STUDIES IN HYDROGENATION OF CARBOXYLIC ACIDS USING SUPPORTED METAL CATALYSTS

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UNDER THE GUIDANCE OF
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AT

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CERTIFICATE

This is to certify that the work incorporated in the thesis, **“Studies in hydrogenation of carboxylic acids using supported metal catalysts.”** submitted by **Mr. Sunil B. Shinde,** for the Degree of **Doctor of Philosophy,** was carried out by the candidate under my supervision in the Homogeneous Catalysis Division, National Chemical Laboratory, Pune – 411 008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Dr. R. M. Deshpande

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DECLARATION BY THE CANDIDATE

I hereby declare that the thesis entitled **"Studies in hydrogenation of carboxylic acids using supported metal catalysts."** submitted by me for the degree of Doctor of Philosophy to the University of Pune is the record of work carried out by me during the period from March 2002 to November 2006 under the guidance of Dr. R. M. Deshpande and has not formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other institution of Higher learning.

I further declare that the material obtained from other sources has been duly acknowledged in the thesis.

May, 2007
Pune

Sunil B. Shinde
(Candidate)

Dedicated to

My Parents

…For always encouraging me
To acquire higher education.

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List of Contents

Description **Page No.**

List of Schemes x

List of Tables xiii

List of Figures xv

List of Abbreviations xxi

Abstract of the Thesis xxiii

CHAPTER 1: Introduction and Literature Survey

1.1 Introduction 1

1.2 Examples of Homogeneous catalysis 2

- 1.2.1 Acid base catalysis 2
- 1.2.2 Organometallic catalysis 2

1.3 Heterogeneous catalysis 2

- 1.3.1 Properties of heterogeneous catalysts 3
- 1.3.2 Hydrogenation with supported metal catalysts 4
- 1.3.3 Hydrogenable functional groups 5
- 1.3.4 Types of selectivity for heterogeneous catalytic hydrogenation 8
- 1.3.5 Importance of hydrogenation products of carboxylic acids 9
- 1.3.6 Literature on hydrogenation of carboxylic acids 11
  - 1.3.6.1 Hydrogenation of aliphatic carboxylic acids and aromatic carboxylic acids to alcohols 11
    - 1.3.6.1.1 Hydrogenation of maleic acid 11
    - 1.3.6.1.2 Hydrogenation of succinic acid 13
    - 1.3.6.1.3 Hydrogenation of glutaric acid 14
    - 1.3.6.1.4 Hydrogenation of adipic acid 15

1.3.6.1.5 Hydrogenation of Dodecanoic acid 16

1.3.6.1.6 Hydrogenation of oleic acid 17

1.3.6.1.7 Hydrogenation of Hexanoic acid 18

1.3.6.1.8 Hydrogenation of lactic acid 19

1.3.6.1.9 Hydrogenation of benzoic acid 20

1.3.6.1.10 Hydrogenation of terephthalic acid 23

1.3.6.1.11 Hydrogenation of isophthalic acid 25

1.3.6.1.12 Hydrogenation of phthalic acid 26

1.3.6.2 Hydrogenation of amino acids to amino alcohols 27

1.3.6.3 Partial hydrogenation of carboxylic acids to aldehydes 29

1.4. Hydrogenation of esters to alcohols 30

1.5 Kinetics of hydrogenation of carboxylic acids 32

1.5.1 Kinetic study for hydrogenation of benzoic acid 33

1.5.2 Kinetic study for hydrogenation of maleic acid 33

1.5.3 Kinetic study for L-Alanine to L-Alaninol 34

1.5.4 Kinetic study for Hydrogenation of lactic acid to propylene glycol 35

1.5.5 Thermodynamic considerations for hydrogenation reactions 36

1.6 Consecutive reactions 39

1.7 Scope and objective of present work 41

References 43

CHAPTER 2: Hydrogenation of aromatic mono and dicarboxylic acids using supported metal catalysts

2.1. Introduction 53

2.2. Experimental 54

2.2.1. Materials 54

2.2.2. Catalyst preparation 54

2.2.3. Reactor set-up for high pressure reactions 56

2.2.4. Experimental procedure for high pressure reactions 57

2.2.5. Analysis 57

2.2.5.1 Procedure for analysis of carboxylic acids by esterification method 58

2.3 Results and discussion 59

2.3.1 Catalyst screening study for hydrogenation of aromatic carboxylic acids 59

2.3.1.1 Hydrogenation of benzoic acid with 5% Pd/C catalyst 61

2.3.1.2 Hydrogenation of benzoic acid with 5% Ru/C catalyst 62

2.3.1.3 Hydrogenation of benzoic acid with 5% Re/C catalyst 63

2.3.1.4 Hydrogenation of benzoic acid with 5%Pd – 2%Re/C bimetallic catalyst 64

2.3.1.5 Hydrogenation of benzoic acid with 1%Ru-6%Re/C catalyst 66

2.3.1.6 Hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst 67

2.3.1.7 Hydrogenation of benzoic acid with cobalt catalysts 69

2.3.2. Hydrogenation of Terephthalic, Isophthalic and Phthalic acid with 5% Ru/C, 5% Pd/C and 5%Ru-29%Sn/Al_2O_3 as catalyst 70

2.3.2.1 Hydrogenation of terephthalic acid (TPA) 70

2.3.2.2 Hydrogenation of isophthalic acid (IPA) 72

2.3.2.3 Hydrogenation of phthalic acid (PA) 75

2.3.3. Hydrogenation of cyclohexane dicarboxylic acids with 5% Ru/C, 5% Pd/C and 5%Ru-29%Sn/Al_2O_3 (Sn/Ru atomic ratio 5) catalyst 77

2.3.4. Hydrogenation of TPA and IPA with 5%Ru-29%Sn/Al_2O_3 (Sn/Ru atomic ratio 5) catalyst 79

2.3.5 Hydrogenation of cinnamic and salicylic acid with 5% Ru/C, 5% Pd/C and 5%Ru-29%Sn/Al_2O_3 catalyst 80

2.3.6 Effect of water as co-solvent for hydrogenation of benzoic acid with ruthenium catalyst 83

2.4 Conclusions 84

References 87

CHAPTER 3: Kinetics of hydrogenation of benzoic acid to cyclohexane carboxylic acid in a batch slurry reactor using 5% Ru/C catalyst

3.1 Introduction 89
3.2 Experimental 90
    3.2.1 Materials 90
    3.2.2 Catalyst preparation 91
    3.2.3 Reactor Set-up for high pressure reactions 91
    3.2.4 Procedure for high pressure reactions 92
    3.2.5 Analysis 92
3.3 Results and discussion 94
    3.3.1 Preliminary experiments for hydrogenation of benzoic acid 94
    3.3.2 Effect of catalyst support on Ru catalyst for hydrogenation of benzoic acid 97
    3.3.3 Effect of ruthenium content in Ru/C catalyst on activity and selectivity for hydrogenation of benzoic acid 98
    3.3.4 Effect of water content in 1,4-dioxane on activity and selectivity 99
    3.3.5 Activity of Ru/C catalyst for hydrogenation of cyclohexane carboxylic acid 100
    3.3.6 Recycle study for 5% Ru/C catalyst for the hydrogenation of benzoic acid to cyclohexane carboxylic acid and cyclohexyl methanol 101
    3.3.7 Experimental procedure for solubility measurement 102
    3.3.8 Preliminary reactions and Analysis of Mass Transfer 103
    3.3.9 Kinetic study for hydrogenation of benzoic acid to cyclohexane carboxylic acid 107
        3.3.9.1 Effect of catalyst loading 107
        3.3.9.2 Effect of benzoic acid concentration 108
        3.3.9.3 Effect of hydrogen partial pressure 109
    3.3.10 Analysis for external and intraparticle mass transfer 111
    3.3.11 Kinetic modeling 115
    3.3.12 Activation energy (E_a) for hydrogenation of cyclohexane 120

carboxylic acid to cyclohexyl methanol on 5% Ru/C catalyst
3.3.13 Determining t_{max} for hydrogenation of benzoic acid to cyclohexyl methanol 123
3.3.13.1 Effect of reaction parameters on t_{max} of cyclohexane carboxylic acid (CCA) 126
3.3.13.1.1 Effect of catalyst loading 126
3.3.13.1.2 Effect of benzoic acid concentration 127
3.3.13.1.3 Effect of Hydrogen partial pressure 128
3.3.13.1.4 Comparison of predicted t_{max} with experimental t_{max} for cyclohexane carboxylic acid 130
3.3.13.2 Determining t_{max} for the intermediate γ-butyrolactone, in hydrogenation of succinic acid to tetrahydrofuran 130
3.4 Conclusion 133
3.5 Nomenclature 135
References 137

CHAPTER 4: Kinetics of hydrogenation of benzoic acid to benzyl alcohol in a batch slurry reactor using Ru-Sn/Al_2O_3 catalyst

4.1 Introduction 139
4.2 Experimental 140
4.2.1. Materials 140
4.2.2. Catalyst preparation 140
4.2.3 Reactor set-up for high pressure reactions 141
4.2.4. Experimental procedure for high pressure reactions 142
4.2.5 Analysis 142
4.2.6 Instrumentation 143
4.3 Results and discussions 144
4.3.1 Preliminary reactions for hydrogenation of benzoic acid 144
4.3.2 Effect of Sn percentage in Ru-Sn/Al_2O_3 catalyst for hydrogenation of benzoic acid to benzyl alcohol 147
4.3.3 Effect of catalyst support for Ru-Sn catalyst on hydrogenation 149

of benzoic acid
4.3.4 Effect of catalyst reduction temperature on activity and selectivity of Ru-Sn/Al_2O_3 catalysts 151
4.3.5 Recycle study for Ru-Sn/Al_2O_3 catalyst for the hydrogenation of benzoic acid to benzyl alcohol 154
4.3.6 Preliminary reactions and analysis of mass transfer 156
4.3.7 Experimental procedure for solubility measurement 159
4.3.8 Analysis for external and intraparticle mass transfer 160
4.3.9 Kinetic study for hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al_2O_3 catalyst 161
4.3.9.1 Effect of catalyst loading 162
4.3.9.2 Effect of benzoic acid concentration 162
4.3.9.3 Effect of hydrogen partial pressure 163
4.3.10 Kinetic modeling 164
4.3.11 Effect of different parameters on leaching of Sn from Ru-Sn/Al_2O_3 catalyst into reaction crude 168
4.4 Conclusion 171
4.5 Nomenclature 173
References 174

CHAPTER 5: Hydrogenation of lauric acid to lauryl alcohol in a batch slurry reactor using Ru-Sn catalysts

5.1 Introduction 175
5.2 Experimental 177
5.2.1. Materials 177
5.2.2. Catalyst preparation 178
5.2.3 Reactor set-up for high pressure reactions 179
5.2.4. Experimental procedure for high pressure reactions 180
5.2.5 Analysis 180
5.3 Results and discussions 182

5.3.1 Preliminary reactions for hydrogenation of lauric acid 182
5.3.2 Effect of support on Ru-Sn catalyst for hydrogenation of lauric acid 184
5.3.3 Effect of Ru/Sn atomic ratio on hydrogenation of lauric acid 185
5.3.4 Effect of catalyst reduction temperature on activity of Ru-Sn on different supports 187
5.3.5 Effect of catalysts reduction temperature for hydrogenation of lauric acid (for different ratio of Sn/Ru in Ru-Sn/TiO_2 catalyst) 188
5.3.6 Recycle study for Ru-Sn/TiO_2 catalyst for the hydrogenation of lauric acid to lauryl alcohol 190
5.3.7 Preliminary reactions and analysis of mass transfer 191
5.3.8 Analysis for external and intraparticle mass transfer 194
5.3.9 Kinetic study for hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO_2 catalyst 195
    5.3.9.1 Effect of catalyst loading 196
    5.3.9.2 Effect of lauric acid concentration 196
    5.3.9.3 Effect of hydrogen partial pressure 197
5.3.10 Kinetic modeling 198
5.4 Conclusion 203
5.5 Nomenclature 205
References 206

CHAPTER 6: Partial hydrogenation of carboxylic acids to aldehydes

6.1 Introduction 208
6.2 Experimental 210
6.2.1. Materials 210
6.2.2. Catalyst preparation 210
6.2.3 Reactor set-up for high pressure reactions 211
6.2.4. Experimental procedure for high pressure reactions 211
6.2.5 Analysis 211
6.3 Results and discussions 212

6.3.1 Preliminary reactions for hydrogenation of lauric acid 212
6.3.2 Effect of support on Ru-Sn catalyst for hydrogenation of lauric acid to lauraldehyde 215
6.3.3 Recycle study of Ru-Sn/TiO_2 catalyst (Sn/Ru atomic ratio=5) for hydrogenation of lauric acid 215
6.3.4 Parametric study for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst in toluene 216
  6.3.4.1 Effect of catalyst loading on selectivity for hydrogenation of lauric acid to lauraldehyde 217
  6.3.4.2 Effect of lauric acid concentration on selectivity for hydrogenation of lauric acid to lauraldehyde 218
  6.3.4.3 Effect of hydrogen partial pressure on selectivity for hydrogenation of lauric acid to lauraldehyde 218
  6.3.4.4 Effect of reaction temperature on hydrogenation of lauric acid to lauraldehyde 219
6.3.5 Effect of catalyst reduction temperature on selectivity of Ru-Sn catalyst supported on different supports 221
  6.3.5.1 Effect of reduction temperature on selectivity of lauraldehyde – 5%Ru-29%Sn/Al_2O_3 catalyst 221
  6.3.5.2 Effect of reduction temperature on selectivity to lauraldehyde – 5%Ru-29%Sn/TiO_2 catalyst 222
  6.3.5.3 Effect of reduction temperature on selectivity to lauraldehyde – 5%Ru-29%Sn/C catalyst 222
6.3.6 Effect of catalyst reduction temperature on activity and selectivity for partial hydrogenation of lauric acid to lauraldehyde - Ru-Sn/TiO_2 catalyst with Sn/Ru varying ratio 223
  6.3.6.1 Sn/Ru atomic ratio 1 (5%Ru-5.8%Sn/TiO_2) 224
  6.3.6.2 Sn/Ru atomic ratio of 2.5 (5%Ru-14.5%Sn/TiO_2) 225
  6.3.6.3 Sn/Ru atomic ratio of 5 (5%Ru-29%Sn/TiO_2) 225
  6.3.6.4 Sn/Ru atomic ratio of 7.5 (5%Ru-43%Sn/TiO_2) 226

    6.3.7 Determining t_{max} for lauraldehyde 228
        6.3.7.1 Effect of reaction parameters on t_{max} of lauraldehyde 229
            6.3.7.1.1 Effect of catalyst loading 230
            6.3.7.1.2 Effect of lauric acid concentration 231
            6.3.7.1.3 Effect of hydrogen partial pressure 231
            6.3.7.1.4 Comparison of predicted t_{max} with experimental t_{max} for lauraldehyde 233
    6.3.8 Hydrogenation of lauric, benzoic and cyclohexane carboxylic acid with Ru-Sn/TiO_2 catalyst in toluene as reaction solvent 233
6.4 Conclusion 235
6.5 Nomenclature 236
References 237

Appendix I 238
Publications / Symposia 256

List of Schemes

Scheme	Description	Page No.
1-1	Hydrogenation of maleic acid with Ru-Re/C catalyst	12
1-2	Hydrogenation of succinic acid Pd-Re/C	14
1-3	Hydrogenation of glutaric acid with Ru-Sn/C catalyst	15
1-4	Hydrogenation of adipic acid with Ru-Pt-Sn/C catalyst	15
1-5	Hydrogenation of adipic acid with Re_2O_7 catalyst	15
1-6	Hydrogenation of lauric acid with copper chromite catalyst	16
1-7	Hydrogenation of lauric acid with zirconia catalyst	16
1-8	Hydrogenation of oleic acid with Ru-Sn catalyst	17
1-9	Hydrogenation of hexanoic acid with Ni or Pt catalyst.	18
1-10	Hydrogenation of lactic acid with Ru/C catalyst	19
1-11	Selective hydrogenation of aromatic ring	20
1-12	Selective hydrogenation of carboxylic group	20
1-13	Hydrogenation of both aromatic ring and carboxylic group	21
1-14	Partial hydrogenation of carboxylic group	21
1-15	Partial hydrogenation of aromatic ring	21
1-16	Hydrogenation of terephthalic acid with Pd or Ru/C catalyst	23
1-17	Hydrogenation of 1,4-cyclohexane dicarboxylic acid with Ru-Sn catalyst	24
1-18	Hydrogenation of terephthalic acid with Ru-Sn catalyst	24
1-19	Hydrogenation of terephthalic acid with ReO_3 catalyst	25
1-20	Hydrogenation of isophthalic acid with Rh/C, Pd/C or Ru/C catalyst	26
1-21	Hydrogenation of isophthalic acid with Ru-Sn/Al_2O_3 catalyst	26
1-22	Hydrogenation of phthalic acid with Pd/C catalyst	27
1-23	Hydrogenation of phthalic acid with Ru-Sn/Al_2O_3	27
1-24	Effect of pH on L-alanine	28
1-25	Hydrogenation of L-alanine with 5% Ru/C catalyst in presence of phosphoric acid	28

Scheme	Description	Page No.
2-1	Possible routes for hydrogenation of terephthalic acid	60
2-2	Reaction scheme for hydrogenation of benzoic acid with 5% Pd/C catalyst	61
2-3	Reaction scheme for hydrogenation of benzoic acid using 5%Ru/C catalyst	62
2-4	Reaction scheme for hydrogenation of benzoic acid with 5% Re/C catalyst	63
2-5	Reaction scheme for hydrogenation of benzoic acid with 5%Pd-2%Re/C catalyst (T = 493 K)	65
2-6	Hydrogenation of benzoic acid with 1%Ru-6%Re/C catalyst	67
2-7	Hydrogenation of benzoic acid with Ru supported on magnesia	68
2-8	Hydrogenation of benzoic acid with Ru-Sn/Al_2O_3	68
2-9	Hydrogenation of terephthalic acid with 5% Ru/C catalyst	71
2-10	Hydrogenation of terephthalic acid with 5% Pd/C catalyst	71
2-11	Hydrogenation of terephthalic acid with 5% Ru/C catalyst at 453 K	72
2-12	Hydrogenation of isophthalic acid with 5% Ru/C catalyst	73
2-13	Hydrogenation of isophthalic acid with 5% Pd/C catalyst	74
2-14	Hydrogenation of isophthalic acid with 5% Ru/C catalyst at 453 K	74
2-15	Hydrogenation of phthalic acid with 5% Ru/C catalyst at 493 K	75
2-16	Hydrogenation of phthalic acid with 5% Pd/C catalyst	76
2-17	Hydrogenation of phthalic acid with Ru-Sn/Al_2O_3 catalyst	76
2-18	Hydrogenation of phthalic acid with 5% Ru/C catalyst at 453 K	77
2-19	Hydrogenation of 1,2-CDCA with Ru-Sn/Al_2O_3 catalyst	78
2-20	Hydrogenation of 1,3-CDCA with Ru-Sn/Al_2O_3 catalyst	78
2-21	Hydrogenation of 1,4-CDCA with Ru-Sn/Al_2O_3 catalyst	78
2-22	Hydrogenation of cinnamic acid with 5% Ru/C catalyst	81
2-23	Hydrogenation of cinnamic acid with 5% Pd/C catalyst	81
2-24	Hydrogenation of cinnamic acid with Ru-Sn/Al_2O_3 catalyst	82

Scheme	Description	Page No.
2-25	Hydrogenation of salicylic acid with Ru/C or Pd/C catalyst	82
3-1	Reaction scheme for hydrogenation of benzoic acid with 5% Ru/C catalyst	95
3-2	Hydrogenation of benzoic acid with 5% Ru/C catalyst	124
3-3	Hydrogenation of succinic acid with 5%Pd-5%Re/C catalyst	131
4-1	Hydrogenation of benzoic acid with 5 % Ru/Al_2O_3 catalyst	145
4-2	Hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst	146
6-1	Hydrogenation of lauric acid with Ru-Sn/Al_2O_3 catalyst in toluene	214

List of Tables

Table No.	Description	Page No.
1-1	Industrial processes using heterogeneous catalysts	4
1-2	Examples of heterogeneously catalyzed liquid phase hydrogenation reactions	6
1-3	Examples of different functional groups which can be hydrogenated using heterogeneous catalyst	7
1-4	Hydrogenation products of carboxylic acid and their application	10
1-5	List for hydrogenation of different functional groups in order of increasing difficulty in hydrogenation	37
2-1	Conditions for gas chromatographic analysis	58
2-2	Catalyst screening for hydrogenation of benzoic acid	69
2-3	Reaction conditions for hydrogenation of aromatic and aliphatic dicarboxylic acids	70
2-4	Hydrogenation of TPA and IPA with Ru-Sn/Al_2O_3 catalyst reduced at 573 and 1073 K	80
2-5	Hydrogenation of benzoic acid with different Ru catalyst in dioxane as solvent	83
2-6	Hydrogenation of benzoic acid with different Ru catalyst in 1,4-dioxane-water (1:1) as solvent	84
3-1	Conditions for gas chromatographic analysis	93
3-2	Range of reaction conditions for hydrogenation of benzoic acid	95
3-3	Henrys constant for hydrogen in water, 1,4-dioxane and 1,4-dioxane-water (1:1) mixture	103
3-4	Range of reaction conditions for kinetic study of hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C catalyst	104
3-5	Parameters used for $k_l a_B$ calculations by Eq-3-4	112
3-6	Rate models for hydrogenation of benzoic acid to cyclohexane carboxylic acid	116

4-1 Reaction parameters used for preliminary studies on hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst 147
4-2 Surface Sn/Ru ratio for Ru-Sn/Al_2O_3 catalyst 149
4-3 Binding energy and oxidation state of Ru, Sn and Al in Ru-Sn/Al_2O_3 catalyst reduced at 573, 723 and 873 K 154
4-4 Henry’s constant for hydrogen in 1,4-dioxane 160
4-5 Range of reaction conditions for parametric study of hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al_2O_3 catalyst 161
4-6 Rate models for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst to benzyl alcohol 165
4-7 Leaching of Sn metal on different support 169
4-8 Effect of catalyst reduction temperature on leaching of Sn metal 170
4-9 Effect of benzoic acid concentration on leaching of Ru and Sn metal 170
5-1 List of catalysts prepared for hydrogenation of lauric acid 178
5-2 Reaction parameters used for hydrogenation of lauric acid with Ru-Sn catalyst 182
5-3 Sn/Ru ratio as obtained from EDX analysis 189
5-4 Range of reaction conditions for hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO_2 catalyst 195
5-5 Rate model for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst to lauryl alcohol 199
6-1 List of catalyst prepared for hydrogenation of lauric acid 210
6-2 Reaction parameters used for hydrogenation of lauric acid with Ru-Sn catalyst 213
6-3 Range of reaction conditions for partial hydrogenation of lauric acid 217

List of Figures

Figure No.	Description	Page No.
2-1	Schematic diagram of silica glass reactor set-up for catalyst reduction	55
2-2	Schematic diagram of reactor set-up for high pressure hydrogenation reactions	56
2-3	Gas chromatograph for esterified reaction sample for hydrogenation of isophthalic acid with 5% Pd/C	59
2-4	Concentration time profile for hydrogenation of benzoic acid with 5% Pd/C catalyst	61
2-5	Concentration time profile for hydrogenation of benzoic acid with 5% Ru/C catalyst	62
2-6	Concentration time profile for hydrogenation of benzoic acid with 5% Re/C catalyst	64
2-7	Concentration time profile for hydrogenation of benzoic acid with 5%Pd-2% Re/C catalyst	66
2-8	Concentration time profile for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst	68
3-1	Gas chromatogram for benzoic acid (BZA) and its hydrogenation products cyclohexane carboxylic acid (CCA) and cyclohexyl methanol (CHM)	94
3-2	Concentration time profile for hydrogenation of benzoic acid with 5%Ru/C catalyst	96
3-3	Effect of support on Ru catalyzed hydrogenation of benzoic acid	97
3-4	Effect of percent Ru in Ru/C catalyst for hydrogenation of benzoic acid	98
3-5	Effect of percentage water in 1,4-dioxane on activity and selectivity of 5%Ru/C catalyst for hydrogenation of benzoic acid	99
3-6	Hydrogenation of cyclohexane carboxylic acid with 5% Ru/C catalyst	101

3-7 Catalyst recycle studies 102

3-8 Hydrogenation of benzoic acid with 5% Ru/C catalyst under reaction conditions for kinetics 104

3-9 Determining initial rate for hydrogenation of benzoic acid at different catalyst loading 105

3-10 Effect of catalyst loading on initial rate of reaction 106

3-11 A plot of initial rate of hydrogenation vs. agitation speed 107

3-12 A plot of rate of hydrogenation vs. catalyst loading 108

3-13 A plot of rate of hydrogenation vs. benzoic acid concentration 109

3-14 A plot of rate of hydrogenation vs. hydrogen partial pressure 110

3-15 A logarithmic plot of rate of hydrogenation vs. hydrogen partial pressure 110

3-16 Effect of catalyst loading on initial rate of hydrogenation of benzoic acid: Comparison of experimental and predicted rates 118

3-17 Effect of benzoic acid concentration on initial rate of hydrogenation of benzoic acid: Comparison of experimental and predicted rates 118

3-18 Effect of hydrogen partial pressure on initial rate of hydrogenation of benzoic acid: Comparison of experimental and predicted rates 119

3-19 ln k and ln k_B versus 1/T 120

3-20 Concentration time profile for hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol 121

3-21 Initial rate for hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol using 5% Ru/C catalyst 122

3-22 Arrhenius plot of hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol 123

3-23 Concentration time profile for hydrogenation of benzoic acid with 5%Ru/C catalyst, with t_{max} 125

3-24 Effect of catalyst loading on t_{max} for CCA 127

3-25 Effect of benzoic acid concentration on t_{max} for CCA 128

3-26	Effect of hydrogen partial pressure on t_{max} for CCA	129
3-27	Comparison of predicted t_{max} with observed t_{max} for cyclohexane carboxylic acid	130
3-28	Concentration time profile for hydrogenation of succinic acid with 5%Pd-5%Re/C catalyst	131
3-29	Comparison of predicted t_{max} with experimental t_{max} for GBL	132
4-1	Gas chromatogram for hydrogenation of benzoic acid to benzyl alcohol	143
4-2	Concentration time profile for hydrogenation of benzoic acid with 5% Ru/Al_2O_3 catalyst	144
4-3	Concentration time profile for hydrogenation of benzoic acid with $Ru\text{-}Sn/Al_2O_3$ (Sn/Ru atomic ratio is 1:5) catalyst	145
4-4	Effect of Sn percentage on activity of $Ru\text{-}Sn/Al_2O_3$ catalyst	148
4-5	Effect of support on Ru-Sn catalyst for hydrogenation of benzoic acid	150
4-6	Effect of reduction temperature on Ru-Sn catalyst for hydrogenation of benzoic acid	151
4-7	XPS characterization for Ru in $Ru\text{-}Sn/Al_2O_3$ catalyst reduced at 573, 723 and 873 K	152
4-8	XPS characterization for Sn in $Ru\text{-}Sn/Al_2O_3$ catalyst reduced at 573, 723 and 873 K	153
4-9	XPS characterization for Al in $Ru\text{-}Sn/Al_2O_3$ catalyst reduced at 573, 723 and 873 K	153
4-10	Recycle study for $Ru\text{-}Sn/Al_2O_3$ catalyst for hydrogenation of benzoic acid	155
4-11	Leaching study for Sn in reaction crude	156
4-12	Determining initial rate for hydrogenation of benzoic acid to benzyl alcohol at different catalyst loading	157
4-13	Effect of catalyst loading on initial rate of reaction	158
4-14	A plot of initial rate of hydrogenation vs. agitation speed	159
4-15	Effect of catalyst loading on rate of hydrogenation of benzoic acid	162

4-16 Effect of benzoic acid concentration on rate of hydrogenation 163
4-17 Effect of hydrogen partial pressure on rate of hydrogenation 164
4-18 Effect of catalyst loading on rate of hydrogenation: Comparison of experimental and predicted rates 166
4-19 Effect of benzoic acid concentration on rate of hydrogenation: Comparison of experimental and predicted rates 167
4-20 Effect of hydrogen partial pressure on rate of hydrogenation: Comparison of experimental and predicted rates 167
4-21 Arrhenius plot for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst 168
5-1 Gas chromatogram for hydrogenation of Lauric acid with Ru-Sn/TiO_2 to lauryl alcohol 181
5-2 Hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst 183
5-3 Effect of support on Ru-Sn catalyst for hydrogenation of lauric acid 184
5-4 Effect of Ru/Sn atomic ratio on Ru-Sn/Al_2O_3 catalyst for hydrogenation 185
5-5 Effect of Sn/Ru atomic ratio on Ru-Sn/TiO_2 and Ru-Sn/Al_2O_3 catalyst for hydrogenation 186
5-6 Effect of reduction temperature on activity of Ru-Sn on different supports 187
5-7 Effect of reduction temperature on Ru-Sn/TiO_2 catalyst with different Sn/Ru atomic ratio for hydrogenation 189
5-8 Recycle study for Ru-Sn/TiO_2 catalyst for hydrogenation of lauric acid 191
5-9 Determining initial rate for hydrogenation of lauric acid to lauryl alcohol at different catalyst loading 192
5-10 Effect of catalyst loading on initial rate of reaction 193
5-11 A plot of initial rate of hydrogenation vs. agitation speed 194
5-12 Effect of catalyst loading on rate of hydrogenation of lauric acid 196

5-13	Effect of lauric acid concentration on rate of hydrogenation	197
5-14	Effect of hydrogen partial pressure on rate of hydrogenation	198
5-15	Comparison of experimental and predicted effect of catalyst loading on rate of hydrogenation	200
5-16	Comparison of experimental and predicted effect of lauric acid concentration on rate of hydrogenation	201
5-17	Comparison of experimental and predicted effect of hydrogen partial pressure on rate of hydrogenation	202
5-18	Arrhenius plot for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst	203
6-1	Gas chromatogram for Lauric acid and its hydrogenation products	212
6-2	Hydrogenation of lauric acid with 5%Ru-43%Sn/Al_2O_3 catalyst in toluene	213
6-3	Effect of support on selectivity of Ru-Sn catalyst for lauraldehyde	215
6-4	Recycle study for Ru-Sn/TiO_2 catalyst	216
6-5	Effect of catalyst loading on hydrogenation of lauric acid to lauraldehyde	217
6-6	Effect of lauric acid concentration on hydrogenation of lauric acid to lauraldehyde	218
6-7	Effect of hydrogen partial pressure on selectivity to lauraldehyde	219
6-8	Effect of reaction temperature on selectivity of lauraldehyde	220
6-9	Effect of catalyst reduction temperature on Ru-Sn/Al_2O_3 catalyst for lauraldehyde	221
6-10	Effect of catalyst reduction temperature on Ru-Sn/TiO_2 catalyst for lauraldehyde	222
6-11	Effect of catalyst reduction temperature on Ru-Sn/C catalyst for lauraldehyde	223
6-12	Effect of reduction temperature on Ru-Sn/TiO_2 catalyst for partial hydrogenation	224

6-13 Effect of reduction temperature on Ru-Sn/TiO_2 (Sn/Ru ratio 2.5) 225
6-14 Effect of reduction temperature on Ru-Sn/TiO_2 (Sn/Ru ratio 5) 226
6-15 Effect of reduction temperature on Ru-Sn/TiO_2 catalyst (Sn/Ru ratio 7.5) 227
6-16 Concentration time profile for hydrogenation lauric acid with Ru-Sn/TiO_2 (Sn/Ru ratio = 5) 228
6-17 Selectivity to lauraldehyde with reaction time for hydrogenation with Ru-Sn/TiO_2 catalyst 229
6-18 Effect of catalyst loading on t_{max} for lauraldehyde 230
6-19 Effect of lauric acid concentration on t_{max} for lauraldehyde 231
6-20 Effect of hydrogen partial pressure on t_{max} for lauraldehyde 232
6-21 Comparison of predicted t_{max} with observed t_{max} for lauraldehyde 233
6-22 Hydrogenation of lauric, benzoic and cyclohexane carboxylic acid in toluene with Ru-Sn/TiO_2 catalyst 234

List of Abbreviations

1,2-BDM	1,2-benzene dimethanol
1,2-CDCA	1,2-cyclohexane dicarboxylic acid
1,2-CHDM	1,2-cyclohexane dimethanol
1,3-BDM	1,3-benzene dimethanol
1,3-CDCA	1,3-cyclohexane dicarboxylic acid
1,3-CHDM	1,3-cyclohexane dimethanol
1,4-BDM	1,4-benzene dimethanol
1,4-CDCA	1,4-cyclohexane dicarboxylic acid
1,4-CHDM	1,4-cyclohexane dimethanol
B. E	Binding energy
BDO	1,4-butanediol
BNBZ	Benzyl benzoate
BuOH	Butanol
BZA	Benzoic acid
BZOH	Benzyl alcohol
CCA	Cyclohexane carboxylic acid
CHM	Cyclohexyl methanol
EDX	Energy dispersive X-ray
FAC	Fumaric acid
FID	Flame ionization detector
GBL	γ-butyrolactone
GC	Gas chromatography
GC-MS	Gas chromatography-Mass spectrometry
GFAAS	Graphite furnace atomic absorption spectrophotometer
HBA	Hydroxy butyric acid
HMBA	Hydroxy methyl benzoic acid
hr	Hour (s)
ICP-AES	Inductive copuplled Plasma- atomic emission spectrophotometry
IPA	Isophthalic acid
LAC	Lauric acid

LALAR	Lauryl laurate
LALD	Lauraldehyde
LAOH	Lauryl alcohol
L-H	Langmuir-Hinshelwood
MAC	Maleic acid
MCH	Methyl cyclohexane
MeOH	Methanol
ml	Milliliter
Mol	Mole
MPa	Megapascal
PA	Phthalic acid
PA	Propionic acid
PG	1,2-Propylene glycol
P_{H2}	Partial pressure of Hydrogen
PMT	Photomultiplier tube
ppm	Parts per million
PrOH	Propyl alcohol
RT	Room temperature
SAC	Succinic acid
SEM	Scanning electron microscopy
T	Temperature
THF	Tetrahydrofuran
t_{max}	Time, when concentration of intermediate is maximum
TOL	Toluene
TOF	Turnover frequency
TPA	Terephthalic acid
XPS	X-ray photoelectron spectroscopy

Abstract of the Thesis

Catalysis has contributed significantly in the replacement of conventional reagent based processes by new catalytic processes that allow efficient utilization of raw materials and energy and produce minimal waste. A majority of processes employ heterogeneous catalysts, particularly since they offer efficient catalyst product separation. Hence, studies related to heterogeneous catalysis and other fundamental aspects like kinetics of these reactions assume significant importance. Tailoring of heterogeneous catalysts for achieving chemoselective reduction has been a challenging task. The design of chemoselective catalyst for hydrogenation of molecules with multiple reducible functions is essential. For achieving high activity and selectivity, mono metallic heterogeneous catalysts are generally doped with other metals to obtain bimetallic catalyst, with the specific requirement[1].

This thesis presents a study related to fundamental issues in catalysis and kinetics for chemoselective hydrogenation of benzoic acid to i) cyclohexane carboxylic acid ii) benzyl alcohol and iii) benzaldehyde. Also, a detail study has been done on supported Ru-Sn bimetallic catalysts for hydrogenation of lauric acid to lauryl alcohol/lauraldehyde.

The conventional method for obtaining cyclohexane carboxylic acid is by hydrogenation of benzoic acid with Pd/C catalyst[2]. Ru/C catalyst is also active for the reaction however; no studies on the selective hydrogenation of benzoic acid to cyclohexane carboxylic acid over Ru/C catalyst are reported. Benzyl alcohol, a commercially important chemical is produced by hydrolysis of benzyl esters[3]. The selective hydrogenation of benzoic acid to benzyl alcohol can offer an alternative route to benzyl alcohol. There is thus a scope for the development of such catalysts with high selectivity to benzyl alcohol.

Considering these issues, the need for development of selective catalysts for hydrogenation is evident. In addition, the studies on the kinetics and mechanism of these reactions also will help in the optimization and understanding of the interactions of catalyst with substrates. The following problems were thus chosen for present work:

- Catalyst synthesis and screening for the hydrogenation of aromatic and aliphatic carboxylic acids. Detailed studies on developing catalysts for chemoselective hydrogenation of benzoic acid to cyclohexane carboxylic acid and benzyl alcohol.
- Achieving high selectivity for hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C and kinetic studies on hydrogenation of benzoic acid to cyclohexane carboxylic acid in batch slurry reactor using 5% Ru/C catalyst.
- Development of catalysts for the selective hydrogenation of benzoic acid to benzyl alcohol and kinetic modeling of the reaction using the chemoselective catalyst.
- Detailed study of supported Ru-Sn catalysts for hydrogenation of lauric acid to lauryl alcohol. Kinetic study for hydrogenation of lauric acid to lauryl alcohol with the best Ru-Sn catalyst.
- Investigations on the partial hydrogenation of carboxylic acids to respective aldehydes

The thesis is presented in six chapters, a brief summary of which is given below

In Chapter 1, a detailed literature review on catalytic hydrogenation of mono and dicarboxylic acids has been presented. Most of the hydrogenation products of carboxylic acids are alcohols which are used as solvents and as monomers for producing polymers, for example the product of succinic acid hydrogenation, 1,4-butanediol, is used as solvent and also as a monomer for polyesters[4]. 1, 6 hexanediol formed by adipic acid hydrogenation finds application in polymers[5].

Most of the literature on hydrogenation of mono and dicarboxylic acids is patented and very few detailed studies have been reported on the hydrogenation of carboxylic acids. The literature available on the hydrogenation of aromatic acids was also reviewed with special emphasis on the chemoselective hydrogenation.

For the hydrogenation of aromatic acids, catalysts like supported Pd[6] and Ru[7] and bimetallic catalysts[8] have been reported. Pd/C is an active and selective catalyst and gives primarily ring hydrogenation[9]. Ru/C on the other hand is active for hydrogenation of the ring and the carboxylic function, and is hence not very selective. The selectivity and activity of Ru catalysts for hydrogenation of carboxylic acid group is enhanced by introduction of additives like Sn[10].

The kinetics of hydrogenation of aliphatic dicarboxylic acid has been reported using Ru-Re/C catalysts[11]. However, no study on the kinetics of hydrogenation of aromatic carboxylic acids has been reported. There are also no major investigations on the development of chemoselective catalysts for the hydrogenation of aromatic mono and dicarboxylic acids, or for the partial hydrogenation of aliphatic and aromatic carboxylic acids[12].

Based on the literature search the following problems were chosen for further detailed studies.

1. Synthesis of mono and bimetallic supported catalysts and their application to hydrogenation of mono and dicarboxylic acids, identification of products. Investigation on the role of solvents etc on the product distribution.
2. Detailed kinetic study of chemoselective hydrogenation of benzoic acid to cyclohexane carboxylic acid using Ru/C catalyst. Studies on the effect of reaction parameters on rate, and optimization of reaction conditions to achieve high selectivity to cyclohexane carboxylic acid. Development of a model to predict t_{max} for cyclohexane carboxylic acid in the hydrogenation of benzoic acid to cyclohexane carboxylic acid and further to cyclohexyl methanol.
3. Development of catalysts for the hydrogenation of benzoic acid to benzyl alcohol in high selectivity. Kinetics of the reaction using Ru-Sn/Al_2O_3 catalysts.
4. Studies on the selective hydrogenation of lauric acid to lauryl alcohol, and kinetics of the reaction.
5. Development of catalysts for the selective partial hydrogenation of aliphatic and aromatic acids to aldehydes, and investigation on the role of various reaction parameters and catalysts on the selectivity to aldehydes. Development of a model for t_{max} of lauraldehyde.

Chapter 2 deals with hydrogenation of aromatic mono and dicarboxylic acids. In this study different supported mono and bimetallic catalysts were synthesized and screened for their activity towards hydrogenation of benzoic acid. The screening study revealed that Pd/C catalyst selectively hydrogenated the aromatic ring to give cyclohexane carboxylic acid whereas Ru-Sn/Al_2O_3 selectively hydrogenated the –COOH group to give benzyl alcohol. Ru/C catalyst hydrogenated both functional groups to give cyclohexyl methanol.

The hydrogenation of phthalic, terephthalic and isophthalic acids was also studied using 5% Ru/C, 5% Pd/C and Ru-Sn/Al_2O_3 catalyst. It was observed that Pd/C and Ru-Sn/Al_2O_3 catalyst selectively hydrogenated the aromatic ring and –COOH group of these carboxylic acids respectively. Ru/C catalyst is observed to give hydrogenolysis products, probably due to high reactivity of cyclohexane dicarboxylic acid intermediates which are formed by hydrogenation of aromatic carboxylic acids. At temperatures of 453 K, hydrogenation of phthalic, isophthalic and terephthalic acid with 5% Ru/C catalyst gives saturated carboxylic acids with hydrogenolysis products < 5%.

Cyclohexane dicarboxylic acid readily undergoes hydrogenolysis with Ru/C catalyst and there is no reaction with Pd/C catalyst. Ru-Sn/Al_2O_3 catalyst selectively hydrogenated the –COOH group of cyclohexane dicarboxylic acid.

Chapter 3 deals with chemoselective hydrogenation of benzoic acid to cyclohexane carboxylic acid. Cyclohexane carboxylic acid is an important chemical used in the preparation of Nylon[13]. From literature it is seen that cyclohexane carboxylic acid is produced from benzoic acid by using Pd/C catalyst, as this catalyst is selective for hydrogenation of the aromatic ring. Although Ru/C catalyst is very active it is not used for producing cyclohexane carboxylic acid from benzoic acid as it hydrogenates –COOH group of cyclohexane carboxylic acid as well, to give cyclohexyl methanol.

In this study we have obtained high selectivity towards cyclohexane carboxylic acid by tailoring of the solvent and by the optimization of process parameters. A kinetic study has also been carried out to understand the role of different parameters on the activity of catalyst.

When hydrogenation of benzoic acid was carried out with Ru/Al_2O_3, Ru/TiO_2 and Ru/SiO_2 catalyst in dioxane solvent, hydrogenolysis products like toluene and methyl cyclohexane were obtained along with cyclohexane carboxylic acid and cyclohexyl methanol. When reactions were carried in 1:1 1,4-dioxane-water as solvent only cyclohexane carboxylic acid was obtained. This change in selectivity results from a change in orientation of benzoic acid molecule at catalyst surface due to the influence of the solvent.

Intrinsic kinetics of hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C catalyst was investigated. The reaction was found to be first order with respect to catalyst concentration and hydrogen partial pressure. The hydrogenation was found to be first order with respect to benzoic acid at lower concentrations and tends to a zero order for higher concentrations of benzoic acid. A semi empirical model has been proposed which predicts the observed rate data in good agreement. Cyclohexane carboxylic acid is an intermediate for hydrogenation of benzoic acid. Like most of the intermediates cyclohexane carboxylic acid also passes through a maximum concentration during reaction. An equation, which predicts the time (t_{max}) for cyclohexane carboxylic acid, was derived using Marquardts method of optimization[14].

In Chapter 4 the development of a catalyst for the selective hydrogenation of benzoic acid to benzyl alcohol has been studied. Different $Ru\text{-}Sn/Al_2O_3$ catalysts were prepared by impregnation method and tested for their activity in hydrogenation of benzoic acid. The effect of Sn percentage, role of support and the catalyst reduction temperature on the activity and selectivity of the catalyst was studied. The stability of catalyst was also checked by recycle studies and monitoring of catalyst leaching.

The product profile in the hydrogenation of benzoic acid is highly dependent on the catalyst employed. With mono metallic Ru/Al_2O_3 along with cyclohexane carboxylic acid and cyclohexyl methanol, hydrogenolysis products (toluene and methyl cyclohexane) were also obtained and with bimetallic $Ru\text{-}Sn/Al_2O_3$ catalyst only benzyl alcohol was obtained.

When the Sn/Ru atomic ratio in Ru-Sn/Al_2O_3 catalyst was increased the conversion of benzoic acid increased up to a Sn/Ru ratio of 5, after which, conversion of benzoic acid remained constant. The selectivity to benzyl alcohol also also unchanged.

The role of supports like alumina, titania and silica on activity and selectivity of Ru-Sn catalyst for the hydrogenation of benzoic acid to benzyl alcohol was studied. It was observed that titania was the best support which gave 72% conversion and 83% selectivity to benzyl alcohol and 17% benzyl benzoate.

The conversion of benzoic acid increased from 40% to 99% as a function of increase in catalyst reduction temperature from 573 to 873 K.

The Ru-Sn/Al_2O_3 catalyst was found to be stable and was recycled four times with no change in activity and selectivity.

The intrinsic kinetics was studied for the hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al_2O_3 catalyst. For this, a parametric study was done in the kinetic regime, which showed the hydrogenation of benzoic acid to benzyl alcohol to be first order with respect to catalyst and benzoic acid concentration and hydrogen partial pressure. First order for hydrogenation with respect to benzoic acid and hydrogen indicates a dual site mechanism.

Chapter 5 deals with screening of different supports for Ru-Sn catalyst and their activity and selectivity for hydrogenation of lauric acid to lauryl alcohol. Effect of catalyst reduction temperature for Ru-Sn on different supports, and for different Ru:Sn compositions on TiO_2 support has also been studied.

Titania supported catalyst was found to be more active and selective for hydrogenation of lauric acid to lauryl alcohol.

When Sn percentage in Ru-Sn/Al_2O_3 and Ru-Sn/TiO_2 was varied, the activity of Ru-Sn/TiO_2 catalyst passed through maximum with varying Sn percent, due to strong metal support interaction (SMSI)[15]. SMSI is absent in Ru-Sn/Al_2O_3 and so the activity of Ru-Sn/Al_2O_3 increased with increasing Sn percentage in the catalyst. Since Ru-Sn/TiO_2 was the best catalyst for hydrogenation of lauric acid to lauryl alcohol, the effect of catalyst reduction temperature for different Sn/Ru ratio was investigated using this support. The activity of Ru-Sn/TiO_2 was highest when the Sn/Ru atomic ratio was 5 for a catalyst with reduction temperature of 573 K. The Ru-Sn/TiO_2 catalyst was found to be stable for four recycles. The kinetics of the hydrogenation of lauric acid to lauryl alcohol was investigated, and it was observed that reaction is first order with respect to catalyst and lauric acid concentration and hydrogen partial pressure. A semi empirical rate model has been fitted to the data which predicts the observed rate within experimental error. The activation energy was also evaluated.

In Chapter 6 we have introduced toluene as a solvent for catalytic hydrogenation with Ru-Sn based catalyst for the first time.

Initially, the stability of toluene as solvent for hydrogenation was assessed, by taking reaction of neat toluene with Ru-Sn/Al_2O_3 catalyst for extended periods at high temperature and pressures. The toluene was found to be in tact, and no hydrogenation products were observed at the end of the reaction.

Different catalysts were synthesized on supports like carbon, silica, alumina and titania and were screened for the hydrogenation of lauric acid with Ru-Sn catalyst. In this study it was found that titania was the best support which gave 32% conversion of lauric acid with 41% selectivity to lauraldehyde. The rest of the products were lauryl alcohol and lauryl laurate. Hence, further studies on catalyst development were done using titania as support.

The effect of catalyst reduction temperature for different Sn/Ru atomic ratio for Ru-Sn/TiO_2 catalyst showed that, the catalyst with Sn/Ru ratio 7.5 and reduced at 1073 K gave high selectivity (87%) to lauraldehyde at 18% conversion.

The Ru-Sn/TiO_2 catalyst was observed to give same conversion of lauric acid and selectivity to lauraldehyde even after four recycles. Further, from the parametric study for hydrogenation of lauric acid, it was clear that selectivity for partial hydrogenation of lauric acid to lauraldehyde was not dependent on reaction parameters.

Hydrogenation of benzoic acid and cyclohexane carboxylic acid with Ru-Sn/TiO_2 catalyst in toluene, also gave benzaldehyde and cyclohexane carboxaldehyde respectively.

During hydrogenation, lauraldehyde concentration was observed to pass through a maximum. An equation to predict the time (t_{max}) when the concentration of lauraldehyde is maximum was derived using Marquardts method of optimization.

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Chapter 1
Introduction and Literature Survey

1.1 Introduction

Catalysis is the key to efficient chemical processing. Most industrial reactions and almost all biological reactions employ catalysts. Catalysis is involved in many chemical processes ranging from large scale refining to fine and specialty chemicals[1]. Catalysis is also central to technologies for industrial waste treatment[2].

A catalyst is a substance that increases the rate of approach to equilibrium of a chemical reaction without being consumed itself. A catalyst changes the rate but not the equilibrium of the reaction. It is well recognized that catalysts function by forming chemical bonds with one or more reactants, thereby opening up pathways to their conversions into products, with simultaneous regeneration of the catalyst. Catalysis is thus cyclic in nature; reactants bond to one form of the catalyst, products are decoupled from another form, and the initial form of the catalyst is regenerated[3].

Most catalysts used in commercial practice are either in dissolved (liquid) state or are surfaces of the solids. Catalysis occurring in a single gas or liquid phase is referred to as homogeneous catalysis (or molecular catalysis) because of the uniformity of the phase in which it occurs. Catalysis occurring in a multiphase mixture such as a gas-solid mixture is referred to as heterogeneous catalysis; usually this is surface catalysis[4].

The performance of a catalyst is measured largely by criteria of chemical kinetics, as catalyst influences the rate and not the equilibrium of a reaction. The selectivity is a measure of the property of catalyst to direct a reaction to particular products. There is no single definition of selectivity, but it is sometimes defined as a ratio of activities, such as the ratio of the rate of desired reaction to the sum of the rates of all the reactions that deplete the reactants[5]. Selectivity may also be represented simply as a product distribution[6]. Because catalysts lose activity and selectivity during operation, they are also evaluated in terms of stability. The stability of a catalyst is a measure of the rate of loss of activity or selectivity. Catalysts that have lost activity are often treated to bring back the activity, i.e. reactivated. Catalytic processes are also evaluated in terms of cost; in a typical process, the cost of catalyst is a small fraction of the total processing cost, often <5% of total raw material cost[7].

1.2 Examples of Homogeneous catalysis

1.2.1 Acid base catalysis:

Inexpensive mineral acids, eg, H_2SO_4, and bases, e.g., KOH, in aqueous solution are widely applied as catalysts in industrial organic synthesis. Catalytic reactions include esterification, hydrations, dehydrations and condensations[8]. Example for such catalysis is synthesis of bisphenol A from phenol and acetone in the presence of a dissociated mineral acid[9].

1.2.2 Organometallic catalysis:

Most of the recent innovations in industrial homogeneous catalysis have resulted from discoveries of organometallic catalysts. Thousands of organometallic compounds, i.e., those with metal-carbon bonds, are known, and the rapid development of organotransition metal chemistry in recent years has been motivated largely by the successes and opportunities in catalysis. The chemistry of organotransition metal catalysis is explained by the bonding and reactivity of organic groups (ligands) bonded to the metals. Examples for organometallic catalysis are: Wilkinson catalyst-$RhCl(PPh_3)_3$ for the hydrogenation[10] of olefins (e.g. cyclohexene and styrene), chiral hydrogenation of methyl ester of acetmidocinnamic acid to 3,4-dihydrooxyphenylalanine (L-dopa), a drug used in the treatment of Parkinson's disease[11], methanol carbonylation by rhodium complex $[Rh(CO)_2I_2]^-$, to give acetic acid, olefin hydroformylation using phosphine-modified rhodium carbonyl complexes (Oxo process)[12], olefin metathesis using Grubb's ruthenium catalysts (converts olefin to lower and higher molecular weight olefins)[13], Wacker oxidation of ethylene to acetaldehyde with $PdCl_2$ as a catalyst[14].

1.3 Heterogeneous catalysis

Most of the large scale catalytic processes take place with gaseous reactants in the presence of solid catalysts. From an engineering viewpoint, these processes offer the following advantages, in contrast to those involving homogeneous catalysts: (i) wide range of temperature and pressure can be applied, (ii) Since these catalysts are stable, temperature of reaction can be increased to increase the activity of catalyst, (iii) catalysts are not corrosive, (iv) the separation of gaseous or liquid products from solid catalyst is simple and costs little, (v) strongly exothermic reactions are routinely carried out with solid catalysts.[7]

1.3.1 Properties of heterogeneous catalysts

Heterogeneous catalysts used on large scale are porous inorganic materials. Various reactions employing heterogeneous catalysts are summarized in Table 1-1[9]. Catalysis takes place as one or more of the reactants are chemisorbed, on the surface of the catalyst and react there. The activity and selectivity of the catalysts depend strongly on the surface composition and structure. The heterogeneous catalysts with the simplest composition are pure metals, and the metals that have the simplest and most uniform surface structures are single crystals. Study on single crystals of Pt confirmed that paraffin hydrogenolysis reactions takes place rapidly on the steps and kinks of platinum surfaces and slowly on flat planes; however, hydrogenation of olefins takes place at approximately the same rate on each kind of surface site[15].

The typical industrial catalyst has both microscopic and macroscopic regions with different compositions and structures. The surfaces of industrial catalysts are much complex than those of the single crystals of metal. Because surfaces of industrial catalysts are very difficult to characterize precisely and catalytic properties are sensitive to small structural details, it is usually not possible to identify the specific combinations of atoms on a surface, called catalytic sites or active sites that are responsible for catalysis. Experiments with catalyst poisons have shown that the catalytic sites are usually a small fraction of the catalyst surface[7].

Important physical properties of heterogeneous catalysts include the particle size and shape, surface area, pore volume, pore size distribution and strength to resist crushing and abrasion. Measurements of physical properties of catalyst are routine and often automated[16]. Pores with diameters <2.0 nm are called micropores; those with diameters between 2.0 and 5.0 nm are called mesopores; and those with diameters >5.0 nm are called macropores. Pore volume and pore size distributions are measured by mercury penetration and by N_2 adsorption methods[17].

Table 1-1: Industrial processes using heterogeneous catalysts.[9]

No.	Catalyst	Reaction
1	Ni, Pd, Pt as powders or on supports or metal oxides (chromium oxide)	hydrogenation of 1,5,9-cyclododecatriene to cyclododecene- an intermediate for 12-laurolactam. hydrogenation of glucose to sorbitol (pharmaceuticals)
2	Fe, Ru	Ammonia synthesis from hydrogen and Nitrogen
3	Supported Cu on ZnO and Al_2O_3	Methanol from carbon monoxide and hydrogen.
4	γ-alumina	Dehydration of alcohol gives olefin and water
5	Pd/zeolite	Paraffin hydrocracking
6	V_2O_5 or Pt	Oxidation of sulphur dioxide to gives sulphur trioxide
7	Mixed oxides of Fe and Mo	Oxidation of methanol to formaldehyde
8	Fe_3O_4 or metal sulfides	Water + carbon monoxide gives hydrogen and carbon dioxide (Water gas shift reaction to remove CO)
9	ZSM-5	Alkylation of benzene to produce ethyl benzene (Mobil-Badger process)[18]

Although a variety of reactions are catalyzed by heterogeneous catalysts, hydrogenation reactions constitute a major class of heterogeneously catalyzed reactions.

1.3.2 Hydrogenation with supported metal catalysts

Hydrogenation is one of the oldest and most widely used applications of supported catalysts, and a lot of literature is available in this field. Metals reported for hydrogenation include cobalt, copper, nickel, palladium, platinum, rhenium, rhodium, ruthenium and silver. These catalysts are supported on supports like carbon, alumina, silica, zeolites and kieselguhr[19].

The reduction of organic compounds is a key step in the synthesis of several chemicals. Conventionally, the reduction was carried out using stoichiometric amounts of reducing agents such as sodium borohydride, lithium aluminum hydride, hydrazine hydrate or iron-acid[20]. The major disadvantages of these reduction process are i) high consumption of reducing agent, ii) disposal of waste generated by the reducing agent, iii) separation of product from the reaction mixture and iv) reducing agents cannot be reused.

Replacement of conventional stoichiometric reduction methods by catalytic hydrogenation is perhaps one of the most significant achievements of modern catalysis. Table 1-2 summarizes a few examples of industrially relevant catalytic hydrogenation processes. From Table 1-2 it is understood that hydrogenation reactions are useful in production of bulk chemicals to produce polymers and dyes and also for production of fine chemicals required in perfumery and pharmaceutical industry.

1.3.3 Hydrogenable functional groups

The organic compounds which can be hydrogenated are alkenes, alkynes, aliphatic aldehydes and ketones, aromatic aldehdydes and ketones, sugars, esters, anhydrides and carboxylic acids, nitriles, nitro compounds, aromatic ring and hetero aromatic compounds[21]. Hydrogenation products of different functional groups heterogeneously catalyzed and their application is given in Table 1-3.

Compared to hydrogenation of nitro, aromatic ring, aldehyde, and ketonic functions, the hydrogenation of carboxylic acids generally requires drastic reaction conditions like 170-200 ^{o}C temperature and 300-400 atmospheres of hydrogen pressure.[6]

Table 1-2: Examples of heterogeneously catalyzed liquid phase hydrogenation reactions.

Sr.	**Substrate**	**Catalyst**	**Product**	**Application**	**Ref.**
1	2,4-Dinitrotoluene	Pd/Al_2O_3	Toluenediamine	Intermediate for TDI	22
2	Chloronitrobenzenes	PtS/C	Chloroanilines	Pharmaceuticals & dyes	23
3	o-Nitroanisole	Pd/C	o-Anisidine	Dyes & fine chemicals	24
4	Butynediol	$Pd\text{-}Zn/CaCO_3$	Cis-Butenediol	Intermediate for vitamin-A & endosulfan	25
5	p-Isobutylacetophenone	Pd/C, Ni/HY	p-Isobutylphenylethanol	Intermediate for Ibuprofen	26
6	Glucose	Raney Ni	Sorbitol	Pharmaceuticals	27
7	Adiponitrile	Raney Ni	Hexamethylenediamine	Intermediate for Nylon6, 6	28
8	1,5,9-Cylododecatriene	Pd/Al_2O_3	Cyclododecene	Intermediate for 121-laurolactum	29
9	Cinnamaldehyde	Pt-Co/C or Pt-Ru/C	Cinnamyl alcohol	Fine chemicals, perfumery	30
10	3-Hydroxypropanal	Ni/support	1,3-propanediol	Fine chemicals	31
11	2,8-Dichloroadenosine	$Pd/BaSO_4$	Adenosine	Neuro-regulatory drug	32
12	Reductive amination of 4-chloroacetylcatechol	Pd/support	Adrenaline	Pharmaceuticals	33
13	4-Aminoacetylphenol	Pd/support	Octapamine	Pharmaceuticals	34
14	Soya bean oil	Ni/support	Saturated oil	Fat industry	35
15	Phenylacetylene	$Pd/C,Al_2O_3$	Styrene	Raw material for polystyrene	36
16	Acetophenone	Ru/Al_2O_3	1-Phenylethanol	Pharmaceuticals, intermediate for styrene	37

Table 1-3: Examples of different functional groups which can be hydrogenated using heterogeneous catalyst

Sr.	Hydrogenable functional groups	Catalyst	Application	Ref.
1.	C=C → CH-CH 1,5,9-Cylododecatriene → Cyclododecene	Pd/Al_2O_3	Intermediate for 121-laurolactum	6
2.	C≡C → CH=CH Butynediol → Cis-Butenediol	$Pd\text{-}Zn/CaCO_3$	Intermediate for vitamin-A & endosulfan	6
3.	RCHO → RCH_2OH Cinnamaldehyde → Cinnamyl alcohol	Pd-Ru/carbon nanotube	Perfumery	38
4.	RCOR → RCH_2OR	Ru/zeolite	Products used as solvents	39
5.	Reductive alkylation Azido sugars → secondary amines	Pd/C	Pharmaceutical and agriculture	40
6.	RC≡N → $RCH_2\text{-}NH_2$ Benzonitrile → Benzyl amine	Pd/C	Drugs, dyestuff and synthetic resins	41
7.	RC=N → RCH-NH Dibenzene imine → dibenzyl amine	Pd/C	Phrmaceuticals & agrochemicals	42
8.	R=NOH → $R\text{-}NH_2$ Cyclohexanone oxime → cyclohexyl amine	Raney Ni	Phrmaceuticals & agrochemicals	43
9.	RNO_2 → RNH_2 p-nitrophenol → p-amino phenol	Pd, Rh, Pt & Raney Ni	Pharmaceutical, Industrial dyes, Photographic developer, coatings.	44
10.	RN_3 → RNH_2 2-azido-2-phenylethanol → 2-amino-2-phenylethanol	Platinum oxide	Gelators	45
11	-COOH → $\text{-}CH_2OH$ Succinic acid → 1,4-butanediol	Ru-Co	Solvent, monomer for polyesters, and for manufacturing Tetrahydrofuran	46

1.3.4 Types of selectivity for heterogeneous catalytic hydrogenation

Numerous functional groups are hydrogenated in the presence of heterogeneous catalysts. For these, the activity and the selectivity of the catalysts is important. Different types of selectivities observed for hydrogenation reactions are well described by Tungler et al.,[47] as follows

a) Chemoselectivity: Hydrogenation of one functional group in the presence of other functional groups which can be hydrogenated, is defined as chemoselective hydrogenation.

   Example: hydrogenation of 4-chloronitrobenzene in methanol with Pd/C catalyst gives aniline. Under similar reaction conditions hydrogenation of 4-chloronitrobnezene with Raney Ni gives 4-chloroaniline. This demonstrates that Raney Ni catalyst is a chemoselective catalyst in the hydrogenation of halogen containing aromatic nitro compounds, as it doesn't cleave the halogen from the aromatic ring.

   The factors which affect the chemoselectivity are the type of catalyst used for hydrogenation, catalyst modification with other metals, poisoning of catalyst, reaction conditions and the solvent used for hydrogenation.

b) Regioselectivity: Selective hydrogenation of a functional group in presence of any other identical group in the same molecule. Regioselectivity can be demonstrated by the palladium catalyzed hydrogenation of β-naphthol, which contains two similar aromatic rings to hydrogenate. Under basic conditions the hydroxyl-substituted ring is hydrogenated, while in the presence of acids the unsubstituted ring is reduced producing aromatic tetralol in excess.

c) Stereoselectivity: Hydrogenation of a functional group to produce one stereo isomer of the product in preference to the other. Palladium catalysts can be used to produce stereochemically-enriched products. The hydrogenation of thymol in water at 383 K and 6 bars of H_2 pressure results in an equilibrium mixture of menthone isomers (60% menthone, 40% isomenthone), which are themselves hydrogenated after the thymol is almost completely converted. Under acidic conditions neomenthol is formed in excess, while under basic conditions menthol is formed with 75% stereoselectivity[48].

d) Enantioselectivity: The most sophisticated type of selectivity is enantioselectivity, where a prochiral compound is converted into a chiral product, and the enantiomers are not produced in a 1:1 ratio. Enantioselective hydrogenation using Raney Ni and platinum catalysts modified with the chiral compounds tartaric acid and cinchonidine respectively has been reported. For example hydrogenation of isophorone with Pd catalyst in presence of proline gave dihydroisophorone with 80% enantiomeric excess.[49]

1.3.5 Importance of hydrogenation products of carboxylic acids:

The hydrogenation of carboxylic acid is an industrially important reaction used for the synthesis of alcohols and aldehydes. These products find applications in cosmetics, surfactants, pharmaceuticals and alcohols and are also used as monomers for polyesters and as solvents. A list of products obtained by hydrogenation of carboxylic acids and their applications are given below in Table 1-4. From Table 1-4 it is clear that the hydrogenation of carboxylic acid using supported metal catalyst is an important reaction.

The hydrogenation of carboxylic acids to alcohols is a sequential reaction, which produces the aldehyde as an intermediate product. There are few studies in literature on the hydrogenation of mono- and dicarboxylic acids. There are still fewer studies on the kinetics of hydrogenation of mono and dicarboxylic acids. The literature on the hydrogenation of carboxylic acids is summarized in the next section.

Table 1-4: Hydrogenation products of carboxylic acid and their application.

Sr.	Carboxylic acid	Catalyst	Product	Application	Ref.
1	Maleic acid	Ru-Re/C	Tetrahydrofuran	Used as solvent	50
2	Succinic acid	Ru-Co	1,4-Butanediol	Solvent, monomer for polyesters, and for manufacturing tetrahydrofuran	51
3	Oleic acid	Ru-Sn/Al_2O_3	Oleyl alcohol	Surfactant, emulsifier and cosmetic products	52
4	Adipic acid	Co	1, 6-hexanediol and hydroxycaproic acid.	For manufacturing polyesters	53
5	Lauric acid	Copper chromite	Lauryl alcohol	Surfactant and cosmetics	54
6	Benzoic acid	Pd/C	Cyclohexane carboxylic acid	For manufacturing Nylon	103
7	Benzoic acid	ZnO	Benzaldehyde	Used in pharmaceuticals, agrochemicals, flavor and perfumery	55
13	1,4-cyclohexane carboxylic acid	Ru-Sn/Al_2O_3	1,4- cyclohexanedimethanol	Used in polyester, paints and synthetic fibers	56
14	Isophthalic acid	Pd/C	1,3-cyclohexane dicarboxylic acid	For manufacturing polymers	57
15	Terephthalic acid	Ru/C	1,4-cyclohexane dicarboxylic acid	For manufacturing polymers	58
16	1,3-cyclohexane carboxylic acid	Ru/C	1,3- cyclohexanedimethanol	For manufacturing polymers	59

1.3.6 Literature on hydrogenation of carboxylic acids

Hydrogenation of carboxylic acids gives primarily alcohols. The catalysts used for hydrogenation of carboxylic acids are Ru/C, Ru/Al_2O_3 and Ru-Sn on alumina[60]. Various other catalysts consisting of Pd-Re on alumina have been used for hydrogenation of nitro benzoic acid[61]. It is reported that Re_2O_7 forms synergistic combinations with Pd, Pt, Rh and Ru for hydrogenation of carboxylic acids[62]. It is also reported that hydrogenation of carboxylic acids is not very efficient at low pressures and temperatures, but when carried at high temperatures and high pressures, side reactions like decarboxylation of the acid and hydrogenolysis of product alcohol take place to give hydrocarbons which may poison the catalyst.[62] For unsaturated carboxylic acids, it is difficult to selectively hydrogenate carboxylic group in the presence of a C=C bond as the activation energy for hydrogenation of C=C is lower as compared to –COOH group.[6] Selective hydrogenation of carboxylic group has been achieved in the presence of the C=C bond by using 5% Pt on charcoal as a catalyst in the presence of ferrous chloride and zinc acetate promoter. Here, zinc ions inhibit the hydrogenation of C=C bond and ferrous ions promote reduction of carbonyl group[63].

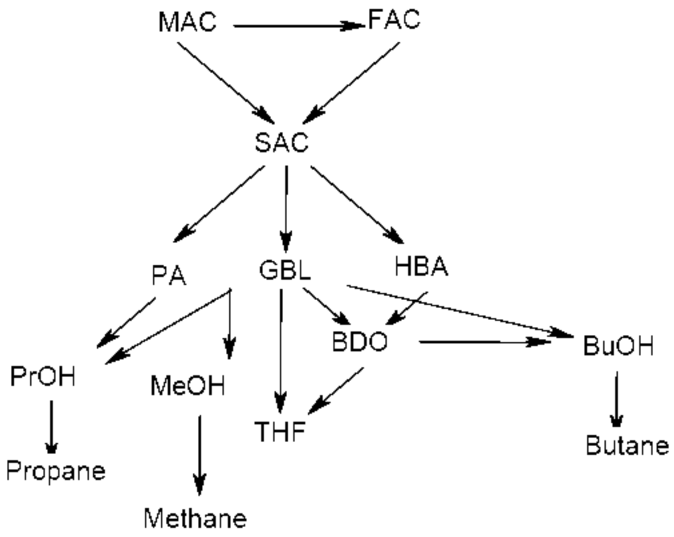
1.3.6.1 Hydrogenation of aliphatic carboxylic acids and aromatic carboxylic acids to alcohols

Studies related to hydrogenation of aliphatic and aromatic carboxylic acid is mostly patented and very little information is available in the open literature. Aliphatic acids which are hydrogenated for commercial purpose are maleic acid, glutaric acid, succinic acid, adipic acid, and oleic acid. Likewise, aromatic carboxylic acids which are hydrogenated are benzoic acid, terephthalic acid, isophthalic acid and phthalic acid.

1.3.6.1.1 Hydrogenation of maleic acid

Hydrogenation of maleic acid (MAC) gives products like gamma butyrolactone (GBL), tetrahydrofuran (THF) and 1,4-butanediol (BDO)[64]. This reaction is now used commercially for manufacture of BDO and THF. The earlier process for obtaining tetrahydrofuran and 1,4-butanediol was the Reppe process, based on acetylene and formaldehyde as starting materials[65]. These starting materials are hazardous as compared to maleic acid; also, maleic acid is obtained economically by oxidation of benzene or C_4 hydrocarbon, which gives maleic anhydride, which on hydrolysis in water gives maleic acid[66].

Hydrogenation of maleic acid is not a single step but involves a series of consecutive and parallel reactions as shown in Scheme 1-1.[50]

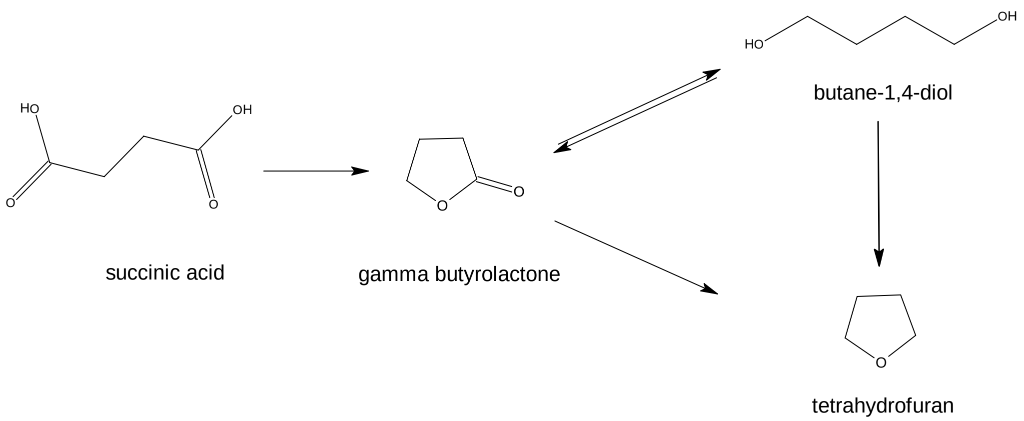


Scheme 1-1: Hydrogenation of maleic acid with Ru-Re/C catalyst.

The catalysts used for the hydrogenation of maleic acid consist of supported Pd, Re, and their combinations with Ni, Co, Mo[67]. Also, catalysts like copper chromites are used for hydrogenation of MAC[68]. This reaction is conducted in solvents like water, tetrahydrofuran, 1,4-dioxane, dimethoxymethane, or dimethoxy ether[69]. In hydrogenation of maleic acid the first step is addition of hydrogen across C=C bond to give succinic acid (SAC) which on further hydrogenation gives a stable intermediate γ-butyrolactone (GBL). Further hydrogenation of GBL gives 1,4-butanediol, and tetrahydrofuran. Under the reaction conditions maleic acid undergoes isomerization to give fumaric acid, which is a non-catalytic reaction. Hydrogenation of fumaric acid to succinic acid also proceeds in the same way as for maleic acid. Therefore, the isomerization step does not affect the overall kinetics of the reaction.[50] Hydrogenation of maleic acid to succinic acid is a fast step but further hydrogenation of succinic acid to GBL and THF are slower steps and require harsh conditions compared to hydrogenation of maleic acid to succinic acid. In this entire sequence, the activation energy for hydrogenation of GBL to THF was the highest compared to other steps, so increasing the reaction temperature and pressure increases the selectivity towards THF[70]. In this reaction THF is obtained by two paths, one by the hydrogenation of GBL and other by the dehydration of BDO. The majority of THF is obtained by hydrogenation of GBL and not by dehydration of BDO. It is observed that dehydration of BDO does not occur in aqueous medium so this step may not be important when the reaction is carried out in presence of water. When acidic medium is used for hydrogenation of MAC, THF formation is favored[71]. There is equilibrium between GBL and BDO, which is dependent on hydrogen pressure and temperature. Higher hydrogen pressure and lower temperature shifts the equilibrium towards BDO[72]. During the reaction, hydrogenation of succinic acid does not commence before the complete hydrogenation of maleic acid. A similar trend is observed for hydrogenation of GBL, which is due to strong substrate inhibition effect shown by maleic acid and succinic acid. The extent of inhibition decreases in following order, MAC > SAC > GBL. Since hydrogenation of maleic acid is multi step consecutive reaction, maxima for concentration of SAC and GBL are observed in the concentration versus time profile for the reaction.

1.3.6.1.2 Hydrogenation of succinic acid

Hydrogenation of succinic acid (SAC) gives the same products as are obtained by hydrogenation of maleic acid as SAC is also a C_4 dicarboxylic acid. The only difference is that succinic acid is a saturated C_4 acid whereas maleic acid is an unsaturated C_4 acid. During hydrogenation of maleic acid as shown in Scheme 1-2, the first step is the hydrogenation of C=C bond of maleic acid to give succinic acid. The product profile and selectivity for other products in the hydrogenation of the SAC remain the same.



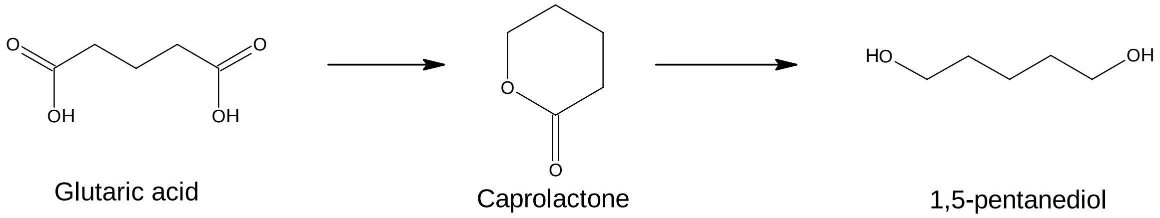
Scheme 1-2: Hydrogenation of succinic acid Pd-Re/C.

Hydrogenation of succinic acid at 473 K and 35 bar of hydrogen pressure in aqueous medium with 1%Pd-4%Re catalyst supported on oxides of Ti and Zr gives 90% selectivity to GBL at a SAC conversion of 100%. Other products which are obtained are THF (2%) and BDO (8%)[73]. Hydrogenation of succinic acid is also reported with Ru-Co catalyst, which was found to show a synergistic effect of Ru and Co. The products formed were BDO, THF and butanol. A comparative study for hydrogenation of succinic acid with mono metallic Ru, Co and bimetallic Ru-Co catalyst showed that activity of Ru-Co catalyst was higher than monometallic Ru and Co catalysts. The rate of 1% Ru-Co catalyst was three times that of pure Co metal catalyst. A 100% conversion of SAC on Ru/C and Co catalyst occurred in 7 and 5.5 hrs respectively, while with 1%Ru-Co 100% conversion of SAC was achieved in 2 hrs. Higher selectivity towards the final products (THF and BDO) was achieved with Ru-Co catalyst. Increasing Ru content in Ru-Co catalyst was found to accelerate hydrogenation of BDO to butanol. Hence optimum Ru content in catalyst was necessary to avoid formation of undesired products.[46]

Hydrogenation of SAC is also reported with trimetallic Ru-Pt-Sn/SiO_2 catalyst at 240 ^oC and a hydrogen pressure of 7 MPa. The products obtained were THF, GBL and BDO, and the major product formed was THF, formed with 67.8% selectivity[74].

1.3.6.1.3 Hydrogenation of glutaric acid

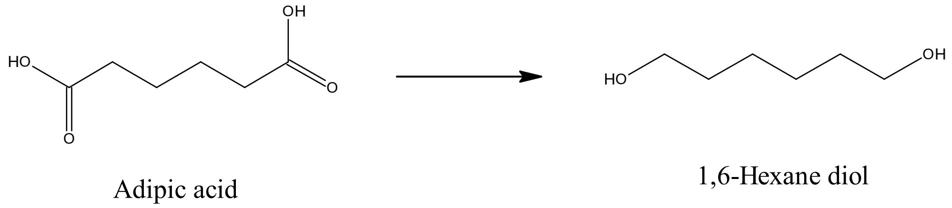
Hydrogenation of glutaric acid with Ru-Sn/C gives 1,5-pentanediol which is used as a monomer for manufacturing polyesters[75]. The reaction scheme for the hydrogenation of glutaric acid is shown in Scheme 1-3.



Scheme 1-3: Hydrogenation of glutaric acid with Ru-Sn/C catalyst.

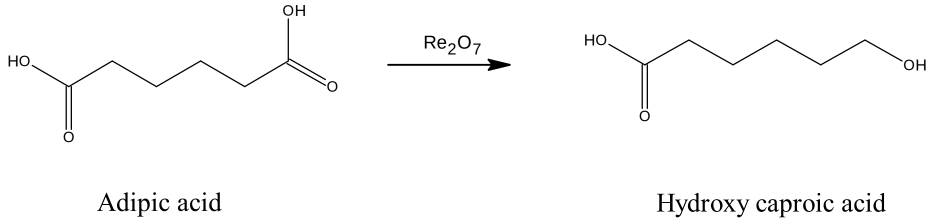
1.3.6.1.4 Hydrogenation of adipic acid.

Adipic acid on hydrogenation with Ru-Pt-Sn/C catalyst at 230° C gives 93.2% 1,6-hexanediol[76] as shown Scheme 1-4. Hydrogenation of adipic acid with Ru-Sn/Al_2O_3 catalyst is reported to give 97.3% conversion with 89.4% selectivity to 1,6-hexane diol[77].



Scheme 1-4: Hydrogenation of adipic acid with Ru-Pt-Sn/C catalyst.

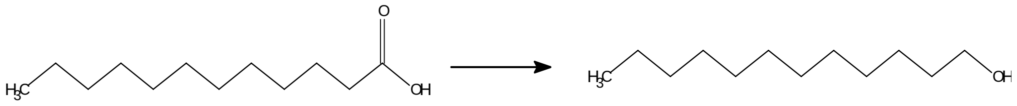
With Mo and Co catalyst hydrogenation of adipic acid at 220 °C and 250 kg/cm^2 hydrogen pressure gave 91% selectivity to 1,6-hexanediol with 40% conversion[78], while with Co catalyst at 210 °C and 50 kg/cm^2 of hydrogen pressure a 75% conversion of adipic acid and 92% selectivity to 1,6-hexanediol was obtained[79]. Hydrogenation of adipic acid with Re_2O_7 catalyst gave hydroxy caproic acid as shown in Scheme 1-5[80].



Scheme 1-5: Hydrogenation of adipic acid with Re_2O_7 catalyst.

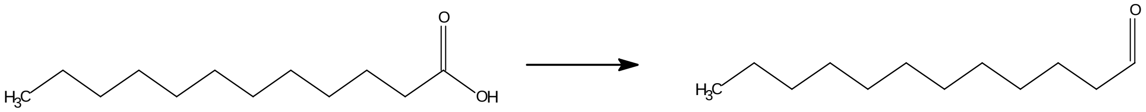
1.3.6.1.5 Hydrogenation of Dodecanoic acid

Hydrogenation of dodecanoic acid (also known as lauric acid) gives dodecanol (lauryl alcohol) and dodecanal (lauraldehyde) as shown in Scheme 1-6 and Scheme 1-7.



Lauric acid Lauryl alcohol

Scheme 1-6: Hydrogenation of lauric acid with copper chromite catalyst.



Lauric acid Lauraldehyde

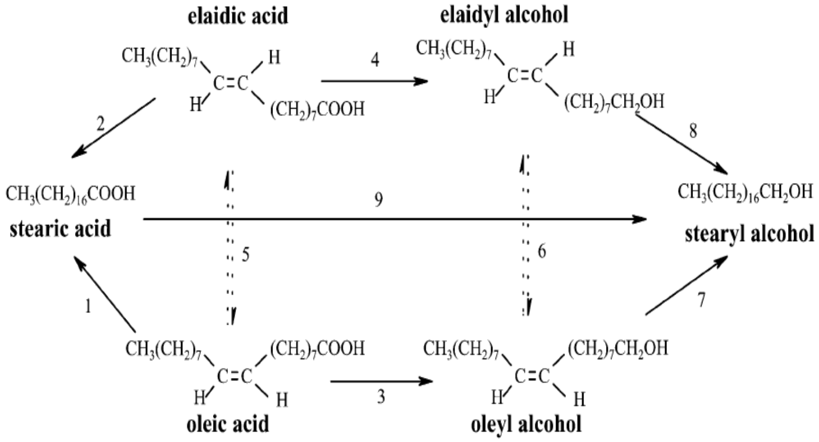
Scheme 1-7: Hydrogenation of lauric acid with zirconia catalyst.

These products are used in detergents, cosmetics and in perfumes[81]. The literature reported for hydrogenation of lauric acid to lauryl alcohol and lauraldehyde is mainly patented and no detailed information is available.

In earlier days, dodecanoic acid was esterified with dodecanol and then hydrogenated to give dodecanol[82]. Various copper based catalysts like copper chromite, Cu/Al_2O_3, Cu/Al_2O_3-SiO_2 and Cu/Al_2O_3-ZnO and Cu/ZnO have been reported for hydrogenation of lauric acid and it was observed that copper chromite catalysts were stable[83].Hydrogenation of lauric acid to lauraldehyde is reportedly conducted in fixed bed reactors using zirconium oxide catalyst doped with chromium. The selectivity for lauraldehyde in this process was 77% with 92.8% conversion of lauric acid[84]. Lauraldehyde can also be obtained by hydroformylation of 1-undecene with rhodium catalyst.[85] These two methods have their limitations as hydroformylation with homogeneous catalyst has catalyst separation problems and hydrogenation with heterogeneous zirconia catalyst has to be carried out at very high temperatures.

1.3.6.1.6 Hydrogenation of oleic acid

Oleic acid is an unsaturated fatty acid and the major challenge for hydrogenation of this acid is to selectively hydrogenate –COOH group to get unsaturated fatty alcohols. Scheme 1-8 shows the possible reaction pathways for the hydrogenation of oleic acid.



Scheme 1-8: Hydrogenation of oleic acid with Ru-Sn catalyst.

As shown, the possible reactions are a) hydrogenation of C=C to give stearic acid; b) the isomerization of C=C bond to give elaidic acid; c) the hydrogenation of the carboxylic group to give unsaturated oleyl alcohol.

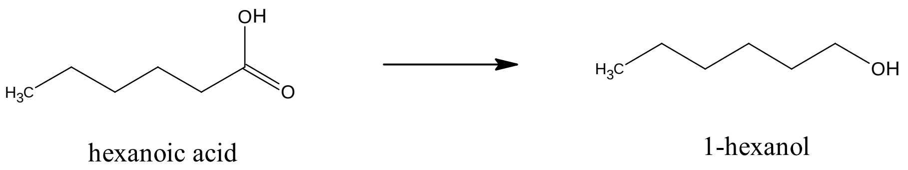
Mizukami and co-workers assessed the performance of different Ru-Sn catalysts in the selective hydrogenation of oleic acid to unsaturated acid and have shown that the activity of the sol-gel Ru-Sn catalyst depends on the nature of the support. They have also reported that alumina was the best support for Ru-Sn catalyst in terms of activity and selectivity in comparison with zirconia, silica and titania[86]. Costa et al. studied the hydrogenation of oleic acid over alumina supported sol-gel Ru and Ru-Sn catalysts and have shown that besides its selective hydrogenation activity, these Ru-Sn catalysts promote the cis-trans isomerization of the unsaturated acid, a reaction which seems to compete with that of alcohol production.[52]

Mendes et al.[87] have reported Ru-Sn/TiO_2 catalyst to be more selective to unsaturated alcohol as compared to Ru-Sn-B/Al_2O_3 catalyst. They also observed Ru-

Sn/TiO_2 catalyst to be more active and selective for hydrogenation of oleic acid to unsaturated alcohol than the alumina supported Ru-Sn catalyst prepared by sol-gel method.

1.3.6.1.7 Hydrogenation of Hexanoic acid

Hexanoic acid (caproic acid) on hydrogenation gives 1-hexanol as shown in Scheme 1-9.



Scheme 1-9: Hydrogenation of hexanoic acid with Ni or Pt catalyst.

The hydrogenation of hexanoic acid was carried out by Aly et al.[88] with copper chromite, nickel and platinum catalysts. The hydrogenation of hexanoic acid with copper chromite catalyst gave the ester and small amounts of hexanol and hexane. The alcohol was formed from the hydrolysis of ester of hexanoic acid and hexanol. The addition of water to the reaction mixture was not found to have much influence on selectivity to hexanol. The nickel and platinum catalyst were found to be more active for the hydrogenation as compared to the copper catalyst, and here too besides 1-hexanol, hexane was also obtained. As the reaction time increases, the selectivity to 1-hexanol was found to increase for all the three catalysts, which might be due to hydrogenation of ester.

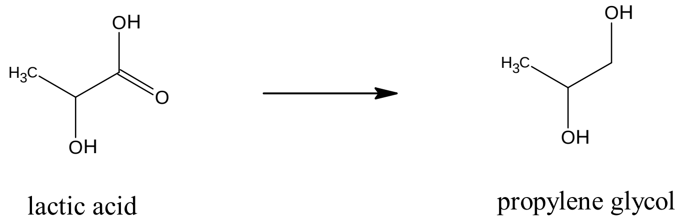
The hydrogenation of acetic acid, oxalic acid and hydroxyacetic acid are some other aliphatic carboxylic acids reported [89]. The catalyst used for the study was 10% Ru/C. Hydrogenation of acetic acid with this catalyst gave ethanol with 88% yield, Hydrogenation of oxalic and hydroxyacetic acids both under similar conditions gave ethylene glycol with 47% and 83% yield respectively.

Other monocarboxylic acids for which the hydrogenation to alcohol is reported are octanoic acid to octyl alcohol (100% selectivity) with Ru-Re catalyst[90], L-ascorbic acid to L-Gulono-γ-lactone with Ru/C catalyst with 87% selectivity[91] and decanoic acid to decanol (>90% selectivity) using Re-Os bimetallic catalyst[92]. Other dicarboxylic acids which are studied for hydrogenation are pentadecanedioic acid with Rh-Re/Al_2O_3 catalyst to give 1,15-pentadecanediol (57%) and sebacic acid to 1,10-decanediol (69%) with Ru-Re/C catalyst.

1.3.6.1.8 Hydrogenation of lactic acid

Biomass-based organic acids are attractive feed stocks for chemical production nowadays because they are increasingly becoming available in commercial quantities at low cost. Lactic acid is one such material. The synthesis of biodegradable poly-lactic acid polymer from lactic acid has sparked extensive research by several major corporations to produce and recover pure lactic acid via fermentation of corn-derived glucose. World wide production of lactic acid has increased steadily since the 1990s[93]. 1,2-Propylene glycol (PG) is a valuable commodity chemical that finds many uses in food, consumer products and chemical applications. Currently the industrial process for producing PG is by hydration of propylene oxide[94]. The earliest production of PG by hydrogenation was reported by Adkins and coworkers who converted ethyl lactate to PG over Raney nickel to obtain PG with 88% yield[95]. The first catalytic hydrogenation of free lactic acid was conducted by Broadbent et al. [96] using unsupported rhenium black as catalyst. They achieved 84% PG after 8 hr at 150 °C and 27 MPa of hydrogen pressure.

Zhang et al.[97] have recently reported hydrogenation of lactic acid with Ru/C catalyst (Scheme 1-10). They have screened catalysts like Pd/C, Ni/Al_2O_3, copper chromite, Raney Ni, Ru/TiO_2 and Ru/Al_2O_3 and it was observed that Ru/C catalyst was the best catalyst for hydrogenation of lactic acid.



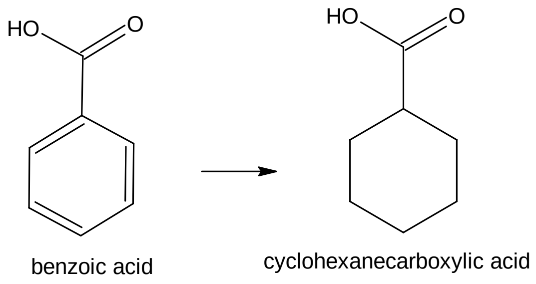
Scheme 1-10: Hydrogenation of lactic acid with Ru/C catalyst.

The parametric effect for this catalyst revealed that increasing reaction temperature increases the conversion but decreases the selectivity to PG due to side reactions. Increasing pressure was observed to increase both conversion and selectivity to PG. Conversion of lactic acid decreases with increasing lactic acid concentration in the reaction mixture. When catalyst loading was increased, the rate increased but selectivity to PG decreased slightly due to the increased exposure of PG to the catalyst. From the parametric study it was understood that optimum reaction conditions are required for achieving high selectivity to PG.[97]

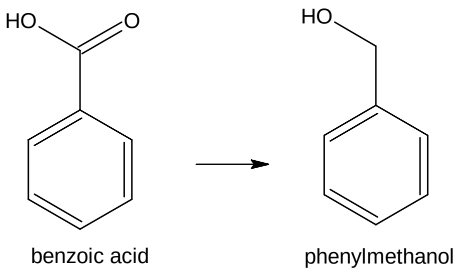
Similar studies are described in patents for the preparation of optically active alcohols by reducing optically active carboxylic acids with hydrogen in presence of ruthenium catalysts. Carboxylic acids with an alpha or beta substituents hydrogenated to alcohols at temperatures lower than 160°C and pressures less than 20 MPa[98].

1.3.6.1.9 Hydrogenation of benzoic acid

Benzoic acid has two functional groups which can be hydrogenated, and depending on the group which is hydrogenated, the product profile varies. Cyclohexane carboxylic acid is obtained when only the aromatic ring of the benzoic acid is hydrogenated and benzyl alcohol is obtained when only the carboxylic group is hydrogenated, as shown in Scheme 1-11 and Scheme 1-12.

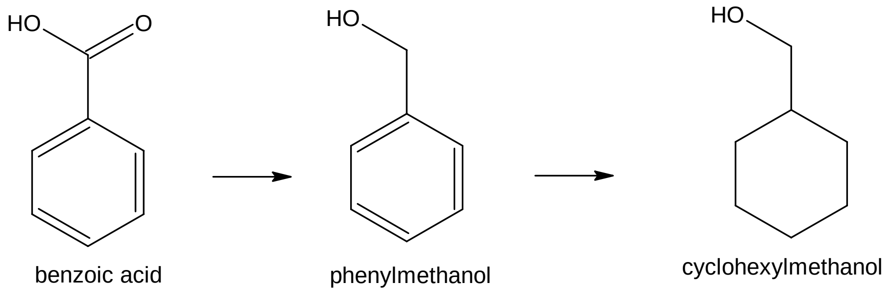


Scheme 1-11: Selective hydrogenation of aromatic ring.



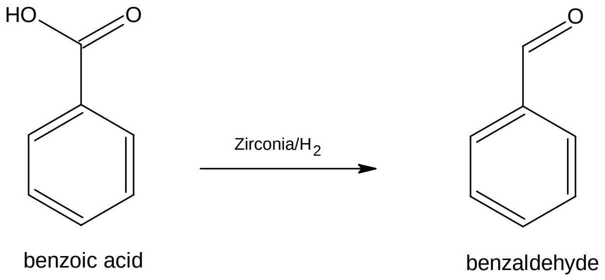
Scheme 1-12: Selective hydrogenation of carboxylic group.

When both the functional groups of benzoic acid are hydrogenated, the product obtained is cyclohexyl methanol as shown in Scheme 1-13.

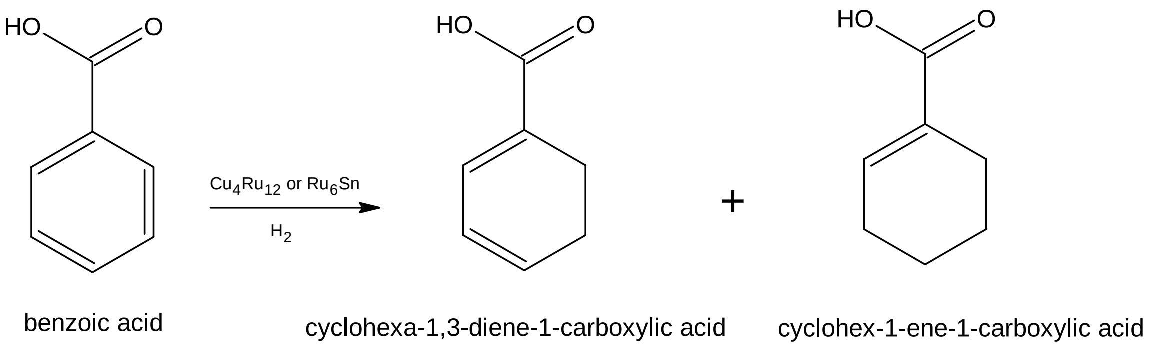


Scheme 1-13: Hydrogenation of both aromatic ring and carboxylic group

Partial hydrogenation of carboxylic group of benzoic acid leads to benzaldehyde. When partial hydrogenation of aromatic ring occurs two products are obtained 1,3-cyclohexadiene-1- carboxylic acid and 1-cyclohexene carboxylic acid as shown in Scheme 1-14 and Scheme 1-15 respectively.



Scheme 1-14: Partial hydrogenation of carboxylic group.



Scheme 1-15: Partial hydrogenation of aromatic ring.

Selectively obtaining benzyl alcohol by hydrogenating carboxylic group of benzoic acid is difficult, as benzyl alcohol formed during reaction undergoes hydrogenolysis to give to products like toluene and methyl cyclohexane[99].

Cyclohexane carboxylic acid is used in the manufacture of caprolactam, which is further used for production of Nylon by Snia Vicosa process[100]. Benzyl alcohol is used as solvent, degreasing agent and as bacteriocide. Although cyclohexyl methanol does not have major industrial applications it is still used as a solvent for polymers. Benzaldehyde is used as intermediate in pharmaceuticals and cosmetics. Hydrogenation of benzoic acid is thus an important subject for catalyst designing as it gives a variety of hydrogenation products.

Cyclohexane carboxylic acid is obtained by hydrogenation of benzoic acid with Ru_5Pt_1 encapsulated in mesoporous silica with 78% conversion and 99.5% selectivity to cyclohexane carboxylic acid. When Ru_6Sn encapsulated in mesoporous silica was used for hydrogenation of benzoic acid, 16% conversion of benzoic acid was obtained with 42% of cyclohexene-1-carboxylic acid and 48% of 1,3-cyclohexadiene-1-carboxylic acid[101].Hydrogenation of benzoic acid with Cu_4Ru_{12} catalyst encapsulated in mesoporous silica, gave 21 % conversion of benzoic acid, with 80% cyclohexene-1-carboxylic acid and 20% 1,3-cyclohexadiene-1-carboxylic acid respectively[101]. Hydrogenation of benzoic acid with Rh/Al_2O_3 at 155°C gives 99% selectivity to cyclohexane carboxylic acid with 98% conversion of benzoic acid was obtained[102]. With 5% Pd/C at 180°C and hydrogen pressure of 600 psi, a yield of 95% for cyclohexane carboxylic acid.[103] Addition of Ni to Pd/C catalyst was found to increase the activity for hydrogenation of benzoic acid to cyclohexane carboxylic acid[104].

Vapor phase hydrogenation of benzoic acid with $MnO_2/ZnO\text{-}ZnAl_2O_4$ catalyst at 380°C gave 83.8% selectivity to benzaldehyde with 100% conversion[105]. Hydrogenation activity for benzoic acid to benzaldehyde over zirconium oxide catalyst was enhanced when the catalyst was doped with Cr_2O_3. The main role of Cr_2O_3 was considered to be activating hydrogen[106]. ZnO is also reported for the hydrogenation of benzoic acid to benzaldehyde at 350°C, with 100% conversion of benzoic acid and 98% selectivity to benzaldehyde[107]. Gas phase hydrogenation of benzoic acid with Ru/SnO_2 catalyst gave

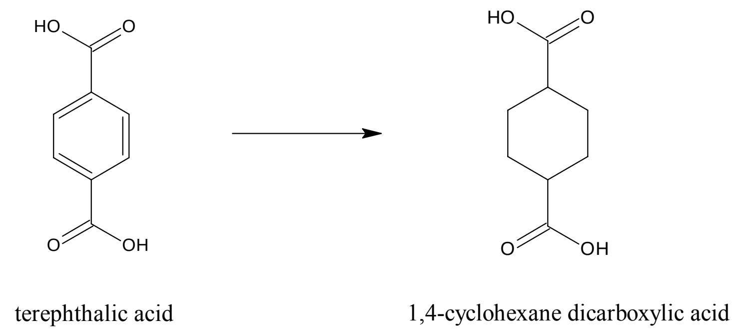
91.3% selectivity to benzaldehyde at 77.4% conversion[108]. Majority of the literature for the hydrogenation of benzoic acid to benzaldehyde is on vapor phase reaction and there is practically no report on liquid phase hydrogenation of benzoic acid to benzaldehyde.

1.3.6.1.10 Hydrogenation of terephthalic acid

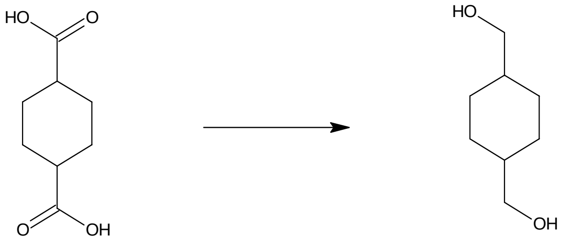
Terephthalic acid is an aromatic dicarboxylic acid which has two carboxylic groups, which can be hydrogenated along with the aromatic ring. The products which can be obtained by hydrogenation of terephthalic acid are 1,4-cyclohexane dicarboxylic acid, 1,4-benzene dimethanol and 1,4-cyclohexane dimethanol. All these products are used in polymer industry for making polyester.

The catalysts reportedly active for hydrogenation of terephthalic to 1,4-cyclohexane dicarboxylic acid are Ru/C[109]**,** Pd/C[110]**,** and Pd-Ba/C[111]**.** Hydrogenation of terephthalic acid to 1,4-cyclohexane carboxylic acid is generally carried out at 303 K to 443 K and a hydrogen pressure of 1-6 MPa.

Hydrogenation of terephthalic acid to 1,4-cyclohexane dimethanol cannot be done simultaneously, as cyclohexane dicarboxylic acids are prone to undergo hydrogenolysis to give products like 4-methyl-1- cyclohexane carboxylic acid, 1,4-dimethyl cyclohexane and methyl cyclohexane[112]. So, first the hydrogenation of terephthalic acid to 1,4-cyclohexane dicarboxylic acid is carried out with Ru/C or Pd/C (Scheme 1-16) catalyst and then the cyclohexane dicarboxylic acid is hydrogenated to cyclohexane dimethanol (Scheme 1-17) using Ru-Sn and Ru-Sn-Pt based catalysts[113]. The reaction conditions used for hydrogenation of 1,4-cyclohexane dicarboxylic acid are reaction temperature of 523 K and hydrogen pressure of 12 MPa.



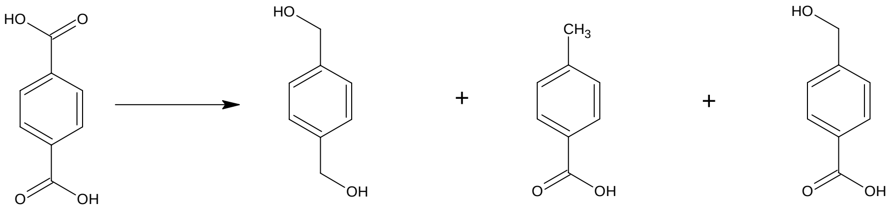
Scheme 1-16: Hydrogenation of terephthalic acid with Pd or Ru/C catalyst.



1,4-cyclohexane dicarboxylic acid 1,4-cyclohexane dimethanol

Scheme 1-17: Hydrogenation of 1,4-cyclohexane dicarboxylic acid with Ru-Sn catalyst.

When the carboxylic groups of terephthalic acid are hydrogenated we obtain 1,4-benzenedimethanol. Hydrogenation of carboxylic groups of terephthalic acid is not an easy task, as other products like p-toluic acid, p-hydroxymethylbenzoic acid are obtained along with 1,4-benezene dimethanol. Ru-Sn/Al_2O_3 catalysts was reported for hydrogenation of terephthalic acid to 1,4-benzenedimethanol.[77] Hydrogenation of terephthalic acid was carried at 513 K and 6.5 Mpa of hydrogen pressure. Overall productivity of this reaction was low as selectivity for benzene dimethanol was low (19.3%) and the selectivity to side products like p-toluic acid and p-hydroxymethylbenzoic acid was 32%,[77] as shown in Scheme 1-18.



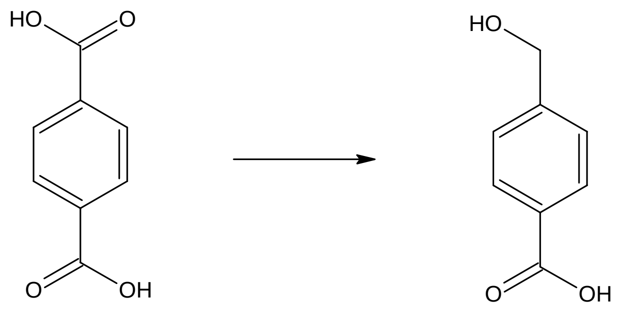
terephthalic acid 1,4-benezenedimethanol Toluic acid p-hydroxymethyl benzoic acid

Scheme 1-18: Hydrogenation of terephthalic acid with Ru-Sn catalyst.

It is reported that as atomic ratio of Ru to Sn in Ru-Sn/Al_2O_3 catalyst increases from 0 to 2 selectivity for hydrogenation of terephthalic acid increases from 0 to 20%.

Toba et al. have reported that highest amount of byproducts are formed for hydrogenation of terephthalic acid as compared to succinic acid, glutaric acid and adipic acid, which confirms the reactivity of terephthalic acid for hydrogenation as compared to the linear carboxylic acids.[77]

Hydrogenation of terephthalic acid when carried out with rhenium oxide (ReO_3) catalyst at 160-175^{o}C at 1800 psi of hydrogen pressure gave 20% conversion of terephthalic acid with 85% selectivity to p-hydroxymethyl benzoic acid as shown in Scheme 1-19.[114]

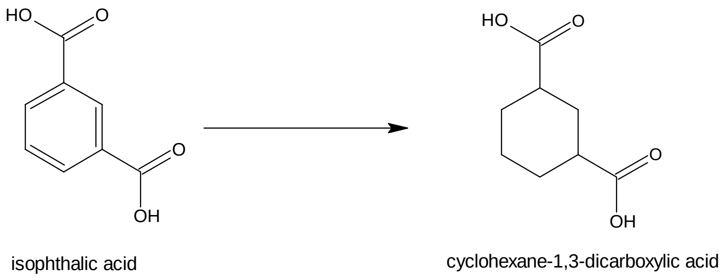


terephthalic acid p-hydroxymethyl benzoic acid

Scheme 1-19: Hydrogenation of terephthalic acid with ReO_3 catalyst.

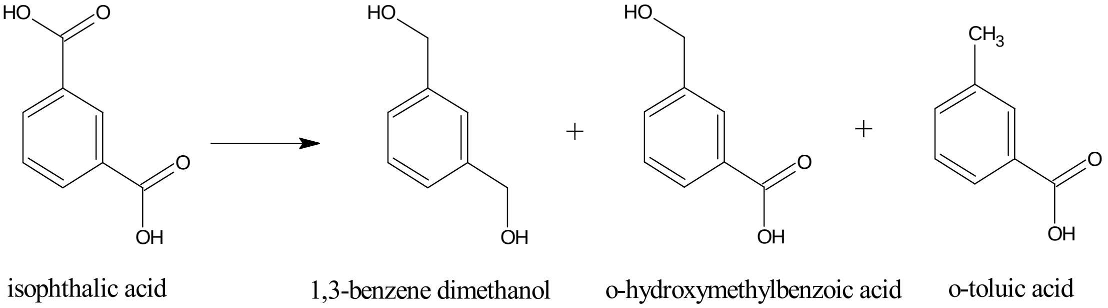
1.3.6.1.11 Hydrogenation of isophthalic acid

There is no detail report in literature on the hydrogenation of isophthalic acid. However, similar to terephthalic acid, hydrogenation of isophthalic acid gives products depending on the functional group which is hydrogenated. Hydrogenation of aromatic ring of isophthalic acid gives 1,3-cyclohexane dicarboxylic acid whereas hydrogenation of carboxylic group gives 1,3-benezenedimethanol. Other products like m-hydroxymethyl benzoic acid and m-toluic acid are also obtained if hydrogenation of single carboxylic group occurs. There is also no report on the partial hydrogenation of aromatic ring to give products like 1,2-cyclohexene dicarboxylic acid or 1,2-cyclohexadiene dicarboxylic acid. Also, no report related to partial hydrogenation of carboxylic group of isophthalic acid to give respective aromatic aldehyde is available. The catalysts which are used for hydrogenation of isophthalic acid to 1,3-cyclohexane dicarboxylic acid (Scheme 1-20) are Rh/C, Pd/C, and Ru/C[115].



Scheme 1-20: Hydrogenation of isophthalic acid with Rh/C, Pd/C or Ru/C catalyst.

1,3-cyclohexane dicarboxylic acid is also obtained by hydrogenation of disodium salt of isophthalic acid[116]. 1,3-cyclohexane dicarboxylic acid is useful as an intermediate for resins with excellent weatherability, thermal resistance and physical strength and is also used in pharmaceuticals[117]. 1,3-benezenedimethanol finds applications in polyesters. Selective hydrogenation of carboxylic group to 1,3-benzenedimethanol is difficult. Hydrogenation of isophthalic acid with Ru-Sn/Al_2O_3 catalyst is reported to give only 9.2% of 1,3-benzenedimethanol and 32.5% 3-hydromethyl benzoic acid and selectivity to the hydrogenolysis products was 33.3% (Scheme 1-21).[77] From this it is understood that the low selectivity to 1,3-benzenedimethanol is due high reactivity of hydroxymethyl group of 3-hydromethyl benzoic acid, which undergoes hydrogenolysis to give o-toluic acid[77].

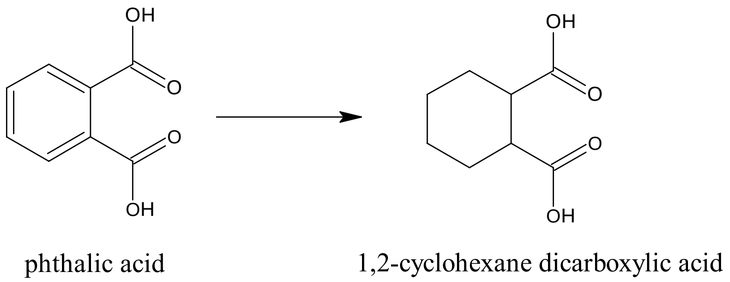


Scheme 1-21: Hydrogenation of isophthalic acid with Ru-Sn/Al_2O_3 catalyst.

1.3.6.1.12 Hydrogenation of phthalic acid

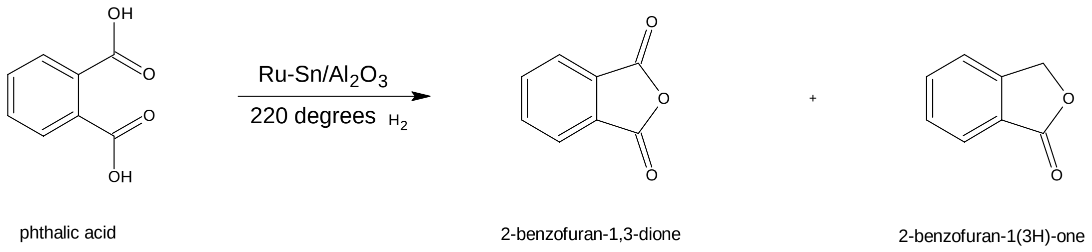
Phthalic acid is an aromatic dicarboxylic acid in which the two carboxylic groups are ortho in position, as a result of which it can undergo dehydration to form an anhydride[118]. Thus the hydrogenation of phthalic acid to 1,2-benzenedimethanol is not achieved easily.

Hydrogenation of phthalic acid is also found to give different hydrogenation products depending on the catalyst used for reaction. In presence of Pd/C catalyst at 170 °C and hydrogen pressure of 0.47 MPa phthalic acid gives 1,2-cyclohexane dicarboxylic acid (Scheme 1-22)[119]. The hydrogenation product of 1,2-cyclohexane dicarboxylic in the form of esters is used as plasticizer [120].



Scheme 1-22: Hydrogenation of phthalic acid with Pd/C catalyst.

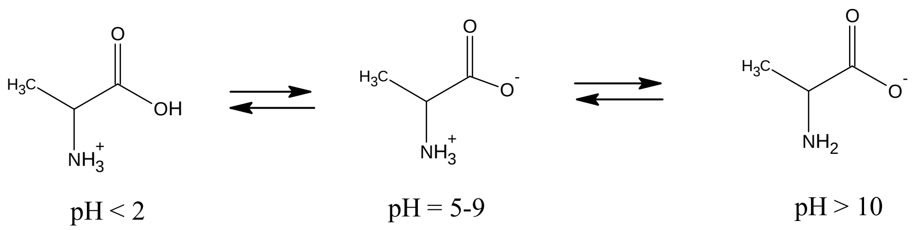
When hydrogenation of phthalic acid is carried out with Ru-Sn/Al_2O_3 catalyst at 513 K and hydrogen pressure of 6.5 MPa, phthalide is obtained with 80.4% selectivity at complete conversion of phthalic acid (Scheme 1-23).[77] This phthalide is used as a pharmaceutical intermediate.



Scheme 1-23: Hydrogenation of phthalic acid with Ru-Sn/Al_2O_3.

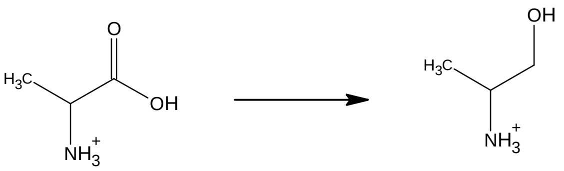
1.3.6.2 Hydrogenation of amino acids to amino alcohols

Amino alcohols are important building blocks in agriculture[121], pharmaceuticals and peptide chemistry[122] and are also used as chiral auxiliaries[123]. Ager et al. have reduced amino acids using expensive and hazardous hydride reagents[124]. Jere et al.[125] have reported hydrogenation of the simplest amino acid, L-alanine [(S)-2-aminopropanoic acid] with 5% Ru/C catalyst to L-alaninol [(S)-2-amino-1-propanol]. The hydrogenation reactions were carried in stirred batch reactors at 90-150°C and 250-1000 psi pressure. Conversion of alanine increases markedly when an excess of phosphoric acid was added to form protonated alanine. This is because in neutral medium alanine is present as a zwitterion which is a carboxylate ion and hydrogenation of carboxylate ion is thermodynamically not feasible. When phosphoric acid is added to the reaction mixture, the carboxylate ion is converted to carboxylic group which can be hydrogenated as shown in Scheme 1-24.



Scheme 1-24: Effect of pH on L-alanine.

With sufficient phosphoric acid L-alaninol was formed with a selectivity >95% and >99% enantiomeric excess (ee). At the end of reaction L-alaninol was found to slowly racemize to D-alaninol along with C–C hydrogenolysis to form ethyl amine. When the reaction was carried out at 100°C instead of 150°C, the rate of hydrogenation decreases and racemization was arrested. They also found that there was no effect of hydrogen pressure above 1000 psi on the activity of catalyst. The hydrogenation of L-alanine with 5% Ru/C catalyst is shown in Scheme 1-25.



L-alanine L-alaninol

Scheme 1-25: Hydrogenation of L-alanine with 5% Ru/C catalyst in presence of phosphoric acid.

1.3.6.3 Partial hydrogenation of carboxylic acids to aldehydes

The ability to synthesize industrially important chemicals like aldehydes from cheap and renewable carboxylic acids is highly desirable, particularly if it can be achieved by direct hydrogenation of carboxylic acids. These reactions are particularly important for long chain aliphatic carboxylic acids like lauric acid to obtain lauraldehyde which is used in cosmetics. However, very few detailed studies have been conducted on these reactions. Aromatic aldehydes too belong to the group of fine chemicals being important as intermediates in organic chemistry[126]. They are used for the production of pharmaceuticals, agrochemicals and some of them are directly used as perfumes and flavours. There are many synthetic routes to produce aromatic aldehydes, but only the partial oxidation of toluene to benzaldehydes and the route via benzyl chloride are applied commercially[127]. Due to many disadvantages of these processes like low yields or low selectivities and large amounts of by-products such as inorganic salts, a new ecologically beneficial and benign synthetic route should be preferred.

The direct hydrogenation of benzoic acid over chromium modified zirconia catalysts was realized as an industrial process by Mitsubishi Chemicals in 1988. Benzaldehyde and its derivative were produced with a product capacity of 2000 tons per year with a 96% selectivity of benzaldehyde at a conversion of 98%. It is reported that the high selectivity obtained by using zirconia catalyst is due to its amphoteric surface properties[128]. Yokoyama et al. [129] reported hydrogenation of benzoic acid to benzaldehyde using ZrO_2 catalyst at 400 ^{o}C. Low conversion of about 53% was obtained with 97% selectivty to benzaldehyde. Holderich et al.[130] have obtained high yields of benzladehyde and various derivatives via direct hydrogenation of aromatic carboxylic acids using zinc oxide catalysts having specific features as very weak acidic sites, in addition to relatively strong basic sites and a rather small specific surface area of about 2-

17 m^2 per gram catalyst. Benzaldehyde was obtained with high yields of about 90% and selectivity upto 96%. They also report that stronger acidic sites on zinc oxide catalyst caused a consecutive hydrogenation of benzaldehyde to toluene and coke formation.

The mechanism for hydrogenation of carboxylic acids to aldehydes is not well studied. Acetic acid is used as a model compound to probe both carboxylic acid adsorption and its kinetic behaviour on metals, metal oxide and supported metal catalyts because of its molecular simplicity. Pestman et al.[131] found that oxides such as Fe_2O_3 and SnO_2 which can be reduced easily were active for hydrogenation of acetic acid to acetaldehyde, and this selective reaction over Fe_2O_3 was suggested to occur via a Mars-Van Krevelen- type of mechanism in which lattice oxygen and oxygen vacancies participate in the reaction. Further investigation on behaviour of acetic acid hydrogenation over Pt supported on TiO_2, SiO_2, Al_2O_3 and Fe_2O_3 was done by Willy Rachmady et al.[132] In their study they observed that hydrogenation of acetic acid to acetaldehyde involves both platinum metal and oxide support, and the reaction takes place at sites on the oxide surface. The principal role of Pt in this case is to serve as source of mobile, activated hydrogen atoms. In their study they also observed that Pt/Fe_2O_3 catalyst gave highest selectivity of 80% (Conversion 4%) as compared to Pt catalyst supported on TiO_2, SiO_2, Al_2O_3, for which the selectivty to actaldehyde was 0% (Conversion 6%). The difference in selectivity for acetaldehyde was related to the adsorption strength of acetic acid and acetaldehyde on the catalyst. A large adsorption equilibrium constant would result in a high surface concentration of acetaldehyde, and would thus favor further hydrogenation to ethanol. Thus, the much higher acetaldehyde selectivity of Pt/Fe_2O_3 catalyst implies a much lower surface coverage of acetaldehyde due to a higher rate of desorption on this catalyst during competitive adsorption compared to Pt/ TiO_2 catalyst[132].

1.4. Hydrogenation of esters to alcohols

Hydrogenation of carboxylic acid esters to alcohols is a high pressure reaction. Industrially, alcohols are produced from carboxylic acid esters using copper chromite based catalysts, which operate in the pressure range 250-300 atmospheres and a temperature of 250-300^o C. A number of variations of copper chromite catalyst systems have been patented.[133]

Turek et al.[134] have studied hydrogenation of dimethyl succinate with copper chromite and copper on silica catalysts. They have proposed that with this catalyst first hydrogenolysis of dimethyl succinate takes place to give γ-butyrolactone and methanol and further hydrogenation of γ-butyrolactone gives tetrahydrofuran and water. They also reported that addition of zinc oxide to copper catalysts increases the hydrogenolysis of dimethyl succinate to γ-butyrolactone. Kinetics of diethyl maleate with copper chromite catalyst was investigated in a fixed-bed catalytic reactor and a rate model was proposed based on Langmuir-Hinshelwood type mechanism. Hydrogenation experiments were also carried out on a pilot plant scale (1.5 kg catalyst capacity) and the reactor performance was found to agree reasonably well with the predictions of a theoretical model.[70]

In addition to the copper catalysts, other catalysts which have been reported for hydrogenation of fatty esters to fatty alcohols are palladium-rhenium and rhodium-tin systems[135]. While there are many reports in the literature on catalysis for the hydrogenation of saturated fatty acid esters to alcohols, hydrogenation of methyl oleate to oleyl alcohol remains a much bigger challenge to catalytic chemists. This process is very important in view of the extensive use of oleyl alcohol to make sufactants. There are few catalyst systems reported in the literature, which can accomplish the task of preserving the olefinic double bond of methyl oleate during the process of its hydrogenation to alcohols. Zinc chromite catalyst was reported first in 1937 to convert methyl oleate to oleyl alcohol in 37-65% yield at 280-300^{o}C and 200 atmospheres of hydrogen pressure[136]. Copper and/ or nickel containing $ZnO-Cr_2O_3$ catalysts were also reported for selective hydrogenation of methyl oleate to oleyl alcohol at a temperature of 340^{o}C at high pressures[137].

In addition to copper catalyst for hydrogenation of esters, Ru-Sn catalysts are also reported for hydrogenation of esters. Among silica, alumina and titania, alumina and titania were found to be better supports for Ru-Sn catalysts for the hydrogenation of 1,4-cyclohexanedicarboxylic acid ester. The yield for cyclohexane dimethanol with Ru-Sn supported on alumina and titania was 78% and 85% respectively. The esters of other carboxylic acids like lauric acid, cyclohexane carboxylic acid, iso-butyric acid , oleic acid and benzoic acid were also hydrogenated to respective alcohols with >95% selectivity, except for methyl benzoate for which selectivity to benzyl alcohol was 18%. The low selectivity for benzyl alcohol is due to formation of cyclohexyl methanol and toluene[138].

The ruthenium-tin boride catalyst is also reported for efficient hydrogenation of methyl oleate to oleyl alcohol at 270 ^{o}C and a hydrogen pressure of 14.2 atmospheres. When Ru:Sn ratio was 1:0, conversion of oleic acid was 100%, with total selectivity to saturated alcohol. No oleyl alcohol was formed. When Ru:Sn ratio was increased to 1:4, the selectivity to oleyl alcohol was increased to 67.7% with 66% conversion of oleic acid. The ruthenium-tin boride catalyst was also used for hydrogenation of methyl palmitate, methyl stearate, hexyl acetate under the same conditions to give corresponding alcohols with yields ranging from 70-85%. A mechanism for hydrogenation of esters, in which Sn^{2+} or Sn^{4+} Lewis acid sites would coordinate to the C=O bond of the ester and polarize it so that hydrogen activated by Ru can attack the C=O bond to give alcohol[139], has also been proposed.

1.5 Kinetics of hydrogenation of carboxylic acids

Kinetic studies provide an understanding of the intrinsic rate behavior of the various steps in hydrogenation. Such information provides the starting basis for further development and optimization of various multiphase reactor performance models for utilization in pilot or commercial scale operations.

A critical step in obtaining reliable quantitative kinetics is to ensure the absence of all transport limitations including external and internal mass transfer effects[140]. The absence of mass transfer limitations typically has been probed by varying stirring speed and/or the catalyst particle size[141]. The Weisz-Prater criterion can also be used to verify the absence of internal diffusion limitations. The Weisz-Prater parameter is a dimensionless number representing the ratio of the reaction rate to the rate of internal diffusion. The value of Weisz-Prater parameter is less than 0.3 for reaction order ≤ 2.[142] Similarly Ramachandran and Chaudhari[143] suggested that the values of α_{gl} (gas to liquid mass transfer), α_{ls} (Liquid to solid mass transfer) and ϕ_{exp} (Thiele constant for intraparticle mass transfer) should be less than 0.1, 0.1 and 0.2 respectively to ensure that the reaction operates under kinetic control.

Intraparticle mass transport resistance can lead to variations in selectivity. If a series reaction A→ B → C takes place in a porous catalyst particle with a small effectiveness factor, the observed conversion to the intermediate B is less than that would be observed in the absence of a significant mass transport influence. This happens because as the resistance to transport of B in the pores increases, B is more likely to be converted to C rather than to be transported from the catalyst interior to the external surface. This result has important consequences in processes such as selective oxidations, in which the desired product is an intermediate and not the total oxidation product CO_2.[7] Such phenomena could also be important for partial/selective hydrogenation reactions.

1.5.1 Kinetic study for hydrogenation of benzoic acid

Konyukhov et al.[144] have proposed a mechanism for benzoic acid hydrogenation in which a benzoic acid-hydrogen adduct is formed on the catalyst surface, isomerized to cyclohexadiene carboxylic acid, and is rapidly hydrogenated to cyclohexane carboxylic acid. Further study revealed that the rate of hydrogenation of benzoic acid on a Pd/C in n-butanol as solvent can be described by the equation $r = kPC/(1+k'PC)$, where P is the hydrogen pressure and C is the concentration of benzoic acid. This equation supports the intermediate formation of benzoic acid-hydrogen adduct on the catalyst surface[145]. Kinetic data for hydrogenation of benzoic acid on palladium catalyst was interpreted in terms of a mechanism in which benzoic acid and hydrogen formed a complex, which is subsequently transformed into cyclohexane dicarboxylic acid. The activation energies for these two steps were 6.9 and 10.5 kcal/mol, respectively[146]. Addition of water to benzoic acid system increased the rate of hydrogenation due to a reduction in catalyst poisoning by carboxylic group, or by decreasing the extent of catalyst pore clogging by tarry by-products formation[147]. The rate equation for hydrogenation of benzoic acid was found to be first order with respect to benzoic acid, hydrogen and catalyst when palladium catalyst was modified with cobalt[148]. Increasing the amount of support (Silica) in palladium catalyst increases the initial rate of hydrogenation but decreased the life of catalyst due to deactivation[149].

1.5.2 Kinetic study for hydrogenation of maleic acid

The kinetics of hydrogenation of maleic acid (MAC) was investigated by Chaudhari et al.[50] using a bimetallic 1%Ru-6%Re/C catalyst in the temperature range of 503-543 K. They reported that maleic acid hydrogenation is a set of parallel and consecutive reactions. The major products obtained in this reaction were succinic acid (SAC), γ-butyrolactone (GBL), and tetrahydrofuran (THF). The reaction rates were found to be strongly inhibited by maleic acid and succinic acid as indicated by L-H type of rate form with a negative reaction order. The selectivity to THF increases only after MAC and SAC are completely converted. The selectivity to THF also increased significantly at higher catalyst loading, hydrogen pressure and temperature. This suggests that GBL to THF is a slower step compared to other steps. The following rate equation based on a dual site Langmuir-Hinshelwood model was found to satisfactorily represent all the data.

$$r_j = \frac{w\,k_j\,A^*\,C_j}{(1 + K_A A^* + K_1 C_1 + K_2 C_2 + K_3 C_3)^2} \qquad \text{Eq-1.1}$$

Where, K_1, K_2 and K_3 are adsorption equilibrium constants (m^3/kmol) for MAC, SAC and GBL. C_1, C_2 and C_3 are concentration of MAC, SAC and GBL respectively. A* denotes the equilibrium solubility of hydrogen (kmol/m^3) and C_j is the concentration of j^{th} species at the catalyst surface. From the temperature dependence of the rate constants, the activation energy for hydrogenation of MAC to SAC was found to be 53.8 kJ/mol, SAC to GBL was 108 kJ/mol and GBL to THF was found to be 165 kJ/mol.

1.5.3 Kinetic study for L-Alanine to L-Alaninol

The kinetics of the aqueous-phase, stereoretentive hydrogenation of alanine over 5% Ru/C catalyst was studied in a three phase stirred batch reactor by Jere et al[150]. Alanine is an amino acid and can be present in protonated, or deprotonated form depending on the pH of solution. Alanine readily undergoes hydrogenation when it is in carboxylic acid form to give alaninol. The reaction mixture for this purpose was acidified with phosphoric acid. Selectivity to alaninol and alaninol optical purity (ee%) was favored by high hydrogen pressure, lower reaction temperatures and a slight excess of phosphoric acid.

Alanine hydrogenation over 5% Ru/C catalyst has been represented by a Langmuir-Hinshelwood-type model. The model assumes that protonated alanine and undissociated phosphoric acid compete for one type of surface catalytic site and that hydrogen dissociatively adsorbs on other site. With reduction of phosphoric acid concentration the rate of hydrogenation decreases.

The authors have also postulated that phosphoric acid adsorbs on the same active sites for alanine hydrogenation, as rate of hydrogenation was found to decrease with excess addition of phosphoric acid. The rate model for alanine hydrogenation based on Langmuir-Hinshelwood mechanism is represented by Eq-1.2.

$$-r_A = k_1 \frac{K_{A+}C_{A+}\ K_{H2}C_{H2}}{(1 + K_{A+}C_{A+} + K_pC_p)\ [1 + (K_{H2}C_{H2})^{1/2}]^2} \qquad \text{Eq-1.2}$$

Where, r_A is rate of consumption of alanine, K_{A+}, K_{H2} and K_p are the equilibrium adsorption constant on catalyst surface for protonated alanine, hydrogen and phosphoric acid respectively. k_1 is the rate constant for the hydrogenation reaction.

The activation energy for alanine hydrogenation based on Eq-1.2 was calculated to be 81.5 kJ/mol.

1.5.4 Kinetic study for Hydrogenation of lactic acid to propylene glycol

Kinetics of lactic acid to propylene glycol (PG) reported by Zhang et al.[151] is relatively simple as it is single step reaction. Hydrogenation of lactic acid was carried out in a stirred batch reactor over 5% Ru/C catalyst. The reaction was checked for gas-liquid, liquid-solid and intraparticle mass transfer and was found to be independent of all mass transfer limitations. The rate of reaction was found to increase with catalyst loading and hydrogen partial pressure. The rates were calculated by applying the differential method. Addition of PG to the reaction mixture was found to have a negligible effect on the initial rate of reaction; therefore the PG term in the denominator of the Langmuir-Hinshelwood rate equation was eliminated. The final form of the L-H kinetic expression is given by Eq-1.3.

$$-r_{LA} = \frac{k\ C_{LA}P_{H2}}{(1 + K_{H2}P_{H2} + K_{LA}C_{LA})^2} \qquad \text{Eq-1.3}$$

Where, r_{LA} is rate of hydrogenation of lactic acid, k rate constant, C_{LA} is concentration of lactic acid, P_{H2} is hydrogen pressure and K_{LA}, K_{H2} are adsorption equilibrium constants for lactic acid and hydrogen respectively.

The activation energy for hydrogenation of lactic acid to PG over 5% Ru/C catalyst was found to be 138 kJ/mol.

1.5.5 Thermodynamic considerations for hydrogenation reactions

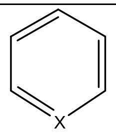
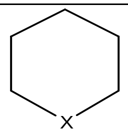
The activation energy for hydrogenation of different functional groups is different and also dependent on the steric environment around the functional group. Augustine[152] has reported a list of the common organic functional groups in an apparent order of decreasing ease of hydrogenation along with typical reaction conditions used for their hydrogenations. Augustine also reported that, it is usually simple to achieve the selective hydrogenation of a functional group listed near the top of Table 1-5 in the presence of one found in the middle or bottom of the list.

For example, hydrogenation of α-β-unsaturated aldehyde (acrolein) over platinum catalyst gives saturated aldehyde (propanaldehyde) and on further hydrogenation, saturated alcohol (n-propanol). The unsaturated alcohol can be achieved by proper choice of catalyst. Over palladium, the only reaction observed is the saturation of C=C bond to give saturated aldehyde (propanaldehyde). With iridium or osmium catalyst, however, the unsaturated alcohol (Allyl alcohol) is formed exclusively[153].

Steric hindrance around the double bond facilitates the selective hydrogenation of the carbonyl group with selectivity for unsaturated alcohol. For example in the hydrogenation of acrolein, crotonaldehdye, 3-methylcrotonaldehyde and cinnamaldehyde, the highest selectivity to unsaturated alcohol is obtained for the hydrogenation of cinnamaldehyde because of its steric hindrance. Steric hindrance at the carbonyl group will reduce the selectivity to unsaturated alcohol. There is no report related to selective hydrogenation of α-β-unsaturated ketone to an unsaturated alcohol. In molecules in which the double bond is not conjugated with the carbonyl group, the selective hydrogenation to the unsaturated alcohol, takes place more easily, particularly when the double bond is highly substituted[154].

Obtaining selectivity when the two functional groups are far apart in the listing shown in Table 1-5[152] is generally very difficult with mono metallic catalyst. For example the hydrogenation of an unsaturated acid or ester gives saturated acid and ester, since the carboxylic group is more difficult to hydrogenate with respect to olefin under standard conditions. However, when a Ru-Sn catalyst was used to hydrogenate an unsaturated fatty acid, the unsaturated alcohol was obtained in about 80% yield[155].

Table 1-5: List for hydrogenation of different functional groups in order of increasing difficulty in hydrogenation.[152]

No.	**Functional group**	**Product**	**Catalyst**	**Reaction conditions (Temperature/Hydrogen pressure)**
1	—C≡C—	—C=C—	Pd	Room temperature, 1 atm.
2	C=C—C=C	C—C=C—C	Pd	Room temperature, 1 atm.
3	C=C—C=C	C=C—C—C	Pd	Room temperature, 1 atm. Low catalyst ratio and deactivated catalyst
4	—$\mathrm{NO_2}$	—$\mathrm{NH_2}$	Pt, Pd, Rh	Room temperature, 1 atm.
5	C=C	HC—CH	Pd, Ni	Room temperature, 1 atm.
6	—C≡N	—$\mathrm{CH_2NH_2}$	Raney Ni, Raney Co	Room temperature, 1-4 atm.
7	>C=N—	>CH—NH—	Pt, Pd	Room temperature, 1-4 atm
8	>C=O	>CHOH	Pt, Rh, Ru	Room temperature, 1-4 atm Room temperature, 1-3 atm
9	 X = C, N, O	 X = C, N, O	Rh Raney Ni Ru	Room temperature, 2-4 atm 100-200°C, 100 atm. 150 °C, 100 atm
10	—$\mathrm{CO_2H}$	—$\mathrm{CH_2OH}$	Ru, CuCrO	High temperature and pressure
11	—$\mathrm{CONR_2}$	—$\mathrm{CH_2NR_2}$	Ru, CuCrO	High temperature and pressure

A detailed study from thermodynamic point of view for hydrogenation of carboxylic acids has been done for acetic acid and its esters over silica supported copper catalyst by Santiago et al.[156]. They have observed that, the rate of dissociation of carboxylic group on copper increases in the order from acetic acid to methyl acetate to ethyl acetate. The corresponding experimental values of the activation energies are estimated to be 83, 67, and 62 kJ/mol, respectively. From kinetic analysis it was also observed that the rate of reduction of n-alkyl acetates is determined by the dissociative adsorption of these molecules and by the surface hydrogenation of surface acyl species[156].

Further Pallassana et al.[157], have studied the hydrogenation of acetic acid over Pd (111), Re (0001) and Pd-Re alloys. They proposed a mechanism, in which acetic acid is hydrogenolysed on catalyst surface to give acetyl intermediate, which on hydrogenation gives acetaldehyde. Further hydrogenation of acetaldehyde gives ethanol. Acetyl formation and acetyl hydrogenation appear to be slow steps. They have calculated the C–OH activation energies on three different metal surfaces. The barriers for C–OH bond activation observe the following trend.

$$\text{Re (0001) [90 kJ/mol]} < \text{Pd (111) [142 kJ/mol]} < \text{Pd}_{\text{ML}}\text{/Re (0001) [158 kJ/mol]}$$

The barriers for acetyl hydrogenation, in contrast, follow nearly the exact opposite trend;

$$\text{Pd (111) [66 kJ/mol]} < \text{Pd}_{\text{ML}}\text{/Re (0001) [69 kJ/mol]} < \text{Re (0001) [88 kJ/mol]}$$

This shows that C–OH activation is more favored on Re (0001) but Re alone, however is not optimal as since it leads to acetic acid decomposition. Group VIII metals such as Pd demonstrate lower activation barriers for hydrogenation and reduced acetic acid decomposition, but they tend to display poor activity for C–O dissociation.

Optimum carboxylic acid hydrogenolysis therefore appears to involve an intricate balance between C–O bond activation and C–H bond formation steps, and C–H bond scission. Catalyst that are capable of preferentially activating the C–O bond, without significantly enhancing β C–H bond activation of the carboxylic acid, are likely to be good catalysts for acid hydrogenation. The ensemble size requirements for acid decomposition and hydrogenation are different. A bimetallic Pd-Re catalyst, with suitably atomically dispersed Re ensembles on Pd, may provide the optimal trade-off between hydrogenation/hydrogenolysis and decomposition activity, rendering it an effective catalyst for acid hydrogenation.

1.6 Consecutive reactions

Some reactions proceed through the formation of an intermediate as shown below, as in the consecutive unimolecular reactions.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The time when the concentration of the intermediate is maximum is given by Eq-1.4[3].

$$t_{max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{(k_1-k_2)} \qquad \text{(Eq-1.4)}$$

Where t_{max} is the time where the concentration of the intermediate is in maximum, k_1 is the rate constant for the first step in the consecutive reaction and k_2 is the rate constant for the second step. For a given value of k_1, as k_2 increases both the time at which B is at maximum concentration and the yield of B increases. This equation can however be used only for unimolecular consecutive reactions. Such equations cannot be used for complex consecutive reactions.[3]

An approach for determining t_{max} for isokinetic consecutive reactions (i.e. reactions having the same reaction rates and the same rate constants) has been established by J. M. Herrmann[158].The equation proposed by Hermann for t_{max} of a consecutive reaction is given by Eq-1.5.

$$t^{n}_{max} = \frac{n}{k} \qquad \text{(Eq-1.5)}$$

Where, t^n_{max} = Time for the nth intermediate, when it goes through maximum, n = the number of the intermediate in a consecutive reaction, k = First order rate constant for all steps in the consecutive reaction.

One of the examples for such type of systems is photo catalytic propane-deuterium isotopic exchange[159].

There is no report regarding development of an equation for t_{max} for intermediate products in reactions involving catalysts. Such equations would focus on increasing selectivity of a catalytic reaction. As discussed above, hydrogenation of many carboxylic acids goes through an intermediate, for e.g. hydrogenation of succinic acid, maleic acid, benzoic acid etc. Thus, developing an equation for t_{max} for complex catalytic consecutive reaction would be of great help in increasing selectivity to industrially important reaction intermediates, like aldehydes etc.

1.7 Scope and objective of present work

From the literature it was observed that the development of catalysts for the selective/partial hydrogenation of aromatic/aliphatic mono and dicarboxylic acids has not been investigated in detail. The optimization of reaction parameters and role of solvents etc. to achieve high selectivity in such partial hydrogenation reactions has also not been studied in enough detail.

The hydrogenation of aromatic/aliphatic acids provides alternate routes for the synthesis of aromatic/aliphatic alcohols with varied applications. The hydrogenation of aromatic dicarboxylic acids also can be a route to obtain compounds like aromatic diols, saturated cyclic dicarboxylic acids/diols. Partial hydrogenation of aliphatic and aromatic acids to aldehydes presents an alternate route to the synthesis of aldehydes. There seems to be lot of scope for development of chemoselective catalysts for such systems.

For consecutive reactions it's important to be able to predict the time for the maximum intermediate concentration. Such consecutive systems are widely found in catalytic hydrogenations. As of now development of such models to predict t_{max} for catalytic hydrogenation are not available.

With the above points in mind the following problems were taken up for detailed study.

1. Synthesis of mono and bimetallic supported catalysts and their application to hydrogenation of mono and dicarboxylic acids, identification of products. Investigations on the role of solvents etc on the product distribution.
2. Detailed kinetic study of chemoselective hydrogenation of benzoic acid to cyclohexane carboxylic acid using Ru/C catalyst. Studies on the effect of reaction parameters on rate, and optimization of reaction conditions to achieve high selectivity to cyclohexane carboxylic acid. Development of a model to predict t_{max} for cyclohexane carboxylic acid for hydrogenation of benzoic acid to cyclohexane carboxylic acid to cyclohexyl methanol.

3. Development of catalysts for the hydrogenation of benzoic acid to benzyl alcohol in high selectivity. Kinetics of the reaction using Ru-Sn/Al_2O_3 catalysts.
4. Studies on the selective hydrogenation of lauric acid to lauryl alcohol, and kinetics of the reaction.
5. Development of catalysts for the selective partial hydrogenation of aliphatic and aromatic acids to aldehydes, and investigation of the role of various reaction parameters and catalysts on the selectivity to aldehydes. Development of a model for t_{max} of lauraldehyde.

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Chapter 2

Hydrogenation of aromatic mono and dicarboxylic acids using supported metal catalysts

2.1 Introduction

The hydrogenation of carboxylic acids or their esters poses major challenges, as; among the carbonyl compounds the acid/ester carbonyl is less reactive than that of ketone and aldehyde[1]. The formation of alcohols by the hydrogenation of the carbonyl group is one of the important reactions, for academia as well as industry, particularly for fatty alcohols, which have been extensively manufactured from fatty acids using hydrogenation technology[2]. For long, copper chromite or copper-zinc catalysts have been used for the hydrogenation of esters, however, they cannot be applied for hydrogenation of carboxylic acids as the copper catalyst reacts with carboxylic acids, leading to an inactive form and also leach into the reaction mixture[3].Hence, there is a need for new type of catalysts that make it possible to hydrogenate carboxylic acids to alcohols under mild reaction conditions. The combination of group VIII metals with metals like rhenium, germanium and tin has resulted in better catalysts for this reaction. The first report on the hydrogenation using these catalysts was by, Louessard et al., who studied the hydrogenation of ethyl acetate to ethanol over Ru-Sn/Al_2O_3 catalyst[4]. Cheath et al. prepared Ru-Sn/Al_2O_3 catalyst by sol-gel method for the hydrogenation of carboxylic acids and esters; this catalyst was found to exhibit high catalytic performance as compared to the catalyst prepared by impregnation/calcination method[5]. They have also reported this catalyst for selectively hydrogenating different carboxylic acids; however, for terephthalic and isophthalic acid the selectivity to the corresponding alcohols was 19% and 9.2% respectively with considerable amount of over hydrogenated products[6].

The bimetallic Ru-Co catalyst has been reported for hydrogenation of succinic acid. The doping of ruthenium in cobalt increases the overall hydrogenation activity and the Ru:Co ratio in the Ru-Co bimetallic catalyst was found to affect the selectivity of gamma butyrolactone and tetrahydrofuran[7].

Hydrogenation of carboxylic acids is not reported in detail and most of the work is patented. Our main aim was thus, to develop catalysts, and compare and correlate their activity for the hydrogenation of aromatic and aliphatic mono and dicarboxylic acids. Since the products obtained by hydrogenation of aromatic dicarboxylic acids are extensively used in polymer industry, it was of interest to develop catalysts for selective hydrogenation of these acids to saturated dicarboxylic acids or diols. For instance ring hydrogenation of terephthalic acid gives 1,4-cyclohexane dicarboxylic acid, which is used for producing polymer Empol 1010[8]. 1,4-cyclohexane dicarboxylic acid is also used as a starting material for producing 1,4-cyclohexane dimethanol, which is also used in polyesters, paint, synthetic fibers and synthetic resins[9].

In this study, a detailed catalyst screening has been done for the hydrogenation of benzoic acid, which was chosen as a standard substrate for the screening of catalysts. In addition, hydrogenation of aliphatic carboxylic acids to alcohols was also investigated. The results have been effectively applied for hydrogenation of other dicarboxylic acids like terephthalic, isophthalic and phthalic acid. Hydrogenation of aliphatic dicarboxylic acids was also studied to understand the behavior of the catalyst for hydrogenation of aromatic and aliphatic cyclic carboxylic groups.

2.2 Experimental

2.2.1 Materials

The substrates, benzoic, terephthalic, isophthalic, phthalic, salicylic and cinnamic acid of analytical reagent grade were purchased from S.D. Fine Chemicals, India. The 5% Ru/C and 5% Pd/C catalysts were obtained from Arora Matthey Ltd., India, and were used as such. Metal salt precursors like $RuCl_3.3H_2O$, $ReCl_3.2H_2O$, $PdCl_2$ and $CoCl_2.6H_2O$ for preparing catalysts were procured from S.D. Fine Chemicals, India. Catalyst supports like alumina, titania, carbon and authentic standards of reaction products like cyclohexane carboxylic acid, 1,2-cyclohexane, 1,3-cyclohexane, and 1,4-cyclohexane dicarboxylic acids were procured from Aldrich Chemicals (USA). Other authentic standards of hydrogenation products like cyclohexyl methanol, 1,2-cyclohexyl, 1,3-cyclohexyl and 1,4-cyclohexyl dimethanol too were obtained from Aldrich Chemicals (USA). Analytical reagent-grade 1,4-dioxane, which was used as the reaction medium, was obtained from Merck India Ltd. Hydrogen and nitrogen with purity of 99.9% were obtained from Indian Oxygen Company Ltd., India.

2.2.2. Catalyst preparation

The catalysts were prepared by impregnation method followed by reduction. The following catalysts were prepared: Ru/C, 5% Pd/C, 5%Re/C, 5% Pd-2% Re/C, 1% Ru-

6% Re/C, 5% Ru/Al_2O_3, 5% Ru/TiO_2, 5% Re/Al_2O_3 , 5% Co/C, 5% Ru-Sn/Al_2O_3 and 5% Ru/MgO.

Catalysts with carbon as support were prepared by impregnating carbon support with metal precursor solution at 333 K with continuous stirring for 1 hr. After impregnation with the metal precursor solution, excess water was removed using rotary evaporator. The dried impregnated catalyst was dried overnight in an oven at 363 K. The catalyst was then reduced at 573 K in a tubular silica glass reactor (as shown in Figure 2-1), under constant flow of hydrogen gas (5 ml/min) for 12 hrs. After the reduction period, the silica glass reactor was cooled under nitrogen to room temperature. The reduced catalyst was transferred into a 50 ml container under nitrogen and stored in the dessicator under nitrogen.

Catalysts with alumina, titania, silica or magnesia supports were also prepared by the procedure described above with the only difference being that, these catalysts were calcined at 773 K for 12 hrs before reducing at 573 K in the silica glass reactor.

Metal catalysts like Co and Ru-Co were prepared by precipitation of respective metal precursors by 5% NH_4OH. The precipitate was filtered and dried at 363 K for 12 hrs. The dried precipitate was calcined at 773 K for 12 hrs. After calcination, the calcined catalyst was reduced at 573 K under constant flow of hydrogen (5ml/min) for 12 hrs.

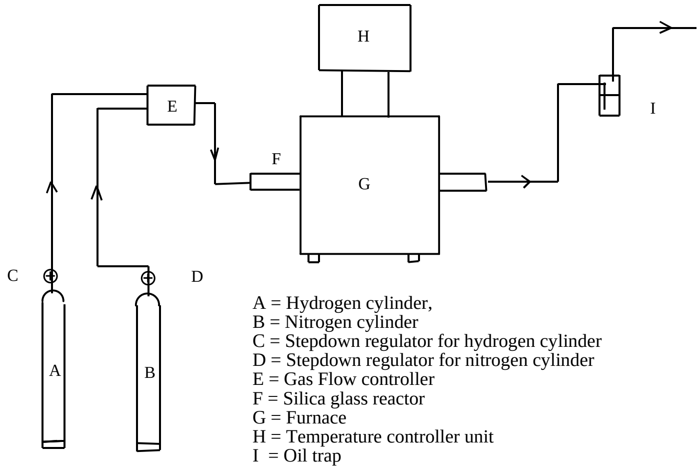
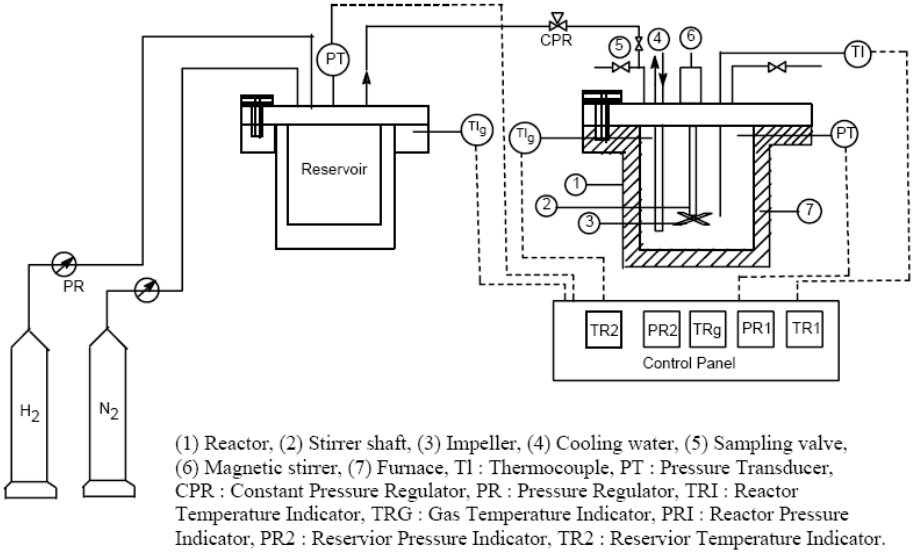


Figure 2-1: Schematic diagram of silica glass reactor set-up for catalyst reduction.

2.2.3 Reactor set-up for high pressure reactions

The reactions were carried out in a 250 ml capacity high pressure – high temperature reactor supplied by Parr Instruments Co. USA. The reactor was provided with a double bladed variable speed stirrer with a magnetic drive and automatic temperature control by means of an external electrically heated jacket and internal cooling coils. A gas inlet / outlet as well as liquid outlet provided a facility for sampling of liquid contents in the reactor. For safety purpose, a high pressure – high temperature cut-off facility was also provided to the reactor, in addition to rupture disc. The autoclave was designed to operate at a temperature up to 623 K and 250 bar pressure.

The reactor was connected to a hydrogen reservoir held at a pressure higher than that of the reactor, through a constant pressure regulator. Hydrogen gas was supplied to the reactor from this reservoir through a non-return valve. The gas consumed during the course of the reaction was determined from the observed pressure drop in the reservoir at different time intervals. A transducer connected to a pressure readout system was used to monitor pressure in the reactor and the hydrogen reservoir. A schematic of the reactor assembly is shown in Figure 2-2.



(1) Reactor, (2) Stirrer shaft, (3) Impeller, (4) Cooling water, (5) Sampling valve, (6) Magnetic stirrer, (7) Furnace, TI : Thermocouple, PT : Pressure Transducer, CPR : Constant Pressure Regulator, PR : Pressure Regulator, TRI : Reactor Temperature Indicator, TRG : Gas Temperature Indicator, PRI : Reactor Pressure Indicator, PR2 : Reservior Pressure Indicator, TR2 : Reservior Temperature Indicator.

Figure 2-2: Schematic diagram of reactor set-up for high pressure hydrogenation reactions.

2.2.4 Experimental procedure for high pressure reactions

In a typical hydrogenation experiment, known quantities of the substrate, catalyst and solvent were charged into a clean and dry reactor. The contents were flushed with nitrogen followed by hydrogen (2-3 times). The contents in the autoclave were heated to a desired temperature under slow stirring. After the desired temperature was attained, the autoclave was pressurized to the requisite pressure with hydrogen and the reaction was started by adjusting the agitation speed to 1200 rpm. The hydrogen consumption was determined from the drop in the hydrogen pressure in the reservoir vessel as a function of time. The liquid samples were withdrawn at specific time intervals and analyzed for reactant and product concentrations. At the end of the reaction, the autoclave was cooled to room temperature and a gas sample was withdrawn for analysing the gas phase products. The gas phase analysis was essential to ensure that cracking of the products to hydrocarbons was negligible. Following this, the contents in the reactor were discharged and the liquid sample was analyzed for reactants and products.

2.2.5 Analysis

The various hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector instrument). The mass spectra of major products are given in Appendix I.

For quantitative analysis, samples from the reaction mixture were filtered to remove the catalyst, and analyzed by gas chromatography (Agilent Systems 6890 GC). For analysis, a HP INNOWax, polyethylene glycol capillary column (30m x 320µm x 0.25 µm) along with flame ionization detector was used on Agilent 6890 gas chromatograph controlled by HP Chemstation software, equipped with an auto sampler unit. Calibration for the hydrogenation products was done using external standard method[10]. The standard conditions under which gas chromatograph was operated for the quantitative analysis of reactants and products are given in Table 2-1.

Table 2-1: Conditions for gas chromatographic analysis

Injection volume	1 μl		
Injector temperature	280 ^{o}C K		
Flame ionization detector Temp	280 ^{o}C K		
Inlet flow-total (He)	505 ml/min		
Split ratio for Injector	100:1		
Oven Temperature	Heating rate (^{o}C/min)	Temperature (^{o}C)	Hold time (min)
		100	5
	30	210	12
	Post run	210	5
Column Pressure	Flow Rate (ml/min)	Pressure (psi)	Hold time (min)
	5.6	24	30

Quantitative analysis of carboxylic acids like terephthalic, isophthalic, phthalic acid, 1,2-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid and 1,4-cyclohexane dicarboxylic acid was not possible on GC as these acids were retained on the HP INNOWax, capillary column due to their polarity and high boiling point. For quantitative analysis, such carboxylic acids were first esterified by procedure given below (Section 2.2.5.1) and then analyzed on GC.

The reproducibility of results was checked and the error in experimental measurements was less than 3%. A mass balance of the reactants consumed during reaction and products formed showed an agreement to about 95%. Similarly gas balance for hydrogen consumed and products formed was found to be 95% or greater.

2.2.5.1 Procedure for analysis of carboxylic acids by esterification method

For these analyses the reaction crude was first filtered to remove the heterogeneous catalyst and was transferred into a 250 ml round bottom flask. To this 100 ml of methanol was added along with 0.2 ml of sulphuric acid. This mixture was then refluxed in an oil bath at 343 K for 4 hrs. After 4 hrs the mixture was cooled to room temperature and was then analyzed by GC for the respective acids. Here, the analysis was done for the ester of the carboxylic acid, from which the concentration of respective carboxylic acid was calculated. A typical gas chromatogram for the derivatised product of hydrogenation of isophthalic acid to 1,3-cyclohexane dicarboxylic acid is shown in

Figure 2-3. The esterification was found to be quantitative and hence this method could be conveniently used for analysis.

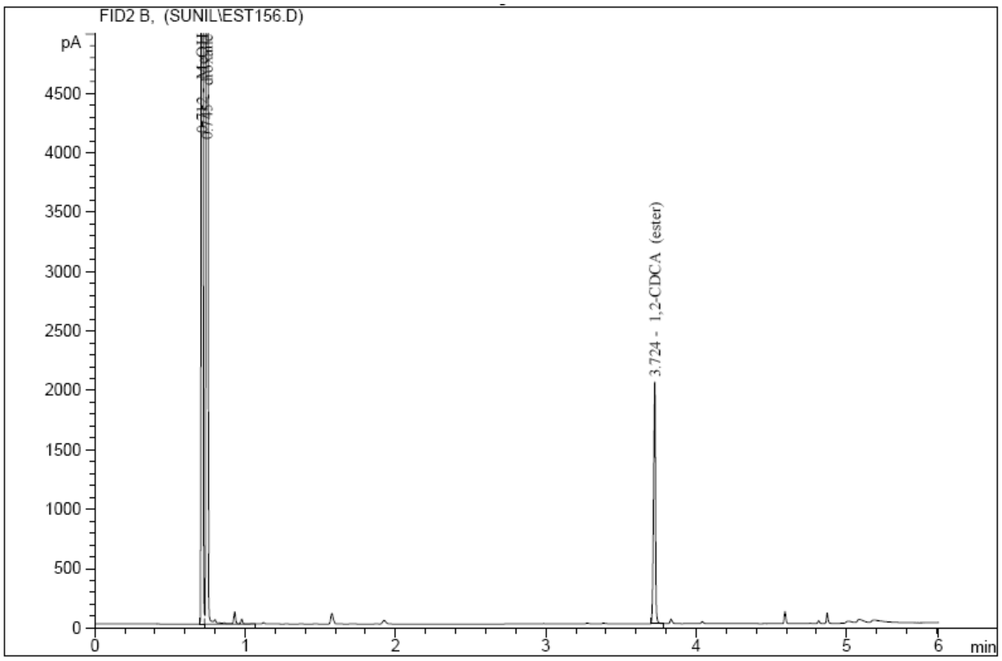
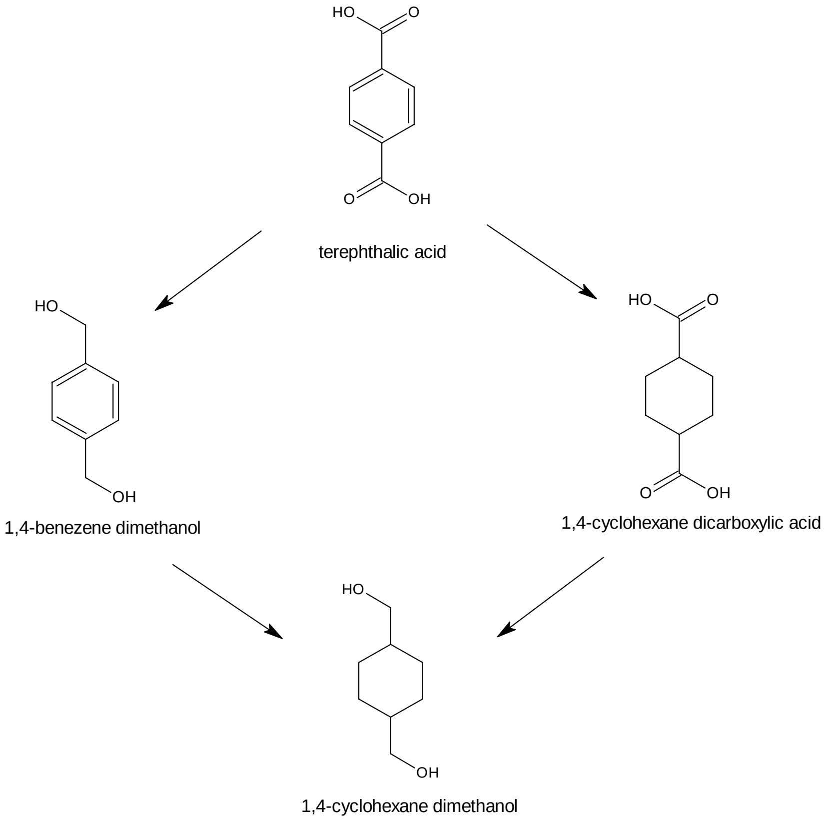


Figure 2-3: Gas chromatograph for esterified reaction sample for hydrogenation of isophthalic acid with 5% Pd/C.

2.3 Results and discussion

2.3.1 Catalyst screening study for hydrogenation of aromatic carboxylic acids

Aromatic acids like benzoic, terephthalic, isophthalic and phthalic acid have two hydrogenable functional groups viz aromatic and carboxylic group. Hydrogenation of a single functional group or both can give an array of products having applications in industry. If hydrogenation of only the aromatic ring takes place then the products obtained are cyclohexane carboxylic or cyclohexane dicarboxylic acid depending on the aromatic acid hydrogenated. If only carboxylic group of the aromatic acid is hydrogenated then the products obtained are aromatic alcohols. When both the functional groups of the aromatic carboxylic acid are hydrogenated, the product obtained is a saturated alcohol. A schematic of the possible products in hydrogenation of terephthalic acid is shown in Scheme 2-1.



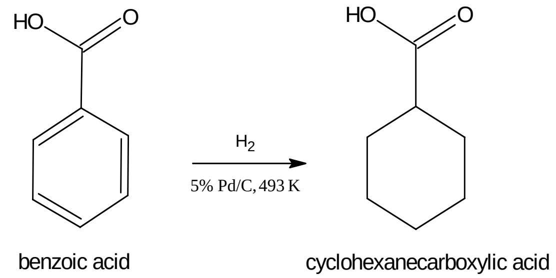
Scheme 2-1: Possible routes for hydrogenation of terephthalic acid.

For this study, initial screening of catalyst was investigated using a simple carboxylic acid – benzoic acid. This substrate has all the functionalities which can be hydrogenated and can hence serve as a model substrate for all aromatic dicarboxylic acids. The major advantage was that the product distribution was uncomplicated unlike the dicarboxylic acids where number of products could be expected. The catalysts which gave the best results for hydrogenation of benzoic acid in terms of selectivity and conversion were further used for hydrogenation of aromatic dicarboxylic acids like phthalic, isophthalic and terephthalic acid.

For catalyst screening study, hydrogenation of benzoic acid was carried out with different supported monometallic catalyst like Pd, Ru, Re, Co and bimetallic catalysts like Ru-Re/C, Ru-Sn/Al_2O_3, and Pd-Re/C. For hydrogenation of benzoic acid, metal catalysts like Co and Ru-Co were also used. The selectivity as well as activity for hydrogenation of benzoic acid was found to be dependent on the catalysts used. The results on catalyst screening study for hydrogenation of benzoic acid are discussed below.

2.3.1.1 Hydrogenation of benzoic acid with 5% Pd/C catalyst

Hydrogenation of benzoic acid (BZA) over 5% Pd/C in 1,4-dioxane (P_{H2} = 6.89 MPa, T = 493 K) proceeds according to the pathway shown in Scheme 2-2. It was observed that, the aromatic ring was selectively hydrogenated to give cyclohexane carboxylic acid (CCA). 59.7% conversion of benzoic acid with 100% selectivity to cyclohexane carboxylic acid was achieved. The concentration versus time profile for hydrogenation of benzoic acid with 5% Pd/C is shown in Figure 2-4. When the reaction was continued for 12 hrs also, only cyclohexane carboxylic acid was observed, no further hydrogenation of CCA was seen.



Scheme 2-2: Reaction scheme for hydrogenation of benzoic acid with 5% Pd/C catalyst

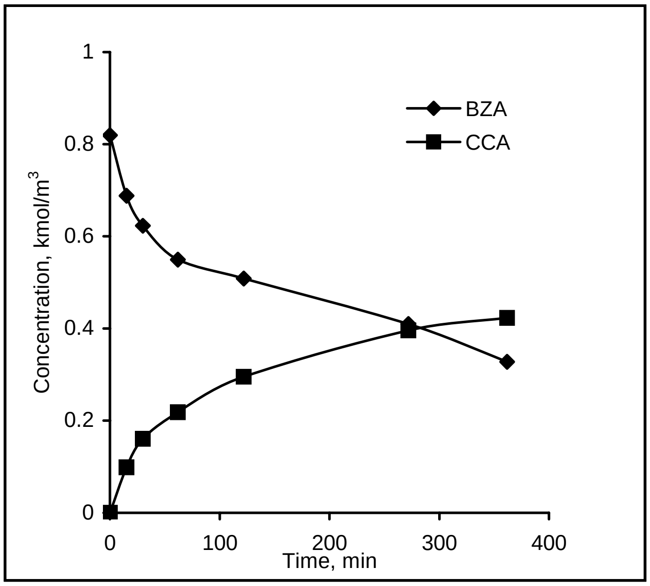
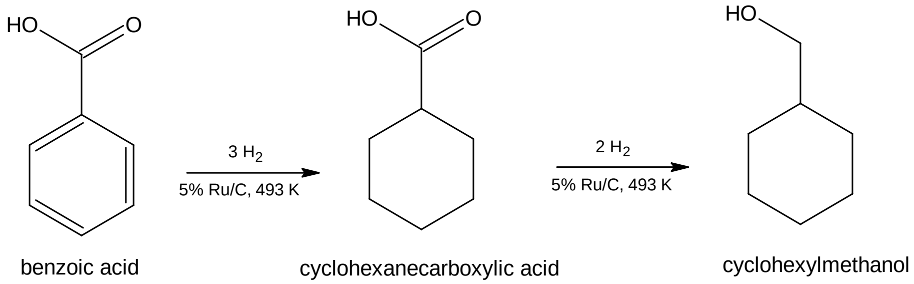


Figure 2-4: Concentration time profile for hydrogenation of benzoic acid with 5% Pd/C catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^{3}.

2.3.1.2 Hydrogenation of benzoic acid with 5% Ru/C catalyst

Under identical conditions (Section 2.3.1.1), 5% Ru/C was an active catalyst as compared to 5% Pd/C. Conversion of benzoic acid at the end of 6 hrs was found to be 99%.The 5% Ru/C catalyst was found to hydrogenate the carboxylic group along with aromatic ring.



Scheme 2-3: Reaction scheme for hydrogenation of benzoic acid using 5%Ru/C catalyst

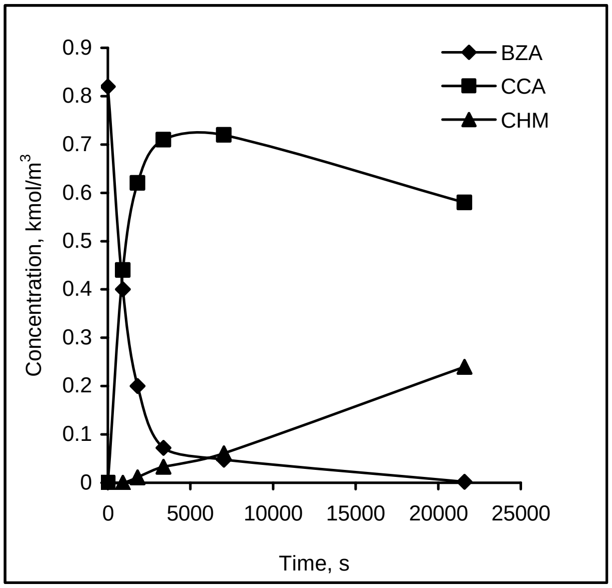


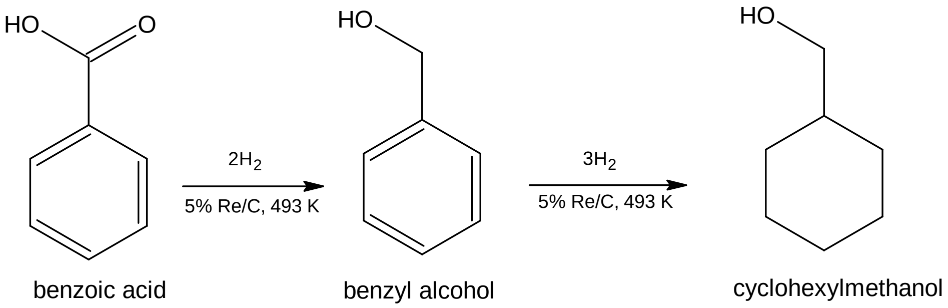
Figure 2-5: Concentration time profile for hydrogenation of benzoic acid with 5% Ru/C catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^{3}.

From the concentration time profile for the reaction shown in Figure 2-5, it is understood that hydrogenation of benzoic acid with 5%Ru/C is a consecutive reaction as shown in Scheme 2-3. Hydrogenation of the aromatic ring in benzoic acid takes place first to give cyclohexane carboxylic acid (CCA); this further hydrogenates to give cyclohexyl methanol (CHM). It is clear from Figure 2-5, that 5% Ru/C can be selective to cyclohexane carboxylic acid (>95%) with 100% conversion of benzoic acid, by optimization of reaction parameters. Under the reaction conditions, the selectivity to cyclohexane carboxylic acid was 70% while that for cyclohexyl methanol, 30%.

2.3.1.3 Hydrogenation of benzoic acid with 5% Re/C catalyst

Hydrogenation of benzoic acid over 5% Re/C is very slow as compared to 5% Ru/C and 5% Pd/C catalysts. The reaction pathway for hydrogenation of benzoic acid over 5% Re/C is also different from that for the other two catalysts as shown in Scheme 2-4. With 5% Re/C, the carboxylic group is hydrogenated first to give benzyl alcohol (BZOH), which is further hydrogenated to give cyclohexyl methanol (CHM), as shown in Figure 2-6. In literature, ReO_3 is reported to be active for selective hydrogenation of terephthalic acid to p-hydroxymethyl benzoic acid[11]. Conversion of benzoic acid was 6.1% and selectivity to benzyl alcohol and cyclohexyl methanol was 50% each.



Scheme 2-4: Reaction scheme for hydrogenation of benzoic acid with 5% Re/C catalyst

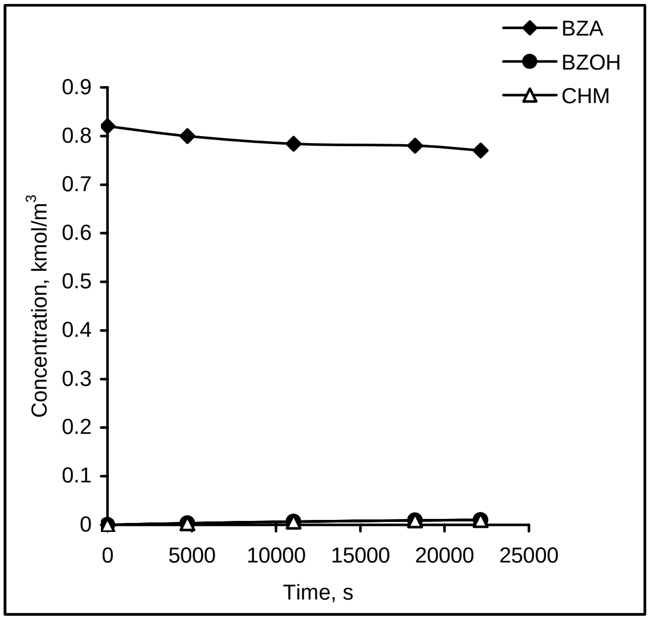
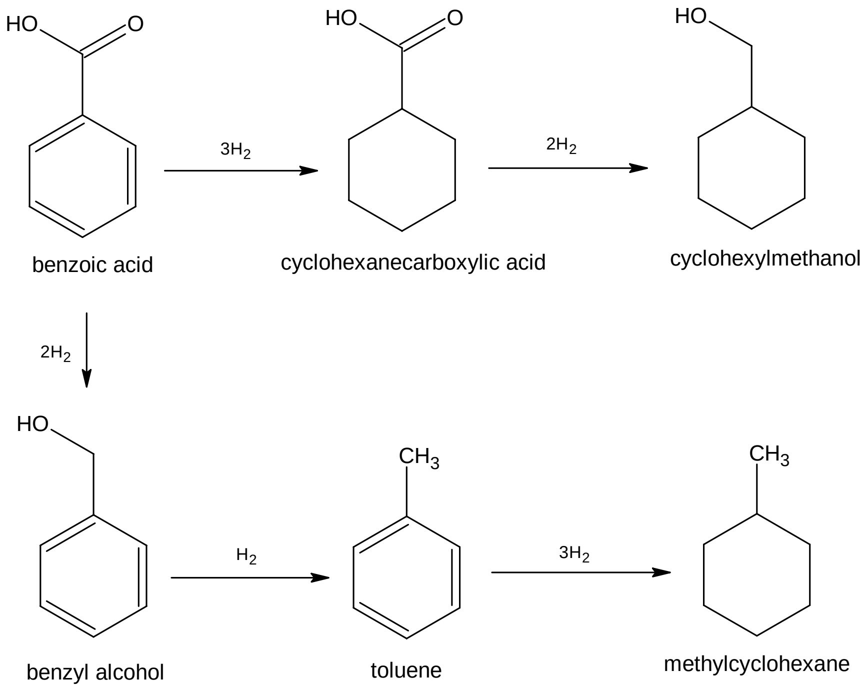


Figure 2-6: Concentration time profile for hydrogenation of benzoic acid with 5% Re/C catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^{3}.

2.3.1.4 Hydrogenation of benzoic acid with 5%Pd – 2%Re/C bimetallic catalyst

The activity of 5%Pd-2%Re/C catalyst was higher than that for 5% Pd/C and 5% Re/C in terms of benzoic acid conversion (98.5%). But the selectivity to benzyl alcohol, cyclohexane carboxylic acid or cyclohexyl methanol was low as compared to the other catalysts like 5% Re/C and 5% Pd/C. This is because hydrogenation of benzoic acid with 5%Pd-2%Re/C catalyst gives benzyl alcohol which undergoes hydrogenolysis. The reaction is thus both consecutive and parallel, which gives a series of products like CCA, CHM, toluene (TOL) and methyl cyclohexane (MCH). The overall reaction scheme for hydrogenation of benzoic acid with 5%Pd-2%Re/C catalyst is given in Scheme 2-5.



Scheme 2-5: Reaction scheme for hydrogenation of benzoic acid with 5%Pd-2%Re/C catalyst.

In the hydrogenation of benzoic acid, toluene and methyl cyclohexane are formed via hydrogenolysis of benzyl alcohol which is formed as an intermediate. This was confirmed by the catalytic hydrogenation of benzyl alcohol and toluene separately under same reaction conditions. Hydrogenation of benzyl alcohol with 5%Pd-2%Re/C catalyst gave both TOL and MCH as products whereas hydrogenation of toluene gave MCH, which confirms that the hydrogenation of BZA with 5%Pd-2%Re/C as a catalyst, occurs with two parallel reaction pathways, (i) only ring is hydrogenated followed by the carboxylic group and (ii) -COOH group is hydrogenated first to give BZOH. The BZOH formed, rapidly undergoes hydrogenolysis to give toluene, which further hydrogenates to give methyl cyclohexane. The concentration time profile for hydrogenation of benzoic acid with 5%Pd-2%Re/C is shown in Figure 2-7. The activity of 5%Pd- 2%Re/C catalyst is high as compared to 5% Pd/C and 5% Re/C catalyst.

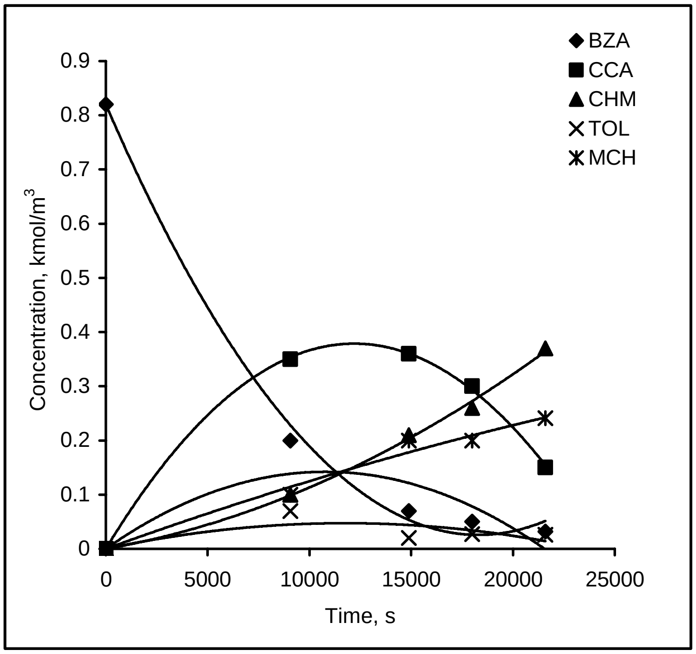


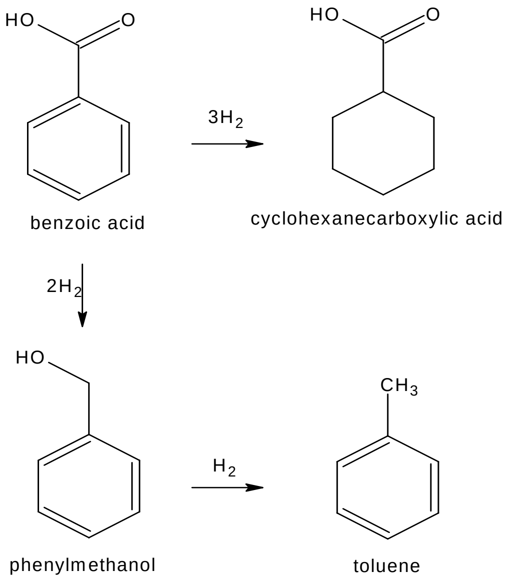
Figure 2-7: Concentration time profile for hydrogenation of benzoic acid with 5%Pd-2% Re/C catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^3.

The selectivity for hydrogenation of BZA with 5%Pd- 2%Re/C to CCA, CHM, TOL and MCH is 19%, 47%, 3.3% and 30.6% respectively (at 6 hrs). Such a difference in activity and selectivity for monometallic and bimetallic catalyst only confirms that Pd and Re form a synergistic combination.

2.3.1.5 Hydrogenation of benzoic acid with 1%Ru-6%Re/C catalyst

As compared to 5%Pd-2%Re/C catalyst, 1%Ru-6%Re/C showed lower activity in terms of BZA conversion (8.1%). This may be attributed to the low percentage of Ru in the catalyst, which alone is a good hydrogenation catalyst for benzoic acid. With 1%Ru-6%Re/C as catalyst it was observed that -COOH group was hydrogenated in preference to the aromatic ring. The advantage of 1%Ru-6%Re/C catalyst over 5%Pd-2%Re/C is that, the benzyl alcohol (33%) formed, does not undergo hydrogenolysis rapidly. The reaction scheme for hydrogenation of benzoic acid with 1%Ru-6%Re/C catalyst is shown in Scheme 2-6.

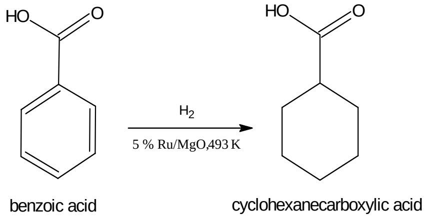


Scheme 2-6: Hydrogenation of benzoic acid with 1%Ru-6%Re/C catalyst

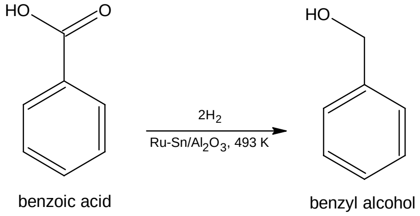
2.3.1.6 Hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst

Hydrogenation of benzoic acid with Ru catalyst on different supports like Carbon (C), alumina (Al_2O_3), silica (SiO_2), titania (TiO_2), and magnesia (MgO) was studied. The activity and selectivity of the catalyst varied with support as seen in Table 2-2. Ru on magnesia was the least active catalyst and hydrogenated only the aromatic ring (Scheme 2-7), while Ru on carbon was very active for hydrogenation of aromatic ring but relatively less active for hydrogenation of carboxylic group. With this catalyst (5% Ru/C) hydrogenation of carboxylic group occurs only after maximum conversion of benzoic acid to cyclohexane carboxylic acid is achieved as shown in Figure 2-5. With Ru on carbon, hydrogenation of BZA to BZOH was not observed. Ru on supports like alumina, silica and titania was active for hydrogenation of carboxylic group as well as for hydrogenation of aromatic ring. With these supports the selectivity to benzyl alcohol was however zero, as hydrogenolysis products of benzyl alcohol i.e. toluene and methyl cyclohexane were obtained.

When Sn is doped in 5% Ru/Al_2O_3 (Sn/Ru atomic ratio 5) catalyst the selectivity of the 5%Ru/Al_2O_3 catalyst is changed completely. This catalyst is observed to hydrogenate only the carboxylic group of benzoic acid to give benzyl alcohol. With Ru-Sn/Al_2O_3 catalyst hydrogenolysis of benzyl alcohol to toluene is not observed, nor is hydrogenation of the aromatic ring. The reaction scheme as shown in Scheme 2-8 for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst was based on the concentration time profile shown in Figure 2-8. The selectivity to benzyl alcohol is 100% with 24% conversion of benzoic acid.



Scheme 2-7: Hydrogenation of benzoic acid with Ru supported on magnesia.



Scheme 2-8: Hydrogenation of benzoic acid with Ru-Sn/Al_2O_3

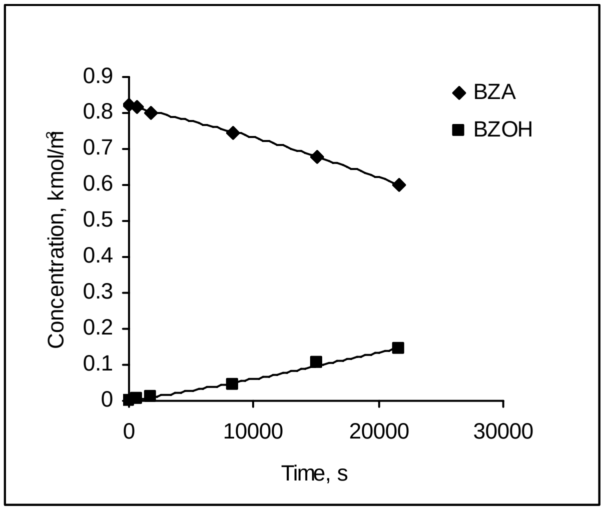


Figure 2-8: Concentration time profile for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

2.3.1.7 Hydrogenation of benzoic acid with cobalt catalysts

Cobalt metal catalyst has been reported for the hydrogenation of carboxylic acid to alcohols[7]. Hydrogenation of benzoic acid was carried out with Co/C, Co metal and Ru-Co catalysts. These catalysts were however, found to be inactive for the hydrogenation of both aromatic and carboxylic group.

The results on screening of catalyst for hydrogenation of benzoic acid with different catalysts are given Table 2-2.

Table 2-2: Catalyst screening for hydrogenation of benzoic acid.

No.	**Catalyst**	**Conversion %**	**Selectivity**				
			CCA %	**CHM %**	**TOL %**	**MCH %**	**BZOH %**
1	5% Ru/C	99	70	30	-	-	-
2	5% Pd/C	59.7	100	-	-	-	-
3	5% Re/C	6	-	50	-	-	50
4	5%Pd-2%Re/C	98.5	19	47	3.3	30.6	-
5	1%Ru-6%Re/C	8.1	15	-	52	-	33
6	5%Ru/Al_2O_3	96.1	56	10	6	28	-
7	5%Ru/TiO_2	65	13	77	7.8	2.2	-
8	1%Ru/C	7.94	62	38	-	-	-
9	1%Pd/C	32	93	7	-	-	-
10	5%Re/Al_2O_3	No reaction					
11	5%Co/C	No reaction					
12	Co metal	No reaction					
13	5% Ru/Co	No reaction					
14	5%Ru-29%Sn/Al_2O_3	24	0	0	0	0	100
15	5% Ru/MgO	29.2	100	0	0	0	0

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

(BZA = Benzoic acid, CCA = Cyclohexane carboxylic acid, CHM = Cyclohexyl methanol, TOL = Toluene, MCH = Methyl cyclohexane and BZOH = Benzyl alcohol)

2.3.2 Hydrogenation of Terephthalic, Isophthalic and Phthalic acid with 5% Ru/C, 5% Pd/C and 5%Ru-29%Sn/Al_2O_3 (Sn/Ru atomic ratio is 5) as catalyst

From catalyst screening studies on the hydrogenation of benzoic acid, it was observed that 5% Pd/C catalyst selectively hydrogenated aromatic ring of benzoic acid to give cyclohexane carboxylic acid, while 5% Ru/C catalyst hydrogenates both the functional groups aromatic ring and carboxylic to give cyclohexyl methanol. Bimetallic Ru-Sn/Al_2O_3 catalyst selectively hydrogenates carboxylic group of benzoic acid to give benzyl alcohol. Thus, hydrogenation of benzoic acid with 5% Pd/C, 5% Ru/C and Ru-Sn/Al_2O_3 catalyst can lead to selective formation of three different products. Hence the performance of 5% Pd/C, 5% Ru/C and Ru-Sn/Al_2O_3 catalyst for hydrogenation of terephthalic (TPA), isophthalic (IPA) and phthalic acid (PA), was assessed. For these reactions the reaction crude was analyzed at the end of the reaction (12 hrs), no intermediate sampling was done. All the reactions were carried out under the reaction conditions given in Table 2-3.

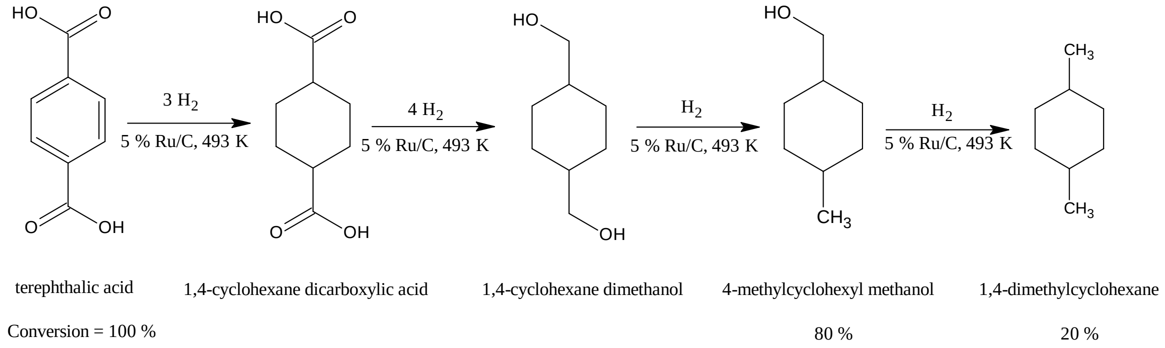
Table 2-3: Reaction conditions for hydrogenation of aromatic and aliphatic dicarboxylic acids.

Reaction parameter	**Range**
Temperature	493 K
Catalyst concentration	10 kg m^{-3}
Carboxylic acid concentration	0.82 $kmolm^{-3}$
Pressure	6.89 MPa
Solvent	1,4-dioxane
Stirring speed	1000 rpm
Total charge	2.5×10^{-5} m^3
Reaction time	12 hrs.

2.3.2.1 Hydrogenation of terephthalic acid (TPA)

Hydrogenation of TPA was carried out with 5% Ru/C, 5% Pd/C and Ru-Sn/Al_2O_3 catalyst respectively under reaction conditions mentioned in Table 2-3.

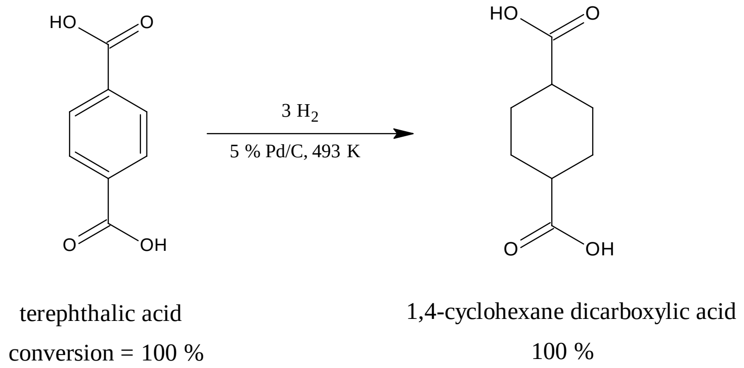
Hydrogenation of TPA with 5% Ru/C catalyst under the conditions mentioned above gave products like 4-methyl cyclohexyl methanol, and 1,4-dimethyl cyclohexane as shown in Scheme 2-9.



Scheme 2-9: Hydrogenation of terephthalic acid with 5% Ru/C catalyst.

These products are obtained from hydrogenolysis of 1,4-cyclohexane dicarboxylic acid (1,4-CDCA) which is formed by hydrogenation of the aromatic ring of TPA[12]. Here the products like 1,4-cyclohexane dicarboxylic acid and 1,4-cyclohexane dimethanol (1,4-CHDM) are not observed due to hydrogenolysis of 1,4-CHDM. This is because of the high activity of Ru/C catalyst for hydrogenation and hydrogenolysis. With this catalyst, conversion of TPA was 100% and selectivity to 4-methyl cyclohexyl methanol and 1,4-dimethyl cyclohexane was 80% and 20% respectively.

Hydrogenation of TPA with 5% Pd/C catalyst at 493 K under the reaction conditions mentioned in Table 2-3, yielded only 1,4-cyclohexane dicarboxylic acid as the product with 100% conversion of TPA as shown in Scheme 2-10 (Pd catalyst are in active for –COOH group[13]).

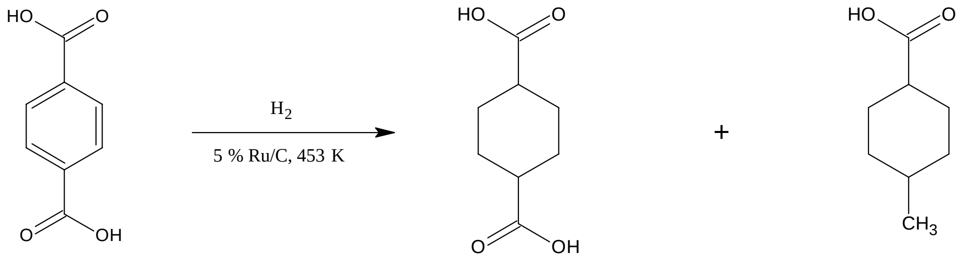


Scheme 2-10: Hydrogenation of terephthalic acid with 5% Pd/C catalyst.

This also confirms that 5% Pd/C catalyst is not active for hydrogenation and hydrogenolysis of carboxylic group of 1,4-CDCA.

Selective hydrogenation of TPA to 1,4-benzene dimethanol (1,4-BDM) does not take place with Ru-Sn/Al_2O_3 catalyst as observed for benzoic acid. The probable reason is that the solubility of TPA in 1,4-dioxane is low and hence the selective hydrogenation of carboxylic group does not occur. In case of the 5% Ru/C and 5% Pd/C catalyst the hydrogenation of the ring takes place giving 1,4-CDCA which is soluble, thereby giving further reaction. For Ru-Sn/Al_2O_3, since ring hydrogenation doesn't occur, no further reaction takes place and hence no hydrogenation products are observed.

When hydrogenation of TPA was carried out at a lower temperature of 453 K with 5% Ru/C catalyst, the hydrogenolysis of 1,4-cyclohexane dicarboxylic acid was reduced from 100% to 5%. The only hydrogenolysis product obtained was 4-methyl cyclohexane carboxylic acid. At 453 K the conversion of TPA was observed to be 100% and selectivity to 1,4-CDCA was 95%. Thus, reducing the temperature of reaction reduces the hydrogenolysis activity of 5% Ru/C catalyst. The probable reaction scheme for hydrogenation of TPA with 5% Ru/C catalyst at lower temperature is shown in Scheme 2-11.



terephthalic acid
Conversion = 100 %

cyclohexane-1,4-dicarboxylic acid
95 %

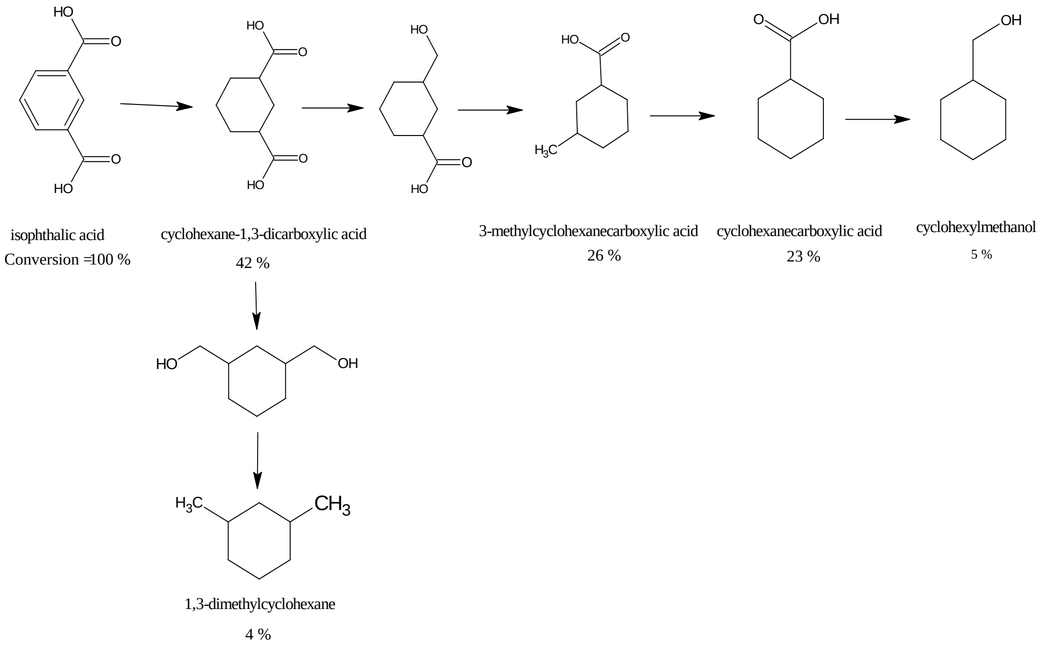
4-methylcyclohexanecarboxylic acid
5 %

Scheme 2-11: Hydrogenation of terephthalic acid with 5% Ru/C catalyst at 453 K.

2.3.2.2 Hydrogenation of isophthalic acid (IPA)

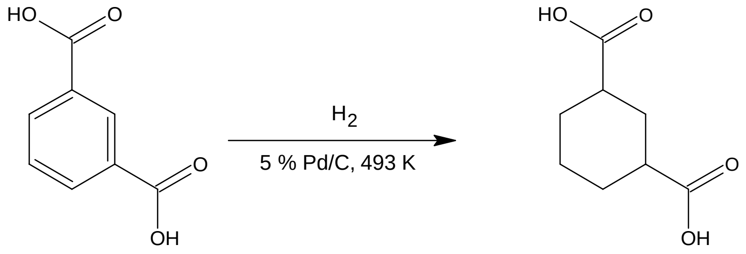
Hydrogenation of isophthalic acid (IPA) was carried out with 5% Ru/C, 5% Pd/C and Ru-Sn/Al_2O_3 catalyst under the reaction conditions mentioned in Table 2-3, to give a variety of products.

Hydrogenation of IPA with 5% Ru/C catalyst at 493 K was also a fast reaction. Here, hydrogenolysis of 1,3-cyclohexane dicarboxylic acid (1,3-CDCA) takes place which gives a range of products like 1,3-dimethyl cyclohexane, cyclohexane carboxylic acid, cyclohexyl methanol and 3-methyl cyclohexane carboxylic acid. Since under the same reaction conditions, hydrogenation of TPA with 5% Ru/C catalyst gave only hydrogenolysis product, it is understood that hydrogenolysis of 1,3-cyclohexane dicarboxylic acid is difficult as compared to 1,4-cyclohexane dicarboxylic acid. The proposed reaction scheme along with the selectivity achieved for different products in the hydrogenation of isophthalic acid with 5% Ru/C catalyst is shown in Scheme 2-12.



Scheme 2-12: Hydrogenation of isophthalic acid with 5% Ru/C catalyst.

Hydrogenation of IPA under the reaction conditions mentioned above with 5% Pd/C catalyst is a very selective reaction yielding a single product 1,3-cyclohexane dicarboxylic acid with 100% conversion of IPA. The reaction scheme for hydrogenation of IPA is shown in Scheme 2-13.



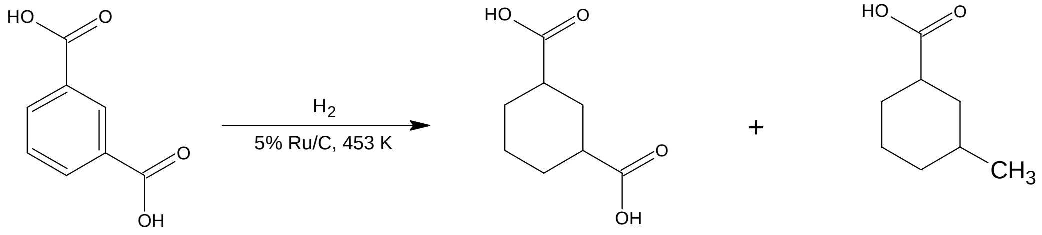
isophthalic acid
Conversion = 100 %

cyclohexane-1,3-dicarboxylic acid
100 %

Scheme 2-13: Hydrogenation of isophthalic acid with 5% Pd/C catalyst.

When hydrogenation of IPA was carried out with Ru-Sn/Al_2O_3 catalyst under the reaction conditions mentioned in Table 2-3, selective hydrogenation of carboxylic group in presence of aromatic ring was not observed as seen in case of benzoic acid, where benzyl alcohol is obtained with 100% selectivity. This is probably due to low solubility of IPA in the reaction medium.

Hydrogenation of IPA with 5% Ru/C catalyst at 453 K, under the same reaction conditions shows a reduction in hydrogenolysis products. A 94% selectivity to 1,3-cyclohexane dicarboxylic acid and 6% selectivity to 3-methyl cyclohexane carboxylic acid were achieved. Conversion of IPA at a reaction temperature of 453 K was 100%. The reaction scheme representing the hydrogenation of IPA with 5% Ru/C catalyst along with product selectivity at 453 K is shown in Scheme 2-14.



isophthalic acid
Conversion = 100 %

cyclohexane-1,3-dicarboxylic acid
94 %

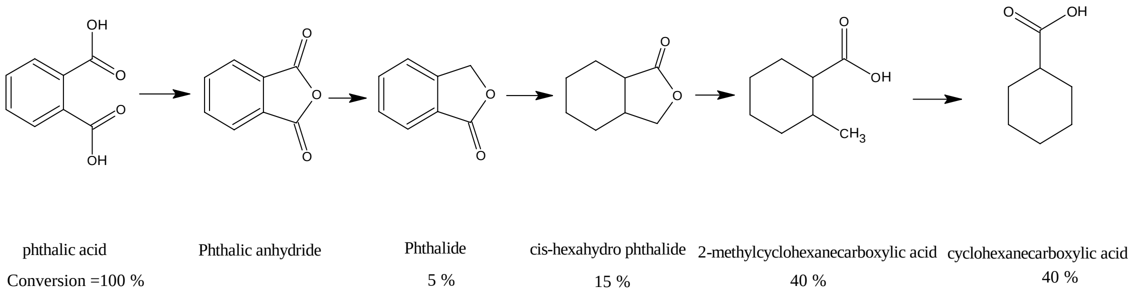
3-methylcyclohexanecarboxylic acid
6 %

Scheme 2-14: Hydrogenation of isophthalic acid with 5% Ru/C catalyst at 453 K.

2.3.2.3 Hydrogenation of phthalic acid (PA)

Hydrogenation of phthalic acid (PA) is more complex as compared to hydrogenation of TPA and IPA. This is due to the proximity of two –COOH groups of IPA, which can undergo dehydration to give phthalic anhydride at higher temperature[14]. Formation of phthalic anhydride from PA is a thermal process and not catalytic. Thus, a low selectivity for hydrogenation products of PA due to formation phthalic anhydride is expected.

Hydrogenation of phthalic acid with 5% Ru/C catalyst was carried out under the reaction conditions mentioned in Table 2-3. Phthalic acid like the other isomers also undergoes hydrogenolysis with 5% Ru/C catalyst at 493 K. The probable reaction scheme for hydrogenation of PA is shown in Scheme 2-15 along with the product selectivity.

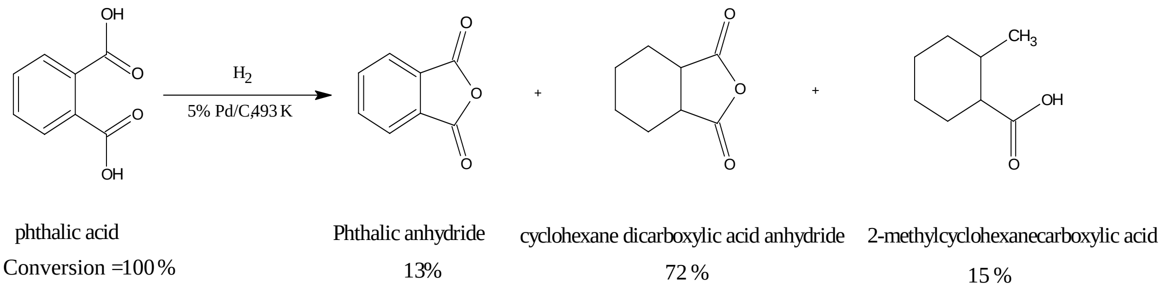


Scheme 2-15: Hydrogenation of phthalic acid with 5% Ru/C catalyst at 493 K.

The major products obtained were 2-methyl cyclohexane carboxylic acid (40% selectivity) and cyclohexane carboxylic acid (40% selectivity); other products which were obtained were cis-hexahydro phthalide (15%) and phthalide (5%). Phthalide and cis-hexahydro phthalide are the hydrogenation products of phthalic anhydride.

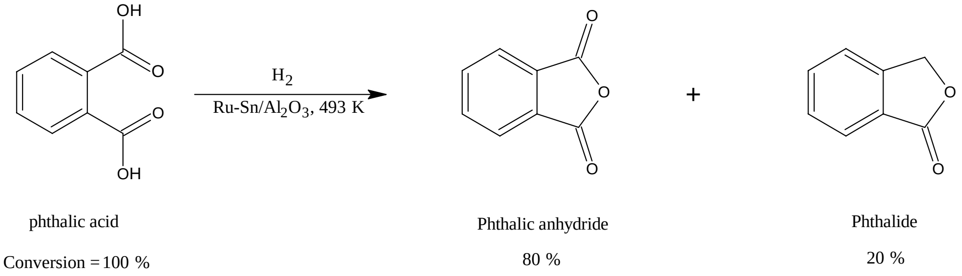
Hydrogenation of PA with 5% Pd/C catalyst under the reaction conditions mentioned in Table 2-3 gave cyclohexane dicarboxylic acid anhydride as a major product (72% selectivity); the other product, 2-methyl cyclohexane carboxylic acid, (15%) was obtained by hydrogenolysis. Hydrogenation of PA with 5% Pd/C catalyst did not produce 1,2-cyclohexane dicarboxylic acid; this is due to formation of phthalic anhydride. In this reaction some unreacted phthalic anhydride (13%) was also observed at the end of 12 hrs.

The reaction scheme for hydrogenation of PA with 5% Pd/C catalyst is shown in Scheme 2-16 along with the selectivity observed.



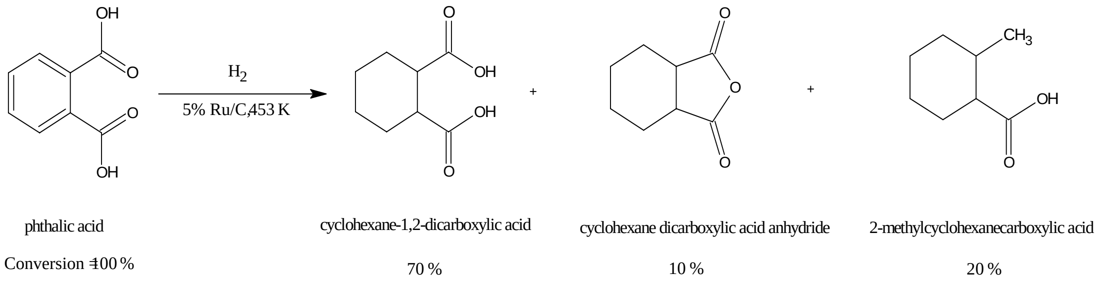
Scheme 2-16: Hydrogenation of phthalic acid with 5% Pd/C catalyst.

Hydrogenation of PA with Ru-Sn/Al_2O_3 catalyst under the reaction conditions mentioned in Table 2-3 gave benzofuranone (Phthalide). Unlike TPA and IPA, PA undergoes hydrogenation with Ru-Sn/Al_2O_3 catalyst since phthalic anhydride formed by dehydration of phthalic acid is soluble in 1,4-dioxane. During reaction the phthalic acid was completely converted to phthalic anhydride. Hydrogenation of C=O group of phthalic anhydride with Ru-Sn/Al_2O_3 catalyst gives phthalide. Conversion of phthalic anhydride is observed to be 20% with 100% selectivity to phthalide. The reaction scheme for hydrogenation of phthalic acid with Ru-Sn/Al_2O_3 catalyst along with product distribution is shown in Scheme 2-17.



Scheme 2-17: Hydrogenation of phthalic acid with Ru-Sn/Al_2O_3 catalyst.

Hydrogenation of PA with 5% Ru/C catalyst was also conducted at 453 K under reaction conditions mentioned in Table 2-3. With lowering of reaction temperature, the formation of phthalic anhydride was drastically reduced and the percentage of hydrogenolysis products obtained was also reduced. Selectivity to 1,2-CDCA was 70%; 2-methyl cyclohexane carboxylic acid was 20% and 10% cyclohexane dicarboxylic acid anhydride was also obtained during reaction. 100% conversion of phthalic acid was observed. The reaction scheme for hydrogenation of phthalic acid with 5% Ru/C catalyst at 453 K is shown in Scheme 2-18 along with product selectivity.



Scheme 2-18: Hydrogenation of phthalic acid with 5% Ru/C catalyst at 453 K.

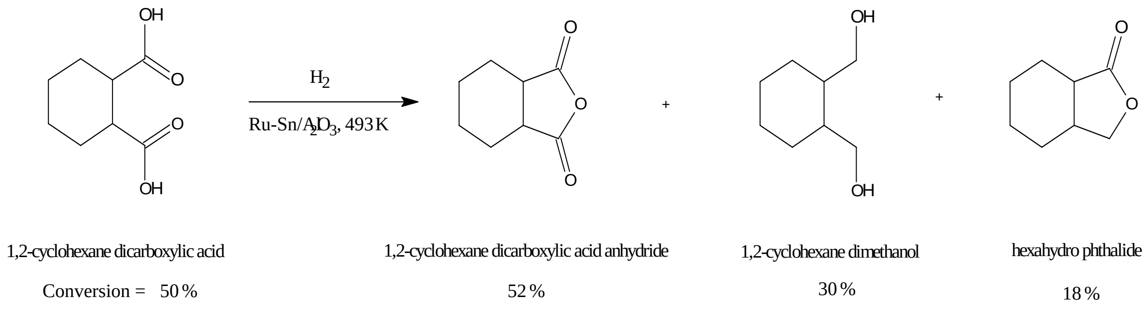
2.3.3 Hydrogenation of cyclohexane dicarboxylic acids with 5% Ru/C, 5% Pd/C and 5%Ru-29%Sn/Al_2O_3 (Sn/Ru atomic ratio 5) catalyst

Cyclohexane dicarboxylic acids are hydrogenation products of TPA, IPA and PA[15]. Hence the activity of 5% Ru/C, 5% Pd/C and Ru-Sn/Al_2O_3 catalyst for hydrogenation of cyclohexane dicarboxylic acids was assessed. Hydrogenation reactions were carried out under reaction conditions mentioned in Table 2-3.

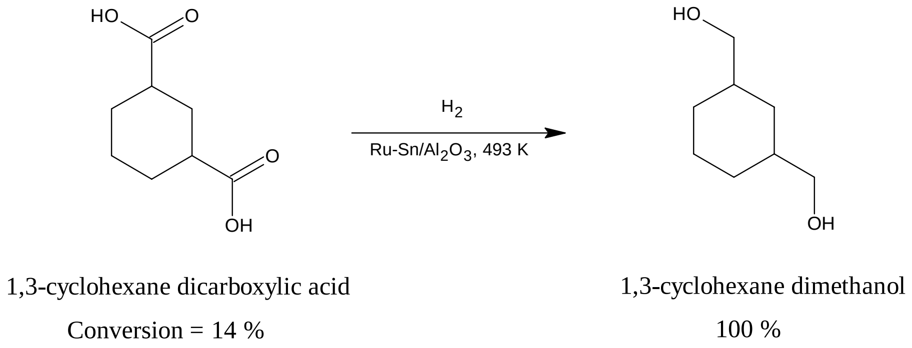
Hydrogenation of 1,4-CDCA, 1,3-CDCA and 1, 2-CDCA with 5% Ru/C catalyst yielded only overhydrogenation products. When the catalyst loading was reduced from 10 kg/m^3 to 0.4 kg/m^3, almost no conversion was seen and hydrogenolysis product was less than 5%.

5% Pd/C catalyst was also found to be inactive for the hydrogenation of 1,4-CDCA, 1,3-CDCA and 1,2-CDCA under the reaction conditions mentioned in Table 2-3. This is because Pd/C is inactive for hydrogenation of carboxylic group.

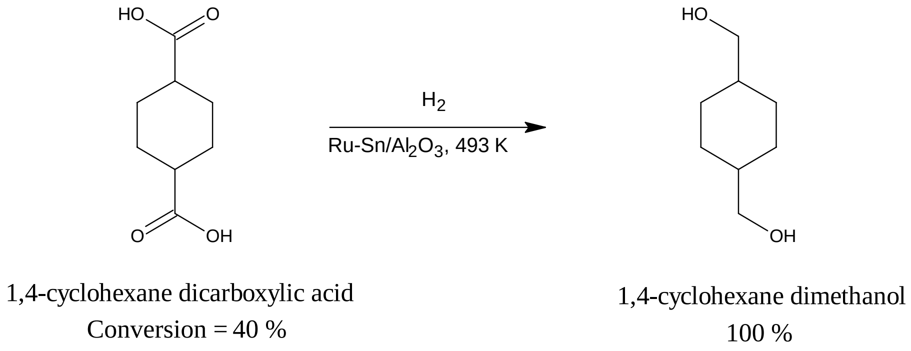
The only catalyst which selectively hydrogenated 1,2-CDCA, 1,3-CDCA and 1,4-CDCA to corresponding 1,2-cyclohexane, 1,3-cyclohexane and 1,4-cyclohexane dimethanol respectively was Ru-Sn/Al_2O_3. The product distribution for hydrogenation with Ru-Sn/Al_2O_3 catalyst is shown in Scheme 2-19, 2-20 and 2-21 for 1,2; 1,3 and 1,4-cyclohexane dicarboxylic acid respectively.



Scheme 2-19: Hydrogenation of 1,2-CDCA with Ru-Sn/Al_2O_3 catalyst.



Scheme 2-20: Hydrogenation of 1,3-CDCA with Ru-Sn/Al_2O_3 catalyst.



Scheme 2-21: Hydrogenation of 1,4-CDCA with Ru-Sn/Al_2O_3 catalyst.

As seen in Scheme 2-19, hydrogenation of 1,2-CDCA gives 18% hexahydro phthalide, 52% 1,2-cyclohexane dicarboxylic acid anhydride and 30% 1,2-cyclohexane dimethanol, at a 1,2-CDCA conversion of 50%.

Hydrogenation of 1,3 and 1,4-CDCA with Ru-Sn/Al_2O_3 gives 100% 1,3 and 1,4-cyclohexane dimethanol with 14% and 40% conversion of 1,3-CDCA and 1,4-CDCA respectively.

2.3.4. Hydrogenation of TPA and IPA with 5%Ru-29%Sn/Al_2O_3 (Sn/Ru atomic ratio 5) catalyst

In Section 2.3.2, it was observed that Ru-Sn/Al_2O_3 catalyst was inactive for hydrogenation of TPA and IPA but was active for the hydrogenation of PA to phthalide. The reason for inactivity of Ru-Sn/Al_2O_3 catalyst for hydrogenation of terephthalic and isophthalic acid was found to be their solubility in the reaction solvent. These aromatic carboxylic acids are insoluble in 1,4-dioxane which is used as reaction solvent.

To study the hydrogenation of these aromatic carboxylic acids the concentration of these acids was reduced from 0.82 kmol/m^3 to 0.03 kmol/m^3. Under these reaction conditions, Ru-Sn/Al_2O_3 (reduced at 573 K) was found to be active for hydrogenation of terephthalic and isophthalic acid but it gave hydrogenolysis products. This is expected because aromatic alcohols are prone to undergo hydrogenolysis [6,16].

When hydrogenation of the aromatic carboxylic acids was carried out with Ru-Sn/Al_2O_3 catalyst reduced at higher temperature i.e. at 1073 K (instead of 573 K) the formation of hydrogenolysis products was suppressed and selectivity to hydroxyl methyl benzoic acid (HMBA) and benzene dimethanol (BDM) was increased, at the expense of the activity of Ru-Sn/Al_2O_3 catalyst, which decreases when reduced at high temperature[17]. A comparison of the results for hydrogenation of TPA and IPA with Ru-Sn/Al_2O_3 catalyst reduced at 573 and 1073 K are shown in Table 2-4.

Table 2-4: Hydrogenation of TPA and IPA with Ru-Sn/Al_2O_3 catalyst reduced at 573 and 1073 K.

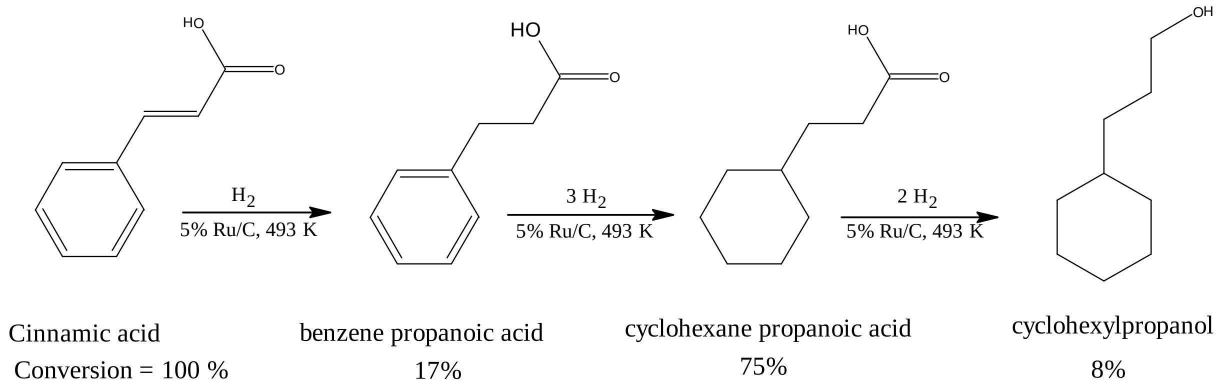
No.	Reduction temperature (K)	Terephthalic acid	Isophthalic acid
1	573	Conversion = 71% 4-HMBA = 0% 1,4- BDM = 0% Other products = 100%	Conversion = 40% 3-HMBA = 0% 1,3- BDM = 0% 3-methyl benzoic acid = 100%
2	1073	Conversion = 48% HMBA = 15% 1,4 BDM = 70% Other products = 15%	Conversion = 21% 3-HMBA = 84% 1,3- BDM = 0% 3-methyl benzoic acid = 16%

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, TPA and IPA = 0.03 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 2.5×10^{-5} m^3.
HMBA = Hydroxy methyl benzoic acid, BDM = Benzene dimethanol, Other products for TPA = 4-methyl benzoic acid and p-xylene.

2.3.5 Hydrogenation of cinnamic and salicylic acid with 5% Ru/C, 5% Pd/C and 5%Ru-29%Sn/Al_2O_3 catalyst

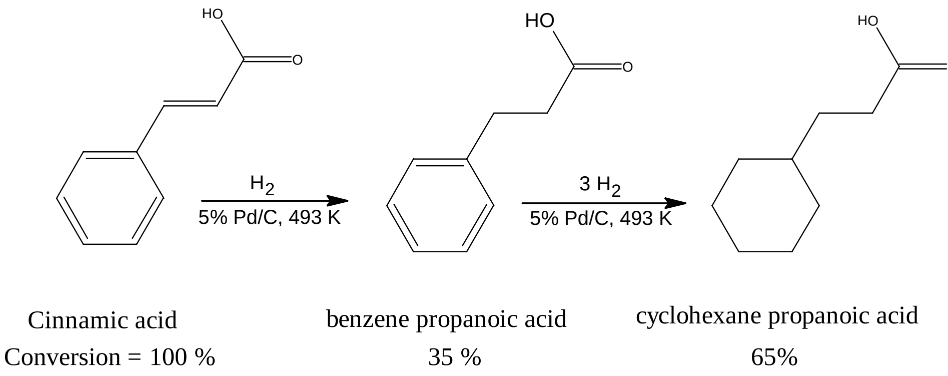
Hydrogenation of cinnamic and salicylic acid was carried out at 493 K, 6.89 MPa of hydrogen partial pressure and catalyst concentration of 5 kg/m^3. The concentration of cinnamic and salicylic acid in 1,4-dioxane was 0.82 kmol/m^3.

Hydrogenation of cinnamic acid with 5% Ru/C catalyst gives benzene propanoic acid, cyclohexane propanoic acid and 3-cyclohexyl propanol at the end of 6 hrs. Conversion of cinnamic acid was 100% and selectivity to benzene propanoic acid, 3-cyclohexane propanoic acid and 3-cyclohexyl propanol was 17%, 75% and 8% respectively. The reaction pathway for hydrogenation of cinnamic acid with 5% Ru/C catalyst is shown in Scheme 2-22.



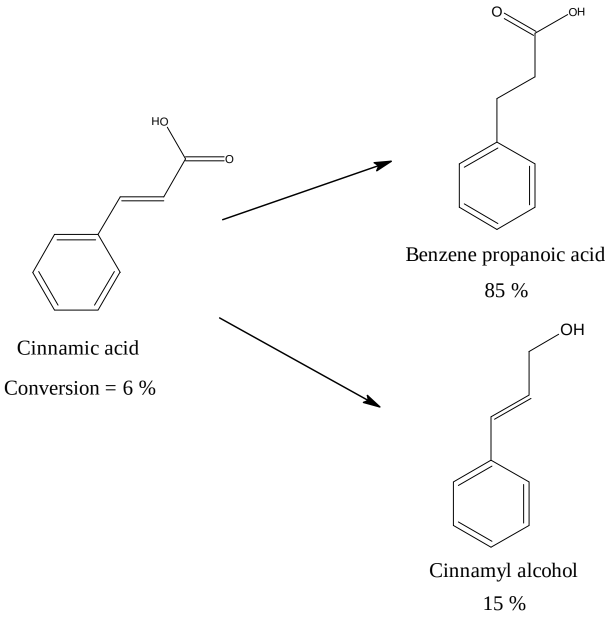
Scheme 2-22: Hydrogenation of cinnamic acid with 5% Ru/C catalyst.

Hydrogenation of cinnamic acid with 5% Pd/C catalyst gives benzene propanoic acid and cyclohexane propanoic acid as shown in Scheme 2-23. Conversion of cinnamic acid was 100% with 35% selectivity to benzene propanoic acid and 65% selectivity to cyclohexane propanoic acid.



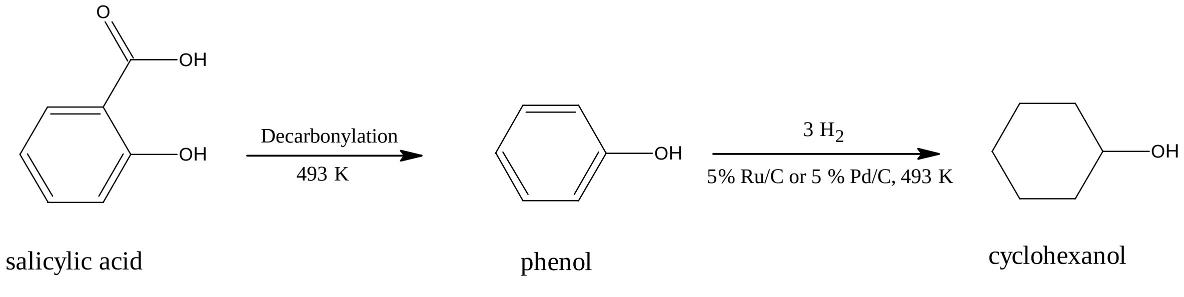
Scheme 2-23: Hydrogenation of cinnamic acid with 5% Pd/C catalyst.

When hydrogenation of cinnamic acid is carried out with Ru-Sn/Al_2O_3 catalyst, hydrogenation of aromatic ring is completely inhibited. A 6% conversion of cinnamic acid with 85% selectivity to benzene propanoic acid and 15% selectivity to cinnamyl alcohol was obtained. The reaction scheme for hydrogenation of cinnamic acid with Ru-Sn/Al_2O_3 catalyst is shown in Scheme 2-24.



Scheme 2-24: Hydrogenation of cinnamic acid with Ru-Sn/Al_2O_3 catalyst.

With 5% Ru/C and 5% Pd/C the hydrogenation of carboxylic group of salicylic acid does not occur at 493 K as decarbonylation of carboxylic group takes place to give phenol followed by the hydrogenation of phenol to cyclohexanol, as shown in Scheme 2-25. Ru-Sn/Al_2O_3 catalyst is inactive for hydrogenation of phenol. With 5% Ru/C catalyst there is a 100% conversion of phenol to cyclohexanol with total selectivity, whereas with 5% Pd/C catalyst a 78% conversion of phenol with 100% selectivity to cylohexanol is observed.



Scheme 2-25: Hydrogenation of salicylic acid with Ru/C or Pd/C catalyst.

2.3.6 Effect of water as co-solvent for hydrogenation of benzoic acid with ruthenium catalyst

The presence of water in the reaction medium is known to influence not only the activity of the catalyst, but also the product distribution. At times it can also entirely change the reaction pathway.

The effect of water as a co-solvent in 1,4-dioxane solvent, in the hydrogenation of benzoic acid was studied in presence of a 1:1 mixture of water and 1,4-dioxane with different ruthenium catalysts. The ruthenium catalysts used for this study were 5% Ru/C, 1%Ru-6%Re/C, 5% Ru/Al_2O_3 and 5% Ru/TiO_2. The results are presented in Table 2-5 and Table 2-6 for the dioxane and water + dioxane solvent respectively.

Table 2-5: Hydrogenation of benzoic acid with different Ru catalyst in dioxane as solvent

No.	Catalyst	Conversion %	Selectivity				
			CCA %	CHM %	TOL %	MCH %	BZOH %
1	5 % Ru/C	100	70	30	-	-	-
2	1%Ru-6%Re/C	8.1	15	-	52	-	33
3	5% Ru/Al_2O_3	96.1	56	10	6	28	-
4	5% Ru/TiO_2	65	13	77	7.8	2.2	-

Reaction conditions: Temperature = 493 K, Hydrogen pressure = 6.89 MPa, Agitation speed = 1000 rpm, Benzoic acid = 0.82 $kmolm^{-3}$, Catalyst = 5 kgm^{-3}, Solvent = 1,4 dioxane, Time = 6 hrs, Total volume = 1.0×10^{-4} m^3.

(BZA = Benzoic acid, CCA = Cyclohexane carboxylic acid, CHM = Cyclohexyl methanol, TOL = Toluene, MCH = Methyl cyclohexane and BZOH = Benzyl alcohol)

From the results shown in Table 2-5 it is clear that initially hydrogenation of carboxylic group takes place followed by hydrogenolysis when hydrogenation is carried in 1,4-dioxane as solvent. This observation is as per reported trend where it is observed that hydrogenolysis is favored in 1,4-dioxane solvent[18].

When hydrogenation of benzoic acid was carried out using the same catalysts in 1:1 water + 1,4-dioxane solvent, the selectivity profile for all the catalysts was changed and for all the four catalysts, cyclohexane carboxylic acid was obtained as a major product. The details of conversion and selectivity are given in Table 2-6. The increase in selectivity to cyclohexane carboxylic acid in presence of water as co-solvent is due to the orientation of aromatic ring towards catalyst surface. Due to interaction of the water molecules in the solvent with the polar carboxylic group[19], the aromatic ring is oriented towards the catalyst surface, while the carboxylic group faces the solvent. This results in selective hydrogenation of the ring to give cyclohexane carboxylic acid.

Table 2-6: Hydrogenation of benzoic acid with different Ru catalyst in 1,4-dioxane-water (1:1) as solvent

No.	Catalyst	Conversion %	Selectivity				
			CCA %	CHM %	TOL %	MCH %	BZOH %
1	5 % Ru/C	100	86	14	-	-	-
2	1%Ru-6%Re/C	13.3	54.1	2.74	5.2	22	16
3	5% Ru/Al_2O_3	85.3	93.7	6.3	0	0	0
4	5% Ru/TiO_2	65.8	99	1	0	0	0

Reaction conditions: Temperature = 493 K, Hydrogen pressure = 6.89 MPa, Agitation speed = 1000 rpm, Benzoic acid = 0.82 $kmolm^{-3}$, Catalyst = 5 kgm^{-3}, Solvent = 1,4 dioxane-water (1:1), Time = 6 hrs, Total volume = 1.0×10^{-4} m^3.

2.4 Conclusion

Catalyst screening study for hydrogenation of benzoic acid suggests that 5% Ru/C catalyst was active for hydrogenation of both aromatic ring and carboxylic group while Pd/C catalyst was observed to be active only for hydrogenation of aromatic ring. With Ru-Sn/Al_2O_3 catalyst hydrogenation of aromatic ring was inhibited completely and hydrogenation of carboxylic group was favored to give benzyl alcohol.

Hydrogenation of aromatic dicarboxylic acids like terephthalic and isophthalic acid gave 100% selectivity to respective cyclohexane dicarboxylic acid with 5% Pd/C catalyst. 5% Ru/C catalyst was observed to be a very active catalyst for hydrogenation of dicarboxylic acids and gave overhydrogenation products at 493 K. At lower temperature (453 K) the selectivity for cyclohexane dicarboxylic acids was increased.

Ru-Sn/Al_2O_3 catalyst was observed to be active for hydrogenation of terephthalic and isophthalic acid and gave hydrogenolysis products. When Ru-Sn/Al_2O_3 catalyst was reduced at higher temperature (1073 K), the hydrogenolysis activity decreased and the selectivity of the catalyst for hydrogenation of terephthalic acid to 1,4-benzene dimethanol was increased to 70%. Similarly the selectivity for hydrogenation of isophthalic acid to 3-hydroxy methyl benzoic acid was increased from 0% to 84% with this catalyst. Hydrogenation of phthalic acid with Ru-Sn/Al_2O_3 catalyst was observed to gave phthalide instead of 1,2-benzene dimethanol or 2-hydroxy methyl benzoic acid.

Hydrogenation of cyclohexane dicarboxylic acids like 1,4-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid and 1,2-cyclohexane dicarboxylic acid was studied using the catalysts Pd/C, Ru/C and Ru-Sn/Al_2O_3. Ru-Sn/Al_2O_3 catalyst selectively hydrogenated the carboxylic group of these cyclohexane dicarboxylic acids to give cyclohexane dimethanol. The selectivity of 1,2-cyclohexane dimethanol formed from hydrogenation of 1,2-cyclohexane dicarboxylic was low (30 %) due to dehydration of 1,2-cyclohexane dicarboxylic acid to give 1,2-cyclohexane dicarboxylic acid anhydride.

Similar trends were observed for hydrogenation of cinnamic acid with 5% Ru/C, 5% Pd/C and Ru-Sn/Al_2O_3 catalysts, as observed for benzoic acid hydrogenation. Selective inhibition of C=C hydrogenation is not possible with 5% Ru/C, 5% Pd/C and Ru-Sn/Al_2O_3 catalyst. Ru-Sn/Al_2O_3 catalyst was observed to suppress hydrogenation of aromatic ring. With Ru-Sn/Al_2O_3 catalyst 6% cinnamic acid was hydrogenated to give 15% cinnamyl alcohol and 85% benzene propanoic acid.

Addition of water in reaction medium (1,4-dioxane) enhanced the selective hydrogenation of aromatic ring of benzoic acid.

The screening of the catalysts showed that with proper choice of catalysts and solvent and by tailoring of reaction conditions it was possible to achieve almost total selectivity to desired products. With this in mind the kinetics of the selective hydrogenation were studied to understand the role of process parameters on activity and selectivity. The systems chosen for study were.

(i) Hydrogenation of benzoic acid to cyclohexane carboxylic acid using 5% Ru/C catalysts in 1,4 dioxane-water (1:1) as solvent.

(ii) Selective hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al_2O_3 catalyst.

(iii) Hydrogenation of lauric acid to lauryl alcohol using Ru-Sn/TiO_2 catalyst

These studies are presented in further chapters.

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Chapter 3

Kinetics of hydrogenation of benzoic acid to cyclohexane carboxylic acid in a batch slurry reactor using 5% Ru/C catalyst

3.1 Introduction

Hydrogenation of benzoic acid (BZA) is an industrially important reaction and there exists a large potential market for benzoic acid-derived hydrogenation products. For example, benzoic acid can be hydrogenated to produce cyclohexane carboxylic acid (CCA), which on further hydrogenation gives cyclohexylmethanol (CHM). The single largest commercial application of CCA is in the manufacture of caprolactam, which is primarily used for production of nylon[1]. CHM is of considerable commercial importance and finds application in the polymer industry.

The liquid-phase catalytic hydrogenation of benzoic acid has been widely studied using supported noble metal catalysts such as Pd, Pt, Rh and Ru[2]. In general, Pd is the most extensively used catalyst for hydrogenation of BZA as, with this catalyst the selectivity to CCA is 100%[3]. The Ru catalyzed systems are also of interest as the selectivity to CCA can be tuned up to 99% with the help of reaction parameters. There is also no information available in the literature on the kinetics of this reaction using Ru/C as catalyst.

Although Ru is a cheap and active catalyst for hydrogenation of aromatic ring, it is not used for hydrogenation of benzoic acid to cyclohexane carboxylic acid as it is also active for the further hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol. Increasing the selectivity for cyclohexane carboxylic acid while retaining the activity of Ru catalyst would be of interest as Ru is cheaper compared to Pd. In the literature there are reports on the effects of solvent on the selective hydrogenation of functional groups with different polarity[4]. In case of benzoic acid, the two functional groups which can be hydrogenated are (i) the aromatic ring and (ii) the carboxylic group. These two functional groups have different polarities, -COOH is polar and has affinity for polar solvents, while the aromatic ring is non-polar, and has affinity for non-polar solvents. If a polar solvent is used for hydrogenation, then the –COOH group is expected to be oriented away from the catalyst surface and towards the solvent. Thus it would favor increasing the selectivity to cyclohexane carboxylic acid for hydrogenation of benzoic acid with Ru/C catalyst.

The hydrogenation of benzoic acid using Ru/C catalyst involves three phases: solid (catalyst), gas (hydrogen) and liquid (reaction solvent) with dissolved reactants. The overall performance of such a multiphase catalytic reaction may depend on various factors such as gas to liquid mass transfer, liquid-solid mass transfer, intraparticle diffusion and intrinsic reaction kinetics etc. Thus, to analyze such a multiphase catalytic reaction, it is important to understand the rate behavior and intrinsic kinetics of this reaction. In Chapter two the catalyst screening studies for hydrogenation of benzoic acid have been presented, wherein it was observed that Ru/C was the most active catalyst for hydrogenation of benzoic acid. It was also observed that addition of water to 1,4-dioxane increases the selectivity of the supported Ru catalyst to cyclohexane carboxylic acid.

The hydrogenation of benzoic acid to cyclohexane carboxylic acid and further to cyclohexyl methanol is a typical case of consecutive hydrogenation. CCA is an important intermediate product and hence it is necessary to achieve high selectivity to CCA. This can be obtained by arresting the reaction at the time at which maximum concentration of CCA is achieved (t_{max}). There are no equations as of now which can predict the t_{max} for such consecutive hydrogenation reactions. It was thus of interest to obtain equations to predict the t_{max} for the system BZA - CCA - CHM.

The first objective of this work was to investigate the effect of co-solvent and various reaction conditions on the activity/selectivity behavior of Ru/C catalyst for catalytic hydrogenation of benzoic acid to cyclohexane carboxylic acid. The second objective was to investigate the kinetics of this reaction and develop rate equations to represent the kinetics observed. Besides the kinetics, we have also proposed an approach to derive an equation for t_{max} for consecutive catalytic reactions using Marquardts method of optimization. The method has been validated by applying to the consecutive hydrogenation of BZA to CCA to CHM.

3.2 Experimental

3.2.1 Materials

Benzoic acid, 1,4-dioxane and $RuCl_3.3H_2O$ were procured from SD Fine Chemicals Ltd. (India). 5% Ru/C catalyst and was procured from Arora Matthey Ltd. (India). Catalyst supports like carbon, alumina, magnesia, titania, silica, and authentic standards of reaction products like cyclohexane carboxylic acid and cyclohexyl methanol were procured from Aldrich Chemicals (USA). Hydrogen and nitrogen used were procured from Indian Oxygen Ltd. Bombay.

3.2.2 Catalyst preparation

Ru/C catalyst was prepared by impregnating carbon support with $RuCl_3.3H_2O$ solution at 333 K with continuous stirring for 1 hr. After impregnation with $RuCl_3.3H_2O$, excess water was removed using rotary evaporator. The dried impregnated catalyst was dried overnight in an oven at 363 K. After this the catalyst was reduced at 573 K in a tubular silica glass reactor placed in a furnace under constant flow of hydrogen gas (5 ml/min) for 12 hrs. After the reduction period, the silica glass reactor was flushed with nitrogen gas till the temperature of the furnace attained room temperature. The reduced catalyst was transferred into 50 ml container under nitrogen flow and stored in the dessicator under nitrogen.

5% Ru/Al_2O_3, 5% Ru/TiO_2 and 5% Ru/SiO_2 catalysts were also prepared by the procedure described above with the only difference that, these catalysts were calcined at 773 K in a furnace for 12 hrs before reducing in silica glass reactor.

The tubular, silica glass reactor assembly for catalyst reduction is discussed in Section 2.2.2.

3.2.3 Reactor Set-up for high pressure reactions

The reactions were carried out in a 250 ml capacity high pressure – high temperature reactor supplied by Parr Instruments Co. USA. The reactor was provided with a double bladed variable speed stirrer with a magnetic drive and automatic temperature control by means of an external electrically heated jacket and internal cooling coils. A gas inlet / outlet as well as liquid outlet provided a facility for sampling of liquid contents in the reactor. For safety purpose, a high pressure – high temperature cut-off facility was also provided to the reactor, in addition to a rupture disc. The autoclave was designed to operate at a temperature up to 623 K and 200 bar pressure.

The reactor was connected to a hydrogen reservoir held at a pressure higher than that of the reactor, through a constant pressure regulator. Hydrogen gas was supplied to the reactor from this reservoir through a non-return valve. The gas consumed during the course of the reaction was determined from the observed pressure drop in the reservoir at different time intervals. A transducer connected to a pressure readout system was used to monitor pressure in the reactor and the hydrogen reservoir. A schematic of the reactor assembly is shown in Section 2.2.3, Figure 2-2.

3.2.4 Procedure for high pressure reactions

In a typical hydrogenation experiment, known quantities of the substrate, catalyst and solvent were charged into a clean and dry reactor. The contents were flushed with nitrogen followed by hydrogen (2-3 times). The contents in the autoclave were heated to a desired temperature under slow stirring (300 rpm). After the desired temperature was attained, the autoclave was pressurized to the requisite pressure with hydrogen and the reaction was started by adjusting the agitation speed to 1200 rpm. The hydrogen consumption was determined from the drop in the hydrogen pressure in the reservoir vessel as a function of time. The liquid samples were withdrawn at specific time intervals and analyzed for reactant and product concentrations. At the end of the reaction, the autoclave was cooled to room temperature and a gas sample was withdrawn for checking the gas phase products if any. The gas phase analysis was essential to confirm that cracking of the products to hydrocarbons was negligible. Following this, the contents in the reactor were discharged and the liquid sample analyzed for reactants and products.

3.2.5 Analysis

The various hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector), as discussed in Section 2.2.5.

Analysis of ruthenium leaching into reaction medium from the catalyst was performed using Inductively Coupled Plasma with Atomic Emission Spectra (ICP-AES) or Graphite Furnace Atomic Absorption Spectrophotometer [GFAAS, GBC Avanta Sigma Instruments Australia, with photomultiplier tube (PMT) detector].

For quantitative analysis, the sample from the reaction mixture was filtered to remove catalyst, and then analyzed by gas chromatography. For analysis a HP INNOWax, (polyethylene glycol) capillary column (30m x 320µm x 0.25 µm) along with flame ionization detector was used on an Agilent 6890 gas chromatograph controlled by HP Chemstation software equipped with an auto sampler unit. Calibration for the hydrogenation products was done using external standard method[5]. The standard conditions under which the gas chromatograph was operated for quantitative analysis of reactants and products are given in Table 3-1. The reproducibility of results was checked and the error in experimental measurements was less than ±3%. A mass balance of the reactants consumed and products formed showed an agreement greater than 95%. Similarly, gas balance for hydrogen consumed and products formed was found to be above 95%. A typical GC chart showing the analysis of benzoic acid hydrogenation reaction is shown in Figure 3-1.

Table 3-1: Conditions for gas chromatographic analysis

Injection volume	1 µl		
Injector temperature	280 ^{o}C		
Flame ionization detector Temp	280 ^{o}C		
Inlet flow-total (He)	500 ml/min		
Split ratio for Injector	100:1		
Oven Temperature	Heating rate (^{o}C/min)	Temperature (^{o}C)	Hold time (min)
		70	5
	30	210	12
	Post run	210	5
Carrier gas (Helium)	Flow Rate (ml/min)	Pressure (Psi)	Hold time (min)
	5.6	24	30

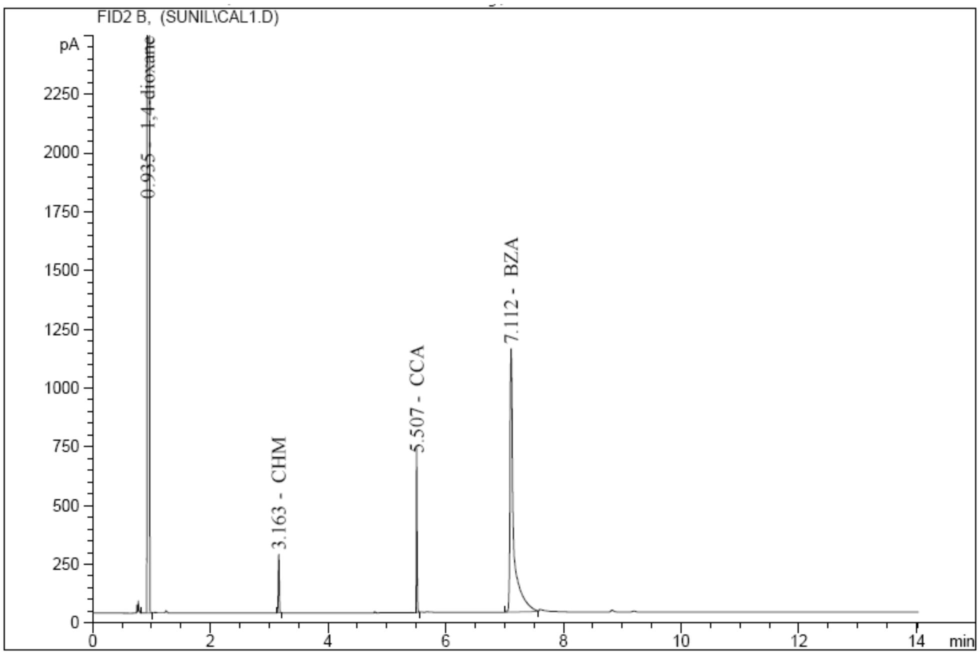


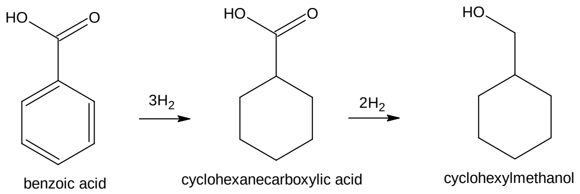
Figure 3-1: Gas chromatogram for benzoic acid (BZA) and its hydrogenation products cyclohexane carboxylic acid (CCA) and cyclohexyl methanol (CHM).

3.3 Results and discussion

As per our observations from the initial experiments (Chapter II) Ru/C was the catalyst of choice for the consecutive hydrogenation of benzoic acid to cyclohexane carboxylic acid and cyclohexyl methanol. Since our main objective was to study the kinetics of benzoic acid hydrogenation to cyclohexane carboxylic acid, it was necessary to standardize the reaction conditions and optimize the solvent composition to obtain total selectivity to cyclohexane carboxylic acid. This would ensure that our study would be representative of hydrogenation of benzoic acid to cyclohexane carboxylic acid.

3.3.1 Preliminary experiments for hydrogenation of benzoic acid

The catalytic hydrogenation of benzoic acid with 5% Ru/C catalyst is a consecutive reaction in which cyclohexane carboxylic acid is formed as an intermediate; further hydrogenation of which gives cyclohexyl methanol as seen in Scheme 3-1.



Scheme 3-1: Reaction scheme for hydrogenation of benzoic acid with 5% Ru/C catalyst

Several experiments were carried out in order to investigate the catalytic activity and selectivity with 5% Ru/C catalyst under different operating conditions. The range of reaction parameters varied for the study is given in Table 3-2.

Table 3-2: Range of reaction conditions for hydrogenation of benzoic acid

Reaction parameter	**Range**
Temperature	493 K
Catalyst concentration	5 kgm^{-3}
Substrate concentration	0.8 kmolm^{-3}
Pressure	6.89 MPa
Stirring speed	1000 rpm
Total charge	1.0 x 10^{-4} m^{3}
Reaction time	6 hrs.

All reactions were carried out to complete conversion of benzoic acid except those related to kinetic studies. The progress of the reactions was followed by monitoring the consumption of benzoic acid and formation hydrogenation products like cyclohexane carboxylic acid and cyclohexyl methanol. A typical concentration time profile of the reaction is shown in Figure 3-2. The conversion of benzoic acid and selectivity to cyclohexane carboxylic acid was calculated as given in Eq-3.1 and Eq-3.2.

$$\text{Conversion of BZA} = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq-3.1}$$

$$\text{Selectivity to CCA} = \frac{C_{CCA}}{C_i - C_f} \times 100 \qquad \text{Eq-3.2}$$

Where,

C_i is initial concentration of benzoic acid, kmol/m^3; C_f is final concentration of benzoic acid, kmol/m^3 and C_{CCA} is the concentration of cyclohexane carboxylic acid, kmol/m^3; formed at end of reaction.

In all experiments the consumption of benzoic acid, hydrogen gas and formation of hydrogenation products were monitored for calculating liquid mass balance and gas balance, which was found to be more than 95%. Following these preliminary hydrogenation reactions, the role of support and the solvent was investigated to optimize the activity of the catalyst and selectivity to cyclohexane carboxylic acid.

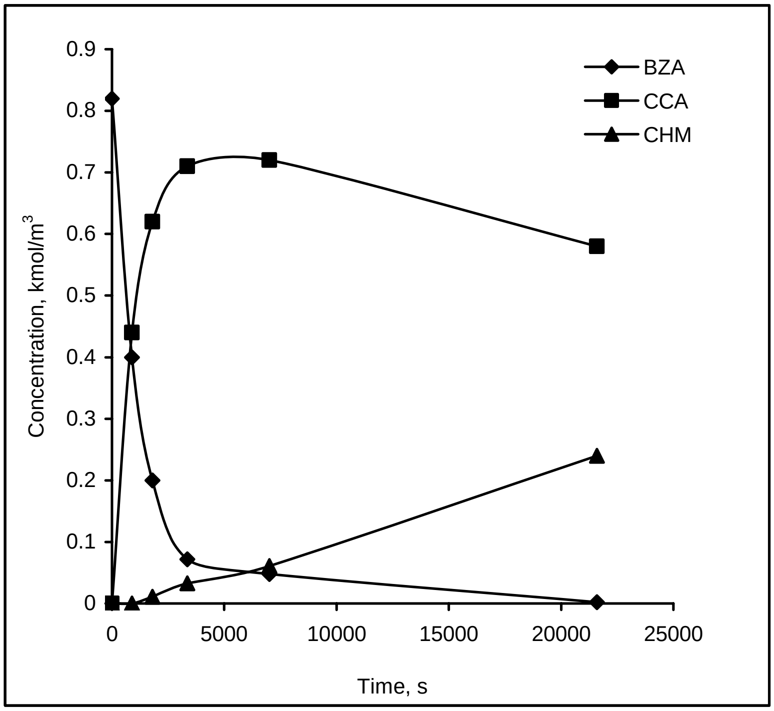


Figure 3-2: Concentration time profile for hydrogenation of benzoic acid with 5%Ru/C catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^3.

3.3.2 Effect of catalyst support on Ru catalyst for hydrogenation of benzoic acid

Supports are known to play a major role in dictating the selectivity of any reaction and hence the activity of Ru supported on different supports was assessed for the hydrogenation of benzoic acid to cyclohexane carboxylic acid. The hydrogenation of benzoic acid in presence of Ru catalysts (prepared by the procedure explained in Section 3.2.2) on different supports like C, Al_2O_3, SiO_2, TiO_2 and MgO was investigated. The results are shown in Figure 3-3.

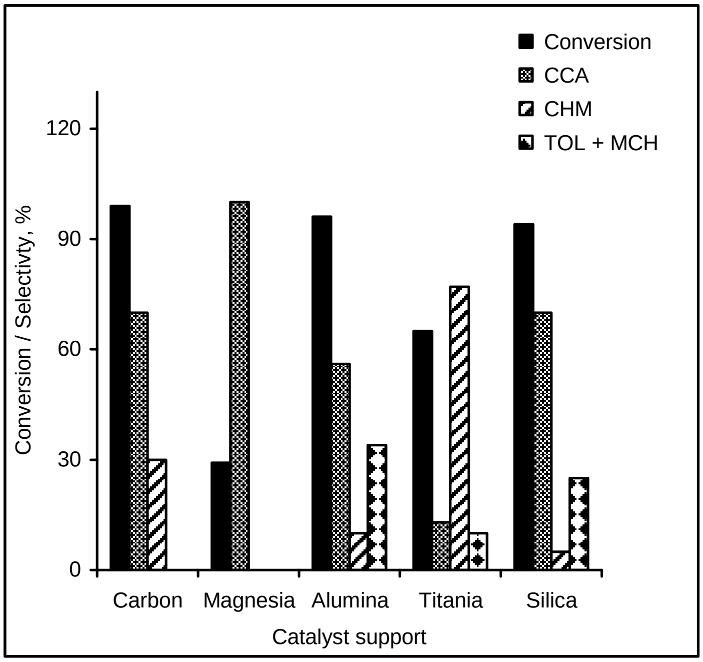


Figure 3-3: Effect of support on Ru catalyzed hydrogenation of benzoic acid

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

Supports like Al_2O_3, SiO_2 and TiO_2 gave the hydrogenolysis products toluene and methyl cyclohexane along with cyclohexane carboxylic acid and cylohexyl methanol. These hydrogenolysis products are obtained from benzyl alcohol which is formed from benzoic acid but undergoes hydrogenolysis[6]. No benzyl alcohol was observed, which indicates that benzyl alcohol hydrogenolysis is extremely rapid under reaction conditions. Ru supported on carbon and magnesia (MgO) gave only cyclohexane carboxylic acid and cyclohexyl methanol. From these investigations it was seen that Ru supported on Al_2O_3,

SiO_2 and TiO_2 is more active for hydrogenation of carboxylic group as compared to Ru on carbon and magnesia. From Figure 3-3 it is clear that carbon is the best support as compared to Al_2O_3, SiO_2, TiO_2 and MgO for hydrogenation of benzoic acid, to cyclohexane carboxylic acid.

3.3.3 Effect of ruthenium content in Ru/C catalyst on activity and selectivity for hydrogenation of benzoic acid

In order to obtain a catalyst with the highest selectivity to cyclohexane carboxylic acid, the effect of Ru loading on activity and selectivity was investigated. Ru/C catalysts with different ruthenium loading were prepared according to the procedure explained in Section 3.2.2. Conversion of benzoic acid increases linearly with increase in ruthenium loading in Ru/C catalyst as shown in Figure 3-4.

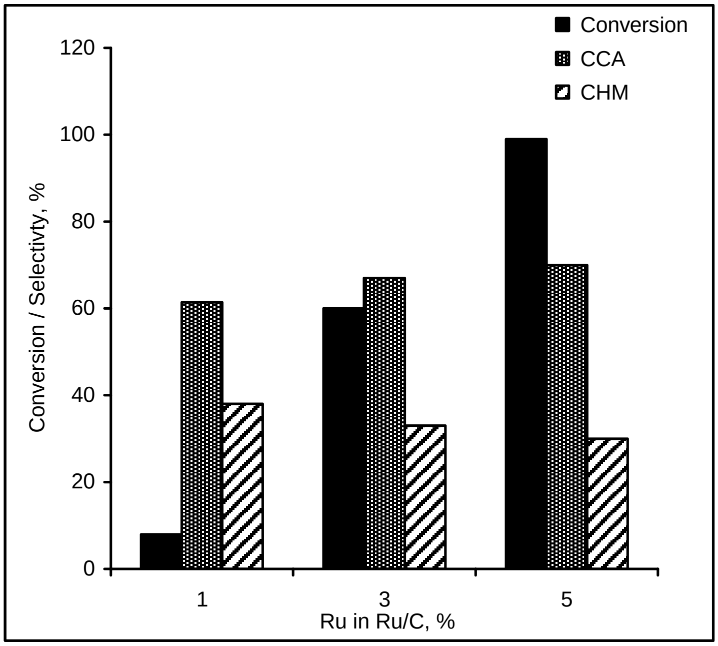


Figure 3-4: Effect of percent Ru in Ru/C catalyst for hydrogenation of benzoic acid
Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.82 kmol^{-3}, Catalyst = 5 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1000 rpm, Time = 6 hrs, Total volume = 1.0 x 10^{-4} m^{3}.

For the catalyst with low ruthenium content, although the conversion of benzoic acid was low, selectivity to cyclohexyl methanol was high as compared to the high ruthenium content catalyst, this is because activation of C=O is favored on highly dispersed metals[7]. The results for selectivity of cyclohexane carboxylic acid and cyclohexyl methanol with different ruthenium loading in Ru/C catalyst are shown in Figure 3-4. Since both activity and selectivity for cyclohexane carboxylic acid was high with 5% Ru/C catalyst, this catalyst was further used for the kinetic study on hydrogenation of benzoic acid.

3.3.4 Effect of water content in 1,4-dioxane on activity and selectivity

In the preliminary experiments it was observed that hydrogenation of benzoic acid with 5% Ru/C catalyst gives 70% cyclohexane carboxylic acid and 30% cyclohexyl methanol with 100% conversion of benzoic acid. From our earlier results (Section 2.3.6), it is understood that addition of water to the reaction solvent increases the selectivity of this catalyst to cyclohexane carboxylic acid. So the effect of water on the selectivity of hydrogenation of benzoic acid with 5% Ru/C catalyst was studied in detail. Hydrogenation of benzoic acid with 5% Ru/C catalyst was carried with varying percentage of water in 1,4-dioxane solvent and the results are presented in Figure 3-5.

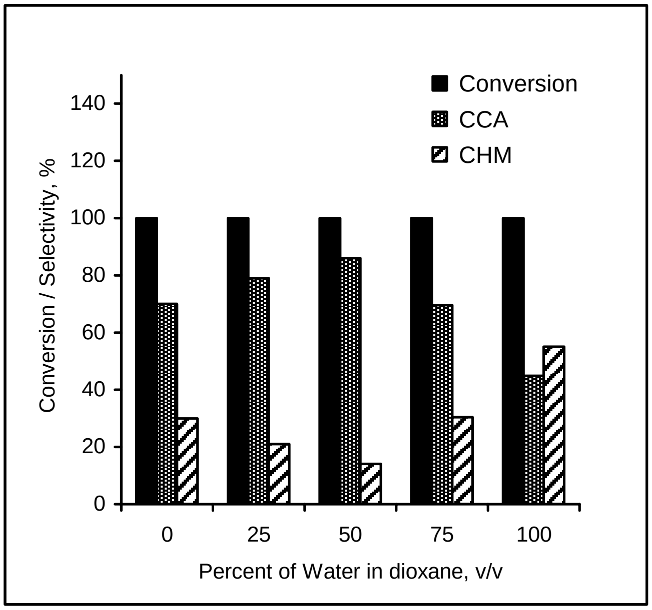


Figure 3-5: Effect of percentage water in 1,4-dioxane on activity and selectivity of 5% Ru/C catalyst for hydrogenation of benzoic acid.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.82 kmolm^{-3}, Catalyst = 5 kgm^{-3}, Agitation speed = 1000 rpm, Time = 6 hrs, Total volume = 1.0 x 10^{-4} m^{3}.

It was observed that, when water content in dioxane was varied from 0-100% there was no change in the conversion of benzoic acid. The selectivity to cyclohexane carboxylic acid, however, increased gradually from 70% to 85% with increasing water content from 0-50% in 1,4-dioxane. Further increase in water content in 1,4-dioxane increased the selectivity to cyclohexyl methanol at the expense of cyclohexane carboxylic acid as seen in Figure 3-5. The selectivity of the reaction to cyclohexyl methanol is increased due to inefficient transport of cyclohexane carboxylic acid from catalyst surface into the reaction medium. Cyclohexane carboxylic acid is sparingly soluble in aqueous 1,4-dioxane with high water content[8]. Since selectivity to cyclohexane carboxylic acid was highest for 50% water in 1,4-dioxane solvent, further studies on hydrogenation of benzoic acid were carried out using this ratio of water to 1,4-dioxane.

3.3.5 Activity of Ru/C catalyst for hydrogenation of cyclohexane carboxylic acid

Since the hydrogenation of benzoic acid to cyclohexyl methanol is a consecutive reaction with cyclohexane carboxylic acid as an intermediate, the activity of 5% Ru/C catalyst for the hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol was also studied with 5% Ru/C catalyst under the same reaction conditions used for hydrogenation of benzoic acid. This study was done to confirm that the high selectivity to cyclohexane carboxylic acid in 1,4-dioxane-water (1:1) solvent was not due to deactivation of Ru/C catalyst after hydrogenation of benzoic acid to cyclohexane carboxylic acid. A 5% conversion of cyclohexane carboxylic acid with 100% selectivity to cyclohexyl methanol was observed after 6 hrs reaction time. Hence the hydrogenation of cyclohexane carboxylic acid with Ru/C catalyst in 1,4-dioxane-water (1:1) solvent is very slow. A Concentration versus time profile for hydrogenation of cyclohexane carboxylic acid with 5% Ru/C catalyst in 1,4-dioxane-water (1:1) as solvent is shown in Figure 3-6.

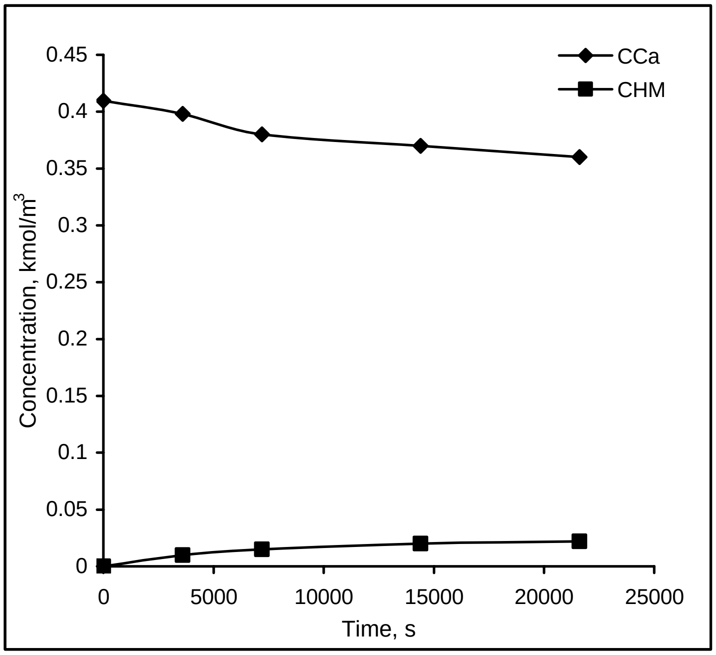


Figure 3-6: Hydrogenation of cyclohexane carboxylic acid with 5% Ru/C catalyst. **Reaction conditions:** Temperature = 493K, Hydrogen partial pressure = 6.89 MPa, Cyclohexane carboxylic acid = 0.41 kmolm^{-3}, Catalyst = 0.5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1000 rpm, Time = 6 hrs, Total volume = 1.0 x 10^{-4} m^3.

3.3.6 Recycle study for 5% Ru/C catalyst for the hydrogenation of benzoic acid to cyclohexane carboxylic acid and cyclohexyl methanol

In order to ensure that the kinetic data collected would be free from any catalyst deactivation phenomenon, the activity of the catalyst on recycle was studied. In these experiments after completion of the reaction, the reactor was cooled to 313 K and the catalyst was allowed to settle. The supernant solution was taken out from the reactor and was used for measuring Ru leaching. The reactor was then charged with benzoic acid solution in 1,4-dioxane-water (1:1) to carry out the recycle experiment. The catalyst recycle experiments were performed at 493 K and a hydrogen partial pressure of 6.89 MPa. The catalyst was found to retain its activity on recycle without affecting the conversion of benzoic acid and selectivity to cyclohexane carboxylic acid and cyclohexyl methanol as shown in Figure 3-7.

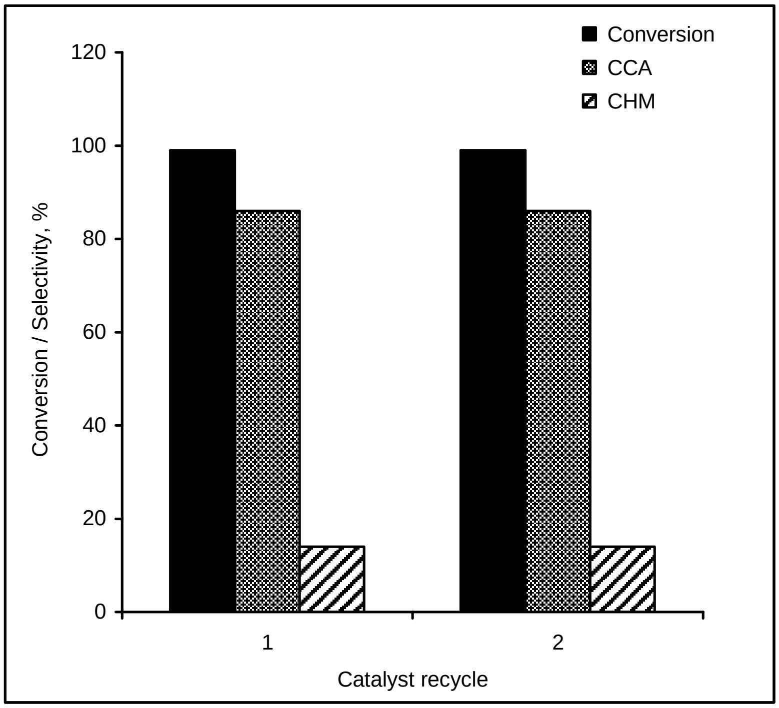


Figure 3-7: Catalyst recycle studies

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.82 kmolm^{-3}, Catalyst = 5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1000 rpm, Time = 6 hrs, Total volume = 1.0 x 10^{-4} m^{3}.

The overall cumulative turn over frequency (TOF) for the catalyst was found to be 3.77 x 10^{3} kmolkg^{-1}hr^{-1}. Leaching of Ru in reaction crude was negligible. Since it was confirmed that the catalyst is stable, the kinetics of the hydrogenation of benzoic acid to cyclohexane carboxylic acid was studied using 5% Ru/C catalyst in 1:1 1,4-dioxane-water solvent.

3.3.7 Experimental procedure for solubility measurement

For interpretation of kinetic data, a knowledge of solubility of gaseous reactants in the reaction medium is essential. The solubility of H_2 in water, dioxane and 1,4-dioxane-water (1:1) mixture was determined experimentally at 453, 473 and 493 K, using the method described by Purwanto et al[9]. The solubility measurements were conducted in the same reactor used for the reaction. The temperature of the liquid in the reactor was controlled within ± 1 K. A pressure transducer having a precision of ± 0.07 atm was used to measure the autoclave pressure.

In a typical experiment, a known volume of liquid mixture, which is same as the volume of reaction charge used for hydrogenation reaction was introduced into the autoclave. The autoclave was flushed with nitrogen and the contents heated to the desired temperature. After thermal equilibrium was attained, the void space in the reactor was pressurized with hydrogen to the pressure required. The contents were then stirred for about ten minutes to equilibrate the liquid phase with the solute gas phase. The drop in the pressure in the autoclave was recorded and used for calculating solubility of hydrogen in the given solvent. In this way Henry's constant for hydrogen in water, 1,4-dioxane, and 1,4-dioxane-water (1:1) mixture were calculated. The results are shown in Table 3-3.

Table 3-3: Henrys constant for hydrogen in water, 1,4-dioxane and 1,4-dioxane-water (1:1) mixture.

No.	**Temperature (K)**	**Henry's constant He, (kmolm^{-3}atm^{-1})**		
		Water	**1,4-dioxane**	**1,4-dioxane-water (1:1)**
1	453	7.0×10^{-4}	8.7×10^{-4}	32.6×10^{-4}
2	473	11.0×10^{-4}	15.4×10^{-4}	39.2×10^{-4}
3	493	21.0×10^{-4}	24.8×10^{-4}	53.0×10^{-4}

3.3.8 Preliminary reactions and Analysis of Mass Transfer

From the results in the preliminary investigations, the conditions given in Table 3-4 were chosen for the kinetic studies. Under these conditions the selectivity to CCA was > 99%, and the liquid and gas balance was >95%. The reaction conditions for studying the kinetics of hydrogenation of benzoic acid to cyclohexane carboxylic acid are given in Table 3-4

Table 3-4: Range of reaction conditions for kinetic study of hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C catalyst.

No.	**Reaction parameter**	**Range**
1	Temperature	453-493 K
2	Catalyst concentration	0.1-0.75 kg m^{-3}
3	Substrate concentration	0.1-0.6 $kmolm^{-3}$
4	Pressure	3 - 10 MPa
5	Stirring speed	1200 rpm
6	Total charge	1.0 x 10^{-4} m^3
7	Reaction time	2 hrs.

A typical concentration time profile for hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C catalyst under the standard reaction conditions mentioned in Table 3-4 is shown in Figure 3-8.

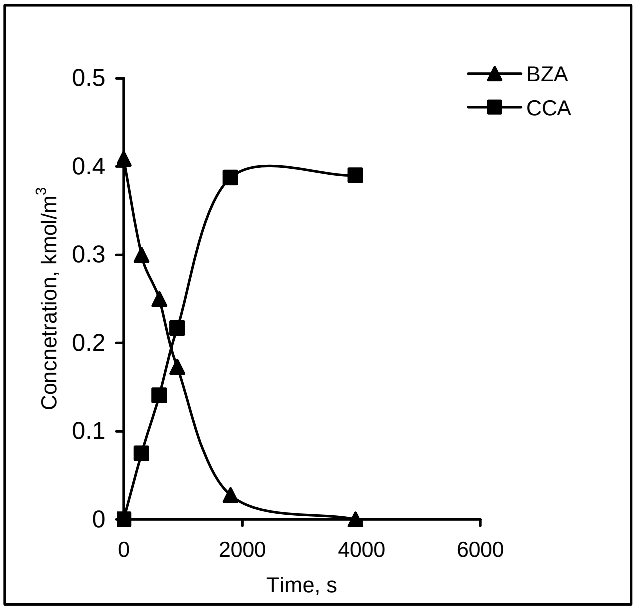


Figure 3-8: Hydrogenation of benzoic acid with 5% Ru/C catalyst under reaction conditions for kinetics.

Reaction conditions: Temperature = 453 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 $kmolm^{-3}$, Catalyst = 0.5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

Analysis of initial rate data provides an approach for understanding the dependency of the reaction rate on individual parameters and also in the evaluation of significance of mass transfer effects. The initial rates for hydrogenation of benzoic acid to cyclohexane carboxylic acid were calculated from the slope of the cyclohexane carboxylic acid formation versus time plots during the initial period of reaction such that the conversion of benzoic acid was less than 15% and differential conditions prevailed. A typical plot to obtain the initial rates from concentration of cyclohexane carboxylic acid formed versus time profile is shown in Figure 3-9.

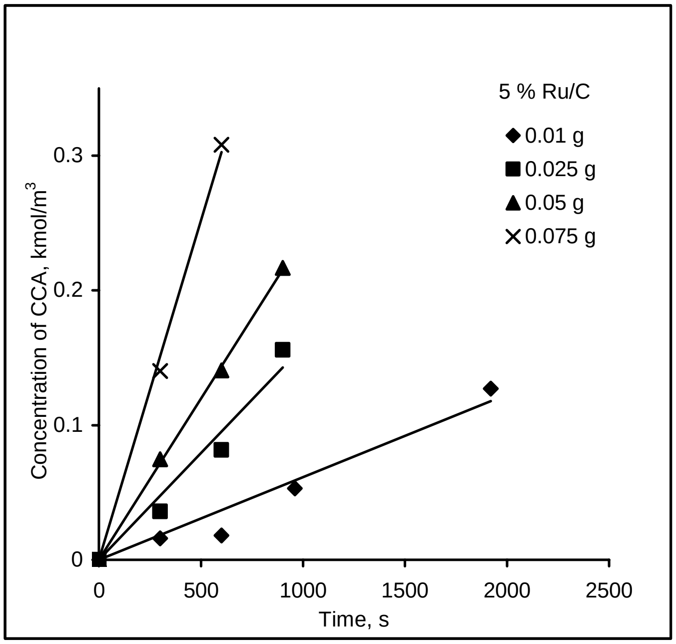


Figure 3-9: Determining initial rate for hydrogenation of benzoic acid at different catalyst loading.

Reaction conditions: Temperature = 453 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^{3}.

This plot pertains to the hydrogenation of benzoic acid to cyclohexane carboxylic acid at 453 K for varying catalyst loadings. The initial rates were calculated from the slopes of these concentration time profiles as shown in Figure 3-9. A plot of initial rate versus catalyst loading based on the initial rates is shown in Figure 3-10, which indicates first order dependence of reaction on catalyst loading.

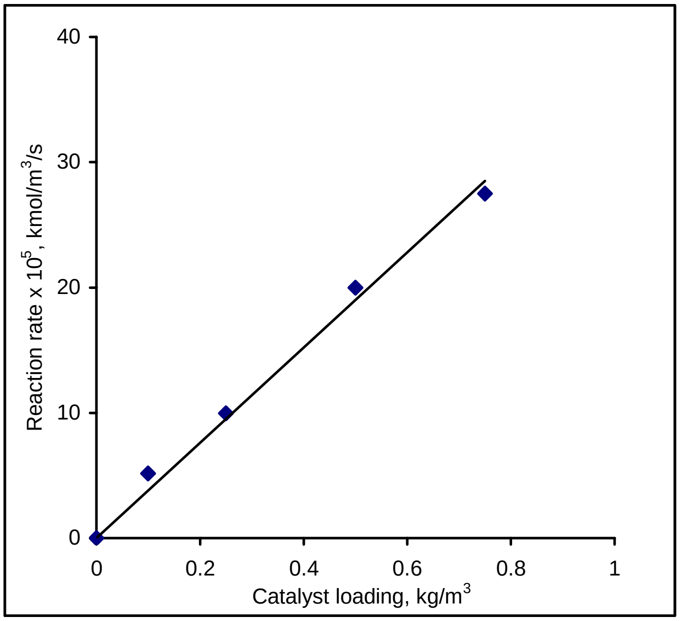


Figure 3-10: Effect of catalyst loading on initial rate of reaction.

Reaction conditions: Temperature = 453 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

Hydrogenation of benzoic acid with 5% Ru/C catalyst is an example of a multiphase reaction involving gas, liquid and solid phases. So this reaction involves (i) transfer of reactant (H_2) from gas into the liquid (ii) the transfer of dissolved reactants (BZA and H_2) from liquid phase on to the catalyst surface (iii) Intraparticle transfer of reactants to the catalytic site. If the rate of transport of reactants in any of these steps is slower as compared to the intrinsic rate of reaction, then the rate of reaction is controlled by the rate of mass transport.

So, before commencing with the kinetic study, it was important to ensure that the reaction occurs in kinetic regime. For this, the effect of agitation speed on the rate of reaction was studied at 493 K in the range of 800-1200 rpm. The agitation speed had no effect on rate of hydrogenation of BZA as shown in Figure 3-11, which confirms that gas-liquid mass transfer is not significant.

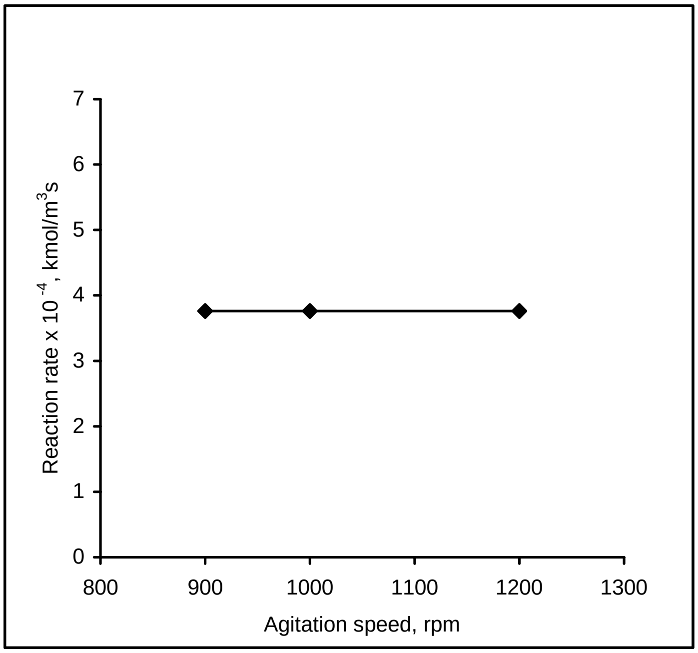


Figure 3-11: A plot of initial rate of hydrogenation vs. agitation speed.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Catalyst = 0.5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

3.3.9 Kinetic study for hydrogenation of benzoic acid to cyclohexane carboxylic acid

In order to study the kinetics of the hydrogenation of benzoic acid using 5% Ru/C catalyst in a 1:1 (v/v) 1,4-dioxane:water mixture as solvent, several experiments were carried out in the range of conditions shown in the Table 3-4.The rates of hydrogenation were calculated from the observed concentration-time profiles as discussed in section 3.3.8. These were essentially initial rates of hydrogenation reaction calculated under low conversion of benzoic acid (Conversion < 10-15%).

3.3.9.1 Effect of catalyst loading

The effect of catalyst concentration on the rate of hydrogenation of benzoic acid to cyclohexane carboxylic acid was studied in the temperature range of 453-493 K, benzoic acid concentration of 0.41 kmolm^{-3} and hydrogen pressure of 6.89 Mpa and 1,4-dioxane-water (1:1) as solvent. The results are shown in Figure 3-12.

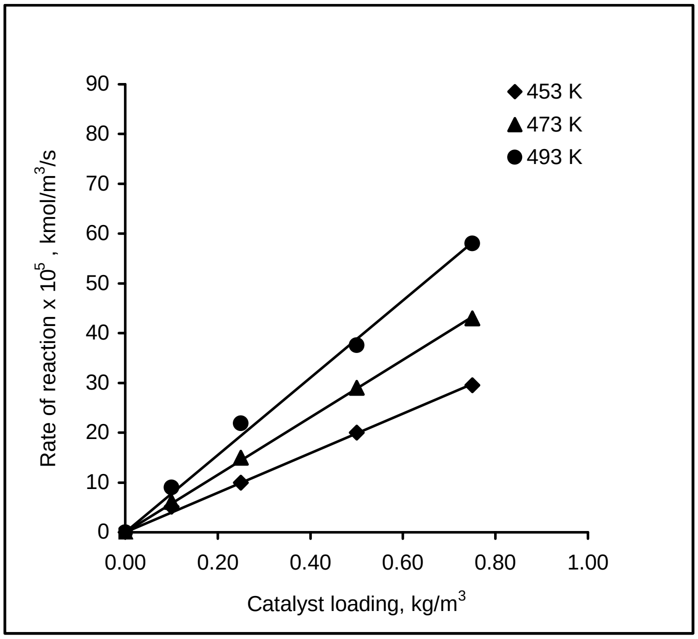


Figure 3-12: A plot of rate of hydrogenation vs. catalyst loading.

Reaction conditions: Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0×10^{-4} m^3.

The rate was found to be linearly dependent on the catalyst concentration, indicating first order kinetics at all temperatures.

3.3.9.2 Effect of benzoic acid concentration

The effect of benzoic acid concentration on the initial rate of hydrogenation was also investigated in the temperature range of 453-493 K, catalyst concentration of 0.5 kgm^{-3} and hydrogen pressure of 6.89 MPa and 1,4-dioxane-water (1:1) as solvent. The results are shown in Figure 3-13.

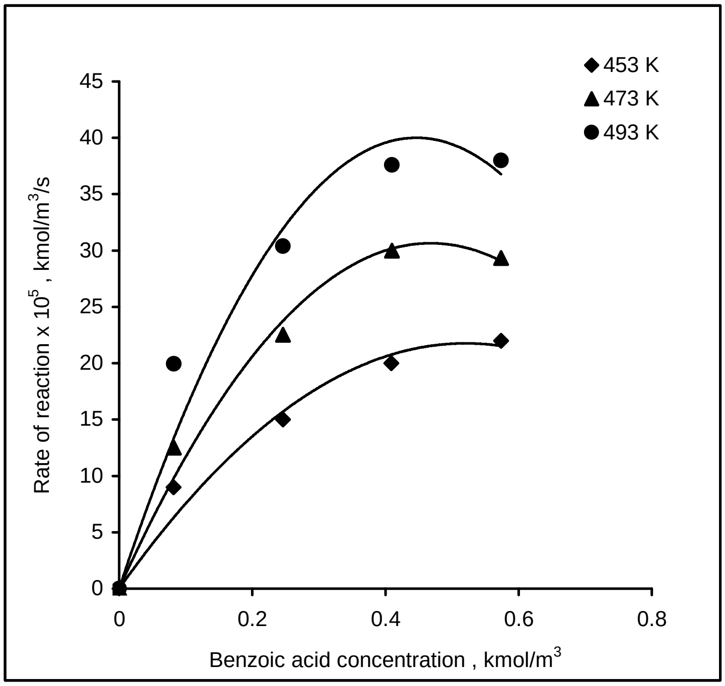


Figure 3-13: A plot of rate of hydrogenation vs. benzoic acid concentration. **Reaction conditions:** Hydrogen partial pressure = 6.89 MPa, Catalyst = 0.5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

The hydrogenation rate showed a first order dependence at lower concentrations of benzoic acid, but at higher concentrations the hydrogenation rate was found to have partial order dependence, tending to a zero order. Since benzoic acid is strongly adsorbed on the active sites of the catalysts, the rate is found to be independent of benzoic acid concentration at high benzoic acid loadings. This is a general trend observed for hydrogenation of aromatic compounds with supported metal catalysts[10].

3.3.9.3 Effect of hydrogen partial pressure

The effect of hydrogen partial pressure on the rate of hydrogenation of benzoic acid to cyclohexane carboxylic acid was studied in the temperature range of 453-493 K, catalyst concentration of 0.5 kgm^{-3}, benzoic acid concentration of 0.41 kmolm^{-3} in 1,4-dioxane-water (1:1) as solvent. The rate showed an order higher than one with respect to hydrogen partial pressure as seen in Figure 3-14 and 3-15. Higher order with respect to hydrogen is reported for the hydrogenation of other aromatic compounds, toluene and benzene[11]. This has been attributed to the presence of multiple bonds in an aromatic ring. A log-log plot of the rate of reaction versus hydrogen partial pressure is shown Figure 3-15 which shows an order in the range of 1.5 to 1.6.

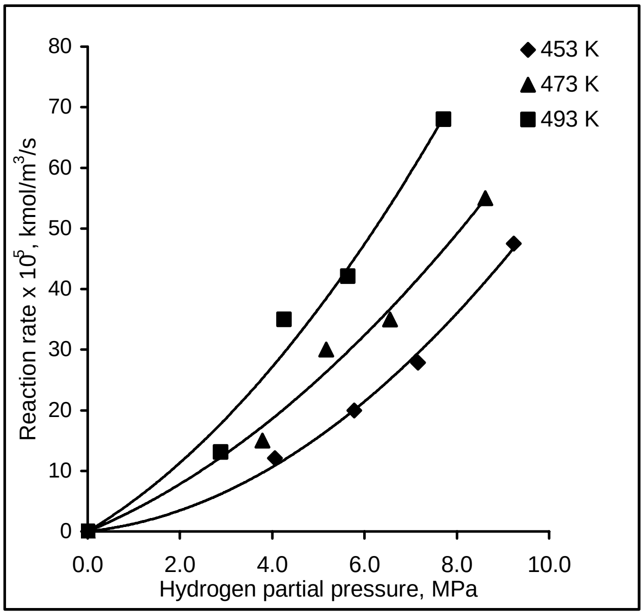


Figure 3-14: A plot of rate of hydrogenation vs. hydrogen partial pressure.

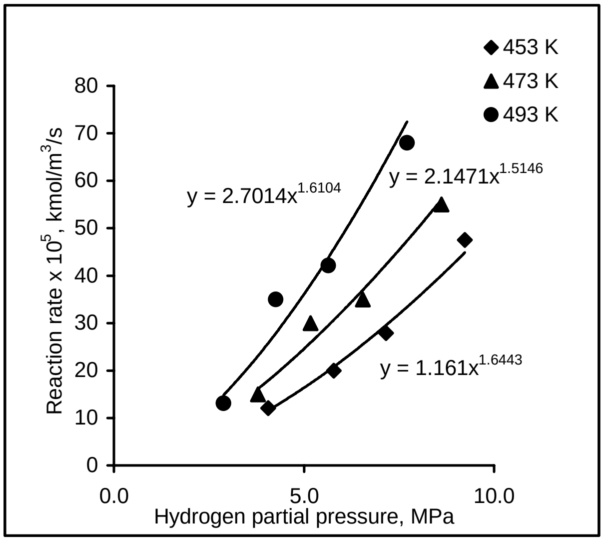


Figure 3-15: A logarithmic plot of rate of hydrogenation vs. hydrogen partial pressure.

Reaction conditions: Benzoic acid = 0.41 kmom^{-3}, Catalyst = 0.5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

3.3.10 Analysis for external and intraparticle mass transfer

The rate of hydrogenation of benzoic acid to cyclohexane carboxylic acid at 493 K is found to be independent of speed of agitation above 800 rpm as shown in Figure 3-11, which suggests that external (gas-liquid) mass transfer is absent under the reaction conditions mentioned in Table 3-4. This is also confirmed by effect of catalyst loading on the rate of reaction, which shows a linear dependence.

However, a detailed analysis to check for the role of external and intraparticle mass transfer is necessary before proceeding further to kinetic modeling. The criteria involves evaluation of factors α_{gl}, α_{ls} and ϕ_{exp}, which are defined as the ratio of observed rate of hydrogenation to the maximum rates of gas-liquid, liquid-solid and intraparticle mass transfer respectively. As suggested by Ramachandran and Chaudhari[12] the values of α_{gl}, α_{ls} and ϕ_{exp} should be less than 0.1, 0.1 and 0.2 respectively to ensure that the reaction operates under kinetic control.

a) Gas-Liquid Mass Transfer

The significance of gas-liquid mass transfer resistance was analyzed by comparing the rate of reaction, R_i ($\text{kmolm}^{-3}\text{s}^{-1}$) and maximum possible rate of gas-liquid transfer. The gas-liquid mass transfer resistance is negligible if the factor α_{gl} as defined in Eq-3.3 is less than 0.1.

$$\alpha_{gl} = \left[\frac{R_i}{k_L a_B C_i^*}\right] < 0.1 \tag{Eq-3.3}$$

Where $k_l a_B$ is the gas-liquid mass transfer coefficient and C_i^* is the saturation solubility of reacting gas (H_2) in equilibrium with the gas phase concentration at the reaction temperature (kmolm^{-3}). The gas-liquid mass transfer coefficient ($k_L a_B$) used in above equation was calculated using a correlation proposed by Chaudhari and coworkers[13] (given in Eq-3.4) for a reactor similar to that used in this work.

$$k_L a_B = 1.48 \text{ x } 10^{-3} (N)^{2.18} \text{ x } (V_g / V_L)^{1.88} \text{ x } (d_I / d_T)^{2.1} \text{ x } (h_1 / h_2)^{1.16} \tag{Eq-3.4}$$

The terms involved in above equation are described in Table 3-5 along with the respective values obtained from the reactor and charge used in the present case.

Table 3-5: Parameters used for $k_l a_B$ calculations by Eq-3-4.

Parameter	Description	Value
V_g	Gas volume (m^3)	1.75×10^{-4}
N	Agitation speed (rpm)	1200
V_L	Liquid volume (m^3)	10×10^{-4}
d_I	Impellar diameter (m)	2×10^{-2}
d_T	Tank diameter (m)	6.3×10^{-2}
h_1	Height of impeller (m)	8.2×10^{-2}
h_2	Liquid height (m)	3.5×10^{-2}

$k_l a_B$ at 1200 rpm (20 Hz) was calculated as 3.7 s^{-1}.
The factor α_{gl} was calculated for hydrogen was in the range of 6.1×10^{-4} to 3.7×10^{-3}. Since the values of α_{gl} are very much less than 0.1 for gaseous reactant, gas-liquid mass transfer resistance can be assumed to be negligible.

b) Liquid-Solid Mass Transfer

The liquid-solid mass transfer resistance can be considered unimportant if a factor α_{ls} (the enhancement factor) defined in Eq-3.5 is less than 0.1.

$$\alpha_{ls} = \left[\frac{R_i}{k_s a_p C_i^*} \right] < 0.1 \qquad \text{(Eq-3.5)}$$

Where, k_s is the liquid to solid mass transfer coefficient (s^{-1}), and a_p is the interfacial area of the particles per unit volume of the liquid phase (m^2/m^3) defined by equation Eq-3.6.

$$a_p = \frac{6w}{\rho_p d_p} \qquad \text{(Eq-3.6)}$$

Where, w is the catalyst mass per unit volume of the reactor (0.5 kg/m^3) ρ_p is the density of the catalyst particle (kg/m^3) and d_p is the particle diameter (m). Substituting for all the required values (w = 6 kg/m^3), average density of the particle = 6.1 x 10^3 kg/m^3 and average particle diameter for catalyst (5% Ru/C) is 1 x 10^{-6} m. We get the value of a_p as 491 m^2/m^3.

k_s, the liquid to solid mass transfer coefficient, can be calculated based on the equation proposed by Sano and coworkers[14] (Eq-3.7)

$$\frac{k_S d_p}{D F_c} = 2 + 0.4\left(\frac{e(d_p)^4(\rho_l)^3}{(\mu_l)^3}\right)^{0.25}\left(\frac{\mu}{\rho_l D}\right)^{0.33} \qquad \text{(Eq-3.7)}$$

Where, d_p is the particle diameter (m), D is the molecular diffusivity (m^2/s), F_c is the shape factor assumed to be unity for spherical particles, ρ_l is the density of the liquid (kg/m^3), μ_l is the viscosity of the liquid (kg/m/s) and e is the energy supplied to the liquid per unit mass (m^2/s). Prasher and Wills[15] give the following equation for calculation of e (Eq-3.8)

$$e = \frac{P}{\rho_L V_L} = \frac{8N^3 d_1{}^5 \psi}{d_T L} \qquad \text{(Eq-3.8)}$$

Where, P is the Power consumption for agitation (kg/m^2/s^3). ρ_L is the density of liquid phase (kg/m^3), V_L is the total volume (m^3), N is the speed of agitation (s^{-1}), d_I is the diameter of the impeller (m), ψ is the correction factor (this correction factor is reported to be significant for low catalyst loadings and for catalysis with low densities), L is the total height of the liquid (m).

Based on the Eq-3.8, the value of overall mass transfer coefficient, k_s (required in Eq-3.7) was calculated as 1.2 x 10^{-3} ms^{-1}, the factor α_{ls} was calculated for hydrogen and was found to be in the range of 3.6 x 10^{-6} to 3.6 x 10^{-5} respectively. Since the values of α_{ls} are less than 0.1 for gaseous reactant, Liquid to solid mass transfer resistance can be assumed to be negligible.

c) Intraparticle diffusion

Pore diffusion is considered to be negligible if a factor ϕ_{exp} defined as follows (Eq-3.9) is less than 0.2.

$$\phi_{\text{exp}} = \frac{d_p}{6}\left(\frac{\rho_p R_A}{w D_e C_i^*}\right)^{0.5} < 0.2 \qquad \text{(Eq-3.9)}$$

Where, C_i^* is the concentration of the dissolved gas at the catalyst surface (kmol/m^3), D_e is the effective diffusivity (m^2/s). Since Gas-liquid and Liquid-solid mass transfer resistance were found to be negligible, in the evaluation criteria, the surface concentration of hydrogen was assumed to be the same as that at the Gas-Liquid interface.

In the absence of complex phenomenon such as surface diffusion and restricted diffusion, the problem of predicting effective diffusivity D_e can be reduced to predicting the tortuosity factor, defined by Eq-3.10.

$$D_e = \frac{D_M \varepsilon_p}{\tau} \qquad \text{(Eq-3.10)}$$

Where, ε_p is the porosity of the catalyst, D_M is the molecular diffusivity of the solute in the liquid medium (m^2/s) and D_M was calculated using a correlation proposed by Wilke and Chang[16] (Eq-3.11).

$$D_{AB} = \frac{7.4\times10^{-8} T\,(\phi M_B)^{1/2}}{\mu_B V_A^{\;0.6}} \qquad \text{(Eq-3.11)}$$

Where, ϕ is the association parameter of the solvent; μ_B is the viscosity of solvent B (kg/m.s), M_B is the molecular weight of the solvent B; T is the temperature (K), V_A is the solute molar volume. Based on the equation given by Eq-3.9, the value of ϕ_{exp} was calculated to be in the range of 2.94 x 10^{-3} to 3.76 x 10^{-2}, which is less than 0.2 and hence, intraparticle diffusion can also be considered unimportant under these conditions.

It was thus observed that the rate data obtained for hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C catalyst is in the kinetic regime, under given set of conditions and can be reliably used to evaluate the intrinsic kinetic parameters. The results are also consistent with the negligible effect of agitation shown in Figure 3-11.

3.3.11 Kinetic modeling

The rate data obtained were fitted to different rate equations based on Langmuir-Hinshelwood (L-H) type models given in Table 3-6. In order to estimate the kinetic constants, the individual rate equations were subjected to a non-linear regression analysis using an optimization routine based on Marquardt's method[17]. The objective function was chosen as follows:

$$\Phi = \sum_{i=1}^{n} (r_{exp} - r_{mod})_i^2 \qquad \text{(Eq-3.12)}$$

Where, r_{exp} is observed rate of hydrogenation and r_{mod} is the predicted rate of hydrogenation.

The non-linear regression analysis was performed to estimate the kinetic constants such that the objective function $\Phi_{\min}$ has minimum value. The values of the kinetic constants obtained using optimization program for different models are given in Table 3-6. Since the magnitude of $\Phi_{\min}$ for all the models was more or less same, model discrimination was necessary. The analysis of the experimental data was performed purely on the mathematical basis and therefore it did not account for the thermodynamic significance of the kinetic constants. Thus, according to the thermodynamic criteria suggested by Kittrel[18], the values for the kinetic constants have to satisfy certain conditions, which are derived from the thermodynamic considerations. This constraint is that, *k* (rate constant) and activation energy should be greater than zero.

Table 3-6: Rate models for hydrogenation of benzoic acid to cyclohexane carboxylic acid:

Model	Rate equation	Temp. (K)	*k*	k_B	Φ_{min}
I	$R_H = \frac{k\ w\ A\ B}{(1+K_A A)}$	453	3.41×10^{-6}	3.98	4.52×10^{-8}
		473	6.01×10^{-6}	5.26	2.91×10^{-8}
		493	13.6×10^{-6}	9.64	7.24×10^{-8}
II	$R_H = \frac{k\ w\ A\ B^2}{(1+K_A A)}$	453	3.9×10^{-9}	4.7	4.22×10^{-9}
		473	8.7×10^{-9}	7.8	5.82×10^{-8}
		493	37.2×10^{-9}	25.3	2.36×10^{-7}
III	$R_H = \frac{k\ w\ A\ B^3}{(1+K_A A)}$	453	5.93×10^{-12}	9.25	2.18×10^{-8}
		473	35.3×10^{-12}	43.17	1.96×10^{-6}
		493	1210×10^{-12}	66.86	7.46×10^{-7}
IV	$R_H = \frac{k\ w\ A\ B^{1.1}}{(1+K_A A)}$	453	1.73×10^{-6}	4.01	3.89×10^{-8}
		473	3.08×10^{-6}	5.31	2.64×10^{-8}
		493	7.97×10^{-6}	11.28	7.75×10^{-8}
V	$R_H = \frac{k\ w\ A\ B^{1.2}}{(1+K_A A)}$	453	9.45×10^{-7}	4.5	3.31×10^{-8}
		473	15.92×10^{-7}	5.44	2.49×10^{-8}
		493	40.1×10^{-7}	10.95	8.52×10^{-8}
VI	$R_H = \frac{k\ w\ A\ B^{1.3}}{(1+K_A A)}$	453	1.67×10^{-7}	4.27	3.16×10^{-8}
		473	2.06×10^{-7}	5.92	7.01×10^{-8}
		493	3.58×10^{-7}	13.78	9.20×10^{-8}
VII	$R_H = \frac{k\ w\ A\ B^{1.4}}{(1+K_A A)}$	453	8.33×10^{-8}	4.27	3.08×10^{-8}
		473	12.48×10^{-8}	5.92	4.23×10^{-8}
		493	83.35×10^{-8}	13.78	1.01×10^{-7}

Model	Rate equation	Temp. (K)	*k*	k_B	Φ_{min}
VIII	$R_H = \frac{k\ w\ A\ B^{1.5}}{(1 + K_A A)}$	453	1.15 x 10^{-7}	4.14	9.82 x 10^{-8}
		473	2.21 x 10^{-7}	5.96	2.78 x 10^{-8}
		493	6.66 x 10^{-7}	14.2	1.24 x 10^{-7}
IX	$R_H = \frac{k\ w\ A\ B^{1.6}}{(1 + K_A A)}$	453	5.89 x 10^{-8}	4.25	1.42 x 10^{-8}
		473	11.50 x 10^{-8}	6.21	3.14 x 10^{-8}
		493	37.82 x 10^{-8}	16.09	1.42 x 10^{-7}
X	$R_H = \frac{k\ w\ A\ B^{1.7}}{(1 + K_A A)}$	453	3.0 x 10^{-8}	4.33	1.08 x 10^{-8}
		473	6.03 x 10^{-8}	6.55	3.62 x 10^{-8}
		493	21.53 x 10^{-8}	8.33	1.62 x 10^{-7}
XI	$R_H = \frac{k\ w\ A\ B^{1.8}}{(1 + K_A A)}$	453	1.53 x 10^{-8}	4.42	8.03 x 10^{-9}
		473	3.1 x 10^{-8}	6.69	4.23 x 10^{-8}
		493	12.22 x 10^{-8}	20.81	1.85 x 10^{-7}

Where, R_H = Initial rate of hydrogenation (kmol/m^3/s), k = Rate constant, w = Catalyst concentration (kg/m^3), A = Benzoic acid concentration (kmol/m^3), B = Hydrogen partial pressure (MPa), K_A = adsorption equilibrium constant for benzoic acid (m^3/kmol).

All models proposed in Table 3-6 had positive values for the kinetic parameters and therefore individual models could not be discriminated using this criterion. To select the model for hydrogenation of benzoic acid to cyclohexane carboxylic acid comparison of Φ_{min} for every model was done, and it was observed that Model VIII has the minimum Φ_{min} at all temperatures. The theoretical rates for hydrogenation of benzoic acid to cyclohexane carboxylic acid were obtained using Model VIII and compared with the experimental rate for hydrogenation as shown in Figure 3-16, 3-17 and 3-18 for the varying catalyst and benzoic acid concentrations and hydrogen partial pressure, respectively. The predictions were in good agreement with the observed trends, within an error of 5%, which is within the range of experimental error.

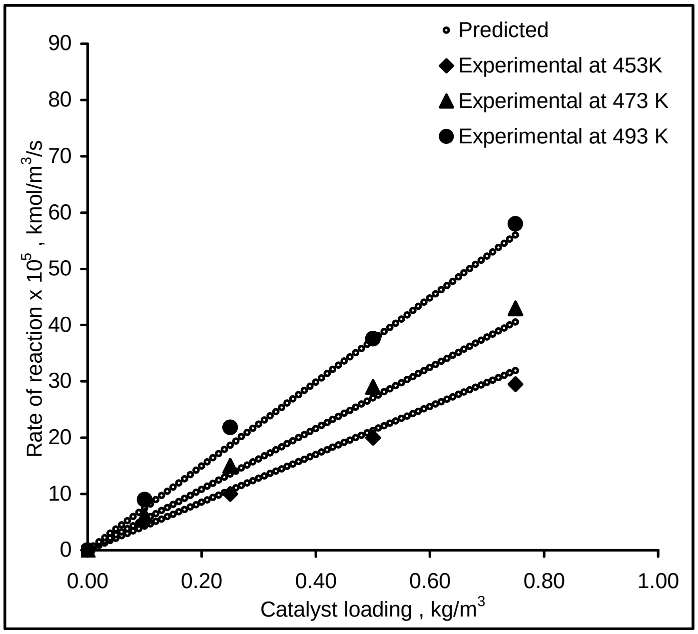


Figure 3-16: Effect of catalyst loading on initial rate of hydrogenation of benzoic acid: Comparison of experimental and predicted rates.

Reaction conditions: Hydrogen partial pressure = 6.89 MPa, Benzoic acid= 0.41 kmol/m^3, Solvent = 1,4-dioxane-water (1:1), Agitation speed= 1200 rpm, Time= 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

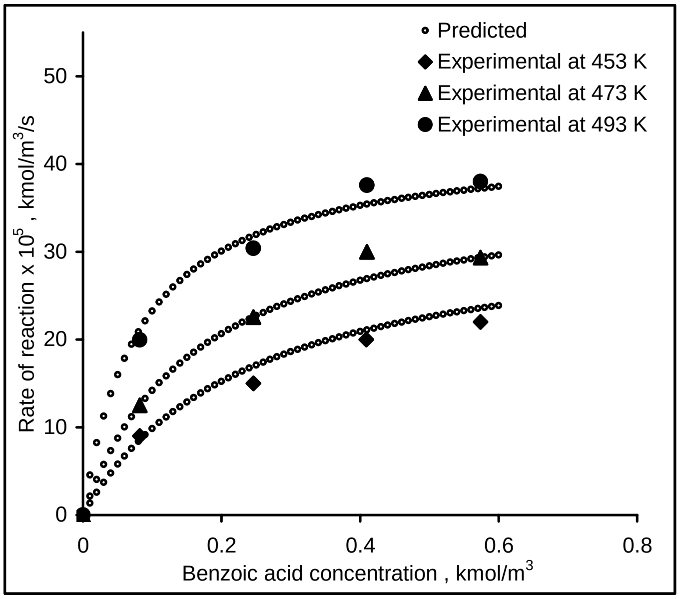


Figure 3-17: Effect of benzoic acid concentration on initial rate of hydrogenation of benzoic acid: Comparison of experimental and predicted rates.

Reaction conditions: Hydrogen partial pressure = 6.89 MPa, Catalyst = 0.5 kg/m^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

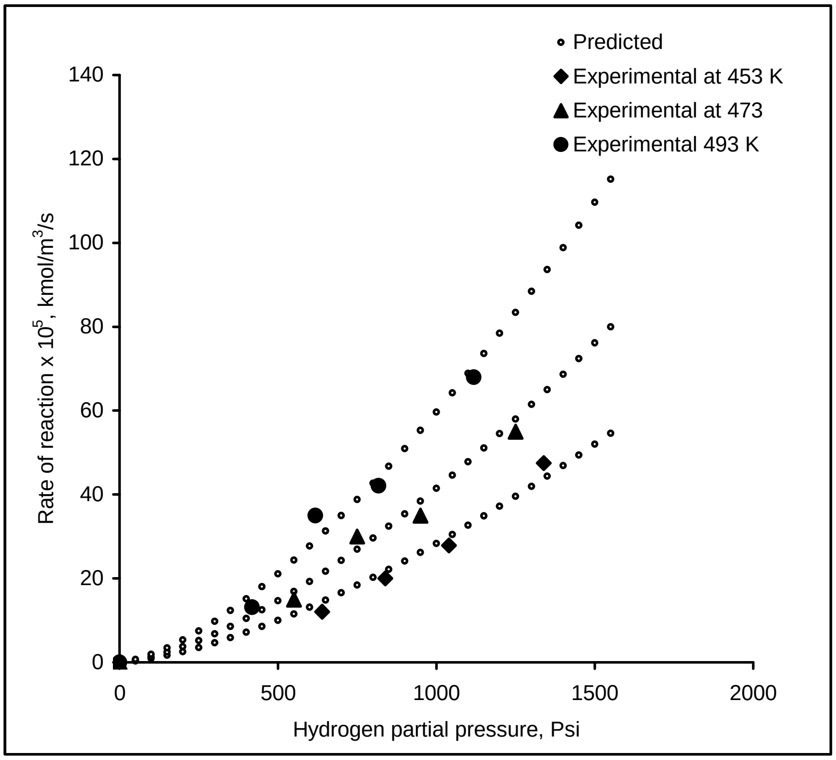


Figure 3-18: Effect of hydrogen partial pressure on initial rate of hydrogenation of benzoic acid: Comparison of experimental and predicted rates.

Reaction conditions: Benzoic acid = 0.41 kmom^{-3}, Catalyst = 0.5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 1.0 x 10^{-4} m^3.

Based on the values of rate constant (k) and adsorption equilibrium constant for benzoic acid (K_A) of this equation, ln k versus 1/T and ln K_A versus 1/T is plotted as shown in Figure 3-19.

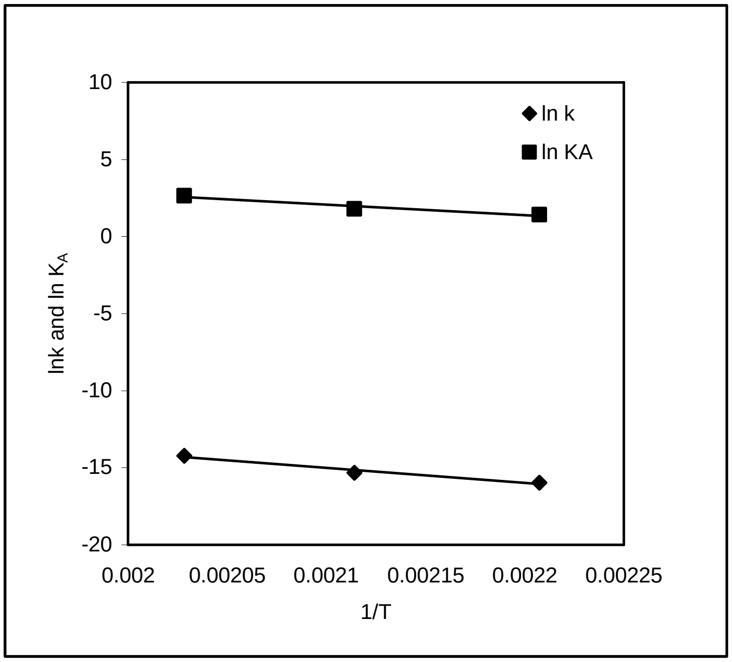


Figure 3-19: ln k and ln k_B versus 1/T.

From Figure 3-19, the activation energy for hydrogenation of benzoic acid was found to be 84.2 kJ/mol and the heat of adsorption of benzoic acid on catalyst surface was calculated to be 58.8 kJ/mol.

3.3.12 Activation energy (E_a) for hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol on 5% Ru/C catalyst

To calculate activation energy for hydrogenation of cyclohexane carboxylic acid a standard reaction was studied in the temperature range of 453 - 493 K, and catalyst concentration of 0.5 kgm^{-3}, hydrogen pressure of 8.27 MPa and benzoic acid concentration of 0.41 kmolm^{-3} in 1,4-dioxane-water (1:1) as solvent. The reaction of benzoic acid hydrogenation was further continued till cyclohexane carboxylic acid hydrogenation to cyclohexyl methanol was observed. From a typical reaction profile shown in Figure 3-20, it can be seen that the hydrogenation of benzoic acid to cyclohexane carboxylic acid is very fast compared to the hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol. The hydrogenation of cyclohexane carboxylic to cyclohexyl methanol is assumed to be in kinetic regime, as it is a slower than the hydrogenation of benzoic acid to cyclohexane carboxylic acid, which occurs in kinetic regime under the reaction conditions mentioned in Table 3-4.

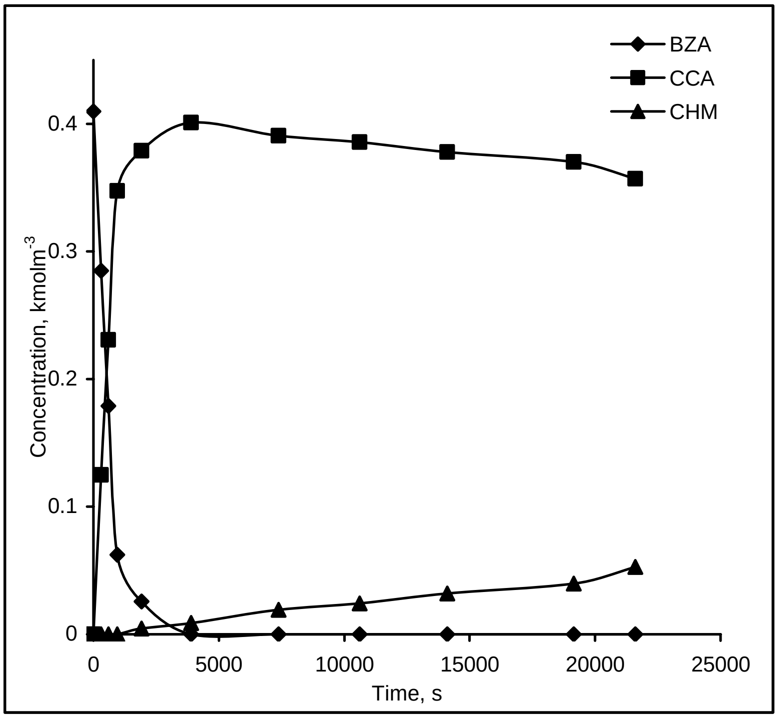


Figure 3-20: Concentration time profile for hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol.

Reaction conditions: Temperature = 493 K, Cyclohexane carboxylic acid = 0.41 kmom^{-3}, Catalyst = 0.5 kgm^{-3}, Hydrogen partial pressure = 8.27 MPa, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 6 hrs, Total volume = 1.0 x 10^{-4} m^{3}.

The initial rates for hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol were calculated from the slope of the cyclohexyl methanol formation versus time plots during the initial period of reaction such that the conversion of cyclohexane carboxylic acid was less than 15% and differential conditions prevailed as shown in Figure 3-21.

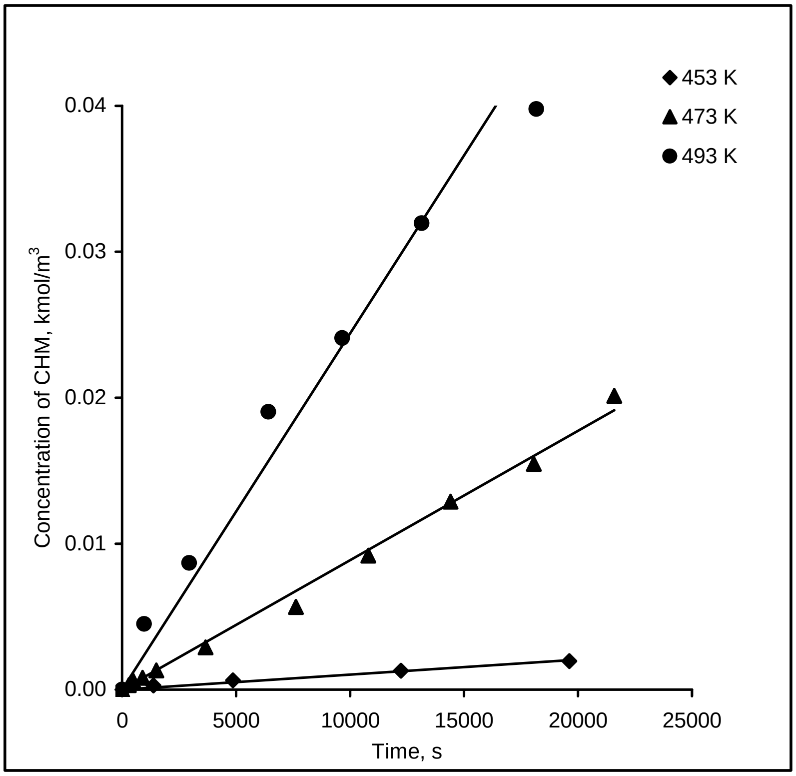


Figure 3-21: Initial rate of hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol using 5% Ru/C catalyst.

Reaction conditions: Cyclohexane carboxylic acid = 0.41 kmolm^{-3}, Catalyst = 0.5 kgm^{-3}, Hydrogen partial pressure = 8.27 MPa, Solvent = 1,4-dioxane-water (1:1), Agitation speed = 1200 rpm, Time = 6 hrs, Total volume = 1.0 x 10^{-4} m^3.

The initial rate for the standard reaction carried out at 453, 473 and 493 K was calculated from Figure 3-21. Further a plot of ln R versus 1/T (Figure 3-22) was used to calculate the apparent activation energy which was found to be 148.3 kJ/mol.

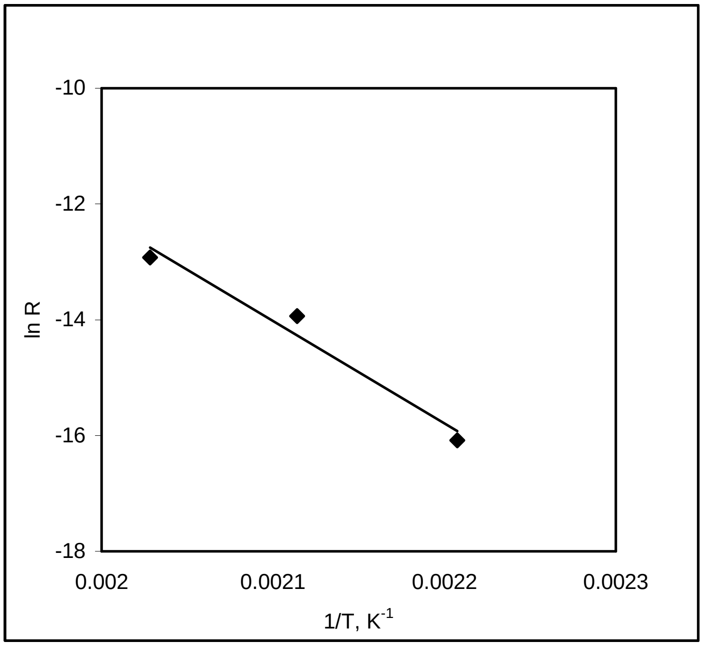


Figure 3-22: Arrhenius plot for hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol.

The activation energy for hydrogenation of cyclohexane carboxylic acid is 148.3 kJ/mol which is greater than the activation energy for ring hydrogenation in benzoic acid, (which was found to be 84.2 kJ/mol). Thus, the selectivity for hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C catalyst in 1,4-dioxane-water (1:1) as solvent under the reaction conditions mentioned in Table 3-4 is high due to the great difference in activation energy for the two functional groups.

3.3.13 Determining t_{max} for hydrogenation of benzoic acid to cyclohexyl methanol

Consecutive reactions are those which proceed with the formation of an intermediate product which further undergoes reaction, as shown below[19].

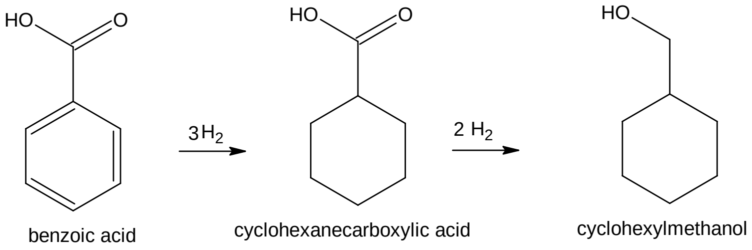
$$A \rightarrow B \rightarrow C$$

A typical trend observed in consecutive reactions is the maximum in the concentration of intermediate product (B). t_{max} is defined as the time for a consecutive reaction, when the concentration of the intermediate is maximum. The t_{max} for unimolecular reactions is obtained by Eq-3.13[20].

$$t_{max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{(k_1-k_2)} \quad \text{(Eq-3.13)}$$

Where, t_{max} = Time when the concentration of the intermediate product is maximum, k_1 = Rate constant for the first step in the consecutive reaction. k_2 = Rate constant for the second step in the consecutive reaction.

Cyclohexane carboxylic acid (CCA) is used for preparing caprolactam which goes into Nylon manufacture [1]. Industrially, cyclohexane carboxylic acid is obtained by hydrogenation of benzoic acid (BZA) with Pd/C catalyst (Snia Vicosa Process)[21]. Although selectivity to cyclohexane carboxylic acid for hydrogenation of benzoic acid with Pd/C catalyst is high, activity of Pd/C catalyst is low as compared to Ru/C catalyst. Hydrogenation of benzoic acid with Ru/C catalyst gives cyclohexane carboxylic acid and cyclohexyl methanol (CHM). The reaction pathway is shown in Scheme 3-2.



Scheme 3-2: Hydrogenation of benzoic acid with 5% Ru/C catalyst.

Hence, knowledge of t_{max} would provide information about the time of reaction when the concentration of cyclohexane carboxylic acid will be highest for a given set of reaction conditions, and thus help in increasing the selectivity of reaction to cyclohexane carboxylic acid. A Typical concentration versus time profile for hydrogenation of benzoic acid is shown in Figure 3-23.

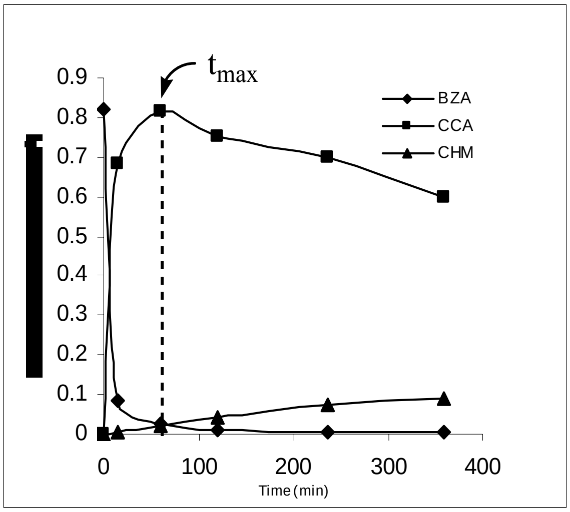


Figure 3-23: Concentration time profile for hydrogenation of benzoic acid with 5%Ru/C catalyst, with t_{max}.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 $kmolm^{-3}$, Solvent = 1,4-dioxane-water (1:1), Time = 6 hrs, Stirring speed = 1200 rpm, Total volume = 1.0 x 10^{-4} m^3.

From Figure 3.23 it is observed that t_{max} for the reaction under the conditions mentioned is 80 minutes. If the reaction is stopped at this time (80 min) then selectivity of the reaction to cyclohexane carboxylic acid is 98%. Thus understanding of t_{max} for a reaction would help to increase the selectivity of a catalytic consecutive reaction.

An approach for determining t_{max} for isokinetic consecutive reactions (i.e. reactions having the same reaction rates and the same rate constants) has been established by J. M. Herrmann[22].The equation proposed by Hermann for t_{max} of a consecutive reaction is given by Eq-3.14.

$$t^{n}_{max} = \frac{n}{k} \qquad \text{(Eq-3.14)}$$

Where, t^n_{max} = Time for the nth intermediate, when it goes through maximum, n = the number of the intermediate in a consecutive reaction, k = First order rate constant for all steps in the consecutive reaction.

One of the examples for such type of systems is photo catalytic propane-deuterium isotopic exchange[23]. Deriving such equations for complex consecutive reactions is difficult and has not been reported to date. Here we report a simplified approach for the determination of t_{max} for intermediate product in complex multiphasic consecutive reactions. In this approach the effect of reaction parameters on t_{max} of hydrogenation of benzoic acid with 5% Ru/C catalyst was studied and an equation derived using Marquardts method of optimization. Such a technique has not been applied for catalytic consecutive reaction, where the evaluation of t_{max} for intermediate product could be relevant.

3.3.13.1 Effect of reaction parameters on t_{max} of cyclohexane carboxylic acid (CCA)

For evaluation of t_{max} for cyclohexane carboxylic acid, in benzoic acid hydrogenation, the complete concentration time profile for hydrogenation of benzoic acid to cyclohexyl methanol via cyclohexane carboxylic acid were studied under different reaction conditions. The t_{max} was obtained from the concentration time profile as shown in Figure 3-23.

3.3.13.1.1 Effect of catalyst loading

The effect of catalyst concentration on the t_{max} of hydrogenation of benzoic acid was studied at 453 K, benzoic acid concentration of 0.41 kmolm^{-3} and hydrogen partial pressure of 6.89 MPa and ratio of water dioxane mixture was 1:1. The results are shown in Figure 3-24.

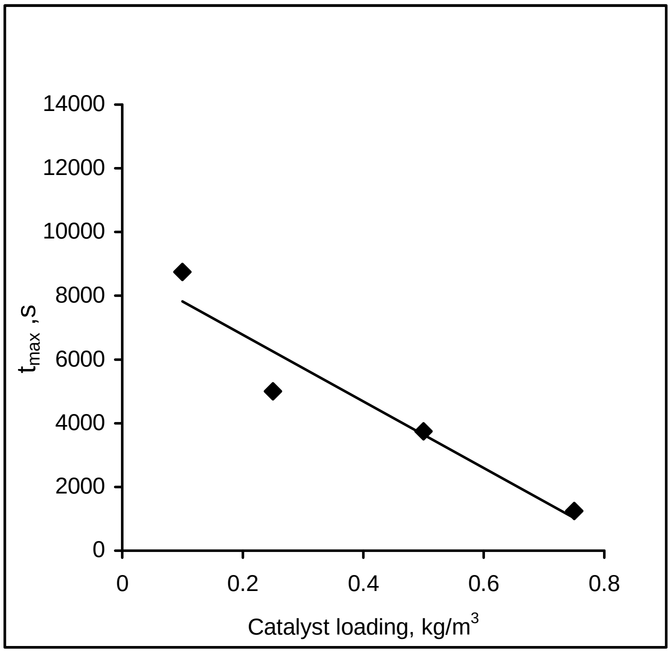


Figure 3-24: Effect of catalyst loading on t_{max} for CCA.

Reaction conditions: Temperature = 453 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 0.5 kgm^{-3}, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane-water (1:1), Time = 6 hrs, Stirring speed = 1200 rpm, Total volume = 1.0 x 10^{-4} m^3.

The t_{max} for cyclohexane carboxylic acid was found to decrease with increase in catalyst concentration as shown in Figure 3-24. Classically the t_{max} is dependent on the ratio of rate of hydrogenation of benzoic acid to cyclohexane carboxylic acid and rate of hydrogenation of cyclohexane carboxylic acid to cyclohexyl methanol. When the catalyst loading is increased the rate of formation and consumption of cyclohexane carboxylic acid are both increased and thus time required for maximum concentration (t_{max}) of cyclohexane carboxylic acid decreases.

3.3.13.1.2 Effect of benzoic acid concentration

The effect of benzoic acid concentration on the t_{max} of hydrogenation of benzoic acid was studied at 453 K, catalyst concentration of 0.5 kgm^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane-water (1:1) as solvent. The results are shown in Figure 3-25.

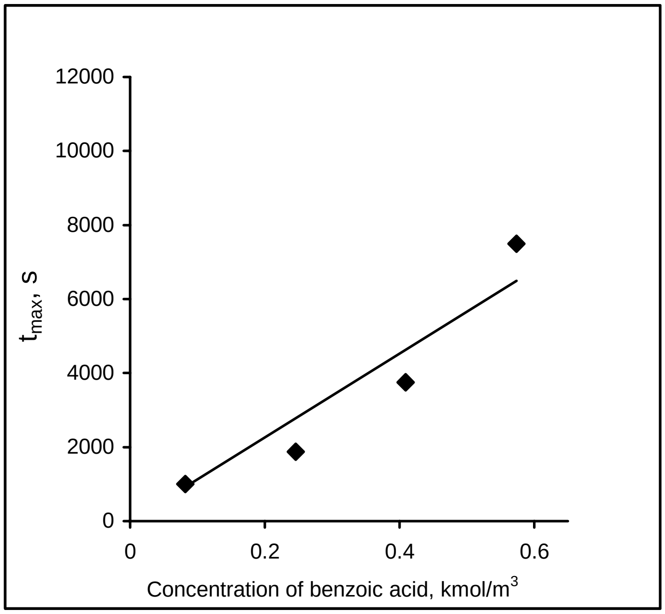


Figure 3-25: Effect of benzoic acid concentration on t_{max} for CCA.

Reaction conditions: Temperature = 453 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 0.5 kgm^{-3}, Solvent = 1,4-dioxane-water (1:1), Time = 6 hrs, Agitation speed = 1200 rpm, Total volume = 1.0 x 10^{-4} m^3.

The t_{max} increases as benzoic acid concentration increases. This is because as benzoic acid is increased, more time is required for building up the concentration of cyclohexane carboxylic acid and hence t_{max} for cyclohexane dicarboxylic acid increases.

3.3.13.1.3 Effect of hydrogen partial pressure

The effect of catalyst concentration on the t_{max} of hydrogenation of benzoic acid was studied at 453 K, benzoic acid concentration of 0.41 kmolm^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane-water (1:1) as solvent. The results are shown in Figure 3-26. The t_{max} for cyclohexane carboxylic acid was found to decrease with increase in hydrogen partial pressure as shown in Figure 3-26. This is due to increase in rate of hydrogenation of both benzoic acid as well as cyclohexane carboxylic acid.

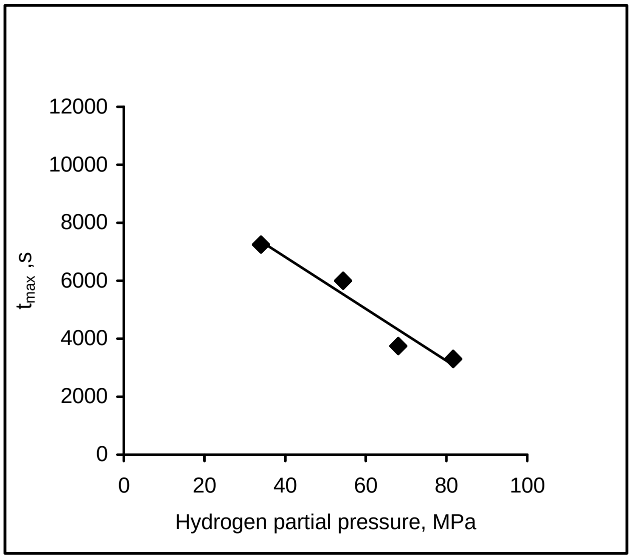


Figure 3-26: Effect of hydrogen partial pressure on t_{max} for CCA.

Reaction conditions: Temperature = 453 K, Catalyst = 0.5 kgm^{-3}, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane-water (1:1), Reaction time = 6 hrs, Agitation speed = 1200 rpm, Total volume = 1.0 x 10^{-4} m^3.

From Figure 3-24, 3-25 and 3-26, it is observed that t_{max} for cyclohexane carboxylic acid is inversely proportional to catalyst loading and hydrogen partial pressure and directly proportional to the concentration of benzoic acid.

Using these parametric trends for t_{max} and Marquardts method for optimization[18] an equation for t_{max} is derived which is given below by Eq-3-15.

$$t_{max} = K \left(\frac{[BZA]}{[CAT][H_2]} \right) \qquad \text{Eq-3.15}$$

Where,

t_{max} Time, where CCA is in maximum concentration (s).

K Constant (s kg bar / kmol)

[BZA] Concentration of benzoic acid (kmol/m^3)

[CAT] Concentration of 5% Ru/C catalyst (kg/m^3)

[H_2] Hydrogen partial pressure (bar)

3.3.13.1.4 Comparison of predicted t_{max} with experimental t_{max} for cyclohexane carboxylic acid

To confirm the validity of Eq-3.15, a plot of predicted t_{max} versus experimental t_{max} was plotted as shown in Figure 3-27.

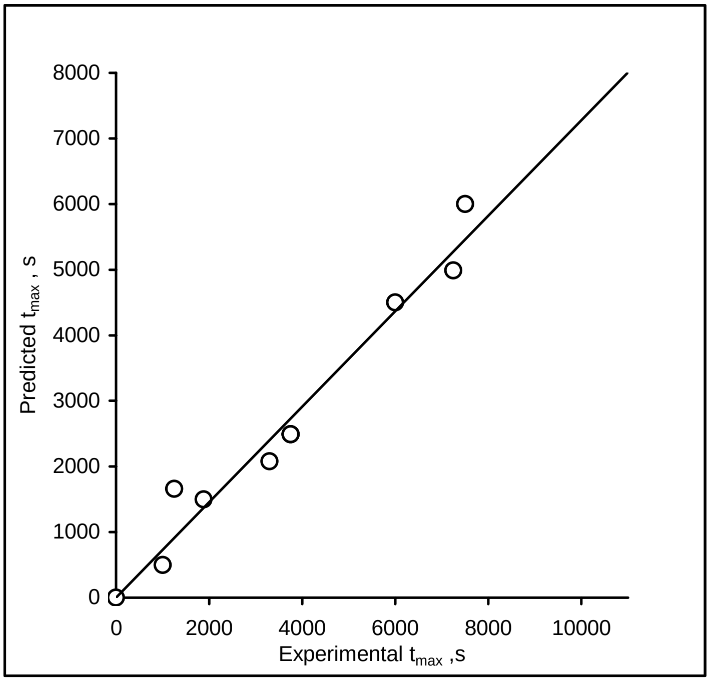
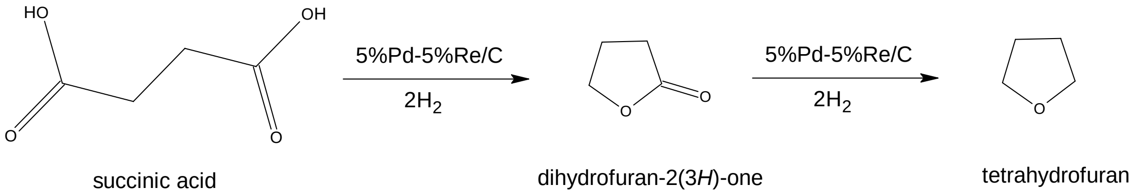


Figure 3-27: Comparison of predicted t_{max} with observed t_{max} for cyclohexane carboxylic acid.

As shown in Figure 3-27, the Eq-3.15 was found to predict t_{max} for cyclohexane carboxylic acid in reasonable agreement. Since, the t_{max} for CCA could be predicted with good agreement with experimental values, using Eq-3.15, the approach was validated for another consecutive hydrogenation system. For this purpose a detailed study on hydrogenation of Succinic acid to tetrahydrofuran through γ-butyrolactone as intermediate reported earlier was used[24].

3.3.13.2 Determining t_{max} for the intermediate γ-butyrolactone, in hydrogenation of succinic acid to tetrahydrofuran

During hydrogenation of succinic acid (SAC) with 5%Pd-5%Re/C catalyst, γ-butyrolactone (GBL) is formed as intermediate and further hydrogenation of GBL gives tetrahydrofuran (THF) as shown in Scheme 3-3.



Scheme 3-3: Hydrogenation of succinic acid with 5%Pd-5%Re/C catalyst.

GBL, the intermediate which is formed by hydrogenation of succinic acid is used as solvent and in pharmaceuticals; GBL is also useful in solvent welding of plastic films. So increasing selectivity to GBL using t_{max} approach will be a much simpler approach. The concentration time profile for hydrogenation of succinic acid with 5%Pd-5%Re/C catalyst is shown in Figure 3-28.

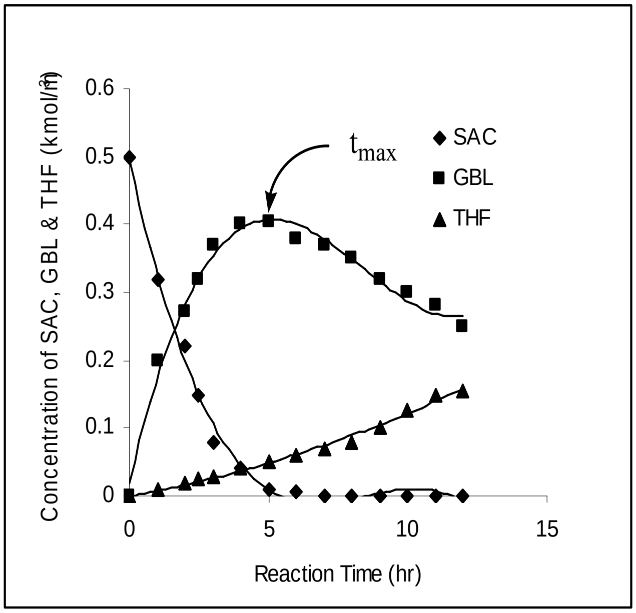


Figure 3-28: Concentration time profile for hydrogenation of succinic acid with 5%Pd-5%Re/C catalyst.

Reaction conditions: Temperature = 523 K, Hydrogen partial pressure = 8.1 MPa, Catalyst = 6.25 kgm^{-3}, Succinic acid = 0.5 $kmolm^{-3}$, Solvent = 1,4-dioxane-water, Time = 12 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

From parametric study reported by Chaudhari et al., it was observed that t_{max} for GBL is inversely proportional to catalyst loading and hydrogen partial pressure and directly proportional to the concentration of succinic acid. Using the data reported by

Chaudhari et al. for t_{max} and Marquardts method for optimization an equation for t_{max} has been derived which is given below by Eq-3.16. The validity of Eq-3.16 was checked by plotting predicted t_{max} versus experimental t_{max} as shown in Figure 3-29, which was found to be in reasonable agreement.

$$t_{max} = K\left(\frac{[SAC]}{[CAT][H_2]}\right) \qquad \text{(Eq-3.16)}$$

Where,

t_{max} Time, where GBL is in maximum concentration (s)

K Constant (s kg bar/kmol)

[SAC] Concentration of succinic acid (kmol/m^3)

[CAT] Concentration of 5% Pd-5% Re catalyst (kg/m^3)

[H_2] Hydrogen partial pressure (bar)

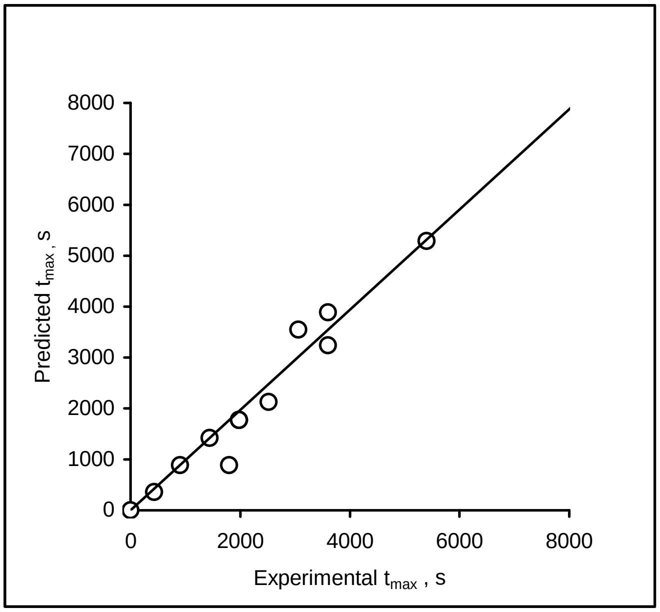


Figure 3-29: Comparison of predicted t_{max} with experimental t_{max} for GBL.

For this system too the approach for t_{max} gave reasonably acceptable fitting with experimental values.

3.4 Conclusion

The hydrogenation of benzoic acid to cyclohexane carboxylic acid using Ru/C catalyst was studied in a laboratory scale slurry reactor. For hydrogenation of benzoic acid with supported Ru catalyst, the catalyst supported on carbon gave highest conversion and selectivity to cyclohexane carboxylic acid. High Ru loading was found to increase the conversion of benzoic acid and selectivity to cyclohexane carboxylic acid. Selectivity for hydrogenation of benzoic acid to cyclohexane carboxylic acid with 5% Ru/C catalyst was increased by addition of water to 1,4-dioxane. The 5% Ru/C catalyst was found to be stable for two recycles without any variation in activity and selectivity. No leaching of Ru into the reaction crude was observed.

The kinetics of hydrogenation of benzoic acid to cyclohexane carboxylic acid was investigated using 5% Ru/C catalyst in a temperature range of 453 to 493 K, hydrogen pressure between 3-10 MPa, catalyst loading between 0.1-0.5 kg/m^3, initial benzoic acid concentration between 0.1-0.6 kmol/m^3.The rates were first order with respect to catalyst and showed order higher than one for hydrogen partial pressure. With benzoic acid a first order tending to zero order was observed.

The following rate equation was found to predict the observed rates in good agreement.

$$R_H = \frac{k\ w\ A\ B^{1.5}}{(1 + k_A A)}$$

The activation energy for hydrogenation of benzoic acid and heat of adsorption for benzoic acid on catalyst surface was found to be 84.2 and 58.8 kJ/mol respectively.

Effect of temperature on hydrogenation of cyclohexane carboxylic acid with 5% Ru/C catalyst in 1:1 1,4-dioxane:water solvent was studied. The activation energy for hydrogenation of cyclohexane carboxylic acid was found to be 148.3 kJ/mol which was higher than the activation energy for ring hydrogenation of benzoic acid

An approach to predict the t_{max} (Eq-3.15) was proposed. The equation proposed for t_{max} was validated for two consecutive hydrogenation systems, hydrogenation of BZA-CCA-CHM and SAC-GBL-THF. A good agreement between the experimental and predicted t_{max} was achieved using the Eq-3.15 for hydrogenation of BZA-CCA-CHM using 5% Ru/C catalyst. This approach for predicting t_{max} for the intermediate of complex consecutive reaction was also successfully applied for determining t_{max} for GBL, an intermediate formed during hydrogenation of succinic acid with 5%Pd-2%Re/C catalyst, based on literature data.

3.5 Nomenclature

A	Benzoic acid concentration, kmol/m^3
a_p	Interfacial area of particles per unit volume of liquid phase, m^2/m^3
B	Hydrogen partial pressure, MPa
$\mathrm{C_{CCA}}$	Concentration of cyclohexane carboxylic acid, kmol/m^3
$\mathrm{C_f}$	Final concentration of benzoic acid, kmol/m^3
$\mathrm{C_i}$	Initial concentration of benzoic acid, kmol/m^3
$\mathrm{C_i}$*	Hydrogen concentration, kmol/m^3
D	Molecular diffusivity, m^2/s
D_e	Effective diffusivity, m^2/s
$\mathrm{d_I}$	Impellar diameter, m
D_M	Molecular diffusivity, m^2/s
d_p	Catalyst particle diameter, m
$\mathrm{d_T}$	Tank diameter, m
e	Energy supplied to the liquid per unit mass, m^2/s
E_a	Activation energy, kJ/mol
F_c	Shape factor
$\mathrm{h_1}$	Height of impeller, m
$\mathrm{h_2}$	Liquid height, m
He	Henrys constant, kmol/m^3/atm
k	Rate constant for hydrogenation
$\mathrm{k_1}$, $\mathrm{k_2}$	Rate constants for the consecutive reaction
K_A	Adsorption equilibrium constant for benzoic acid, m^3/kmol
k_La_B	Gas to liquid mass transfer coefficient, s^{-1}
k_s	Liquid to solid mass transfer coefficient, s^{-1}
M_B	Molecular weight of solvent
N	Agitation speed, rpm
R_H	Initial rate of hydrogenation, kmol/m^3/s
$\mathrm{R_i}$	Initial rate of hydrogenation, kmol/m^3/s
$\mathrm{t_{max}}$	Time for maximum concentration of intermediate, s
$\mathrm{t^n_{max}}$	$\mathrm{t_{max}}$ for n$^{\mathrm{th}}$ intermediate, s

V_A	Solute molar volume
V_g	Gas volume, m^3
V_L	Liquid volume, m^3
w	Catalyst concentration, kg/m^3
w	Catalyst mass per unit volume of the reactor, kg/m^3

Greek symbols

μ_l	Viscosity of reaction solvent, kg/m/s
$ø_{exp}$	Thiele parameter defined by equation Eq-3.9
α_{gl}	Parameter defined by Eq-3.3
α_{ls}	Parameter defined by Eq-3.5
ε_p	Porosity of catalyst
ρ_l	Density of reaction solvent, kg/m^3
ρ_p	Density of the catalyst particle, kg/m^3
Φ	Objective function defined by Eq-3.12

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Chapter 4

Kinetics of hydrogenation of benzoic acid to benzyl alcohol in a batch slurry reactor using Ru-Sn/Al_2O_3 catalyst

4.1 Introduction

Supported Ru-Sn bimetallic catalysts are reported to be active for hydrogenation of carboxylic acids to alcohols. These catalysts are not only active for hydrogenation of carboxylic group but are also selective for hydrogenation of carboxylic group in presence of other hydrogenable functional groups. One such example for selective hydrogenation with Ru-Sn/Al_2O_3 catalyst is the hydrogenation of oleic acid to 9-octadecen-1-ol[1]. A supported Ru-Pt-Sn/C catalyst is reported to suppress hydrogenolysis reaction occurring during hydrogenation of 1,4-cyclohexane dicarboxylic acid to 1,4-cyclohexane dimethanol[2]. Tahara et al. have reported that when the hydrogenation of rosin is carried out with Ru-Sn/Al_2O_3 catalyst without calcination, a 95% selectivity to rosin alcohol was obtained. However, when the catalyst is calcined at 573-1173 K the selectivity of catalyst increased from 95% to 100%[3]. Metal precursors used for preparing Ru-Sn/Al_2O_3 catalyst were also observed to affect the activity and selectivity of catalyst for hydrogenation of carboxylic acids[4]. Aromatic carbonyls are generally hydrogenolysed with ease with supported metal catalysts to give methylene compounds via the formation of intermediate aromatic alcohols during hydrogenation[5].

Benzoic acid is the simplest aromatic carboxylic acid which contains one hydrogenable carboxylic group and an aromatic ring. In Chapter II, Section 2.3.1.6 it has been observed that selective hydrogenation of benzoic acid to benzyl alcohol is not possible with monometallic Ru/Al_2O_3 catalyst, as hydrogenolysis products like toluene and methyl cyclohexane are obtained. This catalyst was also found to be active for the hydrogenation of the aromatic ring to give cyclohexane carboxylic acid. When Sn is doped in Ru/Al_2O_3 catalyst, a 100% selectivity to benzyl alcohol was achieved for hydrogenation of benzoic acid. There is so far no detailed study on the effect of Sn/Ru ratio in Ru-Sn/Al_2O_3 catalyst on the hydrogenation of aromatic carboxylic acids, which would elucidate the role of Sn in inhibiting hydrogenolysis. The influence of support and catalyst reduction temperature on activity and selectivity for hydrogenation of benzoic acid to benzyl alcohol has also not been reported.

For Ru-Sn catalysts, leaching of Sn into the reaction crude is reported for hydrogenation of 1,4 cyclohexane dicarboxylic acid with Ru-Pt-Sn/C trimetallic catalysts, wherein the authors have observed that addition of Pt to Ru-Sn/C catalyst reduces the leaching of Sn [2]. However, a detailed investigation on the parameters which control the leaching of Sn from Ru-Sn catalyst is also lacking.

Since hydrogenation of benzoic acid to benzyl alcohol involves three phases: viz solid (catalyst), liquid (reaction solvent) and gas (hydrogen), the overall performance of such a multiphase catalytic reaction will depend on various factors such as gas to liquid mass transfer, liquid-solid mass transfer, intraparticle diffusion and intrinsic reaction kinetics etc. Thus, to analyze such a multiphase catalytic reaction, it is important to understand the rate behavior and intrinsic kinetics of this reaction. Although in the literature, the mechanism for hydrogenation of carboxylic acid with Ru-Sn/Al_2O_3 catalyst is proposed to be a dual site mechanism, no kinetic study for this system has been reported[6].

In this chapter, we have studied the influence of Sn/Ru ratio, role of support and catalyst reduction temperature on activity and selectivity of Ru-Sn catalysts for hydrogenation of benzoic acid to benzyl alcohol. The leaching of Sn during hydrogenation reaction was also investigated. Also, a kinetic study on chemoselective hydrogenation of benzoic acid to benzyl alcohol has been done and rate equations based on initial rate data have also been proposed.

4.2 Experimental

4.2.1 Materials

Benzoic acid, 1,4-dioxane, $RuCl_3.3H_2O$, Stannous chloride ($SnCl_2.2H_2O$) were procured from SD Fine Chemicals Ltd. (India). Catalyst supports like carbon, alumina, titania and silica were procured from Aldrich Chemicals (USA). Authentic standards of reaction products like cyclohexane carboxylic acid, cyclohexyl methanol, and benzyl alcohol and benzyl benzoate were procured from Merck India Ltd. Hydrogen and nitrogen >99.9% purity were obtained from Indian Oxygen Ltd. Bombay.

4.2.2 Catalyst preparation

The catalysts were prepared by impregnation method followed by calcination and reduction. The following catalysts were prepared: Ru-Sn/Al_2O_3, Ru-Sn/TiO_2 and Ru-

Sn/SiO_2[7]. Ru-Sn/Al_2O_3 catalyst with varying Sn/Ru ratios and different catalyst reduction temperatures were also prepared by this procedure.

For preparing these catalysts, a homogeneous solution of required amount of $RuCl_3.3H_2O$ and $SnCl_2.2H_2O$ was prepared in 50 ml water. To this solution, 10 g of required support was added and the suspension was stirred vigorously for 5 minutes. After stirring for 5 min the slurry was transferred into 100 ml round bottom flask and excess water was removed using rotary evaporator. The dried impregnated catalyst was dried overnight in oven at 363 K. This dried catalyst was then calcined at 773 K for 12 hrs in a calcination furnace. After calcination, the catalyst was reduced at 573 K in a tubular silica glass reactor placed in a furnace as shown in Section 2.2.2 ,Figure 2-1, under constant flow of hydrogen gas (5 ml/min) for 12 hrs. After the reduction period, the silica glass reactor was cooled under nitrogen flow to room temperature. The reduced catalyst was transferred into a 50 ml container and stored in the dessicator under nitrogen.

4.2.3 Reactor set-up for high pressure reactions

The reactions were carried out in a 250 ml capacity high pressure – high temperature reactor supplied by Parr Instruments Co. USA. The reactor was provided with a double bladed variable speed stirrer with a magnetic drive and automatic temperature control by means of an external electrically heated jacket and internal cooling coils. A gas inlet / outlet as well as liquid outlet provided a facility for sampling of liquid contents in the reactor. For safety purpose, a high pressure – high temperature cut-off facility was also provided to the reactor, in addition to a rupture disc. The autoclave was designed to operate at a temperature up to 623 K and 250 bar pressure.

The reactor was connected to a hydrogen reservoir held at a pressure higher than that of the reactor, through a constant pressure regulator. Hydrogen gas was supplied to the reactor from this reservoir through a non-return valve. The gas consumed during the course of the reaction was determined from the observed pressure drop in the reservoir at different time intervals. A transducer connected to a pressure readout system was used to monitor pressure in the reactor and hydrogen reservoir. A schematic of the reactor assembly has been presented in Section 2.2.3, Figure 2-2.

4.2.4 Experimental procedure for high pressure reactions

In a typical hydrogenation experiment, known quantities of the substrate, catalyst and solvent were charged into a clean and dry reactor. The contents were flushed with nitrogen, followed by hydrogen (2-3 times). The contents in the autoclave were heated to a desired temperature under slow stirring. After the desired temperature was attained, the autoclave was pressurized to the requisite pressure with hydrogen and the reaction was started by adjusting the agitation speed to 1200 rpm. The hydrogen consumption was determined from the drop in the hydrogen pressure in the reservoir vessel as a function of time. The liquid samples were withdrawn at specific time intervals and analyzed for reactant and product concentrations. At the end of the reaction, the autoclave was cooled to room temperature and a gas sample was withdrawn for checking the gas phase product. The gas phase analysis was essential to ensure that cracking of the products to hydrocarbons was negligible. Following this, the contents in the reactor were discharged and the liquid sample was analyzed for reactants and products.

4.2.5 Analysis

The various hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector instrument). Mass spectra for major reaction products are given in Appendix I.

For quantitative analysis, the sample from the reaction mixture was filtered to remove catalyst, and analyzed by gas chromatography. For analysis, a HP INNOWax, polyethylene glycol capillary column (30m x 320µm x 0.25 µm) along with flame ionization detector was used on an Agilent 6890 gas chromatograph controlled by HP Chemstation software equipped with an auto sampler unit. Calibration for the hydrogenation products was done using external standard method[8]. The standard conditions under which the gas chromatograph was operated for quantitative analysis of reactants and products are given in Section 3.2.5, Table 3.1. The reproducibility of results was checked and the error in experimental measurements was less than ±3 %. A mass balance of the reactants consumed during reaction and products formed showed > 95% agreement. Similarly, gas balance for hydrogen consumed and products formed was found to be above 95%. A typical GC chart showing the analysis of benzoic acid hydrogenation reaction is shown in Figure 4-1.

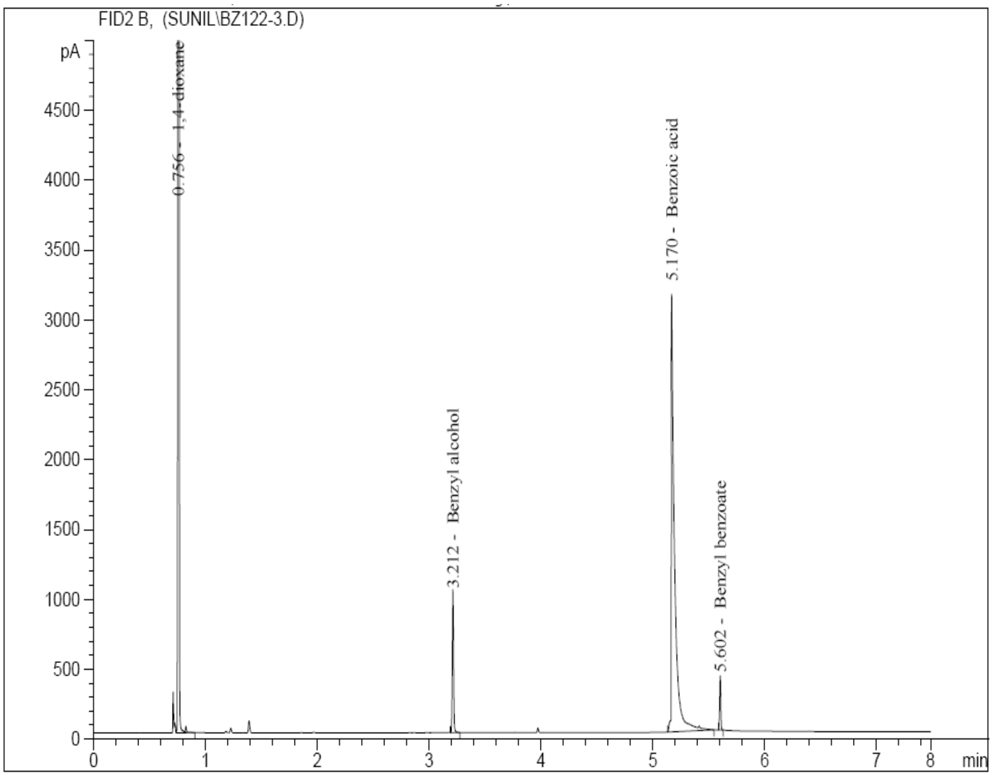


Figure 4.1: Gas chromatogram for hydrogenation of benzoic acid to benzyl alcohol.

4.2.6 Instrumentation

Analysis of ruthenium leaching into reaction medium from the catalyst was performed using Inductively Coupled Plasma with Atomic Emission Spectra (ICP-AES) or Graphite Furnace Atomic Absorption Spectrophotometer [GFAAS, GBC Avanta Sigma Instruments Australia, with photomultiplier tube (PMT) detector].

X-ray photoelectron spectroscopy (XPS) measurements were recorded using a VG Microtech ESCA 3000 instrument at 10^{-10} Torr Pressure, a pass energy of 50 eV, and using monohromatized Mg-K_{α} (Photon energy – 1253.6 eV) as the radiation. EDX was recorded on Perkin Elmer Instrument.

4.3 Results and discussions

4.3.1 Preliminary reactions for hydrogenation of benzoic acid

In Chapter II it was observed that hydrogenation of benzoic acid with monometallic 5% Ru/Al_2O_3 catalyst gives hydrogenolysis products toluene and methyl cyclohexane along with cyclohexane carboxylic acid and cyclohexyl methanol which are obtained by consecutive hydrogenation. A concentration time profile for the hydrogenation of benzoic acid is shown in Figure 4-2. From the profile the reaction pathway proposed is depicted in Scheme 4-1.

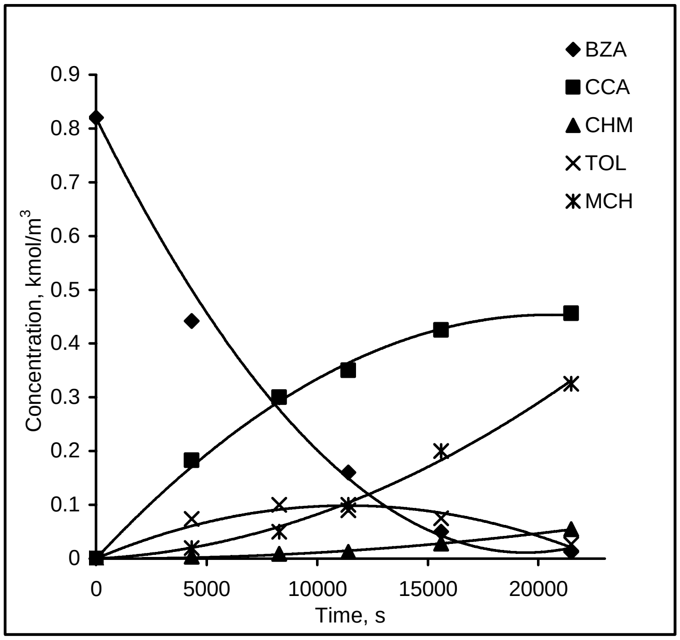
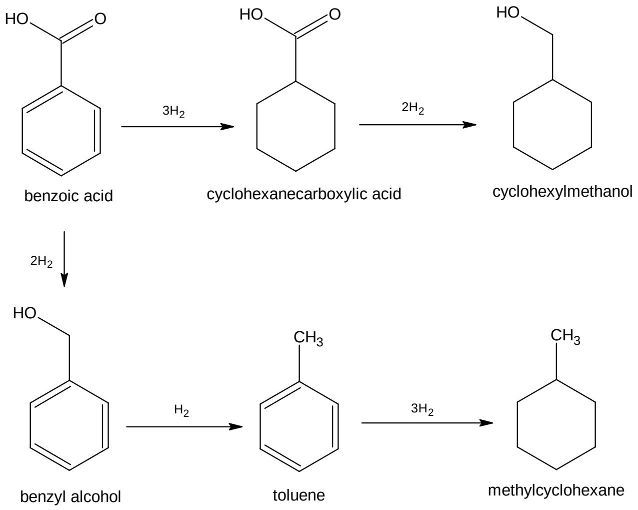


Figure 4-2: Concentration time profile for hydrogenation of benzoic acid with 5% Ru/Al_2O_3 catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^3.



Scheme 4-1: Hydrogenation of benzoic acid with 5 % Ru/Al_2O_3 catalyst

When Sn is added to the Ru/Al_2O_3 catalyst, the reaction profile for the hydrogenation of benzoic acid changes completely. Hydrogenation of the aromatic ring is completely inhibited and hydrogenation of carboxylic group is favored to give benzyl alcohol as shown in Figure 4-3.

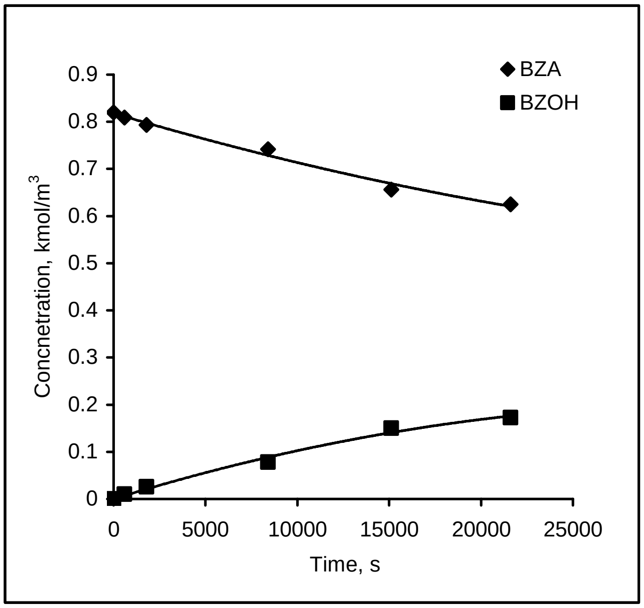
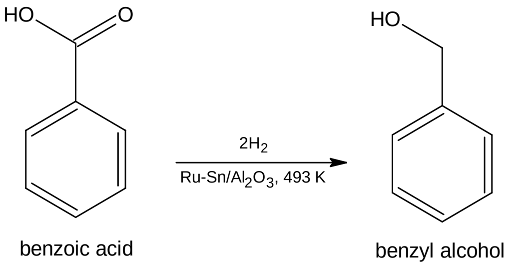


Figure 4-3: Concentration time profile for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 (Sn/Ru atomic ratio is 1:5) catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 5 kgm^{-3}, Benzoic acid = 0.82 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

The benzyl alcohol formed during hydrogenation does not undergo hydrogenolysis to give toluene and methyl cyclohexane as observed with Ru/Al_2O_3 catalyst. The 100% selectivity to benzyl alcohol is probably due to a change in adsorption properties of Ru on addition of Sn to Ru/Al_2O_3 catalyst, which inhibits the hydrogenolysis reaction as proposed by M. Toba et al. using TPR studies[9].

The reaction scheme for hydrogenation of benzoic acid with $Ru\text{-}Sn/Al_2O_3$ catalyst is shown in Scheme 4-2.



Scheme 4-2: Hydrogenation of benzoic acid with $Ru\text{-}Sn/Al_2O_3$ catalyst

Experiments were carried out in order to investigate the catalytic activity and selectivity for benzoic acid hydrogenation with $Ru\text{-}Sn/Al_2O_3$ [5%Ru-29%Sn/Al_2O_3, Ru:Sn atomic ratio is 5] catalyst. The standard reaction conditions for the study are given in Table 4-1. The progress of the reactions was followed by monitoring the consumption of benzoic acid and the formation of hydrogenation product benzyl alcohol and benzyl benzoate (BNBZ). A typical concentration time profile of the reaction is shown in Figure 4-3. The conversion of benzoic acid and selectivity to benzyl alcohol and benzyl benzoate was calculated as given in Eq-4.1, Eq-4.2 and Eq-4.3.

$$\text{Conversion of BZA} = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq-4.1}$$

$$\text{Selectivity to BZOH} = \frac{C_{BZOH}}{C_i - C_f} \times 100 \qquad \text{Eq-4.2}$$

$$\text{Selectivity to BNBZ} = \frac{2 \times C_{BNBZ}}{C_i - C_f} \times 100 \qquad \text{Eq-4.3}$$

Where,

C_i is initial concentration of benzoic acid, kmol/m^3; C_f is final concentration of benzoic acid, kmol/m^3 and C_{BZOH} and C_{BNBZ} is the concentration of benzyl alcohol and benzyl benzoate, kmol/m^3; formed at end of reaction (The factor 2 in Eq-4.3 arises as 1 mole of BNBZ is formed from 1 mole BZOH and 1 mole BZA).

In all experiments the consumption of benzoic acid, hydrogen gas and formation of hydrogenation products were monitored for calculating liquid mass balance and gas balance, which was found to be more than 95%. Following this methodology, the effect of Sn percentage in Ru-Sn/Al_2O_3 catalyst, the role of support and the effect of catalyst reduction temperature on the activity and selectivity of catalyst was studied. The reaction conditions were optimized to achieve highest selectivity to benzyl alcohol.

Table 4-1: Reaction parameters used for preliminary studies on hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst.

Reaction parameter	**Range**
Temperature	493 K
Catalyst concentration	10 kg m^{-3}
Substrate concentration	0.41 kmolm^{-3}
Pressure	6.89 MPa
Stirring speed	1000 rpm
Total charge	1.0×10^{-4} m^3
Reaction time	6 hrs.

4.3.2 Effect of Sn percentage in Ru-Sn/Al_2O_3 catalyst for hydrogenation of benzoic acid to benzyl alcohol

The hydrogenation activity is known to be influenced by the surface Sn concentration in Ru-Sn/Al_2O_3 catalyst[4]. The effect of Sn/Ru ratio on activity of catalyst was studied for benzoic acid hydrogenation and the results are shown in Figure 4-4.

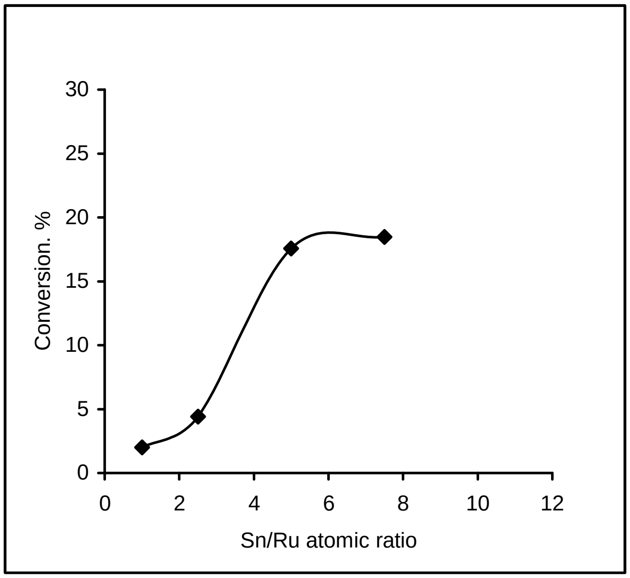


Figure 4-4: Effect of Sn percentage on activity of Ru-Sn/Al_2O_3 catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Benzoic acid = 0.41 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3. Selectivity to benzyl alcohol was 100%.

In absence of Sn the conversion of benzoic acid was 100% but the selectivity to benzyl alcohol was zero, as hydrogenolysis of benzyl alcohol was predominant. Hydrogenation of the aromatic ring was also observed, to give cyclohexane carboxylic acid and cyclohexyl methanol (Figure 4-2). Presence of even a small amount of Sn (Sn/Ru atomic ratio 1 in Ru-Sn/Al_2O_3) in the catalyst inhibits the hydrogenation of aromatic ring and the hydrogenolysis of benzyl alcohol; Further addition of tin to 5% Ru/Al_2O_3 catalyst increases the activity of catalyst for hydrogenation of benzoic acid to benzyl alcohol up to an Sn/Ru atomic ratio of 5 (5% Ru-29% Sn/Al_2O_3 w/w). Further addition of Sn to the catalyst had no effect on activity of catalyst as shown in Figure 4-4. The EDX analysis for the Ru-Sn/Al_2O_3 catalysts at different Sn/Ru atomic ratio is presented in Table 4-2. With increase in Sn loading the surface Sn/Ru ratio increased, along with the activity of the catalyst. A maximum activity was achieved at an Sn/Ru ratio of 5. The increase in activity for hydrogenation of carboxylic group of benzoic acid to benzyl alcohol with increasing Sn/Ru ratio is due to creation of new sites for selective hydrogenation in presence of tin as described by Galvagno et al[10]. Excess addition of Sn i.e. Sn/Ru ratio of 7.5 was found to have no effect on the activity, as surface Ru concentration required for hydrogen activation remains the same. As seen in Table 4-2 the surface Sn/Ru ratio is 4.06. When hydrogenation of benzoic acid was carried out with Sn/Al_2O_3 catalyst conversion of benzoic acid was observed to be zero. Thus, Sn in the catalyst increases the selectivity of benzyl alcohol from 0-100 %, and also increases the activity. Both Ru and Sn are hence essential constituents of the catalyst for the chemoselective hydrogenation of benzoic acid to benzyl alcohol. Hence, for all further studies the catalyst composition employed was 5% Ru-29% Sn. [This catalyst has been referred to as Ru-Sn on support as mentioned].

From the EDX analysis shown in Table 4-2, it seems that a minimum surface Sn/Ru ratio required in the catalyst to achieve maximum activity and selectivity for the hydrogenation should be 3-4.

Table 4-2: Surface Sn/Ru ratio for $Ru\text{-}Sn/Al_2O_3$ catalyst

No.	**Bulk Sn/Ru ratio**	**EDX analysis surface atomic %**		**Surface Sn/Ru ratio**
		Sn	**Ru**	
1	1	0.09	0.109	0.82
2	2.5	0.1004	0.05644	1.77
3	5	0.143	0.03832	3.73
4	7.5	0.1833	0.04515	4.06

4.3.3 Effect of catalyst support for Ru-Sn catalyst on hydrogenation of benzoic acid

The effect of support on Ru/Al_2O_3 catalyst has been investigated in Chapter III, Section 3.3.2 for hydrogenation of benzoic acid. Supports like alumina, titania and silica were observed to be active for hydrogenation of carboxylic group of benzoic acid and promoted hydrogenolysis as well. Carbon and magnesia supports were observed to selectively hydrogenate aromatic ring to give cyclohexane carboxylic acid. So, to study the effect of support on activity and selectivity of Ru-Sn catalyst, Ru-Sn catalysts were prepared using different supports like alumina, titania and silica by the procedure described in Section 4.2.2. The Sn/Ru atomic ratio in Ru-Sn catalyst with different supports was 5. The results for hydrogenation of benzoic acid with Ru-Sn catalyst on different supports are shown in Figure 4-5.

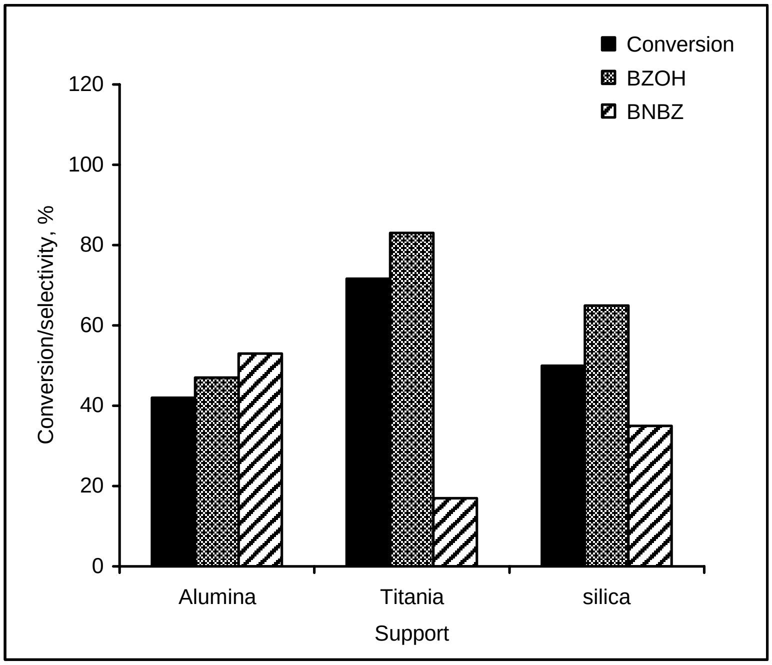


Figure 4-5: Effect of support on Ru-Sn catalyst for hydrogenation of benzoic acid. **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^{3}.

The highest activity for chemoselective hydrogenation of benzoic acid to benzyl alcohol was obtained with Ru-Sn supported on titania, due to the activation of carboxylic group by TiO_2 species (Ti^{+3}) on surface[11]. Ru-Sn/TiO_2 catalyst converted 72% of benzoic acid with 83% selectivity to benzyl alcohol and 17% selectivity to benzyl benzoate. For other supports benzyl benzoate was formed to larger extent.

4.3.4 Effect of catalyst reduction temperature on activity and selectivity of Ru-Sn/Al_2O_3 catalysts

For studying the effect of catalyst reduction temperature on activity and selectivity of Ru-Sn/Al_2O_3 catalyst, alumina was impregnated with $RuCl_3.3H_2O$ and $SnCl_2.2H_2O$ as per the standard procedure and calcined at 773 K for 12 hrs. These calcined catalysts were reduced under hydrogen for 12 hrs at 573, 723 and 873 K respectively as described in Section 4.2.2. The Sn/Ru atomic ratio in Ru-Sn/Al_2O_3 catalyst was maintained as 5.

The reduced catalysts were used for hydrogenation of benzoic acid to benzyl alcohol, the results for which are shown in Figure 4-6.

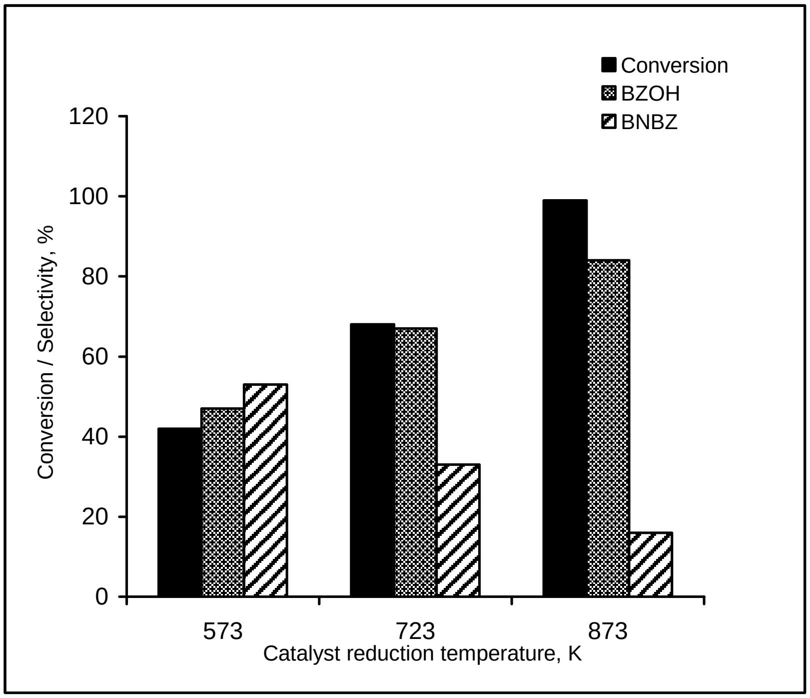


Figure 4-6: Effect of reduction temperature on Ru-Sn catalyst for hydrogenation of benzoic acid.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Benzoic acid = 0.41 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

As seen in Figure 4-6, the activity of Ru-Sn/Al_2O_3 for hydrogenation of benzoic acid increased with reduction temperature. The conversion of benzoic acid for Ru-

Sn/Al_2O_3 catalyst, reduced at 573 K was 40%, while that for the catalyst reduced at 873 K was 99%. The selectivity for benzyl alcohol also increased when catalyst was reduced at 873 K. When the catalyst was reduced at 573 K the selectivity to benzyl alcohol was 47% and 53% benzyl alcohol was in the form of benzyl benzoate. When the same catalyst was reduced at 873 K the selectivity to benzyl alcohol increases from 47% to 84%, this increase in selectivity to benzyl alcohol is mainly due to the increase in activity of Ru-Sn/Al_2O_3 catalyst which consumes benzoic acid rapidly. Very little benzoic acid is free for esterification with benzyl alcohol to give benzyl benzoate.

The catalysts were characterized by X-ray photoelectron spectroscopy (XPS) for the oxidation state of Ru, Sn and Al as shown in Figure 4-7, 4-8 and 4-9. The corrected binding energy and oxidation state for these metals are given in Table 4-3. As there is no change in oxidation state of Ru, Sn and Al, the increase in catalyst activity with reduction temperature was not because of any change in oxidation state of Ru, Sn or Al. The reason for increase in activity of Ru-Sn/Al_2O_3 catalyst is probably due to removal of entrapped Cl (Hydrodechlorination reaction) from the catalyst which is reported to inhibit the hydrogenation of –C=O group[12], giving a more efficient and active catalyst.

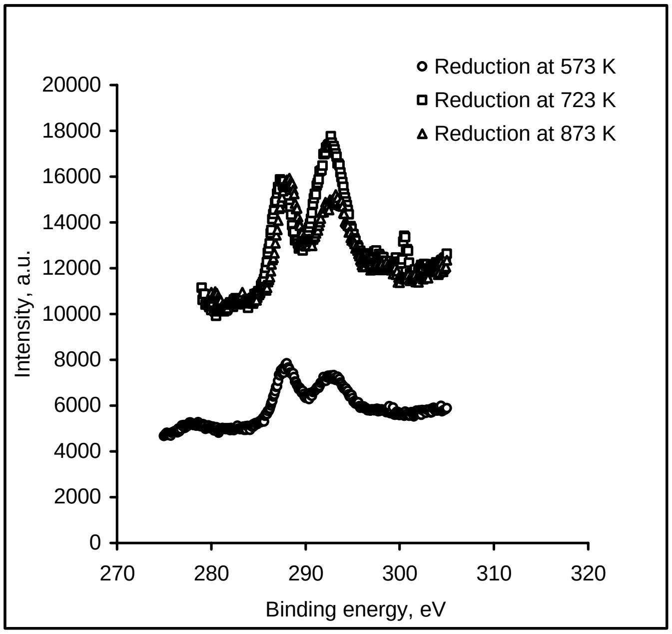


Figure 4-7: XPS characterization for Ru in Ru-Sn/Al_2O_3 catalyst reduced at 573, 723 and 873 K

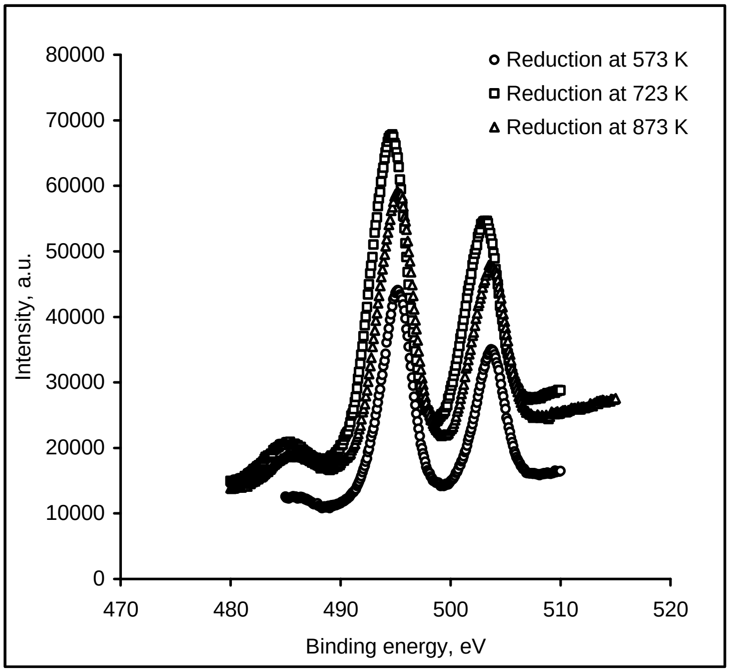


Figure 4-8: XPS characterization for Sn in Ru-Sn/Al_2O_3 catalyst reduced at 573, 723 and 873 K.

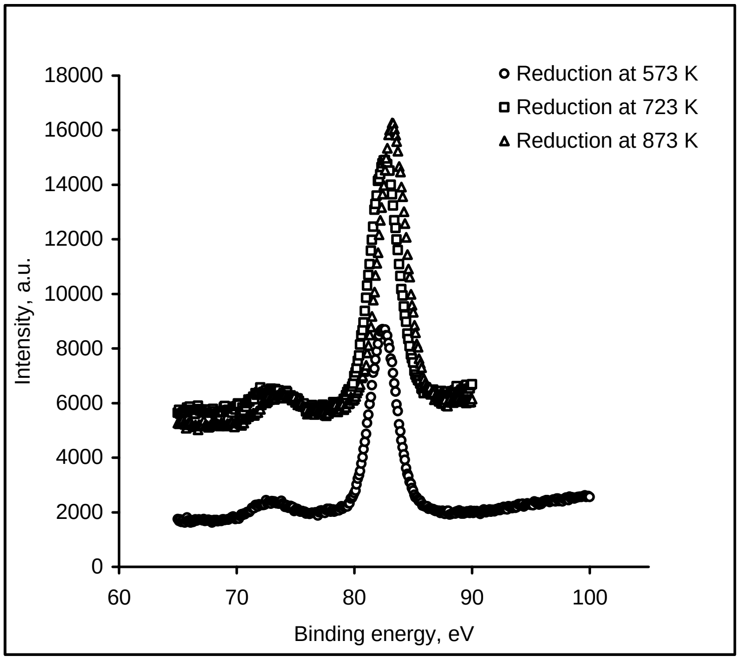


Figure 4-9: XPS characterization for Al in Ru-Sn/Al_2O_3 catalyst reduced at 573, 723 and 873 K.

Table 4-3: Binding energy and oxidation state of Ru, Sn and Al in Ru-Sn/Al_2O_3 catalyst reduced at 573, 723 and 873 K[13].

No.	Reduction temperature (K)	B.E Values (e.V)	Ru (0) ($3d_5$)	Sn(II/IV) ($3d_5$)	Al (III) ($2p_3$)	C (1s)
1	573	Observed	288.3	495.3	82.7	293.1
		Corrected	280.2	487.2	74.6	285
2	723	Observed	287.7	494.8	82.5	292.7
		Corrected	280	487.1	74.8	285
3	873	Observed	288.6	495.5	83.3	293.4
		Corrected	280.2	487.1	74.9	285
		Literature	280	487.3	74.3	285

4.3.5 Recycle study for Ru-Sn/Al_2O_3 catalyst for the hydrogenation of benzoic acid to benzyl alcohol

In order to ensure the stability of the catalyst for hydrogenation of benzoic acid to benzyl alcohol, the catalyst was recycled under same reaction conditions. The Ru-Sn/Al_2O_3 catalyst used for recycle study had Sn/Ru atomic ratio 5. This catalyst was calcined at 773 K for 12 hrs and then reduced at 573 K under hydrogen for 12 hrs.

In these experiments after completion of reaction, the reactor was cooled to 313 K and the catalyst was allowed to settle down and supernant solution was separated from the catalyst. The reactor was then charged with benzoic acid solution to carry out the recycle experiment. The catalyst recycle experiments were performed at 493 K and at a hydrogen partial pressure of 6.89 MPa. The catalyst was found to retain its activity for four recycles without affecting the conversion of benzoic acid and selectivity to benzyl alcohol as shown in Figure 4-10. The overall cumulative turn over frequency (TOF) for the catalyst was found to be 2.73 x 10^{-3} $kmolkg^{-1}hr^{-1}$.

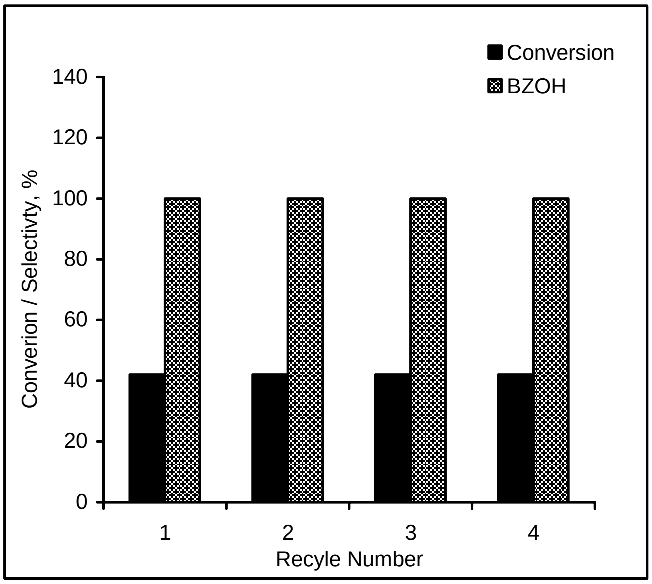


Figure 4-10: Recycle study for Ru-Sn/Al_2O_3 catalyst for hydrogenation of benzoic acid. **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Benzoic acid = 0.41 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0 x 10^{-4} m^3.

In literature, it is reported that Sn leaches out into reaction crude from Ru-Sn catalyst[2]; and hence the leaching of Sn into reaction crude was investigated for the catalyst recycle experiments. For this study at the end of every recycle, the reaction crude was separated from the catalyst and was used for quantitative analysis of Ru and Sn present using AAS/ICP. Ru leaching was not observed in the reaction crude for any recycle reaction. Leaching of Sn into the reaction crude was confirmed and it was also observed that Sn leaching decreased with the catalyst recycle as shown in Figure 4-11. For the first recycle the leaching was maximum (3% of Sn content of catalyst) whereas, at the end of the fourth recycle it was found to be 0.5%. Since activity and selectivity of Ru-Sn/Al_2O_3 catalyst was retained at the end of four recycles, the Sn leaching into the reaction mixture is likely to be the excess superficial Sn, which is not involved in the hydrogenation of benzoic acid.

Following the preliminary experiments and ensuring the stability of catalyst on recycle, the kinetics of the hydrogenation of benzoic acid to benzyl alcohol was studied using Ru-Sn/Al_2O_3 catalysts with Sn/Ru ratio 5, calcined at 773 K and reduced at 573 K for 12 hrs.

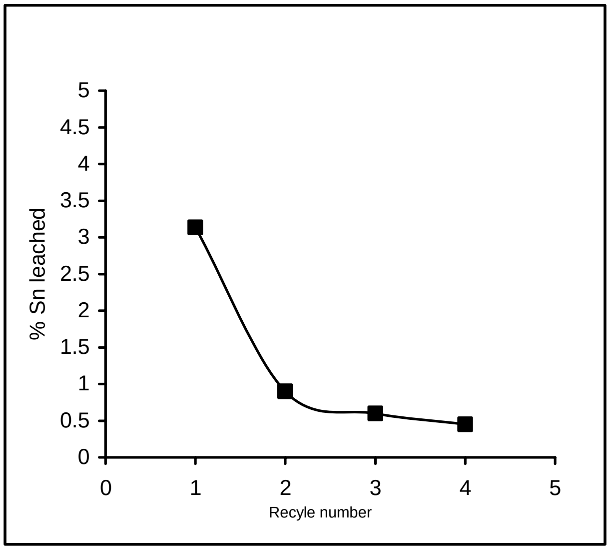


Figure 4-11: Leaching study for Sn in reaction crude.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Benzoic acid = 0.41 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

4.3.6 Preliminary reactions and analysis of mass transfer

The preliminary experiments for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst were carried out to establish the range of reaction conditions like reaction period, catalyst concentration, benzoic acid concentration and hydrogen partial pressure for parametric study. The catalyst used for this study was prepared in-house by the procedure explained in Section 4.2.2. The Sn/Ru ratio in Ru-Sn/Al_2O_3 catalyst was 5, the calcination and reduction temperature for catalyst preparation were 773 K and 573 K respectively. The activity and selectivity for the Ru-Sn/Al_2O_3 catalyst prepared in bulk was observed to be same as for the catalyst prepared in small batch. The mass balance and gas balance for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst prepared in bulk was also found to be greater than 95%.

Analysis of initial rate data provides an approach for understanding the dependency of the reaction rate on individual parameters and also in the evaluation of significance of mass transfer effects. The initial rates for hydrogenation of benzoic acid to benzyl alcohol were calculated from the slope of the benzyl alcohol formation versus time plots during the initial period of reaction, such that, the conversion of benzoic acid was less than 15% and differential conditions prevailed. In the initial period of reaction no benzyl benzoate was formed and hence the rate could be measured as a function of formation of benzyl alcohol with time. A typical plot to obtain the initial rates from concentration of benzyl alcohol formed versus time profile is shown in Figure 4-12.

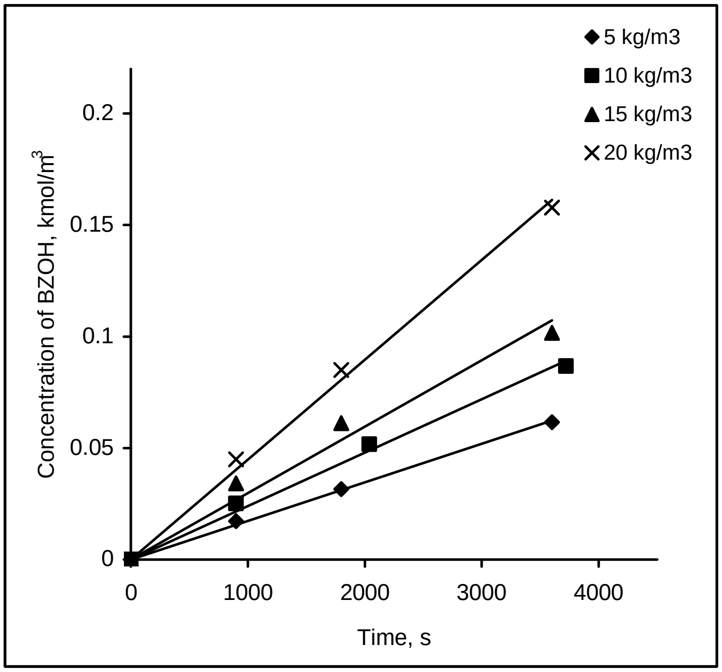


Figure 4-12: Determining initial rate for hydrogenation of benzoic acid to benzyl alcohol at different catalyst loading.

Reaction conditions: Temperature = 513 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^{3}.

This plot pertains to the hydrogenation of benzoic acid to benzyl alcohol at 513 K for varying catalyst loadings. The initial rates were calculated from the slopes of these concentration time profiles as shown in Figure 4-12. A plot of initial rate versus catalyst loading is shown in Figure 4-13 and it indicates first order dependence of reaction on catalyst loading. Effect of other reaction parameters on rate of hydrogenation were studied in same way.

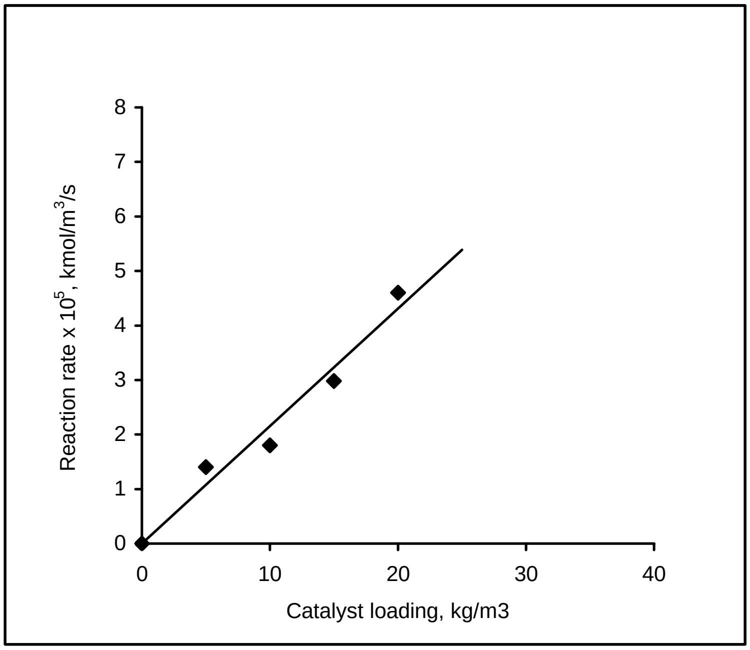


Figure 4-13: Effect of catalyst loading on initial rate of reaction.

Reaction conditions: Temperature = 513 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

Hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst is an example of a multiphase reaction involving gas, liquid and solid phases. So, this reaction involves (i) transfer of reactant (H_2) from gas into the liquid (ii) the transfer of dissolved reactants (BZA and H_2) from liquid phase on to the catalyst surface which is in a solid phase (iii) Intraparticle transfer of reactants to the catalytic site. If the rate of transport of reactants from one phase to the other is slower as compared to the intrinsic rate of reaction, then the rate of reaction is controlled by the rate of mass transport.

So, before commencing with the kinetic study, it was important to ensure that the reaction occurs in the kinetic regime. For this, the effect of agitation speed on the rate of reaction was studied at 513 K in the range of 800-1500 rpm. The agitation speed had no effect on rate of hydrogenation as shown in Figure 4-14, which confirms that gas-liquid mass transfer is not significant.

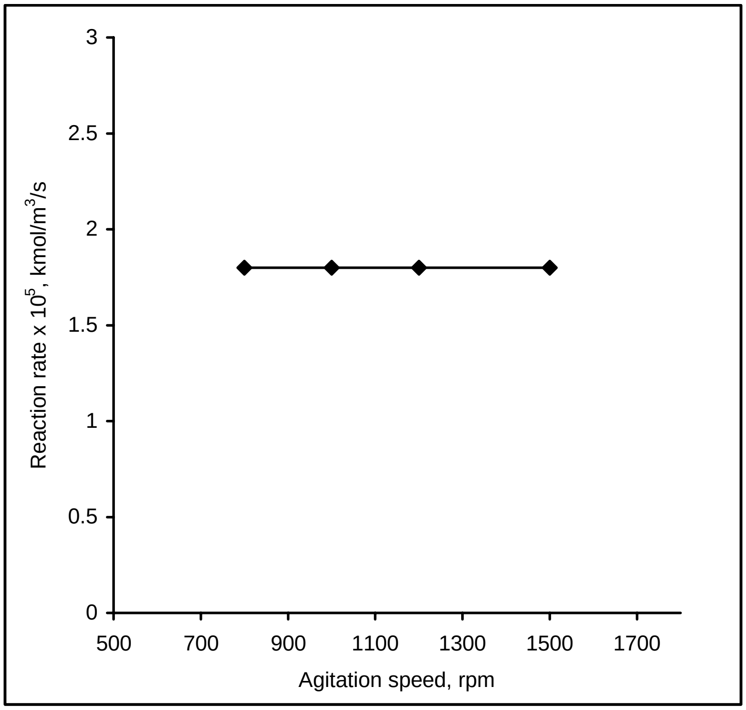


Figure 4-14: A plot of initial rate of hydrogenation vs. agitation speed.

Reaction conditions: Temperature = 513 K, Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Catalyst = 10 kgm^{-3}, Solvent = 1,4-dioxane, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

4.3.7 Experimental procedure for solubility measurement

For interpretation of kinetic data, knowledge of solubility of gaseous reactants in the reaction medium is essential. The solubility of H_2 in dioxane was determined experimentally at 473, 493 K and 513 K using the method described by Purwanto et al[14]. The solubility measurements were conducted in the same reactor used for the reaction. The equipment was provided with automatic temperature control and a pressure display. The temperature of the liquid in the reactor was controlled within ± 1 K. A pressure transducer having a precision of ± 0.07 bar was used to measure the pressure in the autoclave.

In a typical experiment for the measurement of solubility of hydrogen, a known volume of liquid mixture was introduced into the autoclave. The autoclave was flushed with nitrogen and the contents heated to the desired temperature. After thermal equilibrium was attained, the void space in the reactor was pressurized with the required amount of hydrogen. The contents were then stirred for about ten minutes to equilibrate the liquid phase with the solute gas phase. The pressure drop in the autoclave was recorded and used for calculating solubility of hydrogen in the given solvent. In this way Henry's constant for hydrogen in 1,4-dioxane was calculated. The results are shown in Table 4-4.

Table 4-4: Henry's constant for hydrogen in 1,4-dioxane.

No.	**Temperature (K)**	**Henry's constant He, (kmolm^{-3}atm^{-1})**
1	453	8.7×10^{-4}
2	473	15.4×10^{-4}
3	493	24.8×10^{-4}
4	513	35.5×10^{-4}

4.3.8 Analysis for external and intraparticle mass transfer

The rate of hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al_2O_3 catalyst at 493 K was found to be independent of agitation speed above 800 rpm as shown in Figure 4-14, which suggests that external (gas-liquid) mass transfer is absent under the reaction conditions mentioned in Table 4-5. This was also confirmed by studying the effect of catalyst loading on the rate of the reaction. The rate of reaction increased linearly with increasing catalyst concentration, which indicates absence of gas to liquid mass transfer resistance.

However, a detailed analysis to check for the role of external and intraparticle mass transfer is necessary before proceeding to kinetic modeling. The criteria involves evaluation of factors α_{gl}, α_{ls} and ϕ_{exp}, which are defined as the ratio of observed rate of hydrogenation to the maximum rates of gas-liquid, liquid-solid and intraparticle mass transfer respectively. As suggested by Ramachandran and Chaudhari the values of α_1, α_2 and ϕ_{exp} should be less than 0.1, 0.1 and 0.2 respectively to ensure that the reaction operates under kinetic control[15]. The calculation for α_{gl}, α_{ls} and ϕ_{exp} were done as described in Chapter III, Section 3.3.10 and were found to be in the range of 2.8×10^{-5}-3.2×10^{-5}, 1.5×10^{-6}-1.59×10^{-5} and 1.1×10^{-5}-3.8×10^{-4} respectively, which revealed that the reaction was free of external and intraparticle mass transfer.

4.3.9 Kinetic study for hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al_2O_3 catalyst

In order to study the kinetics of hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al_2O_3 catalyst in 1,4-dioxane as solvent, and several experiments were carried out in the range of conditions shown in Table 4-5. The rates for hydrogenation were calculated from the observed concentration-time profiles as discussed in Section 4.3.6. These were essentially initial rates of hydrogenation as they were obtained for low conversion of benzoic acid (Conversion < 10-15%).

Table 4-5: Range of reaction conditions for parametric study of hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al_2O_3 catalyst.

No.	Reaction parameter	Range
1	Temperature	473-513 K
2	Catalyst concentration	5-20 kg m^{-3}
3	Substrate concentration	0.2-0.8 $kmolm^{-3}$
4	Pressure	3.8 – 8.8 MPa
5	Stirring speed	1200 rpm
6	Total charge	1.0×10^{-4} m^3
7	Reaction time	3 hrs.

4.3.9.1 Effect of catalyst loading

The effect of catalyst concentration on the rate of hydrogenation of benzoic acid to benzyl alcohol was studied in the temperature range of 473-513 K, benzoic acid concentration of 0.41 kmolm^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The results are shown in Figure 4-15. The rate was found to be linearly dependent on the catalyst concentration, indicating a first order kinetics.

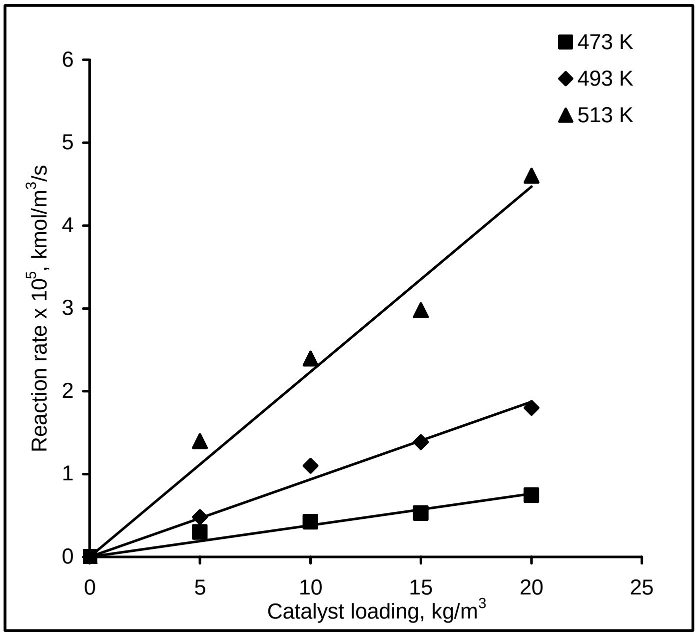


Figure 4-15: Effect of catalyst loading on rate of hydrogenation of benzoic acid. **Reaction conditions:** Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmolm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

4.3.9.2 Effect of benzoic acid concentration

The effect of benzoic acid concentration on the initial rate of hydrogenation was investigated in the temperature range of 473-513 K, catalyst concentration of 10 kgm^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The results are shown in Figure 4-16. The rate showed a first order dependence on benzoic acid concentration also.

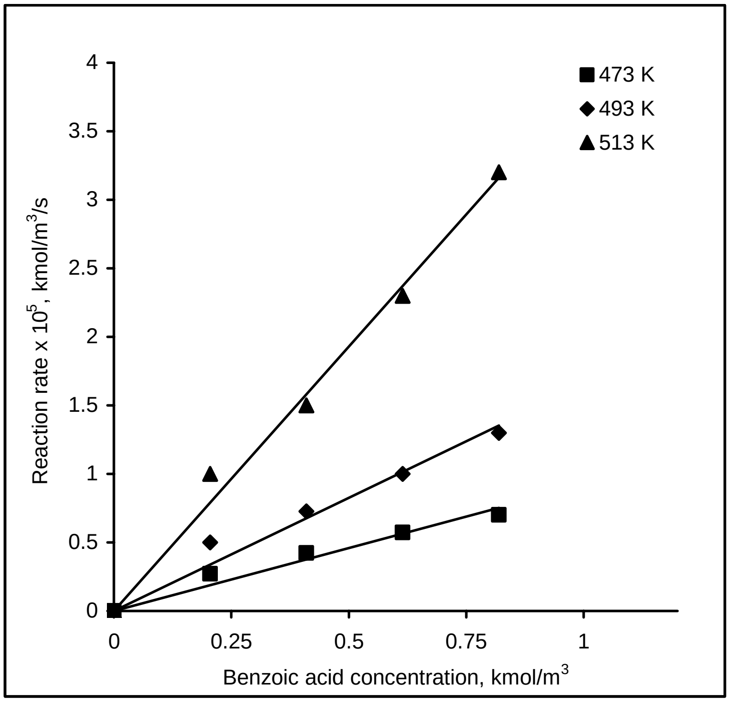


Figure 4-16: Effect of benzoic acid concentration on rate of hydrogenation.

Reaction conditions: Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

4.3.9.3 Effect of hydrogen partial pressure

The effect of hydrogen partial pressure on the rate of hydrogenation of benzoic acid to benzyl alcohol was studied in the temperature range of 473-513 K, catalyst concentration of 10 kgm^{-3} and benzoic acid concentration of 0.41 kmolm^{-3} in 1,4-dioxane as solvent. The rate was found to be linearly dependent on the hydrogen partial pressure, indicating first order kinetics. The results for effect of hydrogen partial pressure are shown in Figure 4-17.

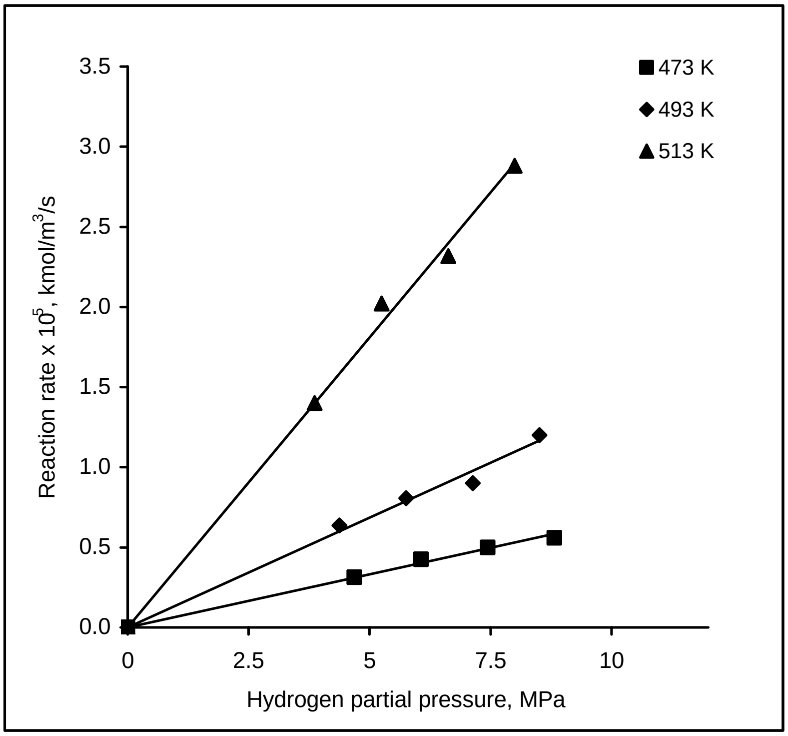


Figure 4-17: Effect of hydrogen partial pressure on rate of hydrogenation. **Reaction conditions:** Benzoic acid = 0.41 kmom^{-3}, Catalyst = 10 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

4.3.10 Kinetic modeling

The rate data obtained were fitted to different rate equations based on Langmuir-Hinshelwood (L-H) type models and the results are shown in Table 4-6. In order to estimate the kinetic constants, the rate equation was subjected to a non-linear regression analysis using an optimization routine based on Marquardt's method[16]. The objective function was chosen as follows:

$$\Phi = \sum_{i=1}^{n} (r_{exp} - r_{mod})_i^2 \qquad \text{(Eq-4.4)}$$

Where, r_{exp} is observed rate of hydrogenation and r_{mod} is the predicted rate of hydrogenation.

Table 4-6: Rate models for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst to benzyl alcohol

Model	Rate equation	T, (K)	*k*	K_A	K_B	Φ_{min}
I	$R_H = k\ w\ A\ B$	473	1.72×10^{-7}	-	-	7.14×10^{-12}
		493	2.99×10^{-7}	-	-	4.07×10^{-11}
		513	8.65×10^{-7}	-	-	2.68×10^{-10}
II	$R_H = \dfrac{k\ w\ A\ B}{(1 + K_A A)}$	473	1.19×10^{-3}	0.37	-	3.16×10^{-10}
		493	2.43×10^{-3}	1.48	-	1.11×10^{-9}
		513	5.41×10^{-3}	2.43	-	1.23×10^{-8}
III	$R_H = \dfrac{k\ w\ A\ B}{(1 + K_B B)}$	473	1.05×10^{-3}	-	0.47	3.15×10^{-10}
		493	1.31×10^{-3}	-	- 0.46	3.19×10^{-9}
		513	2.29×10^{-3}	-	- 0.40	3.09×10^{-8}
IV	$R_H = \dfrac{k\ w\ A\ B}{(1 + K_A A)(1 + K_B B)}$	473	1.38×10^{-3}	0.40	1.34	2.37×10^{-10}
		493	2.79×10^{-3}	1.56	0.86	1.08×10^{-9}
		513	6.39×10^{-3}	2.53	0.78	1.19×10^{-8}

Where, *R_H = Initial rate of hydrogenation (kmol/m^3/s), k = Rate constant ($m^6kg^{-1}kmol^{-1}s^{-1}$), w = Catalyst concentration (kg/m^3), A = Benzoic acid concentration (kmol/m^3), B = Hydrogen concentration (kmol/m^3), K_A = adsorption equilibrium constant for benzoic acid (m^3/mol) and K_B = adsorption equilibrium constant for hydrogen (m^3/kmol).*

The Model I was found to fit the observed rate data with reasonable agreement based on the Φ_{min} value. To verify the model for hydrogenation of benzoic acid to benzyl alcohol, the theoretical rates were obtained using Model I and compared with the experimental rate for hydrogenation as shown in Figure 4-18, 4-19 and 4-20.

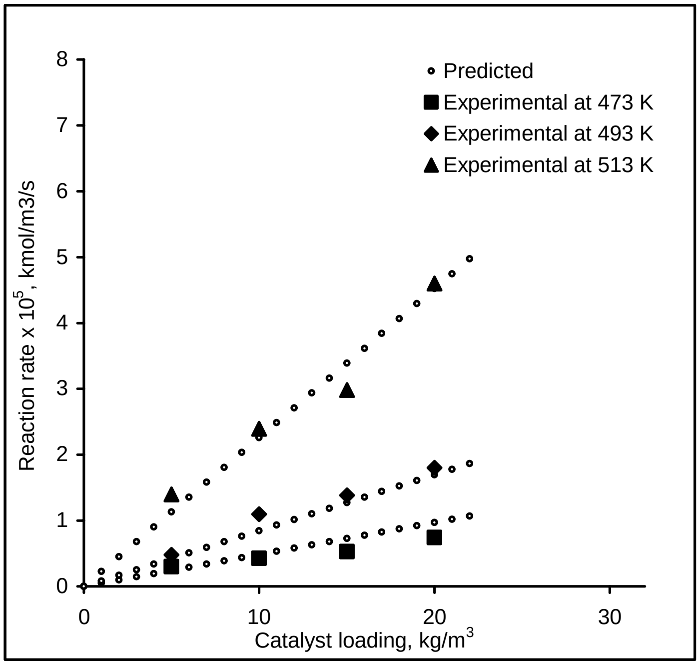


Figure 4-18: Effect of catalyst loading on rate of hydrogenation: Comparison of experimental and predicted rates.

Reaction conditions: Hydrogen partial pressure = 6.89 MPa, Benzoic acid = 0.41 kmol/m^3, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

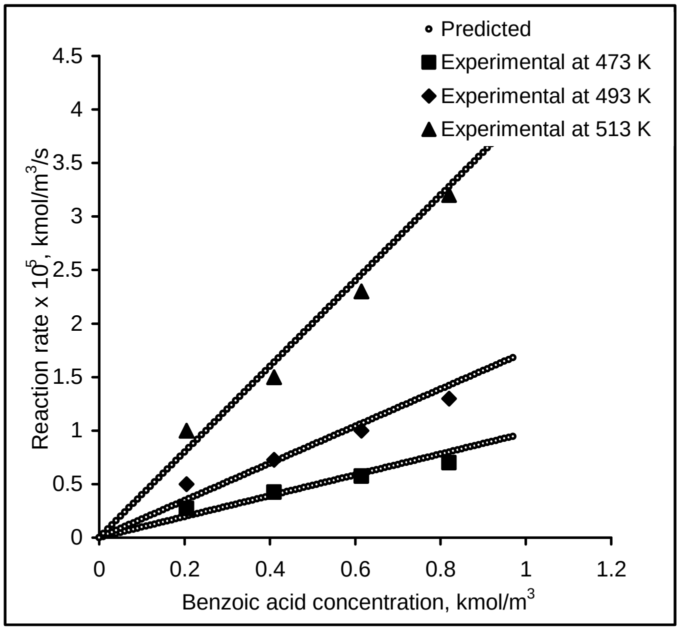


Figure 4-19: Effect of benzoic acid concentration on rate of hydrogenation: Comparison of experimental and predicted rates.

Reaction conditions: Hydrogen partial pressure= 6.89 MPa, Catalyst = 10 kg/m^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

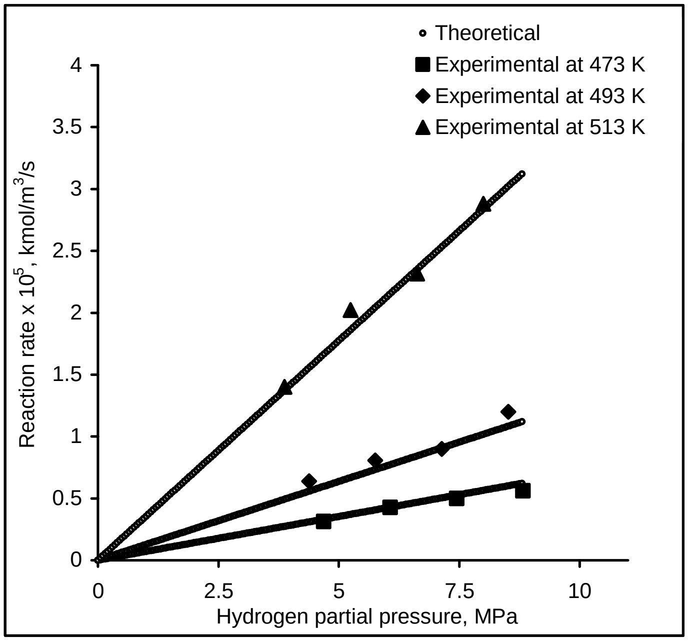


Figure 4-20: Effect of hydrogen partial pressure on rate of hydrogenation: Comparison of experimental and predicted rates.

Reaction conditions: Benzoic acid = 0.41 kmom^{-3}, Catalyst = 10 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 3 hrs, Total volume = 1.0 x 10^{-4} m^3.

From Figure 4-18, 4-19 and 4-20 it is seen that Model I predicts the rate of reaction with an error less than ± 5% which is within the range of experimental error. Based on the values of rate constant (*k*) of this equation, ln *k* versus 1/T (Arrhenius plot) is plotted as shown in Figure 4-21. The activation energy for hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al_2O_3 catalyst was found to be 81.64 kJ/mol.

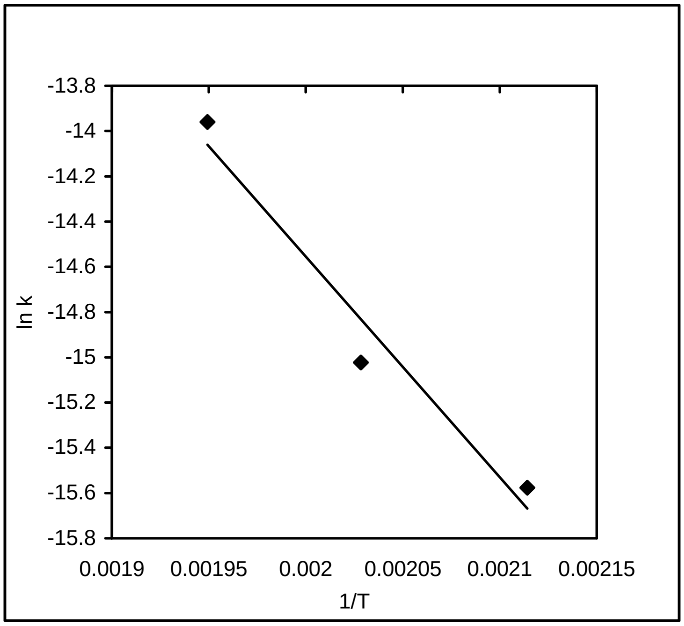


Figure 4-21: Arrhenius plot for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst.

From kinetic study the dual site mechanism as proposed by Kluson and Cerveny[6] was confirmed for hydrogenation of benzoic acid with Ru-Sn/Al_2O_3 catalyst. The mechanism for hydrogenation with this catalyst is dual site mechanism, as the hydrogenation shows first order dependence on the two reaction parameters benzoic acid concentration and hydrogen partial pressure.

4.3.11 Effect of different parameters on leaching of Sn from Ru-Sn/Al_2O_3 catalyst into reaction crude

In Section 4.3.5 it was observed that during recycle of catalyst the leaching of Sn into reaction crude decreased from 3% to 0.45% without change in activity and selectivity of the catalyst. So, a study for leaching of Ru and Sn in reaction crude for different parameters related to catalyst preparation and reaction condition was conducted. Explanation for activity and selectivity for hydrogenation of benzoic acid with respect to these parameters are discussed in Section 4.3.3, 4.3.4 and 4.3.9.2 respectively.

a) Effect of catalyst support:

Analysis of the reaction crudes for Ru-Sn catalyst on different supports shows no leaching of Ru metal from catalyst into the reaction crude. The leaching of Sn into the reaction crude was confirmed for all the Ru-Sn catalysts supported on alumina, titania and silica. Sn Leaching was highest for alumina supported catalyst as shown in Table 4-7.

Table 4-7: Leaching of Sn metal on different support:

No.	Support	% Sn in reaction crude
1	Alumina	3.1
2	Titania	1.0
3	Silica	2.9

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Benzoic acid = 0.41 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

b) Effect of catalyst reduction temperature on leaching of Ru and Sn in Ru-Sn/Al_2O_3 catalyst

GFAAS analysis for reaction crudes of hydrogenation reactions carried out with Ru-Sn/Al_2O_3 catalysts reduced at different temperature revealed that the amount of Sn leaching into reaction solution decreased with increase in the reduction temperature of the catalysts. Ru metal was not detected in the reaction crude for any of these reactions, indicating ruthenium was strongly adhered on to the catalyst surface. The details for Sn percentage leached from the catalyst, reduced at 573, 723 and 873 K are shown in Table 4-8. The leaching of Sn is reduced due strong binding of Sn onto catalyst surface when reduced at higher temperatures[17].

Table 4-8: Effect of catalyst reduction temperature on leaching of Sn metal.

No	Reduction temperature (K)	% Sn in reaction crude
1	573	3.1
2	723	2.5
3	873	1.6

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Benzoic acid = 0.41 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 6 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

c) Effect of benzoic acid concentration on leaching of Ru and Sn in Ru-Sn/Al_2O_3 catalyst

In the literature it is reported that during hydrogenation of benzoic acid over Ru-Sn catalysts, the carboxylic group is activated on Sn and activated hydrogen is transferred to this activated carboxylic group from ruthenium[6]. This mechanism involves chemisorption of carboxylic group on Sn which may also lead to leaching due to interaction with carboxylic group. To verify this, hydrogenation of benzoic acid was carried out at three different concentrations of benzoic acid. At the end of reaction, the reaction crudes were analyzed for Ru and Sn. For these reactions also, leaching of Ru was not observed. The study also confirmed that benzoic acid had no role in leaching of Sn, as the percentage of Sn leached into reaction crude remains constant as is given in Table 4-9.

Table 4-9: Effect of benzoic acid concentration on leaching of Ru and Sn metal.

No	Benzoic acid ($kmol/m^3$)	% Sn in reaction crude
1	0.82	2.26
2	0.41	2.30
3	0.20	2.28

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Solvent = 1,4-dioxane, Time = 3 hrs, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

Thus, in this study it was observed that Ru doesn't leach into the reaction crude under the conditions discussed above. Leaching of Sn was governed by catalyst reduction temperature and the support used for preparing Ru-Sn catalyst. Other parameters like benzoic acid concentration in reaction medium had no effect on leaching of Sn.

4.4 Conclusion

The chemoselective hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al_2O_3 catalyst was studied in a laboratory scale slurry reactor. Monometallic Ru/ Al_2O_3 and Sn/Al_2O_3 were observed to be unproductive catalysts for hydrogenation of benzoic acid to benzyl alcohol, as Ru/Al_2O_3 catalyst gave hydrogenolysis products and Sn/ Al_2O_3 catalyst was found to be inactive for hydrogenation. Ru-Sn/Al_2O_3 catalyst gave 100% selectivity to benzyl alcohol. The conversion of benzoic acid to benzyl alcohol was found to increase with Sn/Ru ratio from 1 to 5 and further increase in Sn/Ru up to 7.5 had no further effect on conversion of benzoic acid.

For hydrogenation of benzoic acid, TiO_2 was observed to be the best support compared to alumina and silica. When the catalyst reduction temperature was increased from 573-873 K the activity of catalyst was found to increase linearly with reduction temperature. The Ru-Sn/Al_2O_3 catalyst was found to be stable for four recycles and although Sn leaching into the reaction crude was observed, it had no effect on the activity and selectivity of the catalyst. The percentage of Sn leached into reaction crude was observed to decrease with the recycle number.

The kinetics of hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al_2O_3 catalyst was investigated in a temperature range of 473-513 K, hydrogen partial pressure between 3-8.8 MPa, catalyst loading between 5-20 kg/m^3, initial benzoic acid concentration between 0.2-0.8 kmol/m^3.The rates were first order with respect to catalyst, benzoic acid and hydrogen partial pressure indicating dual site mechanism for hydrogenation of benzoic acid to benzyl alcohol on Ru-Sn/Al_2O_3 catalyst.

The following rate equation was found to predict the observed rates in good agreement.

$$R_H = k \quad w \quad A \quad B$$

The activation energy for hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al_2O_3 catalyst was found to be 81.64 kJ/mol.

GFAAS analysis for Ru and Sn in reaction crude confirmed that Ru leaching did not occur. Leaching of Sn into reaction crude from catalyst surface was found to be dependent on the support used for catalyst preparation and catalyst reduction temperature.

4.5 Nomenclature

A	Benzoic acid concentration, kmol/m^3
B	Hydrogen partial pressure, MPa
$\mathrm{C}_{\mathrm{BNBZ}}$	Concentration of benzyl benzoate, kmol/m^3
$\mathrm{C}_{\mathrm{BZOH}}$	Concentration of benzyl alcohol, kmol/m^3
C_{f}	Final concentration of benzoic acid, kmol/m^3
C_{i}	Initial concentration of benzoic acid, kmol/m^3
E_a	Activation energy, kJ/mol
He	Henrys constant, kmol/m^3/atm
k	Rate constant for the reaction, m^{6}kg^{-1}kmol^{-1}s^{-1}
K_A	Adsorption equilibrium constant for benzoic acid on catalyst, m^3/kmol
K_B	Adsorption equilibrium constant for hydrogen on catalyst, m^3/kmol
r_{exp}	Observed rate of hydrogenation, kmol/m^3/s
R_H	Rate of hydrogenation, kmol/m^3/s
r_{mod}	Predicted rate of hydrogenation, kmol/m^3/s
w	Catalyst concentration, kg/m^3

Greek symbols

$\o_{exp}$ Thiele parameter defined by equation Eq-3.9

α_{gl} Parameter defined by Eq-3.3

α_{ls} Parameter defined by Eq-3.5

Φ Objective function defined by Eq-4.4

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Chapter 5

Hydrogenation of lauric acid to lauryl alcohol in a batch slurry reactor using Ru-Sn catalysts.

5.1 Introduction

In the last decade, supported ruthenium-tin catalysts have been intensively studied because of their activity and high chemoselectivity in the hydrogenation of unsaturated aldehydes, esters and carboxylic acids to corresponding alcohols[1]. A general conclusion drawn from the studies devoted to Ru-Sn catalyst systems is that ionic tin species, i.e., Lewis acid sites, activate the carbonyl group in hydrogenation reactions, by polarizing the C=O bond[2], followed by hydrogenation, which leads to their highly chemoselective behavior.

It is interesting to note that the ruthenium-tin-boride system exhibited a unique chemoselective hydrogenation of cinnamaldehyde to unsaturated alcohol[3]. Mendes et al.[4] have studied the performance of different supported ruthenium-tin catalysts for the liquid phase hydrogenation of oleic acid to unsaturated alcohol. Titania supported Ru-Sn catalyst prepared by impregnation showed better performance than the alumina supported sol-gel Ru-Sn catalyst. Ru supported on alumina is more active for the hydrogenation of C=C bond, whereas the titania supported catalyst is more active for hydrogenation of the carboxylic group. The introduction of tin to Ru/TiO_2 catalyst resulted in almost total suppression of the C=C bond hydrogenation[4].

In general, it has been observed that titanium oxide, when used as support, greatly improves the activity of platinum group metals in the hydrogenation of carbonyl group, and improves in particular, the selectivity to unsaturated alcohols. The beneficial effect of TiO_2 was attributed to the TiO_{2-x} species on the metal and Ti^{n+} ions that promote the hydrogenation in the desired direction[5]. The enhanced activity of transition metal catalysts supported on reducible oxides for selective hydrogenation of the C=O bond is generally attributed to an interaction of the oxygen end of the C=O bond with exposed cations of the oxide supports. In case of titania these sites can be Ti^{3+} cations or oxygen vacancies. These cations or oxygen vacancies are created via spill-over hydrogen activated by the metal during high temperature reduction. The improved performance of metal catalysts with the addition of promoters such as tin is attributed to the presence of promoter cations on the surface of metal, which activate the C=O bond through the interaction with the lone pair of electron of the carbonyl group oxygen[4].

It is known that an oxide support can strongly interact with another supported oxide, affecting its reducibility, and that the stability of supported oxides is determined by the similarity of the electronegativities of the two cations[6]. It is interesting to note, in this context, that in activated Pt-Sn/SiO_2 and Ru-Sn/SiO_2 catalysts, tin is mainly present as metallic Sn^0 and as metal-tin alloys, while in activated Pt-Sn/Al_2O_3 and Ru-Sn/Al_2O_3, tin is otherwise stabilized as Sn^{2+}.[7] It should also be noted that, in contrast to Pt-Sn system, no alloy phases exist for Ru-Sn bimetallic system. Nevertheless, the existence of two Ru-Sn intermetallic phases, $Ru_{0.4}Sn_{0.6}$ and $Ru_{0.3}Sn_{0.7}$, has been shown[8].

Besides oxide supported, carbon supported Ru-Sn catalysts[9] also find application in hydrogenation reactions.

In recent years, although Ru-Sn catalysts are reported, in addition to other bimetallic systems (Pd-Re, Re-Sn, Rh-Sn, Co-Sn) Ru-Sn/Al_2O_3 catalysts have gained much attention for the hydrogenolysis of fatty esters to fatty alcohols[1]. It has been proposed that in the hydrogenolysis of fatty esters the active centers are metallic Ru particles in interaction with tin oxide acting as Lewis acid centers involved in the activation of the carbonyl group[2].

Barrault and co-workers studied the selective hydrogenation of methyl oleate to oleyl alcohol over Ru-Sn-B/Al_2O_3 catalysts[10]. The yield of oleyl alcohol was 75% at 90% methyl oleate conversion over Ru-Sn-B/Al_2O_3 catalysts for a bulk atomic ratio of Sn/Ru of 4.

Methyl hexadecanoate, methyl-9-octadecanoate and dimethyl succinate were reported to be hydrogenated on α- and γ-alumina and silica and titania supported ruthenium-tin-boride catalysts. Methyl-9-octadecanoate gave the best yield of oleyl alcohol over the γ-alumina supported catalyst with Ru/Sn atomic ratio of 0.5, at 543 K, 44 bar of hydrogen pressure and 7 hrs reaction time. Among Sn, Ge and Pb, tin appeared to be the best promoter. The highest activity and selectivity was attributed to Ru^0 sites interacting with Sn^{2+} and Sn^{4+} Lewis acid sites via oxygen wherein the Lewis acid preferentially activates the C=O group of ester, facilitating activation and H_2 transfer from adjacent Ru-H sites. The role of boron probably lies in increasing the electronic charge density around Ru, thereby facilitating activation of H_2 as a hydride[2]. Ruthenium on alumina, modified by tin compounds, has been also reported as good catalyst for selective reduction of oleic acid to the corresponding unsaturated alcohol. A study on the catalyst preparation indicated that when Ru(acac)$_3$ was loaded on alumina first followed by tin tetra-butoxide, the catalyst showed a better selectivity, but lower activity than that with catalysts prepared with a reversed order of impregnation. Obviously, the selectivity is highest when tin covers the Ru surface and most of the tin remains in the unreduced state[11]. The optimum atomic ratio of ruthenium to tin is about 1:2. Catalysts prepared by an improved sol-gel method showed higher activity and selectivity than those prepared by impregnation and co-precipitation methods. Under optimum reaction conditions the selectivity for 9-octadecen-1-ol and total alcohol (9-octadecen-1-ol + stearyl alcohol) formation was 80.9% and 97%, respectively, at conversion of 81.3%[12].

Despite the detailed studies on supported Ru-Sn catalyst for chemoselective hydrogenation reactions and hydrogenolysis of esters, there is a need to further investigate the effect of catalyst preparation and pretreatment parameters on the performance of this bimetallic system. In this chapter, screening of Ru-Sn catalyst on different supports was done for hydrogenation of lauric acid to lauryl alcohol. Effect of catalyst reduction temperature on activity and selectivity of Ru-Sn catalyst on different supports was studied. Effect of reduction temperature on Ru-Sn/TiO$_2$ catalyst with different Sn/Ru ratio was also studied for hydrogenation of lauric acid to lauryl alcohol. The kinetic study for hydrogenation of lauric acid to lauryl alcohol was investigated using Ru-Sn/TiO$_2$ catalyst. A semi empirical model has been developed which fits the observed rate within experimental error. The activation energy for hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO$_2$ catalyst was calculated using this rate model.

5.2 Experimental

5.2.1 Materials

Lauric acid, 1,4-dioxane and RuCl$_3$.3H$_2$O, Stannous chloride (SnCl$_2$.2H$_2$O) were procured from SD Fine Chemicals Ltd. (India). Catalyst supports like carbon, alumina, titania and silica were procured from Aldrich Chemicals (USA). Authentic standards of reaction products like lauryl alcohol were procured from Aldrich Chemicals (USA).

Lauryl laurate ester was prepared from lauric acid and lauryl alcohol by esterification reaction. Crude lauryl laurate was separated on column, purified and was used as authentic standard. Hydrogen and nitrogen of 99.9% purity were obtained from Indian Oxygen Ltd. Bombay.

5.2.2 Catalyst preparation

The catalysts were prepared by impregnation method followed by calcination and reduction. The following catalysts were prepared in the laboratory: Ru-Sn/Al_2O_3, Ru-Sn/C, Ru-Sn/TiO_2 and Ru-Sn/SiO_2. Ru-Sn/Al_2O_3 and Ru-Sn/TiO_2 catalyst with varying Sn/Ru atomic ratios and different catalyst reduction temperatures were prepared by this procedure. The catalysts prepared are listed in Table 5-1. The general procedure used for preparing the Ru-Sn catalysts is discussed below.

For preparing these catalysts, initially a homogeneous solution of required amount of $RuCl_3.3H_2O$ and $SnCl_2.2H_2O$ is prepared in 50 ml water. To this solution, 10 g of required support is added and is stirred vigorously for 5 minutes. After stirring for 5 min the slurry is transferred into a 100 ml round bottom flask and excess water is removed using a rotary evaporator. The dried impregnated catalyst was dried overnight in an oven at 363 K. This dried catalyst was then calcined at 773 K for 12 hrs in a calcination furnace. After calcination, the catalyst was reduced at 573 K in a tubular silica glass reactor placed in a furnace as shown earlier [Section 2.2.2 ,Figure 2-1] under constant flow of hydrogen gas (5 ml/min) for 12 hrs. After the reduction period, the silica glass reactor was cooled to room temperature under nitrogen flow. The reduced catalyst was transferred into a 50 ml container under nitrogen and stored in the dessicator under nitrogen.

Table 5-1: List of catalysts prepared for hydrogenation of lauric acid.

No.	Catalyst	Sn/Ru atomic ratio	Reduction temperature (K)
1	Ru-Sn/Al_2O_3	1	573
2	Ru-Sn/Al_2O_3	2.5	573
3	Ru-Sn/Al_2O_3	5	573

No.	Catalyst	Sn/Ru atomic ratio	Reduction temperature (K)
4	Ru-Sn/Al_2O_3	7.5	573
5	Ru-Sn/Al_2O_3	5	723
6	Ru-Sn/Al_2O_3	5	873
7	Ru-Sn/SiO_2	5	573
8	Ru-Sn/TiO_2	5	573
9	Ru-Sn/TiO_2	1	573
10	Ru-Sn/TiO_2	2.5	573
11	Ru-Sn/TiO_2	7.5	573
12	Ru-Sn/TiO_2	5	873
13	Ru-Sn/TiO_2	1	873
14	Ru-Sn/TiO_2	2.5	873
15	Ru-Sn/TiO_2	7.5	873
16	Ru-Sn/TiO_2	5	1073
17	Ru-Sn/TiO_2	1	1073
18	Ru-Sn/TiO_2	2.5	1073
19	Ru-Sn/TiO_2	7.5	1073

Conditions: Calcination temperature = 773 K, Calcination time = 12 hrs, Reduction time = 12 hrs.

5.2.3 Reactor set-up for high pressure reactions

The reactions were carried out in a 25 ml capacity high pressure–high temperature reactor supplied by Parr Instruments Co. USA. The reactor was provided with a double bladed variable speed stirrer with a magnetic drive and automatic temperature control by means of an external electrically heated jacket and internal cooling coils. A gas inlet / outlet as well as liquid outlet provided a facility for sampling of liquid contents in the reactor. For safety purpose, a high pressure – high temperature cut-off facility was also provided to the reactor, in addition to rupture disc. The autoclave was designed to operate at a temperature up to 623 K and 250 bar pressure.

The reactor was connected to a hydrogen reservoir held at a pressure higher than that of the reactor, through a constant pressure regulator. Hydrogen gas was supplied to the reactor from this reservoir through a non-return valve. The gas consumed during the course of the reaction was determined from the observed pressure drop in the reservoir at different time intervals. A transducer connected to a pressure readout system was used to monitor pressure in the reactor and hydrogen reservoir. A schematic of the reactor assembly is shown in Section 2.2.3, Figure 2-2.

5.2.4. Experimental procedure for high pressure reactions

In a typical hydrogenation experiment, known quantities of the substrate, catalyst and solvent were charged into a clean and dry reactor. The contents were flushed with nitrogen followed by hydrogen (2-3 times). The contents in the autoclave were heated to a desired temperature under slow stirring. After the desired temperature was attained, the autoclave was pressurized to the requisite pressure with hydrogen and the reaction was started by adjusting the agitation speed to 1200 rpm. The hydrogen consumption was determined from the drop in the hydrogen pressure in the reservoir vessel as a function of time. The liquid samples were withdrawn at specific time intervals and analyzed for reactant and product concentrations. At the end of the reaction, the autoclave was cooled to room temperature and a gas sample was withdrawn for checking the gas phase product. The gas phase analysis was essential to ensure that cracking of the products to hydrocarbons was negligible. Following this, the contents in the reactor were discharged and the liquid sample was analyzed for reactants and products.

5.2.5 Analysis

The various hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector instrument). Mass spectrum for lauric acid, lauryl alcohol and lauryl laurate are shown in Appendix I.

For quantitative analysis, the sample from the reaction mixture was filtered to remove catalyst, and analyzed by gas chromatography. For analysis a HP INNOWax, polyethylene glycol capillary column (30m x 320μm x 0.25 μm) along with flame ionization detector was used on an Agilent 6890 gas chromatograph controlled by HP

Chemstation software, equipped with an auto sampler unit. Calibration for the hydrogenation products was done using external standard method[13]. The standard conditions under which the gas chromatograph was operated for quantitative analysis of reactants and products are given in Section 3.2.5, Table 3.1. The reproducibility of results was checked and the error in experimental measurements was less than ±3 %. A mass balance of the reactants consumed during reaction and products formed showed a greater than 95% agreement. Similarly, gas balance for hydrogen consumed and products formed was found to be above 95%. A typical GC chart showing the analysis of lauric acid hydrogenation reaction is shown in Figure 5-1.

X-ray photoelectron spectroscopy (XPS) measurements were recorded using a VG Microtech ESCA 3000 instrument at 10^{-10} Torr Pressure, a pass energy of 50 eV, and using monohromatized Mg-K_α (Photon energy – 1253.6 eV) as the radiation. EDAX was recorded on Perkin Elmer Instrument.

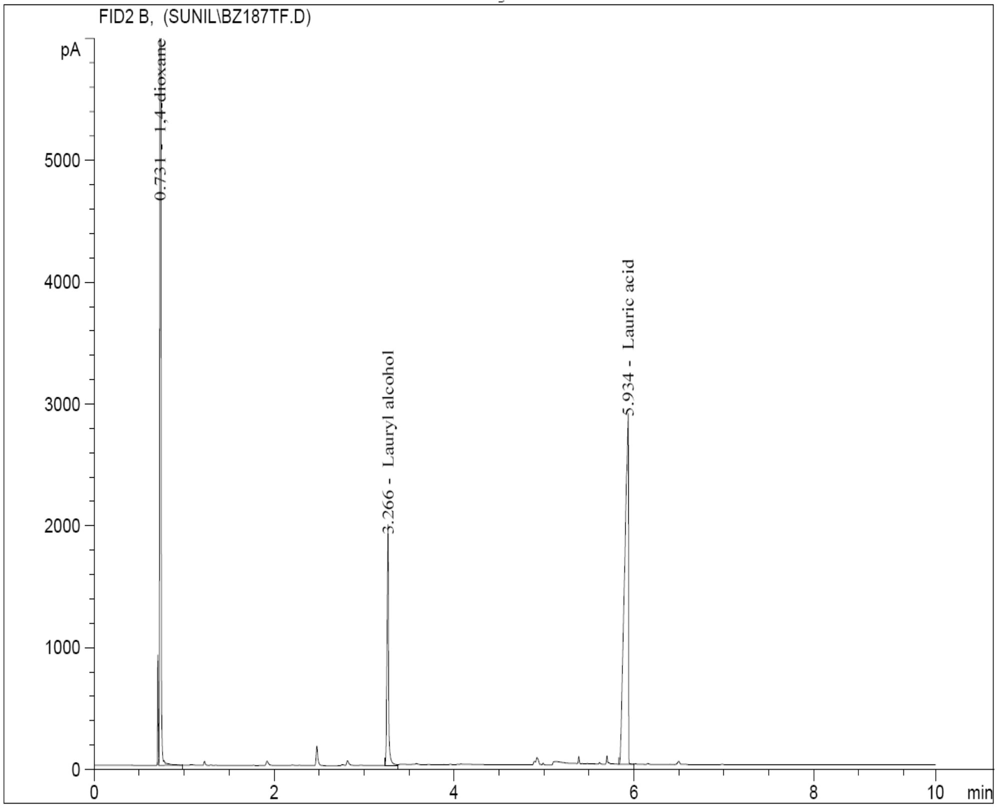

Figure 5-1: Gas chromatogram for hydrogenation of Lauric acid with Ru-Sn/TiO_2 to lauryl alcohol.

5.3 Results and discussions

5.3.1 Preliminary reactions for hydrogenation of lauric acid

Several experiments were carried out in order to investigate the catalytic activity and selectivity of Ru-Sn/TiO_2 catalyst for hydrogenation of lauric acid under different operating conditions. Sn/Ru ratio used for the Ru-Sn/TiO_2 catalyst was 1 and it was reduced at 873 K. The reaction parameters for the study are given in Table 5-2.

Table 5-2: Reaction parameters used for hydrogenation of lauric acid with Ru-Sn catalyst

Reaction parameter	**Range**
Temperature	493 K
Catalyst concentration	10 kg m^{-3}
Substrate concentration	0.25 $kmolm^{-3}$
Pressure	6.89 MPa
Stirring speed	1000 rpm
Total charge	2.5×10^{-5} m^3
Reaction time	4 hrs.

All reactions were carried out for 4 hrs except those related to kinetic studies. The progress of the reactions was followed by monitoring the consumption of lauric acid (LAC) and formation of hydrogenation products lauryl alcohol (LAOH) and lauryl laurate (LALAR). A typical concentration time profile of the reaction is shown in Figure 5-2.

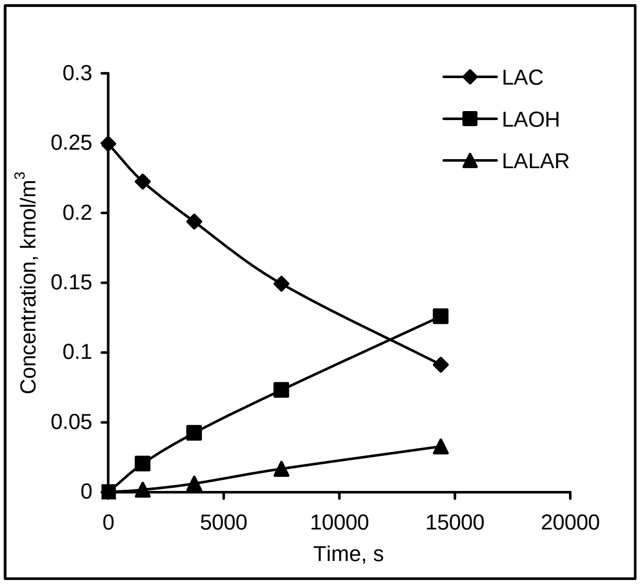

Figure 5-2: Hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5 x 10^{-5} m^3.

The conversion of lauric acid and selectivity to lauryl alcohol was calculated as given in Eq-5.1, Eq-5.2 and Eq-5.3.

$$\text{Conversion of LAC} = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq-5.1}$$

$$\text{Selectivity to LAOH} = \frac{C_{LAOH}}{C_i - C_f} \times 100 \qquad \text{Eq-5.2}$$

$$\text{Selectivity to LALAR} = \frac{2 \times C_{LALAR}}{C_i - C_f} \times 100 \qquad \text{Eq-5-3}$$

Where,

C_i is initial concentration of lauric acid, kmol/m^3; C_f is final concentration of lauric acid, kmol/m^3, C_{LAOH} is the concentration of Lauryl alcohol, kmol/m^3 and C_{LALAR} is the concentration of lauryl laurate formed at end of reaction (The factor 2 in Eq-5.3 arises as 1 mole of LALAR is formed from 1 mole LAOH and 1 mole LAC).

In all the experiments the consumption of lauric acid, hydrogen gas and formation of hydrogenation products was monitored for calculating liquid mass balance and gas balance, which was found to be more than 95% for the hydrogenation. Following these preliminary hydrogenation reactions using Ru-Sn/TiO_2 catalyst, the effect of percentage Sn and Ru in Ru-Sn catalysts, the role of catalyst support and the effect of catalyst reduction temperature was investigated to optimize the activity of the catalyst and selectivity to lauryl alcohol.

5.3.2 Effect of support on Ru-Sn catalyst for hydrogenation of lauric acid

In literature, it is reported that Ru-Sn catalyst has high activity and selectivity when supported on titania as compared to alumina[4]. So, to study the effect of support on activity and selectivity of Ru-Sn catalyst for hydrogenation of lauric acid, the Ru-Sn catalysts on different supports like alumina, titania, silica and carbon were prepared by the procedure described in Section 5.2.2. The Sn/Ru atomic ratio in Ru-Sn catalyst was 5 and reduction temperature was 573 K. The results for hydrogenation of lauric acid with Ru-Sn catalyst on different supports are shown in Figure 5-3.

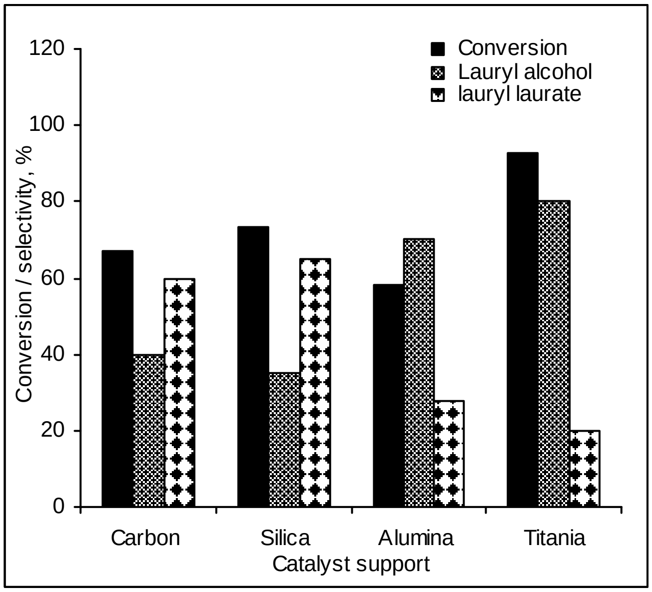

Figure 5-3: Effect of support on Ru-Sn catalyst for hydrogenation of lauric acid.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5×10^{-5} m^3.

The highest activity for hydrogenation of lauric acid to lauryl alcohol is obtained with Ru-Sn supported on titania. This is due to activation of carboxylic group by the partially reduced TiO_2 species on the surface[5]. Ru-Sn/TiO_2 catalyst converted 93% of lauric acid

(LAC) with 80% selectivity to lauryl alcohol (LAOH) and 20% selectivity to lauryl laurate (LALAR). The low selectivity to lauryl laurate with Ru-Sn/TiO_2 catalyst is due to high activity of catalyst for hydrogenation of lauric acid, which consumes lauric acid rapidly, reducing the esterification reaction.

5.3.3 Effect of Ru/Sn atomic ratio on hydrogenation of lauric acid

The hydrogenation activity was affected by the surface Sn concentration of Ru-Sn/Al_2O_3 catalyst. In literature, it is reported that as Sn percentage in the catalyst becomes very high, the activity of catalyst decreases, due to the coverage of Ru by the Sn species[14]. There is however, no study related to the influence of Ru content on catalyst surface. To investigate this, Ru-Sn/Al_2O_3 catalysts with different Ru/Sn ratio were prepared (Reduction temperature 573 K) and tested for their activity for hydrogenation of lauric acid. For these catalysts the Sn content was kept constant (29% w/w). It was observed that as the Ru/Sn atomic ratio increases from 0-1 the conversion of lauric acid increases linearly and further increase in Ru/Sn ratio from 1-2.5 decreases the activity of catalyst. The results are shown in Figure 5-4.

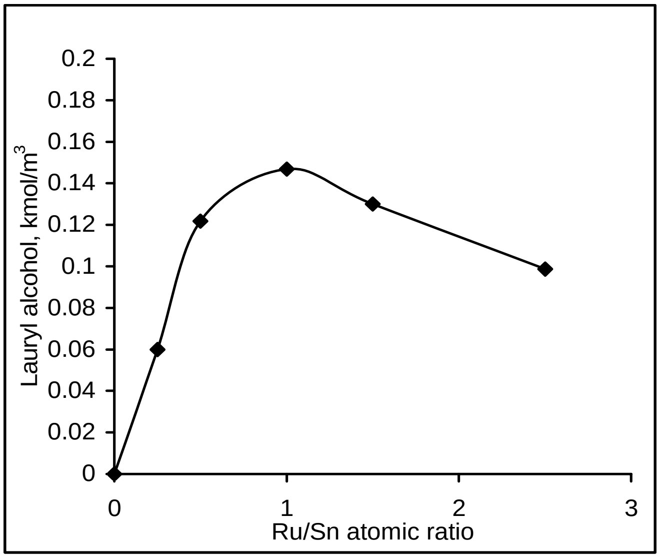

Figure 5-4: Effect of Ru/Sn atomic ratio on Ru-Sn/Al_2O_3 catalyst for hydrogenation*. **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5×10^{-5} m^3. (* Sn content for all catalyst was 29% w/w).

From this it is understood that both Ru and Sn are required in specific amount in the catalyst, and that excess Ru or Sn inhibits the hydrogenation activity.

The Ru-Sn catalysts with different Sn/Ru ratio were prepared on titania and alumina as support. For these catalysts Ru content was kept constant (5% w/w) and only Sn was varied. Hydrogenation of lauric acid was observed to increase with Sn/Ru atomic ratio in Ru-Sn/Al_2O_3 catalyst. In case of Ru-Sn/TiO_2 the activity for the hydrogenation of lauric acid to lauryl alcohol passed through maxima when the Sn/Ru atomic ratio was increased, as seen in Figure 5-5.

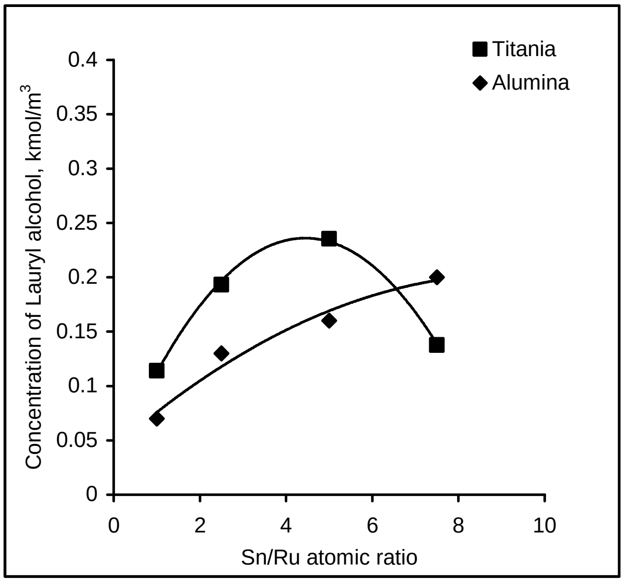

Figure 5-5: Effect of Sn/Ru atomic ratio on Ru-Sn/TiO_2 and Ru-Sn/Al_2O_3 catalyst for hydrogenation*.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5×10^{-5} m^3. (* Ru content for all catalyst was 5% w/w).

Such a different trend for the two supports is observed because in Ru-Sn/Al_2O_3 catalyst only SnO_2 species are present on catalyst surface which activate the –COOH group. The increase in activity is due to activation of carboxylic group by tin as described by Narashimhan et al[15]. In case of Ru-Sn/TiO_2 catalyst both TiO_2 and SnO_2 are present on the Ru surface and both are involved in activation of –COOH group[5]. So, the maximum concentration of Sn required in Ru-Sn/TiO_2 catalyst to achieve highest activity is lower than that in case of Ru-Sn/Al_2O_3 catalyst. The excess of Sn in catalyst is responsible for the deactivation of catalyst, at higher Sn/Ru ratio, for the titania supported catalyst.

5.3.4. Effect of catalyst reduction temperature on activity of Ru-Sn on different supports

In case of Ru-Sn/Al_2O_3 it was observed that the reduction temperature had an important influence on the activity of catalyst (Section 4.3.4). Hence, it was of interest to study the effect of reduction temperature on the activity for Ru-Sn catalyst on different supports. The results for activity in terms of lauryl alcohol formed for Ru-Sn on different supports reduced at 573, 873 and 1073 K are shown in Figure 5-6.

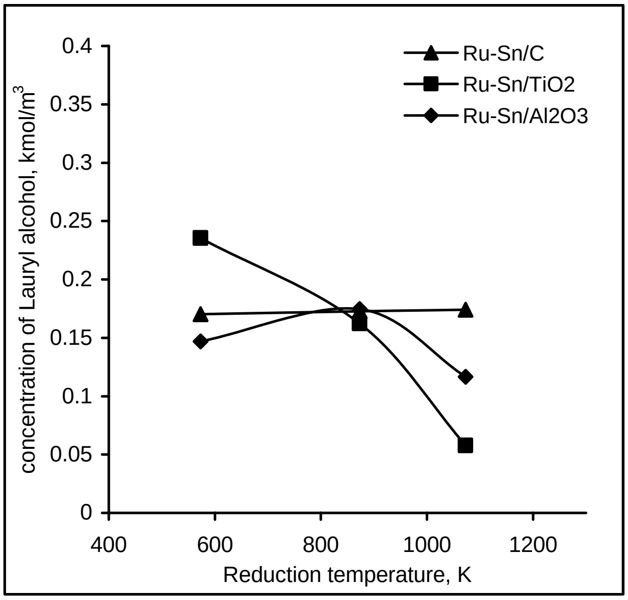

Figure 5-6: Effect of reduction temperature on activity of Ru-Sn on different supports. **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5×10^{-5} m^3.

It was observed that activity of Ru-Sn/TiO_2 catalyst decreased with the increase in reduction temperature of catalyst. For Ru-Sn/Al_2O_3 catalyst the activity of catalyst increased up to a reduction temperature of 873 K and then decreased when it was reduced at 1073 K. For Ru-Sn/C catalyst the activity increased with increase in catalyst reduction temperature, however, the increase in activity was marginal. These trends can be attributed to the transfer of SnO_2 species required for activation of –COOH group, on to the Ru surface[5]. These species, when in excess act as a poison. In Ru-Sn/TiO_2 catalyst, partially reduced TiO_2 is also responsible for activating the -COOH group. As the reduction temperature is increased, both TiO_2 and SnO_2 species move on to the Ru surface, thus blocking the active sites required for hydrogenation. In case of Ru-Sn/Al_2O_3 catalyst, only SnO_2 species moves on to the surface of Ru, and hence it requires a higher temperature for saturation of the Ru surface with SnO_2. This results in a maximum in rate with reduction temperature for Ru-Sn/Al_2O_3 catalyst. In case of Ru-Sn/C catalyst the increase in activity of catalyst with reduction temperature can be due to slow movement of SnO_2 from carbon onto the Ru surface because of which there is no saturation observed for SnO_2 on catalyst surface.

5.3.5 Effect of catalyst reduction temperature on hydrogenation of lauric acid (for different ratio of Sn/Ru in Ru-Sn/TiO_2 catalyst)

In Section 5.3.2, it was observed that the hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst gave a conversion of 93% with 80% selectivity to lauryl alcohol and 20% selectivity to lauryl laurate. It was thus of interest to study the influence of Sn/Ru atomic ratio and also the effect of reduction temperature used for this catalyst for different Sn/Ru ratio on the hydrogenation of lauric acid. For this, Ru-Sn/TiO_2 catalysts with different Sn/Ru ratios and reduced at 573, 873 and 1073 K were synthesized and assessed for their activity in hydrogenation of lauric acid. The results for this study are shown in Figure 5-7. When the catalyst was reduced at 573 K a maximum in rate was observed at Sn/Ru = 5. The maximum was shifted to Sn/Ru of 2.5 when reduction of catalyst was conducted at 873 and 1073 K.

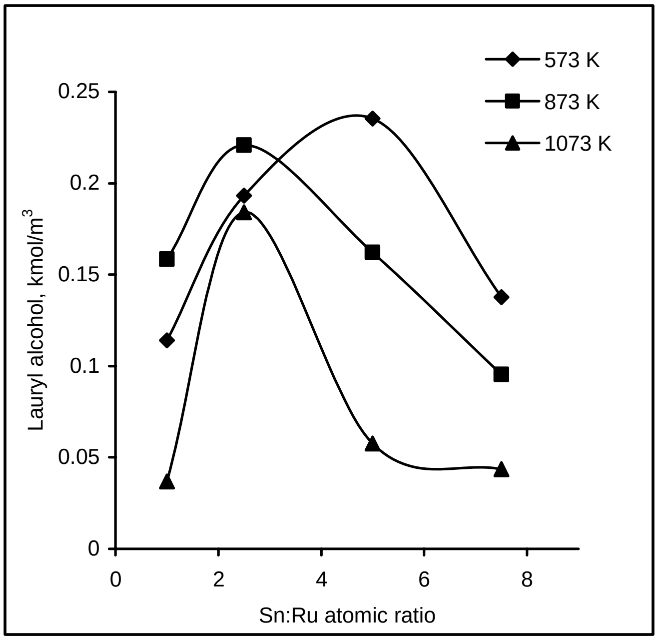

Figure 5-7: Effect of reduction temperature on Ru-Sn/TiO_2 catalyst with different Sn/Ru atomic ratio for hydrogenation.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 kmolm^{-3}, Solvent = 1,4-dioxane, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5 x 10^{-5} m^3.

To understand this phenomenon, surface Sn/Ru atomic ratio were obtained from EDX analysis for the catalysts and the details are shown in Table 5-3.

Table 5-3: Sn/Ru ratio as obtained from EDX analysis.

No.	**Bulk Sn/Ru ratio in Ru-Sn/TiO_2**	**Sn/Ru ratio for different Reduction temperature by EDX**		
		573 K	**873 K**	**1073 K**
1	Sn/Ru = 1	1.09	1.14	1.44
2	Sn/Ru = 2.5	3.93	4.02	5.75
3	Sn/Ru = 5	5.37	9.61	11.11
4	Sn/Ru = 7.5	8.33	12.72	14.31

As seen in Table 5-3, the bulk Sn/Ru ratio was different from the surface ratio. As the catalyst reduction temperature was increased the surface Sn/Ru ratio for all the catalysts increases. The surface Sn/Ru ratio also increased with bulk Sn/Ru ratio used for catalyst. Comparing results in Figure 5-7 and Table 5-3, it is observed that when surface Sn/Ru atomic ratio is 4-6, the activity of Ru-Sn/TiO_2 catalyst is highest. From Table 5-3 it is also understood that the surface Sn/Ru ratio in Ru-Sn/TiO_2 catalyst can be obtained in the range of 4-6 from lower bulk Sn/Ru ratios by increasing the catalyst reduction temperatures. Thus, a catalyst with low bulk Sn/Ru ratio can be tuned to give activity comparable to a catalyst with high bulk Sn/Ru ratio by increasing the reduction temperature used in the catalyst preparation.

5.3.6 Recycle study for Ru-Sn/TiO_2 catalyst for the hydrogenation of lauric acid to lauryl alcohol

In order to ensure that the data observed for the hydrogenation of lauric acid to lauryl alcohol would be free from any catalyst deactivation effects, the catalyst was recycled under same reaction conditions. The Ru-Sn/TiO_2 catalyst used for recycle study had an Sn/Ru atomic ratio 5 and was calcined at 773 K for 12 hrs and further reduced at 573 K under hydrogen for 12 hrs.

In these experiments, after completion of the reaction, the reactor was cooled to 313 K and the catalyst was allowed to settle down. The supernant solution was separated from the catalyst. The reactor was then charged with lauric acid solution to conduct the recycle experiment. The catalyst recycle was performed at 493 K and a hydrogen partial pressure of 6.89 MPa. The catalyst was found to retain its activity for four recycles without affecting the conversion of lauric acid and the selectivity to lauryl alcohol as shown in Figure 5-8. The overall cumulative turn over frequency (TOF) for the catalyst was found to be 3.9×10^{-3} $kmolkg^{-1}hr^{-1}$.

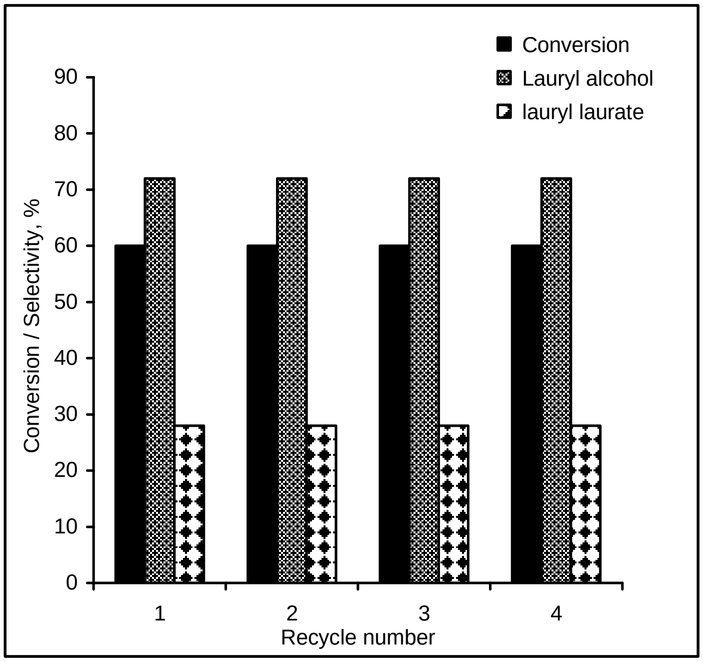

Figure 5-8: Recycle study for Ru-Sn/TiO_2 catalyst for hydrogenation of lauric acid. **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kgm^{-3}, lauric acid = 0.25 $kmolm^{-3}$, Solvent = 1,4-dioxane, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5 x 10^{-5} m^3.

5.3.7 Preliminary reactions and analysis of mass transfer

The preliminary experiments for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst were carried out to establish the reaction conditions like reaction time, catalyst concentration, lauric acid concentration and hydrogen partial pressure for parametric study. The catalyst used for this study was prepared in-house by procedure explained in Section 5.2.2. The Sn/Ru ratio in Ru-Sn/TiO_2 catalyst was 5, the calcination and reduction temperature for catalyst preparation was 773 K and 573 K respectively. The activity and selectivity for the Ru-Sn/TiO_2 catalyst prepared in bulk was observed to be consistent with the catalyst from smaller batch. The mass balance and gas balance for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst prepared in bulk was also found to be greater than 95%.

Analysis of initial rate data provides an approach for understanding the dependency of the reaction rate on individual parameters and also in the evaluation of significance of mass transfer effects. The initial rates for hydrogenation of lauric acid to lauryl alcohol were calculated from the slope of the lauryl alcohol formed versus time plots during the initial period of reaction such that the conversion of lauric acid was less than 15% and differential conditions prevailed. Typical plots to obtain the initial rates from concentration of lauryl alcohol formed versus time profile are shown in Figure 5-9. In the initial period of reaction no lauryl laurate was formed and hence the rate could be measured as a function of formation of lauryl alcohol with time.

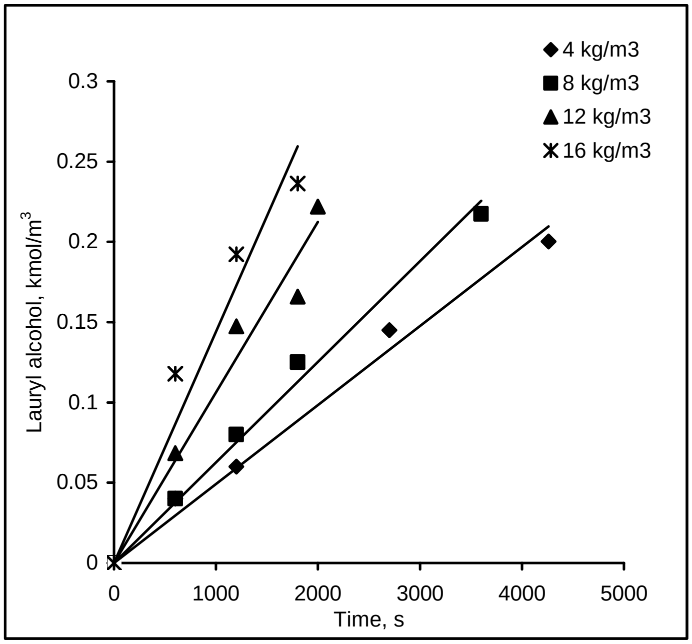

Figure 5-9: Determining initial rate for hydrogenation of lauric acid to lauryl alcohol at different catalyst loading.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Lauric acid = 0.4 kmolm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^3.

This plot pertains to the study on the rate of hydrogenation of lauric acid to lauryl alcohol at 493 K for varying catalyst loading. The initial rates were calculated from the slopes of these concentration time profiles as shown in Figure 5-9. A plot of initial rate versus catalyst loading is shown in Figure 5-10 and it indicates first order dependence of reaction on catalyst loading. The effects of other reaction parameters on rate of hydrogenation were studied in the same way.

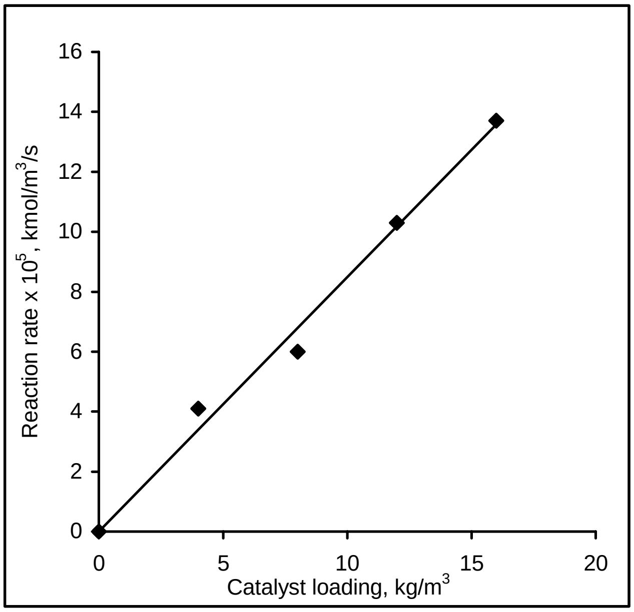

Figure 5-10: Effect of catalyst loading on initial rate of reaction.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, lauric = 0.4 kmolm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^{3}.

Hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst is an example of a multiphase reaction involving gas, liquid and solid phases. So this reaction involves (i) transfer of reactant (H_2) from gas into the liquid (ii) the transfer of dissolved reactants (LAC and H_2) from liquid phase on to the catalyst surface (iii) Intraparticle transfer of reactants to the catalytic site. If the rate of transport of reactants from one phase to the other is slower as compared to the intrinsic rate of reaction, then the rate of reaction is controlled by the rate of mass transport.

So before commencing with the kinetic study, it was important to ensure that the reaction occurs in kinetic regime. For this, the effect of agitation speed on the rate of reaction was studied at 493 K in the range of 1000-1400 rpm. The agitation speed had no effect on rate of hydrogenation as shown in Figure 5-11, which confirms that gas-liquid mass transfer is not significant.

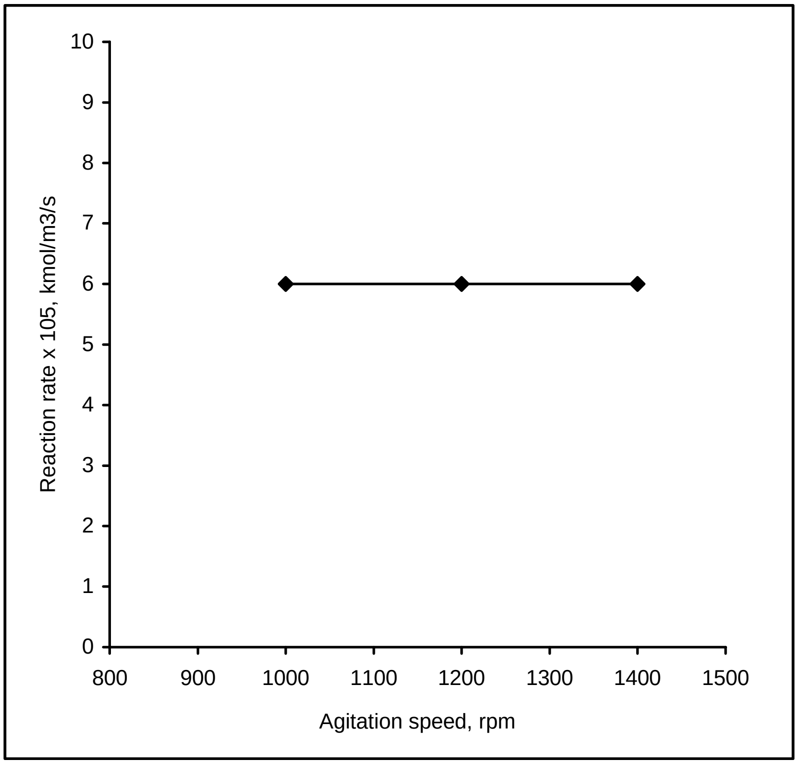

Figure 5-11: A plot of initial rate of hydrogenation vs. agitation speed.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Lauric acid = 0.4 kmolm^{-3}, Catalyst = 8 kgm^{-3}, Solvent = 1,4-dioxane, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^{3}.

5.3.8 Analysis for external and intraparticle mass transfer

The rate of hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO_2 catalyst at 493 K was found to be independent of agitation speed above 1000 rpm as shown in Figure 5-11, which suggests that external (gas-liquid) mass transfer is absent under the reaction conditions mentioned in Table 5-4. This was also confirmed by catalyst loading effect for the reaction, as the rate of reaction increases linearly with increasing catalyst concentration.

However, a detailed analysis to check for the role of external and intraparticle mass transfer is necessary before proceeding for kinetic study. The criteria involves evaluation of the factors α_{gl}, α_{ls} and ϕ_{exp}, which are defined as the ratio of observed rate of hydrogenation to the maximum rates of gas-liquid, liquid-solid and intraparticle mass transfer respectively. As suggested by Ramachandran and Chaudhari, the values of α_{gs}, α_{ls} and ϕ_{exp} should be less than 0.1, 0.1 and 0.2 respectively to ensure that the reaction operates under kinetic control[16]. The calculation for α_{gl}, α_{ls} and ϕ_{exp} were done for hydrogenation of lauric acid to lauryl alcohol as described in Section 3.3.10 and were found to be in the range of 3.5×10^{-6} - 4.4×10^{-5}, 1.5×10^{-7}- 1.9×10^{-6} and 3.2×10^{-5} – 1.1×10^{-4} respectively, which revealed that the reaction was free of external and intraparticle mass transfer.

5.3.9 Kinetic study for hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO_2 catalyst

In order to study the kinetics of hydrogenation of lauric acid to lauryl alcohol using Ru-Sn/TiO_2 catalyst in 1,4-dioxane as solvent, several experiments were carried out in the range of conditions shown in the Table 5-4. The rates for hydrogenation were calculated from the observed concentration-time profiles as discussed in Section 5.3.7. These were essentially initial rates of hydrogenation as they were obtained for low conversion of lauric acid (Conversion < 10-15%).

Table 5-4: Range of reaction conditions for hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO_2 catalyst.

No.	Reaction parameter	Range
1	Temperature	453-493 K
2	Catalyst concentration	4-16 kg m^{-3}
3	Substrate concentration	0.2-0.5 kmolm^{-3}
4	Pressure	3 - 9 MPa
5	Stirring speed	1200 rpm
6	Total charge	2.5×10^{-5} m^3
7	Reaction time	2 hrs.

5.3.9.1 Effect of catalyst loading

The effect of catalyst concentration on the rate of hydrogenation of lauric acid to lauryl alcohol was studied in the temperature range of 453-493 K, lauric acid concentration of 0.4 kmolm^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The results are shown in Figure 5-12. The rate was found to be linearly dependent on the catalyst concentration, indicating first order kinetics.

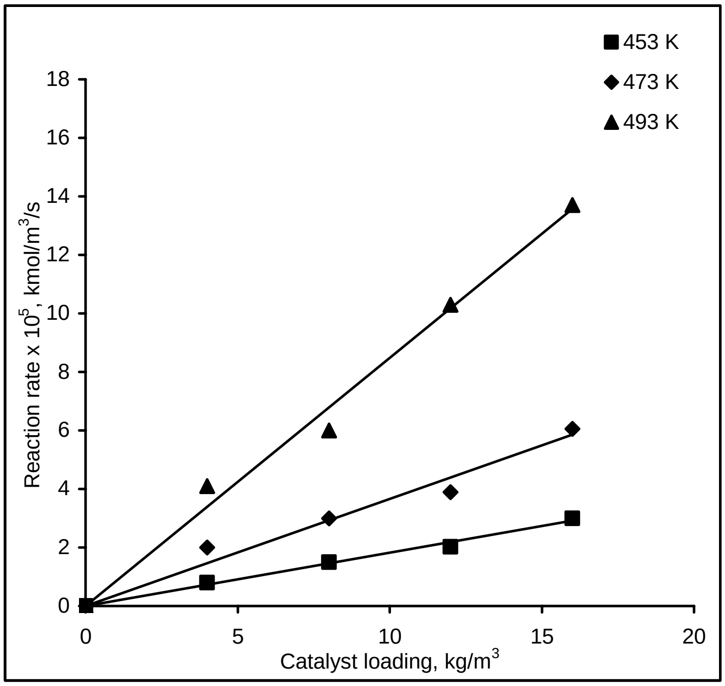

Figure 5-12: Effect of catalyst loading on rate of hydrogenation of lauric acid. **Reaction conditions:** Hydrogen partial pressure = 6.89 MPa, Lauric acid = 0.4 kmolm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^3.

5.3.9.2 Effect of lauric acid concentration

The effect of lauric acid concentration on the initial rate of hydrogenation was investigated in the temperature range of 453-493 K, catalyst concentration of 8 kgm^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The results are shown in Figure 5-13. The hydrogenation rate showed a first order dependence on lauric acid concentration.

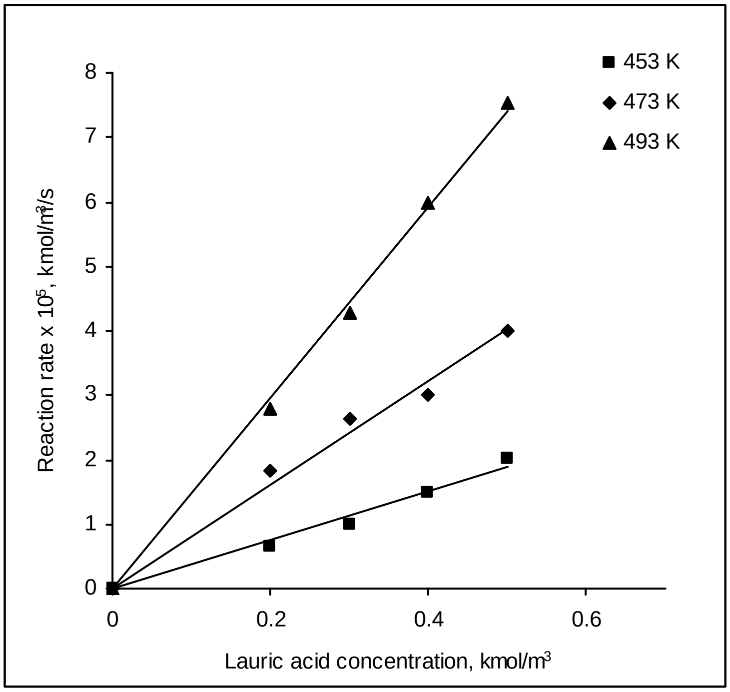

Figure 5-13: Effect of lauric acid concentration on rate of hydrogenation.

Reaction conditions: Hydrogen partial pressure = 6.89 MPa, Catalyst = 8 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^{3}.

5.3.9.3 Effect of hydrogen partial pressure

The effect of hydrogen partial pressure on the rate of hydrogenation of lauric acid to lauryl alcohol was studied in the temperature range of 453-493 K, catalyst concentration of 8 kgm^{-3} and lauric acid concentration of 0.4 kmolm^{-3} in 1,4-dioxane as solvent. The rate was found to be linearly dependent on the hydrogen partial pressure, indicating first order kinetics. The results for effect of hydrogen partial pressure are shown in Figure 5-14.

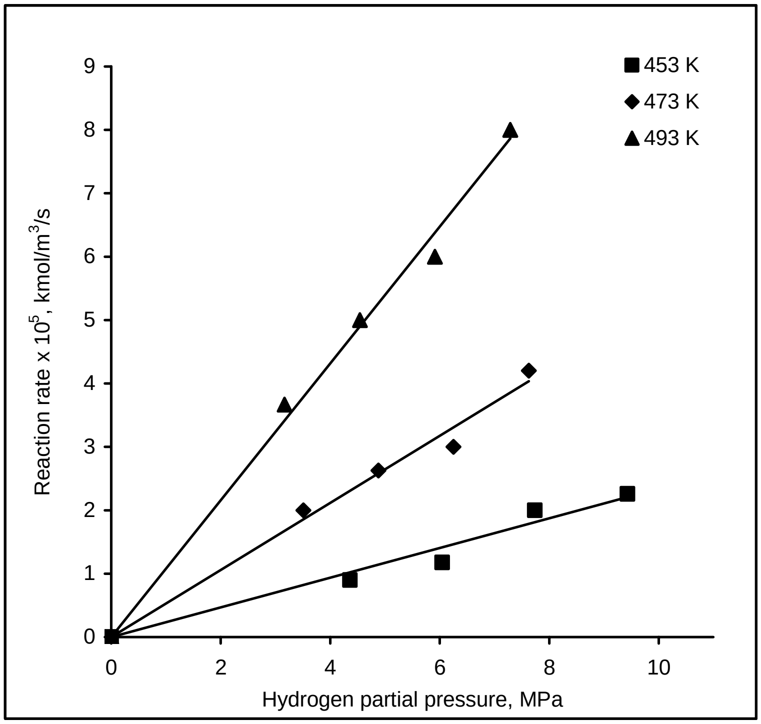

Figure 5-14: Effect of hydrogen partial pressure on rate of hydrogenation.

Reaction conditions: Lauric acid = 0.4 kmom^{-3}, Catalyst = 8 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^3.

5.3.10 Kinetic modeling

The rate data obtained from kinetic study were fitted to simple rate equation based on Langmuir-Hinshelwood (L-H) type model given in Table 5-5. In order to estimate the kinetic constants, the rate equation was subjected to a non-linear regression analysis using an optimization routine based on Marquardt's method[17]. The objective function was chosen as follows:

$$\Phi = \sum_{i=1}^{n} (r_{exp} - r_{mod})_i^2 \qquad \text{(Eq-5.4)}$$

Where, r_{exp} is the observed rate of hydrogenation and r_{mod} is the predicted rate of hydrogenation.

Table 5-5: Rate model for hydrogenation of lauric acid with Ru-Sn/TiO$_2$ catalyst to lauryl alcohol

Model	Rate equation	T, (K)	k	K_A	K_B	Φ_{min}
I	$R_H = k\ w\ A\ B$	453	6.87×10^{-7}	-	-	9.89×10^{-11}
		473	1.53×10^{-6}	-	-	3.33×10^{-10}
		493	3.60×10^{-6}	-	-	5.32×10^{-10}
II	$R_H = \dfrac{k\ w\ A\ B}{(1 + K_A A)}$	453	7.50×10^{-5}	0.45	-	9.61×10^{-10}
		473	9.08×10^{-5}	-0.22	-	3.32×10^{-10}
		493	1.42×10^{-4}	-0.023	-	7.03×10^{-10}
III	$R_H = \dfrac{k\ w\ A\ B}{(1 + K_B B)}$	453	4.03×10^{-5}	-	-10	5.27×10^{-10}
		473	1.00×10^{-4}	-	0.063	3.33×10^{-10}
		493	1.42×10^{-4}	-	-0.026	7.06×10^{-10}
IV	$R_H = \dfrac{k\ w\ A\ B}{(1 + K_A A)(1 + K_B B)}$	473	-5.11×10^{-2}	-1.46×10^{3}	-4.01×10^{-5}	2.28×10^{-10}
		493	-2.29×10^{-2}	-5.96×10^{4}	-6.03×10^{-4}	6.09×10^{-10}
		513	1.53×10^{-4}	-3.53×10^{-2}	-3.39	7.02×10^{-10}

Where,

R_H = Initial rate of hydrogenation (kmol/m^3/s), k = Rate constant, w = Catalyst concentration (kg/m^3), A =Lauric acid concentration (kmol/m^3), B = Hydrogen concentration (kmol/m^3), K_A = adsorption equilibrium constant for lauric acid (m^3/kmol) and K_B = adsorption equilibrium constant for hydrogen (m^3/kmol).

The models proposed in Table 5-5 were discriminated using Φ_{min} values. The Model I had the lowest Φ_{min} values and was hence accepted. To verify the Model I for hydrogenation of lauric acid to lauryl alcohol, the theoretical rates for hydrogenation of lauric acid to lauryl alcohol were obtained using Model I and compared with the experimental rate for hydrogenation as shown in Figure 5-15, 5-16 and 5-17.

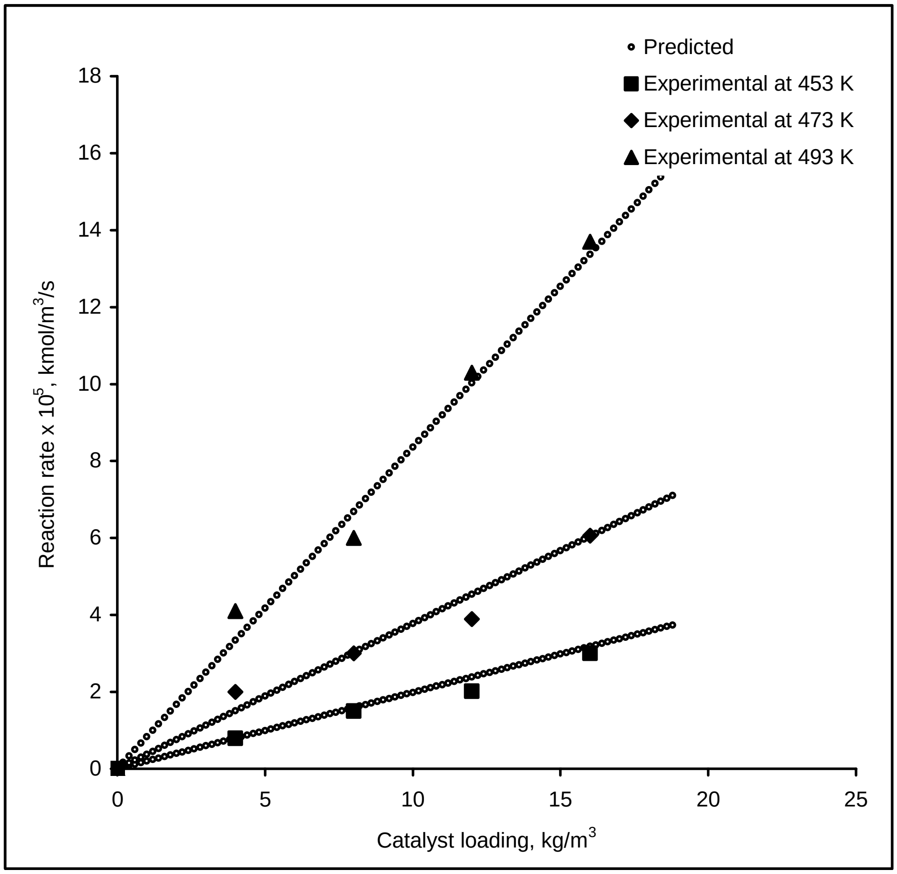

Figure 5-15: Comparison of experimental and predicted effect of catalyst loading on rate of hydrogenation.

Reaction conditions: Hydrogen partial pressure = 6.89 MPa, lauric acid= 0.4 kmol/m^3, Solvent = 1,4-dioxane, Agitation speed= 1200 rpm, Time= 2 hrs, Total volume = 2.5 x 10^{-5} m^3.

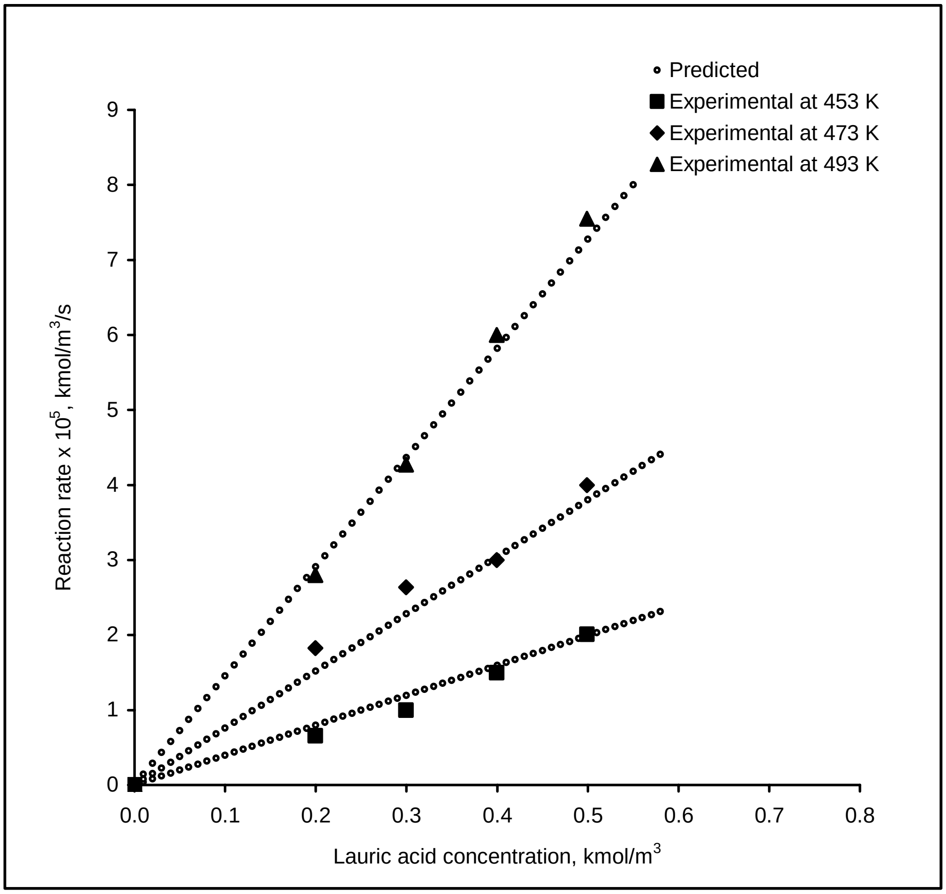

Figure 5-16: Comparison of experimental and predicted effect of lauric acid concentration on rate of hydrogenation.

Reaction conditions: Hydrogen partial pressure= 6.89 MPa, Catalyst = 8 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^{3}.

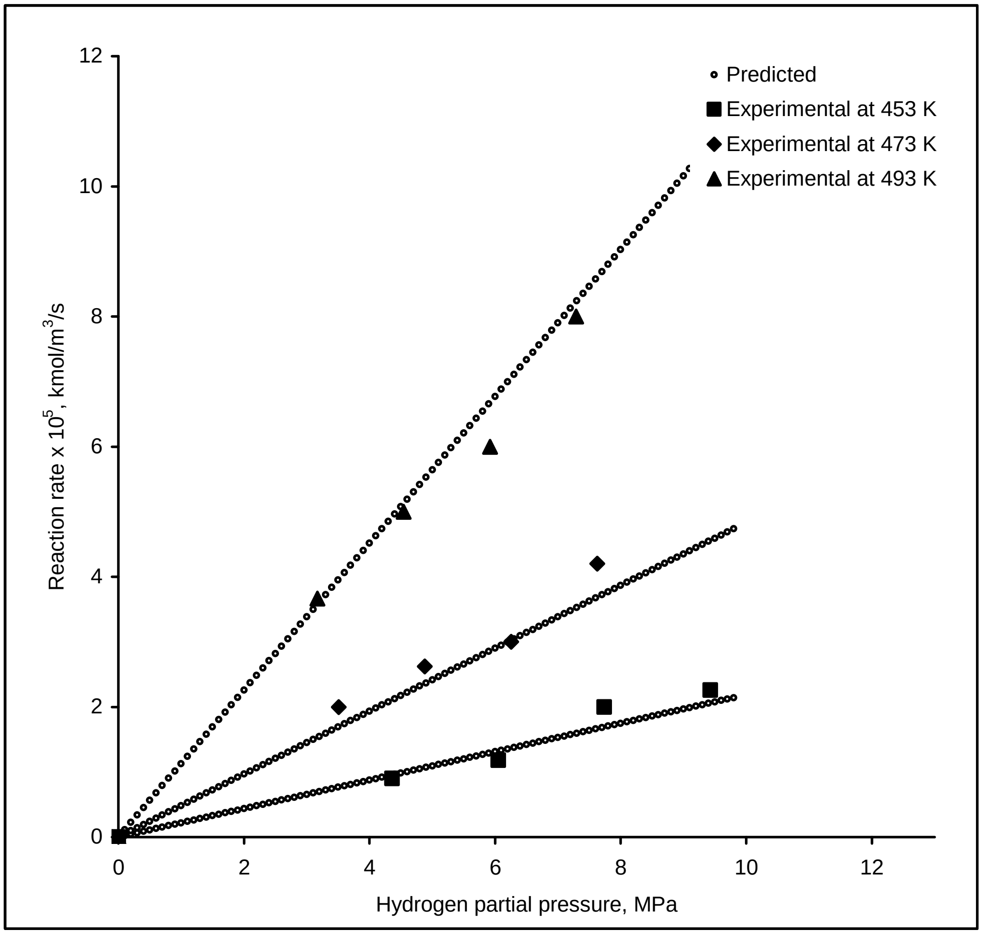

Figure 5-17: Comparison of experimental and predicted effect of hydrogen partial pressure on rate of hydrogenation.

Reaction conditions: lauric acid = 0.4 kmom^{-3}, Catalyst = 8 kgm^{-3}, Solvent = 1,4-dioxane, Agitation speed = 1200 rpm, Time = 2 hrs, Total volume = 2.5 x 10^{-5} m^3.

From Figure 5-15, 5-16 and 5-17 it is observed that Model I predicts the rate of reaction with an error less than ±5 % which is within the range of experimental error. Based on the values of rate constant (*k*) of this equation, ln *k* versus 1/T was plotted as shown in Figure 5-18. From Figure 5-18 the activation energy for hydrogenation of lauric acid to lauryl alcohol using Ru-Sn/TiO_2 catalyst was found to be 77.2 kJ/mol.

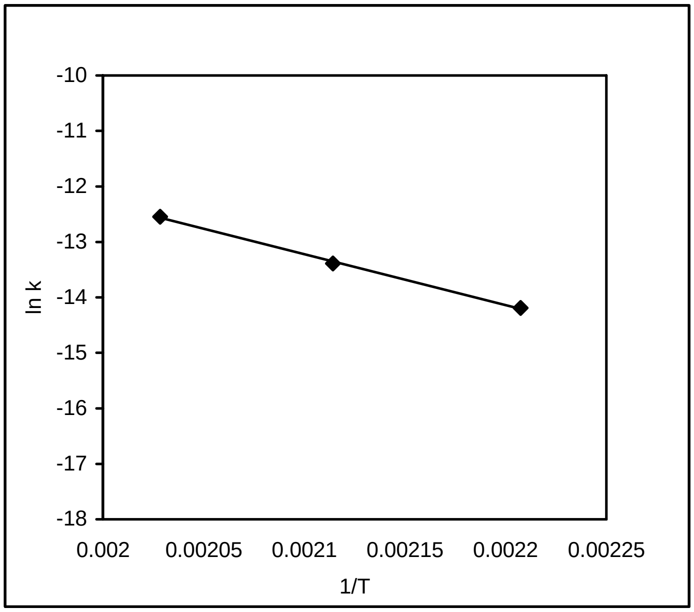

Figure 5-18: Arrhenius plot for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst.

From kinetic study the dual site mechanism proposed by Kluson and Cerveny[18] was confirmed for the hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst. The mechanism for hydrogenation with this catalyst is a dual site mechanism, as the hydrogenation shows first order dependence on the two reaction parameters, lauric acid and hydrogen.

5.4 Conclusion

The hydrogenation of lauric acid to lauryl alcohol using Ru-Sn catalyst was studied in a laboratory scale slurry reactor.

The activity of Ru-Sn on supports like carbon, silica, alumina and titania was assessed for hydrogenation of lauric acid. Titania was observed to be the best support resulting in 93% conversion of lauric acid and 80% selectivity to lauryl alcohol. Effect of both the Ru and Sn percentage on the hydrogenation activity was studied for Ru-Sn/Al_2O_3 catalyst and it was observed that excess Ru or Sn (>Ru:Sn 1:5) decreased the activity of the catalyst signifying the importance of both the metals in the catalyst. A low loading of Sn was required to achieve highest activity in Ru-Sn/TiO_2 as compared to Ru-Sn/Al_2O_3 catalyst which shows that TiO_2 also has a similar effect on catalyst as Sn.

The effect of catalyst reduction temperature on Ru-Sn catalyst on different supports was studied in the range of 573-1073 K. It was observed that the activity of Ru-Sn/TiO_2 catalyst decreases with reduction temperature and for Ru-Sn/Al_2O_3 catalyst the activity of catalyst passes through maximum at 873 K. For Ru-Sn/C catalyst the activity of catalyst increased with increasing reduction temperature. The effect of reduction temperature on Ru-Sn/TiO_2 catalyst with different Sn/Ru ratios showed that activity for the Ru-Sn catalyst with a low Sn/Ru ratio can be enhanced to achieve an activity comparable to Ru-Sn/TiO_2 catalyst with a high Sn/Ru ratio, merely by tuning the reduction temperature used for catalyst preparation.

The Ru-Sn/TiO_2 catalyst was found to be stable for four recycles for the hydrogenation of lauric acid in 1,4-dioxane. The kinetics of hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO_2 catalyst was investigated in a temperature range of 453-493 K, hydrogen partial pressure between 3-9 MPa, catalyst loading between 4-16 kg/m^3, initial lauric acid concentration between 0.2-0.5 kmol/m^3.The rates were first order with respect to catalyst, lauric acid and hydrogen indicating dual site mechanism for hydrogenation of lauric acid to lauryl alcohol on Ru-Sn/TiO_2 catalyst.

The following rate equation was found to predict the rates in good agreement with the experimental data.

$$R_H = k \quad w \quad A \quad B$$

Where, w, A and B are catalyst loading, lauric acid concentration and hydrogen concentration respectively.

The activation energy for hydrogenation of lauric acid to lauryl alcohol using Ru-Sn/TiO_2 catalyst was found to be 77.2 kJ/mol.

5.5 Nomenclature

A	Lauric acid concentration, $kmol/m^3$
B	Hydrogen concentration, $kmol/m^3$
C_{LAOH}	Concentration of lauryl alcohol, $kmol/m^3$
C_{LALAR}	Concentration of lauryl laurate, $kmol/m^3$
C_f	Final concentration of lauric acid, $kmol/m^3$
C_i	Initial concentration of lauric acid, $kmol/m^3$
E_a	Activation energy, kJ/mol
He	Henrys constant, $kmol/m^3/atm$
k	Rate constant, $m^6kg^{-1}kmol^{-1}s^{-1}$
K_A	Adsorption equilibrium constant for lauric acid on catalyst, $m^3/kmol$
K_B	Adsorption equilibrium constant for hydrogen on catalyst, $m^3/kmol$
r_{exp}	Observed rate of hydrogenation, $kmol/m^3/s$
R_H	Rate of hydrogenation, $kmol/m^3/s$
r_{mod}	Predicted rate of hydrogenation, $kmol/m^3/s$
w	Catalyst concentration, kg/m^3

Greek symbols

$\o_{exp}$	Thiele parameter defined by equation Eq-3.9
α_{gl}	Parameter defined by Eq-3.3
α_{ls}	Parameter defined by Eq-3.5
Φ	Objective function defined by Eq-5.4

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Chapter 6

Partial hydrogenation of carboxylic acids to aldehydes

6.1 Introduction

The ability to synthesize industrially important aldehydes from cheap and renewable carboxylic acids is highly desirable, particularly if it can be achieved by direct hydrogenation of carboxylic acids. These reactions are more important for long chain aliphatic carboxylic acids like lauric acid to obtain lauraldehyde which is used in cosmetics. Higher aldehydes/alcohols are manufactured from olefins via the hydroformylation reaction. Synthesis of the aldehydes/alcohols via hydrogenation of naturally occuring fatty acids will be more desirable. Aromatic aldehydes too belong to the group of fine chemicals being important as intermediates in organic chemistry[1]. They are used for the production of pharmaceuticals , agrochemicals and some of them are directly used as perfumes and flavours. Benzaldehyde is an important aldehyde and although there are many synthetic routes to produce benzaldehyde, only the partial oxidation of toluene to benzaldehyde and the route via benzyl chloride are applied commercially[2]. The hydrogenation of benzoic acid to benzaldehdye may provide a more environmentally benign synthetic route.

The direct hydrogenation of aromatic carboxylic acid over chromium modified zirconia catalysts was realized as an industrial process by Mitsubishi Chemicals in 1988. Benzaldehyde and its derivative were produced with a product capacity of 2000 tons per year with a selectivity of benzaldehyde of 96% at a conversion of 98%. It is reported that the high selectivity obtained by using zirconia catalyst is due to its amphoteric surface properties[3]. Holderich et al. [4] have obtained high yields of benzladehyde and various derivatives via direct hydrogenation of aromatic carboxylic acids using zinc oxide catalysts having specific features as very weak acidic sites in addition to relatively strong basic sites and rather small specific surface area of about 2-17 m^2 per gram catalyst. Benzaldehyde was obtained with high yields of about 90% and selectivity upto 96%. They also report that stronger acidic sites on zinc oxide catalyst caused a consecutive hydrogenation of benzaldehyde to toluene and coke formation.

The mechanism of hydrogenation of carboxylic acids to aldehydes is not well studied. Acetic acid is generally used as model compound to probe both carboxylic acid adsorption and its kinetic behavior on metals, metal oxides and supported metal catalysts because of its molecular simplicity. Pestman et al.[5] found that highly reducible oxides such as Fe_2O_3 and SnO_2 were active for hydrogenation of acetic acid to acetaldehyde, and this selective reaction over Fe_2O_3 was suggested to occur via a Mars-Van Krevelen- type of mechanism in which lattice oxygen and oxygen vacancies participate in the reaction. Further investigation on behavior of acetic acid hydrogenation over Pt supported on TiO_2, SiO_2, γ-Al_2O_3 and Fe_2O_3 was done by Rachmady et al.[6] In their study they observed that hydrogenation of acetic acid to acetaldehyde involves both platinum metal and oxide support, and the reaction takes place at sites on the oxide surface. The principal role of Pt in this case is to serve as a source of mobile, activated hydrogen atoms. In their study they also observed that Pt/Fe_2O_3 catalyst gave highest selectivity of 80% as compared to Pt catalyst supported on TiO_2, SiO_2 and γ-Al_2O_3. The difference in selectivity for acetaldehyde was related to the adsorption strength of acetic acid and acetaldehyde on the catalyst. A large adsorption equilibrium constant would result in a high surface concentration of acetaldehyde, and would thus favor further hydrogenation of acetaldehyde to ethanol. Thus, the much higher acetaldehyde selectivity on Pt/Fe_2O_3 catalyst implies a much lower surface coverage of acetaldehyde due to much higher rate of desorption on this catalyst during competitive adsorption compared to Pt/TiO_2 catalyst.

Most of the literature for hydrogenation of carboxylic acids to aldehydes is studied in a continuous reactor using fixed bed reactors with very high reaction temperatures. There is a scope for designing a catalyst containing Ru, with a low adsorption equilibrium constant for the aldehydes, which can yield aldehydes at low temperatures in batch slurry reactors.

Although toluene is used as solvent in many reactions, it cannot be used for hydrogenation reactions, as toluene contains aromatic ring which is susceptible to hydrogenation. In the previous chapters it was observed that the ring hydrogenation activity of Ru-Sn catalysts is negligible (For toluene/Benzoic acid/ benzyl alcohol). Hence, in this work, an attempt has been made to introduce toluene as a solvent for catalytic hydrogenation for the first time with Ru-Sn based catalyst, for the selective hydrogenation of carboxylic acids to aldehydes using batch slurry reactor. Development of catalysts for selective hydrogenation of lauric acid and benzoic acid has been investigated. The influence of reduction temperature, support and Sn/Ru atomic ratio on the selectivity and activity has been studied.

Since lauraldehyde is an intermediate for hydrogenation of lauric acid to lauryl alcohol its concentration passes through a maximum, and hence, lauraldehyde selectivity is also dependent on the reaction time. To achieve high selectivity for hydrogenation of lauric acid to lauraldehyde, an equation for t_{max} (i.e. the time when concentration of lauraldehyde is maximum during reaction) was also obtained using Marquardts method of optimization.

6.2 Experimental

6.2.1 Materials

Benzoic acid, lauric acid, toluene, $RuCl_3.3H_2O$ and Stannous chloride ($SnCl_2.2H_2O$) were procured from SD Fine Chemicals Ltd. (India). Cyclohexane carboxylic acid was procured from Aldrich Chemicals (USA). Catalyst supports like carbon, alumina, titania and silica were procured from Aldrich Chemicals (USA). Authentic standards of reaction products like lauryl alcohol and lauraldehyde were procured from Aldrich Chemicals (USA). Lauryl laurate ester was prepared from lauric acid and lauryl alcohol by esterification reaction, Crude lauryl laurate was separated on column, purified and used as an authentic standard. Hydrogen and nitrogen of 99.9% purity were obtained from Indian Oxygen Ltd. Bombay.

6.2.2 Catalyst preparation

The general procedure for catalyst preparation is described in Section 5.2.2. Various catalysts were prepared for partial hydrogenation of lauric acid to lauraldehyde with varying reduction temperature and Sn/Ru atomic ratio. The list of catalysts prepared is shown in Table 6-1.

Table 6-1: List of catalyst prepared for hydrogenation of lauric acid

No.	Catalyst	Sn/Ru atomic ratio	Reduction temperature (K)
1	5%Ru-29%Sn/Al_2O_3	5	573
2	5%Ru-43%Sn/Al_2O_3	7.5	573
3	5%Ru-29%Sn/Al_2O_3	5	723
4	5%Ru-29%Sn/Al_2O_3	5	873

5	5%Ru-29%Sn/SiO_2	5	573
6	5%Ru-29%Sn/TiO_2	5	573
7	5%Ru-5.8%Sn/TiO_2	1	573
8	5%Ru-14.5%Sn/TiO_2	2.5	573
9	5%Ru-43%Sn/TiO_2	7.5	573
10	5%Ru-29%Sn/TiO_2	5	873
11	5%Ru-5.8%Sn/TiO_2	1	873
12	5%Ru-14.5%Sn/TiO_2	2.5	873
13	5%Ru-43%Sn/TiO_2	7.5	873
14	5%Ru-29%Sn/TiO_2	5	1073
15	5%Ru-5.8%Sn/TiO_2	1	1073
16	5%Ru-14.5%Sn/TiO_2	2.5	1073
17	5%Ru-43%Sn/TiO_2	7.5	1073
18	5%Ru-29%Sn/C	5	573
19	5%Ru-29%Sn/C	5	873
20	5%Ru-29%Sn/C	5	1073

Conditions: Calcination temperature = 773 K, Calcination time = 12 hrs, Reduction time = 12 hrs.

6.2.3 Reactor set-up for high pressure reactions

The reactions were carried out in a 25 ml capacity high pressure – high temperature reactor supplied by Parr Instruments Co. USA. The details of the reactor set-up and schematic of the reactor assembly are given in Section 5.2.3 and Figure 2-2 respectively.

6.2.4. Experimental procedure for high pressure reactions

Experimental procedure for conducting high pressure reaction is discussed in Section 5.2.4.

6.2.5 Analysis

The various hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector instrument), for quantitative analysis, liquid samples were analyzed by gas chromatography. The details for analysis are discussed in Section 5.2.5. Typical gas chromatogram obtained for lauric acid and its hydrogenation products (lauraldehyde, lauryl alcohol and lauryl laurate) is shown in Figure 6-1. The conditions used for GC analysis are given in Section 3.2.5, Table 3-1.

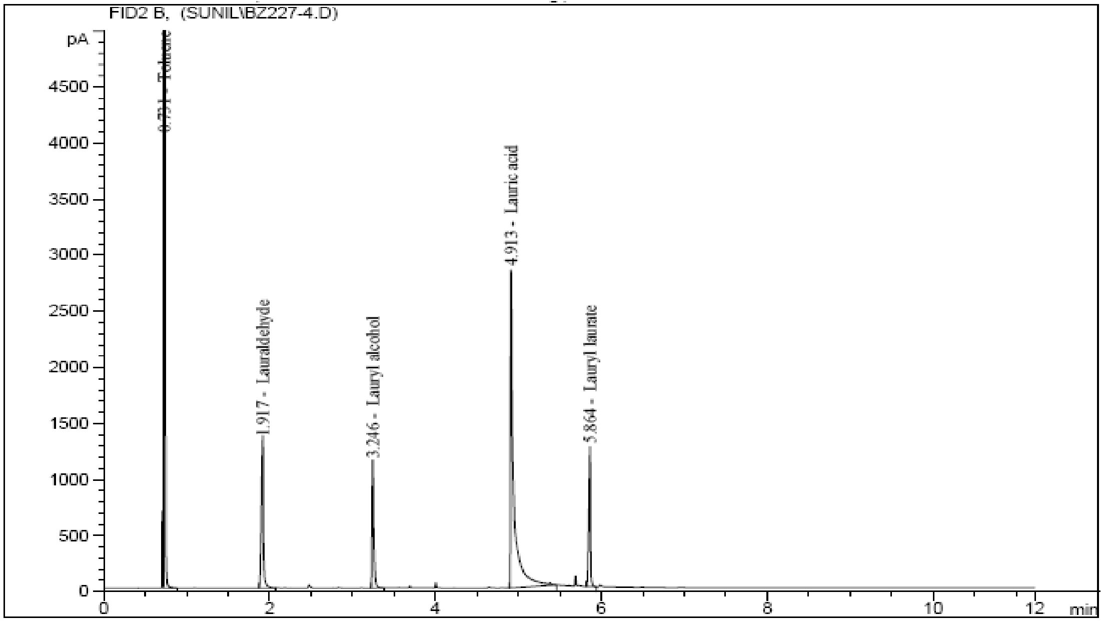


Figure 6-1: Gas chromatogram for lauric acid and its hydrogenation products.

6.3 Results and discussions

6.3.1 Preliminary reactions for hydrogenation of lauric acid

In the preliminary reactions, the activity of Ru-Sn catalyst for toluene hydrogenation was assessed. For this, hydrogenation of neat toluene was conducted with 10 kg/m^3 of 5%Ru-43%Sn/Al_2O_3 (The Sn/Ru atomic ratio was 7.5 and reduced at 573 K) and 6.2 MPa of hydrogen partial pressure. In this experiment it was confirmed that toluene doesn't undergo hydrogenation with Ru-Sn/Al_2O_3 even after 12 hrs reaction at 493 K.

Further to this, several experiments were carried out in order to investigate the catalytic activity and selectivity of Ru-Sn/Al_2O_3 catalyst under different operating conditions, for hydrogenation of lauric acid to lauraldehyde. The ranges of reaction parameters used for the study were as shown in Table 6-2.

Table 6-2: Reaction parameters used for hydrogenation of lauric acid with Ru-Sn catalyst

Reaction parameter	**Range**
Temperature	493 K
Catalyst concentration	10 kg m^{-3}
Substrate concentration	0.25 $kmolm^{-3}$
Pressure	6.2 MPa
Stirring speed	1200 rpm
Total charge	2.5 x 10^{-5} m^3
Reaction time	0.5-1 hr.

The progress of the reactions was followed by monitoring the consumption of lauric acid (LAC) and formation of hydrogenation product lauraldehyde and lauryl alcohol (LAOH) and lauryl laurate (LALAR). A typical concentration time profile of the reaction is shown in Figure 6-2.

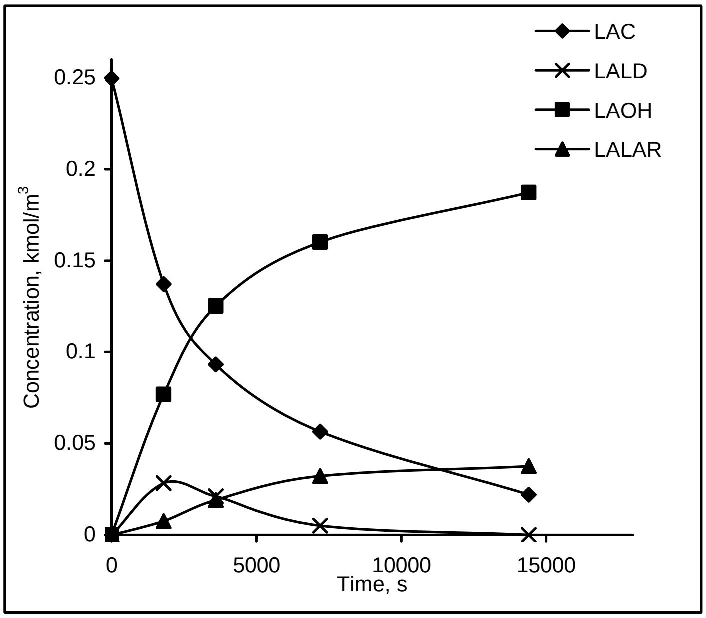
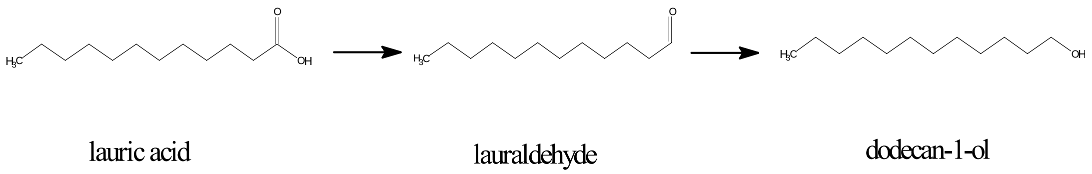


Figure 6-2: Hydrogenation of lauric acid with 5%Ru-43%Sn/Al_2O_3 catalyst in toluene
Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = toluene, Time = 4 hrs, Agitation speed = 1000 rpm, Total volume = 2.5 x 10^{-5} m^3.

Reaction scheme obtained for hydrogenation of lauric acid with Ru-Sn/Al_2O_3 catalyst in toluene from the above concentration time profile is shown in Scheme 6-1.



Scheme 6-1: Hydrogenation of lauric acid with Ru-Sn/Al_2O_3 catalyst in toluene.

The conversion of lauric acid and selectivity to lauraldehyde (LALD), lauryl alcohol (LAOH) and lauryl laurate (LALAR) was calculated as given in Eq-6.1, Eq-6.2, Eq-6.3 and Eq-6.4.

$$\text{Conversion of LAC} = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq-6.1}$$

$$\text{Selectivity to LALD} = \frac{C_{LALD}}{C_i - C_f} \times 100 \qquad \text{Eq-6.2}$$

$$\text{Selectivity to LAOH} = \frac{C_{LAOH}}{C_i - C_f} \times 100 \qquad \text{Eq-6.3}$$

$$\text{Selectivity to LALAR} = \frac{2 \times C_{LALAR}}{C_i - C_f} \times 100 \qquad \text{Eq-6-4}$$

Where,

C_i is initial concentration of lauric acid, kmol/m^3; C_f is final concentration of lauric acid, kmol/m^3, C_{LAOH} is the concentration of Lauryl alcohol, kmol/m^3, C_{LALD} is the concentration of lauraldehyde and C_{LALAR} is concentration of lauryl laurate formed at the end of reaction (The factor 2 in Eq-6.4 arises as 1 mole of LALAR is formed from 1 mole of LAOH and 1 mole of LAC).

In all experiments the consumption of lauric acid, hydrogen gas and formation of hydrogenation products were monitored for calculating liquid mass balance and gas balance, which was found to be more than 95%. Following these preliminary hydrogenation reactions using Ru-Sn/Al_2O_3 catalyst, the effect of catalyst reduction temperature and the role of catalyst support were investigated to optimize the activity and selectivity of the Ru-Sn catalyst to lauraldehyde.

6.3.2 Effect of support on Ru-Sn catalyst for hydrogenation of lauric acid to lauraldehyde

Ru-Sn catalysts were prepared on supports like carbon, silica, alumina and titania by the procedure given earlier (Section 5.2.2). The selective hydrogenation of lauric acid to lauraldehyde was studied in toluene for the different supported Ru-Sn catalysts. The results are shown in Figure 6-3. The maximum selectivity to lauraldehyde was obtained when titania was used as the support. The conversion of lauric acid obtained with Ru-Sn/TiO_2 catalyst was 31%. The selectivity to both lauraldehyde and lauryl alcohol was 41% each and selectivity to lauryl laurate was 18%.

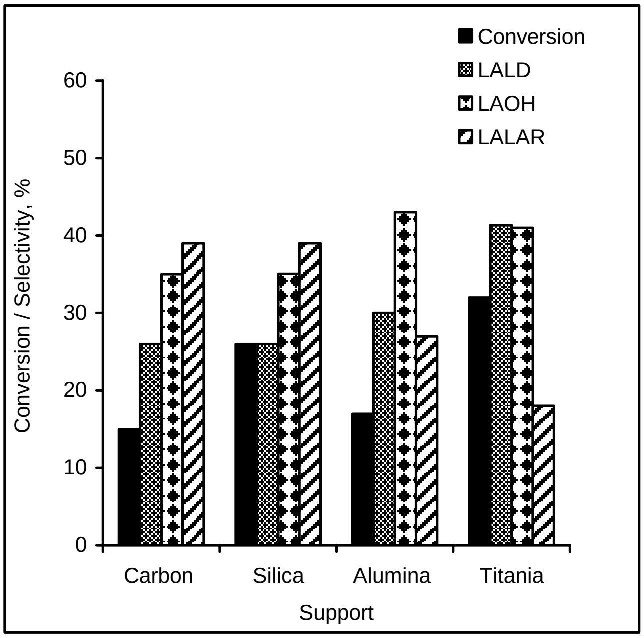


Figure 6-3: Effect of support on selectivity of Ru-Sn catalyst for lauraldehyde

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = toluene, Time = 0.5 hrs, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

6.3.3 Recycle study of Ru-Sn/TiO_2 catalyst (Sn/Ru atomic ratio = 5) for hydrogenation of lauric acid

As Ru-Sn/TiO_2 catalyst gave highest activity and selectivity for hydrogenation of lauric acid to lauraldehyde (as seen Section 6.3.2), it was necessary to ensure that the catalyst is stable and doesn't deactivate in the course of reaction. For this purpose the catalyst was recycled. The Ru-Sn/TiO_2 catalyst used for the recycle study had Sn/Ru atomic ratio 5 and was calcined at 773 K for 12 hrs and further reduced at 573 K under hydrogen for 12 hrs. The results are shown in Figure 6-4.

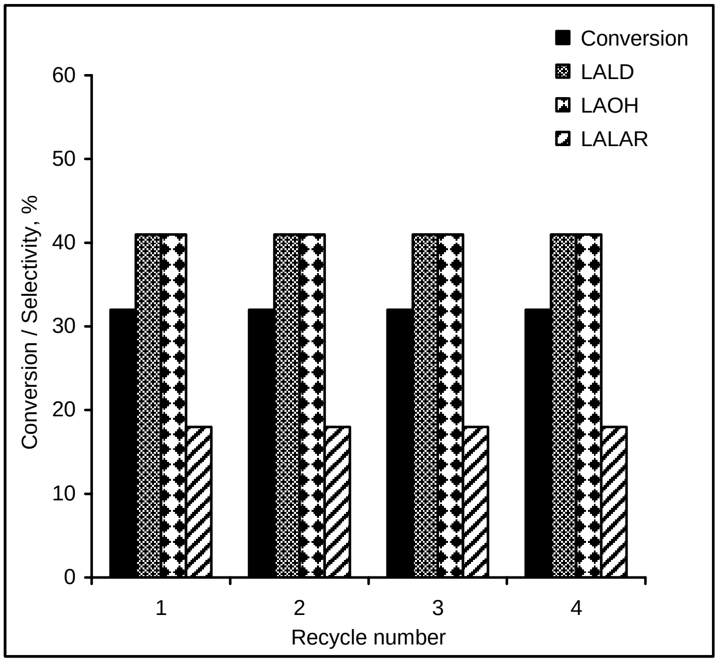


Figure 6-4: Recycle study for Ru-Sn/TiO_2 catalyst.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

The catalyst was found to retain its activity for four recycles without affecting the conversion of lauric acid and the selectivity to lauraldehyde and lauryl alcohol as shown in Figure 6-4.

6.3.4 Parametric study for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst in toluene

From the preliminary experiments it was observed that Ru-Sn/TiO_2 is active for hydrogenation of lauric acid to lauraldehyde. Since the activity of catalyst and selectivity are dependent on reaction parameters, the influence of process parameters on the activity and selectivity of the catalyst was observed.

Several experiments were carried out in the range of conditions given in Table 6-3.

Table 6-3: Range of reaction conditions for partial hydrogenation of lauric acid.

No.	**Reaction parameter**	**Range**
1	Temperature	453-513 K
2	Catalyst concentration	4-16 kg m^{-3}
3	Substrate concentration	0.2-0.5 $kmolm^{-3}$
4	Pressure	4 - 8 MPa
5	Stirring speed	1200 rpm
6	Total charge	2.5 x 10^{-5} m^3
7	Reaction time	0.5 hr.

6.3.4.1 Effect of catalyst loading on selectivity for hydrogenation of lauric acid to lauraldehyde

The effect of catalyst concentration on selectivity for hydrogenation of lauric acid to lauraldehyde was studied at 473 K, lauric acid concentration of 0.4 $kmolm^{-3}$ and hydrogen partial pressure of 6.3 MPa and toluene as solvent. The results are shown in Figure 6-5. The conversion of lauric acid increased with catalyst loading however the selectivity of reaction was found to decrease.

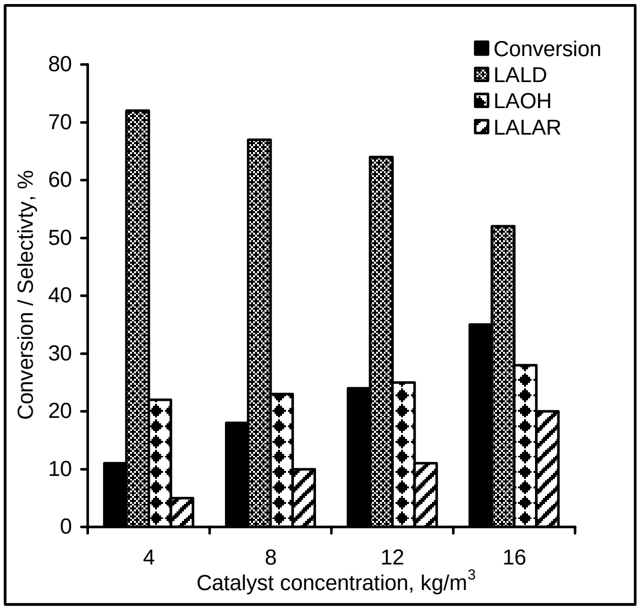


Figure 6-5: Effect of catalyst loading on hydrogenation of lauric acid to lauraldehyde.

Reaction conditions: Temperature = 473 K, Hydrogen partial pressure = 6.3 MPa, Lauric acid = 0.4 $kmolm^{-3}$, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

6.3.4.2 Effect of lauric acid concentration on selectivity for hydrogenation of lauric acid to lauraldehyde

The effect of lauric acid concentration on the selectivity of hydrogenation was investigated at 473 K, catalyst concentration of 8 kgm^{-3} and hydrogen partial pressure of 6.3 MPa in toluene as solvent. The results are shown in Figure 6-6. As the conversion increased with increase in lauric acid concentration, the selectivity to lauraldehyde decreased. The formation of lauryl laurate was enhanced.

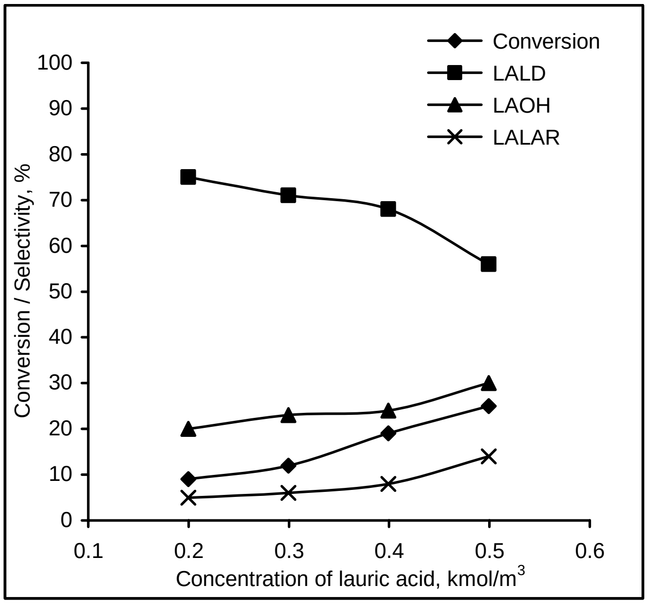


Figure 6-6: Effect of lauric acid concentration on hydrogenation of lauric acid to lauraldehyde.

Reaction conditions: Temperature = 473 K, Hydrogen partial pressure = 6.3 MPa, Catalyst = 8 kgm^{-3}, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

6.3.4.3 Effect of hydrogen partial pressure on selectivity for hydrogenation of lauric acid to lauraldehyde

The effect of hydrogen partial pressure on selectivity for hydrogenation of lauric acid to lauraldehyde was studied at 473 K, catalyst concentration of 8 kgm^{-3} and lauric acid concentration of 0.4 kmolm^{-3} in toluene as solvent. With increase in hydrogen partial pressure conversion of lauric acid was increased from 14% to 25% and selectivity to lauraldehyde decreased from 70% to 64%. The results for effect of hydrogen partial pressure are shown in Figure 6-7.

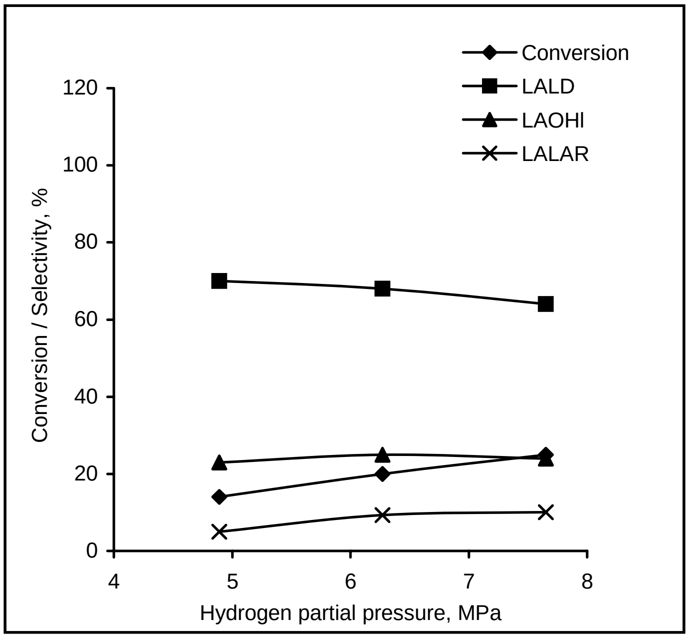


Figure 6-7: Effect of hydrogen partial pressure on selectivity to lauraldehyde.

Reaction conditions: Temperature = 473 K, Catalyst = 8 kgm^{-3}, Lauric acid = 0.4 kmolm^{-3}, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^{3}.

6.3.4.4 Effect of reaction temperature on hydrogenation of lauric acid to lauraldehyde

The effect of reaction temperature on selectivity was studied in the temperature range of 453-513K, at a catalyst and lauric acid concentration of 8 kgm^{-3} and 0.4 kmolm^{-3} respectively and hydrogen partial pressure of 6.3 MPa in toluene solvent. With increase in reaction temperature, conversion of lauric acid increased from 8% to 58% and selectivity to lauraldehyde decreased from 88% to 35%, as shown in Figure 6-8.

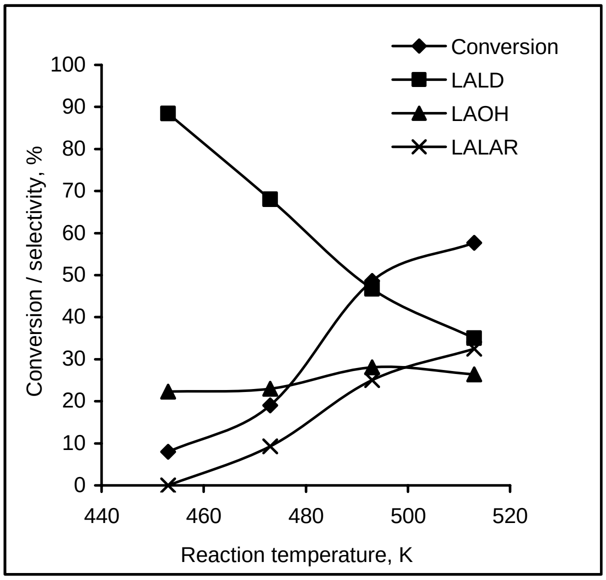


Figure 6-8: Effect of reaction temperature on selectivity of lauraldehyde.

Reaction conditions: Hydrogen partial pressure = 6.3 MPa, Catalyst = 8 kgm^{-3}, Lauric acid = 0.4 kmolm^{-3}, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^{3}.

From the parametric study it is understood that none of the reaction parameters had any major influence on the selective hydrogenation of lauric acid to lauraldehyde. The selectivity of partially hydrogenated product lauraldehyde is dependent on the concentration of lauric acid and lauraldehyde in the reaction medium, as both can compete for the same active site and undergo hydrogenation. As the concentration of lauric acid drops or the concentration of lauraldehyde increases, the probability of lauraldehyde getting adsorbed on catalytic sites increases. Hence the selectivity to lauraldehyde is decreased due to its further hydrogenation to lauryl alcohol. The highest selectivity to lauraldehyde could be achieved at lower conversion of lauric acid.

Since the variation of process parameters had no major influence on the selectivity to lauraldehyde, further catalyst development was undertaken to assess the role of catalyst synthesis parameters on lauraldehyde selectivity.

6.3.5 Effect of catalyst reduction temperature on selectivity of Ru-Sn catalyst supported on different supports

To study the effect of reduction temperature on Ru-Sn catalyst, Ru-Sn/Al_2O_3, Ru-Sn/C and Ru-Sn/TiO_2 catalysts with Sn/Ru atomic ratio of 5 were prepared by the procedure discussed earlier (Section 5.2.2) and each catalyst was reduced at 573, 873 and 1073 K.

6.3.5.1 Effect of reduction temperature on selectivity of lauraldehyde – 5%Ru-29%Sn/Al_2O_3 catalyst

The results for hydrogenation of lauric acid with Ru-Sn/Al_2O_3 catalyst reduced at 573, 873 and 1073 K are shown in Figure 6-9. It was observed that conversion of lauric acid increases from 24% to 42%, when the catalyst reduction temperature was increased from 573 to 873 K. This results in a lowering of lauraldehyde selectivity. However, reduction at 1073 K results in a much less active catalyst due to migration of SnO_2 on to Ru surface. A high selectivity (26%) to lauraldehyde is obtained as a result of having a less active catalyst.

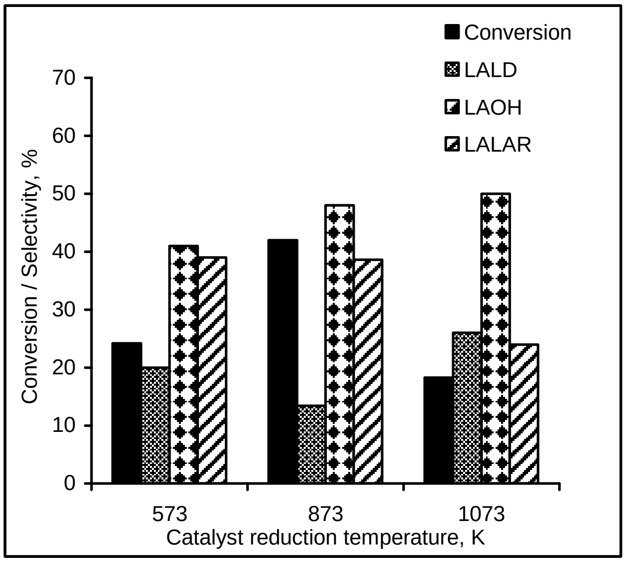


Figure 6-9: Effect of catalyst reduction temperature on Ru-Sn/Al_2O_3 catalyst for lauraldehyde.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = Toluene, Time = 1 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

6.3.5.2 Effect of reduction temperature on selectivity to lauraldehyde – 5%Ru-29%Sn/TiO_2 catalyst

Ru-Sn/TiO_2 catalysts were reduced at 573, 873 and 1073 K and used for hydrogenation of lauric acid in toluene solvent. Activity of catalyst decreased with catalyst reduction temperature, while the selectivity to lauraldehyde increased as shown in Figure 6-10. The highest selectivity to lauraldehyde with Ru-Sn/TiO_2 catalyst was obtained at a reduction temperature of 1073 K. With this catalyst a lauraldehyde selectivity of 82% was obtained at a lauric acid conversion of 20%. The selectivity to lauryl alcohol and lauryl laurate was 10% and 8% respectively.

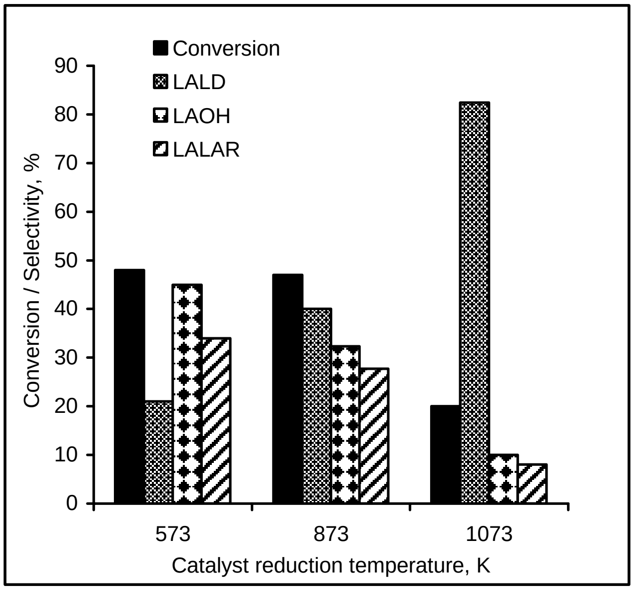


Figure 6-10: Effect of catalyst reduction temperatureon Ru-Sn/TiO_2 catalyst for lauraldehyde.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = Toluene, Time = 1 hr, Agitation speed = 1200 rpm, Total volume = 2.5×10^{-5} m^3.

6.3.5.3 Effect of reduction temperature on selectivity to lauraldehyde – 5%Ru-29%Sn/C catalyst

The effect of reduction temperature on the activity of Ru-Sn/C catalyst for the partial hydrogenation of lauric acid to lauraldehyde was studied at 493 K, catalyst loading

10 kg/m^3, hydrogen partial pressure of 6.2 MPa and lauric acid concentration of 0.25 kmol/m^3. The results for the reactions at the end of 1 hr are shown in Figure 6-11.

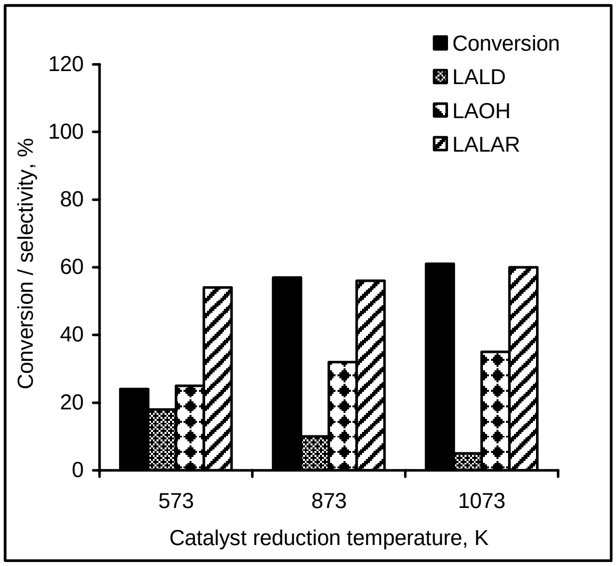


Figure 6-11: Effect of catalyst reduction temperature on Ru-Sn/C catalyst for lauraldehyde.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 kmolm^{-3}, Solvent = Toluene, Time = 1 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

It was observed that activity of Ru-Sn/C catalyst increases when the reduction temperature was increased from 573–1073 K, and hence the selectivity to lauraldehyde decreased. The highest selectivity to lauraldehyde of 18% could be obtained when the catalyst was reduced at 573 K.

In this study it is observed that highest selectivity to lauraldehyde is obtained with Ru-Sn/TiO$_2$ catalyst reduced at 1073 K.

6.3.6 Effect of catalyst reduction temperature on activity and selectivity for partial hydrogenation of lauric acid to lauraldehyde - Ru-Sn/TiO$_2$ catalyst with Sn/Ru varying ratio

Ru-Sn/TiO$_2$ catalysts having Sn/Ru atomic ratio of 1, 2.5, 5 and 7.5 were prepared and reduced at 573, 873 and 1073 K respectively. The results for hydrogenation of lauric acid using these catalysts are discussed below in detail.

6.3.6.1 Sn/Ru atomic ratio 1 (5%Ru-5.8%Sn/TiO_2)

The Ru-Sn/TiO_2 catalyst with Sn/Ru atomic ratio of 1 reduced at 573, 873 and 1073 K, was an active catalyst, however there was no selectivity to lauraldehyde (Figure 6-12). The highest lauric acid conversion for this catalyst was obtained at a reduction temperature of 873 K. The selectivity to lauryl alcohol and lauryl laurate was 75% and 25% respectively. Lauraldehyde is not obtained with these catalysts as the Sn/Ru atomic ratio is very low to reduce the number of Ru sites responsible for hydrogen activation in Ru-Sn/TiO_2 catalyst. The results for hydrogenation of lauric acid with this catalyst reduced at 573, 873 and 1073 K are shown in Figure 6-12.

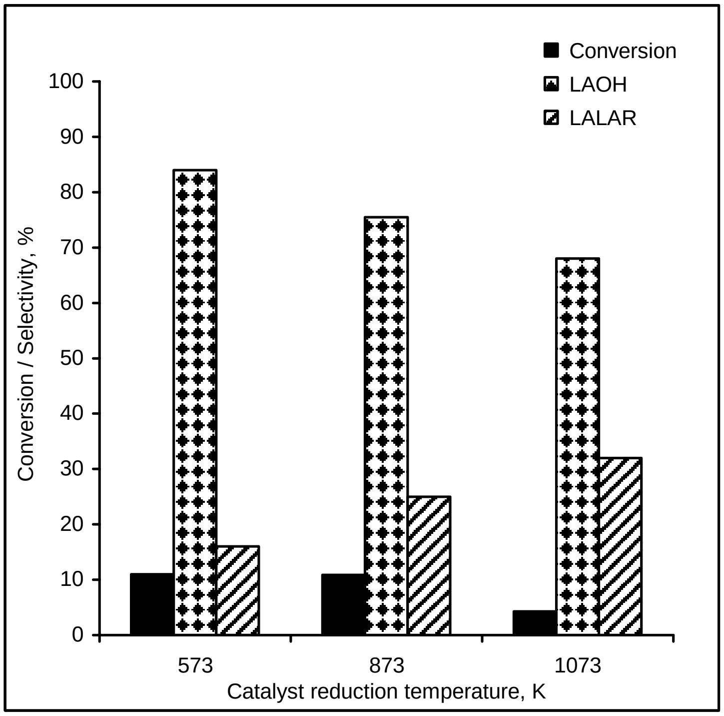


Figure 6-12: Effect of reduction temperature on Ru-Sn/TiO_2 catalyst for partial hydrogenation.

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.3 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

6.3.6.2 Sn/Ru atomic ratio of 2.5 (5%Ru-14.5%Sn/TiO_2)

As shown in Figure 6-13, the highest selectivity to lauraldehyde was 47% at a 55% lauric acid conversion, for a catalyst reduced at 873 K. The conversion of lauric acid and selectivity to lauraldehyde was lower at reduction temperature of 573 and 1073 K.

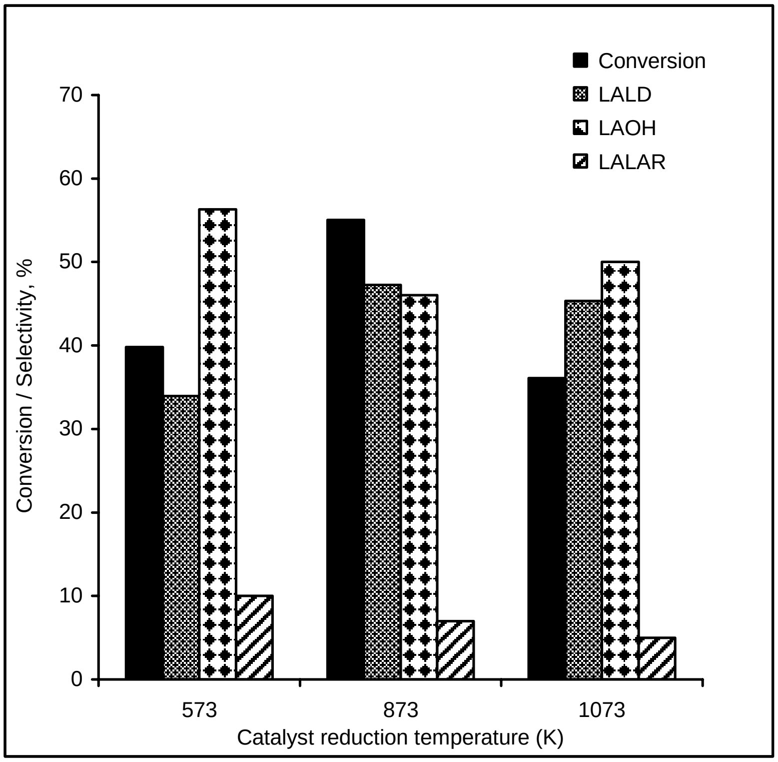


Figure 6-13: Effect of reduction temperature on Ru-Sn/TiO_2 (Sn/Ru ratio 2.5). **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

6.3.6.3 Sn/Ru atomic ratio of 5 (5%Ru-29%Sn/TiO_2)

With increase in reduction temperature, the activity of the catalyst for the hydrogenation of lauric acid increases from a conversion of 32% to 35% when reduction temperature is increased from 573 to 873 K and on further increase in reduction temperature (1073 K), conversion decreases to 14%.

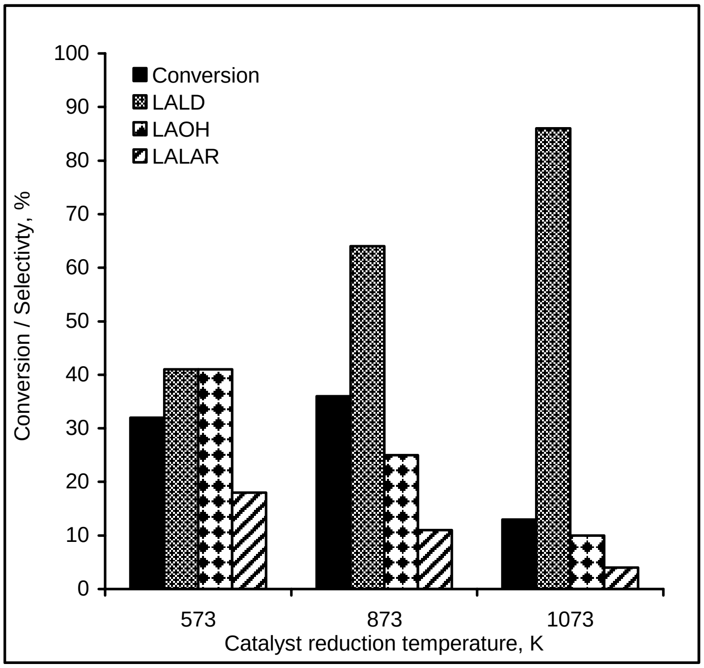


Figure 6-14: Effect of reduction temperature on Ru-Sn/TiO_2 (Sn/Ru ratio 5). **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.3 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

As seen in Figure 6-14, the selectivity to lauraldehyde improved dramatically with the reduction temperature and highest selectivity, 86% was achieved.

6.3.6.4 Sn/Ru atomic ratio of 7.5 (5%Ru-43%Sn/TiO_2)

The results for hydrogenation of lauric acid with Ru-Sn/TiO_2 catalyst (Sn/Ru atomic ratio = 7.5) reduced at 573, 873 and 1073 K are shown in Figure 6-15. It was observed that selectivity to lauraldehyde increased when catalyst reduction temperature was increased and conversion was highest when catalyst was reduced at 873 K indicating that an optimum reduction temperature was required during catalyst preparation, to achieve highest conversion for lauric acid. As in case of Sn/Ru atomic ratio of 5, here also the highest selectivity for lauraldehyde (87%) was obtained when the catalyst was reduced at 1073 K, at an 18% conversion of lauric acid.

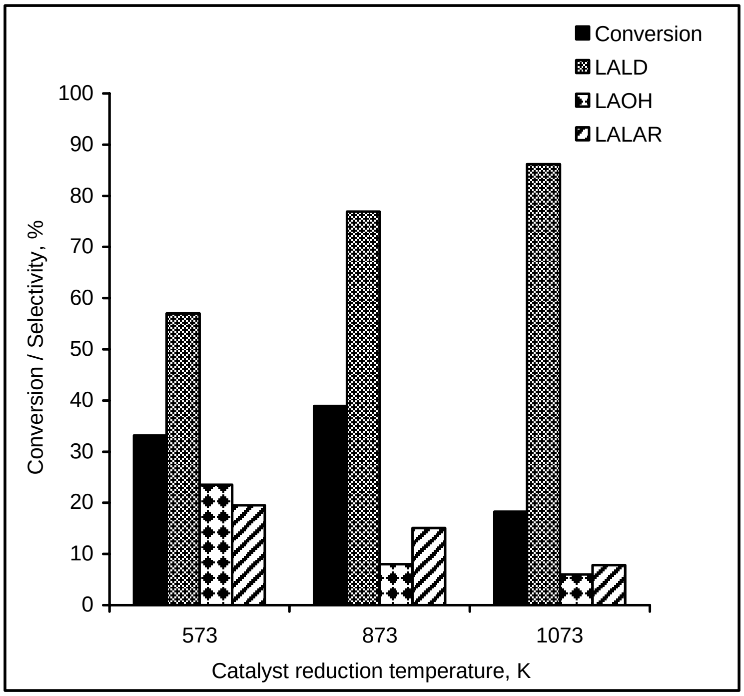


Figure 6-15: Effect of reduction temperature on Ru-Sn/TiO_2 catalyst (Sn/Ru ratio 7.5). **Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.2 MPa, Catalyst = 10 kgm^{-3}, Lauric acid = 0.25 $kmolm^{-3}$, Solvent = Toluene, Time = 0.5 hr, Agitation speed = 1200 rpm, Total volume = 2.5×10^{-5} m^3.

From this study it can be concluded that a high selectivity to lauraldehyde can be achieved by (1) increasing Sn/Ru atomic ratio or (2) by increasing catalyst reduction temperature for the Ru-Sn/TiO_2 catalyst.

6.3.7 Determining t_{max} for lauraldehyde

A concentration time profile for the hydrogenation of lauric acid to lauryl alcohol with lauraldehyde as the intermediate product is presented in Figure 6-16.

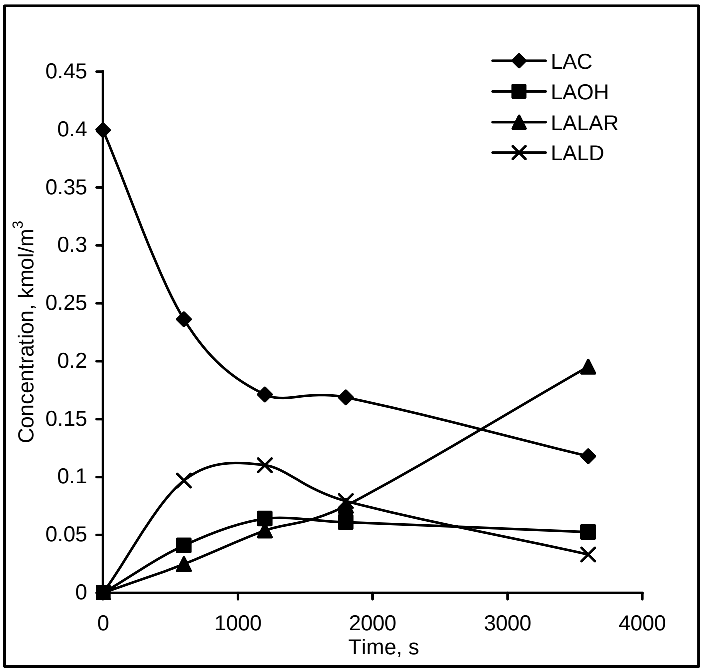


Figure 6-16: Concentration time profile for hydrogenation lauric acid with Ru-Sn/TiO_2 (Sn/Ru ratio = 5).

Reaction conditions: Temperature = 513 K, Hydrogen partial pressure = 5.9 MPa, Catalyst = 8 kgm^{-3}, Lauric acid = 0.4 $kmolm^{-3}$, Solvent = Toluene, Time = 1 hr, Agitation speed = 1200 rpm, Total volume = 2.5×10^{-5} m^3.

It is observed that the selectivity of lauraldehyde varies with lauric acid conversion, and passes through maximum. Under the reaction conditions the highest selectivity to lauraldehyde (60%) was obtained at the end of 10 minutes reaction, at 41% conversion of lauric acid, as seen in Figure 6-16 and 6-17.

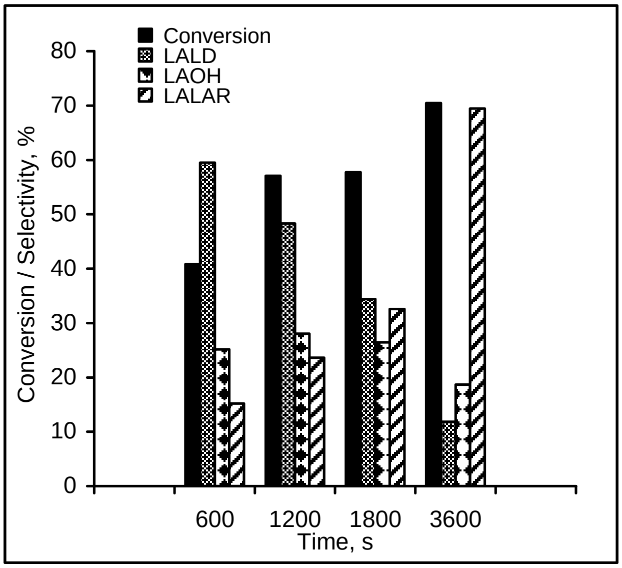


Figure 6-17: Selectivity to lauraldehyde with reaction time for hydrogenation with Ru-Sn/TiO_2 catalyst.

Reaction conditions: Temperature = 513 K, Hydrogen partial pressure = 5.9 MPa, Catalyst = 8 kgm^{-3}, Lauric acid = 0.4 $kmolm^{-3}$, Solvent = Toluene, Time = 1 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

Hydrogenation of lauric acid with Ru-Sn/TiO_2 (Sn/Ru atomic ratio = 5) in toluene is a consecutive reaction proceeding through an intermediate lauraldehyde as shown in Scheme 6-1. A knowledge of t_{max} would thus provide information about the time during the reaction, when the concentration of lauraldehyde will be high, and thus help in increasing the selectivity of the reaction to lauraldehyde.

An approach for determining t_{max} for consecutive catalytic reaction has already been described in Section 3.3.13. Using this approach, the effect of reaction parameters on t_{max} of hydrogenation of lauric acid with Ru-Sn/TiO_2 (Sn/Ru atomic ratio = 5) catalyst was studied and an equation was derived using Marquardts method of optimization.

6.3.7.1 Effect of reaction parameters on t_{max} of lauraldehyde

For evaluation of t_{max} for lauraldehyde, in lauric acid hydrogenation, the complete concentration time profile for hydrogenation of lauric acid to lauryl alcohol through lauraldehyde were monitored under different reaction conditions.

6.3.7.1.1. Effect of catalyst loading

The effect of catalyst concentration on the t_{max} of hydrogenation of lauric acid was studied at 473 K, lauric acid concentration of 0.4 kmolm^{-3} and hydrogen partial pressure of 6.3 MPa in toluene as solvent. The results are shown in Figure 6-18.

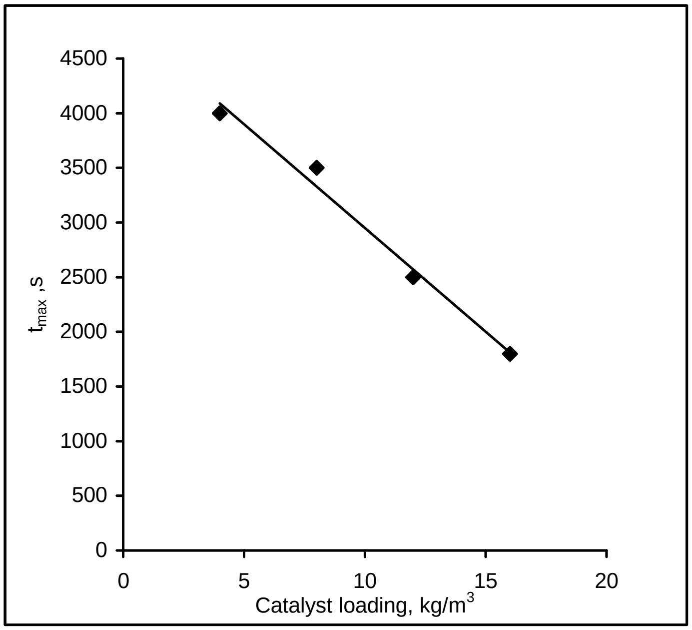


Figure 6-18: Effect of catalyst loading on t_{max} for lauraldehyde.

Reaction conditions: Temperature = 473 K, Hydrogen partial pressure = 6.3 MPa, Lauric acid = 0.4 kmolm^{-3}, Solvent = Toluene, Time = 4 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

The t_{max} for lauraldehyde was found to decrease with increase in catalyst concentration as shown in Figure 6-18. The t_{max} is dependent on the relative rates of hydrogenation of lauric acid to lauraldehyde and lauraldehyde to lauryl alcohol. When the catalyst loading is increased, the rate of formation and consumption of lauraldehyde are both increased and thus time required for maximum concentration (t_{max}) of lauraldehyde reduces.

6.3.7.1.2 Effect of lauric acid concentration

The effect of lauric acid concentration on the t_{max} of lauraldehyde was studied at 473 K, catalyst concentration of 8 kgm^{-3} and hydrogen partial pressure of 6.3 MPa and toluene as solvent. The results are shown in Figure 6-19.

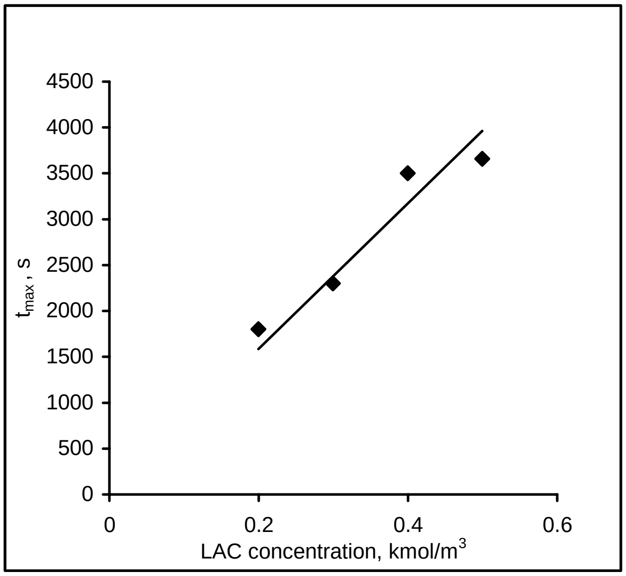


Figure 6-19: Effect of lauric acid concentration on t_{max} for lauraldehyde.
Reaction conditions: Temperature = 473 K, Hydrogen partial pressure = 6.3 MPa, Catalyst = 8 kgm^{-3}, Solvent = Toluene, Time = 4 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

The t_{max} for lauraldehyde increases as lauric acid concentration increases. This is because as the lauric acid concentration is increased, more time is required for building up the concentration of lauraldehyde and hence t_{max} for lauraldehyde increases.

6.3.7.1.3 Effect of hydrogen partial pressure

The effect of hydrogen partial pressure on the t_{max} of hydrogenation of lauric acid was studied at 473 K, lauric acid concentration of 0.4 kmolm^{-3}, catalyst concentration of 8 kg/m^3 and toluene as solvent. The t_{max} for lauraldehyde was found to decrease with increase in hydrogen partial pressure as shown in Figure 6-20. This is due to increase in rate of hydrogenation of both lauric acid as well as lauraldehyde.

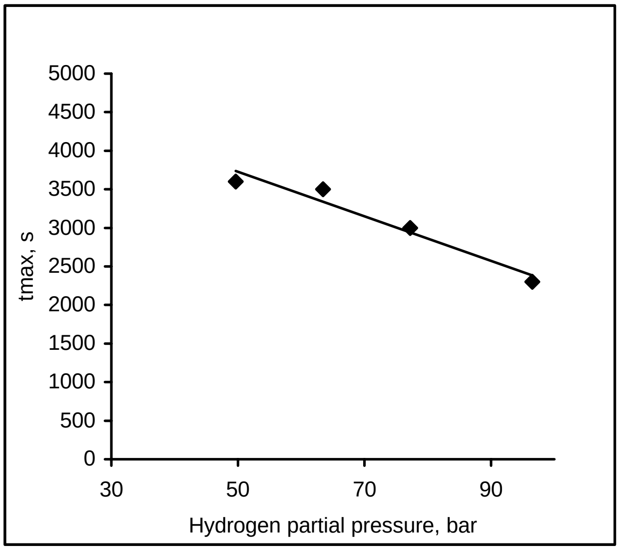


Figure 6-20: Effect of hydrogen partial pressure on t_{max} for lauraldehyde.

Reaction conditions: Temperature = 473 K, Catalyst = 8 kgm^{-3}, Lauric acid = 0.4 kmolm^{-3}, Solvent = Toluene, Time = 4 hr, Agitation speed = 1200 rpm, Total volume = 2.5 x 10^{-5} m^3.

From Figure 6-18, 6-19 and 6-20, it is observed that t_{max} for lauraldehyde is inversely proportional to catalyst loading and hydrogen partial pressure and directly proportional to the concentration of lauric acid.

Using these parametric trends for t_{max} and Marquardts method for optimization[7] an equation for t_{max} is derived which is given below by Eq-6.5.

$$t_{max} = K \left(\frac{[LAC]}{[CAT]\,[H_2]} \right) \qquad \text{Eq-6.5}$$

Where,

t_{max}	Time, where lauraldehyde is in maximum concentration (s).
K	Constant (s kg bar / kmol)
[LAC]	Concentration of lauric acid (kmol/m^3)
[CAT]	Concentration of Ru-Sn/TiO$_2$ catalyst (kg/m^3)
[H$_2$]	Hydrogen partial pressure (bar)

The value for K in Eq-6.5 was evaluated to be 3.65 x 10^6 s kg bar / kmol.

6.3.7.1.4. Comparison of predicted t_{max} with experimental t_{max} for lauraldehyde

To confirm the validity of Eq-6.5, a plot of predicted t_{max} versus experimental t_{max} was plotted as shown in Figure 6-21.

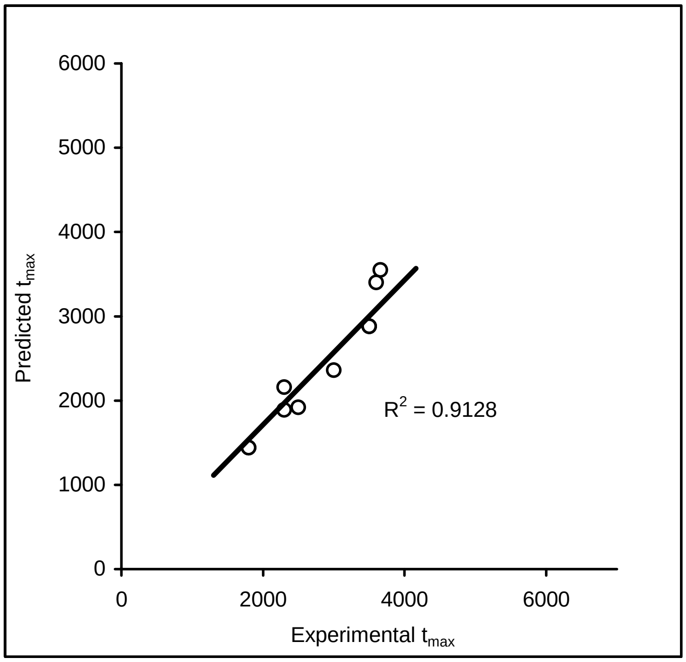


Figure 6-21: Comparison of predicted t_{max} with observed t_{max} for lauraldehyde.

As shown in Figure 6-21, the Eq-6.5was found to predict t_{max} for lauraldehyde satisfactorily.

6.3.8 Hydrogenation of lauric, benzoic and cyclohexane carboxylic acid with Ru-Sn/TiO_2 catalyst in toluene as reaction solvent

The feasibility of selective hydrogenation of other carboxylic acids to respective aldehydes with Ru-Sn/TiO_2 catalyst was assessed in toluene as reaction solvent. The hydrogenation of lauric, benzoic and cyclohexane carboxylic acid were carried out at 513 K, carboxylic acid concentration of 0.4 kmolm^{-3}, catalyst concentration of 8 kg/m^3 and hydrogen partial pressure of 5.9 MPa and toluene as solvent. The Ru-Sn/TiO_2 catalyst used for this study had Sn/Ru atomic ratio of 5 and was prepared according to procedure given in Section 5.2.2 (Reduced at 573 K). The products obtained during hydrogenation of these carboxylic acids were the respective aldehydes, alcohols and the esters, the results for which are shown in Figure 6-22.

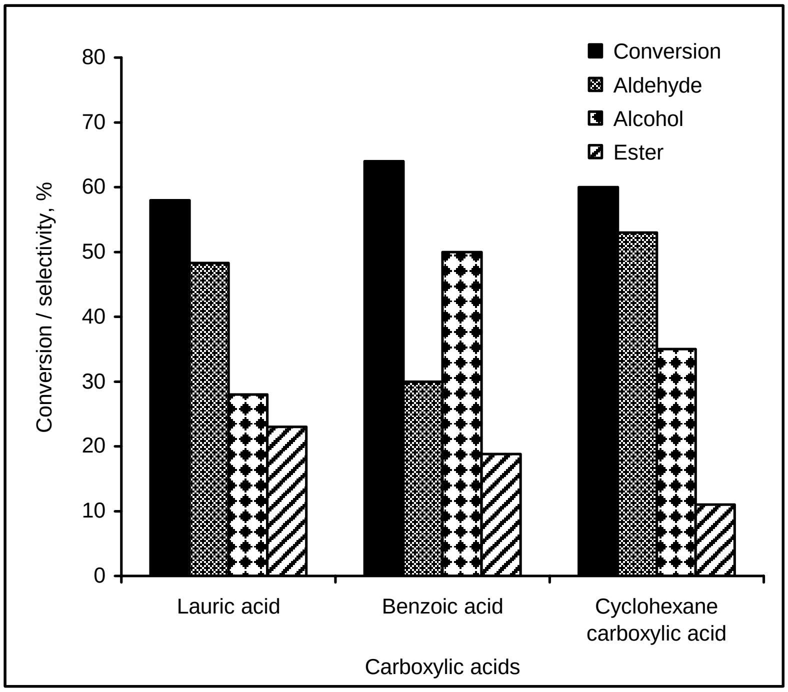


Figure 6-22: Hydrogenation of lauric, benzoic and cyclohexane carboxylic acid in toluene with Ru-Sn/TiO_2 catalyst.

Reaction conditions: Temperature = 513 K, Hydrogen partial pressure = 5.9 MPa, Catalyst = 8 kgm^{-3}, Carboxylic acid = 0.4 $kmolm^{-3}$, Solvent = Toluene, Time = 0.3 hr, Agitation speed = 1200 rpm, Total volume = 2.5×10^{-5} m^3.

The selectivity to lauraldehyde, benzaldehyde and cyclohexane carboxaldehyde was 48%, 30% and 53% respectively after 20 minutes reaction. Since the carboxylic acids used for partial hydrogenation represent aliphatic, aromatic and aliphatic cyclic carboxylic acids, it is established that partial hydrogenation of other such carboxylic acids is possible with Ru-Sn/TiO_2 catalyst using toluene as solvent. The conversion for all the three carboxylic acids was almost 60%.

From this study it can be seen that the partial hydrogenation of carboxylic acids to aldehydes is possible, however a proper optimization of reaction time may be required to achieve higher selectivity to aldehyde.

6.4 Conclusion

The partial hydrogenation of lauric acid to lauraldehyde using Ru-Sn catalyst was studied in a laboratory scale slurry reactor. In this study, toluene was found to be good solvent for partial hydrogenation of lauric acid to lauraldehyde, in presence of supported metal catalyst.

Titania supported Ru-Sn catalyst was the best catalyst for this reaction and 32% conversion of lauric acid with 41% selectivity to lauraldehyde was obtained. Ru-Sn on supports like alumina, silica and carbon were also active for the reaction.

When Ru-Sn/TiO_2 catalysts with Sn/Ru atomic ratio of 1, 2.5, 5 and 7.5 reduced at 573, 873 and 1073 K were screened for hydrogenation, highest selectivity was obtained for Ru-Sn/TiO_2 catalyst with Sn/Ru ratio of 7.5 reduced at 1073 K. With this catalyst selectivity to lauraldehyde was 87% with 18% conversion of lauric acid.

Ru-Sn/TiO_2 catalyst was observed to be stable with same conversion of lauric acid and selectivity to lauraldehyde up to four recycles. The reaction parameters had no major influence on the partial hydrogenation of lauric acid to lauraldehyde, but the selectivity to lauraldehyde was dependent on concentration of lauric acid and lauraldehyde in the reaction medium.

Hydrogenation of lauric acid to lauryl alcohol in toluene as solvent with Ru-Sn/TiO_2 catalyst is a consecutive reaction with lauraldehyde as intermediate. The selectivity to lauraldehyde was found to be dependent on reaction time. The following equation was derived using Marquardts method of optimization for t_{max} of lauraldehyde.

$$t_{max} = K \left(\frac{[LAC]}{[CAT]\,[H_2]} \right)$$

From this equation it is understood that t_{max} is directly proportional to the concentration of lauric acid and inversely proportional to the catalyst loading and hydrogen partial pressure.

Hydrogenation of benzoic and cyclohexane carboxylic acid using Ru-Sn/TiO_2 catalyst in toluene as solvent also gave benzaldehyde and cyclohexane carboxaldehdye with 30% and 53% selectively respectively, indicating that the catalyst synthesis could be further tuned to obtain high selectivity to the desired aldehydes.

6.5 Nomenclature

C_f	Final concentration of lauric acid, kmol/m^3
C_i	Initial concentration of lauric acid, kmol/m^3
C_{LALAR}	Concentration of lauryl laurate, kmol/m^3
C_{LALD}	Concentration of lauraldehyde, kmol/m^3
C_{LAOH}	Concentration of lauryl alcohol, kmol/m^3
K	Constant in Eq-6.5, s kg bar/kmol
t_{max}	Time for maximum concentration of intermediate, s

Reference

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[7] D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **1963**, *11(2)*, 431.

Appendix I

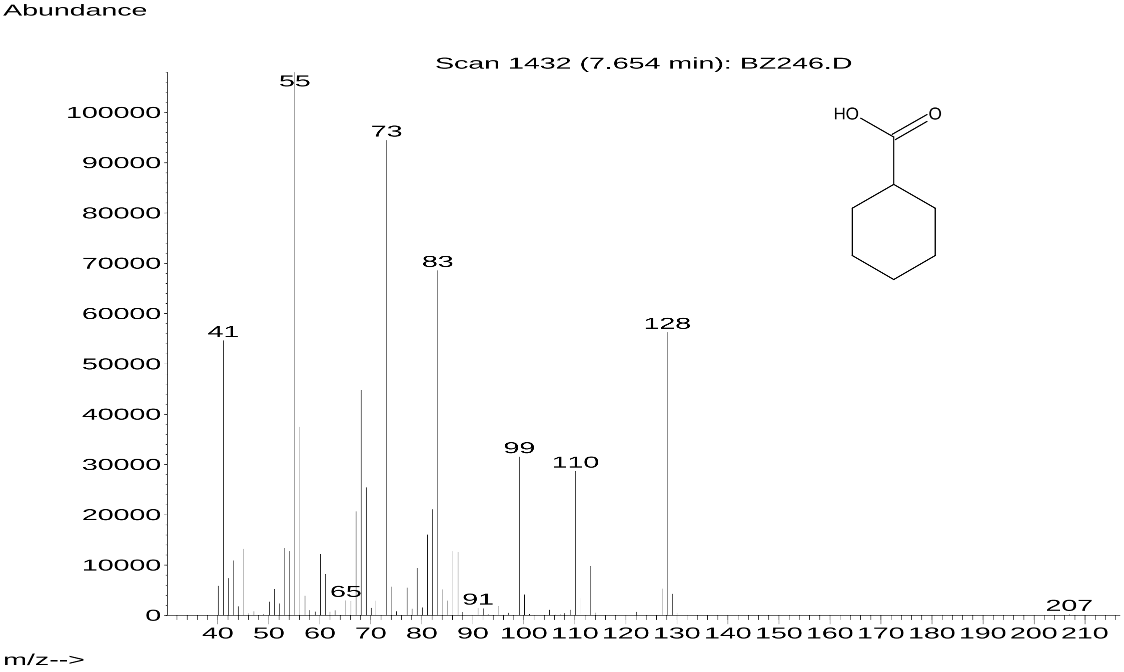

Figure 1: Mass spectra of Cyclohexane carboxylic acid.

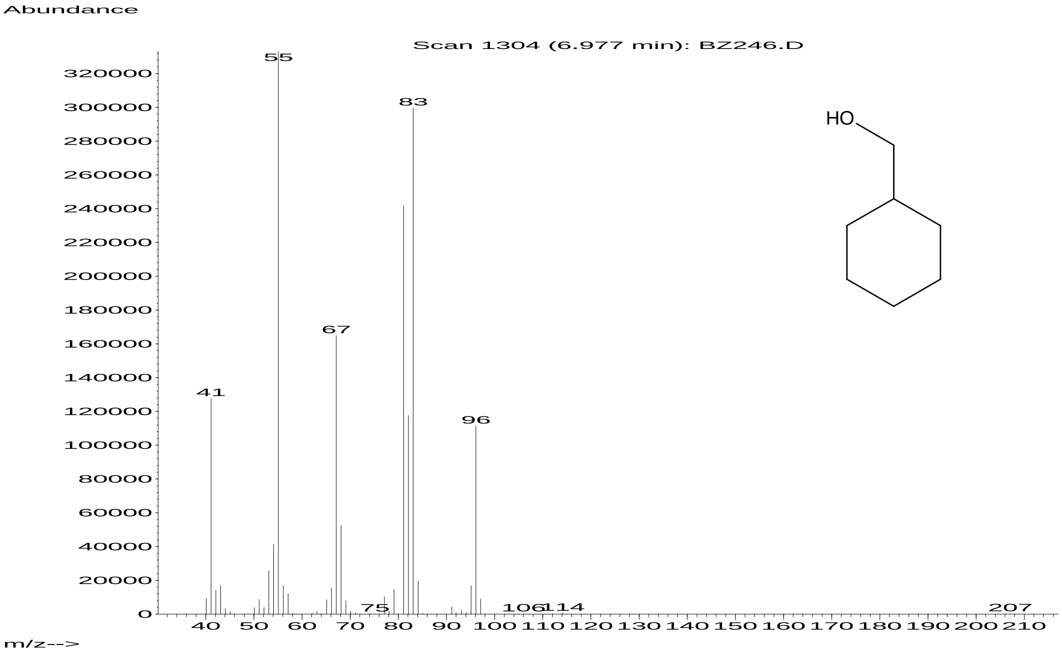

Figure 2: Mass spectra of Cyclohexyl methanol

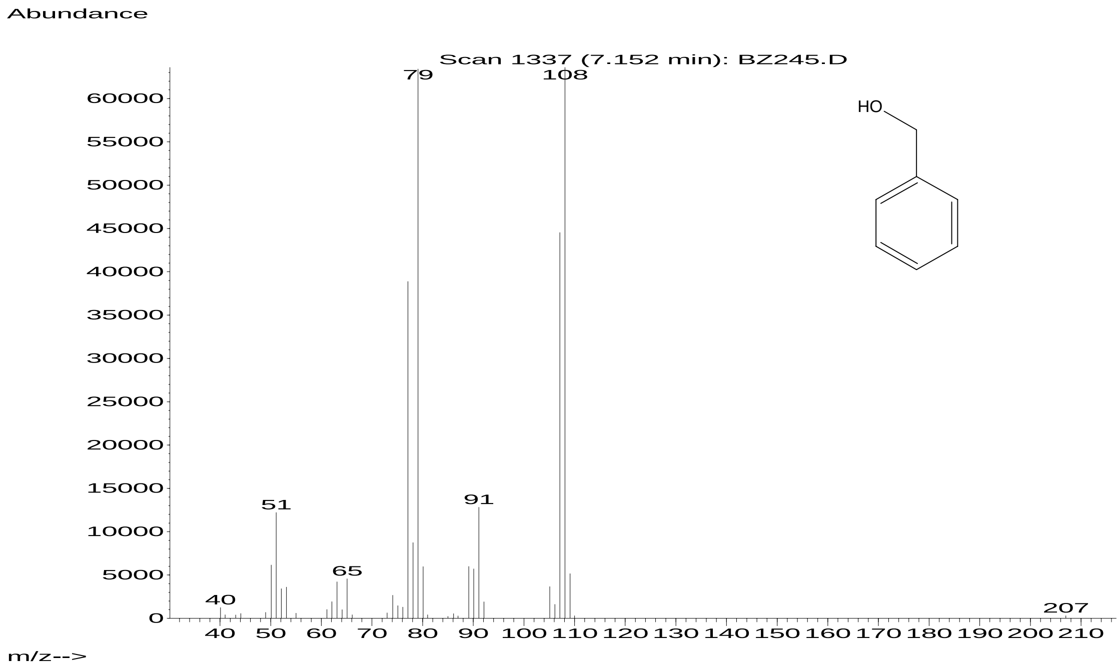

Figure 3: Mass spectra of Benzyl alcohol.

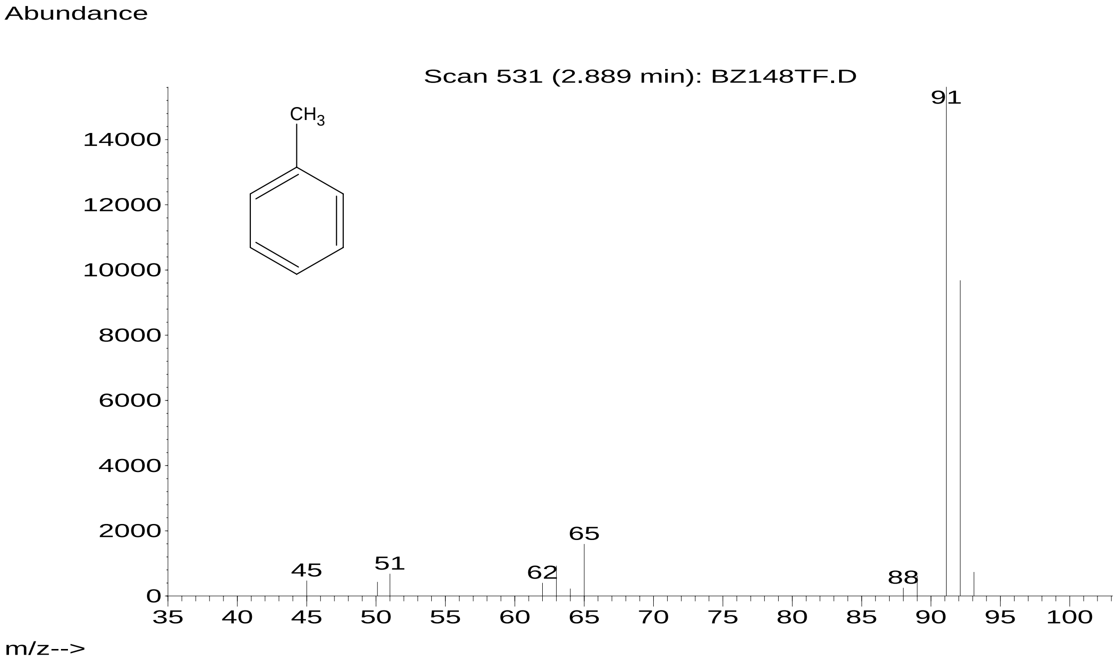

Figure 4: Mass spectra of Toluene.

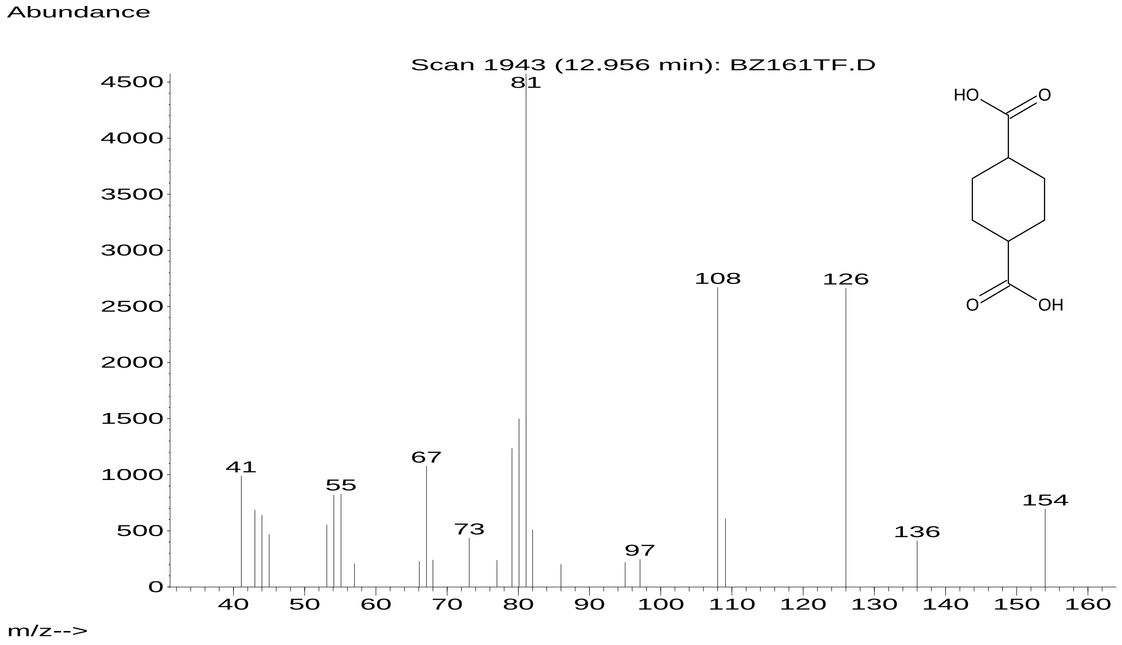

Figure 5: Mass spectra of 1,4-Cyclohexane dicarboxylic acid.

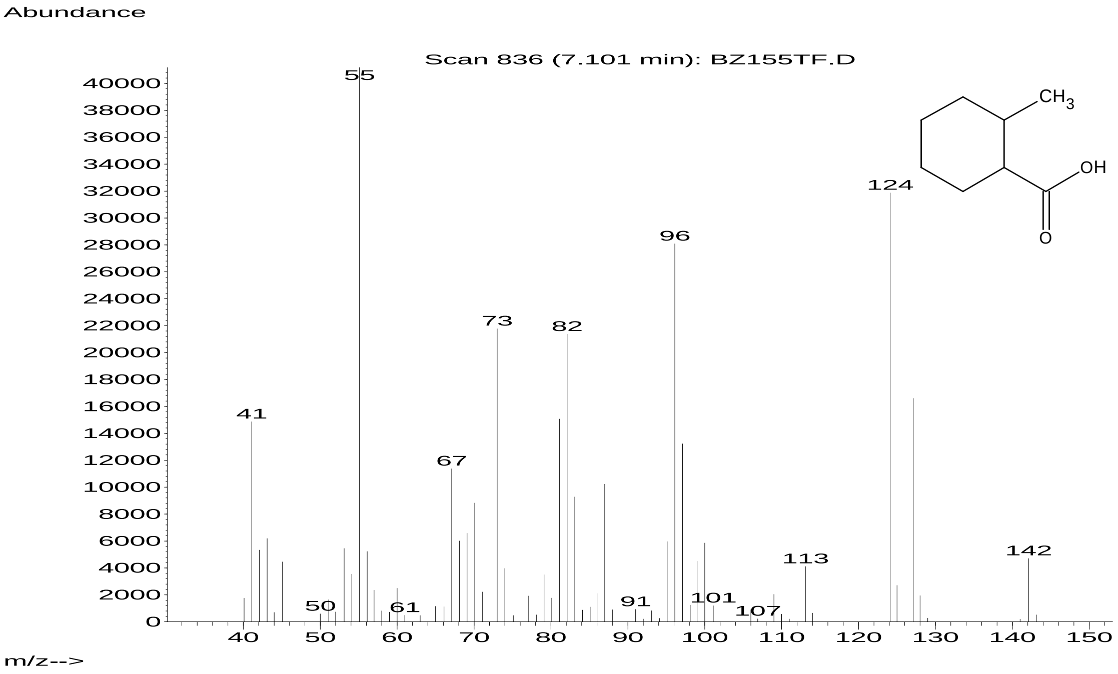

Figure 6: Mass spectra of 2-Methyl cyclohexane carboxylic acid.

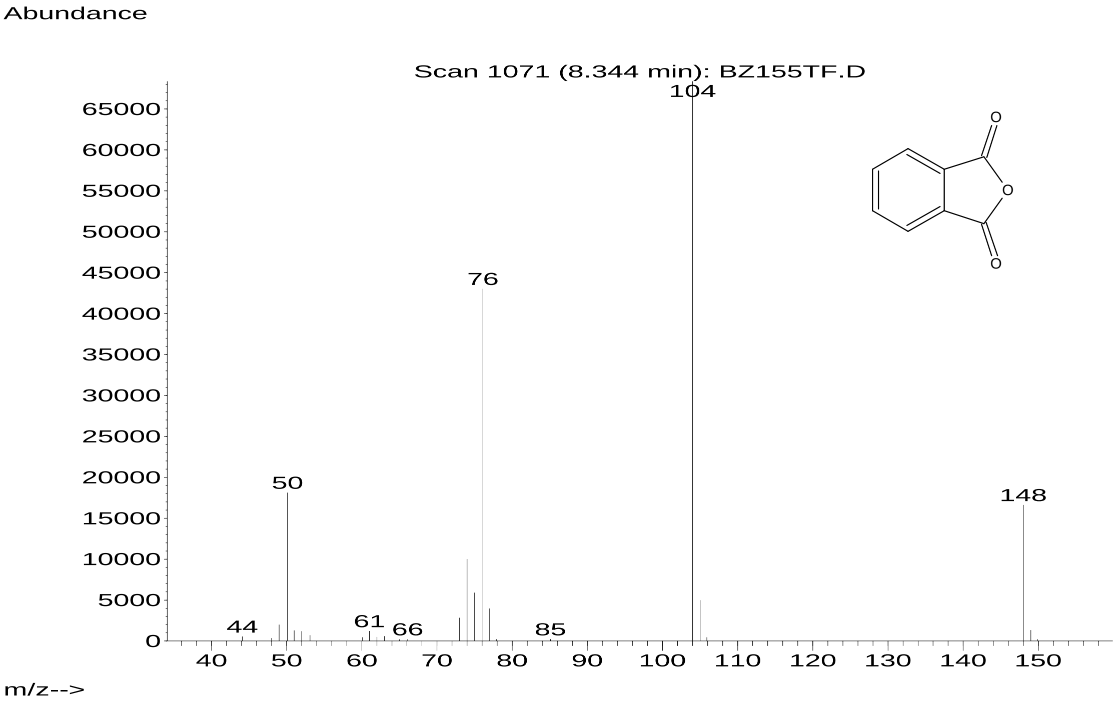

Figure 7: Mass spectra of Phthalic anhydride.

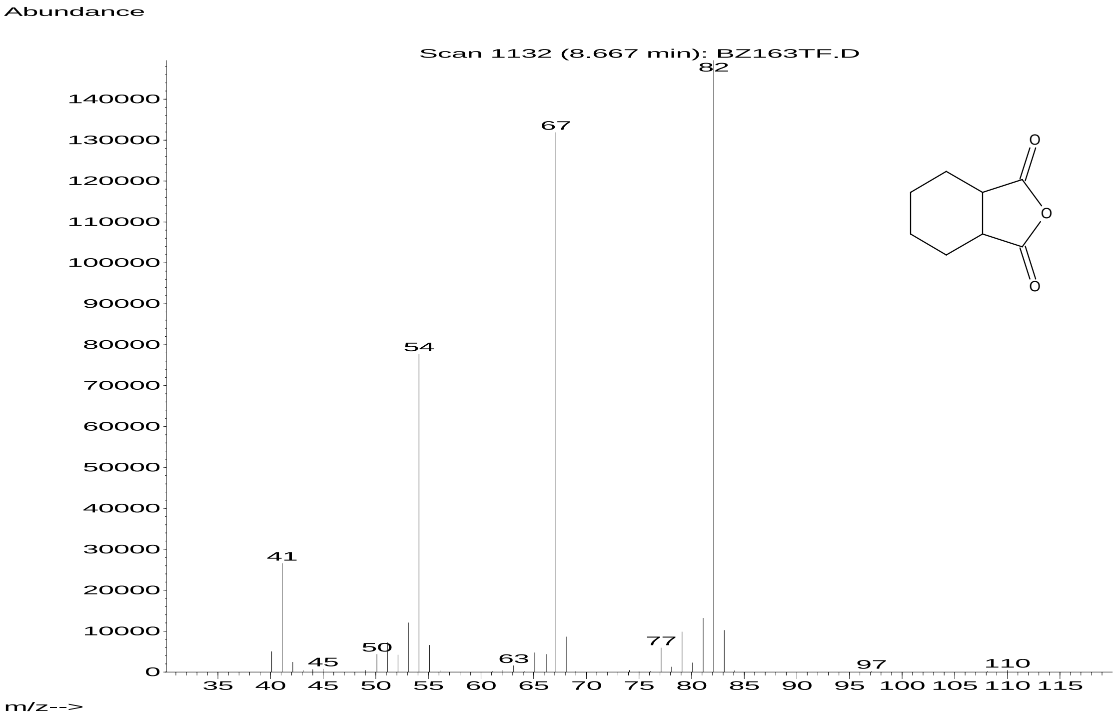

Figure 8: Mass spectra of Cyclohexane carboxylic acid anhydride.

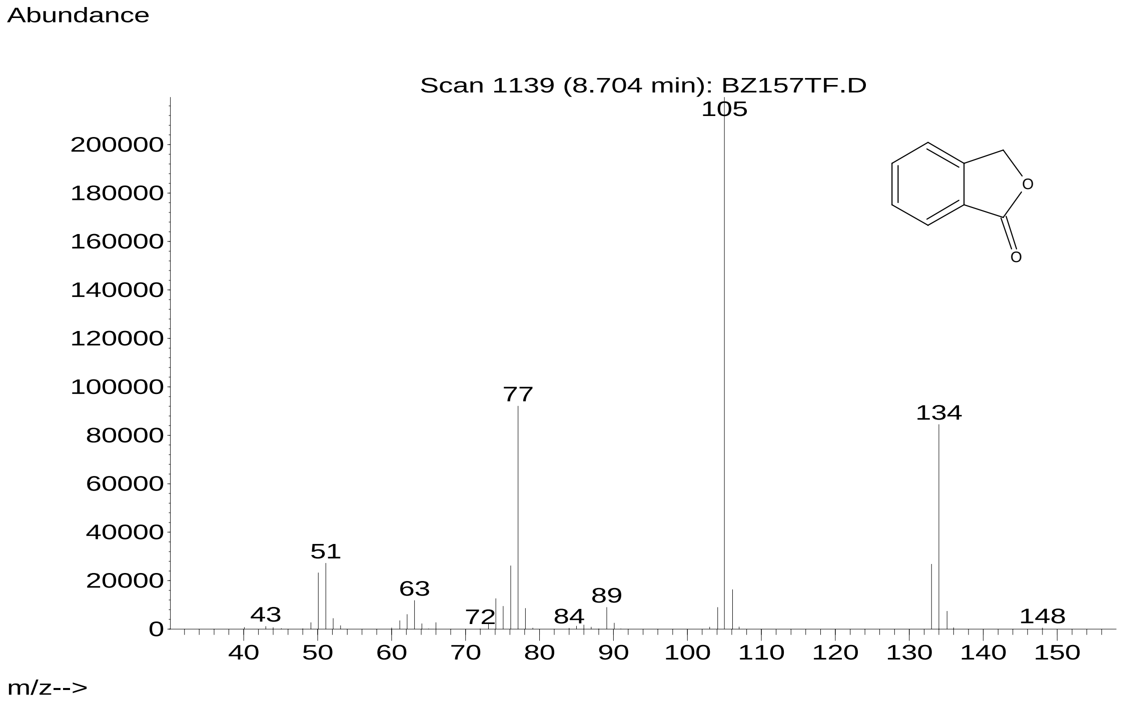

Figure 9: Mass spectra of Phthalide.

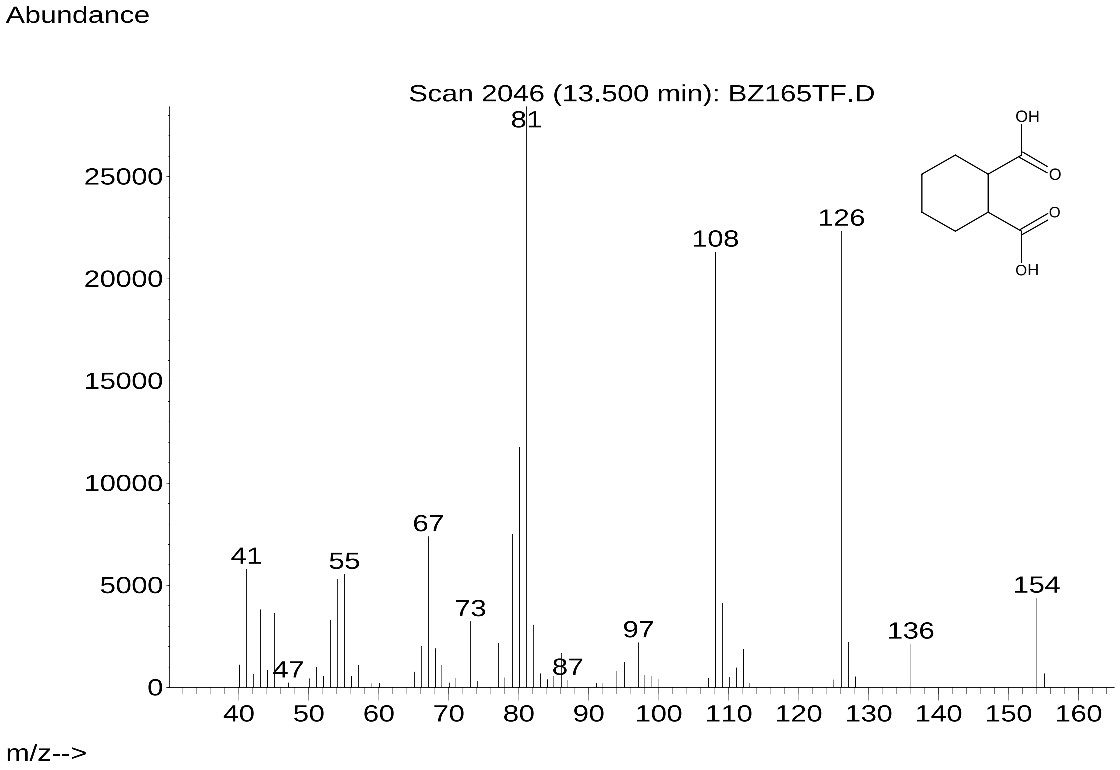

Figure 10: Mass spectra of 1, 2-Cyclohexane dicarboxylic acid.

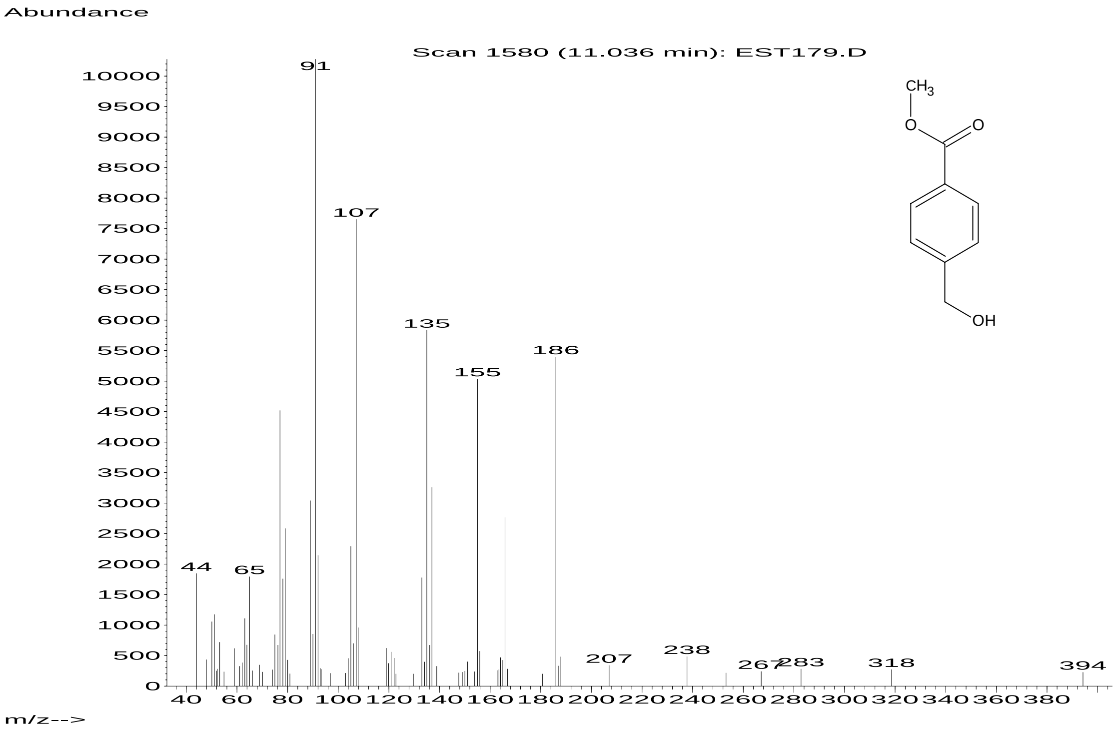

Figure 11: Mass spectra of 4-Hydroxy methyl benzoic acid methyl ester

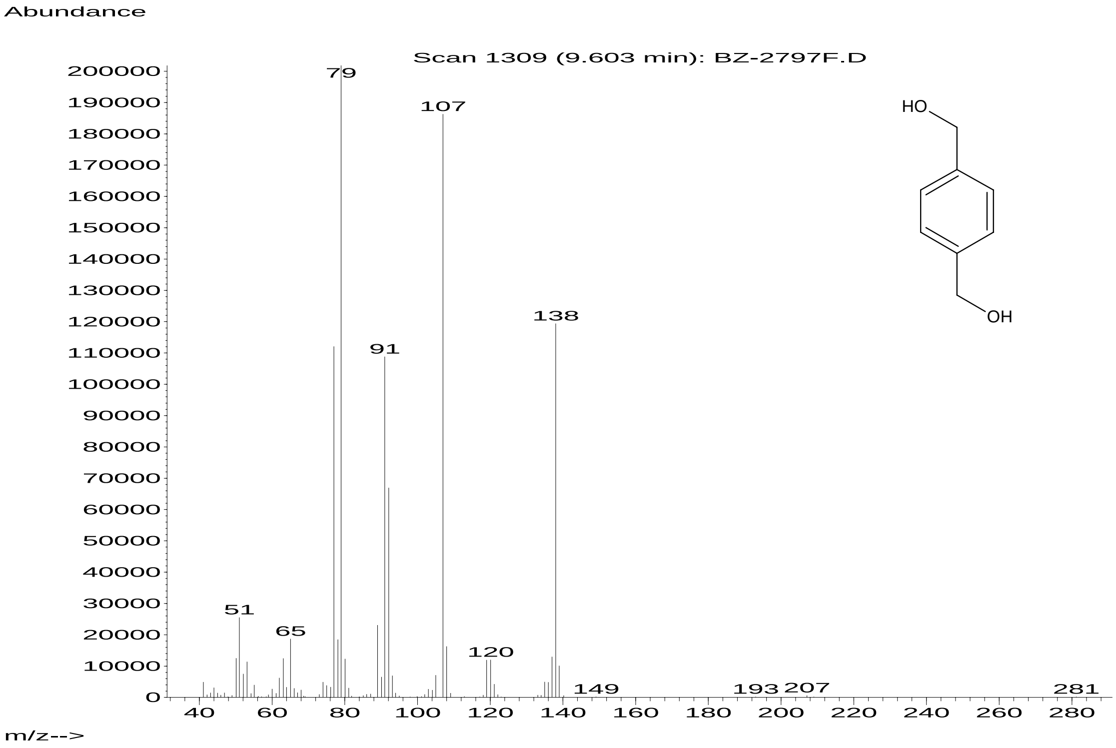

Figure 12: Mass spectra of 1,4-Benzene dimethanol.

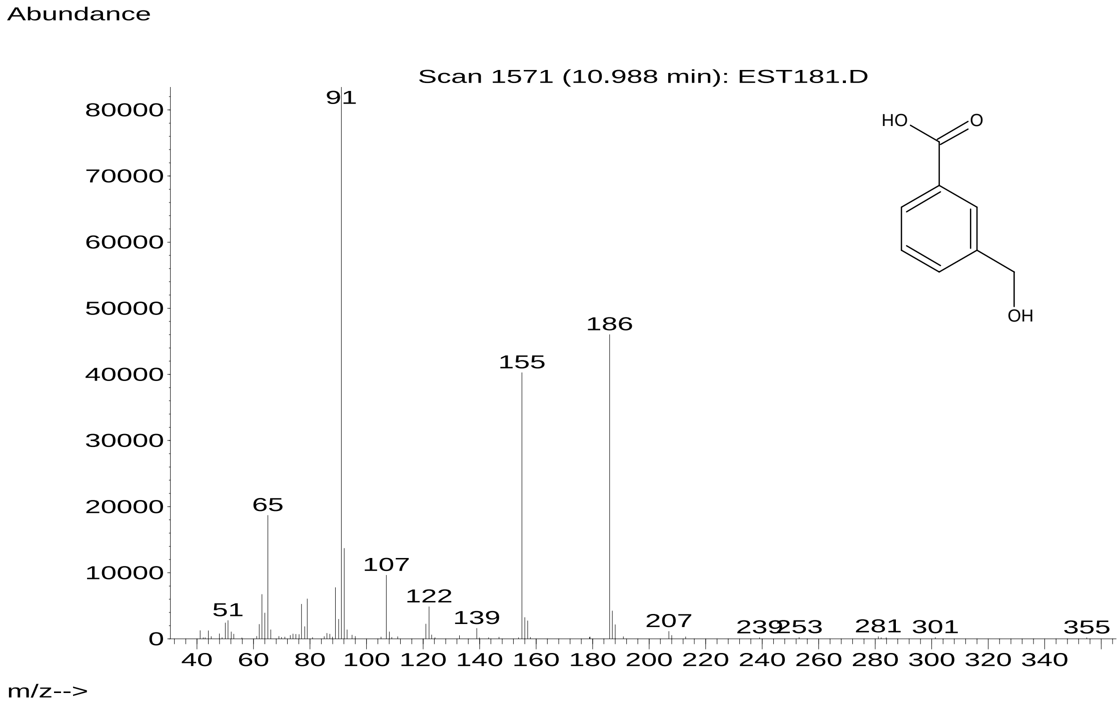

Figure 13: Mass spectra of 3-Hydroxymethyl benzoic acid

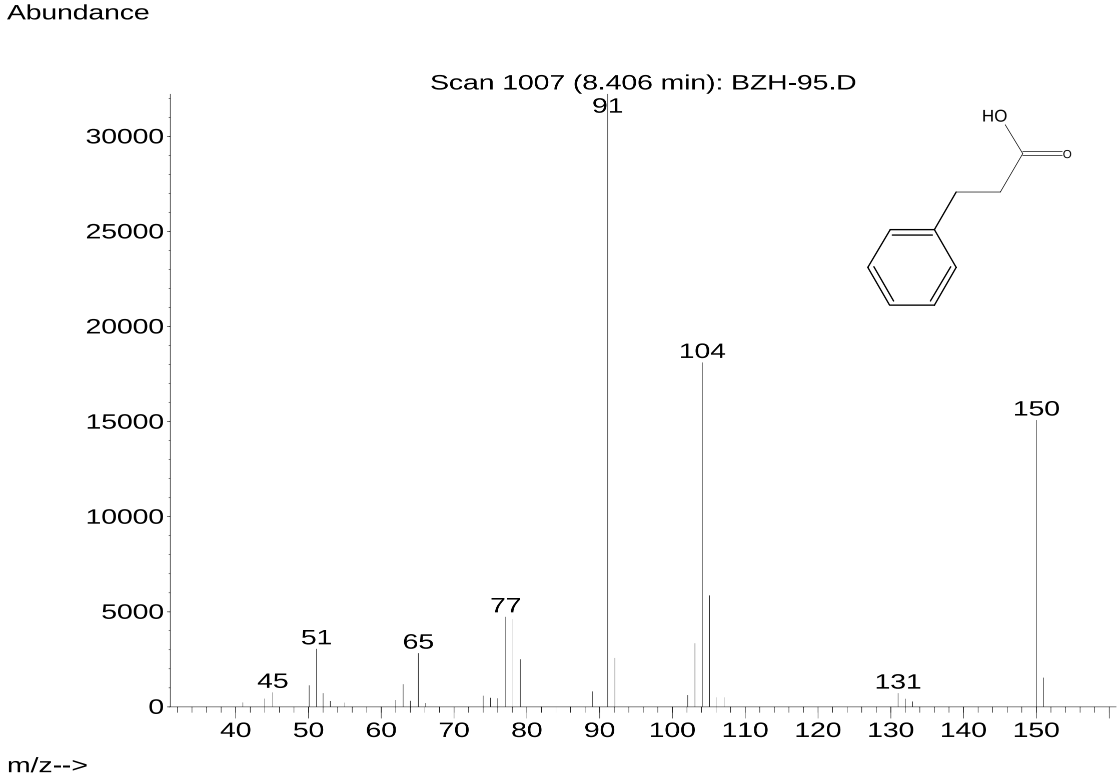

Figure 14: Mass spectra of Benzene propanoic acid.

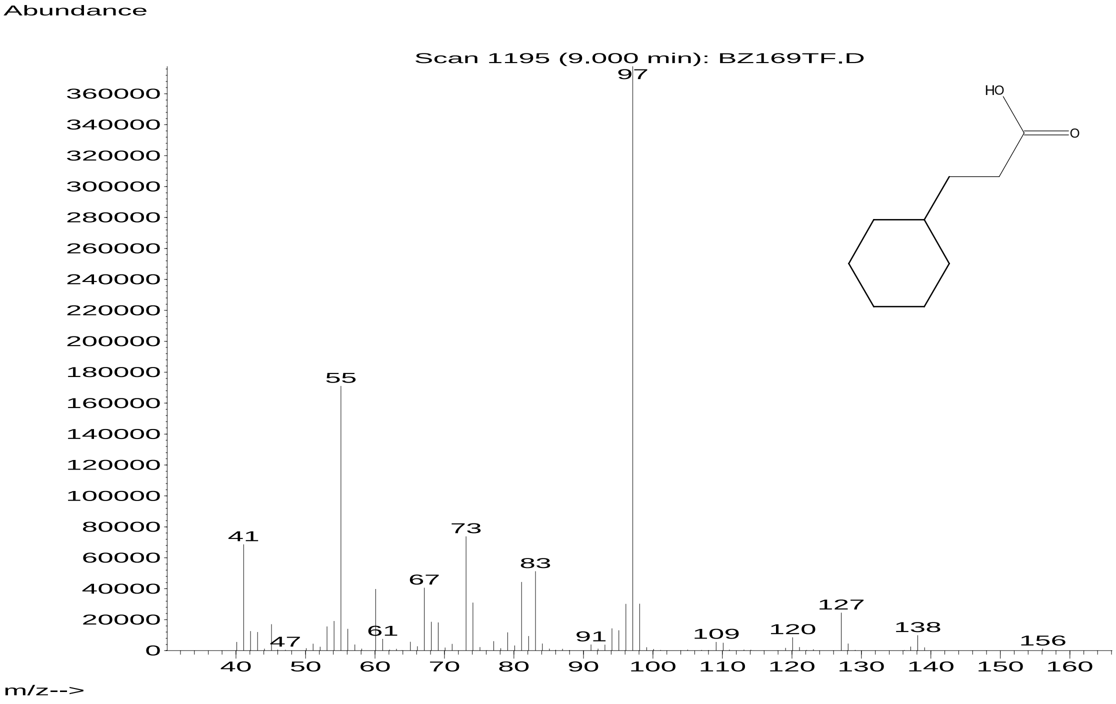

Figure 15: Mass spectra of Cyclohexane propanoic acid.

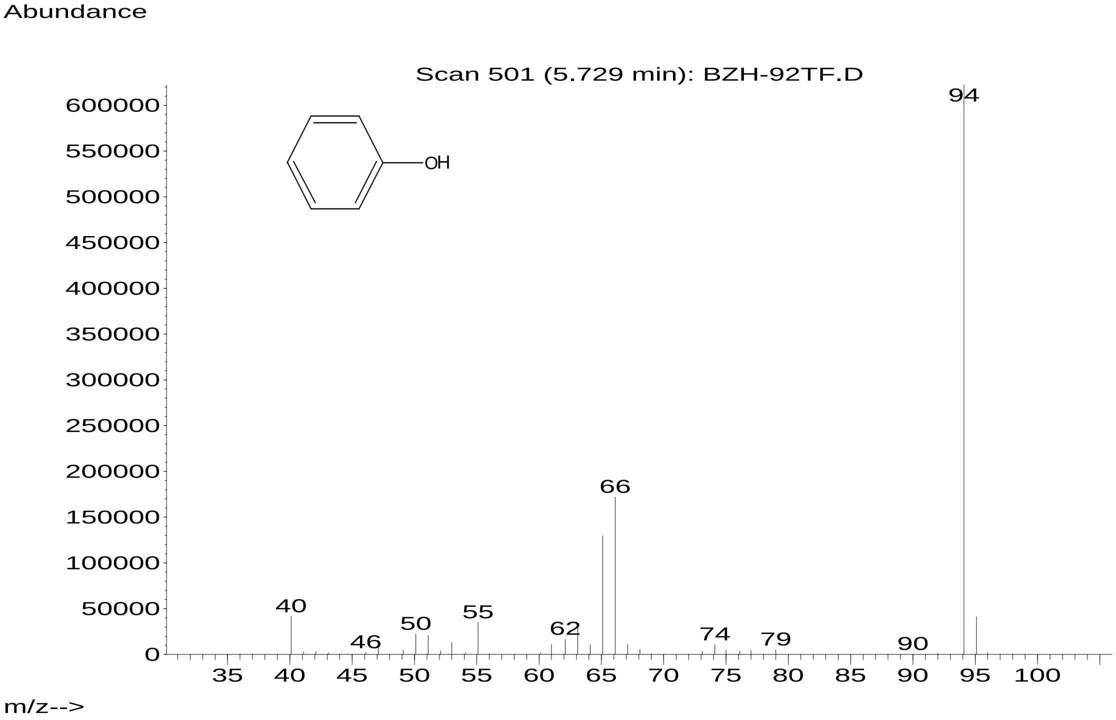

Figure 16: Mass spectra of Phenol.

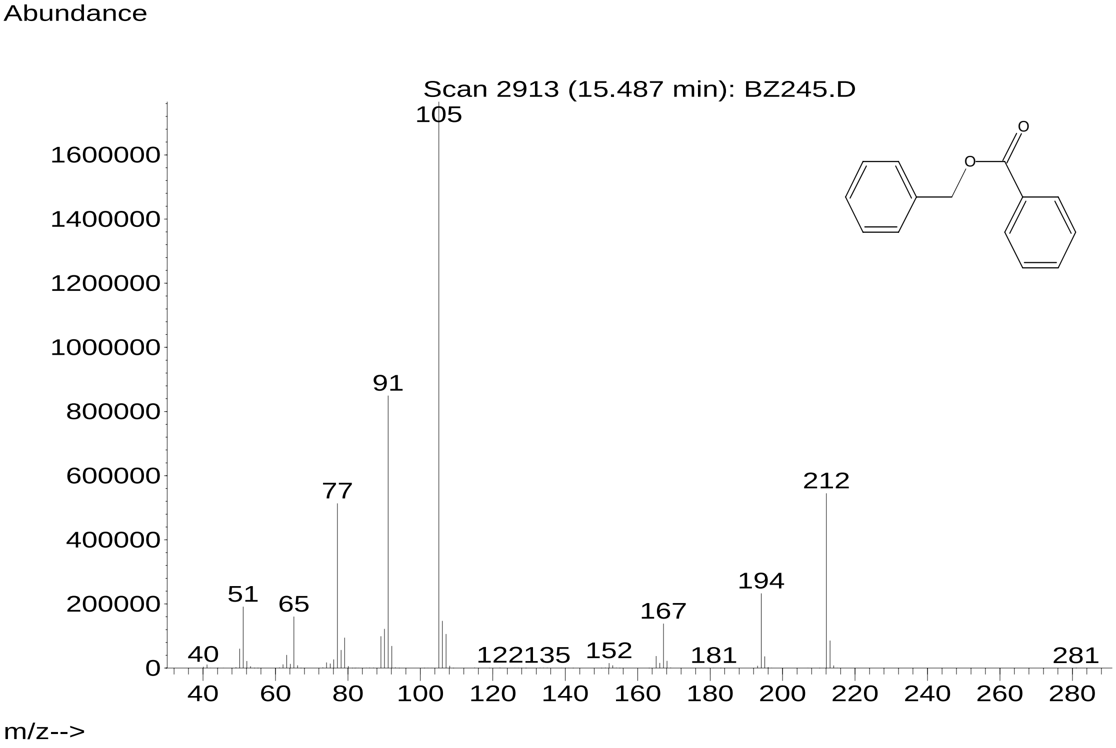

Figure 17: Mass spectra of Benzyl benzoate.

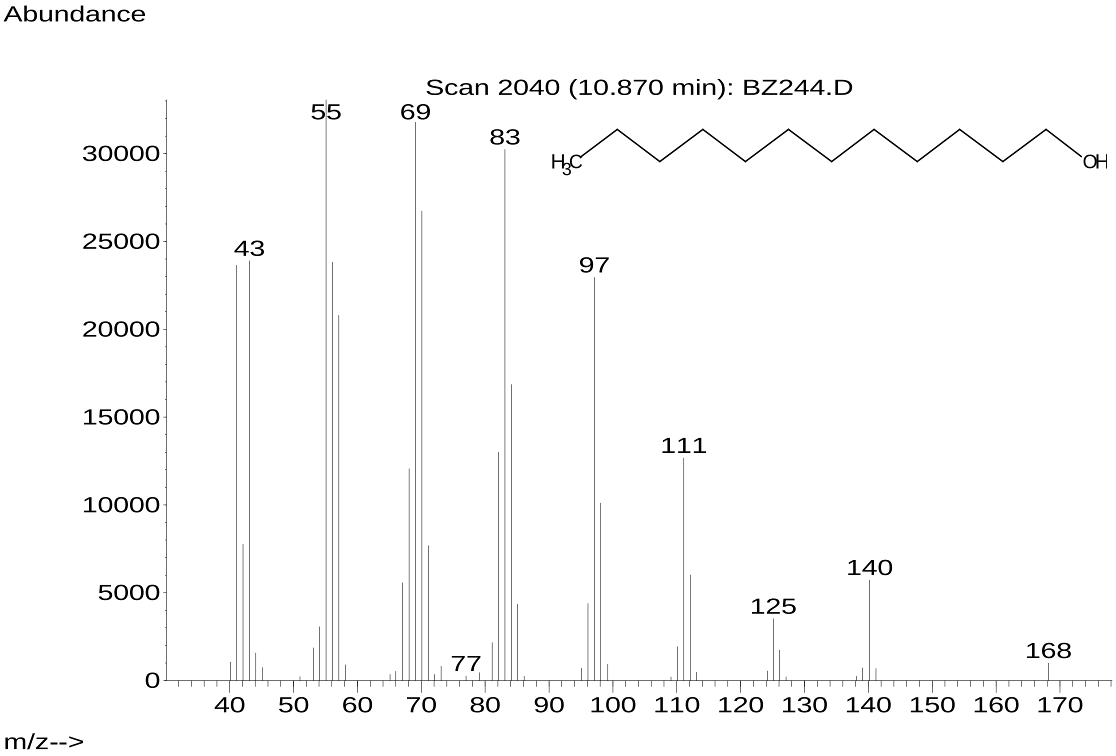

Figure 18: Mass spectra of 1-Dodecanol/lauryl alcohol.

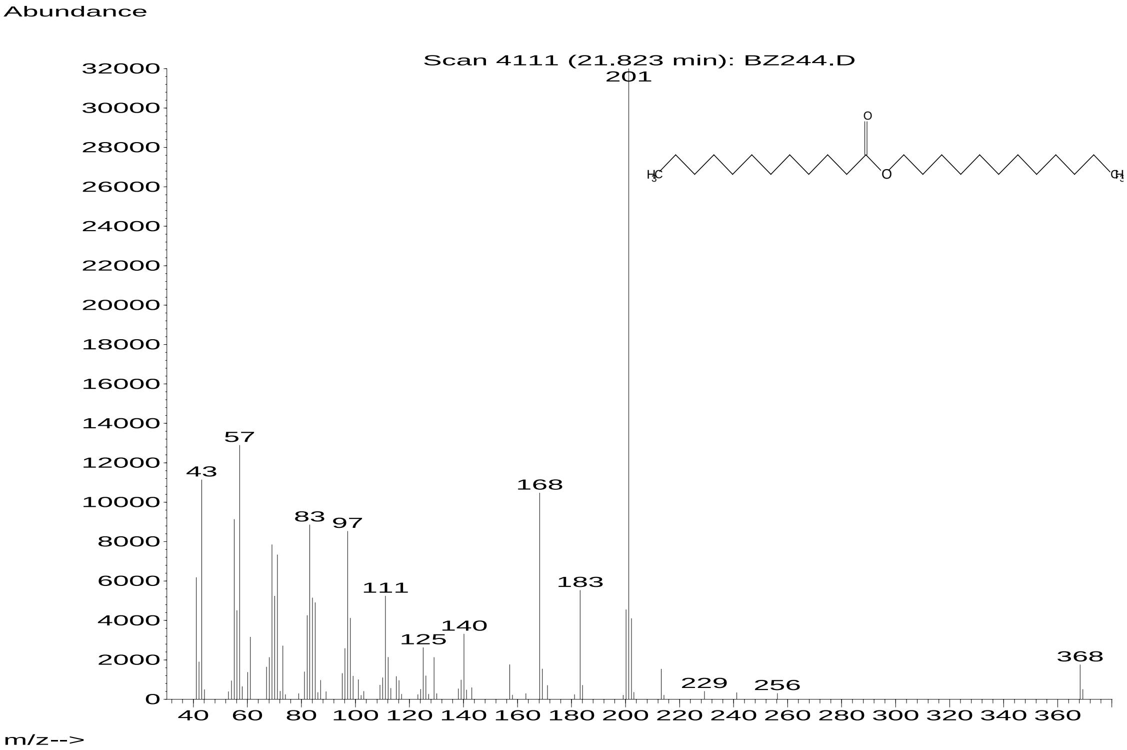

Figure 19: Mass spectra of Lauryl laurate / Dodecanoic acid dodecyl ester.

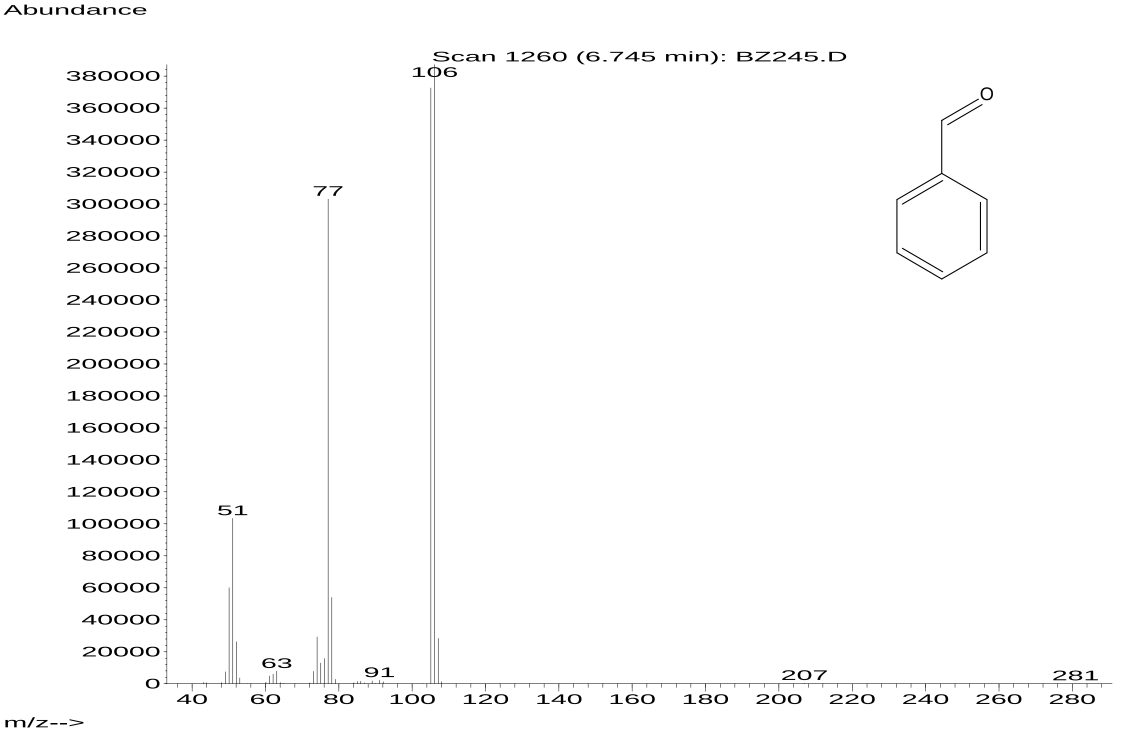

Figure 20: Mass spectra of Benzaldehyde.

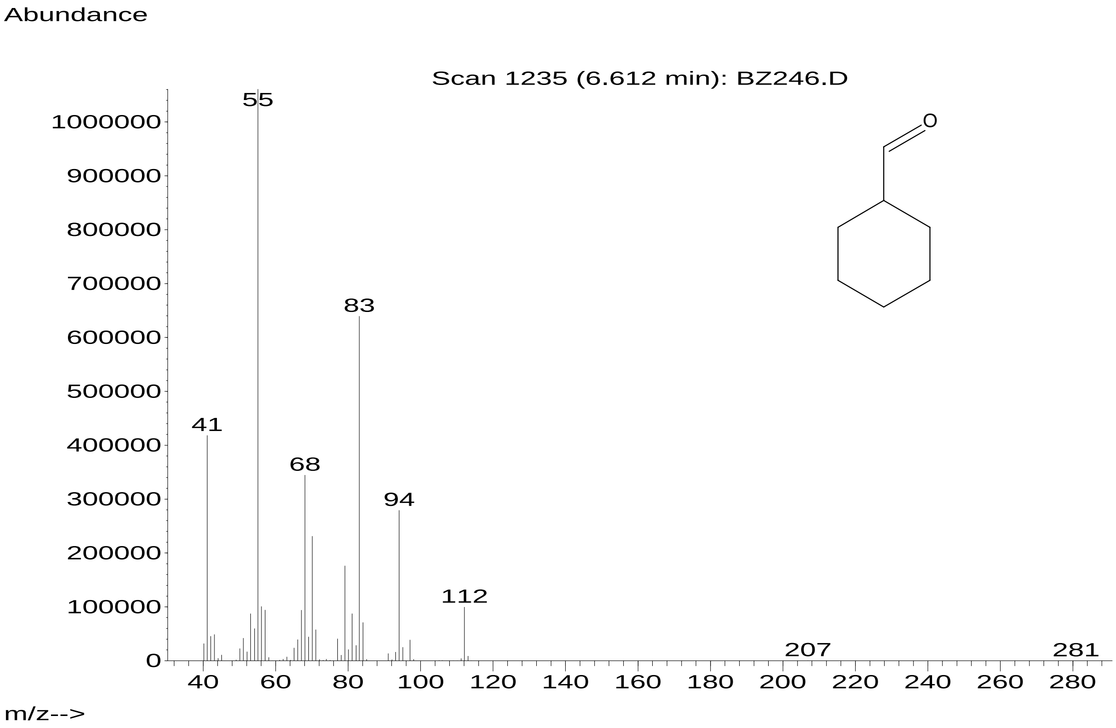

Figure 21: Mass spectra of Cyclohexanecarboxaldehyde.

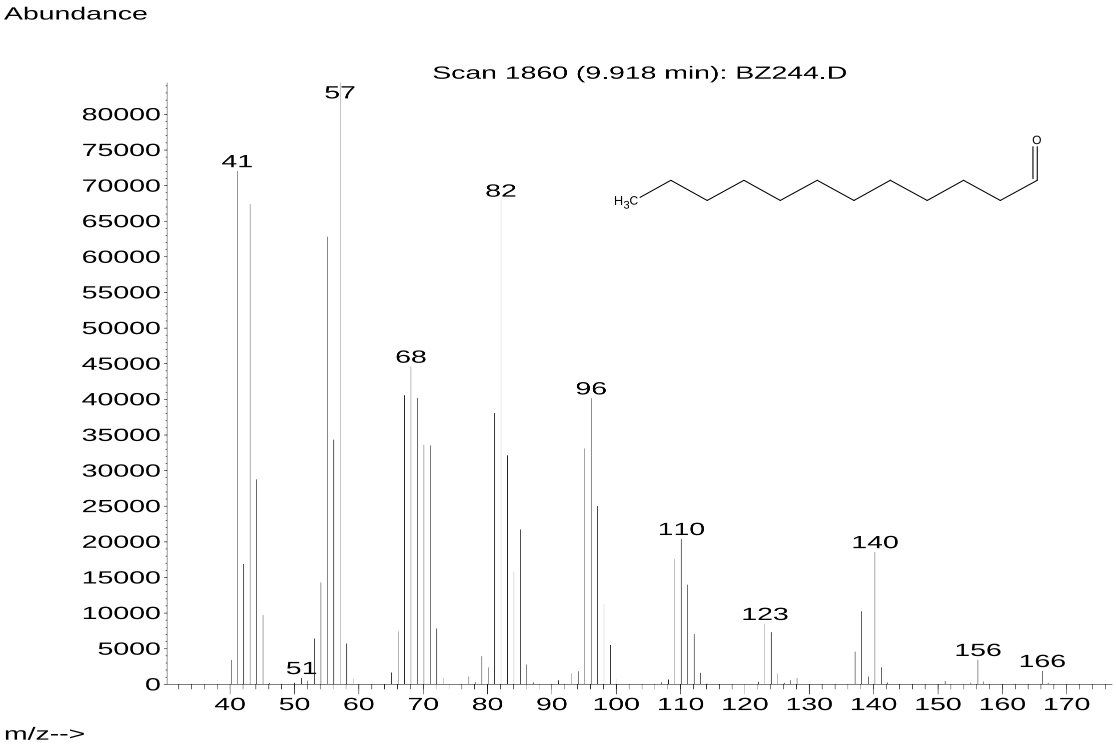

Figure 22: Mass spectra of Dodecanal/Lauraldehyde

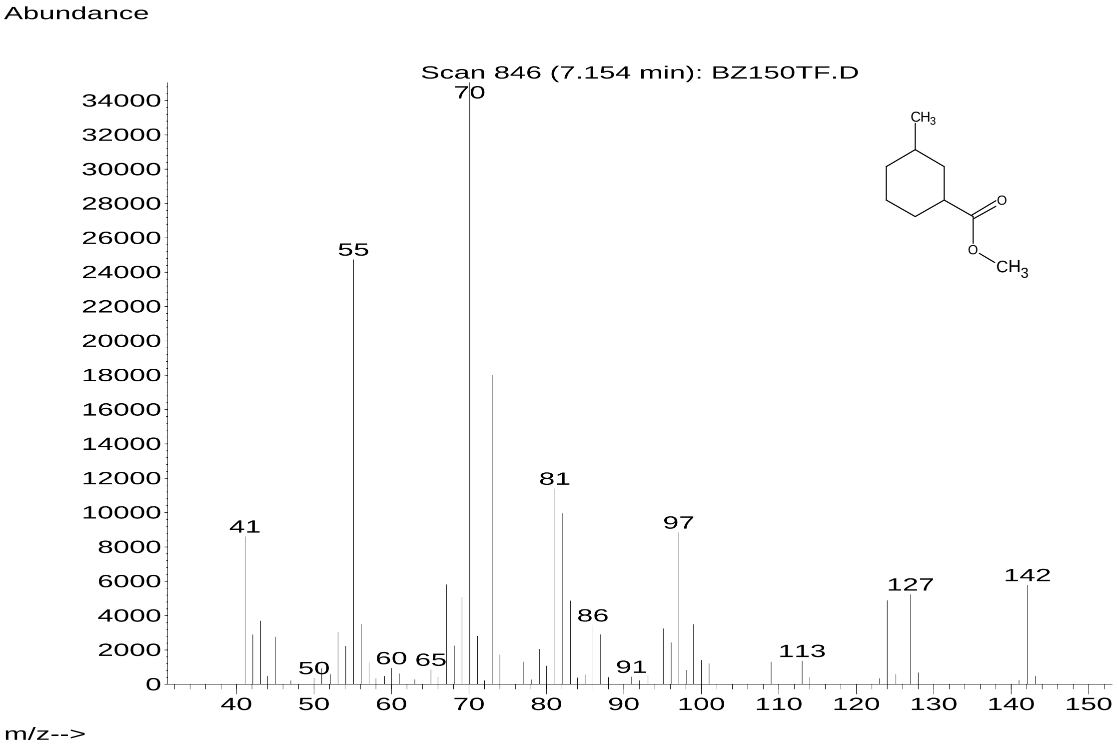

Figure 23: Mass spectra of 3-Methyl cyclohexane carboxylic acid, methyl ester.

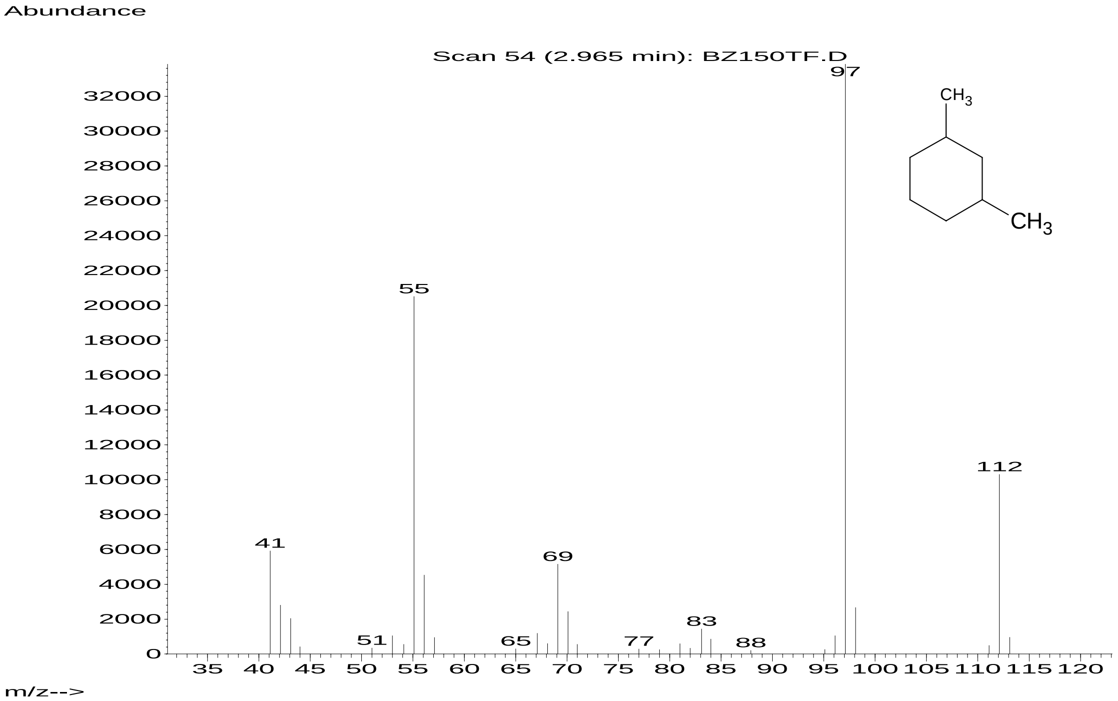

Figure 24: Mass spectra of 1,3-Dimethyl cyclohexane.

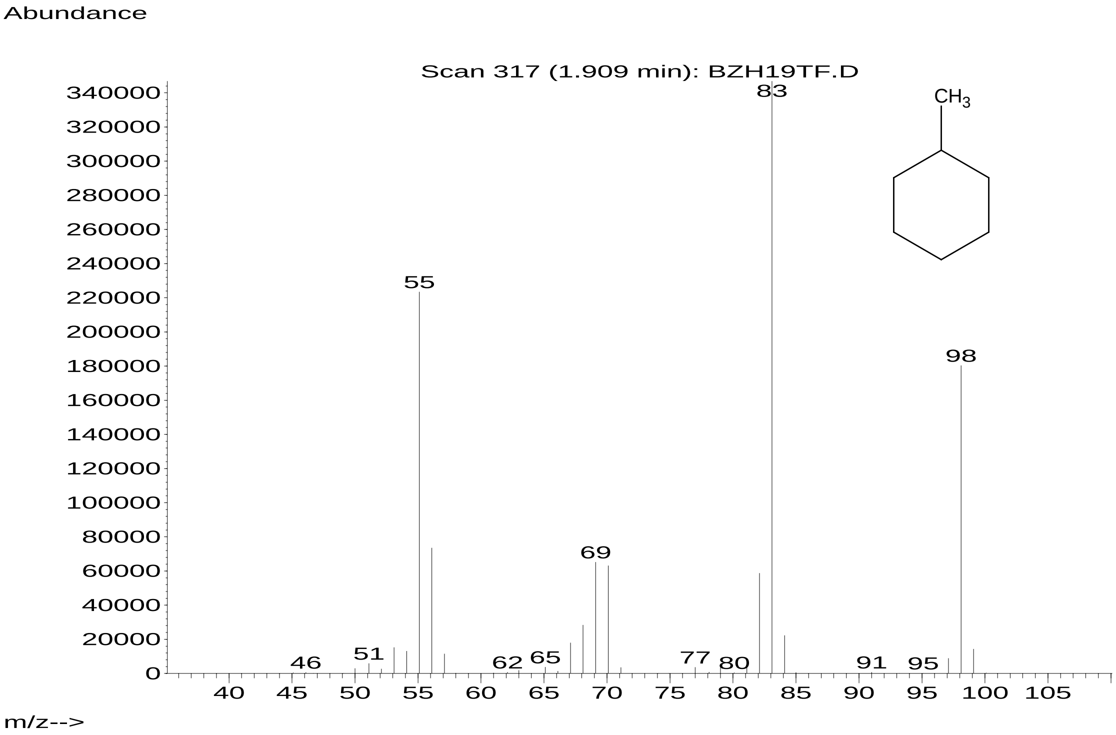

Figure 25: Mass spectra of Methyl cyclohexane

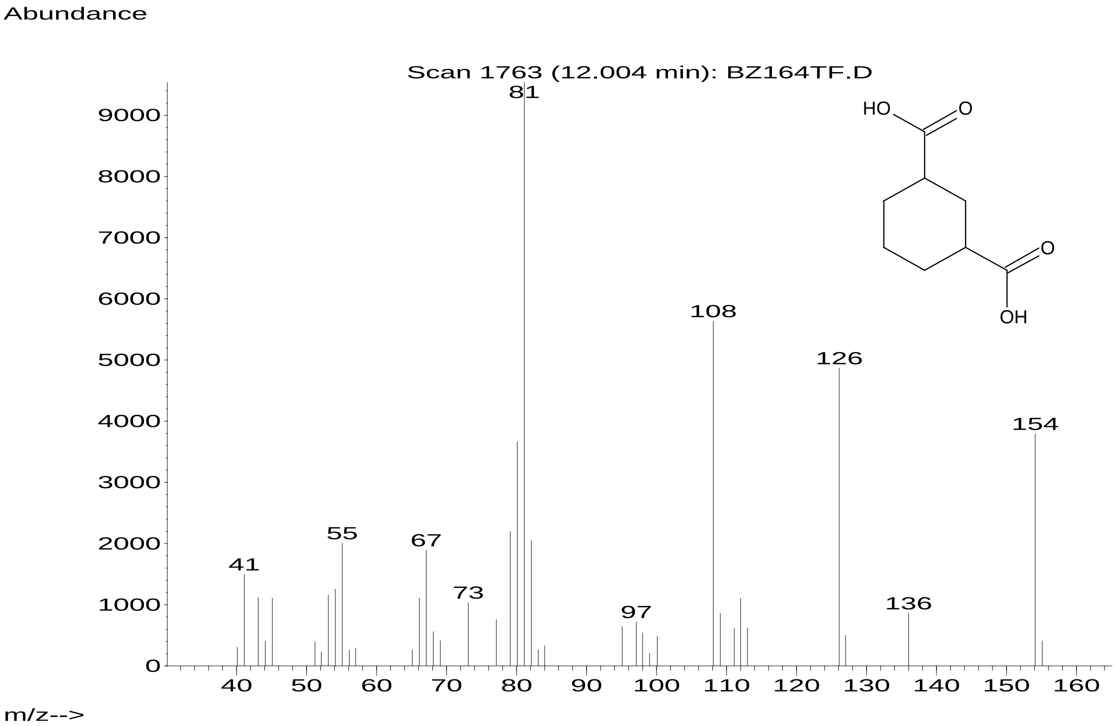

Figure 26: Mass spectra of 1,3-Cyclohexane dicarboxylic acid

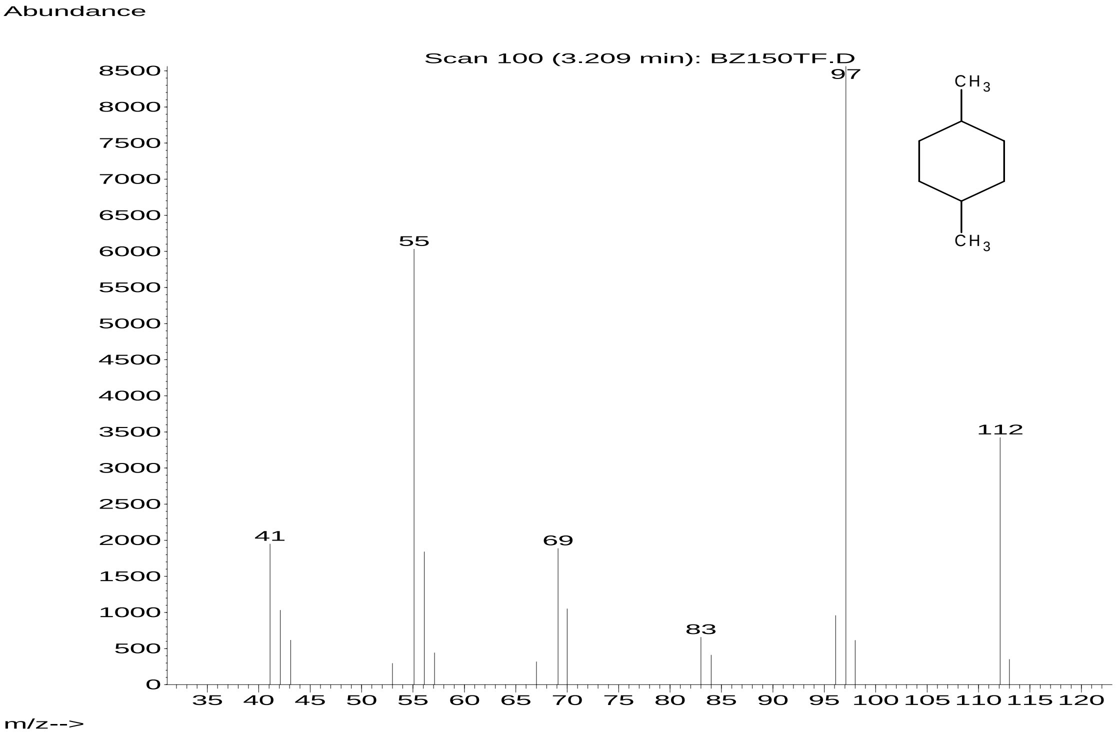

Figure 27: Mass spectra of 1,4-Dimethyl cyclohexane.

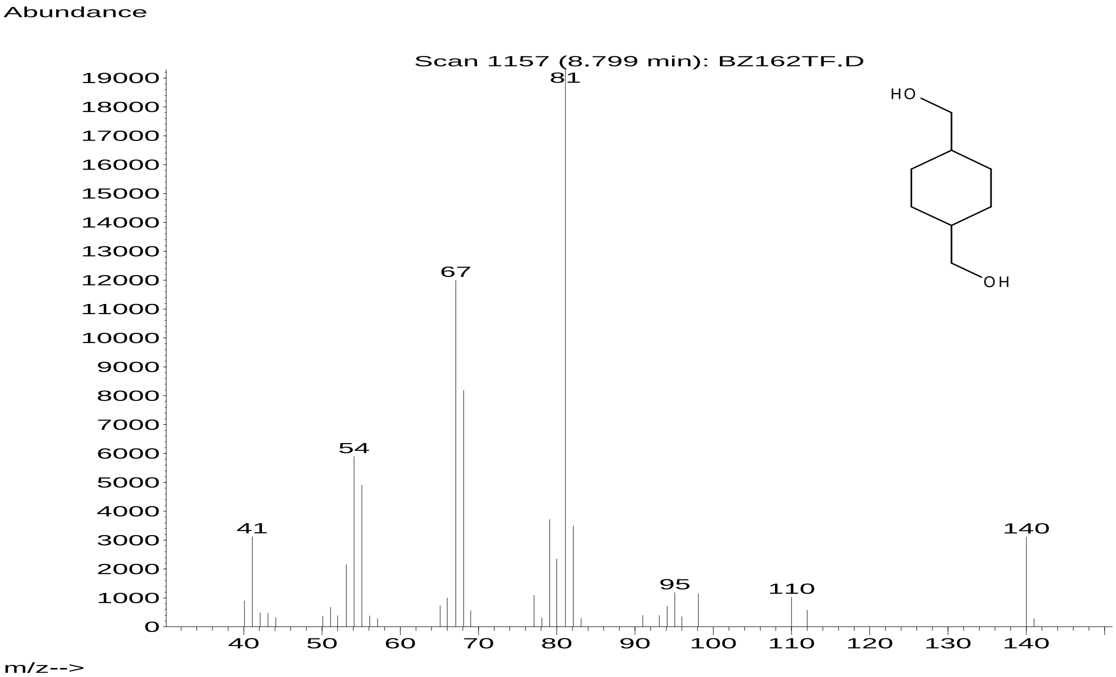

Figure 28: Mass spectra of 1,4-Cyclohexane dimethanol

.

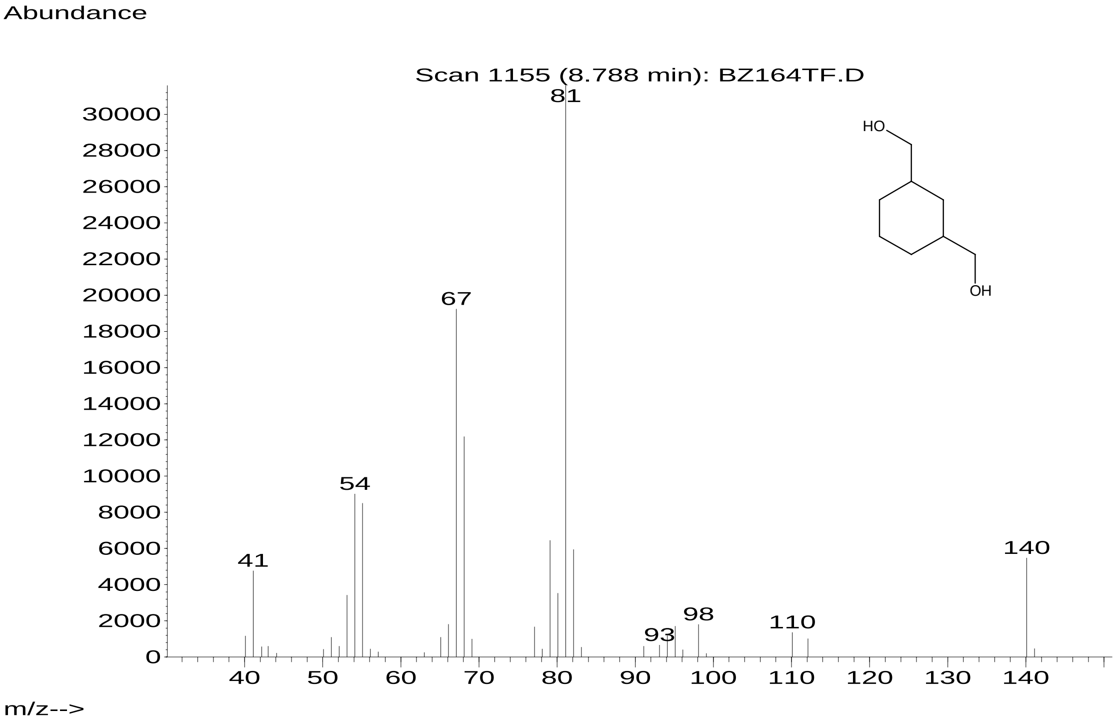

Figure 29: Mass spectra of 1,3- Cyclohexane dimethanol.

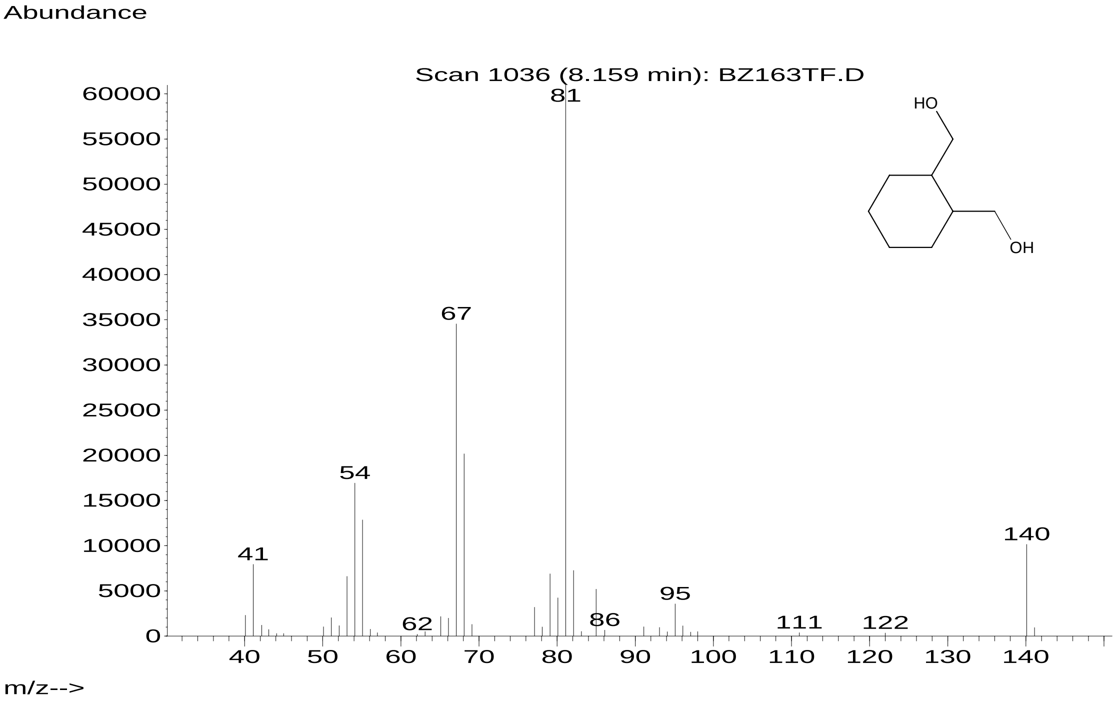

Figure 30: Mass spectra of 1,2-Cyclohexane dimethanol.

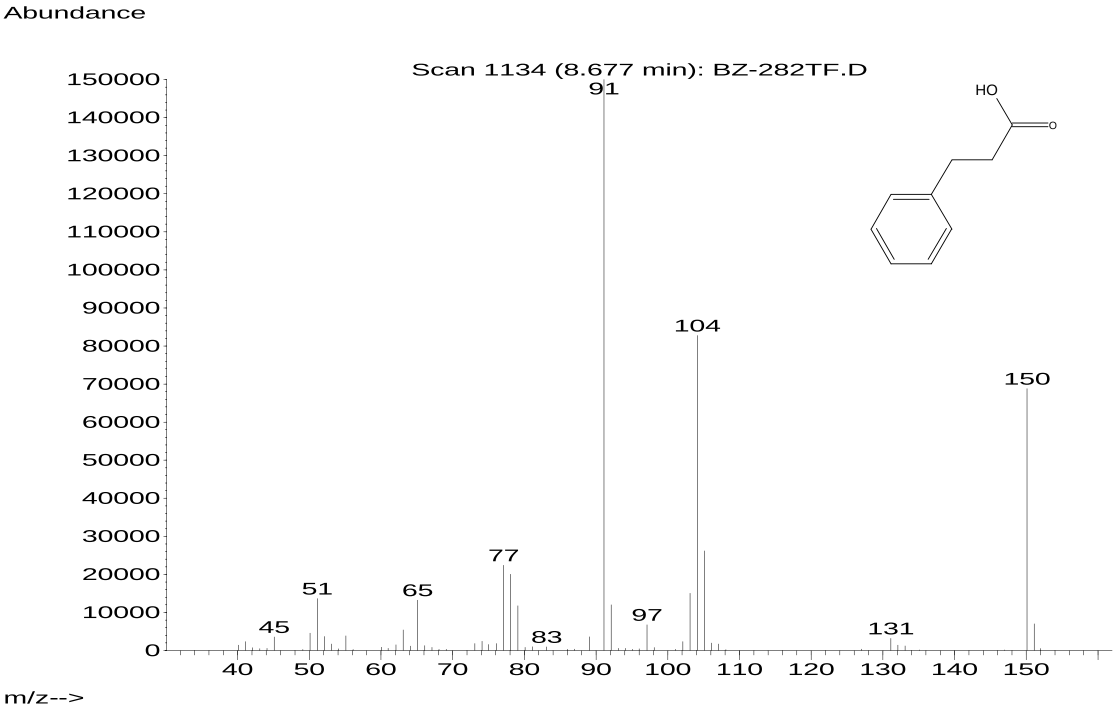

Figure 31: Mass spectra of Benzene propanoic acid.

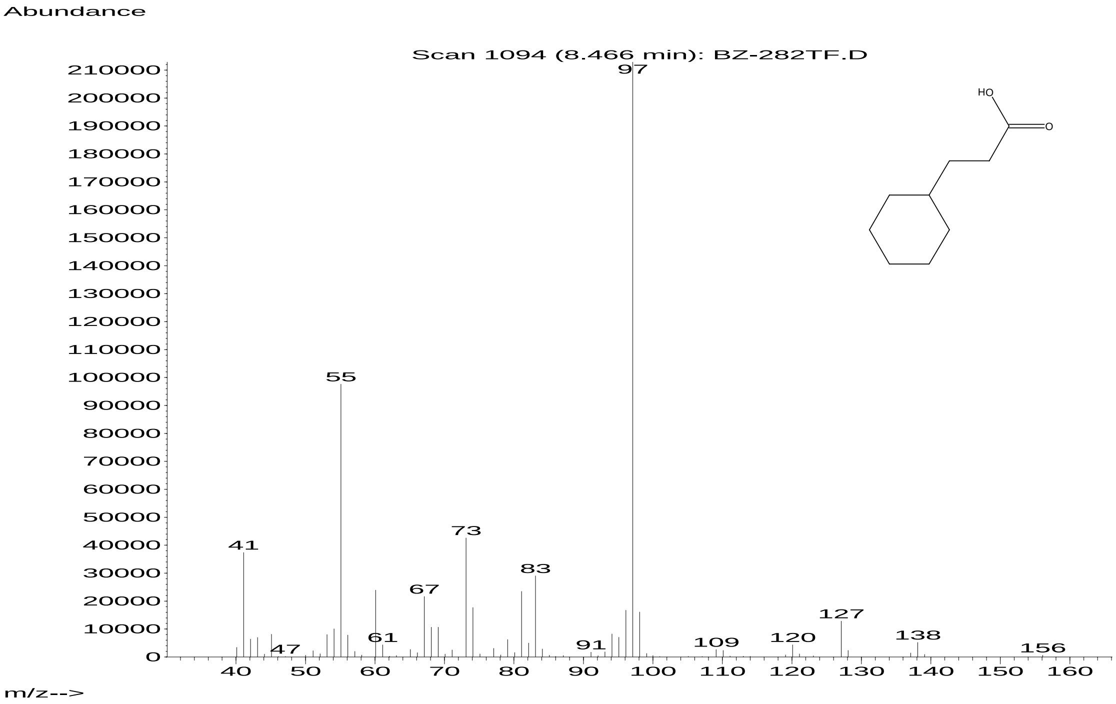

Figure 32: Mass spectra of Cyclohexane propanoic acid.

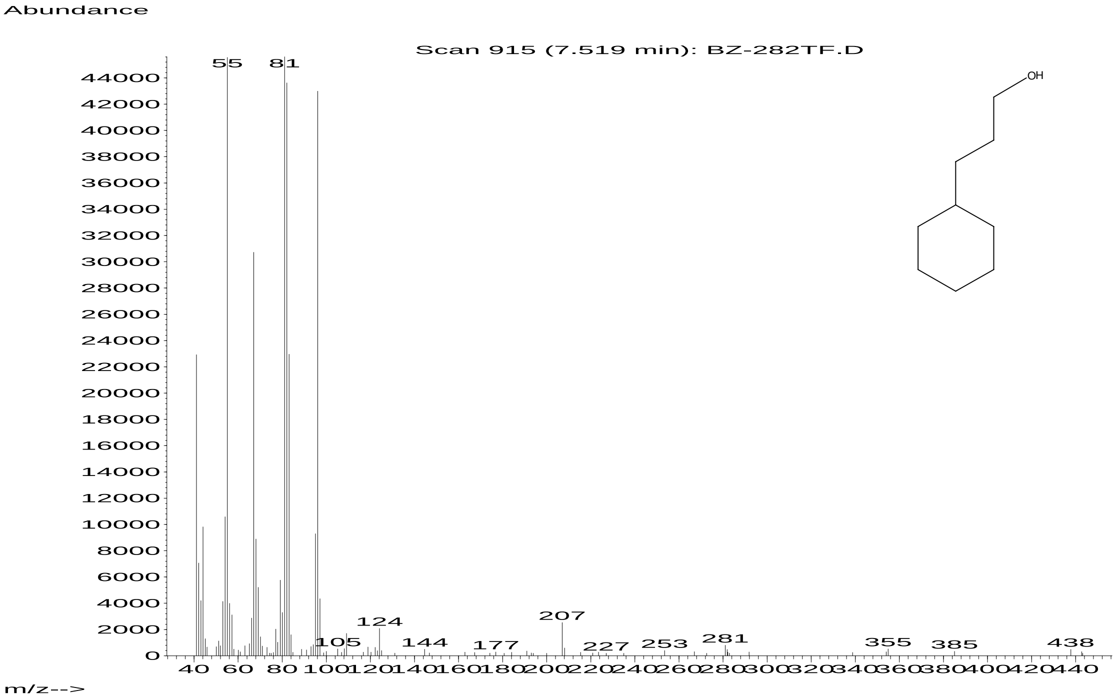

Figure 33: Mass spectra of Cyclohexane propanol.

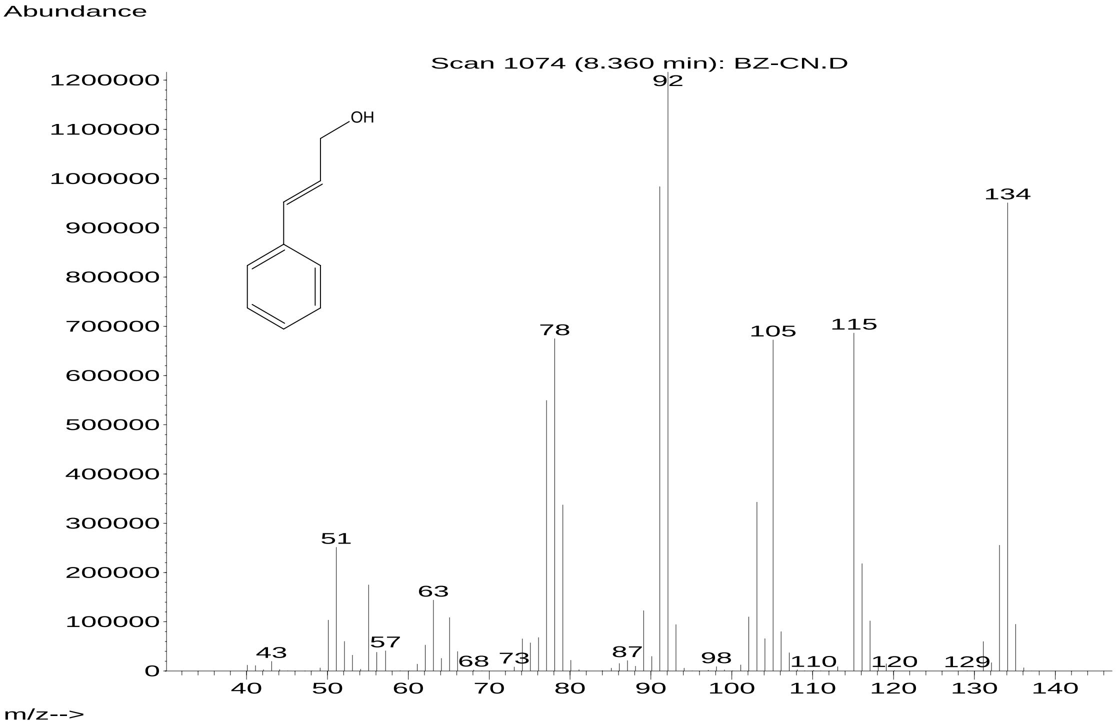

Figure 34: Mass spectra of Cinnamyl alcohol.

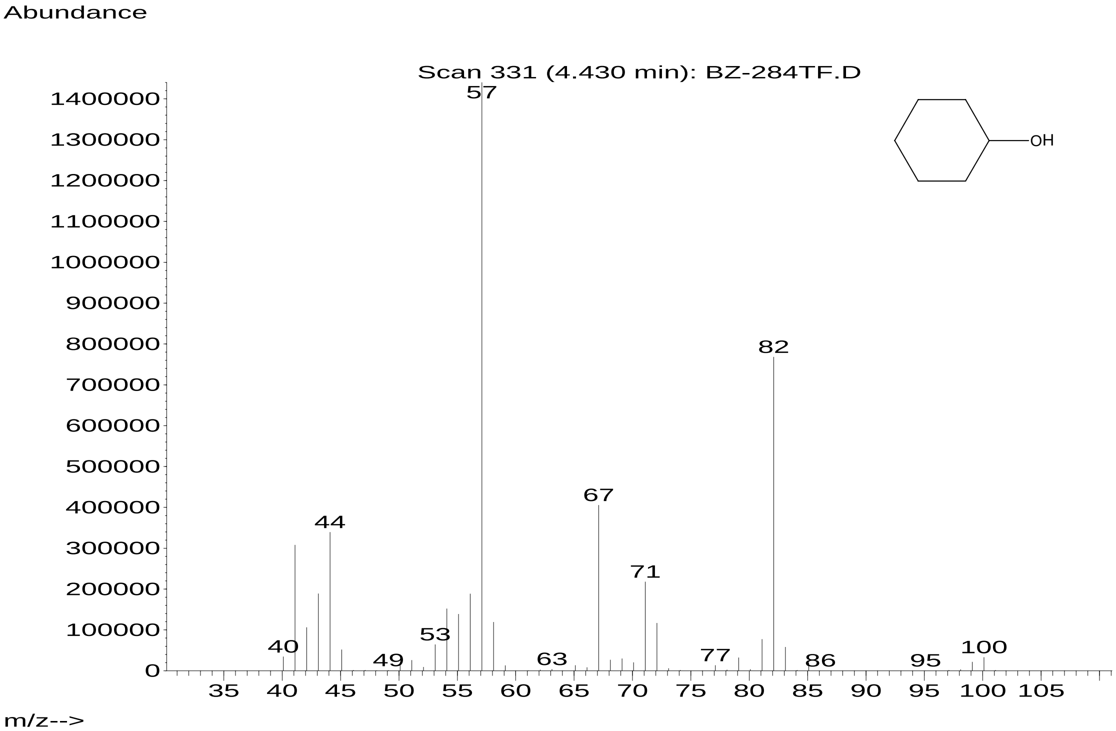

Figure 35: Mass spectra of Cyclohexanol.

Publications/Symposia

- Kinetics of hydrogenation of benzoic acid in a batch slurry reactor using 5% Ru/C catalyst

  S. B. Shinde, R. M. Deshpande and R. V. Chaudhari

  Proceedings of International Conference on Molecules to Materials, 2006, pp 284-288.
- Hydrogenation of benzoic acid.

  S. B. Shinde, R. M. Deshpande and R. V. Chaudhari

  Poster Presentation, Science Day, National Chemical Laboratory, Pune, India, February 2004.
- Kinetics of hydrogenation of benzoic acid in a batch slurry reactor using 5% Ru/C catalyst

  S. B. Shinde, R. M. Deshpande and R. V. Chaudhari

  Oral Presentation in International Conference on Molecules to Materials (ICMM) , 2006, at Punjab, India, March 3-4, 2006.
- A new approach for the determination of time for attainment of maximum concentration (t_{max}) of intermediate product in consecutive reactions using heterogeneous catalysts

  S. B. Shinde, R. M. Deshpande and R. V. Chaudhari

  Poster Presentation in 6th International Symposium on Catalysis in Multiphase Reactors (CAMURE-6) and 5th International Symposium on Multifunctional Reactors (ISMR-5), Pune, India, January 14-17, 2007.
- Development of catalyst for chemoselective hydrogenation of benzoic acid to benzyl alcohol

  S. B. Shinde, R. M. Deshpande and R. V. Chaudhari

  Poster Presented in 18th National Symposium and Indo-US Seminar on Catalysis, Dehradun, India, April 16-18, 2007.