Manisha_Dohade_Thesis

by Manisha Dohade

Chemistry of conversion of furans into value added chemicals using supported metal catalysts

By

Manisha Genulal Dohade

(Enrollment No. 10CC11J26093)

CERTIFICATE

This is to certify that the work incorporated in this Ph.D. thesis entitled "**Chemistry of conversion of furans into value added chemicals using supported metal catalysts**" submitted by **Ms. Manisha Genulal Dohade** to Academy of Scientific and Innovative Research (AcSIR) in fulfilment of the requirements for the award of the Degree of **Doctor of Philosophy in Chemistry,** embodies original research work under my supervision/guidance. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the thesis. Any text, illustration, table etc., used in the thesis from other sources, have.been duly cited and acknowledged.

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Declaration by the candidate

I hereby declare that the thesis entitled "**Chemistry of conversion of furans into value added chemicals using supported metal catalysts**" submitted for the award of the Degree of **Doctor of Philosophy in Chemistry,** to the **Academy of Scientific & Innovative Research (AcSIR),** New Delhi, has been carried out by me at Catalysis & Inorganic Chemistry Division, Council of Scientific and Industrial Research-National Chemical Laboratory, Pune-411008, India, under the supervision of Dr. Paresh L. Dhepe. Research material received from other sources has been duly cited and acknowledged in the thesis. The work is original and has not been submitted as a part or full by me for any degree or diploma to this or any other university.

Date: 13ᵗʰ October, 2017

Place: CSIR-NCL, Pune

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Dedicated to . . . .
My Parents

Brothers and sister

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……………Manisha

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List of Abbreviations

C	Carbon
C-HT	Calcined Hydrotalcite
CPO	Cyclopentanone
CPL	Cyclopentanol
2,5-DMF	2,5-dimethylfuran
2,5-DMTHF	2,5-dimethyltetrahydrofuran
FID	Flame Ionization Detector
FDCA	2,5-furandicarboxylic acid.
FAL	Furfural
FOL	Furfuryl Alcohol
2-MF	2-methylfuran
2-MTHF	2-methyltetrahydrofuran
5-MF	5-methylfurfural
GC	Gas Chromatography
H-ZSM	Zeolite Socony Mobil (H-form)
HMF	5-hydroxymethylfurfural
HPLC	High Performance Liquid Chromatography
HT	Hydrotalcite
ICP-OES	Inductively Coupled Plasma-Opticle Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
NMR	Nuclear Magnetic Resonance
RPM	Rotation per Minute
SMSI	Strong Metal-Support Interaction
TEM	Transmission Electron Microscopy
TOF	Turn Over Frequency
TON	Tons Over Number
THF	Tetrahydrofuran
THFOL	Tetrahydrofurfuryl Alcohol
TOPV	Total pore volume
TPR	Temperature Programmed Reduction
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Abstract of thesis

Introduction

      Lignocellulosic biomass is gaining importance in synthesis of various valuable chemicals and fuels due presence of various functionalities in its structure. Lignocellulosic biomass mainly contains cellulose, hemicelluloses and lignin.[1] The components of these lignocelluloses can be separated into individual compound by physical, chemical or biological treatment.[2-4] The cellulose on hydrolysis produces glucose which on further dehydration produces 5-hydroxymethyl furan (HMF).[5] Hemicelluloses on hydrolysis produces xylose which on dehydration produces furfural (FAL).[6] Both HMF and FAL contains carbonyl functional group which on hydrogenation form furan derived alcohols.[7] These furan derived alcohols have much importance in industrial point of view for synthesis of resins, polymer and other valuable chemicals and fuel additives like tetrahydrofuran (THF), methylfuran (MF), tetrahydrofurfuryl alcohol (THFA), methyl terahydrofuran (MTHF) etc.[6-8] FAL in water medium gets converted in to cyclopentanone (CPO) and cyclopentanol (CPL) which are used for intermediate in medical and perfumed product.[9, 10] Also sugar alcohol like sorbitol and xylitol[11, 12] derived from biomass derived glucose and xylose have wide applications due to its important properties like their low caloric value, glycemic index and anti-cariogenicity they are used in food and pharmaceutical industry.[13] Due to these wide applications of furan derived compounds and sugar derived sugar alcohols global demand for this product has been increased. Considering these facts, it was decided to carryout work hydrogenation of furan derived compound to value added product and also hydrogenation of sugar to sugar alcohol for development of efficient recyclable catalytic process to get better yield of desired product.

      My thesis is divided into seven chapters. chapter one comprises introduction of biomass and biomass derived chemicals, their applications and literature survey. Second chapter includes detailed study for synthesis and characterization of catalyst. Third to sixth chapter includes the results and discussion of all catalytic results including conversion of FAL to FOL, FAL to MF, FAL to CPO, HMF to DMF sugar to sugar alcohol. Seventh chapter comprises summery and conclusion of the thesis.

Problems related to reported method

➢   Use of dilute system: not feasible for industrial application.

- ➤ Use of organic solvent: organic solvent like methanol, ethanol, iso-propanol (IPA) were used preferentially instead of water.
- ➤ High pressure reactions: H_2 pressure in the range of 3-8 MPa were used it makes the process costlier.
- ➤ Leaching of metal: it increases the process costs due to separation of metals from desired product.
- ➤ Deactivation of catalyst: oxidation of active metal during reaction leads to deactivation and requires further reduction treatment.
- ➤ Recyclability of catalyst: due to deactivation of catalyst it cannot be used repeatedly

In view of these limitations it is required to develop an efficient, clean and stable catalytic system at lower H_2 pressure and milder temperature for hydrogenation reactions.

Methodology

- ❖ Various mono and bimetallic catalyst were synthesized from Pt, Co, Ni, Ru and Cu metals and carbon as support by wet-impregnation method.
- ❖ The morphology and chemical nature of catalyst were characterized by various techniques like N_2 physisorption, TPR, TEM, EDAX, XRD, XPS etc.
- ❖ Catalytic reactions were done by Amar make reactor in batch process.
- ❖ Catalyst activity was studied for conversion of FAL to FOL, FAL to MF, FAL to CPO, HMF to DMF and sugar to sugar alcohol.
- ❖ Various reaction parameters like effect of temperature, time, solvent, H_2 and N_2 pressure, concentration of substrate, substrate to catalyst ratio etc. were studied in detailed.

Results of catalytic reactions

Conversion of FAL to FOL:

Conversion of FAL to FOL was studied with different mono and bimetallic catalyst with varying reaction conditions like, temperature, H_2 pressure, solvent, time. It was found that at 100 °C for 5 h, in presence of IPA and 10 bar H_2 the conversion of FAL was complete with 100% yield of FAL. Further reaction was carried out at 50 °C for 10 h under similar reaction condition the conversion reaches to 92% with 91% yield of FOL. In order to carry out reaction at lower temperature it was carried out at 35 in water medium for 10 h it was showing complete conversion with 100% selectivity of FOL. reaction was carryout at 1 bar H_2 for 1 bar H_2 it was

showing 100% yield of FOL. In order to make the process industrially feasible concentrated system was used up to 40% FAL (Table 1) and it was showing 20% FAL with 100% yield and 40% FAL shows 86% yield of FAL with100% conversion.

Table 1. Effect of FAL concentration on the hydrogenation in water as a reaction medium

Entry no.	FAL (wt%)	Temperature (°C)	Time (h)	FAL conversion (%)	FOL yield (%)
1[a]	5	35	10	98	98
2	20	35	10	50	49
3	20	50	6	100	100
4	40	50	6	100	86
5	40	100	3	83	28

Reaction condition: FAL; Pt(3)Co(3)/C; Substrate/Catalyst ratio, 4.45 (wt/wt); water, 35 mL; H_2, 1 MPa pressure was maintained during the reaction by charging H_2 intermittently; 900 rpm; FAL: Furfural, FOL: Furfuryl alcohol. [a] H_2, 1 MPa was charged at room temperature and during reaction no additional H2 was charged in the reactor

Conversion of FAL to MF

One pot conversion of FAL to MF was carried out at 10 bar H_2 180 °C in presence of Pt(3)Co(3)/C catalyst for 8 h in IPA. Under optimized condition 56% yield of MF was obtained with THFA, MTHF and FOL as side product. Effect of N_2 pressure was studied to check proton donor ability of IPA solvent for catalytic transfer reaction. It was observed that at 180 °C 10 bar N_2 80% conversion of FAL with 66% FOL and 14% MF yield was observed. Further increased in N_2 pressure to 20 bar showing no improvement in result with 76% conversion of FAL and 62% yield of FOL with12% yield of MF was observed. This shows that IPA acts as proton donor under reaction condition.

Conversion of FAL to CPO

The conversion of FAL to FOL was carried out in monophasic i.e. water medium as well as in biphasic water: toluene solvent ratio in presence of Pt(3)Co(3)/C catalyst. The results of bi-phasic solvent system are better than mono-phasic solvent system. To optimize the biphasic solvent ratio reaction were carried out with varying water toluene ratio as shown in Figure 2
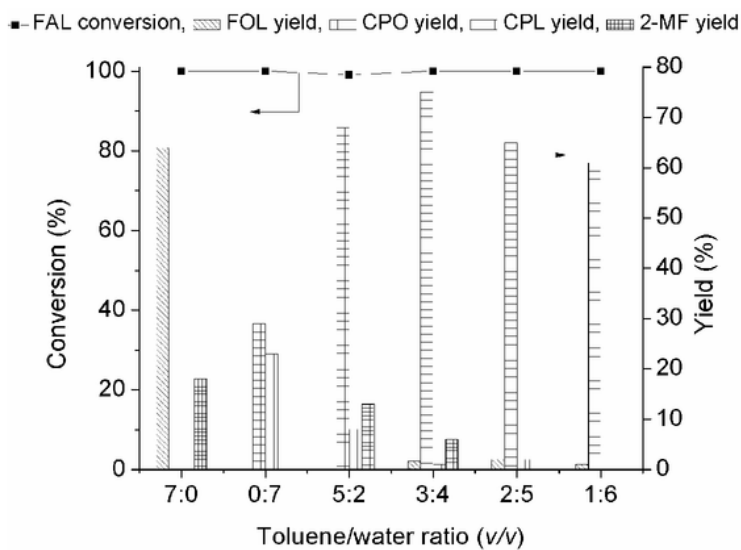
Figure 2. Effect of varying toluene/water *v/v* solvent ratio on conversion of FAL to CPO Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; toluene/water 3:4 (v/v), 35 mL; H_2 Pressure 1 MPa at room temperature; 180 °C; 5 h; 900 rpm, (FAL: furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, CPO: cyclopentanone, CPL: cyclopentanol) .

It was observed that 3:4 toluene water ratio is showing best result compared to all. The best result with 3:4 toluene water ratios is due to solubility of substrate and intermediate product in two different solvents. From the solubility study of FAL, FOL and CPO it was observed that furfural is highly soluble in toluene, FOL is highly soluble in water and CPO is highly soluble in toluene however catalyst is dispersed at interface between toluene and water. Hence furfural which is present in toluene gets converted to FOL and FOL on cyclic ring arrangement in water and get converted to CPO. Hence it is believed that biphasic solvent ratio selectively extracts CPO into toluene layer and increase the rate of conversion of FOL to CPO in water.

Conversion of sugar to sugar alcohol

The hydrogenation of glucose and xylose were performed in water medium by using Pt(3)Co(3)/C and Ru(3)/C catalyst and 2-10 bar H_2. The comparison study of both catalyst shows Ru(3)/C the best catalyst compared to Pt(3)Co(3)/C bimetallic catalyst. Further reactions were carried out at 40 wt% sugar concentration at 10 bar H_2, 100 °C in presence of Ru(3)/c catalyst, Table 2 and it was found that the conversion of sugar was complete with 98% yield of xylitol and

98% yield of sorbitol. Also in presence of Ru(3)/C catalyst the complete conversion of sugar to sugar alcohol was observed under 2 bar H_2 with <95% selectivity for sugar alcohol.

Table 2. Conversion of concentrated solution of sugar to sugar alcohol

Entry No.	Time (h)	Temperature (°C)	Substrate 40 wt%	Substrate Conversion (%)	Yield (%)
1	5	100	Xylose	100	Xylitol 98
2	5	120	Glucose	100	Sorbitol 98

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Chapter 1
Introduction and Literature Survey

1.1 Introduction

1.1.1 Biomass a better substitute to fossil feedstock

The biomass, sun, wind, water and geothermal are the renewable sources for the production of energy however biomass is the only renewable resources for the synthesis of liquid transportation fuels and chemicals. Before the start of petrochemical era in 1920-1930's biomass derived chemicals and fuels were promoted in a significant way in United States.[1] However from 1920-1950's again transition from renewable to non-renewable based economy was started. This leads to high dependence on non-renewable fossil feedstock for the synthesis of daily requisite transportation fuels and chemicals however its availability is limited in nature and huge time is required (millions of years) for its formation. The growing demand of energy, fuels and chemicals in day to day life increased the consumption rate of fossil feedstock attributed to its depletion. The transition of economy from non-renewable to renewable source occurred after 1st oil crises in 1970's. Reasons behind this transition of economy are decreasing resources, political issues and also the adverse effects of released CO_2 during consumption of fossil feedstock on the environment like global warming and environmental pollution.[2-4] Moreover renewable lignocellulosic biomass is the most promising natural and renewable resources in modern industrial society compared to fossil feedstock. It is economical, efficient and easily available alternative[5-9] which is explained in the next coming section. However, besides the huge potential of biomass, unfortunately currently much of the lignocellulosic biomass is used for burning process for the energy generation.

Hence researchers have focused on utilization of various byproducts derived from agricultural practices (separation of edible part from crop plant) for synthesis of fuels and chemicals.

1.1.2 Biomass sources

Biomass generally refers to organic materials derived mostly from plants and also from animals which may be used as feedstock in agriculture and industry. Major sources of biomass are agriculture feedstock, energy crop, lignocellulosic biomass and aquatic plant[8, 10] the examples are mentioned bellow (Figure 1.1).

Agricultural feedstock

Sugar crop - sugar cane, sugar beet

Starch crop - maize, potato

Oil crop - rapeseed oil, soya

Energy crop

Perennial grass - miscanthus, switch grass

Non edible oil plant - jatropha, sorghum

Lignocellulosic biomass

Forest product - lodging residue, tree, shrub

Agriculture crop waste - straw, corn stover, rice husk, barley hull, corn stalks

Industry by - product- bagasse, paper pulp

Aquatic plant

Aquatics weed, Algae

Figure 1.1 Biomass resources

1.1.3 Significance of biomass feedstock

Among the above mentioned sources the lignocellulosic biomass derived from agricultural crop waste is considered to be the best source for the synthesis of chemicals and fuels due to its following properties,

Renewable: takes less time for its re-generation compared to fossil feedstock.

- *Cost effective*: cheaply available.
- *Carbon neutral*: during photosynthetic process plants consumes CO_2 and convert it in carbohydrate which makes the process eco-friendly (Figure 1.2).

- *Non edible*: it is non edible to humans hence dose not compete with food.
- *Abundant availability:* in general the annual production of crop residue in India is 686 MT.[11-13] and annual global production of crop residue is 9667 MT.[14]

Hence lignocellulosic biomass is considered as a sustainable feedstock for the formation of transportation fuels and fine chemicals with net zero carbon emission.[15-18]
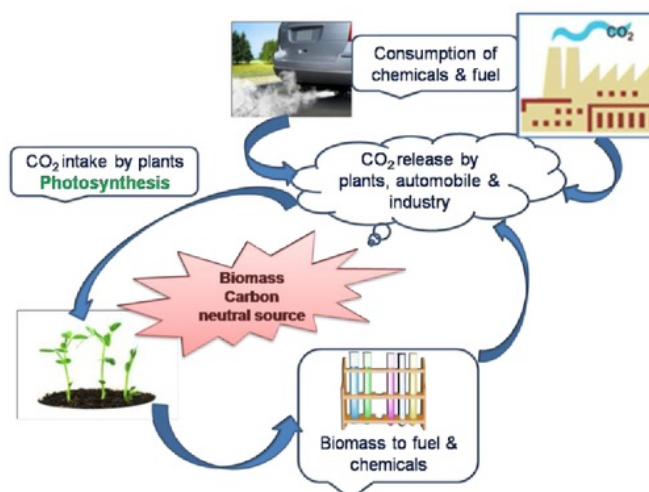
Figure 1.2 Biomass a carbon neutral source for the synthesis of fuel and chemicals

1.2 Chemical composition and structure of lignocellulosic component

1.2.1 Chemical composition of lignocellulosic biomass

The elemental composition of biomass is majorly carbon (47-53%), hydrogen (5.9 to 6.1%), oxygen (41 to 45%)[19] with small amount of nitrogen, sulfur and some minerals like Na, K, Fe, Mn, P, Mg.[20] The biomass feedstock contains more oxygen in its composition than fossil feedstock hence it is more economical to produce chemicals from biomass feedstock than production of fuels. Among the different sources of biomass lignocellulosic biomass contains cellulose 35–50%, hemicelluloses 20–35% and lignin 10–25%.[8,17] Besides this it also contains protein, fats, oil, wax, ash and minerals like Na, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn[21-23] It is estimated that nearly half of the organic carbon in the biosphere is present in the form of cellulose[11-12,24] and around 7.5×10^{10} tonnes of it is consumed for conversion to fuel and valuable chemicals and regenerated every year.[25] The composition of lignocellulose depends on the type

of sources and varies in softwood, hardwood and grasses. Table 1.1 summarizes the composition of lignocellulose in most of the common biomass source.[26-28]

Table 1.1. Composition of lignocellulose in different sources on dry basis.[26]

Entry No.	Lignocellulosic biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
1	Hardwood stems	40–55	24–40	18–25
2	Softwood stems	45–50	25–35	25–35
3	Nut shells	25–30	25–30	30–40
4	Corn cobs	45	35	15
5	Grasses	25-40	35-50	10-30
6	Paper	85-99	0	0-15
7	Wheat straw	30	50	15
8	Sorted refuse	60	20	20
9	Leaves	15-20	80-85	0
10	Cotton seed hairs	80-95	5–20	0
11	Newspaper	40-55	25-40	18-30
12	Waste papers from chemical pulps	60-70	10–20	5–10
13	Primary wastewater solids	8–15	NA	24–29
14	Swine waste	6	28	NA
15	Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
16	Coastal Bermuda grass	25	35.7	6.4
17	Switch grass	45	31.4	12

1.2.2 Structure of cellulose

Cellulose is a carbohydrate polymer made up of D-glucopyranose units linked by β-1,4-glycosidic bonds and form a long chain of polymer (Figure 1.3). It is crystalline in nature due to ordered arrangement of hexoses (glucose). Inter-molecular H-bonds are formed between the hydroxyl groups of one chain with the hydroxyl groups of adjacent parallel chain.[17, 29] The fusion

of several polymer chains leads to the formation of microfibrils which in turn are united to form fibers.
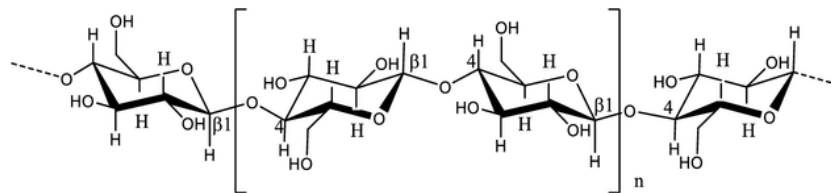
Figure 1.3 Structure of cellulose

1.2.3 Structure of hemicellulose

Hemicellulose is the hetero-polymer made up of pentoses (xylose, arabinose) and hexoses (mannose, glucose, galactose) with short branches on polymer chain which are arranged randomly and hence are amorphous in nature (Figure 1.4).[30-32] Mostly xylan and glucomannan are found in hardwood and softwood respectively.[32-33] In hardwood xylan the back bone chain is made up of xylose unit which are linked by β-(1,4)-glycosidic bond and branched by β-(1,2)-glycosidic bond with 4-O-methyl glucuronic acid group. In addition, the -OH group at C2 and C3 positions sometimes replace O-acetyl group. Depending on the presence of pentoses and hexoses they are grouped as xylan, xyloglucan, glucomannan, galactomannan, glucuronoxylan, arabinoxylan and xyloglucan.
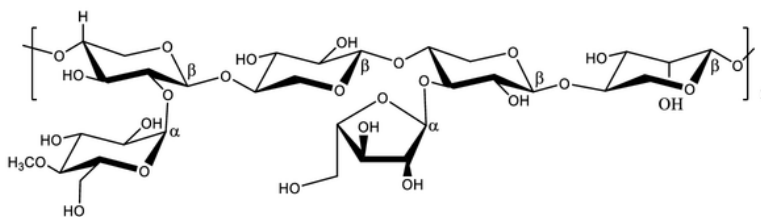
Figure 1.4 Structure of hemicelluloses (xylan)

1.2.4 Structure of lignin monomers

Lignin is a class of complex biopolymer made up of, cross-linked, three-dimensional polyphenolic aromatic network. It is composed of phenylpropane units which are linked to each other by the irregular C–C and C–O bond linkages. Three basic structural monomers unit of lignin are: *p*-phenyl monomer (*H* type) derived from coumaryl alcohol, guaiacyl monomer (*G*

type) derived from coniferyl alcohol and syringyl monomer (*S* type) derived from sinapyl alcohol (Figure 1.5).[29, 34-35] Because of the different monomers units, lignin can be divided into three types: *syringyl lignin* polymerized by syringyl propane, *guaiacyl lignin* polymerized by guaiacyl propane and *hydroxy-phenyl lignin* polymerized by hydroxy-phenyl propane. Usually, gymnosperm contains guaiacyl (*G*) lignin; the dicotyledon mainly contains guaiacyl-syringyl (*GS*) lignin; the monocotyledon mainly contains guaiacyl-syringyl-hydroxy-phenyl (*GSH*) lignin.[36] Because of differences in the chemical composition and structure of these lignocellulosic component they show different chemical reactivity.[37-38]

(a): Sinapyl alcohol   (b): Coniferyl alcohol

(c): Coumaryl alcohol
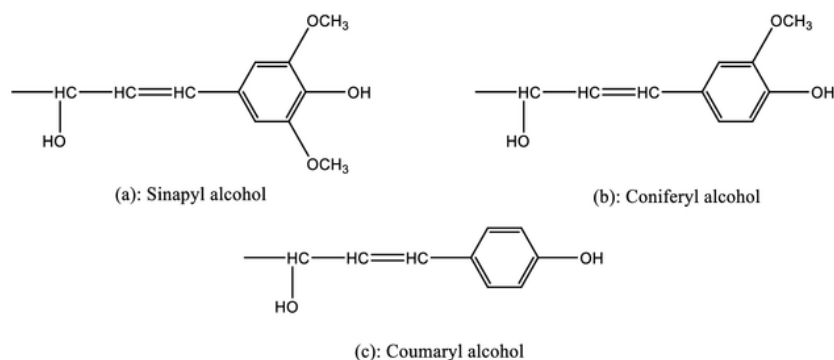
Figure 1.5 Structures of lignin monomers

1.3 Conversion of lignocellulosic biomass to value added chemicals

1.3.1 Chemicals derived from thermo-chemical and bio-chemical process in one pot conversion of lignocellulosic biomass

Different thermo-chemical and bio-chemical processes are used for the direct conversion of lignocellulosic biomass to fuel and value added chemicals (Figure 1.6).[39] Thermo-chemical processes involves a) *combustion*: to produce heat and energy, b) *gasification*: produce various products like hydrogen, alcohols, olefins, gasoline and diesel, c) *hydrothermal*: produce heat and energy, d) *liquefaction*: produce hydrogen, methane, CO and bio-oil, e) *pyrolysis*: produce hydrogen, olefin bio-oil, and speciality chemicals (speciality chemicals are group of chemical with similar functionalities like phenolic fraction which are utilized in production of adhesives, pharmaceuticals or petrochemical industries for production of octane improver).[40] However biochemical process produces bioethanol, biodiesel, biobutanol, methane and speciality chemicals.
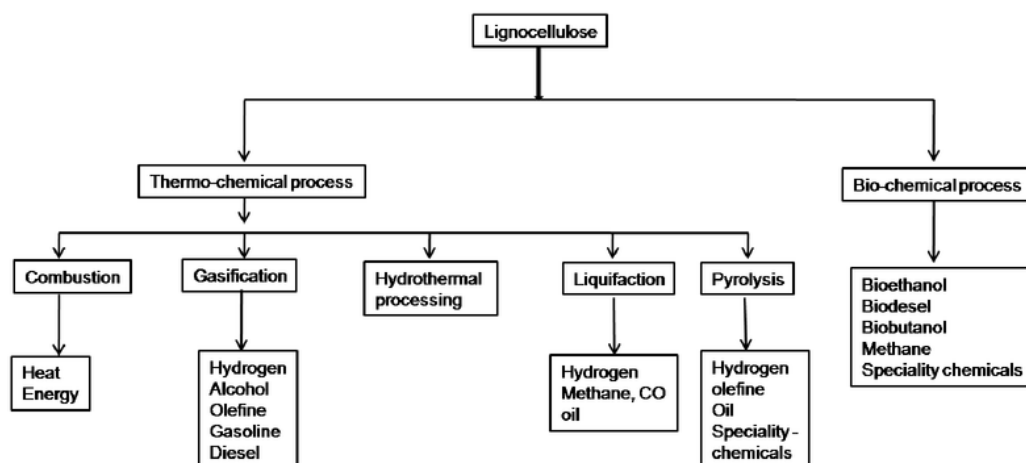
Figure 1.6 Processes for direct conversion of lignocellulosic biomass to energy and chemicals

1.3.2 Pretreatment of biomass

The direct synthesis of chemicals from lignocellulosic biomass in one pot process like pyrolysis is carried out at 400-600 °C in absence of O_2. However it leads to decreased selectivity of desired product(s) due to their thermal degradation. It mainly produces bio-oil that contains the mixture of different products.[41] Mixture of products makes the process complicated due to difficulty in their separation which increases the process cost.
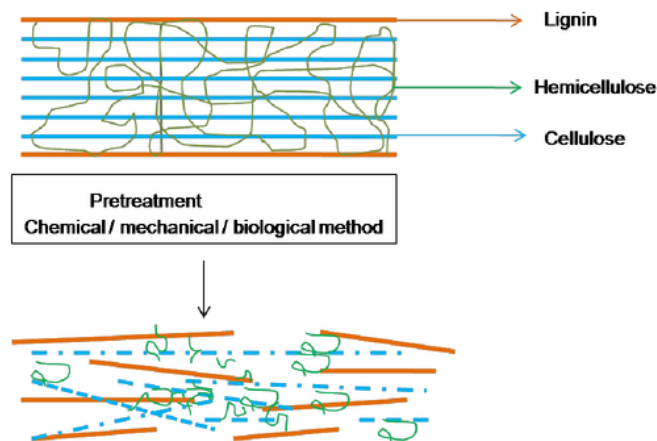
Figure 1.7 Pretreatment of lignocellulosic biomass

As mentioned in section 1.2 lignocellulose is the complex mixture of cellulose, hemicelluloses and lignin where lignin acts as a protective layer around the cellulose and hemicellulose. Hence to get the desired product it is important to separate lignin from cellulose

and hemicelluloses. It requires pretreatment of lignocellulosic biomass to improve the formation of desired product, which prevents the degradation of carbohydrates and desired products. Pretreatment also helps to avoid the formation of byproducts which inhibits the hydrolysis process.[26] Various pretreatment processes like physical, chemical, physico-chemical, mechanical and biological are involved to fractionate, solubilize, hydrolyze and to separate the cellulose, hemicellulose and lignin components (Figure 1.7).[16,42-44]

1.4 Conversion of cellulosic component of lignocellulose to platform chemicals

1.4.1 Conversion of cellulose to 5-hydroxymethylfurfural (HMF)

Considering the abundant availability of lignocellulosic biomass it is worth to convert this cellulosic component to chemicals and fuels. It is well reported that cellulose on hydrolysis in presence of acidic catalyst produces glucose which on further dehydration produces 5-hydroxymethylfurfural (HMF)[45-46] (Scheme 1.1).
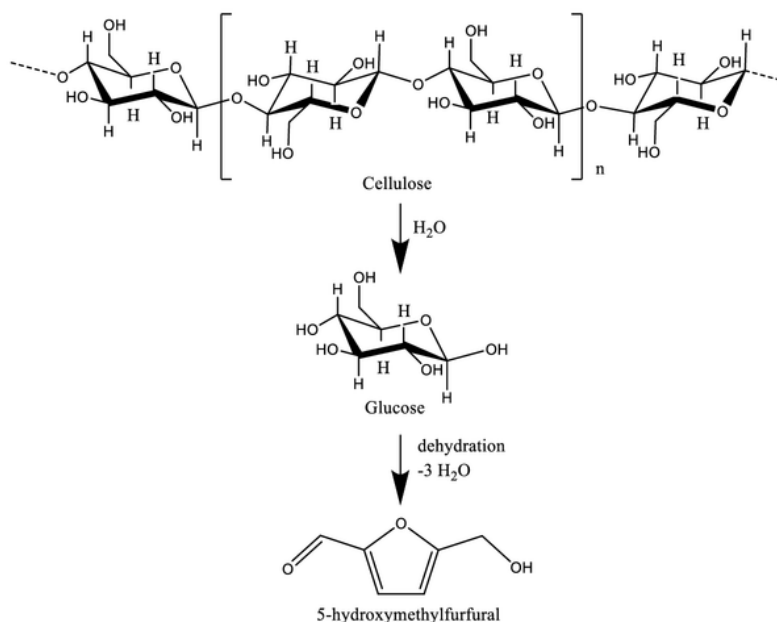
Scheme 1.1 Cellulose to 5-hydroxymethylfurfural (HMF)

1.4.2 Hydrogenation of glucose

Glucose on hydrogenation in presence of H_2 produces sugar alcohols like sorbitol & mannitol[47] (Scheme 1.2) which can be further converted to glycol products by C-C bond cleavage (Scheme 1.3).[48]
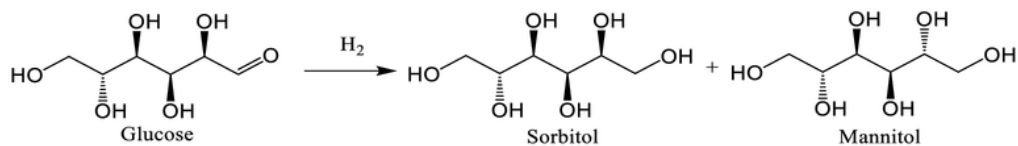
Scheme 1.2 Hydrogenation of glucose to C6 sugar alcohols
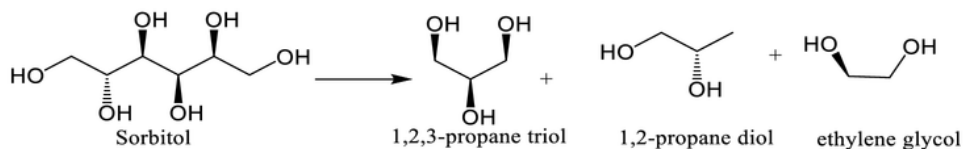
Scheme 1.3 Conversion of sugar alcohol(s) to glycols

1.4.3 Conversion of hemicellulose to furfural (FAL)

Hemicellulose on acid hydrolysis produces xylose which on further dehydration produces furfural (FAL)[49-50] (Scheme 1.4).
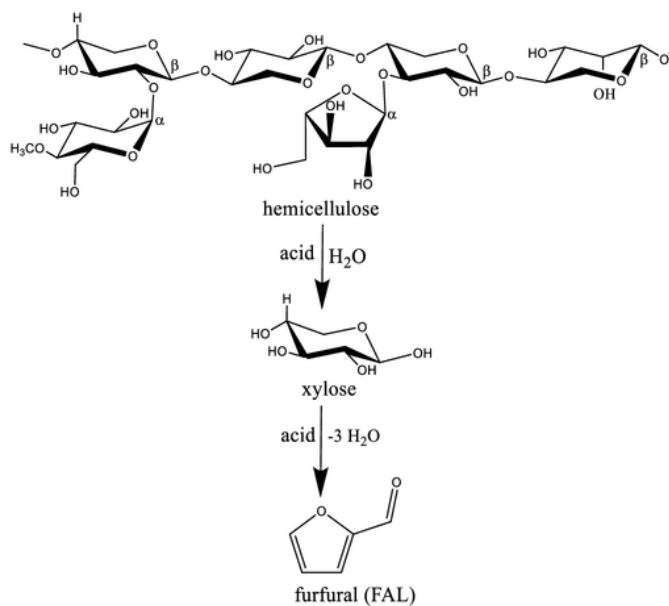
Scheme 1.4 Hemicellulose to furfural

1.4.4 Hydrogenation of xylose

Xylose a pentose sugar containing one carbonyl group and four hydroxyl groups on hydrogenation gives xylitol and arabitol[51] (Scheme 1.5).
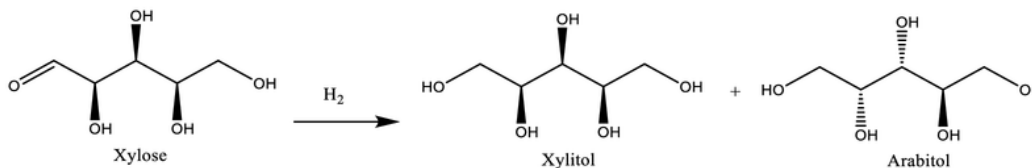
Scheme 1.5 Hydrogenation of xylose to C5 sugar alcohols

1.5 Furans: the platform molecules for the synthesis of fuels and chemicals

1.5.1 Conversion of 5-hydroxymehylfurfural (HMF)

HMF derived from glucose is the platform compound for the synthesis of various chemicals (Scheme 1.6) due to presence of several functionalities in its structure including C=C bonds, hydroxyl and carbonyl group.[52] HMF on hydrogenation of carbonyl group produces bis-hydroxymethyl furfural, which on further C-O bond hydrodeoxygenation produces 2,5-dimethylfuran (2,5-DMF). The ring hydrogenation of 2,5-DMF forms 2,5-dimethyltetrahydrofuran (2,5-DMTHF).[52] Oxidation of HMF produces 2,5-furandicarboxylic acid (FDCA).
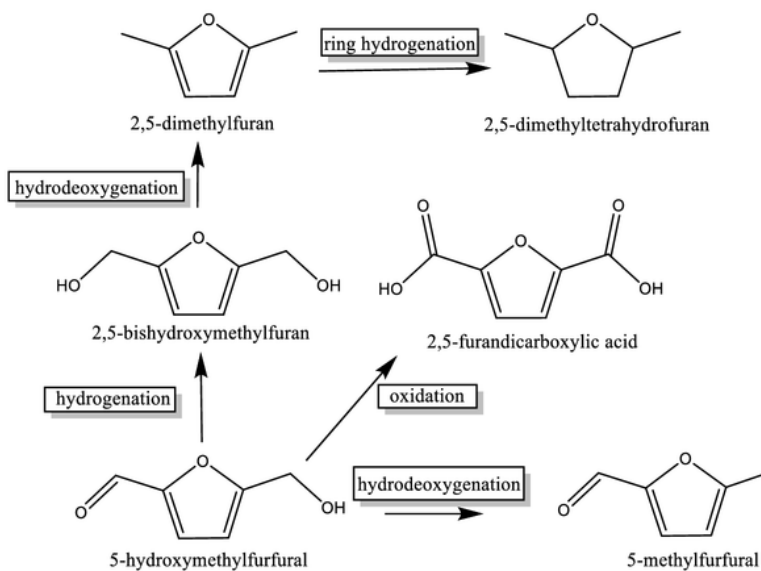
Scheme 1.6 Conversion of HMF to value added chemicals

1.5.2 Conversion of furfural (FAL)
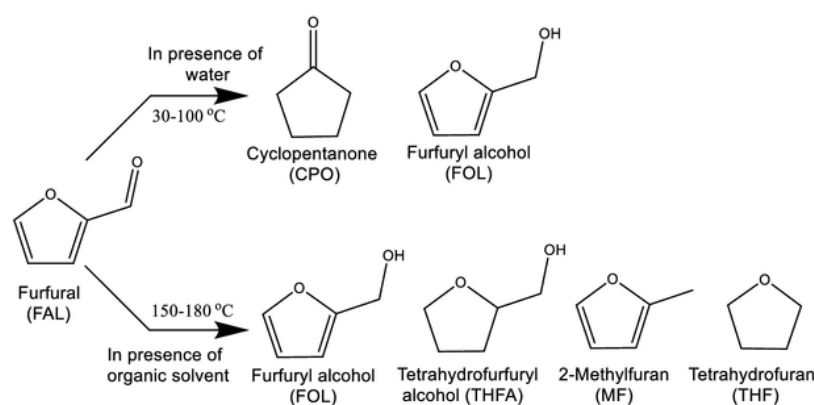
Scheme 1.7 Conversion of furfural to value added chemicals

Hemicellulose derived FAL is an interesting platform chemical due to its conversion to various value added chemicals by simply tuning reaction conditions like temperature, pressure, solvent, catalyst, etc. As shown in Scheme 1.7 in presence of water and organic solvent at temperature range 30-100 °C, FAL can be converted to furfuryl alcohol (FOL).[53-56] In aqueous medium at temperature range between 150-180 °C and in presence of H_2 FAL get converted to cyclopentanone (CPO) and cyclopentanol (CPL).[57] At higher temperature range 170-180 °C FAL converted to 2-methylfuran (2-MF) in presence of organic solvent.[58-59]

1.6 Application of lignocellulose derived chemicals

1.6.1 Applications of furfuryl alcohol (FOL)

FAL as well as FOL both individually or in combination with phenol, acetone or urea can be used to make resins which is resistant to acids, bases and various solvents[60] and for the synthesis of furan cement.[61] These resins are used for surface coatings, chemically resistant resins, boiler floor grouting and also in the production of adhesives, used in foundry cores and in the production and manufacture of casting molds, automotive brake linings, abrasive wheels, refectory products of the steel industry, fiberglass and some aircraft components. FOL was one of the components used as hypergolic starter fluids that ignite liquid rocket fuels spontaneously in space shuttles in the absence of oxygen (i.e. in space).[62] FOL is widely used in producing

various synthetic fibers, rubbers and farm chemicals. It can also be used as good solvent for furan resin, pigment and varnish.[63,60] FOL is also an important intermediate chemical in the synthesis of lysine, vitamin C, lubricants, dispersing agents, plasticizer and tetrahydrofurfuryl alcohol.[64-66]

1.6.2 Applications of cyclopentanone (CPO)

CPO is a fragrance ingredient used in many fragrance mixtures. It is found in fragrances used in decorative cosmetics, fine fragrances, shampoos, toilet soaps and other toiletries as well as in non-cosmetic products such as household cleaners and detergents.[67] CPO is a useful intermediate for medical and perfume products.[68] It is a raw material, widely used for the synthesis of fungicides, pharmaceuticals, pesticides, rubber and chemicals.[69] It can be used for preparation of polyamides,[70] C_{15}–C_{17} diesel or jet fuels and polyolefin stabilizers.[71]

1.6.3 Applications of 2-methylfuran (2-MF) and 2,5-dimethylfuran (2,5-DMF)

Table 1.2 Comparison of properties of 2-MF and 2,5-DMF with gasoline and ethanol[73, 78]

Entry no.	Properties	Gasoline	Ethanol	2,5-DMF	2-MF
1	Chemical formula	C_6-C_9	CH_3CH_2OH	C_6H_8O	C_5H_6O
2	H/C ratio	1.795	3	1.333	1.2
3	O/C ratio	0	0.5	0.17	0.2
4	Density ($Kg.m^{-3}$) at 20 °C	745	791	890	913
5	Octane number (RON)	97	109	119	103
6	Boiling Point (°C)	32.8	78.4	92	64.7
7	Water Solubility ($mg.mL^{-1}$ @ 20 °C)	insoluble	100	26	3

2-MF and its ring hydrogenation derivatives 2-MTHF are used as biofuel due to their intrinsically high research octane number (octane number of 2-MF is 103 and 86 for 2-MTHF).[72-73] 2-MF is also used for the synthesis of chemicals, e.g., toluene in combination with

ethylene. In chemical industry, 2-MF is used for the synthesis of crysanthemate pesticides, perfume inter-mediates and chloroquine lateral chains in medical intermediates.[58] 2,5-DMF is used for synthesis of p-xylene by combination with ethylene.[74-77] Due to attractive physical and chemical properties of 2,5-DMF and 2-MF both have potential to be used as biofuel. The properties of 2,5-DMF and 2-MF are compared with gasoline and ethanol in Table 1.2.

1.6.4 Applications of sugar alcohols (sorbitol and xylitol)

Both xylitol and sorbitol have wide industrial applications due to their beneficial physical and chemical properties. Xylitol is widely used as sweetener and refreshing agent in foods and in toothpastes because of its low calorific value, glycemic index and anti-cariogenicity.[79-81] Sorbitol is largely used in the food and pharmaceutical industries as low calorie sweetener, laxative, humectants. Approximately 60% of the produced sorbitol is utilized in processed foods, confections, toothpaste and other personal care products as humectants, stabilizers, softeners, emulsifiers. An additional 16% of the total market for sorbitol is utilized for the production of L-ascorbic acid (Vitamin C).[82-83] As a consequence sorbitol holds the biggest market share among sugar alcohols with an expected demand of 2148.9 kilo tons in 2018.[84-86]

1.7 Global market of xylose, furfural (FAL), furfuryl alcohol (FOL), cyclopentanone (CPO), sorbitol and xylitol

- According to global one stop (Gos) report center global xylose market is expected worth 270 million USD by 2019.[87]
- Global FAL market demand was 300 kilo tons in 2013 and is expected to reach 652.5 kilo tons by 2020, growing at a CAGR of 11.9% from 2014 to 2020.[88]
- According to grand view research report, FOL emerged as the largest application segment and accounted for over 85% of overall FAL market in 2013.[88]
- CPO has a potential market valued at 100 million USD (year 2014) and has been recognized as a chemical having explosion of market in near future (130 million USD by year 2020).[89]
- Sorbitol market size was estimated at 18.5 lac kilo tons in 2015 and expected to reach 24 lac kilo tons by 2023 (more than USD 4 billion).[90]
- Global market of xylitol was estimated as 190.9 thousand kilo tons (USD 725.9 million) in 2016 expected to reach 266.5 thousand kilo tons in 2022 (above USD 1 billion).[91]

1.8 Literature survey

1.8.1 Literature survey for conversion of furfural (FAL) to furfuryl alcohol (FOL)

The wide application of FOL in resin and chemical industry motivated researchers to carry out work for conversion of FAL to FOL. Literature survey for the conversion of FAL to FOL (Table 1.3) shows that, industrially FOL is produced from FAL by using Cu-Cr catalyst however it is associated with deactivation of catalyst and also due to toxicity of Cr it is difficult to dispose the deactivated catalyst. Hence researchers were promoted to study Cr free catalyst.[59] Various Cu based Cr free catalyst were develop for conversion of FAL to FOL which are showing better performance however those are associated with deactivation of catalyst and also operated at high temperature and high pressure. Cu/Al_2O_3 catalyst is reported for 81% conversion FAL with 100% selectivity of FOL at 90 °C[92] while $Cu/Mg/Al_2O_3$ shows 100% conversion with 100% selectivity but this reaction was operated at 150 °C.[93] $Pt-Sn/SiO_2$ also reported for 99% conversion of FAL with 98% selectivity for FOL but this catalyst undergo deactivation.[55] Cobalt based Co-Mo-B alloy system is reported for 100% selectivity of FOL with 99% conversion of FAL at 100 °C and 1MPa H_2 in ethanol solvent.[63] Polymer stabilized PVP NiB system were reported for 73% conversion with 90% selectivity of FOL but no recycle study was done.[56] Pd(5)Cu(5)/MgO catalyst is reported for 100% conversion of FAL with 99% selectivity of FOL at 110 °C in water medium and catalyst is recyclable upto 4th run.[94] Bimetallic Ir-Re catalyst was reported for 99% conversion of FAL with 99% selectivity of FOL at 30 °C however no recycle study was reported. Another bimetallic $Pt(2)Re(1)/TiO_2-ZrO_2$ catalyst is reported for 100% conversion of FAL with 95% FOL selectivity but reaction were carried out under 5 MPa H_2 pressure and 130 °C and no recycle study was performed.[95] Most of the studies were carried out above 90 °C and 1-5 MPa H_2 pressure also less than 20 *v/v* FAL feed concentration were used as shown in Table 1.3. In order to avoid the use of external H_2 pressure catalytic transfer hydrogenation reaction were carried out with different catalyst like $Cu(10)/Fe_2O_3$, $Ni(10)Fe_2O_3$, $Pd(5)/Fe_2O_3$ however reactions were carried out at 180 °C in presence of IPA as proton donating solvent however no recycle study was performed.[96] As per our knowledge very few reports are available for conversion of FAL to FOL at lower temperature 25-30 °C but those were compromised with high Pt (10%) loading and 2 MPa H_2 pressure.[54, 97-98]

Table 1.3 Literature survey for conversion of FAL to FOL

Entry no.	Catalyst	Sub./Sol. ratio	Temp (°C)/ Solvent	H₂ pressure (MPa)	FAL Conversion (%)	FOL Selectivity (%)	Ref. no.
1	Cu-Cr-alkaline earth metal	100	140/ -	10	100	96	99
2	Cu-Cr-oxide	100	180/ -	3	100	98	100
3	Cu(5)/Al$_2$O$_3$	1 *wt/v*	90/H$_2$O	2	81	100	92
4	Cu(40)/Mg/Al	1.6 *v/v*	150/IPA	-	100	100	93
5	Pd(5)Cu(5)/MgO	6 *wt/v*	110/H$_2$O	0.6	100	98	101
6	Co-Mo-B alloy	10 *v/v*	100/ethanol	1	99	100	63
7	PVP(2)CoNiB	6.7 *v/v*	180/ethanol	1.8	73.9	97	56
8	Co(10)/SBA-15	11 *wt/wt*	150/ethanol	2	92	96	102
9	Ir–ReO$_x$/SiO$_2$	3.2 *wt/wt*	30/H$_2$O	0.8	99	99	97
10	Pt(10)/Al$_2$O$_3$	5 *wt/v*	25/IPA	2	62.5	99.8	54
11	Pt(2)Re(1)/TiO$_2$-ZrO$_2$	18 *v/v*	130/ethanol	5	100	95	95
12	Pt(1)Sn(0.3)/SiO$_2$	4 *v/v*	100/IPA	1	99	98	55
13	Cu(10)/Fe$_2$O$_3$	3.75 *wt/v*	180/IPA	1.5 N$_2$	37	28	96
	Cu(10)/Fe$_2$O$_3$				46	33	
	Pd(5)/Fe$_2$O$_3$				87	57	

1.8.2   Literature survey for conversion of furfural (FAL) to cyclopentanone (CPO)

Cyclopentanone (CPO) is a valuable intermediate for the synthesis of various chemicals as mentioned in section 1.6.2. Different chemical processes were applied for production of CPO like oxidation of cyclopentene to CPO with nitrous oxide having 2.53 MPa pressure and 200 °C temperature.[103] It can also be produced by condensation of hexamethylene glycol at 367 °C[104] and from adipic acid at 285-295 °C.[105] All these processes are carried out at high temperature and high pressure and also the feed used in this process are derived from fossil feedstock which make the process costlier. Hronec *etal.*, is the first who developed the new route for conversion of biomass derived FAL to CPO by catalytic process.[106] Various reports are available for catalytic conversion of FAL to CPO. As shown in Table 1.4, Yan Liang have shown activity of NiCu-50/SBA-15 catalyst at 160 °C with 4 MPa H$_2$ pressure for 62% yield of CPO with 99% conversion of FAL in water medium but no recycle study was performed.[107] Recently Xing-Long reported 100% conversion of FAL with 7% of CPO and 46% yield of CPL at 150 °C and 4 MPa H$_2$ pressure by using 20% Cu/Co$_3$O$_4$ in water medium. However recycle study shows decrease in

catalyst activity due to leaching of metal [108] Jianhua Guo reported the 97% conversion of FAL at 4 MPa H_2 pressure and 150 °C with 60% yield of CPO in water medium in presence of CuAlZn catalyst and recycle study shows loss in activity due to leaching of metal and also due to coke formation.[109] Hydrotalcite based Cu:Ni:Al catalyst reported by Hongyan Zhu for 100% conversion of FAL with 95% yield of CPO at 140 °C under 4 MPa H_2 pressure however catalyst shows deactivation due to agglomeration of catalyst because of repeated calcinations and reduction after each recycle study.[69]

Table 1.4 Literature survey for conversion of FAL to CPO

Entry no.	Catalyst	Temp (°C)/ Solvent	H_2 pressure (MPa)	FAL Conversion (%)	Yield (%)		Ref. no.
					CPO	CPL	
1	NiCu(50)/SBA-15	160/H_2O	4	99	62	3	107
2	Cu(20)/Co$_3$O$_4$	150/H_2O	4	100	46	7	108
	Cu(30)/Co$_3$O$_4$			100	10	58	
	Cu(30)/ZrO$_2$			100	25	40	
	Ni(20)/Co$_3$O$_4$			100	24	29	
3	CuZnAl-500−0.5	150/H_2O	4	97.9	60	2.5	109
	Cu/SBA-15			89.6	10.5	13.7	
4	Cu(1):Ni(14):Al(05)	140/H_2O	4	100	95.8	3	69
5	Pt(5)/C	160/H_2O	8	100	77	5	110
		175/H_2O		100	44.23	36.23	
	Pd(5)/C	160/H_2O	3	97.8	67.08	0.74	
		175/H_2O	8	100	38.89	3.54	
	Ru(5)/C	175/H_2O	8	100	57.33	9.5	
	CoMnCr	175/H_2O		100	7.63	16.49	
6	Pd(5)Cu(10)/C	160/H_2O	3	98	92	0.4	71
7	Cu-Co-OG	160/H_2O	2	100	62	10	108
8	Pt(5)/C	160/H_2O	3	95	51	3.8	111

Milan Hronec reported 77% yield of CPO with 100% conversion of FAL at 160 °C and 8 MPa H_2 pressure in presence of 5% Pt/C catalyst in water medium however no recycle study was performed.[106] In one of the report PdCu/C catalyst was reported for 98% conversion of FAL with 92% yield of CPO with no recycle study.[71] The Cu-Co catalyst is reported for 62% yield of CPO at 160 °C and 2 MPa H_2. Moreover the activity of catalyst decreases due to leaching of metal.[57] All these reports shows that the conversion of FAL to CPO occurs in presence of water medium,

however these reaction are operated under high pressure of H_2 i.e. in the range of 2-8 MPa. In most of the catalytic process the conversion reaches to 100% however selectivity of CPO is low also the activity of catalyst decreases either due to adsorption of byproduct, agglomeration of active site or leaching of metal which increase the process costs. Various noble metals are used like Pt, Pd, Ru and among them Pd facilitates the ring hydrogenation of furan and forms THFA as major product under high pressure and high temperature however Pt and Ru form major product as CPO[57, 110] Yet in one of the study PdCu catalyst is showing better performance at 160 °C and 3 MPa H_2 but the loading of metal is high (5%). Pt(5)/C catalyst achieved 95% conversion of FAL with 51% yield of CPO at 160 °C and 3 MPa H_2 but no recycle study was performed.[111] In Cu-Co bimetallic catalyst Cu_2O species act as electrophilic or Lewis site for polarization of carbonyl group which assist to improve the catalyst performance.[57]

1.8.3   Literature survey for conversion of furfural (FAL) to 2-methylfuran (2-MF)

2-MF is a platform chemical for the synthesis of valuable chemicals and fuel additive. Conversion of FAL to 2-MF were carried out either by vapour phase or liquid phase catalytic process.[112-116] Various reports are available for the conversion of FAL to 2-MF by using external H_2 pressure (Table 1.5). Cu-based catalysts like Raney-Cu, Cu/Al_2O_3 and copper chromite have been widely employed because Cu is known for preferential cleavage of C-O bond during hydrodeoxygenation process of FOL to 2-MF.[117-120] However, the supported Cu-catalysts were found to be rapidly deactivated due to oxidation of Cu or leaching of metal.[72] Carbon-supported copper chromate has also been reported for conversion of FAL to 2-MF, those were undergo deactivation and also contain toxic Cr metal.[121] In order to avoid toxic Cr, hydrotalcite (HT) based Cu-Fe/HT catalyst were developed for conversion of FAL to 2-MF and applied at 220 ºC, 9 MPa H_2 pressure for 14 h in octane. This catalyst achieved 51% yield of 2-MF with 99% conversion of FAL however no recycle study was reported.[120] Pt/C system is reported by M. Hronec in two different conditions in first case H_2 pressure was 8 MPa with 175 °C temperature for 30 min in n-butanol showing 40% yield of 2-MF with 99% FAL conversion but no recycle study was reported.[106] In second study same catalyst under 3 MPa H_2 pressure with H_2O/H_3PO_4 solvent system were used at 175 °C where conversion of FAL was 100% with 36% yield of 2-MF is reported.[111] Another noble metal catalyst i.e Pd/C system is reported for 41% conversion of FAL with very low yield of 2-MF (9%) in presence of acetic acid assisted toluene solvent at 2

MPa H_2 and 150 °C.[122] In yet another report Pd supported on SiO_2 is reported for conversion of FAL to 2-methyltetrahydrofuran (2-MTHF) due to preferential ring hydrogenation under atm H_2 pressure in vapour phase reaction.[123] These results show that Pd metal facilitates ring hydrogenation which reduces the selectivity of 2-MF. In one of the report $CuCo/Al_2O_3$ catalyst is reported for 100% conversion with 78% selectivity for 2-MF however the reaction condition is very harsh (220 °C, 4 MPa H_2) moreover catalyst is recyclable until 3rd run but the spent catalyst need to be calcined.[124] All these reactions are carried out at high H_2 pressure. Hydrogen free reactions were carried out in presence of proton donating solvents like iso-propyl alcohol (IPA), 2-butanol and 2-pentanol in order to avoid the use of external H_2 pressure. In presence of Ru/C catalyst at 180 °C and 2 MPa N_2 pressure and IPA as solvent the conversion of FAL was found to be 95% with 61% yield of 2-MF however after 2nd run catalyst showed decreased in activity for 2-MF yield.[58] $Ru/RuO_2/C$ system were reported for 76% yield of 2-MF from FAL at 180 °C with 2-butanol and 2-pentanol as hydrogen donor and no recycle study was reported.[125] In one of the recent report $PdRu/TiO_2$ catalyst is showing activity for 39% conversion of FAL with 51% selectivity of 2-MF with 0.3 MPa H_2 pressure.[126]

Table 1.5 Literature survey for conversion of FAL to 2-MF

Entry no.	Catalyst	Temp (°C)/Solvent	H_2pressure (MPa)	FAL conversion (%)	2-MF selectivity (%)	Ref. no.
1	$Ru/RuO_2/C$	180/2-butanol/2-Pentanol	PN_2- 2.04	100	76	125
2	Cu–Fe HT	220/octane	9	99	51	120
3	$CuCo/\gamma Al_2O_3$	220/IPA	4	98.8	78	124
4	Pt(5)/C	175/n-butanol	8	99	40	106
5	Pd(5)/C	150/toluene acetic acid	2	41.2	19	122
6	Pd(4)Ru(1)/ TiO_2	RT/octane	0.3	39	18	126
7	Pt(5)/C	175/H_2O, H_3PO_4 85%	3	100	36.6	111
8	Ru(5)/C	180/IPA	PN_2-2.04	95	61	58

Among all of these reports most of the studies have been carried out at high temperature and high pressure. Very few reports are available for conversion of FAL to 2-MF by using Pt metal where Pt loading is 5 *wt*% and the maximum yield of 2-MF is 40% with high hydrogen pressure 3-8 MPa. Mechanistic study carried out for conversion of FAL to 2-MF in presence of Ru/RuO$_2$/C emphases that hydrogenation of carbonyl group occurs via Lewis acid mediated hydride transfer and hydrodeoxygenation occurs by activation of furan ring by both metal and Lewis acid sites.[127] Also in vapour phase reaction over Cu/SiO$_2$ catalyst 100% conversion of FAL and 90% yield of 2-MF at 220 °C due to presence of both metallic Cu and oxide Cu^{2+} species present in catalyst was seen.[113, 115]

1.8.4 Literature survey for hydrogenation of sugar to sugar alcohol

Sugar alcohol i.e. xylitol can be produced by microbial, enzymatic and chemical processes.[80, 128-137] In microbial process, D-xylose is converted into xylitol in presence of wild type yeast and recombinant yeast. Wild type yeast can achieve 65-85% yield of xylitol and recombinant yeast can yield 86-100% xylitol. This process is environmentally friendly and cost effective due to lower consumption of energy however limitations associated with this are, it is time consuming, associated with recycling problem and requires high water consumption.[80, 128, 129, 131, 132, 134, 138] In enzymatic process xylose can be converted into xylitol with 96% yield and it can be recycle, environmental friendly, has a potential for energy and water saving with easy recovery of xylitol. However it is costlier process due to preparation of coenzyme regeneration. Moreover xylitol and sorbitol are currently manufactured in ton per year through the catalytic hydrogenation in presence of RANEY® nickel at elevated temperature and pressure.[80, 81, 130, 139, 140] It is reported that 50-60% xylitol is recovered from total xylan fraction of lignocellulosic biomass. Hence the final product is very expensive due to extensive separation and purification process.[137] This catalytic process is associated with deactivation of catalyst due to adsorption of impurities on the catalyst surface and leaching of Ni metal in reaction mixture.[141-143] Ni form chelating complex with sugar alcohol which is stable in basic medium and makes the resulting sugar alcohol rich in Ni. It requires further purification of sugar alcohol by expensive purification steps like ion exchange, filtering and crystallization.[144, 145] Various noble metals like Ru, Pt and Pd based catalyst were also developed for conversion of xylose to xylitol (Table 1.6) and among them Ru based catalyst showed better performance. Ru supported on NiO-TiO$_2$ is

showing 99.9% conversion of xylose with 99.9% yield of xylitol with 20 *wt%* xylose concentration at 120 °C and 5.5 MPa H_2 pressure.[146] Ru/TiO_2 is reported for 100% conversion of 1 *wt%* xylose with 98% yield of xylitol at 120 °C and 2 MPa H_2.[147] The utilization of Ru@Dowex-H was reported for 99.7% conversion of xylose with 99.3% xylitol yield at 120 °C and 3 MPa H_2 for 0.1 M xylose concentration.[148] Ru supported on HYZ zeolite is reported for 62% conversion of 20 *wt%* xylose with 61% yield of xylitol at 120 °C and 5.5 MPa H_2.[143] Recently Ru/TiO_2 catalyst is reported at 120 °C and 2 MPa H_2 for 100% conversion of 1% xylose solution to 98% xylitol yield without recycle study.[149] PtSn system is reported for 98% conversion with 90% yield of xylitol with 0.43 *wt%* xylose in 1.6 MPa H_2 at 130 °C,[150] Pt/Al_2O_3 in presence of HT at 60 °C and 1.6 MPa H_2 is giving 99% conversion with 78% yield of xylitol with 0.43 *wt%* xylose concentration.[47] Likewise various reports are available for conversion of glucose to sorbitol (Table 1.7). Ni/SiO_2 catalyst is reported to achieved 45% conversion of glucose with 41% yield of FOL at 120 °C and 12 MPa H_2.[145] This catalyst was showing no leaching of metal but activity is low. Pt/ACC catalyst is reported for 100% conversion with 99% yield of sorbitol at 100 °C and 8 MPa H_2 however no recycle study was reported.[151] Our group has reported 98% conversion of glucose with 53% yield of sorbitol in presence of Pt/Al_2O_3 catalyst combination with calcined hydrotalcite (HT) solid base at 90 °C and 1.6 MPa H_2.[47] Conversion of glucose to sorbitol was also reported at 100 °C in presence of Ru/C catalyst for concentrated system with 100% conversion of glucose and 99% yield of sorbitol under 5.5 MPa H_2.[141]

Table 1.6 Literature survey for hydrogenation of xylose to xylitol

Entry no	Catalyst	Temp (°C)	H_2 pressure (MPa)	Xylose conc (*wt%*)	Xylose conversion (%)	Xylitol yield (%)	Ref. no.
1	Ru(1)/NiO (5)-TiO$_2$	120	5.5	20	99.9	99.7	146
2	Ru/TiO$_2$	120	2	1	100	98	147
3	Ru@ Dowex-H	120	3	1.5	99.7	99.3	148
4	Ru/HYZ	120	5.5	1.5	62	61	143
5	PtSn/AL	130	1.6	0.5	98	90	150
6	Pt/Al$_2$O$_3$+ HT	60	1.6	0.5	99	78	47
7	Ru/TiO$_2$	120	2	1	100	98	149

In yet another report Ru catalyst was used at 120 °C and 3 MPa H_2 to achieved 100% conversion with 99% yield but here the feed system was very dilute.[148] All these reports revels that Ru is showing better activity for hydrogenation of xylose however H_2 pressure used is 2 to 8 MPa which is very high. On the contrary few reports are available for Pt metal where 1.6 MPa H_2 is used but they are showing decrease in selectivity of sugar alcohol.

Table 1.7 Literature survey for hydrogenation of glucose to sorbitol

Entry no.	Catalyst	Temp (°C)	H_2 pressure (MPa)	Glucose concentration (*wt%*)	Glucose conversion (%)	Sorbitol yield (%)	Ref no.
1	Ru/C	100	8	40	100	99	141
2	Ru@Dowex-H	120	3	1.5	100	99	148
3	Pt/Al$_2$O$_3$+ HT	90	1.6	0.5	98	53	47
4	Ni(20)/SiO$_2$	120	12	20	45	41	145
5	Pt(10)/ACC	100	8	40	100	99	151
6	Ru/MCM-48	100	2.5	0.73	100	100	152

1.9 Limitations of literature report

1.9.1 Limitation of literature and opportunities for conversion of FAL to FOL

From the literature review for the conversion of FAL to FOL it was found that mostly reactions were carried out in organic solvents like ethanol, methanol, IPA and very few reports are there with water as solvent. The concentrations of FAL used in these reactions were less than 20% which is industrially not economical. Different noble-metals like Pt, Pd, Ir were used in

combination with promoters like Cu, Re, Sn which show good yield of FOL however those are operated in the temperature range of 100-130 °C and 0.6-5 MPa H_2. Moreover in monometallic catalyst higher loading of precious metal (10 wt% Pt) was used.[54] However very few reports are available in which low temperature 25-30 °C is used. No report is available for the conversion of FAL to FOL at lower temperature (<50 °C) and lower H_2 pressure (<0.6 MPa) in presence water medium. Very few reports are available for recycle study of catalyst. It is observed that compared to monometallic catalyst bimetallic catalyst show better performance.

Considering the limitation of literature there is scope to develop efficient catalytic system which will work in water medium at lower temperature (close to room temperature) and at lower H_2 pressure (<1 MPa).

1.9.2 Limitation of literature and opportunities for conversion of FAL to CPO

Literature study for the conversion of FAL to CPO shows that very high H_2 pressures (2-8 MPa) are used for the conversion of FAL to CPO in water medium. Nevertheless, in presence of noble monometallic catalyst, no reports are available under lower H_2 pressure (lower than 2 MPa). In one of the report, PdCu catalyst has showed 98% conversion with 92% yield of CPO at 2 MPa H_2. Most of the reports show decrease in catalyst activity due to either leaching of metal, agglomeration of catalyst or coke formation at high temperature and high pressure with low selectivity to CPO. From reports it is also found that bimetallic catalyst could perform better than monometallic catalyst.

Hence there is opportunity to develop a system which will work under low H_2 pressure in presence of bimetallic catalyst.

1.9.3 Limitation of literature and opportunities for conversion of FAL to 2-MF

Literature survey on the conversion of FAL to 2-MF shows utilization of high H_2 pressure (2-8MPa) in combination with various additives like H_3PO_4, acetic acid in presence of precious metal catalyst. However the yield of 2-MF was not achieved beyond 40%. Also loading of precious metal is high which increase the process cost. Non-noble metal catalysts were used but the reaction conditions are very harsh (150-220 °C and 2-9 MPa H_2) as mentioned in Table 1.5 and also catalyst undergoes deactivation due to leaching of metal. Moreover Ru catalyst is showing good performance due to presence of Ru metal and RuO_2 species.

Considering the literature survey there is an opportunity to develop catalytic system which could work at lower H_2 pressure (1 MPa) with good 2-MF selectivity and recyclable catalyst.

1.9.4 Limitations of literature and opportunities for conversion of sugar to sugar alcohol

Hydrogenation of sugars to sugar alcohols is also reported at 1.6-8 MPa H_2 pressure with different metals like Ni, Pt, Ru etc. Although cheaper catalyst like Ni is useful, however Ni catalyst undergoes deactivation due to leaching in reaction mixture and also formation of chelating complex with sugar alcohols, which requires further purification step.

Considering these limitations of reported results it is important to develop an efficient catalytic system which would be recyclable and work under optimum reaction condition to improve the result.

1.10 Catalyst

1.10.1 Supported metal catalysts

Supported catalysts play a significant role in many industrial processes. These are formed by adsorption or deposition of catalytically active component on the support (Figure 1.8). The role of support in the catalyst is to provide high surface area and stabilize the dispersion of the active component (e.g., metals supported on oxides). The acidic (Pt/Al_2O_3) or basic (Pt/HT) nature of supports also shows activity in the catalytic process in bifunctional catalysts. The most frequently used *binary oxide* supports are α-Al_2O_3, SiO_2, MCM-41, TiO_2 (anatase), ZrO_2 (tetragonal), MgO etc., and ternary oxides including amorphous SiO_2–Al_2O_3 and zeolites. Additional potential catalyst supports are aluminophosphates, kieselguhr, bauxite, and calcium aluminate. *Carbons* in various forms (charcoal, activated carbon, carbon nanofiber, carbon nanotubes, graphaite, etc) can be applied as supports.
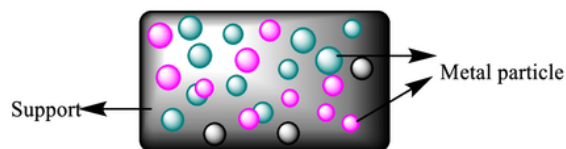
Figure 1.8 Supported metal catalyst

1.10.2 Methods of supported metal catalyst preparation

Supported metal catalyst is synthesized by *impregnation and precipitation method.*[153]

Impregnation: In this method, catalytically active material is impregnated on the surface of preformed oxide or carbon support. In this process a certain volume of solution containing the precursor of the catalytically active element brought in contact with the solid support.

Method of impregnation

❖ *Impregnation by soaking*: excess metal precursor solution is added into support solution and kept for stirring for definite time at room temperature. After a definite time, the excess solvent is removed by drying.

❖ *Incipient wetness impregnation*: in this method volume of solution is either equals or less than the pore volume of the support, is used.

❖ *Co-impregnation* (one step): Co-impregnation has been known as a catalyst preparation method of forming bimetallic particles. Here the precursors of both metals are added in one step.

❖ *Successive impregnation* (two step): In this method precursor of one metal is added in the support solution. Followed by agitation, drying, calcinations and reduction and then precursor of second metal added following the same procedure.

Precipitation method:

Deposition-precipitation: In this process the precipitating agent is injected below the surface of the suspension containing the solid support and the precursor compound. This solution is allowed under the vigorous agitation, which form homogeneous precipitate. This precipitate gets completely adsorbed on the support.

Ion exchange: In this method ionic species of precursor from aqueous solution get transferred towards the support charge site surface by electrostatic force of attraction. For example zeolites are good cationic exchangers where K^+, Na^+, NH_4^+ get exchange with complex like amine cations of Pt or Pd.

Chemical vapour deposition (CVD): CVD is a synthesis process where chemical component are transform into vapour phase with the help of heating, radiation or plasma. This process produces a solid deposit resulting in the formation of powders or coatings on the support. Volatilization of a solid or liquid feed produces the gaseous compound containing the deposit

material. A carrier gas (usually Hydrogen or Nitrogen) is used to transport gaseous materials to hot substrate.

Atomic layer deposition (ALD): Here metals, oxides, and other materials are deposited on surfaces by a sequence of self-limiting reactions. In these method highly uniform thin films is form on substrates by the two consecutive surface sequence reactions. In the first step surface reactions were carried out between precursor A and the available functional groups on the support. After completion of reaction unreacted precursor and any volatile byproducts are removed by purging the inert gas. In second step precursor B is introduced to the support to conduct the second surface reaction, followed by second inert gas purge. For synthesizing heterogeneous catalyst comprising of noble metal nanoparticles supported on the solid surface a volatile metal precursor exposed to the support surface at sufficiently low temperatures to prevent thermal decomposition. The precursor with its ligand get chemisorbs on the support surface followed by sequential calcinations and reduction remove the ligands or exposed to oxidizing and reducing precursor to remove ligand and get metal nano particles.

The sol–gel process: It involves the formation of a sol, followed by the creation of a gel. A sol (liquid suspension of solid particles smaller than 1 μm) is obtained by the hydrolysis and partial condensation of an inorganic salt or a metal alkoxide. Further condensation of sol particles into a three-dimensional network results in the formation of a gel. The porosity and the strength of the gel are strongly affected by conditions of its formation. For example, slow coagulation, elevated temperature or hydrothermal post treatment increase the crystalline fraction of the gel.[153]

1.11 Aims & Objectives of thesis

As mentioned in the section 1.5, the hydrogenation product of lignocellulose derived chemicals have wide applications in the various fields. However these reactions are carried out at either high temperature, high pressure or at higher loading of noble metal in supported metal catalyst. Leaching of metal hampers the recyclability of catalyst is another issue related to supported metal catalyst. Selection of suitable solvent for efficient conversion of substrate to desired product is also important. Nevertheless, the most important is the selection of catalyst for hydrogenation reaction. Considering these facts, it is important to develop an efficient catalytic process which will work at lower temperature and lower H_2 pressure with suitable solvent to

improve the yields, selectivity and conversions. Hence the aims & objectives for my work were set as;

1.11.1 Aims of the work

Development of efficient recyclable catalytic system

Literature survey shows that the supported metal catalyst which is made up of noble metal in combination with electropositive metal can give better results in hydrogenation reactions. Pt metal is known for efficient hydrogenation and its combination with electropositive metal like Co can improve the activity of bimetallic catalyst compared to monometallic catalyst. Also it will help to increase the substrate to catalyst ratio in reaction which decreases the process cost.

Selective hydrogenation of carbonyl functional group of reactant

The furfural molecule contains C=C and carbonyl (C=O) functional group in its structure. The hydrogenation of furfural can be performed either by ring or carbonyl group hydrogenation or hydrogenation of both. Hydrogenation of ring C=C decreases the selectivity of FOL. FOL is the main key intermediate product for desired product formation like CPO, MF. Hence in order to get maximum possible selectivity for FOL, there should be preferential hydrogenation of C=O bond and not the C=C bond.

Conversion of higher substrate concentration to desired product

Literature report shows that conversions of FAL to FOL were carried out by using dilute systems which is not industrially economical. Hence in order to develop industrially relevant process, concentrated system of substrate should be used.

Selective conversion of FAL to FOL at ambient reaction condition in water medium

As mentioned in section 1.7.1 plenty of literature is available for conversion of FAL to FOL in different organic solvents like methanol, ethanol, IPA and also wide range of temperature i.e. 25-180 °C and H_2 pressure 0.6-5 MPa H_2 is reported. Very few reports are available where water is used as reaction medium but those comprised either high temperature or high pressure. Hence aim of this work is selective conversion of FAL to FOL at lower temperature (<50 °C) and lower H_2 pressure (0.1 MPa) in water medium.

Conversion of FAL 2-MF and CPO at lower pressure

As mentioned in the section 1.7.2 and 1.7.3 the conversion of FAL to 2-MF and CPO were carried out at high H_2 pressure which makes the process costlier and not safe under operating

condition hence the aim of this work is development of catalytic process which work at lower pressure by manipulating the reaction parameter like solvent, temperature and catalyst.

Conversion of concentrate sugar solution to sugar alcohol at lower pressure and moderate temperature

Literature survey given in section 1.7.3, shows that hydrogenation of sugar is carried out at mild temperature but higher H_2 pressure. It needs development of catalytic process which will work at moderate temperature and lower H_2 pressure (<1.5 MPa).

Considering the aim of the work objectives were set as follows;

1.11.2 Objectives of the work

Synthesis and characterization of catalyst

Synthesis of noble and non-noble metal based, mono and bimetallic catalyst by wet-impregnation method and characterization of synthesized catalyst by various techniques like TEM, XRD, XPS, ICP-OES, N_2-physisorption, TPR.

Study the effect of bimetallic catalyst over monometallic catalyst for hydrogenation reactions

Bimetallic catalyst having noble metal in combination with electropositive metal is showing improved result than noble monometallic catalyst hence the objective of this work is to study the effect of monometallic catalyst over bimetallic catalyst for hydrogenation of biomass derived different substrates.

Metal loading effect

The precious metals are very costlier and its use in the preparation of catalyst increases the cost of process hence in order to develop optimized catalyst with minimum loading of precious metal it is important to study the effect of metal loading.

Study the effect of temperature, pressure, solvent, time and substrate to catalyst ratio on hydrogenation reaction of FAL to FOL

In order to develop an efficient catalytic process it is important to study the effect of reaction parameters like temperature, pressure, solvent, time, substrate to catalyst ratio etc. to optimize the reaction condition.

Study the effect of higher concentration of substrate in reaction

In order to build the industrially viable catalytic process it is recommended to work on concentrated system which can be preferably use by industry.

<u>**Study the recyclability of catalyst**</u>

In order to make the catalytic process coast effective it is important to develop the recyclable catalyst.

<u>**Characterization of spent catalyst**</u>

In order to correlate the activity of catalyst for recycle study the recovered catalyst should be characterized by various techniques like XRD, XPS, TEM, BET-surface area etc., to see the effect of reaction condition on catalyst.

1.12 Hypothesis of work

1.12.1 Hypothesis behind conversion of FAL to FOL

Careful survey of literature gave us insights to understand the use of bimetallic system containing one metal in reduced state and other metal in oxidized state help to improve the yield of FOL with complete conversion of FAL**.** Due to electronegativity difference between Pt and Co, Pt is found in zero oxidation state and Co is found in II/III oxidation state.[154] Hence in this work noble metal i.e. Pt in combination with oxophilic Co metal was preferred because PtCo system is known for selective hydrogenation of α, β, unsaturated aldehyde.[155-156] Also carbon being neutral with high surface area is used as supports for synthesis of supported bimetallic catalyst.

1.12.2 Hypothesis behind conversion of FAL to CPO

The conversion of FAL to cyclopentanone occurs only in water medium however it is well known that at high temperature, FAL and FOL undergo polymerization reactions which decrease the selectivity of desired product. Hence it was anticipated that biphasic solvent system containing water and organic solvent could be used to improve the yield at lower H_2 pressure in presence of PtCo/C catalyst. Hence combination of metallic Pt with oxophilic Co could be the best catalyst to carry out rearrangement of FAL to CPO. However to carryout reaction under lower H_2 pressure depending on the solubility of substrate and desired product it was anticipated to carryout reaction in presence of biphasic solvent system and bimetallic PtCo/C catalyst.

1.12.3 Hypothesis behind conversion of FAL to 2-MF

Hence it is anticipated that PtCo/C catalyst having both metallic and Lewis acid site would give better performance for conversion of FAL to 2-MF. It is reported that PtCo/C catalyst is showing better performance for hydrogenation of carbonyl group in cinnamaldhyde and conversion of 5-hydroxymethyl furfural to dimethyl furan. Hence in order to study the effect of

bimetallic catalyst Pt modified with Co promoter supported on carbon was used for conversion of FAL to 2-MF.

1.12.4 Hypothesis behind hydrogenation of sugar to sugar alcohol

PtCo/C is reported for hydrogenation of aldehyde group in cinnamaldhyde and 5-hydroxymethylfurfural hence Pt modified with Co supported on carbon was used to study its effect for hydrogenation of sugar to sugar alcohol. Also in addition to that Ru supported on carbon and other non- noble metal containing Cu, Co, Ni catalyst was used for comparative study. High concentration of xylose and glucose were studied to see the hydrogenation of concentrated solution of sugar to sugar alcohol.

From published reports it was observed that catalytic hydrogenation reactions were carried out at high H_2 pressure which increases the cost of process. Hence in order to decrease the hydrogen pressure catalyst having good interaction with substrate and hydrogen is required. It is anticipated that the substrate having polar functional group (carbonyl group) comes in contact with Lewis acid site (electropositive metal) present on catalyst which improve the interaction between catalyst and substrate. Considering all these facts the bimetallic catalyst having noble Pt metal which is known for activation of H_2 in combination with oxophilic Co metal supported on neutral carbon were preferred to carry out these hydrogenation reactions.

1.13 Outline of thesis

This thesis is divided into seven chapters. The present chapter comprises the detailed introduction regarding the biomass, its sources, chemical composition, its component structure, conversion of biomass to value added chemicals, applications of chemicals derived from cellulose and hemicelluloses. It also includes literature survey related to the conversion of FAL to FOL, FAL to MF, FAL to CPO and conversion of sugar to sugar alcohol. This chapter also includes the, detailed discussion on method of supported metal catalyst synthesis and also consists of aim, objectives and hypothesis of thesis. Second chapter comprises discussions on principles of catalyst characterization techniques, synthesis of mono and bimetallic catalyst and detailed study on characterizations of synthesized catalyst and results. Third chapter discusses about detailed study for catalytic activity of mono and bimetallic catalyst on conversion of furfural to furfuryl alcohol. The 4th chapter includes detailed study for activity of catalyst for conversion of FAL to 2-MF and conversion of HMF to 2,5-DMF. Chapter 5th comprises discussion on catalytic activity for conversion of FAL to CPO with effect of biphasic solvent

system. Chapter 6th is related to conversion of sugar to sugar alcohol which again divided into two sections. In section A: discussions are made on conversion of xylose to xylitol and section B: includes conversion of glucose to sorbitol. Lastly Chapter 7th comprises summary and conclusion of thesis.

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Chapter 2
Catalyst Synthesis and
Characterization

2.1 Introduction

As discussed in chapter 1, section 1.10.2, among various catalyst synthesis methods wet impregnation method is simple, efficient and widely used for the synthesis of supported metal catalyst. This chapter comprises the synthesis of Pt and Co based mono and bimetallic catalysts supported on carbon by wet-impregnation method and their characterization by various techniques. The activity of catalyst depends on different factors like nature of support, type of metal, metal-metal interaction and metal-support interaction. It is reported that addition of promoter metal in bimetallic catalyst system helps to increase the activity of catalyst by changing electronic or geometrical property of catalyst. Pt is known for splitting of H_2 to carryout hydrogenation at lower temperatures however it requires higher loading of Pt in monometallic catalyst.[1] Different electropositive metals like Sn, Co, Ga are used as promoters in combination with noble metals. The synergetic effect between noble metal and non-noble metal in bimetallic catalyst increases the activity of catalyst either by changing the electronic or geometrical property of catalyst which increases the interaction between substrate and catalyst.

2.2 Experimental

2.2.1 Materials

Activated carbon used as support for the preparation of mono and bimetallic catalysts was procured from s. d. Fine Chemicals having surface area 750 $m^2 \cdot g^{-1}$. Pt metal precursor, Platinum tetra-ammine nitrate i.e. $(Pt(NH_3)_4(NO_3)_2)$ (99.9%) was purchased from Alfa Aesar. Cobalt nitrate $(Co(NO_3)_2 \cdot 3H_2O)$ (97%) precursor of Co was procured from Thomas Baker, Ruthenium chloride $(RuCl_3 \cdot 3H_2O)$ (99.9%) was procured from Loba Chemicals as precursor of Ru, the precursor of Ni, Nickel nitrate $(Ni(NO_3)_2.6H_2O)$ (99%) was also procured from Loba chemicals and Copper nitrate $(Cu(NO_3)_2.3H_2O)$ (99.9%) was purchased from Merck for Cu metal precursor.

2.2.2 Synthesis of catalyst

Supported monometallic (Pt(3)/C, Co(3)/C, Co(10)/C, Ru(3)/C, Cu(10)/C, Ni(10)/C) catalysts were prepared by wet-impregnation method and bimetallic catalyst (Pt(3)Co(3)/C, Ni(10)Co(3)/C) were prepared by Co-impregnation method (Figure 2.1). The synthesis procedure of monometallic catalyst involves immersion of 1 g of activated carbon (C) in 10 mL water and kept it for stirring. After half an hour, 2.5 mL aqueous solution of $Pt(NH_3)_4(NO_3)_2$ solution (12

mg·mL^{-1} Pt) was added and slurry was allowed to stir for 16 h followed by evaporation of water at 60 °C by rotary evaporator. Powdered monometallic Pt(3)/C catalysts were dried at 60 °C in laboratory oven for 16 h followed by vacuumed drying at 150 °C for 6 h. Dried catalyst was reduced at 400 °C for 2 h in an H$_2$ atmosphere (H$_2$, at a rate of 10 mL·min^{-1}) followed by cooling in argon till room temperature (at a rate of 10 mL·min^{-1}) (Figure 2.2). The rate of linear increase in temperature during thermal processing was 2 °C min^{-1}.
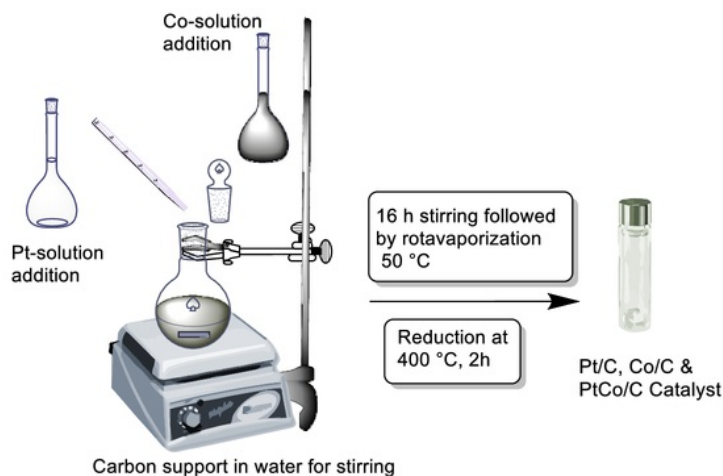
Figure 2.1 Impregnation of metal on support
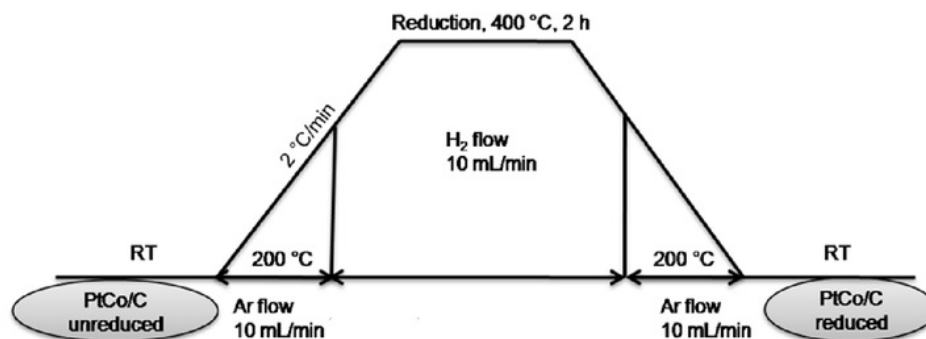
Figure 2.2 Reduction program of catalyst

The same procedure was used for all monometallic catalysts synthesis. Bimetallic PtCo/C catalysts containing 3, 2, 1, 0.5 *wt%* Pt and 0.25, 0.5, 1, 2, 3, 5 *wt%* Co were prepared by co-impregnation on activated carbon with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ and $Co(NO_3)_2 \cdot 3H_2O$. The name of bimetallic catalyst containing Pt, 3 *wt%* and Co, 3 *wt%* were given as Pt(3)Co(3)/C, remaining catalyst were named accordingly.

2.2.2.1 Synthesized mono and bimetallic catalysts in present work

The synthesized catalysts are enlisted in following Tables

Table 2.1 Mono and bimetallic catalysts containing Pt 2 *wt%* with varying Co loading

Entry no.	Catalyst
1	Pt(2)/C
2	Pt(2)Co(0.25)/C
3	Pt(2)Co(1)/C
4	Pt(2)Co(3)/C
5	Pt(2)Co(5)/C

Table 2.2 Mono and bimetallic catalysts containing Pt 3 *wt%* with varying Co loading

Entry no.	Catalyst
1	Pt(3)/C
2	Pt(3)Co(5)/C
3	Pt(3)Co(4)/C
4	Pt(3)Co(2)/C
5	Pt(3)Co(1)/C
6	Pt(3)Co(0.25)/C
7	Pt(3)Co(3)/C

Table 2.3 Mono and bimetallic catalysts containing Co 3 *wt%* with varying Pt, Ni and Ru loading

Entry no.	Catalyst
1	Co(3)/C
2	Pt(1)Co(3)/C
3	Pt(0.5)Co(3)/C
4	Ni(10)Co(3)/C
5	Ru(3)Co(3)/C

Table 2.4 Monometallic catalyst of Co, Ni and Ru

Entry no.	Catalyst
1	Co(10)/C
2	Ni(10)/C
3	Ru(3)/C

2.3 Techniques for characterization of supported metal catalyst

In order to know the exact structural morphology, surface area, particle size, arrangement of atoms, reduction temperature of supported metal, oxidation state of metal present in the supported metal catalyst, various techniques are used. The surface characteristic (surface area, pore size, pore volume) of catalyst is characterized by physical adsorption BET method, arrangement of atom in the solid material is characterized by X-ray diffraction (XRD), structural morphology of the catalyst like particle size, structure, elemental analysis can be characterized by transmission electron microscopy (TEM), reduction temperatures of catalysts were characterized by temperature reduction program (TPR). Oxidation state of metal in the catalyst was measured by X-ray photo electron spectroscopy (XPS). Metal composition is determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis.

2.3.1 Physical adsorption, Brunauer–Emmett–Teller (BET)

This technique is generally used for the measurement of surface area and porosity of powders and porous materials. In these techniques, solid material is exposed to gases or vapors at different conditions and evaluated on the basis of uptake of weight or volume of sample. Analysis of these data provides information regarding the physical characteristics of the solid including: porosity, total pore volume (TOPV) and pore size distribution. Nitrogen gas is used as the probe molecule and is exposed to a solid material during analysis at liquid nitrogen conditions (i.e. 77 K) which gives adsorption isotherms of nitrogen. The surface area is calculated on the basis of measured monolayer adsorption capacity and the cross-sectional area of the molecule being used as a probe. The cross-sectional area of Nitrogen is taken as 16.2 $Å^2$/molecule.

2.3.2 X-ray diffraction (XRD)

This technique is used to characterize the polycrystalline phase of solid material. Solid material can exist in crystalline or amorphous form depending on arrangement of atom (ordered and disordered). When X-ray beam is incident on a pair of parallel plane example P1 and P2 separated by interplaner spacing 'd', two parallel incident ray make an angle 'θ' and reflected beam make an angle '2θ' with these plane. The difference in path length between incident ray and reflected ray must then be an integer (n) of wavelength (λ). This is expressed in term of Bragg's equation (1). When X-ray interacts with crystalline substance it gives characteristic diffraction pattern of that substance which is the fingerprint of that material. Powder diffraction is mainly used for "fingerprint identification" of various solid materials.

XRD diffractions were obtained ex-situ using PAN analytical Xpert Pro, Netherlands with duel goniometer diffractor equipped with a Cu Kα (1.5418 Å) radiation source with Ni filter. Data were collected in the range of 2θ = 5–90° with a step of 4° min^{-1}.

$$n\lambda = 2d\sin\theta \qquad (1)$$

$2d\sin\theta$ – is the path difference between two rays undergoing interference where θ is the scattering angle.

2.3.3 X-ray Photoelectron spectroscopy (XPS)

It is also known as electron spectroscopy and this technique used for surface analysis. It gives valuable quantitative and chemical state information from the surface of the material being studied. The average depth of analysis for an XPS measurement is approximately 5 nm. It has the ability to provide spectra with a lateral spatial resolution as small as 7.5 μm, spatial distribution information can be obtained by scanning the micro focused X-ray beam across the sample. In this technique a samples surface is exciting with mono-energetic Al kα X-rays which results in photoelectrons ejection from the sample surface. An electron energy analyzer is used to measure the energy of the emitted photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state and quantity of a detected element can be determined. The binding energy of emitted electron is calculated by using following formula

$$\text{Binding Energy} = E_{X\text{-}ray} - (E_{kinetic} + \Phi) \qquad (2)$$

Where,

$E_{X\text{-}ray}$ - Energy of X-ray

$E_{kinetic}$ - Kinetic energy of ejected photoelectron

Φ - Work function depends on spectrometer and material.

XPS spectrum is plotted between binding energy vs intensity which gives the oxidation state of metal by comparing with binding energy.

The electronic states of metals were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PH 15000C) having X-ray source Al Kα radiation. The mode of lens was LAXPS and Energy Step Size 0.1 eV. Peak in the spectrum were deconvoluted by XPSPEAK-41. All binding energy values were calibrated using the value of carbon (C1S = 284.4 eV) as a reference.

2.3.4 Transmission electron microscopy (TEM)

In this technique high accelerating voltage (200 kV) electron beam focused by magnetic lens under vacuum passes through the specimen and transmits the light. The source of electron beam is tungsten filament. Transmitted light carries information about the structure of specimen in the form of image. The vacuum is applied throughout the whole optical system to avoid the scattering of electron due to collision of electron with air molecule. In the column, magnetic coils are fixed to focus the electron beam. It works as electromagnetic condenser lens. The specimen stained with an electron dense material and is placed in the vacuum.

TEM images were obtained using FEI TECNAI T20 model instrument working at an accelerating voltage of 200 kV. Samples were dispersed in iso-propyl alcohol (IPA) by sonication and the drop casted on carbon coated copper grid.

2.3.5 Temperature program reduction (TPR)

The TPR studies were done by Micromeritics Autochem-2920 instrument in the temperature range of 50−800 °C in presence of 5% H_2 in He with a ramping rate of 5 °C min^{-1}. The catalyst was treated at 300 °C for 1h in the presence of He gas before the TPR analysis. The quantitative measurement of H_2 consumption in the TPR analysis was done by a thermal conductivity detector (TCD).

2.3.6 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

This technique is used for the analysis of metal in trace amount (in ppm level). It is the type of atomic emission spectroscopy where plasma is used to excite the atoms or ions. After excitation, they emit electromagnetic radiations and goes to the ground state. Wavelength of the

emitted radiation is characteristic for particular element and shows peak in the spectrum at that particular wavelength. The quantitative analysis of the elements can be done by calibrating instrument with standard solutions. Metal contents in the catalysts were determined by ICP-OES analysis using 'SPECTRO ARCOS Germany, FHS 12' instrument. Samples were prepared by calcining catalyst at 600 °C (5 °Cmin^{-1} ramping rate) for 6h in air. After calcination solid residue was dissolved in aquaregia followed by dilution with deionized water and filtered through 0.22 μm syringe filter before analysis.

2.4 Characterization of synthesized catalyst

2.4.1 XRD analysis

XRD analysis of the catalyst was done to know the crystalline planes of Pt and Co present in the catalyst. The XRD patterns of bimetallic Pt(0.5)Co(3)/C catalyst (Figure 2.3a) shows no peak for Pt but show presence of peak for Co$_3$O$_4$. Similarly XRD pattern of Pt(1)Co(3)/C and Pt(2)Co(3)/C shows peak for Co$_3$O$_4$. Species however as the loading of Pt increases to 3 *wt*% appearance of new peak at 41.60 ° attributed to CoPt alloy formation. Similarly as the loading of Co decreases to 0.25% (Figure 2.3b) in Pt(2)Co(0.25)/C catalyst no peak is observed for Co oxides however peak pattern were matching with Pt. Further increase in Co loading to 1 *wt*% in Pt(2)Co(1)/C, the XRD pattern of this catalyst shows appearance of peak for both Pt and Co. Further increase in Co loading to 3-4 *wt*%, appearance of diffraction peak for only Co was observed. Hence from XRD analysis it is concluded that as the loading of Co increases by keeping Pt loading constant predominant peak for Co species were observed and if Pt loading increases by keeping Co constant the peaks for Pt species were predominant. As shown in Figure 2.3c the XRD pattern of support (carbon) shows diffraction peak at 26.51° (002) attributed to the hexagonal graphitic carbon (JCPDS File No. 41-1487) and another peak at 44.64° (111), which is associated with cubic carbon (JCPDS File No. 80-0017).[2] The diffraction peaks in Pt(3)/C catalyst at 2θ of 39°, 46°, 67° and 81° are related to the Pt (111), (200), (220) and (311) crystalline planes, respectively of face-centered cubic (fcc) structure of Pt with a space group Fm-3m (JCPDS File No. 01-088-2343).[3] The XRD pattern of Co(3)/C catalyst shows diffraction peaks at 2θ of 31.47° and 44.24° indicting presence of Co in the form of face-centered cubic Co$_3$O$_4$ with a space group Fd-3m (JCPDS File No. 09-0418). Additionally, peaks at 36.58°, 42.43° reflected the presence of cubic CoO species with space group Fm-3m (JCPDS File No. 09-0402).[4] Hence XRD results, suggest that Co is present in (II)

and (III) oxidation states in the form of CoO and Co_3O_4. However, diffraction pattern of bimetallic catalyst, i.e. (Pt(3)Co(3)/C) shows appearance of new peak at 41.60° for the formation of CoPt alloy[5-7] with a space group P4/mmm (JCPDS File No. 29-0498) having tetragonal structure. The weak peak in this catalyst at 40.5° is attributed to the formation of small quantity of cubic $CoPt_3$ species with a space group Pm-3m (JCPDS File No. 29-0499).
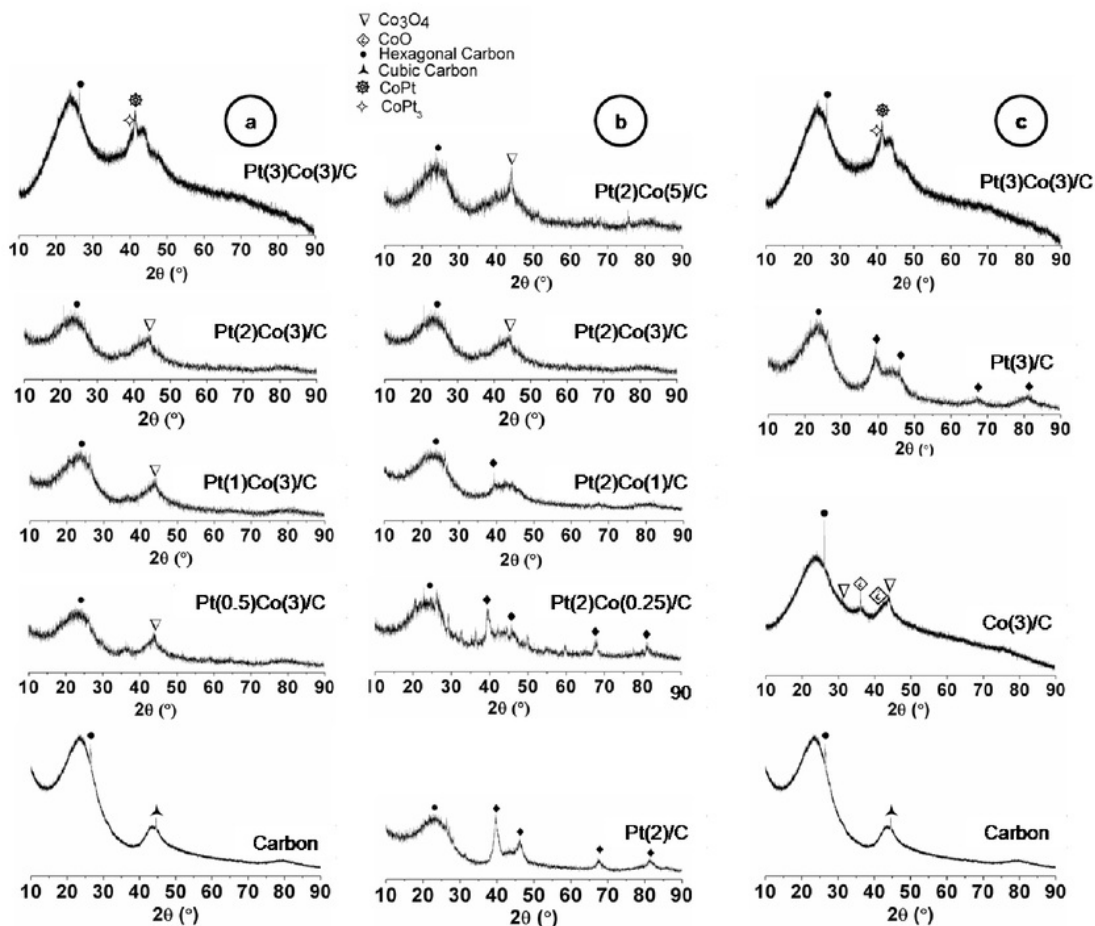
Figure 2.3 XRD patterns of synthesized mono and bimetallic catalysts

The absence of peak(s) for either CoO or Co_3O_4 species in bimetallic Pt(3)Co(3)/C catalyst is because mostly Co is situated close to Pt in the form of CoPt alloy.[5] It is also postulated that due to overall low intensity of peaks and overlapping of many peaks in the same 2θ range, it is probable that many of the peaks are masked. Additionally, it is feasible that Co might be present in the

amorphous form and thus is not detected. Thus, from XRD analysis it is suggested that Pt may assist reduce Co to form Co(0) species unlike in monometallic Co(3)/C catalyst or alloy is formed with electron rich Pt and electron deficient Co. Based on these postulations, XRD analysis of bimetallic catalysts indicates that the Co and Pt interact with each other which may influence the geometric and/or electronic properties of metals. Hence from XRD analysis of bimetallic catalysts it is concluded that the Co and Pt interact with each other which may influence the geometric and/or electronic properties of metals.

XRD pattern of Ru(3)/C catalyst

XRD pattern of Ru(3)/C catalyst (Figure 2.4)shows peaks at 2θ of 38.58°, 44.23°, 58.63°, 69.7°, 78.68°, 86.3° which are attributed to the, (100), (101), (102), (110), (103), (201) crystalline planes, respectively with space group P63/mmc (JCPDS File No 06-0663). The diffraction peak at 26.51° (002) in carbon is assigned to the hexagonal graphitic carbon (JCPDS File No. 41-1487) and the peak at 44.64° (111) is assigned to cubic carbon (JCPDS File No. 80-0017).[2]
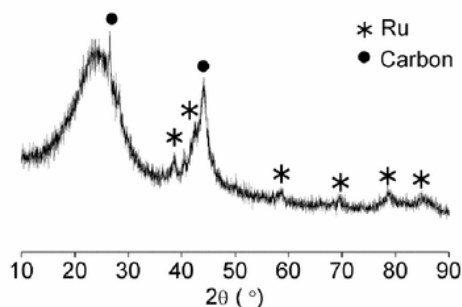
Figure 2.4 XRD pattern of Ru(3)/C catalyst

XRD pattern of Ni(10)/C catalyst

XRD pattern of Ni(10)/C catalyst (Figure 2.5) shows peaks at 2θ of 44.51°, 51.81° and 76.34° which are attributed to the, (111), (200), (220) crystalline planes, respectively with space group Fm-3m (JCPDS File No 04-0850). The diffraction peak at 26.51° (002) in carbon is assigned to the hexagonal graphitic carbon (JCPDS File No. 41-1487).[2]
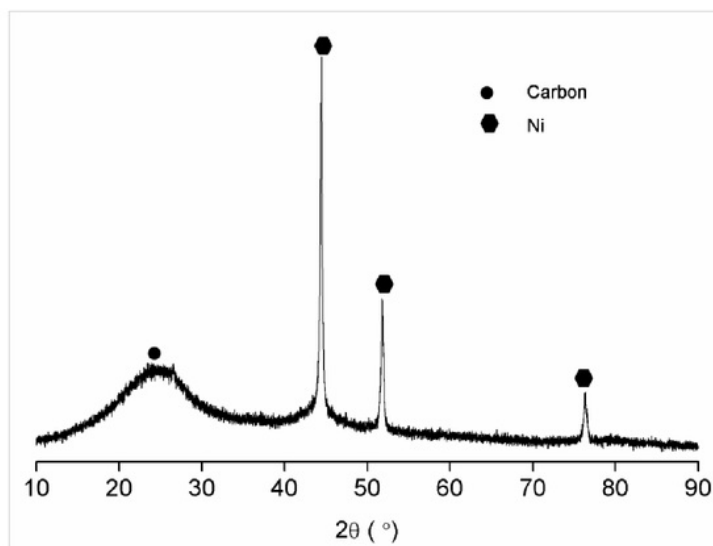
Figure 2.5 XRD pattern of Ni(10)/C catalyst

2.4.2 XPS analysis
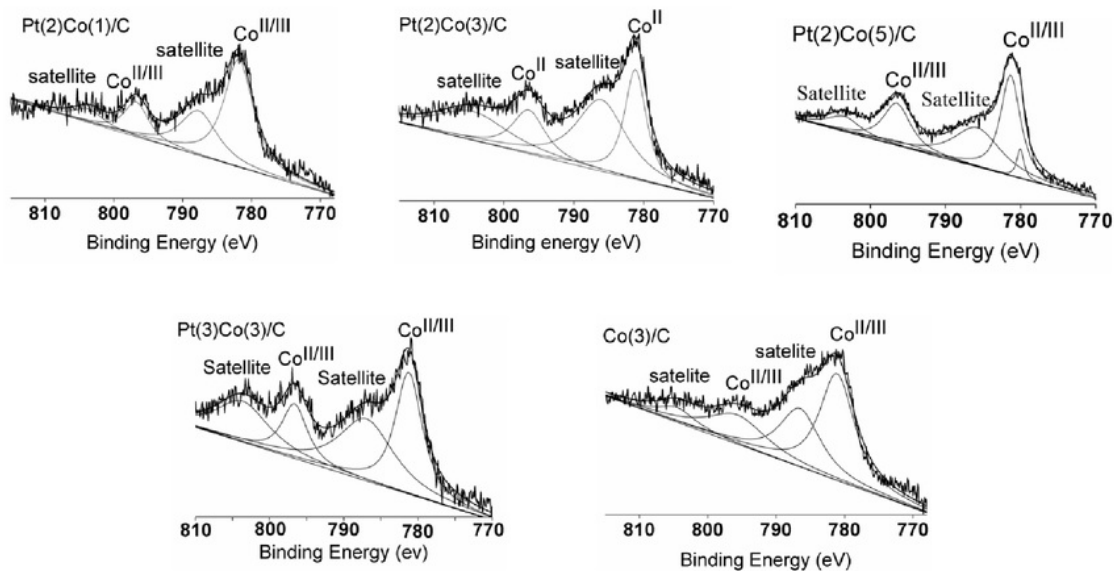
Figure 2.6 XPS deconvolution of the Cobalt core 2p level XPS spectrum

XPS analysis of mono and bimetallic catalysts were done to find the oxidation states of metals present in the catalyst (Figure 2.6-2.7). In the XPS spectrum of Co(3)/C catalyst (Figure 2.6) no peak was detected for Co zero oxidation state at binding energy (B.E) of

778-779 eV and observation of peaks for Co $2p_{1/2}$ (B.E.=796.2 eV) and Co $2p_{3/2}$ (B.E.=781.2 eV) are related to the presence of CoO and Co_3O_4 species.

This observation proves that in monometallic Co(3)/C catalyst, Co is present in II, III oxidation states. However in XPS spectrum of monometallic Pt(3)/C catalyst, strong peaks for $4f_{5/2}$ (74.5 eV) and $4f_{7/2}$ (71.1 eV) levels were observed for Pt in metallic state [Pt(0)]. Same spectrum also shows weak peaks for Pt(II) at $4f_{5/2}$ (76 eV) and $4f_{7/2}$ (72.2eV) level (Figure 2.7).
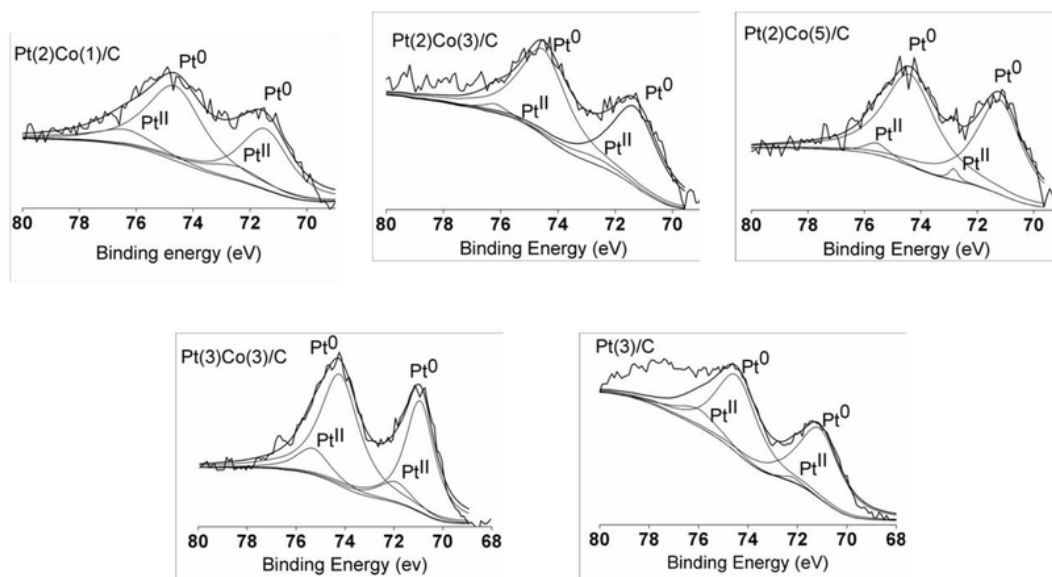
Figure 2.7 XPS deconvolution of the Platinum core 4f level XPS spectrum

From this observation it is concluded that in monometallic catalyst Co is present in CoO and Co_3O_4 oxide forms and Pt is present in metal state and these results are in line with XRD result. The XPS spectrum for bimetallic Pt(3)Co(3)/C catalyst, also shows presence of characteristic peaks for Co (II, III) species like mono metallic Co(3)/C catalyst at 781.2 eV ($2p_{3/2}$) and 796.2 eV($2p_{1/2}$), which proves that in the presence of Pt also; Co is not reduced completely.[8] Moreover the peaks for Pt are shifted to lower binding energy (74.2 eV for $4f_{5/2}$ and 71 eV for $4f_{7/2}$) compared to monometallic Pt(3)/C catalyst. Also weak peaks for Pt(II) species were observed (Figure 2).[9] The presence of Co in oxide form in bimetallic catalyst might be due to electronegativity difference between Co (1.88) and Pt (2.28), which leads to flow of electron from Co to Pt as expected thus Co is present in II

and III state.[9] Hence, with an increase in electron density on Pt metal, decrease in B.E. is observed. Taking into account this, XPS results agrees well with the fact that Pt becomes electron rich in bimetallic catalyst than in monometallic catalyst. It is also known in the literature that the core level B.E. shift, for the noble metals, could be relatively weak (<1eV).[9-11] Thus from XRD and XPS results it is believed that both, in bimetallic Pt(3)Co(3)/C catalyst electronegative Pt and electro positive Co are present in near vicinity to each other in the form of alloy.[5-7] However due to electronegativity difference between Pt and Co, Co found in II oxidation state. Similarly the XPS spectrum of other bimetallic catalyst (Figure 2.5) also shows the presence of peak at binding energy of about 781.1 eV for $Co2p_{3/2}$ which is characteristic peak for Co_2O_3 and CoO species in the form of Co(II) oxidation state.[8,7,11] Binding energy value of Pt (Figure 2.6) confirms that major amount of Pt is present in Pt^0 state and few Pt atoms are present in II oxidation state corresponding to the binding energy (B.E.) of 71, 74 eV for $4f_{7/2}$ and 72 and 76 eV for $4f_{5/2}$ respectively, which is in agreement with the earlier reports.[12,13]

XPS analysis of Ru(3)C catalyst shows the peak at binding energy 280 eV for metallic Ru as shown in Figure 2.8.[14]
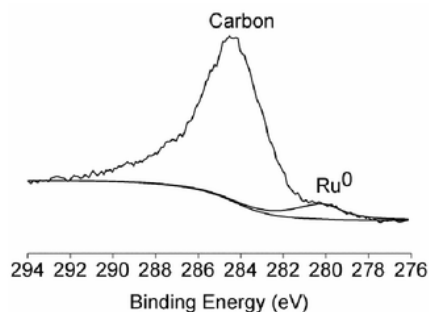
Figure 2.8 XPS spectrum of Ru(3)/C

2.4.3 BET surface area

The N_2 physisorption analysis was done to find out the change in surface area of support without impregnation of metal and also after impregnation of metal on support. The surface area of support without impregnation was found to be 753 $m^2 \cdot g^{-1}$), (Table 2.5). The surface area of supported metal catalyst shows that with loading of metal the surface area decreases as evident from the data summarized in Table 2.5.

Table 2.5 BET surface area, pore volume and pore diameter of support and catalysts

Entry no.	Catalyst	Surface area (m^2g^{-1})	Pore volume (ccg^{-1})	Pore diameter (nm)
1	Carbon	753	0.42	3.2
2	Pt(2)/C	704	0.39	3.0
3	Pt(2)Co(0.25)/C	705	0.44	3.6
4	Pt(2)Co(1)/C	685	0.45	3.0
5	Pt(2)Co(5)/C	582	0.41	3.4
6	Pt(0.5)Co(3)/C	710	0.42	3.2
7	Pt(1)Co(3)/C	720	0.42	3.2
8	Pt(2)Co(3)/C	640	0.47	3.0
9	Pt(3)Co(3)/C	630	0.39	3.0
10	Pt(3)/C	662	0.41	3.0
11	Co(3)/C	712	0.44	3.4
12	Ru(3)/C	694	0.34	3.6
13	Ru(2)/C	692	0.31	3.6

2.4.4 TEM analysis

TEM analysis was done to know the morphology of catalyst and particle size of impregnated metal present in catalyst. TEM images of all the catalysts (Figure 2.9) shows well dispersion of metal on support due to high surface area of support (Table 2.5, Entry no. 1). From TEM analysis the particle size distribution were measured (Table 2.6) and it is observed that the average particle size for monometallic catalyst i.e. Pt(3)/C and Pt(2)/C is 6 nm and for Co(3)/C catalyst average particle size is 13 nm.
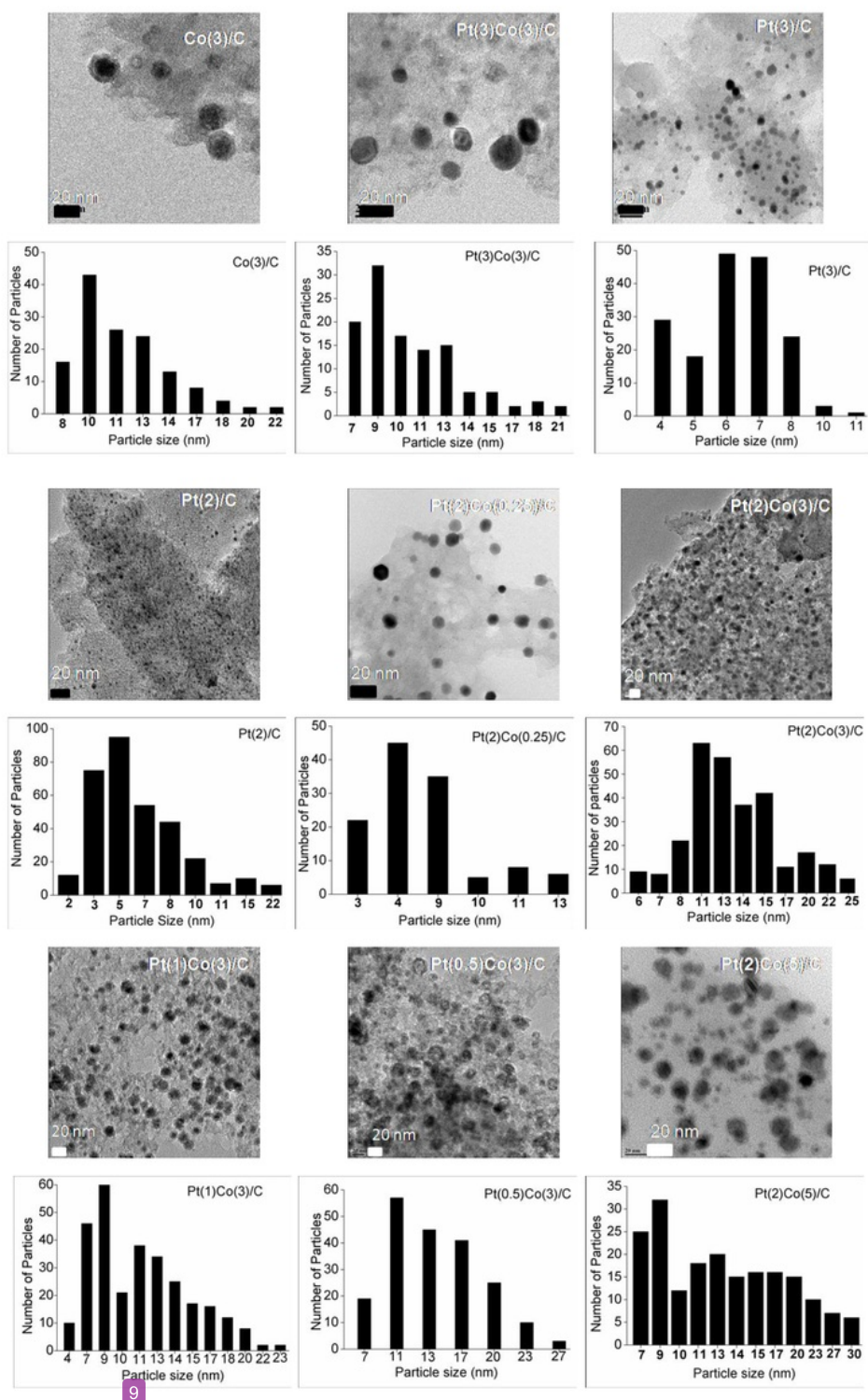
Figure 2.9 TEM images and particle size distributions of mono and bimetallic catalysts
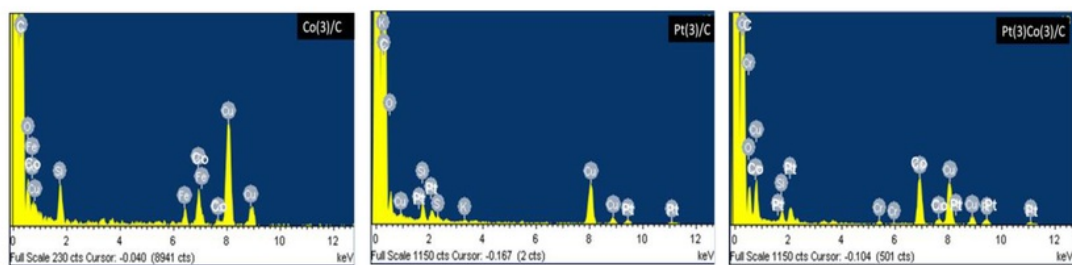
Figure 2.10 EDX spectra of Co(3)/C, Pt(3)/C and Pt(3)Co(3)/C

All bimetallic catalysts except Pt(2)Co(0.25)/C have average particle size between 9-13 nm, which is intermediate between Pt and Co monometallic catalysts. The EDX spectra of mono Pt(3)/C, Co(3)/C and bimetallic Pt(3)Co(3)/C catalyst (Figure 2.10) shows the presence of Pt, Co and Pt and Co metal in respective catalyst.

Table 2.6 Average particle size distribution in mono and bimetallic catalysts

Entry no.	Catalyst	Average particle size (nm)
1	Co(3)/C	13
2	Pt(3)/C	7
3	Pt(0.5)Co(3)/C	13
4	Pt(1)Co(3)/C	11
5	Pt(2)Co(3)/C	12
6	Pt(3)Co(3)/C	10
7	Pt(2)/C	5
8	Pt(2)Co(0.25)/C	7
9	Pt(2)Co(5)/C	11
10	Pt(2)Co(1)/C	9.6

2.4.5 SEM, EDS mapping

Figure 2.11a shows the SEM image of Pt(3)Co(3)/C catalyst and Figure 2.11b shows Energy Dispersive Spectroscopy (EDS) analysis of PtCo bimetallic catalyst elemental composition. Figure 2.11b shows the presence of Pt and Co element in the catalyst. It also shows the elemental mapping image of the bimetallic catalyst. The red and green colour represents Co and Pt element respectively. The mapping images are based on Pt, M line and Co, K line spectra

of element. The overlapping image of Pt and Co is also shown. It is observed that the elements have homogeneous dispersion on the support.
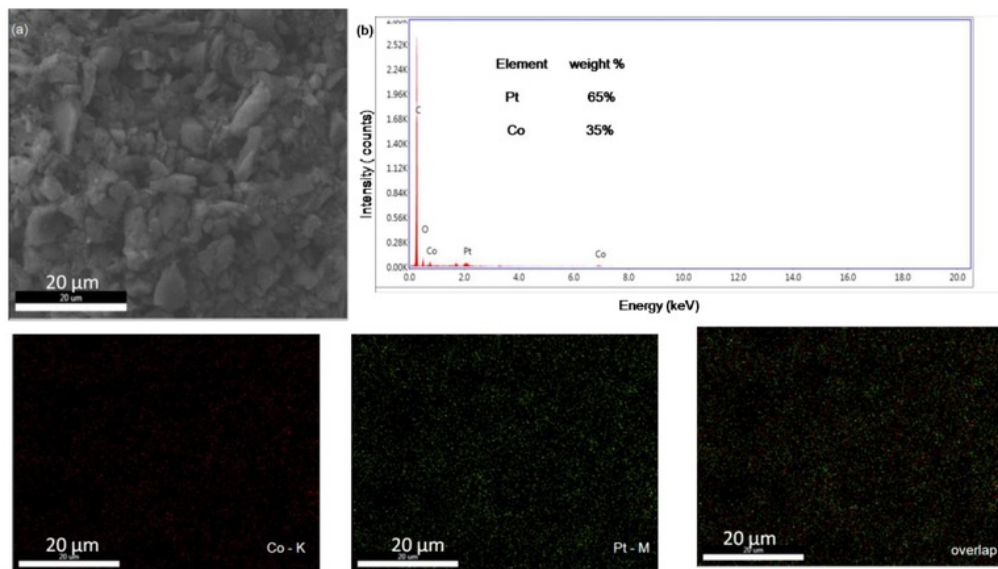
Figure 2.11 a) SEM image of Pt(3)Co(3)/C bimetallic catalyst, b) EDS mapping of Co, Pt and overlap elements

The TEM image of Ru(3)/C catalyst (Figure 2.12) shows well dispersion of metal on support surface. The average particle size of catalyst is 5 nm. EDX spectra conforms the presence of Ru metal in Ru(3)/C catalyst.
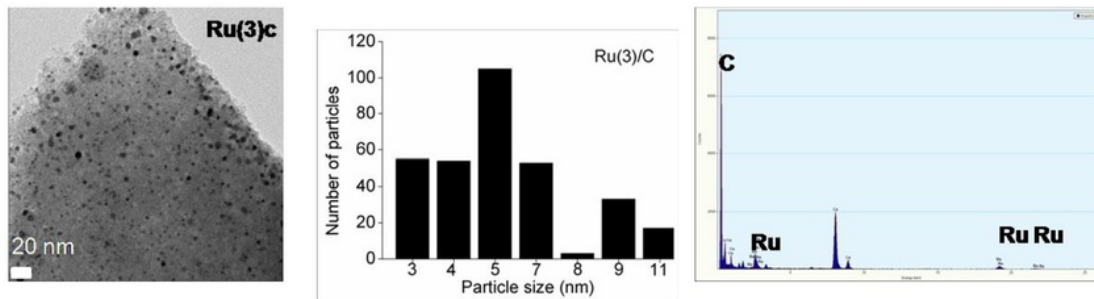
Figure 2.12 TEM image, particle size distribution and EDX spectra of Ru(3)/C catalyst

2.4.5 ICP-OES analysis

ICP analysis was done to know the exact metal loading of synthesized catalysts. It was observed that the metal content was matching with the theoretical values and the results for Pt and Co based catalyst are shown in Table 2.7. The ICP-OES analysis of Ru(3)/C catalyst shows presence of 2.97 *wt%* of Ru in catalyst.

Table 2.7 Result of ICP–OES analysis of mono and bimetallic catalysts

Entry no.	Catalyst	Pt (*wt%*)	Co (*wt%*)
1	Carbon	-	-
2	Pt(2)/C	2.09	-
3	Pt(2)Co(0.25/C	2.07	0.24
4	Pt(2)Co(1)/C	2.11	1.1
5	Pt(2)Co(5)/C	2.14	5.08
6	Pt(0.5)Co(3)/C	0.54	3.11
7	Pt(1)Co(3)/C	1.15	3.13
8	Pt(2)Co(3)/C	1.94	3.08
9	Pt(3)Co(3)/C	3.1	3.12
10	Pt(3)/C	2.98	-
11	Co(3)/C	-	3.15

2.4.6 TPR analysis

The temperature program reduction (TPR) study was carried out to know the reducible species of Pt and Co present in mono and bimetallic catalysts (Figure 2.13). The TPR profile of support (carbon) shows broad peak in the range of 340-700°C which is attributed to reduction of oxides present on carbon.[15, 16] The TPR profile of Pt(3)/C shows two peaks, one with low intensity (170-220 °C) due to reduction of PtO and 2nd broad intense peak in the range 350-799 °C for reduction of oxide species on carbon support.[16, 17] In order to prove this analysis of carbon was done by titration to know the presence of any oxide functionalities present on the carbon species and it was observed that phenolic functional group are present on the carbon surface. In the TPR profile of Co(3)/C catalyst the intense peak with peak maxima at 306 °C corresponding to reduction of Co oxide species i.e. Co(III) to Co(II) species was observed.[18, 19] However the peak intensity for reduction of Co species is high which suppress the intensity of 340-700 °C range peak which is assigned for reduction of oxide species present on carbon moreover small hump can be seen in the same region.
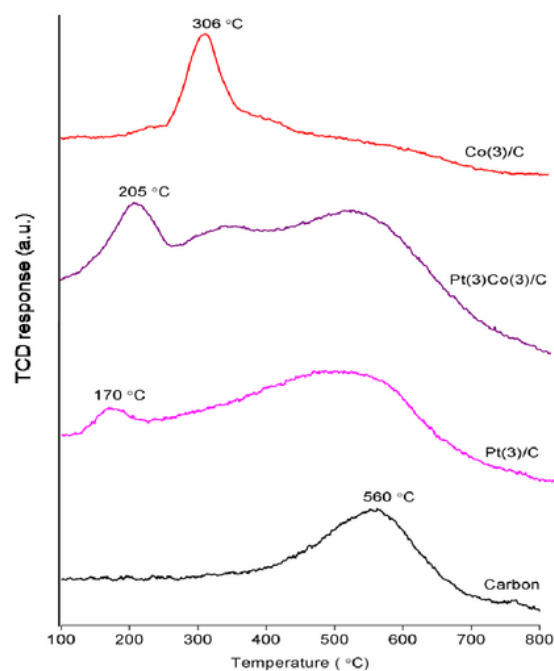
Figure 2.13 TPR profiles of support mono and bimetallic catalyst

However the TPR profile of bimetallic Pt(3)Co(3)/C catalyst is showing shift of PtO peak to lower temperature (170 °C) with increase in intensity than Pt(3)/C catalyst. This shows that Co facilitates the easy reduction of Pt.[20] Additionally shift of peak for Co II/III at lower temperature (294 °C) with weak intensity proves that there is interaction between Pt and Co and the broad peak for oxides of carbon also shifts to lower temperature and appears at 477 °C. This shows the strong interaction between metal and support.[20] The TPR analysis matches well with XRD and XPS analysis which proves that small amount of Pt is present in PtO form in Pt(3)/C catalyst and Co is present in II/III oxidation state in Co(3)/C. It also proves that there is interaction between Pt, Co and carbon.

2.5 Titration method for analysis of oxygen containing groups on the carbon surface

The concentration of oxygen containing group (-OH, -COOH and lactone) on the carbon surface were measured by titration method as reported earlier.[21, 22] The total oxygen containing group was determined by NaOH titration. Free carboxylic group were estimated by amount of 0.05 N NaHCO$_3$ consumed. Amount of lactone group was calculated by the difference between amount

of 0.05 N NaHCO₃ consumed and 0.05 N Na₂CO₃ consumed. Phenolic hydroxyl group was determined as the difference between the amount of 0.05 N NaOH and amount of 0.05 N NaHCO₃ consumed. The basic group contain was calculated as amount of HCl consumed.

2.5.1 Chemicals required

NaOH (0.05 N), NaOH (0.25 N), NaHCO₃ (0.05 N), Na₂CO₃ (0.05 N), HCl (0.05 N), oxalic acid (0.05 N), phenolphthaline, methyl orange, D. I. Water

2.5.2 Methodology

Known weight of carbon (0.020 g) was dispersed in 10 mL of NaOH (0.05 N), NaOH (0.25 N), NaHCO₃ (0.05 N), Na₂CO₃ (0.05 N), HCl (0.05 N) solution separately in 25 mL sealed bottle and sonicated for 4 h. After sonication the solution was filtered with the help of whatman filter paper and titrated with respective acid and base. Each titration was done three times. For titration of NaOH verses HCl and for HCL verses Na₂CO₃ phenolphthalein indicator was used and for titration of NaHCO₃ and HCL methyl orange indicator was used.

2.5.3 Titration results

Table 2.8 Titration results of blank and sample solution

Entry no.	Acid/Base	Normality of blank solution (N)	Normality of Sample (N)	Difference between blank and sample solution (N)
1	NaOH (0.05)	0.05	0.049	0.001
2	NaOH (0.25)	0.254	0.252	0.002
3	Na₂CO₃ (0.05)	0.027	0.027	0
4	NaHCO₃ (0.05)	0.0565	0.057	0
5	HCl (0.05)	0.05	0.045	0.005

1) Free -COOH functional group in 0.02 g carbon = Amount of 0.05 N NaHCO₃ consumed

$$= 0 \text{ N}$$

2) Amount of lactone group in 0.02 g carbon = Amount of NaHCO₃ (0.05 N) consumed - Amount of   Na₂CO₃ (0.05 N) consumed

$$= 0-0$$
$$= 0 \text{ N}$$

3) Amount of phenolic hydroxyl group in 0.02 g carbon = Amount of NaOH (0.05 N) consumed

-   Amount of NaHCO$_3$ (0.05 N) consumed

$$= 0.001\text{-}0$$

$$= 0.001 \text{ N}$$

4) Basic functional group in 0.02 g carbon =Amount of HCl consumed

$$= 0.005 \text{ N}$$

2.6 References

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Chapter 3
Role of Catalyst in Hydrogenation of
Furfural in to Furfuryl Alcohol

3.1 Introduction

As mentioned in chapter 1, section 1.3.3, biomass derived furfural (FAL) is one of the important platform chemical for the synthesis of various valuable chemicals. Presence of different functionalities in FAL like ring double bond, ring C-O bond and aldehyde group make it possible to convert into different valuable chemicals like furfuryl alcohol (FOL), 2-methylfuran (2-MF), tetrahydrofurfuryl alcohol (THFOL), 2-methyltetrahydrofuran (2-MTHF), cyclopentanone (CPO) etc. by tuning the reaction conditions.[1-4] FOL is used for the synthesis of resins which are widely used in chemical industry due to their attractive chemical resistant properties as mentioned in chapter 1, section 1.6.1. Various catalysts are reported for the conversion of FAL to FOL. As mentioned in chapter 1, commercially Cu-Cr catalyst is used for the conversion of FAL to FOL where catalyst show 100% conversion of FAL with 96-98% selectivity of FOL, however those are associated with deactivation and toxic nature of Cr make it difficult to dispose of the deactivated catalyst. Also these catalysts are operated at high temperature (150-180 °C) and high H_2 pressure (8-10 MPa).[5,6] Different metals like Pt, Pd, Co, Ir, Re, Sn are also reported in the form of mono and bimetallic catalyst for the conversion of FAL to FOL which show FAL conversion in the range of 62-100% with 99% selectivity of FOL. These catalysts are operated at the temperature range between 90-150 °C and in the presence of organic solvents like iso-propyl alcohol (IPA), ethanol, methanol for conversion of FAL to FOL.[1, 7-10] Very few catalytic systems are reported at the lower temperature in the range between 25-30 °C, however those are operated at high pressure (0.8-2 MPa) and high loading of precious metal.[11, 12] Due to high temperature and high H_2 pressure, operating conditions remains unsafe and increases the cost of process. Hence in order to replace the molecular hydrogen, catalytic transfer hydrogenation reactions were also performed in presence of proton donating solvent like IPA, with 100% conversion of FAL with 100% yield of FOL[13] and in presence of 2-butanol FAL conversion was 92% with 76% yield of FOL.[14] Moreover these reactions were carried out at high temperature above 150 °C.[15] Very few reports are available where water was used as solvent and few reports are available for recycle study of catalyst.[11,13,16] Considering these limitations it is important to develop an efficient clean catalytic system which works at low temperature and low pressure in water medium with recyclable catalyst.

3.2 Hypothesis of work

Bimetallic catalysts were reported for better results than monometallic catalyst due to change in their electronic and geometrical property in conversion of FAL to FOL in presence of PtSn/SiO$_2$ catalyst.[10] Hence for selective and efficient catalytic hydrogenation of α, β-unsaturated carbonyl group, bimetallic catalyst containing noble metal (Pt) in reduced form combined with non-noble metal like Co, Sn, Ga in oxide form is required. Hence it was anticipated that Pt will help to split H$_2$ molecule in combination with oxophillic Co metal which will polarize the carbonyl group could be the best combination for selective hydrogenation of FAL to FOL (Scheme 3.1).
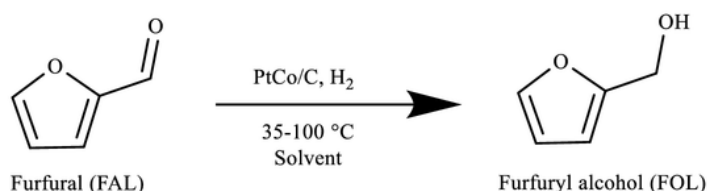
Scheme 3.1 Conversion of furfural (FAL) to furfuryl alcohol (FOL)

3.3 Materials and methods

Furfural (99%), furfuryl alcohol (99%), and 2-methylfuran (99%) were purchased from s.d. Fine chemicals. Tetrahydrofuran (99%), iso-propanol (99.5%), n-propanol (99%), n-butanol (99%), 2-butanol (98%), toluene (98.5%), ethanol (99%), methanol (99%) were procured from Alfa Aesar.

As discussed in chapter 2, supported mono and bimetallic catalyst of Pt and Co were synthesized by wet-impregnation method. The catalysts were characterized by various techniques to know their morphology and chemical property. The detailed study of catalyst characterization is given in chapter 2.

The catalyst activity was measured in Amar make reactor with 50 mL volume. The reactor was charged with 35 mL solvent, 0.35 g FAL, 0.0785 g catalyst. After addition of substrate, solvent and catalyst, reactor was tightly closed and flushed with H$_2$ 3-4 times to remove any air. H$_2$ gas was flushed four-five times in reactor to remove air, followed by filling reactor with required H$_2$ pressure (0.1-1 MPa). Initially stirring speed of reactor was maintained at 300 rpm and increased to 900 rpm after reaching the desired temperature.

The analysis of reaction mixture (organic solvent) was done by Varian GC equipped with HP-5 capillary column (0.25 μm x 0.32 mm x 30 m), a FID detector (30 mL·min^{-1} N$_2$ flow as a carrier gas, 250 °C) and the oven temperature program was as follows: 50 °C (hold time 1 min) to 200 °C (hold time 10 min) at the 15 °C min^{-1} of ramp rate, injector temperature 200 °C. The analysis of aqueous solvent was done by HPLC. The HPLC (Agilent Technologies, 1200 infinity series, USA) equipped with an HC-75 Pb^{2+} column (Hamilton, 7.8 mm × 300 mm, 80 °C) and refractive index detector (Agilent Technologies, 1200 infinity series, 40 °C) were used. The GC-MS (Agilent-7890 GC and Agilent MS-5977A MSD) having DB-MS column (0.25 μm × 0.25 mm × 30 m) was used for the analysis. Temperature programs used were similar to that for GC-FID. The NIST library was used for product identification.

Figure 3.1 Reaction setup

The conversion, yield, TON and TOF were calculated with the help of following formulae.

$$Yield\ (\%) = \left[\frac{Mole\ of\ product\ formed}{Theoretical\ mole\ of\ product}\right] \times 100$$

$$Conversion\ of\ Furfural\ (\%) = \left[\frac{Initial\ mole\ of\ Furfural - Final\ mole\ of\ Furfural}{Initial\ mole\ of\ Furfural}\right] \times 100$$

$$TOF\ (min^{-1}) = \left[\frac{Mole\ of\ substrate\ converted}{Mole\ of\ active\ site \times time}\right] \times 100$$

$$TON = \left[\frac{Mole\ of\ substrate\ converted}{Mole\ of\ active\ site}\right] \times 100$$

3.4 Catalytic activity

3.4.1 Effect of mono and bimetallic catalyst at 100 °C

Initially the reactions were carried out at 100 °C with mono and bimetallic catalyst to see the catalytic performance in the conversion of FAL to FOL and the results are shown in Figure 3.2. Non catalytic reaction shows 2% conversion of FAL with 2% yield of FOL. In presence of carbon the conversion was 8% with 1% yield of FOL. Compared to non-catalytic results, conversion of FAL was high in presence of carbon however formation of FOL was found to be negligible. This was attributed to predominance of side reactions like polymerization of FAL on the surface of carbon which cannot be detected by GC and also adsorption of substrate on the surface of carbon. This shows that carbon is inactive for hydrogenation of FAL to FOL. In presence of Pt(3)/C catalyst, the conversion was 34% with 33% yield of FOL due to activation of hydrogen molecules by Pt metal. This catalyst shows good selectivity for FOL however activity is low. In presence of monometallic Co(3)/C catalyst the conversion was 12% with 3% yield of FOL. The result obtained in presence of Co(3)/C catalyst was comparable to that of carbon. This fact indicates that under reaction condition, Co and carbon alone have no potential to activate H_2 molecule. Hence the rate of formation of FOL was negligible in presence of Co monometallic catalyst and carbon. However it promotes side reaction like polymerization or adsorption of FAL on catalyst surface attributed to 8-12% conversion of FAL.
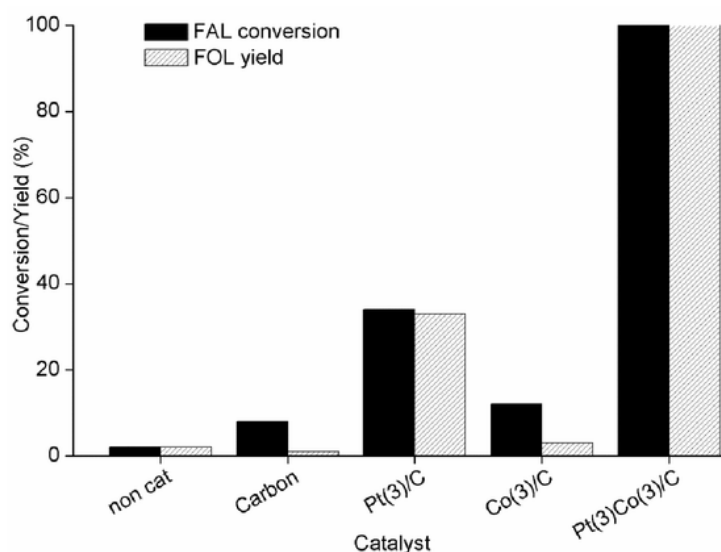
Figure 3.2 Effect of mono and bimetallic catalysts on the hydrogenation of FAL to FOL

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; 100 °C; 5 h; H_2 pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol).

Moreover, bimetallic catalyst shows significant improvement in the result with 100% conversion of FAL and 100% yield of FOL was obtained. From the activity of Co(3)/C catalyst it is concluded that monometallic Co(3)/C catalyst is inactive for hydrogenation of FAL under reaction condition. However Pt(3)/C catalyst was active and promote hydrogenation of FAL but the rate of reaction was slow. Moreover addition of Co with Pt in bimetallic Pt(3)Co(3)/C catalyst showed tremendous improvement in the activity of catalyst. Combining these results with XPS data it is proposed that due to synergetic effect of Pt(0) and Co(II/III) in bimetallic catalyst where Pt activates H_2 molecule and Co polarize the carbonyl group facilitates easy reduction of carbonyl group than ring double bond and selectively hydrogenate carbonyl group to form FOL.

3.4.2 Effect of varying Pt loading with Co(3) in bimetallic catalyst on hydrogenation of FAL to FOL

Earlier results showed better performance of bimetallic catalyst than monometallic catalysts in hydrogenation of FAL to FOL. Hence, the role of both metals (Pt and Co) in

bimetallic catalyst with varying loading were checked to see their effect. Initially reactions were carried out with various bimetallic catalysts with 3 *wt*% Co and varied Pt metal loading from 0.5-3 *wt*% as shown in Figure 3.3. Bimetallic catalyst (Pt(3)Co(3)/C) is showing best activity among all the catalysts with 100% conversion of FAL and 100% yield of FOL. The TON of catalyst was calculated to be 2582. Under similar condition Pt(2)Co(3)/C catalyst showed 92% conversion with 91% yield and TON was 4275. This shows that Pt(2)Co(3)/C is the most efficient catalyst. With increase in Pt loading, the conversion and yield of FAL and FOL increases. The enhancement in activity of bimetallic catalyst with increased Pt loading attributed to the availability of more active sites for adsorption of H_2 molecule leading to heterolytic splitting of H_2 into H^+ and H^- ions, which gets spill over on the catalyst surface where it comes in contact with adsorbed carbonyl group resulting in its reduction. However, Pt(0.5)Co(3)/C catalyst showed 51% FAL conversion with 23% FOL yield (FOL selectivity 45%) and in presence of Pt(1)Co(3)/C catalyst 69% conversion of FAL with 45% yield of FOL (FOL selectivity 65%) was observed.
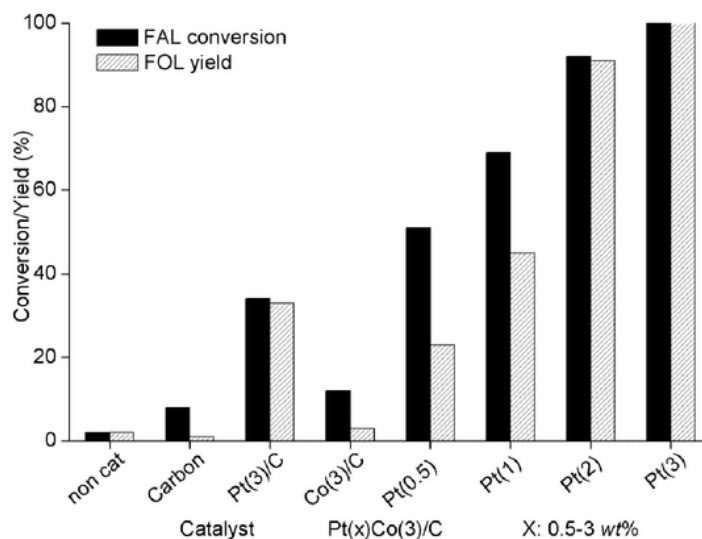
Figure 3.3 Effect of varying Pt loading with Co(3) in bimetallic catalyst

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; 100 °C; 5 h; H_2 pressure 1 MPa, at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol).

The lower selectivity of FOL at lower loading of Pt (Pt(0.5)Co(3)/C, Pt(1)Co(3)/C) is due to lesser availability of active site for activation of H_2 molecules. It diverts the reaction towards the formation of side (polymerized) products which could not be detected by GC. Hence it was concluded that the optimum Pt loading (2 *wt%*) was required for better performance of catalyst.

3.4.3 Effect of varying Co loading with Pt(3) in bimetallic catalyst

To study the role of Co metal, various bimetallic catalysts having 3 *wt%* Pt with varied Co loading from 0.25 to 5 *wt%* were checked as shown in Figure 3.4. With increase in Co loading from 0.25 to 3 *wt%* the conversion of FAL reaches to 100% with 100% yield of FOL and further increase in Co loading from 3 to 5 *wt%*, decrease in the activity of catalyst was observed. This decrease in activity of catalyst with increased in Co loading to 5 *wt%* could be attributed to covering of the active Pt sites by excess Co metal which reduce the accessibility of Pt metal to H_2 molecule. Metal loading study of Pt and Co in bimetallic catalyst proves that both metals (Pt and Co) were playing synergetic role in selective conversion of FAL to FOL as shown in Figure 3.5.[10]
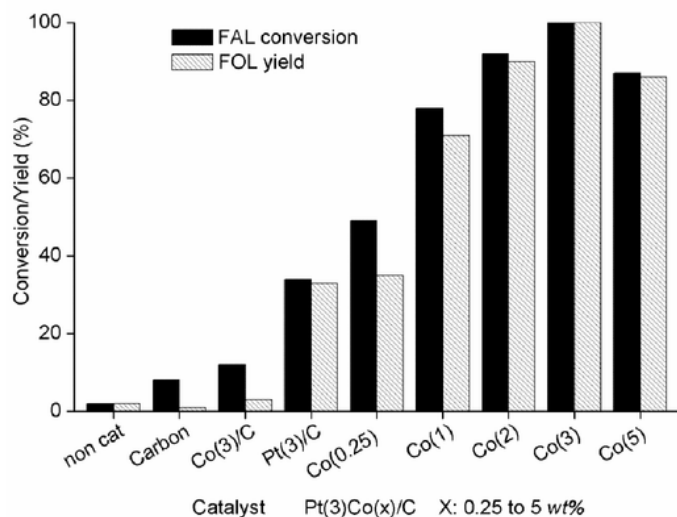
Figure 3.4 Effect of varying Co loading with Pt(3) in bimetallic catalyst

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; 100 °C; 5 h; H_2 pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol).
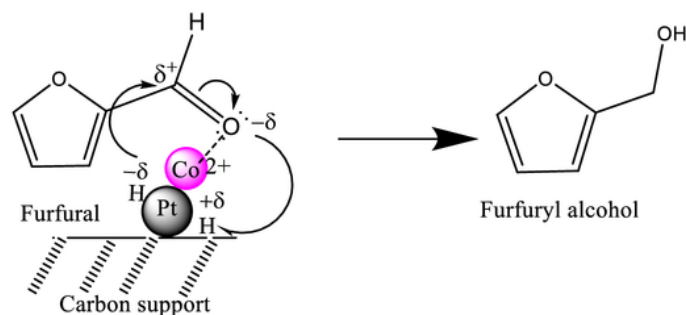
Figure 3.5 Proposed reaction mechanism for hydrogenation of FAL to FOL

3.4.4 Conversion of FAL to FOL at 50 °C and 1 MPa H₂

Bimetallic Pt(3)Co(3)/C catalyst was showing best activity among all catalyst at 100 °C with 100% yield of FOL. Hence to study the conversion at lower temperature, the reaction was carried out at 50 °C,1 MPa H₂ pressure for 10 h (Figure 3.6).
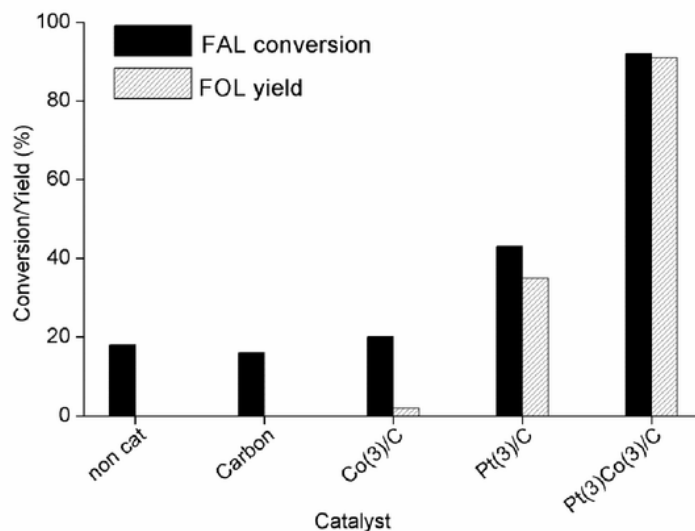
Figure 3.6 Hydrogenation of FAL to FOL at 50 °C

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; 50 °C; 10 h; H₂ pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol).

The results show that bimetallic Pt(3)Co(3)/C catalyst gives good activity even at 50 °C with 92% FAL conversion and 99% selectivity of FOL in IPA solvent. However the results obtained from non-catalytic reaction, carbon and Co(3)/C catalyst were almost similar (conversion of FAL becomes 16-20% with negligible amount of FOL formation) which indicates that at 50 °C, with longer time (10 h) and unavailability of active sites promotes undesired side reaction. The activity of bimetallic catalyst was found to be more than monometallic catalyst even at lower temperature.

3.4.5 Effect of H_2 pressure on conversion of FAL to FOL at 50 °C

Under 1 MPa H_2 pressure and 50 °C appreciable results were observed. Hence in order to study the effect of lower H_2 pressure, the reactions were carried out with varying H_2 pressure from 0.1 to 1 MPa as shown in Figure 3.7.
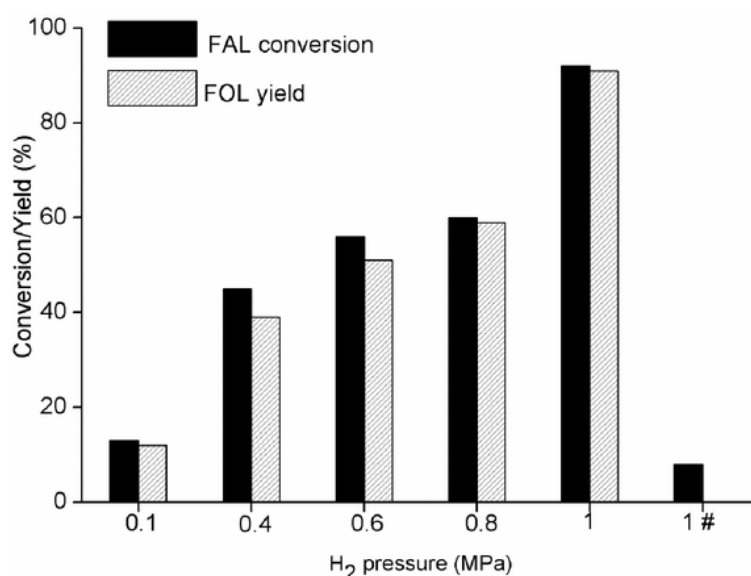
Figure 3.7 Effect of H_2 pressure on the hydrogenation of FAL to FOL
Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; iso-propyl alcohol, 35 mL; 50 °C; 10 h; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, # - N_2 pressure).

The results represent that with increase in H_2 pressure from 0.1 to 1 MPa the conversion of FAL and yield of FOL increases.[17] This was attributed to increase in solubility of gas with

increase in pressure known from Henry's law. It is reported in the literature that with increase in pressure of H_2 from 0.751 to 1.10 MPa, the mole fraction of H_2 in IPA increases from 0.18 to 0.61 x 10^{-4} at 25 °C and at 50 °C with 0.698 to 1.22 MPa pressure the mole fraction of H_2 increases from 21.20 to 37.14 x 10^{-4}.[18, 19] Hence with increase in pressure the solubility of H_2 increases which ultimately enhances interaction between catalyst and H_2 leading to improvement in FOL yield. Further to study the source of H_2, the reactions were done under 1 MPa N_2 pressure and it was observed that under N_2 atmosphere the conversion reaches to 10% without formation of FOL which represents that external H_2 pressure is required to carry out reaction. However in literature it is known that IPA acts as H_2 donor at higher temperature above 140 °C.[20] Hence to study the effect of temperature on catalytic transfer hydrogenation in IPA, further reactions were carried out at higher temperature (100 °C and 150 °C) under 1 MPa N_2 pressure. The experimental results at 100 °C showed only 7% conversion of FAL without formation of FOL. However at 150 °C the conversion of FAL was 8% with 100% selectivity of FOL.[20] Hence at 150 °C as reported earlier the catalytic transfer hydrogenation occurred however the activity was very low. This result again proves that the source of H_2 is external pressurized H_2 and not the IPA under reaction condition at lower temperature (50-100 °C).

3.4.6 Effect of catalyst loading under 0.1 MPa H_2

Hence to improve the FOL yield under 0.1 MPa H_2 pressure, the catalyst loading was increased from 0.080 to 0.12 g. With increase in catalyst loading, FAL conversion reaches to 26% with 24% yield of FOL. Considering these encouraging results the loading of catalyst further increased to 0.16 g. With increased in catalyst loading FAL conversion improves to 59% with 57% yield of FOL. Hence under similar condition reaction was performed for longer time (20 h) to improve the yield. Within 20 h, 84% FOL yield was achieved with 90% conversion. This result showed that in presence of IPA solvent under 0.1 MPa H_2 pressure FOL yield improved to 84% however the rate of reaction was slow due to decreased solubility of H_2 at lower H_2 pressure (0.1 MPa). It is reported in the literature that at 50 °C and 0.02 MPa H_2 the mole fraction of H_2 was zero however at 0.698 MPa mole fraction of H_2 increased to 21.20 x10^{-4}.[18, 21] Pressure study shows that catalyst was giving activity at 50 °C and 0.1MPa H_2 pressure with 12% yield of FOL and 13% conversion of FAL (Figure 3.8) however the rate of reaction was slow.
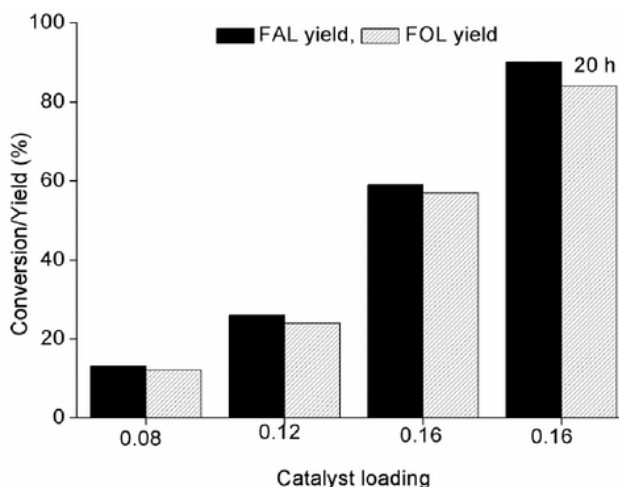
**Figure 3.8** Effect of catalyst loading at 0.1 MPa H_2 pressure on hydrogenation of FAL to FOL **Reaction condition:** FAL, 0.35 g; Pt(3)Co(3)/C; iso-propyl alcohol, 35 mL; 50 °C; 10 h; H_2 pressure, 0.1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfurylalcohol)

3.4.7 Effect of solvent polarity with different time

Table 3.1 Effect of solvent polarity on conversion of FAL to FOL

Entry no.	Solvent	1 h		2 h		10 h	
		FAL conversion (%)	FOL yield (%)	FAL conversion (%)	FOL yield (%)	FAL conversion (%)	FOL yield (%)
1	water	95	95	100	100	100	98
2	methanol	60	30	87	82	100	96
3	ethanol	48	40	68	52	100	98
4	1-propanol	18	16	61	39	100	95
5	2-propanol	17	15	45	36	92	91
6	1-butanol	17	13	54	43	100	94
7	2-butanol	17	11	55	41	94	90
8	toluene	7	6	10	10	87	68

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; solvent, 35 mL; 50 °C; H_2 pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol).

From the earlier study it was observed that in IPA medium at 100 °C the yield of FOL was 100% however decreases to 92% at 50 °C. Hence in order to study the effect of polarity of

solvent at lower temperature on the yield of FOL reactions were carried out in different solvents with varying polarity. Various solvents like methanol, ethanol, propanol, butanol and toluene were used to carry out reactions for 1, 2 and 10 h and the results are summarized in Table 3.1. Among all solvents water is showing the best activity even at shorter time (1 h, 95% FAL conversion and 95% FOL yield).

The order of activity of solvent in the conversion of FOL was as follows; water>methanol> ethanol>propanol>butanol> toluene. This order corresponds with the polarity index and Hansen solubility parameter of solvent as shown in Table 3.2. The best activity was observed in water medium within 1 h with 95% yield of FOL due to its high polarity index among all solvents. Poor activity of toluene for conversion of FAL to FOL attribute to its lower polarity index. From these facts it is proposed that with increase in polarity of solvent (water) the interaction between the FOL and solvent increases and carbon from catalyst being hydrophobic in nature reduces the adsorption competition of water on catalyst surface. FAL adsorption on the catalyst surface increases leading to increase in interaction between FAL and catalyst. From the previous report it is known that hydrophilic catalyst preferentially adsorb water than FAL. It decrease the accessibility FAL on catalyst surface resulting in decreased catalyst activity.[22] The polar nature of solvent helps to desorbed FOL from catalyst surface which creates new active sites for adsorption of FAL. In addition to this, Hansen solubility parameter is playing role. FAL has an HSP value of (22.9 δ/MPa) and FOL has HSP value of (25.6 δ/MPa). Moreover water has higher HSP value 47.9 and among all organic solvents methanol has higher HSP value (29.7 δ/MPa) hence it is observed that water and methanol is showing better activity among all tested organic solvents.[23, 24]

Another factor which is responsible for change in activity is the solubility of H_2 in different solvents. The K_H value of H_2 in water is 7.45 x 10^{-3} MPa and ethanol have K_H value 0.44 x 10^{-3} MPa at 50 °C.[25, 26] Hence solubility of H_2 is more in water than ethanol however among alcohols, methanol is showing higher activity due to higher solubility of H_2 in methanol than other alcohols.[17] The solubility of H_2 in methanol is 3.75 M, in ethanol 2.98 M and in toluene 3.50 M.[27]

Table 3.2 Polarity index and Hansen solubility parameter of solvents

Entry no.	Solvent	Polarity index	Hansen solubility parameter HSP (δ/MPa)
1	water	10.2	29.7
2	methanol	5.2	26.0
3	ethanol	4.3	24.3
4	1-propanol	4.0	23.5
5	2-propanol	3.9	23.1
6	2-butanol	4.0	22.1
7	1-butanol	4.0	18.2
8	toluene	2.4	47.9
9	furfural	-	22.9
10	furfuryl alcohol	-	25.6

One more additional factor is side reaction of substrate with solvent. It is well known that FAL in presence of alcohols like ethanol, methanol and propanol forms acetal like products. FAL in the presence of methanol as a solvent, forms 2-hydroxy, 1-methoxy ethylfuran, and in the presence of ethanol, 2-furaldehyde diethyl acetal formation is observed.[28-31] In presence of methanol, the conversion was 87% but the yield of FOL was 82% due to the formation of 2-hydroxy, 1-methoxy ethylfuran which was confirmed from GC-MS analysis (m/z, 142, 111, 95, 53) and when the reaction was carried out in the ethanol medium, formation of 2-furaldehyde diethyl acetal product was observed (m/z, 170, 125, 97, 95). Hence from this it was concluded that different factors were responsible for change in activity of catalyst in different solvents.

3.4.8 Activity of catalyst at 35 °C and 1MPa H_2 in water medium

Bimetallic Pt(3)Co(3)/C catalyst was giving 100% FOL yield in water medium at 50 °C in 2 h which shows high activity of catalyst. Hence it was decided to carry out reaction close to room temperature (35 °C). With bimetallic Pt(3)Co(3)/C catalyst at 35 °C, in presence of water medium and 1 MPa H_2 pressure 100% yield of FOL was achieved.
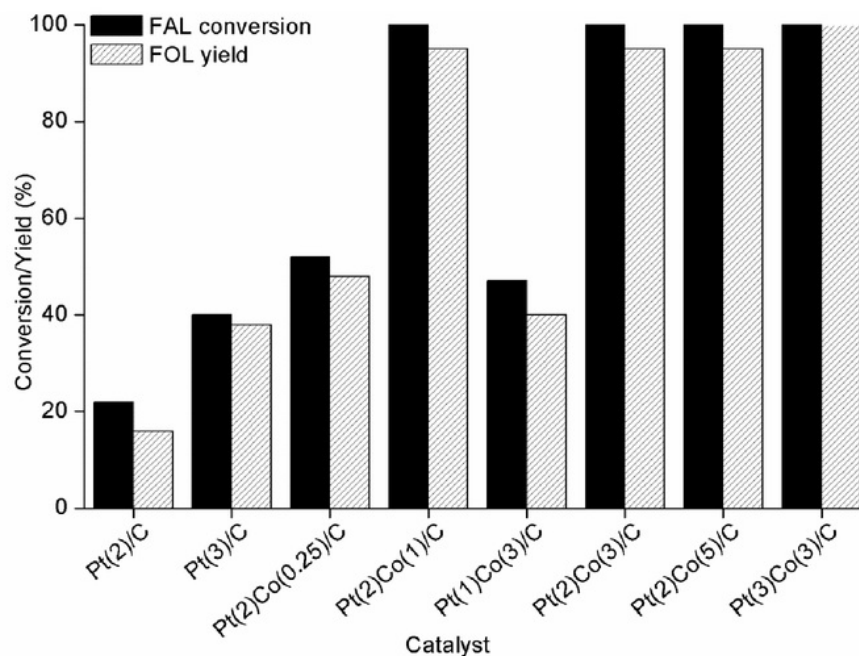
Figure 3.9 Activity of bimetallic catalyst in water medium at 35 °C and 1 MPa H_2

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; water, 35 mL; 35 °C; 10 min; H_2 pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol).

Similarly, the catalytic performance of all catalysts with varying metal loading was tested under identical reaction condition and the results are shown in Figure 3.9. Monometallic Pt(2)/C catalyst shows decrease in activity with 22% conversion of FAL and 16% FOL yield and with increase in Pt loading by 1 *wt*% (Pt(3)/C) shows 40% conversion and 38% FOL yield. The increase in activity of Pt(3)/C catalyst with that of Pt(2)/C catalyst was due to increase in active sites. However, bimetallic Pt(2)Co(0.25)/C catalyst shows increase in conversion from 22 to 52% and FOL yield reaches to 48%. This shows that addition of Cobalt improves the catalytic activity. Further, increase in loading of cobalt from 0.25 to 1 *wt*% (Pt(2)Co(1)/C) the conversion of FAL reaches to 100% with 95% yield of FOL. However decrease in loading of Pt to 1% and increase in loading of Co to 3% i.e. Pt(1)Co(3)/C catalyst shows decrease in yield of FOL. The Pt(2)Co(3)/C and Pt(2)Co(5)/C catalyst shows 100% conversion with 95% yield of FOL. However Pt(3)Co(3)/C catalyst shows 100% conversion with 100% yield of FOL. Among all catalysts, Pt(3)Co(3)/C catalyst is showing best activity. This fact shows that the optimum

loading of Pt and Co was 3 *wt%*. In order to calculate the TOF values, the reactions were carried out for 10 min with Pt(3)Co(3)/C, Pt(3)/C and Co(3)/C catalyst. The Pt(3)Co(3)/C catalyst gives 28% conversion of FAL and 27% yield of FOL with TOF value 753.1 min^{-1}.
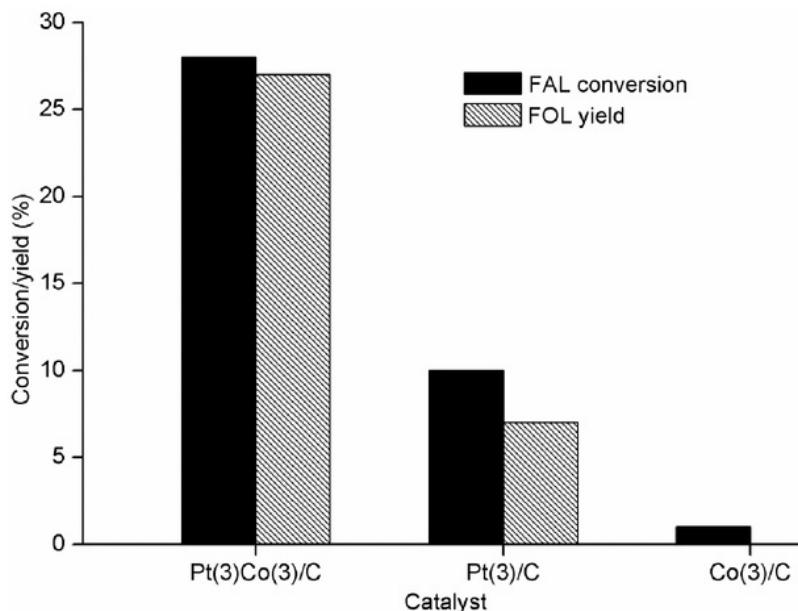
Figure 3.10 Activity of bimetallic catalyst in water medium at 35 °C for shorter time
Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; water, 35 mL; 35 °C; 10 min; H$_2$ pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol)

The monometallic Pt(3)/C catalyst shows 10% FAL conversion with 7% yield of FOL and TOF calculated was 161.3 min^{-1} and monometallic Co(3)/C catalyst shows 1% conversion with no FOL formation (Figure 3.10). This shows that the activity of Pt(3)Co(3)/C bimetallic catalyst significantly increased in water medium even at 35 °C.

3.4.9 Recycle study of catalyst

Recycle study of catalyst was done to check the reusability of catalyst. The spent catalyst was recovered by centrifugation of reaction mixture (reaction condition: Pt(3)Co(3)/C, 0.0785 g, water 35 mL, 35 °C, 1 MPa H$_2$, 10 h) followed by filtration and the recovered catalyst was used as it is without further treatment. The recycle study shows that catalyst is recyclable until 4th run with marginal loss in activity (Figure 3.11). The loss in activity of catalyst is due to handling error which leads to loss of catalyst. To see the effect of loss of catalyst on the conversion and

yield, further recycle study was done by keeping the substrate to catalyst ratio constant. For this study the reaction mixture was centrifuged and recovered catalyst was dried at 60 °C for 12 h and activated at150 °C for 3 h and dried catalyst was used for next run without further treatment. This shows that the catalyst is recyclable until 3rd run without loss in activity as shown in Figure 3.12.
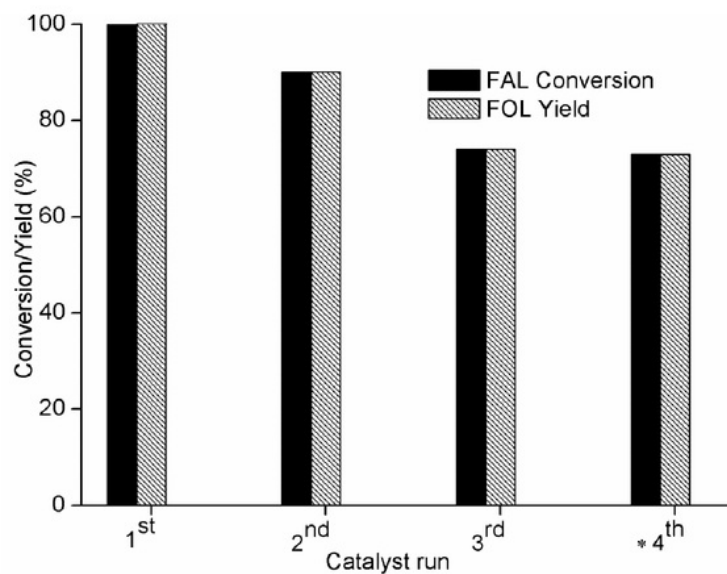
Figure 3.11 Recycle study of catalyst at 35 °C with 1 MPa H$_2$

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; water, 35 mL; 35 °C; 10 h; H$_2$ pressure, 1 MPa at room temperature; 900 rpm (*0.050 g catalyst was recovered from 3rd run and before 4th catalytic run, catalyst recovered from 3rd catalytic run was reduced at 400 °C for 2 h under H$_2$ flow) (FAL: Furfural, FOL: Furfuryl alcohol)
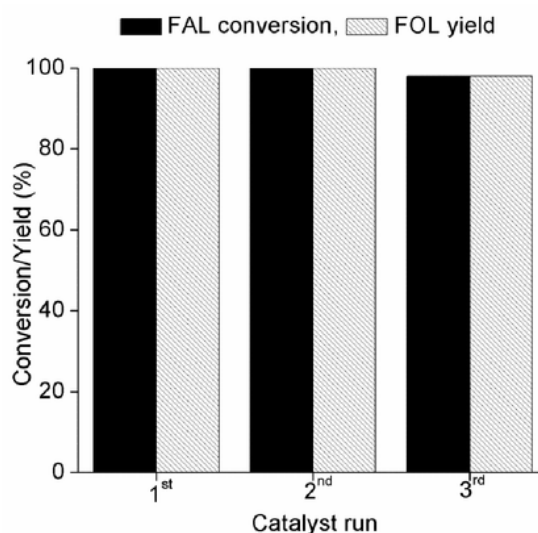
Figure 3.12 Recycle study of catalyst with substrate/catalyst ratio constant

Reaction condition: FAL: catalyst ratio, 4.43 *wt/wt*; water, 35 mL; 35 °C; 10 h; H_2 pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol)

3.4.10 Conversion of FAL to FOL at 0.1 MPa H_2

The catalyst is showing best activity at 35 °C and 1MPa H_2 hence in order to study the effect of lower pressure, the reaction was carried out at 35 °C and 0.1 MPa H_2. Initially reaction was carried out for 5 h with 0.1 MPa H_2 at 35 °C as shown in Table 3.3. Result showed that catalyst gave 65% conversion of FAL with 63% FOL yield. In order to improve the result, the reactions were carried out with increase in catalyst loading to 0.16 g under similar reaction condition. With increased in catalyst loading the yield of FOL achieved to be 72% with 83% conversion of FAL. However, considering the result of 5 h reaction, it was decided to carry out reaction for 10 h to achieved 100% conversion of FAL with maximum yield of FOL. Hence the reaction was carried out for 10 h and it was observed that the yield of FOL reached to 100%. Moreover, the rate of reaction was very slow, hence in order to increase the rate of reaction, temperature was increased to 100 °C and within 4 h, 100% conversion with 100% yield of FOL was obtained, and HPLC profile show single peak of FOL (Figure 3.13).

3.4.11 Extraction of product from reaction mixture

To confirm the purity of the formed FOL product, it was extracted by solvent extraction method in ethyl acetate from reaction mixture (water). Ethyl acetate layer was separated and

subjected to rotavapour at 35 °C to remove ethyl acetate from product. After separation of ethyl acetate, the product obtained was subjected to NMR analysis. As shown in Figure 3.14 and 3.15 NMR analysis showed that product was pure without FAL impurity which confirm that Pt(3)Co(3)/C bimetallic catalyst is active at lower pressure in water medium.

Table 3.3 Hydrogenation of FAL under 0.1 MPa H_2

Entry no.	Time (h)	FAL conversion (%)	FOL yield (%)
1	5	65	63
2[a]	5	83	72
3	10	100	100
4[b]	4	100	100

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; water, 35 mL; 35 °C, H_2 pressure 0.1 MPa, at room temperature, 900 rpm. [a] Catalyst, 0.16 g; [b] 100 °C.
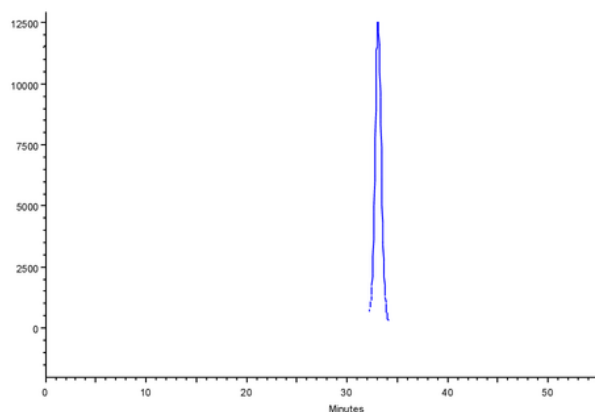
Figure 3.13 HPLC profile of reaction mixture
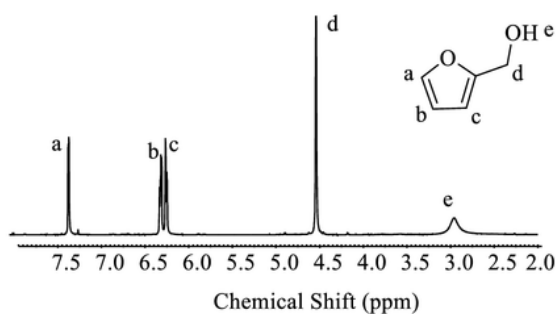
Figure 3.14 ^{1}H NMR spectrum of FOL (extracted product)
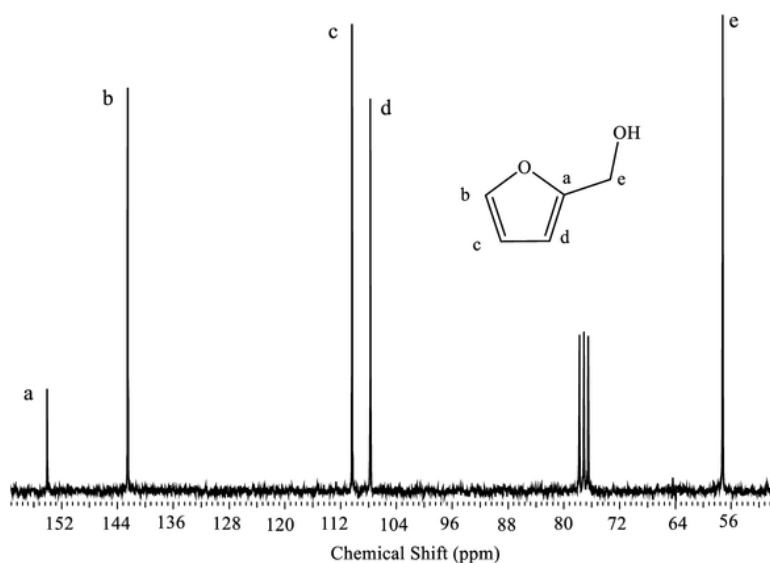
Figure 3.15 ^{13}C NMR spectrum of FOL (extracted product)

3.4.12 Characterization of spent catalyst

After carrying out reaction at 35 °C and 0.1 MPa H_2 pressure, the spent catalyst was characterized by different techniques like XRD, XPS, TEM BET surface area and ICP-OES analysis. XRD patterns (Figure 3.16) of fresh catalyst were matching with the spent catalyst.
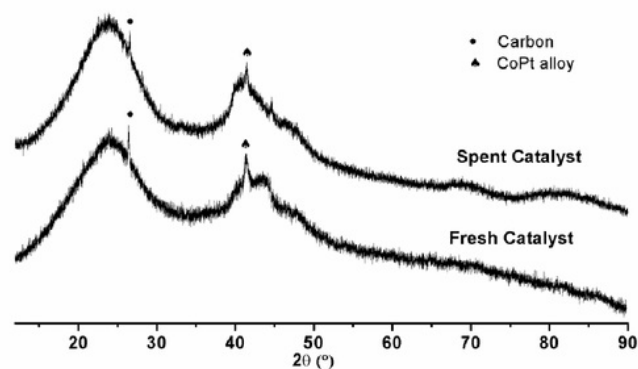
Figure 3.16 XRD patterns of fresh and spent catalysts (35 °C, 0.1 MPa H_2, 20 h)

XPS analysis (Figure 3.17) shows presence of Pt in zero oxidation state and Co in II/III oxidation state like fresh catalyst. BET surface area of spent catalyst (635 $m^2 \cdot g^{-1}$) was matching with fresh catalyst (630 $m^2 \cdot g^{-1}$). TEM analysis of spent catalyst (Figure 3.18), shows particle size distribution nearly similar to fresh catalyst with no sintering of metal. ICP-OES analysis shows loss of Co metal (1.94 ppm) however no leaching of Pt metal was found. All these characterizations show no change in the morphology of catalyst but small loss of Co was observed.
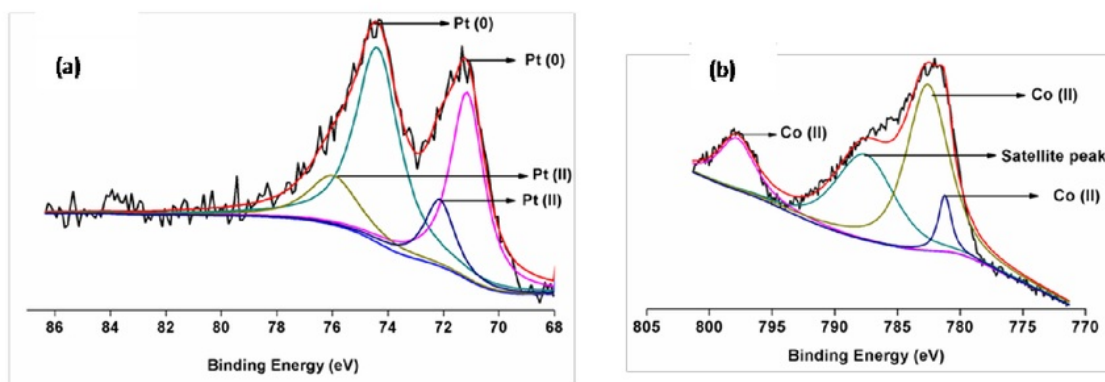
Figure 3.17. Deconvoluted XPS spectra of (a) Pt 4f level of Pt(3)Co(3)/C spent catalyst and (b) Co 2p level of Pt(3)Co(3)/C spent catalyst
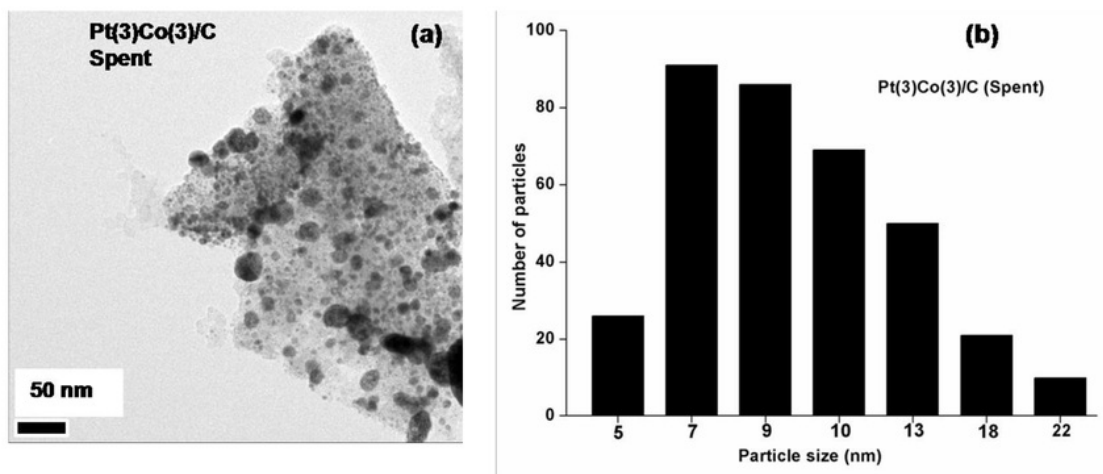
Figure 3.18. (a) TEM image of Pt(3)Co(3)/C spent catalyst and (b) Particle size distribution of Pt(3)Co(3)/C spent catalyst

3.4.13 Conversion of concentrated solution of FAL

Literature study reveals that the maximum FAL concentration reported in reaction were 20 *wt%*. In order to make the process industrially feasible, it is significant to work with higher substrate concentration under safer operating condition (low temperature, lower H_2 pressure and in green solvent like water). Hence in order to study the effect of higher concentration of FAL, the reactions were carried out at 5, 20 and 40 *wt%* of FAL concentrations (Table 3.4). Initially, the reaction was carried out with 5 *wt%* FAL at 1 MPa H_2 for 10 h with FAL/catalyst ratio 4.43. It was observed that conversion was 98% with 100% selectivity of FOL. Then the reaction was carried out for 20 *wt%* FAL under similar reaction condition. However, the H_2 pressure of reaction was maintained at 1 MPa by charging the H_2 in between. Under this reaction condition the yield of FOL achieved to be 49% with 50% yield of FOL which shows that the rate of reaction was slow. Hence in order to increase the rate of reaction temperature was increased to 50 °C. With increase in temperature to 50 °C, 100% conversion of FAL was achieved with 100% yield of FOL within 6 h. With this encouraging result reaction was carried out with 40*wt%* FAL concentrations which gave 100% conversion of FAL with 86% yield of FOL however the rate of reaction was slow. Slow rate of reaction was attributed to lesser solubility of FAL in water to prove this solubility of 40 *wt%* FAL and FOL were checked in water medium at room temperature and it was observed that the solubility of FAL was found to be 8% and solubility FOL was found to be 96%. As shown in Figure 3.19, two layers are clearly visible of FAL and

water. It is also known that solubility of FAL in water is 8% at 25 °C[32] which increases to infinity above 120 °C.[33] Hence to study the rate of reaction in water medium at higher temperature, further reaction was carried out at 100 °C. However, the results were surprising with 83% conversion of FOL within 3 h but the yield of FOL was only 28%. This proves that as the temperature of reaction increases, the solubility of FAL increase leading to side reaction like polymerization of FAL due to availability of excess soluble FAL amount which ultimately reduce the yield of FOL. Hence for better FOL yield controlled solubility of FAL is required which get converted to FOL and reaction move in forward direction at lower temperature.
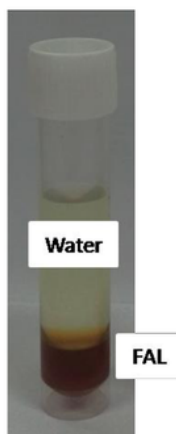
Figure 3.19 Solubility of 40 *wt*% FAL in water

Table 3.4 Hydrogenation of concentrated solution of FAL

Entry no.	FAL (*wt%*)	Temp. (°C)	Time (h)	FAL conversion (%)	FOL yield (%)
1[a]	5	35	10	98	98
2	20	35	10	50	49
3	20	50	6	100	100
4	40	50	6	100	86
5	40	100	3	83	28

Reaction condition: FAL; Pt(3)Co(3)/C; Substrate/Catalyst ratio, 4.43 (*wt/wt*); water, 35 mL; H_2 pressure, 1 MPa was maintained during the reaction by charging H_2 in-between; 900 rpm; FAL: Furfural, FOL: Furfuryl alcohol. [a] H_2 pressure 1 MPa was charged at room temperature and during reaction no additional H_2 was charged in the reactor

3.5 Conclusions

The conversion of FAL to FOL was carried out in presence of different metal loading of Pt and Co on carbon support. Among all Pt(3)C(3)/C is showing best activity which shows that there is synergetic effect present between Pt and Co metals. Various organic solvents with different polarity index were studied at 50 °C along with water and activity of catalyst was found to be best in water among all solvent seven at 35 °C. Most of the reactions were carried out in IPA solvent however IPA was not source of H_2 under reaction conditions and requires external hydrogen for conversion of FAL to FOL. With Pt(3)Co(3)/C catalyst, 100% of FAL conversion with 100% yield of FOL at 35 °C and 0.1MPa H_2 was achieved. However the rate of reaction is slow but at 100 °C and 0.1 MPa H_2, 100% yield of FOL can be achieved with faster reaction rate due to increased solubility of FAL. With 20 *wt*% of FAL solution, 100 % yield of FOL was obtained and with 40 *wt*% solution of FAL 86% yield of FOL was obtained. For better catalytic activity at higher FAL concentrations, reaction was carried out at lower temperature(s) to control the solubility of FAL i.e. solubility of FAL in water is only 8% hence FAL which is soluble in water is converted to FOL which ultimately decreases the concentration of soluble FAL in water and facilitates the solubility of insoluble FAL. Pt(3)Co(3)/C catalyst is showing best activity in water medium for the conversion of FAL to FOL at lower temperatures and lower pressures and with concentrated FAL solution than ever reported due to synergetic effect of Pt and Co metal.

3.6 References

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Chapter 4
Activity of Bimetallic Pt-Co Catalyst in Conversion of Furfural and 5-hydroxymethylfurfural in to Fuel Additives

4.1 Introduction

In present era, fossil feedstock is the major resource for the generation of liquid transportation fuels and chemicals for our day-to-day requirements. However its rate of consumption is faster than rate of formation leading to the depletion of non-renewable fossil feedstocks. Moreover, this feedstock is associated with environmental issues like global warming due to emission of CO_2. Hence, researchers are motivated for development of methods for the production of fuel and chemicals from abundantly available renewable potential resources i.e. nonedible lignocellulosic biomass which is carbon neutral in nature and cheaply available. The major component of lignocelluloses is cellulose (polysaccharide made up of C6 sugar) and hemicelluloses (polysaccharide made up of C5 and C6 sugars) which on hydrolysis produce glucose (C6 sugar) and xylose, arabinose, mannose, etc. respectively.[1] Various reports are available for the formation of furfural (FAL) from xylose by undergoing acid catalyzed dehydration reaction.[2, 3] FAL is a promising platform chemical for the synthesis of fuel additives and chemicals due to various functionalities (C=O group and Π bond of furan ring) present in its structure. FAL on partial hydrogenation produces FOL which on further hydrodeoxygenation (by removing excess oxygen) produces 2-methylfuran (2-MF). 2-MF has potential to be used as fuel additive because of its high energy density (27.6 MJ/L) compared to ethanol 20 MJ/L.[4] It is also used for the formation of crysanthemate pesticides, perfume inter-mediates, chloroquine lateral chains in medical intermediates and for synthesis of toluene.[56] Its ring hydrogenation derivative, 2-methyltetrahydrofuran (2-MTHF) is used as biofuel due to their intrinsically high research octane number (86).[7-9] Complete hydrogenation of FAL produces tetrahydrofurfuryl alcohol (THFOL) used as specialty solvent in chemical industry.[10] FAL on decarbonylation produces furan which on hydrogenation produces tetrahydrofuran (THF) which is used as solvent in various chemical reactions As mentioned in chapter 1, section 1.6.3, HMF is used for the synthesis of 2,5-dimethylfuran (2,5-DMF) which has attractive fuel additive properties like high octane number (119), high energy density (30 MJ/L) and low solubility in water (<1mg·mL^{-1}). Oxidation of HMF produce furan dicarboxylic acid (FDCA) which act as monomer for synthesis polymers.[11] As explained in chapter 1 section 1.8.3, various noble metal catalysts based on Pt and Ru metals were reported for the conversion of FAL to 2-MF however those are active at high temperatures (180-220 °C) and under high H_2 pressures (3-9 MPa). With these catalysts, maximum 61% selectivity to 2-MF was achieved. Attaining better selectivity to 2-MF without

formation of ring hydrogenation and ring opening products under lower H_2 pressure (<1 MPa) is a challenging task. The conversion of FAL to 2-MF in presence of $Ru/RuO_2/C$ emphasizes that hydrogenation of carbonyl group occurs via Lewis acid mediated hydride transfer.[12] Also vapour phase reaction in presence of Cu/SiO_2 catalyst shows 100% conversion of FAL and 90% yield of 2-MF at 220 °C due to the presence of both metallic Cu and oxide Cu(II) species present in catalyst.[8, 13] It is known that the presence of Lewis acid site helps to break the C-O bond during hydrogenolysis[14-16] and conversion of FAL to 2-MF was carried out at higher temperature (>170 °C).[17, 18] As shown in chapter 3, 100% FOL yield can be achieved in IPA solvent at 100 °C in presence of Pt(3)Co(3)/C catalyst.[19] It is proposed that Pt and Co play synergistic effect to achieve better results. Hence, it was hypothesized that Pt in combination with Co catalyst having both metallic and Lewis acid site could show better performance in the conversion of FAL to 2-MF (Scheme 4.1).
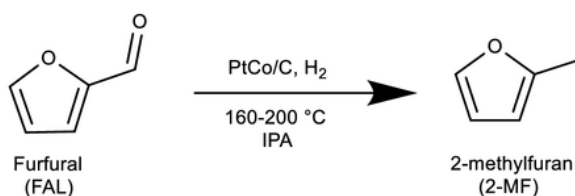
Scheme 4.1 Conversion of furfural (FAL) to 2-methylfuran (2-MF)

4.2 Materials and methods

Furfural (99%), 2-methylfuran (2-MF) (99%), tetrahydrofurfurylalcohol (99%), and 2-methyltetrahydrofuran (99.5%) were procured from Sigma Aldrich, USA. iso-propyl alcohol (IPA) (99%), tetrahydrofuran (THF) (99.5%) and toluene (99%) were procured from Alfa Aesar, India. All the materials were used as received without giving any treatment.

Typically, hydrogenation of FAL was performed in a 50 mL stainless steel Amar make reactor containing 35 mL IPA, 0.35 g FAL and 0.0785 g catalyst. The reactor was flushed with H_2 repeatedly for four-six times to remove air. Then, the reactor was filled with H_2 up to 1 MPa and was heated slowly until desired temperature. At the beginning of reaction, stirring rate was 300 rpm and increased to 900 rpm after final temperature was reached to ensure the elimination of the diffusion.

4.3 Catalytic activity

4.3.1 Catalytic activity for conversion of furfural (FAL) to 2-methylfuan (2-MF)

4.3.1.1 Effect of mono and bimetallic catalyst

Literature report for the conversion of FAL to 2-MF shows that most of the reactions were carried out at 175-220 °C[14, 20-22] in presence of Lewis acid site which helps for dissociation of C-O bond during hydrodeoxygenation reaction. Considering this it was thought that bimetallic catalyst which will contain noble metal in combination with oxophilic metal will perform better in the conversion of FAL to 2-MF. In chapter 3 it is shown that PtCo/C catalyst is giving better activity for conversion of FAL to FOL and it is known from the literature that conversion of FAL to 2-MF is a two-step process and in 1st step, FAL converts in to FOL and in second step FOL is converted to 2-MF. Thus it was decided to use same catalyst (Pt(3)Co(3)/C) for conversion of FAL to 2-MF and carry out reaction at 180 °C.

Therefore, reactions were carried out in the presence of monometallic Pt(3)/C, Co(3)/C and bimetallic Pt(3)Co(3)/C catalysts and also with bare carbon support at 180 °C for 8 h under 1 MPa H$_2$.
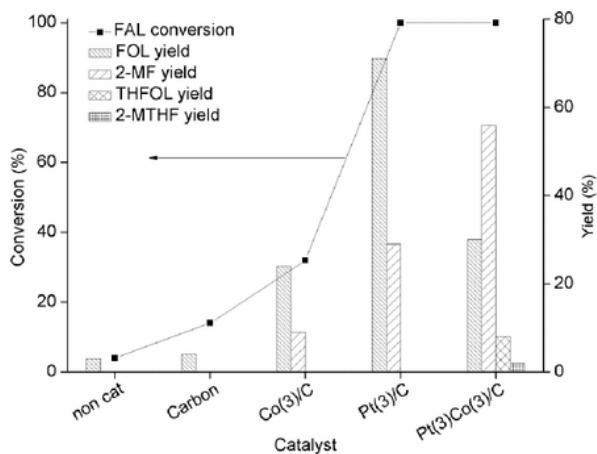
Figure. 4.1 Effect of mono and bimetallic catalysts in the conversion of furfural (FAL) to 2-methylfuran (2-MF)

Reaction condition: FAL, 0.35 g; catalyst, 0.0785g; iso-propyl alcohol, 35 mL; H$_2$ pressure, 1 MPa at room temperature; 180 °C; 8 h; 900 rpm. (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: Tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran).

As observed from Figure 4.1, in presence of Pt(3)/C catalyst complete conversion of FAL with 72% yield of FOL and 29% yield of 2-MF (selectivity of 2-MF, 29%) along with ca. 100% carbon balance was observed. The activity of Co(3)/C catalyst was found to be lower than Pt(3)/C catalyst which represents that Co metal is not efficient in splitting of H_2. Reaction was carried out in presence of monometallic Co(3)/C catalyst to see the effect of Lewis acid site on the conversion of FAL to 2-MF by polarising carbonyl group. However, the results were not encouraging as only 32% conversion of FAL with 24% yield of FOL and 9% 2-MF yield (selectivity of 2-MF, 28%) having 101% carbon balance was observed with this catalyst (Figure 4.1). Though, in presence of Co(3)/C catalyst the hydrogenation of FAL to FOL happened to a little extent, it might be due to the donation of proton from IPA solvent and not by splitting of H_2 under reaction condition (as Co is not known for splitting of hydrogen). Further small amount of FOL gets converted to 2-MF in presence of Co. The selectivity of 2-MF was observed to be same (29%) in both the catalysts. The rate of hydrogenation of carbonyl group was found to be more in presence of Pt(3)/C catalyst than rate of hydrodeoxygenation (HDO) because Pt is known for hydrogenation reaction by splitting of H_2 molecule but on the contrary in HDO reaction 1st C-O bond gets cleaved resulting in deoxygenation followed by addition of H_2 to form CH_3. In presence of monometallic Pt(3)/C catalyst the rate of hydrogenation is fast but rate of C-O bond cleavage is slow. In presence of bimetallic Pt(3)Co(3)/C catalyst almost two times improvement in the yield of 2-MF (56%) was observed compared to Pt(3)/C catalyst (29%) as seen from the Figure 4.1. In addition to 2-MF there is a formation of 30% FOL and trace amount of ring hydrogenated products i.e. THFOL (8%) and 2-MTHF (2%). Also formation of Furan,2-(2-furanylmethyl)-5-methyl was observed, which is expected to be formed from FOL. Nevertheless, in order to confirm whether 2-MF is a source of Furan,2-(2-furanylmethyl)-5-methyl formation, reaction with 2-MF was carried out under similar conditions (180 °C, 2 h) but no such products were observed with 2-MF (the details of these reactions are given in 2-MF stability study section, section 4.4.5).

Increase in the activity of bimetallic catalyst over monometallic catalysts show that Pt and Co are playing synergistic role. In presence of bimetallic catalyst, the rate of HDO increases due to presence of Co(II) species as Lewis acid site. As mentioned earlier, conversion of FAL to 2-MF is a two-step process wherein first, FAL is converted to FOL as intermediate and further FOL gets converted to 2-MF. Hence, to study this reaction path, reaction was performed with

FAL and FOL as substrate for shorter time (2 h instead of 8 h). Initially reaction was carried out with FAL [FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; IPA, 35 mL; H_2 pressure, 1 MPa at RT; 180 °C]. Under this reaction condition complete conversion of FAL was observed with 87% FOL formation and 12% 2-MF formation. Also under similar condition, reaction was performed with FOL as a substrate. The result shows decrease in activity of catalyst towards conversion of FOL (26%) to yield 2-MF (13% yield, 50% selectivity) along with formation of by-products (THFOL, 3%; 2-MTHF, 1%; 1,2-pentanediol, 4% & 1,5-pentanediol, 2%). This result emphasizes that conversion of FAL to FOL is a fast step however 2nd step which is the conversion of FOL to 2-MF is a slow step. In order to calculate TOF for slow step i.e conversion of FOL to 2-MF the reactions were carried out in presence of Pt(3)/C, Co(3)/C and Pt(3)Co(3)/C catalysts for shorter time (2 h). The reaction was carried out with FOL at 180 °C, in IPA (35 mL) and 1 MPa H_2 at room temperature. In presence of Co(3)/C catalyst, conversion of FOL was 4% but no identified products were observed. In presence of Pt(3)/C catalyst conversion was 15% with 3% 2-MF formation (20% selectivity) along with formation of other compounds (5% THFOL; 2% 1,5-pentanediol and 3%, 2-MTHF). In this reaction formation of furfuryl ether (Furan, 2,2-[oxybis(methylene)]bis) was also observed. However in presence of Pt(3)Co(3)/C catalyst conversion of FOL was 26% with 13% 2-MF formation (50% selectivity) along with formation of side products like THFOL (3%), 2-MTHF (1%), 1,2-pentanediol (4%) & 1,5-pentanediol (2%) were observed. As expected TOF for Pt(3)Co(3)/C catalyst was found to be higher (17482 h^{-1}) than Pt(3)/C (7564 h^{-1}) and Co(3)/C (3227 h^{-1}) catalysts.

4.3.1.2 Time study at 180 °C

When reaction was carried out at 180 °C for 8 h, the yield of 2-MF was 56% along with formation of ring hydrogenated product therefore in order to minimize the formation of ring hydrogenated product it was thought to carry out the reaction for shorter time (5, 6 and 7 h). Time study was done in presence of Pt(3)Co(3)/C catalyst at 180 °C and 1 MPa H_2 at room temperature (Figure 4.2). Initially, reaction was carried out for 5 h and it was observed that FAL underwent complete conversion with an yield of 33% of 2-MF and 60% yield of FOL along with good carbon balance (93%) was achieved. Also in the reaction formation of Furan,2-(2-furanylmethyl)-5-methyl was observed. In 6 h the yield of 2-MF reached to 39% with 55% FOL yield and other products like 1% 2-MTHF and 2% THFOL were formed.

Figure 4.2 Effect of time on the conversion of FAL to 2-MF

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; iso-propyl alcohol, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 900 rpm. (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: Tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran).
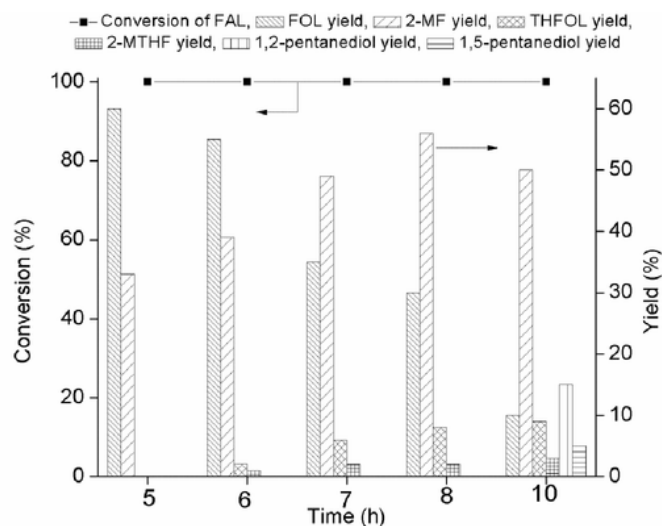
This shows that with longer reaction time, the yield of 2-MF was not improving drastically but the ring hydrogenation products derived from 2-MF and FOL were formed. With further increase in time to 7 h, yield of FOL decreased to 35% with formation of 49% 2-MF, 6% THFOL and 2% 2-MTHF. Within 8 h, yield of 2-MF increased to 56% with formation of 30% FOL, 8% THFOL and 2% 2-MTHF. When reactions were carried out for longer time (10 h) FOL yield decreased to 10% but no improvement in the yield of 2-MF (50%) was seen. Additionally, formation of 1,2-pentanediol (15%) and 1,5-pentanediol (5%) was seen. It is suggested that these ring opening products were formed from THFOL by cleavage of ring C-O bond. Hence, it was concluded that FOL and 2-MF both were undergoing side reactions when longer reaction times are employed. In shorter reaction time the rate of conversion of FOL to 2-MF was slow compared to conversion of FAL to FOL.

4.3.1.3 Effect of temperature

As seen above, maximum 56% yield of 2-MF was achieved in 8 h at 180 °C in presence of Pt(3)Co(3)/C catalyst however the rate of formation of 2-MF was very slow. Hence in order to increase the rate of reaction it was decided to carry out reaction at 200 °C for 2 h and 4 h in IPA

solvent. The result of 2 h reaction shows formation of 45% 2-MF, 18% FOL and 4% THFOL products (Figure 4.3). Under similar reaction condition within 4 h the products were 2-MF (51%), THFOL (8%) and 2-MTHF (3%). Under this reaction condition (200 °C, 1 MPa H_2) the yield of 2-MF was not improving beyond 51% and carbon balance was poor due to degradation of products to gaseous compounds. It is observed that after completion of reaction (4 h) at 200 °C, the final pressure in the reactor at room temperature was 1.2 MPa which is higher than initial reaction pressure (1 MPa). This indicates that some gaseous products were formed under the reaction conditions and hence gas analysis was done by GC-TCD but no products were observed other than H_2. IPA giving hydrogen at 200 °C and it is not getting fully used during reaction and hence build up of hydrogen is possible.
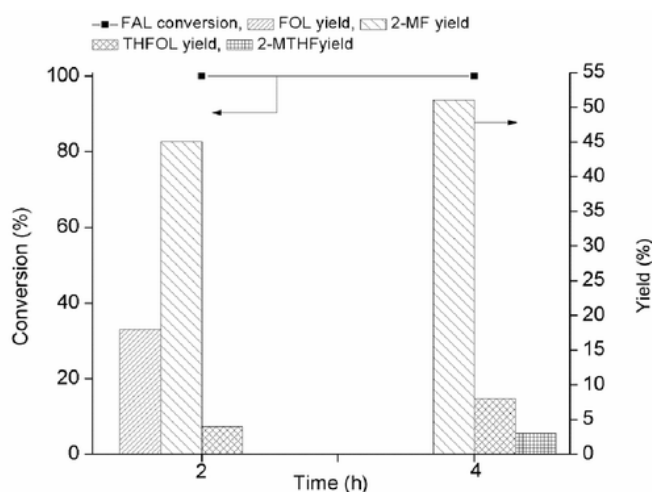
Figure 4.3 Conversion of furfural (FAL) to 2-methylfuran (2-MF) at 200 °C
Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; iso-propyl alcohol, 35 mL; H_2 pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran).

At higher temperature (200 °C) carbon balance was very poor (62%) and hence reactions were studied at lower temperature (160, 170) and also at 180 °C for longer time (10 h) as shown in Figure 4.4. As expected at lower temperature (160 °C), the yield of 2-MF was low (30%) and the yield of FOL was 72% with good (100%) carbon balance. This shows that at 160 °C, formation of ring hydrogenated products was not promoted. Further increase in temperature to

170 °C show the formation of 2-MF with 50% yield, FOL (26%) and THFOL (10%). At 180 °C (10 h) formation of 2-MF (53%), FOL (10%), THFOL (9%) and 2-MTHF (2%) was observed. Compared to this when reaction was done at 180 ºC for 8 h, 56% yield of 2-MF was observed. Temperature study shows that with increase in temperature the yield of 2-MF increases however carbon balance decreases. As seen, at 160 °C the 100% carbon balance was observed but the rate of formation of 2-MF was slow and above this temperature (170-200 °C) the rate of formation of 2-MF increases with decrease in carbon balance. From this study, it is concluded that for achieving better activity with bimetallic catalyst 180 ºC is an optimized reaction temperature.
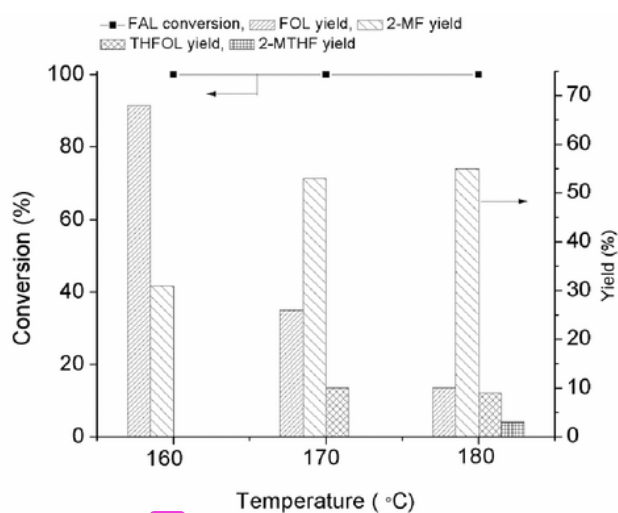
Figure 4.4 Effect of temperature on the conversion of furfural (FAL) to 2-methylfuran (2-MF) **Reaction condition:** FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; iso-propyl alcohol, 35 mL; H$_2$ pressure, 1 MPa at room temperature; 10 h; 900 rpm. (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: Tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran).

4.3.1.4 Time study for conversion of furfuryl alcohol (FOL) to 2-MF

From the earlier results (section 4.4.1) it is observed that rate of formation of 2-MF from FOL is very slow and longer time or higher temperatures are not improving the 2-MF yield beyond 56% (180 ºC, 8 h). Under reaction condition (180 °C, 1 MPa H$_2$, 8 h) FOL and 2-MF are undergoing ring hydrogenation, thus time study of FOL was done for different time (2, 4 and 6 h) and the results are shown in Figure 4.5. When reaction was carried out for 2 h the conversion of FOL was 26% with 13% 2-MF yield (50% selectivity) along with formation of byproducts

like THFOL (3%), 2-MTHF (1%), 1,2-pentanediol (4%) & 1,5-pentanediol (2%) was seen. Further increase in time to 4 h showed increase in conversion of FOL to 46% with increase in 2-MF yield to 25% (54% selectivity) along with formation of side products (THFOL, 4%; 2-MTHF, 6%; 1,2-pentanediol, 6% & 1,5-pentanediol, 1%).
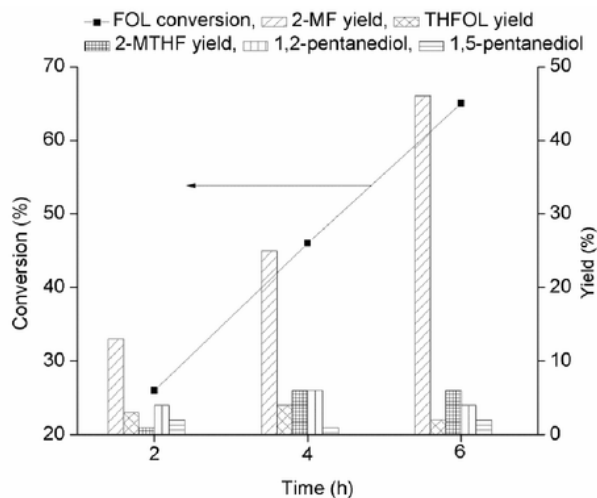
Figure 4.5 Time study for conversion of FOL to 2-MF

Reaction condition: FOL, 0.35 g; Pt(3)Co(3)/C, 0.0785 g; iso-propyl alcohol, 35 mL; H$_2$ pressure, 1 MPa at room temperature; 180 °C; 900 rpm. (FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: Tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran).

Considering increase in the yield of 2-MF with increase in time the reaction was performed for 6 h and it was observed that conversion of FOL reached to 65% with 45% 2-MF yield (70% selectivity of 2-MF) along with formation of side products (THFOL, 2%; 2-MTHF, 6%; 1,2-pentanediol, 4% & 1,5-pentanediol, 2%). Moreover in all these reactions other side products were also observed like 2,2'-(2-Furylmethylene)bis(5-methylfuran); furfuryl ether (Furan, 2,2'-[oxybis(methylene)]bis) and Furan, 2-(2-furanylmethyl)-5-methyl which were confirmed from GC-MS. It is expected that these side products were formed from either FOL or 2-MF. In order to investigate this, reactions were done with 2-MF however no such products were observed from 2-MF as discussed in next section. This confirms that these products were formed from FOL and not from 2-MF. This result also shows that the selectivity of 2-MF increases when reaction was carried out directly with FOL.

4.3.1.5 Thermal stability of 2-MF

With varying reaction condition, the yield of 2-MF was not improving beyond 56%, hence it was thought that 2-MF may not be stable under these conditions. Hence, the stability study of 2-MF was performed under different temperatures at constant time (2 h) in presence of Pt(3)Co(3)/C catalyst. As shown in Figure 4.6 at 160 °C conversion of 2-MF was 28% with only 4% yield of 2-MTHF and at 170 °C, 2-MF conversion increased to 36% with 6% yield of 2-MTHF. Further increase in temperature to 180 °C, 53% conversion of 2-MF along with only 6% yield of 2-MTHF was seen. In all these reactions only 2-MTHF was seen as the identified product but the rate of formation of 2-MTHF was very slow and no any other byproducts were observed like FOL reaction as discussed in section 4.4.4. This shows that 2-MF is either adsorbing on the catalyst surface or undergoing some side reaction(s). When the reaction was performed at 160 °C with FAL as substrate, formation of 2-MTHF was not observed but on the contrary when 2-MF was used as a starting compound, at 160 °C the conversion of 2-MF was 28% with 4% 2-MTHF formation was observed.
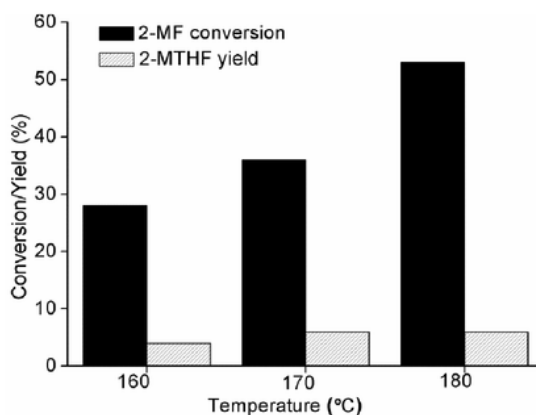
Figure 4.6 Thermal stability of 2-MF

Reaction condition: 2-MF, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; 2 h; H$_2$ pressure, 1 MPa at room temperature; 900 rpm. (2-MF: 2-methylfuran, 2-MTHF: 2-methyltetrahydrofuran).

The reason behind this could be concentration effect which suppress the formation of 2-MTHF. To investigate this further, reaction was carried out with the mixture of FAL and 2-MF (FAL, 0.25 g + 2-MF, 0.1 g) at 160 °C, 1 MPa H$_2$ for 2 h and the result shows no formation of 2-

MTHF.This confirms that presence of FOL and FAL suppress the formation of 2-MTHF. Considering the result of FAL reaction at 160 °C with good carbon balance without formation of side product it was thought to carry out reaction under milder conditions but as seen from earlier results with temperature (4.4.3) and time (4.4.2), it is very clear that at lower temperatures (160 °C, 31% yield) the rate of formation of 2-MF is very slow. In anticipation of this it is apparent that there is an optimum reaction condition under which maximum 2-MF yield is possible to achieve.

4.3.1.6 Effect of metal loading

Considering the better performance of bimetallic catalyst, (Pt(3)Co(3)/C) over monometallic catalysts study was further extended to see the effect of metal loading for decreasing the Pt loading. Hence bimetallic catalysts with altering the Pt metal loading (0.5, 1, 2, 3 *wt%*) by keeping Co loading (3 *wt%*) constant with Pt/Co *wt* ratio of 0.16, 0.33, 0.66 and 1 were prepared. Also by varying Co loading (1 and 2 *wt%*) by keeping Pt loading (3 *wt%*) constant bimetallic catalyst with Pt/Co *wt* ratio of 3 and 1.5 were prepared. The activities of the prepared catalysts were checked for 3 h instead of 8 h because earlier result showed (Figure 4.2 & 4.5) that conversion of FAL to FOL is a fast step however conversion of FOL to 2-MF is slow process. In 2 h the conversion of FAL was complete however conversion of FOL to 2-MF was slow hence in order to investigate the activity of different catalyst for formation of FAL to 2-MF, reactions were carried out for 3 h. As seen from Figure 4.7, when reaction was carried out with lower Pt loading with Pt/Co *wt* ratio 0.16, 93% conversion of FAL was achieved with 83% FOL and 9% 2-MF yield. This shows that even lower loading of Pt is effective for almost complete conversion of FAL to FOL. With increase in loading of Pt to 1 *wt%* in Pt(1)Co(3)/C catalyst it was possible to achieve 97% conversion of FAL with 87% FOL and 6% 2-MF yield. Following this, further reaction was carried out with Pt(2)Co(3)/C catalyst with 0.66 Pt/Co *wt* ratio and in this reaction, complete conversion of FAL with 76% FOL and 26% 2-MF yield was obtained. When reaction was carried out with Pt(3)Co(3)/C catalyst with Pt/Co *wt* ratio 1, complete conversion of FAL with 71% FOL and 30% 2-MF yield was achieved. It was observed that as Pt/Co *wt* ratio increases, the yield of 2-MF also increases and hence reactions were carried out in presence of catalysts with Pt/Co *wt* ratio 1.5 and 3.
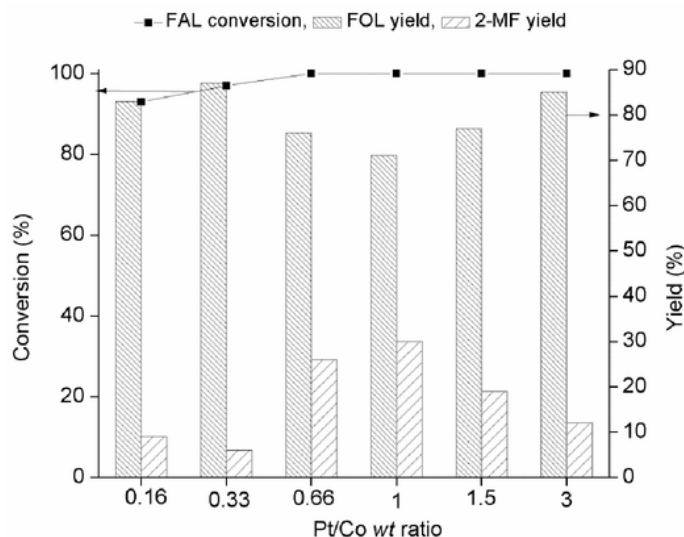
Figure 4.7 Role of Pt and Co loading

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 3 h; 900 rpm. (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran).

In presence of Pt(3)Co(2)/C catalyst further decrease in the yield of 2-MF (19%) was observed with 77% FOL yield. This fact shows that as the loading of Co decreases the yield of 2-MF decreases. In order to study the effect of Co loading further reaction was carried out with Pt(3)Co(1)/C catalyst, and it was seen that the yield of 2-MF decreases to 12% with 85% yield of FOL. This result proves that Pt and Co metal present synergistic effect in bimetallic catalyst (Pt(3)Co(3)/C) where Pt is playing role in adsorption and dissociation of H_2 molecule and Co in the form of (II) state polarizing carbonyl group and this overall increases the rate of hydrogenation of carbonyl group. Further the Co(II) assist the C-O bond cleavage during HDO step. Hence, it is proposed that Pt enhances the hydrogenation reaction and Co in the form of Lewis site helps to cleave C-O bond (Figure 4.8). In all the reactions it was observed that in shorter time (3 h) there is no formation of ring hydrogenated products which are observed in 8 h reaction. From the earlier results of 3 h reaction in presence of Pt(1)Co(3)/C catalyst 93% conversion of FAL with 87% FOL and 6% 2-MF yield was observed with good carbon balance. Therefore, in order to study its performance for longer time, reaction was carried out for 8 h.

Unfortunately, no improvement in the yield of 2-MF (25%) was noticed with formation of 70% FOL.
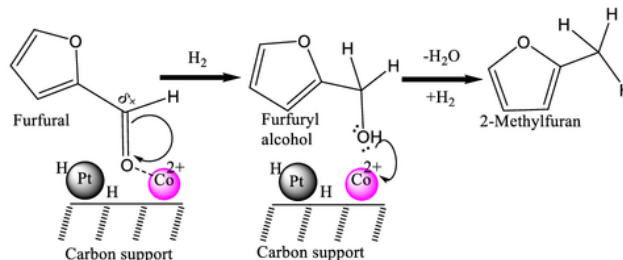
Figure 4.8 Proposed reaction mechanism

4.3.1.7 Effect of pressure (H₂/N₂)

At 180 °C under 1 MPa H_2 pressure ring hydrogenation products were obtained along with 2-MF possibly due to presence of excess H_2. Hence to check the effect of lower H_2 pressure, reactions were carried out under 0, 0.1, 0.5 MPa H_2 pressure (Figure 4.9) and under 1 and 2 MPa N_2 pressure. When reaction was carried out without H_2 atmosphere under unpressurized environment the conversion of FAL was 48% with 29% yield of FOL and 4% yield of 2-MF. This proves that under reaction condition at 180 °C, IPA is donating hydrogen to carry out the hydrogenation of FAL to FOL however the rate of HDO was very slow compared to 1 MPa H_2 pressure. With no hydrogen at 180 °C, 8 h the yield of 2-MF was 4% but when 1 MPa H_2 was used the yield of 2-MF increases to 56%. More over in order to study the reaction under pressurized condition the reaction was performed at 1 MPa N_2 pressure where the conversion was 80% with 66% FOL and 14% 2-MF yield. This fact shows that under N_2 pressure hydrogen donation activity of IPA increases leading to increase in conversion of FAL and yield of FOL. However further increase in the N_2 pressure from 1 to 2 MPa, the results remain almost same (conversion of FAL 76%, FOL yield 62% and 2-MF yield 12%). When reaction was carried out with 0.1 MPa H_2 pressure, conversion was 61% with 37% yield of FOL and very less yield of 2-MF (4%). This shows that 0.1 MPa H_2 pressure is not sufficient for the formation of 2-MF. Moreover, significant improvement in 2-MF yield (59%) was found under

0.5 MPa H_2 pressure along with 27% FOL yield without formation of ring hydrogenated side products.
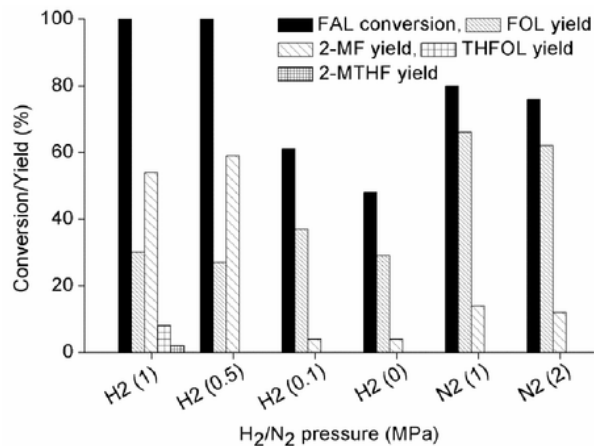
Figure 4.9 Effect of H_2 and N_2 pressures

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; iso-propyl alcohol, 35 mL; H_2/N_2 pressure, at room temperature; 180 °C; 8 h; 900 rpm, (FAL: furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: Tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran).

Though under 1 MPa H_2 pressure, the yield of 2-MF decreases to 56% with 30% FOL yield along with 8% 2-MTHF and 2% THFOL yield. The increased selectivity of 2-MF under 0.5 MPa H_2 pressure compared to 1 MPa H_2 pressure attributed to decrease in side product formation due to less availability of excess H_2 for ring hydrogenation. Under 1 MPa N_2 the conversion of FAL is 80% but the formation of 2-MF is only 14% moreover under 1 MPa H_2 yield of 2-MF increases this tells that to get maximum yield of 2-MF external H_2 pressure is required. Hence from pressure study it is concluded that at 180 °C IPA act as hydrogen donor and leading to catalytic transfer hydrogenation however its rate was slow and with increase in H_2 pressure the solubility of H_2 increases leading to increase in the yield of 2-MF.

4.3.1.7 Effect of solvent

As mentioned in chapter 3, section (3.4.7) solvent study was performed for the conversion of FAL to FOL, where the yield of FOL increases with increase in the polarity of solvent. Hence it was believed that with increased in the polarity desorption of FOL from

catalyst surface increases which make availability of new active sites for the adsorption of FAL on catalyst surface. Conversion of FAL to 2-MF is a two-step process where FAL is 1st converted to FOL and FOL is further converted to 2-MF. So, considering the earlier effect of solvent polarity on the conversion of FAL to FOL, solvent study was carried out with different solvents to know the optimum polarity required for this reaction (Figure 4.10). The activity of Pt(3)Co(3)/C catalyst was tested in different solvents like methanol (polarity index, 5.1), ethanol (5.2), iso-prpopyl alcohol (IPA, 3.9), tetrahydrofuran (THF, 4.0) and toluene (2.4). When reaction was carried out in methanol, 97% conversion of FAL was observed with 72% FOL and 16% 2-MF formation along with Furan,2-(methoxymethyl) and 2-Furanethanol, β-methoxy and 2-(2-furanylmethyl)-5-methyl products were also observed which was confirmed from GC-MS.
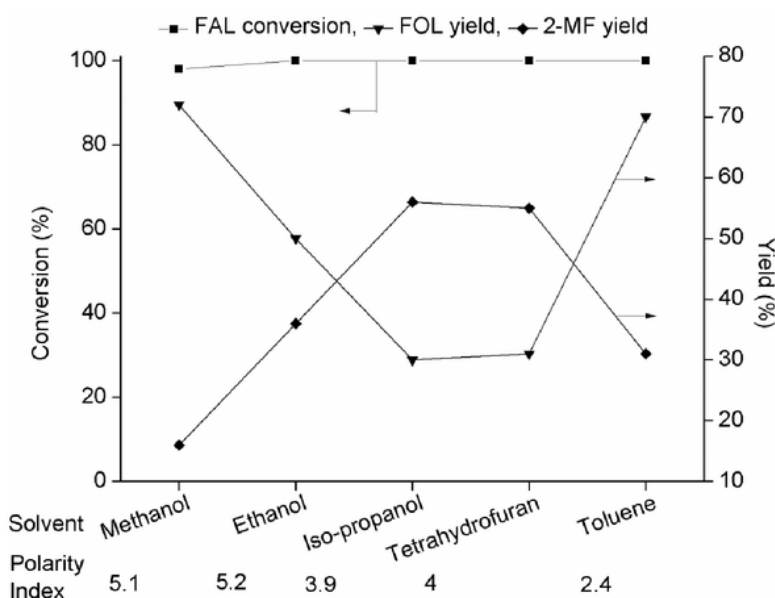
Figure 4.10 Effect of solvent polarity

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; solvent, 35 mL; H_2 pressure, 1 MPa at room temperature; 8 h; 900 rpm. (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran).

In presence of ethanol, 100% conversion of FAL with 50% FOL and 36% 2-MF formation was observed in addition to formation of 1,2-pentanediol; Furan, 2,5-diethoxytetrahydro and Furan, 2-(2-furanylmethyl)-5-methyl. However, in presence of IPA, 100% conversion of FAL with 56% 2-MF, 30% FOL, 8% 2-MTHF and 2% THFOL yield was

observed along with 2-(2-furanylmethyl)-5-methyl formation from FOL. In presence of THF 100% conversion with 55% 2-MF and 31% FOL along with 6% 2-MTHF formation was observed. However, in toluene medium conversion was 100% with 71% FOL and 30% 2-MF formation. Among all the solvents, IPA and THF are showing better performance. Hence from earlier results (conversion of FAL to FOL in presence of different solvent) as mentioned in chapter 3 and the results obtained for conversion of FAL to 2-MF in presence of different solvents it is believed that with decrease in polarity the desorption of FOL from catalyst surface decreases which fasten the rate of formation of 2-MF from FOL. From these results it is concluded that optimum polarity is required for the conversion of FAL to 2-MF, which helps in desorption of products from the surface of catalyst.

4.3.1.8 Effect of catalyst loading
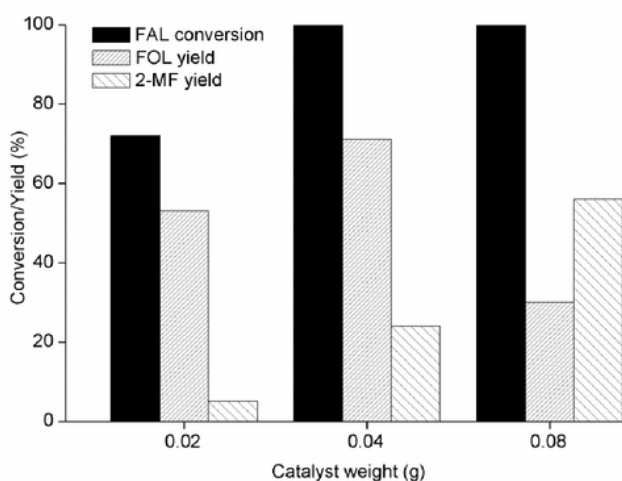
Figure 4.11 Effect of catalyst loading

Reaction condition: FAL, 0.35g; catalyst, Pt(3)Co(3)/C; iso-propyl alcohol, 35 mL; 180 °C; 8 h; H_2 pressure, 1 MPa at room temperature; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran).

In order to know the minimum catalyst loading with higher substrate to catalyst ratio optimization of catalyst loading were done. The, reactions were carried out with 0.02, 0.04 and 0.08 g of catalyst (Figure 4.11). The best results were obtained with 0.08 g catalyst due to availability of more active sites. Charging of 0.04 g catalyst gives 71% FOL and 24% 2-MF

yield with complete conversion of FAL. As the loading of catalyst decreased from 0.04 to 0.02 g the conversion of FAL becomes 72% with 52% FOL and 5% 2-MF yield. The decrease in the yield of 2-MF and FOL with decreased catalyst loading attributed to less availability of active sites for the hydrogenation and HDO reactions.

4.3.1.9 Recycle study of catalyst
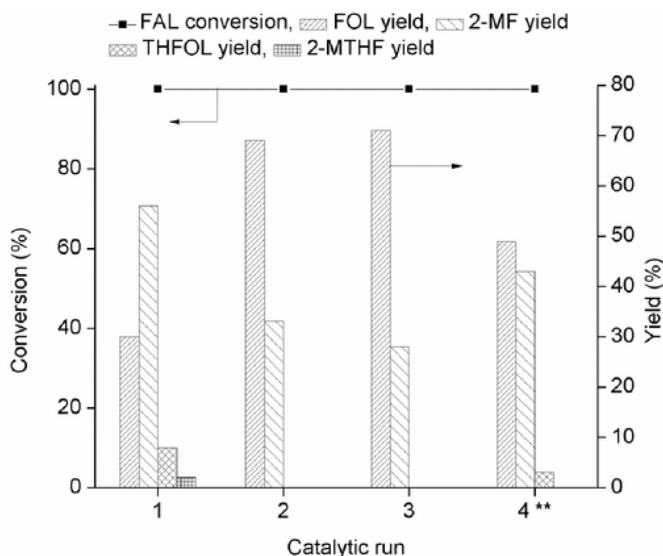
Figure 4.12 Recycle study with Pt(3)Co(3)/C catalyst

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 8 h; 900 rpm. (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: Tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran, ** - spent catalyst recovered from 3rd run was reduced at 400 °C for 2 h under 20 mL·min^{-1} flow).

Results of recycle study of Pt(3)Co(3)/C catalyst (Figure 4.12) shows that after the 1st catalytic run, the activity of a catalyst is decreased for the conversion of FOL to 2-MF. In the first catalytic run the yield of 2-MF was 56% with 30% yield of FOL. For 2nd and 3rd runs the conversion was 100% but the yield of 2-MF decreases to 33 and 28%, respectively. During the recycle study the catalyst was recovered by centrifugation from the reaction mixture and this was followed by filtration to remove any suspended particle and same catalyst was used for next run without any further treatment. After 2nd and 3rd run the loss in activity of catalyst was observed

due to either loss of catalyst because of handling error or due to adsorption of some side product(s) on the catalyst surface which deactivated the active sites. Hence to check this, after 3rd run, spent catalyst was regenerated by reducing the same at 400 °C for 2 h. With this catalyst, in 4th run, increase in the 2-MF yield to 43% and FOL yield 49% was observed. This shows that the activity of catalyst increases after regeneration of catalyst due to removal of any adsorbed species from catalyst surface.

4.3.1.10 Characterization of spent Catalyst

The spent catalyst after 1st run was characterized by XRD (Figure 4.13), TEM (Figure 4.14), ICP-OES and BET-surface area. TEM and XRD analysis showed no change in morphology of catalyst. BET-surface analysis showed 620 $m^2 \cdot g^{-1}$ surface area of catalyst, which is almost similar to that of fresh catalyst (630 $m^2 \cdot g^{-1}$). However, ICP-OES analysis showed slight leaching of Co metal (0.40 ppm) in the solution. Considering this, it is suggested that the catalyst is almost stable under reaction conditions and the decrease in activity in recycle runs is mainly due to change of S/C ratio and adsorption of some products.
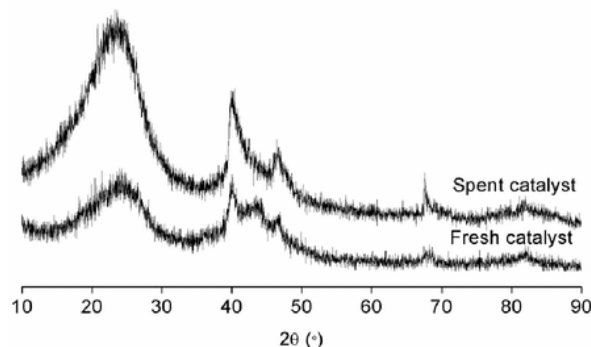
Figure 4.13 XRD patterns of fresh and spent Pt(3)Co(3)/C catalysts
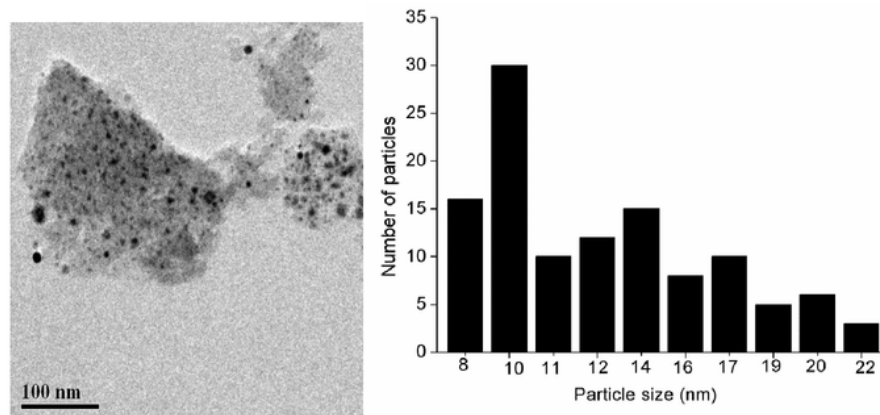
Figure 4.14 TEM images and particle size distribution of spent Pt(3)Co(3)/C catalyst

4.4 Conversion of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (2,5-DMF)

HMF is derived from dehydration of glucose/fructose in presence of acidic catalysts. Like FAL, HMF also contains carbonyl group and additional hydroxyl group. The carbonyl group on hydrogenation and further HDO of both hydroxyl groups form 2,5-dimethylfuran. (2,5-DMF) can be used as fuel additive and intermediate in various chemicals reactions as discussed in chapter 1, section 1.6.3. Hence considering the applications of 2,5-DMF and structural similarity of HMF with that of FAL, reactions were carried out for the conversion of HMF to 2,5-DMF in presence of optimized Pt(3)Co(3)/C catalyst.

4.4.1 Time study

To optimize the time, reaction was carried out for 2, 3 and 5 h and the results are summarized in Table 4.1. It was observed that within 2 h the conversion of HMF was almost complete with formation of 79% 2,5-DMF. Further increased in time to 3 h the conversion become complete with 81% yield of 2,5-DMF this is due to conversion of intermediate products like 2,5-bishydroxymethylfuran or 5-methylfurfuryl alcohol to 2,5-DMF. In order to improve the yield of 2,5-DMF reaction was carried out for longer time (5 h) which gives 89% yield of 2,5-DMF along with formation of 2,5-dimethyltetrahydrofuran this confirms that presence of intermediate product increases the yield of 2,5-DMF. From this study it is observed that in 2 & 3 h reaction the yield of 2,5-DMF remains almost constant with complete conversion of HMF however further longer time (5 h) slight increase in the yield (89%) of 2,5-DMF along with 2,5-dimethyltetrahydrofuran as ring hydrogenated product was observed. It was concluded that

further increase in time will not improve the yield of 2,5-DMF. Hence 5 h was considered as the optimum reaction time for conversion of HMF to 2,5-DMF.

Table 4.1 Effect of time on conversion of HMF to 2,5-DMF

Entry no.	Time (h)	HMF conversion (%)	2,5-DMF yield (%)	Other products (%)
1	2	98	79	20
2	3	100	81	19
3	5	100	89	10

Reaction condition: HMF, 0.15 g; Pt(3)Co(3)/C, 0.785 g; iso-propyl alcohol, 30 mL; H_2 pressure, 1 MPa at room temperature, 180°C; 900 rpm. (HMF: 5-hydroxymethyl furan, 2,5-DMF: 2,5-dimethylfuran, other products, 2,5-bishydroxymethylfuran, 5-methylfurfual, 5-methylhydroxyfuran, 2,5-dimethyltetrahydrofuran).

4.4.2 Pressure study

At 180 °C and 1 MPa H_2 pressure the yield of 2,5-DMF reaches to 89% hence in order to reduce the H_2 pressure it was decided to study the effect of lower H_2 pressure (Table 4.2). Reaction was carried out in absence of H_2 atmosphere where the conversion of HMF was 70% with 10% 2,5-DMF formation and no other identified products were observed. At 180 °C IPA act as proton donor to carry out reaction however the yield of 2,5-DMF is very low and no other identified products were observed. However, under 0.1 MPa H_2 pressure conversion of HMF was 100% with 40% yield of 2,5-DMF along with small yield of 5-MF (5%) and also formation of 2,5-bishydroxymethylfuran and 5-methylfurfuryl alcohol product was observed. With increase in H_2 pressure to 0.5 MPa the yield of 2,5-DMF reaches to 70% also formation of 2,5-bishydroxymethylfurfural and 2,5-dimethyltetrahydrofuran was observed. Further increase in pressure to 1 MPa, the yield of 2,5-DMF reached to 89% along with formation of 2,5-dimethyltetrahydrofuran. From this it is concluded that with an increase in pressure, solubility of H_2 gas increases which increases the interaction between substrate catalyst and H_2 leading to increased yield of 2,5-DMF which is also seen earlier in section (4.3.1.7). Also, it is concluded that external hydrogen pressure is required to attain maximum yield of 2,5-DMF.

Table 4.2 Effect of pressure on conversion of HMF to 2,5-DMF

Entry no.	Pressure (MPa)	HMF conversion (%)	2,5-DMF yield (%)	Other products (%)
1	0	70	10	-
2	0.1	100	40	10
3	0.5	100	70	30
4	1	100	89	10

Reaction condition: HMF, 0.15 g; Pt(3)Co(3)/C, 0.785 g; iso-propyl alcohol, 30 mL; H_2 pressure, at room temperature, 180 °C; 5 h; 900 rpm. (HMF: 5-hydroxymethyl furan, 2,5-DMF: 2,5-dimethylfuran, other products, 2,5-bishydroxymethylfuran, 5-methylhydroxyfuran, 5-methyltetrahydrofurfuryl alcohol, 2,5-dimethyltetrahydrofuran).

4.4.3 Solvent study

Table 4.3 Effect of solvent polarity on conversion of HMF to 2,5-DMF

Entry no.	Solvent	Polarity Index	HMF conversion (%)	2,5-DMF yield (%)	Other products (%)
1	IPA	3.9	100	89	10
2	THF	4	100	88	12
3	Toluene	2.4	100	62	40

Reaction condition: HMF, 0.15 g; Pt(3)Co(3)/C, 0.078 g; solvent, 30 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 5 h; 900 rpm. (HMF: 5-hydroxymethyl furan, 2,5-DMF: 2,5-dimethylfuran, other products: 2,5-bishydroxymethylfuran, 5-methylfurfuryl alcohol, 5-methyltetrahydrofurfuryl alcohol, 2,5-dimethyltetrahydrofuran).

In order to study the effect of solvent polarity, reactions were carried out in IPA, THF and toluene solvents (Table 4.3). It was observed that the yield of 2,5-DMF was same in IPA and THF (88-89%) with the formation of side products like 5-methylfurfuryl alcohol, 5-methyltetrahydrofurfuryl alcohol, 2,5-dimethyltetrahydrofuran however the yield decreased to

62% in toluene solvent. These results are comparable with the results obtained during solvent study for conversion of FAL to 2-MF (4.4.7). This shows that with the decrease in polarity of solvent, yield of 2,5-DMF decreases.

4.4.5 Catalyst loading study

Catalyst loading (0.02, 0.04, 0.08 g) study was carried out at 180 °C, 1 MPa H_2 for 5 h in presence of Pt(3)Co(3)/C catalyst and the results are given in Table 4.4. In non-catalytic reaction, only 2% HMF conversion but no formation of 2,5-DMF was observed. In presence of 0.02 g catalyst, conversion was 100% however the yield of 2,5-DMF was found to be 54% along with 23% 5-methylfurfural (5-MF) formation. Further increase in loading to 0.04 g, complete conversion of HMF and 77% yield of 2,5-DMF was achieved with formation of side products (2,5-bishydroxymethylfuran, 5-methylfurfual, 5-methylhydroxyfuran, 5-methyltetrahydrofurfuryl alcohol). Moreover, with 0.08 g catalyst loading, the yield of 2,5-DMF reaches to 89% with 100% conversion of HMF. This shows that with an increase in catalyst loading, the yield of 2,5-DMF increases due to sufficient availability of active sites. Hence with lower loading of catalyst, less active sites are available which promotes the side reactions and ultimately lowers the carbon balance.

Table 4.4 Catalyst loading study at 180 °C

Entry no.	Catalyst (g)	HMF conversion (%)	2,5-DMF yield (%)	5-MF yield (%)	Other products (%)
1	Non-cat	2	-	-	-
2	0.02	100	54	23	10
3	0.04	100	77	-	20
4	0.08	100	89	-	10

Reaction condition: HMF, 0.15 g; Pt(3)Co(3)/C; iso-propyl alcohol, 30 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 5 h; 900 rpm. (HMF: 5-hydroxymethyl furan, 2,5-DMF: 2,5-dimethylfuran, other products: 2,5-bishydroxymethylfuran, 5-methylfurfual, 5-methylhydroxyfuran, 5-methyltetrahydrofurfuryl alcohol).

4.5 Conclusions

By using bimetallic (Pt(3)Co(3)/C) catalyst having 3 *wt%* Pt and 3 *wt%* Co composition the maximum possible yield of 2-MF achieved was 59% at 180 °C and 0.5 MPa H_2 pressure. Catalyst is stable under reaction condition as is seen from the spent catalyst analysis. By studying the effect of Pt and Co metal loading on the conversion of FOL to 2-MF it is concluded that the Pt is playing important role in dissociation of H_2 molecules required for hydrogenation of carbonyl group of FAL. Also Co is helping through its Lewis acidity dissociation of C-O bond for HDO reaction. To achieve the maximum selectivity of 2-MF reaction should be done at low temperature and low H_2 pressure to avoid any side products formation. At low temperature and low pressure, the rate of formation of 2-MF decreases. Polarity study of solvent indicates that optimum polarity of solvent required for conversion of FAL and HMF to 2-MF and 2,5-DMF respectively. 89% yield of 2,5-DMF was attained with same catalyst under 180 °C, 1 MPa H_2 and 5 h. However further study is required to improve the yield of 2-MF.

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Chapter 5
Role of Catalyst in the Conversion of Furfural
to Cyclopentanone/Cylcopentanol

5.1 Introduction

The non-edible lignocellulosic biomass due to its renewability and abundant availability has attracted lot of attention of researchers for the synthesis of chemicals and fuels. Hydrolysis of hemicellulose (xylan type) produces xylose (C5 sugar), from which furfural (FAL) can be synthesized as a dehydrated product.[1-5] It is estimated that, worldwide more than 280,000 tons of FAL is produced annually[6] which is considered as one of the important route to get commercially important valuable chemicals. Moreover, due to recent interests and advances made in the synthesis of FAL from hemicellulose it is predicted that in near future its production will increase rapidly. Catalytic reduction of biomass derived FAL gives partial hydrogenated product furfuryl alcohol (FOL, hydrogenation of $-CHO$ to $-CH_2OH$)[7] in presence of hydrogen and followed by hydrodeoxygenation to get 2-methylfuran (2-MF, hydrodeoxygenation of $-CH_2OH$ to $-CH_3$) and 2-methyltetrahydrofuran (2-MTHF, ring hydrogenation) efficiently.[8-9] In water medium FAL undergoes ring rearrangement reaction to yield cyclic alcohol, cyclopentanol (CPL) and cyclic ketone, cyclopentanone (CPO) via formation of FOL.[10-16]

As explained in chapter 1, section 1.6.2, CPO is an important raw material for the synthesis of fungicides, pharmaceuticals, pesticides and rubber.[11,13-15,17-18] It is also used in the synthesis of polyamides,[19] C15–C17 range diesel or jet fuels,[20] polyolefin stabilizer[21] and formation of CPL.[22-25] CPO is likely to offer plentiful opportunities in flexible electronic displays and pharmaceutical formulations in upgrowing economies of the world. Also CPO and CPL act as raw materials for the synthesis of jasmine family fragrances. Moreover, both CPO and CPL were found as an important precursor in the synthesis of cyclopentyl methyl ether and cyclopentyl ethyl ether, which used as a prime solvent in Grignard reaction, coupling reaction and several other important chemical reactions.[11, 26]

Literature discussed in chapter 1 shows that CPO is synthesized by vapour phase catalytic cyclization of 1,6-hexanediol and adipic ester or also by decarboxylation of adipic acid.[27-28] Liquid phase oxidation of cyclopentene with nitrous oxide is also another route to synthesize CPO.[24] However, these routes are based on the use of fossil feedstock derived raw materials and reactions are carried out at high temperatures (230-475 °C) and high O_2/N_2O pressures (10-25 atm).[22, 24, 27, 30-33] Hence there is a need to develop a general

method which operates at milder conditions. Moreover, worldwide demand to replace fossil feedstock at least partially with renewable feedstock like biomass for the synthesis of chemicals of importance is considered as major attraction to work with renewable biomass.

As discussed in chapter 1 various catalytic processes are reported for the conversion of biomass derived FAL to CPO. In presence of SBA-15, supported NiCu catalyst, 62% yield of CPO at 160 °C under 4 MPa H_2 pressure from FAL (>99% conversion) could be obtained in water medium.[10] Recently, it is reported that with the complete conversion of FAL, synthesis of 7% CPL and 46% CPO at 150 °C and 4 MPa H_2 pressure over 20% Cu/Co_3O_4 in water medium is possible.[34] Although in another report, with 97% conversion of FAL at 4 MPa H_2 pressure and 150 °C, 60% yield of CPO is claimed in water medium with CuZnAl system.[12] Formation of CPO in high yields (95%) over Cu:Ni:Al hydrotalcite based catalyst at 4 MPa H_2 pressure is recently explored.[13] Use of 5% Pt/C catalyst is also reported to yield 67% CPO with 97% conversion of FAL at 160 °C under 3 MPa pressure.[35] High loading of noble metal i.e. Pt (5%) is reported for conversion of FAL to CPO (76% yield) at 175 °C and 8 MPa H_2 pressure in water medium. Pd (5%) catalyst is shown to yield 67% of CPO at 160 °C under 3 MPa H_2 and Ru (5%) is reported for obtaining 57% yield of CPO at 175 °C and 8 MPa H_2.[14] Yet, another report, it is claimed that over Cu-Co catalyst which operates at bit milder conditions (2 MPa hydrogen pressure, 160 °C) than discussed above, can yield 67% of CPO.[34] Whereas it is also reported that, PdCu catalyst with 5% Pd and 10% Cu is responsible for 92% yield of CPO at 160 °C in presence of 3 MPa H_2 pressure.[16] Although all the above discussed reports claimed the formation of CPO with high yields, but use of high pressure (>3 MPa) of H_2 is required in these methods. It is reported that the selectivity of CPO decreases due to formation of furanic polymer in water medium at high temperature when lower pressures are used.[36] Hence researchers have used high pressure of H_2 to enhance the formation of CPO. However, due to this, high pressure reactor is required to carry out reactions which would increase the process costing and also use of high pressures is not safe.

It is well known from the literature that by manipulating the reaction conditions such as use of biphasic solvent systems can improve the yields of desired products. For

e.g. it is reported that by employing biphasic solvent systems in the conversion of xylose to FOL,[37] sugars into FAL and HMF[38] and hemicelluloses to FAL[3] etc. yields of desired products have improved. This improvement in yields of desired product is possible because of selective extraction of products (in suitable organic solvents) which is scavenged away from coming in contact with water and catalyst by which further side reactions are avoided. This in turn also increases the interaction between substrate and catalyst in water by tuning solvent ratio that would help to suppress the side reactions and improve the reaction rate (due to development of concentrated substrate and catalyst solutions). Additionally, use of bimetallic systems were also known from the literature to tune the reaction pathway by virtue of designing a catalyst which would give favorable geometric and electronic properties to enhance the yields of desired products.[10, 15, 39-43] For example it is shown that the use of PtSn catalyst could give higher yields of sugar alcohols (xylitol, 90%) from xylose compared to monometallic catalyst (Pt).[43] The PtSn catalyst also has a potential to give ca. 99% conversion of FAL with 98% FOL yield.[41] The NiCu catalyst is reported to form 62% of CPO with 99% conversion of FAL.[10] IrRe catalyst is also reported for achieving ca. 99% conversion of FAL with 99% yield of FOL.[40] Bimetallic PtRe system is reported for 100% conversion of FAL with 95% yield of FOL.[42]

After considering above points such as use of biomass derived FAL to produce CPO and CPL under milder reaction conditions it was decided to carry out reactions in biphasic solvent system (Scheme 5.1) in presence of PtCo/C bimetallic catalyst.
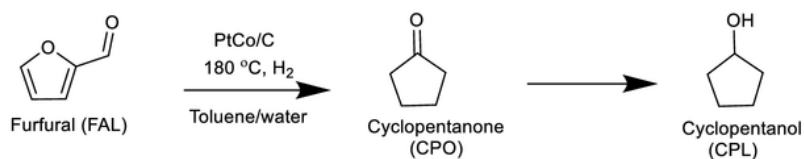
Scheme 5.1 Conversion of furfural (FAL) to cyclopentanone (CPO) and cyclopentanol (CPL)

5.2 Materials and method

Cyclopentanone (CPO) (99%), cyclopentanol (CPL) (99%) were purchased from Loba Chemie, India. 2-cyclopentene-1-one was procured from Aldrich (98%), Furfural (FAL) (99%), furfuryl alcohol (FOL) (99%) and 2-methylfuran (99%) was purchased from s. d. Fine chemicals,

toluene (98.5%) was procured from Alfa Aesar, India. Synthesis of Pt, Co based mono and bimetallic catalyst is given in chapter 2.

Batch mode reactions were done in high temperature high pressure 50 mL stainless steel Amar make reactor. The reactor was charged with 35 mL solvent with varying (toluene/water) (*v/v*) solvent ratio, 0.0785 g catalyst and 0.35 g substrate. H_2 gas was flushed four-five times in reactor to remove air, followed by filling reactor with required H_2 pressure (0.1-2 MPa). The reactor was heated slowly to reach at desired temperature (150-180 °C). Until final temperature reached the stirring speed was maintained at 300 rpm. After final temperature was attained the stirring speed was increased to 900 rpm and the time was noted down as starting time of the reaction.

5.3 Catalytic activity

5.3.1 Effect of mono and bimetallic catalyst on the conversion of furfural (FAL) to cyclopentanone (CPO)/(CPL)in water medium

The non-catalytic and catalytic reactions were carried out for 30 min at 180 °C under 1 MPa H_2 in water medium to check the activity of mono and bimetallic catalysts (Figure 5.1). It was found that in non-catalytic reaction, only 10% conversion of FAL was possible whereas the formation of CPO and CPL were negative. The resultant reaction mixture was dark brown in color and some brown color solid was deposited on the walls of reactor which is considered as a degradation of some amount of FAL under non-catalytic reaction condition. Further reaction was carried out in presence of catalyst support i.e. carbon which showed 10% conversion but again formation of desired products was not observed, which leads to the conclusion that carbon is not active for the conversion of FAL to CPO but there could be adsorption of FAL on the surface of carbon leading to formation of condensation product of furfural. Like non-catalytic reaction, no solid formation was observed on reactor wall in presence of carbon support. In presence of monometallic catalyst i.e. Co(3)/C conversion of FAL was 5% but no identified products were observed. Later, in presence of Pt(3)/C catalyst, conversion of FAL was 60% but the yield of CPO was only 6%. However, when reaction was done with Pt(3)Co(3)/C bimetallic catalyst, significant increase in the yield of CPO (50%) was observed with 2% FOL yield and 85% conversion of FAL.
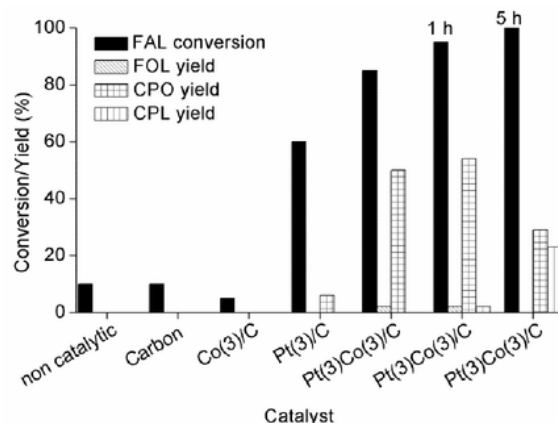
Figure 5.1 Catalytic activities of mono and bimetallic catalysts in the conversion of FAL to CPO/CPL in water medium

Reaction condition: FAL, 0.35 g; catalyst, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 30 min; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol).

This shows that bimetallic catalyst is more active than monometallic catalyst for the synthesis of CPO. Considering the catalytic activity of bimetallic catalyst for 30 min, reactions were carried out for longer time i.e. 1 h and 5 h at 180 °C (Figure 5.1). It was observed that in 1 h, conversion of FAL was 95% with 54% CPO, 2% FOL and 2% CPL yield. With further increase in time to 5 h, decrease in the yield of CPO to 29% and formation of 23% CPL with complete conversion of FAL was observed. This indicates that with an increase in time, yield of CPO is not improving due to hydrogenation of CPO to CPL. These result leads to the conclusion that in water medium at low H_2 pressure (1 MPa, lower compared to literature), high temperature (180 °C) and low loading of Pt (3%), CPO yield cannot be improved beyond 54%. This fact is also supported from the literature where high H_2 pressure (8 MPa) is used at 160 °C for this reaction in presence of monometallic Pt(5%)/C catalyst.[35] The reason behind this could be at high temperature solubility of FAL increases FAL, which can be a result of condensation reaction.[36]

5.3.2 Effect of biphasic solvent system with varying time

When reaction was carried out in pure water medium for shorter time (1 h) the yield of CPO was 54% and with further increase in time to 5 h at 180 °C and 1 MPa H_2 at room temperature the conversion of FAL was complete but yield of CPO decreased to 29% due to formation of CPL (23% yield). The results obtained in monophasic solvent system were not encouraging and hence to improve the yield of CPO the reactions were carried out in biphasic toluene/water solvent system as per hypothesis.
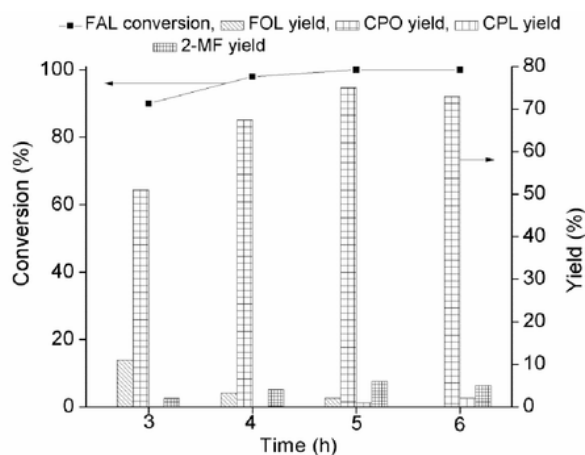
Figure 5.2 Time study for conversion of FAL to CPO in biphasic solvent system

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; toluene/water 3:4 *v/v*, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol, 2-MF: 2-methylfuran).

Toluene was used as organic solvent in biphasic system because of it is immiscible nature in water and solubility of FAL is more in toluene rather than that of water, which suppresses the formation of side products. For better understanding the solubility details are given in the next section 5.3.3. From the monophasic solvent system it is observed that, activities of bimetallic catalysts is better than monometallic catalyst and hence activity of Pt(3)Co(3)/C catalysts were scrutinized in biphasic toluene/water solvent system with 3:4 *v/v*, ratio at 180 °C for different time (3, 4, 5, 6 h) under 1 MPa H_2 (Figure 5.2). Initially reaction was carried out for 3 h where the conversion of FAL reaches to 90% and the yield of CPO achieved was 51% (56% CPO selectivity) with 11% FOL and 2% 2-MF yield. In 4 h reaction time, the conversion

achieved to be 98% with 67% yield of CPO (68% selectivity) and 4% 2-MF formation. The conversion becomes 100% with 75% yield of CPO (75% CPO selectivity) with 1% CPL and 6% 2-MF yield within 5 h. When reaction proceeds further for 6 h, no improvement in the yield of CPO was observed and remains 73% along with 6% 2-MF formation. It was clear from these above experiments that, with increasing the time from 2 to 5 h, conversion of FAL and FOL increases, which in turns increases the yield of CPO and beyond 5 h it remains almost constant. With increased in time the selectivity of CPO increases due to increase in conversion of FAL, FOL and intermediate products into CPO. However, the yield is not improving beyond 75%. This is attributed to the fact that water soluble FAL undergo side reaction like condensation which will not contribute for formation of CPO.

5.3.3 Effect of different toluene/water, (*v/v*) solvent ratio in presence of bimetallic catalyst

Pt(3)Co(3)/C catalyst is showing better result (75% CPO yield) in 5 h with 3:4 *v/v* toluene water ratio hence in order to optimize the solvent ratio reactions were carried out with different toluene/water *v/v* ratio (7:0, 0:7, 5:2, 2:5, 1:6) and the results are shown in Figure 5.3. When toluene was used as a solvent, the conversion of FAL was found to be complete with 64% yield of FOL and 18% yield of 2-MF but negative formation of CPO was observed (Figure 5.3).[36] It proved that the formation of CPO is solvent dependent and form only in aqueous solvent as observed in water and toluene/water solvent system and not in organic solvent this fact is also supported by literature.[16] As discussed in earlier section 5.3.1, in presence of water the yield of CPO was 29% with 23% CPL formation. In biphasic solvent system with 5:2 *v/v*, toluene/water ratio, the conversion of FAL was completed with 68% yield of CPO, 13% 2-MF and 8% CPL yield. In 2:5 *v/v*, toluene/water ratio FAL undergoes complete conversion and the yield of CPO remains almost same (65%) with 2% FOL and 2% CPL yield. Further decrease in toluene/water ratio to 1:6 *v/v*, the yield of CPO decreases to 61% and 1% FOL yield without formation of CPL. From this result it is concluded that solubility of substrate and product varies in biphasic solvent system with varying solvent ratio which ultimately affects the yield of desired product. Hence solubility study of FAL and FOL in all toluene/water solvent ratios was carried out as shown in Table 5.1-5.2.

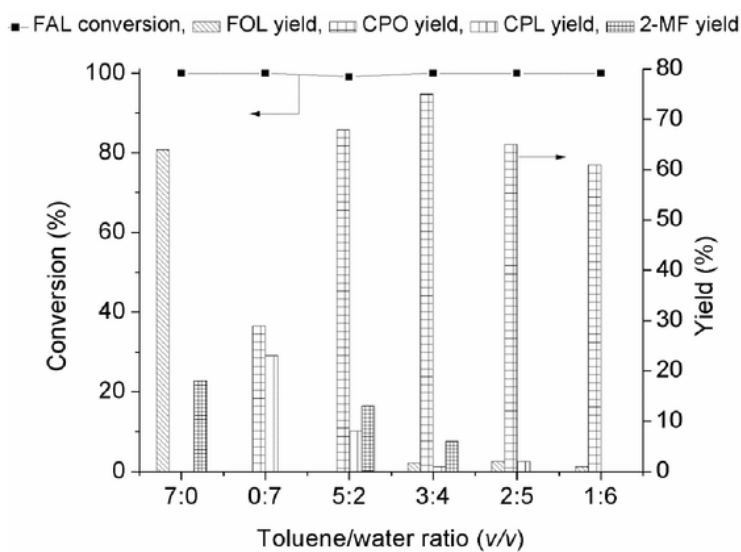**Figure 5.3** Effect of varying toluene/water *v/v* solvent ratio on conversion of FAL to CPO

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; toluene/water ratio *v/v*, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 5 h; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol, 2-MF: 2-methylfuran).

Table 5.1 Distribution of FAL in different toluene/water (*v/v*) solvent ratio

Toluene/Water (*v/v*)	FAL distribution		Partition coefficient
	Organic phase (g)	Aqueous phase (g)	
5:2	0.29	0.03	0.99
3:4	0.23	0.09	0.38
2:5	0.18	0.13	0.14
1:6	0.14	0.19	-0.12

Conditions: FAL, 0.35 g; toluene/water ratio *v/v*, 35 mL; 28 °C; 1 h; 600 rpm; FAL: Furfural

Table 5.2 Distribution of FOL in different toluene/water (*v/v*) solvent ratio

Toluene/Water (*v/v*)	FOL distribution		Partition coefficient
	Organic phase (g)	Aqueous phase (g)	
5: 2	0.15	0.15	-0.00
3:4	0.05	0.24	-0.65
2:5	0.03	0.27	-0.86
1:6	0.02	0.29	-1.16

Conditions: FOL, 0.35 g; toluene/water ratio *v/v*, 35 mL; 28 °C; 1 h; 600 rpm; FOL: Furfuryl alcohol

It is observed that with decrease in toluene/water ratio from 3:4 to 1:6, the distribution of FAL increase more in water than toluene leading to increased rate of polymerization reaction of FAL. It is reported in the literature that FAL is not stable at high temperature and facilitate the condensation product formation. With increase in toluene/water ratio from 3:4 to 5:2, concentration of FOL in water decreases which ultimately affect the yield of CPO. Considering the better catalytic (75% CPO yield) and distribution result in 3:4 (*v/v*) ratio solubility studies of FAL, FOL, CPO and CPL were carried out in the same solvent ratio at room temperature (Table 5.3).

Table 5.3. Distribution of substrate and product in biphasic toluene/water 3:4 *v/v* solvent ratio 35 mL

Substrate and product	Distribution of substrate and product		Partition coefficient
	Organic phase (g)	Aqueous phase (g)	
FAL	0.23	0.09	0.38
FOL	0.05	0.24	-0.65
CPO	0.25	0.07	0.53
CPL	0.15	0.18	-0.087

Conditions: Substrate and product 0.35 g; toluene/water 3:4 *v/v*, 35 mL; 28 °C; 1 h; 600 rpm (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol)
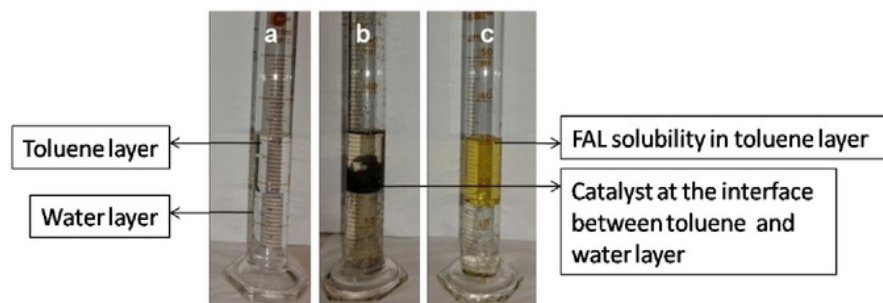
Figure 5.4 a) Toluene and water biphasic solvent system, b) Distribution of catalyst at the interface between water and toluene layer, c) Distribution of FAL in toluene layer (FAL: Furfural)

From this study it was investigated that FAL is more soluble in toluene than water and the catalyst is present at the interface between toluene and water layer (Figure 5.4) which converts

FAL into FOL and since the solubility of FOL is much more in water (Table 5.3), it gets extracted in water layer and undergoes ring rearrangement to form CPO which gets extracted in toluene due to its higher solubility in toluene.

5.3.4 Effect of Pt metal loading in bimetallic catalyst

In order to minimize the loading of Pt below $3wt\%$ the effect of Pt loading in bimetallic catalyst was investigated by carrying out reaction in presence of bimetallic catalyst having different Pt loading with constant Co (3 $wt\%$) loading at 180 °C, 1 MPa H_2, 3:4 (v/v), toluene/water solvent ratio for 30 min as shown in Figure 5.5. The bimetallic Pt(0.5)Co(3)/C catalyst gives 24% conversion of FAL with 15% FOL and 4% CPO yield and TOF calculated was 537 min^{-1} with 79% mass balance. Increase in loading of Pt from 0.5 to 1 $wt\%$ in Pt(1)Co(3)/C catalyst, increases the FAL conversion to 43% with 18% FOL and 13% CPO yield and mass balance is 72%, the TOF calculated was 407 min^{-1}. Further increase in Pt loading (Pt(2)Co(3)/C catalyst) gives 60% conversion of FAL with 19% CPO and 23% FOL yield, mass balance 70% and the TOF was 309 min^{-1}. In presence of Pt(3)Co(3)/C catalyst the conversion of FAL was 66% with 21% CPO and 17% FOL, mass balance is 58%, and the TOF 189 min^{-1}.
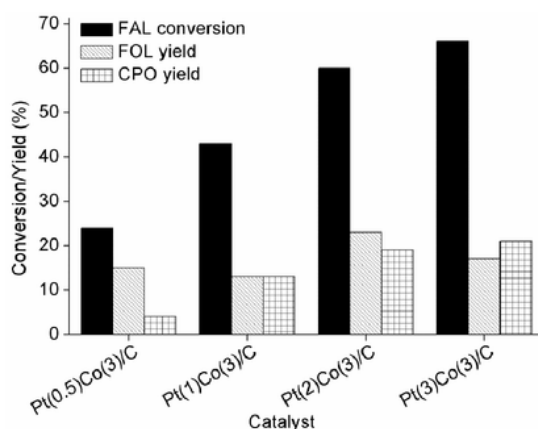
Figure 5.5 Effect of Pt metal loading in bimetallic catalyst in the conversion of FAL to CPO

Reaction condition: FAL, 0.35 g; Catalyst, 0.0785 g; toluene/water 3:4 v/v, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 30 min; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone).

The TOF of Pt(2)Co(3)/C catalyst is greater than Pt(3)Co(3)/C catalyst but the conversion of Pt(3)Co(3)/C is more than Pt(2)Co(3)/C catalyst. Hence Pt(3)Co(3)/C catalyst was considered as optimized catalyst to carry out further reactions. Interestingly in all of these reactions the conversion of FAL increases but the mass balance of identified product decreases. Hence to investigate the reason behind this the adsorption study of FAL, FOL, CPO and CPL on carbon support was carried out at room temperature and the results are shown in Table 5.5.

Table 5.5 Adsorption of substrate and product in biphasic toluene/water 3:4 (*v/v*), 35 mL solvent system

Chemical	FAL	FOL	CPO	CPL
Adsorption (%)	5	7	3	5

Conditions: Substrate and product 0.35 g, toluene/water 3:4 *v/v*, 35 mL; 28 °C; 600 rpm; 1 h; carbon 0.078 g, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol).

From the adsorption study it was observed that the adsorption of FAL became 5%, FOL 7%, CPO 3% and CPL 5%. Hence it was believed that adsorption of product and substrate on carbon support is the possible reason behind loss of mass balance.

5.3.5 Thermal stability of product (intermediate)

In order to know the formation of intermediate products during reaction the reaction was carried out for 30 min. (Pt(3)Co(3)/C, 3:4 *v/v* toluene/water, 1 MPa H_2). In this reaction conversion of FAL was 66% with 17% FOL and 21% CPO yield was obtained. From this result it is observed that in the initial stage the FAL converted to FOL which further gets converted to CPO by ring rearrangement mechanism (Figure 5.5). Time study showed that the yield of CPO was not improving beyond 75% even with complete conversion of FAL. This could be possible due to side reaction of intermediate product like FOL or final product like CPO and CPL, The thermal stability of FOL, CPO, CPL and 2-cyclopentene-1one were studied in presence of Pt(3)Co(3)/C catalyst and the

results are shown in Figure 5.6. Initially reaction was carried out with FOL as substrate which has shown 100% conversion with formation of CPO 62%, CPL 4%, 1,2-pentanediol 2% and 2-MF 1%. The mass balance of this reaction is only 69% which is very poor.
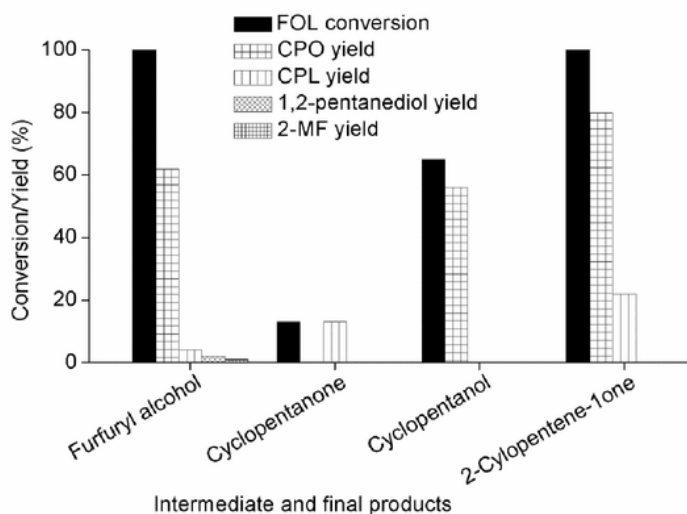
Figure 5.6 Thermal stability study of intermediate and final products in presence of catalyst **Reaction condition**: Substrate, 0.35 g; Pt(3)Co(3)/C, 0.078 g; toluene/water 3:4 (*v/v*), 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 5 h; 900 rpm, (FOL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol, 2-MF: 2-methylfuran).

This leads to the conclusion that during reaction FOL is undergoing parallel reaction like condensation and conversion to CPO which decreases the yield of CPO.[44, 45] Hence time study was carried out for 2, 3 and 5 h to check the activity of FOL under reaction condition and the results are shown in Figure 5.7. In all these reactions conversion of FOL was 100% with varying yield of CPO. In 2 h 47% yield of CPO with 6% CPL, 2% 2-MF and 6% 1,2-pentanediol side product formation was observed.
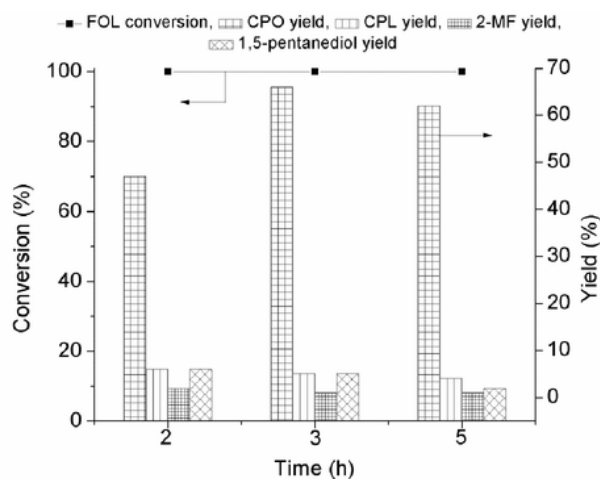
Figure 5.7 Activity of FOL with varying time

Reaction condition: FOL, 0.35 g; Pt(3)Co(3)/C, 0.0785 g; toluene/water 3:4 *v/v*, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol, 2-MF: 2-methylfuran).

In 3 h the yield of CPO reaches to 66% with 5% CPL, 5% 1,2-pentanediol and 1% 2-MF yield formation was observed. For 5 h reaction 62% CPO, 4% CPL, 1% 2-MF and 2% 1,2-pentanediol yields were obtained. In 2 h the conversion of FOL is complete but yield of CPO was 47%. In 3 h it reaches to 66% which shows that FOL forms intermediate product by ring rearrangement and as the reaction proceeds the intermediate product converted to CPO. Moreover, after 3 h the yields of CPO remain almost constant which conclude that condensation of FOL and formation of CPO is a simultaneous process.

Under the same reaction condition (substrate, 0.35 g; Pt(3)Co(3)/C, 0.078 g; toluene/water 3:4 *v/v*, 35 mL; 180 °C; 5 h; 900 rpm; 1 MPa H_2 at room temperature) when reaction was carried out with CPO surprisingly 65% CPL was converted into 56% CPO (Figure 5.6). When reaction was carried out with CPO it shows 13% conversion with 12% CPL formation which proves that CPO is stable under reaction condition. Thermal stability study of CPO and CPL shows that CPO is stable under reaction condition and CPL get converted into CPO without undergoing any degradation reaction. Hence to investigate the active metal among Pt and Co in bimetallic catalyst Pt(3)Co(3)/C for conversion of CPL to CPO under reaction conditions, reaction were carried out with CPO and CPL in presence of Pt(3)/C and Co(3)/C

monometallic catalyst and the data is summarized in Table 5.6. It proves that Pt is playing active role for conversion of CPL to CPO under reaction condition[45-48] which leads to CPO as major product under reaction condition.

Table 5.6 Role of active metal for interconversion of cyclopentanol to cyclopentanone

Entry no.	Catalyst	Substrate	CPL/CPO conversion (%)	Yield (%)	
				CPO	CPL
1	Co(3)/C	CPL	10	2	0
2	Co(3)/C	CPO	12	0	3
3	Pt(3)/C	CPL	93	73	0
4	Pt(3)/C	CPO	15	0	4

Reaction condition: CPO, CPL, 0.35 g; Catalyst, 0.0785 g; toluene/water 3:4 *v/v*, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 5 h; 900 rpm, (CPO: Cyclopentanone, CPL: Cyclopentanol).

5.3.6 Activity of bimetallic catalyst in water medium for conversion of FAL and FOL to CPO

Further to investigate the stability of FOL and FAL in water medium the reactions of FAL and FOL were carried out in pure water medium and the results are summarized in Table 5.7. FAL and FOL are showing 100% conversion in presence of water at 180 °C, 5 h, 1 MPa H_2 at room temperature. FAL is showing formation of 29% CPO and 23% CPL yield and FOL gives 9% CPO, 30% CPL and 5% 1,2-pentanediol yield. It is observed from the results that formation of CPO occurs through FOL and in water, CPO come in contact with catalyst and converted to CPL.

Table 5.7 Activity of FAL and FOL in water medium

Substrate	FAL/FOL conversion (%)	Yield (%)		
		CPO	CPL	1,2-pentanediol
FAL	100	29	23	0
FOL	100	9	30	5

Reaction condition: FAL, FOL, 0.35 g; Pt(3)Co(3)/C, 0.0785 g; water 35 mL; H_2 pressure, 1 MPa, at room temperature; 180 °C; 5 h; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol).

When reaction was carried out with FAL the yield of CPO is good and obviously with FOL formed CPO get converted to CPL because CPO remain longer time in contact with catalyst under reaction which ultimately reduce the yield of CPO. It again proves that FOL and FAL are undergoing side reaction in presence of water and FOL also undergoing ring opening reaction to form diol.[45-48]

5.3.7 Effect of H_2 pressure

In order to see the effect of H_2 pressure reactions were done with varying pressure from 0.1 to 1 MPa (Figure 5.8). From the results it was found that as the H_2 pressure decrease from 1 to 0.5 MPa the FAL conversion decrease to 64% with 7% CPO, 8% FOL and 7% CPL yield. Further decrease in H_2 pressure upto 0.1 MPa, the FAL conversion decreases to 48% and only 1% FOL formation was observed.
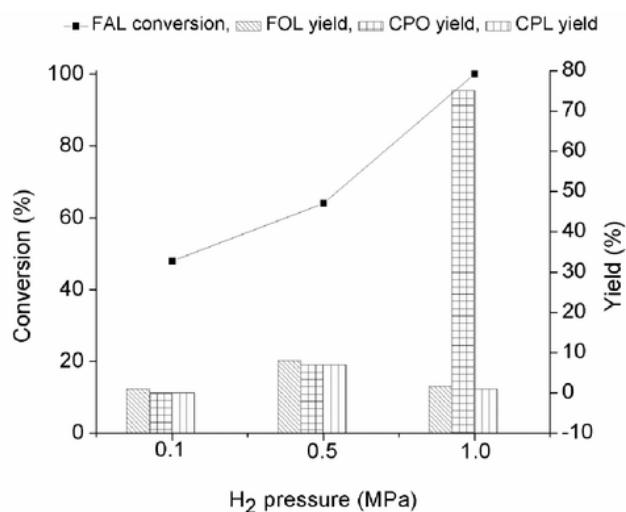
Figure 5.8 Effect of H_2 pressure

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; toluene/water 3:4 v/v, 35 mL; H_2 pressure, at room temperature, 180 °C; 5 h; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol).

Figure 5.8 shows that lower pressure of H_2 is not sufficient for conversion of FAL to FOL leading to side reaction.[35] At 1 MPa H_2, conversion of FAL is complete with 75% yield of CPO. It implies that the conversion of FAL and yield of CPO is depending on H_2 pressure because with increase in H_2 pressure solubility of H_2 increases and also

interaction between catalyst and substrate also increases which ultimately improve the yield of CPO.

5.3.8 Effect of catalyst loading

Effect of catalyst loading was studied to know the optimized weight of catalyst required for maximum yield of CPO. Reactions were carried out with 0.02, 0.04, 0.08 g catalyst loading as shown in Figure 5.9. With 0.02 g loading of catalyst 80% conversion achieved but yield of FOL is 6% and CPO is 2%. For 0.04 g catalyst loading the conversion is nearly same to that of earlier loading but the yield of CPO reaches to 22% with 1% FOL.
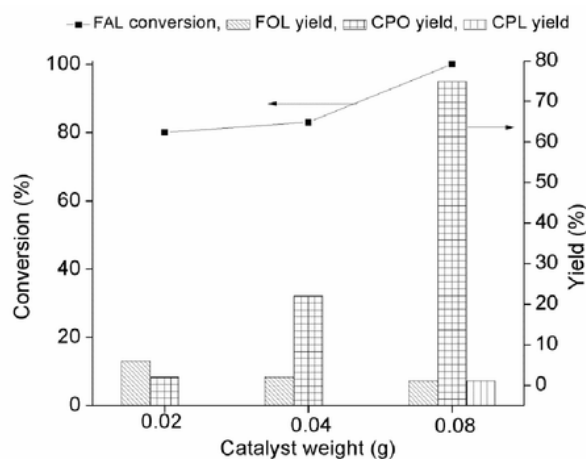
Figure 5.9 Effect of catalyst loading

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C; toluene/water 3:4 *v/v*, 35 mL; H_2 pressure, 1 MPa, at room temperature; 180 °C; 5 h; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cylclopentanone, CPL: Cyclopentanol).

When loading of catalyst increases to 0.08 g, the yield of CPO achieved was 75% with 2% FOL and 1% CPL yield and complete conversion of FAL. This shows that as the loading of catalyst increases availability of active metal sites increases for conversion of FAL to CPO which suppress the side reaction leading to increases in the yield of CPO.

5.3.9 Effect of stirring speed

In order to investigate the effect of stirring speed under reaction condition reactions were carried out with varying stirring speed (Figure 5.10). It was found out that at 300 rpm conversion of FAL is 91% with 20% CPO and 10% FOL yield, at 600 rpm 95% conversion with 36% yield of CPO and at 900 rpm 100% conversion with 75% yield of CPO was obtained. Increase in stirring speed from 300 to 900 rpm the interaction between substrate, catalyst and diffusion of H_2 from gas to liquid phase increases which suppress the side reactions hence improve the yield of CPO.
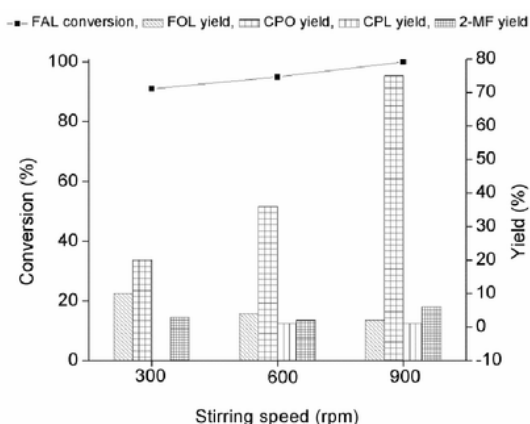
Figure 5.10 Effect of stirring speed

Reaction condition: FAL, 0.35 g; Catalyst, 0.0785 g; toluene/water 3:4 *v/v*, 35 mL; H_2 Pressure, 1 MPa at room temperature; 180 °C; 5 h, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol, 2-MF: 2-methylfuran).

5.3.10 Effect of lower temperature

At higher temperature formation of side products were predominant which decreases the yield of CPO. Hence the reaction was carried out at lower temperature (150 °C) for 5 h in water medium under 1 MPa H_2 and it was observed that 73% yield of CPO and 2% CPL was achieved with 100% conversion of FAL. Considering the result of monophasic solvent system (water) at 150 and 180 °C it is concluded that at lower temperature (150 °C) rate of formation of furfural condensation products suppressed than

rate of conversion of FAL to CPO and hence at 150 °C the yield of CPO improve to 73%.In order to compare the effect mono and biphasic solvent system on conversion of FAL to CPO the reactions were carried out at 150 °C in biphasic solvent system at different time and the results are shown in Figure 5.11. For 3 h reaction FAL conversion was almost compete with 31% FOL, 44% CPO, 8% CPL, 10% 2-MF and 5% 1, 2-pentanediol yield was obtained. With increase in time to 6 h yield of FOL decreases to 10% with 60% CPO, 18% CPL, 8% 2-MF, 3% 1,2-pentanediol yield. Within 9 h, the conversion of FAL was 100% with formation of 3% FOL, 54% CPO, 30% CPL, 7% 2-MF and 3% 1,2-pentanediol yield. It shows that at lower temperature with increase in time the selectivity of CPO decreases with formation of CPL, 2-MF and 1,2-pentanediol side products.
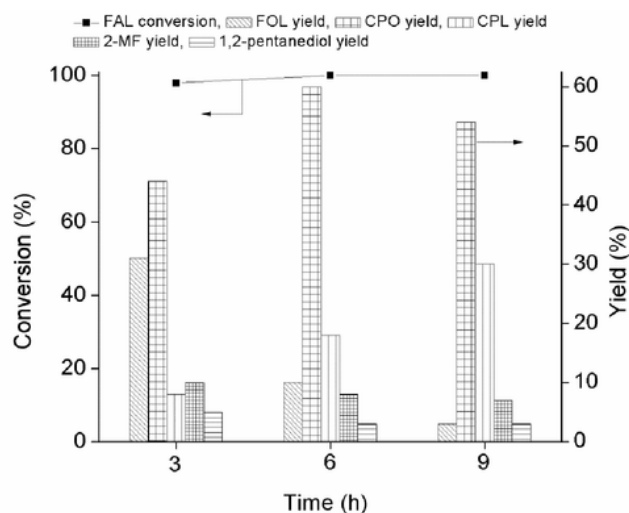
Figure 5.11 Time study for conversion of FAL to CPO at 150 °C

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C catalyst, 0.0785 g; toluene/water, 3:4 *v/v*, 35 mL; H_2 pressure, 1 MPa at room temperature; 150 °C; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone, CPL: Cyclopentanol, 2-MF: 2-methylfuran)

In order to study the effect of higher pressure at 150 °C the reaction was carried out at 2 MPa H_2 pressure for 6 h in 3:4 (*v/v*), toluene/water solvent ratio in presence of Pt(3)Co(3)/C catalyst. It shows that under higher pressure CPO converted to CPL with formation of 1% FOL, 8% CPO,

71% CPL and 5% 2-MF. This result shows that higher pressure and lower temperature is favorable for the formation of CPL than CPO.

5.3.11 Effect of formic acid as additional H^{+} source

Considering the results of bimetallic catalyst in biphasic solvent at 150 °C for 3 h, the reaction was carried out in presence of 1.75 mmol formic acid as an additional H^{+} source to enhance the yield of CPO under 150 °C, 1 MPa H_2, 3 h, 3:4 (*v/v*), toluene/water solvent ratio and in presence of Pt(3)Co(3)/C catalyst. It was found that addition of formic acid leading to lower activity of catalyst with 77% FAL conversion with 16% CPO, 5% FOL, 6% CPL and 6% 2-MF yields. It indicates that formic acid is deactivating the catalyst.[16]

5.3.12 Recycle study of catalyst
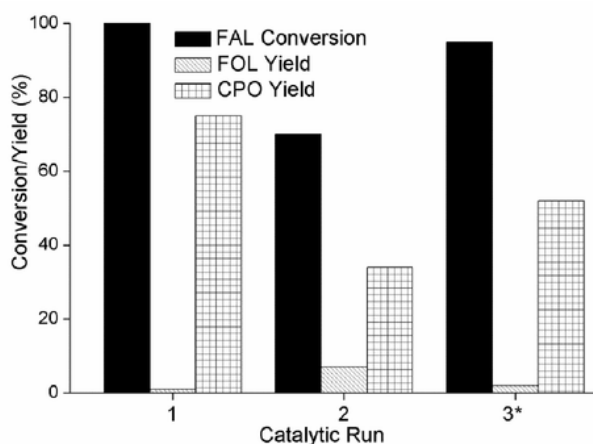
Figure 5.12 Recycle study of catalyst

Reaction condition: FAL, 0.35 g; Catalyst, 0.0785 g for 1st run; toluene/water 3:4 *v/v*, 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 5 h; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, CPO: Cyclopentanone)

After completion of reaction, the catalyst was separated from reaction mixture by centrifugation and the recovered catalyst was dried at 60 °C for 12 h followed by activation for 3 h at 150 °C and used for next run without any pre-treatment. After 2nd run

dried spent catalyst was reduced at 400 °C for 2 h and used for 3rd run. The results of recycle study (Figure 5.12) shows decrease in catalyst activity after 1st run. The conversion of FAL decreases to 75% with 36% yield of CPO. This could be due to deactivation of active side by the adsorption of some side product. To check the adsorption of side product on catalyst surface the recovered catalyst after 2nd run was reduce at 400 °C for 2 h then again used for reaction it shows increase in activity of catalyst with 95% conversion and 57% yield of CPO.
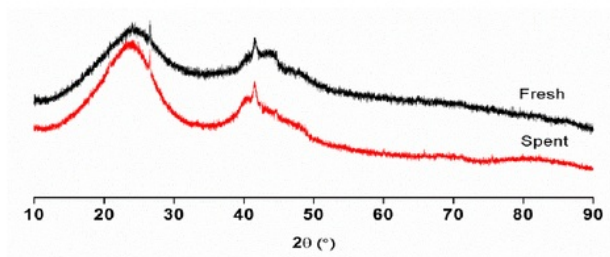
Figure 5.13 XRD of fresh and spent catalyst
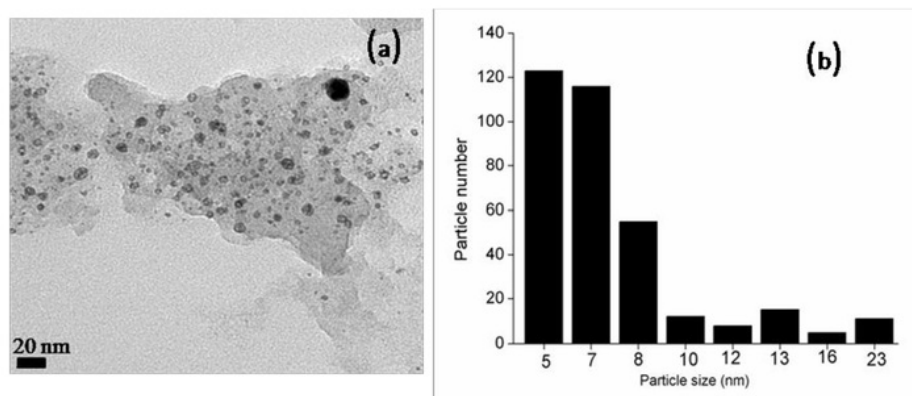
Figure 5.14 a) TEM image of spent catalyst and b) particle size distribution of spent catalyst

In order to understand the reason behind the decrease in activity of catalyst the characterization of spent catalyst was done after 1st run. The XRD pattern (Figure 5.13) observed to be slightly changed but retention of CoPt alloy peak. BET surface area shows decrease in surface area of spent catalyst i.e. 550 $m^2 \cdot g^{-1}$ compared to fresh catalyst (630 $m^2 \cdot g^{-1}$) which could be due to adsorption of side product on the catalyst surface. The

particle size distribution obtained from TEM data shown in Figure 5.14 is correlating with fresh catalyst which proves that no sintering of metal occurs under reaction condition. ICP-OES study of spent catalyst shows 0.36 ppm loss of Co and similar amount was found in reaction mixture without loss of Pt metal.

5.3.13 Proposed reaction mechanism for conversion of FAL to CPO

From the catalytic reactions of FAL, FOL, CPO, 2-cyclopentene-1-one in biphasic solvent system, it is postulated that the mechanistic route of reaction is 1st FAL get converted to FOL and FOL is undergoing ring rearrangement by ring opening and closing to CPO as major product via 2-cylopentene-1one intermediate which is highly unstable intermediate (Figure 5.15).
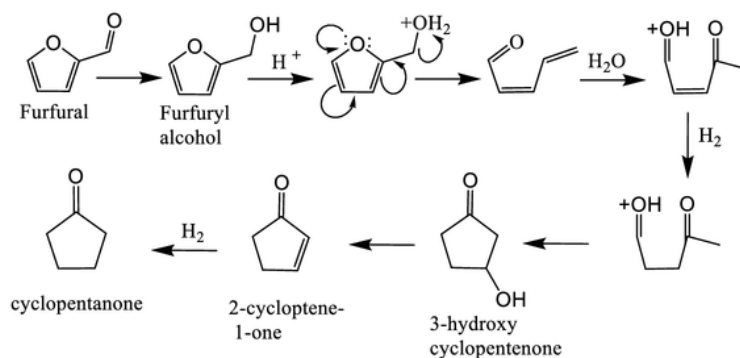
Figure 5.15 Proposed reaction mechanism for conversion of furfural to cyclopntanone

The mechanism of reaction is adsorption of FAL on the catalyst surface through the interaction between carbonyl group of FAL and Co(II) cation of Pt(3Co(3)/C catalyst which converts FAL to FOL by splitting of hydrogen molecule on Pt metal surface followed by attack of H_2O on FOL to undergo cyclic rearrangement and formation of CPO via unstable intermediate product.[10, 16]

5.4 Conclusions

It has been seen that the conversion of FAL to CPO is highly depending on solvent system. Instead of pure water, biphasic solvent system is more efficient under lower H_2

pressure (1 MPa) at 180 °C and reduces the side reactions of FAL and FOL which are more likely to prominent in water medium. At 1 MPa H_2, 75% CPL yield was obtained at 180 °C. At 150 °C with 2 MPa H_2, 71% CPL formation was observed. The yield of CPO achieved to be 73% in water medium at 150 °C. Bimetallic catalyst with 3 *wt*% Pt and 3 *wt*% Co is giving better activity than monometallic catalyst. Both catalyst and solvent system were helping out simultaneously to get better yield of CPO. CPO is the stable product under reaction condition as observed from substrate and product stability study. In presence of toluene, FAL is converted to FOL and 2-MF without formation of CPO and hence only toluene system was not used in the reaction. It has been visualized that CPO is formed only in water medium and thus biphasic system is used, which proved to be useful in achieving better yields of CPO. When FOL was used as starting substrate, 1,2-pentanediol is formed along with CPO and this decreased the selectivity of CPO. In recycle study the activity of catalyst was observed to be decreased after 1st run due to loss of catalyst and deactivation of catalyst due to adsorption of side products on catalyst surface.

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Chapter 6
Hydrogenation of Sugars to Sugar alcohols

Chapter 6
Section A: Hydrogenation of Xylose to Xylitol

6A.1 Introduction

Patients suffering from diabetes were recommended to use artificial low calorie and dietetic sweeteners. About 100 years ago, saccharine was introduce as artificial sweetener which is 300 times sweeter than glucose but it leaves bitter metallic after test[1] which was objectionable to some users. In 1950s sodium and calcium salt of cyclamates were introduce which is 30-40 times sweeter than sugar but it has negative impact on health and leads to the formation of bladder tumor, hence it was banned by Food and Drug Administration (FDA). Presently, the source of xylitol is the biomass derived non edible sugar i.e. xylose. As explained in chapter 1, section 1.6.4, xylitol is the better artificial sweetener due to its attractive properties like sweetness, inertness, solubility and anticarcinogenicity. It is 20-25 times sweeter than sugar and is highly soluble in water (62.4% at 25 °C). It does not get caramelize at higher temperature and does not require insulin hence is suitable for diabetics patients.[1,2] Due to the relative inertness of xylitol during storage, it is used in several other industries such as in pharmaceutical, cosmetic and synthetic resin.[3] xylitol has antimicrobial property and hence is used to prevent dental infection.[4] Various products are made up of xylitol like mouth wash, toothpaste, chewing gum, sugar free candy etc.[5,6]

In general three processes are used for the production of xylitol i.e. chemical, microbial (fermentation) and enzymatic (Figure 6A.1). The microbial process is time consuming due to sterilization, inoculum development and high consumption of water and it is associated with recycling problem,[7-13] while enzymatic process is pH, nutrient and temperature dependent and also costlier process due to cost of enzyme preparation and regeneration.[14,15] Chemical process involves high temperature and high pressure but still used by industrially for production of xylitol.[4,7,8]
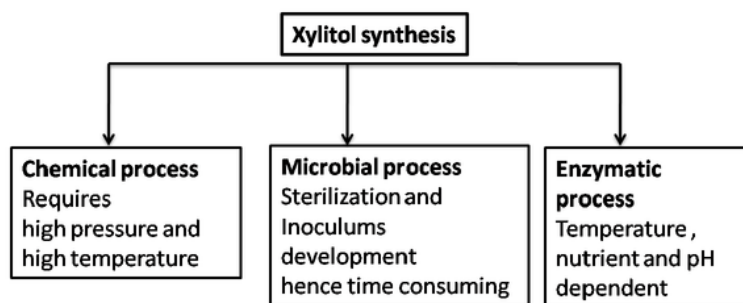

Figure 6A.1 Xylitol synthesis processes and their drawbacks

In chemical process, xylitol is obtained by batch mode hydrogenation of aqueous xylose solution under hydrogen pressure. Lignocellulose is the potential source for synthesis of glucose and xylose. By hydrolysis of cellulose and hemicelluloses these sugar on hydrogenation produces sugar alcohols like sorbitol, xylitol, mannitol and arabitol.[16, 17] Industrial synthesis of xylitol is done from xylose hydrogenation in presence of cheaper Raney Ni catalyst at 80-140 °C and 5-12 MPa H_2 pressure giving 50-60% xylitol yield.[18, 19] However, it is associated with deactivation of catalyst due to adsorption of impurities on the catalyst surface and leaching of metal.[20-22] Leaching of Ni in reaction mixture further increases the process cost to purify the xylitol which involves expensive steps like ion exchange, filtering and crystallization.[23] Noble metals like Ru, Pt, Pd are reported for conversion of xylose to xylitol at the temperature range between 120-130 °C and H_2 pressure 1.6-5.5 MPa.[24,16] From known literature, it is observed that Ru is showing better activity for hydrogenation of xylose. However, H_2 pressure used is very high (2.0 to 5.5 MPa). On the contrary few reports are available for Pt catalytic system where 1.6 MPa H_2 is used at 60 °C in presence of calcined hydrotalcite (CHT) but it has been showing decrease in selectivity of xylitol. In our group, $PtSn/Al_2O_3$ catalyst has shown 98% conversion of xylose with 89% yield of xylitol. Besides the catalytic activity in most of the works recycle study is not shown.

Hence, the objective of the present work was to develop a catalytic system which will efficiently convert xylose to xylitol at low pressure (< 1.6 MPa) than reported with better selectivity of xylitol, recyclable catalyst and hydrogenation of concentrated sugar solution (≈40 *wt*%).

In earlier work, as discussed in chapter 3, Pt(3)Co(3)/C catalyst have shown the selective hydrogenation of FAL to FOL (100% conversion of FAL with 100% yield of FOL) in water medium. Hence it was hypothesized that bimetallic catalyst with Pt modified Co metal supported on carbon could be used for the hydrogenation of xylose to xylitol. In addition to PtCo/C catalyst, Ru and other non-noble metal (Cu, Co, Ni) supported catalyst were also used for comparative study. In order to make the process industrially feasible, the concentrated xylose solution were used (Scheme 6A.1).
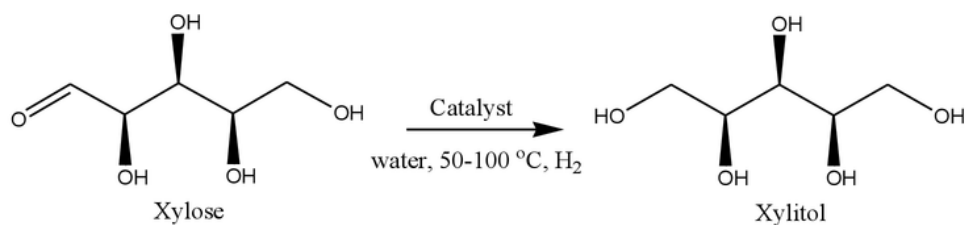
Scheme 6A.1 Hydrogenation of xylose to xylitol

6A.2 Materials and methods

Xylose (99%) and arabinose (99%) were purchased from Loba Chemicals, India. Xylitol (99%), arabitol (99%), ethylene glycol (99%), were procured from s.d. fine chemicals, India. Synthesis of Pt, Co based mono and bimetallic catalyst is described in chapter 2.

Batch mode reactions were carried out in high temperature high pressure 50 mL stainless steel Amar make reactor. The reactor was charged with 35 mL water, 0.0785 g catalyst and 0.35 g substrate. H_2 gas was flushed four-five times in reactor to remove air. After pressurisation of H_2 gas up to required pressure (0.2-2 MPa), the reactor was heated slowly to reach at desired temperature (50-120 °C). Until final temperature reached, the stirring speed was maintained at 300 rpm. After final temperature was attained, the stirring speed was increased to 900 rpm and the time was noted down as starting time of the reaction.

6A.3 Catalytic activity

6A.3.1 Activity of mono and bimetallic catalyst

Initially, the reactions were carried out with Co(3)/C, Pt(3)/C and Pt(3)Co(3)/C catalyst and the results are shown in Figure 6A.2. In presence of carbon, the xylose conversion was 6% without formation of desired product due to adsorption of xylose on carbon.

When reaction was carried out with Co(3)/C catalyst the conversion of xylose was 24% but no formation of xylitol. While in presence of Pt(3)/C catalyst, the xylose conversion of 17% with 12% yield of xylitol was observed. The difference in the activity of Co(3)/C and Pt(3)/C was observed because Pt is known for hydrogenation reaction by splitting H_2 molecule. Moreover, the bimetallic catalyst is showing significant increase in the activity with 79% conversion of xylose and 76% yield of xylitol with 4% yield of arabitol as side product.
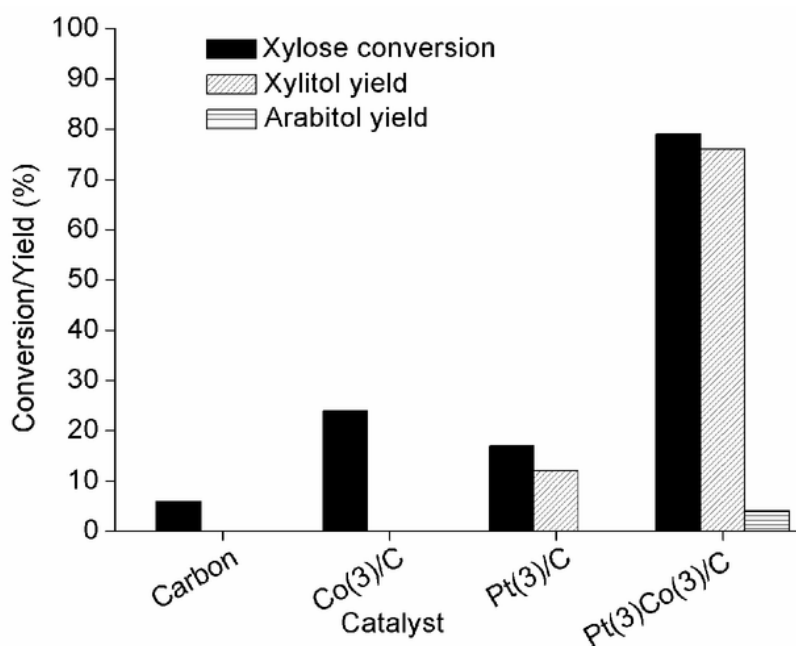
Figure 6A.2 Effect of mono and bimetallic catalyst

Reaction condition: Xylose, 0.35 g; Catalyst, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 100 °C; 11 h; 900 rpm.

These result are encouraging at lower H_2 pressure (1 MPa) with better selectivity of xylitol than earlier reports where H_2 pressure is >1 MPa.[3, 16] Improvement in the yield of xylitol in presence of bimetallic catalyst in comparison to monometallic catalyst is due to change in electronic nature of metals by charge transfer of electron from electropositive Co to electronegative Pt metal (the details are given in Chapter 2, section 2.4.2). The Pt in metallic state activates the heterolytic dissociation of H_2 to H^+ and H^- ions, and Co in II oxidation state activates the carbonyl group. Hence both the metals showed synergetic effect for improvement in the activity of bimetallic catalyst. Adsorption study of xylose and xylitol was done on carbon support at room temperature. It shows that 6% xylose was adsorbed on the carbon but no adsorption of xylitol was found on carbon which also help to increase the interaction between catalyst and xylose. However due to lower interaction between catalyst and xylitol, it gets easily desorbed and provide active sites for hydrogenation at lower H_2 pressure.

6A.3.2 Effect of temperature on conversion of xylose to xylitol

To see the activity of catalyst for conversion of xylose to xylitol at different temperatures (50, 80 and 100 °C), the reactions were carried out for shorter time 5 h in presence of Pt(3)Co(3)C catalyst. It was observed that with increase in temperature from 50 to 100 °C, the conversion of xylose and yield of xylitol increases (Figure 6A.3). At 50 °C, the conversion of xylose was 15% with 15% yield of xylitol (100% selectivity of xylitol) was observed. As the temperature increases to 80 °C, the xylose conversion reaches to 35% with 34% xylitol yield and 1% arabitol yield.
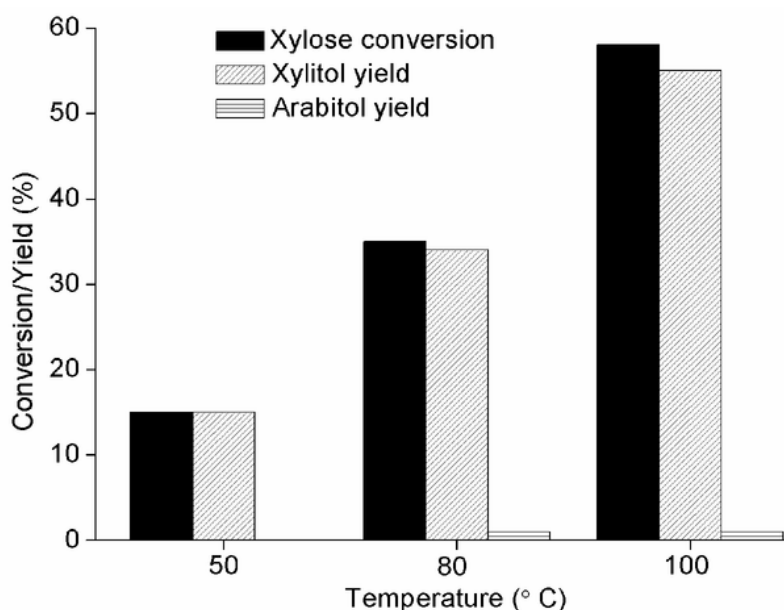
Figure 6A.3 Effect of temperature on the conversion of xylose to xylitol

Reaction condition: Xylose, 0.35 g; Pt(3)Co(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 5 h; 900 rpm.

At 100 °C, the conversion of xylose reaches to 58% with 55% yield of xylitol and 1% yield of arabitol. This study shows that as the temperature increases, the conversion of xylose increases with marginal decreases in the selectivity of xylitol due to the formation of arabitol. At 50 °C, there is no formation of arabitol. However as the temperature increases from 50 to100 °C, the formation of arabitol was observed. To find the source of arabitol reaction was carried out with xylitol at 100 °C under 1 MPa. However, there was no formation of arabitol. This proves

that arabitol is not formed from xylitol but directly form xylose. Formation of arabitol was also observed at 90 °C but no arabitol formation was observed below 90 °C.[25] As per kinetic modeling study, the xylose get isomerise to xylulose which is then converted into xylitol or arabitol due to presence of Lewis acid site on catalyst.[25, 26] The optimum reaction temperature of 100 °C is used for further study.

6A.3.3 Effect of time

In order to study the effect of time on the conversion of xylose to xylitol, the reaction were carried out with varying time from 3 to 14 h at 100 °C. It was observed that the conversion of xylose increases with time from 40 to 89% as shown in Figure 6A.4. However, the rate of xylose conversion was very slow. Within 3 h, the conversion was 40% with 36% xylitol and 1% arabitol yield. Within 5 h, the conversion reaches to 58% with 55% yield of xylitol and 1% arabitol. For longer reaction time of 11h, the converison of xylose become 79% with 76% xylitol and 4% arabitol yield. Futher, the increased in reaction time to 14 h, the conversion reaches to 89% with 81% xylitol and 2% arabiol yield. Under 1 MPa H_2 pressure for longer time (11 h) the rate of xylose conversion became very slow. This could be due to either decrease in H_2 pressure during reaction as a result of the consumption of H_2 or adsorption of xylose on catalyst surface which reduce the active sites. The earlier reports clearly showed that these reactions were carried out at high H_2 pressure 2-5.5 MPa.[24,16] Hence it was decided to carry out reaction for 11 h by maintaing 1 MPa H_2 pressure during reaction by pressurising H_2 after 3 h. However, the results were not encouraging.

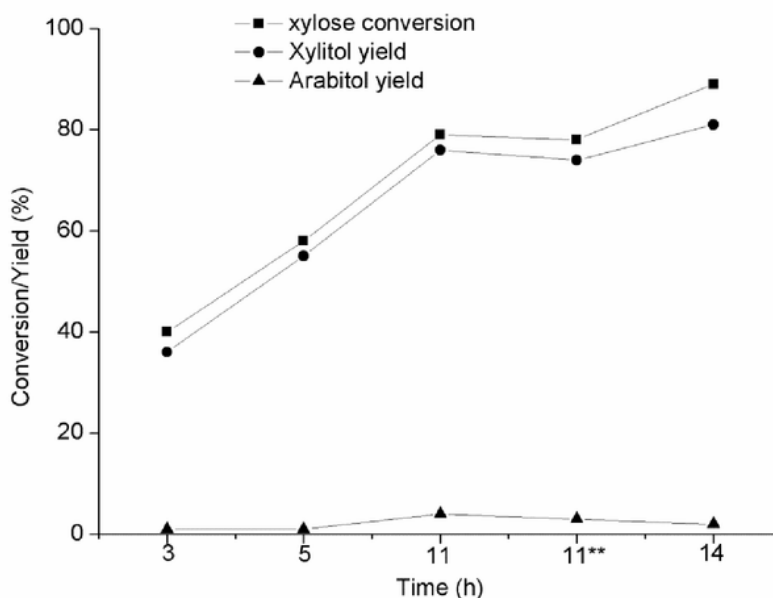**Figure 6A.4** Effect of time on conversion of xylose to xylitol

Reaction condition: Xylose, 0.35 g; Pt(3)Co(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 100 °C; 900 rpm. ** H_2 pressurised after 3 h.

6A.3.4 Effect of H_2 pressure

Literature survey for hydrogenation of xylose to xylitol in presence of noble metal catalyst showed the better activity of catalyst under higher H_2 pressure i.e. in the range of 2.0-5.5 MPa. Hence the pressure study was done with varying H_2 pressure from 0.5 to 2.0 MPa for 5 h and the results are shown in Figure 6A.5. Under 0.5 MPa H_2 pressure, the conversion was 45% with 38% yield of xylitol and 2% arabitol yield. Under 1.0 MPa H_2 pressure, the conversion increases to 58% with 55% xylitol and 1% arabitol yield. With increase in pressure to 1.5 MPa, the conversion increase to 70% with 63% yield of xylitol and 1% arabitol yield.
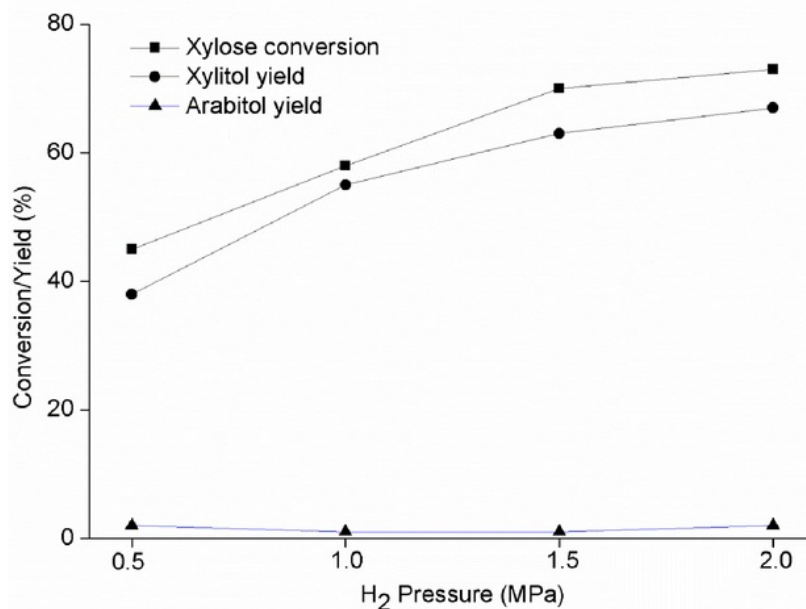
Figure 6A.5 Effect of pressure on the conversion of xylose to xylitol

Reaction condition: Xylose, 0.35 g; Pt(3)Co(3)/C, 0.0785 g; water, 35 mL; H_2 pressure at room temperature;100 °C; 5 h; 900 rpm.

Further, the increase in H_2 pressure to 2.0 MPa does not improve the conversion of xylose which remains almost constant with 73% conversion and 67% xylitol and 2% arabitol yield. These results show that with increase in pressure from 0.5 to 1.5 MPa, the improvement in conversion and yield was observed. As reported earlier that with increases in pressure, the solubility of H_2 increases at 100 °C the absorption coefficient of H_2 per g of water under 2.5, 5.0 and 7.5 MPa was 0.4615, 0.9120, 1.355, respectively.[27] Further increase in pressure, the conversion and yield remains almost constant. This showed that the reaction is not totally depend on pressure but also associated with other factors like adsorption of substrate on catalyst surface which decreases the activity of catalyst.

6A.3.5 Effect of solid base

Pressure study shows that the conversion of xylose to xylitol was not improved much beyond 1.5 MPa. Hence in order to improve the results, it was decided to study the effect of solid base on the conversion of xylose to xylitol. Earlier report from our group showed 99%

conversion of xylose in presence of Pt/Al_2O_3 and calcined CHT.[16,28] The better performance of catalyst in presence of CHT was due to ring opening phenomenon of sugars in presence of base. It is known that in alkaline medium glucose get converted into fructose by Lobry de Bruyn-Albeda Van Ekenstein transformation reaction. It makes C=O group easily available for hydrogenation. Hence, the reactions with Pt(3)/C, Co(3)/C and Pt(3)Co(3)/C catalyst in combination with CHT (basicity 0.8 mmol/g) were carried out and the results are shown in Figure 6A.6. When the reaction was carried out in presence of Pt(3)Co(3)/C catalyst without CHT, the conversion of xylose was 79% with 76% xylitol and 4% arabitol formation. The pH of reaction mixture was 7.4 after completion of reaction.
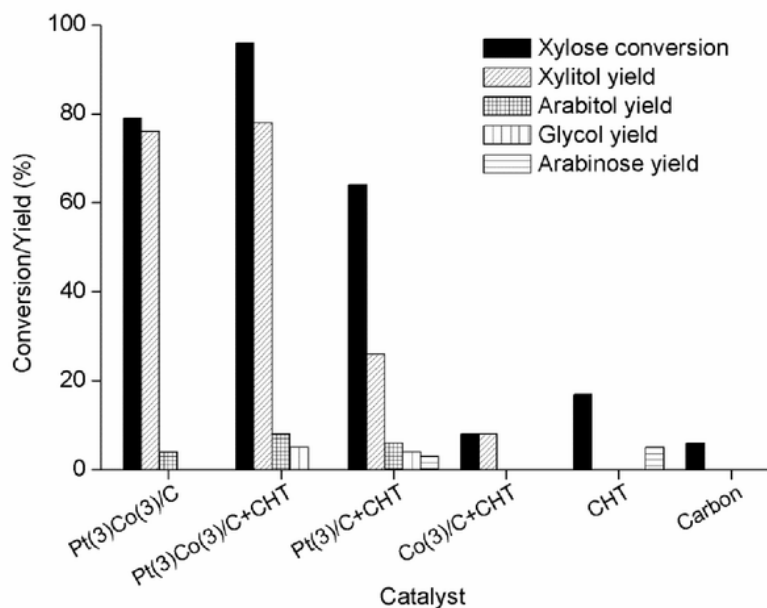
Figure 6A.6 Effect of solid base on hydrogenation of xylose

Reaction condition: Xylose, 0.35 g; catalyst, 0.0785 g; CHT, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 100 °C; 11 h; 900 rpm, (CHT-calcined hydrotalcite).

However in presence of Pt(3)Co(3)/C + CHT, 96% xylose conversion with 78% xylitol, 8% arabitol and 5% glycol yield formation was observed. The resulting pH of reaction mixture after completion was 9.1. With Pt(3)/C+CHT the conversion reaches to 64% with 26% xylitol, 3% arabinose, 6% arabitol and 4% ethylene glycol formation. In presence of Co(3)/C + CHT

catalyst, the conversion was 8% with 8% yield of xylitol. In presence of solely solid base, CHT, the conversion reaches to 17% with 5% arabinose formation, but no sugar alcohol or glycol product formation was observed. In presence of carbon, the xylose conversion was only 6% and the xylitol formation was not observed. This result shows that the presence of CHT improves the conversion of xylose. However, the selectivity of xylitol decreases due to formation of side product like arabinose, arabitol and also ethylene glycol. The similar results were also reported in presence of base.[28] Hence, it was concluded that in presence of base, the isomerization and C-C bond breaking occurs which increases the conversion of xylose and yield of xylitol along with formation of ethylene glycol as side product.

6A.4 Activity of Ru(3)/C catalyst for hydrogenation of xylose to xylitol

Activity study of Pt(3)Co(3)/C catalyst for different time and different H_2 pressure showed no improvement in the conversion of xylose and yield of xylitol. In presence of CHT, the conversion reaches to 96%, however, the yield of xylitol was 78% (81% selectivity of xylitol) due to the formation of side products (8% arabitol and 5% glycol yield). Moreover, from the literature it is known that Ru shows good activity. Hence it was decided to carry out the reactions with Ru(3)/C catalyst for comparison study. The synthesis of Ru/C catalyst is given in chapter 2, section 2.4.1.

6A.4.1 Effect of time

Initially, the reaction was carried out at 100 °C in presence of Ru(3)/C catalyst for 11 h. The result showed 100% conversion of xylose with 98% yield of xylitol. Ru(3)/C catalyst has shown drastic improvement in result compared to PtCo/C catalyst (79% xylose conversion, 76% xylitol yield, 4% arabitol yield) at 100 °C and 11 h. Hence the time study was done with varying time as shown in Figure 6A.7. Within 1h reaction, the xylose conversion was 53% with 49% yield of xylitol. Within 2 h, the conversion reached to 69% with 65% yield of xylitol. Within 3 h, the complete conversion of xylose was achieved with 98% yield of xylitol. After 5 h of reaction time, the steady state was achieved and the xylitol yield was remains constant (98%) with no arabitol formation. This shows that Ru in comparison to Pt is showing better activity for hydrogenation of xylose. Various factors are responsible for activity of catalyst like Surface structures, electronic property of active metal, adsorption geometries, bond strengths and the

ability of a surface to bind or react with a particular molecule. Transition metals, which are used in catalysts, have partially filled or completely filled d-orbitals. When substrate gets adsorbed on the metal surface it forms metal-adsorbate bonding and metal- adsorbate antibonding orbitals. In periodic table there are two general trends in the interaction between metal and adsorbate i.e. 1) farther to the left (left to right) in the periodic table, the stronger the bond, and 2) down the periodic table, the weaker the interaction hence the 5d metals are more noble than the 4d and 3d metals. The position of Ru in periodic table is right to Pt and also the atomic size of Pt is larger than that of Ru. Hence the interaction of H_2 with Ru is more than Pt. This could be one of the reasons behind the more activity of Ru than Pt in hydrogenation of xylose to xylitol.
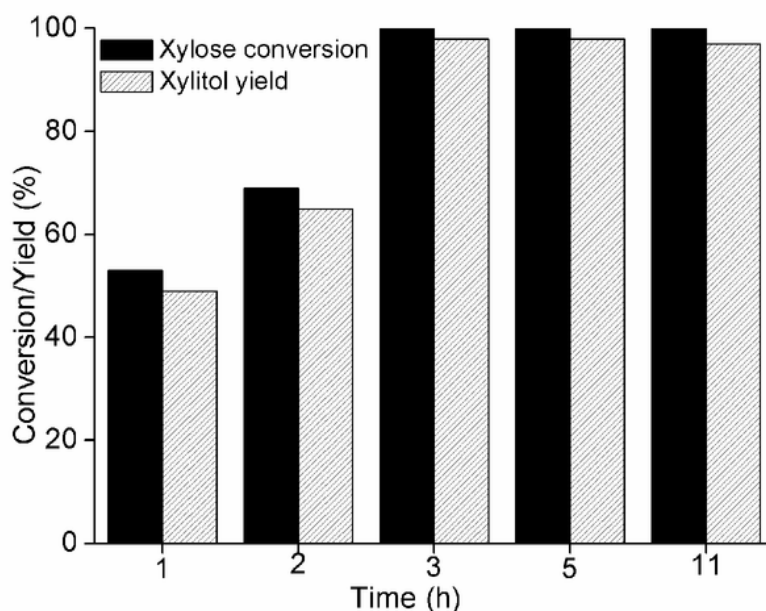
Figure 6A.7 Effect of time on the conversion of xylose to xylitol in presence of Ru(3)/C catalyst **Reaction condition:** Xylose, 0.35 g; Ru(3)/C, 0.0785 g; 100 °C; H_2 pressure, 1 MPa at room temperature; 35 mL water, 900 rpm.

6A.4.2 Effect of temperature

In presence of Ru(3)/C catalyst at 100 °C within 3 h, the conversion of xylose was 100% with 98% yield of xylitol. Hence it was thought that this reaction can be carried out at temperature below 100 °C.
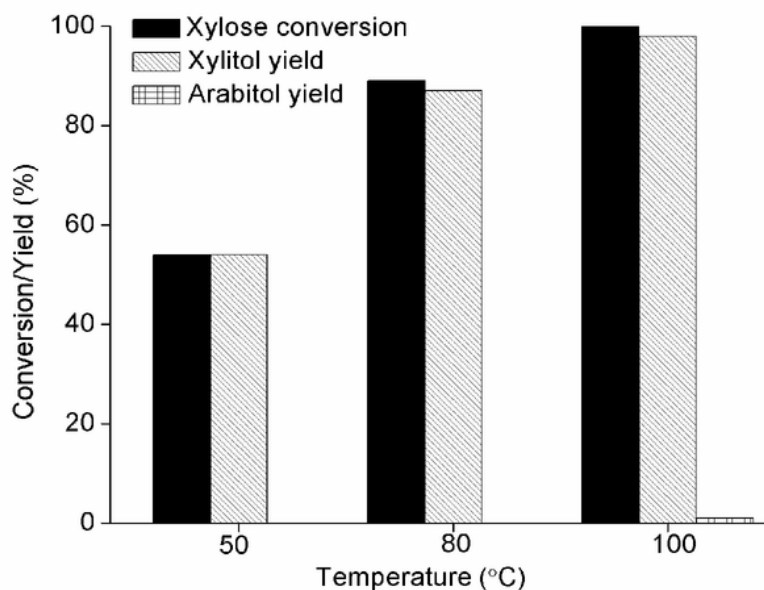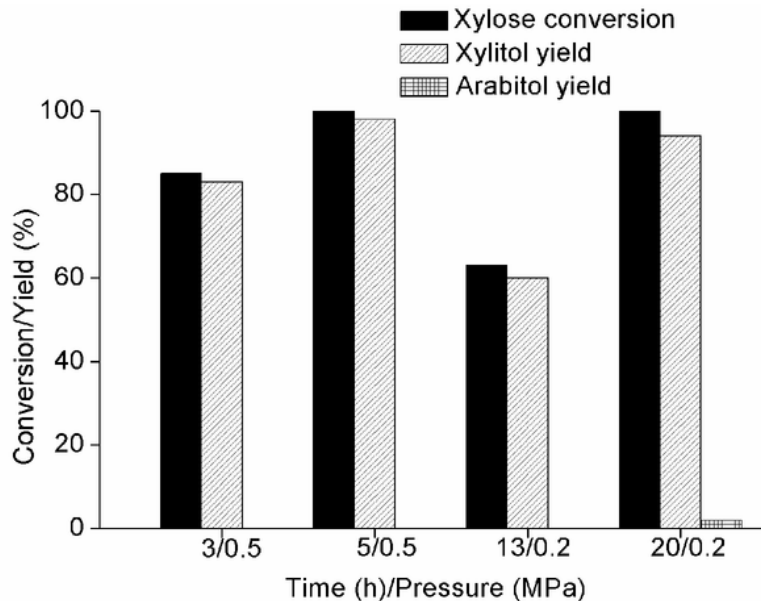
Figure 6A.8 Effect of temperature

Reaction condition: Xylose, 0.35 g; Ru(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 3 h; 900 rpm.

The reactions were optimized in the temperature range from 50 to 100 °C to study the activity of catalyst as shown in Figure 6A.8. Temperature study shows that in presence of Ru(3)/C catalyst at 50 °C, the conversion of xylose reaches to 54% with 54% xylitol yield (100% selectivity for xylitol). At 80 °C, the conversion of xylose was found to be 89% with 87% yield of xylitol. With further increased in temperature to 100 °C, the conversion reaches to 100% with 98% yield of xylitol. These results showed that with increase in temperature, the conversion of xylose and yield of xylitol was increased with marginal loss in the selectivity of xylitol as compared to PtCo/C catalyst where the formation of arabitol was observed.

6A.4.3 Effect of low pressure

Ru(3)/C catalyst has shown best activity at 100 °C and 1MPa H_2 pressure in 3 h with 100% xylose conversion and 98% yield of xylitol. Hence it was decided to carry out the reactions at lower H_2 pressure from 0.2 to 0.5MPa and the results are shown in Figure 6A.9. Under 0.5 MPa H_2 pressure, the conversion of xylose was found to be 85% with 83% xylitol

yield in 3 h. Hence, to achieve the complete conversion, the reaction was carried out for 5 h under similar reaction conditions and it was observed that conversion of xylose achieved to be 100% with 98% yield of xylitol.

Figure 6A.9 Effect of low pressure on conversion of xylose to xylitol

Reaction condition: Xylose, 0.35 g; Ru(3)/C, 0.0785 g; water, 35 mL; H_2 pressure at room temperature; 900 rpm.

The catalyst was found to be active under 0.5 MPa H_2 pressure. Hence the reaction was carried out under 0.2 MPa to see the effect of lower H_2 pressure and it was found that under 0.2 MPa, the conversion was 63% with 60% yield of xylitol within 13 h. Under similar reaction condition for longer time (20 h), 100% xylose conversion was observed with 94% yield of xylitol; however the rate of reaction decreases.

6A.4.4 Effect of substrate/catalyst ratio for concentrated xylose (5-40 *wt%*) system

The objective of this work was to develop an efficient catalytic system with higher concentration of xylose and lower catalyst loading for the selective hydrogenation of xylose to xylitol. Hence the effect of higher concentration of substrate with lower catalyst loading was studied with different substrate to catalyst ratio as shown in Table 6A.1. It was observed that the

16 substrate/catalyst ratio was showing best activity with 40 *wt*% xylose concentration achieving 100% conversion of xylose with 98% yield of xylitol.

Table 6A.1 Effect of substrate/catalyst ratio for higher *wt*% of xylose

Entry No.	Substrate /Catalyst (*wt/wt*) ratio	Xylose (*wt%*)	Xylose conversion (%)	Yield (%)		
				Xylitol	Arabitol	Not identified
1	22	5[a]	30	26	-	4
2	5.5	20	100	98	2	0
3	5.3	40	100	99	1	0
4	8	40	100	98	1	1
5	11	40	100	98	1	1
6	16	40	100	98	1	1
7	20	40	74	62	1	11

Reaction condition: Ru(3)/C; water, 35 mL; 900 rpm; 3 h, H_2 pressure 1 MPa was maintained during the reaction by charging H_2 intermittently, 100 ºC; 900 rpm; [a] 1 MPa H_2 was charged at room temperature and during reaction no additional H_2 was charged in the reactor.

After completion of reaction the catalyst was separated from the reaction mixture by filtration and filtrate was subjected to rotavapour in order to remove the solvent (water). The obtained product was subjected for HR-MS analysis (Figure 6A.10) and the result proves the formation of xylitol.
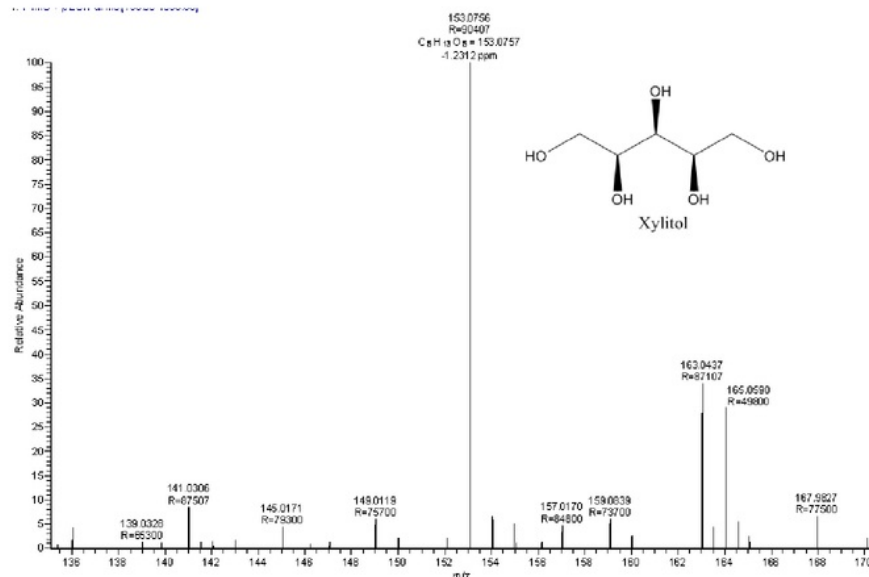
Figure 6A.10 HR-MS profile of extracted (xylitol) product

6A.4.5 Recycle study of catalyst

Ru(3)/C catalyst is giving best activity at 100 °C under 1 MPa H_2 pressure with 100% xylose conversion and 98% yield of xylitol. Hence, the recycle study of Ru(3)/C catalyst was done.

Figure 6A.11 Recycle of Ru/C catalyst in hydrogenation of xylose to xylitol

Reaction condition: Xylose, 0.35 g; Ru(3)/C for only fresh catalyst in 1st run catalyst, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 3 h; 900 rpm.

After completion of reaction, the reaction mixture was centrifuged to separate the catalyst and same catalyst was used for next run without any further treatment. It was observed that catalyst was recyclable until 4th run as shown in Figure 6A.11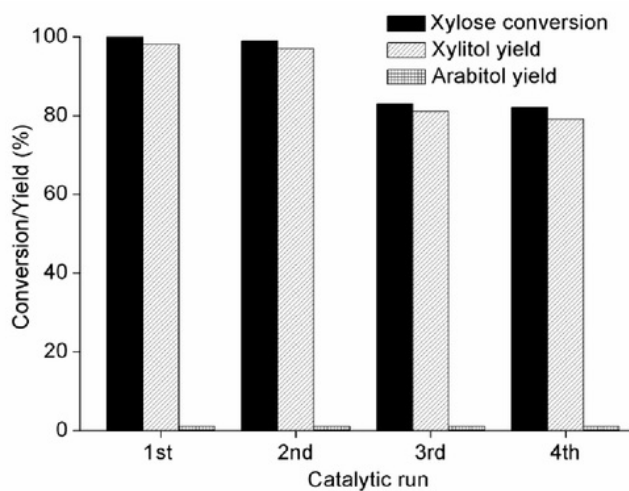. However, the lowering in catalytic activity of was observed due to handling loss of catalyst after each run which increases the substrate to catalyst ratio.

6A.4.6 Characterization of spent catalyst

Ru(3)/C spent catalyst, after 1st catalytic run, was characterized by XRD, TEM-EDX, ICP-OES, and nitrogen adsorption-desorption analysis. The XRD pattern (Figure 6A.12) of spent catalyst was matching well with that of fresh catalyst, suggesting no structural alterations in the catalyst under reaction conditions. Moreover, the TEM image (Figure 6A.13) of the spent catalyst shows no change in the morphology and particle size distribution of catalyst (Figure 6A.14). The elemental analysis of spent catalyst by ICP-OES analysis showed no leaching of Ru metal. An addition to this, the BET surface area of spent catalyst was found to be 680 m^2g^{-1} which is comparable with fresh catalyst (694 m^2g^{-1}). These observation shows that the catalyst is stable under reaction conditions.
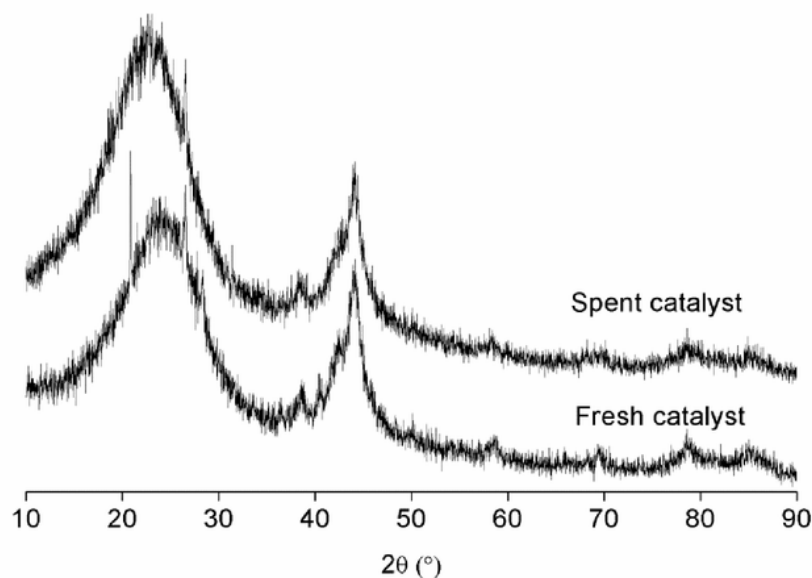
Figure 6A.12 XRD patterns of fresh and spent Ru(3)/C catalyst
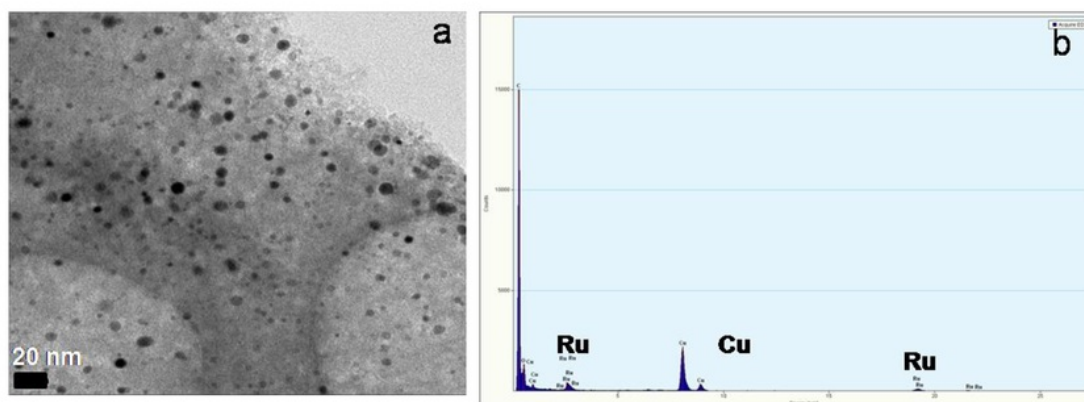
Figure 6A.13 (a) TEM image and (b) EDX of spent Ru(3)/C catalyst
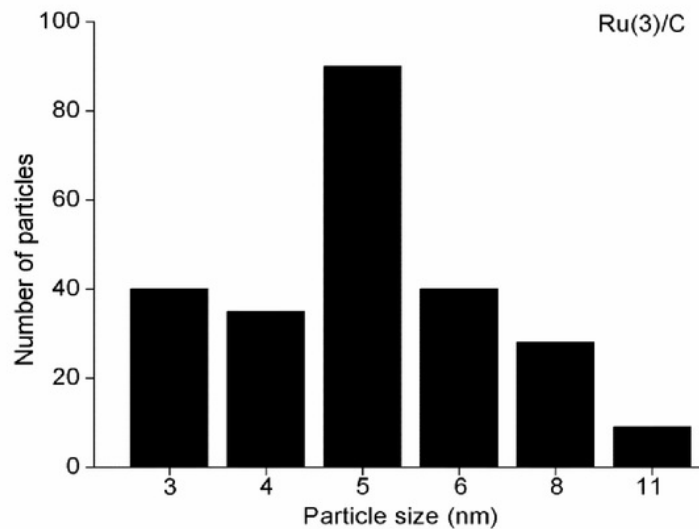
Figure 6A.14 Particle size distribution of spent catalyst

6A.5 Effect of different noble and non-noble metal supported catalyst

In order to compare the activity of noble metal catalyst with non-noble metal catalyst, different noble and non-noble metals were used to study the hydrogenation of xylose to xylitol as shown in Table 6A.2. Commercially Ni catalyst is used for conversion of xylose to xylitol because it is cheaper and the noble metals are costlier.

The hydrogenation activity of different catalyst shows that among all the catalysts, as expected, Ru catalyst is showing better activity with 100% conversion of xylose, 98% yield of.

Table 6A.2 Effect of different noble and non-noble metal supported catalyst

Entry no	Catalyst	Xylose conversion (%)	Xylitol yield (%)	Arabitol yield (%)	Unidentified (%)
1	Pt(3)/C	5	3	-	2
2	Co(3)/C	8	-	-	8
3	Pt(3)Co(3)/C	40	36	1	3
4	Ru(3)/C	100	98	1	1
5	Co(10)/C	31	12	2	17
6	Cu(10)/C	0	-	-	-
7	Ni(10)/C	18	16	-	2
8	Ni(10)Co(3)/C	42	28	1	13

Reaction condition: Xylose, 0.35 g; Catalyst 0.0785 g; water, 35 mL; H_2 pressure 1 MPa at room temperature; 100 °C; 3 h; 900 rpm.

xylitol and 1% arabitol yield. While Pt(3)Co(3)/C catalyst has shown 40% conversion with 36% yield of xylitol. Ni(10)Co(3)/C catalyst has shown 42% conversion of xylose with 28% yield of xylitol, while Ni(10)/C catalyst shown 18% conversion with 16% xylitol yield. It shows that among all catalyst, Ru is the best followed by bimetallic catalyst for PtCo/C catalyst and Ni(10)/C. However, the activity of all monometallic catalyst is low for hydrogenation of xylose to xylitol

6A.6 Conclusions

Bimetallic Pt(3)Co(3)/C catalyst is showing better activity (76% xylitol yield) for hydrogenation of xylose to xylitol at lower H_2 pressure (1 MPa) than monometallic catalyst (12% xylitol yield). However, the rate of xylose conversion was lower after certain reaction time because of the reduction of available active sites by adsorption of xylose on catalyst surface. Ru catalyst was showing best activity (100% xylose conversion) with 98% xylitol yield even at low temperature (100 °C) and low H_2 pressure (0.5 MPa). The hydrogenation of concentrated solution of xylose (40 *wt*%) was carried out in presence of Ru(3)/C catalyst. The presence of solid base (CHT) enhances the rate of reaction as well as conversion of xylose (96%). However selectivity of xylitol (81%) decreased due to formation of ethylene glycol. The xylitol yield of 98% was obtained by hydrogenation of 40 *wt*% xylose solution in presence of Ru(3)/C catalyst

under 1MPa H_2 pressure, at 100 °C. Ru(3)/C catalyst is recyclable until third run, however, the activity of catalyst decreases due to handling loss of catalyst.

6A.7 References

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Chapter 6
Section B : Hydrogenation of Glucose to Sorbitol

6B.1 Introduction

Glucose on hydrogenation produces sorbitol and mannitol. Sorbitol has wide industrial importance, as mentioned in chapter 1, section 1.7. Approximately 60% of the produced sorbitol is utilized in processed foods, confections, toothpaste and other personal care products as humectants, stabilizers, softeners and emulsifiers. An additional 16% of the total market for sorbitol is utilized for the production of L-ascorbic acid (Vitamin C).[1, 2] As a consequence; sorbitol holds the biggest market share among all the sugar alcohols with an expected demand of 2148.9 kilo tons in 2018.[3-5] Industrially, the sorbitol is produced from glucose by catalytic hydrogenation in presence of Ni catalyst. However this catalyst undergoes deactivation due to leaching of metal. Other noble metal based catalysts were also used like Pt, Ru and amongst them Ru based catalyst are show better activity.[6,7-10]

In earlier work in chapter 6A, the activity of Pt(3)Co(3)/C bimetallic catalyst and Ru/C catalysts showed for the hydrogenation of xylose to xylitol. Hence same catalysts were used for the conversion of glucose to sorbitol (Scheme 6B.1).
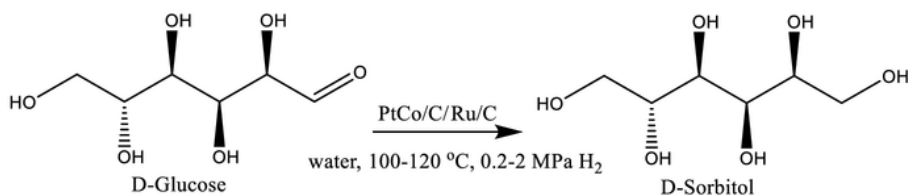
Scheme 6B.1 Hydrogenation of glucose to sorbitol

6B.2 Materials and methods

Glucose (99%), galactose (98%), fructose (99%), galactitol (99%), mannitol (99.5%), ethylene glycol (99%), were procured from s. d. Fine chemicals, India. Sorbitol (99.9%) was purchased from Aldrich Chemicals, USA. Synthesis of Pt, Co, Ru based mono and bimetallic catalyst are given in chapter 2.

Batch mode reactions were carried out in high temperature and high pressure 50 mL stainless steel Amar make reactor. The reactor was charged with 35 mL water, 0.0785 g catalyst and 0.35 g substrate. H_2 gas was flushed four-five times in reactor to remove air. After pressurization H_2 gas up to required pressure (0.2-2 MPa) the reactor was heated slowly to reach at desired temperature (50-120 °C). Until final temperature reached the stirring speed was

maintained at 300 rpm. After final temperature was attained the stirring speed was increased to 900 rpm and the time was noted down as starting time of the reaction.

6B.3 Catalytic activity

6B.3.1 Activity of mono and bimetallic catalysts in the conversion of glucose to sorbitol
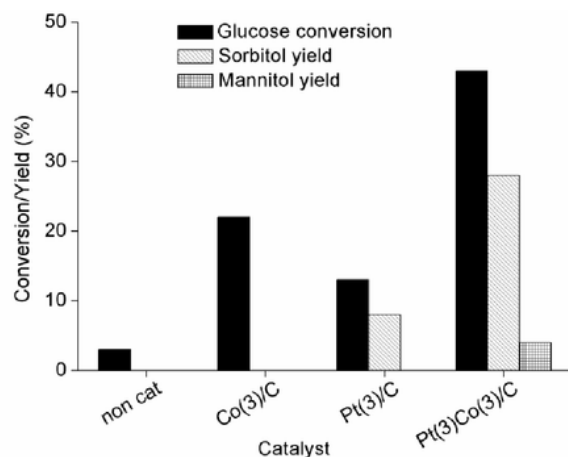
Figure 6B.1 Effect of mono and bimetallic catalyst

Reaction condition: Glucose, 0.35 g; Catalyst, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 100 °C; 11 h; 900 rpm.

To check the activity of mono and bimetallic catalyst, the reactions were carried out in presence of Co(3)/C, Pt(3)/C and Pt(3)Co(3)/C catalysts at 100 °C, for 11 h under 1 MPa H_2 pressure (Figure 6B.1). Non catalytic reaction shows only 3% glucose conversion but the sorbitol formation is not observed. In presence of Co(3)/C catalyst the conversion was 22% with no desired product formation. It represents that monometallic Co catalyst is not active for hydrogenation under the given reaction conditions. This may be due to the adsorption of glucose on the catalyst surface. To confirm the experimental results, the adsorption study of glucose and sorbitol was done which shows 7% adsorption of glucose and 4% adsorption of sorbitol. In presence of Pt(3)/C catalyst, the conversion was 13% with 8% sorbitol yield. Pt catalyst is giving better activity than Co catalyst because Pt is known for hydrogenation reaction by splitting H_2 unlike Co metal. Moreover in presence of bimetallic Pt(3)Co(3)/C catalyst conversion was 43% with 28% sorbitol and 4% mannitol yield. This indicates that compared to monometallic catalysts

bimetallic catalyst shows better result, however the rate of reaction was very slow. In order to achieve complete conversion, the reaction was further carried out for 15 h (Table 6B.1). But there was no improvement in sorbitol yield as 60% conversion of glucose and 45% sorbitol and 6% mannitol yield formation was observed. Under 1 MPa H_2 pressure, the results were not encouraging. Hence to further study the effect of increase in the H_2 pressure the reaction was carried out under 2 MPa H_2 pressure. The result showed 70% conversion of glucose with 68% yield of sorbitol but still the rate of reacion was slow. Hence in order to improve the catalytic activity, the reaction temperature was increased to 120 °C under 1 MPa H_2 pressure which gave 81% conversion of glucose, however the yield of sorbitol and mannitol was 60% and 8%, respectively. From these results, it is concluded that at higher reaction temperature (120 °C, 1 MPa H_2, 12 h), the rate of reaction increases with increase in selectivity of sorbitol (from 65% at 100 °C to 74% at 120 °C). Further reaction was carried out under 2 MPa H_2 pressure for 6 h and it was observed that within 6 h at 120 °C the conversion was 82% with 66% yield of sorbitol and 6% mannitol formation, but the carbon balance (90%) was not good. The results conclude that with increase in temperature (from 100 to 120 °C) and H_2 pressure (1-2 MPa) the conversion of glucose increases (82%) with increase in selectivity of sorbitol (80%) within 6 h.

Table 6B.1 Effect of temperature, H_2 pressure and time on the conversion of glucose to sorbitol

Entry No.	Temperature (°C)	H_2 Pressure (MPa)	Time (h)	Glucose conversion (%)	Sorbitol yield (%)	Mannitol yield (%)
1	100	1	5	33	23	1
2	100	1	11	43	28	4
3	100	1	15	60	45	5
5	120	1	12	81	60	8
6	120	2	6	82	66	6

Reaction condition: Glucose, 0.35 g; Pt(3)Co(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, at room temperature; 900 rpm.

6B.4 Activity of Ru catalyst for conversion of glucose to sorbitol

6B.4.1 Effect of time on activity of Ru catalyst for conversion of glucose to sorbitol

With Pt(3)Co(3)/C catalyst the conversion and selectivity were not improving satisfactorily. Hence Ru(3)/C catalyst was evaluated for hydrogenation of glucose to sorbitol (Figure 6B.2). In presence of Ru(3)/C catalyst within 11 h at 100 °C the glucose conversion was 100% with 97% yield of sorbitol. With this encouraging results the reaction was carried out for 5 h which gives 100% conversion with 98% yield of sorbitol. Hence further reaction was performed for shorter time (3 h). Within 3 h conversion reaches to 67% with 66% sorbitol yield. Hence the optimized reaction condition was 5 h, 100 °C and 1 MPa H_2 pressure in presence of Ru(3)/C catalyst. This result shows that Ru catalyst is giving better performance than Pt(3)Co(3)/C catalyst. This could be due to Ru is more active for dissociation of H_2 molecule than Pt. As Ru has smaller atomic size than Pt hence Pauli's repulsion is less in Ru and interaction between H_2 and Ru metal increases compared to that of Pt.
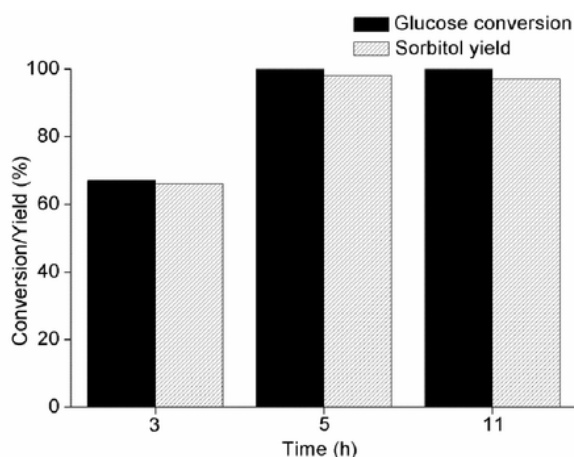

Figure 6B.2 Time study in presence of Ru(3)/C catalyst

Reaction condition: Glucose, 0.35 g; Ru(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 100 °C; 900 rpm.

6B.4.2 Effect of pressure

In presence of Ru(3)/C catalyst, 100% conversion of glucose with 98% yield of sorbitol under 1 MPa H_2 pressure was observed. In order to reduce the operating pressure, further reactions were carried out under lower H_2 pressure (0.2 and 0.5 MPa).
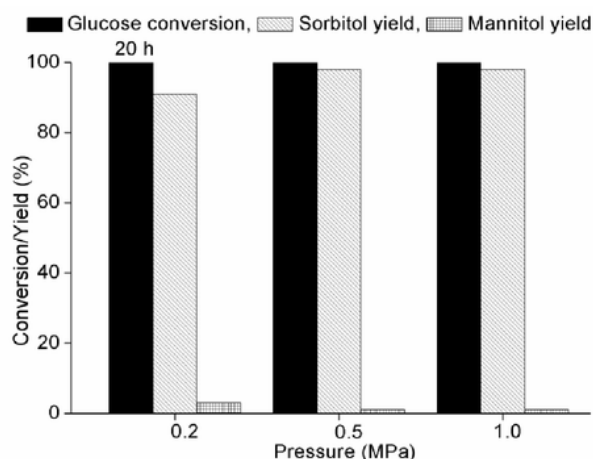
Figure 6B.3 Effect of lower H_2 pressure

Reaction condition: Glucose, 0.35 g; Ru(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, at room temperature; 100 °C; 5 h; 900 rpm.

As shown in Figure 6B.3, under 0.5 MPa H_2 pressure the conversion was 100% with 98% yield of sorbitol. Hence further reaction was carried out under 0.2 MPa which showed 100% conversion with 91% yield of sorbitol, however this reaction was performed for longer time (20 h). From the above result it is observed that under H_2 pressure ranging from 0.2 to 1 MPa, the conversion of glucose is 100%, however under 0.2 MPa the yield of sorbitol was decreased to 91%. these results show that 0.2 is not sufficient for better yield of sorbitol. Thus it is concluded that maximum 0.5 MPa H_2 pressure is the optimized reaction pressure at 100 °C for 5 h.

6B.4.3 Recycle study of catalyst

Ru(3)/C catalyst was giving better activity at 100 °C and 1 MPa H_2 within 5 h. The recycle study was done till 4th run for Ru(3)/C catalyst (Figure 6B.4). For recycle study the spent catalyst was recovered by centrifugation of reaction mixture and the recovered catalyst was used for next run without any further treatment. Recycle study shows that the activity of catalyst was decreasing after each run. This could be due to adsorption of substrate on catalyst surface which block the active sites. To confirm this, the adsorption study of glucose and sorbitol on the fresh catalyst was done and it was observed that glucose was showing 6% adsorption while sorbitol was showing 1% adsorption on carbon.
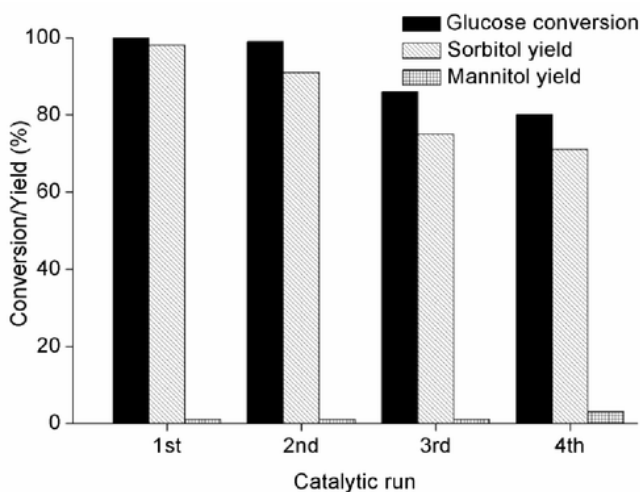
Figure 6B.4 Recycle study of catalyst

Reaction condition: Glucose, 0.35 g; Ru(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 100 °C; 11 h; 900 rpm).

6B.4.4 Characterization of spent catalyst

To know the reasons behind the decrease in the catalytic activity of catalyst, the spent catalyst was characterized after second run by TEM-EDX, XRD and ICP-OES and nitrogen adsorption-desorption analysis. TEM-EDX analysis (Figure 6B.5a) confirms the presence of Ru metal. Further, the TEM image (Figure 6B.5b, c) showed no sintering of metal and the particle size of fresh and spent catalyst is matching (5 nm). The XRD patterns (Figure 6B.6) of spent catalyst is matching with fresh catalyst which shows no structural changes in the Ru catalyst after reaction. ICP-OES analysis shows the active metal loading of fresh catalyst was 2.97 *wt*% and spent catalyst also showed 2.97 *wt*% loading which confirms no leaching of metal. The BET surface area of spent catalyst was found nearly similar (687 m^2 g^{-1}) to that of fresh catalyst (694 m^2 g^{-1}). From all the characterizations, it is concluded that there is no change in the morphology of catalyst and therefore, the catalyst was stable under reaction conditions. Hence, the possible reason for decrease in activity of catalyst could be due to adsorption of substrate (sugar) on the catalyst surface which block the active sites on the catalyst.
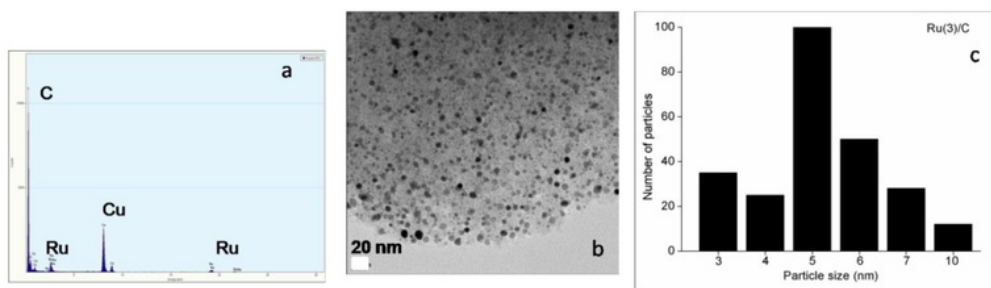
Figure 6B.5 (a) EDX, (b) TEM image and (c) particle size distribution of spent Ru(3)/C catalyst
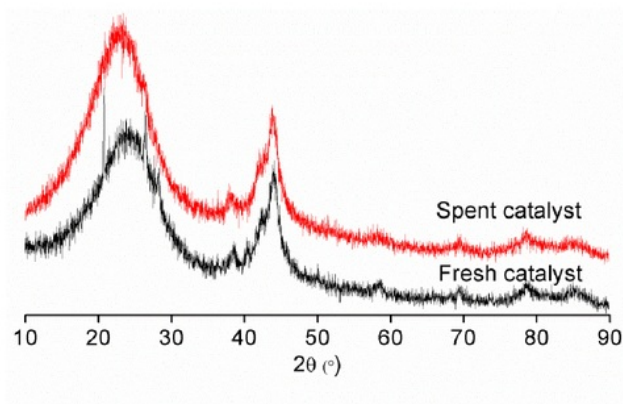

Figure 6B.6 XRD spectra of spent and fresh Ru(3)/C catalysts

6B.4.5 Hydrogenation of concentrated solution of glucose

Ru(3)/C catalyst is showing best activity at 100 °C, 5 h, 1 MPa H_2 with 1 *wt*% glucose solution. In order to make the process industrially economical, the reactions were carried out with concentrated (40 *wt*%) glucose solution and the results are summarized in Table 6B.1. Entry no. 1 shows 99% yield of sorbitol with substrate to catalyst ratio of 8. Further increased in substrate to catalyst ratio to 15, 98% yield of sorbitol was observed. To check the purity of product, the catalyst was separated by filtration of reaction mixture and the product was extracted by rotavapour. The extracted product was subjected to HR-MS (Figure 6B.7) analysis. The peak corresponding to m/z is 183 attributed to sorbitol which confirms formation of sorbitol.

Table 6B.2 Conversion of concentrated solution of glucose to sorbitol

Entry no.	Weight of glucose (g)	Weight of Ru(3)/C catalyst (g)	Substrate/Catalyst *(wt/wt)* ratio	Glucose conversion (%)	Sorbitol yield (%)
1	8	1	8	100	99
2	8	0.4	15	100	98

Reaction condition: Glucose 40 *wt%;* Ru(3)/C; water, 20 mL; H_2 pressure, 1 MPa at room temperature was maintained during the reaction by charging H_2 intermittently; 100 °C; 5 h; 900 rpm
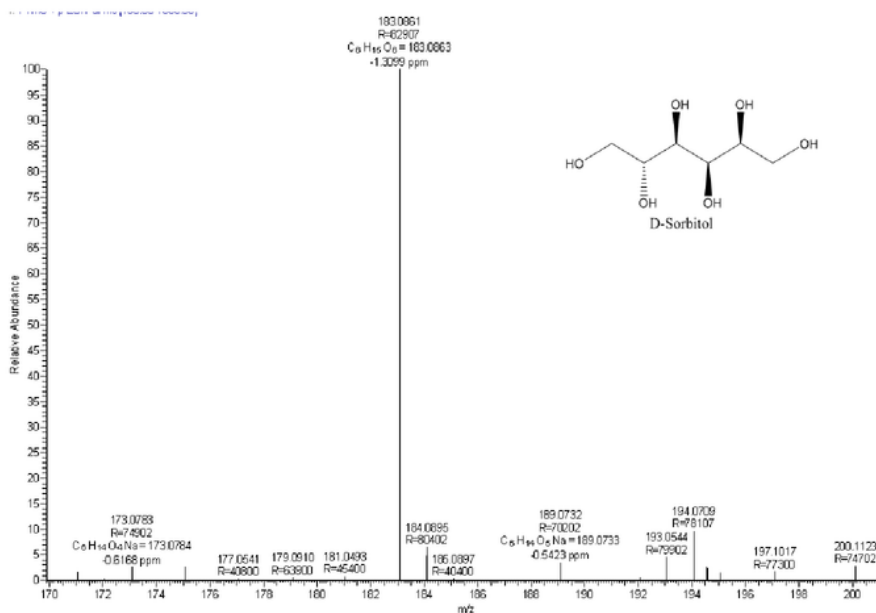

Figure 6B.7 HR-MS profile of extracted product

6B.5 Conclusions

Bimetallic Pt(3)Co(3)/C catalyst is showing better activity with 81% conversion of glucose and 60% yield of sorbitol at 120 °C and 1 MPa H_2 pressure than monometallic catalyst Pt(3)/C (13% glucose conversion with 8% sorbitol yield). However, the rate of reaction is slow due to blocking of active sites by adsorption of glucose on catalyst surface. Ru(3)/C catalyst was showing best catalytic activity 100% conversion of glucose and 98% yield of sorbitol even at low temperature (100 °C) and low H_2 pressure 0.5 MPa. The hydrogenation of concentrated

solution of glucose (40 *wt*%) was performed in presence of Ru(3)/C catalyst giving 98% yield of sorbitol. The recycle study of Ru catalyst showed decrease in activity of catalyst after each run could be due to adsorption of glucose on the catalyst surface.

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Chapter 7
Summary and conclusions

Summary and conclusions

Now-a-days lignocellulosic biomass is gaining lot of attention from researchers for the synthesis of chemicals and fuels due to their abundant availability, renewability and carbon neutral nature. Lignocellulosic biomass has potential to replace conventional fossil feedstock for the synthesis of day to day chemicals and fuels. Cellulose, the major component of lignocellulose on hydrolysis produces glucose. Glucose can be converted into ethanol by fermentation process. Beside this, glucose on dehydration produce 5-hydroxymethylfurfural (HMF) which is the platform chemical for the synthesis of various chemicals like 2,5-furandicarboxylic acid and 2,5-bishydroxymethylfuran which can be used as monomers for the synthesis of furan based polymers. Also hydrodeoxygenation of HMF produces 2, 5-dimethylfuran (DMF) which can be used as fuel additives. Second component of lignocellulose is hemicellulose, which on hydrolysis produces xylose. The dehydration of xylose in presence of catalyst produces furfural (FAL). FAL is the platform chemical for the synthesis of various chemicals like furfuryl alcohol (FOL), 2-methylfuran (2-MF), 2-methyltetrahydrofuran (2-MTHF), tetrahydrofurfuryl alcohol (THFA), tetrahydrofuran (THF) and cyclopentanone (CPO). FOL is used for the formation of furan based resins, THFOL and THF are used as solvent, 2-MF and 2-MTHF are used as fuel additives, and CPO is used in perfumery industry. Further, glucose and xylose on hydrogenation can be converted into sorbitol and xylitol, respectively. Both sugar alcohols are used as low calorie sweeteners. Lignin is made up of aromatic monomers and these monomers can be further upgraded to fuel grade chemicals. In earlier chapters catalytic activity for conversion of FAL to FOL, 2-MF, CPO, HMF to DMF and also hydrogenation of sugars to sugar alcohols is discussed. This chapter comprises the summary and conclusion of important results from all the chapters.

Chapter 1

In this chapter discussions are made on the significance of non-edible lignocellulosic biomass and its application in the conversion of value added chemicals. Lignocellulosic biomass is made up of three components; cellulose, hemicellulose and lignin. Different processes like thermo-chemical and bio-chemical are reported for the valorization of lignocellulosic biomass. Cellulose on hydrolysis produces glucose which on dehydration produces HMF. Hemicellulose on hydrolysis produces xylose which on dehydration produces FAL. These furans (HMF and FAL) are the platform chemicals for synthesis of various value added chemicals. It is reported

that compared to monometallic catalyst, bimetallic catalyst shows better activity due to change in electronic and geometrical property. Hence the objectives of this work were set to prepare mono and bimetallic catalysts based on Pt and Co with different metal loadings by wet-impregnation method, for the catalytic hydrogenation reactions under mild reaction condition, with recyclable catalyst and hydrogenation of concentrated substrate solutions.

Chapter 2

This chapter comprises synthesis and characterizations of mono and bimetallic catalysts.

➢ The catalysts were synthesized by wet impregnation method with varying metal loadings

➢ Characterization of catalyst was done by XRD, XPS, Nitrogen adsorption-desorption, TEM, SEM and TPR techniques

➢ The XRD patterns of bimetallic catalyst Pt(0.5)Co(3)/C, Pt(1)Co(3)/C and Pt(2)Co(3)/C shows peak for Co_3O_4 species, however no peaks were observed for Pt. Similarly Pt(2)Co(0.25)/C shows peaks for Pt but no peaks were observed for Co. Moreover, Pt(2)Co(3)/C catalyst shows peaks for both Pt and Co. However, in case of Pt(3)Co(3)/C catalyst, the appearance of new peak at higher degree than Pt peak shows the formation of CoPt alloy.

➢ In XPS analysis of mono and bimetallic catalyst, Pt is found in zero oxidation state in major amount with less amount of II oxidation state and Co is found in II/III state in both mono and bimetallic catalyst however no metallic peak was observed for Co.

➢ BET surface area of carbon is 753 m^2g^{-1}. However, in catalyst the surface area decreases due to loading of metal.

➢ ICP-OES analysis shows the theoretical loading of metal is matching with the experimental value.

➢ TEM analysis shows well dispersion of metal on supports and the average particle size for monometallic catalyst i.e. Pt(3)/C and Pt(2)/C is 6 nm and for Co(3)/C catalyst average particle size is 13 nm. All bimetallic catalysts, except Pt(2)Co(0.25)/C have average particle size between 9-13 nm, which is intermediate between Pt and Co monometallic catalysts. The EDX spectra of mono Pt(3)/C, Co(3)/C and bimetallic Pt(3)Co(3)/C catalyst shows the presence of Pt and Co metal in respective catalyst.

➤ TPR analysis shows the reduction peak for oxide functionalities present on carbon support and also reduction peak for Pt oxide and Co oxide species in mono and bimetallic catalyst.

➤ Presence of phenolic group on the carbon surface was proved by titration analysis of carbon sample.

Chapter 3

In this chapter, detailed catalytic activity of PtCo bimetallic catalyst for the conversion of FAL to FOL is discussed. FAL contains furan ring with aldehyde functional group, which on hydrogenation gives FOL. In most of the reports, hydrogenation of FAL to FOL was carried out at 100 °C, IPA solvent and 1 MPa H_2. Hence in order to carry out the reactions at lower temperatures and lower H_2 pressures; it was decided to prepare PtCo bimetallic catalyst, where Co in oxide form can act as Lewis acid site and helps to polarize the carbonyl group and Pt will split the H_2 molecule required for hydrogenation.

➤ Initially reactions were carried out in IPA at 100 °C under 1 MPa H_2 for 5 h in presence of Pt(3)Co(3)/C catalyst. 100% conversion of FAL with 100% yield of FOL was obtained.

➤ Effect of Pt and Co loading was studied under similar reaction conditions and it was observed that with decrease in Pt and Co loading, the conversion of FAL and yield of FOL decreases. However, the optimum *wt*% loading of Pt and Co is 3 [Pt(3)Co(3)/C catalyst].

➤ Reaction was carried out at 50 °C for 10 h under 1 MPa H_2 pressure in IPA medium and it was observed that the conversion of FAL was 92% with 91% yield of FOL.

➤ Pressure study was done at 50 °C and it was observed that IPA is not acting as a source of H_2 and the source of H_2 is molecular H_2 which was charged externally.

➤ Activity of Pt(3)Co(3)/C catalyst was studied in different solvent (methanol, ethanol, 2-propanol, n-propanol, n-butanol, 2-butanol, toluene and water) and among all the solvents, water is showing best activity at 50 °C (100% conversion of FAL with 100% FOL yield). The results show that the polarity of solvent is playing important role in the conversion of FAL to FOL.

➢ Further reaction was studied at 35 °C and 1 MPa H_2 which shows 100% conversion of FAL with 100% FOL yield. The recycle study of catalyst under similar condition shows that catalyst is recyclable at least till 3rd run.

➢ Pt(3)Co(3)/C catalyst is showing best activity even at 0.1 MPa and 35 °C with 100% conversion of FAL with 100% FOL yield.

➢ Higher concentration reactions were done where 40 *wt*% FAL solution shows 100% conversion with 86% yield of FOL at 50 °C in 6 h and 1 MPa H_2 as shown in Table 7.1.

Table 7.1 Hydrogenation of concentrated solution of FAL

Entry no.	FAL (*wt%*)	Temperature (°C)	Time (h)	FAL conversion (%)	FOL yield (%)
1[a]	5	35	10	98	98
2	20	35	10	50	49
3	20	50	6	100	100
4	40	50	6	100	86
5	40	100	3	83	28

Reaction condition: FAL; Pt(3)Co(3)/C; Substrate/Catalyst ratio, 4.43 (*wt/wt*); water, 35 mL; H_2 pressure, 1 MPa was maintained during the reaction by charging H_2 in-between; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol. [a] H_2, 1 MPa was charged at room temperature and during reaction no additional H_2 was charged in the reactor)

Chapter 4

This chapter comprises the results on catalytic activity in the conversion of FAL to 2-MF and HMF to 2,5-DMF. Both, 2-MF and 2,5-DMF have potential to be used as fuel additives.

➢ At 180 °C, the conversion of FAL was 100% with 56% 2-MF formation along with FOL and ring hydrogenated products like 2-MTHF and THFA.

➢ Conversion of FAL to 2-MF occurs in two step; in 1st step FAL gets converted to FOL and in second step FOL gets converted to 2-MF. However, the formation of 2-MF is slow compared to formation of FOL.

➢ Temperature study shows that with decrease in temperature below 180 °C, the decrease in the rate of formation of 2-MF was seen. However, with increase in temperature above 180

°C, the rate of reaction increases but carbon balance of reaction decreases. Hence the optimum temperature is 180 °C.

➢ Pressure study shows that in absence of H_2, 48% conversion of FAL was occurred with 29% yield of FOL and only 4% yield of 2-MF (Figure 7.1). This proves that the catalytic transfer hydrogenation activity is possible with catalyst. However, the rate of reaction was very slow.
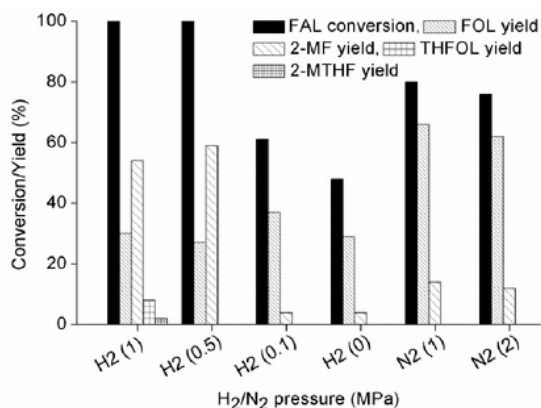
**Figure 7.1** Effect of H_2 and N_2 pressures on the conversion of furfural (FAL) to 2-methylfuran (2-MF)

Reaction condition : FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; iso-propyl alcohol, 35 mL; H_2/N_2 pressure is at room temperature; 180 °C; 8 h; 900 rpm. (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran, THFOL: Tetrahydrofurfuryl alcohol, 2-MTHF: 2-methyltetrahydrofuran)

➢ The yield of 2-MF increases with decrease in polarity of solvent.

➢ Recycle study shows the decrease in activity of catalyst for formation of 2-MF after each run due to adsorption of side product(s) on the catalyst surface and also due to loss of catalyst.

➢ Conversion of HMF to 2,5-DMF was carried out at 180 °C and 1 MPa H_2 and the result shows 100% conversion of HMF with 89% yield of 2,5-DMF.

Chapter 5

This chapter consists of catalytic conversion of FAL to CPO in biphasic solvent system and in presence of Pt(3)Co(3)/C catalyst. Conversion of FAL to CPO occurs via formation of FOL. The solubility of FAL is more in organic solvent and FOL is highly soluble in water. CPO

is highly soluble in organic solvent (Figure 7.2). Considering this solubility of product and substrate, reactions were carried out in toluene/water biphasic solvent system in presence of Pt(3)Co(3)/C catalyst.
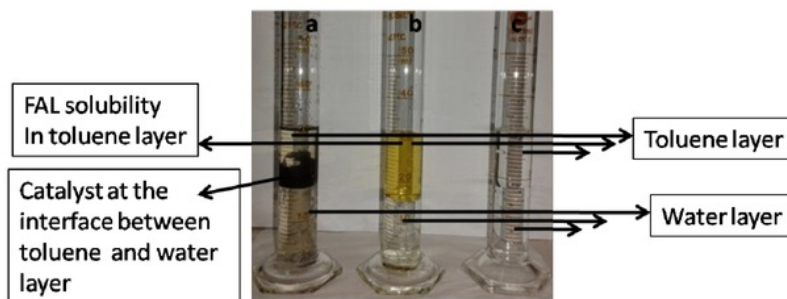
Figure 7.2 a) Distribution of catalyst at the interface between water and toluene layer b) Solubility of FAL in toluene layer c) Toluene and water biphasic solvent system; (FAL: Furfural)

➤ When reaction was carried out in pure water for 5 h under 1 MPa H_2 at 180 °C, 29% yield of CPO was obtained along with 23% CPL yield (Figure 7.3). However, when reaction was carried out in toluene/water biphasic solvent system the yield of CPO reaches to 75% which shows that the biphasic solvent system is more effective than monophasic solvent system.

➤ CPO is the major product, formed during reaction because CPL gets converted into CPO.

➤ Recycle study of catalyst shows decrease in activity of catalyst due to adsorption of side products on the catalyst surface.

➤ At lower temperature (150 °C) and biphasic solvent system, formation of CPO was 60% under 1 MPa H_2 pressure. At the same temperature and 2 MPa H_2 pressure the yield of CPO was decreased to 8% with increase in yield of CPL to 71%.

➤ When reaction was carried out in presence of formic acid as hydrogen donor the activity of catalyst was observed to be decrease.

➤ When reaction was carried out in pure water at 150 °C, 73% yield of CPO was obtained. This shows that at lower temperature the formation of side product is suppressed that improves the yield of CPO.
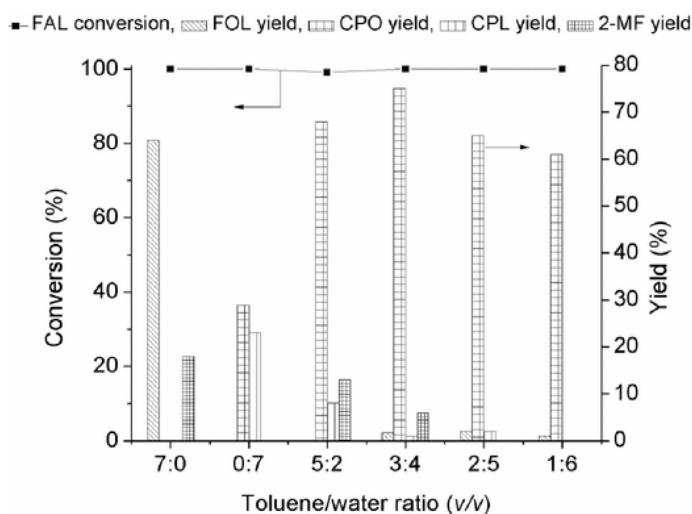
Figure 7.3 Effect of varying toluene/water (*v/v*) solvent ratio on conversion of FAL to CPO **Reaction condition**: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; toluene/water (*v/v*), 35 mL; H_2 pressure, 1 MPa at room temperature; 180 °C; 5 h; 900 rpm, (FAL: Furfural, FOL: Furfuryl alcohol, 2-MF: 2-methylfuran CPO: Cyclopentanone, CPL: Cyclopentanol)

Chapter 6

This chapter includes hydrogenation of biomass derived sugar to sugar alcohol. Xylose and glucose derived from hemicellulose and cellulose which on hydrogenation produced xylitol and sorbitol, respectively. Most of the hydrogenation reactions reported until now were carried out in presence of Ni or Ru catalysts under high H_2 pressures (5-5.5 MPa). Very few reports are available for monometallic Pt catalyst at 1.6 MPa H_2 hence in order to improve the activity of Pt catalyst at lower H_2 pressure PtCo/C bimetallic catalyst were studied for hydrogenation of sugar to sugar alcohol and also activity of Ru catalyst was compared with PtCo/C catalyst. This chapter is divided into two sections; section A includes hydrogenation of xylose to xylitol and section B includes hydrogenation of glucose to sorbitol.

Section A

This chapter includes hydrogenation of xylose to xylitol. Xylitol has wide applications in industry as low calorie sweetener. However, hydrogenation of xylose to xylitol under low pressure is challenging task. In this work, the activity differences between monometallic (Pt

based), bimetallic (Pt and Co based) and Ru based catalysts were studied for hydrogenation of xylose to xylitol.

➢ Pt(3)Co(3)/C bimetallic catalyst is showing good activity in comparison to Pt(3)/C and Co(3)/C monometallic catalysts for hydrogenation of xylose to xylitol (Pt(3)Co(3)/C catalyst showed 79% conversion of xylose and 76% yield of xylitol under 1 MPa H_2 at 100 °C and 11 h). However, further increase in time to 14 h shows no substantial improvement in the yield of xylitol (81%) could be due to adsorption of xylose on catalyst surface.

➢ With increase in H_2 pressure from 0.5 to 2.0 MPa, the rate of formation xylitol increases with 67% yield of xylitol within 5 h.

➢ In presence of solid base, calcined hydrotalcite (CHT), the conversion of xylose reaches to 96% however the yield of xylitol remains at 78%. This is because of formation of glycol as side product. This shows that the presence of CHT in reaction favors the C-C bond breakage.

➢ Ru(3)/C catalyst is showing 100% conversion of xylose with 98% yield of xylitol at 100 °C and 1 MPa H_2 in 3 h. This shows that Ru is the most efficient catalyst than PtCo/C catalyst where adsorption of substrate and desorption of xylitol is fast process.

Table 7.2 Effect of substrate/catalyst weight ratio for higher *wt*% of xylose

| Entry no.	Substrate /Catalyst *(wt/wt)* ratio	Xylose *(wt%)*	Xylose conversion (%)	Yield (%)		
				Xylitol	**Arabitol**	**Not identified**
1	22	5[a]	30	26	-	4
2	5.5	20	100	98	2	0
3	5.3	40	100	99	1	0
4	8	40	100	98	1	1
5	11	40	100	98	1	1
6	16	40	100	98	1	1
7	20	40	74	62	1	11

Reaction condition: Ru(3)/C; water, 35 mL; 900 rpm; 3 h, H_2 pressure, 1 MPa was maintained during the reaction by charging H_2 intermittently, 100 ºC; 900 rpm; [a] 1 MPa was charged at room temperature and during reaction no additional H_2 was charged in the reactor.

➢ Ru(3)/C catalyst is active under 0.2 MPa H_2 pressure and shows 100% conversion of xylose with 94% yield of xylitol. Under 0.5 MPa H_2, the yield of xylitol reaches to 98%, hence, 0.5 MPa is the minimum optimized H_2 pressure required for hydrogenation of xylose to xylitol.

➢ High concentration of xylose (40 *wt%*) is showing 100% conversion of xylose with 98% yield of xylitol under 1 MPa H_2 and 100 °C with substrate to catalyst *wt/wt* ratio of 16, as shown in Table 7.2.

➢ Recycle study of catalyst shows no loss in activity of Ru(3)/C catalyst.

Section B

This chapter includes hydrogenation of glucose to sorbitol. Sorbitol is extensively used in the food and pharmaceutical industries as low calorie sweetener, laxative, humectants and synthesis of l-ascorbic acid. Due to structural similarity between xylose and glucose, the activity of Pt(3)Co(3)/C and Ru(3)/C catalyst was also studied for hydrogenation of glucose to sorbitol.

➢ Bimetallic Pt(3)Co(3)/C catalyst is showing good performance than monometallic catalyst with 43% conversion of glucose and 28% yield of sorbitol at 100 °C, 1 MPa H_2 and 11 h. With increase in temperature to 120 °C, the conversion of glucose increases to 81% with 60% yield of sorbitol.

➢ At 120 °C and 2 MPa H_2, the conversion of glucose increases to 82% with 66% yield of sorbitol.

➢ Ru(3)/C catalyst is showing best activity with 100% conversion of glucose and 98% yield of sorbitol at 100 °C, 1 MPa H_2 and 5 h.

➢ The activity of both Pt(3)Co(3)/C and Ru(3)/C catalyst for hydrogenation of glucose required longer time than hydrogenation of xylose under similar reaction condition.

➢ Ru(3)/C catalyst is showing 100% conversion of glucose with 91% yield of sorbitol under 0.2 MPa H_2 within 20 h. However, under 0.5 MPa H_2 100% conversion of glucose with 98% yield of sorbitol was obtained (Figure .7.3).
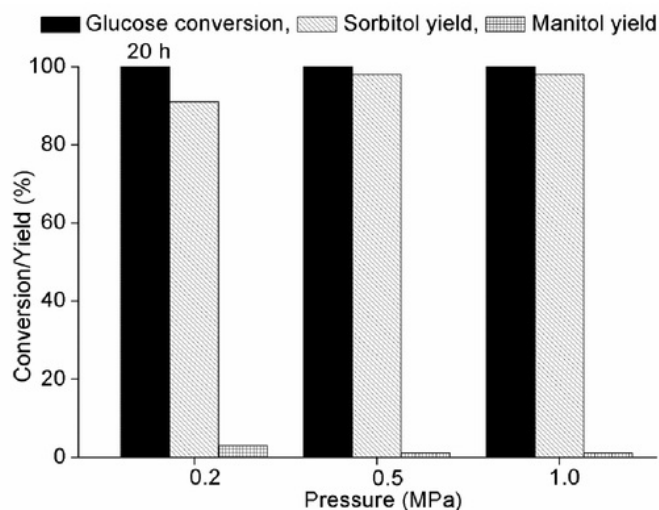
Figure 7.3 Effect of lower H_2 pressure

Reaction condition: Glucose, 0.35 g; Ru(3)/C, 0.0785 g; water, 35 mL; H_2 pressure, 1 MPa at room temperature; 100 °C; 5 h; 900 rpm.

➤ Recycle study of Ru/C catalyst shows decrease in activity of catalyst due to adsorption of substrate on catalyst surface.

Finally, it is concluded that in 3rd, 4th, 5th and 6th chapters, discussions on the catalytic hydrogenation reactions were done in presence of Pt(3)Co(3)/C catalyst. As per the objectives, reactions were performed at lower H_2 pressure which is showing efficient hydrogenation of substrate in presence of catalyst at H_2 lower pressure. This catalyst is also showing good activity for hydrogenation of concentrated solution (40 *wt*%) of FAL and sugars. In 6th chapter, Ru(3)/C catalyst is used for hydrogenation of sugar to sugar alcohol which showed best activity at lower H_2 pressure (0.5 MPa) with 98% yield of sugar alcohol.

List of Publications

❖ M. G. Dohade, P. L. Dhepe, Efficient hydrogenation of concentrated aqueous furfural solutions in to furfuryl alcohol under ambient conditions in presence of PtCo bimetallic catalyst, *Green chemistry*, 2017**, 19,** 1144-1154

❖ M. G. Dohade, P. L. Dhepe, Hydrodoxygenation of furfural to methylfuran in presence of PtCo bimetallic catalyst. *Clean Technology and Environmental Policy*, 2017**,** DOI 10.1007/s 10098-017-1408-z

❖ M. G. Dohade, P. L. Dhepe, Achieving improvements in cyclopentanone and cyclopentanol yields from furfural under mild conditions with the help of solubility differences of substrate, intermediates and products, (communicated).

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Work presented

- Poster presentation: International conference on membrane, ICM 2013, organized by center of environmental and technology, Kottayam during, Oct. 03-06, 2013

- Poster presentation: National science day at CSIR-National Chemical Laboratory, Pune, Feb. 2013

- Poster presentation: 3rd FAPS polymer congress and MACRO 2013 conference, held at the Indian Institute of Science Bangalore from, May 15-18, 2013

- Poster presentation: ICSIC 2014 jointly hosted by NCL-Pune, IISER-Pune, and SP Pune University-Pune during, Dec. 04-05, 2014.

- Attended: CATSYMP-22, the 22nd National Symposium on Catalysis organized by CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Bhavnagar, India during, Jan. 07-09 2015.

- Oral presentation: APCAT-7 Mumbai, India, Jan. 17-21st 2017

- Poster presentation: National science day at CSIR-National Chemical Laboratory, Pune, Feb. 2017

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