Exploration of the effects of supports, metals and promoters on the catalytic conversion of biomass derived mono- and poly-saccharides in to sugar alcohols

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In CHEMISTRY

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This is to certify that the work incorporated in this Ph.D. thesis entitled "**Exploration of the effects of supports, metals and promoters on the catalytic conversion of biomass derived mono- and poly-saccharides in to sugar alcohols**" submitted by **Mr. Anup Prakash Tathod** to Academy of Scientific and Innovative Research (AcSIR) in fulfillment 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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I hereby declare that the thesis entitled "**Exploration of the effects of supports, metals and promoters on the catalytic conversion of biomass derived mono- and poly-saccharides in to sugar alcohols**" 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, CSIR-National Chemical Laboratory, Pune-411008, India, under the supervision of Dr. Paresh L. Dhepe. 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.

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Dedicated to…………

My Parents

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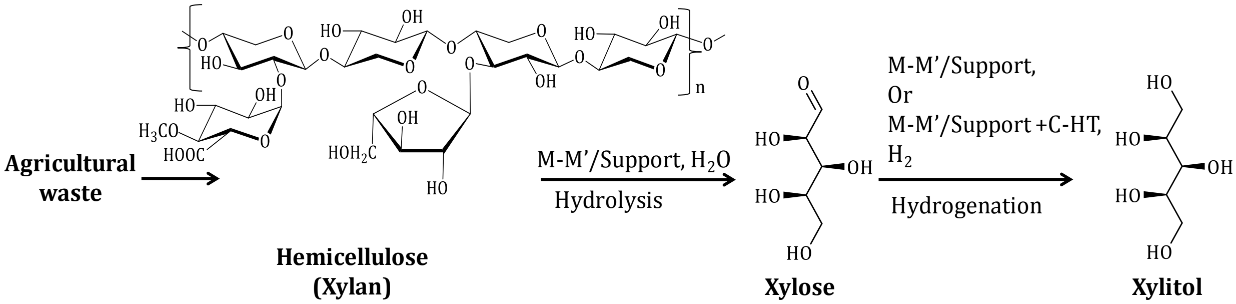
List of Abbreviations

AL	γ-Alumina
C	Carbon
C-HT	Calcined Hydrotalcite
DP	Degree of Polymerization
FAS	Ferrous Ammonium Sulfate
FDCA	2, 5-furan dicarboxylic acid
FID	Flame Ionization Detector
GC	Gas Chromatography
GVL	γ-valerolactone
HAP	Hydroxyapatite
H-BEA	Beta Zeolite (H-form)
H-MOR	Mordenite (H-form)
H-USY	Ultra Stable Zeolite Y (H-form)
H-ZSM	Zeolite Socony Mobil (H-form)
HMF	5-hydroxymethylfurfural
HPLC	High Performance Liquid Chromatography
HT	Hydrotalcite
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
MCM	Mobil Composition of Matter
MMT	Million Metric Tons
NMR	Nuclear Magnetic Resonance
RPM	Rotation per Minute
SA	Silica-Alumina
SBA	Santa Barbara Amorphous
SMSI	Strong Metal-Support Interaction
TAPPI	Technical Association of the Pulp and Paper Industry
TEM	Transmission Electron Microscopy
TOF	Turn Over Frequency
TPA	Tons per Annum
TPD	Temperature Programmed Desorption
UV-Vis	Ultra violet- Visible
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Abstract of the Thesis

Introduction

Since biomass is the alternate to fossil feedstock, lots of efforts are directed towards development of efficient methods for its conversion in to chemicals. Plant derived lignocellulosic biomass consists of cellulose (ca.50%), hemicellulose (ca.30%) and lignin (ca.20%). Cellulose is made up of glucose and hemicelluloses are made up of different pentoses (xylose, arabinose) and/or hexoses (glucose, galactose, etc), while lignin is highly branched polymer of aromatic compounds. Polysaccharides can be hydrolyzed to monomer sugars which further can be converted in to various sugar derivatives like, furans, sugar acids, sugar alcohols, glycols, etc.[1-6] Sugar alcohols are used as low calorie sweetener, in cosmetics and in pharmaceutical industries and also can act as platform chemicals.[7-9] Hence, the conversion of monosaccharides, polysaccharides and agricultural wastes in to sugar alcohols over supported metal catalysts was undertaken as my Ph.D. work (Scheme 1).[5, 6, 10]



Scheme 1. One pot conversion of hemicellulose and agricultural waste in to sugar alcohols.

Excluding introduction chapter, my thesis is divided into five chapters. Synthesis of various supported metal catalysts, characterizations of catalysts and catalytic methods are described in second chapter. Remaining chapters comprises results and discussion for the conversion of monosaccharides, isolated polysaccharides and agricultural wastes in to sugar alcohols over various monometallic and bimetallic catalysts. The effect of solid base on the above mentioned conversions has been explored.

Statement of Problem

Following are few problems associated with the earlier known methods in the synthesis of sugar alcohols,

- Use of homogeneous catalysts (enzymes and mineral acids): difficult recovery and corrosiveness of catalysts.[11, 12]
- Use of edible feedstock as substrate: may create food crisis in society.[13]
- Multiple step methods: needs additional set-up.[12]
- Low yield and selectivity for sugar alcohols.[14]
- Unstable catalyst: poor recyclability.[15, 16]

To resolve above mentioned issues, an efficient, green and one pot method needs to be developed for the conversion of lignocellulosic biomass in to sugar alcohols. Another important concern is the stability of catalysts. Catalyst which can be used for the conversion of variety of substrates (mono and poly-saccharides, agricultural wastes), with good recyclability and exploitable at wide range of reaction conditions should be developed.

Methodology Used

- Monometallic and bimetallic supported metal catalysts were synthesized by wet co-impregnation method using various supports (activated carbon (C), γ-alumina (AL), silica-alumina (SA), calcined-hydrotalcite (C-HT)), metals (Pt, Ru) and promoters (Sn, Ga, Fe). Along with this, synthesis of solid base (calcined-hydrotalcite (C-HT)) was also undertaken. Catalysts were characterized using XRD, XPS, NH_3-TPD, CO_2-TPD, N_2 sorption, ICP-AES, TEM techniques.
- Detailed compositional analysis of 3 different types of agricultural wastes (bagasse, rice husk, wheat straw) was undertaken by TAPPI method.
- Reactions were carried out in batch mode autoclave and analysis of reaction mixture was done using HPLC.

Sample Results

Monometallic and bimetallic supported metal catalysts were evaluated for the conversion of C5 sugars, C6 sugars, polysaccharides and agricultural wastes. Among all the monometallic and bimetallic catalyst screened, Pt-Sn/γ-Al_2O_3 (Pt-Sn/AL) catalyst showed best activity for the production of sugar alcohols from all types of substrates.

Conversion of monosaccharides: Enhancement in the yield of sugar alcohols (more than 2 times) was achieved using 2wt%Pt-0.25wt%Sn/γ-Al_2O_3 (Pt(2)Sn(0.25)/AL) compared to the 2wt%Pt/γ-Al_2O_3 (Pt(2)/AL). Maximum 91% yield of sugar alcohols (xylitol+arabitol) was obtained from xylose over Pt(2)Sn(0.25)/AL at 130°C (2 h) and 73% at 190°C (15 min). Effect of reaction parameters such as temperature, H_2 pressure, reaction time, catalyst concentration and metal loading have been studied. Reaction conditions have been optimized to achieve maximum yield of sugar alcohols. It was observed that, with increase in the reaction temperature from 130°C to 190°C, yield of sugar alcohols decreases (from 91% to 73%). Similar results were observed in the conversion of arabinose, glucose, galactose and fructose.

Conversion of polysaccharides and agricultural wastes: Similar to the conversion of monosaccharides, over Pt(2)Sn(0.25)/AL catalyst 1.5 to 3 times more yield of sugar alcohols was obtained compared to the Pt(2)/AL in the conversion of polysaccharides and agricultural wastes. Higher temperature and longer time was required to achieve optimum yields (xylan: 190°C (sugar alcohols yield 43%), arabinogalactan: 180°C (yield 47%), inulin: 110°C (yield 77%) and agricultural wastes: 160°C (yield 72, 60 & 49% from bagasse, rice husk & wheat straw, respectively)).[10] Pt(2)Sn(0.25)/AL catalyst gave higher yield of sugar alcohols compare to Pt(2)/AL catalyst because of two reasons i) Sn cannot be reduced to (0) state and remain in (II) or (IV) on alumina support as it interacts with alumina and form surface shell. Hence it prevents sintering of the Pt particles during calcination and reduction. ii) Sn (II) or (IV) can polarize C=O bond of carbonyl group of sugar molecules, thus help for faster hydrogenation. Characterization of the spent catalyst proved that catalyst is stable at reaction conditions and showed good recyclability.[6]

Effect of solid base: After successful improvement in the yields of sugar alcohols over bimetallic catalyst, effect of solid base on the conversion of monosaccharides and polysaccharides was studied.[5, 17] When solid base i.e. calcined hydrotalcite (C-HT) was used in the combination with supported metal catalyst, exceptionally high yield of sugar alcohols was obtained at much milder reaction conditions (50°C, 6 h).

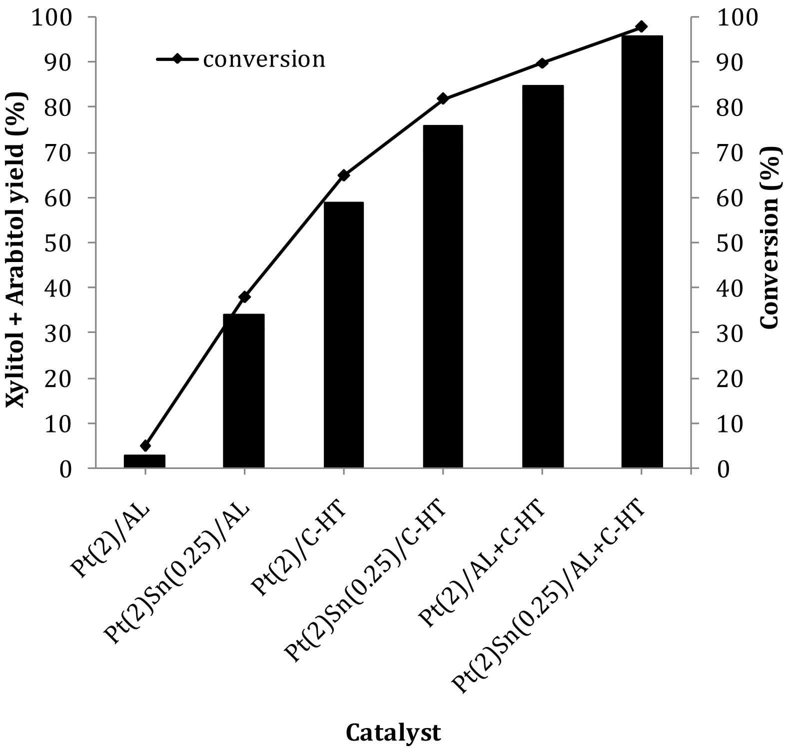


Figure 1. Effect of C-HT on the conversion of xylose over various catalysts.
Reaction conditions: xylose 0.15 g, catalyst 0.075 g, **C**-HT 0.075 g, H_2O 35 mL, 16 bar H_2, 50°C, 6 h.

Pt(2)/C-HT and Pt(2)Sn(0.25)/C-HT catalysts showed better activity than Pt(2)/AL and Pt(2)Sn(0.25)/AL catalysts but highest yield of sugar alcohols could be achieved using Pt(2)Sn(0.25)/AL+C-HT catalytic system. Results for the conversion of xylose over various catalysts are as shown in Figure 1. Similarly, in the conversion of arabinose, glucose and galactose, Pt(2)Sn(0.25)/AL+C-HT showed the best activity. Conversion of xylose, arabinose, glucose and galactose was conducted at room temperature to yield 96, 97.5, 84 and 91% of sugar alcohols, respectively.[17] After addition of C-HT, pH of reaction mixture becomes alkaline (pH=8.5-9). In alkaline medium sugar molecules tend to be in open chain form. UV-Vis study of aqueous solution of glucose at alkaline pH showed characteristic peak of C=O bond (at 268 nm) which proved that more glucose molecules are in open chain form.[5] Sugar molecules in open chain form can be hydrogenated easily. At higher temperature selectivity for sugar alcohols was less. Hence addition of C-HT along with the Pt(2)Sn(0.25)/AL did not show any improvement in the yield of sugar alcohols in the conversion of polysaccharides as these conversions are feasible only at higher temperature e.g. xylan at 190°C.

It can be concluded that over Pt(2)Sn(0.25)/AL improvement in the yields of sugar alcohols was achieved compared to Pt(2)/AL. Further enhancement in the yields at milder reaction conditions was observed using Pt(2)Sn(0.25)/AL+C-HT catalytic system in the conversion of C5 and C6 sugars.

References

1. R. Rinaldi and F. Schüth, *ChemSusChem*, 2009, **2**, 1096-1107.
2. R. Sahu and P. L. Dhepe, *ChemSusChem*, 2012, **5**, 751-761.
3. S. B. Kim and Y. Y. Lee, *Applied Biochemistry and Biotechnology*, 1988, **17**, 55-72.
4. A. Wang and T. Zhang, *Accounts of Chemical Research*, 2013, **46**, 1377-1386.
5. A. Tathod, T. Kane, E. S. Sanil and P. L. Dhepe, *Journal of Molecular Catalysis A: Chemical*, 2014, 388-389, 90-99.
6. A. P. Tathod and P. L. Dhepe, *Green Chemistry*, 2014, **16**, 4944-4954.
7. J. P. Mikkola and T. Salmi, *Catalysis Today*, 2001, **64**, 271-277.
8. R. R. Davda and J. A. Dumesic, *Chemical Communications*, 2004, 36-37.
9. J. Sun and H. Liu, *Green Chemistry*, 2011, **13**, 135-142.
10. A. P. Tathod and P. L. Dhepe, *Bioresource Technology*, 2014, **178**, 36-44.
11. G. Yi and Y. Zhang, *ChemSusChem*, 2012, **5**, 1383-1387.
12. L. Canilha, W. Carvalho, M. d. G. a. A. Felipe and J. o. B. d. A. e. Silva, *Brazilian Journal of Microbiology*, 2008, **39**, 333-336.
13. B. Kusserow, S. Schimpf and P. Claus, *Advanced Synthesis & Catalysis*, 2003, **345**, 289-299.
14. B. T. Kusema, L. Faba, N. Kumar, P. i. Mäki-Arvela, E. DÃaz, S. Ordóñez, T. Salmi and D. Y. Murzin, *Catalysis Today*, 2012, **196**, 26-33.
15. L. Faba, B. T. Kusema, E. V. Murzina, A. Tokarev, N. Kumar, A. Smeds, E. DÃaz, S. Ordóñez, P. i. Mäki-Arvela, S. Willför, T. Salmi and D. Y. Murzin, *Microporous and Mesoporous Materials*, 2014, **189**, 189-199.
16. P. Gallezot, N. Nicolaus, G. Fleche, P. Fuertes and A. Perrard, *Journal of Catalysis*, 1998, **180**, 51-55.
17. A. P. Tathod and P. L. Dhepe. manuscript communicated **2014**.

Chapter 1

General introduction and literature survey

1.1. Introduction

1.1.1. Biomass

Living organisms are being evolved since their origin on the earth. These living organisms are potential resource of energy and often called as biomass. Biomass is the biological material derived from living organism. More specifically it can be defined as "the total mass of living or dead organisms in given area".[1] Chemically biomass is the carbon based material and consists of various organic compounds. These organic compounds contain hydrogen, oxygen and nitrogen in addition to carbon. Alkali metals, alkaline earth metals and some heavy metals are very often found in biomass as a part of important biological molecules. Plants can synthesize carbohydrates from CO_2 and H_2O in the presence of sunlight by the process of photosynthesis. Synthesized carbohydrates are stored in the plant body and further eaten by animals. If plant is not eaten by animal, it undergoes microbial decomposition and such decomposition releases carbon back to the atmosphere. If plant is eaten by animal, after death of animal its body is decomposed by microorganisms which again return carbon to the atmosphere. This is called as carbon cycle in which plants are the primary source of energy.

Scientific world is looking towards biomass as a renewable resource for the synthesis of chemicals and fuels. Since last few decades biomass has attracted the attention of researchers. Various studies to ascertain the chemical composition, physicochemical properties and applications of biomass and biomass derived compounds in different fields are ongoing.

1.1.2. Classification and composition of biomass

Depending upon the origin, biomass can be classified into two main categories i.e. animal derived and plant derived. Animal derived biomass includes animal residues and various products obtained from them. Chitin is the most abundant animal derived biomass and second most abundant amongst animal and plant derived biomass. Plant derived biomass consists of plant residues and its products which can further be classified as edible and non edible biomass. Non edible plant derived biomass commonly termed as lignocellulosic biomass which consists of cellulose, hemicellulose and lignin as main components. These components are bound to each other by various covalent and non covalent linkages.[2] Based on the above discussion classification of biomass can be done as represented in Figure 1.1.

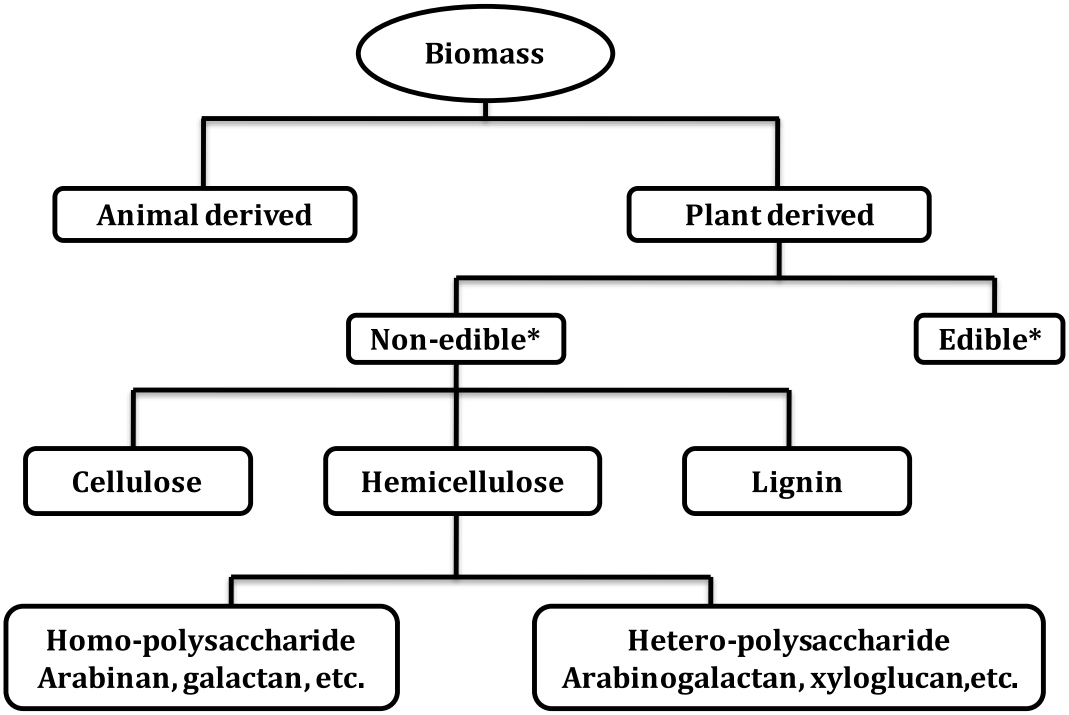


Figure 1.1. Classification of biomass.

*edible/non edible for humans

Cellulose is the most abundant polysaccharide and comprises ca. 50% of lignocellulosic biomass. Cellulose is the homo-polysaccharide of linearly arranged D-glucose monosaccharide units linked together by β-(1→4) glycosidic linkages (Figure 1.2).[3] Cellulose is crystalline in nature due to the presence of intra-molecular and inter-molecular hydrogen bonds.[4, 5] These β-(1→4) glycosidic linkages in cellulose make it indigestible to humans, rather cellulose cannot be digested by any vertebrate directly. Symbiotic bacteria in the digestive track of the herbaceous animals possess the enzyme to digest the cellulose. Although cellulose is non edible to humans, it finds many application in our day to day life e.g. in paper and garment industry.

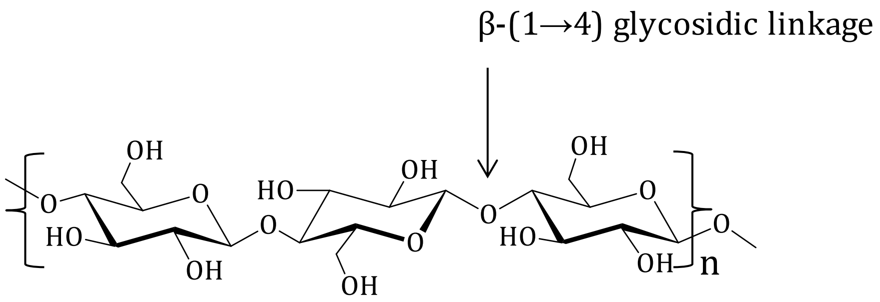


Figure 1.2. Structure of cellulose.

Hemicelluloses are the second most abundant plant derived polysaccharides and comprise ca. 30% of lignocellulosic biomass. Unlike cellulose, hemicelluloses can be hetero-polysaccharide or homo-polysaccharide made-up of various C5 and C6 sugars depending upon the plant in which it occurs. According to the composition, hemicelluloses are named as xylan (polysaccharide of xylose), arabinan (arabinose), glucomannan (glucose and mannose), arabinogalactan (arabinose and galactose), etc. Xylan present in oat spelt, beech wood, etc. contains some amount of other monosaccharide like arabinose and glucuronic acid. Oat spelt xylan (more precisely arabinoglucuronoxylan) has linear chain of β-(1→4) linked xylose with α-(1→2) bonded 4-O-methyl-D-glucuronic acid unit and α-(1→3) bonded L-arabinose unit (Figure 1.3).[4] Pure xylan (homopolymer of xylose) occurs only in oceanic algae. Generally hardwood hemicellulose is mainly composed of xylan while softwood hemicellulose contains glucomannan as major component.[6, 7]

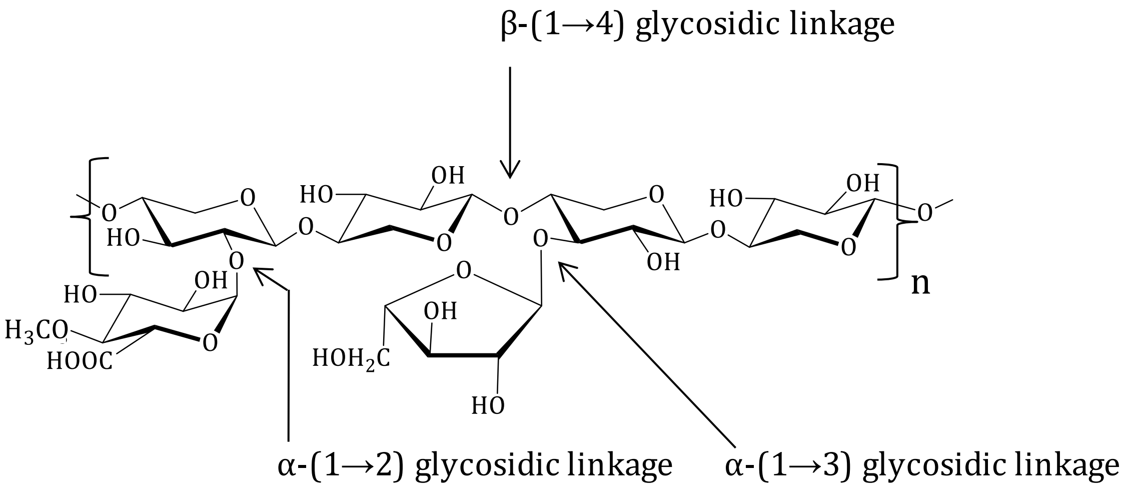
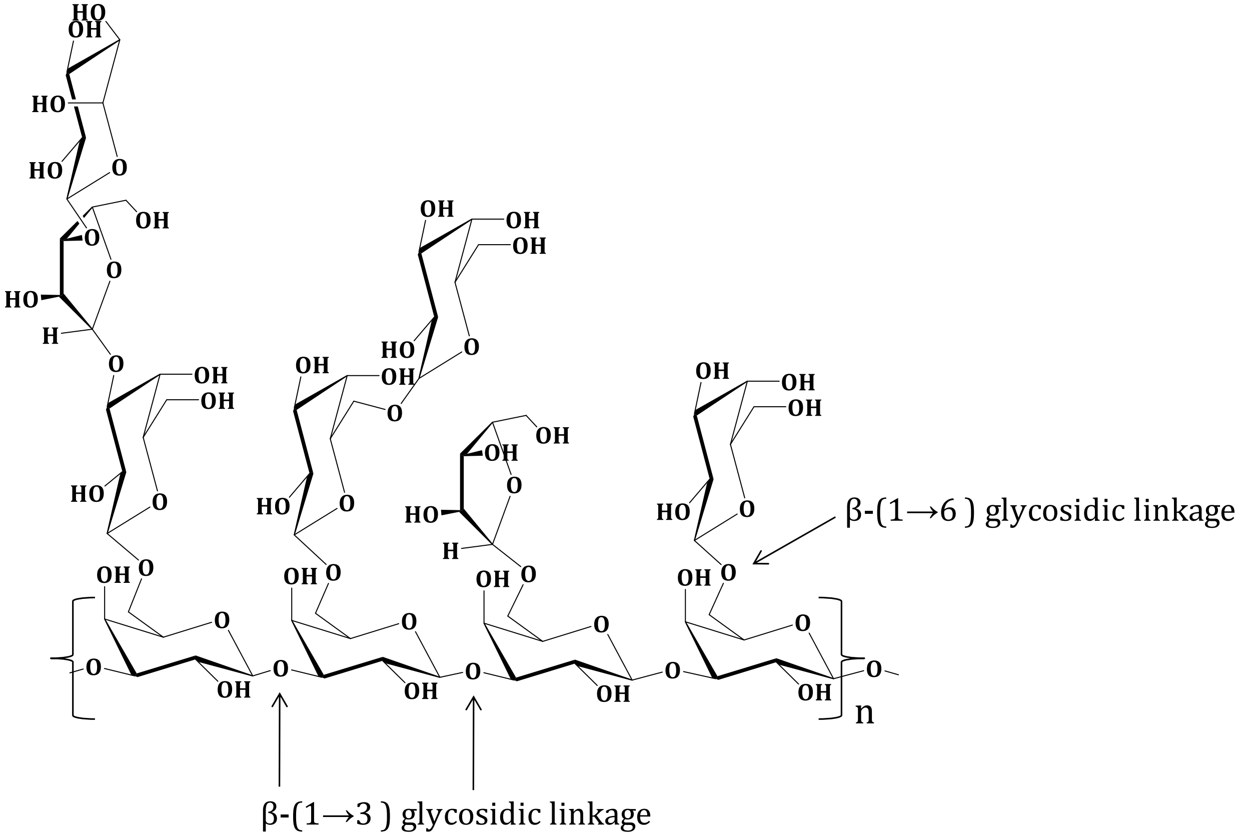


Figure 1.3. Structure of oat spelt xylan.

Arabinogalactan is yet another type of hemicellulose mainly made up of arabinose and galactose. Larch wood arabinogalactan has a chain of β-(1→3) linked D-galactose with the branches made up of β-(1→6) linked D-galactose units and L-arabinose units (some D-glucuronic acid units may present) (Figure 1.4). Unlike most of the other hemicelluloses, larch wood arabinogalactan is water soluble.[7, 8]



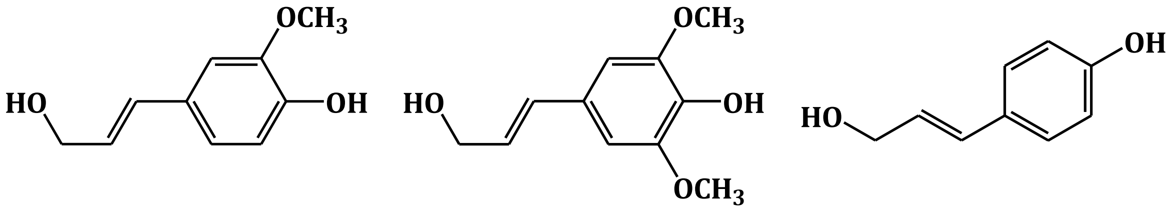
β-(1→6) glycosidic linkage

β-(1→3) glycosidic linkage

Figure 1.4. Structure of larch wood arabinogalactan.

Lignin is a complex branched polymer of aromatic compounds comprising ca. 20% of lignocellulosic biomass.[7] Lignin conversion has significant potential for the production of fuels and chemicals as is discussed several times in the literature.[9-12] Some of the common building blocks of lignin are coniferyl alcohol, sinapyl alcohol and coumaryl alcohol (structures are shown in Figure. 1.5). The exact structure of lignin is not very clear since it depends on various factors such as type of plant, location of plant and age of plant.

Moreover, studies have concluded that lignin may undergo some structural changes during its isolation, so the structure and functional groups present in lignin are significantly governed by the method of isolation.[13, 14] Composition and amount of lignin in plants varies from species to species and even in woods from different parts of the same plant. Softwoods are known to contain higher amount of lignin, followed by hardwoods and grasses contains least amount of lignin.[13]



Coniferyl alcohol Sinapyl alcohol Coumaryl alcohol

Figure 1.5. Structures of primary building blocks of lignin.

Inulin is a polymer mainly made up of fructose units linked together via β-(2→1) fructosyl-fructose linkages. Glucose unit may be present at the starting of the chain but not essentially. Inulin is present in the vegetables and fruits like onion, garlic, chicory, wheat, banana, etc. as a storage carbohydrate. Chicory root consists of abundant amount of inulin and is a major feedstock used for the industrial production of inulin. In chicory inulin, number of fructose units linked to a terminal glucose unit, varies from 2-70. Inulin from plants has low DP (200 maximum) which varies with the plant species and weather conditions. Inulin which is extracted from the roots of plant, consists of fructose as a major component and sucrose, glucose and oligosaccharides in small amount. On the other hand, bacterial inulin has high DP (10,000-100000) and is highly branched.[15] As mentioned above there are two types of inulin polymers, with and without terminal glucose unit. Inulins with a terminal glucose unit are called as α-D-glucopyranosyl-[β-D-fructofuranosyl]$_{n-1}$D-fructofuranoside, while those only constitutes fructose are called as β-D-fructopyranosyl-[α-D-fructofuranosyl]$_{n-2}$-D-fructofuranoside.[16] Structure of the inulin with terminal glucose unit is represented in Figure 1.6. As mentioned earlier, inulin is present in the vegetables and fruits which are the part of daily diet and hence its conversion in to chemicals has to compromise with food. Nevertheless, real substrates which are not suitable for human consumption, like rotten wheat and low quality garlic can be used efficiently as a feedstock for the production of fructose and its derivatives.

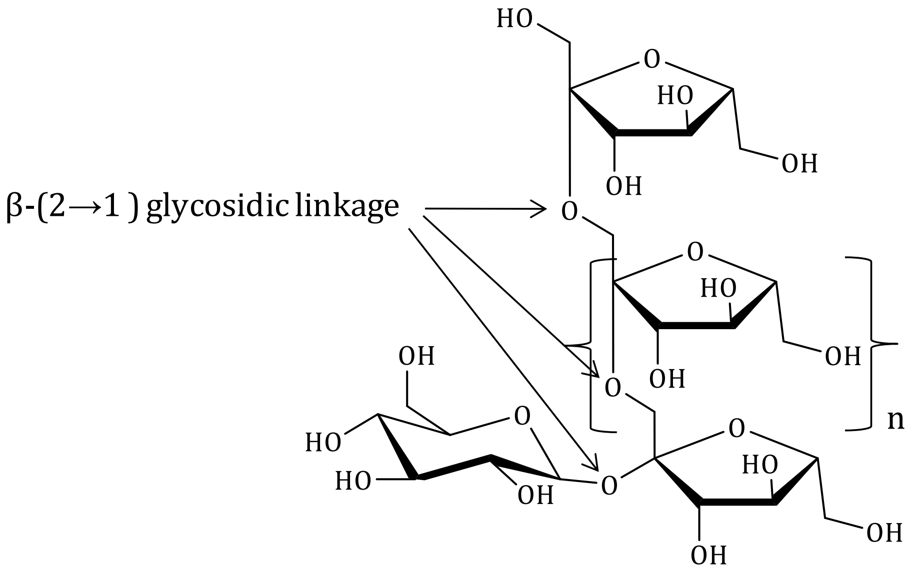


Figure 1.6. Structure of inulin.

1.1.3. Concept of biorefinery

Biorefinery integrates biomass conversion processes to produce fuels and value added chemicals while petrorefinery produces fuels and chemicals from fossil feedstock. Petrorefinery depends on fossil feedstock which is non-renewable and unevenly distributed throughout the world, whereas in biorefinery, renewable feedstock i.e. biomass is used. Hence, concept of biorefinery is the step towards sustainable system for the production of fuels and chemicals. “Sustainable development is the development that meets the needs of present without compromising the ability of future to meet their own needs”.[17] Biorefinery deals with the optimum utilization of organic waste which may resolve waste management issue up to some extent. Biorefinery concept is still in the early stage of development and scientific community around the globe is taking efforts for its progress. Though the biorefinery concept is interesting still there are few factors such as raw material availability and its supply, technology exploitable at commercial level and cost of production which need to be addressed for its success.

1.1.4. Biomass as the potential source of chemicals

As discussed above, biomass has a great potential to replace fossil feedstock for the synthesis of fuels and chemicals. Useful chemicals and materials can be obtained from biomass through various conversion processes which can be chemical, thermo-chemical, bio-chemical or physical. Lignocellulosic biomass in the form of agricultural wastes, forest wastes, municipal wastes or agro-based industry wastes can be used as a feedstock in biorefinery for the production of value added chemicals. Figure 1.7 represents various types of processes for the conversion of aforementioned wastes in to a variety of products like chemicals, fuels, materials and energy.

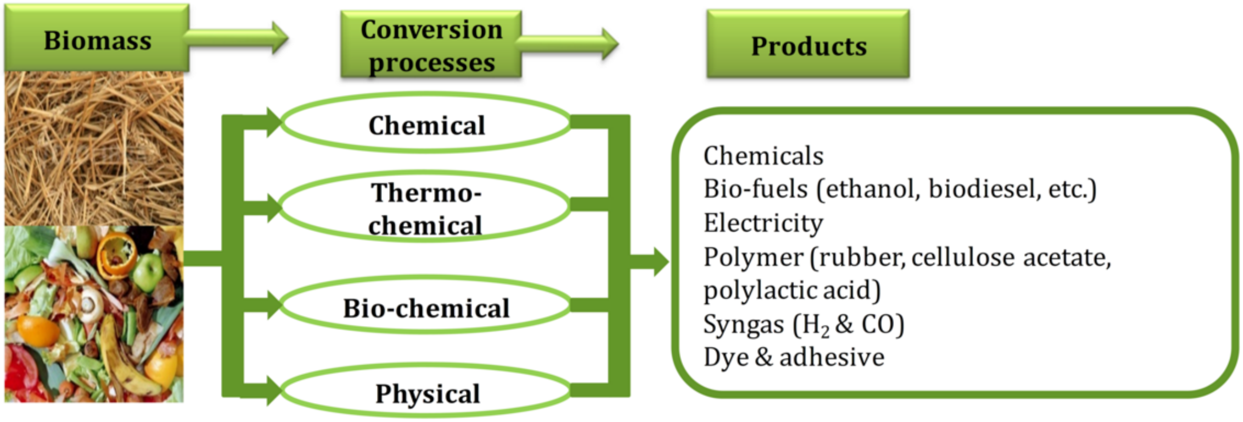


Figure 1.7. Biomass conversion methods.

Before going into the details about chemicals obtained from the lignocellulosic biomass through various types of conversion processes, it is necessary to be acquainted with these processes. Conversion processes represented in Figure 1.7 are explained very briefly in next few paragraphs.

Chemical processes: These processes involve chemical conversion of biomass or biomass derived feedstock in to various products. Conversion of lignocelluloses i.e. cellulose, hemicellulose and lignin in to various value added chemicals is well studied. Although edible feedstock like starch can be used in biorefinery, this discussion is restricted to the conversion lignocellulosic biomass which is non-edible for human being. Homogeneous catalyst like mineral acid (HCl, H_2SO_4)[18-20] and heterogeneous catalyst like solid acids (metal oxides, amberlyst, sulphonated carbon, heteropolyacids, zeolites),[21-23] supported metal catalysts (Pt/γ-Al_2O_3, Ru/AC)[24] are often used for the conversion of lignocellulosic biomass in to sugars, furans, sugar acids, sugar alcohols, glycols, etc.[25-32]

Thermo-chemical processes: These are the processes which not necessarily produce energy but converts biomass in to chemical compounds which can be used for the production of energy more conveniently. Such compounds are more energy dense and have more predictable combustion properties relative to the untreated biomass. For an instance bio-oil, the liquid fuel obtained by subjecting biomass to pyrolysis has higher calorific value (ca. 10,000Kcal/Kg) compared to wood (ca. 3000Kcal/Kg).[33] Under pyrolysis condition, biomass is subjected to high temperatures (350-500°C) in the absence of any oxidant for short period of time to yield pyrolysis oil, generally called as bio-oil. Along with this oil, formation of char and tar is also observed. Syngas can be obtained from biomass by subjecting it to the gasification condition i.e. to high temperature (700-900°C) under controlled oxygen supply. In this process, biomass is partially combusted to form producer gas and some amount of charcoal. CO_2 and H_2O produced in the partial combustion are further reduced to form CO and H_2. Composition of the gaseous product formed in gasification is ca. 20% H_2, ca. 20% CO, ca. 3% CH_4 and ca. 10% CO_2 (rest is nitrogen).

Bio-chemical processes: These processes involve use of micro-organism for the conversion of biomass in to various products. Anaerobic fermentation of biomass (animal manure and crop waste) for the production of methane rich biogas is one of the oldest known bio-chemical processes. Culture of methanogenic bacteria converts biomass in to biogas (containing ca. 55% of methane) under anaerobic condition. Enzymatic hydrolysis of polysaccharides like cellulose and hemicellulose to yield constituting monomer sugars and fermentation of sugars for the production of ethanol is reported several times in the literature.[34-36]

Physical process: Extraction is the simple method to obtain valuable vegetable oil or seed oil from the biomass. For example vegetable oil from the plant like Jatropha (*Jatropha curcas*), Soapnut (*Sapindus mukorossi*) are considered as excellent feedstock for the production of bio-diesel. Oils extracted from the plant can be converted in to fuel (bio-diesel) after undergoing base catalyzed trans-esterification reaction.[37] Other than vegetable oils, plants are the source for rubber (rubber tree, *Hevea brasiliensis*), adhesives, dyes (*Indigofera* plant, *Pomegranate* peels), etc.

As mentioned earlier, lignocellulosic material is made up of three main components, cellulose, hemicellulose and lignin, out of which cellulose and hemicelluloses are polysaccharides made up of several monomer sugars (monosaccharides) linked together. Cellulose and hemicelluloses undergo hydrolysis reaction to yield monomer sugars (C6 and C5 sugars) which can further be converted in to various chemicals depending upon the catalyst used and reaction conditions applied. Similarly many chemical compounds can be obtained from lignin which is made up of various types of aromatic monomers. Amongst several biomass derived chemicals, some are recognized as 'Top value added chemicals from biomass' by U.S. Department of Energy (in the report 'Top Value Added Chemicals From Biomass, Vol. 1: Results of Screening for Potential Candidates from Sugars and Synthesis Gas, 2004').

Top value added chemicals from biomass

C3- glycerol, 3-hydroxypropionic acid

C4- succinic acid, fumaric acid, malic acid, aspartic acid, 3-hydroxybutyrolactone

C5- glutamic acid, itaconic acid, levulinic acid, xylitol

C6- 2,5-furan dicorboxylic acid, glucaric acid, sorbitol

Since cellulose is made up of several glucose units linked together, upon hydrolysis it yields glucose. Unlike to cellulose hemicelluloses are made up of various C5 sugars (xylose, arabinose) and C6 sugars (glucose, galactose, mannose), hence upon hydrolysis it gives different types of sugars according to its composition. Homogeneous mineral acids as well as heterogeneous solid acids can be used for the hydrolysis of polysaccharides. Sugars thus obtained, undergoes various reactions to form many useful chemicals. Sugars upon dehydration yields furans i.e. 5-hydroxymethylfurfural from glucose and furfural from xylose while upon hydrogenation C5 and C6 sugar alcohols can be obtained from respective sugars. Furans can further be converted in to levulinic acid, lactic acid, furan dicarboxylic acid, furfuryl alcohols, etc. Other than this, useful chemicals like glycols (ethylene glycol, 1,2-propanediol, glycerol) can also be obtained either from sugars or from sugar alcohols.

Some of the sugar derivatives are used as fuel additive, e.g. ethyl levulinate, γ-valarolactum, methyltetrahydrofuran, etc. while others are important platform chemicals. Figure 1.8 represents the formation of some important chemicals from cellulose and hemicellulose via sugar formation.

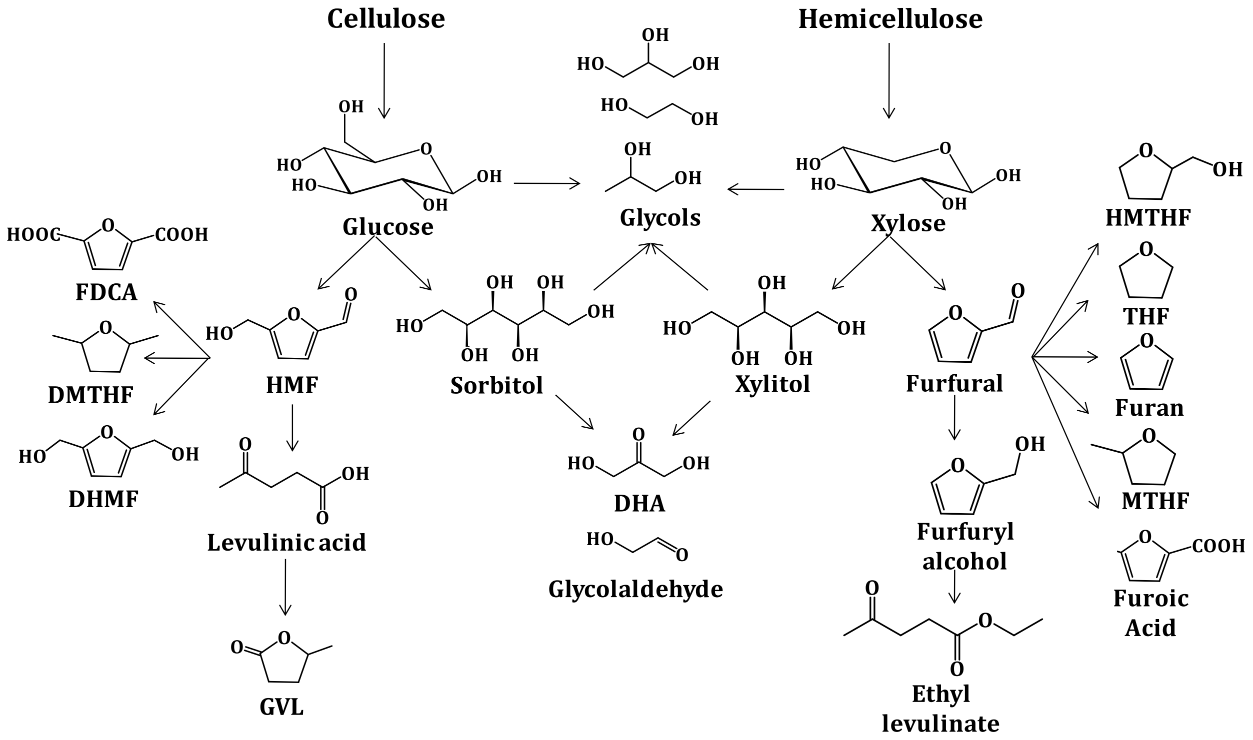


Figure 1.8. Production of chemicals from cellulose and hemicellulose.

(FDCA: furandicarboxylic acid; DMTHF: dimethyltetrahydrofuran; DHMF: dihydroxymethylfuran; HMF: hydroxymethylfurfural; GLV: γ-valarolactum; DHA: dihydroxyacetone; HMTHF: hydroxymethyltetrahydrofuran; THF: tetrahydrofuran; MTHF: methyltetrahydrofuran).

1.2. Sugar alcohols

Sugar alcohols are the hydrogenation products of sugars. Sugars are of two types; aldoses (having aldehyde as a functional group) and ketoses (having ketone as a functional group). In the presence of active metal and H_2, aldehyde or ketone group in sugar molecule is hydrogenated to form sugar alcohol. Sugar alcohols are the organic compounds with multiple hydroxyl groups and are also often called as polyols, polyhydric alcohols or polyalcohols. Sugar alcohols have the general formula $HOCH_2(CHOH)_nCH_2OH$ with two hydrogen extra than corresponding sugar (general formula of sugars is $HOCH_2(CHOH)_nCHO$

(aldoses) or $HOCH_2(CHOH)_{n-1}C(O)CH_2OH$ (ketoses)). Sugar alcohols are classified according to the length of carbon chain, e.g. tretriol (C4), pentitol (C5), hexitol (C6), etc. Most of the sugar alcohols have their names derived from the name of respective sugars. Xylitol is the sugar alcohol named according to the sugar from which it is derived i.e. xylose. But some sugar alcohols are named differently like sorbitol which is hydrogenation product of glucose. Sugar alcohols have one -OH group attached to each C atom in the chain. The orientation of these -OH groups differentiate one sugar alcohol from other with similar molecular formula. For example xylitol and arabitol or sorbitol and mannitol are the epimers of each other and do have same molecular formula but different orientation of one -OH group (Figure 1.9).

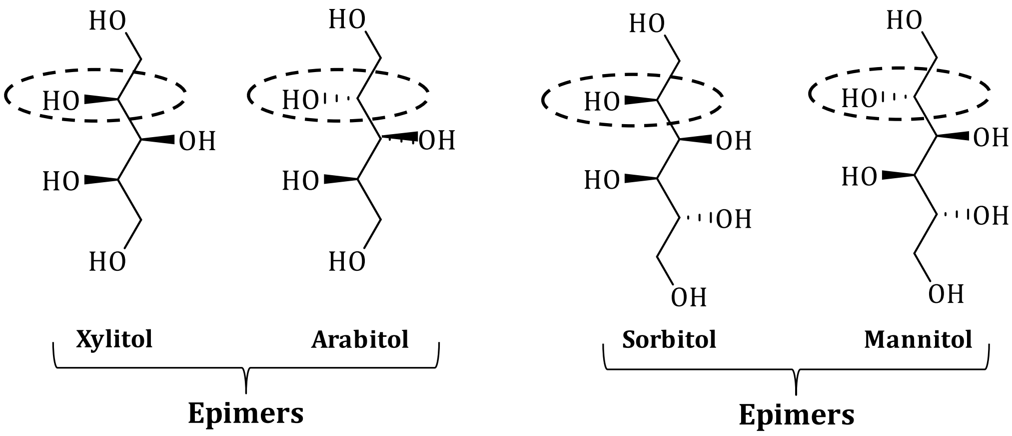


Figure 1.9. Structures of sugar alcohols.

Sugar alcohols occur naturally in some fruits and berries or can be synthesized from sugars. Sugar alcohols like sorbitol, mannitol and xylitol have some general physicochemical properties as mentioned below.

Properties of sugar alcohols

- Sweet in taste
- High solubility in water
- High thermal stability
- High chemical stability
- Stable at wide range of pH

- Excellent moisture stabilizing effect
- Preserving effect
- High microbial stability
- Excellent compressibility

Because of the aforementioned properties, sugar alcohols find applications in various fields such as pharmaceutical industry, cosmetics and food. DOE (department of energy, U.S.) includes sorbitol and xylitol in the list of 'top value added chemicals from biomass' which itself reflects their importance in the day to day life.

1.2.1. Importance of sugar alcohols

Sugar alcohols find many applications in daily life because of their above discussed characteristic properties. Although, most accredited use of sugar alcohols is as a low calorie sweetener. Other than this, its importance is well recognized in food industry, pharmaceutical industry, cosmetics and for the production of chemicals. Sorbitol is a C6 sugar alcohol obtained by hydrogenation of glucose which is extensively used for the production of oral hygiene products such as mouth freshener, chewing gums, toothpaste, etc. as well as it is used in humectants. It is used as a precursor for the synthesis of ascorbic acid and out of total sorbitol produced in the world ca. 15% is consumed for ascorbic acid synthesis.[38] Lactic acid can be produced from sorbitol under alkaline hydrothermal condition.[39] It is possible to obtained C3 and C4 polyols from sorbitol by the process of hydrogenolysis..[40] A dehydration product of sorbitol, isosorbide has many applications in the field of medicine, cosmetic and in the synthesis of polymer materials.[41-43] Recently, use of sorbitol for the production of hydrogen is also explored.[44, 45] Use of mannitol, (epimer of sorbitol) in medical field is well renowned for its osmotic diuretic properties, as laxative, in the treatment of cerebral oedema and oliguric renal failure.[46] C5 sugar alcohol, xylitol is well known for its utility as a low calorie sweetener, in cosmetics as well as in pharmaceutical industry.[47, 48] Xylitol is used as an ingredient in the preparation of chewing gums, mouth wash and toothpaste very often because of its property to prevent dental decay. [49-51] Chewing of xylitol containing gum is proved to minimize dental caries and its regular use can prevent acute otitis media in childrens.[52] [53] Because of its low calorie content (for xylitol 2.4 cal/g while for sucrose 4.0 cal/g) and insulin independent metabolism, xylitol can be used as a substitute for sugars by diabetics.[54-56] Because of remineralization properties and anticarcinogenicity, xylitol is important in odontological industries.[57] Applications of sugar alcohols in various fields are summarized in Table 1.1.

Table 1.1. Applications of sugar alcohols.

Sr. No.	Sugar alcohol	Applications
1	Sorbitol	Low calorie sweetener, oral hygiene products, humectants, for the production of chemicals and hydrogen.
2	Mannitol	Low calorie sweetener, in the treatment of celebral oedema and oliguric renal failure, as a laxative
3	Xylitol	Low calorie sweetener, having non-diabetes and anti-caries properties, in cosmetics and pharmaceutical industry.
4	Arabitol	Food and pharmaceutical industry

1.2.2. Methods for the conversion of biomass in to sugar alcohols

Worldwide production of xylitol is ca. 2.4 x 10^4 TPA (tons per annum)[58] and of sorbitol is 6.5 x 10^5 TPA.[59] Demand for sugar alcohols is continuously increasing because of its aforementioned applications in various fields.[60, 61] To fulfill the increasing demand, researchers are taking efforts to develop efficient catalytic methods for the synthesis of sugar alcohols. Some reports for the synthesis of sugar alcohols from mono- and polysaccharides are discussed below.

1.2.2.1. Conversion of monosaccharides

Generally sugar alcohols are synthesized either from monosaccharides (by hydrogenation) or from polysaccharides (by hydrolytic hydrogenation). There are two types of catalysts used for the production of sugar alcohols from monosaccharides or polysaccharides (cellulose, hemicellulose, inulin, etc.) viz. i) Homogeneous catalysts and ii) Heterogeneous catalysts. Homogeneous catalysts are the catalysts which operate in the same phase where the reaction occurs. Very often these catalysts are co-dissolved in solvent along with reactant. Homogeneous catalysts like enzymes (microbial conversion or bio-conversion) are known for the conversion of sugars in to sugar alcohols since many years. Conversion of xylose to xylitol by *Saccharomyces cerevisiae* or *Candida* is reported in the literature.[58] Application of micro-organisms like *Corynebacterium, Enterobacter liquefaciens, Mycobacterium smegmatis, Petromyces albertensis, Candida* guilliermondii, *Candida tropical*, *Saccharomyces cerevisiae* and many more are known for the conversion of xylose to xylitol.[57, 62-67] Similarly, conversion of glucose to sorbitol using *Zymmonas mobilis*, fructose to mannitol by *Candida magnolia*,[68] arabinose to arabitol using *Candida entomaea* and *Pichia guilliermondii* are reported.[69, 70] Homogeneous catalysts have advantage of good contact with reactant and hence good activity. But it has some obvious drawbacks e.g. difficult separation from product solution and difficulty in reuse. Moreover some methods involve use of mineral acid, hence needs post reaction neutralization.

Heterogeneous catalysts have overcome the drawbacks of homogeneous catalysts and have attracted the attention of researchers. Conversion of monosaccharides (C5 and C6 sugars) over heterogeneous catalysts like supported metal catalysts is well known. Raney nickel is used for the production of sugar alcohols (xylitol and sorbitol) on industrial scale.[47, 48, 71-73] Deactivation of the catalyst because of leaching of nickel and thus high content of nickel in the sugar alcohol solution are the major drawbacks of the methods.[74, 75] Therefore purification of sugar alcohol is needed to make it nickel free and suitable for the use in food and pharmaceutical industry.[75] Conversion of glucose to sorbitol over Ni/SiO_2, shows negligible leaching but low activity was observed (maximum 45% glucose conversion with 82% selectivity for sorbitol, at 120°C, 5 h).[76] Fructose conversion over Ni based catalyst gives 50% yield of mannitol and sorbitol.[77] Noble metal (Pt, Ru, Rh, Pd) based catalysts were used for the hydrogenation of xylose and glucose to achieve better yield and selectivity for sugar alcohols.[78-81] Although Ru catalyst showed better activity than Ni catalyst, it undergoes deactivation by poisoning of Ru surface by impurities and sintering of metal particles.[82] Effect of support material (MgO, Al_2O_3, SiO_2, Carbon, TiO_2) on the catalytic activity of Ru based catalyst in the conversion of lactose was undertaken. 5wt%Ru/Carbon showed highest activity with 96-98% yield of lactitol, however high metal loading (5wt%Ru), high H_2 pressure (50 bar) and catalyst deactivation due to metal leaching are the issues to be resolved.[83] Yet another report on the glucose hydrogenation over Pt supported on the activated carbon cloth reveals that high yield of sorbitol (99%)

can be achieved. Although this catalyst has some advantages over typical activated carbon catalyst, like high rate of mass transfer and good recyclability, it requires high H_2 pressure (80 bar) and very high metal loading (10wt%Pt) to carry out the conversion.[84] Conversion of xylose to yield 99% yield of xylitol was reported over 1wt%Ru-5wt%NiO/TiO_2 and catalyst is observed to be stable at reaction conditions (120°C, 2 h, H_2 pressure 55 bar).[60] Although few of the above mentioned catalysts give good yield of sugar alcohols from sugars, activities of these catalysts need to be ascertained for the direct conversion of polysaccharides or agricultural waste in to sugar alcohols.

1.2.2.2. Conversion of polysaccharides

Sugar alcohols can be obtained from polysaccharides by hydrolytic hydrogenation in one pot method. Conversion of polysaccharides (cellulose, hemicellulose, inulin) in to sugar alcohols comprises two steps in cascade manner, i.e. hydrolysis of polysaccharides to obtain monosaccharides and subsequent hydrogenation of monosaccharides in to sugar alcohols. Thus catalyst should have bi-functional nature (should have active sites for hydrolysis and hydrogenation both). Multistep reaction in single pot has advantages like, reduction in the number of steps to obtain final product and reduction in the operating time. Sorbitol production from cellulose over various homogeneous and heterogeneous catalysts is well known.[15, 24, 31, 85-90] However, relatively less number of reports are available for the conversion of hemicelluloses and inulin in to sugar alcohols. Few reports are available in the literature for the production of xylitol from hemicellulose using mineral acids and enzymes as catalyst. Enzymatic conversion of hemicellulose (xylan) using *Candida guilliermondii, Candida athensensis* SB18, *Candida guilliermondii, E. Coli* strain is reported. [91-95] Recently, exploitation of supported metal catalyst (Ru/C) with the combination of mineral acid (H_2SO_4) for the production of xylitol (83% yield) from hemicellulose (xylan) has been reported.[96] Even so, due to homogeneous system, reutilization of these catalysts becomes complicated. To overcome these problems, conversion of hemicellulose in to corresponding sugar alcohols over supported metal catalysts is evaluated without using any mineral acid. Arabinan from beet fibers has been converted to yield arabitol over Ru/AC.[97] Similarly arabinogalactan was converted in to arabitol and galactitol over Ru/MCM-48.[98] But the low yield of sugar alcohols and poor recyclability were the limitations of these catalytic systems. Metal modified beta zeolites can catalyze hydrolytic hydrogenation of hemicellulose, but yield obtained was very low (ca.15% of sugar alcohols).[99] As mentioned above, hydrolysis of hemicellulose (xylan) to xylose by solid acid catalysts is extensively studied [25, 26, 28-30, 100] and use of supported metal catalysts in the xylose hydrogenation reaction is well documented.[60, 61, 72, 74, 101] Nevertheless, an efficient one pot method for the production of sugar alcohols directly from hemicellulose with superior yields needs to be developed.

Inulin is mainly made up of fructose and upon hydrolytic hydrogenation gives mannitol and some amount of sorbitol. Not many reports are available for direct conversion of inulin to mannitol over heterogeneous catalyst. Hydrolysis of inulin to yield fructose over acidic zeolite LZ-M-48[102] and conversion of inulin to mannitol over Ru supported on the acidic carbon (acidity was introduced with ammonium per-oxydisulfate) is known to yield 37-40% yield of mannitol.[103] Agricultural waste like wheat straw and bagasse have been used as a substrate for the production of sugar alcohols, but microbe or/and mineral acids were used as catalyst.[93, 95] Application of solid acid catalysts for the conversion of hemicellulose and agricultural waste to C5 sugars and furfural is known.[26, 27, 104] Despite that, reports on the direct one pot conversion of untreated agricultural wastes or raw biomass using heterogeneous catalyst are scanty. With regards to all above reports on the conversion of monosaccharides, polysaccharides and agricultural wastes in to sugar alcohols, the heterogeneous catalyst having good activity and recyclability needs to be developed to overcome the drawbacks associated with known methods.

1.3. Solid acid

Role of acid in the field of catalysis is well known to scientific society since long time. Importance of the heterogeneous catalyst to develop green methods has been recognized by researchers in last few decades. There are many natural and synthetic solid acids know to catalyze several acid catalyzed reactions.[105, 106] These heterogeneous solid acid catalysts shows two types of acidity i.e. Brønsted and/or Lewis acidity. Type of acidity, amount and strength of acid site and morphological properties like surface area, porosity varies from material to material.[107] Clays have acidic properties and potential to be used as a solid acid catalyst. Montmorillonite-KSF, K-10 and bentonite are some of the clays known for their catalytic properties.[107] Another extensively studied, well known class of solid acid is zeolite. Zeolites are the alumino-silicates having tetrahedral structure of Si and Al surrounded by oxygen atoms. Though the naturally occurring zeolites are microporous, pore size can be controlled in synthetic zeolites. Tetravalent Si bonded with four oxygen atoms is neutral while trivalent Al bonded with four oxygen atoms is negatively charged, hence associated with positively charge counter ions (Na^+). Replacement of these counter ions with protons gives acidity to the zeolites. Typical structure of the zeolite after replacement of counter ions with protons is shown in Figure 1.10.[108]

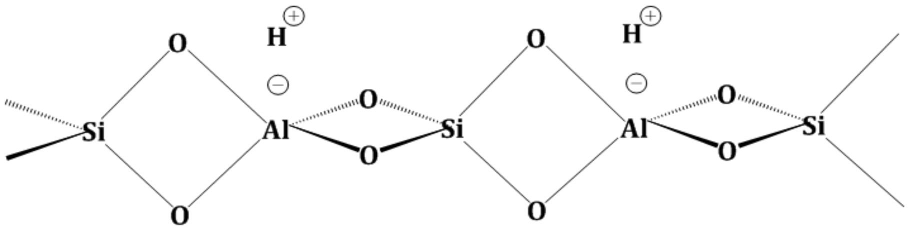


Figure 1.10. Structure of zeolite.

Metal oxides like silica, alumina, titania, zirconia, etc. and acidified materials like sulphonated silica and carbon in which acidity is introduced by sulphonation reaction, ion exchange resins, etc. shows acidic property and have potential to be used as acidic catalyst.[109, 110] Mesoporous material like MCM-41, SBA-15, etc. are of common choice for many acid catalyzed reactions.[111, 112] Alumina is often used as a solid acid catalyst or as a support material to prepare supported metal catalysts owing to its thermal stability. Among all forms of alumina, γ-alumina (γ-Al_2O_3) has wide applications in the field of catalysis.[113, 114] Different forms of alumina can be obtained by subjecting boehmite (γ-AlO(OH)) to thermal treatment at various temperatures.[115-117] Acidic character of γ-alumina is mainly determined by its surface composition. It shows cubic defect spinel type structure in which Al atoms occupy octahedral and tetrahedral sites while non-spinel sites can be occupied by cations.[118, 119] Moreover, γ-Al_2O_3 shows interesting interaction with water. Lewis acid sites are associated with the Al atom and basic sites are associated with oxide anions at the surface which interact with H_2O to form –OH group.[120-122] This interaction involves the adsorption of H_2O on the Lewis acid site and subsequent transfer of electron density to the Lewis acid site. After this dissociative adsorption of H_2O to modify surface Al coordination with –OH group takes place.[118] γ-Al_2O_3 upon rehydration loses tetrahedrally coordinated Al from surface and creates hydroxylated octrahedrally coordinated Al. Interaction of the γ-Al_2O_3 with water which results in the formation of hydroxylate Al can be represented as Figure 1.11.

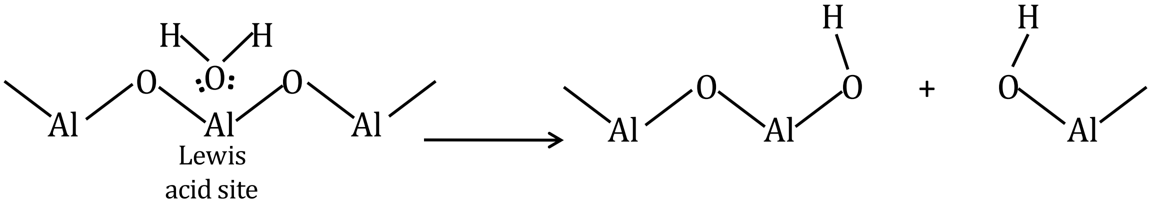


Figure 1.11. Interaction of alumina with water.[118]

In supported metal catalysts, γ-Al_2O_3 is used as support material and may show various interactions with metal precursor depending upon the nature of precursor (support-metal interaction is briefly discussed in section 1.5). Density of adsorption sites on the surface is low and hence high dispersion can be achieved but higher metal loading is restricted. Because of these characteristic features γ-Al_2O_3 is widely used in the preparation of supported metal catalysts. Other than the above mentioned catalysts there are many more solid acids which could find applications in the field of catalysis. Some of the commonly used solid acids are listed category wise in the Table 1.2.

Table 1.2. Examples of solid acids.

Sr. No.	Type	Example
1	Metal oxides	SiO_2, Al_2O_3, ZrO_2
2	Mixed metal oxides	SiO_2-Al_2O_3, WO_3-ZrO_2, Al_2O_3-TiO_2-ZnO
3	Zeolites	H-USY, H-BEA, H-ZSM-5, H-MOR.
4	Heteropoly acids	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, CsHPW, $H_3PW_{12}O_{40}.6H_2O$
5	Ion exchange resins	Amberlist-15, Nafion-NR50
6	Mesoporous materials	MCM-41, SAB-15,

7	Sulphonated catalysts	Sulfonated-carbon, Sulfonated-ZrO_2, Sulfonated-Silica, Sulfonated-MCM-41
8	Clays	Montmorillonite-KSF, Montmorillonite-K10, Bentonite

1.4. Solid base

Solid acid catalysts are well known in the field of catalysis and since last few decades it could succeed in replacing the homogeneous catalysts (mineral acids) in acid catalyzed conversions. Even though solid base catalysts have been used in several industries, extensive catalytic studies on them are scanty compared to the solid acid catalysts.[123] Application of homogeneous bases in reactions such as isomerization, addition, alkylation and cyclization is well documented. But the homogeneous nature makes their separation and recycling very tricky. Beside this, use of homogeneous bases makes the overall process corrosive and most of the times it needs to be added in the stoichiometric amount. On the other hand, solid bases are easily separable from reaction mixture, safe to handle and can be recycled easily.

Analogous to solid acid which has acid sites, solid base has basic sites. In solid acids, acid sites are generated by mixing different kinds of metal oxides but rarely basic sites can be generated by mixing two different kinds metal oxides. In general, basic sites in the form of exposed 'O' atom of metal oxides are generated by removal of H_2O or CO_2 from surface, hence pretreatment at high temperature is needed.[123] Strength of basic sites varies from material to material or the same material may show basic sites with different strength. Strength of the basic site in a particular material is determined mainly by the optimum pretreatment temperature. Strength of the base required for base catalyzed reactions varies from reaction to reaction and depends on abstraction of proton from reactant. As a result, all base catalyzed reactions are not feasible by using same base catalyst. Some of the commonly used solid bases are listed in Table 1.3.[124] These materials shows some typical properties of base like color change of the acid-base indicator, adsorption of acidic molecules and poisoning of active sites by acidic molecules such as HCl, CO_2, etc.

Table 1.3. Examples of solid bases.

Sr. No.	Type	Example
1	Metal oxides	CaO, MgO, ZrO_2, SiO-CaO, SiO-MgO, Al_2O_3-MgO (calcined hydrotalcite)
2	Alkali compounds supported on Al_2O_3	KF/Al_2O_3, K_2CO_3/Al_2O_3, $NaOH/Al_2O_3$, KOH/Al_2O_3, etc.
3	Supported alkali metal	Na/Al_2O_3, K/Al_2O_3, K/MgO, Na/zeolite
4	Anion exchangers	Anion exchange resins
5	Zeolites	K, Rb, Cs-exchanged X-zeolite
6	Clay	Sepiolite
7	Phosphates	Natural phosphates, hydroxyapatite

Among all the above mentioned solid bases, hydrotalcite is the most studied and used solid base. "Hydrotalcites (HT) are the synthetic or natural layered materials made of positively charged two-dimensional sheets of mixed hydroxides with water and exchangeable charge-compensating anions".[125, 126] Mg-Al hydrotalcites including their calcination products are very often used as solid base to catalyze various reactions.[127-129] Hydrotalcite can be prepared with various bivalent (Ni, Cu, Co) and trivalent (Fe, Cr) cations other than Mg, Zn and Al. HT exhibit certain characteristic properties which make it exploitable for various base catalyzed reactions. Reactivity of as synthesized HT is governed by the intercalated anion and amount of water present.[127] Two metal hydroxide layers in Mg-Al type HT shows brucite like structure ($Mg(OH)_2$) in which some bivalent metal cations (Mg^{+2}) are replaced by trivalent metal cations (Al^{+3}). These bivalent metal cations are in close proximity of -OH group. Two brucite layers are placed one over other and held by weak hydrogen bonding. Substitution of bivalent cation by trivalent cation (almost of equal radius) creates excess positive charge which is compensated by intercalating anion.[130] Intercalating compensating anions and water molecules are present in the interlayer space between two brucite layers. HT in as synthesized form does not have activity for some base catalyzed reactions because adsorbed water molecules hinder the access of basic sites, hence needs thermal activation typically at 400-500°C for 12-48 h.[131-134] During heat treatment intercalating anions and water molecules are decomposed and brucite layers are converted into (Mg(Al)O) mixed oxide with higher surface area and porosity.[132, 135] Moreover the basicity of HT is tunable and fine tuning of basicity is important factor for achieving good catalytic activity.[128] Change in the M^{+3}/M^{+2} ratio or change in the intercalating anions can change the basicity.[136] Basicity of hydrotalcite can be increased by thermal activation.[135] Thermally activated i.e. calcined HT shows good activity in number of reactions.[137-142] After loss of intercalating anions, O^{-2}-M^{+2} ion pair and strong Lewis basic sites associated with the isolated O^{-2} ions are created which can act as active site for base catalyzed reaction[131, 143] and strength of the active site depends on the calcination temperature.[144, 145] Calcined HT can be rehydrated to obtained lamellar material (memory effect).[130] Structure of as synthesized HT with two brucite like layers can be represented as Figure 1.12.

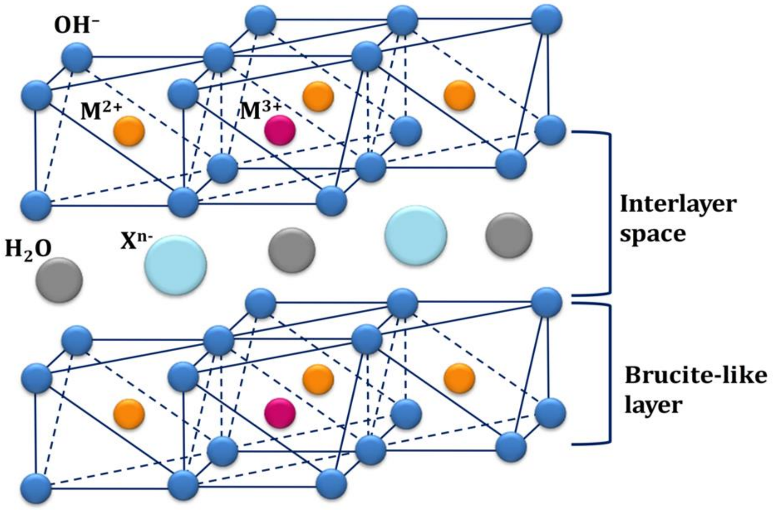


Figure 1.12. Structure of hydrotalcite.

M^{2+}: bivalent metal ion; M^{3+}: trivalent metal ion; X^{n-}: intercalating anion

1.5. Supported metal catalysts

Supported metal catalysts are the heterogeneous catalysts prepared by anchoring the metal or metals on the suitable support and hence have bi-functional nature. Supported metal catalyst integrates the properties of support as well as the metal. Overall catalytic properties of supported metal catalysts are determined by three factors.

i) Nature of support material: Support materials can be of three types i.e. acidic, basic or neutral. Solid acids, solid bases and neutral materials like carbon are frequently used as support in the preparation of supported metal catalysts (solid acids and solid bases are discussed in details in section 1.3 and 1.4). Porosity and surface area of support material governs the total binding sites available for anchoring of metal precursor on the support material.

ii) Nature of metal: Metals are being used to catalyze various reactions and ability to catalyze particular reaction is the characteristic property of metal. Neither all the reactions can be catalyzed by a single metal, nor can single reaction be catalyzed by all the metals. Electronic properties of metals are mainly responsible for its catalytic activity towards the reaction. Electronic effect is the result of change in electron density on the metal atom after interaction with support or with other metal.

iii) Support-metal interaction: Support-metal interaction is one of the most important factors which determine the activity of supported metal catalyst. Hence, while choosing a supported metal catalyst to carry out certain reaction, one should consider all above mentioned three aspects. Studies on supported metal catalysts revealed that, various types of interactions may present between supports and metals. Nature of interaction depends on the nature of support and nature of metals as well as on the experimental conditions during its synthesis (pH of solution, temperature of calcination and reduction, etc.) Dispersion of metal is one of the most significant properties of supported metal catalysts. It depends on the support-metal interaction and method of synthesis. Dispersion indicates the number of metal atoms present on the surface out of the total atoms present in the catalyst.[146] Hence, dispersion 'D' can be calculated as;

$$\mathbf{D = N_S/N_T}$$

N_S: number of atoms present on the surface

N_T: total number of atoms present.

Smaller the particle size of metal particles higher is the dispersion and specific surface area is inversely proportional to the particle size.[146] Relation between the specific surface area and dispersion can be represented as;

$$\mathbf{S_{sp} = A(N_A/M)D}$$

S_{sp}: specific surface area

A: area occupied by an atom on the surface.

N_A: avogadro's number (6.022×10^{23})

M: atomic mass

Other than aforementioned features, supported metal catalysts show effects like spillover effect and steric effect. "Spillover involves the transport of an active species sorbed or formed on the first phase on to another phase that does not sorb or form the species under same condition". For example in 'hydrogen spillover' over supported metal catalyst, metal act as donor on which hydrogen species is adsorbed and subsequently migrates to the support which acts as an accepter. Steric effect inhibits the access of reactant molecule to the active site on the catalyst because of bulky groups near the active center.[146] Inhibition of catalytic activity of supported metal catalysts may occur because of adsorption of inhibitory substances, leaching of metal from the support and sintering of metal particle during reaction.

1.5.1. Methods for the synthesis of supported metal catalysts.

It is very important to select the proper method for catalyst synthesis while preparing the supported metal catalyst as it has significant effect on the catalyst properties.[147, 148] Impregnation is one of the most practiced methods for the preparation of supported metal catalysts. In this method solution of metal precursor (active phase) is stirred with support which allows the metal precursor to interact with support material. Two types of impregnation techniques are being used i.e. dry impregnation and wet impregnation. Dry impregnation method is also known as incipient wetness or pore volume impregnation. An adequate amount of precursor solution is used to fill the pores on the supports. Quantity of precursor solution used is just enough to fill the pore volume and not more than that. While in wet impregnation method excess quantity of metal precursor solution is used. In impregnation techniques three processes are involved i.e. transport of metal precursor solution into the pores of support material and diffusion of metal precursor within pores followed by interaction of metal precursor with sites on pore wall. Metal precursors get attached to the support by adsorption (chemical or physical), or by replacement of ligands with surface -OH groups of support. Adsorption of the precursor depends on the surface charge of support. At the pH equals to the point of zero charge, support surface will be neutral, at pH below point of zero charge surface will be positively charged and at pH higher than point of zero charge, surface will be negatively charged. On negatively charged surface, adsorption of positively charged ions will be stronger. Some other methods used for synthesis of supported metal catalysts are homogeneous deposition precipitation, co-precipitation, sol-gel, chemical vapor deposition, etc.[149]

1.5.2. Monometallic and bimetallic catalysts

Monometallic supported metal catalysts are the catalysts which consist of single metal other than support material. As mentioned above, properties of monometallic catalysts are governed by nature of metal, nature of support and support-metal interaction. Bimetallic catalysts consist of two metals other than support material hence the properties of bimetallic catalysts are governed by support-metal interaction and metal-metal interaction along with nature of metal and support. Bimetallic catalyst may exhibit different catalytic properties than individual monometallic catalysts. Generally second metal in bimetallic catalyst act as a promoter. "Promoter is the substance that is added to a catalyst in small amounts in order to improve its properties such as activity, selectivity or stability."[150] It is interesting to study the properties of bimetallic catalyst and effects of promoter on the catalytic behavior. Addition of second metal (promoter) may have various effects like, increase in the catalyst activity, better selectivity for particular product or it may improve the catalyst stability. Promoter may cause significant effect because of various interactions or phenomena out of which some are mentioned below;[151]

i) Hydrogen spillover effect: Activated hydrogen species can be transferred from promoter to the accepter metal which may help for the reduction of latter.

ii) Geometric effect: This effect is caused by alteration in the geometry of catalytically active sites due to addition of promoter. Such addition may change the size of 'ensemble' significantly.[151] If adsorbed substrate molecule is in close contact with one particular surface atom, then adsorption site is associated with single atom. If adsorbed substrate molecule is in close contact with more than one atom, then adsorption site is associated with more than one atom or 'ensemble' of atoms. If the size of ensemble is decreased after addition of promoter, then the reaction which needs the larger ensembles will be inhibited. This type of effect is generally referred as ensemble effect.[146]

iii) Electronic effect: Electron transfer may occur between active metal and promoter, which alter the electronic properties of metal. This eventually leads to the change in the catalytic activity of metal. When the interaction or bonding between metal and promoter is strong, this effect is called as ligand effect. Electronic effect does not necessarily include the significant charge transfer but it implies any type of electronic perturbation because of promoter.[146]

iv) Stabilizing effect: Promoter may inhibit the sintering of metal particles which help to improve the dispersion of metal. Promoter can interact with support and hence can form surface shell because of which mobility of metal particles is restricted.[151]

v) Synergistic effect: In this effect, both metal and promoter participate in chemical bonding with reaction intermediate and help to improve the catalytic activity.[151] Promoter may exhibit any one or more than one promoter effect at a time.

1.6. Objectives and scope of the thesis

Importance of the sugar alcohols in food, pharmaceutical and cosmetic industries has been explained earlier (section 1.2.1). Demand for sugar alcohols like sorbitol and xylitol is increasing incessantly as food habits of human beings are changing. Often use of sugar alcohols as low calorie sweetener opened new market for these chemicals.[152]

To execute on growing demand of sugar alcohols, efficient synthesis route is obligatory. Conventional methods for sugar alcohols synthesis are allied with some obvious drawbacks such as low yield of sugar alcohols, poor recyclability, requisite of harsh reaction conditions, etc. (explained in section 1.2.2). Objective of the current work is to develop an efficient and green one pot method for the production of sugar alcohols. More specifically objectives can be stated as;

- To convert mono- and poly-saccharides in to sugar alcohols over monometallic and bimetallic catalysts.

Sugar alcohols can be produced by hydrogenation of monosaccharides. Conversion of C5 sugars (xylose, arabinose) and C6 sugars (glucose, galactose, fructose) will be conducted to yield corresponding sugar alcohols. Hydrolytic hydrogenation of polysaccharides (xylan, arabinogalactan, inulin) will be carried out in one pot manner for the synthesis of sugar alcohols.

➢ To analyze agricultural wastes and selective conversion of hemicellulose in to sugar alcohols.

Utilization of agricultural wastes for the production of sugar alcohols is one of the convenient options since isolation of various components (cellulose, hemicellulose, lignin) with purity from raw biomass is difficult. Isolation and purification steps will increase the total number of steps to obtain desired product, time and capital and ultimately cost of production will be increased. Secondly, during isolation process some physicochemical properties of product may change. Hence, in current work one pot conversion of agricultural wastes in to sugar alcohols will be studied. Moreover, selective conversion of single component i.e. hemicellulose by optimizing reaction conditions to achieve better selectivity for sugar alcohols will be carried out. Complete compositional analysis of agricultural wastes to find out exact percentage of various components will be done by TAPPI (Technical Association of Pulp and Paper Industry) method.

➢ To explore the effects of supports, metals and promoters on the catalytic conversion of mono- and poly-saccharides.

Activity of supported metal catalyst towards particular reaction is governed by nature of support, metal and support-metal interaction. In bimetallic catalyst promoter metal can alter properties of catalyst. It is interesting to study the effect of various supports, metals and promoters on the catalytic activity. For this study various monometallic and bimetallic catalysts will be prepared and will be evaluated for entitled conversions. Variety of support materials (γ-Al_2O_3, SiO_2-Al_2O_3, activated carbon, calcined hydrotalcite), metals (Pt, Ru) and promoters (Sn, Ga, Fe) will be used for the synthesis of catalysts.

➢ To develop recyclable catalyst exploitable at wide range of reaction conditions.

Some of the known supported metal catalysts shows good activity for the conversion of monosaccharides and polysaccharides in to sugar alcohols but the common problem associated with these catalysts is poor recyclability. Hence it is necessary to develop stable catalyst having good recyclability.

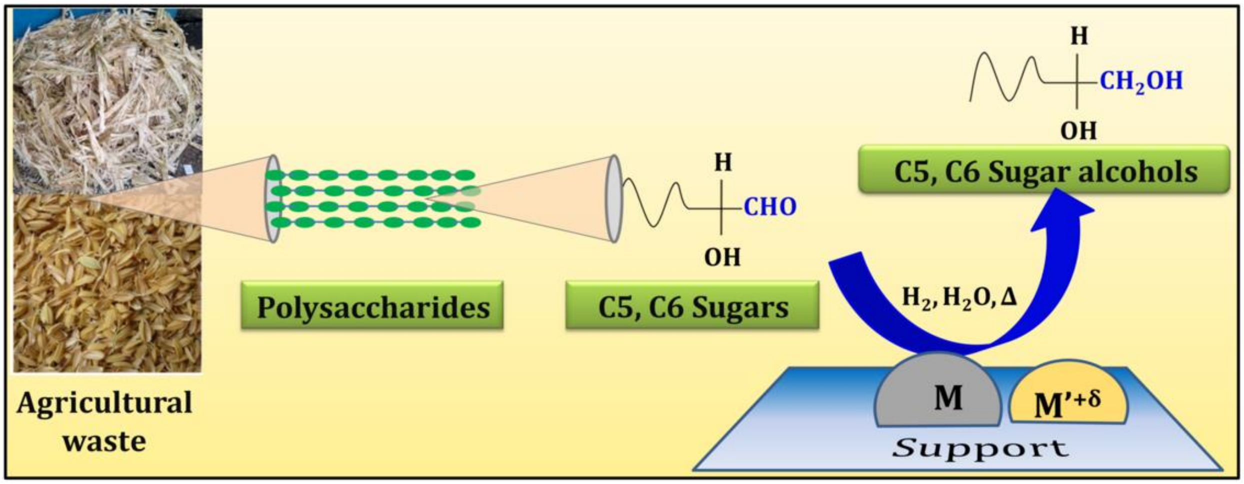
- To study the effect of solid base as an additive or support on the conversion of mono- and poly-saccharides in to sugar alcohols over monometallic and bimetallic catalysts.

To study the effect of solid base on the entitled conversion, solid base (calcined hydrotalcite) will be synthesized and will be used as a support or in the combination with supported metal catalysts as an additive. Effect of commercially available solid bases will be compared with synthesized solid base.

- To study the effect of catalyst properties on catalytic activity.

Various properties of synthesized catalysts will be determined with the help of characterization techniques (ICP-AES, XRD, NH_3-TPD, CO_2-TPD, N_2-Sorption, TEM, XPS, etc.) and will be correlated with its catalytic activity.

Overall, conversion of the monosaccharides, polysaccharides and agricultural wastes will carried out over monometallic and bimetallic catalysts for the production of sugar alcohols, which can be stated schematically as Figure 1.13.



Scheme 1.1. Conversion of monosaccharides, isolated polysaccharides and agricultural wastes in to sugar alcohols over supported metal catalysts.

Hypothesis

- In bimetallic catalyst, promoter can alter the properties of catalyst by electronic or/and geometric effect.

As explained in section 1.5.2, bimetallic catalyst may show better activity for particular reaction. Better yield and selectivity can be achieved using bimetallic catalysts. Either electronic or geometric or both effects can alter catalyst properties. Considering this, various bimetallic catalysts will be prepared and will be evaluated for entitled reaction.

➢ With the addition of solid base, pH of solution becomes alkaline, which help generate sugar molecules in open chain form.

Sugar molecules can undergo 'Lobry de Bruyn-Alberda van Ekenstien transformation' in alkaline medium and sugar molecule can be converted in to its isomer through intermediates (enolate ions and endiol). According to this transformation in alkaline medium, sugar molecule would be in open chain form which further can be transformed in to isomeric sugar. Sugar molecules in open chain form can be converted in to sugar alcohols in the presence of active catalyst and hydrogen. Hence, solid base in combination with supported metal catalyst will be used for the conversion of mono- and poly-saccharides to produce sugar alcohols.

Outline of the thesis

Current chapter comprises brief introduction about biomass, classification and composition of biomass, brief description about biomass conversion methods, etc. Methods for sugar alcohol synthesis and importance of sugar alcohols have been explained in this chapter. Excluding this chapter, thesis has been divided into five chapters. Second chapter comprises catalyst synthesis method and characterizations of synthesized catalysts. Results for various characterizations are included in the same chapter. In third chapter, detailed experimental procedure and methods for analysis of reaction mixture has been explained. Results for the conversion of monosaccharides over monometallic and bimetallic catalysts are summarized and catalyst properties were correlated with catalytic activity. Effects of supports, metals and promoters on the conversion of C5 sugars (xylose, arabinose) and C6 sugars (glucose, galactose, fructose) have been explained in this chapter. Fourth chapter comprises the results for the conversion of polysaccharides. This chapter is divided into two sub-chapters i.e. part A (4th A) and part B (4th B). Part A consists of results for the conversion of isolated polysaccharides (xylan, arabinogalactan, inulin) in to sugar alcohols while part B includes results for compositional analysis of agricultural wastes (sugarcane bagasse, rice husk, wheat straw) and selective conversion of hemicellulose in these agricultural wastes to yield sugar alcohols. Effect of solid base (calcined hydrotalcite) on the conversion of monosaccharides (C5 sugars and C6 sugars) and polysaccharides over monometallic and bimetallic catalysts is discussed in fifth chapter of the thesis. In sixth chapter, summary and conclusions of the work are consolidated.

1.7. References

1. http://www.biomassenergycentre.org.uk.
2. J. Pérez, J. Muñoz-Dorado, T. de la Rubia and J. Martínez, *International Microbiology*, 2002, **5**, 53-63.
3. M. Berchel, J. Haddad, S. p. S. Le Corre, J.-P. Haelters and P.-A. JaffrÃ¨s, *Tetrahedron Letters*, **56**, 2345-2348.
4. A. Demirbas, *Energy conversion and Management*, 2000, **41**, 633-646.
5. M. Hall, P. Bansal, J. H. Lee, M. J. Realff and A. S. Bommarius, *FEBS Journal*, 2010, **277**, 1571-1582.
6. D. Fengel, G. Wegener, Wood. Chemistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin, Germany,1989.
7. E. Sjöström, Wood Chemistry. Fundamentals and Applications, 2nd edition, Academic Press, San Diego, CA, USA, 1993.
8. K. Shimizu, Chemistry of hemicelluloses; in: Wood and Cellulosic Chemistry. 2nd edition, Eds. D.N.-S. Hon, N. Shiraishi, Marcel Dekker Inc., New York, USA, 2001.
9. J. Harkin, in *Naturstoffe*, Springer Berlin Heidelberg, Editon edn., 1996, **6**, 101.
10. C. Amen-Chen, H. Pakdel and C. Roy, *Bioresource Technology*, 2001, **79**, 277-299.
11. G. W. Huber, S. Iborra and A. Corma, *Chemical Reviews*, 2006, **106**, 4044-4098.
12. E. Dorrestijn, L. J. J. Laarhoven, I. W. C. E. Arends and P. Mulder, *Journal of Analytical and Applied Pyrolysis*, 2000, **54**, 153-192.
13. J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chemical Reviews*, 2010, **110**, 3552-3599.
14. R. J. Evans, T. A. Milne and M. N. Soltys, *Journal of Analytical and Applied Pyrolysis*, 1986, **9**, 207-236.
15. P. Dhepe and A. Fukuoka, *Catalysis Surveys from Asia*, 2007, **11**, 186-191.
16. S. b. N. Ronkart, C. S. Blecker, H. l. n. Fourmanoir, C. Fougnies, C. Deroanne, J.-C. Van Herck and M. Paquot, *Analytica Chimica Acta*, 2007, **604**, 81-87.
17. H. W. Doelle, *Biotechnology, Ed. Horst W. Doelle*, 2003.

18. F. Bergius, *Industrial & Engineering Chemistry*, 1937, **29**, 247-253.
19. Y. Lu and N. S. Mosier, *Biotechnology and Bioengineering*, 2008, **101**, 1170-1181.
20. J. F. Saeman, J. L. Bubl and E. E. Harris, *Industrial & Engineering Chemistry Analytical Edition*, 1945, **17**, 35-37.
21. Y. B. Huang and Y. Fu, *Green Chemistry*, 2013, **15**, 1095-1111.
22. F. Guo, Z. Fang, C. C. Xu and R. L. Smith Jr, *Progress in Energy and Combustion Science*, 2012, **38**, 672-690.
23. P. L. Dhepe and A. Fukuoka, *ChemSusChem*, 2008, **1**, 969-975.
24. H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chemistry*, 2011, **13**, 326-333.
25. P. L. Dhepe and R. Sahu, *Green Chemistry*, 2010, **12**, 2153-2156.
26. R. Sahu and P. L. Dhepe, *ChemSusChem*, 2012, **5**, 751-761.
27. P. Bhaumik and P. L. Dhepe, *RSC Advances*, 2014, **4**, 26215-26221.
28. Y. Kim, R. Hendrickson, N. Mosier and M. R. Ladisch, *Energy & Fuels*, 2005, **19**, 2189-2200.
29. P. D. Cara, M. Pagliaro, A. Elmekawy, D. R. Brown, P. Verschuren, N. R. Shiju and G. Rothenberg, *Catalysis Science & Technology*, 2013, **3**, 2057-2061.
30. R. Ormsby, J. R. Kastner and J. Miller, *Catalysis Today*, 2012, **190**, 89-97.
31. A. Fukuoka and P. L. Dhepe, *Angewandte Chemie International Edition*, 2006, **45**, 5161-5163.
32. A. Onda, T. Ochi and K. Yanagisawa, *Green Chemistry*, 2008, **10**, 1033-1037.
33. Y. M. Chang, *Resources, Conservation and Recycling*, 1996, **17**, 125-139.
34. B. Yang, Z. Dai, S. Y. Ding and C. E. Wyman, *Biofuels*, 2011, **2**, 421-449.
35. M. Yoshida, Y. Liu, S. Uchida, K. Kawarada, Y. Ukagami, H. Ichinose, S. Kaneko and K. Fukuda, *Bioscience, Biotechnology, and Biochemistry*, 2008, **72**, 805-810.
36. J. R. Mielenz, J. Doran-Peterson, A. Jangid, S. Brandon, E. DeCrescenzo-Henriksen, B. Dien and L. Ingram, in *Biofuels*, Humana Press, Editon edn., 2009, **581**, 263-280.
37. U. Schuchardt, R. Sercheli and R. r. M. Vargas, *Journal of the Brazilian Chemical Society*, 1998, **9**, 199-210.
38. P. Gallezot, P. J. Cerino, B. Blanc, G. Fleche and P. Fuertes, *Journal of Catalysis*, 1994, **146**, 93-102.
39. C. A. Ramírez-López, J. R. Ochoa-Gómez, S. Gil-Río, O. Gómez-Jiménez-Aberasturi and J. Torrecilla-Soria, *Journal of Chemical Technology & Biotechnology*, 2011, **86**, 867-874.
40. X. Chen, X. Wang, S. Yao and X. Mu, *Catalysis Communications*, 2013, **39**, 86-89.
41. J. Li, A. Spina, J. A. Moulijn and M. Makkee, *Catalysis Science & Technology*, 2013, **3**, 1540-1546.

42. R. M. Gohil, *Polymer Engineering & Science*, 2009, **49**, 544-553.
43. Y. Zhu, M. Durand, V. Molinier and J.-M. Aubry, *Green Chemistry*, 2008, **10**, 532-540.
44. R. R. Davda and J. A. Dumesic, *Chemical Communications*, 2004, **0**, 36-37.
45. L. He and D. Chen, *ChemSusChem*, **5**, 587-595.
46. H. Shawkat, M.-M. Westwood and A. Mortimer, *Continuing Education in Anaesthesia, Critical Care & Pain*, 2012.
47. J. P. Mikkola and T. Salmi, *Chemical Engineering Science*, 1999, **54**, 1583-1588.
48. J. P. Mikkola and T. Salmi, *Catalysis Today*, 2001, **64**, 271-277.
49. G. Hildebrandt, I. Lee and J. Hodges, *Special Care in Dentistry*, 2010, **30**, 53-58.
50. P. Lif Holgerson, C. Stecksén-Blicks, I. Sjöström, M. Öberg and S. Twetman, *Caries Research*, 2006, **40**, 393-397.
51. H. Sano, S. Nakashima, Y. Songpaisan and P. Phantumvanit, *Journal of Oral Science*, 2007, **49**, 67-73.
52. K. K. Makinen, C. A. Bennett, P. P. Hujoel, P. J. Isokangas, K. P. Isotupa, H. R. Pape and P. L. Makinen, *Journal of Dental Research*, 1995, **74**, 1904-1913.
53. M. Uhari, T. Kontiokari, M. Koskela and M. Niemela, *Xylitol chewing gum in prevention of acute otitis media: double blind randomised trial*, 1996.
54. S. S. r. da Silva, A. K. Chandel, R. de Căssia Lacerda Brambilla Rodrigues, E. Canettieri, E. Martinez, L. Canilha, A. Solenzal and J. o. de Almeida e Silva, in *D-Xylitol*, Springer Berlin Heidelberg, Editon edn., 2012.
55. N. de Kalbermatten, E. Ravussin, E. Maeder, C. Geser, E. Jĕquier and J. P. Felber, *Metabolism*, 1980, **29**, 62-67.
56. S. S. Natah, K. R. Hussien, J. A. Tuominen and V. A. Koivisto, *The American Journal of Clinical Nutrition*, 1997, **65**, 947-950.
57. X. Chen, Z. H. Jiang, S. Chen and W. Qin, *International Journal of Biological Sciences*, 2010, **6**, 834-844.
58. T. Granstrom, K. Izumori and M. Leisola, *Applied Microbiology and Biotechnology*, 2007, **74**, 273-276.
59. F. W. Lichtenthaler, *Acc Chem Res*, 2002, **35**, 728-737.
60. M. Yadav, D. K. Mishra and J. S. Hwang, *Applied Catalysis A: General*, 2012, **425-426**, 110-116.
61. J. Zhang, A. Geng, C. Yao, Y. Lu and Q. Li, *Bioresource Technology*, 2012, **105**, 134-141.
62. J. Yoshitake, H. Ohiwa, M. Shimamura and T. Imai, *Agricultural and Biological Chemistry*, 1971, **35**, 905-911.
63. J. Yoshitake, H. Ishizaki, M. Shimamura and T. Imai, *Agricultural and Biological Chemistry*, 1973, **37**, 2261-2267.

64. J. Yoshitake, M. Shimamura, H. Ishizaki and Y. Irie, *Agricultural and Biological Chemistry*, 1976, **40**, 1493-1503.
65. K. Izumori and K. Tuzaki, *Journal of Fermentation Technology*, 1988, **66**, 33-36.
66. J. S. Dahiya, *Canadian Journal of Microbiology*, 1991, **37**, 14-18.
67. D. K. Oh, S. Y. Kim and J. H. Kim, *Biotechnology and Bioengineering*, 1998, **58**, 440-444.
68. H. Baek, K. H. Song, S. M. Park, S.-Y. Kim and H.-H. Hyun, *Biotechnology Letters*, 2003, **25**, 761-765.
69. G. S. Erzinger, M. M. d. Silveira, J. P. C. L. d. Costa, M. Vitolo and R. Jonas, *Brazilian Journal of Microbiology*, 2003, **34**, 329-333.
70. B. C. Saha and R. J. Bothast, *Applied Microbiology and Biotechnology*, 1996, **45**, 299-306.
71. J. P. Mikkola and T. Salmi, *Catalysis Today*, 2001, **64**, 271-277.
72. M. Herskowitz, *Chemical Engineering Science*, 1985, **40**, 1309-1311.
73. K. van Gorp, E. Boerman, C. V. Cavenaghi and P. H. Berben, *Catalysis Today*, 1999, **52**, 349-361.
74. P. Gallezot, N. Nicolaus, G. Flěche, P. Fuertes and A. Perrard, *Journal of Catalysis*, 1998, **180**, 51-55.
75. J. P. Mikkola, R. Sjöholm, T. Salmi and P. i. Mäki-Arvela, *Catalysis Today*, 1999, **48**, 73-81.
76. S. Schimpf, C. Louis and P. Claus, *Applied Catalysis A: General*, 2007, **318**, 45-53.
77. F. Devos, Process for the production of mannitol, U.S. Patent, 1995, 5466-795.
78. W. Y. Jeon, B. H. Yoon, W. Y. Shim and J. H. Kim, *Journal of Biotechnology*, 2010, **150**, 345-346.
79. H. Ling, K. Cheng, J. Ge and W. Ping, *New Biotechnology*, 2011, **28**, 673-678.
80. B. Kusserow, S. Schimpf and P. Claus, *Advanced Synthesis & Catalysis*, 2003, **345**, 289-299.
81. B. W. Hoffer, E. Crezee, P. R. M. Mooijman, A. D. van Langeveld, F. Kapteijn and J. A. Moulijn, *Catalysis Today*, 2003, **79-80**, 35-41.
82. B. J. Arena, *Applied Catalysis A: General*, 1992, **87**, 219-229.
83. J. Kuusisto, A. V. Tokarev, E. V. Murzina, M. U. Roslund, J. P. Mikkola, D. Y. Murzin and T. Salmi, *Catalysis Today*, 2007, **121**, 92-99.
84. A. Perrard, P. Gallezot, J.-P. Joly, R. Durand, C. d. Baljou, B. Coq and P. Trens, *Applied Catalysis A: General*, 2007, **331**, 100-104.
85. J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs and B. Sels, *Chemical Communications*, 2011, **47**, 5590-5592.
86. L. N. Ding, A.-Q. Wang, M. Y. Zheng and T. Zhang, *ChemSusChem*, **3**, 818-821.

87. A. Shrotri, A. Tanksale, J. N. Beltramini, H. Gurav and S. V. Chilukuri, *Catalysis Science & Technology*, 2012, **2**, 1852-1858.
88. V. I. Sharkov, *Angewandte Chemie International Edition in English*, 1963, **2**, 405-409.
89. C. Luo, S. Wang and H. Liu, *Angewandte Chemie International Edition*, 2007, **46**, 7636-7639.
90. T. Deng and H. Liu, *Green Chemistry*, 2013, **15**, 116-124.
91. M. G. A. Felipe, M. Vitolo, I. M. Mancilha and S. S. Silva, *Biomass and Bioenergy*, 1997, **13**, 11-14.
92. J. Zhang, A. Geng, C. Yao, Y. Lu and Q. Li, *Bioresource Technology*, 2011, **105**, 134-141.
93. L. Canilha, W. Carvalho, M. d. G. a. A. Felipe and J. o. B. d. A. e. Silva, *Brazilian Journal of Microbiology*, 2008, **39**, 333-336.
94. N. U. Nair and H. Zhao, *Metab Eng*, 2010, **12**, 7-7.
95. W. Carvalho, S. S. Silva, M. Vitolo, M. G. Felipe and I. M. Mancilha, *Z Naturforsch C*, 2002, **57**, 109-112.
96. G. Yi and Y. Zhang, *ChemSusChem*, **5**, 1383-1387.
97. S. K. Guha, H. Kobayashi, K. Hara, H. Kikuchi, T. Aritsuka and A. Fukuoka, *Catalysis Communications*, 2011, **12**, 980-983.
98. B. T. Kusema, L. Faba, N. Kumar, P. i. Mäki-Arvela, E. DÃaz, S. Ordóñez, T. Salmi and D. Y. Murzin, *Catalysis Today*, 2012, **196**, 26-33.
99. L. Faba, B. T. Kusema, E. V. Murzina, A. Tokarev, N. Kumar, A. Smeds, E. DÃ-az, S. Ordóñez, P. i. Mäki-Arvela, S. Willför, T. Salmi and D. Y. Murzin, *Microporous and Mesoporous Materials*.
100. C. M. Jinesh, C. A. Antonyraj and S. Kannan, *Applied Clay Science*, 2010, **48**, 243-249.
101. N. Li, G. A. Tompsett, T. Zhang, J. Shi, C. E. Wyman and G. W. Huber, *Green Chemistry*, **13**, 91-101.
102. A. E. Abasaeed and Y. Y. Lee, *Chemical Engineering & Technology*, 1995, **18**, 440-444.
103. A. W. Heinen, J. A. Peters and H. van Bekkum, *Carbohydrate Research*, 2001, **330**, 381-390.
104. P. Bhaumik and P. L. Dhepe, *ACS Catalysis*, 2013, **3**, 2299-2303.
105. A. Corma, *Chemical Reviews*, 1995, **95**, 559-614.
106. A. Corma and H. Garcia, *Catalysis Today*, 1997, **38**, 257-308.
107. K. Wilson, J. H. Clark, *Pure and Applied Chemistry,* 2000, **72**, 1313–1319.
108. Y. M. Sani, W. M. A. W. Daud and A. R. Abdul Aziz, *Applied Catalysis A: General*, 2014, **470**, 140-161.
109. W. M. Van Rhijn, D. E. De Vos, B. F. Sels and W. D. Bossaert, *Chemical Communications*, 1998, 317-318.

110. Y. C. Sharma, B. Singh and J. Korstad, *Biofuels, Bioproducts and Biorefining*, 2010, **5**, 69-92.

111. E. A. Gunnewegh, S. S. Gopie and H. van Bekkum, *Journal of Molecular Catalysis A: Chemical*, 1996, **106**, 151-158.

112. K. Richard Kloetstra and J. C. Jansen, *Chemical Communications*, 1997, 2281-2282.

113. M. E. Dry, *Applied Catalysis A: General*, 1996, **138**, 319-344.

114. C. Bianchi, *Catalysis Letters*, 2001, **76**, 155-159.

115. S. J. Wilson and M. H. Stacey, *Journal of Colloid and Interface Science*, 1981, **82**, 507-517.

116. K. I. Shimizu, Y. Kato, H. Yoshida, A. Satsuma, T. Hattori and T. Yoshida, *Chemical Communications*, 1999, 1681-1682.

117. J. A. Wang, X. Bokhimi, A. Morales, O. Novaro, T. Lŏpez and R. Gŏmez, *The Journal of Physical Chemistry B*, 1998, **103**, 299-303.

118. M. Trueba and S. P. Trasatti, *European Journal of Inorganic Chemistry*, 2005, **2005**, 3393-3403.

119. R. S. Zhou and R. L. Snyder, *Acta Crystallographica Section B*, 1991, **47**, 617-630.

120. A. A. Tsyganenko and P. P. Mardilovich, *Journal of the Chemical Society, Faraday Transactions*, 1996, **92**, 4843-4852.

121. A. Ionescu, A. Allouche, J. P. Aycard, M. Rajzmann and F. o. Hutschka, *The Journal of Physical Chemistry B*, 2002, **106**, 9359-9366.

122. D. Coster and J. J. Fripiat, *Chemistry of Materials*, 1993, **5**, 1204-1210.

123. H. Hattori, *Chemical Reviews*, 1995, **95**, 537-558.

124. Gāmiăt al-Bitrūl wa-'l-Māādin, 20th Annual Saudi-Japan Symposium Catalysts in Petroleum Refining & Petrochemicals Dhahran, Saudi Arabia - December 2010.

125. G. Centi and S. Perathoner, *Microporous and Mesoporous Materials*, 2008, **107**, 3-15.

126. A. Vaccari, *Catalysis Today*, 1998, **41**, 53-71.

127. D. Tichit and B. Coq, *CATTECH*, 2003, **7**, 206-217.

128. A. Corma, S. Iborra, C. G. Bruce and K. z. Helmut, in *Advances in Catalysis*, Academic Press, Editon edn., 2006, **49**, 239-302.

129. F. O. Figueras, *Topics in Catalysis*, 2004, **29**, 189-196.

130. D. P. Debecker, E. M. Gaigneaux and G. Busca, *Chemistry – A European Journal*, 2009, **15**, 3920-3935.

131. J. C. A. A. Roelofs, D. J. Lensveld, A. J. van Dillen and K. P. de Jong, *Journal of Catalysis*, 2001, **203**, 184-191.

132. Y. Liu, E. Lotero, J. G. Goodwin Jr and X. Mo, *Applied Catalysis A: General*, 2007, **331**, 138-148.

133. M. Turco, G. Bagnasco, U. Costantino, F. Marmottini, T. Montanari, G. Ramis and G. Busca, *Journal of Catalysis*, 2004, **228**, 43-55.
134. K. K. Rao, M. Gravelle, J. S. Valente and F. O. Figueras, *Journal of Catalysis*, 1998, **173**, 115-121.
135. F. Li, X. Jiang, D. Evans and X. Duan, *Journal of Porous Materials*, 2005, **12**, 55-63.
136. S. K. Sharma, P. A. Parikh and R. V. Jasra, *Journal of Molecular Catalysis A: Chemical*, 2007, **278**, 135-144.
137. M. Di Serio, M. Cozzolino, M. Giordano, R. Tesser, P. Patrono and E. Santacesaria, *Industrial & Engineering Chemistry Research*, 2007, **46**, 6379-6384.
138. Y. Xi and R. J. Davis, *Journal of Catalysis*, 2008, **254**, 190-197.
139. V. K. Dīez, C. R. Apesteguīa and J. I. Di Cosimo, *Journal of Catalysis*, 2003, **215**, 220-233.
140. P. Kuśtrowski, D. Sułkowska, L. Chmielarz, A. Rafalska-Łasocha, B. Dudek and R. Dziembaj, *Microporous and Mesoporous Materials*, 2005, **78**, 11-22.
141. A. Corma, V. Fornés, R.M. Martín-Aranda and F. Rey, *Journal of Catalysis*, 1992, **134**, 58-65.
142. W. M. e. Antunes, C. u. d. O. Veloso and C. A. Ã. o. Henriques, *Catalysis Today*, 2008, **133-135**, 548-554.
143. W. Xie, H. Peng and L. Chen, *Journal of Molecular Catalysis A: Chemical*, 2006, **246**, 24-32.
144. P. Kuśtrowski, L. Chmielarz, A. Rafalska-Łasocha, B. Dudek, A. Pattek-Janczyk and R. Dziembaj, *Catalysis Communications*, 2006, **7**, 1047-1052.
145. D. Tichit, C. Gĕrardin, R. Durand and B. Coq, *Topics in Catalysis*, 2006, **39**, 89-96.
146. G. Ertl, H. Kn¨ozinger, J. Weitkamp, Handbook of Heterogeneous Catalysis, Vol. 2, 2nd Edition, Wiley-VCH, Weinheim, 2007.
147. G. Ertl, H. Kn¨ozinger, J. Weitkamp, Handbook of Heterogeneous Catalysis, Vol. 1, 2nd Edition, Wiley-VCH, Weinheim, 2007.
148. J. W. Geus, J. R. van Veen, An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Eds.: J. A. Moulijn, P.W. N. M. van Leeuwen, R. A. van Santen, Elsevier, Amsterdam 1999.
149. http://www.worldscibooks.com/chemistry/p354.html.
150. http://eng.thesaurus.rusnano.com/wiki/article14001.
151. D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chemical Society Reviews*, 2012, **41**, 8075-8098.
152. Y. Mahalaxmi, T. Sathish and R. S. Prakasham, *Letters in Applied Microbiology*, 2009, **49**, 533-538.

Chapter 2

Catalyst synthesis and characterizations

2.1. Introduction

As discussed in chapter 1 (section 1.2.2), it is necessary to develop an efficient catalyst for the conversion of mono- and poly-saccharides (C5 & C6 sugars, xylan, arabinogalactan, inulin, etc.) in to sugar alcohols (xylitol, arabitol, sorbitol, mannitol, galactitol). Supported metal catalysts are well known to catalyze hydrogenation of monosaccharides and hydrolytic hydrogenation of polysaccharides. Considering the importance of supported metal catalysts in the field of heterogeneous catalysis, various supported metal catalysts were synthesized and evaluated in the conversion of above mentioned mono- and poly-saccharides. Various types of support materials have been used to check the effect of support's properties on the catalytic activity. Moreover, effect of metals (Pt & Ru) and promoter effect of second metal (promoter: Sn, Fe, Ga) was explored by preparing various monometallic and bimetallic catalysts. The synthesized monometallic and bimetallic catalysts were subjected to various characterization techniques to correlate catalytic activity with their physicochemical properties. Further all synthesized catalysts were evaluated for the production of sugars alcohols from monosaccharides, polysaccharides and untreated agricultural wastes. Characterization of spent catalyst recovered after completion of the reaction was done to check its stability and effect of reaction conditions on its properties.

Current chapter comprises the step wise synthesis procedure for monometallic and bimetallic catalysts as well as it includes the details on materials used for the synthesis (support materials and metal precursors). Techniques and methods used for the characterization of catalysts along with the results for every characterization are also explained in detail.

2.2. Catalyst synthesis

2.2.1. Materials

Support materials: Acidic support materials like γ-Al_2O_3**,** SiO_2-Al_2O_3 and neutral support material like activated carbon have been used for the synthesis of catalysts. γ-Al_2O_3 (AL) and SiO_2-Al_2O_3 (SA) were purchased from Aldrich Chemicals, USA. Activated carbon-black pearl BP-2000 (C) was obtained from Cabot, Japan. Basic support material, calcined hydrotalcite (C-HT) was prepared by known co-precipitation method.[1] Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) (99%) was purchased from Merck, India while aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) (99%) was purchased from Thomas Baker, Germany. Sodium carbonate (Na_2CO_3) (99.5%) and sodium hydroxide (NaOH) (98%) were purchased from Loba Chemicals, India. In the synthesis of hydrotalcite, NaOH was used to maintain the pH, while Na_2CO_3 was used as a carbonate source. An aqueous solution 'A' (37.5 mL) of $Mg(NO_3) \cdot 6H_2O$ (0.279 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.093 mol) were slowly added into aqueous solution 'B' (37.5 mL) of NaOH (0.4375 mol) and Na_2CO_3 (0.1125 mol) under vigorous stirring over a period of 2 h. During addition, pH of the solution was maintained between 8-10. The white precipitate thus obtained was kept in autoclave at 60°C for 16 h. Precipitate was then washed with deionized water until pH becomes neutral. Solid thus obtained was dried at 80°C for 18 h in oven and properly dried powder was calcined at 550°C in the air atmosphere for 8 h. In this way hydrotalcite with Mg/Al ratio 3 was obtained and this calcined hydrotalcite (C-HT) was used for further studies during current research work. C-HT was used as a support material and as an additive along with other supported metal catalysts.

Metal precursors: Monometallic supported metal catalysts were prepared by using noble metals i.e. Platinum (Pt) and Ruthenium (Ru). Tetraamine platinum nitrate ($Pt(NH_3)_4(NO_3)_2$) (99.9%) from Alfa Aesar, UK, was used as a precursor of Pt. Ruthenium trichloride trihydrate ($RuCl_3 \cdot 3H_2O$) (99.9%) from Loba Chemicals, India, was used as metal precursor for the synthesis of Ru catalyst. Various monometallic catalysts were synthesized using AL, SA, C and C-HT as a support and Pt or Ru as metal. Likewise, bimetallic catalysts were prepared by adding second metal (promoter) to the above mentioned monometallic catalysts during synthesis. Tin (Sn), gallium (Ga) and iron (Fe) were used as a promoter in the preparation of Pt and Ru based bimetallic catalysts. Stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) (98%) from Loba Chemicals, India, was used as a precursor of tin while gallium nitrate hydrate ($GaNO_3 \cdot H_2O$) (99.9%) obtained from Alfa Aesar, UK and ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) (98%) procured from Merck Chemicals, India, were used as a precursor for Ga and Fe, respectively.

2.2.2. Synthesis procedure

Monometallic supported metal catalysts were prepared by wet impregnation method using γ-Al_2O_3 (AL), SiO_2-Al_2O_3 (SA), activated carbon-black pearl BP-2000 (C) and calcined hydrotalcite (C-HT) as support material.[2] Prior to impregnation of metal, supports were evacuated at 150°C for 6 h under vacuum (-700 Torr). Accurately weighed support material was stirred with known quantity of water for half an hour. After that, metal precursor solution of accurately known concentration was added drop wise to the suspension of support. Aqueous solution of $Pt(NH_3)_4(NO_3)_2$ was used to prepare Pt catalyst while to prepare Ru catalyst aqueous solution of $RuCl_3·3H_2O$ was added. Quantity of precursor solution added was according to the respective wt% loading of the metal.

Bimetallic catalysts were prepared by wet co-impregnation method. During the synthesis of bimetallic catalysts, addition of aqueous solution of Pt or Ru was followed by the addition of precursor solution of promoter metal to the suspension of support. $SnCl_2·2H_2O$ solution in 3M HCl (quantity according to the respective wt% loading) was added to prepare Pt-Sn bimetallic catalysts. Similarly, aqueous solutions of $Ga(NO_3)3·H_2O$ and $Fe(NO_3)_3·9H_2O$ were added instead of $SnCl_2·2H_2O$ solution to prepare Pt-Ga and Pt-Fe bimetallic catalysts, respectively. After stirring the mixture at room temperature (30-35°C) for 16 h, solvent was removed by rotary vacuum evaporator. Powder thus obtained was dried overnight (16 h) at 60°C in oven followed by drying under vacuum (-700 Torr) at 150°C for 3 h. All monometallic and bimetallic catalysts i.e. M-M'/Support (M=Pt/Ru, M'=Sn, Ga, Fe, Support=AL/SA/C-HT) were calcined at 400°C for 2 h followed by reduction at 400°C for 2 h under the flow of oxygen (20 mL/min) and hydrogen (20 mL/min), respectively.

Monometallic and bimetallic catalysts in which C was used as support material i.e. M-M'/C (M=Pt/Ru, M'=Sn) were reduced at 400°C for 2 h without calcinations. Various catalysts synthesized in current work are listed in the Table 2.1 (catalyst indicated as Pt(3.5)/AL is 3.5wt%Pt/γ-Al_2O_3, Pt(3.5)Sn(0.22)/AL is 3.5wt%Pt-0.22wt%Sn/γ-Al_2O_3 and likewise other catalysts are indicated).

Table 2.1. Monometallic and bimetallic catalysts synthesized in current work.

Sr. No.	Catalyst	Pt/Ru (wt%)	Sn/Ga/Fe (wt%)
1	Pt(3.5)/AL	3.5	--
2	Pt(3.5)Sn(0.22)/AL	3.5	0.22
3	Pt(3.5)Sn(0.43)/AL	3.5	0.43
4	Pt(3.5)Sn(0.87)/AL	3.5	0.87
5	Pt(3.5)Sn(1.75)/AL	3.5	1.75
6	Pt(3.5)Sn(3.5)/AL	3.5	3.50
7	Sn(0.43)/AL	--	0.43
8	Sn(3.5)/AL	--	3.50
9	Pt(2)/AL	2.0	--
10	Pt(2)Sn(0.25)/AL	2.0	0.25
11	Pt(2)Ga(0.25)/AL	2.0	0.25
12	Pt(2)Fe(0.25)/AL	2.0	0.25
13	Pt(2)Fe(0.5)/AL	2.0	0.50
14	Pt(2)/SA	2.0	--
15	Pt(2)Sn(0.25)/SA	2.0	0.25
16	Pt(2)/C	2.0	--
17	Pt(2)Sn(0.25)/C	2.0	0.25
18	Pt(3.5)/C-HT	3.5	--
19	Pt(2)/C-HT	2.0	--
20	Pt(2)Sn(0.25)/C-HT	2.0	0.25
21	Ru(2)/AL	2.0	--
22	Ru(2)Sn(0.25)/AL	2.0	0.25
23	Ru(2)/C	2.0	--
24	Ru(2)Sn(0.25)/C	2.0	0.25
25	Ru(3.5)/C	3.5	--
26	Ru(3.5)Sn(0.87)/C	3.5	0.87

Other than above mentioned catalysts, monometallic Pt(3.5)/AL$^{\$}$-acidified catalyst was synthesized. During the synthesis of this catalyst (0.075 g), 0.062 mL of 3M HCl was added (HCl quantity is equal to the quantity used during the preparation of Pt(3.5)Sn(0.43)/AL catalyst). Similarly, Pt(3.5)Sn(0.43)AL$^{\#}$-extra acidified catalyst (0.075 g) was prepared by adding 0.5 mL HCl (typically, 0.062 mL was added for the preparation of catalyst). These acidified catalysts were calcined and reduced under the similar conditions mentioned above (at 400°C for 2 h each, under oxygen and hydrogen flow). Activity of these catalysts was evaluated in the conversion of mono- and poly-saccharides to yield sugar alcohols.

2.3. Catalyst characterizations

All prepared catalysts were characterized using various characterization techniques such as ICP-AES, XRD, TEM, XPS, N_2 sorption and TPD. The details of characterization techniques (instruments used and operating conditions, etc.) and results for characterizations are discussed elaborately in this section.

2.3.1. Catalyst characterization techniques

2.3.1.1. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is also known as 'Inductively coupled plasma-optical emission spectroscopy' (ICP-OES). This is an analytical technique used for the elemental analysis and most frequently for the detection of metals in trace amount (in ppm level). It is a type of atomic emission spectroscopy in which plasma is used to excite the atoms or ions. These excited atoms or ions emit electromagnetic radiations when revert back to the ground state. Wavelength of the emitted radiation is a characteristic feature of particular element, hence shows peak in the spectrum at that characteristic wavelength. It is possible to perform quantitative analysis of the elements by calibrating instrument with standard solutions of accurately known concentrations.

Metal contents in the catalysts were determined using 'SPECTRO ARCOS Germany, FHS 12' instrument. Samples for ICP-AES analysis were prepared by dissolving known amount of catalyst in acidic solvent. M-M'/support (M=Pt/Ru, M'=Sn, Ga, Fe, support =AL, C-HT) catalysts were dissolved in freshly prepared aquaregia ($HCl:HNO_3$ =3:1 (*Vol/Vol*)) while Pt/SA and Pt-Sn/SA catalysts were first treated with HF, then leftover HF was evaporated by heating at 60°C. Further, solid residue obtained after HF treatment was dissolved in freshly prepared aquaregia and diluted with deionized water. Catalysts in which C was used as a support, were calcined at 600°C (5°C/min ramping rate) for 6 h in air atmosphere and solid residue after calcination was dissolved in aquaregia. All ICP-AES samples were diluted with deionized water and filtered (through 0.22 μm syringe filter) before analysis.

2.3.1.2. X-ray diffraction (XRD)

XRD is one of the most important analytical techniques to determine the crystallographic structure of material. X-ray diffractogram for particular sample can be recorded by measuring the angle at which diffraction of X-ray occurred. Inter-planner distance between two lattice planes (hkl miller indices) can be calculated using Bragg's equation, if angle of diffraction is known. Bragg's equation can be represented as below;

$$\mathbf{2d\ Sin\theta = n\lambda}$$

where, d: inter-planner distance, θ: angle of diffraction, n: integer (order of plane) and λ: wavelength of X-ray. Inter-planner spacing (d) which is characteristic feature of the crystal is used for its identification.

XRD analysis of catalysts was performed using 'PANanalytical X'pert Pro' machine (Netherland) with duel goniometer diffractor. X-ray source was Cu Kα radiation (λ=1.540598Å) and XRD patterns were recorded at the scanning rate of 4.3° min^{-1}. Samples were dried and grinded before analysis.

2.3.1.3. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopic technique in which electron beam is transmitted through very thin layer of sample. Image is formed because of these transmitted electrons. Images can be magnified up to certain extent with the help of magnifying devices. TEM is capable for imaging of very small objects with high resolution due to small wavelength of electrons (de Broglie wavelength). This technique is routinely used for the determination of morphological features of material such as shape and size of metal particles. In current work, TEM images of supported metal catalysts were obtained using FEI Tecnai TF-30 instrument. Suspension of supported metal catalyst in isopropyl alcohols was prepared and one or two drops of catalyst suspension were added onto the copper grid. Sample on the copper grid was allowed to dry and used for TEM analysis.

2.3.1.4. X-ray photoelectron spectroscopy (XPS)

XPS is the surface sensitive spectroscopic technique which being used for the determination of composition, chemical state and electronic state of the element in the sample. To obtain XPS spectra, sample is irradiated with the beam of X-ray which initiates the ejection of photoelectrons. Kinetic energy and number of ejected photoelectrons are analyzed under ultrahigh vacuum. In principle, XPS can be employed for the detection of all elements but in practice, elements with atomic number 3 and above can be detected by XPS. It is very difficult to determine element with lower atomic number like hydrogen and helium by XPS technique. Energy of the incident X-ray is known (e.g. Al Kα X-ray is 1486.7 eV) and kinetic energy of ejected photoelectron is measured, hence electron binding energy can be calculated using equation;

$$\textbf{Binding energy} = E_{\text{X-ray}} - (E_{\text{kinetic}} + \phi)$$

Where,

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

E_{kinetic}: Kinetic energy of ejected photoelectron

Φ : Work function depend on spectrometer and material.

XPS spectrum is the plot of intensity against the binding energy. In this work, oxidation state of metals is determined using VG Micro Tech ESCA-3000 instrument (operating under ultrahigh vacuum).

2.3.1.5. N_2 sorption study

Specific surface area of the sample can be determined by means of gas sorption technique. In this technique, the known volume of the gas (adsorbate, typically N_2) is allowed to adsorb on the surface of the sample at low temperature (at cryogenic temperature). Volume of gas adsorbed is calculated by measuring the reduced pressure after adsorption. Adsorption isotherm is plotted with volume of gas adsorbed against relative pressure at constant temperature. Material shows any one type of isotherm out of commonly known six types (Figure 2.1). Type of isotherm shown by sample depends on the surface area, porosity and pore size distribution. Hence the technique can be used for the determination of the surface area, pore volume and pore size distribution.

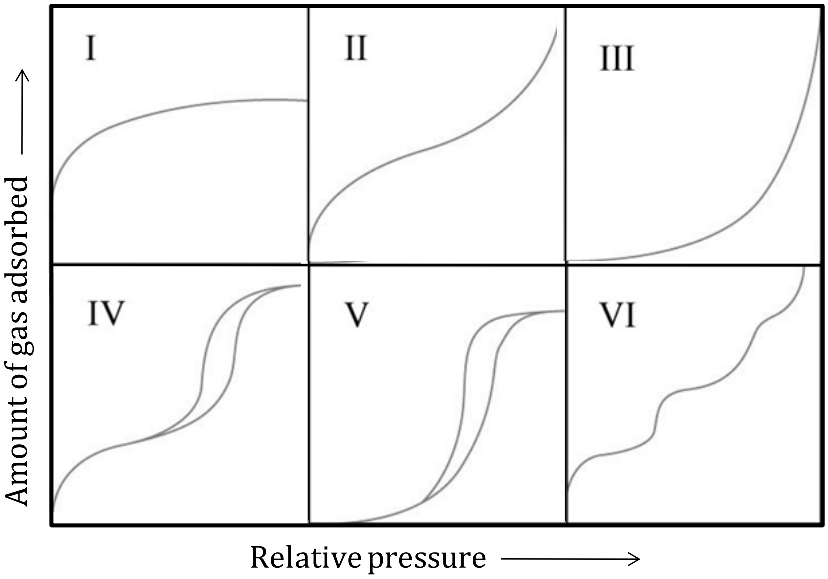


Figure 2.1. Types of adsorption isotherm.

Type I isotherm is generally shown by the microporous solid materials while type II isotherm is obtained from nonporous or macroporous solids. Type III isotherm is given by macroporous adsorbent where the cohesive forces between adsorbate molecules are greater than adhesive forces. Type IV is typically shown by mesoporous material. Hysteresis loop associated with capillary condensation taking place in mesopore is the characteristic feature of type IV isotherm. Type V isotherm is given by the solids in which adsorbate-adsorbent interaction is greater than that of adsorbate-adsorbate interaction. Type VI isotherm is typically arises because of layer by layer adsorption on the highly uniform surface.

Nitrogen sorption studies were performed using a Dona Quantachrome Nova 4200e instrument. Samples were activated in-situ at 200°C for 3 h before analysis and surface area was determined by BET method.

2.3.1.6. Temperature programmed desorption (TPD)

Temperature programmed desorption (TPD) is the analytical technique used for the determination of amount and strength of acidic or basic sites in the catalytic materials. Generally NH_3 (basic probe) is used to detect the acidic sites while CO_2 (acidic probe) is used for the determination of basic sites. During typical experiments probe molecules are allowed to adsorb onto the sample. Probe molecules interact with the acidic or basic sites on the surface. Nature of the interaction between probe molecule (adsorbate) and site on the surface (adsorbent) depend upon strength of the surface site. Stronger acid or basic site interact strongly with basic (NH_3) or acidic (CO_2) probe, respectively. Amount of probe molecule adsorbed is directly proportional to the number of acidic or basic sites available on the sample surface. Adsorbed amount of the probe molecule is calculated by heating the sample at precise ramping rate which cause desorption of the adsorbed molecules. Strongly adsorbed molecule desorbs at higher temperature indicating strong acidic or basic sites.

In current work, amount and strength of acidic sites was determined using NH_3 as a probe while CO_2 was used as a probe molecule to determine the amount of basic sites. Micrometrics Autochem-2910 instrument was employed to carry out all TPD experiments. In a typical experiment to determine acidity, sample was activated in-situ for 30 min at 550°C, in a helium flow (30 mL/min). Then the temperature was allowed to decrease to 50°C. Next, 10% NH_3 in helium was passed over the sample for 1 h, at 50°C. Subsequently, temperature of the sample was increased and maintained at 100°C for 30 min. under the flow of helium gas (30 mL/min). This allowed desorption of any physisorbed NH_3 which is weakly bounded to the sample surface. Later, at the rate of 10°C/min temperature was increased from 100°C to 700°C in helium flow (30 mL/min) and TPD profile was recorded during temperature ramping. To determine amount and strength of basic site, sample activation and adsorption-desorption of the CO_2 was carried out similar to the NH_3-TPD except CO_2 was used as a probe (acidic) instead of NH_3 (basic), rest of the experimental procedure was similar.

2.3.2. Results and discussion

Results for all characterizations of monometallic and bimetallic catalysts used in the current work are consolidated and discussed below.

2.3.2.1. Inductively coupled plasma-atomic emission spectroscopic (ICP-AES) analysis

All synthesized catalysts were analyzed using ICP-AES to determine metal contents. Metal contents (determined by ICP-AES) of all catalysts were found to be in close proximity to the expected metal contents. Results for the ICP-AES analysis are show in Table 2.2.

Table 2.2. Summary of the metal contents in the synthesized catalysts quantified by ICP-AES technique.*

Sr. No.	Catalyst	M (wt.%)	M' (wt.%)	Sr. No.	Catalyst	M (wt.%)	M' (wt.%)
1	Pt(3.5)/AL	3.58	-	14	Pt(2)/SA	2.11	-
2	Pt(3.5)Sn(0.22)/AL	3.54	0.20	15	Pt(2)Sn(0.25)/SA	2.09	0.28
3	Pt(3.5)Sn(0.43)/AL	3.45	0.47	16	Pt(2)/C	2.11	-
4	Pt(3.5)Sn(0.87)/AL	3.41	0.83	17	Pt(2)Sn(0.25)/C	2.10	0.29
5	Pt(3.5)Sn(1.75)/AL	3.54	1.79	18	Pt(3.5)/C-HT	3.56	-
6	Pt(3.5)Sn(3.5)/AL	3.47	3.41	19	Pt(2)/C-HT	2.12	-
7	Sn(0.43)/AL	-	0.41	20	Pt(2)Sn(0.25)/C-HT	2.07	0.21
8	Sn(3.5)/AL	-	3.39	21	Ru(2)/AL	2.19	-
9	Pt(2)/AL	2.14	-	22	Ru(2)Sn(0.25)/AL	2.09	0.22
10	Pt(2)Sn(0.25)/AL	2.19	0.23	23	Ru(2)/C	2.17	-
11	Pt(2)Ga(0.25)/AL	2.11	0.21	24	Ru(2)Sn(0.25)/C	2.14	0.21
12	Pt(2)Fe(0.25)/AL	2.19	0.23	25	Ru(3.5)/C	3.52	-
13	Pt(2)Fe(0.5)/AL	2.13	0.54	26	Ru(3.5)Sn(0.87)/C	3.55	0.89

M=Pt/Ru and M'=Sn/Ga/Fe; *Error: ± 0.05wt%

2.3.2.2. X-ray diffraction (XRD) analysis

XRD study was done for the various supported metal catalysts and bare support materials. Figure 2.2.A represents the XRD patterns for AL, SA and C-HT supported monometallic and bimetallic catalysts. XRD patterns for Pt(2)/AL and Pt(2)Sn(0.25)/AL depict that in both the catalysts, Pt is present in the metallic state and do not form alloy or intermetallic system on bulk level. In both the catalysts, characteristic peaks for Pt at 2θ°= 39.8, 46.3, 67.5, 81.3 and 85.8 were observed and are assigned to planes (111), (200), (220), (311) and (222), respectively (Joint Committee on Powder Diffraction Standards, JCPDS file no. 01-088-2343). In case of bimetallic Pt(2)Sn(0.25)/AL catalyst, peaks for PtSn or Pt_3Sn species were not seen (JCPDS file no. 25-0614 and 35-1360, respectively) indicating that Pt and Sn might be present as separate species. Even if such intermetallic systems were formed, its concentration must be very low and could not be detected by XRD. Intensity of the Pt peaks was lower in the case of Pt(2)Sn(0.25)/AL than in Pt(2)/AL, because of fine dispersion of Pt in Pt(2)Sn(0.25)/AL. Similarly, in Pt(2)Sn(0.25)/SA, intensity of Pt peaks was much lower compared to Pt(2)/SA and no peaks for intermetallic systems were observed.

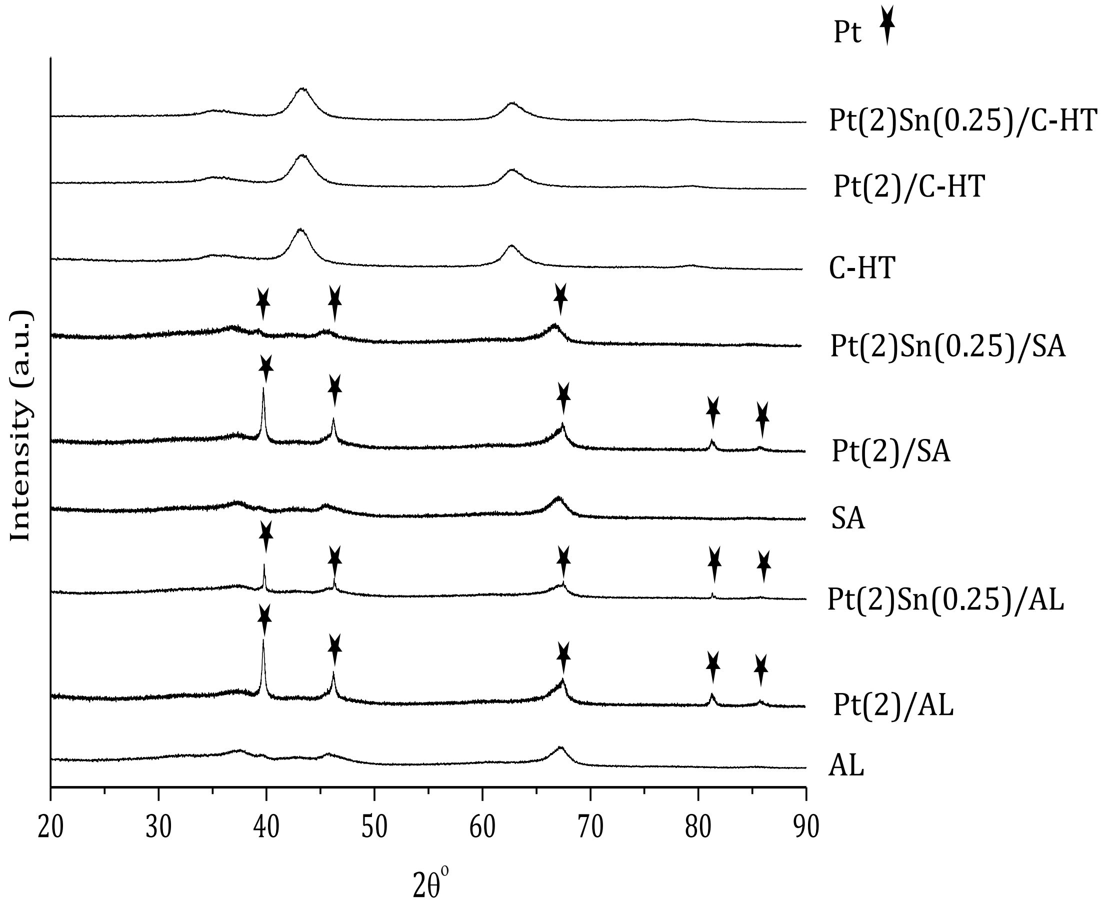


Figure 2.2.A. XRD patterns of various Pt/Support and Pt-Sn/Support catalysts.

In Pt(2)/C-HT and Pt(2)Sn(0.25)/C-HT peak intensity was very low to observe, indicating very small metal particle size in these catalysts. Furthermore, no peaks for PtSn or Pt_3Sn intermetallic systems were observed indicating that similar to the Pt(2)Sn(0.25)/AL in Pt(2)Sn(0.25)/SA and Pt(2)Sn(0.25)/C-HT too most of Pt and Sn are present as separate species. On the contrary, when Pt(2)/C and Pt(2)Sn(0.25)/C catalysts were subjected to XRD analysis (Figure 2.2.B), even with lower concentration of Sn (0.25wt%), peaks due to PtSn intermetallic system were clearly visible in Pt(2)Sn(0.25)/C (JCPDS file no. 25-0614). Above results indicate that, dispersion of metal on the support varies from support to support as support-metal interaction might be different. Another interesting conclusion drawn from the aforementioned facts is that the formation of intermetallic systems (PtSn or Pt_3Sn) depends on the support material used. Hence formation of PtSn was observed over C support but not over AL or SA, in spite of similar metal loading.

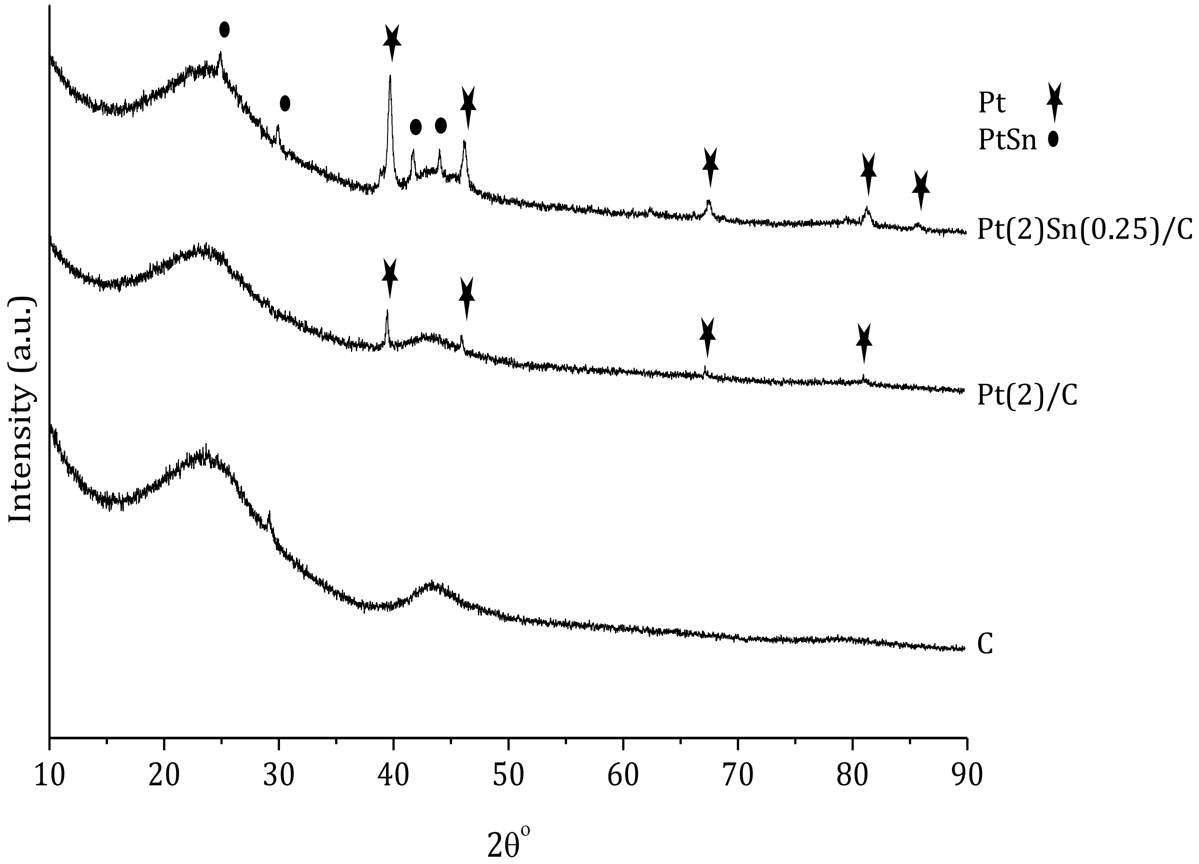


Figure 2.2.B. XRD patterns of carbon (C) supported catalysts.

To verify the dependency of the formation of PtSn or Pt_3Sn on the Pt:Sn ratio, bimetallic Pt-Sn/AL catalysts were prepared with constant Pt loading (3.5wt%) and varying Sn loading (0 to 3.5wt%). Diffractograms of Pt-Sn/AL bimetallic catalysts with varying Pt:Sn ratio are shown below (Figure 2.2.C).

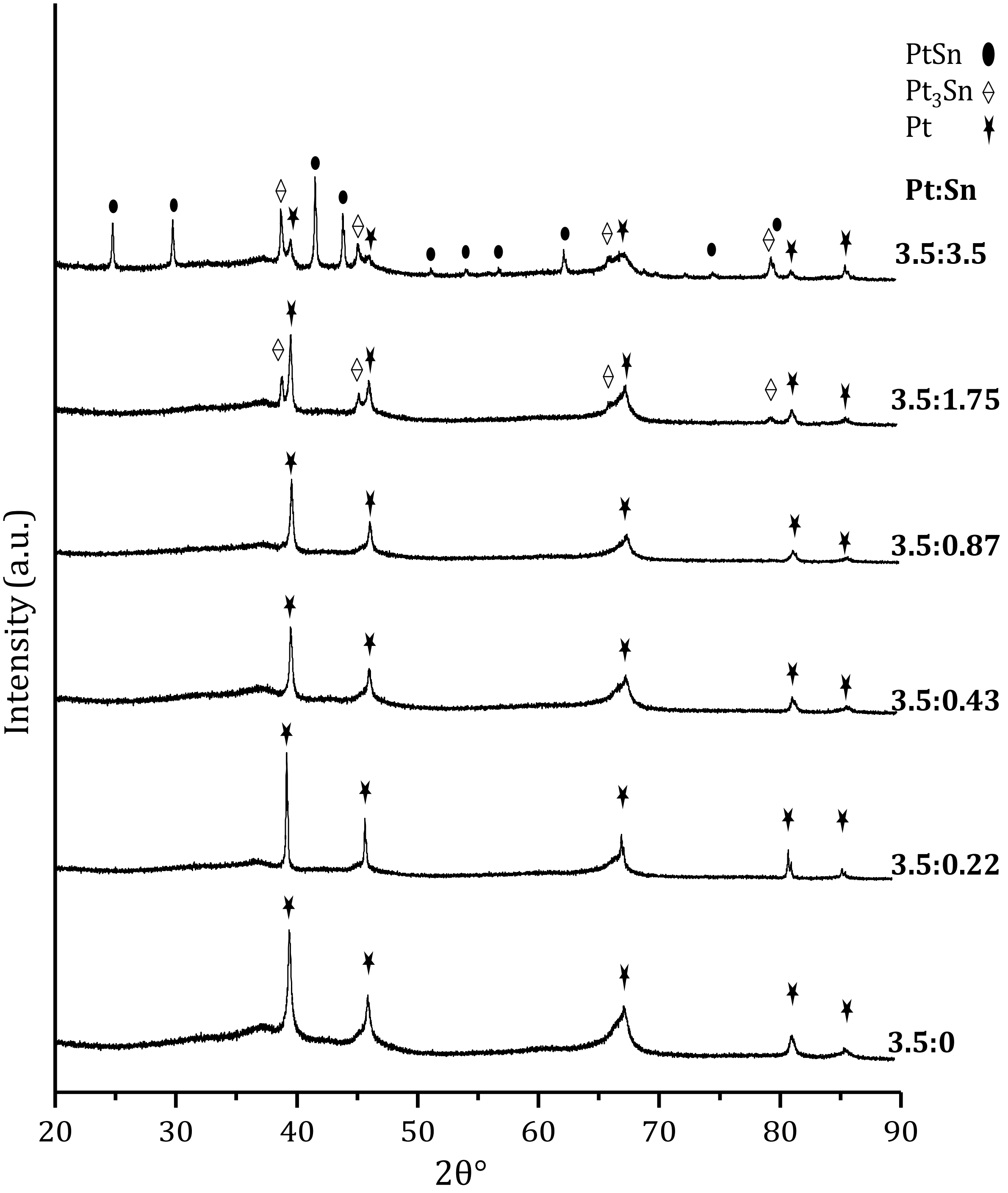


Figure 2.2.C. XRD patterns of Pt-Sn/AL catalysts with varying Pt:Sn ratio.

In Pt(3.5)/AL catalyst, the characteristic peaks for Pt at 2θ° = 39.8, 46.3, 67.5, 81.3 and 85.8 were observed (JCPDS file no. 01-088-2343). In case of bimetallic catalysts, peaks owing to Pt were clearly noticeable until 0.87wt% of Sn loading. However, when the loading of Sn was increased to 1.75wt%, extra peaks start appearing at 2θ° = 39.0, 45.4, 66.1 and 79.8, which were assigned to the Pt_3Sn species (JCPDS file no. 35-1360). Moreover, the peaks for PtSn along with the peaks for Pt_3Sn and very low intensity peaks for Pt were observed in the XRD pattern of Pt(3.5)Sn(3.5)/AL at 2θ° = 25.0, 30.0, 41.8, 44.0, 51.4, 54.3, 57.0, 62.4, 74.7, and 79.5 (JCPDS file no. 25-0614). This specifies that with higher Sn loading (1.75, 3.5wt%) formation of Pt_3Sn and PtSn species over AL is doable. Effect of formation of these intermetallic systems on the activity of catalysts in the conversion of mono- and poly-saccharides is discussed in next chapeters (Chapeter 3 and 4).

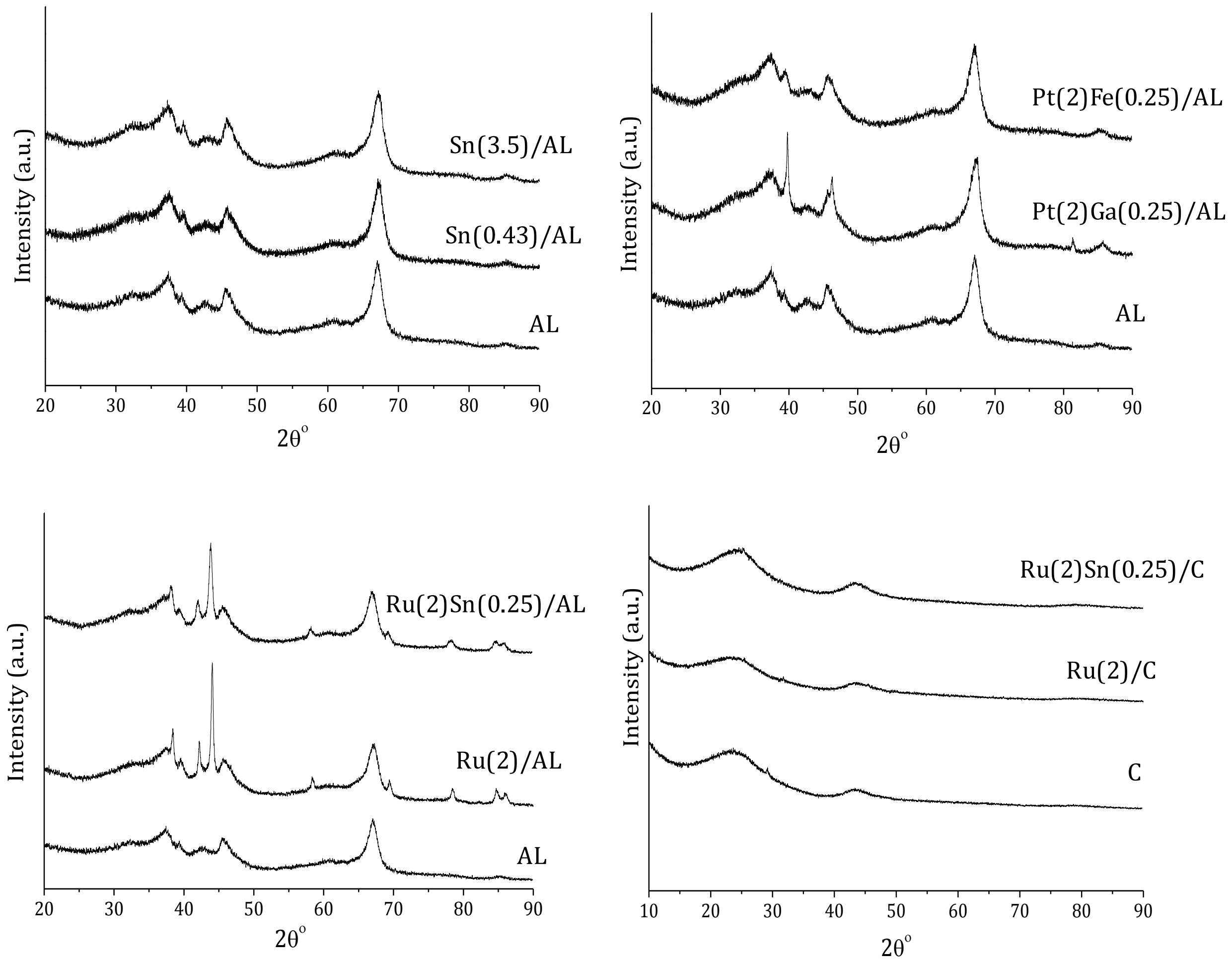


Figure 2.2.D. XRD patterns of various monometallic and bimetallic catalysts.

The XRD patterns for Sn(0.43)/AL and Sn(3.5)/AL did not show characteristic peaks for Sn species, which indicates fine dispersion of Sn on AL support (Figure 2.2.D). Pt(2)Ga(0.25)/AL and Pt(2)/Fe(0.25)/AL catalysts showed low intensity peaks for Pt. In diffractograms of Ru(2)/AL and Ru(2)Sn(0.25)/AL peaks for Ru were visible but no peak for $RuSn_2$, Ru_2Sn_3 or Ru_3Sn_7 (JCPDS file no. 18-1143, 50-1244 and 73-7217, respectively) intermetallic systems was obzerved. On the other hand, in XRD pattern of Ru(2)/C and Ru(2)Sn(0.25)/C no peak for Ru or Ru_2Sn_3 and Ru_3Sn_7 was visible owing to very small particle size. Diffractograms of all these catalysts are consolideted in Figure 2.2.D.

2.3.2.3. Transmission electron microscopic (TEM) analysis

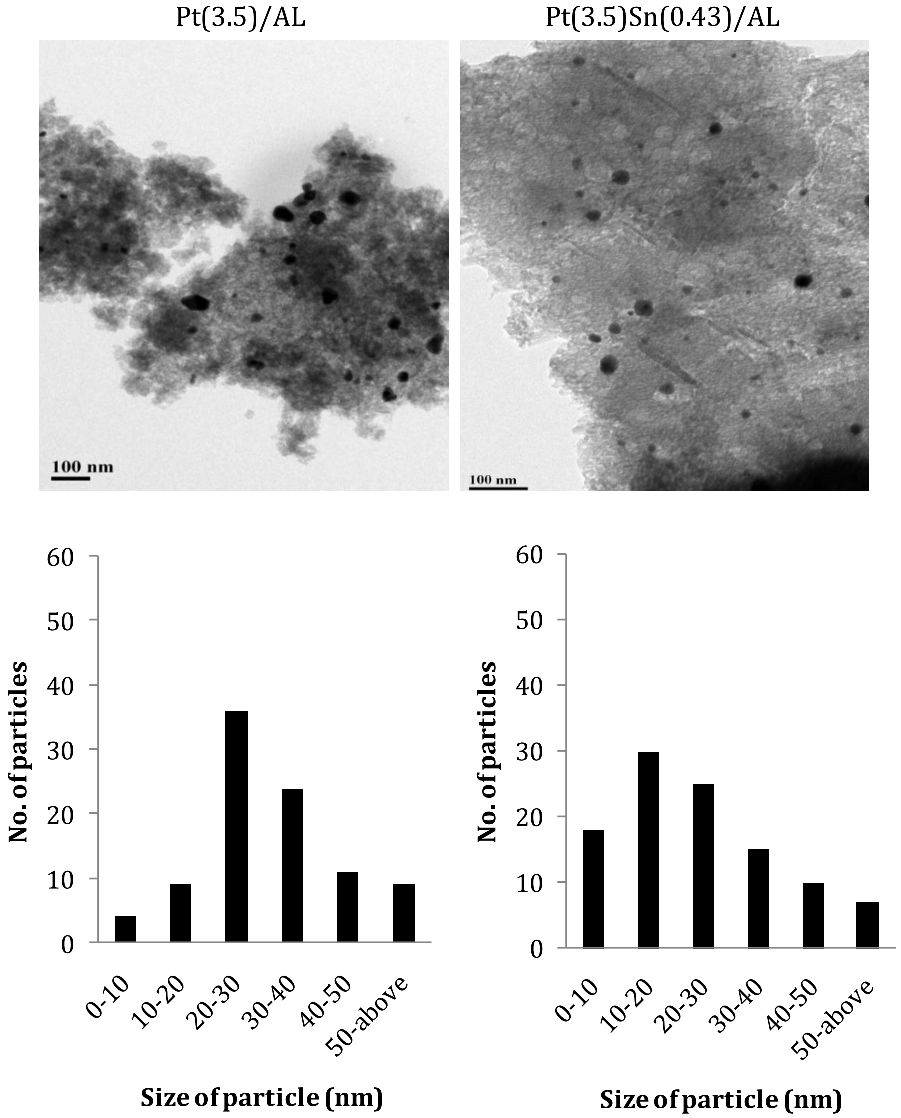
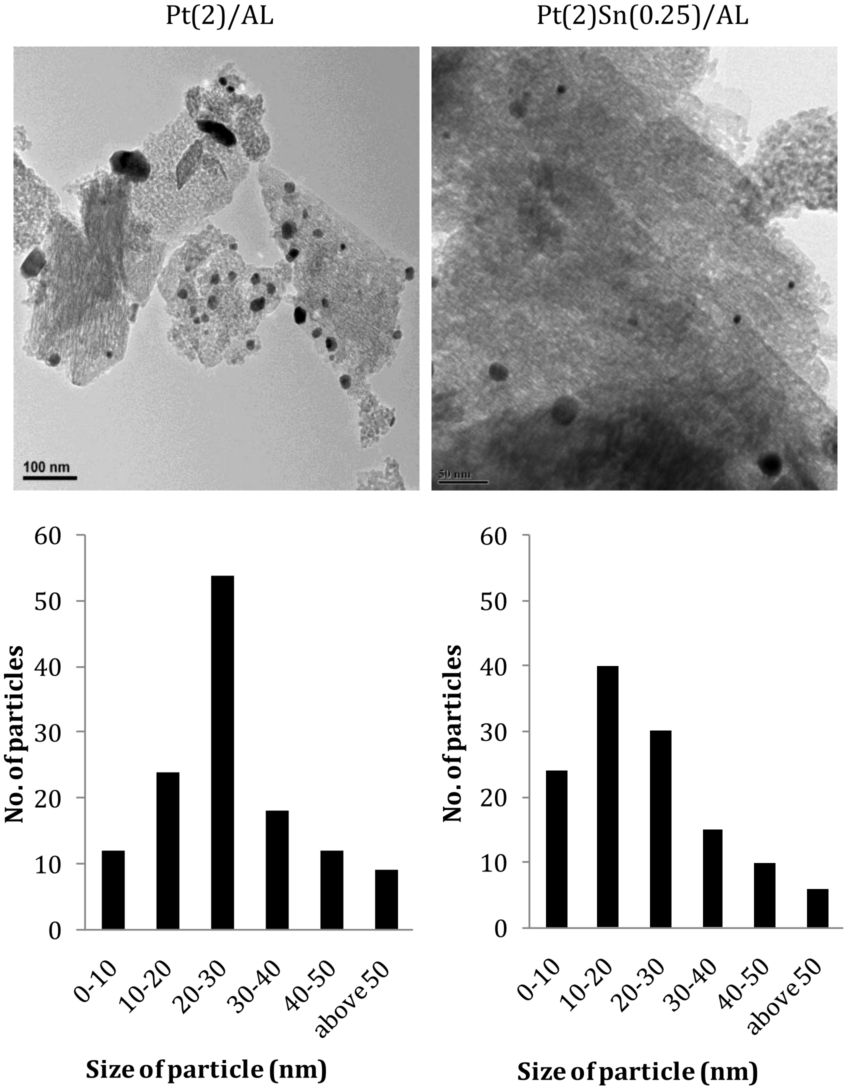


Figure 2.3.A. TEM images of Pt(3.5)/AL and Pt(3.5)Sn(0.43)/AL catalysts.

From TEM analysis, average particle size of Pt in the monometallic Pt(3.5)/AL catalyst was calculated to be 20-30 nm. On the contrary, in case of Pt(3.5)Sn(0.43)/AL catalyst average particle size of 10-20 nm was observed (Figure 2.3.A). The data advocates that with the addition of Sn, the migration of Pt on the support is minimized (during calcinations/reduction) and hence higher dispersion is acheived and smaller particles are formed. Moreover, it is reported that the catalytic activity of Pt/AL catalyst depends on the dispersion of the Pt.[3, 4] Pt-Sn/AL bimetallic catalyst showed higher dispersion for Pt than the monometallic Pt/AL catalyst. Similar conclusion was drawn from the XRD study of Pt/AL and Pt-Sn/AL catalysts where peak intentisity for Pt was low in Pt-Sn/AL owing to higher dispersion contrast to Pt/AL.



Pt(2)/AL

Pt(2)Sn(0.25)/AL

Figure 2.3.B. TEM images of Pt(2)/AL and Pt(2)Sn(0.25)/AL catalysts.

Similar results were observed from TEM analysis of Pt(2)/AL and Pt(2)Sn(0.25)/AL (Figure 2.3.B). Particle size of Pt was smaller in Pt(2)Sn(0.25)/AL (10-20 nm) than in Pt(2)/AL (20-30 nm). Although the particle size of Pt in bimetallic catalysts (Pt(3.5)Sn(0.43)/AL & Pt(2)Sn(0.25)/AL) was smaller than in monometallic catalysts (Pt(3.5)/AL & Pt(2)/AL), bigger particles (30-40 nm) were observed when Sn loading is higher (1.75wt% & 3.5wt%). These bigger particles can be assigned to intermetallic systems like Pt_3Sn and PtSn. From XRD, it was concluded that intermetallic systems like Pt_3Sn and PtSn were formed at higher Sn loading. Moreover, the morphological study of various Pt-Sn intermetallic systems is also reported.[5] According to this report, Pt_3Sn and PtSn species show triangular, cubic or hexagonal morphology. In current work, TEM images of Pt(3.5)Sn(3.5)/AL showed some particles with cubic and hexagonal morphology (Figure 2.3.C).

These results reinforce the formation of Pt_3Sn and PtSn intermetallic systems in the catalyst with higher Sn loading. TEM images of various monometallic and bimetallic catalysts are shown in Figure 2.3.C and average particle size of metal is mentioned below each image. Metal particle size varies from catalyst to catalyst even when metal is same and support was changed. For example, Pt particle size was very small over C (5-10 nm) and C-HT support (<3 nm) than over AL and SA support (20-30 nm). Ru(2)/C and Ru(2)Sn(0.25)/C showed metal particle size less than 3 nm, while Ru(2)/AL and Ru(2)Sn(0.25)/AL showed metal particles of 20-30 and 30-40 nm, respectively. Bigger particle size in Ru(2)Sn(0.25)/AL indicates some kind of interaction between Ru and Sn. It is reported that Sn can interact strongly with Ru which can alter the catalytic properties of Ru.[6] Addition of Sn to Ru catalyst causes the decrease in active site Ru surface which are responsible for hydrogen activation.[7, 8] Furthermore, formation of intermetallic systems such as Ru_2Sn_3 and Ru_3Sn_7 is also reported and these intermetallic systems are less active towards hydrogenation than monometallic Ru catalyst.[9] But in current study formation of Ru-Sn intermetallic systems was not visible from XRD analysis of Ru(2)Sn(0.25)/AL catalyst.

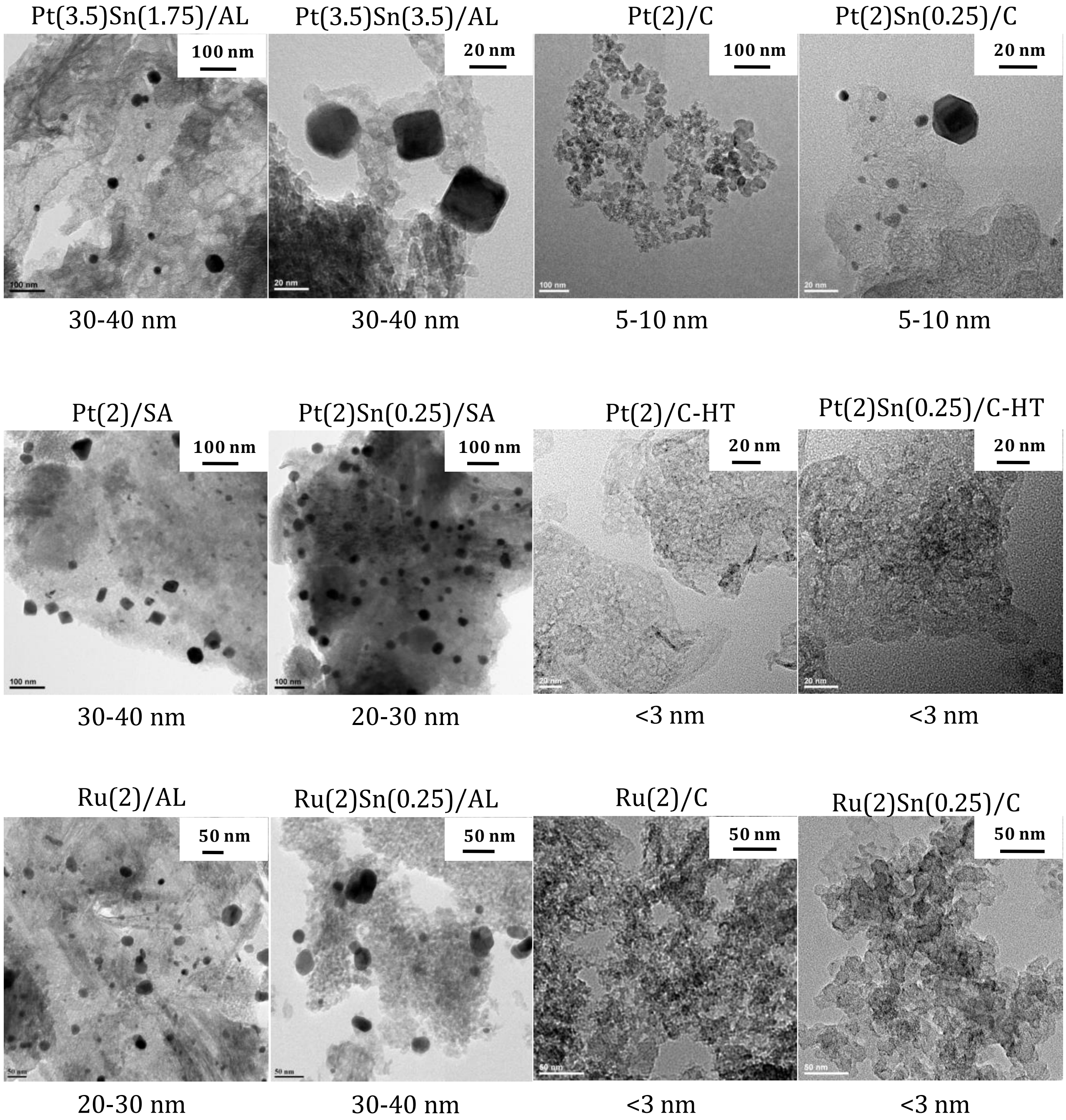


Figure 2.3.C. TEM images of various catalysts.

2.3.2.4. X-ray photoelectron spectroscopic (XPS) analysis

Oxidation states of Pt and Sn may play crucial role in catalytic activity of Pt-Sn/AL bimetallic catalysts. Hence, several researchers have studied Pt-Sn bimetallic systems to understand the consequence of oxidation states on the catalyst performance.[10-15] In one of the such studies, it is reported that even after reduction of metals at 500°C in hydrogen flow, Sn can still be present in (II) oxidation state.[11, 16, 17] In the present study, catalysts was reduced at 400°C for 2 h and therefore it is expected that Sn may be present in the higher oxidation state (ionic species). Researchers have also stated that in hydrogenation reaction of α, β unsaturated aldehydes like citral, metallic Sn can poison the active sites of Pt catalyst inhibiting the activation of hydrogen molecules whereas non-metallic Sn (in ionic form) can promote the activity of a catalyst .[11, 18] Hence in current study it might be advantageous, if Sn is present as ionic species in bimetallic catalysts. In view of this, it was indispensable to know the oxidation state(s) of Sn in the synthesized catalysts. For this, XPS experiments were carried out for Pt-Sn/AL bimetallic catalysts with varing Pt:Sn ratio (Figure 2.4).

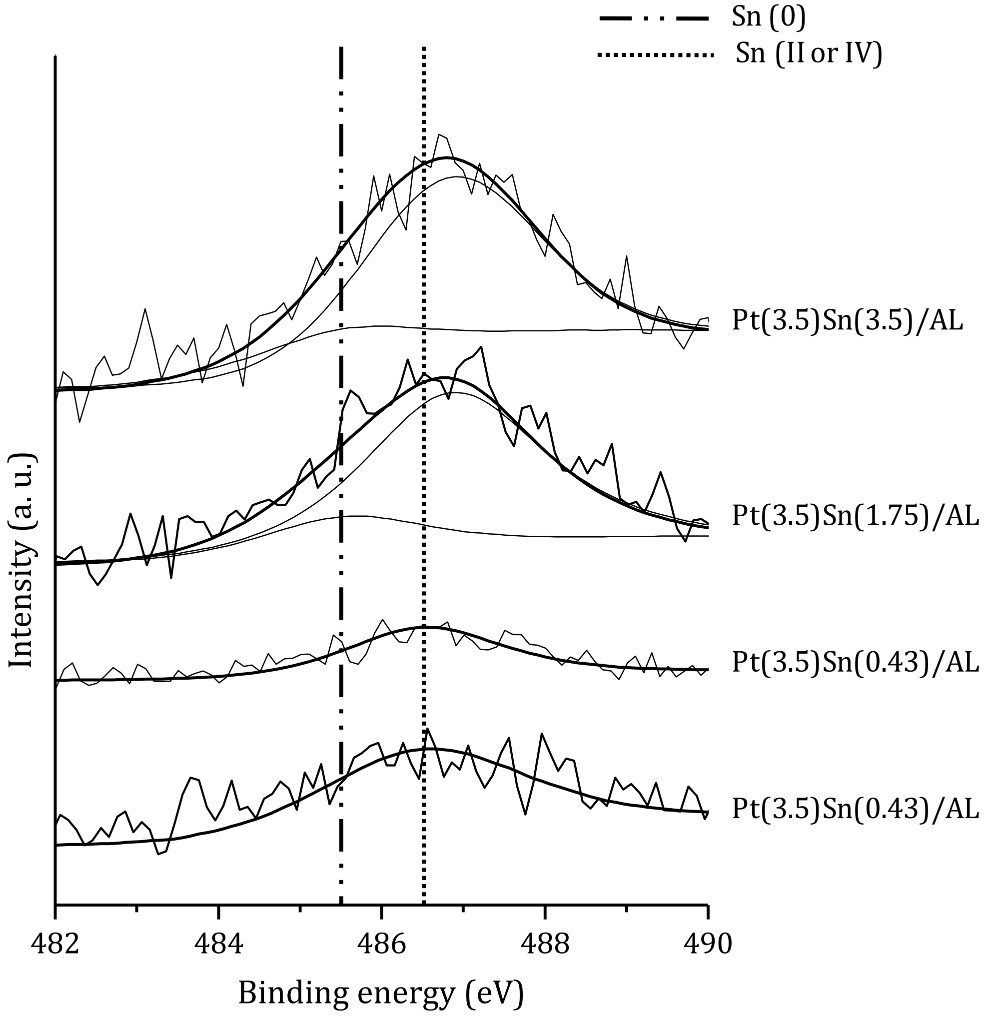


Figure 2.4. XPS stectra of Pt-Sn/AL bimetallic catalysts.

The Sn $3d_{5/2}$ XPS spectra of various Pt-Sn/AL catalysts (Figure 2.4) showed the presence of two types of Sn species i.e. Sn (II) or (IV) and Sn (0) states in the catalyst having higher Sn loading (1.75wt% and 3.5wt%). As against this, single species of Sn i.e. Sn (II) or (IV) was present when Sn loading was lower (0.43wt% and 0.87wt%). As summarized in Table 2.3, peak at 486.5±0.32eV was present in all the four catalysts while in Pt(3.5)Sn(3.5)/AL and Pt(3.5)Sn(1.75)/AL catalysts extra peak at 485.55 eV was also present. The major peak at 486.5±0.32 eV is a characteristic peak for the oxidized Sn species (II) or (IV) and the peak at 485.55 eV can be assigned to the metallic Sn (0) or alloyed Sn species. It is quite tricky to distinguish between Sn (II) and Sn (IV) species as the difference in binding energy is very small (0.2 eV).[19] Hence from XPS study, it can be concluded that Pt-Sn/AL catalyst having lower Sn content (0.43wt% and 0.87wt%) has Sn present in either (II) or (IV) state. But when the loading of Sn was increased to 1.75wt% and 3.5wt% then part of Sn was also present in the (0) state (metallic) and part of Sn was present in (II) or (IV) oxidation state. Unfortunately the XPS study for Pt was not possible because XPS spectra of Pt $4f_{7/2}$ and Al 2p interfere with each other.

Table 2.3. Results for XPS study of Pt-Sn/AL bimetallic catalysts.

Sr. No.	**Catalyst**	**Peak position**	**Sn species present**
1	Pt(3.5)Sn(0.43)/AL	486.23 eV	Sn (II) or (IV)
2	Pt(3.5)Sn(0.87)/AL	486.50 eV	Sn (II) or (IV)
3	Pt(3.5)Sn(1.75)/AL	486.82 eV & 485.55 eV	Sn (II) or (IV) & Sn (0)
4	Pt(3.5)Sn(3.5)/AL	486.82 eV & 485.55 eV	Sn (II) or (IV) & Sn (0)

2.3.2.5. N_2 sorption study

To determine the surface area of bare supports and change in their surface areas after impregnation of metals, N_2 sorption study was done. Results obtained for the N_2 sorption study of various supports and catalysts are shown in Table 2.4. From the data in this table, it is clear that surface area of all types of support materials i.e. AL (acidic), C (neutral) and C-HT (basic) was decreased after impregnation of metals. Higher metal dispersion can be achieved if support material has larger surface area. This might be the reason that over C better dispersion is achieved than AL. From XRD and TEM study it was proven that metal particle size was much smaller when C was used as a support. On the contrary, difference in the surface area of AL and C-HT is not so large, but the difference observed in the metal particle size is considerably large. This proves that factors other than surface area like support-metal interaction may play crucial role in governing the metal dispersion.

Table 2.4. Results for N_2 sorption study.

Sr. No.	**Catalyst**	**BET surface area** (m^2/g)	**Sr. No.**	**Catalyst**	**BET surface area** (m^2/g)
1	AL	179	7	Ru(2)/C	969
2	Pt(2)/AL	157	8	Ru(2)Sn(0.25)/C	943
3	Pt(2)Sn(0.25)/AL	164	9	C-HT	212
4	C	997	10	Pt(2)/C-HT	148
5	Pt(2)/C	958	11	Pt(2)Sn(0.25)/C-HT	134
6	Pt(2)Sn(0.25)/C	966			

2.3.2.6. Temperature programmed desorption (TPD) analysis

NH_3-TPD analysis: Acidity of the synthesized catalysts was determined by NH_3-TPD technique and acid amount of AL, Pt(2)/AL and Pt(2)Sn(0.25)/AL was found to be 0.4, 0.24 and 0.22 mmol/g respectively, while Pt(2)/C and Pt(2)Sn(0.25)/C did not show any acidity. NH_3-TPD profiles for AL supported catalysts are represented in Figure 2.5.A and profiles for C supported catalysts are represented in Figure 2.5.B.

TPD profile for AL support showed one broad peak at 180°C, which can be assigned to the presence of weak acid sites (0.4 mmol/g) on AL. However, after impregnation of Pt and Pt-Sn on AL, sharp decrease in the peak intensity was seen. A careful observation suggests that in Pt(2)Sn(0.25)/AL catalyst a new peak appears between 350-550°C may be due to the presence of Sn as $Sn^{+\delta}$ species (Lewis acid site). From this analysis, total acid amount was calculated and it was observed that after impregnation of metal(s) on the AL, total acid amount was decreased from 0.4 mmol/g (AL) to 0.24 mmol/g (Pt(2)/AL) and 0.22 mmol/g (Pt(2)Sn(0.25)/AL). This is obvious since it is expected that during the synthesis of catalysts, Pt and Sn will interact with the acidic sites of AL. On the contrary, carbon supported catalysts, Pt(2)/C and Pt(2)Sn(0.25)/C did not show any major peak since support (C) itself do not have any acidity. In Pt(2)Sn(0.25)/C catalyst a very low intensity peak between 400-500°C was observed, which may arise because of possible presence of $Sn^{+\delta}$ species. Even so, the calculation of acid amount based on this peak was almost impossible as the intensity of this peak was too low compared to the peak observed in Pt(2)Sn(0.25)/AL catalyst. This clearly indicates that, if at all Sn is present in +δ state, its concentration in Pt(2)Sn(0.25)/C catalyst is less than Pt(2)Sn(0.25)/AL catalyst. This implies, most of the Sn in Pt(2)Sn(0.25)/C is present in (0) state which can form intermetallic system with Pt. Formation of such intermetallic system (i.e. PtSn) in Pt(2)Sn(0.25)/C was evidenced from XRD analysis. For comparison purpose, NH_3-TPD study for Sn(0.25)/AL catalyst was performed and the profile shows a very low intensity peak at 400-500°C (Figure 2.5.A) due to the presence of $Sn^{+\delta}$ species. Here also, decrease in the peak intensity for AL was seen which imply that Sn may interact with AL and thus reduce the amount of acid sites on AL. Based on the NH_3-TPD study, it can be concluded that Sn interacts with the acid sites on AL to decrease their concentration[13] and also forms new type of acid sites which may be assigned to the formation of Lewis acid sites. Results for the NH_3-TPD experiments are consolidated in Table 2.5.

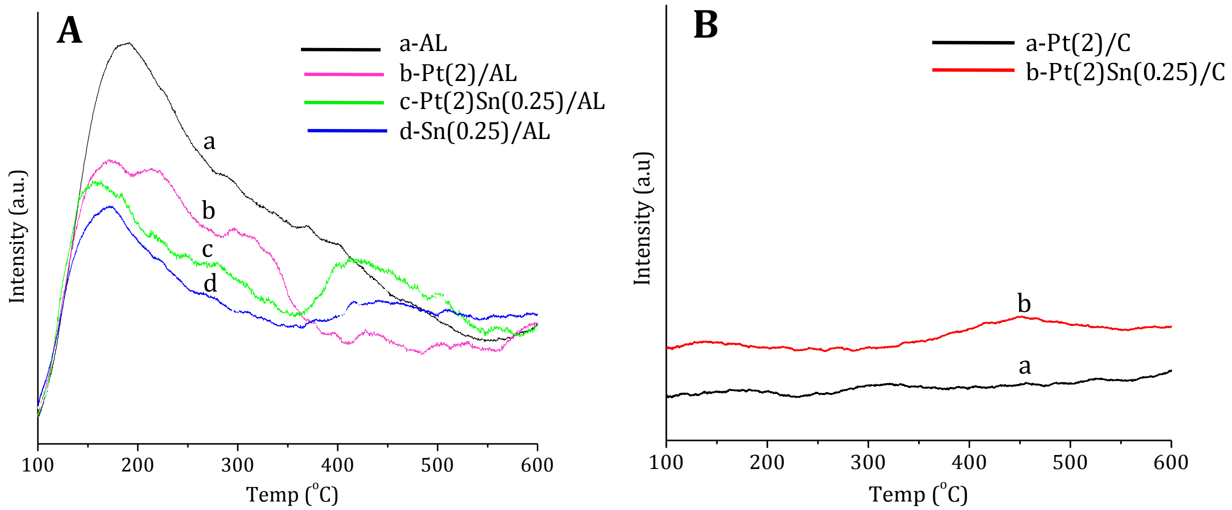


Figure 2.5. NH_3-TPD profiles of various catalysts.

CO_2-TPD analysis: CO_2-TPD technique was used for the determination of basicity of the synthesized catalysts. Basicity of calcined hydrotalcite (C-HT) was found to be 0.88 mmol/g, while for Pt(2)/C-HT and Pt(2)Sn(0.25)/C-HT it was 0.78 and 0.61 mmol/g, respectively. CO_2-TPD profiels for various catalysts are reprented in Figure 2.6.

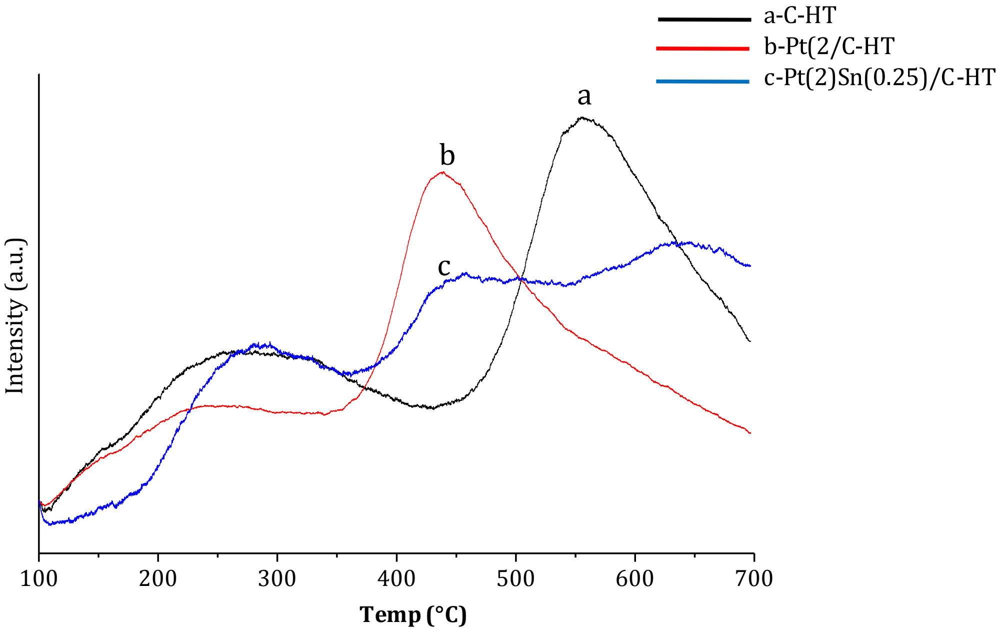


Figure 2.6. CO_2-TPD profiles of various catalysts.

CO_2-TPD profiles depict that after impregnation of Pt over C-HT, basicity was decreased. Moreover there is a shift in the peak position from 550°C to 450°C. This indicates that stronger basic sites are killed after impregnation. In case of Pt(2)-Sn(0.25)/C-HT further decrease in the basicity was observed. Basicity of the catalyst determined by CO_2-TPD is summarized in Table 2.5.

Table 2.5. Results for TPD analysis of various catalysts.

Sr. No.	**Catalyst**	**Acidity**[a] (mmol/g)	**Sr. No.**	**Catalyst**	**Basicity**[b] (mmol/g)
1	AL	0.40	5	C-HT	0.88
2	Pt(2)/AL	0.24	6	Pt(2)/C-HT	0.78
3	Pt(2)Sn(0.25)/AL	0.22	7	Pt(2)Sn(0.25)/C-HT	0.61
4	Sn(0.25)/AL	0.20	8	-	-

[a]determined using NH_3-TPD and [b]determined using CO_2-TPD

2.4. Conclusions

Various monometallic and bimetallic catalysts were synthesized for the conversion of mono- and poly-saccharides in to sugar alcohols. To explore the effect of supports in the entitled conversions, different types of support materials (acidic: AL, SA; Neutral: C; basic: C-HT) have been used. To study the effect of metals and promoters, monometallic and bimetallic catalysts using Pt or Ru as metal and Sn or Ga or Fe as promoter were synthesized. All supported metal catalysts were synthesized by wet impregnation method (co-impregnation for bimetallic catalysts).

Activity of the catalyst towards the particular reaction is governed by many physicochemical properties of the catalyst. Hence the detail characterizations of all synthesized catalysts were done using various characterization techniques. ICP-AES proved that the metal loading in all supported metal catalysts is nearly equal to the expected (theoretical) metal loading. XRD patterns of monometallic catalysts showed the characteristic peaks of the metal. Peak intensity varies from support to support according to the dispersion of metals. Diffractograms of the bimetallic catalysts showed interesting results and are much informative to interpret the support-metal and support-promoter interaction. When support-metal interaction is strong, mobility of metal particles on the support is restricted which results in the higher dispersion of metal on that particular support. Such a catalyst in which metal is finely dispersed on the support shows very low intensity peaks for metal in XRD pattern. On the other hand, if two metals in the bimetallic catalyst interact to form intermetallic system, characteristic peaks for the intermetallic system appears in XRD pattern of the catalyst. Pt(2)Sn(0.25)/C showed peaks for PtSn intermetallic system while Pt(2)Sn(0.25)/AL does not show any peak for PtSn. This is because Sn interacts with AL to form complex (surface shell), hence could not be reduced to Sn (0) state. Sn can interact with alumina through oxygen to form tin-aluminate like structure in which Sn is in (II) state.[17, 20] It is suggested that formation of surface shell prevents migration of Pt particles during calcinations and reduction, consequently smaller metal particle size was observed for Pt-Sn/AL catalyst in TEM analysis. On the other hand Sn could not interact with C to form the surface shell and hence could be reduced to Sn (0) which could form PtSn intermetallic system. XRD analysis of Pt-Sn/AL bimetallic catalysts with higher Sn loading (3.5wt% and 1.75wt%) evidenced the formation of PtSn and Pt_3Sn. It can be concluded that, Sn up to certain loading (less than 0.87wt%) can form complex with AL therefore cannot be reduced to Sn (0). At higher loading surplus Sn can be reduced to Sn (0) which can form intermetallic systems with Pt. XPS analysis reinforce the fact that up to optimum loading (0.87wt%), Sn is present in (II) or (IV) oxidation state while at higher loading, Sn (0) state is also observed along with (II) or (IV) state. TPD analysis of AL supported catalysts revealed that metal (Pt or Sn) interact with acidic sites on the AL support and hence acid amount was observed to be decreased in Pt/AL and Pt-Sn/AL catalysts. Similarly in C-HT supported catalysts, basicity of Pt/C-HT and Pt-Sn/C-HT was slightly less than bare C-HT support.

From aforementioned results it is comprehensible that physicochemical properties of the catalysts are governed by nature of support, metal and promoter. Effects of the various properties of the catalysts on the conversion of mono- and poly-saccharides in to sugar alcohols have been studied. Next chapters include the results and discussion for above mentioned conversions over monometallic and bimetallic catalysts.

2.5. References

1. R. Salomão, L. M. Milena, M. H. Wakamatsu and V. C. Pandolfelli, *Ceramics International*, 2011, **37**, 3063-3070.
2. J. M. Campelo, D. Luna, R. Luque, J. M. Marinas and A. A. Romero, *ChemSusChem*, 2009, **2**, 18-45.
3. C. Corolleur, D. Tomanova and F. G. Gault, *Journal of Catalysis*, 1972, **24**, 401-416.
4. B. Veldurthy, J. M. Clacens and F. Figueras, *Advanced Synthesis & Catalysis*, 2005, **347**, 767-771.
5. X. Wang, L. Altmann, J. r. Stöver, V. Zielasek, M. Bäumer, K. Al-Shamery, H. Borchert, J. r. Parisi and J. Kolny-Olesiak, *Chemistry of Materials*, 2013, **25**, 1400-1407.
6. V. A. Mazzieri, M. R. Sad, C. R. Vera, C. L. Pieck and R. Grau, *QuÃmica Nova*, 2010, **33**, 269-272.
7. S. Galvagno, C. Milone, A. Donato, G. Neri and R. Pietropaolo, *Catalysis Letters*, 1993, **17**, 55-61.
8. S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, *Catalysis Letters*, 1991, **8**, 9-14.
9. S. G. Wettstein, J. Q. Bond, D. M. Alonso, H. N. Pham, A. K. Datye and J. A. Dumesic, *Applied Catalysis B: Environmental*, 2012, **117-118**, 321-329.

10. A. C. Muller, P. A. Engelhard and J. E. Weisang, *Journal of Catalysis*, 1979, **56**, 65-72.
11. R. Burch, *Journal of Catalysis*, 1981, **71**, 348-359.
12. R. Burch and L. C. Garla, *Journal of Catalysis*, 1981, **71**, 360-372.
13. R. Bacaud, P. Bussiĕre and F. Figueras, *Journal of Catalysis*, 1981, **69**, 399-409.
14. B. Coq and F. Fgiueras, *Journal of Molecular Catalysis*, 1984, **25**, 87-98.
15. H. Lieske and J. Völter, *Journal of Catalysis*, 1984, **90**, 96-105.
16. G. T. Baronetti, S. R. de Miguel, O. A. Scelza and A. A. Castro, *Applied Catalysis*, 1986, **24**, 109-116.
17. B. A. Sexton, A. E. Hughes and K. Foger, *Journal of Catalysis*, 1984, **88**, 466-477.
18. G. Neri, C. Milone, S. Galvagno, A. P. J. Pijpers and J. Schwank, *Applied Catalysis A: General*, 2002, **227**, 105-115.
19. J. Llorca, P. R. r. de la Piscina, J. L. G. Fierro, J. Sales and N. s. Homs, *Journal of Molecular Catalysis A: Chemical*, 1997, **118**, 101-111.
20. K. Balakrishnan and J. Schwank, *Journal of Catalysis*, 1991, **127**, 287-306.

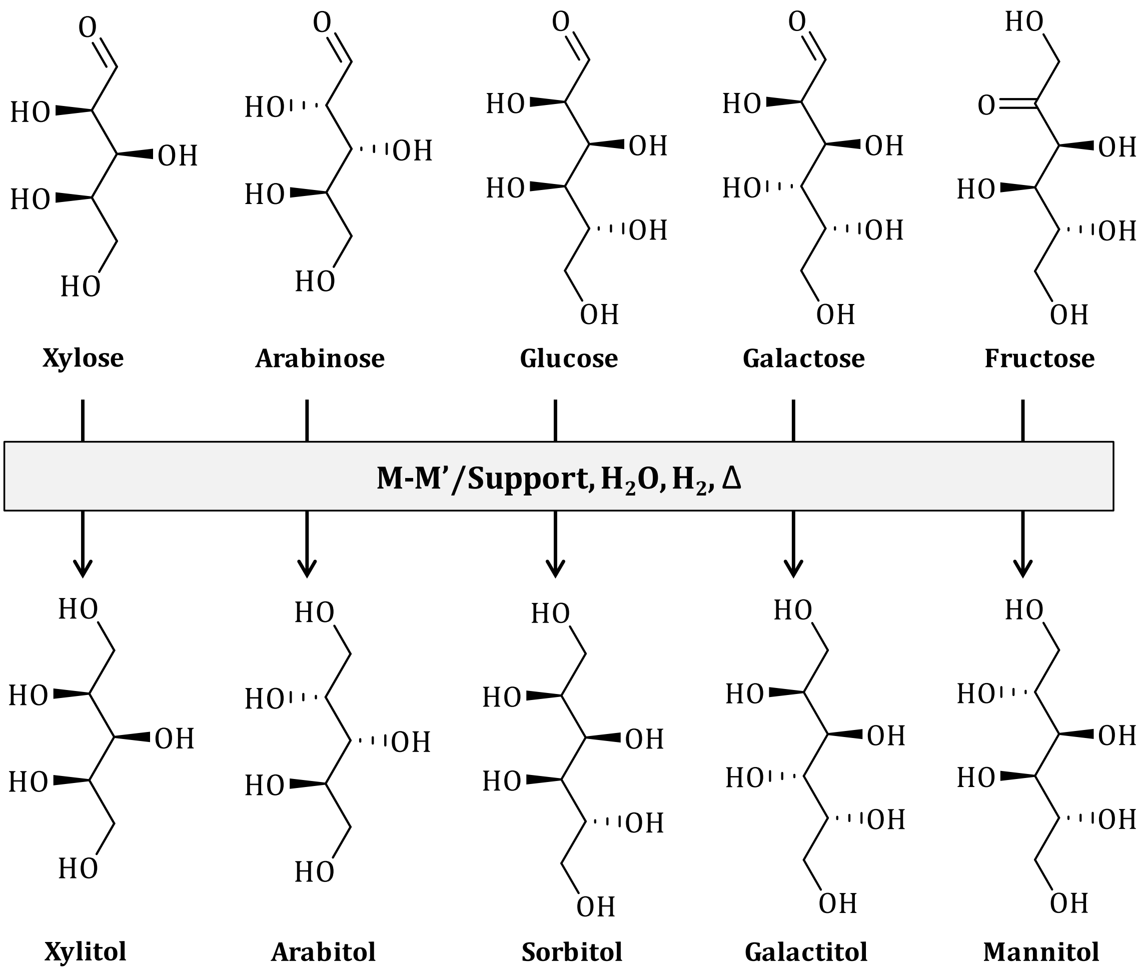
Chapter 3

Conversion of monosaccharides in to sugar alcohols

3.1. Introduction

Importance of the sugar alcohols in food, pharmaceutical and cosmetic industries is well recognized since last few decades (for more details refer chapter 1, section 1.2.1).[1-9] Sugar alcohols are often used in oral hygiene products because of its anti caries property. Low calorie content and non-diabetic nature of sugar alcohols make them promising alternative sweetener for diabetes patients.[10, 11] Owing to these applications in day to day life, demand for sugar alcohols is increasing persistently.[12, 13] Several processes for the conversion of mono- and poly-saccharides in to sugar alcohols are known, but those are associated with some common drawbacks like low yields of sugar alcohols, use of homogeneous catalysts, requisite of strong reaction conditions and poor recyclability of the catalyst (refer chapter 1, section 1.2.2).[14]

To overcome the shortcomings of conventional methods, monometallic and bimetallic supported metal catalysts were synthesized and evaluated for the conversion of mono- and poly-saccharides in to sugar alcohols. In current chapter results for the conversion of monosaccharides i.e. C5 sugars (xylose and arabinose) and C6 sugars (glucose, galactose and fructose) to yield sugar alcohols are discussed comprehensively. Effects of support materials, metals and promoters on the catalytic activity of the catalyst were studied as well as reaction parameters like time, temperature, H_2 pressure, catalyst quantity, etc. were optimized for better yields of sugar alcohols. Catalytic activities of catalysts towards the entitled conversions were correlated with their physicochemical properties determined by various characterization techniques. Furthermore, plausible reaction pathway for the formation of sugar alcohols and other side products like glycols (glycerol, ethylene glycol, 1,2-propanediol) and furans (furfural and furfuryl alcohol) from monosaccharides over supported metal catalyst is also discussed. Recycle study was done to check the stability of catalysts at applied reaction conditions. Alteration of catalyst properties during reaction was checked by subjecting spent catalyst to various characterization techniques. Work undertaken for the production of sugar alcohols by hydrogenation of C5 and C6 sugars over supported metal catalysts is represented in Scheme 3.1.



(M=Pt/Ru, M'=Sn/Ga/Fe, Support=AL/SA/C)

Scheme 3.1. Conversion of C5 and C6 sugars in to sugar alcohols.

3.2. Materials and methods

3.2.1. Materials

Chemicals: Xylose (99%) and arabinose (99%) were purchased from Loba Chemicals, India. Glucose (99%), galactose (98%), fructose (99%), galactitol (99%), mannitol (99.5%), xylitol (99%), arabitol (99%), glycerol (98%), ethylene glycol (99%), 1,2-propanediol (99.5%), furfural (99%), were procured from s.d. fine chemicals, India. Levulinic acid (98%), furfuryl alcohol (98%), sorbitol (99.9%) were purchased from Aldrich Chemicals, USA.

Catalysts: Various monometallic and bimetallic catalysts were prepared by wet impregnation method and evaluated for titled conversion. Detail information about supports, metal precursors and synthesis procedure is given in chapter 2 (refer section 2.2.1 and 2.2.2).

3.2.2. Experimental set-up and catalytic methods

All the catalytic and non-catalytic runs were carried out in batch mode autoclave (Amar Equipments make batch reactor) with 50 mL capacity. In a typical reaction, 0.15 g substrate (monosaccharide), 0.075 g catalyst (substrate/catalyst ratio was kept constant as 2 (*wt/wt*)) and 35 mL of water was charged in reactor. H_2 with required pressure (8-24 bar at room temperature) was fed in the reactor after flushing the reactor with H_2 for 3-4 times. Reactions were performed at desired reaction temperature ranging between 110°C and 190°C, for various times (15 min- 2 h). Reaction mixture was stirred at 150 rpm until desired reaction temperature is reached and after that stirring was increased to 900 rpm. This time was considered as starting time of the reaction. Upon completion of reaction, autoclave was cooled to room temperature under the flow of air. The gas was vent off and the reaction mixture was collected. Catalyst was separated from the reaction mixture by centrifugation and the liquid was filtered through 0.22 μm syringe filter and was analyzed using high performance liquid chromatography (HPLC).

3.2.3. Analysis of reaction mixture

The collected reaction mixture was centrifuged and upper layer was decanted. The solution was filtered through 0.22 μm syringe filters before analysis. Reaction mixtures were analyzed using HPLC (Agilent Technologies, 1200 infinity series, USA) equipped with HC-75 Pb^{++} (Hamilton, 7.8 mm x 300 mm) column maintained at 80°C and refractive index detector (Agilent Technologies, 1200 infinity series) maintained at 40°C. HPLC grade water was used as an eluent, at a flow rate of 0.6 mL/min. Reaction mixture was also analyzed using HPLC (Agilent Technologies, 1200 infinity series, USA) equipped with HC-75 H^+ (Phenomenex, 7.8 x 300 mm) column (maintained at 60°C). Sulfuric acid (0.5 mmol) was used as an eluent (0.6 mL/min) and for the detection of products, the RID (Agilent Technologies, 1200 infinity series) was used. Standards were used to calibrate all the compounds.

3.2.4. Calculations

Conversion of the substrate was calculated by following formula:

Conversion of monosaccharide (%) = {Moles of monosaccharide charged – Moles of monosaccharide unconverted / Moles of monosaccharide charged} × 100

In the conversion of monosaccharides, moles unconverted were calculated by HPLC analysis of reaction mixture before and after reaction.

Yield (%) = {Moles of product formed / Theoretical moles of product} × 100

3.3. Results and discussion

Results for the conversion of monosaccharides in to sugar alcohols over monometallic as well as bimetallic catalysts are consolidated in this section. Xylose, a C5 sugar is the main component of xylan (hemicellulose) and gives xylitol as a major product upon hydrogenation. With regards to the importance of xylitol (as explained in chapter 1, section 1.2.1) and availability of xylose in the form of hemicelluloses (second most abundant plant derived polysaccharides), the conversion of xylose for the production sugar alcohols was studied.

3.3.1. Conversion of xylose over monometallic catalysts

Xylose hydrogenation was carried out over Pt and Ru catalysts synthesized using various support materials like γ-Al_2O_3, SiO_2-Al_2O_3 and activated carbon to check the effect of supports and metals on the entitled conversion.

3.3.1.1. Effect of supports (γ-Al_2O_3, SiO_2-Al_2O_3, activated carbon) and metals (Pt and Ru)

To examine the effects of supports, Pt based catalysts were prepared using γ-Al_2O_3 (AL), SiO_2-Al_2O_3 (SA) and activated carbon (C) as a support material and evaluated in xylose hydrogenation reactions at 190°C for 15 minutes of reaction time. Experiments were carried at 16 bar H_2 pressure with substrate/catalyst ratio (*wt/wt*) of 2. It is clear from the Figure 3.1 that, conversion of xylose and yield of sugar alcohols varies with support material. While 28% yield of sugar alcohols (xylitol+arabitol) was achieved over Pt(2)/AL catalyst, 22 and 15.5% sugar alcohols yields were obtained over Pt(2)/SA and Pt(2)/C catalysts, respectively. Highest yield and conversion was observed over Pt catalyst when AL was used as a support in comparison with SA and C which emphasizes that AL is a better support for preparation of Pt based catalysts.

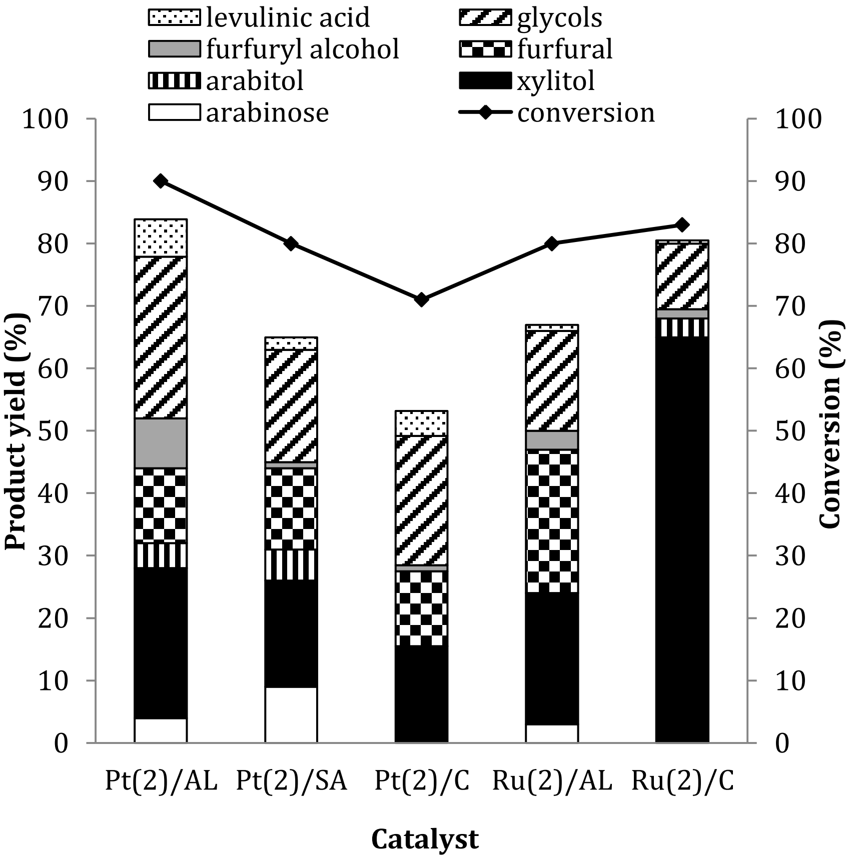
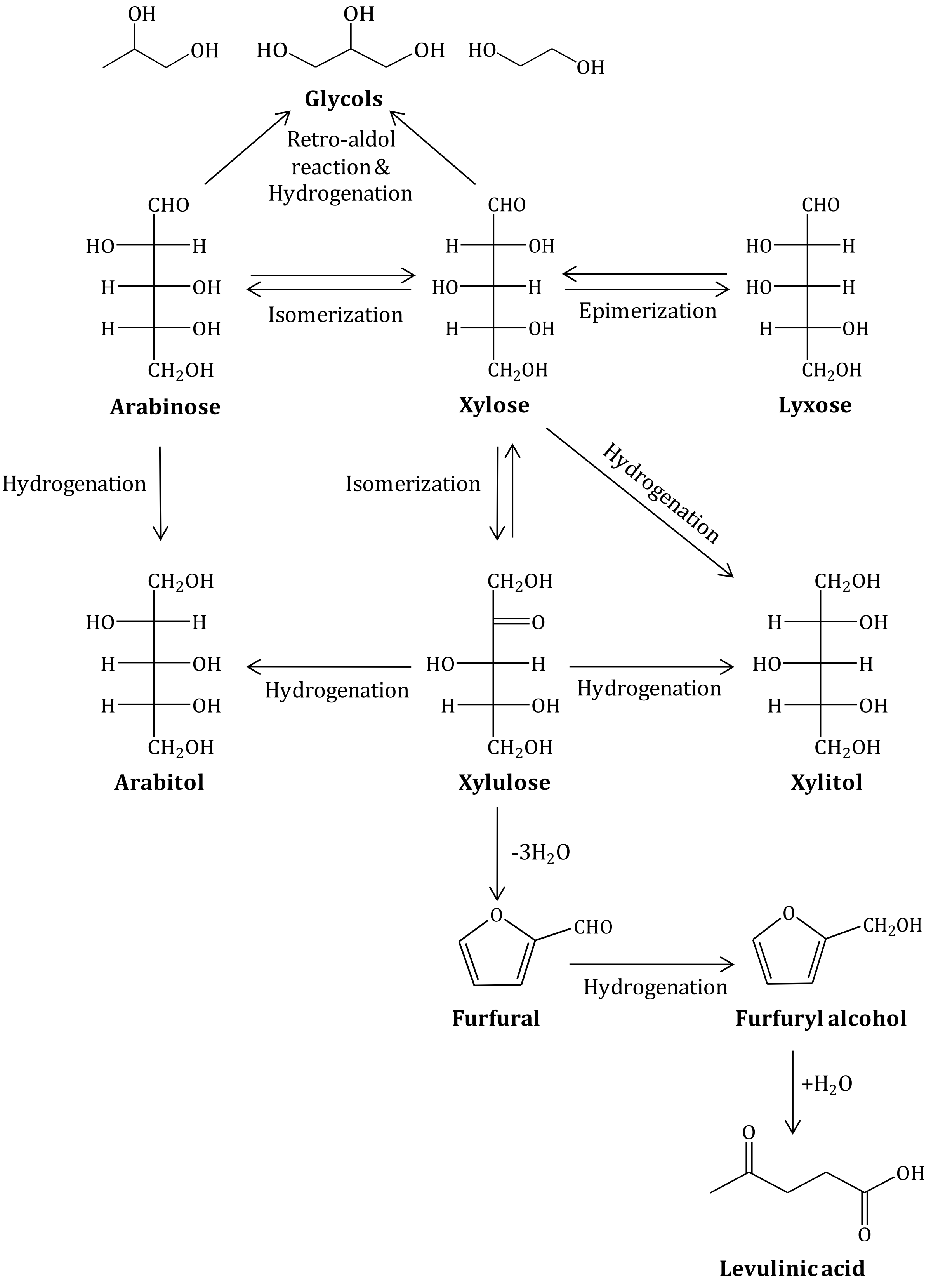


Figure 3.1. Effect of supports and metals on xylose conversion over monometallic catalyst.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

Though sugar alcohols are the desired products, undesired products like furfural, furfuryl alcohol, glycols (ethylene glycol, 1,2-propanediol, glycerol) and levulinic acid were formed. These byproducts have importance of their own in many fields. Pathway for the formation of various products from xylose is represented in Scheme 3.2.



Scheme 3.2. Conversion of xylose in to various products.

Further to confirm, whether the better yield of sugar alcohols over Pt(2)/AL is because of support (AL) or because of metal (Pt), other catalysts using Ru metal (Ru(2)/AL and Ru(2)/C) were synthesized and evaluated in the xylose hydrogenation reaction. Figure 3.1 shows that the performance of Ru(2)/AL catalyst was inferior (21% sugar alcohols yield) to Pt(2)/AL catalyst (28% sugar alcohols yield), while Ru(2)/C catalyst showed better yield of sugar alcohols (68%) than Pt(2)/C and Pt(2)/AL catalyst. This implies that activity of the catalyst towards the hydrogenation of xylose is governed by support-metal pair collectively and not by support or metal individually. Tendency of various monometallic catalysts towards sugar alcohols formation is as follows. Ru(2)/C (68% yield) > Pt(2)/AL (28% yield) > Pt(2)/SA (22% yield) > Ru(2)/AL (21% yield) > Pt(2)/C (15.5% yield).

Above results can be explained with the help of TEM analysis of catalysts (refer chapter 2, section 2.3.2.3) and varying tendency of xylose to get adsorbed on the different support. Average metal particle size in Ru(2)/C was 3 nm or less, in Pt (2)/C it was 8-10 nm while for Pt(2)/AL, Pt(2)/SA , Ru(2)/AL it was nearly 20-30 nm. As particle size goes on decreasing, dispersion of the metal i.e. number of the metal atoms present on the particle surface goes on increasing which eventually creates more active metal sites for hydrogenation reaction. Hence it was obvious to get highest yield of sugar alcohols over Ru(2)/C catalyst owing to highest dispersion of the metal compared to other catalysts. Pt(2)/C catalyst was supposed to show better yield than Pt(2)/AL, Pt(2)/SA , Ru(2)/AL catalysts because of smaller particle size of metal. In spite of smaller particles size (8-10 nm), its activity towards hydrogenation was less than all other catalysts. This miscellaneous result can be explained with the help of adsorption study of xylose over AL and C. Adsorption of substrate, xylose on support might be the reason for poor activity of Pt(2)/C catalyst towards xylose hydrogenation. To explain this result beyond doubt adsorption study of xylose on the support materials i.e. AL and C was undertaken. For this study, 1 g of support was added to the 1wt% xylose solution (200 mg xylose in 20 mL H_2O) and stirred at room temperature for 2 h in round bottom flask. Upon completion of the reaction, amount of xylose adsorbed on support was calculated by determining the concentration of xylose solution using HPLC. It was observed that, 1 g of C adsorbed 32 mg of xylose while 1 g of AL adsorbed merely 0.7 mg of xylose. This proves that considerable amount of substrate was adsorbed on C support which restricts the contact of substrate with active metal sites. Therefore Pt(2)/C showed poor activity than Pt(2)/AL or Ru/AL towards hydrogenation of xylose. On contrary, better activity over Ru(2)/C catalyst was achieved compared to Ru(2)/AL or Pt(2)/AL catalyst, in spite of using C as a support (which can significantly adsorb xylose). This is because of very small metal particle size in Ru(2)/C (<3 nm) which creates large number of finely dispersed active metal sites. As there were enough active metal sites on the catalyst surface most of the adsorbed substrate molecules could find active metal site in the close vicinity. Adsorbed substrate molecules were hydrogenated and other fresh molecules could access the active metal site. This was not the case when Pt(2)/C was used because of comparatively larger metal particle size and less number of active metal sites. These results depict that Ru(2)/C gave maximum yield of sugar alcohols (68%) among all monometallic catalysts screened for xylose conversion, hence further study was done using Ru(2)/C as a catalyst.

3.3.1.2. Effect of metal loading

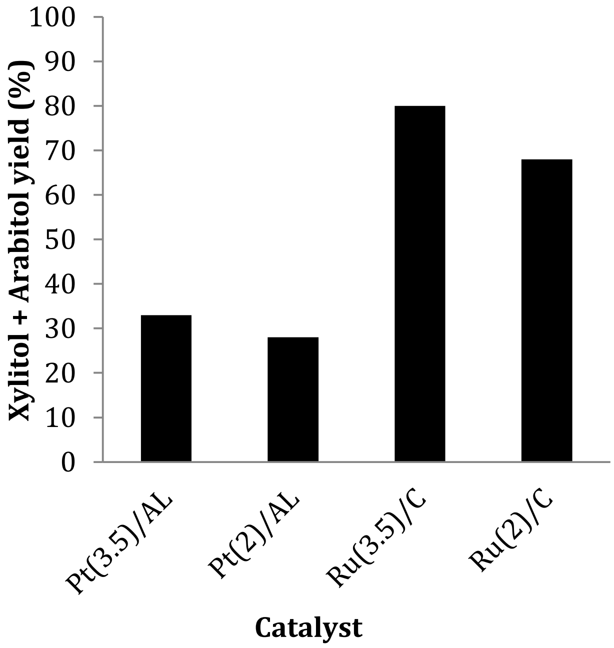


Figure 3.2. Effect of metal loading on xylose conversion over monometallic catalyst. Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

Effect of metal content in catalyst on its activity towards xylose hydrogenation was investigated, because number of active metal sites present in the catalyst varies with metal content. Activity of Ru(3.5)/C was compared with the Ru(2)/C at 190°C, for 15 minutes of reaction time at 16 bar H_2 pressure. As expected better yield of sugar alcohols (80% yield of xylitol+arabitol) was achieved over Ru(3.5)/C. This is much obvious because with increasing metal content in catalyst, number of active metal sites increases. Hence substrate molecules can easily locate the active site which gives better results. Even so, yield of sugar alcohols was improved by merely 12% in spite of increasing metal content to 3.5wt% from 2wt% (Figure 3.2).

Similar results were observed when activity of Pt(3.5)/AL was compared with the Pt(2)/AL catalyst. Maximum 33% yield of sugar alcohols was obtained over Pt(3.5)/AL against 28% yield over Pt(2)/AL (Figure 3.2). Other conclusion drawn from the above observations is, even though Pt loading was increased to 3.5wt%, sugar alcohol yield could not be improved more than 33% over Pt/AL catalyst. Owing to the good yield of sugar alcohols over Ru(2)/C, effect of other reaction parameters was studied using Ru(2)/C as a catalyst.

3.3.1.3. Effect of reaction parameters

Effect of reaction parameters like temperature, time, H_2 pressure and substrate/catalyst (S/C) (*wt/wt*) ratio was explored and reaction conditions were optimized to achieve the maximum yield of sugar alcohols over Ru(2)/C catalyst.

Effect of temperature and time: Conversion of xylose over Ru(2)/C was carried out at the reaction temperature ranging between 110°C and 190°C for various times (15 min-2 h) at 16 bar H_2 pressure. Figure 3.3 implies that at 110°C, 48% yield of sugar alcohols (52% conversion) could be achieved within 2 h. Higher conversions (87% and 91%) could be achieved at higher temperatures (130°C and 150°C) within short period of time (2 h), but the selectivity for sugar alcohols was less at higher temperature than at lower temperature. Selectivity for sugar alcohols was 92% at 110°C, while at 130°C and 150°C it was 90% and 85%, respectively. When temperature was further increased to 190°C, 83% conversion was observed in 15 minutes with 68% yield of sugar alcohols. Maximum 75% yield of sugar alcohols (93% conversion) could be obtained over Ru(2)/C within 30 minutes (80% selectivity).

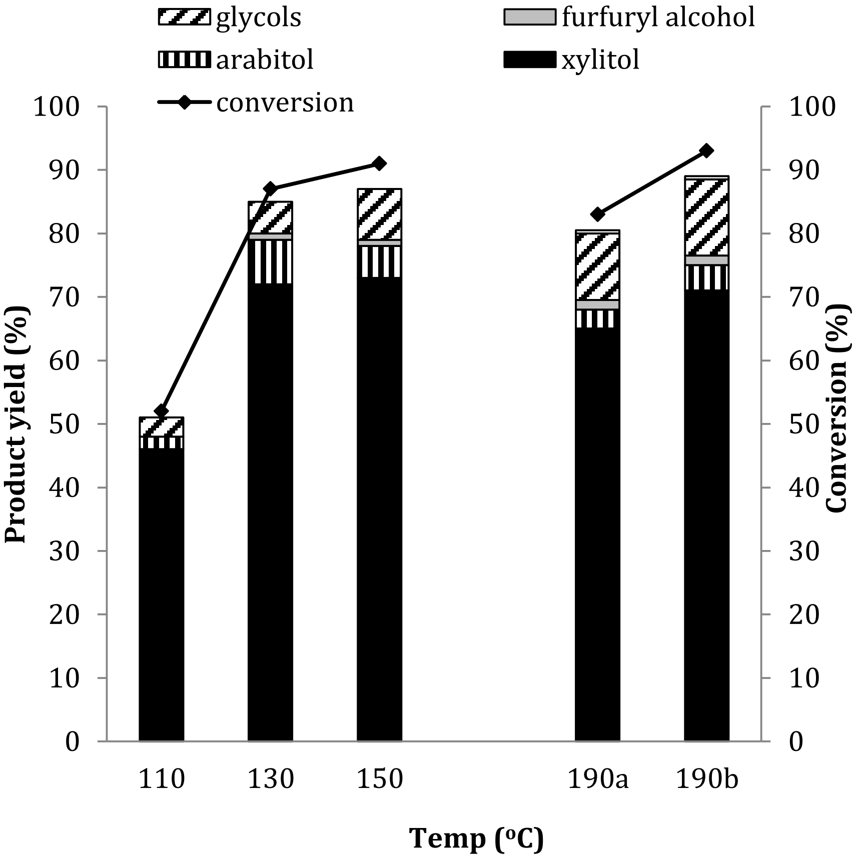


Figure 3.3. Effect of temperature and time on xylose conversion over Ru(2)/C catalyst.

Reaction condition: xylose 0.15 g, catalyst (Ru(2)/C) 0.075 g, water 35 mL, 16 bar H_2 at R.T., 2 h, a-15 min; b-30 min.

This is because, at lower temperature selectively C=O bond of carbonyl group of sugar molecules is hydrogenated rather than C-C bond breaking reactions which gives products like glycols and dehydration reactions to yield furfural, while at higher temperature side reactions are relatively more prominent than lower temperature. Conversion of sugar (here xylose) in to glycols takes place through retro-aldol reaction (which gives glyceraldehydes and glycoldehyde) followed by hydrogenation. But formation of glyceraldehydes and glycoldehyde by retro-aldol mechanism is favored at higher temperature (>160°C).[15-18] Hence with increasing reaction temperature, yield of glycols was observed to be increased and yield of sugar alcohols was decreased. On contrary hydrogenation of sugar to yield sugar alcohols is favored at lower temperature and sugar alcohols does not undergo further decomposition reactions at this temperature (130-190°C). Better yield and selectivity for sugar alcohols can be achieved by conducting reactions at lower temperature for longer time. On the other hand complete conversion is possible to achieve within short time at higher reaction temperatures, but with comparatively lower selectivity for sugar alcohols. Though the selectivity was low, other reaction parameters were optimized at higher temperature (190°C), because the stability of the catalyst needs to be verified at strong reaction conditions and it should give optimum yield at wide range of reaction conditions. Moreover, subsequent aim in the current work is to convert polysaccharides in to sugar alcohols. From literature it can be understood that such conversions need higher temperature. Therefore, other reaction parameters were optimized at higher reaction temperature, to presume the activity of catalyst in the polysaccharides conversion.

Effect of H_2 pressure: In hydrogenation reactions, pressure of H_2 gas in the reactor may significantly affect the yield of hydrogenation product (here sugar alcohols). Typically all xylose hydrogenation reactions were performed after charging 16 bar H_2 at room temperature. Though, to check the effect of H_2 pressure on the sugar alcohols formation, reactions were conducted after charging 8 and 24 bar H_2 at room temperature (Figure 3.4). Over Ru(2)/C catalyst after charging 8 bar H_2, 55% yield for sugar alcohols was observed. Against this, when 16 bar H_2 was charged, 68% yield was obtained. Next, after charging 24 bar H_2 in the reactor, no considerable improvement in the sugar alcohols yield (70%) was observed.

These results imply that until attaining the optimum H_2 pressure, sugar alcohols formation depends on the H_2 pressure. The solubility of gases in solvent is a function of temperature & pressure and hence with the increase in pressure enhancement in solubility of gas is predictable. One of the report states that, solubility of H_2 in water increases with increase in partial pressure of H_2 and respectively at 8, 16 and 24 bar approximately 0.21, 0.39 and 0.63 mL/g of H_2 is soluble in water at 198°C.[19] Hydride ion and proton (H^- and H^+) are generated from H_2 molecules on the active metal sites,[20-23] which further initiates hydrogenation of carbonyl group of sugar molecules.

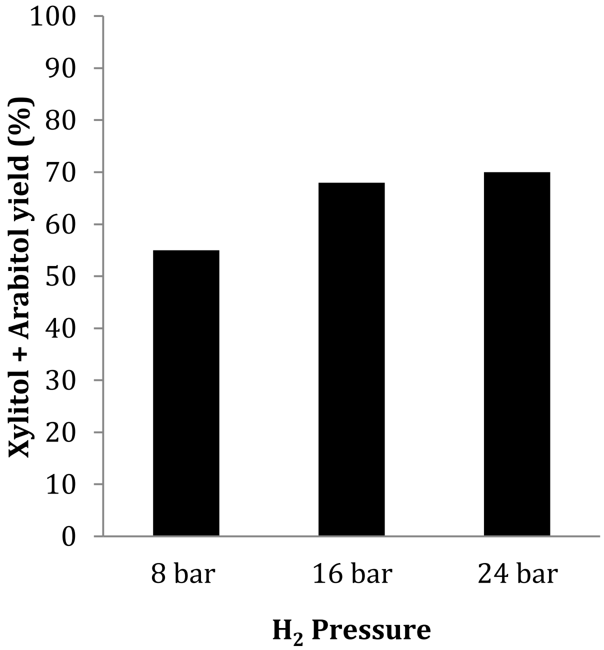


Figure 3.4. Effect of H_2 pressure on xylose conversion over Ru(2)/C catalyst. Reaction condition: xylose 0.15 g, catalyst (Ru(2)/C) 0.075 g, water 35 mL, 190°C, 15 min.

Hence the rate of reaction will be determined by concentration of H_2 molecules available in the reaction mixture, when concentration of substrate and number of active metal sites is constant. Accordingly, if solubility of H_2 in water improves with the increase in pressure from 8 to 16 bar then generation of sufficient amount of H^- and H^+ species (over active metal site) is probable.[19] Further improvement in the yield of sugar alcohols was not observed when pressure was increased to 24 bar. This is because, although with increase in pressure solubility of H_2 might have improved but number of active sites available for the activation of H_2 molecules remained same (as catalyst quantity was kept constant). In general for reaction to occur, substrate and H_2 molecule should get adsorbed on the metal surface. At lower pressure (8 bar) concentration of H_2 is lower at metal surface and at higher pressure (16 bar) concentration is more which help to achieve better catalytic activity but after certain pressure concentration of H_2 on the metal surface cannot be improved by further increment in pressure. Consequently similar yields were observed at 16 and 24 bar pressure, as active sites available for H_2 adsorption were same.

Effect of substrate/catalyst ratio: substrate/catalyst (S/C) ratio (*wt/wt*) is one of the crucial factors which can alter the conversion and product yields. Experiments were carried out with S/C ratio of 1, 2 and 4 at 190°C for 15 minutes, at 16 bar H_2 over Ru(2)/C. It was observed that with S/C ratio of 4 (catalyst quantity 0.038 g and xylose quantity 0.15 g in 35 mL H_2O) 58% yield of sugar alcohols was obtained (78% conversion) while with S/C ratio of 2 it was 68% (83% conversion). Considerable improvement in the yield of sugar alcohols was observed when catalyst quantity was increased from 0.038 g to 0.075 g. Further increment in yield (73%) was observed when 0.15 g catalyst was used i.e. S/C=1 (Figure 3.5).

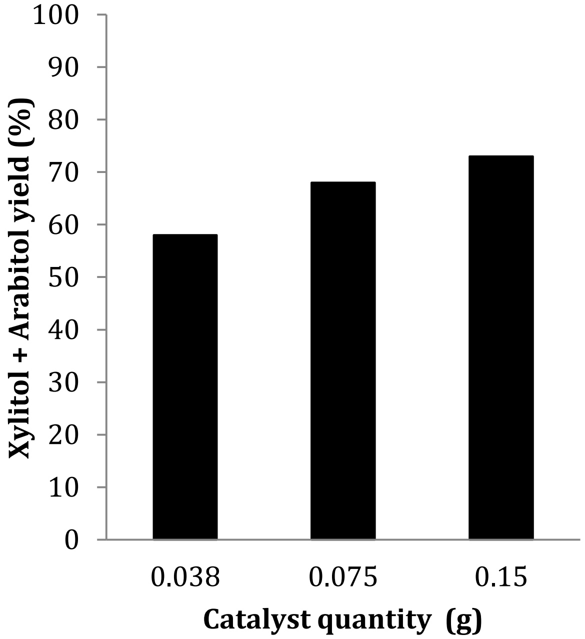


Figure 3.5. Effect of catalyst (Ru(2)/C) quantity on xylose conversion.
Reaction condition: xylose 0.15 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 15 min.

When 0.038 g of catalyst was used, active metal sites available for reaction were less and might be insufficient to convert all substrate molecules in to sugar alcohols in given time (15 minutes), because lower metal surface is available for the adsorption of substrate and H_2 molecules. Hence lower yield (58%) of sugar alcohols was observed. But when, 0.075 g catalyst was used to carry out the reaction, more active metal sites were available and hence better yield (68%) could be achieved, because higher metal surface is available for the adsorption of substrate and H_2 molecules. Relatively less improvement in the yield of sugar alcohols was observed over 0.15 g of catalyst in spite of having more active metal sites, because number of substrate molecules and H_2 molecules available for adsorption on the active sites was same.

3.3.1.4. Recycle study

Ru(2)/C showed best activity for the production of sugar alcohols among all monometallic catalysts in xylose hydrogenation. Hence the recyclability of the catalyst was checked for xylose hydrogenation at 190°C and 16 bar H_2. After reaction, catalyst was recovered from reaction mixture by centrifugation. Recovered catalyst was washed with distilled water thoroughly to get rid of any adsorbed product or unconverted substrate. This wet catalyst without drying or any other treatment (i.e. without calcination and reduction) was evaluated in next run at similar reaction conditions. The catalyst Ru(2)/C showed good recyclability up to 5th run (Figure 3.6). Minor loss of activity was observed after each run owing to the loss of some catalyst quantity during separation from reaction mixture. This ultimately, altered the S/C ratio in each run (0.15 g xylose was charged in each run).

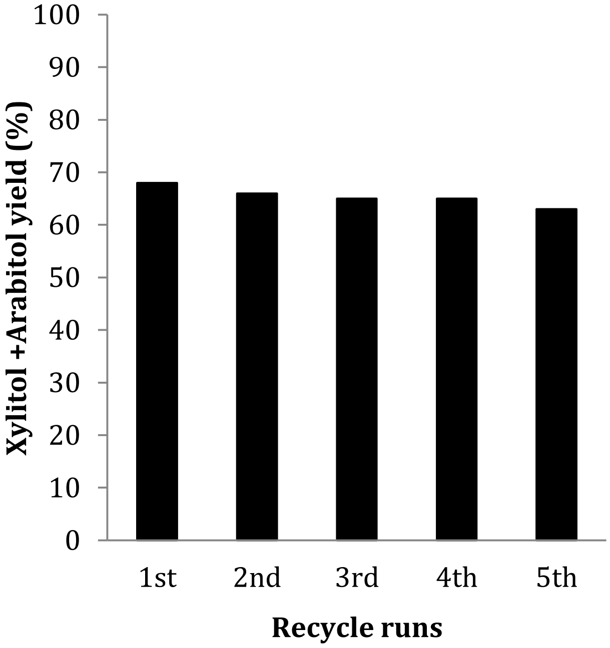


Figure 3.6. Recycle study for xylose conversion over Ru(2)/C catalyst.

Reaction condition: xylose 0.15 g, catalyst (Ru(2)/C) 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

It can be concluded from above discussion that, Ru(2)/C shows optimum yield of sugar alcohols (68% xylitol+arabitol) from xylose at 190°C and 16 bar H_2 pressure with (S/C) ratio 2 in 15 minutes of reaction time and catalyst shows good recyclability up to 5th run.

3.3.2. Conversion of xylose over bimetallic catalysts

As discussed earlier, good yield of sugar alcohols can be achieved from xylose over Ru/C catalysts. Nevertheless, there is definite scope to improve the sugar alcohol yield up to some extent. Furthermore, these monometallic catalysts, Ru(2)/C or Pt(2)/AL did not show good activity in the conversion of hemicelluloses. Results on the conversion of hemicelluloses in to sugar alcohols are discussed elaborately in next chapter (chapter 4.A). However, the conversion of xylan (a hemicellulose mainly composed of xylose) over monometallic catalyst is discussed here in brief to accentuate the need of bimetallic catalysts. In xylan conversion over Ru(2)/C, maximum 23% yield of sugar alcohols (xylitol+arabitol) was seen while over Pt(2)/AL maximum 15.5% yield of sugar alcohols was obtained. Yields could not be improved much by increasing metal loading of the catalysts. Over Ru(3.5)/C catalyst 25% yield of sugar alcohols was obtained and over Pt(3.5)/AL it was 18% (for more details refer chapter 4.A, section 4A.3.1.1.1).

In view of this, catalyst having good activity for the conversion of monosaccharides as well as for polysaccharides in to sugar alcohols needs to be developed. It is well known that activity of the supported metal catalysts can be improved by adding promoter to it. Role of promoter in enhancing the activity of the catalysts towards the particular reaction is discussed in chapter 1 (refer section 1.5.2). There are many reports in the literature in which metal promoters have been used to improve the activity of the catalysts.[24-34] In this work, to obtain sugar alcohols with better yields from sugars, it is vital to improve the efficiency of carbonyl group hydrogenation. From the earlier works it is learnt that better selectivity for unsaturated alcohols can be achieved from unsaturated aldehydes over bimetallic catalysts compared to monometallic catalysts, if an appropriate promoter is added.[35-37] Majority of the studies reveal that with Pt or Ru as a base metal, the selectivity for carbonyl group hydrogenation can be improved with the addition of promoters such as, Sn, Ga (non-transition element) or Fe (transition metal). Though, to enhance the performance of these catalysts it is essential that promoters are present in the ionic form ($Sn^{+\delta}$, $Ga^{+\delta}$, $Fe^{+\delta}$).[37] From most of the studies it is found that among all the promoters, Sn shows better results to obtain unsaturated alcohols from unsaturated aldehydes.[34, 37-43] For example, in carvone conversion selectivity for carveol was improved up to 70% from 30% using Pt-Sn/AL bimetallic catalyst.[42] Yet another report showed that in citral conversion, selectivity for nerol was increased from 20% to 83% using Pt-Sn/AL catalyst instead of Pt/AL.[43] Taking this into consideration, exploration of catalytic behavior of supported M-M'/Support catalyst (M, metal=Pt/Ru; M', promoter=Sn, Ga, Fe; support= AL, SA, C) in the synthesis of sugar alcohols (xylitol, arabitol) from xylose is studied.

3.3.2.1. Effect of Sn as promoter in Ru/C and Pt/AL catalysts

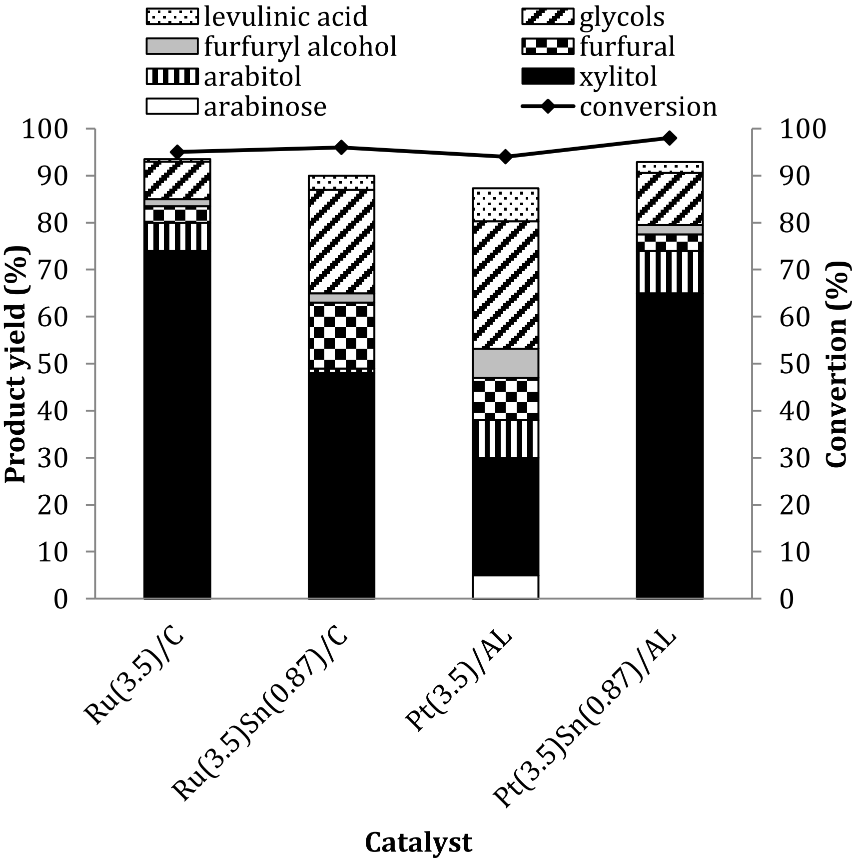


Figure 3.7. Effect of Sn as a promoter on xylose conversion.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

Among all monometallic catalysts evaluated for the xylose hydrogenation, Ru/C showed best yield of sugar alcohols followed by Pt/AL. Hence the effect of Sn as a promoter in these two catalysts was examined. Ru(3.5)Sn(0.87)/C and Pt(3.5)Sn(0.87)/AL were prepared and the activity of these bimetallic catalysts was compared with Ru(3.5)/C and Pt(3.5)/AL for xylose hydrogenation. Reactions were carried out at 190°C and 16 bar H_2 for 15 minutes. Results obtained for the xylose conversion over monometallic and bimetallic catalysts are shown in Figure 3.7. When Ru(3.5)Sn(0.87)/C was used instead of Ru(3.5)/C, yield of sugar alcohols was observed to be decreased by 31% (from 80% to 49%). In contrast, over Pt(3.5)Sn(0.87)/AL, 74% yield of sugar alcohols was obtained in comparison with 33% over Pt(3.5)/AL. This implies that activity of Pt/AL towards hydrogenation of xylose can be improved by adding Sn (promoter) in the catalyst, but the addition of Sn does not help to improve the activity of Ru/C catalyst. Before investigating the reasons for poor activity of Ru-Sn/C, efforts were taken to improve the yield of sugar alcohols over Pt-Sn/AL bimetallic catalysts. Pt:Sn ratio in bimetallic catalyst and other reaction parameters like temperature, time, S/C ratio, etc. were optimized for superior activity. Explanation for dwindle in the yield of sugar alcohols over Ru-Sn/C compared to Ru/C catalyst and reasons for the enhancement in the yield over Pt-Sn/AL are given in section 3.3.2.4 of this chapter.

3.3.2.2. Effect of Pt:Sn ratio on xylose conversion.

Effect of Pt:Sn ratio (*wt/wt*) on the catalytic activity of the catalyst was studied by preparing the series of catalysts having constant Pt loading (3.5wt%) and varying Sn loading (0-3.5wt%). When all these catalysts were evaluated at 190°C to verify their catalytic activity in xylose hydrogenation then following trend in the sugar alcohols yield was observed,

Pt(3.5)Sn(0.43)/AL (79% yield) ≥ Pt(3.5)Sn(0.22)/AL (77% yield) > Pt(3.5)Sn(0.87)/AL (74% yield) > Pt(3.5)Sn(1.75)/AL (68% yield) > Pt(3.5)Sn(3.5)/AL (45% yield) > Pt(3.5)/AL (33% yield)

From the above trend it is clear that bimetallic catalyst with 0.43wt% of Sn and 3.5wt% Pt on AL support gave best sugar alcohols yield (79%). It is noteworthy here that in all these reactions >90% xylose conversion was observed (except non-catalytic and reaction with bare support i.e. AL). Maximum yield of sugar alcohols (79%) over

Pt(3.5)Sn(0.43)/AL was allied with the decrease in the yield of side products (glycols and furans) to ca. 21% (Figure 3.8).

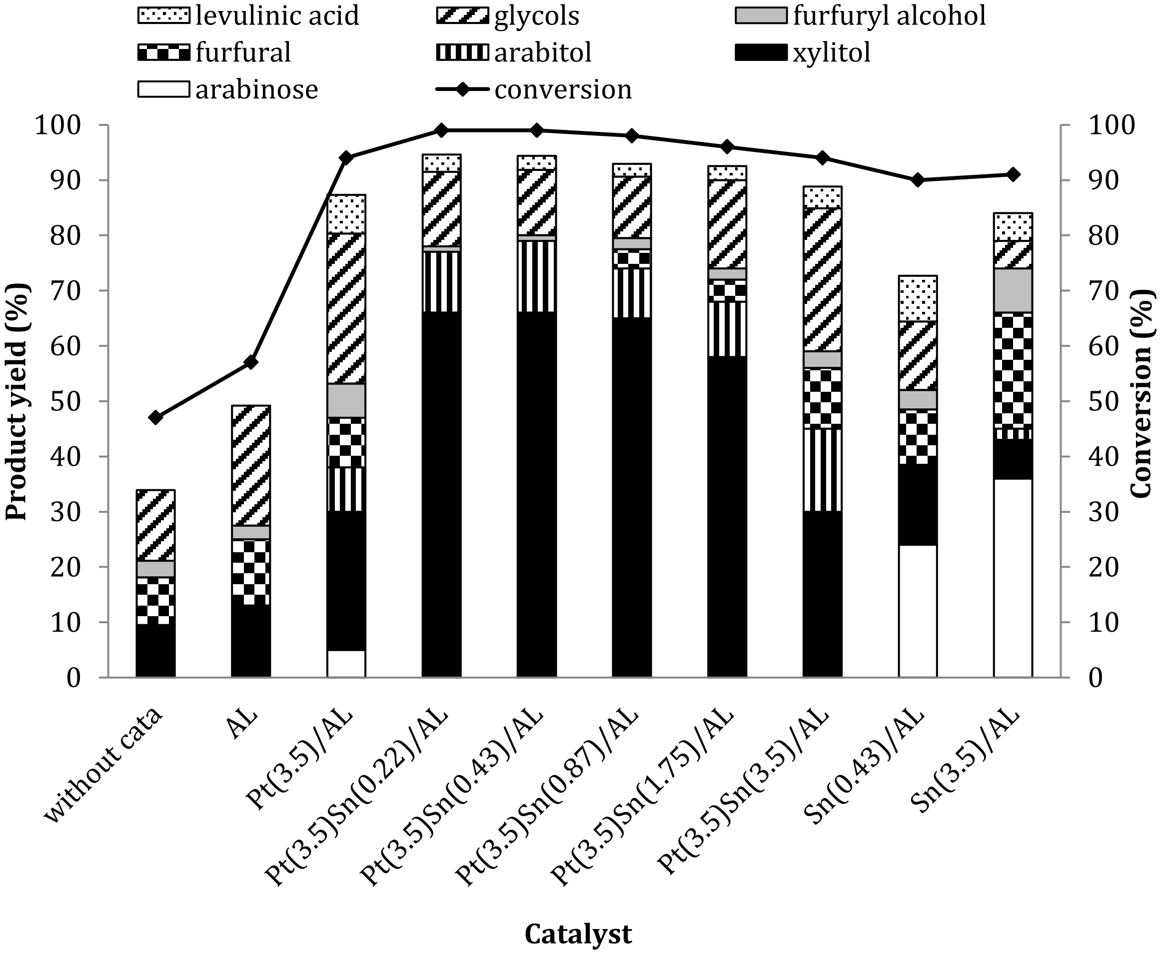


Figure 3.8. Effect of Pt:Sn ratio on the formation of sugar alcohols from xylose. Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

Above results also point out that, ca. 61% of side products formation (94% conversion) was observed over Pt(3.5)/AL catalyst. This raises a point that formation of the side products may happen directly from xylose since even though high concentration of sugar alcohols were present in the solution (over bimetallic catalyst) still side products were obtained in lower concentration. To confirm the pathway for side products formation, stability study of sugar alcohol, xylitol was carried out over Pt(3.5)Sn(0.43)/AL catalyst at 190°C for 1 h (instead of 15 minutes for which typical reactions are carried out). After the reaction it was found that only 8% of xylitol underwent conversion to yield 3% glycols and 4% arabitol. This implies that xylitol is almost stable under reaction conditions, so it is proposed that contribution from xylose in the formation of side products cannot be neglected as about ca. 21% yield for side products was achieved within 15 minutes of reaction time over Pt(3.5)Sn(0.43)/AL catalyst (Figure 3.8). From literature, it is known that glycols can be obtained from both sugars (by retro-aldol reaction followed by hydrogenation) as well as from sugar alcohols (by hydrogenolysis).[16] One of the report stated that conversion of sugars (glucose and fructose) in to glycols by retro-aldol mechanism occurs only at higher temperature (>160°C), while at lower temperature formation of sugar alcohols is suggested.[15] Moreover, formation of glycols from xylose by retro-aldol reaction in presence of solid base and supported metal catalyst at 200°C is known.[44] In current study reactions were carried out at 190°C, hence there is the possibility of glycols formation from sugars. Similarly, when xylitol stability was checked over Pt(3.5)/AL catalyst, merely 5% yield for glycols was observed. This again confirmed that the side products can be obtained directly from xylose. Based on this data it is apparent that bimetallic catalysts drive the reaction towards the augmentation of desired product, sugar alcohol by suppressing side reactions to yield side products such as glycols and furans. From Figure 3.8, it is obvious that over Pt(3.5)/AL catalyst, furfural was formed which is expected only when xylose undergoes dehydration reaction in acidic medium. The formation of furfural also explains that Pt(3.5)/AL catalyst is not capable for immediate formation of sugar alcohols by hydrogenating xylose. However, further conversion of furfural to furfuryl alcohol (hydrogenation reaction) is feasible over Pt(3.5)/AL catalyst up to some extent. Besides this, formation of levulinic acid was also observed on this catalyst. Contrast to this over bimetallic catalysts having Sn loading of 0.22 and 0.43wt% formation of furfural was not observed but sugar alcohols yields were enhanced. Vigilant observation of the results shows that considerable amount of furans (furfural and furfuryl alcohol) was formed over Pt(3.5)Sn(1.75)/AL and Pt(3.5)Sn(3.5)/AL (6% and 14%, respectively). This indicates that with increasing Sn content, yield of furans was increasing. Another information can be gathered from the Figure 3.8 is that with Pt(3.5)Sn(0.43)/AL catalyst, formation of arabitol (13%) was observed which means that Sn plays a role in the epimerization of xylitol. To verify whether Sn alone can catalyze the hydrogenation reaction, experiments were done with Sn/AL monometallic catalysts at 190°C for 15 minutes. Both, Sn(0.43)/AL and Sn(3.5)/AL catalysts showed very pitiable yields of sugar alcohols, 14.5% and 9%, respectively indicating that Sn alone is not capable of converting xylose in to sugar alcohols. Although in these reactions the yield of sugar alcohols was low but the formation of arabinose and furans was visible. Careful observation of Figure 3.8 depicts that 5% yield of arabinose and 8% yield of arabitol was obtained over Pt(3.5)/AL catalyst. On the other hand with Sn(3.5)/AL as a catalyst, 36% yield for arabinose and 2% yield of arabitol along with 29% yield of furan was obtained. When reaction of xylose was performed under inert atmosphere (N_2, 16 bar at R.T.) with Sn(3.5)/AL catalyst, 30% yield of arabinose and 8% yield of furans (at 52% xylose conversion) was observed in 15 minutes at 190°C. These results confirm that Sn catalyzes the isomerization reaction of xylose as well as dehydration of xylose to furfural. It is reported in the literature that Sn can act as Lewis acid center ($Sn^{+\delta}$) and is capable of catalyzing isomerization reactions.[45-47] Lewis acid catalyzed dehydration of xylose is also know over Sn catalysts.[45] Reactions carried out without catalyst and with bare support i.e. AL showed 47% and 57% of xylose conversion, respectively with the formation of sugar alcohols in minor quantities (9.5 & 13%) (Figure 3.8).

3.3.2.3. Effect of metal loading

Similar to the monometallic catalyst, effect of metal content was examined on xylose hydrogenation over Pt-Sn/AL bimetallic catalysts. For this, Pt-Sn/AL catalysts with varying metal loading but fixed Pt:Sn ratio (1:0.12 (*wt/wt*)) were prepared and evaluated in xylose conversion at 190°C and 16 bar H_2 for 15 minutes. Maximum 79% yield of sugar alcohols (99% conversion) was achieved over Pt(3.5)Sn(0.43)/AL, whereas 73% (98% conversion) and 51% (88% conversion) yield was observed over Pt(2)Sn(0.25)/AL and Pt(1)Sn(0.12)/AL, respectively (Figure 3.9). Even though Pt loading was reduced to 2wt% from 3.5wt% in Pt-Sn/AL catalyst, yield was decrease merely by 6%. But when Pt(1)Sn(0.12)/AL was used, yield was decreased by 22% compared to Pt(2)Sn(0.25)/AL. Lower yield of sugar alcohols over Pt(1)Sn(0.12)/AL was allied with higher yield of side products. Hence for further studies Pt(2)Sn(0.25)/AL catalyst was used because of the better activity towards hydrogenation with optimum metal loading.

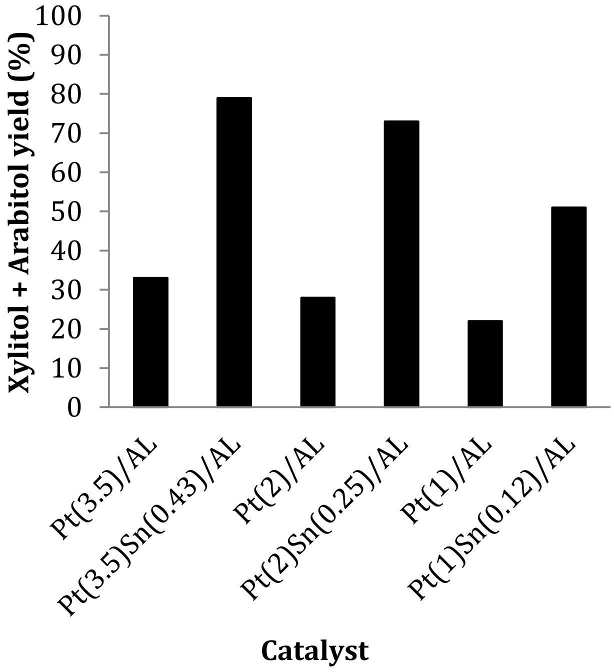


Figure 3.9. Effect of metal loading on xylose conversion over Pt-Sn/AL catalyst. Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

3.3.2.4. Effect of supports (γ-Al_2O_3, SiO_2-Al_2O_3, activated carbon) and metals (Pt and Ru)

Effect of supports and metals was studied for monometallic catalysts and it was found that metals interact differently with different support materials. Consequently properties of catalyst like dispersion of metals vary with support. Effect of support and metals can be more prominent in bimetallic catalysts. Because, excluding support-metal interaction, support-promoter and metal-promoter interactions exist in bimetallic catalysts. Hence, it is mandatory to inspect the consequence of supports and metals on the catalytic activity of bimetallic catalysts. Taking this into account, bimetallic catalysts using Sn as a promoter, Pt or Ru as a metal and AL, SA or C as a support, were synthesized and evaluated for xylose hydrogenation at 190°C and 16 bar H_2 for 15 minutes. As discussed earlier, Pt(2)Sn(0.25)/AL showed superior yield of sugar alcohols (73%) than Pt(2)/AL (28%) catalyst. Similarly, Pt(2)Sn(0.25)/SA showed enhanced yield of sugar alcohols (68%) compared to Pt(2)/SA (22%). To check the effect of C as a support on the hydrogenation activity, Pt(2)/C and Pt(2)Sn(0.25)/C were evaluated in the conversion of xylose under similar conditions. While over Pt(2)/C catalyst, 15.5% yield of sugar alcohols (xylitol+arabitol) with 71% conversion was obtained, Pt(2)Sn(0.25)/C catalyst yielded 22% of sugar alcohols (65% conversion) (Figure 3.10). These results indicate that there is no considerable improvement in the yield of sugar alcohols when Pt(2)Sn(0.25)/C was used instead of Pt(2)/C catalyst.

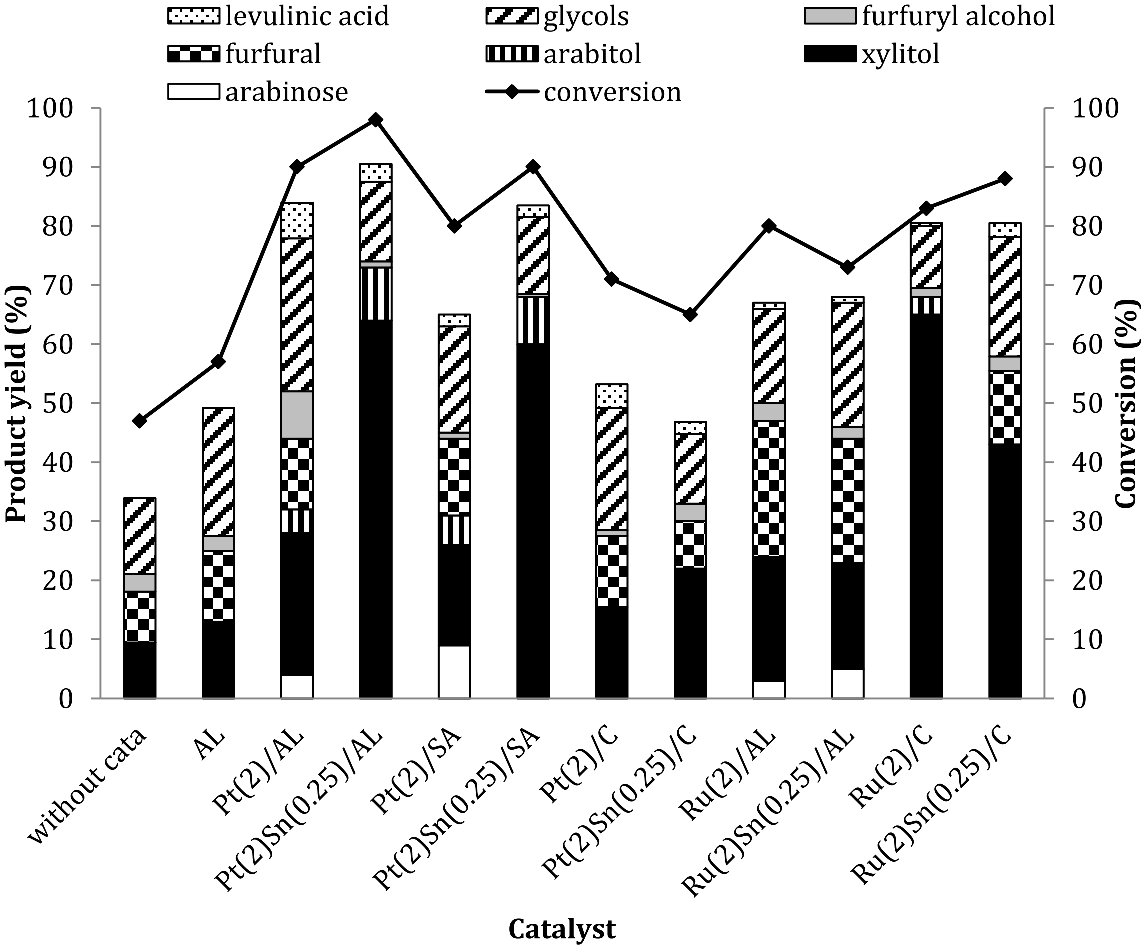


Figure 3.10. Effect of supports and metals on xylose conversion over bimetallic catalyst.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

Moreover, results presented in Figure 3.10 indicate that formation of furans (furfural and furfuryl alcohol) from xylose was possible even in the absence of catalyst

(11.6%). It is interesting to note that over Pt(2)/C catalyst similar yield for furans (13%) was seen as observed in non-catalytic reaction but, over Pt(2)/AL catalyst yield of furans was relatively more (20%). Difference in the furans yield over C and AL supported catalysts can be attributed to the presence of acidic sites on AL (0.4 mmol/g, refer chapter 2, section 2.3.2.6) those can catalyze dehydration reactions of sugars to yield furans. Nevertheless, formation of furan compounds was almost suppressed (1%), after incorporation of Sn in the Pt(2)/AL catalyst. However, over C supported catalyst (Pt(2)Sn(0.25)/C), almost similar yield of furans (11%) was observed after incorporation of Sn. Superior yield of sugar alcohols over Pt(2)Sn(0.25)/AL catalyst was possibly due to the availability of higher number of active metal sites (average particle size, 10-20 nm) than monometallic Pt(2)/AL catalyst (average particle size, 20-30 nm). Besides increase in active sites some other factors were also playing role in enhancing the sugar alcohols formation over Pt(2)Sn(0.25)/AL catalyst. It is reported in the literature that Sn interacts with the acidic sites of AL to form a complex and this in turn may decrease the number of acid sites in the catalyst.[28] In this work also, based on the NH_3-TPD analysis, it is proved that in Pt(2)Sn(0.25)/AL catalyst (0.22 mmol/g), less number of acid sites are present compared to Pt(2)/AL (0.24 mmol/g). The above discussions reveal that, increase in number of active metal sites and suppression of acidic sites were helpful to obtain higher yields of sugar alcohols over Pt(2)sn(0.25)/AL catalyst. AL supported catalysts were capable of isomerizing xylose to yield arabinose which in turn gives rise to arabitol which was almost not observed with C supported catalysts, since C catalysts do not show acidity unlike AL catalysts. It was also possible that once xylitol was obtained from xylose, it can undergo acid catalyzed epimerization reaction to yield arabitol over AL supported catalysts. This implies that formation of various products from the xylose is strongly affected by nature of support.

Furthermore, when promoter effect of Sn was explored in Ru catalysts, inferior yields were obtained over bimetallic Ru(2)Sn(0.25)/AL and Ru(2)Sn(0.25)/C catalysts. Ru(2)/AL and Ru(2)/C showed 21% and 68% yield of sugar alcohols while Ru(2)Sn(0.25)/AL and Ru(2)Sn(0.25)/C showed 18% and 43% yields, respectively. Over Ru(2)Sn(0.25)/AL sugar alcohol yield could not be improved even though AL was the support. Similar to the Pt(2)Sn(0.25)/C, in the case Ru(2)Sn(0.25)/C too, augmentation in the yield of sugar alcohols was not seen in comparison with Ru(2)/C catalyst. It can be concluded that improved activity of the bimetallic catalyst in together is govern by support, metal and promoter. The discrepancy in results over various catalysts is explained and correlated with the catalyst properties in next section (refer section 3.3.2.7).

3.3.2.5. Effect of reaction parameters

Reaction conditions in terms of temperature, time, H_2 pressure and catalyst quantity were optimized to achieve better yield over Pt-Sn/AL catalyst.

Effect of temperature and time: Pt(2)/AL monometallic and Pt(2)Sn(0.25)/AL bimetallic catalysts were evaluated to check the effect of reaction temperature on their catalytic activities in the hydrogenation of xylose. As observed from Figure 3.11, with the change of catalyst from monometallic Pt(2)/AL to bimetallic Pt(2)Sn(0.25)/AL catalyst, enhancements in the conversion of xylose was possible from 67 to 97% at 130°C in 2 h. It is important to note that along with increase in conversion, bimetallic Pt(2)Sn(0.25)/AL catalyst also improved the yield for sugar alcohols to 91% from 37% observed with monometallic Pt(2)/AL catalyst. A careful observation also suggests that, over monometallic catalyst, higher amount of furfural and glycols formation was possible compared to bimetallic catalyst. When hydrogenation reactions of xylose were carried out at 190°C, similar trend of product formation was observed i.e. increase in sugar alcohols yields and suppression of undesired product formation (glycols, furfural) over bimetallic Pt(2)Sn(0.25)/AL catalyst. At higher (190°C) temperature too, yield of sugar alcohols was higher over Pt(2)Sn(0.25)/AL (73%) than Pt(2)/AL (28%).

It should be noted here that with increase in the temperature to 190˚C, decrease in the yield of sugar alcohols and increase in the yield of glycols was observed compared with reactions done at 130°C. This means that, higher temperatures are favorable for the formation of side products like glycols and not for sugar alcohols from xylose. From earlier study, it is clear that xylitol is stable under reaction conditions (190°C, 16 bar H_2, 1 h) and formation of glycols is possible directly from xylose (section 3.3.2.2 in this chapter). Based on the above discussions, it is suggested that at higher temperature there is a possibility of enhancement of the rate of xylose to glycols reaction (as in non-catalytic reaction at 190°C, 12.8% yield of glycols was obtained, Figure 3.8) and hence lower yields for sugar alcohols were obtained at 190°C than yields at 130°C. Nevertheless, over Pt-Sn/AL bimetallic catalyst, at any temperature (130 or 190°C) yield of sugar alcohols was more than the yield of glycols, but relatively it was better at 130°C than at 190°C.

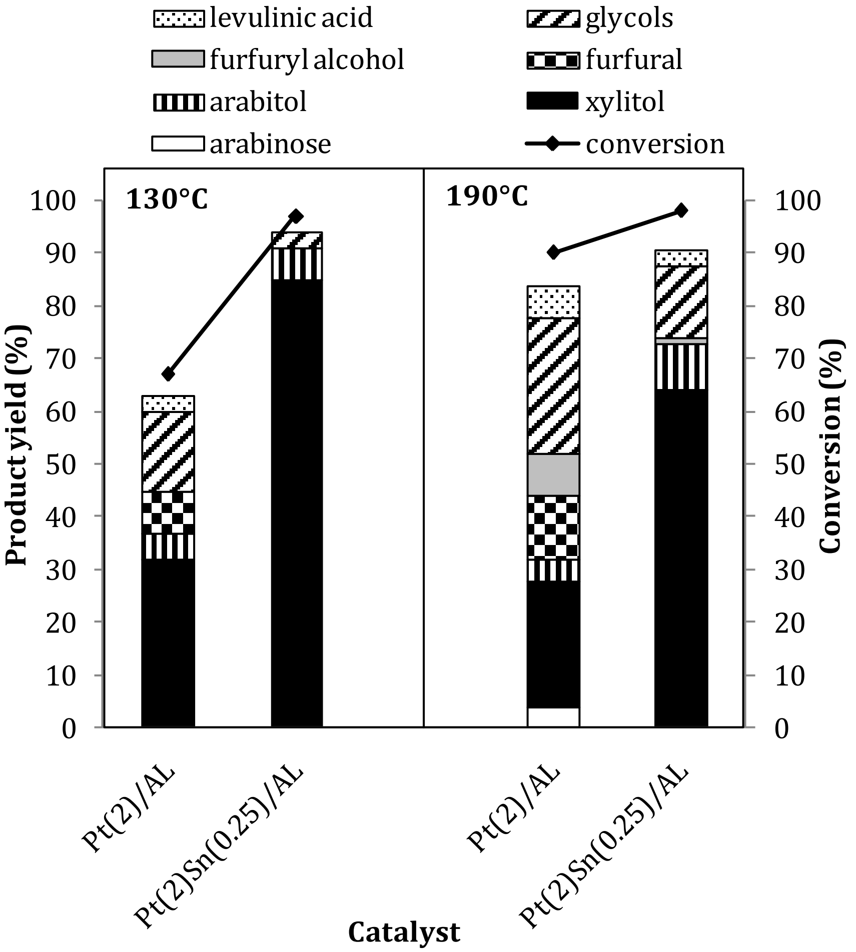


Figure 3.11. Effect temperature and time on xylose conversion over bimetallic catalyst.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 16 bar H_2 at R.T., 130˚C-2 h, 190˚C-15 min.

Though the yield of sugar alcohols over bimetallic catalyst was low (73%) at 190°C than the yield obtained at 130°C (91%), further study was done at 190°C. This is because, complete conversion was achieved over Pt(2)Sn(0.25)/AL within 15 minutes at 190°C whereas it took 2 h for complete conversion at 130°C. Over Pt(2)/AL catalyst even longer time (8 h) was required at 130°C for complete conversion (with sugar alcohols yield of

61%). Furthermore, activities of these catalysts will be tested for polysaccharide conversion in to sugar alcohols which is feasible at higher temperatures only. So the catalyst needs to be active and stable at higher temperature. Above results shows that Pt(2)Sn(0.25)/AL is exploitable at wide range of temperature as decrease in the yield of sugar alcohols was only 18% (from 91% to 73%) when reaction was carried out at 190°C instead of 130°C.

Effect of H_2 pressure: Solubility of hydrogen in water depends on the pressure of the gas at constant temperature. Solubilized H_2 is actually responsible for hydrogenation reaction. Analogous to the monometallic Ru(2)/C (section 3.3.1.3), effect of pressure was studied for xylose hydrogenation over Pt(2)Sn(0.25)/AL catalyst. Xylose conversion at 190°C was carried out for 15 minutes after charging 8 bar H_2 at room temperature and 54% yield of sugar alcohols was seen (89% conversion). When reaction was conducted after charging 16 bar and 24 bar H_2 almost similar yields i.e. 73% (98% conversion) and 75% (99% conversion) were observed. This indicates, amount of H_2 available in solvent is not sufficient at 8 bar pressure. At 16 bar more H_2 is available in reaction mixture hence better yield could be achieved.

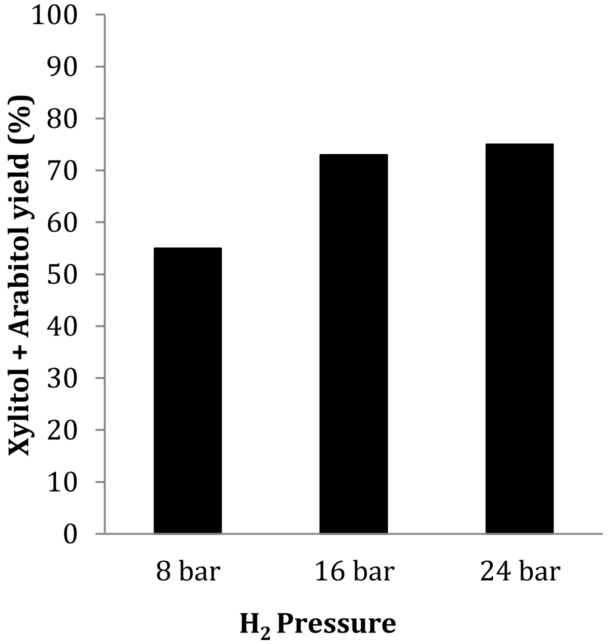


Figure 3.12. Effect H_2 pressure on xylose conversion over bimetallic catalyst. Reaction condition: xylose 0.15 g, catalyst (Pt(2)Sn(0.25)/AL) 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

But further rise in the yield was not possible when pressure was increased to 24 bar. This gives insinuation that even if amount of H_2 solubilized in water might have improved, but number of H_2 molecules adsorbed on the active metal sites remained same and activity could not be improved (for more explanation, refer section 3.3.1.3). To confirm, whether 16 bar pure H_2 is essential to achieve optimum yield, xylose hydrogenation at 190°C was carried out after charging H_2 and N_2 together. 8 bar H_2 was charged and then 16 bar pressure was maintained by feeding nitrogen (8 bar) to the reactor at room temperature. 64% yield of sugar alcohols (92% conversion) was achieved signifying that 16 bar pressure of pure H_2 is required since with 16 bar H_2, 73% yield was achieved (Figure 3.12). This implies that, merely high pressure is not enough for adsorption of more H_2 molecules on to the active metal sites, but higher concentration of solubilized H_2 molecules is also essential. When there is enough number of H_2 molecules available in reaction medium, only then sufficient H_2 molecules will be available on metal surface which eventually results into better activity towards hydrogenation.

Effect of substrate/catalyst ratio: The xylose hydrogenation reaction was carried out at 190°C using S/C ratio of 4 (*wt/wt*) instead of 2, to check the effect of catalyst quantity on sugar alcohols formation (Figure 3.13). When 0.038 g of Pt(2)Sn(0.25)/AL catalyst was used, slight decrease in the sugar alcohols yield (66% at 89% conversion) was seen compared to 0.075 g catalyst (73% at 98% conversion). Though, catalyst loading was decreased by half, only slight decrease in the yields was seen which indicates that, it is possible to carry out the reactions even with lower catalyst concentrations. Moreover selectivity for the sugar alcohols is almost similar at both the catalyst quantities i.e 74.15% for 0.038 g and 74.48% for 0.075 g of catalyst. This implies that better yield can be obtained with lower catalyst quantity (0.038 g), if reaction is carried out for longer time (within 30 min, 98% conversion with 71% yield was observed). When reaction was carried out over 0.15 g of catalyst, within 15 minutes 76% yield (99% conversion) of sugar alcohols was obtained. Considering this, all experiments were carried out with 0.075 g catalyst i.e. S/C ratio of 2 (*wt/wt*) because it showed almost complete conversion with higher yield of sugar alcohols than 0.038 g catalyst and yield similar to 0.15 g catalyst quantity in short period of time (Figure 3.13).

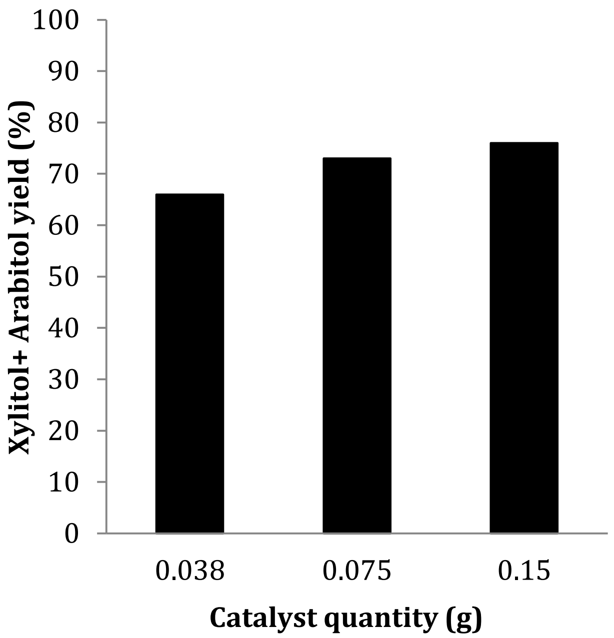


Figure 3.13. Effect of catalyst (Pt(2)Sn(0.25)/AL) quantity on xylose conversion. Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 15 min.

3.3.2.6. Effect of Fe and Ga as promoter in Pt/AL catalyst.

To inspect the promoter effect of other metals in Pt/AL system, Pt-Fe/AL and Pt-Ga/AL catalysts were synthesized (refer chapter 2, section 2.2.1 and 2.2.2 for more details on synthesis) and were used in the xylose hydrogenation reactions at 190°C and 16 bar H_2 for 15 minutes. While, bimetallic Pt(2)Sn(0.25)/AL catalyst gave 73% yield of sugar alcohols, Pt(2)Ga(0.25)/AL and Pt(2)Fe(0.25)/AL showed poor performance by yielding only 14% and 43% sugar alcohols, respectively. Among Ga and Fe promoters, Fe showed better activity hence next catalyst was prepared by higher Fe content (Pt(2)Fe(0.5)/AL). However, almost similar amount of sugar alcohols formation (40%) was observed with this catalyst as that observed with Pt(2)Fe(0.25)/AL catalyst (43%). On the other hand, over Pt(2)Ga(0.25)/AL formation of side products like glycols and arabinose was prominent. Decrease in the sugar alcohols yields over Pt-Ga/AL catalyst is attributed to the reduction (at temperature more than 350°C) of Ga to (0) state and encapsulation of Pt particle by reduced Ga species.[48] As mentioned earlier in the current study catalysts were oxidized and reduced at 400°C, hence possibility of encapsulation of some Pt particle by reduced Ga species cannot be neglected. Results for xylose hydrogenation over various bimetallic catalysts are represented in Figure 3.14.

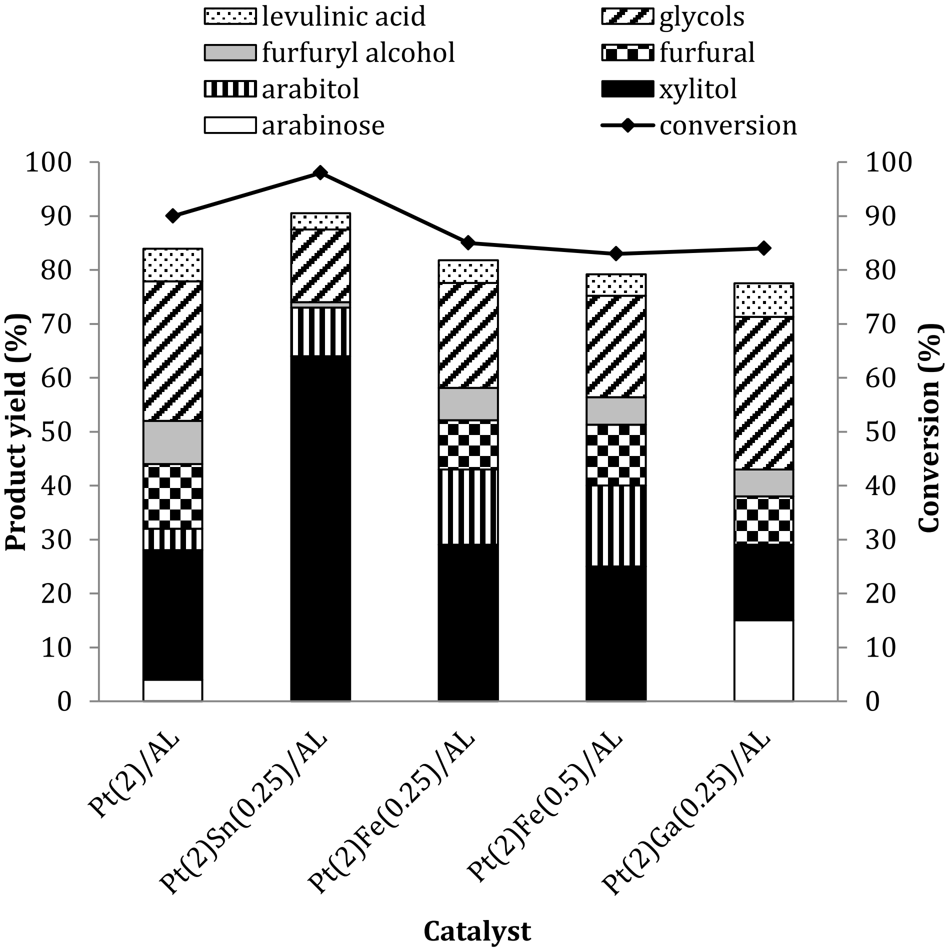


Figure 3.14. Effect of Fe and Ga as a promoter on xylose conversion.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 15 min.

Summarizing all above results, the following tendency of sugar alcohols formation was observed over various catalysts;

Pt(2)Sn(0.25)/AL (73% yield) > Pt(2)Fe(0.25)/AL (43% yield) > Pt(2)Fe(0.5)/AL (40% yield) > Pt(2)/AL (28% yield) > Pt(2)Ga(0.25)/AL (14% yield).

The data elucidates that amongst all the promoters (Sn, Ga, Fe), Sn shows superior activity in xylose hydrogenation reactions.

3.3.2.7. Correlation of catalyst properties with activity

From the above results it is evident that in xylose reactions, bimetallic Pt-Sn/AL catalyst showed enhanced sugar alcohols yields compared to the monometallic Pt/AL and other bimetallic catalysts (Pt-Fe/AL and Pt-Ga/AL). To realize the reason behind enhanced yields of sugar alcohols and role of Sn in the promotion of activity of Pt/AL catalyst towards hydrogenation, various properties of catalyst were correlated with the activity. It is believed that the catalytic activity of the Pt-Sn/AL catalysts is mainly governed by the oxidation state of the metals, dispersion of Pt on the support material, composition and amount of alloys or intermetallic system formed (if any).

From XRD analysis (chapter 2, section 2.3.2.2, Figure 2.2.C), it is confirmed that at higher Sn content (1.75wt% and 3.5wt%), Pt_3Sn and PtSn species were formed in Pt-Sn/AL catalysts. It is reported that there is a possibility of PtSn alloy formation when Sn is in higher concentration, which can reduce the surface area of Pt.[49] Moreover, XPS analysis also confirmed formation of metallic Sn in these catalysts (chapter 2, section 2.3.2.4, Figure 2.4). One of the report also discusses the possibility of Pt helping reduction of Sn by hydrogen spillover effect.[50] These results imply that in the catalysts having higher Sn content, alloy (PtSn or Pt_3Sn) formation is possible and it is predicted that it will have adverse effect on the catalytic activity.[49, 51, 52] Hence to achieve maximum yield of sugar alcohols, Sn content in the Pt-Sn/AL bimetallic catalyst should be optimum, as with higher Sn content formation of intermetallic system is prominent. In current study maximum yield was observed when Sn loading was 0.43wt% (over Pt(3.5)Sn(0.43)/AL) and it start decreasing with further increase in the Sn content in Pt-Sn bimetallic catalyst. In one of the study, correlation is drawn between concentration of Sn and oxidation state of it (from the amount of oxygen consumed during reoxidation of previouly reduced Sn supported on AL) and it is evidenced that until 0.6wt% of Sn loading in Sn/AL catalyst, Sn is not reduced to metallic state since it forms complex with alumina support.[28] It is observed that AL helps in the stabilization of Sn (II) or (IV) by forming tin-aluminate surface shell (complex).[53, 54] Sn can interact with alumina through oxygen atom and forms tin-aluminate like structure which is very stable and Sn is in (II) oxidation state.[53, 54] This phenomenon in turn suppresses the sintering of active (base) metal by hindering its movement on the support during calcinations, reduction and reactions.[54] It is recognized in the literature that, with the addition of Sn in optimum concentration, increase in the dispersion of Pt on AL support is possible. Consequently, with higher dispersion catalyst gives enhanced activity as dispersion is one of the important factors governing the activity of Pt-Sn bimetallic catalyst.[55] In this work, TEM analysis proved that Pt was well dispersed in bimetallic Pt(2)Sn(0.25)/AL or Pt(3.5)Sn(0.43)/AL catalyst (10-20 nm) than in monometallic Pt(2)/AL or Pt(3.5)/AL catalyst (20-30 nm).

From the catalytic results it is clear that Pt-Sn/AL catalysts having lower Sn content (0.43wt%) shows best catalytic performance and from XRD and XPS characterizations it is apparent that in the catalyst with Sn loading lower than 0.87wt%, Sn is present as ionic species (higher oxidation state) and Pt is in metallic form. These results were in line with the NH_3-TPD analysis of Pt-Sn/AL catalyst, wherein observance of new peak possibly due to formation of Lewis acid sites ($Sn^{+\delta}$) was seen at 400-500°C due to absence of alloy formation (chapter 2, section 2.3.2.6, Figure 2.5.A). It is understood that when Sn is present in higher oxidation state it can act as Lewis acid site (electron deficient) and thus Sn is ready to accept the electrons. It is proposed that in this reaction when sugar molecule interacts with catalytically active site, the lone pair of electrons on oxygen of carbonyl group interacts with Sn and thus polarization of double bond of carbonyl group takes place. This in turn gives rise to electron deficient carbon which ultimately gives higher hydrogenation activity.[29, 39-43] In case of Pt-Sn/AL catalysts having higher Sn loading (1.75wt% and 3.5wt%), it is believed that the combined effect of Sn present in metallic state and formation of alloy is responsible for observing poor activity (for sugar alcohols formation) than Pt-Sn/AL catalysts having lower Sn content (with 0.87wt% and 0.43wt% Sn). Nevertheless, presence of some Sn in higher oxidation state in Pt(3.5)Sn(1.75)/AL and Pt(3.5)Sn(3.5)/AL catalysts (refer chapter 2, section 2.3.2.4, Figure 2.4 and Table 2.3) shows slightly higher sugar alcohols formation activity compared to monometallic Pt(3.5)/AL catalyst (Figure 3.8).

Besides this, Sn in electron deficient state (II) or (IV) act as a Lewis acid site and hence can catalyze isomerization and epimerization reactions of sugars and sugar alcohols, respectively. Conversion of xylose to furfural over Sn catalyst is achievable because of these Lewis acid sites.[45] In this context, researchers have studied the conversion of xylose to xylulose (isomer) and lyxose (epimer) using Sn-Beta zeolite as a catalyst.[46] Similarly, isomerization of glucose over Lewis acid catalyst (Sn containing zeolite, Sn-Beta catalyst) is also known.[45-47, 56] Though; formation of xylulose or lyxose could not be observed from HPLC analysis, this might be due to the fact that once these sugars are formed those are instantaneously undergoing hydrogenation reactions to yield sugar alcohols. This is feasible since at 190°C within 15 minutes complete conversion of xylose to yield 79% sugar alcohols was seen (Figure 3.8) making it hard to detect the intermediate products formation.

Moreover, quite a few studies have shown that support plays a vital role in governing the effect of promoter on the catalytic activity. It is shown that the neutral support like activated carbon does not demonstrate strong interaction with Sn and thus restricts the promoter effect of Sn.[35] Furthermore, use of silica as a support gives rise to Sn(0) species and these Sn (0) species cannot improve the catalytic activity.[53, 54] In current study, when bimetallic carbon catalysts (Pt(2)Sn(0.25)/C and Ru(2)Sn(0.25)/C) were tested for xylose hydrogenation, none of them showed enhanced yields of sugar alcohols compared to the corresponding monometallic catalysts (Pt(2)/C and Ru(2)/C, respectively). This proves that Sn does not show any promoter effect when carbon is the support. From XRD analysis of Pt(2)Sn(0.25)/C it was understood that Sn (at this low concentration) can be reduced to Sn (0) and formation of PtSn intermetallic system is possible over carbon support (chapter 2, section 2.3.2.2, Figure 2.2.B). Unfortunately in case of Ru(2)Sn(0.25)/C catalyst peaks for any Ru-Sn intermentallic systems (i.e. $RuSn_2$, Ru_2Sn_3 or Ru_3Sn_7) were not observed. XRD pattern of Ru(2)Sn(0.25)/C does not show any peak for Ru or intermetallic systems, probably because of very fine dispertion (chapter 2, section 2.3.2.2, Figure 2.2.D). Surprisingly against the expectation, in Ru(2)Sn(0.25)/AL catalyst promoter effect of Sn was not visible in spite of AL was the support. Careful study of literature shows that Sn can interact very strongly with both AL and Ru, because of this catalytic properties of Ru can be altered.[57] Active metal sites on the Ru surface which are responsible for hydrogen activation can be poisoned due to addition of Sn to Ru catalyst.[58, 59] This might be the reason for obtaining low yield over Ru(2)Sn(0.25)/AL catalyst.

3.3.2.8. Recycle study and characterization of spent catalyst

Since, Pt(3.5)Sn(0.43)/AL catalyst showed the best possible sugar alcohols yields from xylose, the recycle studies were performed with this catalyst. The catalyst used in first xylose reaction was recovered from the reaction mixture by centrifugation and then was washed with distilled water. This catalyst was used in the next reaction without any additional treatment (drying/calcination/reduction etc.). It is observed that catalyst could give roughly similar sugar alcohols yields in at least five recycle runs (1st run:79%, 2nd run: 78%, 3rd run: 78%, 4th run: 76%, 5th run: 75%). Similar results were obtained when recycle study was done over Pt(2)Sn(0.25)/AL (1st run:73%, 2nd run: 72%, 3rd run: 70%, 4th run: 68%, 5th run: 67%) (Figure 3.15).

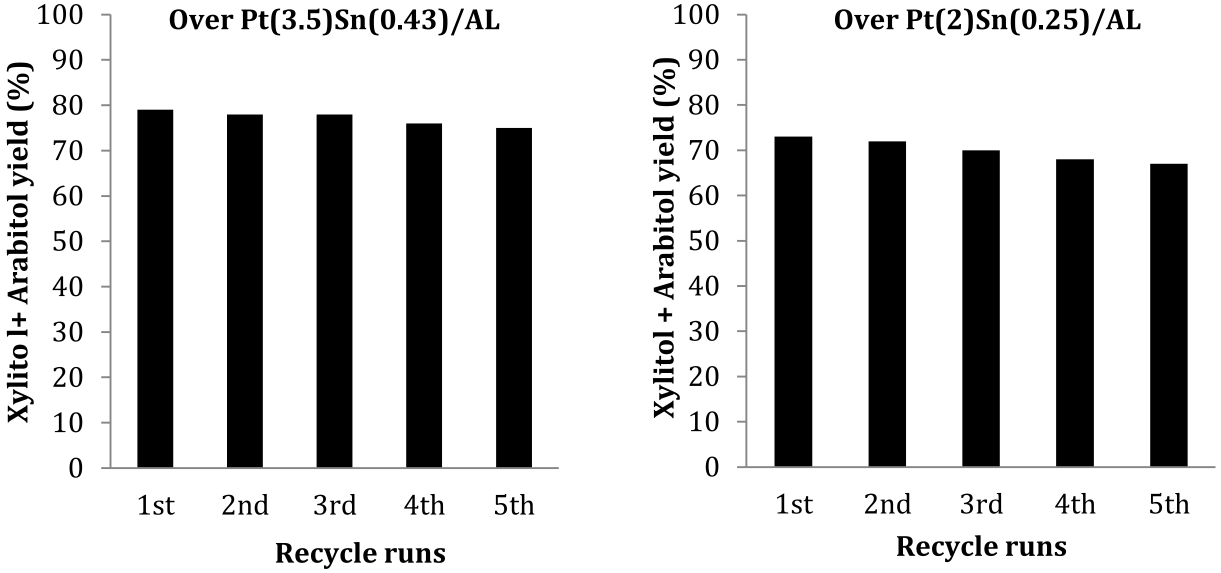


Figure 3.15. Recycle study for xylose conversion over Pt-Sn/AL catalyst. Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 15 min.

The Minor decrease in the activity was observed due to the loss of some catalyst quantity during separation of catalyst from reaction mixture. Also is it important to note here that recovered wet catalyst was charged in next reaction without drying and wieghing. This ultimately, altered the S/C ratio in each run (since 0.15 g of xylose was charged in each run). To check the effect of reaction condition on the physicochemical properties of the catalyst, spent Pt(2)Sn(0.25)/AL catalyst (used in xylose conversion at 190°C for 15 min) was subjected to various characterizations. XRD pattern of the spent and fresh catalysts were compared to confirm no structural deformation occurred in the catalyst during reaction (Figure 3.16). Peaks characteristic for metallic Pt were clearly visible in both, fresh and spent catalysts. Transformation of alumina to form boehmite is reported under similar reaction conditions (190°C, 24 h, 50 bar H_2 pressure).[23] However XRD pattern for spent catalyst did not show any peak at 2θ°= 14.45, 28.24, 38.40, 45.81, 48.97, 49.31, 51.68 and 55.30 characteristic for boehmite (JCPDS file no. 21-1307). This proves that boehmite was not formed on bulk level to be detected by XRD.

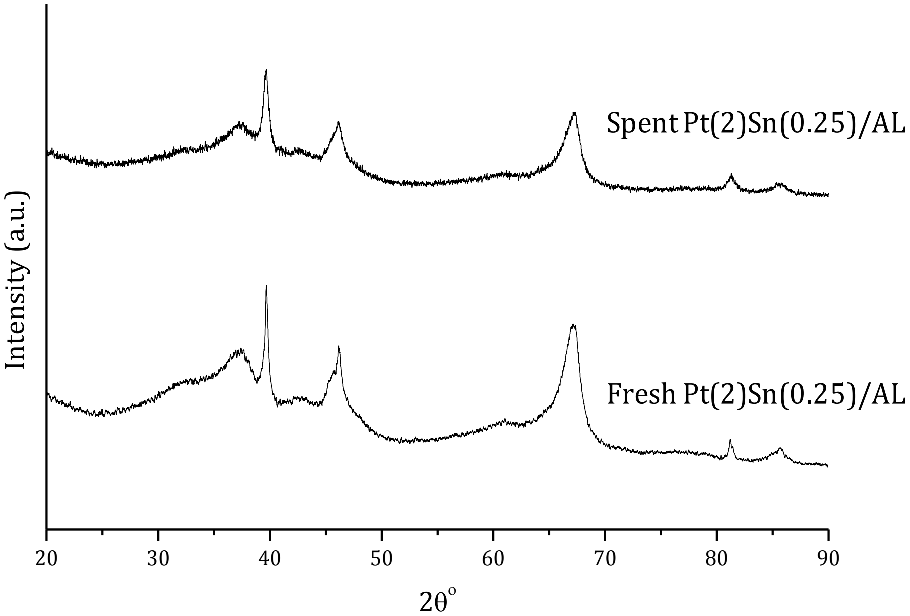
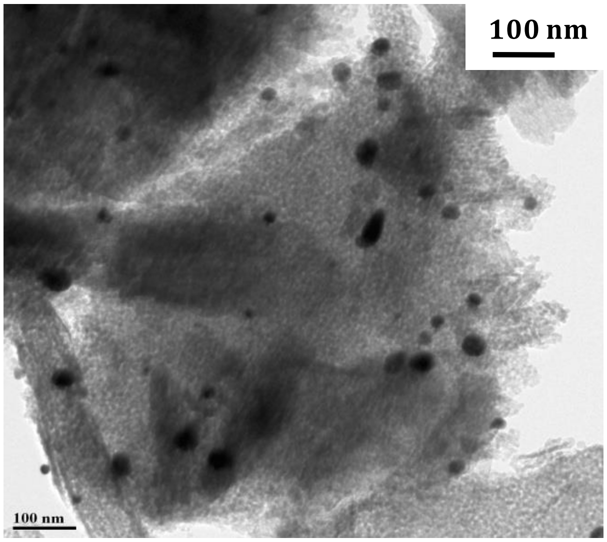


Figure 3.16. XRD patterns of fresh and spent Pt(2)Sn(0.25)/AL catalyst.*

*Spent catalyst: catalyst used for xylose conversion at 190°C for 15 min. at 16 bar H_2.

Other than XRD, analysis like ICP-AES and N_2 sorption reinforces the stability of Pt-Sn/AL catalyst during reaction. ICP-AES analysis of spent catalyst showed, metal content in the catalyst remained almost unaltered after reaction. Pt contents in the fresh and spent Pt(2)Sn(0.25)/AL were 2.19wt% and 2.14wt% which are quite comparable and so as the Sn contents (fresh 0.23wt% and spent 0.21wt%). Slight change in the metal contents may arise because of handling error during sample preparation (ICP-AES results are subjected to ±0.05wt% of error). TEM analysis showed that metal particle size in spent catalyst is almost similar to the fresh catalyst i.e. 10-20 nm (Figure 3.17). This proves sintering of metal particles was restricted during reaction. Additionally, N_2-sorption study revealed that surface area of the catalyst was not changed appreciably (fresh 164 m^2/g while spent 152 m^2/g). From aforementioned discussion it is unambiguous that catalyst is pretty stable under reaction condition and can be reused for the synthesis of sugar alcohols from xylose with minimal loss of activity.

Spent Pt(2)Sn(0.25/AL)



20-30 nm

Figure 3.17. TEM image of spent Pt(2)Sn(0.25)/AL catalyst.*

*Spent catalyst: catalyst used for xylose conversion at 190°C for 15 min. at 16 bar H_2.

3.3.3. Effect of residual Cl^- on catalytic activity

As explained in second chapter, during synthesis of Pt-Sn/AL catalysts, hydrochloric acid (HCl) was used to dissolve the Sn precursor and therefore it is probable that some amount of Cl^- may remain on the catalysts even if catalysts were calcined (O_2 flow, 20 mL/min) and reduced (H_2 flow, 20 mL/min) at 400°C for 2 h each (refer catalyst synthesis, chapter 2, section 2.2.2). In case, Cl^- are present on the catalyst, there is a possibility that these residual Cl^- may alter the catalytic activity for Pt-Sn/AL catalysts compared to Pt/AL, Pt-Fe/AL and Pt-Ga/AL catalysts. Moreover, reactions over Pt-Sn/AL catalysts with higher Sn loading showed lower yield of sugar alcohols and higher yield of side products like glycols and furfural. Therefore it was absolutely necessary to verify whether Cl^- are present on the catalyst and if Cl^- are present then what effect those will have on the activity. Presence of Cl^- on catalysts was confirmed by silver chloride test for all Pt-Sn bimetallic catalysts. For this test, 0.075 g of Pt(3.5)Sn(3.5)/AL catalyst was suspended in the distilled water (35 mL) and the resulting mixture was stirred for 30 minutes over magnetic stirrer at R.T (30-35°C). Next, by centrifugation, solid catalyst was separated from the water. The liquid was decanted and was then titrated with 0.01M aq. solution of $AgNO_3$. Formation of white precipitate (AgCl) was observed to confirm the presence of Cl^- in the solution. Presence of Cl^- in Pt(3.5)Sn(0.22)/AL, Pt(3.5)Sn(0.43)/AL, Pt(3.5)Sn(0.87)/AL and Pt(3.5)Sn(1.75)/AL catalysts was confirmed by performing similar experiments. Formation of white precipitate of AgCl in this test implied that even after subjecting the catalysts for calcinations and reduction treatments at 400°C some amount of Cl^- was still present on Pt-Sn/AL catalysts.

Next, to understand whether these residual Cl^- are contributing towards the reaction, some experiments were carried out using xylose as substrate (results are represented in Table 3.1).

Table 3.1. Effect of residual Cl^- in the conversion of xylose.*

Catalyst	Conv. (%)	Product yield (%)						pH
		xylitol	arabitol	glycols^	furfural	FA$^{\Delta}$	LA$^{\lozenge}$	
Pt(3.5)/AL	94	25	8	27.1	9	6.2	7	5.61
Pt(3.5)/AL$^{\$}$	90	17	10	24	11	7	6	5.28
Pt(3.5)Sn(0.43)/AL$^{\$}$	99	66	13	11.8	0	1	2.6	5.32
Pt(3.5)Sn(0.43)/AL$^{\#}$	98	69	8	9	1.1	1	3	5.08

^glycols = glycerol+ethylene glycol+1,2-propanediol; $^{\Delta}$FA = furfuryl alcohol; $^{\lozenge}$LA = levulinic acid.

*Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 15 min.

$^{\$}$During synthesis of 0.075 g of catalyst, 0.062 mL of 3M HCl was used.

$^{\#}$During synthesis of 0.075 g of catalyst, 0.5 mL of 3M HCl was used instead of 0.062 mL.

For these experiments monometallic Pt(3.5)/AL$^{\$}$-acidified catalyst was prepared (HCl was added during the synthesis of Pt(3.5)/AL$^{\$}$ catalyst. For details on catalyst preparations, refer chapter 2, section 2.2.2). Along with this, Pt(3.5)Sn(0.43)/AL$^{\#}$ catalyst was also prepared by adding extra HCl (instead of 0.062 mL of HCl normally added during preparation of Pt(3.5)Sn(0.43)/AL catalyst (for 0.075 g), 0.5 mL of HCl was added during synthesis). Presence of Cl^- in these catalysts was confirmed by performing silver chloride test. When monometallic Pt(3.5)/AL catalyst (normal catalyst preparation, without addition of HCl) was tested for xylose hydrogenation reaction at 190˚C for 15 minutes, 33% sugar alcohols yield was obtained. Compared to this, under similar reaction conditions (190˚C, 15 min.) with monometallic Pt(3.5)/AL$^{\$}$ catalyst (in which 0.062 mL HCl was added during synthesis) 27% sugar alcohols (xylitol+arabitol) yield was observed.

Above results imply that even if HCl was added during the synthesis of Pt(3.5)/AL catalyst there was no considerable difference in the yield of sugar alcohols from xylose. Furthermore, in xylose hydrogenation reaction both the catalysts, Pt(3.5)Sn(0.43)/AL$^{\$}$ (79% yield) and Pt(3.5)Sn(0.43)/AL$^{\#}$ synthesized with extra HCl (77% yield) showed similar sugar alcohol yields. Besides this, reactions with the addition of HCl directly in the reactor along with substrate and Pt(3.5)/AL catalyst were intended. However; due to the restrictions of the reactor (corrosion/leaching), those reactions could not be performed. Nevertheless, aforementioned results indicate that even if higher quantity of HCl was added during the synthesis of catalyst, most of it is lost during calcination and reduction steps. From above results and discussion it can be concluded that, there is almost no contribution from Cl^- in the reaction and decrease in the sugar alcohols yield at higher Sn content may be the effect of Pt and Sn and not of Cl^-, because at higher Sn loading formation of PtSn and Pt_3Sn intermetallic systems were observed.

3.3.4. Conversion of arabinose, glucose, fructose and galactose in to sugar alcohols over Pt-Sn/AL catalyst

As discussed above, Pt-Sn/AL bimetallic catalyst was successfully employed to enhance the yield of sugar alcohols (xylitol+arabitol) from xylose. Next, activity of this catalyst was tested for the conversion other C5 sugar (arabinose) and C6 sugars (glucose, fructose and galactose). Reactions were carried out using above mentioned substrates over monometallic Pt(2)/AL and bimetallic Pt(2)Sn(0.25)/AL catalysts.

3.3.4.1. Results and discussion

Similar to the xylose conversion, from arabinose also better yields could be achieved over Pt-Sn/AL bimetallic catalyst at both higher (190°C) and lower (130°C) temperatures. At 130°C, 43% yield of sugar alcohols (arabitol+xylitol) was obtained (67% conversion) over Pt(2)/AL in 2 h of reaction time. While, at similar reaction conditions, 92% yield of sugar alcohols (99% conversion) was achieved over Pt(2)Sn(0.25)/AL catalyst. Formation of side products was more over monometallic catalyst than bimetallic catalyst (Table 3.2).

Table 3.2. Conversion arabinose in to sugar alcohols.

Temp (°C)	Catalyst	Product yield (%)						Conv. (%)
		xylitol	arabitol	glycols^	furfural	FA[Δ]	LA[◊]	
130	Pt(2)/AL	14	29	14	3	-	2	65
	Pt(2)Sn(0.25)/AL	1	92	2.5	-	-	-	99
190	Pt(2)/AL	3	31	36	6	2	6	86
	Pt(2)Sn(0.25)/AL	2	80	11.9	-	2	-	99

^glycols = glycerol+ethylene glycol+1,2-propanediol; [Δ]FA = furfuryl alcohol; [◊]LA = levulinic acid.

Reaction condition: arabinose 0.15 g, catalyst 0.075 g, water 35 mL, 16 bar H_2 at R.T., 190˚C-15 min, 130°C-2 h.

When hydrogenation reactions of arabinose was carried out at 190°C, similar trend of product formation was observed i.e. raise in sugar alcohols yields and decrease in undesired product formation (glycols, furfural, levulinic acid) over bimetallic Pt(2)Sn(0.25)/AL catalysts. 34% yield of sugar alcohols (86% conversion) was observed over Pt(2)/AL whereas 82% yield (99% conversion) was seen over Pt(2)Sn(0.25)/AL in 15 minutes of reaction time (Table 3.2).

The catalytic performances of Pt(2)/AL and Pt(2)Sn(0.25)/AL were also evaluated in the hydrogenation of C6 sugars i.e. glucose, galactose and fructose at 190°C and 130°C (Table 3.3).

Table 3.3. Conversion C6 sugars in to sugar alcohols.

Substrate	Temp (°C)	Catalyst	Product yield (%)				Conv. (%)
			sorbitol	mannitol	galactitol	glycols^	
Glucose	130	Pt(2)/AL	20	10	-	8	45
		Pt(2)Sn(0.25)/AL	78	6	-	2	90
	190	Pt(2)/AL	16	7	-	23	73
		Pt(2)Sn(0.25)/AL	59	9	-	9	85
Galactose	130	Pt(2)/AL	-	10	31	14	65
		Pt(2)Sn(0.25)/AL	-	8	80	4	98
	190	Pt(2)/AL	-	7	27	21	75
		Pt(2)Sn(0.25)/AL	-	8	67	9	93
Fructose	130	Pt(2)/AL	20	28	-	17	70
		Pt(2)Sn(0.25)/AL	40	50	-	3	97
	190	Pt(2)/AL	16	28	-	28	85
		Pt(2)Sn(0.25)/AL	29	45	-	10	95

^glycols = glycerol+ethylene glycol+1,2-propanediol

Reaction condition: substrate 0.15 g, catalyst 0.075 g, water 35 mL, 16 bar H_2 at R.T., 130°C-2 h, 190°C-15 min.

Analogous to the results obtained with C5 sugars, C6 sugars also showed improvement in the sugar alcohols (sorbitol, galactitol, mannitol) yields with the use of bimetallic Pt(2)Sn(0.25)/AL catalyst against monometallic Pt(2)/AL catalyst. It was observed that maximum of 84% sugar alcohols (sorbitol+manntiol) yield can be obtained from glucose while with fructose as a substrate maximum of 90% yield was achievable at 130°C. As expected, with fructose as a substrate high yield of mannitol (50%) was observed as against high concentration of sorbitol formation was seen in case of glucose as substrate.

Because of acidic nature of AL, it is capable of epimerizing sugar alcohols; to yield mannitol from sorbitol and vice-versa. However, it was surprising to note here that when glucose was used as substrate, yield of mannitol was not higher which suggest that either isomerization of glucose to yield fructose or epimerization of sorbitol to yield mannitol was restrictive. However, sorbitol and mannitol stability study performed under similar reaction conditions did not show much conversion (ca. 5%) and hence it is suggested that in the presence of AL preferably, glucose and fructose undergo isomerization reactions. Moreover the isomerization of fructose to glucose is faster than glucose to fructose formation since in fructose reaction higher amount of sorbitol (hydrogenation product of glucose) was formed but when glucose was used as a substrate, formation of mannitol (hydrogenation product of fructose) was less. With galactose as a substrate, 80% yield for galactitol was seen at 130°C. In all the reactions, isomerization products of sugars and epimerization products of sugar alcohols were observed. Results obtained with C6 sugars at 190°C showed lower yield of sugar alcohols, which again confirms that from monomer sugars to achieve best possible yields for sugar alcohols, lower temperatures is preferable.

3.3.4.2. Recycle study

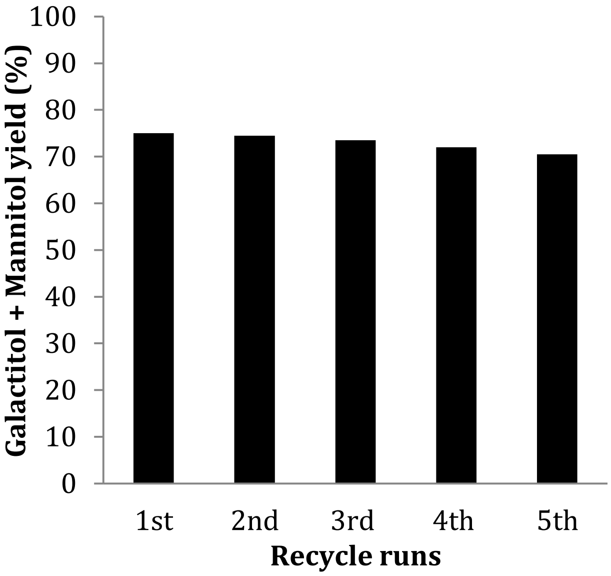


Figure 3.18. Recycle study for galactose conversion over Pt(2)Sn(0.25)/AL catalyst.
Reaction condition: galactose 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 15 min.

Similar to the xylose hydrogenation, recyclability of Pt(2)Sn(0.25)/AL was tested for the galactose conversion (procedure was same as recycle study in xylose conversion, refer section 3.3.2.8). Catalyst showed good recyclability up to 5th run with negligible decrease in the yield of sugar alcohols (galactitol+mannitol). This minor decrease in the yields can be attributed to the loss of some catalyst quantity during separation of catalyst from reaction mixture. Results for the recycle study of the Pt(2)Sn(0.25)/AL catalyst are represented in Figure 3.18 (1st run:75%, 2nd run: 74.5%, 3rd run: 73.5%, 4th run: 72%, 5th run: 70.5%). Results indicate that Pt-Sn/AL bimetallic catalyst shows good recyclability in the conversion of C5 sugars as well as C6 sugars.

3.4. Proposed reaction mechanism

Pt catalysts are well known for hydrogenation reactions and role of Pt in the generation of H^+ and H^- from H_2 molecule is well documented in the literature. H^+ and H^- species generated on the active metal site of Pt surface are responsible for hydrogenation of functional groups (C=O of carbonyl group in sugar molecule). In case of monometallic Pt/AL catalyst, hydrogenation of C=O bond is initiated by hydride ion transfer to the electron deficient carbon atom of the carbonyl group. While over Pt-Sn/AL bimetallic catalyst, Pt plays its role to generate H^+ and H^- ions from H_2 molecules, at the same time Sn plays very significant role because of which it acts as a promoter in the hydrogenation reaction. Sn interacts with AL to form tin-aluminate like complex, hence cannot be reduced to (0) state and remain in ionic state (II) or (IV) on alumina. As reported earlier, Sn in ionic state can polarize the C=O bond of carbonyl group.[40, 60]

In current work, XPS study proved that Sn is present in ionic state (II) or (IV) in Pt-Sn/AL bimetallic catalysts which interacts with the C=O bond of carbonyl group in sugar molecules to polarize it. Simultaneously, H^+ and H^- generated on the Pt surface can easily hydrogenate the polarized C=O bond of carbonyl group of sugars. In this way, Sn in ionic state can speed up the hydrogenation reaction of sugars. Plausible reaction mechanism of the hydrogenation of the sugar molecule over Pt-Sn/AL bimetallic catalyst is represented in the Figure 3.19.

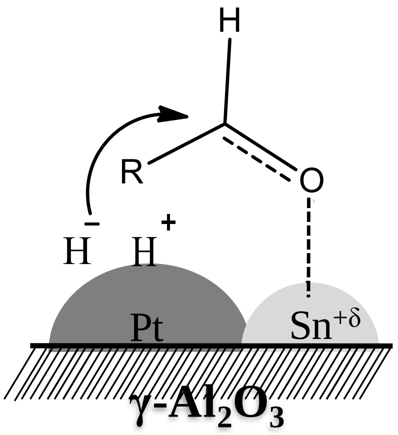


Figure 3.19. Proposed mechanism for the hydrogenation of sugar molecule over Pt-Sn/AL catalyst.

3.5. Conclusions

From aforementioned results and discussions, it can be concluded that yields of sugar alcohols from sugars can be improved, if appropriate combination of metal, promoter and support is achieved. Various monometallic and bimetallic catalysts were synthesized and evaluated in the conversion of sugars to yield sugar alcohols. Effects of supports (AL, SA, C) and metals (Pt, Ru) on the formation of sugar alcohols was studied. Amongst all monometallic catalyst, Ru(2)/C showed superior yield of sugar alcohols (68%) in xylose conversion. With the intension to obtain better yields, bimetallic catalysts using Sn as a promoter were synthesized. Although Ru/C showed best results for sugar alcohols production, yields could not be improved by adding promoter (Sn) to the catalyst. On the other hand, yield of sugar alcohols (xylitol+arabitol) was increased dramatically over Pt(2)Sn(0.25)/AL (73%) against Pt(2)/AL catalyst (28%). Further improvement in the sugar alcohols yield (79%) was observed when catalyst with higher metal loading (Pt(3.5)Sn(0.43)/AL) was employed in xylose hydrogenation. Effect of varying Pt:Sn ratio was studied and Pt:Sn = 1:0.12 (*wt/wt*) showed highest yield of sugar alcohols. Other reaction parameters like temperature, time, H_2 pressure, S/C ratio, etc. were optimized to achieve superior yields of sugar alcohols from various C5 and C6 sugars. Temperature study revealed that, at higher temperature yield of sugar alcohols was less as compared to lower temperature, as at high temperature side reactions to form glycols and furans were prominent. At 130°C, maximum 93% yield of sugar alcohols from xylose could be achieved over Pt(3.5)Sn(0.430/AL catalyst against 79% at 190°C. Promoter effect of other metal like Fe and Ga was studied but Pt-Sn/AL showed best activity for the synthesis of sugar alcohols.

In the conversion of various C5 sugars (xylose, arabinose) and C6 sugars (glucose, galactose, fructose), yield of respective sugar alcohols was enhanced by more than 2 times over Pt-Sn/AL compared with Pt/AL. Pt-Sn/AL catalyst is exploitable at wide range of reaction conditions. Cautious study of the results obtained from various characterization techniques helped to correlation of catalyst activity with its physicochemical properties. Sn interacts with alumina support to form tin-alumina complex (surface shell) which restrict the reduction of Sn to Sn (0) on alumina support. NH_3-TPD showed the decrease in the acid amount of alumina after incorporation of Sn which proves the interaction of Sn with acid site of alumina. Moreover, XPS study depicts that at lower loading of Sn (up to 0.87wt%), it was present in Sn (II) or (IV) state. The formation of Pt_3Sn and PtSn type intermetallic systems was not discernible in the catalyst with lower loading of Sn (up to 0.87wt%) over AL support. But in the catalyst with higher Sn content (Pt(3.5)Sn(1.75)/AL and Pt(3.5)Sn(3.5)/AL) formation of Pt_3Sn and PtSn was clearly visible (XRD study). This implies that optimum amount of Sn can form complex with alumina and cannot be reduced to Sn (0), but, if Sn loading is higher than optimum loading, some of the Sn can form complex and surplus Sn can be reduced to Sn (0) and hence can form intermetallic systems (Pt_3Sn and PtSn) over AL support. Formation of surface shell prevents sintering of Pt particles during calcination, reduction and during reaction too. Furthermore, Sn in ionic form ((II) or (IV)) polarizes the C=O bond of the carbonyl group in the sugar molecules which can be hydrogenated easily. Neutral support like carbon (C) does not interact with Sn to form surface shell and hence Sn can be reduced to Sn (0) state to form PtSn intermetallic system even with optimum loading. Consequently Sn cannot demonstrate any promoter effect when C is the support. Characterization of the spent Pt-Sn/AL catalyst proved the stability of catalyst at applied reaction condition and catalyst can be reuse with negligible loss of activity after each run.

Efficient bimetallic catalyst has been developed for the conversion of monosaccharides (various C5 and C6 sugars) in to sugar alcohols. The catalyst is exploitable at wide range of reaction condition for assort of substrates with good recyclability. In next chapter activity of this bimetallic catalyst will be examined in the conversion of isolated polysaccharides and agricultural wastes in to sugar alcohols in one pot method.

3.6. References

1. P. Gallezot, P. J. Cerino, B. Blanc, G. Fleche and P. Fuertes, *Journal of Catalysis*, 1994, **146**, 93-102.
2. C. A. Ramírez-López, J. R. Ochoa-Gómez, S. Gil-Río, O. Gómez-Jiménez-Aberasturi and J. Torrecilla-Soria, *Journal of Chemical Technology & Biotechnology*, 2011, **86**, 867-874.
3. X. Chen, X. Wang, S. Yao and X. Mu, *Catalysis Communications*, 2013, **39**, 86-89.
4. J. Li, A. Spina, J. A. Moulijn and M. Makkee, *Catalysis Science & Technology*, 2013, **3**, 1540-1546.
5. R. M. Gohil, *Polymer Engineering & Science*, 2009, **49**, 544-553.
6. Y. Zhu, M. Durand, V. Molinier and J.-M. Aubry, *Green Chemistry*, 2008, **10**, 532-540.
7. R. R. Davda and J. A. Dumesic, *Chemical Communications*, 2004, **0**, 36-37.
8. L. He and D. Chen, *ChemSusChem*, **5**, 587-595.
9. H. Shawkat, M. M. Westwood and A. Mortimer, *Continuing Education in Anaesthesia, Critical Care & Pain*, 2012.
10. N. de Kalbermatten, E. Ravussin, E. Maeder, C. Geser, E. Jéquier and J. P. Felber, *Metabolism*, 1980, **29**, 62-67.
11. S. S. Natah, K. R. Hussien, J. A. Tuominen and V. A. Koivisto, *The American Journal of Clinical Nutrition*, 1997, **65**, 947-950.
12. M. Yadav, D. K. Mishra and J. S. Hwang, *Applied Catalysis A: General*, 2012, **425-426**, 110-116.
13. J. Zhang, A. Geng, C. Yao, Y. Lu and Q. Li, *Bioresource Technology*, 2012, **105**, 134-141.
14. A. Corma, S. Iborra, C. G. Bruce and K. z. Helmut, in *Advances in Catalysis*, Academic Press, Editon edn., 2006, **49**, 239-302.
15. G. Zhao, M. Zheng, J. Zhang, A. Wang and T. Zhang, *Industrial & Engineering Chemistry Research*, 2013, **52**, 9566-9572.
16. R. Ooms, M. Dusselier, J. A. Geboers, B. Op de Beeck, R. Verhaeven, E. Gobechiya, J. A. Martens, A. Redl and B. F. Sels, *Green Chemistry*, 2014, **16**, 695-707.
17. Z. Tai, J. Zhang, A. Wang, M. Zheng and T. Zhang, *Chemical Communications*, 2012, **48**, 7052-7054.

18. M. Y. Zheng, A. Q. Wang, N. Ji, J. F. Pang, X. D. Wang and T. Zhang, *ChemSusChem*, 2009, **3**, 63-66.
19. H. A. Pary, C. E. Schweickert and B. H. Minnich, *Industrial & Engineering Chemistry,* 1952, **44**, 1146-1152.
20. V. Jollet, F. Chambon, F. Rataboul, A. Cabiac, C. Pinel, E. Guillon and N. Essayem, *Green Chemistry*, 2009, **11**, 2052-2060.
21. E. Crezee, B. W. Hoffer, R. J. Berger, M. Makkee, F. Kapteijn and J. A. Moulijn, *Applied Catalysis A: General*, 2003, **251**, 1-17.
22. A. Fukuoka and P. L. Dhepe, *Angewandte Chemie International Edition*, 2006, **45**, 5161-5163.
23. H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chemistry*, 2011, **13**, 326-333.
24. X. Wang, L. Altmann, J. R. Stöver, V. Zielasek, M. Bäumer, K. Al-Shamery, H. Borchert, J. R. Parisi and J. Kolny-Olesiak, *Chemistry of Materials*, 2013, **25**, 1400-1407.
25. V. Grolier and R. Schmid-Fetzer, *Journal of Alloys and Compounds*, 2008, **450**, 264-271.
26. R. Burch and L. C. Garla, *Journal of Catalysis*, 1981, **71**, 360-372.
27. C. Corolleur, D. Tomanova and F. G. Gault, *Journal of Catalysis*, 1972, **24**, 401-416.
28. F. M. Dautzenberg, J. N. Helle, P. Biloen and W. M. H. Sachtler, *Journal of Catalysis*, 1980, **63**, 119-128.
29. P. Gallezot, P. J. Cerino, B. Blanc, G. Flèche and P. Fuertes, *Journal of Catalysis*, 1994, **146**, 93-102.
30. H. Lieske and J. Völter, *Journal of Catalysis*, 1984, **90**, 96-105.
31. S. Karski, T. Paryjczak and I. Witonnska, *Kinetics and Catalysis*, 2003, **44**, 618-622.
32. J. L. Margitfalvi, M. L. Hegedüs and E. Tálas, *Journal of Molecular Catalysis*, 1989, **51**, 279-284.
33. M. Wenkin, P. Ruiz, B. Delmon and M. Devillers, *Journal of Molecular Catalysis A: Chemical*, 2002, **180**, 141-159.
34. J. M. Ramallo-Lăpez, G. F. Santori, L. Giovanetti, M. L. Casella, O. A. Ferretti and F. G. Requejo, *The Journal of Physical Chemistry B*, 2003, **107**, 11441-11451.
35. F. Coloma, A. Sepŭlveda-Escribano, J. L. G. Fierro and F. Rodrīguez-Reinoso, *Applied Catalysis A: General*, 1996, **136**, 231-248.
36. V. Ponec, *Applied Catalysis A: General*, 1997, **149**, 27-48.
37. T. B. L. W. Marinelli, S. Nabuurs and V. Ponec, *Journal of Catalysis*, 1995, **151**, 431-438.
38. G. J. Siri, J. M. Ramallo-Lăpez, M. n. L. Casella, J. L. G. Fierro, F. l. G. Requejo and O. A. Ferretti, *Applied Catalysis A: General*, 2005, **278**, 239-249.
39. M. Englisch, V. S. Ranade and J. A. Lercher, *Journal of Molecular Catalysis A: Chemical*, 1997, **121**, 69-80.

40. N. Homs, J. Llorca, P. R. de la Piscina, F. Rodriguez-Reinoso, A. Sepulveda-Escribano and J. Silvestre-Albero, *Physical Chemistry Chemical Physics*, 2001, **3**, 1782-1788.
41. A. B. Merlo, V. Vetere, J. F. Ruggera and M. n. L. Casella, *Catalysis Communications*, 2009, **10**, 1665-1669.
42. G. C. Torres, S. D. Ledesma, E. L. Jablonski, S. R. de Miguel and O. A. Scelza, *Catalysis Today*, 1999, **48**, 65-72.
43. P. D. Zgolicz, V. I. Rodrīguez, I. M. J. Vilella, S. R. de Miguel and O. A. Scelza, *Applied Catalysis A: General*, 2011, **392**, 208-217.
44. J. Sun and H. Liu, *Green Chemistry*, 2011, **13**, 135-142.
45. V. Choudhary, A. B. Pinar, S. I. Sandler, D. G. Vlachos and R. F. Lobo, *ACS Catalysis*, 2011, **1**, 1724-1728.
46. V. Choudhary, S. Caratzoulas and D. G. Vlachos, *Carbohydrate Research*, 2013, **368**, 89-95.
47. J. P. Mikkola, R. Sjöholm, T. Salmi and P. Mäki-Arvela, *Catalysis Today*, 1999, **48**, 73-81.
48. F. Domīnguez, G. Carruyo, R. Andrade, R. Solano, D. Rodrīguez, J. Sănchez and G. Arteaga, *Catalysis Letters*, 2008, **123**, 207-212.
49. H. Verbeek and W. M. H. Sachtler, *Journal of Catalysis*, 1976, **42**, 257-267.
50. G. T. Baronetti, S. R. de Miguel, O. A. Scelza and A. A. Castro, *Applied Catalysis*, 1986, **24**, 109-116.
51. R. Bacaud, P. Bussiĕre and F. Figueras, *Journal of Catalysis*, 1981, **69**, 399-409.
52. R. Bacaud and P. Biloen, *Surfce Science,* 1974*,* **41***,* 348-358..
53. K. Balakrishnan and J. Schwank, *Journal of Catalysis*, 1991, **127**, 287-306.
54. B. A. Sexton, A. E. Hughes and K. Foger, *Journal of Catalysis*, 1984, **88**, 466-477.
55. V. N. Seleznev, Y. V. Fomichev and M. E. Levinter, *Neftekhimiya*, 1974, **14**, 205-208..
56. Y. Román-Leshkov, M. Moliner, J. A. Labinger and M. E. Davis, *Angewandte Chemie International Edition*, 2010, **49**, 8954-8957.
57. V. A. Mazzieri, M. R. Sad, C. R. Vera, C. L. Pieck and R. Grau, *QuÃmica Nova*, 2010, **33**, 269-272.
58. S. Galvagno, C. Milone, A. Donato, G. Neri and R. Pietropaolo, *Catalysis Letters*, 1993, **17**, 55-61.
59. S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, *Catalysis Letters*, 1991, **8**, 9-14.
60. R. Burch, *Journal of Catalysis*, 1981, **71**, 348-359.

Chapter 4

Conversion of polysaccharides in to sugar alcohols

Chapter 4A

Conversion of isolated polysaccharides in to sugar alcohols

4A.1. Introduction

As mentioned earlier (chapter 1, section 1.2.2.1 and 1.2.2.2), sugar alcohols can be synthesized from monosaccharides (C5 and C6 sugars) by hydrogenation or from polysaccharides by hydrolytic hydrogenation. In previous chapter (chapter 3, section 3.3.1 and 3.3.2), conversion of monosaccharides in to sugar alcohols over various monometallic and bimetallic catalysts is discussed. Bimetallic Pt-Sn/AL catalyst was successfully employed in the hydrogenation of C5 and C6 sugars to improve the yields of sugar alcohols (up to 90%). Nevertheless, the production of monosaccharides from polysaccharides with high selectivity is tedious because such acid catalyzed hydrolysis is associated with some other acid catalyzed reactions. Most of the sugars occur naturally in the form of polysaccharides i.e. cellulose, hemicellulose, starch, inulin, etc. Production of sugar alcohols from polysaccharides is a two step process including hydrolysis of polysaccharides in to constituting monosaccharides and subsequent hydrogenation of monosaccharides in to sugar alcohols. Production of sugar alcohols from polysaccharides by hydrolytic hydrogenation in a one pot manner is the better alternative as it avoids separation and purification of intermediate chemical compound (sugars) and save time as well as resources. Considering above facts, conversions of hemicelluloses and inulin were undertaken to yield sugar alcohols in one pot fashion. Hemicelluloses are the second most abundant plant derived polysaccharides after cellulose and non edible for humans; therefore were selected for the entitled conversion. Inulin can be obtained from vegetables and grains which are not suitable for human consumption e.g. rotten grains (wheat), low grades garlic, asparagus, etc. Moreover the conversion methods for inulin to yield sugar alcohols are scanty and understudied.

Hence this chapter consolidates results for the conversions of hemicelluloses (xylan and arabinogalactan) and inulin in to sugar alcohols over monometallic and bimetallic catalysts. Various experiments were carried out to optimize reaction conditions to achieve maximum yield of sugar alcohols from above mentioned polysaccharides. Effects of supports, metals and promoters were explored and correlated with catalytic activity.

4A.2. Materials and methods

4A.2.1. Materials

Chemicals : xylan (oat spelt; Product No. X0627; xylose ≥70%, arabinose ≤ 10%, glucose ≤ 15%), levulinic acid (98%), furfuryl alcohol (98%), sorbitol (99.9%) were purchased from Aldrich Chemicals, USA. Xylose (99%) and arabinose (99%) were purchased from Loba Chemicals, India. Glucose (99%), galactose (98%), fructose (99%), galactitol (99%), mannitol (99.5%), xylitol (99%), arabitol (99%), glycerol (98%), ethylene glycol (99%), 1,2-propanediol (99.5%), furfural (99%), were procured from s.d. fine chemicals, India. Inulin and arabinogalactan (larch wood) were purchased from TCI Chemicals, Japan. Xylo-oligosaccharides (2<DP<7) standard was purchased from Cascade analytical reagents & biochemicals, USA.

Catalysts: Monometallic and bimetallic catalysts were synthesized by wet impregnation method (co-impregnation method for bimetallic catalyst). Synthesized catalysts were evaluated for the conversion of polysaccharides. Detail information about supports, metal precursors used for the catalyst synthesis and details about synthesis procedure is given in chapter 2 (refer section 2.2).

4A.2.2. Experimental set-up and analysis of reaction mixture

Various catalytic and non-catalytic runs were carried out in a batch mode autoclave and reaction mixtures were analyzed using HPLC. Details about experimental set-up, catalytic methods and analysis of reaction mixture are mentioned in chapter 3 (refer section 3.2.2 and 3.2.3). Experiments were carried out at temperature ranging between 70°C and 200°C for various times (6 h-20 h). Typical experiments were carried out at 16 bar H_2 and with substrate/catalyst ratio 2 (substrate 0.15 g and catalyst 0.075 g, 35 mL H_2O). Other than typical experiments, some experiments at 8-24 bar H_2 pressure and with different substrate/catalyst ratio (S/C= 4, 2, 1, 0.66) were conducted.

4A.2.3. Calculations

In all reactions (with hemicelluloses and inulin) conversions were calculated based on the weights. Reaction mixture was centrifuged to separate liquid and solid. Liquid was decanted and solid was dried and weighed. By subtracting weight of catalyst taken from the weight of dried solid obtained after centrifugation, weight of unconverted substrate was calculated.

Conversion of the substrate was calculated by formula:

Conversion (%) = [Weight of substrate charged, initial – Weight of substrate unconverted, final / Weight of substrate charged, initial] × 100

Yields of various products were calculated using following formula:

Yield (%) = [Moles of product formed (HPLC)/ Theoretical moles of product] × 100

For example, yield of sugar alcohol obtained from xylan is calculated by considering molecular weight of xylan as 132, due to loss of one H_2O (molecular weight =18) by each xylose molecule (molecular weight =150), while forming polysaccharide. So, 132 g of xylan gives 150 g of xylose which on hydrogenation gives 152 g sugar alcohols (xylitol/arabitol, molecular weight =152) considering 100% conversion and selectivity. Eventually, 132 g of xylan gives 152 g of sugar alcohol. Weight can be converted to mole by dividing with molecular weight.

Yield of sugar alcohol (%) = [Moles of sugar alcohol formed (HPLC)/ Theoretical moles sugar alcohol] × 100

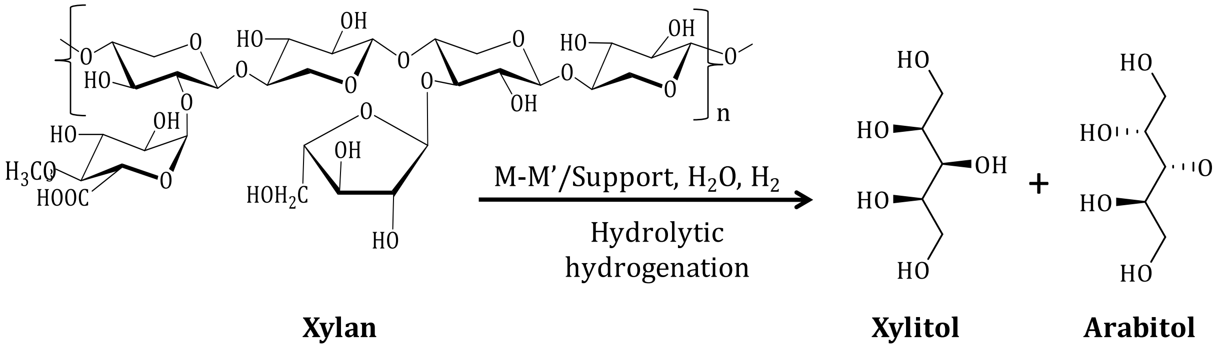
4A.3. Results and discussion

4A.3.1. Conversion of hemicelluloses in to sugar alcohols over monometallic and bimetallic catalysts

As mentioned earlier, in this chapter results for the conversions of hemicelluloses and inulin are consolidated. First, we will discuss results for the conversion of hemicelluloses. To check the effect of composition of the substrate, two different types of hemicelluloses having completely different compositions were used. Xylan which is mainly made up of xylose and arabinogalactan which is composed of arabinose and galactose were subjected for various catalytic and non-catalytic experiments to produce sugar alcohols. Details about the composition of xylan and arabinogalactan are discussed in chapter 1 (refer section 1.1.2).

4A.3.1.1. Conversion of xylan in to sugar alcohols

Conversion of oat spelt xylan was carried out over monometallic and bimetallic catalysts for the production of sugar alcohols (xylitol+arabitol) (scheme 4A.1). Xylan is mainly made-up of xylose and hence xylitol is the major desired product. Besides this, arabitol is one of the expected products, as xylan itself contains some amount of arabinose (ca. 10%) and xylose can undergo isomerization to form arabinose which upon hydrogenation yields arabitol.



Scheme 4A.1. Conversion of xylan in to sugar alcohols.

(M=Pt, Ru; M'=Sn, Ga, Fe; Support= AL, SA, C)

4A.3.1.1.1. Effect of supports (γ-Al_2O_3, SiO_2-Al_2O_3, activated carbon) and metals (Pt and Ru)

Results for the conversion of monosaccharides over various monometallic catalysts depict that support plays important role in determining catalytic properties. In the conversion of polysaccharides like xylan, support may play more significant role. Conversion of polysaccharide in to sugar alcohols is a two step process, i.e. hydrolysis of polysaccharide to yield monosaccharides and further hydrogenation of monosaccharides to yield sugar alcohols out of which hydrolysis is acid catalyzed reaction. Use of solid acid catalysts for hydrolysis of polysaccharides like cellulose and hemicellulose is reported earlier in the literature.[1-9] Hence, supported metal catalyst having acidic support may behave differently than the catalyst having neutral support. Since acidic functionality helps to catalyze the hydrolysis reaction, it is very interesting to study the effect of supports on the conversion of polysaccharides. To study this imperative effect, Pt catalysts using different supports (AL, SA, C) were prepared and evaluated in the conversion of xylan (Figure 4A.1). From the literature it is known that conversion of xylan over heterogeneous catalysts is feasible only at higher temperature (170°C),[9, 10] so experiments were carried out at reaction temperature of 190°C at 16 bar H_2 for 16 h. Similar to the xylose hydrogenation, amongst all monometallic catalysts, Ru(2)/C showed highest yield (21%) for sugar alcohols (xylitol+arabitol) from xylan. Trend of sugar alcohols formation from xylan over various catalysts was as follows:

Ru(2)/C (21%) > Pt(2)/AL (15.5%) > Pt(2)/SA (13%) = Pt(2)/C (13%) > without catalyst (12.5%)

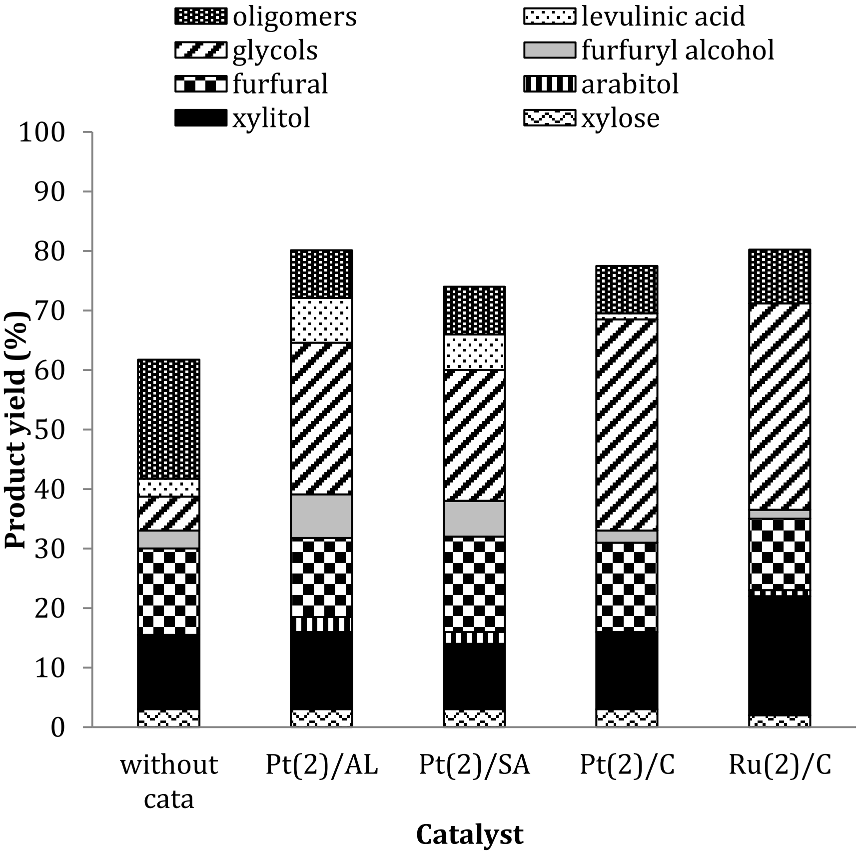


Figure 4A.1. Effect of supports and metals on xylan conversion.

Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C,16 bar H_2 at R.T., 16 h.

In non-catalytic reaction, besides sugar alcohols, furans (furfural and furfuryl alcohol) were formed (17.5%) indicating, such conversions are possible without any catalyst at this reaction condition. Over Pt(2)/AL and Pt(2)/SA (catalyst having acidic support) yield of furans was more as compare to non-catalytic reaction (20.6% and 22%, respectively). On the other hand over Pt(2)/C and Ru(2)/C (catalyst having neutral support) yield of furans was less (17% and 13.5%) compared to non-catalytic reaction. This is obvious since acidic support may catalyze dehydration of xylose to yield furfural. In all catalytic and non-catalyst runs conversion was more than 90%.

From the results obtained for the conversion of monosaccharides (C5 and C6 sugars), it was concluded that at higher temperature (190°C) selectivity for the sugar alcohols is low compare to lower temperature (130°C) (refer chapter 3, section 3.3.1.3, 3.3.2.5 and 3.3.4.1). Hence with the intention to boost the yield of sugar alcohols, conversion of xylan over Ru(2)/C was conducted at 170°C to check the effect of temperature. However, comparison between the results at 190°C and 170°C showed that better yields can be achieved at 190°C (21%) than at 170°C (12%) in 16 h. These results proved that even though the hydrogenation of monosaccharides is favorable at lower temperature but hydrolysis step requires higher temperature. Attempts were done to improve the yield of sugar alcohols by increasing the metal loading in the catalysts. Unfortunately much improvement in the yield was not observed. Over Ru(3.5)/C and Pt(3.5)/AL maximum 25% and 18% yields of sugar alcohols (xylitol+arabitol) from xylan were obtained, respectively. Hence the exploitation of bimetallic catalyst is mandatory to achieve better yield of sugar alcohols from xylan.

4A.3.1.1.2. Effect of Sn as promoter and effect of Pt:Sn ratio on xylan conversion

Effect of Sn as promoter in the conversion of xylan was investigated by evaluating various Pt-Sn/AL catalysts with varying Pt:Sn ratio. Pt-Sn/AL catalysts with constant Pt loading (3.5wt%) and varying Sn loading (0-3.5wt%) were prepared and tested in xylan conversion at 190°C for 16 h at 16 bar H_2 pressure (Figure 4A.2). In contrast to monometallic Pt(3.5)/AL catalyst (18%), all the bimetallic Pt-Sn/AL catalysts showed enhanced sugar alcohols yields. Among all Pt-Sn/AL catalysts, highest sugar alcohols formation was observed with Pt(3.5)Sn(0.43)/AL (50%) and compared to monometallic Pt(3.5)/AL catalyst this activity is 2.8 times higher. In addition to sugar alcohols, formation of other products such as, glycols (ethylene glycol, glycerol, 1,2-propanediol), furfural, furfuryl alcohol, levulinic acid, and some oligomers was also observed.

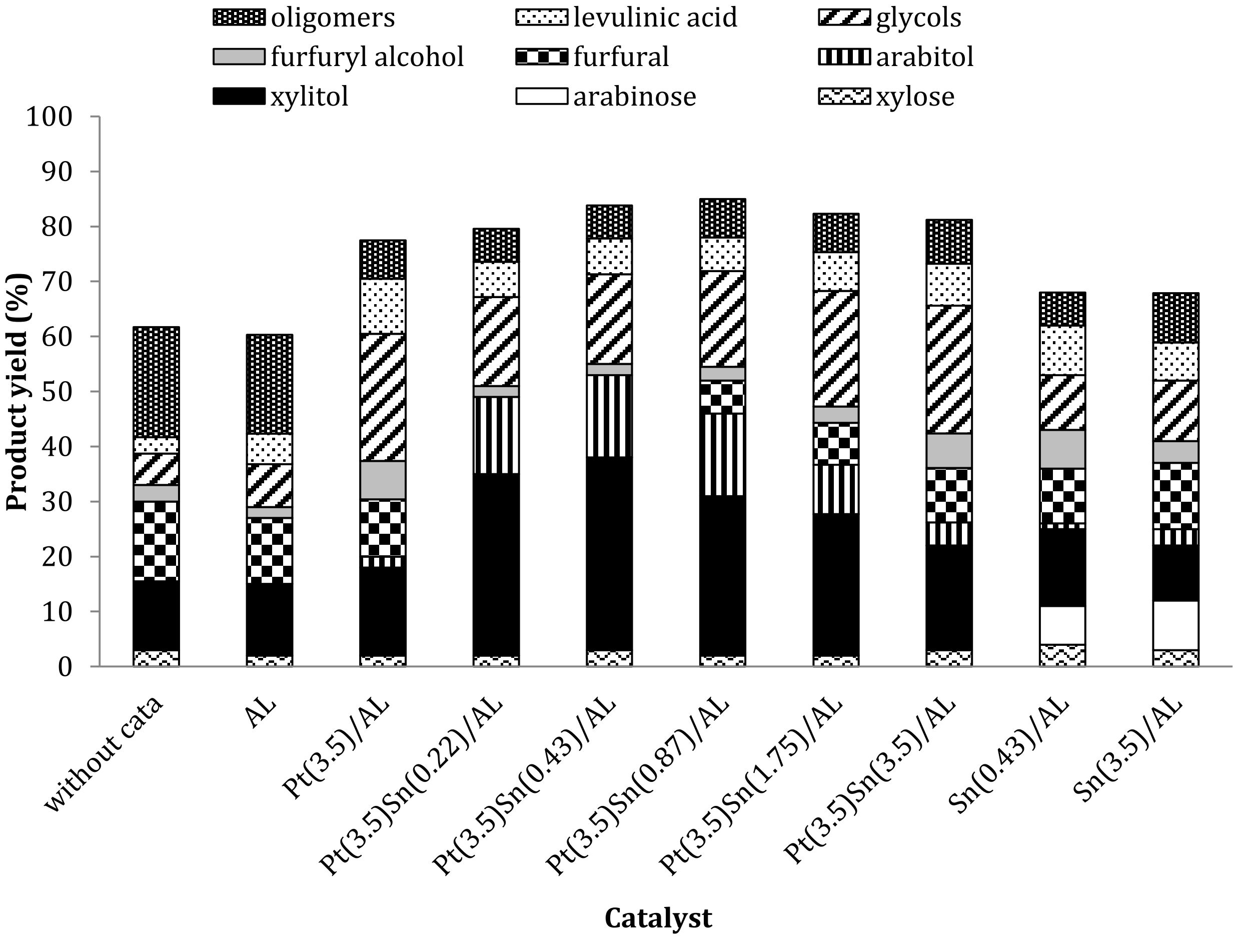


Figure 4A.2. Effect of Pt:Sn ratio on the formation of sugar alcohols from xylan. Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 16 h.

Yiled of sugar alcohols was observed to be decreasing with increasing Sn loading in Pt-Sn/AL catalyst. At the same time yield of side products like glycols and furans was more over Pt-Sn/AL catalysts with higher Sn loading. Over Pt(3.5)Sn(0.22)/AL and Pt(3.5)Sn(0.43)/AL no furfural formation was observed and yield of furfuryl alcohol was merely 2%. But over Pt(3.5)Sn(0.87)/AL, Pt(3.5)Sn(1.75)/AL and Pt(3.5)Sn(3.5)/AL catalysts, furans yield was 8.5, 10.6 and 16.2%, repectively. Analogous to xylose reaction (chapter 3, section 3.3.2.2), in xylan reaction too, Sn(0.43)/AL and Sn(3.5)/AL catalysts showed very low yields of sugar alcohols but considerable amount of furans was formed (17 and 16%, repectively). Along with these products, arabinose (7 and 9%) was formed over Sn(0.43)/AL and Sn(3.5)/AL catalysts. Xylan reactions without catalyst and with bare support, AL gave 12.5 and 13% yield for sugar alcohols. In all the catalytic and non catalytic reactions more than 90% conversion of xylan (on weight basis) was observed in 16 h. Aformentioned data shows that, Sn (if added in appropriate amount) can promote the activity of Pt/AL for the production of sugar alcohols from xylan. Maximum yield of sugar alcohols can be achieved at optimum Pt:Sn ratio i.e. Pt(3.5)Sn(0.43)/AL catalyst showed better yield (50%) than monometallic Pt(3.5)/AL (18%) and Ru(3.5)/C (25%) too. Explanation for the variation in activity towards formation of sugar alcohols of different catalysts on the basis of catalyst properties is given in coming section (refer section 4A.3.3).

4A.3.1.1.3. Effect of metal loading

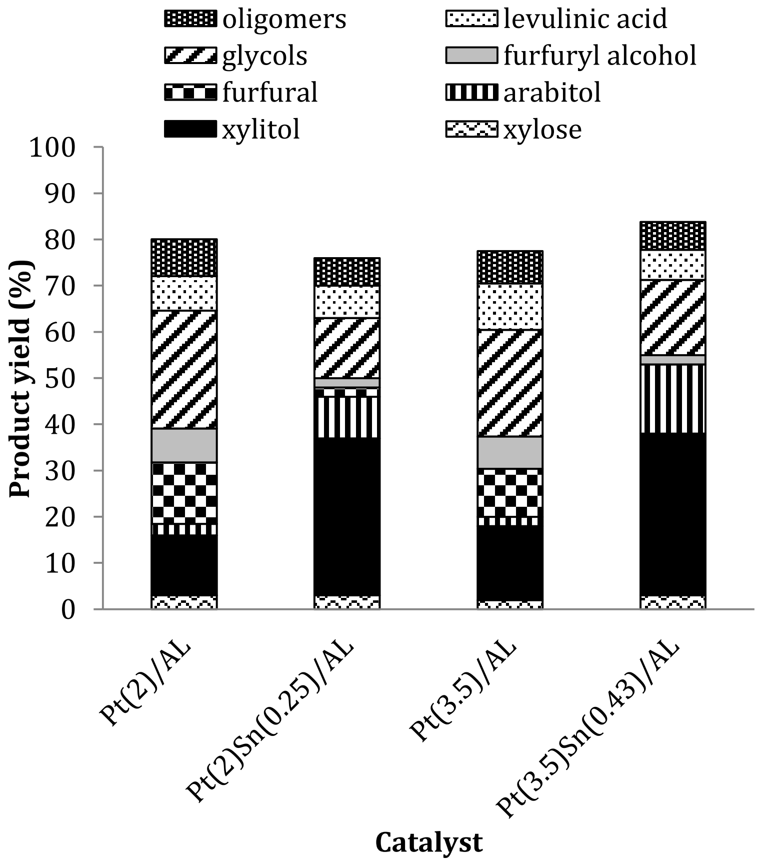


Figure 4A.3. Effect of metal loading on xylan conversion.

Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 16 h.

Since, in the xylose hydrogenation reaction not much disparity in the catalytic activity between Pt(3.5)Sn(0.43)/AL (79% sugar alcohols yield) and Pt(2)Sn(0.25)/AL (73% sugar alcohols yield) was observed (chapter 3, section 3.3.2.3), it was decided to carry out xylan reactions with Pt(2)Sn(0.25)/AL catalyst. The results presented in Figure 4A.3 shows marginal decrease in the sugar alcohols formation over Pt(2)Sn(0.25)/AL catalyst (43%) as against Pt(3.5)Sn(0.43)/AL catalyst (50%). These results are understandable since availability of Pt and Sn is reduced when same quantity (0.075 g) of Pt(2)Sn(0.25)/AL catalyst is used in the reaction. As discussed in chapter 2 (section 2.3.2.3), average particle size of Pt in both the catalysts, Pt(2)Sn(0.25)/AL and Pt(3.5)Sn(0.43)/AL is similar (10-20 nm), therefore total number of Pt atom exposed on the surface will be more in the case of Pt(3.5)Sn(0.43)/AL which altimately gives better yields. Although Pt loading was decreased to 2wt% from 3.5wt%, decrease in the yield of sugar alcohols was only 7%. This implies that, good yield of sugar alcohols can be obtained over catalyst with lower metal loading in the entitled conversion.

4A.3.1.1.4. Effect of reaction parameters

Effect of temperature and time: Effect of reaction temperature was studied by conducting experiments at 170, 190 and 200°C for 12 h (Figure 4A.4).

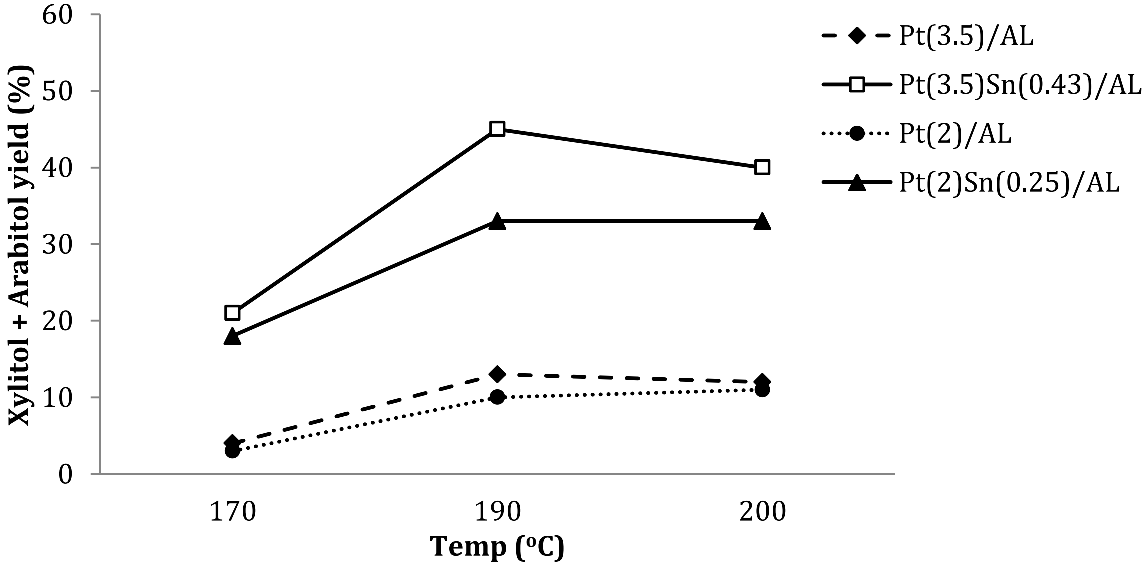


Figure 4A.4. Effect of temperature on xylan conversion.

Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 16 bar H_2 at R.T., 12 h.

When reactions were carried out at 170°C for 12 h, very poor yields of sugar alcohols were obtained over monometallic Pt(3.5)/AL (4%) and bimetallic Pt(3.5)Sn(0.43)/AL (21%) catalyst with oligomers as major product. Significant improvement in the yield was observed, when temperature was increased to 190°C. In 12 h of reaction time 45, 33, 13 and 10% yield of sugar alcohols were achieved over Pt(3.5)Sn(0.43)/AL, Pt(2)Sn(0.25)/AL, Pt(3.5)/AL and Pt(2)/AL, respectively. But further increase in the temperature to 200°C, did not show any enhancement in the yields (40, 33, 12 and 11% yield over Pt(3.5)Sn(0.43)/AL, Pt(2)Sn(0.25)/AL, Pt(3.5)/AL and Pt(2)/AL, respectively). Hence other reaction parameters were optimized at reaction temperature of 190°C. To achieve complete conversion with maximum yield for sugar alcohols, experiments were carried out at 190°C for various times. Over Pt(3.5)Sn(0.43)/AL maximum 50% yield of sugar alcohols was achieved in 16 h, however yield could not be improved by conducting reaction for longer time (20 h). Over Pt(2)Sn(0.25)/AL maximum 43% yield was observed in 16 h and not much improvement (45% yield) was seen in 20 h.

Effect of H_2 pressure: In xylan conversions, reactions were done after charging 16 bar H_2 in the reactor at room temperature. Though, to check the effect of H_2 pressure on xylan conversion and product yields, reactions were conducted after charging 8, 16 and 24 bar H_2 at room temperature (Figure 4A.5). Over Pt(3.5)Sn(0.43)/AL catalyst 35% yield for sugar alcohols was observed in the reaction at 8 bar H_2 pressure, while at 16 bar H_2 50% yield was obtained. No improvement in the sugar alcohols yield compare to 16 bar was observed when reaction was carried out at 24 bar H_2 pressure (52%). Similar to xylose conversion in xylan conversion also, until attaining certain H_2 pressure yield for sugar alcohols was observed to be increased with increase in H_2 pressure. The solubility of gases (H_2) in solvent (H_2O) is a function of temperature & pressure and hence with the increase in pressure, enhancement in solubility of gas is expected. With increase in the solubility, higher concentration of H_2 is adsorbed on the metal surface which will be available for reactions.[11, 12] In this way sugar alcohols yield can be improved by increasing H_2 pressure from 8 bar to 16 bar (for more discussion, refer chapter 3, section 3.3.1.3). Similar results were obtained (25, 43 and 44% yield) when reactions were carried out over Pt(2)Sn(0.25)/AL with 8, 16 and 24 bar H_2, respectively (Figure 4A.5).

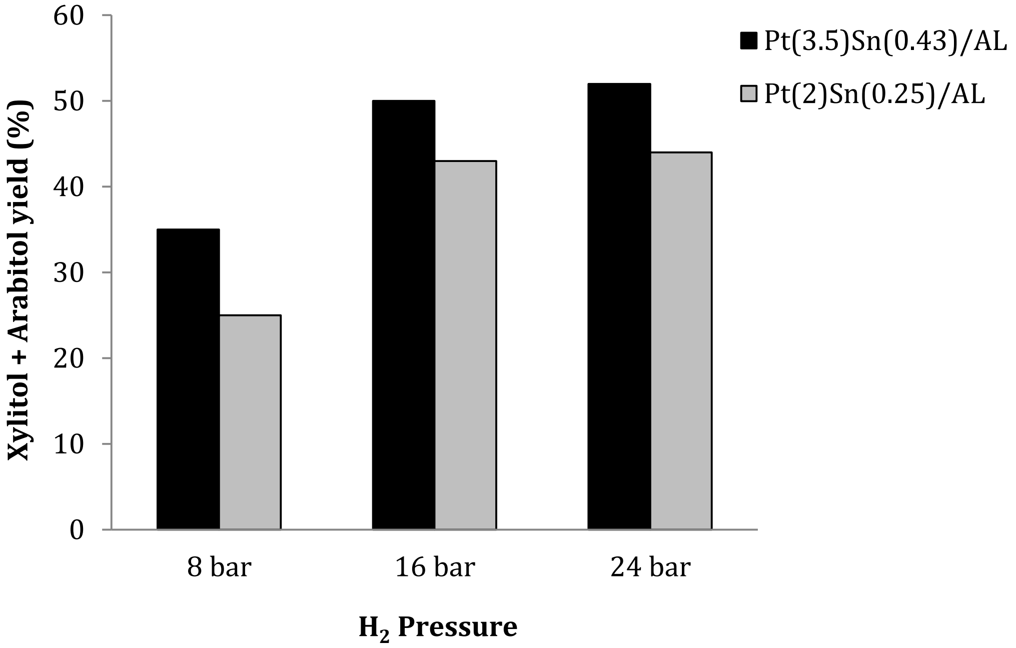


Figure 4A.5. Effect of H_2 pressure on xylan conversion.

Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 h.

Effect of substrate/catalyst ratio: Xylan reactions were carried out over Pt(2)Sn(0.25)/AL with varying catalyst quantity by using constant substrate quantity (0.15 g xylan) to check the effect of different S/C ratio (*wt/wt*) on the yield of sugar alcohols. Experiments were done with catalyst quantity of 0.038, 0.075, 0.15 and 0.225 g (S/C = 4, 2, 1 and 0.66, respectively) at 190°C for 16 h and results are represented in Figure 4A.6. With increase in the catalyst quantity from 0.038 to 0.15 g, yield of sugar alcohols was increased from 30 to 55%. Further increase in the catalyst quantity to 0.225 g did not show considerable improvement in the yield (57%). When higher amount of catalyst was added, obviously more active sites for hydrolysis and hydrogenation were available, hence better yields were obtained. But after optimum quantity, yield cannot be improved only by increasing the catalyst quantity at constant H_2 pressure and with constant substrate quantity. Because, rate of reaction depends on substrate quantity and H_2 adsorbed on the metal surface which is govern by number of active metal sites (catalyst quantity) and solubilized H_2 in the reaction mixture (H_2 pressure). For more discussion on the effect of S/C ratio, refer chapter 3, section 3.3.1.3. These observations advocate that sufficient quantity of catalyst should be available in the reaction to improve the yields.

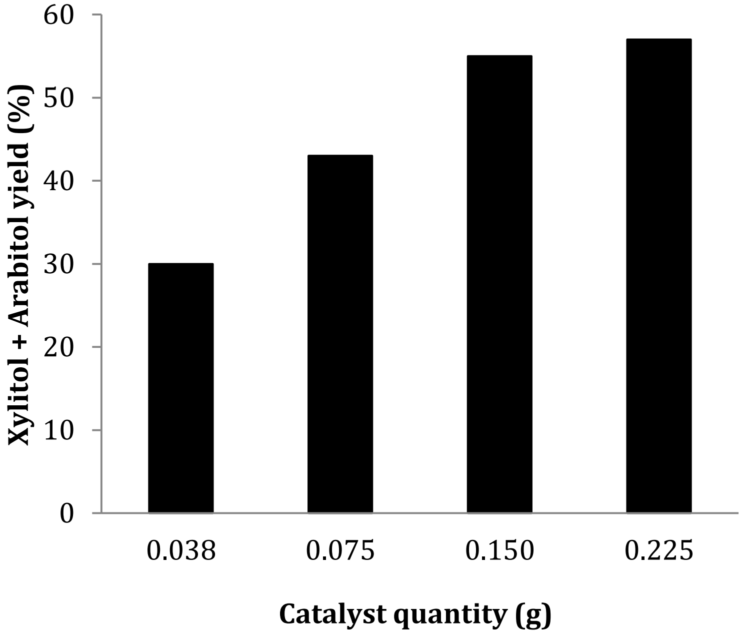


Figure 4A.6. Effect of catalyst quantity on xylan conversion.

Reaction condition: xylan (oat spelt) 0.15 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 16 h.

4A.3.1.1.5. Effect of Fe and Ga as promoter in Pt/AL catalyst

Activity of the Pt/AL catalyst for the production of sugar alcohols from xylan was improved successfully by adding small amount of Sn. Sugar alcohols yield was increased from 15.5% to 43% over Pt(2)Sn(0.25)/AL compare to Pt(2)/AL. Xylan reactions were also carried out using Pt(2)Fe(0.25)/AL (17% yield) and Pt(2)Ga(0.25)/AL (12% yield) and as observed in xylose hydrogenation reactions (chapter 3, section 3.3.2.6), in xylan reactions too, Pt(2)Sn(0.25)/AL catalyst showed the highest yield of sugar alcohols (43%). Lower yields of sugar alcohols over Pt-Fe/AL and Pt-Ga/AL catalysts were allied with higher amount of side products like glycols (Figure 4A.7). Yield of sugar alcohols obtained over Pt(2)Fe(0.25)/AL was better than Pt(2)/AL catalyst while Pt(2)Ga(0.25)/AL catalyst showed poor yield of sugar alcohols. However side reactions to yield glycols are more prominent over Pt(2)Fe(0.25)/AL and Pt(2)Ga(0.25)/AL than Pt(2)/AL, Pt(2)Sn(0.25)/AL and non-catalytic reaction. Deprived activity of the Pt(2)Ga(0.25)/AL towards formation of sugar alcohols can be attributed to the reduction of Ga and encapsulation of Pt by reduced Ga which can significantly affect the catalytic activity.[13]

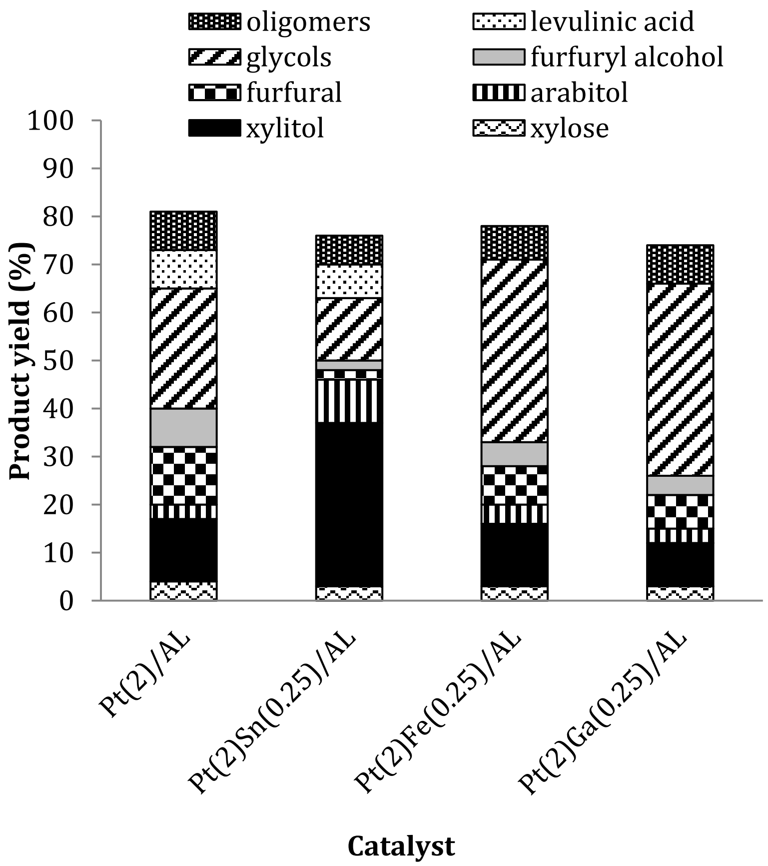


Figure 4A.7. Effect of Fe and Ga as a promoter on xylan conversion.
Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190˚C, 16 bar H_2 at R.T., 16 h.

Besides this, effect of supports in Pt-Sn bimetallic catalysts was studied by preparing catalysts with SA and C as a support material and their activities were evaluated in the conversion of xylan at 190°C for 16 h. Improvement in the yield of sugar alcohols was observed over Pt(2)Sn(0.25)/SA (36%) compare to Pt(2)/SA (13%). On the other hand promoter effect of Sn was not doable in the C supported catalysts, hence significant improvement in the yield was not observed over Pt(2)Sn(0.25)/C (19%) compare to Pt(2)/C (13%). Furthermore slightly low yield of sugar alcohols was observed over Ru(2)Sn(0.25)/C (14%) than Ru(2)/C (21%). Above results are in correlation with trend observed in the conversion of monosaccharides over various catalysts. This once again proved that Pt-Sn/AL bimetallic catalyst shows superior activity for the formation of sugar alcohols from xylan amongst all monometallic and bimetallic catalysts.

4A.3.1.1.6. Effect of residual Cl¯ on catalytic activity

Effect of residual Cl¯ was studied in xylose hydrogenation and it was clear from the results that Pt-Sn/AL catalysts do have residual Cl¯ but it does not have any significant effect on the conversion and product yields (refer chapter 3, section 3.3.3). Even so, the effect of Cl¯ on xylan conversion was studied because residual acidity due to Cl¯ can alter the activity of catalyst towards hydrolysis (as hydrolysis is the acid catalyzed reaction). For more details on experimental procedure to confirm the presence of Cl¯ ions in the Pt-Sn/AL catalysts refer chapter 3, section 3.3.3.

Table 4A.1. Effect of residual Cl¯ on xylan conversion.*

Catalyst	Conv. (%)	Product yield (%)						pH
		xylitol	arabitol	glycols^	furfural	FA$^{\Delta}$	LA$^{\lozenge}$	
Pt(3.5)/AL	94	16	2	23.1	10.4	7	10	5.66
Pt(3.5)/AL$	96	14	6	21	12.2	6	8.1	5.25
Pt(3.5)Sn(0.43)/AL$	94	35	15	16.3	0	2	6.5	5.34
Pt(3.5)Sn(0.43)/AL#	95	37	16	15	1	3	8.5	5.06

^glycols = glycerol+ethylene glycol+1,2-propanediol; $^{\Delta}$FA = furfuryl alcohol; $^{\lozenge}$LA = levulinic acid.

*Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C, 16 bar H_2 at R.T., 16 h.

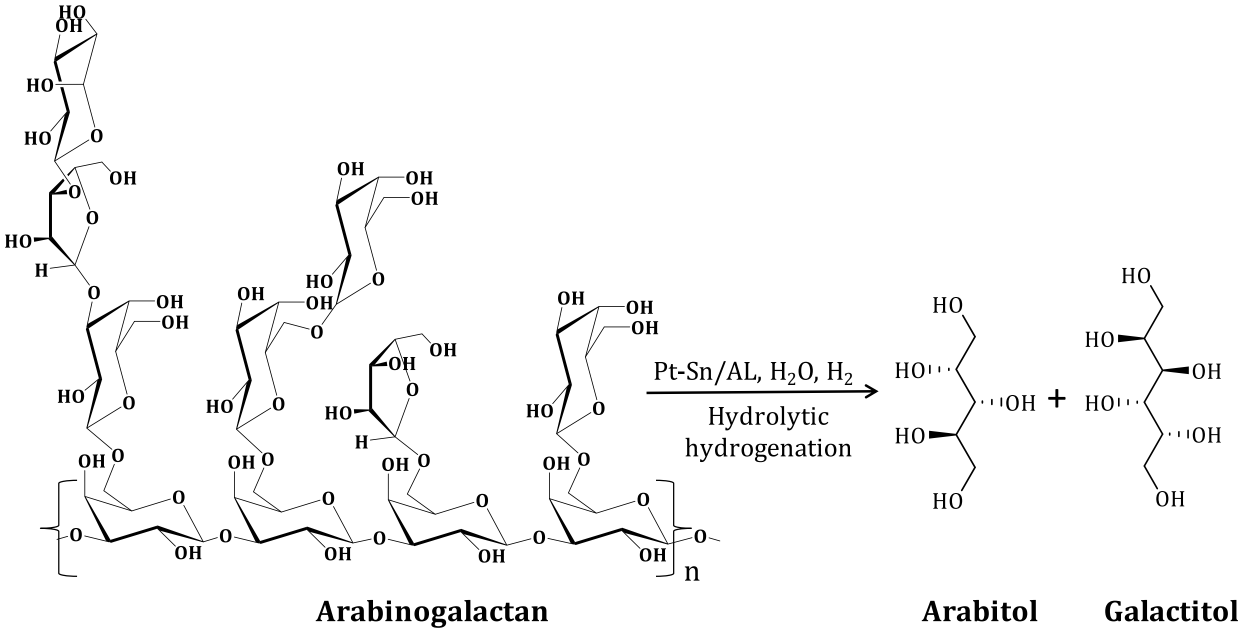
$During synthesis of 0.075 g of catalyst, 0.062 mL of 3M HCl was used.

#During the synthesis of 0.075 g of catalyst, 0.5 mL of 3M HCl was used instead of 0.062 mL of HCl.

Xylan reaction was conducted with Pt(3.5)/AL$-acidified catalyst (for synthesis procedure, refer chapter 2, section 2.2.2) at 190°C for 16 h at 16 bar H_2 and 20% yield of sugar alcohols (xylitol+arabitol) could be achieved. On the other hand when reaction was performed with typical Pt(3.5)/AL catalyst (without addition of HCl), 18% yield was obtained. Above results imply that even if HCl was added during the synthesis of Pt(3.5)/AL catalyst there was no difference in the sugar alcohols formation from xylan.

Over Pt(3.5)Sn(0.43)/AL# catalyst prepared by adding extra HCl (instead of 0.062 mL of HCl normally added during preparation of Pt(3.5)Sn(0.43)/AL catalyst (for 0.075 g), 0.5 mL of HCl was added during synthesis) yield (53%) similar to the yield over typical Pt(3.5)Sn(0.43)/AL (50%) was obtained (Table 4A.1). It can be concluded from above results that similar to the xylose conversion in xylan conversion too, residual Cl^- ions does not play any significant role. Variation in the yields of sugar alcohols was because of metals and supports but not because of residual Cl^- ions.

4A.3.1.2. Conversion of arabinogalactan in to sugar alcohols



Scheme 4A.2. Conversion of arabinogalactan in to sugar alcohols.

Results for the conversion of xylan in to sugar alcohols (xylitol+arabitol) proves that Pt-Sn/AL catalyst shows enhanced yields compare to Pt/AL, not only in the conversion of monosaccharides but also in the conversion of polysaccharides. Effect of supports, metals and promoters was studied for xylan conversion and Pt-Sn/AL showed the best results. Hence catalytic activity of Pt-Sn/AL catalyst was tested in the conversion of arabinogalactan, to check if the composition of substrate affects the activity (Scheme 4A.2). Details about structure and composition of arabinogalactan are mentioned in chapter 1 (refer section 1.1.2). Arabitol and galactitol are two major desired products in the entitled conversion, since arabinogalactan mainly composed of arabinose and galactose.

4A.3.1.2.1. Effect of reaction parameters

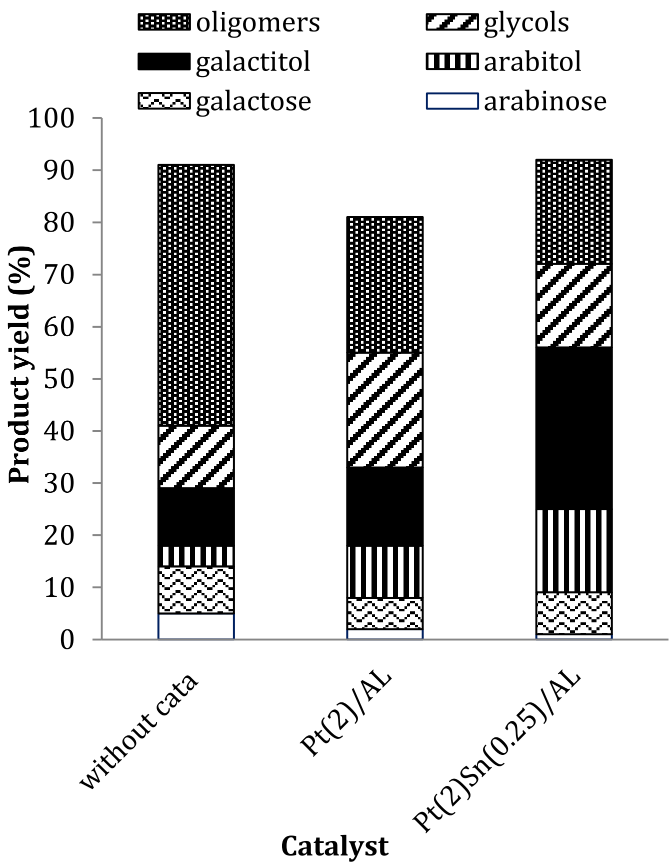


Figure 4A.8. Conversion of arabinogalactan in to sugar alcohols.

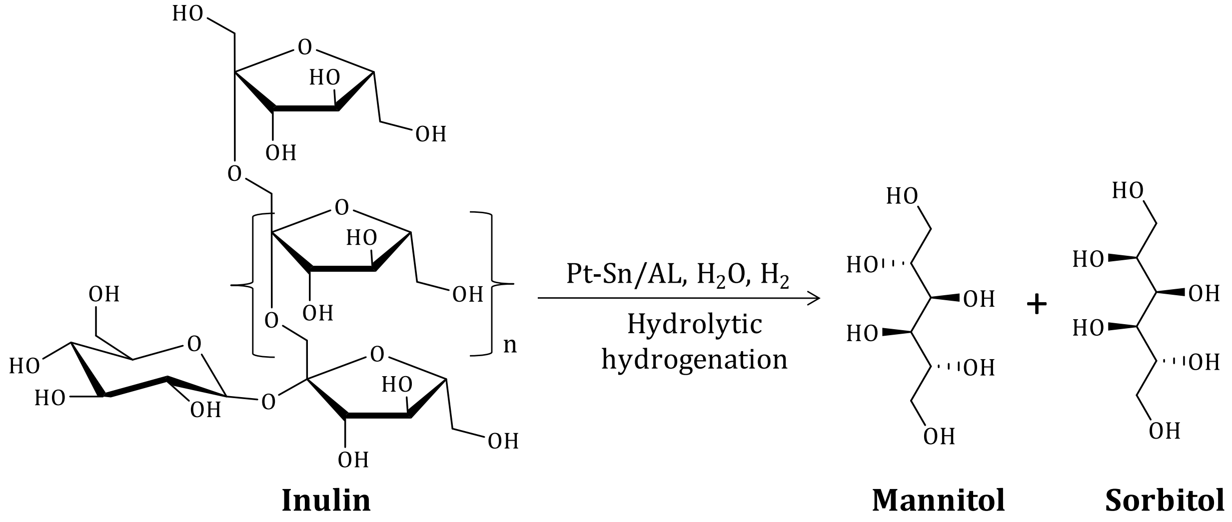
Reaction condition: arabinogalactan (larch wood) 0.15 g, catalyst 0.075 g, water 35 mL, 180°C, 16 bar H_2 at R.T., 12 h.

Reactions were carried out with arabinogalactan over Pt(2)Sn(0.25)/AL catalyst at various temperatures for 12 h. Reactions at 170, 180 and 190°C showed 23, 47 and 35% yield of sugar alcohols in 12 h. To achieve maximum yield of sugar alcohols, reactions were conducted at 180°C for various times. 47% yield was obtained in 12 h compared to 32% in 8 h, but further improvement in the yield was not seen at reaction time of 16 h (48%). When arabinogalactan conversion was carried out over Pt(2)/AL catalyst at 180°C and 16 bar H_2 for 12 h then 25% yield of sugar alcohols (galactitol+arabitol) was obtained (Figure

4A.8). Under similar reaction conditions, without catalyst 15% yield of sugar alcohols was observed.

4A.3.2. Conversion of inulin in to sugar alcohols

Inulin is the polysaccharide mainly composed of fructose (details of structure and composition is given in chapter 1, section 1.1.2). Inulin can be used as potential source for the production of valuable sugar alcohols i.e. mannitol (hydrogenation product of fructose) and sorbitol (hydrogenation product of glucose and isomer of mannitol). After enhancement in the yields of sugar alcohols from monosaccharides and hemicelluloses (xylan and arabinogalactan) using Pt-Sn/AL catalyst, activity of this bimetallic catalyst was evaluated in the conversion of inulin (scheme 4A.3). It is interesting to study the effect of reaction parameters on the inulin conversion and product yield as inulin has different structure and composition than hemicelluloses.



Scheme 4A.3. Conversion of inulin in to sugar alcohols.

4A.3.2.1. Effect of reaction parameters

In the view of above discussion, inulin conversion was studied at temperature ranging between 70 to 170°C over Pt(2)Sn(0.25)/AL for 12 h at 16 bar H_2 pressure. Maximum 77% yield of sugar alcohols (mannitol+sorbitol) was achieved at 110°C (almost complete conversion), while maximum 43 and 47% yield could be obtained from xylan and arabinogalactan. Better yield of sugar alcohols could be achieved from inulin at comparatively milder reaction condition than xylan and arabinogalactan probably because of difference in bonding between adjacent monomers and difference in the structures (refer chapter 1, section 1.1.2).

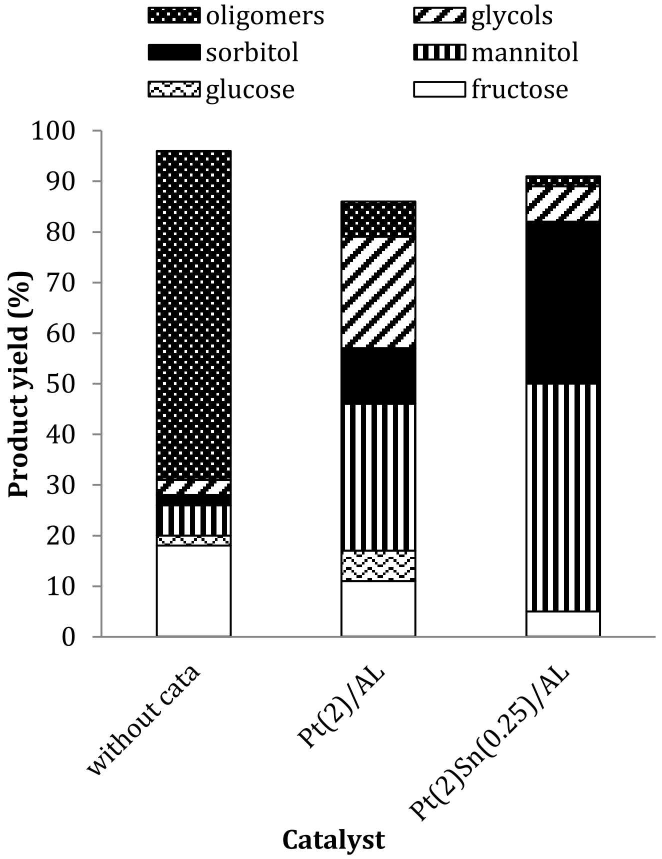


Figure 4A.9. Conversion of inulin in to sugar alcohols.

Reaction condition: inulin 0.15 g, catalyst 0.075 g, water 35 mL, 110°C, 16 bar H_2 at R.T., 12 h.

When reaction was carried out at lower temperature (90°C), poor yield was obtained (66%) and at higher temperature (>110°C) not much improvement was observed in the yield of sugar alcohols. Next, reactions were conducted at 110°C for 8, 12 and 16 h to achieve better yield, but it was not possible to improve the yield of sugar alcohols significantly in spite of longer reaction time. Almost similar yields were obtained in 12 h (77%) and 16 h (79%). Hence further reactions were carried out at 110°C and for 12 h. Inulin showed total sugar alcohols yield of 40% over Pt(2)/AL catalyst but the improvement in yield to 77% was seen over Pt(2)Sn(0.25)/AL catalyst (Figure 4A.9). Other than sugar alcohols, formation of glucose, fructose, glycols (glycerol, ethylene glycol, 1,2-propanediol) and oligomers was also observed. However, the yields of these products were more over Pt(2)/AL catalyst. In non catalytic reaction, oligomers were formed as major product and yields of sugar alcohols and other products were very low (Figure 4A.9).

4A.3.3. Correlation of catalyst properties with activity

Alike to the monosaccharides conversion, in the conversion of polysaccharides (xylan, arabinogalactan and inulin) activity of the Pt-Sn/AL catalyst towards the hydrolytic hydrogenation is governed by oxidation state of metals, dispersion of metals and formation of intermetallic systems. In the conversion of all three substrates (xylan, arabinogalactan and inulin), Pt-Sn/AL showed best yields of sugar alcohols amongst all monometallic and bimetallic catalysts. As explained in chapter 3 (refer section 3.3.2.7), from TEM study it is clear that Pt is well dispersed in the Pt-Sn/AL (10-20 nm particle size) than Pt(2)/AL (20-30 nm particle size), hence more number of active metal sites are available in Pt-Sn/AL catalyst. Moreover from XPS analysis, it can be concluded that Sn is present in (II) or (IV) state in the Pt-Sn/AL catalyst (catalysts with Sn loading up to 0.87wt%), because Sn interacts with alumina to form surface shell (tin-alumina complex) and cannot be reduce to Sn (0) state. Surface shell formation prevents the sintering of Pt particles during calcination, reduction and reaction, eventually better dispersion was achieved in Pt-Sn/AL catalyst. Further, Sn in (II) or (IV) states plays significant role in the second step of polysaccharide conversion i.e. hydrogenation of monosaccharides in to sugar alcohols. Sn in (II) or (IV) state can polarize the C=O bond of carbonyl group of sugar molecules which can be hydrogenated easily. Formation of intermetallic system like Pt_3Sn and PtSn was evident from XRD in the catalyst having higher Sn loading (1.75 and 3.5wt%). Hence over these catalyst comparatively low yields of sugar alcohols (xylitol+arabitol) were obtained in xylan conversion (similar trend was observed in xylose conversion, refer chapter 3, section 3.3.2.2).

4A.3.4. Recycle study and characterization of spent catalyst

Since in the conversion of all three substrates (xylan, arabinogalactan and inulin) Pt-Sn/AL catalyst showed best results, recycle study was done for xylan conversion over Pt(3.5)Sn(0.43)/AL and Pt(2)Sn(0.25)/AL catalyst and reactions were carried out at 190°C for 16 h at 16 bar H_2. On completion of reaction, catalyst was separated from product solution by centrifugation and then washed with water before its reuse in next run of xylan conversion. Recovered catalyst was reused without drying or any other treatment like calcination and reduction. Results from the Figure 4A.10 depict that yield of sugar alcohols was observed to be decreasing after each run by 8-12% over (3.5)Sn(0.43)/AL and Pt(2)Sn(0.25)/AL catalyst.

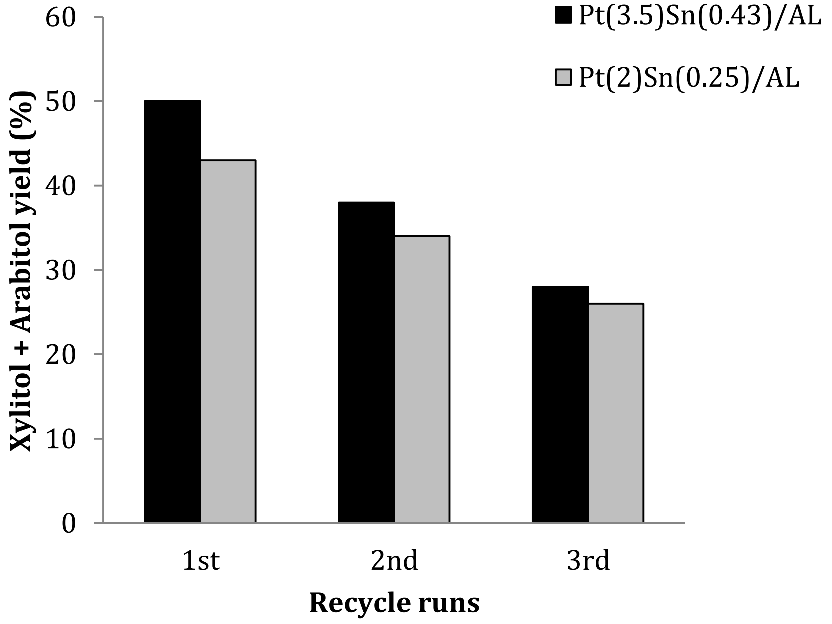


Figure 4A.10. Recycle study for xylan conversion over Pt-Sn/AL catalyst.

Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C,16 bar H_2 at R.T., 16 h.

The decrease in the yield is may be because of change in the S/C ratio, since loss of some catalyst quantity is possible during separation from reaction mixture and each time same amount of xylan (0.15 g) and solvent (H_2O, 35 mL) was added. Besides this, spent catalyst may have some amount of unconverted substrate or adsorbed product associated with it which can alter its catalytic activity. Over Pt(3.5)Sn(0.43)/AL catalyst 50, 38 and 28% yield of sugar alcohols (xylitol+arabitol) was obtained in 1st, 2nd and 3rd run, while over Pt(2)Sn(0.25)/AL yield was 43, 34 and 26% for 1st, 2nd and 3rd run, respectively (Figure 4A.10). Similar results were obtained when recycle study was done for arabinogalactan (at 180°C, 12 h, 16 bar H_2) and inulin (at 110°C, 12 h, 16 bar H_2) over

Pt(2)Sn(0.25)/AL. In arabinogalactan conversion yield obtained was 47, 44 and 40% whereas in inulin conversion it was 77, 70 and 55% in 1st, 2nd and 3rd run, respectively (Figure 4A.11).

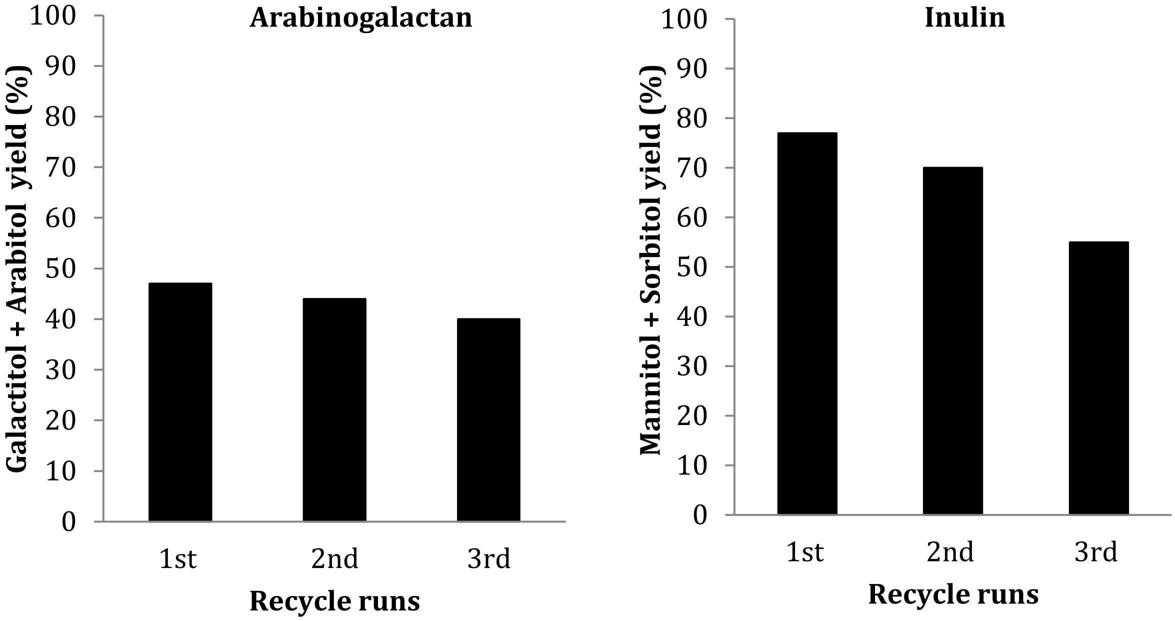


Figure 4A.11. Recycle study for the conversion of arabinogalactan and inulin over Pt(2)Sn(0.25)/AL catalyst.

Reaction condition: substrate 0.15 g, catalyst 0.075 g, water 35 mL, 16 bar H_2 at R.T., arabinogalactan-180°C, 12 h; inulin-110°C, 12 h.

To minimize the loss of activity during recycle runs, it was decided to calcine and reduce the spent catalyst before reuse. As mentioned above, unlike to the conversion of monosaccharides (water soluble) in the conversion of polysaccharides (water insoluble), spent catalyst may be associated with little amount of unconverted substrate and some adsorbed products. Such impurities cannot be removed from catalyst surface just by washing with water and hence spent catalyst was subjected to calcination before reuse for next run. To study the effect of calcination treatment on the recyclability, spent Pt-Sn/AL catalyst recovered from xylan reaction (190°C, 16 h) was washed with water, dried overnight (16 h) in oven at 60°C and in vacuum (-700 Torr) for 3 h at 120°C. Dried catalyst was subjected to calcination at 500°C for 6 h followed by reduction at 400°C for 2 h and then used in the next reaction. After this treatment, spent catalyst showed almost comparable conversions with marginal decrease (ca. 4%) in sugar alcohols yields from xylan. Over Pt(3.5)Sn(0.43)/AL catalyst 50, 46 and 41% yield of sugar alcohols (xylitol+arabitol) was obtained, while over Pt(2)Sn(0.25)/AL 43, 40 and 35% yield was achieved in 1st, 2nd and 3rd run after calcination and reduction of spent catalyst (Figure 4A.12). This proves that activity of spent catalyst in the formation of sugar alcohols can be improved by subjecting spent catalyst to calcination and reduction before reuse because after this treatment active sites on the catalyst will be free from adsorbed impurities.

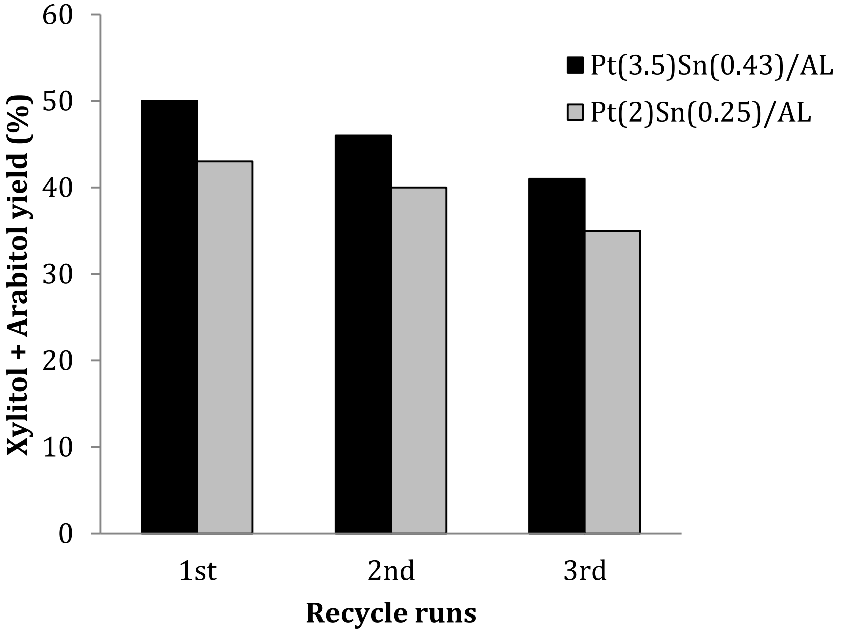


Figure 4A.12. Recycle study for the conversion of xylan over Pt-Sn/AL catalyst: effect calcination and reduction of spent catalyst.

Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C,16 bar H_2 at R.T., 16 h. (spent catalyst-calcined at 500°C for 6 h and reduced at 400°C for 2 h).

Spent Pt(3.5)Sn(0.43)/AL catalyst (calcined and reduced) from xylan conversion (190°C, 16 h, 16 bar H_2) was subjected to various characterizations to check the effect of reaction conditions on the physicochemical properties of the catalyst. XRD patterns of the fresh and spent catalysts showed characteristic peaks for the metallic Pt and alumina. Possibility of conversion of alumina to the boehmite in presence of water is predicted at similar reaction condition (190°C, 24 h, 50 bar H_2 pressure).[14] However in the XRD pattern of spent (in both uncalcined and calcined) catalyst, peaks for boehmite (at 2θ°= 14.45, 28.24, 38.40, 45.81, 48.97, 49.31, 51.68 and 55.30) were not visible (Figure 4A.13).

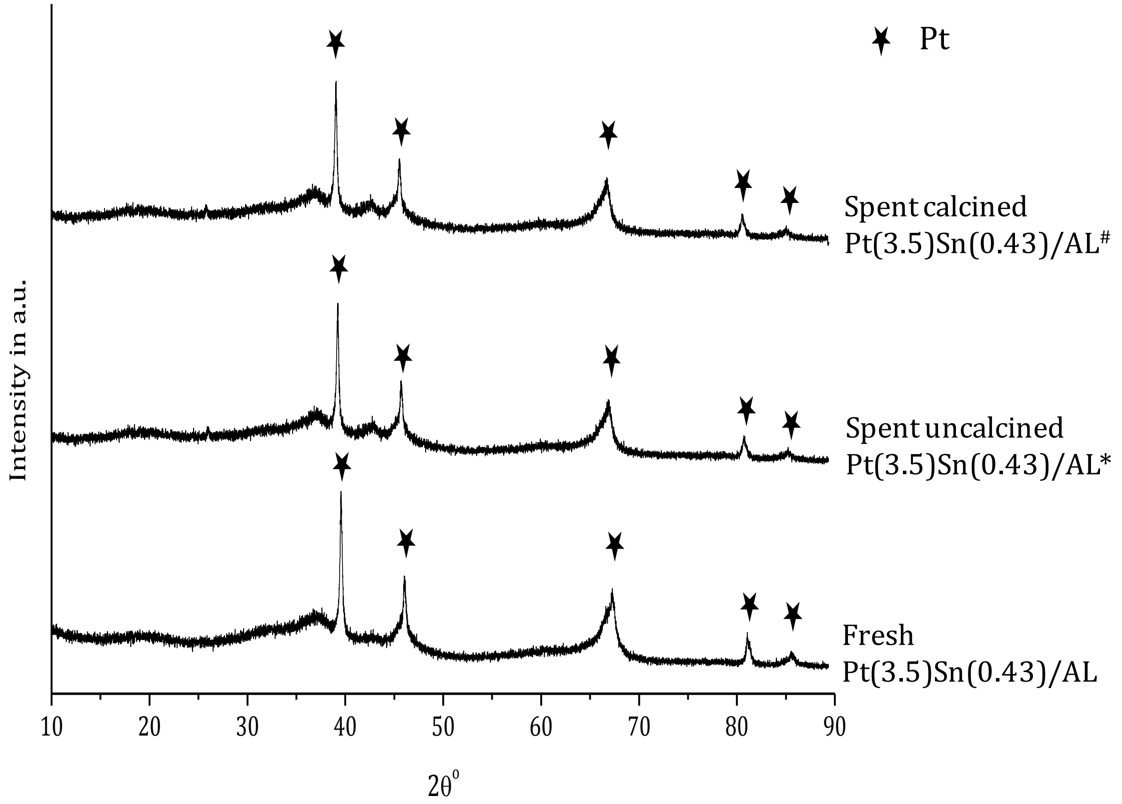


Figure 4A.13. XRD patterns of fresh and spent Pt(3.5)Sn(0.43)/AL catalyst.

*catalyst used for xylan conversion at 190°C for 16 h, at 16 bar H_2.

#spent catalyst was calcined at 500°C for 6 h and reduced at 400°C for 2 h.

TEM analysis of spent calcined catalyst showed similar particle size as in fresh catalyst (10-20 nm) (Figure 4A.14). This proves that sintering of the metal particles during reaction was inhibited. Moreover, calcination and reduction treatment to the spent catalyst did not affect the dispersion of metal. The ICP-AES analysis of reaction mixture and spent catalyst was performed to check whether metals are leached out in the solution during the reaction and the results divulge that though Sn is not leached out in the solution; Pt showed negligible leaching (0.37 ppm).

Spent Pt(3.5)Sn(0.43)/AL (calcined)

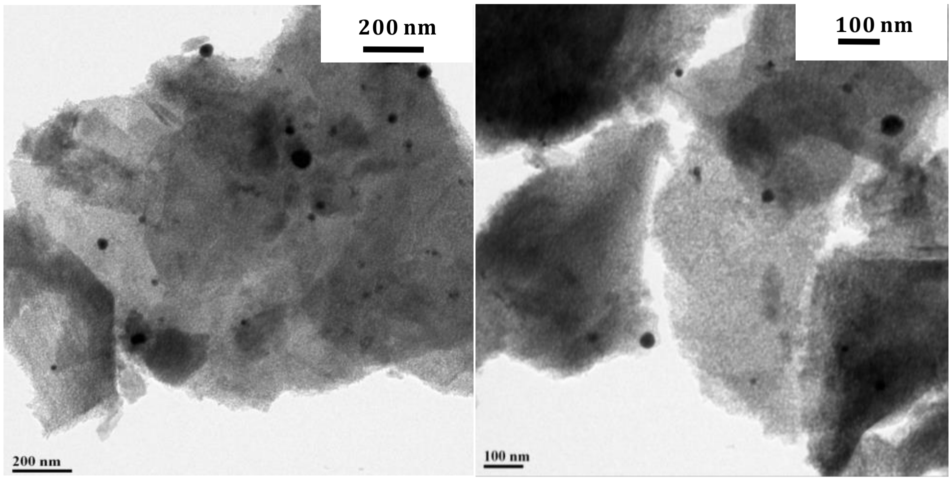


Figure 4A.14. TEM images of spent Pt(3.5)Sn(0.43)/AL (calcined) catalyst.*

*calcined catalyst: spent catalyst (xylan conversion at 190°C for 16 h, at 16 bar H_2) was calcined at 500°C for 6 h and reduced at 400°C for 2 h.

Surface area was almost unaltered in spent catalyst (161 m^2/g) compare to fresh catalyst (179 m^2/g) (determined by N_2 sorption study). The elemental analysis of the spent (Pt(3.5)Sn(0.43)/AL) catalyst before calcination and reduction showed presence of carbon (3%), but after calcination catalyst did not show any carbon. Above characterization proved that catalyst is stable under applied reaction conditions and can be reuse in the conversion of polysaccharides with minor loss of activity after each run.

4A.4. Conclusions

Aforesaid results and discussion suggest that similar to the monosaccharides conversions, in the conversions of isolated polysaccharides (xylan, arabinogalactan and inulin), Pt-Sn/AL bimetallic catalyst shows superior activity than Pt/AL monometallic catalyst. Over Pt(2)Sn(0.25)/AL maximum 43, 47 and 77% yields of sugar alcohols were obtained from xylan, arabinogalactan and inulin at optimized reaction condition which is 1.8-2.7 times more than yields over Pt(2)/AL catalyst. Optimum reaction conditions (temperature and time) at which maximum yield of sugar alcohols could be obtained varies from substrate to substrate. This is obvious as structures and compositions of substrates are dissimilar. Moreover, time and temperature required for the complete conversion of polysaccharides is higher than that for monosaccharides because conversion of polysaccharide in to sugar alcohols comprises of two steps (hydrolysis and hydrogenation). Since the complete conversion of monosaccharides was observed within 15 minutes, hydrolysis of polysaccharide in to monosaccharides is the rate determining step.

Results for the conversions over various bimetallic catalysts implied that analogous to monosaccharides conversions in the conversions of polysaccharides too, promoter effect of Sn is not achievable in carbon supported catalysts. Sn forms surface shell with alumina and hence cannot be reduced to Sn (0) which inhibits the sintering of Pt particle during calcination and reduction. In Pt-Sn/AL catalyst, ionic Sn (II) or (IV) improve the activity of catalyst by polarizing C=O bond of the sugar molecules and speed up the hydrogenation reaction. Maximum yield of sugar alcohols was attainable at optimum Pt:Sn ratio of 3.5:0.43 (*wt/wt*). Altogether, better dispersion of Pt, higher oxidation state of Sn and optimum ratio of Pt:Sn in Pt-Sn/AL catalyst govern the enhancement in the yield of sugar alcohols.

Catalyst showed good recyclability with the minor loss of activity towards sugar alcohols formation after each run. Calcination and reduction of spent catalyst before reuse helps to improve the recyclability, hence Pt-Sn/AL bimetallic catalyst proved to be superior for the production of sugar alcohols from isolated polysaccharides. Next chapter (4B) deals with the selective conversion of hemicellulose in agricultural wastes to yield sugar alcohols in one pot manner.

4A.5. References

1. S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *Journal of the American Chemical Society*, 2008, **130**, 12787-12793.
2. A. Onda, T. Ochi and K. Yanagisawa, *Green Chemistry*, 2008, **10**, 1033-1037.
3. J. Zakzeski, R. J. H. Grisel, A. T. Smit and B. M. Weckhuysen, *ChemSusChem*, **5**, 430-437.
4. A. Takagaki, C. Tagusagawa and K. Domen, *Chemical Communications*, 2008, 5363-5365.
5. J. Pang, A. Wang, M. Zheng and T. Zhang, *Chemical Communications*, 2010, **46**, 6935-6937.
6. P. D. Cara, M. Pagliaro, A. Elmekawy, D. R. Brown, P. Verschuren, N. R. Shiju and G. Rothenberg, *Catalysis Science & Technology*, 2013, **3**, 2057-2061.

7. R. Ormsby, J. R. Kastner and J. Miller, *Catalysis Today*, 2012, **190**, 89-97.
8. L. Faba, B. T. Kusema, E. V. Murzina, A. Tokarev, N. Kumar, A. Smeds, E. Díaz, S. Ordóñez, P. Mäki-Arvela, S. Willför, T. Salmi and D. Y. Murzin, *Microporous and Mesoporous Materials*, 2013, **189**, 189-199.
9. P. L. Dhepe and R. Sahu, *Green Chemistry*, 2010, **12**, 2153-2156.
10. R. Sahu and P. L. Dhepe, *ChemSusChem*, 2012, **5**, 751-761.
11. A. E. Abasaeed and Y. Y. Lee, *Chemical Engineering & Technology*, 1995, **18**, 440-444.
12. A. Fukuoka and P. L. Dhepe, *Angewandte Chemie International Edition*, 2006, **45**, 5161-5163.
13. F. Domīnguez, G. Carruyo, R. Andrade, R. Solano, D. Rodrīguez, J. Sănchez and G. Arteaga, *Catalysis Letters*, 2008, **123**, 207-212.
14. H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chemistry*, 2011, **13**, 326-333.

Chapter 4B

Selective conversion of hemicellulose in agricultural wastes in to sugar alcohols

4B.1. Introduction

Until now, results for the conversion of monosaccharides (C5 and C6 sugars) and isolated polysaccharides (xylan, arabinogalactan and inulin) in to sugar alcohols are discussed in chapter 3 and chapter 4A. In all above mentioned conversions, enhancement in the yield of sugar alcohols was achieved by employing bimetallic catalyst (Pt-Sn/AL). Effects of various supports, metals and promoters were also studied. Discrepancy in the yields of sugar alcohols over various catalysts was correlated with the properties of catalyst. After successful conversion of monosaccharides and polysaccharides in to sugar alcohols with high yield, attempts were made to obtain sugar alcohols from agricultural wastes in one pot manner. Pt-Sn/AL catalyst was preferred for the conversion, considering its exceptionally superior performance in all previous conversions.

Agricultural wastes i.e. bagasse, rice husk and wheat straw were collected from different regions of India (Maharashtra, Uttar Pradesh and Orissa). These agricultural wastes are the rich sources of various C5 and C6 sugars, since they consist of cellulose and hemicelluloses as major components. Nevertheless, only handful of reports have discussed the use of untreated agricultural wastes instead of isolated polysaccharide, in the production of sugars and other chemicals like furans, sugar alcohols, levulinic acids and its esters.[1-4] According to the survey made by ‘Food and Agriculture Organization of the United Nations’, it is estimated that India produces ca. 342 MMT of sugarcane, ca. 158 MMT of rice and ca. 86 MMT of wheat per annum (year 2013) and the production of these crops is increasing along the years. Approximate yield of crops (sugarcane, rice and wheat) per annum in India and in world in the year of 2013 is given in Table 4B.1.

Table 4B.1. Crop yield of sugarcane, rice and wheat in India and World.*

Sr. No.	Crop	India (MMT/year)	World (MMT/year)
1	Sugarcane	342	1877
2	Rice	158	745
3	Wheat	86	710

*yields are approximate and according to survey (2013) by ‘Food and Agriculture Organization of the United Nations’.

Considering this, huge amounts of agricultural wastes (bagasse, rice husk, wheat straw, etc.) generated from these crops, which are typically lignocellulosic materials can be used for the production of chemicals and particularly, in the production of sugar alcohols. Although this discussion is restricted to above mentioned three crops only, many more crops are being cultivated around the world which can generate large quantity of agricultural wastes.

In current chapter, selective conversion of hemicellulose in the agricultural wastes to yield sugar alcohols is discussed. Reaction conditions were optimized to convert hemicellulose selectively keeping other components (cellulose and lignin) unconverted. It is interesting to study the selective conversion of single component when all other components are present and to study the effect of these unconverted components on the product yield. Direct conversion of agricultural wastes is much efficient method for the production of sugar alcohols, since it skip over the two important processes i.e. isolation of hemicellulose from raw agricultural wastes and conversion of hemicellulose in to sugars (which further can be converted in to sugar alcohols upon hydrogenation). Hence it saves time and capital both. Compositional analysis of agricultural wastes was done using TAPPI (Technical Association of the Pulp and Paper Industry) method to estimate the percentages of each components in particular agricultural waste. Metal contents in the agricultural wastes were determined using ICP-AES, as metal can poison the catalyst and may alter the catalytic activity.

4B.2. Materials and methods

4B.2.1. Materials

Substrates: Agricultural wastes i.e. bagasse, wheat straw and rice husk were collected from agricultural fields located in different parts of India. Bagasse was collected from agricultural field in Maharashtra while wheat straw from Uttar Pradesh and rice husk from Orissa. Before use these agricultural wastes were washed (with room temperature water), dried (in oven at 60°C, 16 h and vacuum drying (-700 Torr) at 80°C, 6 h) and sieved to obtain ca. 2 mm size particles. Agricultural wastes were then subjected to catalytic and non-catalytic conversions to yield sugar alcohols. Details for the other chemicals like sugars, sugar alcohols, glycols, furfural and oligomers are given in chapter 3 (section 3.2.1) and chapter 4A (section 4A.2.1).

Catalysts: Monometallic Pt(2)/AL and bimetallic Pt(2)Sn(0.25)/AL catalysts were synthesized and evaluated for the conversion of agricultural wastes to yield sugar alcohols. Detail information about supports, metal precursors used for the catalyst synthesis and synthesis procedure is given in chapter 2 (refer section 2.2.1 and 2.2.2).

4B.2.2. Experimental set-up and analysis of reaction mixture

Catalytic and non-catalytic runs were carried out in batch mode autoclave (50 mL capacity) and reaction mixtures were analyzed using HPLC. Details regarding experimental set-up, catalytic methods and analysis of reaction mixture are discussed in chapter 3 (refer section 3.2.2 and 3.2.3). Experiments were carried out at temperature ranging between 140°C and 190°C for various times (8 h-20 h). Typically, experiments were carried out at 16 bar H_2 and with substrate/catalyst ratio 2 (substrate 0.15 g and catalyst 0.075 g, 35 mL H_2O).

4B.2.3. Calculations

Yields of various products obtained by selective conversion of hemicellulose in agricultural waste were calculated based on the percentage of pentosan in the respective agricultural waste. Percentage of pentosan in each type of agricultural wastes was determined using TAPPI method. Detail procedure of the determination of various components by TAPPI method is explained in following section (section 4B.3.2). Molecular weight of pentosan was taken as 132, because loss one H_2O molecule (molecular weight =18) by each C5 sugar molecule (molecular weight =150) while forming pentosan. So, 132 g of pentosan gives 150 g of C5 sugars which on hydrogenation gives 152 g C5 sugar alcohols (xylitol or arabitol, molecular weight =152) considering 100% conversion and selectivity.

Yield of sugar alcohol (%) = [Moles of sugar alcohol formed / Theoretical moles of sugar alcohol] × 100

For example, bagasse consists of 21.7% of hemicellulose (pentosan), which means 0.15 g of bagasse consist of 0.03255 g (0.246 mmol) of hemicellulose which gives 0.03748 g (0.246 mmol or 0.000246 mol) of C5 sugar alcohols. Hence, in bagasse conversion,

Yield of sugar alcohol (%) = [Moles of sugar alcohols formed (HPLC)/0.000246] × 100

Likewise, yields for other products were calculated for bagasse and other agricultural wastes. Conversions of the agricultural waste were calculated on weight basis, as follows;

Conversion (%) = [Weight of agricultural waste converted/ Weight of agricultural waste charged] × 100

4B.3. Analysis of agricultural wastes

It is known that during the growth, crops use various nutrients and since no pre-treatment besides washing of agricultural wastes with cold water was given prior to reaction, the presence of any metals on these substrates was checked by ICP-AES study. Besides this, to quantify the various components; these materials were analyzed by TAPPI method to understand the composition (hollocellulose, pentosan, lignin, ash, etc.).

4B.3.1. Determination of metal contents in agricultural wastes

For the determination of various metal contents, accurately weighed (1 g) dried (in oven at 60°C for 16 h and vacuum drying at 80°C for 6 h) agricultural wastes was subjected to the calcination at 600°C for 5 h in presence of air. Solid residue thus obtained was treated with HF to get rid of silica content because silica reacts with HF (in excess) to form H_2SiF_6 which is miscible with water (chemical reaction can be represented as follows).

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$$

After HF treatment, leftover residue was dissolved in freshly prepared aquaregia and after dilution with deionized water; solutions were analyzed using ICP-AES to obtained metal contents in agricultural wastes. From ICP-AES results, it was observed that agricultural wastes contains variable amount of various metals as represented in Table 4B.2. It is important to determine metal contents of the agricultural wastes because these metals may get adsorbed on the catalyst surface during reaction and can alter the catalytic activity.

Table 4B.2. Various elements present in agricultural wastes.

Element (mmol/g)$^{\$}$	Bagasse	Rice husk	Wheat straw
Na	0.000	0.000	0.000
Mg	0.032	0.039	0.023
Al	0.019	0.022	0.018
K	0.021	0.068	0.14
Ca	0.072	0.032	0.028
P	0.011	0.048	0.013

$^{\$}$Determined by ICP-AES (mmol of element in 1 g of agricultural waste)

4B.3.2. Compositional analysis of agricultural wastes

Agricultural waste is the lignocellulosic material having cellulose, hemicellulose and lignin as a main components. TAPPI method is one of the most practiced methods for the compositional analysis of lignocellulosic biomass. Compositional analysis was done by T203 cm 99-procedure.[5]

Procedure for the compositional analysis

1) Determination of moisture content: Accurately weighed agricultural wastes were allowed to dry at 100°C for 12 h under vacuum (-700 Torr). Amount of moisture was determined by calculating difference in the weight of the sample before and after drying.

2) Determination of ash content: Vacuum dried samples of agricultural wastes were subjected to calcination in the presence of air to determine amount of ash in it. Accurately weighed samples were calcined at 600°C for 5 h in the presence of air. At this temperature all other components (cellulose, hemicellulose and lignin) were oxidized, leaving behind the ash which consists of silica and some of the metals. Obtained ash was weighed to calculate the exact amount of ash present in the given quantity of sample.

3) Determination of hollocellulose: Hollocellulose is the delignified pulp of lignocellulosic biomass. Hollocellulose consists of cellulose and hemicellulose part of lignocelluloses. Furthermore hollocellulose is made-up of three types of components i.e. α-cellulose, β-cellulose and γ-cellulose. This method can be used for the compositional analysis only of delignified pulp of lignocellulosic biomass. Hence agricultural wastes were delignified before subjected to analysis.

Delignification of agricultural waste: Accurately weighed agricultural waste (2.5 g) was taken in 250 mL capacity conical flask and 80 mL distilled water was added. Mouth of the flask was covered with glass stopper. Flask was heated at 70°C for 3 h in water bath. During heating 0.75 g sodium chlorite ($NaClO_2$) and 0.5 mL acetic acid was added 4 to 5 time (with the interval of 40 minutes) with constant stirring. Then mixture was allowed to cool and filtered through sintered glass crucible-G2 (with pore size 15-40 μm). Lignin is soluble in the above solution and hence lignin free or delignified hollocellulose pulp can be obtained after filtration as a solid residue. However, some lignin can be associated with hollocellulose even after this treatment. Hence, hollocellulose pulp was further subjected to claisen delignification method to ensure the complete removal of lignin. Amount of lignin can be calculated from the difference in the weight of agricultural waste taken and dried hollocellulose pulp. Hollocellulose thus obtained consist of ash, therefore while considering weight of hollocellulose weight of ash has to be subtracted (ash correction).

Determination of α-cellulose, β-cellulose and γ-cellulose: Quantity of α-cellulose was calculated indirectly, by subtracting quantity of β-cellulose and γ-cellulose from hollocellulose. β-cellulose and γ-cellulose in the sample were determined by the treatment with 17.5% solution of NaOH at room temperature (ca. 25°C). These two components are soluble in NaOH solution while α-cellulose is insoluble. Quantitative analysis of β-cellulose and γ-cellulose was done by oxidation with potassium dichromate ($K_2Cr_2O_7$) followed by titration with ferrous ammonium sulfate (FAS). α-cellulose consist of high molecular weight cellulose (generally insoluble in dilute alkali) while β-cellulose and γ-cellulose consist of low molecular weight cellulose and hemicellulose, respectively. β-cellulose is soluble in NaOH and can be reprecipitated on acidification. While γ-cellulose is soluble in NaOH but cannot be reprecipitated by acidification.

To determine percentage of α-cellulose, β-cellulose and γ-cellulose, delignified pulp of agricultural waste was allowed to dry at 60°C for 12 h. Accurately weighed quantity of dry pulp was taken (1.5 g) in 500 mL conical flask and 100 mL of NaOH (17.5%) was added to it and suspension was stirred to achieve well dispersed mixture. Then after 30 minutes (after addition of NaOH), 100 mL distilled water was added and suspension was stirred for another 30 minutes (so total stirring time was 1 h after addition of NaOH). During addition and stirring, temperature was maintained at 25±2°C. Mixture thus obtained was filtered through sintered glass crucible-G2 and filtrate was collected for further analysis (first 20 mL filtrate was discarded and remaining was used). This filtrate (F1) consists of β-cellulose and γ-cellulose while solid residue is α-cellulose and ash, hence exact amount of α-cellulose was calculated by subtracting weight of ash from weight of residue.

Determination of α-cellulose: 25 mL of filtrate (F1) was pipette out in conical flask of 250 mL capacity and 10 mL aqueous solution of $K_2Cr_2O_7$ (0.5N) was added slowly into the flask with caution. Then 50 mL conc. H_2SO_4 was added and solution was kept as it is for 15 minutes. Next, 50 mL water (room temperature) was added in this solution and it was cooled to room temperature by keeping under running tap. Cold solution was titrated against 0.1N FAS with ferroin as an indicator (3-4 drops). β-cellulose and γ-cellulose was oxidized by $K_2Cr_2O_7$ and quantified by volumetric titration with FAS (end point at the appearance of purple color). Volume of FAS required in the titration was recorded (V_1). Blank titration was done by following same procedure but instead of pulp filtrate (F1), 12.5 mL NaOH (17.5%) and 12.5 mL of water was used. Volume required for blank titration was also recorded (V_2). Total amount of β-cellulose + γ-cellulose can be calculated by formula;

$$[\beta\text{-cellulose }(\%) + \gamma\text{-cellulose }(\%)] = 6.85\,(V_2 - V_1) \times N \times 20/A \times W$$

where,

V_1 : Volume of FAS required for sample titration (mL)

V_2 : Volume of FAS required for blank titration (mL)

N : Normality of FAS

A : Volume of pulp filtrate (F1) taken (mL)

W : Weight of hollocellulose (ash corrected) taken (g)

Percentage of α-cellulose was calculated by subtracting percentage of β-cellulose + γ-cellulose from 100.

$$\alpha\text{-cellulose }(\%) \quad = 100 - [(6.85(V_2 - V_1) \times N \times 20)/(A \times W)]$$

= 100 – [β-cellulose(%) + γ-cellulose (%)]

Determination of γ-cellulose: 50 mL pulp filtrate (F1) was taken into graduated cylinder with stopper and 50 mL H_2SO_4 (3N) was added into it with caution. Solution was mixed properly by thorough shaking and inverting the cylinder. Solution was heated at 80-90°C for 15-20 minutes by keeping cylinder in water bath (this allows coagulation of β-cellulose). Precipitate thus obtained was allowed to settle down by keeping cylinder undisturbed for 16 h. Precipitate was separate out by filtration through sintered glass crucible-G2 and filtrate (F2) thus obtained after separation of precipitate (mainly consist of β-cellulose) was treated with $K_2Cr_2O_7$ and titrated against 0.1N FAS solution. For this titration, 50 mL of filtrate (F2) obtained after β-cellulose separation, was taken into 250 mL conical flask and 90 mL conc. H_2SO_4 was added slowly. Solution was allowed to remain hot for 15 minutes and then cooled to room temperature. 3-4 drops of ferroin indicator was added in the cold (room temperature) solution and solution was titrated against 0.1N FAS. End point was recorded at the appearance of purple color (V_3). Blank titration was done by substituting filtrate (F2) with 12.5 mL NaOH (17.5%), 12.5 mL water and 25 mL H_2SO_4 (3N) and end point was recorded at change in color to purple (V_4). Percentage of γ-cellulose was calculated using following formula;

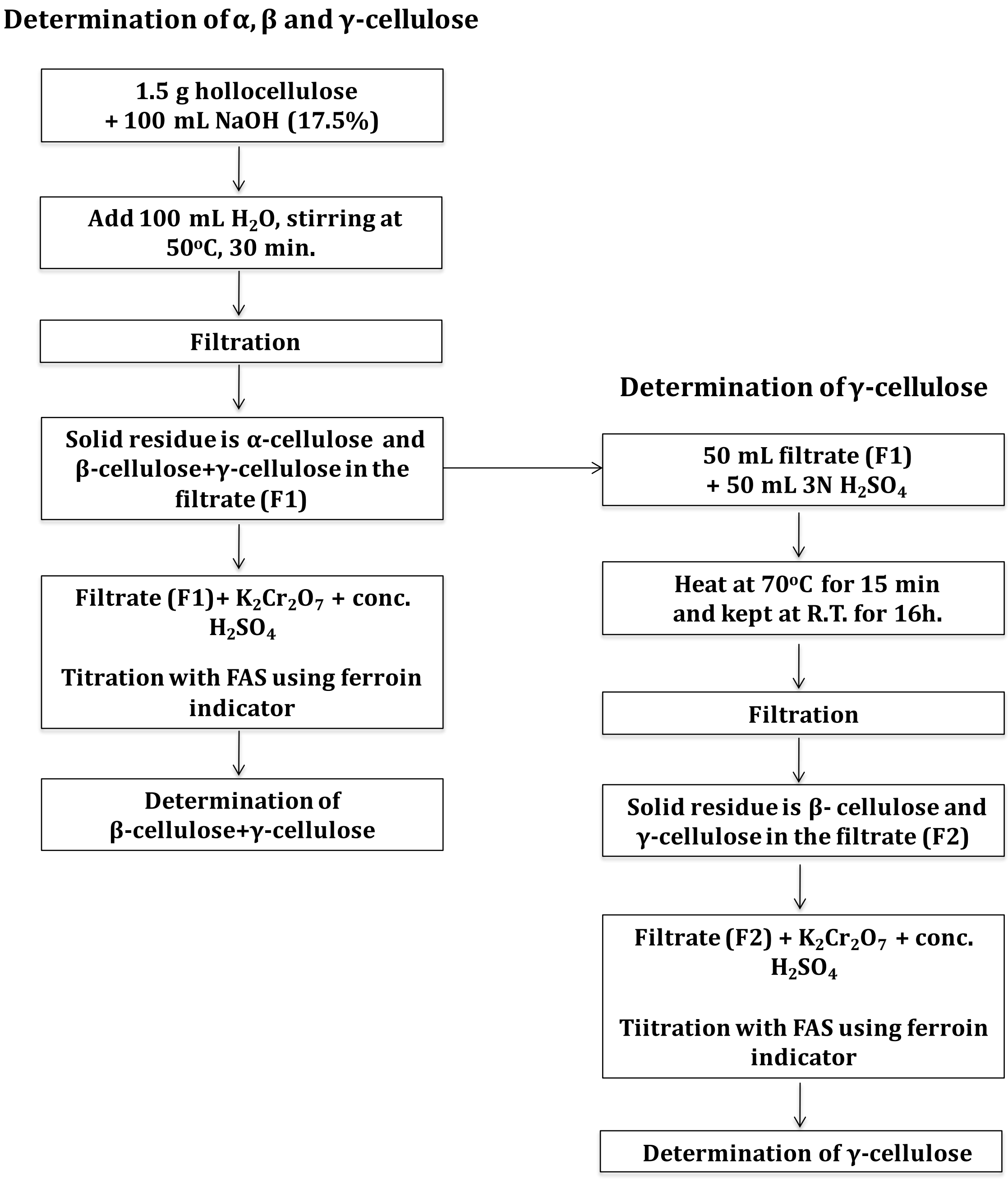
γ-cellulose (%) = (6.85(V_4 – V_3) × N × 20)/(25 × W)

where,
V_3 : Volume of FAS required for sample titration (mL)
V_1 : Volume of FAS required for blank titration (mL)
N : Normality of FAS
W : Weight of hollocellulose (ash corrected) taken (g)

β-cellulose (%) in hollocellulose was calculated by subtracting α-cellulose (%) and γ-cellulose (%) from 100;

β-cellulose (%)= 100 – [α-cellulose (%) + γ-cellulose (%)]

This way, percentage of ash, lignin and hollocellulose (α-cellulose, β-cellulose and γ-cellulose) was determined for all three types of agricultural wastes and percentage of all the components is consolidated in Table 4B.3. Overall procedure for the determination of α-cellulose, β-cellulose and γ-cellulose can be represented as Scheme 4B.1.



α-cellulose (%) = 100 – [β-cellulose(%) + γ-cellulose (%)]

β-cellulose (%)= 100 – [α-cellulose (%) + γ-cellulose (%)]

Scheme 4B.1. Procedure for the determination of α-cellulose, β-cellulose and γ-cellulose.

4) Determination of pentosan: Percentage of γ-cellulose represents the amount of hemicellulose in the biomass. Hemicelluloses present in the agricultural wastes used in the current work mostly consist of pentosan. Furthermore reactions were carried out to yield C5 sugar alcohols selectively (mostly from hemicellulose), hence determination of accurate amount of the pentosan in the agricultural wastes was unavoidable. For pentosan determination, 5 gm dried sample of agricultural waste and 300 mL of HCl (13.5M) was taken into 500 mL round bottom flask attached with distillation assembly as shown in Figure 4B.1.

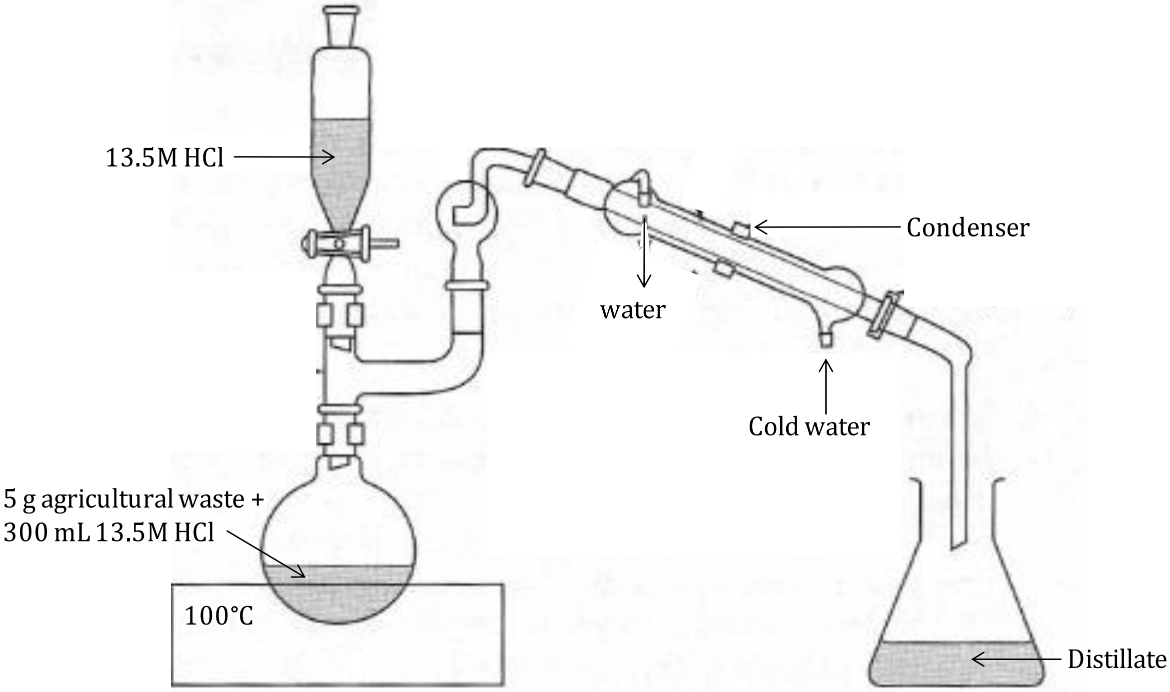


Figure 4B.1. Experimental set-up for the determination of pentosan.

Mixture was heated at 100°C and distillate was collected in conical flask (approximately 250 mL distillate was collected). During distillation pentosan was expected to come with solvent in distillate. During distillation volume of the reaction mixture was maintained to 300 mL by drop wise addition of 13.5M HCl. Distillate (consisting pentosan) was diluted with distilled water and subjected to UV-Vis analysis (at 280 nm) to determine percentage of pentosan. Percentage of pentosan in the agricultural waste was calculated using formula;

Pentosan (%) = (absorbance × 1.563)/151 × weight of agricultural waste) × 100

Corrected weight of agricultural wastes should be considered by taking into account the moisture and ash corrections. Percentage of various components in agricultural wastes determined by aforementioned procedure is shown in Table 4.B.3.

Table 4B.3. Composition of agricultural wastes.

Component (%)*	Bagasse	Rice husk	Wheat straw
Lignin	21.5	22.6	17.9
Pentosan	21.7	12.5	21.5
Hollocellulose	68.4	52.6	63.1
α-cellulose	40	34.4	36.8
β-cellulose	15.2	6.7	17.2
γ-cellulose	13.2	11.5	9.3
Ash	3.2	16.4	12.1

*Determined by TAPPI method

Results obtained for the compositional analysis of agricultural wastes in the current work are similar to the reported results with minor differences. According to the earlier reports bagasse, rice husk and wheat straw comprises 22±3, 20±5 and 22±3% of hemicellulose, respectively.[6-9] Nevertheless composition of the particular agricultural wastes (or any plant derived biomass) may vary from place to place.

4B.4. Results and discussion

Since, very high yields of sugar alcohols were achieved over bimetallic Pt(2)Sn(0.25)/AL catalyst from monosaccharides (chapter 3, section 3.3.2 and 3.3.4) and isolated polysaccharides (chapter 4A, section 4A.3.1 and 4A.3.2) it was thought of extending this catalytic system to produce sugar alcohols from agricultural wastes.

4B.4.1. Effect of reaction parameters

In this work, three different substrates i.e. bagasse, rice husk and wheat straw were used without any pre-treatment for the production of sugar alcohols. All three substrates were subjected for the reactions at different temperatures ranging between 140- 190°C for different time durations (8 - 20 h) at 16 bar H_2, to find out the optimum reaction conditions at which highest sugar alcohols yields can be obtained. When reactions were carried out at 140, 160 and 180°C for 12 h over Pt(2)Sn(0.25)/AL catalyst, maximum yield of sugar alcohols (xylitol+arabitol) were obtained at 160°C from all three substrates (bagasse: 62%, rice husk: 60% and wheat straw: 49%). With the increase in temperature to 180 and 190°C, no increament in the sugar alcohols yield was observed (Figure 4B.2.A). Hence reactions were carried out at 160°C for various times to achieve maximum yield. Maximum 72% yield of sugar alcohols was obtained from bagasse in 16 h of reaction time while 60% and 49% yields were obtained from rice husk and wheat straw in 12 h. Reactions were carried out for longer time but there was no significant enhancement in the yields (Figure 4B.2.B).

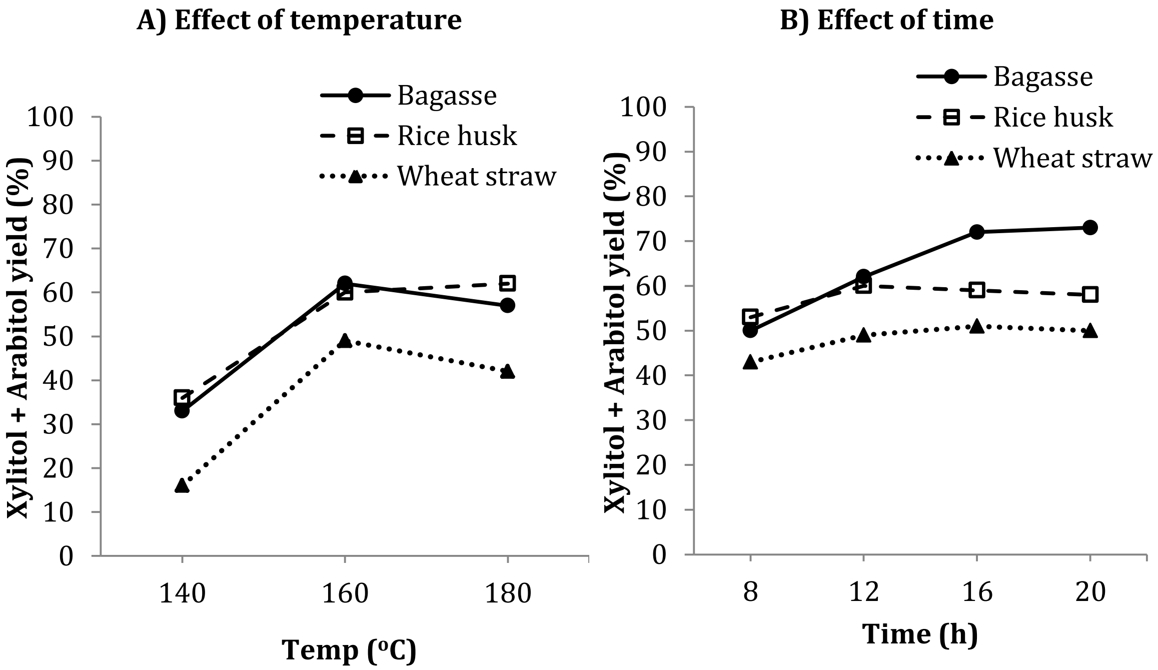


Figure 4B.2. Effect of reaction parameters on the conversion of agricultural wastes over Pt(2)Sn(0.25)/AL catalyst.

Reaction condition: substrate 0.15 g, catalyst 0.075 g, water 35 mL, 16 bar H_2 at R.T.,
A) 12 h; B) 160°C.

Activities of Pt(2)/AL and Pt(2)Sn(0.25)/AL were compared in the conversion of bagasse, rice husk and wheat straw at above mentioned optimized reaction conditions. In case of bagasse, at 160°C within 16 h, 43 and 72% yields for C5 sugar alcohols (xylitol+arabitol) were obtained over Pt(2)/AL and Pt(2)Sn(0.25)/AL catalysts, respectively (Figure 4B.3). When instead of bagasse, rice husk was used as a substrate and the reaction was performed at 160°C for 12 h, 32% yield of C5 sugar alcohols was obtained over Pt(2)/AL catalyst. Improvement in the yield to 60% was seen when bimetallic, Pt(2)Sn(0.25)/AL catalyst was used under similar reaction conditions (Figure 4B.3). Similar trend of increase in C5 sugar alcohols yield from 29 to 49% was observed with Pt(2)/AL and Pt(2)Sn(0.25)/AL catalysts, respectively with wheat straw as a substrate (Figure 4B.3). To verify the effect of catalyst concentration on the sugar alcohols yield, when experiment was carried out with 0.038 g of Pt(2)Sn(0.25)/AL and 0.15 g bagasse (S/C = 4 (*wt/wt*)) at 160°C for 16 h, decrease in the sugar alcohols yield to 56% was observed. With decrease in the sugar alcohols yield, increase in the side products formation was seen, which implies that side reactions becomes predominant (glycols, furans formation) under thermal conditions when catalyst quantity is less.

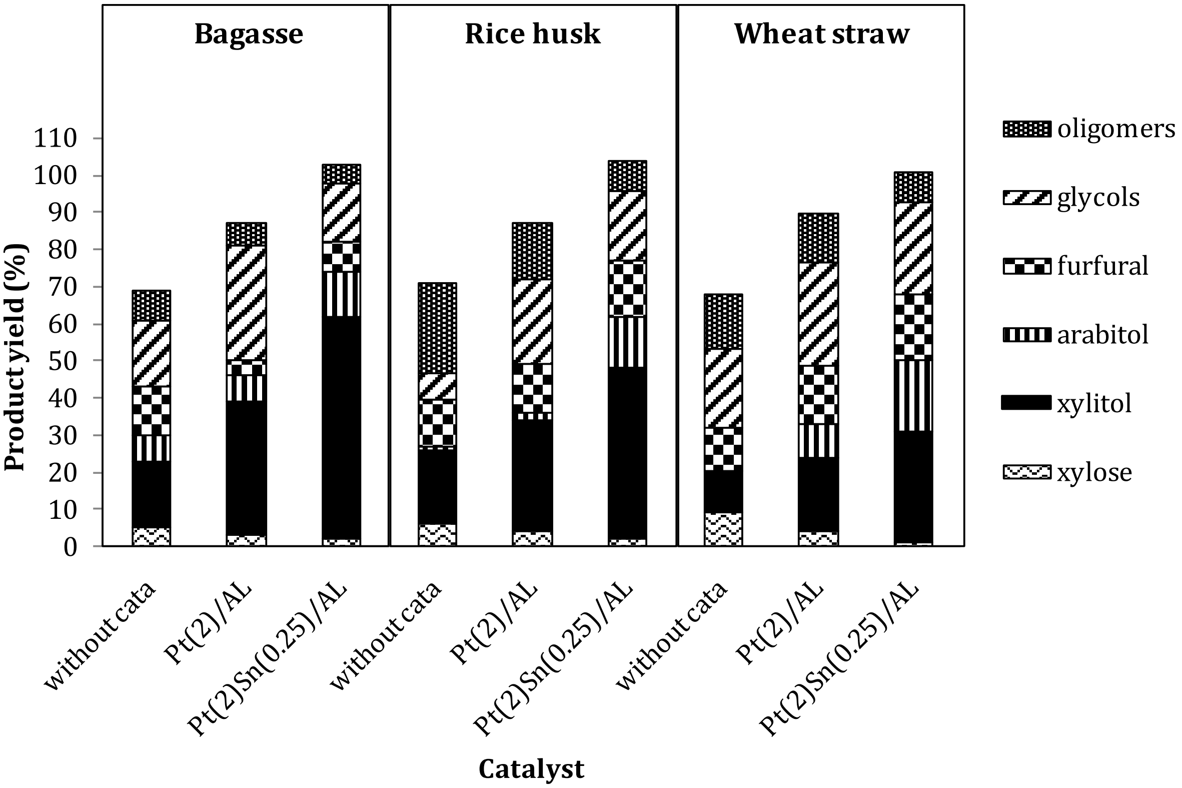


Figure 4B.3. Conversion of agricultural wastes in to sugar alcohols.

Reaction condition: substrate 0.15 g, catalyst 0.075 g, water 35 mL, 160˚C, 16 bar H_2 at R.T., bagasse-16 h; rice husk-12 h; wheat straw-12 h.

In the reactions of bagasse, rice husk and wheat straw over Pt(2)Sn(0.25)/AL catalyst, conversion values were 25.33, 26 and 16% respectively. Conversions were calculated on weight basis using following formula;

Conversion of bagasse: Over Pt(2)Sn(0.25)/AL catalyst at 160°C, 16 h.

Conversion (%) = [Weight of bagasse converted/Weight of bagasse charged] × 100

= [0.038/0.15] × 100 = 25.33%

Conversion of rice husk: Over Pt(2)Sn(0.25)/AL catalyst at 160°C, 12 h.

Conversion (%) = [0.039/0.15] × 10 = 26%

Conversion of wheat straw: Over Pt(2)Sn(0.25)/AL catalyst at 160°C, 12 h.

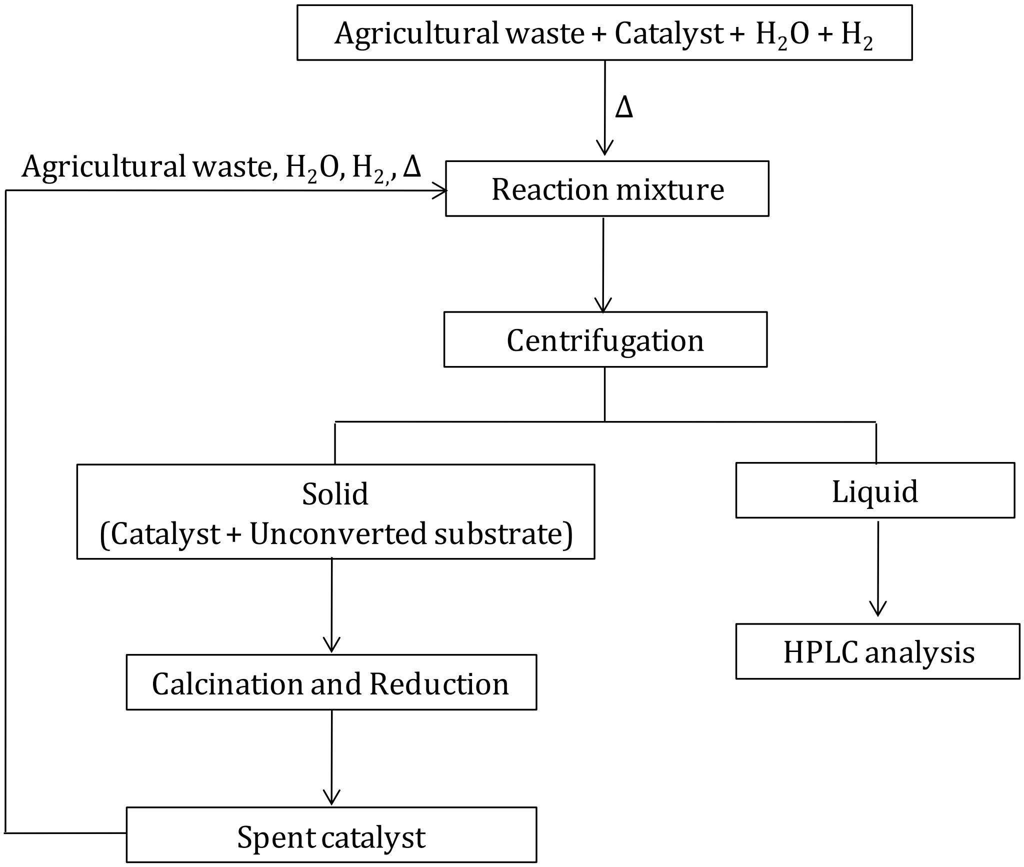
Conversion (%) = [0.024/0.15] × 100 = 16%

These conversion values are similar (slightly greater) to the percentage of pentosan present in respective agricultural waste, indicating complete conversion of pentosan might have achieved. Formation of C6 sugar alcohols was not observed; hence it was assumed that cellulose remained unconverted during reactions. This is how; selective conversion of hemicellulose (pentosan) in various agricultural wastes was accomplished over Pt-Sn/AL catalyst with superior yields of sugar alcohols.

4B.4.2. Recycle study

Recycle study was done for the conversion of bagasse and rice husk over Pt(2)Sn(0.25)/AL at optimized reaction conditions. It is important to note here that when catalyst was recovered from bagasse and rice husk reactions after successful selective conversion of hemicelluloses in to sugar alcohols; along with catalyst, water insoluble unconverted cellulose and lignin were also recovered as solids. Next, the recovered solid (containing catalyst, cellulose and lignin) was washed with water and without any other treatment was charged in the autoclave for next reaction. The results on the catalyst reuse study for bagasse and rice husk substrates showed decrease in the sugar alcohols yield by ca. 10-12% with respect to the yield obtained in earlier run. The decrease in the activity in these reactions was obvious since along with recovered catalyst, unconverted cellulose and lignin from earlier run were also charged in the reactor. This way in next run, after addition of 0.15 g of substrate (which was charged afresh), the total charged substrate (or solid) was higher compared to earlier run. This essentially changed the substrate/catalyst (S/C) ratio and due to this yields might have decreased after each run.

To overcome this issue, catalyst reuse study was done using another method. Upon completion of bagasse reaction using Pt(2)Sn(0.25)/AL catalyst, reaction mixture was centrifuged to separate the solid (catalyst + unconverted agricultural waste) and liquid. Solid was then washed with water and dried at 60°C for 12 h and then at 120°C under vacuum (-700 Torr) for 3 h. Dried solid was calcined at 550°C (ramping rate 2°C/min) for 5 h (in O_2 flow, 20 mL/min) to remove the unconverted part of substrate (cellulose and lignin). Later, catalyst was reduced at 400°C for 2 h (in H_2 flow 20 mL/min) to obtain Pt in metallic state which otherwise might be present in the higher oxidation state because of calcinations carried out at higher temperatures. Procedure of recycle study after calcination and reduction of spent catalyst in conversion of bagasse can be schematically represented as Scheme 4B.2.



Scheme 4B.2. Procedure of the recycle study for bagasse conversion.

Although, after this treatment catalyst is expected to be free from cellulose and lignin, some contamination may be associated with the spent catalyst in the form of ash. As mentioned earlier, all the agricultural wastes have significant ash content which will be there in calcined spent catalyst (refer section 4B.3.1). Elemental analysis of the spent catalyst recovered from bagasse reaction did not show any carbon content after calcination treatment. Nevertheless, ICP-AES analysis of this catalyst showed presence of metal like Mg, Al, K, P and Ca in trace quantity (0.001 -0.007 mmol) which is obvious as ash associated with spent catalyst contains these metals. When this spent catalyst [Pt(2)Sn(0.25)/AL] was used in the next reaction at 160°C for 16 h, slight decrease (7-9% compared to earlier reaction yield) in the yield of C5 sugar alcohols (xylitol+arabitol) was observed which can be attributed to the loss of some catalyst quantity during recovery. Furthermore, spent catalyst has some metal content which may affect the catalytic activity (however this is not very clear at this point). Even so this decrease in yield was less than the earlier procedure employed where total solid (catalyst and unconverted substrate) was used. Results for the recycle study for bagasse conversion over spent catalyst (after calcination and reaction) is as shown in Figure 4B.4.

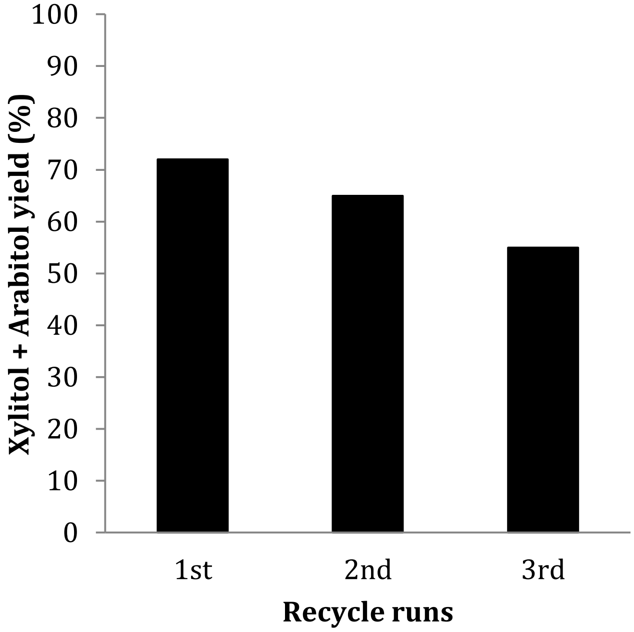


Figure 4B.4. Recycle study for bagasse conversion.

Reaction condition: bagasse0.15 g, catalyst 0.075 g, water 35 mL, 160°C, 16 bar H_2 at R.T., 16 h.

4B.5. Conclusions

It can concluded from above results that Pt-Sn/AL catalyst shows superior activity in sugar alcohols formation from agricultural wastes compare to Pt/AL catalysts. This proves that enhancement in the yield of sugar alcohols is achievable using Pt-Sn/AL bimetallic catalyst from monosaccharides, isolated polysaccharides and untreated agricultural wastes irrespective of their structure, composition and source from which it is obtained. Nonetheless increment in the yield compare to monometallic Pt/AL catalyst varies from substrate to substrate.

1.5 to 2 times more yields for sugar alcohols were obtained from different types of agricultural wastes over Pt(2)Sn(0.25)/AL contrast to Pt(2)/AL catalyst. The catalyst showed good recyclability with minimum loss of activity after each run. Proposed catalytic method can be used for the production of sugar alcohols from various types of agricultural wastes. More than 50 times value addition is possible by converting cheaply available agricultural wastes (ca. 3-5 Rs/Kg) in to valuable sugar alcohols (ca. 300-400 Rs/Kg).[10] Although, in current work conversion of only three agricultural wastes is studied, similar catalytic method can be use for the production of sugar alcohols from other agricultural waste too. Therefore, such an efficient catalytic methods need to be employed on commercial level for cost effective synthesis of sugar alcohols.

4B.6. References

1. P. L. Dhepe and R. Sahu, *Green Chemistry*, 2010, **12**, 2153-2156.
2. R. Sahu and P. L. Dhepe, *ChemSusChem*, 2012, **5**, 751-761.
3. G. Yi and Y. Zhang, *ChemSusChem*, 2012, **5**, 1383-1387.
4. S. K. Guha, H. Kobayashi, K. Hara, H. Kikuchi, T. Aritsuka and A. Fukuoka, *Catalysis Communications*, 2011, **12**, 980-983.
5. T203 cm 99-procedure. , approved by the Chemical Properties Committee of the Process and Product Quality Division, TAPPI.
6. D. W. Templeton, C. J. Scarlata, J. B. Sluiter and E. J. Wolfrum, *Journal of Agricultural and Food Chemistry*, 2010, **58**, 9054-9062.
7. C. Rezende, M. de Lima, P. Maziero, E. deAzevedo, W. Garcia and I. Polikarpov, *Biotechnology for Biofuels C7 - 54*, 2011, **4**, 1-19.

8. P. S. Kumar, K. Ramakrishnan, S. D. Kirupha and S. Sivanesan, *Brazilian Journal of Chemical Engineering*, 2010, **27**, 347-355.

9. O. D. Montañez Valdez, E. O. García Flores, J. A. Martínez García, J. Salinas Chavira, R. Rojo Rubio and J. J. Germán Peralta Ortiz, *Interciencia*, 2008, **33**, 435-438.

10. http://www.alibaba.com/showroom.html.

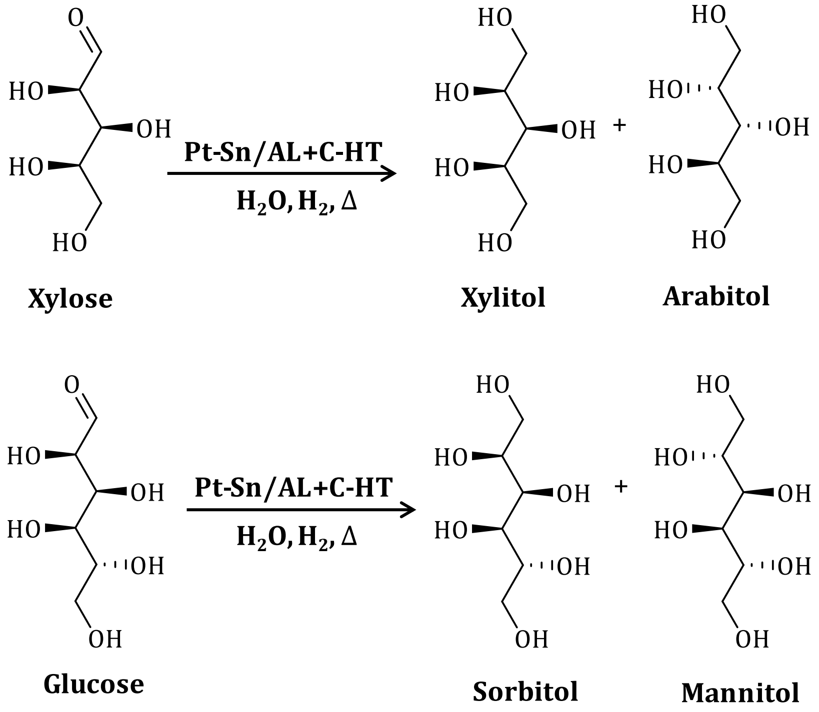
Chapter 5

Effect of solid base on the conversion of mono- and poly-saccharides in to sugar alcohols

5.1. Introduction

In last two chapters (chapter 3 and 4), promoter effect of second metal (Sn) in the supported metal catalyst (Pt/AL) on the conversion various monosaccharides (C5 and C6 sugars) and polysaccharides is discussed elaborately. It was observed from the results that, Sn can polarize the C=O bond of the carbonyl group of sugar molecules and such polarization is possible only if sugar molecule is present in open chain form. However, in aqueous solution (under neutral condition) more sugar molecules (ca. 98%) are in cyclic form and very less molecules are present in open chain form at equilibrium.[1] By taking this into account, to improve the conversion of sugars to yield sugar alcohols, more sugar molecules should be available in open chain form. Conscious study of the literature showed that under alkaline condition, sugar molecules undergo isomerization reaction (Lobry de Bruyn-Alberda van Ekenstein transformation).[2] Such isomerization reactions proceed essentially through the open chain intermediates to yield isomerized form of the sugar. Therefore, it might be possible to generate sugar molecules in open chain form under alkaline condition which may undergo hydrogenation reaction instead of isomerization if active metal and hydrogen is available. Hence it was decided to conduct hydrogenation reaction of C5 and C6 sugars in alkaline reaction medium i.e. in the presence of base (Scheme 5.1). Owing to the heterogeneous nature of solid base, it is advantageous to use solid base instead of homogeneous base because of its easy separation from reaction mixture.

Among various solid bases, hydrotalcites including its calcined form are well known for the base catalyzed reactions. In current work, Mg-Al hydrotalcite was prepared considering its importance in the field of catalysis and its effect on the production of sugar alcohols was evaluated in the conversion of C5 and C6 sugars. Mg-Al hydrotalcite was prepared by known method[3] and was calcined at 550°C before use (for more details on the synthesis of hydrotalcite, refer chapter 2, section 2.2.1). This calcined form of hydrotalcite (C-HT) was used as a solid base in the entitled conversions either as a support or as an additive along with supported metal catalyst. Firstly, effect of solid base (C-HT) was studied in the conversion of sugars over monometallic catalyst. Intentionally monometallic catalysts were used, to check whether solid base alone can improve the yield of sugar alcohols in the absence of promoter metal. Next, the effect of solid base was studied in the conversions of sugars over bimetallic catalysts. Similarly, this effect was studied in the conversion of polysaccharides like xylan, arabinogalactan and inulin.



Scheme 5.1. Effect of solid base in the conversion of C5 and C6 sugars.

5. 2. Materials and methods

5.2.1. Materials

Chemicals: Details for the various chemicals used i.e. monosaccharides (C5 and C6 sugars) and polysaccharides (xylan, arabinogalactan, inulin) as well as standards for various products are given in chapter 3 (section 3.2.1) and chapter 4A (section 4A.2.1).

Catalysts: Monometallic and bimetallic catalysts were synthesized and evaluated for the conversion of mono- and poly-saccharides to yield sugar alcohols. Detail information about supports, metal precursors used for the catalyst synthesis and synthesis procedure is given in chapter 2 (refer section 2.2.1 and 2.2.2). Calcined hydrotalcite (C-HT) was used as a support material to prepare various monometallic and bimetallic catalysts. Moreover C-HT was used as an additive along with supported metal catalyst (physical mixture). Detail procedure for the synthesis of hydrotalcite is explained in chapter 2 (section 2.2.1).

Synthesized hydrotalcite was subjected to XRD analysis before calcination and XRD pattern showed that layered double hydroxide structure has been formed (JCPDS file no. 14-0191). On the other hand calcined form of hydrotalcite showed the drastic change in XRD patter in which characteristic peaks for periclase (mixed oxide of Mg(Al)O) were clearly visible at 2θ° = 35.23°, 43.34° and 62.63° correspond to the lattice plane (111), (200), and (220), respectively (JCPDF file No. 45-0946). Formation of (Mg(Al)O) mixed oxide after calcination (thermal activation) of synthesized hydrotalcite (layered double hydroxide structure) is well reported in the literature.[4, 5] Structural features of hydrotalcite and origin of its basicity is already explained in chapter 1 (section 1.4).

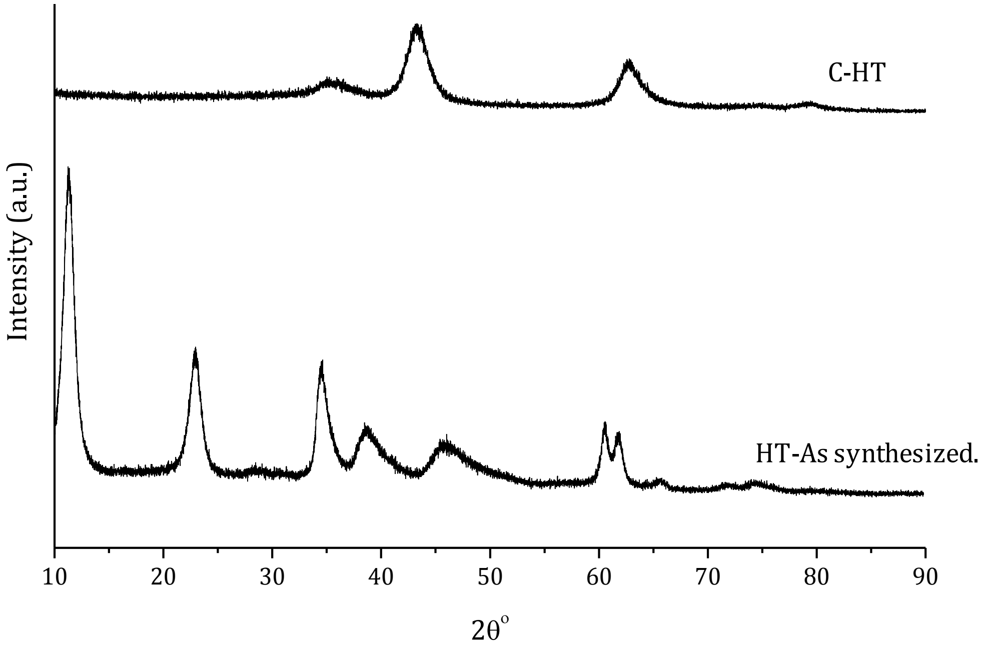


Figure 5.1. XRD patterns of as synthesized and calcined hydrotalcite.

5.2.2. Experimental set-up and analysis of reaction mixture

Catalytic and non-catalytic runs were carried out in a batch mode autoclave (50 mL capacity) and reaction mixtures were analyzed using HPLC. Information about experimental set-up, catalytic methods and analysis of reaction mixture is given in chapter 3 (refer section 3.2.2 and 3.2.3). Experiments were carried out at various temperatures ranging between room temperature (32±3°C) and 190°C for various times (15 min-20 h). Typically, experiments were carried out at 16 bar H_2 and with substrate/catalyst ratio 2 (substrate 0.15 g and catalyst 0.075 g, 35 mL H_2O and C-HT 0.075 g if added).

5.2.3. Calculations

Conversions and yields of various products were calculated on mole basis in the reactions of monosaccharides (for details refer chapter 3, section 3.2.4). In the reaction of polysaccharides, conversions were calculated on weight basis and product yields were calculated on mole basis (refer chapter 4A, section 4A.2.3).

5.3. Results and discussion

5.3.1. Effect of calcined hydrotalcite as a support or additive on the conversion of xylose over monometallic catalyst

Effect of calcined hydrotalcite (C-HT) as a support was examined by preparing Pt(3.5)/C-HT catalyst and its activity was compared with Pt(3.5)/AL in the conversion of xylose at 130°C for 2 h (Figure 5.2).

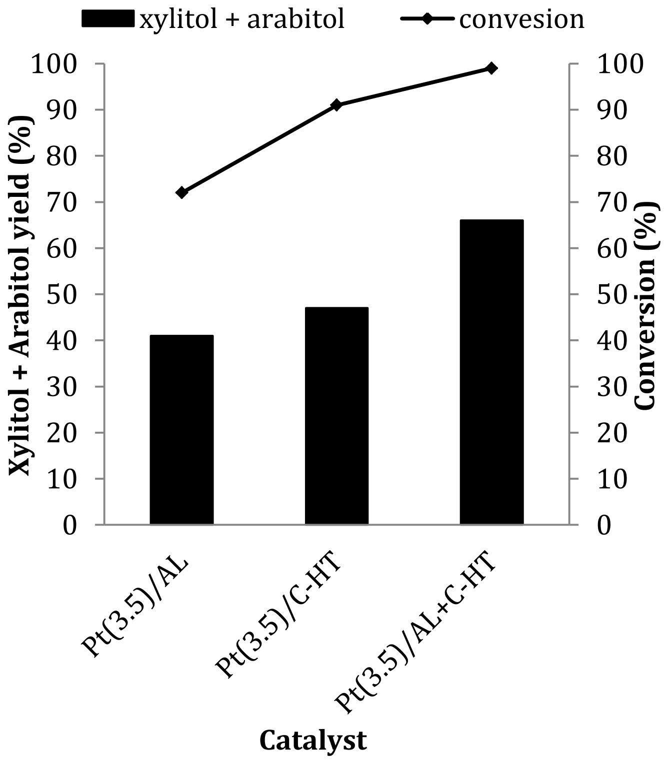


Figure 5.2. Effect of C-HT as a support and additive on xylose conversion.

Reaction conditions: xylose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, water 35 mL, 130°C, 16 bar H_2 at R.T., 2 h.

Although higher conversion (91%) was achieved over Pt(3.5)/C-HT, selectivity for sugar alcohols (xylitol+arabitol) was low (51.64%) compare to Pt(3.5)/AL (conversion 72%, selectivity 56.94%). But when bare C-HT (without Pt) was used as an additive along with Pt(3.5)/AL (physical mixture of Pt(3.5)/AL, 0.075 g and C-HT, 0.075 g), complete conversion with better selectivity (66.66%) was achieved within 2 h. From Figure 5.2, it is clear that Pt(3.5)/AL catalyst is more selective for the sugar alcohol formation than Pt(3.5)/C-HT at 130°C. Nevertheless, better conversion and selectivity was observed over Pt(3.5)/AL+C-HT catalytic system. In this system, Pt(3.5)/AL is the catalyst and C-HT act as an additive or promoter. Probable mechanism for the promoter effect of the C-HT is discussed in details in section 5.3.4 of this chapter.

5.3.1.1. Effect of reaction parameters

Since Pt(3.5)/AL+C-HT catalytic system showed best results for the production of sugar alcohols, reaction parameters like temperature, time, H_2 pressure, etc. were optimized for this catalytic system.

Effect of temperature and time: The effect of temperature was studied by conducting reactions at 60, 90 and 130°C for 2 h at 16 bar H_2 (Figure 5.3). Although at 60°C conversion was less (82%) than other temperatures, the selectivity for sugar alcohols was highest i.e. 87.8% (72% yield). While at 90 and 130°C complete conversion of xylose with sugar alcohols yields of 76 and 66% were observed. This proves that lower reaction temperature favors the formation of sugar alcohols while at higher temperature formation of undesired products like glycols is more prominent. As observed in Figure 5.3, 4% yield of glycols was obtained at 60°C while 15% and 28% glycols yield was observed at 90°C and 130°C, respectively. These results indicate that, although addition solid base C-HT, along with supported metal catalyst improved the yield of sugar alcohols at lower temperature (60°C), at higher temperature (90 and 130°C) side reaction to yield glycols are more prominent. These results are in line with literature, wherein it is reported that formation of glycols from sugar is favored by high temperature.[6, 7] Considering this, further study was done at 60°C to achieve maximum yield of sugar alcohols.

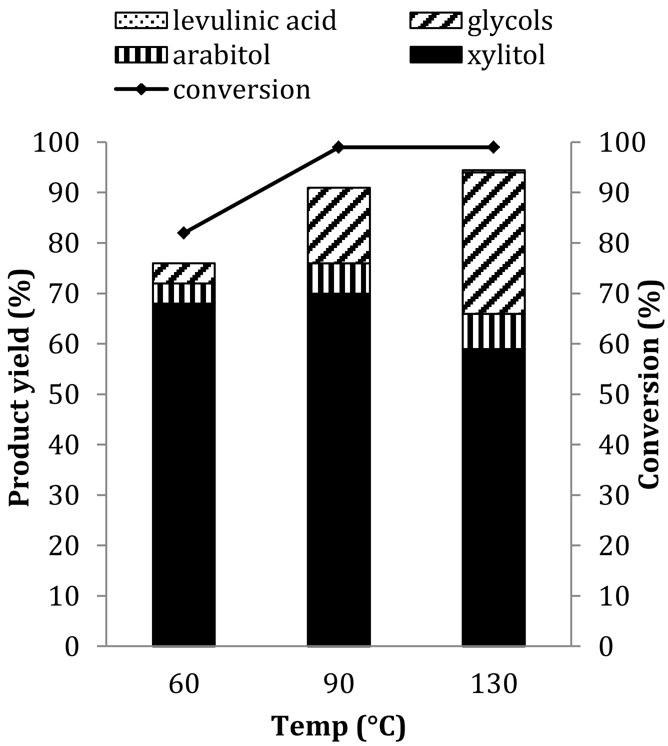


Figure 5.3. Effect of temperature on xylose conversion over Pt(3.5)/AL+C-HT catalyst.

Reaction conditions: xylose 0.15 g, catalyst (Pt(3.5)/AL) 0.075 g, C-HT 0.075 g, water 35 mL, 16 bar H_2 at R.T., 2 h.

To achieve complete conversion with better yields, reactions over various catalysts i.e. Pt(3.5)/AL, Pt(3.5)/C-HT and Pt(3.5)/AL+C-HT were carried out at 60°C for longer time (Table 5.1). In non-catalytic reaction, merely 2% conversion of xylose was observed with 0.5% yield of sugar alcohols (xylitol+arabitol) within 6 h while reaction over Pt(3.5)/AL showed 9% conversion with 4.5% yield in 6 h. Higher conversion (72%, 6 h) was achieved over Pt(3.5)/C-HT with sugar alcohols yield of 55%. Amongst all the catalysts evaluated, Pt(3.5)/AL+C-HT catalytic system showed highest yield of sugar alcohols (82%) with almost complete conversion of xylose in 4 h of reaction time. This implies that though Pt(3.5)/AL catalyst does not show good activity at 60°C for xylose hydrogenation, its activity can be improved drastically when C-HT is used as an additive with the catalyst. When C-HT was used as a support, catalyst (Pt(3.5)/C-HT) showed better activity than Pt(3.5)/AL but not as good as Pt(3.5)/AL+C-HT.

Table 5.1. Effect of different catalysts on the conversion of xylose.

Catalyst	Time (h)	Conv. (%)	Product yield (%)		
			Sugar alcohols		Glycols^
			Xylitol	Arabitol	
Without catalyst	2	-	-	-	-
	4	-	-	-	-
	6	2	0.5	-	-
Pt(3.5)/AL	2	4	3.3	-	-
	4	6	3	-	1
	6	9	4.5	-	1.5
Pt(3.5)/C-HT	2	41.5	36	6	-
	4	59	50	6	1.5
	6	72	55	4	3.5
Pt(3.5)/AL+C-HT	2	82	68	4	4
	4	99	79	3	6
	6	99	78	3	6

^Glycols: ethylene glycol, glycerol and 1,2-propanediol.

Reaction conditions: xylose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, water 35 mL, 16 bar H_2 at R.T., 60°C.

Effect of H_2 pressure: As mentioned earlier, H_2 pressure plays crucial role in the hydrogenation reaction of sugars and may affect the yield of sugar alcohols significantly. Literature suggest that solubility of hydrogen in water is directly proportional to pressure and temperature.[8] Hence it is obligatory to study the effect H_2 pressure on product yields in the conversion of sugars over Pt(3.5)/AL+C-HT catalytic system. Xylose reactions were conducted at 60°C for 2 h with H_2 pressure ranging between 8-24 bar (Figure 5.4). Yield of sugar alcohols obtained after complete conversion at any pressure seems to be similar (ca. 80%). But the noteworthy point is that, time required for total conversion of xylose was different at different pressure. Xylose conversion was 95% at 24 bar (80% yield of sugar alcohols), 82% at 16 bar (72% yield) and 63% at 8 bar (58% yield) within 2 h of reaction time (Figure 5.4). Complete conversion with 82% yield occurs within 4 h at 16 bar pressure but it takes 6 h for complete conversion at 8 bar. It is suggested that above 16 bar pressure, enough concentration of hydrogen (solubilized) was present in reaction mixture; hence more concentration of H_2 adsorbed on the metal surface is available to carry out the reaction which is not the case when pressure is 8 bar. Therefore to achieve optimum yield of sugar alcohols from xylose, further conversions were carried out at 16 bar H_2 pressure.

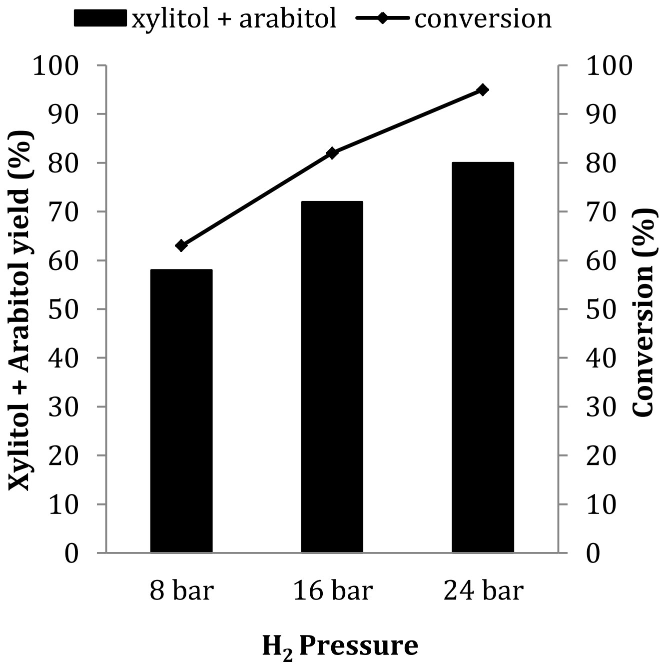


Figure 5.4. Effect of H_2 pressure on xylose conversion over Pt(3.5)/AL+C-HT catalyst. Reaction conditions: xylose 0.15 g, catalyst (Pt(3.5)/AL) 0.075 g, C-HT 0.075 g, water 35 mL, 60°C, 2 h.

5.3.1.2. Effect of metal loading: Xylose conversion was studied at 60°C for 4 h over Pt(2)/AL+C-HT catalytic system and results were compared with Pt(3.5)/AL+C-HT, to check the effect of metal content in the catalyst (Figure 5.5). 75% yield of sugar alcohols (96% conversion) was observed over Pt(2)/AL+C-HT against 82% yield over Pt(3.5)/AL+C-HT. Decrease in the yield of sugar alcohols is obvious as with lower metal loading, less number of active site for hydrogenation are available. Although, Pt loading was reduced to 2wt% from 3.5wt%, sugar alcohols yield was decreased merely by 7%, this indicates that good yield can be obtained in the entitled conversion, in spite of using catalyst with lower loading of Pt.

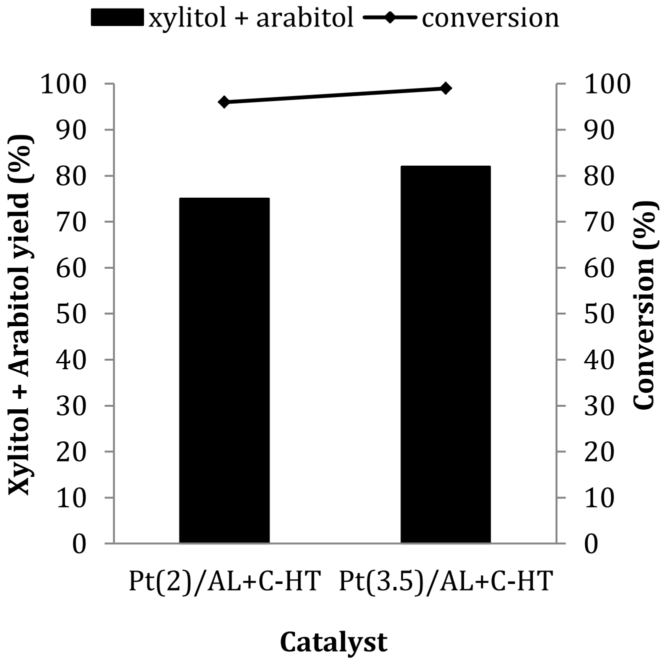


Figure 5.5. Effect of metal loading on the conversion of xylose.

Reaction conditions: xylose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, water 35 mL, 60°C, 16 bar H_2 at R.T., 4 h.

5.3.1.3. Recycle study and characterization of spent catalyst

Recycle study was done for Pt(3.5)/AL+C-HT catalytic system for xylose hydrogenation at 60°C for 4 h at 16 bar H_2. Catalyst showed good recyclability up to 4th cycle with negligible decrease in the yield after each run (1st run: 82%; 2nd run: 80%; 3rd run: 74%; 4th 71%). During recycle study, catalyst (Pt(3.5)/AL+C-HT) was separated from the reaction mixture by centrifugation and washed with water. Spent catalyst was reused in next run without drying, weighing or any other treatment like calcination and reduction. Minor decrease in the yields after each run is because of probable loss of some catalyst quantity during separation (Figure 5.6). Stability of the catalyst was checked by subjecting the spent catalyst to various characterizations. ICP-AES analysis of the spent catalyst and reaction mixture showed that Pt was not leached out in the reaction mixture.

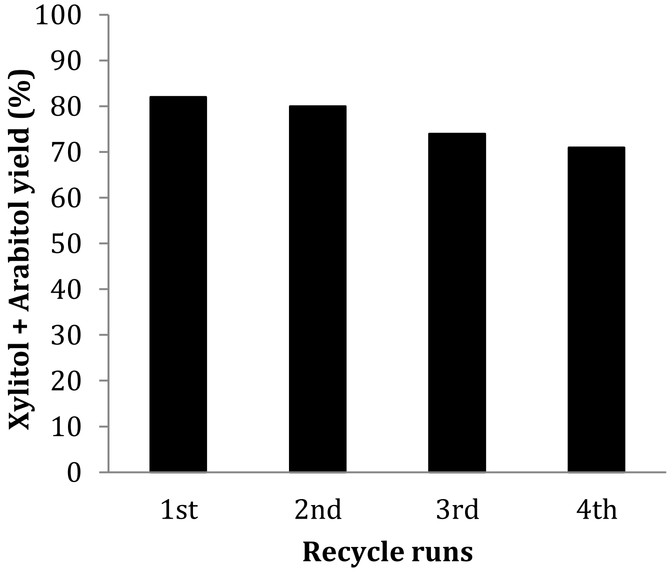


Figure 5.6. Recycle study for xylose conversion over Pt(3.5)/AL+C-HT catalyst. Reaction conditions: xylose 0.15 g, catalyst (Pt(3.5)/AL) 0.075 g, C-HT 0.075 g, water 35 mL, 60°C, 16 bar H_2 at R.T., 4 h.

XRD patterns of fresh and spent catalysts used in hydrogenation reactions of xylose conducted at 60°C are shown in Figure 5.7. It can be observed that most of the peaks were retained in the spent catalysts. Peaks for Pt were not visible in C-HT supported catalyst because of very fine dispersion. Calcined hydrotalcite can regain its layered double hydroxide structure in presence of water (rehydration) by memory effect,[9] however in XRD

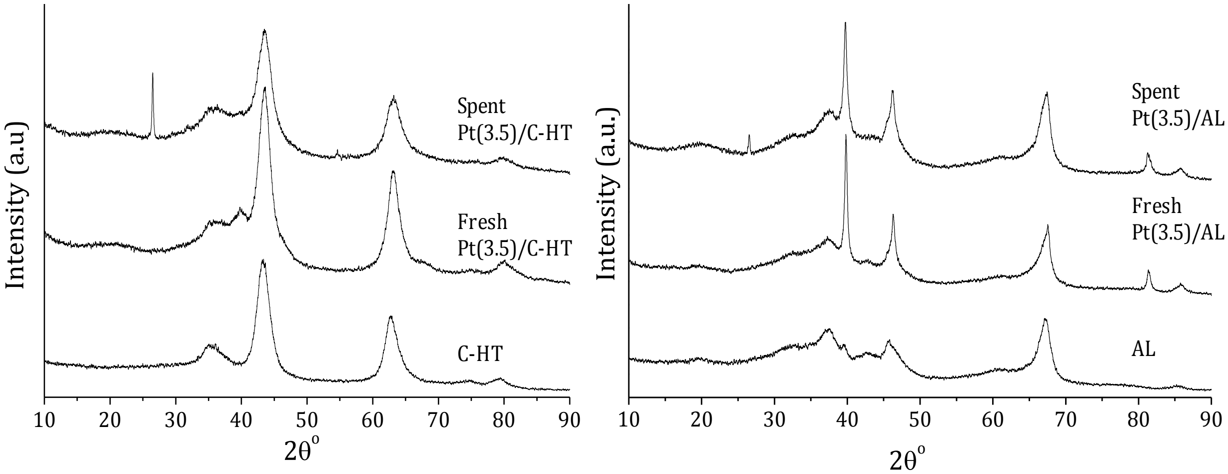


Figure 5.7. XRD patterns of fresh and spent catalysts.*

*Spent catalyst: used in the conversion of xylose at 60°C, 16 bar H_2 and 4 h.

pattern of spent Pt(3.5)/C-HT catalyst peaks for the double layer structure of hydrotalcite were not observed. This proved that C-HT is stable at applied reaction condition and does not form double layer structure. On the contrary in Pt(3.5)/AL catalyst, sharp peaks for Pt could be seen at characteristic peak positions. In spent catalyst too all characteristic peaks for Pt were retained. These sharp peaks imply bigger particle size of Pt on AL support. The additional peak at 24.5° in both spent catalysts can originate from adsorbed carbon species. TEM analysis of the spent Pt(3.5)/C-HT and Pt(3.5)/AL showed the comparable particle size of Pt with fresh catalysts i.e. 2-3 nm in spent Pt(3.5)/C-HT and 20-30 nm spent Pt(3.5)/AL. This proves that sintering of Pt particles during reaction is not doable irrespective of the support material used, thus catalysts are stable and can be reused with minimum loss of activity.

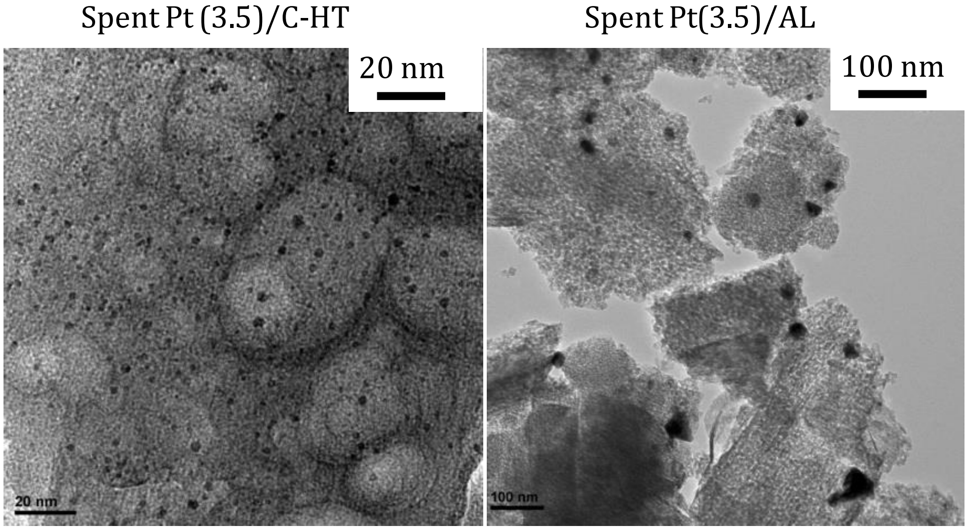


Figure 5.8. TEM images of spent Pt(3.5)/C-HT and Pt(3.5)/AL.*

*Spent catalyst: used in the conversion of xylose at 60°C, 16 bar H_2 and 4 h.

5.3.2. Effect of calcined hydrotalcite as a support or additive on the conversion of glucose over Pt monometallic catalyst

As seen in previous section (section 5.3.1), Improvement in the yield of sugar alcohols (xylitol+arabitol) was achieved at much milder reaction conditions in the presence of solid base, C-HT from xylose (C5 sugar) over Pt/AL catalyst. Similar to the xylose conversion, effect of C-HT as a support and as an additive was studied in the conversion of glucose (C6 sugar) in to sorbitol and mannitol, because these sugar alcohols have vital application in various field (refer chapter 1, section 1.2.1).

5.3.2.1. Effect of reaction parameters

Since Pt(3.5)/AL+C-HT catalytic system showed best results in the conversion of xylose in to sugar alcohols, reaction parameters were optimized for the same catalytic system in the conversion of glucose.

Effect of temperature and time: Figure 5.9 depicts the effect of temperature on the catalytic activity of Pt(3.5)/AL+C-HT for the conversion of glucose in to sugar alcohols (sorbitol+mannitol).

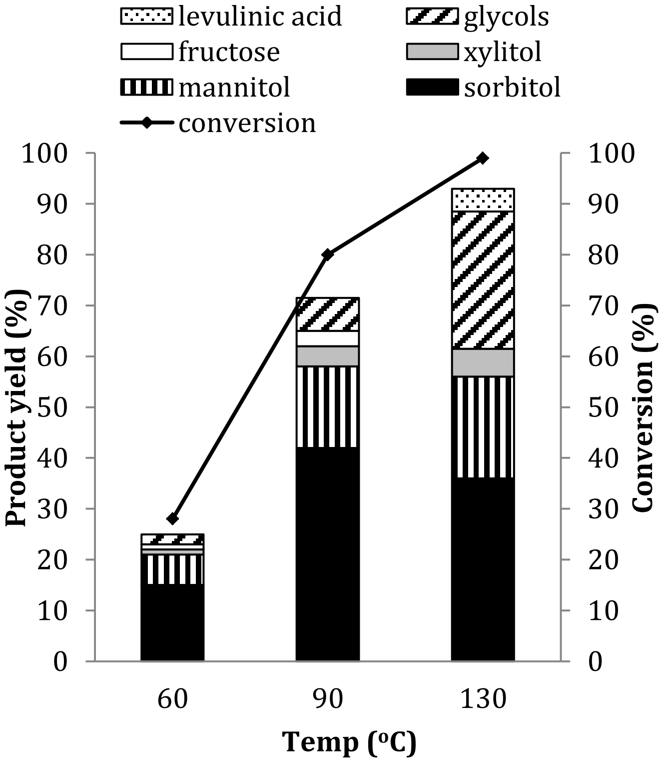


Figure 5.9. Effect of temperature on glucose conversion over Pt(3.5)/AL+C-HT catalyst.

Reaction conditions: glucose 0.15 g, catalyst (Pt(3.5)/AL) 0.075 g, C-HT 0.075 g, water 35 mL, 16 bar H_2 at R.T., 2 h.

Increase in temperature to 130°C did not necessarily increase the sugar alcohols yield even though conversion was increased to 99% in 2 h. This in fact lowered the yield for

C6 sugar alcohols (sorbitol+mannitol) formation (56%) at the expense of increase in yields for glycols and other products like levulinic acid and xylitol. On the other hand decrease in temperature to 60°C reduced the conversion levels to 28% with 21% yield of C6 sugar alcohols. In view of above results, 90°C reaction temperature was optimum to obtain higher conversions (80%) and 58% C6 sugar alcohols yield in 2 h of reaction time. Hydrogenation of glucose was studied over Pt(3.5)/AL, Pt(3.5)/C-HT and Pt(3.5)/AL+C-HT at 90°C at 16 bar H_2 pressure for various times (Table 5.2).

Table 5.2. Effect of different catalysts on the conversion of glucose.

Catalyst	Time (h)	Conv. (%)	Product yield (%)				
			Sugar alcohols			Fructose	Glycols^
			Sorbitol	Mannitol	Xylitol		
Without catalyst	2	-	-	-	-	-	-
	4	2	0.5	-	-	-	
	6	4	1.5	0.5	-	-	
Pt(3.5)/AL	2	8	5.7	-	-	-	
	4	15	8.4	-	-	-	1.5
	6	25	9.8	-	1	-	3.5
Pt(3.5)/C-HT	2	60	12	13.3	2	15	3.7
	4	80	19.4	19.6	4.5	16	6.5
	6	85	26	19.5	5	14	9
Pt(3.5)/AL+ C-HT	2	80	42	16	4	3	6.5
	4	92	54	14	4	-	7
	6	98	53	12	4	-	8

^Glycols: Ethylene glycol, glycerol and 1,2-propanediol.

Reaction conditions: glucose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, water 35 mL, 16 bar H_2 at R.T., 90°C.

As observed, Pt(3.5)/AL+C-HT showed 68% sugar alcohols yield with 92% conversion. Under similar reaction conditions, Pt(3.5)/C-HT showed 39% sugar alcohol yield (80% conversion) and the lowest activity was observed for Pt(3.5)/AL catalyst (8.4% yield, 15% conversion). In the absence of any catalyst only 2% conversion with 0.5% sugar alcohol yields was observed. Besides C6 sugar alcohols, formation of C5 sugar alcohol (xylitol), fructose and glycols (ethylene glycol, 1,2-propanediol, glycerol) was observed. Xylitol (C5 sugar alcohol) and glycols can be formed in the glucose conversion because of hydrogenolysis and/or retro-aldol reaction. Formation of polyols with less number of carbon from sugar and sugar alcohols with higher number of carbon is explained in chapter 3 (refer section 3.3.1.3). Aforementioned results clearly indicate that Pt(3.5)/AL+C-HT catalytic system gave maximum yield (68%) of C6 sugar alcohols compared to any other catalysts.

Careful observation of the data from Table 5.2 reveals that when Pt(3.5)/AL was used no fructose formation was observed. However, when Pt(3.5)/C-HT catalyst was used, fructose (isomerization product of substrate, glucose) was obtained in high quantity (14%, 6 h). Over Pt(3.5)/+C-HT catalyst also, fructose formation (3%, 2 h) was seen. The results imply that change in support affects the activity of catalyst and hence reactions with bare supports were carried out (Table 5.3). It is interesting to note here that without catalyst and with AL as a catalyst maximum of 4% conversion was possible after 6 h. However, when basic C-HT was introduced, the conversion increased to 80% yielding 39% fructose and 16% sugar alcohols. This implies that glucose isomerization reaction occurs in the alkaline medium. It is evidenced that the C-HT has alkaline nature which may help to achieve higher activity in the isomerization of sugars.[10] Reaction with AL+C-HT also showed higher glucose conversions (72%) with 42% fructose and 18.6% sugar alcohol formation. As mentioned in chapter 2 (section 2.3.2.6), C-HT has 0.88 mmol/g basic sites which can catalyze the isomerization of glucose to yield fructose by 'Lobry de Bruyn-Alberda van Ekenstein transformation'.

In the absence of Pt metal, hydrogenation of the sugar is restricted hence poor yield of sugar alcohols was observed and fructose was formed as a major product. Recently Cu/Ni/Al hydrotalcite was used to achieve better yield of sorbitol (73%) from glucose,[11] wherein it was shown that after addition of NaOH along with hydrotalcite, yield of sorbitol was observed to be decreased compare to reaction over hydrotalcite only. This is because in the presence of NaOH formation of glycols (by hydrogenolysis of sorbitol) was prominent.

Table 5.3. Contribution of supports to the conversion of glucose.

Catalyst	Time (h)	Conv. (%)	Product yield (%)		
			Sugar alcohols		Fructose
			Sorbitol	Mannitol	
Without catalyst	2	-	-	-	-
	4	2	0.5	-	-
	6	4	1.5	0.5	-
AL	2	-	-	-	-
	4	2	-	-	-
	6	4	2.5	-	-
C-HT	2	65	8	4.2	37
	4	78	7.7	5.8	39
	6	80	8.6	7.4	39
AL+C-HT	2	50	5.4	8	35
	4	66	9.9	11	41
	6	72	8.7	9.9	42

Reaction conditions: glucose 0.15 g, catalyst 0.075 g, water 35 mL, 16 bar H_2 at R.T., 90°C.

Considering this, it is obvious to expect that if basic support is used to impregnate Pt then higher concentrations of mannitol should form in the reaction (via fructose formation). Now, again looking at sugar alcohols formation data from Table 5.2, with Pt(3.5)/C-HT catalyst 26% sorbitol was formed while 19.5% mannitol (a hydrogenation product of fructose) was observed. Whereas with Pt(3.5)/AL+C-HT system, 53% sorbitol yield was obtained with 12% mannitol yield. Moreover, when Pt(3.5)/AL catalyst was used (without addition of any base) formation of mannitol was not observed. These results are very obvious since formation of 39% fructose (80% glucose conversion) was observed over bare C-HT and 42% fructose formation (72% glucose conversion) was observed over

AL+C-HT. Over Pt(3.5)/C-HT and Pt(3.5)/AL+C-HT catalytic system also, conversion of glucose in to fructose is possible which can further be converted in to mannitol. Nevertheless, extent of isomerization of glucose to fructose over Pt(3.5)/C-HT and Pt(3.5)/AL+C-HT was less as it has to compete with hydrogenation reaction (because of Pt metal) compare to C-HT and AL+C-HT (without Pt). Above data indicates that in the presence of C-HT fructose formation is possible, hence the formation of mannitol was observed along with sorbitol.

5.3.3. Correlation of catalyst properties with activity.

Discrepancy in the activities of Pt(3.5)/AL and Pt(3.5)/C-HT can be explained on the basis of their properties. From XRD and TEM analysis it is very clear that Pt particle size is much smaller in Pt(3.5)/C-HT (2-3 nm) compare to Pt(3.5)/AL (20-30 nm). This shows strong support metal interaction in Pt(3.5)/C-HT and number of active sites available for hydrogenation are more owing to the high dispersion. It is well documented that solid base can suppress the cracking reaction, which generally occur on acidic catalysts.[12] It is suggested that over solid bases no strong adsorption of complexes (through 'O' of the product) is possible which means that the products formed will be readily removed from the surface to avoid undergoing further reactions (glycols, coke). To prove this, experiments were conducted to check the adsorption of sorbitol on C-HT and AL. The results showed that there was no considerable difference in the adsorption of sorbitol on either C-HT or AL. This implies that, to obtain enhanced activity over Pt(3.5)/C-HT catalyst compared to Pt(3.5)/AL catalyst, weak or strong adsorption of product may not be the reason. It is known from the literature that at the surface of a basic support typically, oxide ions form ion pairs with low coordinated metal ions.[13] It is possible that hydrogen ions are immobilized on the set of active sites (O^{2-} - metal cation pair) and these sites are separated from each other and hence migration and recombination of hydrogen ions to form hydrogen molecule is not possible.[14] This ultimately gives rise to rich environment of hydrogen ions on the support. This pool of hydrogen ions then may be available for the hydrogenation reaction thus increasing the activity of a catalyst.

The other possibility for increased activity in case of Pt supported on basic support is that the basic support can give rise to electron-rich metallic particles. In fact it is reported that electron rich Pd particles are possibly formed when MgO is used as a support.[15] A similar phenomenon is also reported for Pt particles supported on hydrotalcites.[16, 17] In another report it is evidenced that when Pt particle size is almost same in different catalysts, it is the electronic ligand effect produced by basic support that enhances the hydrogenation activity.[18] The strong metal-support interaction (SMSI) is first reported for Pt/MgO catalyst and it was shown that higher metal dispersion achieved by SMSI enhances the hydrogenation activity. [19] In this study, better hydrogenation activity with Pt/C-HT may arise due to SMSI in Pt/C-HT compared to Pt/AL catalyst. Even so, best yield of sugar alcohols was achieved over the Pt/AL+C-HT catalytic system in the conversion of both xylose and glucose. This indicates that better yield of sugar alcohols can be achieved over Pt/AL catalyst in the presence of C-HT. Thus, C-HT plays very crucial role which dramatically improved the activity of Pt/AL catalyst towards hydrogenation reaction. In xylose conversion turn over frequency (TOF) of the Pt(3.5)/AL was improved from 0.38 min^{-1} to 13.01 min^{-1} when C-HT, solid base was used along with catalyst. Similar enhancement in the TOF was observed in the conversion of glucose (Table 5.4). It can be concluded that better yield of the sugar alcohols over Pt/C-HT was not only because of fine dispersion of the Pt but also because of presence of C-HT, a solid base.

Table 5.4. Turn over frequencies of various catalysts.*

Catalytic system	TOF (min^{-1}) xylose conversion at 60°C	TOF (min^{-1}) glucose conversion at 90°C
Pt(3.5)/AL	0.38	0.91
Pt(3.5)/C-HT	0.42	0.98
Pt(3.5)/AL+C-HT	13.01	10.21

*TOF was calculated at initial stage of reaction at almost similar conversion levels (±5% difference) in all the reactions.

5.3.4. Proposed reaction mechanism

The best hydrogenation activity for Pt/AL+C-HT catalytic system can be attributed to the fact that presence of C-HT may influence the isomerization of glucose to make it available in open chain form. It is reported that concentration of glucose in open chain form in water at equilibrium is very small. In alkaline medium glucose can be converted in to isomerization product (fructose) by undergoing Lobry de Bruyn-Albeda van Ekenstein transformation reaction (Figure 5.10).[2]

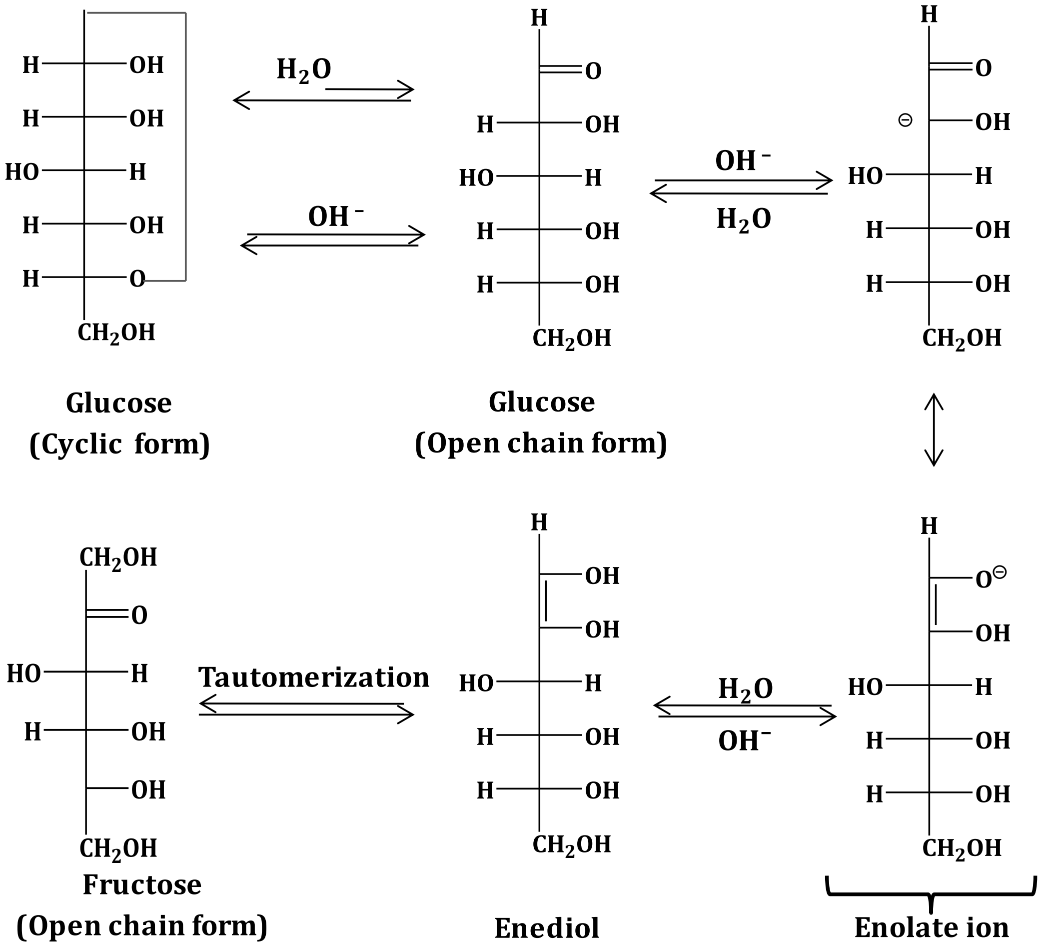


Figure 5.10. Isomerization of glucose to fructose in alkaline medium.

The enolate ion thus formed as an intermediate is present in an open chain form (in water) and these ions in high concentration are available for hydrogenation. It is not possible to obtain similar concentration of glucose in open chain form under neutral and acidic reaction conditions and hence it is suggested that higher yields were possible when Pt/AL+C-HT catalyst was used for the reaction. Moreover, pH of the reaction solution in case of Pt/C-HT catalyst was observed to be 9.3 while with Pt/AL+C-HT catalyst it was 8.5 and with Pt/AL it was 5.5. This difference in pH makes the variation in products yield, since alkaline pH enhances the concentration of glucose in the enolate form (open chain) which ultimately leads to fructose formation. Hence in glucose conversion over bare C-HT and

AL+C-HT formation of fructose (39% and 42%, respectively) and over Pt(3.5)/C-HT and Pt(3.5)AL+C-HT catalysts formation of mannitol; hydrogenation product of fructose (19.6 and 14%, respectively) was seen (Table 5.2 and 5.3). As discussed above, glucose may undergo Lobry de Bruyn-Alberda van Ekenstein transformation (Figure 5.10) under alkaline medium to yield enolate ions, enediol and fructose. Similar transformation of xylose to xylulose through open chain intermediates is also possible under alkaline medium.[20] Glucose molecule is UV active if it is present in open chain form due to exposure of –CHO group, while absence of –CHO group in cyclic form makes glucose UV inactive. Based on this fact, UV absorption study of glucose was done to confirm that more glucose molecules are in open chain form under alkaline condition (Figure 5.11).

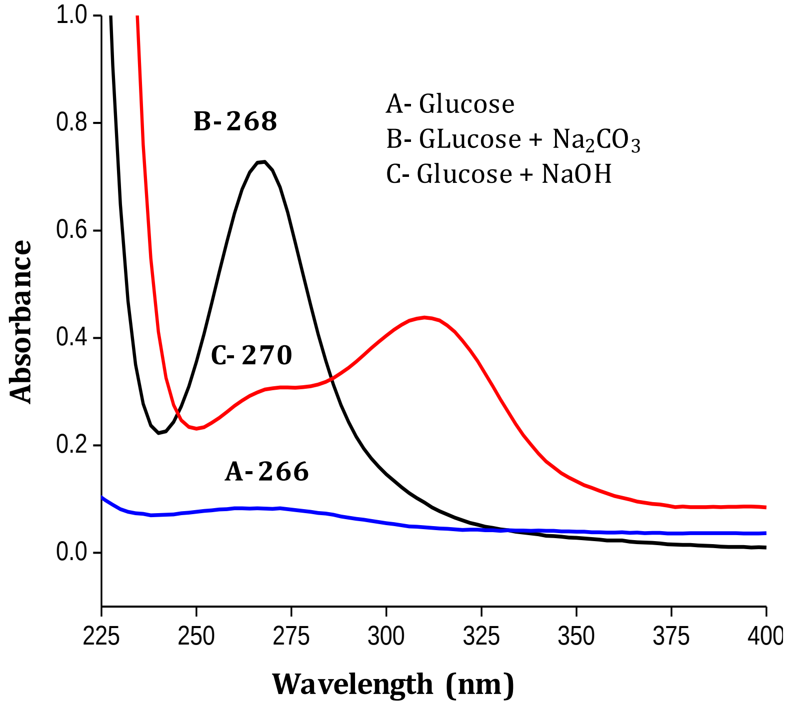


Figure 5.11. UV-Vis absorption study of glucose.

For this study, glucose (0.7 g) was dissolved in water (30 mL) and subjected to UV absorption analysis without addition of any base (under neutral conditions, pH = 6.7). The peak at λmax = 266 nm, characteristic for C=O of carbonyl group was visible as a small hump indicating low concentration of glucose in open chain form (Figure 5.11). Next, UV absorption study was intended after addition of C-HT in the glucose solution.

Unfortunately, experiments with the addition of C-HT were not possible since it is a solid base and after adding the same it is difficult to do UV analysis and if C-HT is filter off, the pH of the solution will become neutral since basicity is due to solid C-HT added. However, after addition of mineral base (Na_2CO_3, 0.2 g) in the glucose solution (glucose, 0.7 g in 30 mL water) intense peak at λmax = 268 nm was observed. This proves that under alkaline conditions, glucose is present in open chain form. Moreover, another study was carried out by using NaOH instead of Na_2CO_3 as a base. With the addition of NaOH, along with the peak at λmax = 270 nm (ascribed to –CHO group) additional peak was observed at λmax = 310 nm, which can be assigned to enediol anion as reported earlier.[21] To understand why after addition of NaOH additional peak appears at 310 nm, pH of the solution was checked and found to be 13.8 while after addition of Na_2CO_3, pH of the solution was 11.8. It is hence understood that in the presence of NaOH (at 13.8 pH) glucose is converted from cyclic form to open chain form to yield enolate ion and subsequently gives rise to enediol formation. This results are in line with literature where formation of enediol is favored in the presence of strong base compare to weak one (here NaOH is stronger base than Na_2CO_3).[21] This proves that use of weak base, Na_2CO_3 may be better in these reactions compared to addition of NaOH. Considering above discussion, it can be concluded that in alkaline medium (in presence of Pt/C-HT, Pt/AL+C-HT) higher concentration of glucose is present in open chain form (than cyclic) which will readily undergoes hydrogenation reaction.

5.3.5. Effect of calcined hydrotalcite as a support or additive on the conversion of xylose over Pt-Sn/AL bimetallic catalyst

In the conversion of various mono- and poly-saccharides, Pt-Sn/AL bimetallic catalyst showed superior yields of sugar alcohols compare to Pt/AL monometallic catalyst at any reaction condition (refer chapter 3, section 3.3.2 & 3.3.4 and chapter 4A, section 4A.3.1 & 4A.3.2). As discussed earlier, yields of sugar alcohols over monometallic Pt/AL catalyst can be improved by adding C-HT along with catalyst during reaction. It might be possible to achieve even better results for the production of sugar alcohols, if C-HT is used in combination with bimetallic Pt-Sn/AL catalyst. From previous results on the conversion of xylose (chapter 3, section 3.3.2), it is clear that maximum yields of sugar alcohols (xylitol+arabitol) can be obtain over Pt-Sn/AL bimetallitc catalyst with Pt:Sn ratio equals to

1:0.12 (*wt/wt*). Maximum 79% sugar alcohols yield was observed over Pt(3.5)Sn(0.43)/AL while Pt(2)Sn(0.25)/AL showed 73% yield which implies that when Pt loading was decreased from 3.5wt% to 2wt%, decrease in the yield was only 7%. Hence the conversion of xylose over Pt(2)/AL+C-HT and Pt(2)Sn(0.25)/AL+C-HT was studied at 60°C for 4 h at 16 bar H_2. As expected Pt(2)Sn(0.25)/AL+C-HT showed superior yield of sugar alcohol (yield 97%, complete conversion) compare to Pt(2)/AL+C-HT (yield 75%, conversion 96%). Effect of reaction parameters like temperature, time, H_2 pressure and quantity of C-HT was studied to optimize reaction condition for xylose conversion over Pt(2)Sn(0.25)/AL+C-HT catalytic system.

5.3.5.1. Effect of reaction parameters

Effect of temperature and time: Conversion of xylose was studied over Pt(2)Sn(0.25)/AL+C-HT catalytic system at 40, 50 and 60°C for 2, 4 and 6 h at 16 bar H_2 pressure.

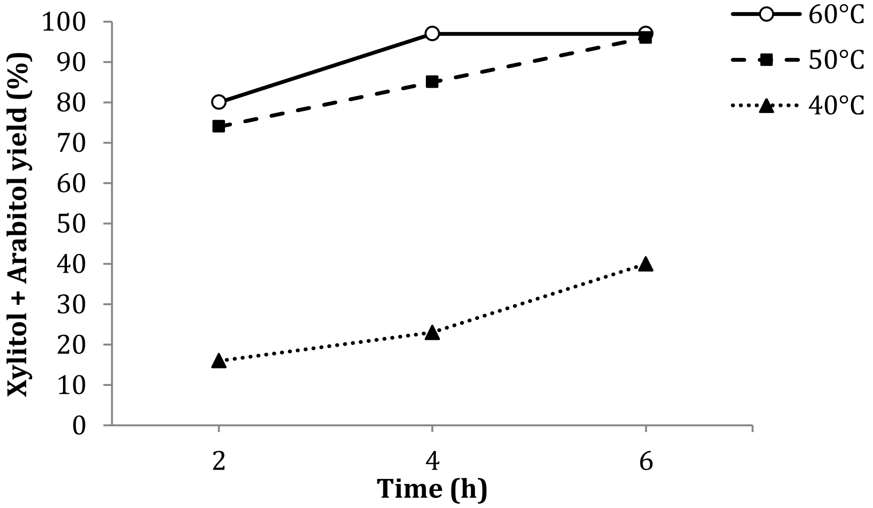


Figure 5.12. Effect of temperature on xylose conversion over Pt(2)Sn(0.25)/AL+C-HT catalyst.

Reaction conditions: xylose 0.15 g, catalyst (Pt(2)Sn(0.25)/AL) 0.075 g, C-HT 0.075 g, water 35 mL, 16 bar H_2 at R.T.

Figure 5.12 depicts that almost complete conversion was achieved within 4 h at 60°C with 97% yield of sugar alcohols while at 50°C it took 6 h for complete conversion with 96% yield. On the other hand only 42% conversion with 40% yield could be achieved at 40°C within 6 h. Another noteworthy point is that formation of side products like glycol was negligible at all the temperatures. This data once again reinforces the fact that formation of sugar alcohols is favorable at lower temperatures while side reactions to yield glycols are prominent at higher temperature. Since complete conversion was achieved with good yield of sugar alcohols within 6 h of reaction time at 50°C, further study was done at 50°C.

Effect of H_2 pressure: As mentioned earlier, solubility of H_2 in the solvent (H_2O) depends on temperature and pressure. Hence effect of H_2 pressure was studied by conducting xylose reactions at 50°C after charging 8, 16, 24 bar H_2 (Figure 5.13).

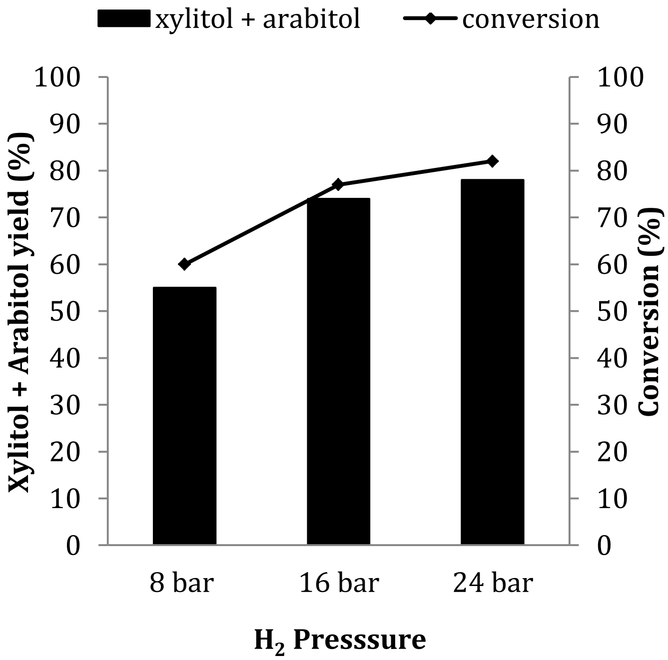


Figure 5.13. Effect of H_2 pressure on xylose conversion over Pt(2)Sn(0.25)/AL+C-HT catalyst.

Reaction conditions: xylose 0.15 g, catalyst (Pt(2)Sn(0.25)/AL) 0.075 g, C-HT 0.075 g, water 35 mL, 50°C, 2 h.

At 8 bar H_2 pressure 55% yield (60% conversion) of sugar alcohols was achieved within 2 h. Improvement in the yield (74% yield and 77% conversion) was noticed at 16 bar pressure but further increase in the pressure to 24 bar did not show considerable increment in the yield (78%) and conversion (82%). This indicates that at 8 bar pressure, sufficient H_2 was not solubilized in reaction mixture and hence concentration H_2 adsorbed on the metal surface is low which results into poor yield of sugar alcohols. At 16 bar pressure sufficient amount of H_2 was solubilized therefore concentration of H_2 adsorbed on the metal surface is high; hence better yield could be achieved (for more details on the pressure effect, refer chapter 3, section 3.3.1.3). Further increase in H_2 pressure to 24 bar did not show considerable improvement in the yield because adsorption of the H_2 on metal surface might not be improved in spite of increase in pressure (Figure 5.13).

Effect of C-HT quantity: Effect of substrate/catalyst (S/C) ratio (*wt/wt*) was studied in previous chapters and it was observed that lower yields of sugar alcohols were obtained, if S/C is more than 2 (chapter 3, section 3.3.2.5). Considering this, effect of quantity of C-HT was examined in xylose conversion by maintaining S/C ratio at 2 (*wt/wt*) i.e. 0.15 g xylose and 0.075 g Pt(2)Sn(0.25)/AL catalyst in 35 mL H_2O. Sugar alcohol yield was decreased to 67% from 96% when 0.038 g of C-HT was used instead of 0.075 g at similar reaction conditions, probably because of drop in pH of reaction mixture to 7.9 from 9.2 when 0.038 g C-HT was added instead of 0.075 g. When double quantity of C-HT was added (0.15 g) pH of the reaction mixture was 9.8, however similar yield was observed (95% yield, 99% conversion). As explained earlier, more sugar molecules are in open chain form in alkaline medium and hence can be converted easily in to sugar alcohols in the presence of active metal and H_2.

When activities of various catalysts were compared at the optimized reaction conditions (50°C, 16 bar H_2 and 6 h) Pt(2)Sn(0.25)/AL+C-HT showed highest yield of sugar alcohols (96%) amongst all catalysts (Figure 5.14). When Pt(2)/AL and Pt(2)Sn(0.25)/AL were used as a catalyst 3% and 34% yield was observed with 5% and 38% conversion, respectively. This is because; pH of the reaction mixture after addition of these catalysts was slightly acidic since AL is acidic support and 3M HCl was used during preparation of Pt-Sn/AL catalyst. In acidic medium less number of sugar molecules must be present in open chain form, hence lower conversion were observed over these catalysts. When C-HT was used as a support or added as an additive, pH of the reaction mixture was alkaline (9-10) and in alkaline medium more number of sugar molecules must be present in open chain form. Therefore, higher conversion with better yields could be achieved over Pt(2)/C-HT (59% yield) and Pt(2)Sn(0.25)/C-HT (76% yield) catalytic systems. Further enhancement in the yield of sugar alcohols was observed when Pt(2)/AL+C-HT (85%) and Pt(2)Sn(0.25)/AL+C-HT (96%) were used as catalyst. Enhancement in the yields of sugar alcohols over Pt(2)Sn(0.25)/AL bimetallic catalyst with or without presence of C-HT compare to Pt(2)/AL is because of the promoter effect of Sn (promoter effect of Sn is explained thoroughly in chapter 3 and 4).

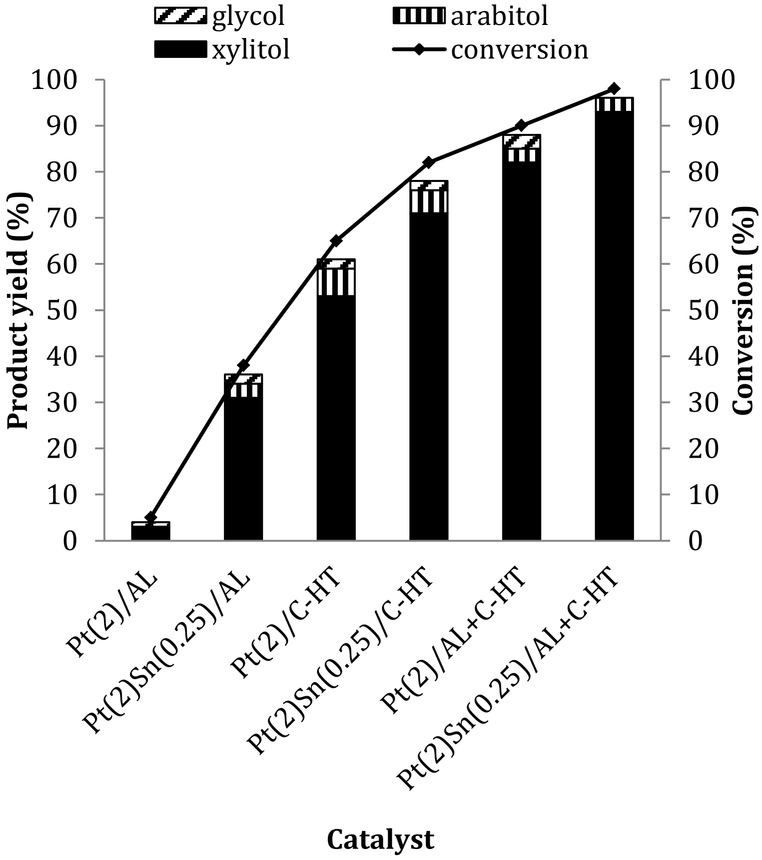


Figure 5.14. Conversion of xylose over various catalysts.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, H_2O 35 mL, 16 bar H_2 at R.T., 50°C, 6 h.

Since Pt(2)Sn(0.25)/AL+C-HT catalytic system showed good activity at much milder reaction condition (50°C) compare to Pt(2)Sn(0.25)/AL catalyst (130°C), it is interesting to check the efficiency of Pt(2)Sn(0.25)/AL+C-HT catalytic system to convert xylose in to sugar alcohols at room temperature (32±3°C). Moreover, from previous study it can be concluded that selectivity for sugar alcohols in the conversion of sugars is higher at lower temperature as side reactions to yield glycols and furans are not much prominent at this temperature. Hence, with the intension to achieve maximum possible yield of sugar alcohols, xylose reactions were carried out at room temperature. To check the effect of H_2 pressure on the conversion of xylose at room temperature, reactions were done over Pt(2)Sn(0.25)/AL+C-HT catalytic system at 16 and 24 bar H_2 pressure for various times. Yields obtained at 16 bar and 24 bar pressure were similar (95 and 96%, respectively) upon complete conversion, but the time required to achieve complete conversion was different at different pressures; 32 h at 16 bar and 28 h at 24 bar. This is obvious because at room temperature solubility of the H_2 is less compare to higher temperatures, hence needs elevated pressure for higher solubility. Considering this, xylose reactions over various catalysts were carried out at room temperature with 24 bar H_2 pressure to achieve complete conversion in short period. Over monometallic Pt(2)/AL catalyst 18% yield of sugar alcohols (xylitol+arabitol) was obtained with 20% conversion within 28 h, while over bimetallic Pt(2)Sn(0.25)/AL catalyst 38.5% yield with 40% conversion could be achieved (Table 5.5). Further improvement in the yield was observed when Pt(2)/C-HT (80.5%) and Pt(2)Sn(0.25)/C-HT (84%) catalysts were used. Highest yield of sugar alcohols (96%) was obtained with almost complete conversion (98%) over Pt(2)Sn(0.25)/AL+C-HT catalytic system. Other than sugar alcohols, side products like glycols (glycerol, ethylene glycol, 1,2-propanediol) were formed but in negligible quantity.

Table 5.5. Conversion of xylose over various catalysts at room temperature.

Catalyst	Product yield (%)			Conv. (%)
	Xylitol	Arabitol	Sugar alcohols	
Pt(2)/AL	17	1	18	20
Pt(2)Sn(0.25)/AL	36	2.5	38.5	40
Pt(2)/C-HT	77	3.5	80.5	85
Pt(2)Sn(0.25)/C-HT	80	4	84	89
Pt(2)/AL+C-HT	85	2.5	87.5	90
Pt(2)Sn(0.25)/AL+C-HT	94.5	1.5	96	98

Reaction condition: xylose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, H_2O 35 mL, 24 bar H_2 at R.T., 32±3°C, 28 h.

5.3.5.2. Comparison of other solid bases with calcined hydrotalcite as an additive

Effect other bases such as, hydroxyapatite (HAP), magnesium oxide (MgO) and calcium oxide (CaO) was compared with the effect of C-HT as an additive on xylose conversion over Pt(2)Sn(0.25)/AL catalyst (Figure 5.15). Among all the catalytic system evaluated, Pt(2)Sn(0.25)/AL+MgO showed best yield for sugar alcohols (98%), however MgO is soluble in water and hence difficult to reuse. When HAP was used as an additive with Pt(2)Sn(0.25)/AL, 37% yield of sugar alcohols (40% conversion) was achieved while 96% yield (complete conversion) could be obtained using Pt(2)Sn(0.25)/AL+C-HT catalytic system. Complete conversion was observed over Pt(2)Sn(0.25)/AL+CaO catalytic system within 6 h but yield of sugar alcohols obtained was 64%. For comparison, xylose reaction was carried out with Pt(2)Sn(0.25)/AL+Na_2CO_3 at similar reaction conditions and 79% (96% conversion) yield was obtained.

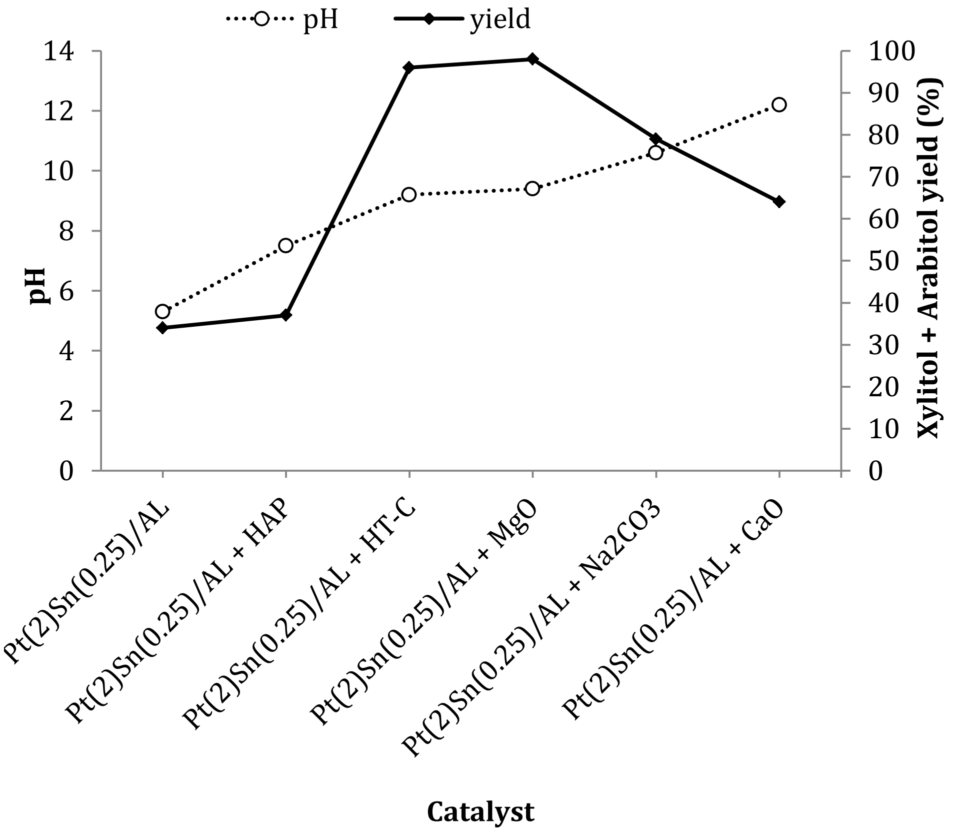


Figure 5.15. Effect of various bases on the xylose conversion.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, base 0.075 g, H_2O 35 mL, 16 bar H_2 at R.T., 50°C, 6 h.

To check the effect of pH on entitled conversion, yields obtained over various catalytic systems were correlated with pH of the reaction mixture after addition of corresponding catalyst (Figure 5.15). Increase in the yield of sugar alcohols was observed when pH of reaction mixture was increased from 7.5 (using HAP) to 9.2 or 9.4 (using C-HT and MgO, respectively) and again decreased with further increase in pH to10.6 and 12.2 (using Na_2CO_3 and CaO). Aforementioned results indicate that optimum yield can be achieved when pH of reaction mixture is 9-10 and start decreasing at pH higher than 10 and lower than 9, because at lower pH (7.5 or less) less number of sugar molecules is present in open chain form while at higher pH side reactions may prevail. But when pH of the reaction mixture was adjusted to 10.2 by adding sufficient amount of C-HT, 95% yield of sugar alcohols was obtained which is very much similar to the yield obtained at pH of 9.2. This indicates that some other factors (other than pH) also plays role in governing the activity of catalyst towards the hydrogenation of sugars.

5.3.5.3 Recycle study

Recyclability of Pt(2)Sn(0.25)/AL+C-HT was checked for xylose conversion (50°C, 16 bar H_2, 6 h) up to 4 recycle runs and showed good result with negligible decrease (2-4%) in the yield after each run (Figure 5.16).

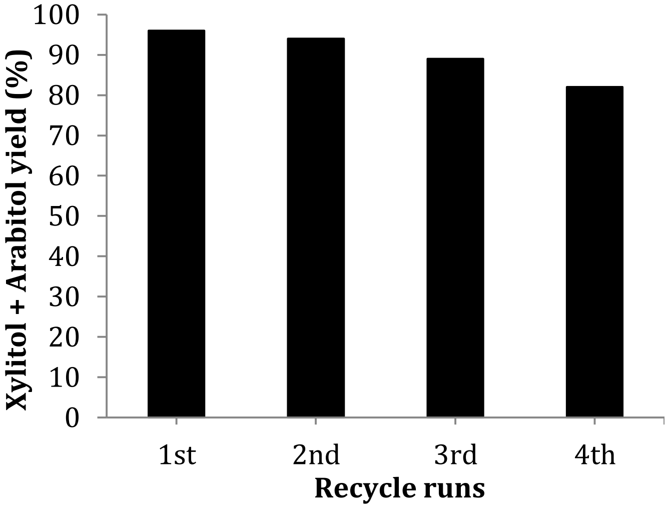


Figure 5.16. Recycle study for xylose conversion over Pt(2)Sn(0.25)/AL+C-HT catalyst.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, H_2O 35 mL, 16 bar H_2 at R.T., 50°C, 6 h.

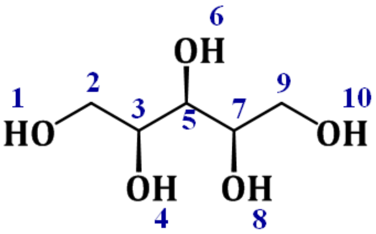
Upon completion of reaction, catalyst was recovered from reaction mixture by centrifugation, washed with distilled water and used in next run without drying and without calcination and reduction. Yields of sugar alcohols obtained in 1st, 2nd, 3rd and 4th run were 96, 94, 89 and 82%, respectively. Slight decrease in the yield is because of loss of some catalyst quantity during separation from reaction mixture.

NMR-study was done for the products obtained in the conversion of xylose to check the purity of products formed. After reaction (xylose conversion at 50°C, 6 h, over Pt(2)Sn(0.25)/AL+C-HT catalyst), reaction mixture was centrifuged to separate catalyst and product solution. Water was evaporated from product solution by rotary vacuum evaporator and a solid residue thus obtained was dissolve in D_2O for NMR study. NMR study depicts that products formed in the entitled conversion of xylose (xylitol 93% and arabitol 3%, determined by HPLC) does not have any considerable impurity of other chemicals as spectrum matches well with xylitol structure. ^1H NMR spectrum recorded at 200 MHz is represented in Figure 5.17 while Table 5.6 represents the peak assignment for various protons.

Table 5.6. ^1H NMR details for product of xylose hydrogenation.*

Sr. No.	Chemical shift (ppm)	No. H-atoms	Type	Position of H-atom
1	3.53-3.56	3	Multiplet	9,2,5
2	3.61-3.64	2	Multiplet	9,2
3	3.69-3.72	2	Double triplet	7,3

* Products obtained are xylitol (93%) and arabitol (3%).



Xylitol

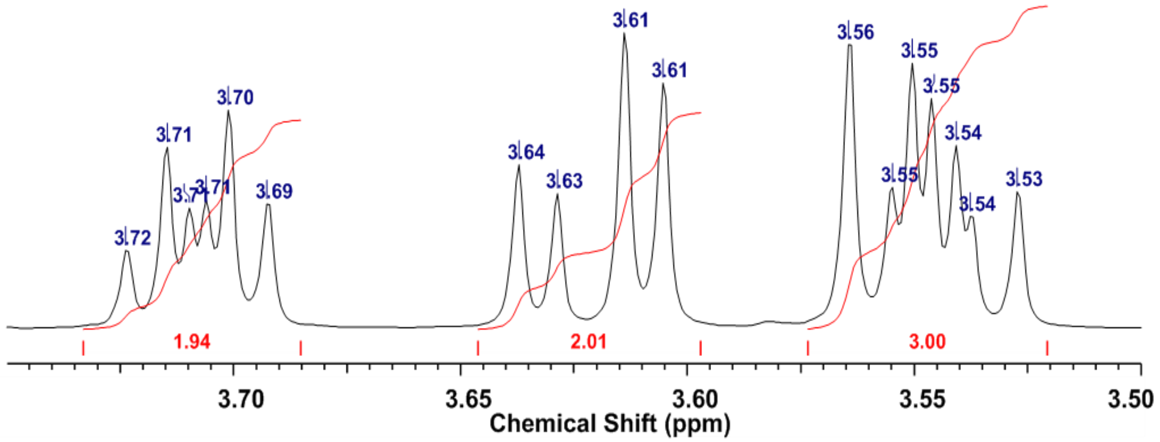


Figure 5.17.^{1}H NMR spectrum of the product obtained from xylose hydrogenation.

5.3.5.4. Correlation of catalyst properties with activity

Variation in yields of sugar alcohols over different catalysts can be explained with the help of characterization of these catalysts. From XRD analysis it can be concluded that no alloy or intermetallic species was formed in bulk quantity in Pt(2)Sn(0.25)/AL, even if formed its concentration must be very less, hence cannot be detected by XRD. Because of high dispersion of Pt, peak intensity was lower in Pt(2)Sn(0.25)/AL than in Pt(2)/AL while in Pt(2)/C-HT and Pt(2)Sn(0.25)/C-HT peak intensity was very low because of highly dispersed Pt on C-HT support compare to AL support (refer chapter 2, section 2.3.2.2). TEM analysis showed that particle size of Pt in Pt(2)/AL and Pt(2)Sn(0.25)/AL was 20-30 nm and 10-20 nm, respectively. Whereas in both Pt(2)/C-HT and Pt(2)Sn(0.25)/C-HT particle size was observed to be 2-3 nm (refer chapter 2, section 2.3.2.3). Better dispersion in Pt(2)Sn(0.25)/AL catalyst is because of interaction of Sn with support (AL) in which Sn interacts strongly with alumina to form tin-aluminate type structure.[22] It is reported that, on AL support, Sn cannot be reduced to (0) oxidation state even after reduction at 500°C[23] and hence Sn can form surface shell which prevents mobility of Pt particle during calcinations and reduction.[22-24] In this study catalysts were reduced at 400°C, so Sn may present in (II) or (IV) oxidation state. In this work, XPS spectra of Pt-Sn/AL bimetallic catalysts showed peak at 486.5 eV which is characteristic for Sn (II) or (IV) (chapter 2, section 2.3.2.4) and hence it is suggested that Sn is not present in (0) state. As mentioned earlier (chapter 3, section 3.4) ionic Sn helps to polarize the C=O bond in carbonyl group of sugars and hydrogenation of polarized C=O bond is easier. Hence it is believed that increase in the yield over Pt(2)Sn(0.25)/AL catalyst compare to Pt(2)/AL, is due to promoter effect of Sn (II) or (IV).

Amongst all the catalytic systems evaluated for xylose conversion, highest yield of sugar alcohols was achieved over Pt(2)Sn(0.25)/AL+C-HT catalyst. This is because of the combined effect of Sn (in ionic form) and presence of C-HT; a solid base by addition of which pH of the reaction medium becomes alkaline. It is proposed that more sugar molecules must be present in open chain form in alkaline medium and these sugar molecules in the open chain form undergo hydrogenation more easily. UV absorption study proves that more sugar molecules are in open chain in alkaline medium than in neutral medium (section 5.3.4, Figure 5.11 in this chapter).

5.3.6. Effect of calcined hydrotalcite as a support or additive on the conversion of arabinose, glucose and galactose over Pt-Sn/AL bimetallic catalyst

Similar to the xylose, conversion of arabinose was studied at 50°C and at room temperature (32±3°C) (Table 5.7).

Table 5.7. Conversion of arabinose over various catalysts.

Catalyst	50°C[a]		Room temperature[b]	
	Arabitol+Xylitol yield (%)	Conv. (%)	Arabitol+Xylitol yield (%)	Conv. (%)
Pt(2)/AL	5	7	34	35
Pt(2)Sn(0.25)/AL	32	35	44	46
Pt(2)/C-HT	51	56	84	87
Pt(2)Sn(0.25)/C-HT	64	69	90	92
Pt(2)/AL+C-HT	85	92	93	95
Pt(2)Sn(0.25)/AL+C-HT	96.5	99	97.5	99

Reaction condition: arabinose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, H_2O 35 mL, a:50°C-16 bar H_2 at R.T., 6 h, b: 32±3°C- 24 bar H_2 at R.T., 28 h.

Maximum 96.5% yield of sugar alcohols (arabitol+xylitol) was obtained within 6 h over Pt(2)Sn(0.25)/AL+C-HT catalytic system from arabinose at 50°C and 16 bar H_2. Likewise 97.5% yield of sugar alcohols was achieved from arabinose within 28 h of reaction time at room temperature and at 24 bar H_2 pressure. Conversions and yields obtained over various catalysts at 50°C and at room temperature are shown in Table 5.7. Amongst all catalysts, Pt(2)Sn(0.25)/AL+C-HT system showed best results for the production of sugar alcohols from arabinose.

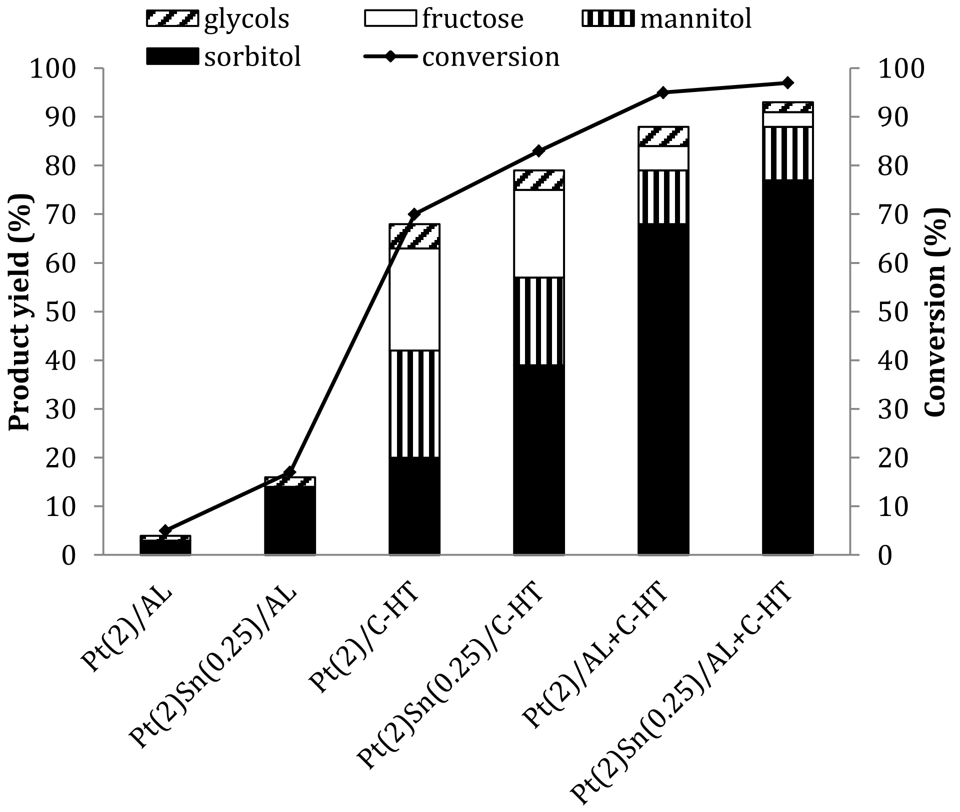


Figure 5.18. Conversion of glucose over various catalysts.

Reaction condition: glucose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, H_2O 35 mL, H_2 16 bar at R.T., 80°C, 6 h.

After achieving very high yield and selectivity of sugar alcohols from C5 sugars (xylose and arabinose), catalyst Pt(2)Sn(0.25)/AL+C-HT was evaluated for the conversion of C6 sugars (glucose and galactose) at room temperature and 24 bar H_2 pressure. For complete conversion of glucose, time required was 60 h and 84% yield of C6 sugar alcohols; sorbitol 76% and mannitol 8% was obtained, while galactose was converted completely at room temperature within 48 h to yield 87% galactitol and small amount of mannitol (3%). To check the effect of temperature in the conversion of glucose, reactions were conducted at 50°C under 16 bar H_2, but only 43% conversion was observed with 36% yield of sugar alcohols in 6 h. When temperature was switched to 80°C, complete conversion of glucose was achieved in 6 h to yield 88% sugar alcohols (sorbitol+mannitol). Comparison of catalytic activities of various catalysts to yield sugar alcohols from glucose at 80°C is represented in Figure 5.18.

5.3.7. Effect of calcined hydrotalcite as a support or additive on the conversion of hemicelluloses and inulin over Pt-Sn/AL bimetallic catalyst

As explained earlier, C5 and C6 sugars can be obtained from polysaccharides by hydrolysis which can further be converted in to sugar alcohols upon hydrogenation. Likewise, it is possible to convert polysaccharides directly in to sugar alcohols in one pot fashion by hydrolytic hydrogenation. In chapter 4A, we have discussed the conversion of isolated polysaccharides (xylan, arabinogalactan and inulin) to yield sugar alcohols and enhanced yields were achieved over Pt-Sn/AL catalyst compare to Pt/AL monometallic catalyst. In the current chapter, the effect of solid base (C-HT) on the conversion of monosaccharides is discussed in earlier sections. Exceptionally high yields of sugar alcohols were obtained from C5 and C6 sugars over Pt-Sn/AL+C-HT catalytic system. Hence it was decided to study the effect of solid base (C-HT) on the conversion of polysaccharides (xylan, arabinogalactan and inulin) to yield sugar alcohols. From earlier data, it is clear that xylan conversion is not feasible at temperature lower than 190°C (chapter 4A, section 4A.3.1.1.4). Therefore catalytic activity of various catalysts for the xylan conversion was compared at 190°C, 16 bar H_2 and 16 h of reaction time (Figure 5.19). Against expectation, much lower yield of sugar alcohols (xylitol+arabitol, 9%) was obtained over Pt(2)Sn(0.25)/AL+C-HT and Pt(2)Sn(0.25)/C-HT (7%) compare to Pt(2)Sn(0.25)/AL (43%). When reactions were carried out with bare supports; AL and C-HT, 13% and 9% yields of sugar alcohols were obtained, respectively (Figure 5.19).

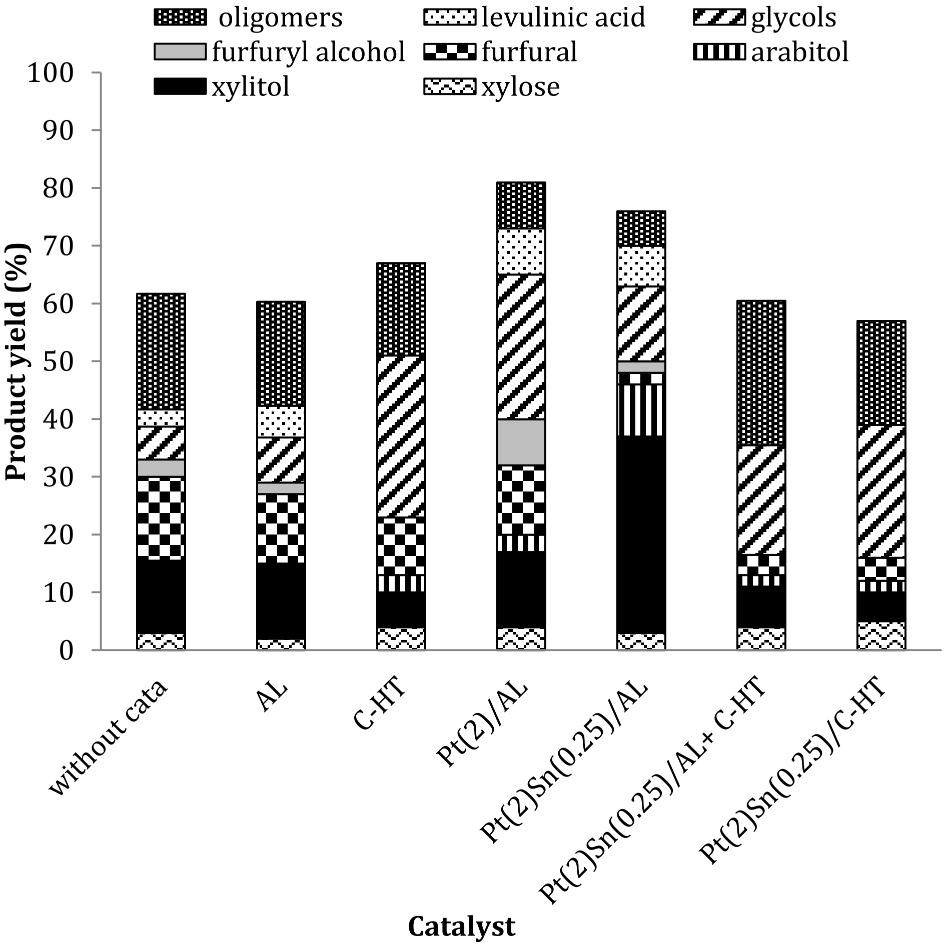


Figure 5.19. Effect of C-HT on the conversion of xylan (oat spelt).

Reaction condition: xylan (oat spelt) 0.15 g, catalyst 0.075 g, C-HT 0.075 g, H_2O 35 mL, H_2 16 bar at R.T., 190°C, 16 h.

These results imply that, although better yields of sugar alcohols were achieved from sugars after addition of C-HT (solid base) along with Pt-Sn/AL catalyst, in xylan conversion yields were decreased after addition of C-HT. Moreover, higher yield of oligomers was observed over Pt(2)Sn(0.25)/AL+C-HT (26%) and Pt(2)Sn(0.25)/C-HT (18%) catalyst against Pt(2)Sn(0.25)/AL (6%). This clearly indicates that C-HT may affect the first step of xylan conversion i.e. hydrolysis up to some extent (most likely to be catalyzed by acidity of AL). This is possible as C-HT is a solid base which may affect the acidity of AL and hence the activity towards the hydrolytic hydrogenation of xylan. Further, in the presence of C-HT, reactions to yield glycols from xylose are more prominent at higher temperature (section 5.3.1.1). To check the effect of temperature on the conversion of xylose in presence of C-HT, xylose reactions were carried out at 190°C and results are represented in Figure 5.20. When reaction was conducted over bare C-HT, 15% yield of sugar alcohols was obtained within 15 min (80% conversion) while 22, 38 and 45% yields were obtained over Pt(2)/C-HT, Pt(2)Sn(0.25)/C-HT and Pt(2)Sn(0.25)/AL+C-HT from xylose at 190°C (Figure 5.20). If these results were compared with earlier data, where 73% yield of sugar alcohols was obtained over Pt(2)Sn(0.25)/AL at 190°C (chapter 3, section 3.3.2.5), it can be concluded that after addition of C-HT along with Pt-Sn/AL catalyst, side reactions are more prominent at higher temperature like 190°C.

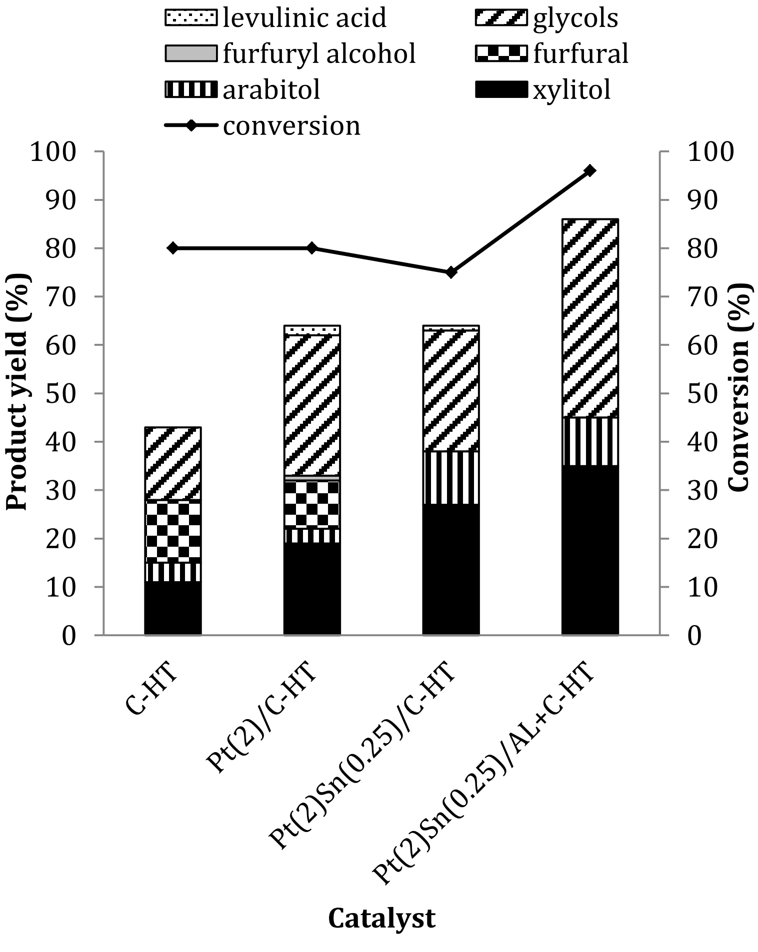


Figure 5.20. Effect of C-HT on the conversion of xylose at higher temperature.

Reaction condition: xylose 0.15 g, catalyst 0.075 g, C-HT 0.075 g, H_2O 35 mL, 190°C, H_2 16 bar at R.T. 15 min.

Hence, decrease in the yield of sugar alcohols in xylan conversion over Pt(2)Sn(0.25)/AL+C-HT catalytic system can be attributed to the effect of C-HT on the hydrolysis step (up to some extend) and conversion of xylose (formed after hydrolysis of xylan, which is partially suppressed after addition of C-HT) in to undesired products like glycols at higher temperature.

Activity of the Pt(2)Sn(0.25)/C-HT and Pt(2)Sn(0.25)/AL+C-HT catalytic system was evaluated for arabinogalactan and inulin conversion at optimized reaction conditions (180°C, 12 h and 16 bar H_2 for arabinogalactan and 110°C, 12 h and 16 bar H_2 for inulin, refer chapter 4A, section 4A.3.1.2 and 4A.3.2). In these conversions too, poor yields were obtained over Pt(2)Sn(0.25)/C-HT and Pt(2)Sn(0.25)/AL+C-HT compare to Pt(2)Sn(0.25)/AL. From arabinogalactan 19% and 23% yields were obtained while from inulin only 5% and 6% yields of sugar alcohols were observed over Pt(2)Sn(0.25)/C-HT and Pt(2)Sn(0.25)/AL+C-HT, respectively.

5.4. Conclusions

Hydrogenation of C5 and C6 sugars over Pt/AL catalyst in presence of solid base (C-HT) is an efficient method for the production of sugar alcohols. Up to 82 and 68% yields of C5 and C6 sugar alcohols were achieved over Pt supported catalyst in the presence of C-HT from corresponding sugars. Yields of sugar alcohols can be improved up to 96-97%, if combination of bimetallic Pt-Sn/AL and C-HT is used in the hydrogenation of sugars at room temperature. Complete conversion of various sugars with good selectivity for sugar alcohols is attainable at much milder reaction conditions (low temperature like 30-80°C and at H_2 pressure of 16 to 24 bar) over Pt-Sn/AL+C-HT catalytic system. Formation of sugar alcohols is favorable at lower temperature and hence it is suggested to conduct conversion of sugars at lower temperature to improve the selectivity. Amongst all catalytic system examined, Pt-Sn/AL+C-HT showed best results. Combined effect of Sn (in ionic form) and solid base (C-HT) furnish the high yield of sugar alcohols from sugars. Solid base, C-HT help to generate sugar molecules in open chain form, while ionic Sn polarize the C=O bond of carbonyl group of sugars. In presence of active metal i.e. Pt hydrogenation of polarized C=O bond takes place more rapidly. Sugar alcohols in high yield i.e. 96%, 97.5%, 84% and 90% were obtained from xylose, arabinose, glucose and galactose respectively at room temperature. Unfortunately in the conversion of polysaccharides Pt-Sn/AL+C-HT did not show any enhancement in sugar alcohols yields, because hydrolysis of polysaccharides to yield corresponding monosaccharides (C5 or C6 sugars) might be restricted after addition of C-HT. Moreover such conversions need higher temperature and Pt-Sn/AL+C-HT catalytic system is less selective towards sugar alcohols at higher temperature. Hence one pot conversion of polysaccharides in to sugar alcohols over Pt-Sn/AL+C-HT with good yield of sugar alcohols is not feasible. Nevertheless, Pt-Sn/AL+C-HT catalyst shows exceptionally high yields of sugar alcohols and good recyclability in the conversion of both C5 and C6 sugars with negligible loss of activity after each run.

5.5. References

1. J. M. Berg, J. L. Tymoczko and L. Stryer, Biochemistry, 5th Edition, New York: W H freeman, 2002.
2. H. Singh, A. Gupta, A. Singh and B. Singh, *Transition Metal Chemistry*, 1998, **23**, 277-281.
3. R. Salomão, L. M. Milena, M. H. Wakamatsu and V. C. Pandolfelli, *Ceramics International*, 2011, **37**, 3063-3070.
4. Y. Liu, E. Lotero, J. G. Goodwin Jr and X. Mo, *Applied Catalysis A: General*, 2007, **331**, 138-148.
5. F. Li, X. Jiang, D. Evans and X. Duan, *Journal of Porous Materials*, 2005, **12**, 55-63.
6. R. Ooms, M. Dusselier, J. A. Geboers, B. Op de Beeck, R. Verhaeven, E. Gobechiya, J. A. Martens, A. Redl and B. F. Sels, *Green Chemistry*, 2014, **16**, 695-707.
7. Z. Tai, J. Zhang, A. Wang, M. Zheng and T. Zhang, *Chemical Communications*, 2012, **48**, 7052-7054.
8. N. Kolev, in *Multiphase Flow Dynamics 4*, Springer Berlin Heidelberg, Editon edn., pp. 209-239.
9. D. P. Debecker, E. M. Gaigneaux and G. Busca, *Chemistry – A European Journal*, 2009, **15**, 3920-3935.
10. C. Moreau, J. Lecomte and A. Roux, *Catalysis Communications*, 2006, **7**, 941-944.
11. J. Zhang, S. Wu, Y. Liu and B. Li, *Catalysis Communications*, 2013, **35**, 23-26.
12. F. King and G. J. Kelly, *Catalysis Today*, 2002, **73**, 75-81.
13. M. Y. He, *Catalysis Today*, 2002, **73**, 49-55.

14. S. Coluccia, A.J. Tench, Proceeding of the 7th International Congress on Catalysis, Tokyo, 1980.
15. M. Kappers, C. Dossi, R. Psaro, S. Recchia and A. Fusi, *Catalysis Letters*, 1996, **39**, 183-189.
16. F. Humblot, F. Lepeltier, J. P. Candy, J. Corker, O. Clause, F. Bayard and J. M. Basset, *Journal of the American Chemical Society*, 1998, **120**, 137-146.
17. Z. Gandao, B. Coq, Charles, L. de Menorval and D. Tichit, *Applied Catalysis A: General*, 1996, **147**, 395-406.
18. S. Recchia, C. Dossi, N. Poli, A. Fusi, L. Sordelli and R. Psaro, *Journal of Catalysis*, 1999, **184**, 1-4.
19. R. C. Everson, H. Mulder and M. J. Keyser, *Applied Catalysis A: General*, 1996, **142**, 223-241.
20. G. Heller, B Boron Compounds: 3rd Supplement Volume 2 Boron and Oxygen, Springer Science & Business Media, 2013.
21. G. de Wit, C. de Hann, A. P. G. Kieboom and H. van Bekkum, *Carbohydrate Research*, 1980, **86**, 33-41.
22. K. Balakrishnan and J. Schwank, *Journal of Catalysis*, 1991, **127**, 287-306.
23. G. T. Baronetti, S. R. de Miguel, O. A. Scelza and A. A. Castro, *Applied Catalysis*, 1986, **24**, 109-116.
24. B. A. Sexton, A. E. Hughes and K. Foger, *Journal of Catalysis*, 1984, **88**, 466-477.

Chapter 6

Summary and Conclusions

Summary and Conclusions

Importance of the lignocellulosic biomass as a renewable feedstock for the production of various value added chemicals has been recognized in last few decades by researchers. Cellulose and hemicelluloses are the major components of plant derived biomass and are made up C6 and C5 sugars. These C6 and C5 sugars can be converted in to important derivatives like furans, sugar acids, sugar alcohols, glycols, etc. through some conversion processes. In current work, conversion of monosaccharides, polysaccharides and agricultural wastes to yield sugar alcohols was carried out. In previous chapters, results for the entitled conversions were discussed in details; however, important results and conclusion drawn from those results are consolidated in this chapter.

Chapter 1

Sugar alcohols are the vital chemical compounds having applications in various fields such as food and pharmaceutical industries, in oral hygiene products, for the production of chemicals, hydrogen generation and most importantly as a low calorie sweetener. These sugar alcohols can be synthesized from C5 or C6 sugars upon hydrogenation as well as from polysaccharides by hydrolytic hydrogenation. Cautious study of the literature shows that, although there are many reports for the production of sugar alcohols from monosaccharides (C5 and C6 sugars) are available, very few methods for the conversion of polysaccharides and even less for the one pot conversion of agricultural wastes are known. Moreover, conventional methods are allied with some drawbacks like low yield of sugar alcohols, requisite of strong reaction conditions and poor recyclability due to deactivation of the catalyst. Because of significant applications, demand for sugar alcohols is increasing continuously; hence it is indispensable to develop an efficient method for the synthesis of sugar alcohols.

In current work, conversion of various C5 and C6 sugars (xylose, arabinose, glucose, galactose and fructose), isolated polysaccharides (xylan, arabinogalactan and inulin) and agricultural wastes (bagasse, rice husk and wheat straw) was carried to yield C5 and C6 sugar alcohols (xylitol, arabitol, sorbitol, mannitol and galactitol) using monometallic and bimetallic supported metal catalysts.

Chapter 2

Considering the superior catalytic activity in the hydrogenation of sugars, Pt and Ru based supported metal catalysts were synthesized by wet impregnation method and were evaluated in the entitled conversions.

- Monometallic and bimetallic catalysts were prepared using various supports (AL, SA, C and C-HT), metal (Pt and Ru) and promoters (Sn, Fe and Ga), to study the effects of supports, metals and promoters on the catalytic conversion of mono- and poly-saccharides.
- Physicochemical properties of the synthesized catalysts were studied using characterization techniques like ICP-AES, XRD, TEM, XPS, NH_3-TPD, CO_2-TPD, N_2-Sorption, etc.
- ICP-AES analysis proved that, metal contents in all monometallic and bimetallic catalysts are comparable with the expected (theoretical) metal contents.
- XRD patterns of monometallic catalysts showed characteristic peaks of the impregnated metal and intensity of the peaks varies with support. This is because, with change in support or metal nature of support-metal interaction changes which ultimately leads to the change in dispersion. Strong metal-support interaction gives rise to finely dispersed metal particles on the support which shows very low intensity peaks, while metal particles of bigger size shows peaks with high intensity.
- In bimetallic catalyst formation of intermetallic system is possible; however formation of such intermetallic systems or alloy depends on the nature of support and metal content. Pt(2)Sn(0.25)/AL and Pt(2)Sn(0.25)/SA did not show peaks for intermetallic systems and intensity of the Pt peaks was also low compare to the Pt(2)/AL and Pt(2)/SA catalyst, indicating fine dispersion of Pt in case of Pt-Sn bimetallic catalyst. Same conclusion can be made from the TEM analysis of various monometallic and bimetallic catalysts. Pt(2)/C-HT and Pt(2)Sn(0.25)/C-HT did not show any peak owing to the fine dispersion in both the catalysts. While peaks for Pt were visible in Pt(2)/C catalyst, bimetallic Pt(2)Sn(0.25)/C showed peaks characteristic for PtSn intermetallic system along with Pt peaks. Formation of Pt_3Sn and PtSn intermetallic systems was observed in Pt-Sn/AL catalyst with higher Sn loading (Pt(3.5)Sn(1.75)/AL and Pt(3.5)Sn(3.5)/AL).

This proves that dispersion of the metal and formation of intermetallic system is governed by nature of support material.

- In Pt-Sn/AL catalysts with lower loading of Sn, formation of intermetallic systems was not observed, moreover dispersion of the Pt in these catalyst was higher compare to Pt/AL catalyst. Because, Sn can interact with AL to form tin-aluminate type complex (surface shell) in which Sn is in (II) state, hence cannot be reduced to (0) state. It is suggested that, formation of such a surface shells prevents mobility of Pt particle on the support during calcination and better dispersion can be achieved.
- XPS study of the Pt-Sn/AL bimetallic catalysts with varying Pt:Sn ratio, suggest that Sn was present in (II) or (IV) state when Sn loading was low (up to 0.87wt%). However, in catalysts with higher Sn loading (greater than 0.87wt%), reduction of Sn to (0) state is possible and Sn in (0) state can interact with Pt to form intermetallic systems. From XRD it is clear that Pt_3Sn and PtSn intermetallic systems were formed in Pt(3.5)Sn(1.75)/AL and Pt(3.5)Sn(3.5)/AL catalysts. This implies that up to certain loading (<0.87wt%), Sn can form complex (surface shell) with AL and cannot be reduced to Sn(0), but at higher loading some amount of Sn forms complex and surplus Sn can be reduced to Sn (0) State.
- TPD analysis of AL supported catalysts revealed that metal (Pt or Sn) interact with acidic sites on the AL support and hence acid amount was observed to be decreased in Pt/AL and Pt-Sn/AL catalysts. Similarly in C-HT supported catalysts, basicity of Pt/C-HT and Pt-Sn/C-HT was slightly less than bare C-HT support.

Chapter 3

Catalytic activity of the synthesized monometallic and bimetallic catalysts towards the formation of sugar alcohols from monosaccharides was evaluated and correlation between activity and physicochemical properties of the catalyst was established.

- It was observed that Pt-Sn/AL catalyst (with Pt:Sn ratio equals to 1:0.12 (*wt/wt*)) showed best results for the production of C5 and C6 sugar alcohols from corresponding sugars. Sn in ionic state, (II) or (IV) promotes the activity of Pt/AL catalyst towards hydrogenation of sugars.

- As mentioned above, from XPS study it is clear that Sn was present in (II) or (IV) state when Sn loading was low (<0.87wt%) and from XRD analysis it can be concluded that formation of intermetallic systems like Pt_3Sn and PtSn occurred only in the catalysts with higher Sn loading (Pt(3.5)Sn(1.75)/AL and Pt(3.5)Sn(3.5)/AL). Even if such intermetallic systems were formed in the catalysts with lower Sn loading (Pt(3.5)Sn(0.22)/AL, Pt(3.5)Sn(0.43)/AL and Pt(3.5)Sn(0.87)/AL), its concentration must be very low and hence cannot be detected by XRD.
- Sn can improve the dispersion of Pt by forming surface shell on the AL and this ultimately increases the number of active metal sites in the catalyst. Consequently better results for the hydrogenation of sugars can be achieved over Pt-Sn/AL bimetallic catalyst than Pt/AL monometallic catalyst.
- Furthermore, Sn (II) or (IV) can polarize the C=O bond of the carbonyl group of sugar molecules which can be hydrogenated easily. Hence maximum yield (79%) of sugar alcohols (xylitol+arabitol) could be obtained over Pt(3.5)Sn(0.43)/AL catalyst at 190°C in 15 minutes of reaction time.
- Yield was observed to be decreasing with increasing Sn loading in Pt-Sn/AL catalysts, because formation of Pt_3Sn and PtSn intermetallic systems is possible in these catalysts. Nevertheless, yield of sugar alcohols obtained over Pt-Sn/AL bimetallic catalyst with any Pt:Sn ratio was better than monometallic Pt/AL catalyst as in bimetallic catalyst with higher Sn loading too, some amount of Sn was present in (II) or (IV) state.
- Temperature study proved that better yield of sugar alcohols could be obtained from sugars at lower temperature, since at higher temperature side reactions to yield undesired products like glycols and furans were prominent (at 130°C, 93% yield was observed over Pt(3.5)Sn(0.43)/AL catalyst, while 79% yield was achieved at 190°C).
- Effect of metal loading in the catalyst was studied by conducting xylose hydrogenation reaction at 190°C over Pt(2)Sn(0.25)/AL and results showed that although Pt loading was decreased from 3.5wt% to 2wt%, decrease in the yield of sugar alcohols was only 6%. This implies that catalyst with lower metal loading can be used efficiently for the production of sugar alcohols.
- When effect of supports, metals, promotes was examined in the conversion of xylose, best results were observed over Pt-Sn/AL bimetallic catalyst compared with any other

catalytic system. Sn could not demonstrate promoter effect when C was used as support, since Sn cannot form complex with C and can be reduce to Sn (0), hence formation of PtSn intermetallic system is possible. Formation of PtSn intermetallic system was evident from XRD analysis of Pt(2)Sn(0.25)/C catalyst in spite of optimum metal loading. Ru can interact strongly with Sn; therefore Ru-Sn/AL catalyst did not show any improvement in the yield of sugar alcohols compare to Ru/AL catalyst. Further, promoter effect of Fe and Ga was examined in the Pt/AL catalyst, but Pt-Sn/AL catalyst showed superior results than Pt-Fe/AL and Pt-Ga/AL catalysts at similar reaction conditions.

- Similar to xylose, hydrogenation of arabinose, glucose, galactose and fructose was carried over Pt(2)Sn(0.25)/AL catalyst and yield of sugar alcohols was observed to be enhanced by more than 2 times compared with Pt(2)/AL catalyst. Pt-Sn/AL catalyst showed good recyclability in the conversion of C5 and C6 sugars.

Chapter 4A

Since improved yields of sugar alcohols were obtained over Pt-Sn/AL catalyst compare to Pt/AL catalyst in the conversion of C5 (xylose and arabinose) and C6 (glucose, galactose and fructose) sugars, efficiency of Pt-Sn/AL catalyst was evaluated in the conversion of isolated polysaccharides to yield sugar alcohols. Conversions of isolated polysaccharides (xylan, arabinogalactan and inulin) were carried over Pt-Sn/AL catalyst and reaction conditions were optimized to achieve maximum yield of sugar alcohols.

- Maximum 43% yield of sugar alcohols could be obtained from xylan over Pt(2)Sn(0.25)/AL catalyst against 15.5% yield over Pt(2)/AL at optimized reaction conditions (190°C, 16 bar H_2, 16 h and S/C ratio of 2). Enhancement in the yield was observed with increase in metal loading (over Pt(3.5)Sn(0.43)/AL, maximum 50% yield was obtained) and with increase in catalyst quantity (with 0.15 g of Pt(2)Sn(0.25)/AL, maximum 55% yield was observed).
- Similarly, maximum 47% yield of sugar alcohols could be achieved over Pt(2)Sn(0.25)/AL from arabinogalactan against 25% over Pt(2)/AL catalyst at 180°C within 12 h of reaction time. In the conversion of inulin at 110°C, 77% yield of sugar

alcohols was obtained over Pt(2)Sn(0.25)/AL catalyst within 12 h compared to 40% over Pt(2)/AL catalyst.

- ❖ Characterization of spent catalyst proved that Pt-Sn/AL catalyst is stable under reaction conditions and showed good recyclability with minor loss of activity after each run.
- ❖ Time required for complete conversion of polysaccharides is much longer than that for conversion of monosaccharides. This is because, conversion of polysaccharides in to sugar alcohols comprises two steps; hydrolysis of polysaccharides to yield monosaccharides and subsequent conversion of monosaccharides in to sugar alcohols. Since complete conversion of monosaccharides was achieved within 15 minutes at 190°C, hydrolysis step should be rate determining step.

Chapter 4B

One pot conversion of agricultural wastes in to sugar alcohols is much convenient method as it skip over two steps, e.g. isolation of polysaccharides and hydrolysis of polysaccharides to monosaccharides. Considering this, selective conversion of hemicellulose in the agricultural wastes to produce sugar alcohol (C5 sugar alcohols) was conducted over Pt-Sn/AL catalyst.

- ❖ Before studying the selective conversion of hemicellulose in agricultural wastes (bagasse, rice husk and wheat straw), compositional analysis was done to determine percentage of various components. TAPPI method was employed for the compositional analysis of bagasse, rice husk and wheat straw.
- ❖ When conversion of agricultural wastes was carried out over Pt(2)Sn(0.25)/AL catalyst, yield of sugar alcohols was observed to be improved by 1.5 to 2 times compared to Pt(2)/AL. Moreover catalyst showed good recyclability and better yields were achieved after subjecting spent catalyst to calcination and reduction before reuse.
- ❖ It can be concluded that Pt-Sn/AL catalyst is exploitable at wide range of reaction conditions and can be used for the synthesis of sugar alcohols from variety of substrates with good recyclability.

Chapter 5

Dramatic improvement in the yield of sugar alcohols was observed over Pt-Sn/AL catalyst compare with Pt/AL catalyst in the conversion of monosaccharides, polysaccharides and agricultural wastes. Promoter effect of Sn in Pt/AL catalyst can be explained with the help of ability of ionic Sn to polarize the C=O bond in sugar molecules. Polarization of C=O bond is possible only if sugar molecule is present in open chain form, hence efforts were taken to generate sugar molecule in open chain form in reaction mixture. It is known that under alkaline condition sugars can undergo isomerization reaction (Lobry de Bruyn-Alberda van Ekenstein transformation) through open chain intermediates (like enolate and enediol). This means more sugar molecules must be present in open chain form in alkaline medium than neutral or acidic medium, which can be hydrogenated if active metal and hydrogen is available. Considering this, effect of solid base, C-HT in the conversion of monosaccharides and polysaccharides over monometallic and bimetallic catalysts was examined.

- Use of solid base along with supported metal catalyst is a convenient method to improve the yields of sugar alcohols from sugars. Maximum 82% and 68% yield of C5 and C6 sugar alcohols could be achieved from xylose and glucose, respectively over Pt(3.5)/AL+C-HT catalytic system.
- Complete conversion of the sugars with better yields of sugar alcohols could be achieved at much milder reaction conditions (60-80°C) within short period of reaction time (4 h), in the presence of C-HT (solid base).
- UV-Vis study of glucose proved that more sugar molecules are in open chain form in alkaline medium than in neutral medium. Sugar molecule in open chain form can be hydrogenated easily at milder reaction conditions. Hence it is possible to achieve complete conversion at low temperature in presence of C-HT (as it makes pH of reaction mixture alkaline). Moreover, at lower temperatures side reactions to yields undesired products like glycols and furans are not prominent; therefore better selectivity for sugar alcohols could be achieved.
- Exceptionally high yields of sugar alcohols was obtained from C5 and C6 sugars over bimetallic Pt-Sn/AL catalyst in the presence of C-HT at milder reaction conditions. Up to

96-97% sugar alcohols (xylitol+arabitol) yield could be achieved over Pt(2)S(0.25)/AL+C-HT catalytic system from xylose and arabinose at 50°C within 6 h. Similarly, from glucose 88% yield of sugar alcohols (sorbitol+mannitol) was observed over Pt(2)Sn(0.25)/AL+C-HT catalytic system within 6 h at 80°C.

- Pt(2)S(0.25)/AL+C-HT catalytic system showed good results in the conversion of C5 and C6 sugar to yield corresponding sugar alcohols at room temperature too. Sugar alcohols in high yield i.e. 96%, 97.5%, 84% and 90% were obtained from xylose, arabinose, glucose and galactose, respectively at room temperature.
- Enhancement in the yield of sugar alcohols over Pt(2)Sn(0.25)/AL+C-HT catalytic system was because of combined effect of C-HT and Sn in (II) or (IV) state. C-HT help to generate sugar molecule in open chain form and ionic Sn can polarize the C=O bond of sugar molecules (already in open chain form under alkaline condition) which can be easily hydrogenated.
- Unfortunately, in the conversion of polysaccharides yields could not be improved by adding C-HT along with Pt-Sn/AL catalyst, because such conversions need higher temperature (110-190°C) and at higher temperatures side reactions to yield glycols and furans are prominent.

It can be concluded that, Sn acts as a promoter in the Pt-Sn/AL bimetallic catalyst and improvement in the yields of sugar alcohols can be achieved over Pt-Sn/AL catalyst in the conversion of C5 and C6 sugars, polysaccharides and agricultural wastes. Further improvement in the yields can be observed from C5 and C6 sugars, if solid base (C-HT) is used as an additive along with the Pt-Sn/AL catalyst.

List of Publications and Patents

- Solid base supported metal catalysts for the oxidation and hydrogenation of sugars.
  Anup Tathod, Tanushree Kane, E.S. Sanil, Paresh Dhepe∗ *Journal of Molecular Catalysis A: Chemical*, 2014, 388–389, 90–99.

- Towards efficient synthesis of sugar alcohols from mono- and poly-saccharides: role of metals, supports & promoters.
  Anup Tathod, Paresh Dhepe* *Green Chemistry*, 2014, 16, 4944-4954.

- Efficient method for the conversion of agricultural waste into sugar alcohols over supported bimetallic catalysts.
  Anup Tathod, Paresh Dhepe* *Bioresource Technology,* 2014, 178, 36-44.

- Room temperature conversion of sugars into sugar alcohols over supported metal catalyst.
  Anup Tathod, Paresh Dhepe* Manuscript communicated, 2015.

- Patent (India): Production of sugar alcohols, xylitol and arabitol using bimetallic supported metal catalysts, IN 0017/DEL/2014.
  Anup Tathod, Paresh Dhepe.

Contributions to Symposia and Conferences

- Best poster award in 'The Seventh Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT-7)' held at Kyoto, Japan during 1st to 6th June 2014.
- Best poster award in international conference on "Global Opportunities for Latest Developments in Chemistry and Technology" held at North Maharashtra University Jalgaon, India during 6th to 8th Feb 2014.
- Oral presentation in '22nd National Symposium on Catalysis for Better Tomorrow' held at CSIR-CSMCRI Bhavnagar, India during 7th to 9th Jan 2015.
- Presented poster in 'The International Conference on Structural and Inorganic Chemistry' held at CSIR-NCL Pune, India during 4th & 5th Dec 2014.
- Presented poster in '21st National Symposium on Catalysis for Sustainable Development' held at CSIR-IICT Hyderabad, during 11th to 13th Feb 2013.
- Attended a workshop on 'Gel Permeation Chromatography' held at CSIR-NCL-Pune, during Feb 2012.
- Attended '20th National Symposium on Catalysis' held at IIT-MADRAS, during 19th to 22nd Dec 2010.

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