

Value addition to lignocellulosics and biomass-derived sugars: An insight into solid acid-based catalytic methods

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Abstract. For the synthesis of important platform chemicals such as sugars (xylose and arabinose) and furans (furfural and 5-hydroxymethylfurfural (HMF)) from carbohydrates (hemicellulose and fructose) solid acid catalysts are employed. Similarly, over solid acid catalysts, conversion of lignin into aromatic monomers is performed. It is observed that in the dehydration of fructose, because of higher hydrothermal stability, silicoaluminophosphate (SAPO) catalysts give better activity (78% HMF yield) compared with other solid acid catalysts (<63% HMF yield) at 175°C. Particularly, SAPO-44 catalyst can be reused at least 5 times with marginal decrease in the activity. Zeolite, HUSY (Si/Al = 15) is active in the conversion of isolated (pure) hemicellulose to produce 41% C₅ sugars in water. The catalyst is also active in the selective conversion of hemicellulose from bagasse to yield 59% C₅ sugars. It is possible to obtain high yields of furfural (54%) directly from bagasse if instead of water, water+toluene solvent system is used. Depolymerization of lignin using HUSY catalyst produced aromatic monomers with 60% yield at 250°C. A detailed catalyst characterization study is performed to understand the correlation between catalyst activity and morphology. To understand the effect of impurities present in the substrate over solid acid catalysts, metal-exchange study is carried out.

Keywords. Aromatic monomers; biomass; furans; hemicellulose; lignin; solid acid catalyst.

1. Introduction

A keen interest shown by Government as well as researchers towards the use of abundant, renewable feedstock, biomass for the synthesis of chemicals may take care of most of the issues related to depleting fossil resource.^{1–6} Worldwide production of lignocelluloses is around 1.8 trillion tons⁷ and India alone generates ca. 624 million tons of crop waste annually in the form of lignocellulosics (crop waste).⁸ Major components of crop waste are cellulose (β -1, 4-D-glucose; 40–50%), hemicelluloses (co-polymer of C₅ and C₆ sugars; 25–35%) and lignin (macromolecular network of phenyl-propane units; 15–20%).⁹ Robustness in structure and high O/C ratio in biomass disapprove its compatibility with the present catalytic system and demands development of modified processes. The most attractive and promising approach is to produce furan derivatives from biomass, for e.g., furfural from hemicelluloses/xylose and 5-hydroxymethylfurfural (HMF) from cellulose/glucose/fructose, because of their importance

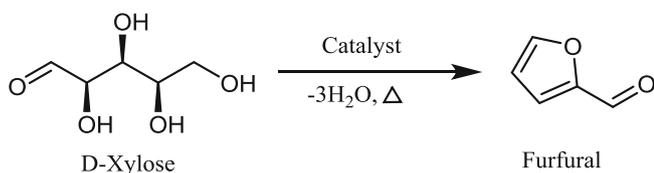
as platform chemicals.^{10–12} Recently, researchers have also been engaged in lignin valorization to yield versatile aromatic chemicals that can be used as fuel additives or can find niche applications.¹³

Typically, hemicellulose is hydrolysed to form C₅ sugars (xylose+arabinose) and which on further dehydration (loss of water molecules) produce furfural.¹⁴ Furfural can be further converted into various important chemicals such as furfuryl alcohol,¹⁵ 2-methylfuran (MF),¹⁵ 2-methyltetrahydrofuran (MTHF),¹⁵ linear alkanes,¹⁶ phenol–formaldehyde resin,¹⁷ furoic and maleic acid¹² which for decades have well-known industrial scale processes/applications. Furfural can be produced from xylose or directly from hemicellulose and the available processes are described here.

1.1 Xylose as substrate

Literature describes that furfural is mainly produced from xylose (scheme 1) and the traditional processes are based on homogeneous catalysis. Homogeneous acids such as HCl, H₂SO₄, HNO₃, CH₃COOH, H₃PO₄ and HCOOH were studied for the conversion of xylose at 135–180°C in water to yield furfural.^{18–20}

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Scheme 1. Production of furfural from xylose.

Due to obvious hazards in handling these acids, solid acid catalysed method has been proposed to provide a cleaner and environment friendly production of furfural. Zeolite, HZSM-5 in water at 200°C yields 46% of furfural from xylose.²¹ Lewis acid type catalyst Sn-beta was also studied with the formation of furfural (14% yield).²² Graphene, graphene oxide, sulphonated graphene and sulphonated graphene oxides at 200°C in water produce 51–62% of furfural from xylose.²³ Though water is the most preferred solvent, it is observed that reactions carried out only in water accelerate undesired side reactions and lower furfural yield.²⁴ In view of this, polar aprotic solvent such as acetonitrile, dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) were tried. Among studies on polar aprotic solvents, DMSO yields highest amount of furfural (78%) in presence of Amberlyst-15 at 170°C.^{25–30} DMSO minimizes side reactions but at the same time its high boiling point and poor sugar solubility severely affects the process.¹¹ To improve the yields, water miscible organic solvent system is also used. H₂O–acetone–DMSO system was studied in presence of SO₄²⁻/C catalyst at 230°C, yielding very less furfural yield (11.5%).³¹ However, H₂O/1-butanol solvent system improves the yield (44%) with MCM-41 at 170°C.³² Introduction of immiscible biphasic solvent system (water+organic solvent) improves furfural yield since organic solvent extracts furfural from the aqueous layer and thereby diminishes the possibility of undesired reactions. Studies on H₂O/MIBK (methyl *iso*-butyl ketone) biphasic system with catalysts such as HMOR,³³ HY³³ and MCM-41-SO₃H²⁷ yields furfural in the range of 20–51%. Very good extracting ability of toluene for furfural makes it the best solvent for furfural synthesis.³⁴ A wide range of solid acid catalysts such as H-form of zeolites,^{28,33,35} H₃PW₁₂O₄₀/MCM-41,³⁰ Cs₃PW₁₂O₄₀/MCM-41,²⁹ HMCM-22,³⁶ MCM-41-SO₃H,²⁷ H-Al-MCM-41,³⁷ SO₄²⁻/ZrO₂-Al₂O₃/SBA-15,³⁸ BEA-TUD-1,³⁶ ITQ-2,³⁶ SO₄²⁻/SnO₂,³⁹ (VO)₂P₂O₇,⁴⁰ SBA-15/SO₃H,⁴¹ Amberlyst-70,⁴² SAPO-11,⁴³ Del-Nu-6³⁷ and H₄TiNbO₅-MgO⁴⁴ were studied in H₂O/toluene biphasic system. Zeolite, HMOR³⁵ yields highest amount of

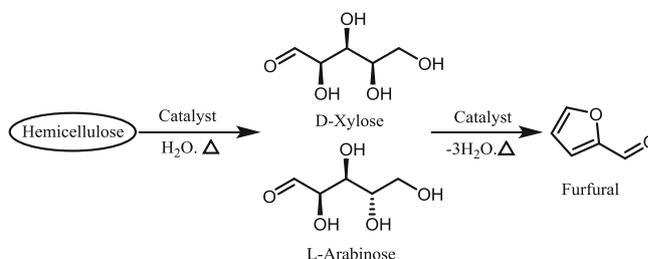
furfural (98 mole%) from xylose in plug-flow reactor at 260°C, 55 bar pressure. For other catalysts, yields remain in the lower range of 31–71%. It is important to note here that though several catalysts show activity in these reactions, their stability in water is questionable. For e.g., ion-exchange resins are mostly unstable in water above 130°C, and mesoporous silicas tend to undergo structural changes above 150°C in water medium. The HPAs are also hydrothermally less stable and show leaching of active species.

The tunable properties of ionic liquids (ILs) also attract researchers. ILs are used as a solvent and also as a catalyst for furfural production.^{45,46} Although, good yields are obtained, various drawbacks such as homogeneous nature of catalyst and difficulties associated with recyclability of ILs indicates that more work should be done in this area.

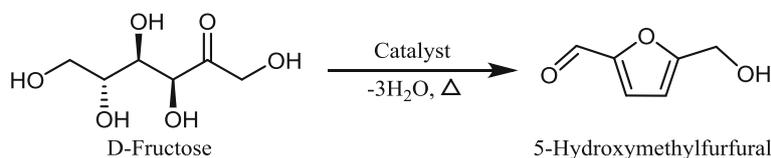
1.2 Furfural from hemicellulose (via xylose and arabinose)

Use of isolated (pure) xylose as a feedstock for the production of furfural is not economical as it is mainly obtained from hemicelluloses after hydrolysis in a separate reactor. Hence, it is desirable to obtain furfural directly from hemicellulose via xylose formation in a one-pot method (scheme 2). Very few reports are available on this reaction using solid acid catalysts.^{47,48} A two-step process is also reported for this reaction, where in the first step (auto-hydrolysis), formation of water soluble oligomers from hemicellulose (xylan) at 160°C is carried out; and then in the second step ion-exchange resin (Amberlyst-15) is used to produce C₅ sugars (90%).^{49,50} Arabinogalactan (hemicellulose) can produce arabinose in high yield (95%) with the help of Smopex-101 catalyst.⁵¹

HMF is a multifunctional molecule as it contains aromatic aldehyde and aromatic alcohol functional groups and is made up of a furan ring system. By converting



Scheme 2. Production of furfural from hemicelluloses as substrate.



Scheme 3. Production of 5-hydroxymethylfurfural (HMF) from fructose.

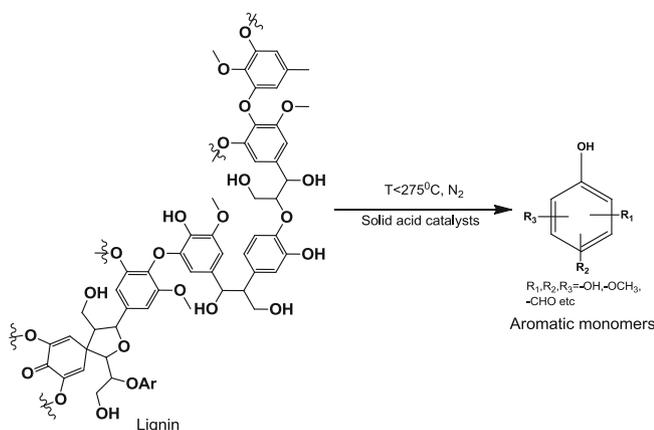
these functional groups, it is possible to synthesize various products and hence HMF is described as a ‘sleeping giant’.^{52,53} HMF is used for the production of 2, 5-dihydroxymethylfuran (DHMF),⁵⁴ 2, 5-dimethylfuran (DMF),⁵⁴ 2, 5-dimethyltetrahydrofuran (DMTHF),⁵⁵ 2, 5-diformylfuran (DFF),⁵⁶ 2, 5-furandicarboxylic acid (FDCA),⁵⁷ formic and levulinic acid⁵⁸ and liquid alkanes.⁵⁹ HMF is mainly produced from fructose (scheme 3), though other substrates such as glucose, inulin, maltose, cellobiose, cellulose, starch, etc., can also be used.

1.3 Fructose as feedstock

A study on water-only system in presence of TiO₂, ZrO₂ and TiO₂ nanoparticles showed very low yields of HMF (30–38%) from fructose since water favours side reactions.^{60,61} To minimize the formation of unwanted side products, use of organic solvent was initiated. Use of DMSO solvent can improve HMF yield to 54% compared to water (34% yield) in presence of TiO₂ nanoparticles.⁶¹ Amberlyst-15 in presence of DMSO showed the best activity (100% HMF yield) while Nafion-H catalyst has comparatively poor activity (75%).⁶² It appears that DMSO is the best solvent but as mentioned earlier due to its drawbacks it cannot be probed further. Other organic solvents such as DMF (73%), tetrahydrofuran (THF; ~45%) and isopropanol (~45%) yields HMF in lower concentrations in presence of Amberlyst-15.^{63–65} Incorporation of biphasic solvent system improves the HMF yield due to its preferential extraction in organic solvent and thereby protects it from further degradation or condensation reactions. In H₂O/MIBK system, HMOR showed the best activity (74% HMF yield) among other zeolites such as HZSM-5 and Hβ.^{66,67} Cs_{2.5}H_{0.5}PW₁₂O₄₀ and Ag₃PW₁₂O₄₀ were also examined in H₂O/MIBK system to yield 74–77% of HMF.^{68,69} Study on H₂O/2-butanol system showed that hydrated Ta-oxide (Ta-p) has better activity than Nb₂O₅ and Ta₂O₅.⁷⁰ Mixed organic solvent system such as acetone/DMSO were studied with ion-exchange resin giving 89% HMF yield.⁷¹

1.4 Other monomers, dimers and polymers as feedstock

The reports mentioned here depict that dehydration of fructose to HMF is possible; however, in terms of availability of feedstock, this process is not proficient. Considering this, to obtain HMF, use of inexpensive and abundant feedstock glucose is desirable. Glucose to HMF reaction is a two-step process, where the first step involves isomerization reaction to form fructose from glucose (base-catalysed) and second step involves dehydration of fructose to HMF (acid-catalysed). Many catalytic systems which favour fructose conversion to HMF show disappointing results in the glucose to HMF reaction since glucose forms a stable pyranose ring in water and first needs to be converted to fructose. So, the lower fraction of open chain molecules available in solution gave lower rate of enolization, which is the rate determining step for HMF formation from glucose. Realizing that formation of HMF from glucose is a two-step process carried out using catalysts having varying properties (basic and acidic), it is very difficult to carry out this scheme in one pot. Combination of base and acid catalysts such as HT and Amberlyst-15 is used in DMF solvent for achieving maximum of 42% HMF yield at 100°C in 9 h.⁶³ This report showed three-time recyclability of HT/Amberlyst-15 at 100°C, 3 h with ca. 25% HMF yield. It was proposed that presence of Lewis acid sites in Sn-beta catalyst can promote isomerization reaction of glucose to fructose.^{72,73} Further addition of HCl to the reaction with Sn-beta catalyst gave 57% HMF yield.^{72,73} Recyclability of Sn-beta catalyst was shown for isomerization reaction with 30% fructose yield over four runs.⁷² TiO₂, ZrO₂ and TiO₂ nanoparticles were also studied to yield lower amount of HMF (10–29%).^{60,61} Sn–W oxide catalyst was evaluated in this reaction and it yielded 48% of HMF from glucose.⁷⁴ HT/Amberlyst-15 was tried for the conversion of sucrose and cellobiose in DMF solvent to yield 54% and 34% of HMF, respectively.⁶³ Sn–W oxide was also efficient in converting cellobiose and starch to yield ~40% HMF.⁷⁴ A major drawback in most of these reports is that catalyst morphology and recyclability is not mentioned.



Scheme 4. Lignin depolymerization using solid acid catalysts.

Valorization of lignin produces a variety of chemicals such as aromatic monomers and gases which have diverse industrial applications (scheme 4). Conversion of lignin into value-added products using competent and green process is required to achieve favourable economics for the cellulose to bioethanol process.⁷⁵ Lignin is made up of a complex three-dimensional amorphous aromatic biopolymer consisting of main building blocks of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. In the literature, several methods of valorizing lignin are mentioned. A well-known base-catalysed depolymerization (BCD) method^{76,77} uses homogeneous mineral bases (NaOH/KOH) for the conversion of lignin into aromatic monomers above 260°C. Use of mineral bases to yield either aromatic monomers or gases has been claimed by others.^{78,79}

However, soluble base method generates neutralization waste, corrosion to reactor and thus is not eco-friendly. Efforts have been diverted towards the use of supported metal catalysts (Pt, Ru, Pd, Ni, Co-Mo, Ni-Mo supported on C, Al₂O₃, SiO₂-Al₂O₃ or zeolites) under hydrogen atmosphere to convert lignin into aromatic monomers and gases.^{80–84} Although good results are achieved, use of precious metals and hydrogen make these methods economically unviable. Reports claim that pyrolysis of lignin produces bio-oils in the absence of oxygen at higher temperatures (>250°C).⁸⁵ Lignin conversion under supercritical water conditions (>275°C) is reported to yield various gases depending upon the reaction conditions employed.^{86,87} Catalytic cracking of bio-oils is also known over HZSM-5 \geq 340°C to form aromatic hydrocarbons.⁸⁸ Pre-treatment of lignin with homogeneous reagents NaOH, H₂O₂ and Ca(OH)₂ followed by pyrolysis using heterogeneous catalysts to yield ca. 90% yield however defeats the purpose of using heterogeneous catalysts.⁸⁹ Yet, majority of studies are done using lignin model compounds (dimers and trimers) instead of real lignin as a substrate. This particularly, hampers in developing a catalytic systems as actual substrates contain several impurities and much more complex structures.

This manuscript mainly describes the recent developments happened in our group related to the production of sugars and furfural from hemicellulose, HMF from fructose and aromatic monomers from lignin with various solid acid catalysts. Physico-chemical characteristics of heterogeneous catalysts used in these studies are mentioned in table 1.

Table 1. Physico-chemical properties of catalysts.

Catalyst	Surface area (m ² g ⁻¹) [#]	Total acid amount (mmolg ⁻¹) [*]
HUSY (Si/Al=15)	873	0.55
HMOR (Si/Al=10)	528	1.20
H β (Si/Al=19)	761	0.91
HZSM-5 (Si/Al=11.5)	405	0.98
K10	246	0.42
Al-MCM-41 (Si/Al=50)	980	0.14
Al-SBA-15 (Si/Al=100)	1011	0.08
γ -Al ₂ O ₃	225	0.40
Nb ₂ O ₅	115	0.30
SiO ₂ -Al ₂ O ₃ (Si/Al=5.8)	532	0.63
SAPO-44	369	1.20
SAPO-5	309	0.80

[#] N₂-sorption analysis; ^{*} NH₃-TPD analysis

2. Experimental

2.1 Materials

Zeolite, HMOR (Si/Al=10), H β (Si/Al=19), HUSY (Si/Al=15) and HZSM-5 (Si/Al=11.5) were obtained from Zeolyst International. Prior to use, zeolites were calcined at 550°C for 16 h in air flow. Pseudoboehmite (Marathwada Chemical Industries Pvt. Ltd., grade: MCI-1524, 65–78% Al₂O₃), fumed silica (Aldrich), γ -alumina (Aldrich), silica-alumina (Aldrich), K10 clay (Aldrich), niobium pentoxide (Spectrochem, 99.95%), orthophosphoric acid (Fisher Scientific, 85%), cyclohexylamine (Spectrochem, 99%), hemicellulose/xylan (softwood; xylose \geq 70%, glucose 15%, arabinose 10%) (Aldrich), dealkaline lignin (Aldrich), xylose (LOBA, 99.5%), arabinose (s. d. fine, 100%), glucose (s. d. fine, 100%), furfural (LOBA, 98%), HMF (Aldrich, 99%), sodium chloride (LOBA, 99.5%), potassium chloride (LOBA, 99.8%), triethyl amine (LOBA, 99%), toluene (LOBA, 99.5%), *p*-xylene (LOBA, 98.5%), MIBK (LOBA, 99%), THF (LOBA, 99.5%) and methanol (LOBA, 99.8%) were purchased and used as received.

2.2 Synthesis of catalysts

Synthesis of crystalline silicoaluminophosphate materials was carried out according to a published report.^{90,91} Pseudoboehmite, fumed silica and orthophosphoric acid were used as source of Al₂O₃, SiO₂ and P₂O₅, respectively during synthesis.

A molar gel composition of 1.0 CHA:1.0 Al₂O₃:1.0 SiO₂:1.0 P₂O₅:60.0 H₂O was used in synthesis of SAPO-44 material.⁹⁰ Typically, 4.60 g pseudoboehmite was added slowly (within 2 h) to the diluted phosphoric acid solution (7.69 g H₃PO₄+ 12.50 g water) to form gel A. Gel B was prepared by mixing of 2.05 g of fumed silica in 23.50 g water followed by addition of 3.33 g CHA (cyclohexylamine). Now, gel B was added to gel A and stirred for 6 h. The homogeneous solution was transferred to Teflon lined steel autoclave and aged (crystallization) for 176 h at 200°C. Solid materials were filtered, washed with water, dried and calcined at 550°C for 6 h in air.

A molar gel composition of 1.0 TEA:1.0 Al₂O₃:0.4 SiO₂:1.0 P₂O₅:50.0 H₂O was used to synthesize SAPO-5 material.⁹¹ Typically, 1.00 g of pseudoboehmite was added (within 2 h) to diluted phosphoric acid (1.58 g H₃PO₄+ 5.95 g water) to prepare gel A. 0.16 g fumed silica was mixed thoroughly with 0.69 g TEA (triethylamine) to get gel B. Both the gels were mixed together and stirred for 3 h at RT. Obtained solution was aged in an autoclave with teflon liner for 4 h at 200°C. Solid

materials were filtered, washed with water, dried and calcined at 550°C for 6 h in air.

2.3 Catalytic reactions

Furfural formation reactions were carried out with either hemicellulose or bagasse as a substrate. In a typical reaction, 0.6 g substrate and 0.3 g catalyst were added to 60 mL water or water+organic solvent=30 + 30 mL in a Parr autoclave. Autoclave was flushed twice with N₂ and finally 50 bar N₂ was charged at RT and heated to desired temperature for definite time. Intermediately, samples were withdrawn to monitor the progress of reaction. After reaction, autoclave was cooled to room temperature; catalyst was separated from reaction mixture by centrifugation.

In fructose dehydration reaction, 0.5 g of fructose, 0.143 g catalyst were mixed with water+organic solvent=5 mL + 25 mL or 30 mL water in Parr autoclave and heated at desired temperature under stirring. At the end of reaction, reactor was cooled to room temperature and catalyst was separated from reaction mixture by centrifugation and aqueous and organic layers were separated from each other.

In lignin valorisation reaction, 0.5 g of dealkaline lignin and 0.5 g catalyst were mixed with water+methanol=5 mL + 25 mL in Parr reactor and filled with 7 bar N₂ at RT. Reactor was heated up to 250°C for 0.5 h. At the end of reaction, reactor was cooled to room temperature and catalyst was separated from reaction mixture by centrifugation.

In metal exchange study, different concentrations (20 or 240 ppm) of metal chloride salt solution were added to catalyst and stirred for 24 h at 60°C. Then catalysts were separated through centrifugation and washed with water carefully and dried (oven at 60°C, 16 h; vacuum at 150°C, 16 h).

2.4 Analysis of reaction mixture

For hemicellulose and fructose reaction, quantification of aqueous layer components was carried out with HPLC, equipped with Pb²⁺ column (300 mm \times 7.8 mm, 80°C), RI detector (40°C) and Millipore water as mobile phase with 0.6 mL flow rate. Organic layer components were quantified on a Varian gas chromatograph, equipped with HP-5 column (50 m \times 0.22 μ m ID) and flame ionization detector (FID).

Lignin reaction mixture is analysed using Varian 3800 model GC equipped with FID and CPSIL 8CB capillary column (30 m \times 0.25 mm). The molecular weight of the products was analysed using Varian 3800

GC-MS (Saturn 2000MS) with VF-5 capillary column (50 m × 0.25 mm) 2.5 Conversion and yield calculations

Conversion (fructose) = $\{[\text{Initial fructose} - \text{unreacted fructose (HPLC)}] / \text{Initial fructose}\} \times 100\%$

Conversion (hemicellulose) = $\{[\text{Initial hemicellulose} - \text{unreacted hemicellulose (solid recovery basis)}] / \text{Initial hemicellulose}\} \times 100\%$

Yield = $\{\text{Weight (from HPLC and GC)} / \text{Theoretical weight}\} \times 100\%$

2.6 Recycle study

Catalyst recycle study was carried out with the spent catalyst after calcination at 550°C for 12 h in air.

3. Results and discussion

3.1 Synthesis of furfural

It is shown that the solid acid catalysts could convert hemicellulose (xylan) to either C₅ sugars (xylose, arabinose) and/or furfural depending upon the solvent system used in the reaction. Figure 1 summarizes the results for the catalytic activity observed in aqueous medium for the conversion of isolated xylan to C₅ sugars (as major) and furfural (as minor) at 170°C using solid acid catalysts. Detail studies on reaction parameters were conducted to find the optimum reaction conditions. Among all the catalysts studied, HUSY (Si/Al = 15) zeolite showed the best activity; (41% yield of xylose+arabinose and 12% yield of furfural). On the other hand, yields of C₅ sugars were less with other

solid acid catalysts such as HMOR (Si/Al = 10), Hβ (Si/Al = 19), K10, Al-MCM-41 (Si/Al = 50), Al-SBA-15 (Si/Al = 100), γ-Al₂O₃ and Nb₂O₅. Non-catalytic reaction under similar reaction condition showed only 5% C₅ sugars yield which clarified the effect of catalyst in this reaction. LC-MS technique proved the step-wise formation of polymer (xylan) → pentamer → tetramer → trimer → oligomer → monomer (C₅ sugars, xylose and arabinose) → furfural. It was shown that HUSY catalyst can be recycled up to 5th run with almost similar activity.⁴⁷

Same strategy was applied to the unpurified hemicellulose (i.e., without separation of cellulose, hemicellulose and lignin from lignocellulose), obtained from bagasse as it is the real crop waste. Bagasse used in this study contains ca. 43% cellulose, ca. 30% hemicellulose, ca. 20% lignin and ca. 7% extractive+ash. When solid acid catalysts were used in the same S/C ratio of 2 as in previous study, the reaction time gets shorter to 1 h at 170°C to yield maximum amount of xylose+arabinose (figure 2).⁴⁸ With increasing reaction time, decrease in monomer yield was observed. This

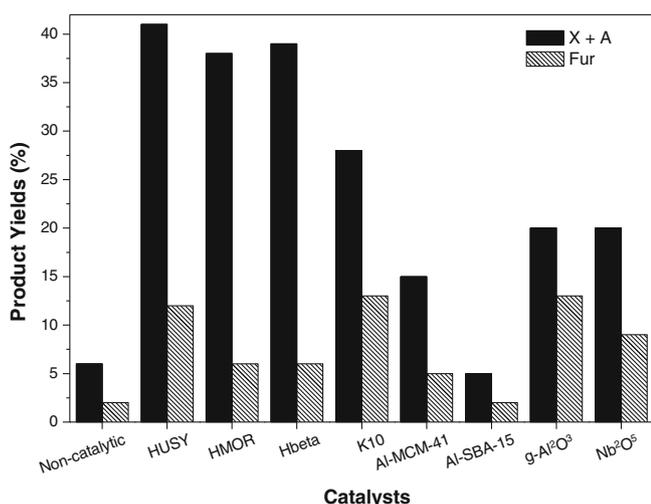


Figure 1. Conversion of hemicellulose to xylose+arabinose (X+A) and furfural (Fur) using solid acid catalysts. Reaction condition: hemicellulose (0.6 g), catalyst (0.3 g), water (60 mL), 50 bar N₂ initial pressure at RT, 170°C, 3 h.

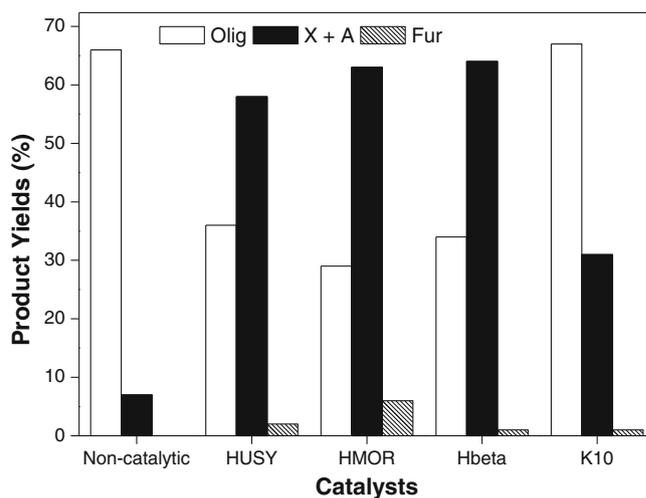


Figure 2. Conversion of bagasse hemicellulose to oligomers (Olig), xylose+arabinose (X+A) and furfural (Fur) using solid acid catalysts. Reaction condition: bagasse (0.6 g), catalyst (0.3 g), water (60 mL), 50 bar initial N₂ at RT, 170°C, 1 h.

could be compensated to form furfural. Zeolite HUSY (Si/Al = 15), HMOR (Si/Al = 10) and H β (Si/Al = 19) were evaluated under reaction condition and showed almost similar yield of C₅ sugars (60 \pm 4%) from bagasse, whereas K10 clay gave 31% yield for C₅ sugars. In case of zeolite, almost 29–36% oligomers and 3% furfural were obtained in addition to sugars which allow a total mass balance of 98 \pm 7% (considering ca. 30% of hemicellulose present in bagasse). Under similar condition, non-catalytic results showed oligomer as a major product (65% yield) with minor amount of C₅ sugars (7%) formation. Non-catalytic conversion of bagasse to oligomer occurs due to thermal hydrolysis and generation of acidic species (H₃O⁺) from water at 170°C. Formation of acidic species can be attributed to change in *pK_w* value of water from 13.99 to 11.64 when the temperature was increased from 25°C to 150°C.⁹² It is important to know whether selectively hemicellulose (part of bagasse) was converted to yield oligomers, C₅ sugars and furfural or that the other components (cellulose, lignin) are also undergoing any conversions. To resolve this, reactions were carried out with purified (isolated) cellulose and lignin under similar reaction conditions. The analysis of reaction mixture by GC and HPLC did not show any products formed from these substrates, which confirmed that selectively hemicellulose from bagasse was converted to yield high amount of products.

Since it has been reported that biphasic reaction system improves furfural yield, in our study, we used three different biphasic solvent systems in presence of HUSY as a catalyst for bagasse conversion.⁴⁸ An improved yield of 54% for furfural was possible by using H₂O/toluene (1:1 *v/v*) biphasic system at 170°C, 6 h in contrast to aqueous-only system; 30% furfural yield. Also, H₂O/toluene system produced 23% oligomer and 18% C₅ sugars along with furfural with a total carbon balance of 95% based on GC and HPLC analysis. With other biphasic solvent system such as H₂O/MIBK and H₂O/*p*-xylene, improvement in the yield of furfural (55 \pm 1%) compared to water-only system was seen. It was observed that higher mass balance can be possible in biphasic system (95 \pm 1%) compared to water-only system (79%). Recycle study was carried out with the recovered catalyst after calcining the catalyst at 550°C for 12 h. A decrease in the activity (45% furfural yield) was observed in the recycle run of a catalyst. This is due to the deposition of carbon or poisoning of active sites on the catalyst during first catalytic run. Further, it was seen that catalyst undergoes morphological changes which was confirmed through various physico-chemical characterizations of catalyst such as XRD, SEM, ICP-OES, solid

state NMR, N₂-sorption study and NH₃-TPD.⁴⁸ For the simplicity of the discussion, we present here, catalyst characterization for HUSY (Si/Al = 15) catalyst. XRD pattern for spent HUSY showed peaks at similar positions as observed in the fresh catalyst; however, with 30% decrease in the intensity (figure 3). SEM images confirmed the change in sharp-edge cubic morphology of fresh HUSY to round-edge spherical morphology in spent catalyst. Presence of Na and K in the spent HUSY catalyst was proved by ICP-OES study. In the fresh HUSY catalyst, we observed 0.017 mmol g⁻¹ of Na; however, on spent catalyst 0.139 mmol g⁻¹ of Na and 0.138 mmol g⁻¹ of K was found. This indicates that source of Na and K is the substrate which is obvious since plants require nutrients for their growth and also during the isolation of hemicelluloses from lignocelluloses, NaOH and Na₂S are used (Kraft process). From the ICP analysis of reaction solution, we conclude that Al is not leached out. Comparison of ²⁷Al-NMR spectra between fresh and spent HUSY showed decrease in Al^{IV} species in spent catalyst wherein intensity of Al^{VI} species remained same in both. The decrease in Al^{IV} species may be attributed to the formation of NMR invisible species in the spent HUSY. Change in intensity of Q¹, Q², Q³ and Q⁴ species in spent HUSY was observed in ²⁹Si-NMR spectra. Increase in Q⁴ [Si(OAl)] species intensity in spent HUSY indicates leaching of Al from the catalyst leading to deactivation. Further, catalyst morphology change was confirmed through N₂-sorption and NH₃-TPD studies which showed decrease in surface area from 873 to 704 m² g⁻¹, pore volume from 0.45 to 0.38 cc/g and total acid amount from 0.55 to 0.21 mmol g⁻¹. A similar phenomenon of change in the properties is observed with other zeolite catalysts. Hence, it is essential to develop stable and reusable catalysts.

3.2 HMF production

As mentioned earlier, HMF has a hidden potential to secure the demand of various chemicals and fuel. It can be synthesized from different substrates such as fructose,^{66,67} glucose,⁶³ starch,⁴⁶ cellulose⁴⁶ and inulin⁵² by the application of homogeneous and heterogeneous catalytic systems. Earlier studies show that in water-mediated sugar chemistry with use of high temperature and pressure, changes in the morphology of structured catalysts are possible.^{47,48} Considering this hydrothermally stable (600°C under 20% steam) solid acid catalysts, silicoaluminophosphates (SAPOs) were prepared and used in the study. Small pore (0.4 nm) SAPO-44 and large pore (0.8 nm) SAPO-5 were synthesized as per procedures reported in literature.^{90,91}

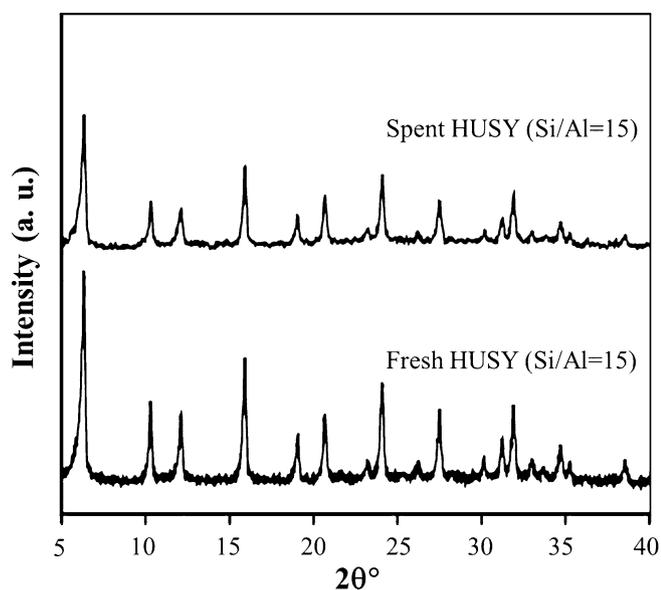


Figure 3. Comparison of XRD patterns of fresh and spent HUSY.

We have evaluated various solid acid catalysts such as SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, HMOR (Si/Al = 10), SAPO-5 and SAPO-44 for fructose dehydration to HMF reaction and the results are shown in figure 4. SAPO-44 was able to produce 78% of HMF with 88% selectivity from fructose at 175°C, 1 h in presence of air (1 bar) and $\text{H}_2\text{O}/\text{MIBK}$ solvent system.⁹³ A total mass balance of 94% was attained to indicate negligible carbon loss due to side reactions or else due to error in analysis. Under similar reaction condition, non-catalytic reaction gave only 29% HMF yield with 74% fructose conversion. Result was compared with HMOR catalyst as it has been shown in literature as one of the best catalysts.⁶⁶

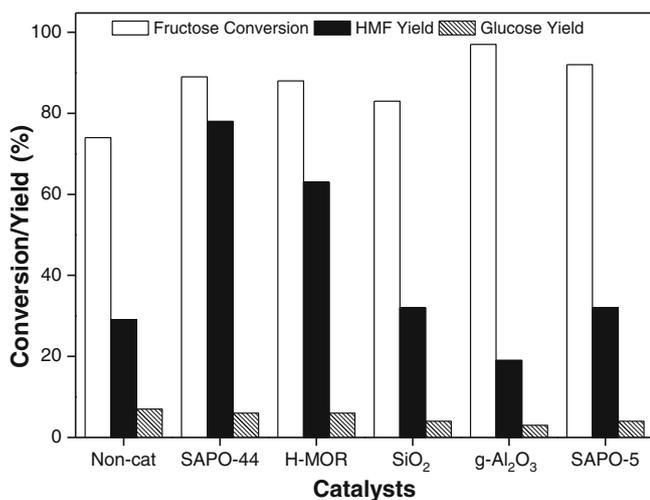


Figure 4. Conversion of fructose to HMF using solid acid catalysts. Reaction condition: fructose (0.5 g), catalyst (0.143 g), $\text{H}_2\text{O}+\text{MIBK}$ = 30 mL (1:5 v/v), 175°C, 1 h.

Under similar condition, HMOR catalyst showed poor performance (63% yield, 72% selectivity), though both SAPO-44 and HMOR catalysts have same total acid amount (1.2 mmol g^{-1}). We also tried SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and SAPO-5 catalysts but the HMF yield remains in the range of 19–32%.

Various solvent systems were studied in presence of SAPO-44 catalyst to check the HMF formation. Water-only system showed lower yield (39%) of HMF compared to ethanol-only system (56%). Shifting to biphasic solvent system $\text{H}_2\text{O}/\text{MIBK}$, promotes HMF extraction from water phase to MIBK phase to improve the HMF yield (78%). It was also observed that 1:5 ratio (v/v) of $\text{H}_2\text{O}/\text{MIBK}$ yields more HMF (78%) compared to that with 1:1 ratio (47%); although in both cases HMF selectivity remained similar ($\sim 85\%$).⁹³

Catalyst recycle study showed a slight decrease in activity for SAPO-44 catalyst up to 3rd run and beyond that, activity remains the same minimum up to 5th run (66%). Slight decrease in activity (78% to 66%) can be attributed to trivial structural modification in catalyst due to re-positioning of Al, P and Si atoms in the framework. This data also coincided well with various physico-chemical characterizations such as XRD, ICP-OES, solid state NMR and SEM images of fresh and spent catalyst.⁹³

XRD pattern for SAPO-44 and SAPO-5 resembles CHA and AFI topology, respectively, whereas that of spent SAPO-44 showed slight change in peak intensity (figure 5). This can be compared with decrease in HMF yield in recycle runs. Now, it is essential to check whether Al and/or P were leached out during the reaction which is responsible for change in activity. To confirm this, ICP-OES analysis of fresh and spent SAPO-44 was carried out and analysis indicates that amount

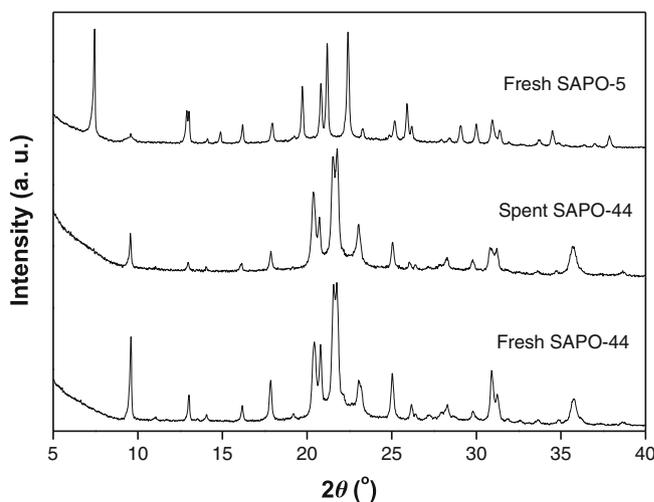


Figure 5. XRD patterns of SAPO catalysts.

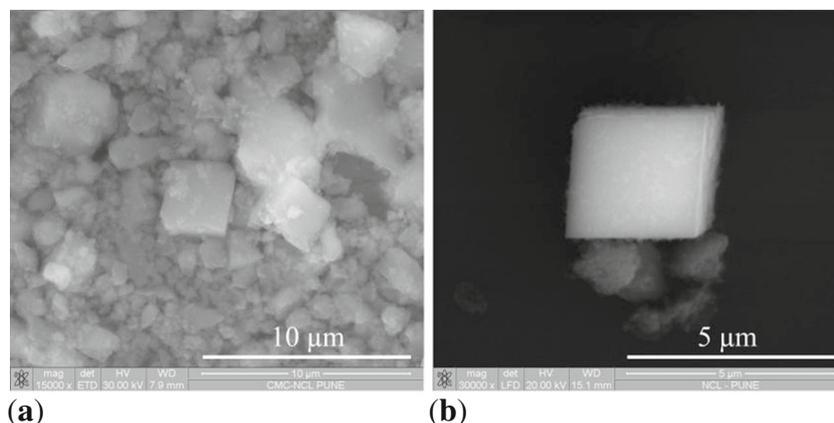


Figure 6. SEM images of SAPO-44; (a) fresh and (b) spent.

of Al and P remains same in both, fresh and spent catalysts. This indicates that in case of SAPO-44 catalyst, morphological changes are due to the repositioning of Al and P. The SEM images show cubic morphology with similar edge length for both fresh and spent SAPO-44 which indicate catalyst stability (figure 6). From all the above discussions, it can be concluded that the actual active phase in the catalyst is the CHA morphology.

The catalyst in this study was used in order to introduce a more stable catalytic system compared to earlier known catalysts. However, we experienced a slight change in the morphology of SAPO during the reaction, even though it is a hydrothermally stable catalyst (600°C under 20% steam). Another reason behind using SAPO catalyst was its expected superior hydrophilicity rather than zeolites due to presence of ‘P’ in its structure. Hydrophilicity of SAPO catalyst allows it to be present in water phase where actual dehydration reaction takes place and it does not interact with extracted HMF in organic phase (condensation or degradation reaction).

3.3 Lignin valorization

Problems associated with known methods encourage researchers to develop a discrete method based on heterogeneous catalysts to convert real lignin substrates into aromatic monomers. Hence, the objective of our study was to develop a method to depolymerize lignin into aromatic monomer units using solid acid catalysts.

Depending on the source of plant species and also the method of extraction, the structure of lignin will differ. So before performing the reactions, lignin was well-characterized using various techniques. It was observed from MALDI-TOF analysis that dealkaline lignin had high molecular weight (60 kDa). Since this

lignin was isolated by Kraft process, both ICP-OES and EDAX analyses showed that Na contamination (29 mg Na/1 g lignin) and CHNS elemental analysis showed the presence of sulphur. The CHNS elemental analysis also showed that the lignin is composed of 65% C and 7% H. TGA analysis showed presence of 17% ignition residue in dealkaline lignin under air atmosphere and 30–40% residue under N₂ atmosphere.

Lignin depolymerization was done using various solid acid catalysts such as HUSY (Si/Al = 15), HZSM-5 (Si/Al = 11.5), HMOR (Si/Al = 10), K10 clay and SiO₂–Al₂O₃. Under inert atmosphere, we observed conversion of lignin to value-added aromatics with high yield of 60% and ca. 95% mass balance. Figure 7 summarizes the catalytic results obtained over various solid acid catalysts. Under the same conditions in the absence of catalyst, aromatic monomer yield was only 11%, while zeolites (HUSY, HZSM-5) gave the highest

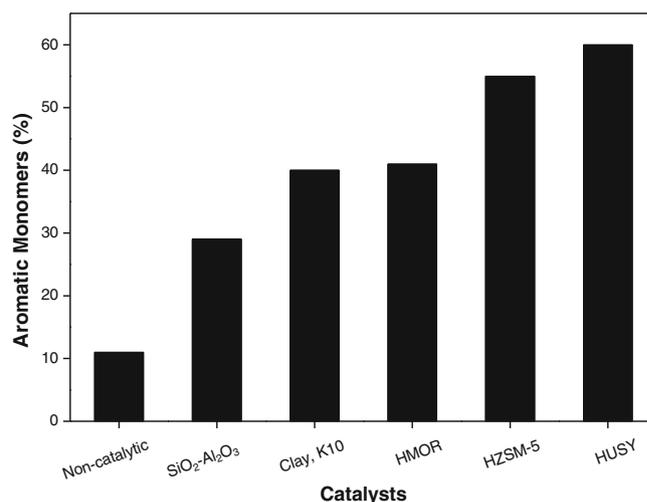


Figure 7. Study on lignin depolymerization over various solid acid catalysts. Reaction conditions: Dealkaline lignin (0.5 g), solid acid catalyst (0.5 g), H₂O+CH₃OH = 30 mL (1:5 v/v), 250°C, 0.5 h, 7 bar N₂ at RT.

yield of ca. 60% for organic solvent soluble (THF soluble) products. Most of the other catalysts gave aromatic monomers yield of 30–40%.⁹⁴

Formation of char/tar or gas (CO, CO₂, CH₄, H₂, C₂–C₄) was not observed under the reaction conditions employed. Also, the products formed in all the reactions were similar. These observations indicate that lignin depolymerization under these reaction conditions is selective in the formation of aromatic monomers. Even though zeolites showed very high activity, those were unstable under the reaction conditions. XRD, NH₃-TPD, ²⁹Si and ²⁷Al NMR of these catalysts revealed that its well-defined porous channel structure has collapsed. Hence, SiO₂–Al₂O₃, a non-structured (amorphous) catalyst was used for further studies. Reaction parameters such as the temperature and pressure were studied. It revealed that 250°C is the optimum temperature for the formation of aromatic monomers (29%), since further increase in temperature (270°C) yields char and at lower temperatures (230°C) yield of aromatic monomers was slightly decreased (25%). Effect of pressure was also studied by charging the reactor with different pressures of N₂ gas (1 bar and 7 bar N₂ at RT) for the reaction. It was observed that 7 bar N₂ pressure was the optimum pressure (29%) for the reaction, while 1 bar N₂ pressure reduced product formation (20%). This study reveals that lignin depolymerization using solid acid catalysts is dependent on both temperature and pressure.

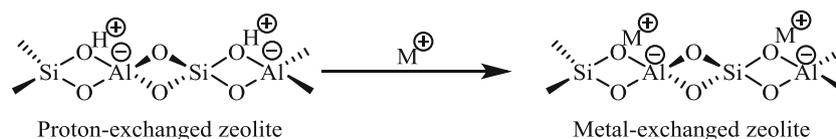
3.4 Metal-exchange studies

Recycle study of unpurified hemicellulose from bagasse showed decrease in activity of zeolite catalyst, which can be attributed to the catalyst morphology change during the reaction.⁴⁸ As mentioned earlier (section 3.1), presence of Na and K was seen from the ICP-OES studies of spent catalyst. This change can be explained on the basis of metal ions present in the raw biomass which might have exchanged with Brönsted acid sites, leading to deactivation of catalyst (scheme 5). To investigate further, we carried out Na and K metal-exchange

study on zeolites [HUSY (Si/Al = 15), HMOR (Si/Al = 10)] and silica–alumina (SA, Si/Al = 5.8). All the fresh and metal-exchanged catalysts were characterized with XRD, ICP-OES and NH₃-TPD.

XRD patterns of all the fresh and metal-exchanged catalysts showed no detectable change in the peak positions, which emphasizes the fact that after the metal exchange treatment, morphology of the zeolites is retained (figure 8a, b). ICP-OES and NH₃-TPD data for fresh and metal-exchanged catalysts is presented in table 2. Presence of Na and K is clearly seen on the catalyst after the metal exchange treatment. This might lead to decrease in the acid amount for treated catalysts. The NH₃-TPD study revealed that in case of HUSY catalysts, acid amount decreased to 0.59 and 0.56 mmolg⁻¹ after 20 and 240 ppm treatment. Also, it is observed that the exchange tendency of K ion in catalyst is more pronounced than Na ion. From this study, it can be claimed that the presence of metal ions in raw biomass has an effect on catalyst activity reduction. However, we wish to point out here that even with 240 ppm treatment, not much decrease in the acidity compared to 20 ppm treatment, was observed (table 2). This gives us a rough idea about the presence of equilibrium between the adsorption of metal on zeolite and presence of metal in the solution. However, to prove this hypothesis, more elaborate studies are ongoing in our laboratory.

Development of a process based on biomass feedstock is advantageous and environment-friendly as discussed. However, at the same time, lignocellulosic biomass is a very complicated substrate since the composition of cellulose, hemicellulose and lignin together make it more complex and presence of nutrients (metals) in biomass kills the catalytically active sites and disrupts the catalytic process. One of the approaches to convert components of lignocellulosic biomass is to first pretreat the lignocellulose to isolate cellulose, hemicellulose and lignin and then develop individual process for them to synthesize value-added chemicals. However, pretreatment of lignocellulose has some disadvantages such as it can contaminate the substrates with additional minerals (Na; Kraft process), incurs extra cost and produces waste. Considering all this, it is essential that future research delves on these facts



Scheme 5. Metal exchanged on protonated zeolite.

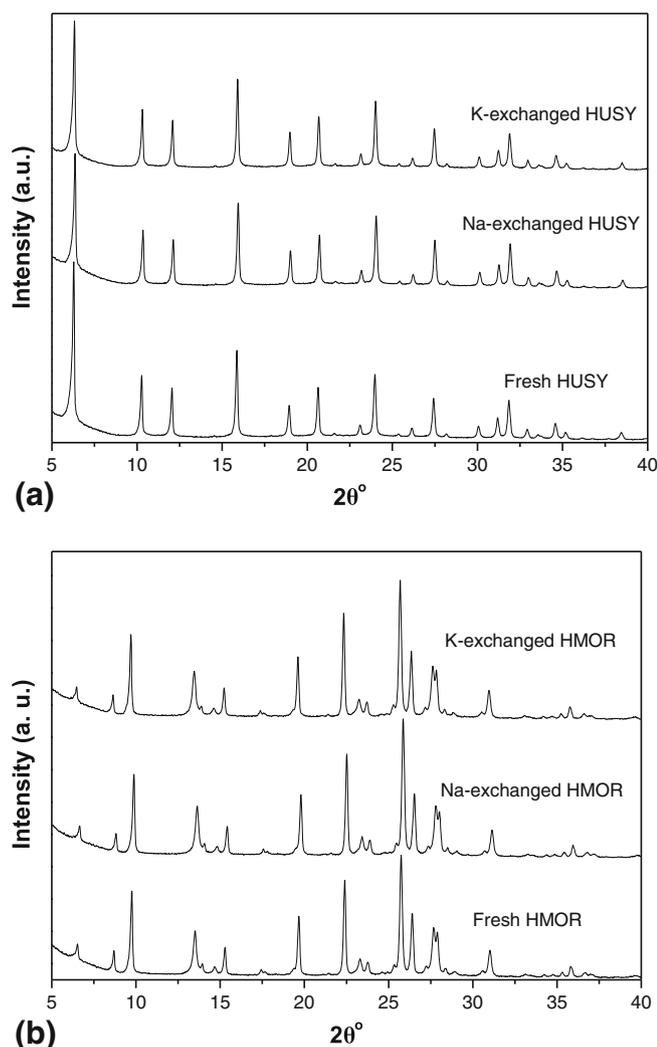


Figure 8. (a). Comparison of XRD patterns of HUSY. (b). Comparison of XRD patterns of HMOR.

and devotes efforts towards developing a stable catalytic system which can convert individual parts (isolated) of lignocelluloses selectively. Another approach is that the whole lignocellulosic materials can be used as a substrate for step-by-step conversion of each components by virtue of developing multifunctional catalysts which are stable under reaction conditions. Thus, drawbacks associated with the isolation procedure can be overcome. However, development of these catalysts and fine tuning the reaction conditions is a major challenge. Hence, it is essential to work on both the approaches and try to develop efficient methods for the conversion of components of lignocellulosic biomass.

4. Conclusion

In summary, literature available on the use of solid acid catalysts for the formation of C_5 sugars (xylose, arabinose), furan derivatives (furfural and HMF) and aromatic monomers from biomass (hemicellulose, fructose, and lignin) has been discussed here. In our study it is shown that ratio of sugars to furfural yield can be controlled by employing a specified solvent system. Recycle runs proved that zeolite catalyst was stable when pure (isolated) hemicellulose was subjected to furfural production; whereas use of bagasse (unpurified hemicellulose) did not render zeolite stability. The metal-exchange study partially explained deactivation of zeolite catalyst. To overcome the problems of zeolite catalysts, employment of SAPO catalysts because of their higher hydrothermal stability is discussed. SAPO-44 catalyst showed very high activity

Table 2. Summary on the metal-exchange study and NH_3 -TPD analysis of catalyst.

Catalyst	Na/K metal detected (ppm) [#]	Total acid amount ($mmol\ g^{-1}$) [*]
Fresh HUSY	0.26/0.02	0.69
20 ppm Na exchanged HUSY	2.04	0.59
240 ppm Na exchanged HUSY	3.64	0.56
20 ppm K exchanged HUSY	2.08	0.64
240 ppm K exchanged HUSY	6.08	0.52
Fresh HMOR	0.17/0.21	1.20
20 ppm Na exchanged HMOR	1.06	1.10
240 ppm Na exchanged HMOR	1.92	1.10
20 ppm K exchanged HMOR	1.87	1.10
240 ppm K exchanged HMOR	5.36	0.90
Fresh SA	2.26/0.17	0.66
20 ppm Na exchanged SA	3.16	0.62
240 ppm Na exchanged SA	5.25	0.52
20 ppm K exchanged SA	2.29	0.30
240 ppm K exchanged SA	9.37	0.47

[#] ICP-OES analysis; ^{*} NH_3 -TPD study

and selectivity for HMF formation from fructose. Even though a slight change in the morphology of SAPO-44 was observed in spent catalyst after 1st run, it can show similar activity after 3rd recycle run onwards. Valorization of lignin to aromatic monomers with high yield was also described with zeolite catalyst but its stability is an issue. This problem can be overcome by using amorphous catalysts.

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