A solid-acid-based process for the conversion of hemicellulose[†]

Paresh Laxmikant Dhepe* and Ramakanta Sahu

Received 10th March 2010, Accepted 19th October 2010 DOI: 10.1039/c004128a

We describe a solid-acid-catalyzed conversion of hemicellulose (a component of lignocellulosic material) into xylose, arabinose and furfural in aqueous media.

The conversion of biomass into chemicals, fuels and energy using the bio-refinery concept has attracted lot of attention.^{1,2} In particular, lignocellulosic biomass, consisting of cellulose (*ca.* 50%), hemicellulose (*ca.* 30%) and lignin (*ca.* 20%) is of special interest because it is non-edible and in plentiful supply.¹⁻³

Hemicellulose is a heterogeneous polymer, made up of C_5 and C_6 sugars (such as xylose, arabinose, mannose, glucose, *etc.*) depending on the source. In the hydrolysis of hemicellulose, selective cleavage of the C–O bonds present between adjacent sugar molecules is very important to yield intact monomer sugar molecules. Conventionally, mineral acids and enzymes are used to hydrolyze these materials,^{4,5} but recently, it has been shown that heterogeneous catalysts can convert cellulose into sugars and its derivatives in a one-pot reaction.^{6–14} Conversion of hemicellulose into monomeric sugars in a two-step process over ion-exchange resins has also been reported. However, in these reports initial autohydrolysis of hemicellulose was carried out at around 160 °C to yield water-soluble oligomers. Ion-exchange resins were then added to the solutions to yield sugar monomers.^{15,16}

In this report, we describe for the first time a one-pot process for the conversion of solid hemicellulose (without any pretreatment) into xylose, arabinose and furfural using solid acid catalysts (zeolites, clays, and metal oxides) in aqueous media (Scheme 1). Also, we show that it is possible to selectively convert just the hemicellulose in lignocellulosic materials using solid acid catalysts. Moreover, we show that the catalysts can be re-used in 5 runs with almost the same activity.

 C_5 and C_6 sugars are important building blocks for the synthesis of chemicals and fuels, and the importance of xylose and furfural is reported in a US Department of Energy report on the 12 top value-added chemicals.¹⁷ The hydrogenation of xylose using supported metal catalysts gives xylitol, which finds use as a sweetener in food and pharmaceutical industries.¹⁸ In addition, it is possible to convert xylose/xylitol into glycols, while under acidic conditions xylose undergoes dehydrocyclization to yield furfural.^{19,20} Furfural is used in the agricultural, plastics, and oil-refining industries, and is a raw material in the synthesis of furfuryl alcohols, furan and THF.²¹



Scheme 1 Conversion of hemicellulose using solid acid catalysts.

In this work, experiments were carried out using softwoodand hardwood-derived hemicellulose. The reason we chose solid acid catalysts with Brønsted acidity is that soluble Brønsted acids (H₂SO₄, HCl) are already known to catalyze conversion of hemicellulose. The solid acids used in this study have various natures: zeolites are microporous crystalline materials with pore diameters of 0.5 nm (HZSM-5) to 0.74 nm (HUSY) and different Si/Al ratios,²² the clays have a layered structure,²³ and Al-incorporated mesoporous silicas (Al-MCM-41 and Al-SBA-15) have a mesoporous channel structure with wide pore openings (>2.4 nm). In addition to these catalysts, sulfated zirconia and Cs-exchanged heteropolyacid and metal oxides (Nb₂O₅, and γ -Al₂O₃) were also tried.²⁴ In a typical reaction, 0.6 g (4.54 mmol) of solid hemicellulose was placed in an autoclave, and 60 mL water and 0.3 g catalyst were added. The substrate-to-catalyst molar ratio was 27.5 [based on HUSY (Si/Al = 15) having 0.55 mmol acid per g, and hemicellulose having a molecular weight of 132]. Analysis of the reaction mixture was carried out using HPLC and LC-MS (for details, see ESI[†]).

With water as a reaction medium and HUSY (Si/Al = 15) as the catalyst, 41% yield of xylose + arabinose could be achieved at 170 °C within 3 h (Fig. 1). Without catalyst under similar reaction conditions only 5% yield for xylose + arabinose was observed, which implies that conversion of hemicellulose is a catalytic reaction. Furthermore, we found that several other solid acid catalysts such as HBeta zeolite (Si/Al = 19), HMOR zeolite (Si/Al = 10), and K10 montmorillonite clay, were active

Inorganic and Catalysis Division, National Chemical Laboratory, Dr Homi Bhabha Road, Pune, 411 008, India. E-mail: pl.dhepe@ncl.res.in; Fax: +91 20-25902633; Tel: +91 20-25902024

[†] Electronic supplementary information (ESI) available: Detailed experimental procedure and results. See DOI: 10.1039/c004128a



Fig. 1 Results for the conversion of hemicellulose using various solid acid catalysts. *Reaction conditions*: softwood hemicellulose (0.6 g), catalyst (0.3 g), water (60 mL), 170 $^{\circ}$ C, 5 MPa N₂, 3 h.

for this reaction (Fig. 1) and resulted in a xylose + arabinose yield of 30–40%. It is reported in the literature that solid acids convert xylose into furfural in a dehydrocyclization reaction.^{19,20} Under our reaction conditions, *ca.* 12% furfural yield was observed with HUSY (Si/Al=15) and K10 montmorillonite clay catalysts (Fig. 1).

Though other solid acid catalysts were also active for this reaction, these showed slightly lower xylose + arabinose yields. For example, γ -Al₂O₃ and Nb₂O₅ gave 20% yield, and sulfated zirconia (SO₄²⁻/ZrO₂) gave 19% yield, while aluminaincorporated mesoporous silica Al-MCM-41 (Si/Al = 50) and Al-SBA-15 (Si/Al=100) showed 15% and 5% yield, respectively. The Cs-exchanged heteropolyacid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) gave 35% xylose + arabinose yield during the first run. However, in subsequent reaction activity dropped to only 5%, implying that HPA was not stable under the reaction conditions. In addition to xylose, arabinose and furfural as the products, oligomers (dimer, trimer, tetramer, pentamer) were also observed, as confirmed by LC-MS analysis (see Fig. S1[†]). These oligomers were the intermediates in the hydrolysis reaction and hence eventually can undergo hydrolysis reaction to yield xylose and arabinose.

To compare our results obtained for solid acid catalysts with homogeneous acid, we carried out the reaction at 170 °C using sulfuric acid (1 wt%) as the catalyst, and found that 50% xylose + arabinose and 10% furfural could be obtained after 1 h. With increase in reaction time, the yield of xylose + arabinose decreased, implying that they undergo further reactions. However, no increase in furfural was observed, indicating that xylose and arabinose undergo degradation reactions. When sulfuric acid was used as a catalyst, the reaction mixture was dark brown, suggesting that product degradation might have occurred. In the case of the solid-acid-catalyzed reaction, the mixture was pale brown after reaction. The higher xylose + arabinose yield with sulfuric acid (50% at 1 h) compared to HUSY (Si/Al = 15) (15% at 1 h) can be explained by the fact that while sulfuric acid

releases 12 mmol H^+ in the reaction mixture, HUSY releases 0.165 mmol H^+ under the reaction conditions employed.

It is clear that as the reaction temperature increases the time required for the formation of the same amount of xylose + arabinose decreases. For example, a reaction carried out at 170 °C gave 41% xylose + arabinose yield within 3 h. However, to obtain a similar yield at 130 °C, 48 h was required.

Catalyst recycling studies were carried out with HUSY (Si/Al = 15) as the catalyst and with 3 wt% hemicellulose loading. After 2 h reaction time (when the maximum xylose + arabinse yield was achieved), the catalyst showed almost the same activity ($50 \pm 4\%$) for up to 5 catalytic runs (Fig. 2). It should be noted that an increase in the xylose + arabinose yield was observed (from 41% to 54%) with increasing catalyst and hemicellulose loading.



Fig. 2 Results of the catalyst [HUSY (Si/Al = 15)] recycling study. *Reaction conditions*: softwood hemicellulose (1.8 g), catalyst (0.9 g), water (60 mL), 170 $^{\circ}$ C, 5 MPa N₂, 2 h.

It is reported in the literature that an increase in water content decreases the acid strength,14 so experiments were carried out at 170 °C using 3 wt% hemicellulose solutions (1.8 g hemicellulose, 0.9 g HUSY (Si/Al = 15), 60 mL water), and within 2 h a 54% xylose + arabinose yield was observed (the same as in the recycling experiment). This implies that with concentrated solutions, increased, as suggested in the literature, and also there is a possibility that hemicellulose and catalysts might have a more efficient interaction. However, further increasing the hemicellulose concentration to 10 wt% (3.6 g hemicellulose, 1.8 g HUSY (Si/Al = 15), 36 mL water) gave slightly lower yields (35% xylose + arabinose) after 2 h. It was observed from HPLC analysis that after 30 min of reaction, peaks for humenes and oligosaccharides start increasing. This is common phenomenon, wherein as the substrate concentration increases, formation of products also increases - in addition, these products may undergo side reactions to form undesired compounds (oligomers, humenes), since there is a high possibility of catalyzed/uncatalyzed reactions between two or more product molecules.19,20

While hemicellulose derived from softwood has a degree of polymerization (DP) of *ca.* 100, hemicellulose derived from hardwood typically has a DP of *ca.* $200.^{25}$ However, we observed almost same results (*ca.* 40% yield) under our reaction conditions (see Fig. S3[†]).

It is known that plants require several nutrients (K, Ca, Mg etc.) for their growth and survival, so it was decided to carry out ICP analysis of the recovered reaction mixture and spent catalysts. ICP analysis of the spent catalyst showed the presence of 7.3 ppm Na and 6.4 ppm K, while the fresh catalyst had 1 ppm Na and no K. ICP analysis of the reaction mixture showed the presence of 110 ppm Na and 39 ppm K. These results indicate that the hemicellulose might be the source of Na and K, the first possibility being that the Na and K are from the plants themselves. The second possibility is that during the separation of hemicellulose from cellulose and lignin by the Kraft process, alkaline solutions are used, resulting in Na and K getting trapped in the hemicellulose.² It is interesting to note that even though Na and K are present in the catalyst and reaction mixture, the catalyst was active, since there is a possibility that Na and K can replace H⁺.

To probe this aspect further, we carried out a TPD-NH₃ study. This revealed that the fresh catalyst had total acid content of 0.55 mmol g^{-1} , which decreased after reaction to 0.19 mmol g^{-1} , indicating that Na and K have replaced H⁺. Based on the ICP analysis results for spent catalyst, the presence of Na and K should decrease the acid amount in the spent catalyst by 0.33 mmol g^{-1} . This implies that 0.22 mmol g^{-1} of acid should remain in the spent catalyst. This value is in good correlation with the amount of acid (0.19 mmol g^{-1}) obtained from the TPD-NH₃ study. XRD characterizations performed on the spent and fresh catalysts proves that the catalyst morphology remains intact after the reaction (see Fig. S2†).

Although zeolites are the most active catalysts, diffusion limitation might be affecting utilization of all the active sites present in the zeolites. The pore diameter of HUSY (Si/Al = 15) is 0.74 nm, but as the hemicellulose molecule has a length of several hundred nm, entry into the zeolite channels might not be possible. It is postulated that hemicellulose hydrolyzes on the external acid sites, and that once dimers and trimers are formed these can enter the zeolite pores and interact with internal acid sites (present inside the pores of zeolites) to yield monomer sugars, xylose and arabinose. These monomeric sugars might then undergo dehydrocyclization to give furfural on these internal sites. The other solid acid catalysts might show lower activity due to their instability in water, and also because of their irregular structure (except Al-incorporated mesoporous silicas). Further studies on the catalyst characterization and mechanistic aspect of this reaction are ongoing, to establish if there is a relation between catalytic activity and catalyst morphology.

Preliminary results on selective conversion of hemicellulose from lignocellulosic material (bagasse, without separation of cellulose, hemicellulose and lignin) at 170 °C using HUSY (Si/Al = 15) indicates that 45% xylose + arabinose yield and 9% furfural yield can be obtained after 2.5 h. The total product yield of 54% is calculated based on 0.18 g hemicellulose being present in bagasse (for details of the calculations, see ESI†). It was earlier reported that with zeolite as the catalyst, cellulose (Fluka) hydrolysis gave *ca.* 12% glucose yield after 24 h.¹¹ Therefore, to confirm that under the reaction conditions employed in this study cellulose and lignin undergo hydrolysis/degradation, experiments were carried out with cellulose (Aldrich) and lignin (Aldrich) as substrates at 170 °C for 2.5 h. However, HPLC and GC peaks from cellulose- and lignin-derived products (glucose, 5-(hydroxymethyl)furfural, aromatic compounds *etc.*) were not observed. This clearly indicates that under the reaction conditions employed in this study, the hemicellulose in the bagasse is being converted selectively.

In summary, we have reported a one-pot conversion of hemicellulose into chemicals by solid acid catalysis. These catalysts are easily separable and reusable, and thus avoid waste generation. This study provides a way to convert both hemicellulose and cellulose together using newer catalysts by tuning the reaction conditions. For example, if a catalyst such as Pt/zeolite were synthesized, then the solid acid part of this catalyst could convert just the hemicellulose into sugars and furfural under the conditions employed in this study (<170 °C, N_2) while cellulose and lignin will remain intact. Furthermore, by increasing the reaction temperature to 190 °C and replacing N_2 with H_2 , one could selectively convert cellulose to sugar alcohols, as reported in earlier work.⁶ In this way, in a multistep one-pot reaction, it might be possible to selectively convert hemicellulose and cellulose into soluble products by tuning the reaction conditions. Work is therefore in progress on catalyst characterization, improvement of the yields, and the preparation of new solid acid catalysts.

Acknowledgements

The authors thank Dr D. Srinivas and Dr Tambe for discussion and LC–MS analysis.

Notes and references

- L. T. Fan, M. M. Gharpuray and Y.-H. Lee, *Cellulose hydrolysis*, Springer Verlag, Berlin, 1987.
- 2 G. Centi and R. A. van Santen, *Catalysis for renewables: from feedstock to energy production*, Wiley-VCH, Weinheim, 2007.
- 3 D. L. Klass, *Biomass for renewable energy, fuels, and chemicals*, Academic Press, San Diego, 1998.
- 4 Y. Lu and N. Mosier, Biotechnol. Bioeng., 2008, 101, 1170.
- 5 B. C. Saha, J. Ind. Microbiol. Biotechnol., 2003, 30, 279.
- 6 A. Fukuoka and P. L. Dhepe, Angew. Chem., Int. Ed., 2006, 45, 5161.
- 7 C. Luo, S. Wang and H. Liu, Angew. Chem., Int. Ed., 2007, 46, 7636.
- 8 R. Rinaldi, R. Palkovits and F. Schüth, *Angew. Chem., Int. Ed.*, 2008, **47**, 8047.
- 9 N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang and J. G. Chen, *Angew. Chem.*, *Int. Ed.*, 2008, 47, 8510.
- 10 S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, J. Am. Chem. Soc., 2008, 130, 12787.
- 11 A. Onda, T. Ochi and K. Yanagisawa, *Green Chem.*, 2008, **10**, 1033.
- 12 A. Onda, T. Ochi and K. Yanagisawa, Top. Catal., 2009, 52, 801.
- 13 A. Takagaki, C. Tagusagawa and K. Domen, Chem. Commun., 2008,
- 5363. 14 D. Yamaguchi, M. Kitano, S. Suganuma, K. Nakajima, H. Kato and
- M. Hara, J. Phys. Chem. C, 2009, 113, 3181.
 Y. Kim, R. Hendrickson, N. Mosier and M. R. Landisch, Energy Fuels, 2005, 19, 2189.
- 16 S. B. Kim and Y. Y. Lee, Biotechnol. Bioeng. Symp., 1985, 15, 83.

- 17 *Top value added chemicals from biomass: Volume 1*, ed. T. Werpy and G. Petersen, US Department of Energy, 2004.
- 18 J-P. Mikkola, H. Vainio, T. Salmi, R. Sjöholm, T. Ollonqvist and J. Vayrynen, Appl. Catal., A, 2000, 196, 143.
- 19 C. Moreau, R. Durand, D. Peyron, J. Duhamet and P. Rivalier, *Ind. Crops Prod.*, 1998, 7, 95.
- 20 S. Lima, M. Pillinger and A. A. Valente, *Catal. Commun.*, 2008, 9, 2144.
- 21 K. J. Zeitsch, *The Chemistry and Technology of Furfural and Its Many By-Products*, Sugar series, vol. 13, Elsevier, The Netherlands, 2000.
- 22 A. Corma, Chem. Rev., 1995, 95, 559.
- 23 Y. Izumi, K. Urabe and M. Onaka, *Microporous Mesoporous Mater.*, 1998, 21, 227.
 24 T. Okubara, *Chem. Rev.* 2002, 102, 3641.
- 24 T. Okuhara, Chem. Rev., 2002, 102, 3641.
- 25 E. Sjöstrom, in *Wood chemistry: fundamentals and applications*, Academic Press, San Diego, 1993.