

Letter

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Efficient, Stable and Reusable Silicoaluminophosphate for the Onepot Production of Furfural from Hemicellulose

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ABSTRACT: Development of stable, reusable and water tolerant solid acid catalysts in the conversion of polysaccharides to give value added chemicals is vital since catalysts are prone to undergo morphological changes during the reactions. With the anticipation that silicoaluminophosphate (SAPO) catalysts will have higher hydrothermal stability those were synthesized, characterized and employed in the one-pot conversion of hemicellulose. SAPO-44 catalyst at 170 °C within 8 h could give 63% furfural yield with 88% mass balance and showed similar activity at least up to 8 catalytic cycles. The morphological studies revealed that SAPO catalysts having hydrophilic characteristics are stable under reaction conditions.

Utilization of renewable biomass, particularly nonedible lignocellulosic materials consisting of cellulose, hemicellulose and lignin serves considerable potential to fulfil our future chemical needs. In this context, furfural, one of the most important platform chemical derived from biomass emerges as a potential building block¹ for its possible use in the synthesis of value-added chemicals, fuels and intermediates such as, furfuryl alcohol, 2methylfuran, 2-methyltetrahydrofuran, phenolformaldehyde resin, furoic acid, maleic acid and linear alkanes.²⁻⁴ Employment of homogeneous acid catalysts for the dehydration of xylose, a C_5 sugar (derived from hemicellulose) to furfural are known however, those face serious drawbacks such as difficulty in recovering the catalyst, environmental issues, toxicity, corrosiveness etc.⁵⁻⁷ To overcome these drawbacks, improvements in the conversion technologies of xylose to yield furfural over solid acid catalysts such as zeolites with various Si/Al ratio, Snbeta zeolite etc. are reported.⁸⁻¹⁰ However, it would be desirable to derive furfural directly from hemicellulose (via xylose formation). Studies on two-pot method for converting hemicellulose to xylose (by hydrolysis reaction) and furfural (by dehydration of xylose) are known.¹¹⁻ ¹³ In these methods first hemicellulose in hot water is converted into soluble oligomers, which later in a separate reactor over solid acid catalysts can yield xylose and furfural. Nonetheless, it is essential to produce furfural directly from hemicellulose in a one-pot reaction instead of using xylose or soluble oligomers as the substrates. Recently, one-pot conversion of hemicellulose into xylose and furfural over solid acid catalysts such as zeolites with varying Si/Al ratio in presence of aqueous and biphasic media is shown.^{14,15} Most of the zeolites showed good activity (54% furfural yield at 170 °C), but are observed to be unstable under the reaction conditions.^{14,15} Therefore careful design of the stable catalyst in these reactions is required. In this respect, it is expected that silicoaluminophosphate (SAPO) catalysts can be potential catalyst since they have higher hydrothermal stability (600 °C under 20% steam).¹⁶

In this communication, we reveal the synthesis of SAPO-44, SAPO-11, SAPO-5 and SAPO-46 catalysts having varying properties such as, pore diameter, Si/P ratio (Table S1, Supporting Information), acid amount and type. Further these catalysts were employed in the conversion of hemicellulose to yield xylose, arabinose and furfural (Scheme 1). SAPO-44 catalyst exhibited remarkable activity for furfural synthesis and was observed to be stable under reaction conditions.

Scheme 1. Production of furfural from hemicellulose using solid acid catalyst



Hemicellulose conversions are carried out in a Parr autoclave under 2 bar nitrogen pressure and reaction mixture was analyzed by GC and HPLC (for details, see Supporting Information). With only water as a solvent over

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SAPO-44 catalyst we observed $41\pm2\%$ furfural yield along with $4\pm1\%$ oligomers and $14\pm2\%$ monomers (xylose, arabinose and glucose) formation at 170 °C within 8 h. In the reaction, $86\pm2\%$ conversion of softwood derived hemicellulose could be successfully achieved however the total mass balance was only ca. 59%. In comparison, over HMOR (Si/Al=10) catalyst, $36\pm2\%$ furfural yield was seen with $87\pm2\%$ conversion and ca. 52% mass balance.

The presence of organic solvent along with water improves the furfural formation¹⁵ hence it was decided to carry out the reactions in a biphasic solvent system. In our study, significant improvement in furfural yield $(63\pm 2\%)$ with water+toluene (1:1 v/v) solvent system over SAPO-44 catalyst was observed when reactions were conducted at 170 °C for 8 h. Compared to this water+p-xylene (55±2%) and water+methyl iso-butyl ketone (MIBK) (53±2%) system with 1:1 v/v ratio showed lower furfural yields. To understand the influence of organic solvent on the yields of furfural we calculated partition co-efficient of furfural in these solvents (Table S2, Supporting Information). We found partition co-efficient of 0.73, 0.58 and 0.91 in water+toluene, water+p-xylene, and water+MIBK solvent system, respectively. In case of toluene and pxylene furfural yields are in good correlation with the partition co-efficient observed. However, in water+MIBK system partition coefficient is higher than even in water+toluene but we observed less yields. This may be due to higher miscibility of MIBK in water (19.1 g/L at 20 °C) compared to toluene (0.47 g/L at 20 °C) and p-xylene (0.18 g/L at 20 °C) which leads to a situation wherein degradation or side reactions of xylose and furfural are possible in presence of catalyst. Study on solvent stability under reaction condition revealed that toluene is stable but MIBK forms few of the degradation products which were detected on FID-GC. Incidentally, in the greener aspect also, toluene is considered as a preferred solvent as it has a better life cycle assessment (LCA) value of 2 compared to *p*-xylene and MIBK (LCA=3 and 9, respectively).¹⁷ Taking into account these points further reactions were carried out with water+toluene system.

The catalytic activities of various solid acid catalysts in the conversion of hemicellulose are presented in Figure 1. The SAPO-44 catalyst showed the best catalytic performance by yielding 63±2% furfural (ca. 68% selectivity) directly (one-pot) from softwood derived hemicellulose. Along with furfural over SAPO-44 catalyst, formations of ca. 7±1% oligomers and ca. 6±2% xylose+arabinose were also observed. Softwood hemicellulose consists of ca. 15% glucose and hence under reaction conditions it is converted to yield 5% fructose and 2% 5-hydroxymethyl furfural (HMF). Incidentally, we also observed 5% of unconverted glucose. Isomerization of glucose to fructose over Lewis acid sites and further dehydration of fructose to HMF over Brönsted acid sites is possible since both the acid sites are available on SAPO-44 catalysts as is evidenced by IR studies. The possibility of participation of Lewis acid sites in the isomerization of glucose is already discussed in the literature.¹⁸ In view of the above results, over SAPO-44 catalyst, ca. 88% mass balance is achievable while ca. 92% of hemicellulose is converted. Under similar reaction conditions, in the absence of catalyst very poor (26±2%) furfural yield was attained and only ca. 53% mass balance was observed. Possibility of the thermal reactions (blank reaction) cannot be ruled out as pK_w value of water is 13.99 at 25 °C and it decreases to 11.64 at 150 °C and hence water can act as an acid.¹⁹ The difference in the reaction results for blank and catalytic reactions clearly emphasizes the fact that catalyst plays a major role in diverting the reaction to produce desired products. Besides SAPO-44, other SAPO series catalysts (SAPO-5, SAPO-11, SAPO-46) were also evaluated for the reaction and furfural yield in the range of 30-50% was obtained over these catalysts (Figure 1). Although moderate yields (44-56%) for furfural were possible using zeolite as a catalyst, these catalysts cannot be reused effectively since those undergo morphological changes as is shown earlier.14,15



Figure 1. Evaluation of catalysts for the conversion of softwood hemicellulose to produce furfural. Reaction condition: hemicellulose (0.3 g), catalyst (0.075 g), water+toluene=30+30 mL, 170 °C, 8 h.

To make the process more effective, it is desirable to use concentrated solutions of the substrates. Therefore, we carried out the reactions with 1, 3, 5 and 10 wt% hemicellulose concentration (with respect to water) keeping S/C ratio same. Results showed that furfural formation remains constant ($62\pm1\%$) when 1, 3 and 5 wt% hemicelluloses concentrations solutions were used. However, with the use of 10 wt% hemicellulose solutions lower furfural yield (42%) was observed. This might be due to the formation of by-product (humin) which can be recognized from the dark brown color of reaction solution obtained after reaction.

Figure S1 (Supporting Information) plots the studies on effect of temperature on the reactions. Reaction carried out at 160 °C yields 31±2% furfural, 42±2% monomers and 25±1% oligomers. If reactions are conducted at 170 and 180 °C, similar furfural yields (63±2%) were observed. This suggests that to reach valuable performance, reactions should be done at least at 170 °C. When reactions with furfural as a substrate were carried out with or without Page 3 of 6

catalyst no measurable conversions were observed indicating that furfural does not undergo any conversion under reaction condition.



Figure 2. Recycle runs for SAPO-44 catalyst. Reaction condition: hemicellulose (0.3 g), SAPO-44 (0.075 g), water+toluene=30 +30 mL, 170 °C, 8 h.

The SAPO-44 catalyst could be reused at least eight times almost without loss of any activity (Figure 2). The catalyst recovered from the reaction mixture was simply washed with water and without any further treatment was subjected to next reaction (for detail, see Supporting Information). After 8 h of reaction time, the same conversion (ca. 91%) and furfural yield (64%) were obtained even after 8th reuse of catalyst. Concurrently to affirm the reusability of SAPO-44 catalyst and to check the activity at initial reaction time reactions were carried out for 2 h. The result shows that almost similar furfural yield $(16\pm 2\%)$. 2 h) can be obtained in all the 8 recycle runs. To explain this behavior detailed catalyst characterization studies were conducted. To compare, recycle studies with HMOR catalyst were also carried out and we observed ca. 10% decrease in the activity after each catalytic run (1st run: 51%, 2nd run: 43%, 3rd run: 33%).



Figure 3. XRD patterns of SAPO catalysts.

To understand the morphology of catalysts (fresh and spent) X-ray diffraction (XRD) study was carried out (Figure 3). The XRD pattern for SAPO-44 showed characteristic peaks for CHA structure. The XRD patterns for SAPO-5, SAPO-11 and SAPO-46 also showed characteristic patterns for AFI, AEL and AFS structures, respectively. All the XRD patterns coincided well with those in the literature.²⁰⁻²³ For spent SAPO-44 catalyst XRD peak pattern matches well with the fresh SAPO-44 catalyst. This demonstrates that the crystal structure of catalyst remains same and that it is stable under reaction conditions. XRD patterns for fresh and spent HMOR are presented in Figure S2 (Supporting Information). It can be seen from the peak pattern that spent HMOR has lower peak intensity compared to fresh catalyst and this in turn indicate morphological changes. Moreover in our earlier report it is shown by various physico-chemical characterization (XRD, SEM, N2-sorption, ICP-OES, NH3-TPD and solid state NMR) techniques that zeolites undergo morphological changes.¹⁵

Table 1. Physico-chemical properties of catalysts

Catalyst	Weak acid amount (100- 250°C) (mmol/g) ^a	Strong acid amount (350- 500°C) (mmol/g) ^a	Total acid amount (mmol/g) ^a	Surface area (m²/g) ^b
Fresh SAPO-44	0.7	0.5	1.2	369
Spent SAPO-44	0.6	0.5	1.1	353
Fresh SAPO-5	0.8	0	0.8	309
Fresh SAPO-11	0.3	0	0.3	42
Fresh SAPO-46	0.4	0.4	0.8	132
Fresh HMOR (Si/Al=10)	0.5	0.7	1.2	528
Fresh HUSY (Si/Al=15)	0.1	0.5	0.6	909
Fresh Hβ (Si/Al=19)	0.2	0.7	0.9	761

^aNH₃-TPD study, ^bN₂-sorption study.

TPD-NH₃ was carried out to compare the amount of acid sites of the SAPO and zeolite samples (Table 1). The total acid amount is decreased in the following order, SAPO-44 = HMOR > H β > SAPO-46 = SAPO-5 > HUSY > SAPO-11. While the number of sites with strong acid strength decreased in the sequence of, HMOR = H β > SAPO-44 =HUSY > SAPO-46. In case of SAPO-5 and SAPO-11 only weak acidity is observed while in other catalysts both weak and strong acidity is seen. Thus, this difference in acid amount may influence the catalytic activity as over SAPO-46 higher activity (51%) is observed than SAPO-5 (35%) though both have same total acid amount. The possibility of SAPO-44 undergoing any morphological changes during reaction is ruled out as we observed only marginal difference between the acid amount in fresh and spent catalyst (Table 1). It would be unfair to compare the catalyst activity and acidity correlation between SAPO and zeolite and also only among different zeolites since during reaction those undergo morphological changes as shown earlier.¹⁵

Since in all the reactions water is used as a reaction media we postulated that the presence of water may play an important role in deciding why catalysts behave differently. Hence we examined the effect of water on the catalyst morphology by studying the hydrophilic character of SAPO-44 and HMOR catalyst. The studies were carried out with zeolite, HMOR as amongst all zeolite samples it has a lowest Si/Al ratio and thus is expected to be more hydrophilic in nature. We took same amount of HMOR and SAPO-44 catalysts in two similar test tubes and to it water and organic solvents (either toluene, d=0.86 g/mL at 25 °C or carbon tetrachloride, CCl₄, d=1.58 g/mL at 25 °C) were added by maintaining 1:1 v/v ratio (Figure S₃, Supporting Information). Both the test tubes were stirred vigorously to mix well with the water and organic solvent layers. As observed in Figure S₃ (Supporting Information), after vigorous stirring most of the SAPO-44 is present in water layer however; HMOR is largely present in organic layer. Although the density of SAPO-44 (0.61 g/L) is higher than that of HMOR (0.35 g/L), SAPO-44 was observed to be separated from lower CCl₄ layer due to its higher hydrophilicity. Because of higher hydrophilicity in SAPO-44 catalyst, it prefers to remain in water phase and thus is completely available for hydrolysis and dehydration reactions and at the same time may suppress the degradation reactions. On the contrary HMOR catalyst present in both the layers hampers the hydrolysisdehydration reaction rates and also increases the chances of degradation reactions. This property of SAPO-44 may also help in achieving higher activity and reusability of catalyst.

TGA-DTG profile (Figure S4, Supporting Information) for SAPO-44 shows 7.9% mass loss at 92.7 °C, which corresponds to loss of water. Further loss of o.8% at 400 °C is due to decomposition of remaining structure directing agent (SDA). Further increase in temperature up to 1000 °C did not show any loss indicating that catalyst is stable.

Presence of both Brönsted acid (v_{max}/cm^{-1} 1634 and 1542), Lewis acid (v_{max}/cm^{-1} 1612 and 1452) and Brönsted+Lewis acid (v_{max}/cm^{-1} 1490) sites in SAPO catalysts was proved with pyridine IR analysis (Figure S5, Supporting Information). In SAPO-44 catalysts, the peaks occur at almost similar positions. Though the concentration of acid sites in SAPO-44 measured through TPD-NH₃ is higher compared to SAPO-5, SAPO-11 and SAPO-46, the peak intensity of IR bands for the Lewis and Brönsted acid sites in SAPO-44 are much smaller than those observed in other SAPO catalysts. This might be due to the smaller pore diameter (0.43 nm) in SAPO-44 that hinders the access of pyridine molecules (Figure S6, Supporting Information). This data was in same line with the earlier literate report which described the same observation.²⁴

The cubic morphology for SAPO-44 (Figure S7, Supporting Information) observed in SEM photographs matches well with the literature.²⁵ Apparently we did not observe any change in morphology in fresh and spent catalysts, which indicates that catalyst is stable under reaction conditions. The possibility of leaching of Al and/or P was also verified by subjecting the SAPO-44 catalysts to ICP-OES analysis. As summarized in Table S₃ (Supporting Information), no leaching of Al and/or P during reaction was observed and the result could be equated to the theoretical value (for detail, see Supporting Information). ICP analysis of reaction mixture also supports our above observations (Table S3, Supporting Information). Specific surface area were measured for all catalysts and described in Table 1. Porosity analysis for both fresh and spent SAPO-44 is carried out and the result shows that fresh SAPO-44 has a pore diameter of 0.45 nm and spent SAPO-44 has a pore diameter of 0.49 nm. This data implies that the SAPO-44 catalyst is stable under the reaction condition. However, the fact that SAPO-44 has small pore opening suggest that hydrolysis of hemicellulose may occur on the external acid sites of the catalysts and once saccharides are produced those may undergo further reactions by diffusing inside the pores. All the characterization studies strengthen the fact that SAPO-44 catalyst is highly stable catalyst.

In conclusion, it is shown that SAPO-44 catalyst is very efficient in converting cheaply and abundantly available hemicellulose directly in a one-pot method into furfural with very high yields. The work allows us to eliminate processing hemicellulose in a separate reactor to obtain water soluble fractions first and then further process these fractions in another reactor to obtain furfural. Various physico-chemical characterizations revealed that SAPO-44 is highly stable catalyst and can be reused at least 8 times without losing any activity. The strong hydrophilic nature of SAPO-44 compared to zeolite (HMOR) can be helpful in achieving higher activity. This work tries to establish the fact that in several processes wherein water is an essential part of reaction system, SAPO type of catalysts having high hydrophilic character and hydrothermal stability can be effectively used.

ASSOCIATED CONTENT

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Supporting Information. Detailed description of catalyst synthesis, characterization techniques, materials, experimental process, calculations, partition co-efficient calculation, temperature effect on reaction, catalyst physico-chemical properties are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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