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Efficient, Stable, and Reusable Silicoaluminophosphate for the One-Pot Production of Furfural from Hemicellulose

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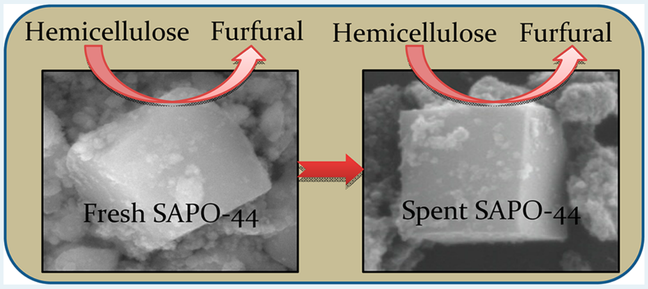
S *Supporting Information*

ABSTRACT: Development of stable, reusable, and water-tolerant solid acid catalysts in the conversion of polysaccharides to give value-added chemicals is vital because 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 a 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 up to at least 8 catalytic cycles. The morphological studies revealed that SAPO catalysts having hydrophilic characteristics are stable under reaction conditions.



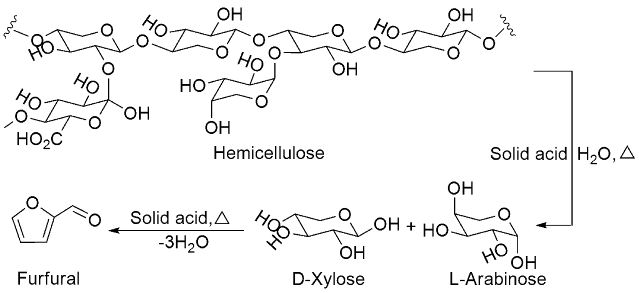
KEYWORDS: *furfural, hemicellulose, hydrophilicity, SAPO, water-tolerant catalyst, zeolite*

Utilization of renewable biomass, particularly nonedible lignocellulosic materials consisting of cellulose, hemicellulose, and lignin serves considerable potential to fulfill our future chemical needs. In this context, furfural, one of the most important platform chemicals derived from biomass emerges as a potential building block[1] for its possible use in the synthesis of value-added chemicals, fuels, and intermediates, such as furfuryl alcohol, 2-methylfuran, 2-methyltetrahydrofuran, phenol formaldehyde 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, Sn-beta zeolite, etc., are reported.[8−10] However, it would be desirable to derive furfural directly from hemicellulose (via xylose formation).

Studies on a 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 ratios in the 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 catalysts because 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



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Hemicellulose conversions are carried out in a Parr autoclave under 2 bar nitrogen pressure, and the reaction mixture was analyzed by GC and HPLC (for details, see Supporting Information). With only water as a solvent over SAPO-44 catalyst, we observed 41 ± 2% furfural yield along with 4 ± 1% oligomers and 14 ± 2% monomers (xylose, arabinose, and glucose) formation at 170 °C within 8 h. In the reaction, 86 ± 2% conversion of softwood derived hemicellulose could be successfully achieved; however, the total mass balance was only ~59%. In comparison, over HMOR (Si/Al = 10) catalyst, 36 ± 2% furfural yield was seen with 87 ± 2% conversion and ~52% mass balance.

The presence of organic solvent along with water improves the furfural formation;[15] hence, it was decided to carry out the reactions in a biphasic solvent system. In our study, significant improvement in furfural yield (63 ± 2%) with a water + toluene (1:1 v/v) solvent system over SAPO-44 catalyst was observed when reactions were conducted at 170 °C for 8 h. Comparing to this water + *p*-xylene (55 ± 2%) and water + methyl *iso*-butyl ketone (MIBK) (53 ± 2%) system with a 1:1 v/v ratio showed lower furfural yields. To understand the influence of organic solvent on the yields of furfural, we calculated the partition coefficient of furfural in these solvents (Table S2, Supporting Information). We found partition coefficients of 0.73, 0.58, and 0.91 in water + toluene, water + *p*-xylene, and water + MIBK solvent systems, respectively. In the case of toluene and *p*-xylene, furfural yields are in good correlation with the partition coefficient observed. However, in the water + MIBK system, the partition coefficient is higher than even in water + toluene, but we observed lower yields. This may be due to higher miscibility of MIBK in water (19.1 g/L at 20 °C) compared with 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 the presence of catalyst. Study of solvent stability under reaction condition revealed that toluene is stable, but MIBK forms few of the degradation products that were detected on FID-GC. Incidentally, in the greener aspect also, toluene is considered as a preferred solvent because 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 the 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 (~68% selectivity) directly (one-pot) from softwood-derived hemicellulose. Along with furfural over SAPO-44 catalyst, formations of ~7 ± 1% oligomers and ~6 ± 2% xylose + arabinose were also observed. Softwood hemicellulose consists of ~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, ~88% mass balance is achievable, whereas ~92% of hemicellulose is converted.

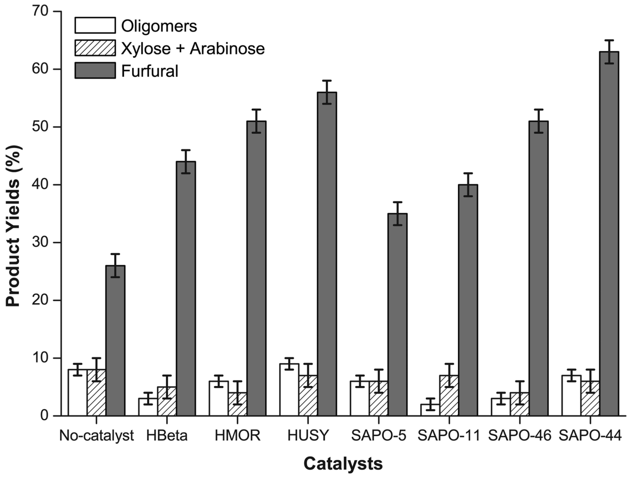

Figure 1. Evaluation of catalysts for the conversion of softwood hemicellulose to produce furfural. Reaction conditions: hemicellulose (0.3 g), catalyst (0.075 g), water + toluene = 30 + 30 mL, 170 °C, 8 h.

Under similar reaction conditions in the absence of catalyst, very poor (26 ± 2%) furfural yield was attained, and only ~53% mass balance was observed. Possibility of the thermal reactions (blank reaction) cannot be ruled out because the pK_w value of water is 13.99 at 25 °C and it decreases to 11.64 at 150 °C; hence, water can act as an acid.[19] The difference in the reaction results for blank and catalytic reactions clearly emphasizes the fact that the catalyst plays a major role in diverting the reaction to produce the desired products.

In addition to SAPO-44, other SAPO series catalysts (SAPO-5, SAPO-11, SAPO-46) were also evaluated for the reaction, and a 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]

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 the S/C ratio the same. Results showed that furfural formation remained constant (62 ± 1%) when 1, 3, and 5 wt % hemicelluloses concentrations solutions were used. However, with the use of 10 wt % hemicellulose solutions, a lower furfural yield (42%) was observed. This might be due to the formation of byproduct (humin), which can be recognized from the dark brown color of the reaction solution obtained after the reaction.

Figure S1 (Supporting Information) plots the studies on the effect of temperature on the reactions. Reaction carried out at 160 °C yields 31 ± 2% furfural, 42 ± 2% monomers, and 25 ± 1% oligomers. When reactions were conducted at 170 and 180 °C, similar furfural yields (63 ± 2%) were observed. This suggests that to reach a valuable performance, reactions should be done at least at 170 °C. When reactions with furfural as a substrate were carried out with or without catalyst, no measurable conversions were observed, indicating that furfural does not undergo any conversion under reaction conditions.

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 the next reaction (for details, see Supporting Information). After 8

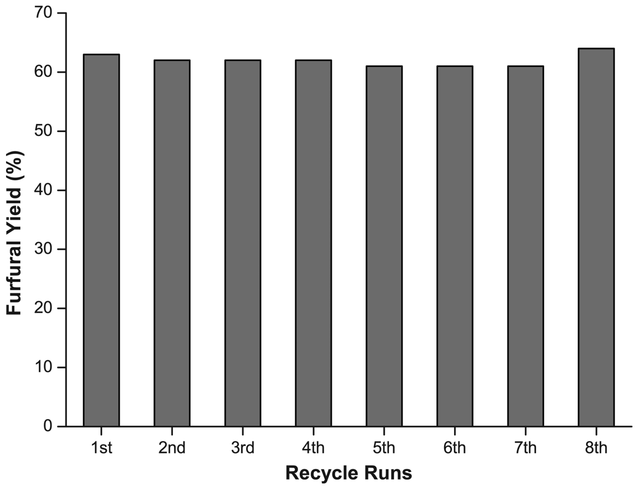

Figure 2. Recycle runs for SAPO-44 catalyst. Reaction conditions: hemicellulose (0.3 g), SAPO-44 (0.075 g), water + toluene = 30 + 30 mL, 170 °C, 8 h.

h of reaction time, the same conversion (~91%) and furfural yield (64%) were obtained, even after the eighth reuse of the catalyst. Concurrently, to affirm the reusability of SAPO-44 catalyst and to check the activity at the initial reaction time, reactions were carried out for 2 h. The result shows that almost similar furfural yields (16 ± 2%, 2 h) could be obtained in all eight 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 an ~10% decrease in the activity after each catalytic run (1st run, 51%; second run, 43%; third run, 33%).

To understand the morphology of the catalysts (fresh and spent) an X-ray diffraction (XRD) study was carried out (Figure 3). The XRD pattern for SAPO-44 showed characteristic peaks for the CHA structure. The XRD patterns for SAPO-5, SAPO-11, and SAPO-46 also showed characteristic patterns for the AFI, AEL, and AFS structures, respectively. All the XRD patterns coincided well with those in the literature.[20−23] For the spent SAPO-44 catalyst, the XRD peak pattern matches well with the fresh SAPO-44 catalyst. This demonstrates that the crystal structure of the catalyst remains the 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 a lower peak intensity compared with fresh catalyst, and this, in turn, indicates morphological changes. Moreover, in our earlier report, it is shown by various physicochemical characterizations (XRD, SEM, N_2-sorption, ICP-OES, NH_3-TPD, and solid state NMR) techniques that zeolites undergo morphological changes.[15]

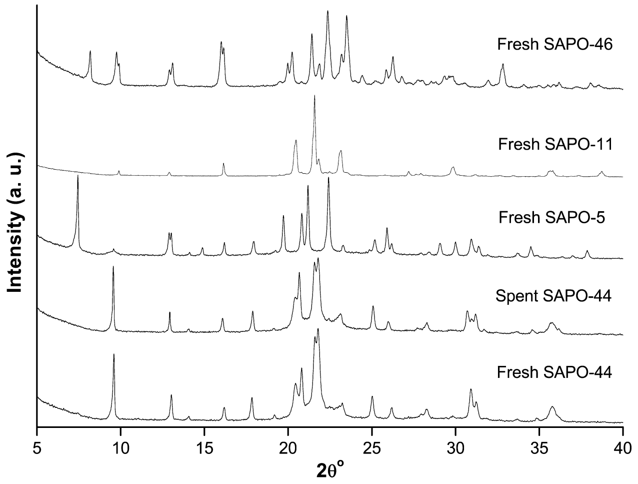

Figure 3. XRD patterns of SAPO catalysts.

TPD-NH_3 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 > Hβ > SAPO-46 = SAPO-5 > HUSY > SAPO-11, although the number of sites with strong acid strength decreased in the sequence of HMOR = Hβ > SAPO-44 = HUSY > SAPO-46. In the case of SAPO-5 and SAPO-11, only weak acidity is observed, whereas in other catalysts, both weak and strong acidities are seen. Thus, this difference in the acid amount may influence the catalytic activity because over SAPO-46, higher activity (51%) is observed than for SAPO-5 (35%), although both have the same total acid amount. The possibility of SAPO-44 undergoing any morphological changes during the reaction is ruled out because we observed only a marginal difference between the acid amount in the 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 because during the 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 because among all zeolite samples, it has the lowest Si/Al ratio and, thus, is expected to be more hydrophilic in nature. We took the 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, CCl_4, $d = 1.58$ g/mL at 25 °C) were added, maintaining a 1:1 v/v ratio (Figure S3, Supporting Information). Both 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 the water layer; HMOR is largely present in the 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 the lower CCl_4 layer because of its higher hydrophilicity. Because of the higher hydrophilicity in the SAPO-44 catalyst, it prefers to remain in the water phase and, thus, is completely available for hydrolysis and dehydration reactions and at the same time may suppress the degradation reactions. In contrast, the HMOR catalyst present in both layers hampers the hydrolysis−dehydration 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 the catalyst.

The TGA-DTG profile (Figure S4, Supporting Information) for SAPO-44 shows a 7.9% mass loss at 92.7 °C, which corresponds to a loss of water. Further loss of 0.8% at 400 °C is due to decomposition of the remaining structure-directing agent (SDA). A further increase in temperature up to 1000 °C did not show any loss, indicating that the catalyst is stable.

Table 1. Physicochemical 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 (m^2 /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

[a] NH_3-TPD study. [b] N_2-sorption study.

The presence of both Brönsted acid (ν_{max}/cm^{-1} 1634 and 1542), Lewis acid (ν_{max}/cm^{-1} 1612 and 1452), and Brönsted + Lewis acid (ν_{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. Although the concentration of acid sites in SAPO-44 measured through TPD-NH_3 is higher compared with SAPO-5, SAPO-11, and SAPO-46, the peak intensity of the 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 the same line with the earlier literature report that 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 the fresh and spent catalysts, which indicates that the 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 details, see Supporting Information). ICP analysis of the reaction mixture also supports our above observations (Table S3, Supporting Information). The specific surface area was measured for all catalysts and is described in Table 1. Porosity analysis for both fresh and spent SAPO-44 was 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. These data imply that the SAPO-44 catalyst is stable under the reaction conditions. However, the fact that SAPO-44 has a small pore opening suggests 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 the SAPO-44 catalyst is a highly stable catalyst.

In conclusion, it is shown that the SAPO-44 catalyst is very efficient in converting inexpensive 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 processing these fractions in another reactor to obtain furfural. Various physicochemical characterizations revealed that SAPO-44 is a highly stable catalyst and can be reused at least eight times without losing any activity. The strong hydrophilic nature of SAPO-44 compared with the 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 catalysts having high hydrophilic character and hydrothermal stability can be effectively used.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed description of catalyst synthesis, characterization techniques, materials, experimental process, calculations, partition coefficient calculation, temperature effect on reaction, catalyst physicochemical properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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