SAPO-34/5A Zeolite Bead Catalysts for Furan Production from Xylose and Glucose

Joelle E. Romo, † Ting Wu, ‡ Xinlei Huang, § Jolie Lucero, † Jennifer L. Irwin, † Jesse Q. Bond, § Moises A. Carreon, †* and Stephanie G. Wettstein* ‡

† Department of Chemical and Biological Engineering, Montana State University, 306 Cobleigh Hall, Bozeman, Montana 59717, United States
‡ Chemical and Biological Engineering Department, Colorado School of Mines, 255 Alderson Hall, Golden, Colorado 80401, United States
§ Department of Biomedical and Chemical Engineering, Syracuse University, 329 Link Hall, Syracuse, New York 13244, United States

ABSTRACT: SAPO-34 zeolite crystals were grown on zeolite 5A beads, characterized, and then used to produce furfural from xylose and 5-hydroxymethylfurfural (HMF) from glucose. The SAPO-34/5A bead catalysts resulted in moderate furfural and HMF yields of 45% from xylose and 20% from glucose (463 K; 3 h) and were easier to recover than the SAPO-34 powder catalyst. At 463 K, the SAPO-34/5A beads were more selective than 0.02 M sulfuric acid for producing HMF and, unlike the sulfuric acid system, no levulinic acid was formed. The SAPO-34/5A bead catalysts had no significant loss in activity after three rounds of recycle when water washed or heated overnight between reactions; however, the heat-treated beads did show signs of thermal stress after the second reuse. The SAPO-34/5A bead catalysts show promise for dehydration reactions to produce furfural and HMF from xylose and glucose, respectively, and tailoring the catalyst and the support bead could lead to even higher selectivities and yields.

1. INTRODUCTION

Increasing energy demands have motivated research for alternative forms of energy and chemicals derived from non-petroleum sources. Biofuels derived from biomass are recognized as viable alternative energy sources, and the production of bio-based platform chemicals is an area of significant interest. Versatile chemical intermediates, such as furfural, 5-hydroxymethylfurfural (HMF), and levulinic acid (LA), can be derived from lignocellulosic biomass, and any of the aforementioned can deliver a variety of fuels and chemical commodities. For example, furfural, identified as one of the top 12 value-added chemicals from biomass by the DOE, has useful applications as a building block for carbon-rich C_{10-15} fuel additives and can be upgraded for incorporation into biofuels, which is achieved through hydrogenation, rearrangement, and carbon—carbon coupling. HMF is a precursor for 2,5-furan dicarboxylic acid, another top 12 value-added chemical, and can be upgraded for many chemical applications.

Existing pathways for furfural and HMF production from lignocellulose are typically energy-intensive and result in only moderate yields. Significant research has been dedicated to producing furfural and HMF using homogeneous acid catalysts such as sulfuric acid and hydrochloric acid; however, homogeneous acids are corrosive, require special handling, and can have negative effects on downstream catalytic processes. Heterogeneous catalysts are an attractive alternative to homogeneous acids, and many researchers have looked at biomass and sugar conversion to furans and other products, including LA.

Different classes of solid acid catalysts have been demonstrated as effective catalysts for both furfural and HMF production, including ion exchange resins, metal oxides, and carbon-based catalysts. Of particular interest are zeolites, which are known for their chemical and thermal stability, versatility, and wide range of pore sizes (0.2 nm to over 1.0 nm) that are available. Zeolites have been widely used in biomass conversion. For example, research by Gao et al. found that xylose dehydration reactions with ZSM-5 resulted in furfural yields of 15.1% in an aqueous system and Ordomsky et al. used MOR, H-ZSM-5, and H-BEA to convert fructose to HMF with selectivities ranging from 30 to 68% at around 80% conversion (165 °C) in an MIBK/H_2O biphasic system. The high HMF selectivity found with MOR was attributed to its high acid site strength compared to other zeolites tested. Other researchers have looked at the use of powdered silicoaluminophosphates (SAPOs), a class of small-pore zeolites, in various solvent systems to maximize furfural production.
production from xylose, achieving moderate yields. For dehydration reactions that are typically favored at higher temperatures, SAPOs are particularly favorable because of their hydrothermal stability, up to 873 K under steam conditions. Additionally, small-pore zeolites have high versatility because of being able to control the physicochemical functionalities such as acidity and hydrophobic—hydrophilic nature. SAPOs with different acidities, pore sizes, and silica to alumina ratios have been used for furfural synthesis in biphasic systems, achieving yields of up to 63% furfural. Other research has shown promising results on powdered catalysts as well.

Despite the general promise of microporous zeolites for sugar dehydration, prior demonstrations have typically been performed with powdered catalysts having average particle sizes on the micrometer scale. Unfortunately, these materials are impractical for utilization in industrial flow reactors because of excessive pressure drop and potential for entrainment. For heterogeneously catalyzed sugar dehydration to be feasible industrially, it is important to demonstrate that sugar dehydrations can be performed on macroscale catalysts, which have additional challenges relative to powdered catalysts. Most significantly in the system of interest here, the small zeolite pore size can create a diffusion-limited system. This is particularly true for substrates like sugars, which have large kinetic diameters. Powdered catalysts are able to mitigate this to some extent as their small particle sizes ensure that the bulk of catalytic active sites remain in relatively close proximity to the external particle surface, that is, they have a short diffusion path. In contrast, pelletized catalysts have large particle sizes and diffusion lengths such that mass transfer limitations are generally severe. Often, the small fraction of catalytic active sites at or near the external surface of the pellet participate in the reaction, while the vast majority of the active sites within the interior of the pellet are inaccessible and thus underutilized.

Hybrid, composite materials offer a potential resolution. Specifically, by depositing a micron-scale layer of the catalyst onto the exterior surface of a macrostructure, all of the active sites remain concentrated in the first few microns of the bead diameter. Thus, the short diffusion path of a powdered catalyst is maintained in an industrially relevant material. Despite their promise, active layers of zeolites grown on a bead support remain an unexplored area of solid acid catalyst use, particularly for furan production. In addition to the aforementioned concerns over diffusion limitations, catalysts will typically undergo some form of deactivation during application and thus be subjected to periodic regeneration. Normally, this occurs through thermal cycling in air (calcination) to oxidize surface carbon and regenerate catalytic active sites. It is critical that industrial catalysts retain their macrostructure through repeated catalyst regeneration cycles, and the thermal stability of composite bead catalysts has not been well established.

In this work, we show that novel SAPO-34/SA bead catalysts can be used for the dehydration of xylose and glucose to furans in aqueous systems, exploring the possible diffusion limitations and catalyst recyclability.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. Figure 1 shows representative scanning electron microscopy (SEM) images of a single composite catalyst bead composed of a SAPO-34 layer grown on zeolite SA. Figure 1a shows the coverage of SAPO-34 crystals collected from the autoclave after synthesis of SAPO-34/SA beads. Figure 2i agrees with the known structure of zeolite SA, which crystallizes in the LTA topology, and after the incorporation of SAPO-34, the XRD pattern of SA beads is preserved (Figure 2ii). The XRD peak of SAPO-34 (Figure 2ii) overlaps with the XRD peak of the SAPO-34/SA beads (Figure 2ii) at 2θ ≈ 16°, suggesting the incorporation of

Table 1. Acidity and Textural Properties of the Materials Used in This Study

| Material     | Brønsted acid sites (μmol/g) | Surface area (m²/g) | Micropore area (m²/g) | Fraction of micropore area |
|--------------|------------------------------|---------------------|-----------------------|---------------------------|
| SAPO-34/SA  | 134                          | 454                 | 378                   | 0.83                      |
| SAPO-34      | 400                          | 520                 | 521                   | 1                         |
| SAPO-34C     | 1100                         | 510                 | 517                   | 1                         |
| 5A bead      | 184                          | 387                 | 332                   | 0.86                      |

Figure 2. (a) XRD patterns of (i) SA beads, (ii) SAPO-34/SA beads, and (iii) SAPO-34 crystals collected during SAPO-34/SA synthesis; (b) representative SEM image of SAPO-34 crystals collected from the autoclave after SAPO-34/SA synthesis.
SAPO-34 on the surface of 5A beads. Also, it was evident from these XRD patterns that the peaks shift slightly for some of these diffraction peaks. The XRD pattern of the crystals collected in the bottom of the autoclave after synthesis (Figure 2iii) corresponded to the CHA topology characteristic of SAPO-34.34 The crystal size of SAPO-34 powders collected from the autoclave after synthesis of SAPO-34/5A beads was approximately 1−5 μm (Figure 2b).

2.2. Xylose Reactions. After 6 h at 423 K, all of the catalysts evaluated dehydrated xylose to furfural to some extent. The SAPO-34/5A beads and 0.02 M H₂SO₄ had the highest furfural yields of 16 and 23%, respectively, and the other catalysts had yields less than 10% and were not significantly different than the system that had no catalyst present (7%; Table 2). This was an unexpected result because both SAPO-34 powders had substantially higher acid site densities than the SAPO-34/5A beads (Table 1); therefore, the powdered catalysts would be expected to be more active and result in higher yields at a given time. However, it is important to note that it is impossible to know how many active sites are accessible to the large sugar molecules and therefore, turn-over frequency may not be representative of the actual activity of the catalyst. The average pore diameter of SAPO-34 is in the range of 0.38 nm,35 which is smaller than the kinetic diameter of xylose (0.68 nm36,37); accordingly, xylose dehydration over the powdered SAPO catalyst is likely to be diffusion-limited. This may explain why the powdered SAPO-34 catalysts show little more than background activity at 423 K. However, the SAPO-34/5A beads had twice the furfural yield than the background activity which may be explained by the higher mesoporosity, whereas both SAPO-34 powders were entirely microporous materials (Table 1). For diffusion-limited systems, it stands to reason that introducing mesoporosity into the SAPO-34 structure would substantially improve catalyst activity by facilitating access to interior Brønsted sites. Similar results have been observed previously with modified H-USY zeolites as reported by Pande et al.38

Increasing the temperature to 443 K significantly increased the furfural yields for all systems (Figure 3). The SAPO-34/5A bead catalyst had a significantly lower furfural yield (32%) than 0.02 M H₂SO₄ (51%) at similar conversions and was within error of the SAPO-34 (34%) and SAPO-34C (27%) powder catalysts (Table 2). Because the powder and the bead yields were similar, the increased mesoporosity of the beads did not seem to affect the reaction at 443 K as much as it may have at 423 K. Further increasing reaction temperature to 463 K led to the highest furfural yield with the SAPO-34/5A beads which was 45% at 95% xylose conversion (Table 2). The furfural selectivities of the SAPO-34 catalysts were in the range of 46−54%, which was at least double that of the 5A beads (21%). The 5A beads had similar Brønsted acidity and micropore area fraction (Table 1) as the SAPO-34/5A bead catalysts, but resulted in significantly lower furfural yields at all temperatures evaluated. One difference between zeolite SA and SAPO-34 is

### Table 2. Xylose Conversion and Furfural Selectivity and Yield for H₂SO₄ and Heterogeneous Zeolites at Different Temperatures

| catalyst          | temperature (K) | time (h) | xylose conversion (%) | selectivity (%) | yield (%)   |
|-------------------|-----------------|----------|-----------------------|----------------|-------------|
| 0.02 M H₂SO₄      | 423             | 6        | 35                    | 66             | 23          |
|                   | 443             | 6        | 82                    | 62             | 51          |
|                   | 463             | 2        | 87                    | 69             | 60          |
| SAPO-34/5A bead   | 423             | 6        | 53                    | 31             | 16          |
|                   | 443             | 6*       | 87                    | 37             | 32          |
|                   | 463             | 3        | 95                    | 47             | 45          |
| SAPO-34 powder    | 423             | 6        | 27                    | 31             | 8           |
|                   | 443             | 6        | 80                    | 43             | 34          |
|                   | 463             | 3        | 85                    | 46             | 39          |
| SAPO-34C powder   | 423             | 6        | 17                    | 37             | 6           |
|                   | 443             | 6*       | 53                    | 51             | 27          |
|                   | 463             | 3        | 57                    | 54             | 31          |
| 5A bead           | 423             | 6        | 75                    | 13             | 10          |
|                   | 443             | 6        | 95                    | 20             | 20          |
|                   | 463             | 3        | 97                    | 21             | 21          |
| no catalyst       | 423             | 6        | 10                    | 69             | 7           |
|                   | 443             | 6        | 41                    | 51             | 21          |
|                   | 463             | 3        | 58                    | 54             | 31          |

*aReaction conditions: 2 wt % xylose, 4 mL H₂O, and 0.02 M H₂SO₄ or 0.048 g of catalyst. Experimental error is ±4%, based on multiple trials of reactions marked with an asterisk.

![Figure 3. Effect of temperature on furfural yield at 443 K (6 h; gray) and 463 K (3 h for all except H₂SO₄ at 2 h; black). Reaction conditions: 2 wt % xylose, 4 mL H₂O, and 0.02 M H₂SO₄ or 0.048 g of catalyst.](image-url)
the framework structure. The SA zeolites have an LTA framework with a pore size of 0.41 nm and interior cages that can include molecules up to 1.1 nm, while SAPO-34 has a CHA framework with 0.38 nm pores and cages that can include molecules up to 0.74 nm.21 This may affect the product selectivity39 because furfural degradation generally occurs through condensation,3 which may be more facile in the more open cages of LTA.

The effect the catalysts had on the reaction kinetics was more evident when conversion was compared with time at 443 K (Figure 4). The xylose conversion of all catalysts systems was at least double that of the no catalyst system at a given time, excluding the SAPO-34C powder. With the exception of SA beads, for which furfural selectivities range from 15 to 20%, the heterogeneous catalysts had furfural selectivities generally in the 30−55% range over the reaction times presented (Table 2), which resulted in furfural yields of approximately half of the xylose conversion (Figure 5). The SAPO-34/5A bead and SAPO-34 powder catalysts showed similar kinetic trends to the 0.02 M H₂SO₄ system where the furfural yield increased through 8 h and then the yield decreased at 24 h (not shown). For these systems, the xylose conversion was above 80% at 8 h, and the decrease in furfural yield at 24 h was likely due to degradation reactions, which lead to formation of humins and other by-products. The SA bead catalyst had the highest xylose conversion at a given time, but had the lowest furfural yields. The increased activity of the SA bead catalyst relative to all other systems may have several causes. First, the slightly larger pore size and increased mesoporosity (Table 1) of the SA catalyst may decrease mass transfer resistance relative to the SAPO-34 based systems. In addition, after reaction, the SA beads showed signs of partial and sometimes complete disintegration. Because the SA beads were held together using a binder and not composed of a single crystal, partial dissolution of the bead may have created a suspension of fine LTA particles in solution, which would, generally, increase access to active sites relative to intact beads.

### 2.3. Recyclability.

The retention of the SAPO-34/SA bead structure in multiple use recycle reactions is critical to the demonstration of the feasibility of the composite catalysts. Recyclability experiments were performed after catalyst regeneration by (1) only washing catalysts with water and (2) not washing the catalyst and only heating it overnight at 523 K. The catalysts showed good performance after three times recycling with the water washing (Figure 6; gray bars) and overnight heating led to a slight increase in furfural yield during the third reuse compared to the nonheated sample (Figure 6; black bars). The decrease in catalyst activity seen for SAPO-34/SA with the second water washing was within experimental error but may be attributed to the blocking of acid sites from surface deposition of carbonaceous species. Similar conclusions have been previously reported for SAPO-34 in other research studies.24,40 Suprun et al. hypothesized that the relatively high acidity and small pores of SAPO-34 are both factors that lead to accumulation of carbonaceous deposits blocking its surface.40 The overnight heating process could remove some of these species, regenerating more acid sites than with just water washing thus, maintaining activity.

The water-washed beads maintained their structure and after the third reuse, the beads still had a spherical shape with no significant mass loss. However, after the second reuse, several of the heat regenerated SAPO-34/SA beads had cracked.
resulting in nonspherical beads with approximately 38% mass loss (Figure 7a). This damage likely occurred because of thermal stressing since the water-washed beads did not show signs of cracking. In a third reuse, the heat-regenerated SAPO-34/SA beads still showed good activity, and the SAPO-34 layer remained intact and was a similar thickness (Figure 7b) to the starting beads (Figure 1b).

2.4. Glucose Reactions. Starting with glucose led to a moderate amount of HMF formed at 443 K (6 h) and 463 K (3 h) for all heterogeneous catalysts tested (Figure 8). The SAPO-34/SA bead catalyst resulted in the highest HMF yield (20%) with no detectable amount of LA formed, while the SAPO-34C and SAPO-34 powders had HMF yields within the experimental error (19 and 18%, respectively). The reaction solutions from all SAPO-34 catalysts also had fructose peaks present after reaction, indicating that the acid sites isomerized the glucose to fructose, whereas no fructose peak was present for the H₂SO₄ system. Although the yields with the SAPO catalysts were low to moderate, it is worth noting that they had a molar composition of 1.0 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:1.0 tetraethylammonium hydroxide (TEAOH):0.16 dipropylamine (DPA):200 H₂O, similar to that reported elsewhere. To prepare the gel, aluminum isopropoxide [Al(i-C₃H₇O)₃, Sigma-Aldrich 98% (all U.S. suppliers)] and deionized water were stirred for another 2 h under stirring. Ludox AS-40 colloidal silica was added (Sigma-Aldrich, 40 wt % suspension in water) and the resulting solution was transferred into a 45 mL stainless-steel autoclave containing 5 g of pure zeolite SA beads. Zeolite SA beads were selected because of their chemical, thermal, and mechanical stability. Hydrothermal synthesis was carried out in a conventional oven at 503 K for 6 h. After the autoclave was cooled to room temperature using a cold water bath, the SAPO-34-covered SA beads were taken out from the autoclave, washed with deionized water, and dried at 373 K overnight. To remove the templates, the SAPO-34/SA beads were calcined using an oven at 763 K for 4 h with heating and cooling rates of 0.8 K/min.

4. METHODS

4.1. Catalyst Preparation. The SAPO-34 synthesis gel had a molar composition of 1.0 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:1.0 tetraethylammonium hydroxide (TEAOH):1.6 dipropylamine (DPA):200 H₂O, similar to that reported elsewhere. To prepare the gel, aluminum isopropoxide [Al(i-C₃H₇O)₃, Sigma-Aldrich 98% (all U.S. suppliers)] and deionized water were stirred for another 2 h under stirring. Ludox AS-40 colloidal silica was added (Sigma-Aldrich, 40 wt % suspension in water) and the resulting solution was stirred for another 2 h under stirring. Ludox AS-40 colloidal silica was added (Sigma-Aldrich, 40 wt % suspension in water) and the resulting solution was stirred for another 2 h under stirring. Ludox AS-40 colloidal silica was added (Sigma-Aldrich, 40 wt % suspension in water) and the resulting solution was stirred for another 2 h under stirring. Ludox AS-40 colloidal silica was added (Sigma-Aldrich, 40 wt % suspension in water) and the resulting solution was stirred for another 2 h under stirring.

4.2. Catalyst Characterization. The synthesized SAPO-34/SA beads were inspected by XRD using a Siemens Kristalloflex 810 diffractometer operating at 30 kV and 25 mA with Cu Kα1 radiation (λ = 1.54059 Å). The morphology of the samples was inspected by SEM model JEOL JSM-7000F.

Specific surface areas were determined from Brunauer–Emmett–Teller analysis of N₂ physisorption isotherms at 77 K. t-Plot analysis of the same isotherms was used to determine the micropore area for each sample. N₂ uptake isotherms were obtained using Micromeritics ASAP 2020. Each experiment...
used roughly 75 mg of catalyst, and all samples were outgassed under vacuum at 623 K for 4 h prior to N₂ dosing.

Bronssted site densities were determined from molar quantities of ethylene evolved between 470 and 870 K during temperature-programmed desorption of ethylamine.\textsuperscript{15} Approximately 70 mg of catalyst was loaded into a quartz tube (1/2") on top of a quartz wool plug, and the tube was positioned in a high-temperature furnace (Omega) and connected to a gas flow manifold. Prior to analysis, catalysts were calcined in situ at 673 K for 4 h under 50 mL min\(^{-1}\) of air (Airgas, Ultra Zero). Subsequently, samples were cooled to 423 K and purged with 100 mL min\(^{-1}\) of He that was dried over molecular sieves. After pretreatment, the samples were held at 423 K and contacted with ethylamine (99%, Sigma). Ethylamine was introduced into the He stream (60 mL min\(^{-1}\)) by vaporization of liquid ethylamine through a 50 μm capillary tube. The point of ethylamine surface saturation was determined by monitoring the off-gas with a mass selective residual gas analyzer (Stanford Instruments RGA 100). After ethylamine saturation, the cell was purged with He (423 K, 400 mL min\(^{-1}\)) for 1 h and subsequently ramped to 973 K (10 K min\(^{-1}\)). The sweep gas for this experiment contained 1.0 mol % Ar, which was used as an internal standard to facilitate quantitative analysis. During the temperature ramp, the cell effluent was monitored using a mass selective residual gas analyzer (Stanford Instruments RGA 100). Signals corresponding to ethylamine (m/z = 30), ethylene (m/z = 27), and Ar (m/z = 40) were monitored continuously. Bronsted site densities were calculated from evolved ethylene based on the assumption that one molecule of ethylene forms at one accessible Bronsted site.

### 4.3. Catalytic Reactions
Reactions were performed in 15 mL pressure tube reactors with magnetic stirring. Reactors were heated in a silicone oil bath held at the reaction temperature by a heated stir plate. For a typical reaction, 2 wt % xylose (Sigma-Aldrich, X1500) or glucose (Fisher Scientific, D16-500), 4 mL H₂O, and the catalyst were added to the reactors with a stir bar and sealed. SAPO-34 powder was purchased commercially (ACS Material) and used as received. To differentiate between the SAPO-34 powder that was synthesized (SAPO-34 powder) and the commercial SAPO-34 (SAPO-34C), a “C” will be used for the commercial SAPO-34 powder. The heterogeneous catalysts were stored in a 403 K oven overnight to remove water prior to reaction. Either 0.02 M sulfuric acid (H₂SO₄) or 0.048 g of catalyst was added to the pressure tube, and the sealed pressure tubes were placed in the heated oil bath. The mass of the heterogeneous catalyst was the same for both the powder and bead catalysts. After the reaction, external airflow was used to cool the reactors to room temperature. Products were analyzed by high-performance liquid chromatography (Agilent 1100, Bio-Rad Aminex HPX-87H column, trifluoroacetic acid mobile phase) with a refractive index detector and diode array detector.

For the recrystallizability experiments, two methods were used to regenerate the SAPO-34/SA bead catalysts. A fresh catalyst was used in 6 h xylose reactions that were run as described previously, and for both methods, the catalysts were recovered after reaction using tongs. For the first method, the recovered catalyst was washed with water five times and then used for a 6 h xylose reaction and the process was repeated. For the second method, no washing occurred, but the catalyst was placed in a 523 K oven overnight. The regenerated catalysts were then used again for a 6 h xylose reaction as described above.

### 4.3.1. Effect of Recycling Catalysts

For this experiment contained 1.0 mol % Ar, which was used as an internal standard to facilitate quantitative analysis. During the temperature ramp, the cell effluent was monitored using a mass selective residual gas analyzer (Stanford Instruments RGA 100). Signals corresponding to ethylamine (m/z = 30), ethylene (m/z = 27), and Ar (m/z = 40) were monitored continuously. Bronsted site densities were calculated from evolved ethylene based on the assumption that one molecule of ethylene forms at one accessible Bronsted site.
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