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Production of 1,6 Hexanediol from Tetrahydropyran-2-methanol by Dehydration-Hydration and Hydrogenation

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In this work we present an alternate method for the conversion of tetrahydropyran-2-methanol (THP2M), a cellulosederived renewable building block, to 1,6-hexanediol (1,6-HDO). Our method is composed of three consecutive steps that either use relatively inexpensive catalysts or no catalyst at all. First, THP2M is catalytically dehydrated to 2,3,4,5tetrahydrooxepine (THO) in up to 40% yield. THO is then hydrated to 2-oxepanol (OXL) and 6-hydroxyhexanal (6HDHX) with a combined yield of 85% in the absence of a catalyst. OXL and 6HDHX are then quantitatively hydrogenated to 1,6-HDO over a commercially available Ni/C or Ru/C catalyst. Various silicoaluminates were screened for the first acidcatalyzed reaction, and it was found that K-BEA shows the highest THO yield (40% over fresh catalyst, 20 % after 25h on stream). An overall 1,6-HDO yield of 34% from THP2M was obtained.

Introduction

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Terminal diols such as 1,4-butanediol (1,4-BDO) and 1,6hexanediol (1,6-HDO) are important building-block chemicals and find application in the synthesis of specialty chemicals and a variety of polymers, primarily in polyesters and polyurethanes, and polyamides such as nylon-6,6.^{1,2} Their synthesis from petrochemical resources involves multiple reaction steps, and produces significant amounts of by-products. Therefore, sustainable catalytic systems that could use a renewable feedstock such as biomass are desired. In particular for short chain diols such as ethylene glycol and 1,4-BDO,^{3,4} renewable alternatives have recently been proposed in the literature. Currently, 1,6-HDO is produced industrially from cylohexanone/cyclohexanol (KA oil) by oxidation with nitric acid to form adipic acid, followed by hydrogenation of the dimethoxy ester to yield 1,6-HDO. The attractiveness of the overall process is tempered by low conversions (4-8% for the oxidation of KA oil), difficult separations, the use of non-renewable fossil feedstocks, and emission of greenhouse gasses, namely N2O.⁵ Most recently an alternative route to 1,6-HDO via hydroformylation of 1.3-butadiene was proposed.⁶ Although showing high yields, the use of homogeneous Rh complexes as catalyst and the multistep process hampers its industrial applicability.⁶ Various attempts to synthesize 1,6-HDO, as well as other α,ω -diols, from biomass resources have been reported. Using supported catalysts that contain precious metals with a reducible metal oxide such as Pt-ReOx,⁷ Rh-ReOx,⁸⁻¹⁴ and Ir-ReOx,^{15,16} tetrahydropyran-2-methanol (THP2M), a biomass-derived feedstock,¹⁷ can be converted into 1,6-HDO with high selectivity. However, the high cost of the catalyst, in combination with a low productivity, limits the industrial applicability of those systems.¹⁸

The dehydration of THP2M to 2,3,4,5-tetrahydrooxepine (THO) over amorphous silicoaluminates was observed in the 1960s.^{19,20} THO can then be re-hydrated to 2-oxepanol (OXL) and 6hydroxyhexanal (6HDHX), both of which can be subsequently hydrogenated to 1,6-HDO giving an overall yield as high as 29%.² Slightly higher 1,6-HDO yields were achieved using a copper chromite catalyst for the initial dehydration, but this introduces a toxic metal that could make this system environmentally harmful.²⁰⁻ ²² No time-on-stream data were reported to assess the stability of these catalysts. Moreover, only amorphous catalysts were tested for the dehydration reaction. This opens the door for a wide range of zeolites to be tested, which have been found to outperform their amorphous counterparts in many reactions.^{23,24} The shape selectivity of zeolites is also ideal for biomass conversion, because the choice of framework can be used to encourage production of oxygenated products, aromatics, or larger polymers.

In this study, we present a three-step approach for the synthesis of 1,6-HDO from THP2M *via* THO (see Scheme 1).





In a first step, THP2M is dehydrated to THO over BEA zeolites, followed by hydration to OXL, which is in equilibrium with 6HDHX. Finally, 6HDHX and OXL are hydrogenated to 1,6-HDO over Ru/C or Ni/C. In this work, we present the highest reported overall yields to 1,6-HDO from THP2M using a silicoaluminate as a dehydration catalyst, and without the use of expensive metals such as Pt, Ir, and Rh. We show effects of the framework topology and exchange

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cation on THO yields and present a catalytic system for a renewable route to 1,6-HDO.

Results

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THP2M Dehydration

Initial experiments on the catalytic conversion of THP2M into THO were performed over Na-BEA (SiO₂/Al₂O₃ = 25) and compared with an amorphous $SiO_2-Al_2O_3$ ($SiO_2:Al_2O_3 = 13$) benchmark catalyst similar to that reported earlier²⁰ for this reaction (see Figure 1). The SiO₂-Al₂O₃ catalyst used in a previous study is no longer commercially available.²⁰ The SiO₂-Al₂O₃ used in this study produced low THO yields over a temperature range from 330 to 430 $^{\circ}$ C (see Figure S1). Amorphous SiO₂ did not show any activity towards THO, and over Al₂O₃ primarily cyclopentanecarbaldehyde (CPC) was produced. Na-BEA was initially selected because sodium was previously reported to enhance the THO yield in the case of amorphous SiO₂-Al₂O₃.²⁰ Ion-exchange of commercial H-BEA was conducted with a 1M aqueous NaNO₃ solution resulting in a Na/Al molar ratio of 0.66 (exchange ratios of all zeolites synthesized in this manner can be found in Table S1). Na-BEA shows higher THO yields compared to amorphous SiO₂-Al₂O₃, suggesting that the pore structure and/or Na⁺ incorporation influence the catalytic performance.



Figure 1. THP2M dehydration over Na-BEA (\Box , SiO₂:Al₂O₃ = 25) and amorphous SiO₂-Al₂O₃ (•, SiO₂:Al₂O₃ = 12). Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate, STP), 30 mL/min (STP) H₂, 1 atm, 150 mg catalyst. Error bars shown are the result of four identical tests with Na-BEA. Error bars are assumed to be the same for each catalyst in this study.

Na-exchanged zeolites with SiO₂:Al₂O₃ ratios of 20-30 were screened for THP2M dehydration to investigate the influence of the zeolite topology on the catalytic activity. Out of the four tested framework types—MFI, MOR, FAU, BEA—the latter shows the highest yields towards THO (see Figure 2). As this is an acid-catalyzed dehydration, Temperature Programmed Desorption of NH₃ (NH₃-TPD) was performed (see Table 1, Figure S2) to rationalize the differences in activity between the various zeolite frameworks.

The curves in Figure S2 were fitted to identify individual acid sites responsible for NH₃ desorption at specific temperatures, which is displayed in Table 1. From this point on, all acid sites that desorb NH_3 in the range of 150-230 $^{\circ}C$ will be denoted as weak acid sites. Those that desorb NH₃ in the range of 230-350 °C will be denoted as moderate-strength acid sites, and we will not show any strong acid sites.²⁶ According to Table 1, Na-BEA, the framework with the highest yields to THO, has a weak and a moderate acid site. Na-ZSM-5 and Na-MOR also have a weak and moderate acid site (in different concentrations). The latter two catalysts produce much less THO than Na-BEA, so it is not immediately obvious which is the active site for THO production. Furthermore, Na-Y has no moderate acid site, and yet shows higher THO yields than Na-ZSM-5 and Na-MOR at nearly every time-on-stream. This would seem to indicate that the weak acid site is active for THO production, and the moderate site is not.



Figure 2. THO yields (a) and THP2M conversion (b) over Naexchanged zeolites. Reaction conditions: 400 $^{\circ}$ C, 0.628 mL/hr THP2M (liquid flow rate, STP), 30 mL/min (STP) H₂, 1 atm, 150 mg catalyst.

Temperature programmed oxidation (TPO) experiments in a ThermoGravimetric Analyzer (TGA) were done to investigate the cause of deactivation. Spent catalysts were heated to 600 °C (ramp

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rate 5 °C/min) under a flow of air. Each spent catalyst shows a mass loss in the range of 16 to 37% during heating in air, due to coking over the course of the reaction (see Table S2, Figure S4). These experiments show that the less active zeolites (Na-ZSM-5 and Na-MOR) produce roughly half the amount of coke than do more active zeolites (Na-Y and Na-BEA).

Table 1. NH_3 desorption signals fitted for strong, moderate, and weak acid Sites on Na-exchanged zeolites. Ramp Rate = 10 °C/min



Figure 3. THO yields (a) and THP2M conversion (b) over alkaliexchanged BEA zeolites. Reaction conditions: 400 $^{\circ}$ C, 0.628 mL/hr THP2M (liquid flow rate, STP), 30 mL/min (STP) H₂, 1 atm, 150 mg catalyst.

BEA samples exchanged with each alkali metal were prepared to determine the effect of the exchange cation on THO yields. Moreover, the THO yields of these catalysts were compared with those of H-BEA, *i.e.* the starting material in the synthesis of all BEA zeolites in this study. The catalysts display clear differences in THO yields (see Figure 3), however, no clear periodic trend among the catalysts with regards to THO production is immediately observed. K- and H-BEA show the highest THO yields amongst the tested catalysts with initial yields of up to 40% for K-BEA. Furthermore, as shown in Figure 3b, Rb- and Cs-BEA show the lowest conversions at all times-on-stream. This will be addressed further later.

We regenerated the spent K- and H-BEA catalysts under flowing air at 580 $^{\circ}$ C and then retested their catalytic activity as shown in Figure 4. K-BEA has the higher initial and final yields compared to H-BEA, with the highest single-point yield of 40% obtained after 7 hours on stream in the first cycle. It appears that for both catalysts the initial activity cannot be fully recovered even after regeneration. However, after the second regeneration the catalyst does not continue to lose activity.



Figure 4. Regeneration of K-BEA (\Box) and H-BEA (X). Reaction conditions: 400 °C, 0.628 mL/hr THP2M (liquid flow rate, STP), 30 mL/min (STP) H₂, 1 atm, 150 mg catalyst.

NH₃-TPD was performed on the alkali-exchanged BEAs (see Table 2, Figure S3). NH₃ desorption below 150 °C is likely due to physisorbed NH₃, as seen previously.^{27,28} It is clear that Rb- and Cs-BEA are less acidic than the other catalysts. This correlates with low conversions obtained with these catalysts. Next, Li- and Na-BEA have similar TPD profiles to each other, with large quantities of a weak acid site and comparable quantities of a moderate acid site. Figure 3a shows that these catalysts produce less THO than K- and H-BEA, but more than Rb- and Cs-BEA. Finally, K-BEA shows more weak acid sites than Rb- and Cs-BEA, and essentially no moderate acid sites. K-BEA is the best of all metal-exchanged catalysts in terms of THO yield, as shown by the data in Figure 3a. These observations are in line with our working hypothesis that the weak acid site is responsible for THO production. Furthermore, the parent catalyst, H-BEA, shows high levels of this weak acid site, along with a smaller, but still significant amount of moderate acid sites. H-BEA

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has a higher ratio of weak sites to moderate sites than any other catalyst except K-BEA. This, along with the fact that K- and H-BEA are the two catalysts in this study that have the highest THO yield, further supports the weak acid site being active for THO production.

Table 2. NH_3 -desorption signals fitted for strong, moderate, and weak acid Sites on alkali-exchanged BEAs. Ramp Rate = 10 °C/min

Catalyst	NH ₃	Assignment	Quantity
	Desorption		Desorbed
	Temp. (°C)		(µmol NH₃/g
			catalyst)
H-BEA	144	Physisorbed NH ₃	150
	161	Weak Acid	615
	289	Moderate Acid	89.8
Li-BEA	176	Weak Acid	669
	258	Moderate Acid	135
Na-BEA	174	Weak Acid	549
	238	Moderate Acid	214
K-BEA	174	Weak Acid	399
	290	Moderate Acid	7.02
Rb-BEA	142	Physisorbed NH ₃	74.9
	168	Weak Acid	145
Cs-BEA	151	Weak Acid	55.3
	244	Moderate Acid	21.7

FTIR of adsorbed pyridine was performed on each catalyst to determine the Brønsted/Lewis acid nature of the active site for THO production. Pyridine was adsorbed on dehydrated samples at 25 °C, which were subsequently heated to 250 °C under a flow of dry N₂. Table 3 shows the Brønsted and Lewis acid concentrations for each catalyst. Concentrations were calculated by multiplying the Brønsted/Lewis acid ratios—determined by FTIR—by the overall concentration of acid sites—determined by NH₃-TPD (physisorbed NH3 was not included in this calculation). H-BEA shows much more Brønsted acid sites (an order of magnitude in most cases) than all other catalysts. This indicates that the aqueous ion-exchange performed for the synthesis of the metal-exchanged catalysts effectively exchanges with Brønsted sites.

Table 3 also shows that the two catalysts that have the highest THO yield—K-BEA and H-BEA—have Brønsted acid concentrations that differ by nearly two orders of magnitude, while their Lewis acid concentrations differ by only a factor of two. This indicates that Brønsted acids are irrelevant towards THO production, and Lewis acids are the active sites. This, along with the data from NH_3 -TPD, leads us to the conclusion that THO production from THP2M is catalyzed by weak Lewis acid sites.

TPO was used to characterize the alkali-exchanged catalysts after reaction (Table S2, Figure S5). As expected, Rb- and Cs-BEA show the least amount of mass loss due to coking, as these are the least active catalysts (similar effect seen with Na-MOR and Na-ZSM-5). Furthermore, Li- and Na-BEA show 1.2-1.9 times the amount of coke that other BEA catalysts produce. In fact, Table S2 and Figure S5 show that the amount of coke formed on BEA catalysts is directly related to the concentration of moderate-strength acid sites on the catalyst. Table S2 and Figure S4 show that this trend does not apply for other frameworks. This could be due to several reasons, such as the possibility that the frameworks with five-membered rings (MFI and MOR) are inaccessible by the reactant or certain intermediates, thus decreasing reactivity and coke formation.

Table 3. Brønsted/Lewis acid concentrations determined by FTIR of pyridine remaining on each catalyst at 250 °C after adsorption at 25 °C. 1540 cm⁻¹ band used for Brønsted site, 1450 cm⁻¹ band used for Lewis site.²⁹ Extinction coefficients shown in Experimental Section.

Catalyst	Brønsted Acid	Lewis Acid
	Concentration	Concentration
	(µmol/g catalyst)	(µmol/g catalyst)
H-BEA	483	222
Li-BEA	322	482
Na-BEA	84.0	679
K-BEA	11.4	394
Rb-BEA	4.63	140
Cs-BEA	3.09	73.9
Na-Y	25.7	348
Na-MOR	199	1140
Na-ZSM-5	78.9	892

Complete product distributions for all dehydrations can be found in the supporting information (see Tables S5-S13 and Table S4 for explanation of abbreviations). Carbon balances in the range of 75-90% can be attributed to coke formation and a large amount of insoluble carbon compounds in the reactor effluent, which could not be accurately quantified. THO selectivity as high as 58% for H-BEA at 28% conversion was obtained.

Figure 5 shows the major products of THP2M dehydration at four different contact times over K-BEA. Scheme 2 shows a possible reaction pathway based on Figure 5. Yields to 6,8dioxabicyclooctane (DBO)-while relatively low at all contact times-decrease with increasing contact time, indicating it is formed early in the reaction network. Yields to tetrahydropyran-2carbaldehyde (THP2C) stay relatively constant with contact time. However, not shown in the figures, THP2M conversion increases with increasing contact time, meaning the selectivity to THP2C drops with increasing contact time. This supports the hypothesis that THP2C is indeed formed early in the reaction sequence, as shown in Scheme 2. The fact that yields to THO reach a maximum at an intermediate contact time indicates that it can be degraded into further reaction products, also shown in Scheme 2. This would explain why we were unable to obtain higher THO yields with these catalysts; at low contact times, THO intermediates are formed, while at higher contact times, THO degradation occurs. Oxepane (OXE), (CPC), cyclopentanecarbaldehyde 5-hexenal dihydromethylpyran (DMP), and 2-methylcyclopentanone (2MCP) increase in yield with increasing contact time, indicating that they are among the degradation products formed late in the reaction network. Due to the high cost and unavailability of reaction intermediates (including THO) in their pure forms, we could not Published on 06 February 2017. Downloaded by University of Florida Libraries on 07/02/2017 08:11:04

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perform reactions using each intermediate as a reactant. These experiments would provide a more definitive reaction network, and should be part of the scope of future work. In our current work, Scheme 2 represents a possible reaction pathway supported by our data and similar reactions in the literature.³⁰⁻⁴⁰



Figure 5. Product distribution with changing catalyst contact time (a), same data zoomed in on byproducts (b). Low time-on-stream (4 hrs) was used for all measurements to minimize the effects of coking, although this led to relatively low carbon balances, in the range of 77-79% for each measurement. K-BEA used for each test.

The final desirable step in our network, that is, the dehydration of DBO to THO, cannot be found in literature, as the mechanism of THO formation has not been studied. We have already shown that DBO is likely formed early in the reaction network, and DBO is the only product formed early in the reaction network that has a sevenmembered ring. It seems likely, therefore, that THO is formed from the dehydration of DBO. The portrayal of DBO in Scheme 2 shows that one oxygen atom of DBO is part of a seven-membered ring, and the other (bridging) oxygen is part of a five-membered ring. To find out which of these sites is more prone to dehydration to THO, quantum-chemical calculations were performed. The C-O-C bond angle of the oxygen in the seven- membered ring in DBO was compared to that of the same bond in OXE, the fully hydrogenated

seven-membered cyclic ether (see Table S3). Furthermore, the C-O-C bond angle of the oxygen in the five-membered ring of DBO was compared to that of the same bond in tetrahydrofuran (THF), the fully hydrogenated five-membered cyclic ether. Table S3 indicates that the C-O-C bond in the five-membered ring of DBO is more strained than that of the seven-membered ring. The C-O-C bond angle of the DBO five-membered ring is 8.0° smaller than that of THF, while the C-O-C bond angle of the DBO seven-membered ring is only 2.4° smaller than that of OXE. The higher strain on the oxygen atom in the five-membered ring of DBO (bridging oxygen) indicates that it is the less stable bond. Moreover, Table S3 shows that the C-O bonds in the five-membered ring of DBO is 0.013 Å longer than the C-O bonds in the seven-membered ring of the same compound, once again indicating that the oxygen in the fivemembered ring is more reactive. If DBO dehydrates at the oxygen in the five-membered ring, it will likely form THO. Therefore, our calculations indicate that DBO could be the precursor to THO.



OXE **Scheme 2.** Possible reaction network for dehydration of THP2M (major products shown).

THO Hydration

The product from THP2M dehydration over K-BEA was then subjected to hydration conditions to produce OXL and 6HDHX from THO (see Scheme 1). The hydration of the THO in the reaction mixture proceeded homogeneously in water at 70 °C for 5h in an autoclave. This resulted in the complete conversion of THO and the formation of one main gas chromatogram (GC) signal. Nuclear Magnetic Resonance (NMR) spectroscopy was performed on the product mixture. As shown in the Quantitative ¹³C NMR spectrum in Figure 6, there exists two compounds that are only surpassed in intensity by unconverted THP2M from the dehydration step.^{41,42}

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The relative ratio of peak intensities of THP2M to the two unknown species in ¹³C NMR matches those of THP2M to the hydration product in GC analysis, indicating these are indeed the hydration products and that their GC peaks overlap one another. The NMR peak at 91.38 ppm is very likely the hemiacetal carbon of OXL, the direct hydration product of THO. The NMR peak at 209.31 ppm is indicative of an aldehyde, likely 6HDHX, the ring-opened tautomer of OXL (see Scheme 1). This is further evidenced by Dept. 135 NMR analysis (see Figure S7),^{41,42} which indicates both peaks are either primary or tertiary carbons, likely the primary carbons of OXL and 6HDHX. Heteronuclear single quantum correlation (HSQC) and heteronuclear multiple bond correlations confirmed the 6 carbons of each hydration product (see Figs. 6 and S7).^{41,42}



Figure 6. Quantitative ¹³C NMR spectra of reaction solution formed via hydration of THP2M dehydration product.

Hydrogenation to 1,6-HDO

The hydration product was then hydrogenated over a prereduced Ru/C catalyst in a batch reactor. Prior to the reaction, Quantitative ¹³C NMR was used to quantify the concentration of OXL and 6HDHX in the feed (28.5 mM) by using the peak ratio of THP2M to the hydration products.^{41,42} The hydrogenation reaction resulted in the complete conversion of the hydration products and ~98% carbon yield to 1,6-HDO after 22 h (see Figure 7). There was no appreciable side-product formation in the hydrogenation step. A maximum of 85% 1,6-HDO yield from THO was achieved. Any loss in 1,6-HDO yields from THO was likely the result of oligomer/polymer formation in the hydration step. In fact, hydrations at higher temperature (100 °C) resulted in the formation of solid residue in the reactor. Moreover, essentially identical results over this time scale were achieved using a Ni/C catalyst instead of Ru/C for the hydrogenation, under the same reaction and reduction conditions. However, Inductively Coupled Plasma (ICP) analysis of the product streams of the Ru/C and Ni/C hydrogenations displayed the instability of Ni/C catalysts, with 31% of the Ni originally present in Ni/C leached into the product stream. In contrast, less than 1% of the Ru originally present in Ru/C leached into the product stream during its reaction.



Figure 7. OXL + 6HDHX (\Box) and 1,6-HDO (\bullet) concentration at various time points in a batch reactor (130 mg Ru/C diluted 20x in Silica gel [6.5 mg Ru/C], T=120 °C, P=6.4 MPa).

As the ring-opening tautomerization of OXL to 6HDHX is thermodynamically favorable (as shown by gas-phase thermochemistry calculations), it is likely that 6HDHX is the main product of the hydration step and was the main 1,6-HDO precursor. This is further corroborated by the fact that 1,6-HDO can be formed via simple hydrogenation with a monometallic hydrogenation catalyst; ring-opening of OXL would require the use of a bimetallicoxophilically promoted catalyst.⁹ Additionally, the reaction was determined to be 1st-order in 6HDHX (see Figure 7 insert). The reaction rate of 994 μ mol gcat⁻¹ min⁻¹ is an order of magnitude higher than achieved in typical C-O-C bond hydrogenolysis reactions,⁹ and suggests the hydrogenation of an aldehyde to be rate determining.⁴³

Conclusions

An alternative to the conventional Pt, Rh, and Ir-based catalysts for the conversion of tetrahydropyran-2-methanol (THP2M) to 1,6hexanediol (1,6-HDO) is presented. While the existence of this pathway has been known since at least the 1960s, it has been essentially ignored over the past 40-50 years. In the first of three steps, THP2M is dehydrated to 2,3,4,5-tetrahydrooxepine (THO) in a continuous flow, gas-phase reactor over a silicoaluminate catalyst. While this study was not able to replicate THO yields over amorphous SiO_2 -Al₂O₃ cited in the literature,^{19,20} data from this study indicates that zeolite materials produce nearly three times higher yields of THO than amorphous SiO₂-Al₂O₃. Various zeolite frameworks, as well as various alkali metals as exchange ions were tested in this dehydration reaction. Maximum THO yields of 40% were achieved over K-BEA. THO production over K-BEA benefits from the catalyst's large quantity of moderate-strength Lewis acid sites (399 cm³ NH₃ desorbed/g catalyst), and very few, if any, strong or weak (Brønsted or Lewis) acid sites. Without the use of any catalyst, THO was then hydrated in 85% yields to 6-hydroxyhexanal

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(6HDHX) and 2-oxepanol (OXL), as confirmed by NMR. 6HDHX and OXL (likely through 6HDHX) were then hydrogenated to 1,6-HDO with Ru/C or Ni/C nearly quantitatively. Therefore, our pathway affords an overall yield of 34% to 1,6-HDO from THP2M, higher than previously reported 1,6-HDO yields from THP2M without using toxic metals.²⁰ In future research, optimizing Lewis acid strength and concentration could potentially lead to higher THO selectivity, and therefore improve the overall viability of this route.

Experimental Details

Materials Synthesis

Amorphous $SiO_2-Al_2O_3$ (Sigma, grade 135) was used for comparison to zeolites in THP2M dehydration. All zeolite frameworks were purchased from Zeolyst in their hydrogen form with $SiO_2:Al_2O_3$ ratios of 20-30:1. All alkali exchanges were done at 80 °C in 1 M solutions of the corresponding nitrate in water for 8 hours. After exchange, the catalyst was washed with one liter of distilled water per gram of catalyst and dried at 110 °C overnight. This ion-exchange was repeated two additional times, using two liters of distilled water per gram of catalyst for the final washing. After the final drying step, the catalyst was calcined under a flow of air to 580 °C at a rate of 3 °C/min, holding at 580 °C for 6 hours. 5 wt% Ru/C was purchased from Sigma-Aldrich. 5 wt% Ni/C was prepared by incipient wetness impregnation of nickel nitrate hexahydrate (Sigma, >98.5% (KT))in water onto Vulcan XC-72 (Cabot Corp.)

Catalyst Characterization

Exchange rates of zeolites synthesized in this study were determined by ICP-AES after digesting the solid samples in HF. NH_3 -TPD measurements were carried out with a Micromeritics Autochem II Chemisorption Analyzer. Prior to NH_3 -TPD analysis, samples were dehydrated at 580 °C for three hours (10 °C/min) under a flow of He. Samples were then cooled to 100 °C for NH_3 adsorption. Adsorption was performed for 30 min at 100 °C under a flow of 40 mL/min 10%NH₃-Ar (Airgas). NH₃ was desorbed under a 40 mL/min flow of He while heating at 10 °C/min.

FTIR experiments were performed with a Bruker Vertex 70 Fourier Transform Infrared Spectrometer equipped with an MCT detector. 32 scans were averaged to give one spectrum with a resolution of 4.00 cm⁻¹. A flow-through transmission cell was loaded with approximately 25 mg of sample that was pressed into a selfsupporting wafer with a diameter of 13 mm. Samples were dehydrated at 350 °C (10 °C/min, hold for 1 hour) under 10⁻⁷ mbar. Samples were then cooled to 25 $^{\circ}$ C, and the time-zero spectrum was taken. Pyridine was then flowed over the catalyst for 10 min by way of a bubbler with a carrier gas of dry N₂ at atmospheric pressure. The cell was then flushed with dry N₂ for 10 min to remove physisorbed pyridine. Samples were then heated at 10 $^{\circ}$ C/min to 250 $^{\circ}$ C, and held at that temperature for 20 min while taking spectra of the catalyst. Samples were also heated to 150 °C and 350 °C with the same procedure, showing similar results. The final spectrum at 250 °C was used for contribution to this paper. The Opus 7.0 software package was used to analyze the data. Each

spectrum was background subtracted and normalized by the intensity of silica framework signals in the range of 1800-2100 cm⁻¹. The time-zero spectrum was subtracted from each of the spectra taken at 250 °C so that only signals due to interaction with pyridine remained. Finally, the signals at 1540 and 1450 cm⁻¹ were integrated for Brønsted and Lewis acid sites, respectively. Extinction coefficients of 1.3×10^6 cm⁻¹/mol and 1.5×10^6 cm⁻¹/mol were used to compare quantities of Brønsted and Lewis acid sites, respectively.⁴⁴

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Temperature-programmed oxidation experiments with spent catalysts were carried out with a Mettler Toledo TGA-DSC1. Samples were heated to 600 °C at 5 °C/min under a 20 mL/min flow of 20%O₂-N₂ (Airgas). Samples were then held at 600 °C for two hours under the same gas flow.

Reaction Testing

Dehydration of THP2M was performed in a continuous flow (down-flow) reactor in the gas phase. The reactor was a quartz tube (52 cm long, 1.1 cm internal diameter) with a quartz frit in the middle to support the catalyst. The reactor was packed with 150 mg catalyst between layers of glass wool. Temperature was monitored and controlled by a thermocouple placed inside the reactor, just above the catalyst bed. The reactant was mixed with carrier gas above the furnace (Carbolite, VST12/300), and preheated in a layer of glass beads within the furnace before reaching the catalyst bed. Gas flow was controlled by mass flow controllers (Bronkhorst, EL-FLOW). Reactant flow was controlled by syringe pump (Chemyx, Fusion 200). Products were collected in a glass collection vessel inside a dry ice/acetone bath. Samples were taken at 4, 7, 10, 13, 16, and 25 hours on stream. The 4-hour sample normally showed lower carbon balances, likely due to the need to fully coat the reactor at the beginning of the reaction. That being the case, the 4hour sample is not reported in this study, except when investigating the reaction network. The 4-hour sample is used for this purpose to minimize the effects of coking on our analysis. Products were analyzed by an Agilent gas chromatograph (HP6890) equipped with an HP-5 column and a flame ionization detector.

The organic product solution formed from THP2M dehydration over K-BEA was added dropwise to DI water up to 2wt% organic fraction in a 50mL Hastelloy Parr reactor. This was done slowly while stirring in order to prevent organic fraction loss to reactor walls and the stir bar. An insoluble organic layer was formed upon addition. The reactor was closed and pressurized to 500 psi with helium after 2 purge cycles. The reactor was heated to reaction temperature while stirring (500 rpm). An ice bath was used to quench the reaction after the desired reaction time. A single, water-soluble phase was formed after hydration. Liquid product samples were filtered with Restek PES syringe filters prior to GC analysis (Shimadzu GC2010 equipped with a flame ionization detector and an RTX-VMS column).

The catalyst used for hydrogenation was a 5wt% Ru/C catalyst (Sigma Aldrich #206180) diluted 20x in Davisil silica gel (Sigma Aldrich #236845). The catalyst was pre-reduced in UHP H₂ (Airgas, 100 mL/min) at 300°C (4 °C/min ramp rate, 1 hr hold time) in a glass

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tube reactor with Ultratorr fittings and ball valves at the inlet and outlet. Upon cooling to room temperature, the H₂ flow was stopped and the ball valves shut. The catalyst was transferred to a glove box with He atmosphere at positive pressure and stored. Prior to the hydrogenation, 130 mg of total catalyst (6.5 mg Ru/C) was added to a 75 mL Hastelloy Parr reactor equipped with a dip tub for time-on-stream sampling in the glove box. After isolating the catalyst and removing the reactor from the glove box, 40 mL of the product from the hydration step was added to the reactor with an HPLC pump after removing any residual oxygen from the lines. The reactor was pressurized to 6.4 MPa with H₂, heated to 120 °C, and stirred at 750 rpm. Samples were taken at desired reaction times with a dip tube and the reactor re-pressurized to 6.4 MPa after each sample. Samples were filtered with Restek PES syringe filters prior to GC analysis (Shimadzu GC2010 equipped with a flame ionization detector and an RTX-VMS column).

NMR

The hydration product was characterized by NMR with quantitative ¹³C, ¹³C DEPT-135, 2D HSQC, and 2D HMBC experiments. D_2O was added to the sample (1:9 v/v). The ¹³C NMR experiments were acquired on a Bruker Biospin (Billerica, MA) AVANCE III 500 MHz spectrometer fitted with a DCH (¹³C-optimized) cryoprobe. Bruker standard pulse sequence 'zgig30' was used for the quantitative ¹³C experiments with the following parameters: an inter-scan relaxation delay of 40 s, a sweep width of 240 ppm centered at 110 ppm, acquiring 59,520 data points with an acquisition time of 1 s, and 256 scans. The ¹³C DEPT-135 experiments used the Bruker standard pulse sequence 'deptsp135' with the following parameters: an inter-scan relaxation delay of 2 s, a sweep width of 240 ppm centered at 110 ppm, acquiring 59,520 data points with an acquisition time of 1 s, and 256 scans. Mestrelab Research's MestReNova software was used to process the spectra.

The 2D NMR (HSQC and HMBC) experiments were carried out on a Bruker Biospin (Billerica, MA) AVANCE III HD 600 MHz spectrometer fitted with a TCI-F cryoprobe. Bruker standard pulse sequence 'hsqcedetgpsisp2p3' was used for the HSQC experiment with the following parameters: 14 ppm sweep width in F2 (¹H), centered at 4.7 ppm, acquiring 3,366 data points, 240 ppm sweep width centered at 110 ppm in F1 (¹³C) acquiring 1,309 increments, 4 scans per increment, and a 2.0 s relaxation delay. Bruker standard pulse sequence 'hmbcgplpndprqf' was used for the HMBC experiment with the following parameters: 14 ppm sweep width centered at 4.7 ppm in F2 (¹H) acquiring 3366 data points, 240 ppm sweep width centered at 110 ppm in F1 (¹³C) acquiring 1,309 increments, 4 scans per increment, and a 2.0 s relaxation delay. Bruker's Topspin 3.5 software was used to process spectra.

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