A Base Metal Catalyzed Route to 1,6-hexanediol from Biomass-Derived Feedstock

Samuel P. Burt,[1,2] Kevin J. Barnett,[2] Daniel J. McClelland,[2] Patrick Wolf,[1,3] James A. Dumesic,[2] George Huber,[2] and Ive Hermans*[1,2]

[1]*Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave, Madison, WI, 53706*

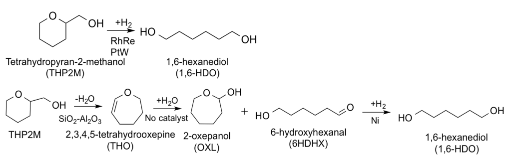
[2]*Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Dr, Madison, WI, 53706*

[3]*Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1-5/10, 8093 Zurich, Switzerland*

*hermans@chem.wisc.edu

Introduction

α,ω-diols are highly sought-after compounds in the chemical industry and find application in the synthesis of specialty chemicals and a variety of polymeric systems, such as polyesters and polyurethanes. Conventionally, 1,6-HDO is produced from KA oil, via hydrogenation of adipic acid. The overall process is hampered by low conversions, difficult separations, and high emissions, prompting the search for an alternate route. Consequently, it has been demonstrated that 1,6-HDO can be synthesized from tetrahydropyran-2-methanol (THP2M, Scheme 1).[1,2] These studies, while promising, are far from being industrially applicable, due to the high cost of catalysts containing precious metals such as Pt and Rh,[1,2] and the low productivity of these catalysts to α,ω-diols.



Scheme 1. Precious metal catalyzed direct conversion of THP2M to 1,6-HDO (top). Base metal catalyzed conversion of tetrahydropyran-2-methanol (THP2M) to 1,6-hexanediol (1,6-HDO) (bottom).

In this study, we present a three-step approach for the synthesis of 1,6-HDO from THP2M through 2,3,4,5-tetrahydrooxepine (THO) using only base metal catalysts (Scheme1). In a first step, THP2M is dehydrated to THO over BEA zeolites, followed by hydration to 2-oxepanol (OXL), which is in equilibrium with 6-hydroxyhexanal (6HDHX). This second step requires no catalyst. 6HDHX and OXL are then hydrogenated to 1,6-HDO over Ru/C or Ni/C.

Materials and Methods

Amorphous SiO_2-Al_2O_3 with a SiO_2:Al_2O_3 ratio of 12:1 was used for initial studies. Zeolite frameworks were purchased from Zeolyst in hydrogen form, and contained SiO_2:Al_2O_3 ratios of 20-30:1. Alkali ions were substituted into the frameworks by wet impregnation of a 1 M solution of the corresponding nitrate precursor. Dehydration reactions were carried out at 400 °C with H_2 and THP2M (liquid) flow rates of 30 mL/min and 0.628 mL/hr, respectively. All reaction products were analyzed by GC. Hydration products were additionally analyzed by ^{13}C, ^{13}C DEPT-135, 2D HSQC, and 2D HMBC NMR.

Results and Discussion

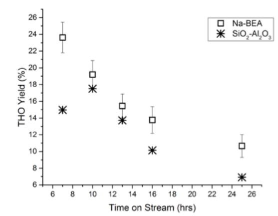


Figure 1. THP2M dehydration over Na-BEA and amorphous SiO_2-Al_2O_3

Previous literature indicates Na doping of SiO_2-Al_2O_3 improves THO yields from THP2M.[3] Figure 1 shows that Na-BEA produces significantly more THO than does amorphous SiO_2-Al_2O_3. In order to examine framework and metal effects separately, we perform a framework screening and an alkali metal screening. Of four common frameworks (BEA, Y, MOR, ZSM-5), BEA produces the highest THO yields. Using only BEA for the alkali screening, K-BEA shows the highest single point THO yield, at 40%. The two most promising dehydration catalysts, K- and H-BEA, were tested for regeneration under a flow of air at 550 °C. Neither catalyst regains initial activity in the second cycle, but the third cycle produces just as much THO as the second cycle. This indicates that these catalysts could be regenerated a number of times while maintaining significant activity. THO is then hydrated (without catalyst) to OXL and 6HDHX with total yields of 85%. While the GC signals of these two products overlap, quantitative NMR confirms the presence of both compounds in the hydration product stream. Both of these compounds are then hydrogenated to 1,6-HDO with quantitative yields over monometallic Ru/C or Ni/C, as shown in Figure 3.

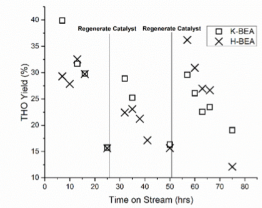


Figure 2. Regenerability of K- and H-BEA.

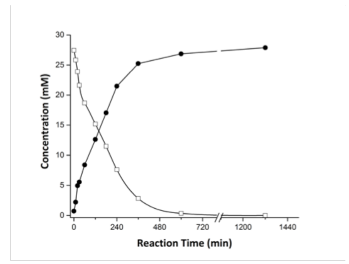


Figure 3. 2-oxepanol + 6HDHX (□) and 1,6-HDO (●) concentration at various time points in a batch reactor (130mg Ru/C diluted 20x in Silica gel [6.5mg Ru/C], T=120°C, P=6.4MPa).

Significance

This is the highest reported 1,6-HDO yield (34%) from THP2M using a silicoaluminate catalyst for THP2M dehydration. This is also the first study of THP2M dehydration with zeolites. As this is the most difficult step in this process, it is likely that further research will bring this route closer to industrial applicability.

References

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