# **Supplementary Information**

## On the selective acid-catalysed dehydration of 1,2,6-hexanetriol

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### **Appendix A: Mass Spectra of Dehydration Products**

A number of the molecules from reaction testing could be identified directly from the NIST mass spectral libraries; these molecules included 1,2,6-hexanetriol, 1,6-hexanediol, THP-2-M, the aldehyde form of THP-2-M (THP-aldehyde), caprolactone, and 5-hexenal, which are illustrated in Figure S1.



Figure S1: Molecules commonly observed in 1,2,6-hexanetriol dehydration experiments, which were readily identified by the NIST mass spectral libraries.

However, several other molecules could not be identified directly from the NIST libraries and these required some interpretation in order to be identified. One of these products was 6-hydroxyhexanal, which is neither commercially available nor available in the NIST libraries. Its existence was suggested by the formation of caprolactone over the zeolite catalysts, along with the spectrum given in Figure S2. 6-hydroxyhexanal would be expected to have a molecular weight of 116, but the presence of both an aldehyde and an alcohol lends itself to rapid loss under the ionization conditions, which is why the molecular ion is not seen and instead peaks at 98 (dehydration) or 88 (decarbonylation) were observed.

The peak at 85 corresponds to  $\alpha$ -cleavage of the hydroxy group (loss of 31) or to a pyran that is generated as an intermediate in the fragmentation of this molecule. This conclusion could be made as pyran rings are always the base peak in their respective MS spectra by a large margin if the molecule being studied begins as a pyran.

In other words, if the molecule were a pyran, the peak at 85 should be taller than the next tallest peak by at least a factor of 2, often much more. The same is true for 1,5 diols, which readily form a pyran upon ionization. The additional peak at 83 also shows the formation of an unsaturated pyran as an intermediate. The likely cause for both peaks is due to a ring being formed in order for the molecule to stabilize the primary carbocation generated by the removal of an oxygen, as shown in Figure S3. The peak at 70 corresponds to both a dehydration and decarbonylation (loss of 18 and 28) which is expected for an alcohol-aldehyde pair, and the two peaks at 55 and 57 indicate the final degradation of the intermediate pyrans to a butenyl group or butyl group, respectively.



Figure S2: Mass spectrum of 6-hydroxyhexanal



Figure S3: Proposed mass spectral degradation scheme for 6-hydroxyhexanal

The other linear product of interest is an unsaturated 1,6-hexanediol that is produced directly from dehydration of 1,2,6-hexanetriol (mass spectrum shown in Figure S4). In this case, the very faint molecular ion once again indicated the presence of alcohols on the molecule. The large peak at 84 corresponded to a loss of 32, which is an unusual loss, but would correspond to  $\alpha$ -cleavage of an alcohol with the loss of an extra proton. The molecule was postulated to be 1,6-hex-2-enediol, as the double bond may aid in the loss of the additional hydrogen. After this loss, the remaining fragment undergoes a McLafferty rearrangement, giving up an ethylene fragment (loss of 27) and leaving behind a propenol fragment (m/z=57). An alternative degradation pathway includes the formation of a pyran ring to give a peak at 83, followed by a CO loss (loss of 28) to give the peak at 55. These two pathways are illustrated in Figure S5. The peaks in the 67-70 range correspond to further degradation pathways involving either isomerization of the double bond or a McLafferty rearrangement.



Figure S4: Mass spectrum of an unsaturated 1,6-hexanediol, which was proposed to be 1,6-hex-2enediol.



Figure S5: Proposed degradation pathways in the mass spectrum of 1,6-hex-2-enediol.

Finally, some condensation products were also detected by GC and we have not been able to definitively identify them. However, these products showed a large peak at 85, which is typical of a

pyran. Based on suggestions from the NIST libraries, the following products as shown in Figure S6 were possible candidates. The two repeating occurrences among the suggested products were the presence of six-membered (typically pyran) rings, and short carbon chains. These results were suggestive that the condensation reactions that were occurring were either the dimerization of pyrans or condensation of pyrans and hexenals.



Figure S6: Condensation products suggested by the NIST libraries.

#### Appendix B: TPD-MS data and data processing

One of the challenges associated with characterizing spent catalyst is the catalyst changing during pretreatment steps, such as high-temperature drying to remove water and other physisorbed gases from a catalyst sample. TPD-MS can be used to qualitatively measure changes in catalyst acid properties, as it can identify molecules based on molecular weight. However, molecules such as water and ammonia can decompose under ionizing conditions in the mass spectrometer, leading to the formation of [M-1]<sup>+</sup> ions in addition to the molecular ion. Since [M-1] for water corresponds to the molecular ion for ammonia, we used a technique of subtracting out the water contribution to the signal for ammonia.

The method uses that fact that the ratio of water and OH<sup>+</sup> ions tends to remain constant, and the ratio can be calculated by observing the m/z=18 and m/z=17 signals for water in the absence of physisorbed ammonia. To measure the ratio, the TPD-MS method mentioned in the experimental section was performed on 0.1000g of amorphous silica-alumina in the absence of ammonia or any other probe gas. Using the m/z=18 and m/z=17 curves from the run, we multiplied the m/z=17 slope by a constant, and calculated an R<sup>2</sup> value. The ratio of water to hydroxonium was found to be 3.258:1, giving an R<sup>2</sup> of 0.9915.

Using this information, water contributions can be subtracted from the m/z curves of the TPD-MS data to get the ammonia curve. The ammonia curves constructed from this water-subtraction method are shown in Figures S7 and S8:



Figure S7: TPD-MS of fresh amorphous niobia catalyst. The three curves are the m/z=18 curve (solid), m/z=17 curve (dot-dash), and the constructed ammonia curve (dotted)



Figure S8: TPD-MS of spent amorphous niobia catalyst. The three curves are the m/z=18 curve (solid), m/z=17 curve (dot-dash), and the constructed ammonia curve (dotted)

### Appendix C: Activity vs. Time on Stream

Figure 1 in the main paper shows activities for the catalysts over the duration of the experiment. The chart below is a reproduction of the same data except showing activity versus time on stream instead of activity versus acid strength.



Activity as a function of Time on Stream (TOS)

Figure S9: Plot of activity vs. time on stream (TOS) for each tested catalyst.