Regioselective Epoxide Ring Opening with Alcohols Using Heterogeneous Lewis Acid Catalysts

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Abstract: The regioselectivity of epoxide ring opening reactions for alcohols is examined using Lewis acidic catalysts. Through comparing catalytic activities, it is found that Sn-Beta is more active than other similar Lewis acidic catalytic materials such as Sn-MFI and Sn-SBA-15. For all materials, high regioselectivity of >99% is obtained. With large substrates such as epoxy octane, diffusion limitations are encountered that can be overcome through creating zeolites with particle sizes less than 100 nm. These materials can be readily recycled while retaining high catalytic activity and selectivity. Hot filtration tests demonstrate that these catalysts are heterogeneous in nature and stable.

Keywords: Sn-Beta; Epoxide Ring Opening; Regioselectivity; Lewis Acid

1. Introduction

Epoxides are versatile intermediates that can be ring opened using different nucleophiles to produce a wide variety of valuable chemicals. The key challenge for this reaction is selectivity. Indeed, the ring opened epoxide can form oligomeric byproducts. At the same time, the reaction can produce either a terminal ether or a terminal alcohol, resulting in low regioselectivity. Previous work with Bronsted acidic catalyst results in low regioselectivity. Higher regioselectivity has been observed for Lewis acidic catalysts such as Co-Salen and Co-Porphyrin. Unfortunately, these catalysts tend to deactivate through loss of the counterion used to maintain the Co in the +3 oxidation state.[1,2] Intriguingly, Lewis acidic zeolites have been demonstrated for the water ring opening of epoxides to produce a diol.[3,4] In this work, we will discuss the regioselective epoxide ring opening reaction with alcohols for Lewis acidic catalytic materials.

2. Experimental

All materials are synthesized using procedures that are similar to previously reported work: Sn-BEA,[5] Sn-MFI, and Sn-SBA-15.[6–8] The target composition of the silica materials is a Sn:Si of 1:200. All materials are characterized using standard techniques, including powder X-ray Diffraction, N_2 physisorption, and elemental analysis (Sn and Si).

Catalytic Testing. The different Lewis acidic catalytic materials are tested for catalytic activity and selectivity for the epoxide ring opening reaction of epichlorohydrin with methanol. The reaction is performed using 0.4 mol% Sn at a temperature of 60°C using an epoxide concentration of 0.4 M in neat methanol. Additional substrates are tested that demonstrate the scope of these catalytic materials using similar reaction conditions.

Catalyst Reuse Testing. The catalytic materials are reused through collecting the catalyst after reaction through using filtration. The catalyst are characterized and reused to determine conversion over time in a second round of catalytic testing. A hot filtration test is used to demonstrate that framework sites are responsible for the catalytic activity.

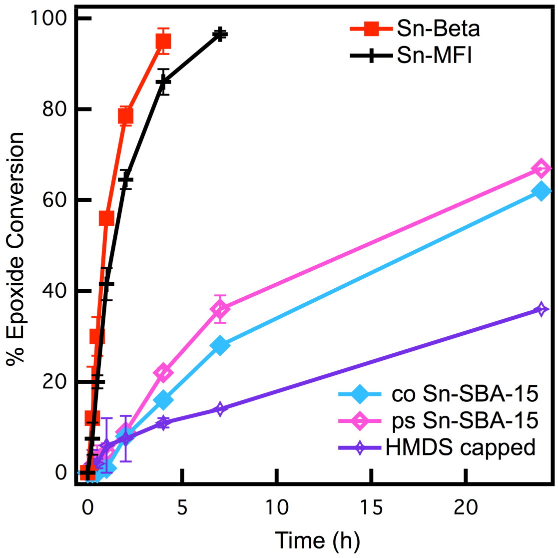

Figure 1. Comparison of catalytic conversion of epichlorohydrin in the epoxide ring opening reaction with methanol using 0.4 mol% Sn at 60°C with Sn-Beta, Sn-MFI, co-condensed Sn-SBA-15, post-synthetically prepared Sn-SBA-15, and hexamethyldisilazane capped PS-SBA-15.

3. Results & Discussion

All materials are successfully synthesized with characterization data showing that the materials are of similar quality to previous reported materials. The Lewis acidic materials are tested for catalytic activity and selectivity in the epoxide ring opening reaction of epichlorohydrin with methanol, as described in the experimental section. Initial tests with Sn-SBA-15 made through a co-condensation (co Sn-SBA-15) route reveal that the Lewis acidic materials are catalytic activity, achieving a conversion of 60% after 24 hours, as shown in Figure 1. Slightly higher catalytic activity is observed if the material is prepared through a post-synthetic route (ps Sn-SBA-15) since this method ensures that Sn sites are present on the surface.

While the materials exhibit high regioselectivity (>99%) for this reaction, the activity is modest potentially because Sn-SBA-15 has numerous silanols that can hydrogen bond to the substrates and products.[9] The number of silanols in a Lewis acidic catalyst can be limited through using a zeolite catalyst with few defects such as Sn-Beta or Sn-MFI. Both Sn-Beta and Sn-MFI had high catalytic activity with initial turnover frequencies (TOF_0) of 75 and 50 hr^{-1}, respectively. In all cases, the catalysts had high regioselectivity with the primary byproduct formed being water. Through drying methanol, only a single product is observed (not shown). Furthermore, it is demonstrated that higher concentrations of epoxide can be used such as 4 M (of commercial interest) with similar regioselectivity and a higher rate of reaction. Additional bulkier substrates are investigated to determine the scope of Sn-Beta. It is found that the nucleophile has little effect on regioselectivity, but can impact the catalytic activity, as demonstrated using n-butanol, 2-butanol, and tert-butnol. For large substrates, diffusion limitations are observed, resulting in incomplete conversion of the epoxide. These diffusion limitations can be overcome through synthesizing Sn substituted zeolites with particle sizes less than 100 nm (not shown).

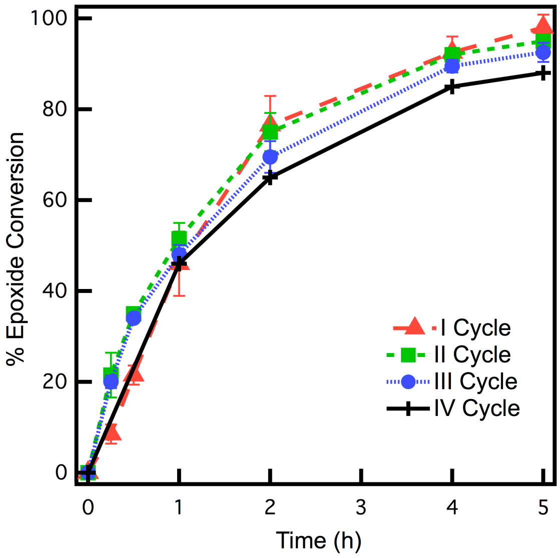

Figure 2. Comparison of the conversion over time for Sn-Beta over four different reaction cycles. After each cycle, the catalyst is filtered and reused without the need for calcination.

The stability of these catalysts is investigated using a hot filtration test and through recycling the catalytic material. For the hot filtration test, it is found that no additional conversion occurs after the catalyst has been removed from the reaction mixture (not shown), confirming the heterogeneous nature of this catalyst for this reaction. The catalytic activity could be retained over multiple catalytic cycles, as shown in Figure 2. Indeed, the catalyst could be recovered through filtration and re-used with no loss in catalytic activity. Overall, the results demonstrated that Sn-Beta is a promising catalyst for this reaction.

4. Conclusions

High catalytic regioselectivity is achieved for the epoxide ring opening reaction of epichlorohydrin with methanol. Of the different Lewis acidic catalysts tested, Sn-Beta exhibits the highest catalytic activity. A hot filtration tests demonstrates that this catalyst is heterogeneous in nature since no conversion of the epoxide is observed once the catalyst is removed. The catalyst is stable to reuse over multiple catalytic cycles, demonstrating that this is a promising catalyst for this reaction.

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