

# Synthesis of Higher Carbon Ethers from Methanol and Olefins

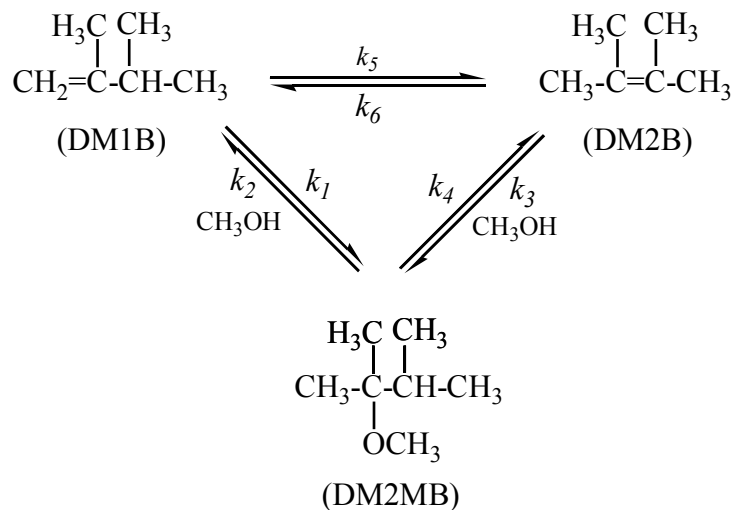
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Oxygenated compounds such as ethers have a great potential as environmental enhancing additives for transportation fuels. The oxygenates can be produced from methanol and olefins or directly from alcohols, which can be produced from syngas by the Fischer-Tropsch process. The objective of our research is to study the production of higher ( $C_6$  or greater) ethers, which have desirable properties as transportation fuel additives. Higher molecular weight oxygenates have lower water solubility and vapor pressures than lower molecular weight oxygenates, e. g. MTBE, which have recently come under environmental pressures. The goal of the current project is to develop optimal reaction conditions and to develop new and improved catalysts for the reactions involved. In the previous year, our study has been focused on kinetics, reaction conditions and new catalysts for the production of a  $C_7$  ether, 2,3 dimethyl-2-methoxybutane (DM2MB), from dimethyl butenes and methanol. We have also investigated the production of other higher ethers from this olefin and butanol, propanol and ethanol as well as binary mixtures of these alcohols. We have explored the development of new catalysts for these reactions as well. Reactions were performed in microautoclave reactors at several conditions using the commercial catalyst, Amberlyst-15, as well as several new laboratory-prepared catalysts and relevant kinetic and equilibrium parameters have been determined. Performance of the new laboratory developed catalysts has also been studied.

## **I. Catalytic behavior of the reference catalyst: Amberlyst 15.**

As part of our first year's work, the reaction parameters for the production of one higher ether oxygenate, 2,3-dimethyl-2-methoxybutane (DM2MB), were investigated in a batch reactor at 50-70 °C using a macroporous cation exchange resin, Amberlyst 15, as catalyst for the etherification of 2,3-dimethyl-1-butene (DM1B) and 2,3-dimethyl-2-butene (DM2B) with methanol. The basic reaction scheme for olefins and DM2B with methanol is given below with the kinetic rate constants numbered as shown in the diagram. The kinetic rate constants were obtained by fitting the experimental data to kinetic equations based on a pseudohomogeneous model. Experimental results obtained in our investigations reveal the effect of temperature on simultaneous etherification and isomerization of DM1B and DM2B and differences in the reactivities of the two olefins were studied. Kinetic and equilibrium parameters obtained from the Arrhenius and

Van't Hoff equations agreed well with the values obtained from similar studies in the literature. The details of our work in the above area have been presented in a paper submitted for publication [1].



In our more recent work, we have studied the etherification reactions of butanol, propanol and ethanol with DM1B to compare the results with our work using methanol. The reaction routes with other alcohols are similar to the ones shown with methanol. The basic procedures were as follows: Amberlyst 15 was used as the catalyst. Before use, the catalyst was sieved and dried overnight in a vacuum oven at 90 °C. A catalyst particle size range of 0.4-0.7 mm was used in the kinetic experiments. Batch reactions were performed in 20 cm<sup>3</sup> 316ss tubing bomb microreactors (TBMRS) agitated in a fluidized sand bath. TBMRS were charged with 250 psig He (inert) pressure in order to guarantee a liquid-phase reaction. Products were analyzed with a Varian 3300 gas chromatograph equipped with a FID using heptane as an internal standard at 35°C. The product ether DM2MB was identified by GC/MS.

Reaction rate constants obtained by fitting the data shown in Figures 1 and 2 for the reactions of DM1B with four different alcohols at 70°C are shown in Table 1. Not all of the results in Table 1 are in the same order as those reported in the literature. The finding that the etherification rate constant of methanol is greater than that of ethanol is different from the results obtained in the etherification of isobutene[2]. In the etherification of isobutene, an activity order of n-butanol = n-propanol > ethanol > methanol has been found, which was explained by the effect of alcohols on the acidity of active sites. The acidity in the resin interior decreases in the

order n-propanol > ethanol > methanol [3]. This leads to increase in both etherification and isomerization reaction rates. In our work shown in Table 1, all rate constants, except those for methanol etherification, are in an agreement with above explanation. These results imply that the effect of alcohols on the acidity of the proton may not be the only reason for the different reactivities.

Table 1. Rate Constants for Reactions with Different Alcohols at 70 °C

<b>Alcohol</b>	$k_1 \times 10^4$ (L·mol <sup>-1</sup> ·min <sup>-1</sup> )	$k_3 \times 10^4$ (L·mol <sup>-1</sup> ·min <sup>-1</sup> )	$k_5 \times 10^4$ (min <sup>-1</sup> )
<b>Methanol</b>	<b>2.48</b>	<b>1.0</b>	<b>39</b>
<b>Ethanol</b>	<b>1.94</b>	<b>0.88</b>	<b>49.6</b>
<b>n-Propanol</b>	<b>4.1</b>	<b>1.6</b>	<b>117</b>
<b>n-Butanol</b>	<b>6.5</b>	<b>2.0</b>	<b>196</b>

Figures 1 and 2 show the concentration profiles of ethers and isomer DM2B with time, respectively. The order of the isomer DM2B concentrations is the same as that of rate constants shown in Table 1. Also, as shown in Figure 1, except for the ether formed from methanol, the order of the ether concentrations is the same as that of rate constants in Table 1. The much higher concentration of methyl ether may be attributed to a consequence of the isomerization reaction. In the isomerization reaction, less DM2B is formed from DM1B in the presence of methanol. Due to the slower rate of isomerization, more DM1B, which is more active in etherification, will be available for the etherification and thus ether production with methanol is higher. For ethanol, n-propanol, n-butanol, the effect of isomerization on etherification is not apparent. Similar behaviors in etherification rates of isoamylenes with different alcohols were also reported by Linnekoski et al. [4]. They believed that the special reactivity of methanol might be related to its small molecule size, which provides easier access to the olefin DM1B, which has two branch methyl groups.

Figures 3-8 show concentration profiles of ethers and isomer DM2B in reaction of DM1B with equimolar binary mixtures of methanol/n-butanol, ethanol/n-butanol and n-propanol/n-butanol, respectively. In Figure 3, the concentrations of methyl ether and butyl ether from binary alcohol mixtures are lower than those from pure alcohols at same reaction time. This result is due

to the sharing of DM1B between the two alcohols. Analogous results are observed in Figure 4 and 5. It's interesting to note that the concentrations of butyl ether were always lower than the other ether when alcohol mixtures were used, despite the fact that the reaction rate constant of butyl ether is the highest with pure alcohol. These interesting results may be attributed to the different distribution coefficients for various alcohols. For example, Ancillotti et al. [2] experimentally determined the distribution coefficients for a methanol/n-butanol mixture on Amberlyst 15 resin, obtaining 1.14 for the methanol and 0.67 for the n-butanol. The sum of the ether concentration in reactions with alcohol mixtures lies approximately between the concentrations of ether in the reaction of DM1B with pure alcohols. Similar results for the isomer DM2B can be found in Figures 6-8.

## **II. Design and evaluation of new catalyst systems for ether production.**

### **1. Acid-treated solid catalysts**

Several acid-treated solid catalysts were prepared and their catalytic activity in the etherification of 23DM1B with methanol was investigated. The effects of acid property and nature of solid on activity were studied. Among the catalysts prepared,  $\text{SiO}_2\text{-H}_2\text{SO}_4$  exhibits high activity and ether yield, which is better than the commercial ion-exchange resin catalysts. The factors influencing the catalytic behavior of  $\text{SiO}_2\text{-H}_2\text{SO}_4$  catalysts were also investigated.

It is believed that acid treatment on solids will change their acid/base properties and their catalytic behavior will depend on nature of solids and acids employed as well as the preparation methods. Various acid-treated solid catalysts were prepared and tested under the same conditions and their catalytic activities were compared with the data obtained using some typical commercial ion-exchange resin catalysts. During the investigation, we firstly used several inorganic acids to modify the solids and found that sulfuric acid treated catalysts exhibited higher activity in terms of conversion and ether yield than that of other acids such as hydrochloric acid and nitric acid. Therefore, further study was concentrated on sulfuric acid treated catalysts.

Table 2 shows the catalytic behavior of the prepared solid catalysts and commercial catalysts. Three commercial catalysts show varying activity and the Amberlyst 15 exhibits the best performance, however, it shows low selectivity to ether production. The catalytic activity is believed to be related to the acidity of the catalysts [5]. Among the acid-treated catalysts,  $\text{SiO}_2\text{-H}_2\text{SO}_4$  shows similar activity to Amberlyst 15. Montmorillonite- $\text{H}_2\text{SO}_4$  gives

moderate conversion and high ether yield. Others show low activity but high ether selectivity around 50%. Based on Table 2, SiO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> is a good candidate and deserves further investigation.

Table 2. Catalytic activity of various acid-treated solids and commercial catalysts in 23DM1B etherification with methanol. \*

Catalyst	23DM1B conv (%)	23DM2B sel (%)	Ether sel (%)	Ether yield (%)
Amberlyst 15	91.0	78.7	20.6	18.8
Nafion	29.0	44.0	53.9	15.6
Nafion SAC-13	3.2	21.7	58.9	1.9
Bentonite-H <sub>2</sub> SO <sub>4</sub>	17.0	36.6	59.6	10.1
Montmorillonite-H <sub>2</sub> SO <sub>4</sub>	44.4	46.2	52.6	23.4
C-H <sub>2</sub> SO <sub>4</sub>	3.2	30.5	54.9	1.8
SiO <sub>2</sub> -H <sub>2</sub> SO <sub>4</sub>	90.3	80.0	19.6	17.7
ZrO <sub>2</sub> - H <sub>2</sub> SO <sub>4</sub>	0	0	0	0
Fe <sub>2</sub> O <sub>3</sub> - H <sub>2</sub> SO <sub>4</sub>	0	0	0	0
Al <sub>2</sub> O <sub>3</sub> - H <sub>2</sub> SO <sub>4</sub>	0	0	0	0

\* Reaction conditions: 0.5 g catalyst, 0.2 g methanol+ 0.5 g 23DM1B + 4g heptane, 80°C, 2h. Catalysts were obtained by treating 3 g SiO<sub>2</sub> in 25 ml sulfuric acid solution (0.5 M) and calcined at 300° C for 2h.

In order to achieve high selectivity and ether yield over the SiO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> system, we have studied some modifications of SiO<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> by varying the sulfur content and calcination temperature. Figure 9 and Figure 10 show the results, respectively. Calcination temperature affects the catalytic activity. High temperature calcination reduces 23DM1B conversion but enhances the ether selectivity. The highest ether yield is obtained at 400°C. Sulfuric acid treatment will increase the 23DM1B conversion and ether yield and the conversion will reach the highest level of 75% at the sulfur acid volume of 15 ml. However, the best ether yield of 30% is attained at a sulfuric acid volume of 20 ml.

## **2. Sulfated zirconia and supported sulfated zirconia catalysts.**

A series of superacid catalysts such as sulfated zirconia(SZ), tungstated zirconia and supported sulfated zirconia were prepared. The effect of support in the supported sulfated zirconia system on the catalytic activity was investigated. It was found that silica supported sulfated zirconia catalysts produced high ether yield and the composition of this type of catalyst

was optimized. Some metal oxide-promoted SZ/SiO<sub>2</sub> catalysts were also prepared and the effect of these promoters on catalytic activity was investigated.

Sulfate, tungstate and molybdate oxide containing solids are found to show high acidity and can be active for some acid-catalyzed reactions. We have prepared sulfated zirconia, tungstated zirconia and supported sulfated zirconia catalysts and investigated their activity. Figure 11 shows the results of 23DM1B etherification with methanol over the various laboratory-prepared and commercial catalysts. Sulfated zirconia exhibits higher conversion than that of Nafion SAC-13 while tungstated zirconia shows the lowest activity but similar isomerization selectivity to that of Nafion SAC-13 and SZ. Silica supported SZ gives a similar conversion and ether yield to that over Nafion NR50, but still lower than that of the Amberlyst 15. Acid-treated SZ/SiO<sub>2</sub> exhibits much high conversion with a desirably lower selectivity for isomerization, giving an ether yield of 30%, which is higher than that of the Amberlyst 15 reference catalyst.

Sulfated zirconia supported on other solids such as alumina, bentonite (BT), and montmorillonite (MT) were also prepared and tested. It was found that the catalytic activity follows an order of SZ/SiO<sub>2</sub> > SZ/MT > SZ/BT > SZ/Al<sub>2</sub>O<sub>3</sub>. Further investigation on the SiO<sub>2</sub> supported system with added W and Mo oxides was also conducted and the results revealed that SiO<sub>2</sub> supported sulfated zirconia give higher activity than the other two catalysts.

The effects of varying the compositions of Zr(SO<sub>4</sub>)<sub>2</sub> and SiO<sub>2</sub> in acid-treated SZ/SiO<sub>2</sub> and calcination temperature were further investigated and the results are presented in Figures 12 and 13, respectively. It is seen that the loading of Zr(SO<sub>4</sub>)<sub>2</sub> in SZ/SiO<sub>2</sub>(H<sub>2</sub>SO<sub>4</sub>) greatly influences the catalytic activity and selectivity. Both 23DM1B conversion and 23DM2B selectivity generally increase as the Zr(SO<sub>4</sub>)<sub>2</sub> loading increases. Ether yield increases with increasing Zr(SO<sub>4</sub>)<sub>2</sub> loading and reaches a stable level of *ca.* 30% when the wt% Zr(SO<sub>4</sub>)<sub>2</sub> exceeds 50%. Calcination temperature also exerts an influence on catalytic behavior. Catalysts calcined at 400-550 °C can give a much high conversion over 80%. When catalysts were calcined at higher temperatures over 600 °C, the selectivity to ether was remarkably enhanced, although the overall conversion drops off. In terms of ether yield, 600 °C was the optimal temperature at which the highest ether yield was achieved.

It has been reported that certain metal oxides in supported SZ catalysts show a promoting effect on the acidity of those catalysts and thus we have prepared some promoted catalysts using Mn, Ni, Fe and Pt as promoters. The results showed that Ni and Pt increase the catalytic activity,

Fe will have no significant influence on 23DM1B conversion while Mn reduces the catalytic activity.

### 3. Si-MCM41 supported catalysts

Three types of silica with different textural properties were employed as supports to prepare the supported sulfated zirconia and the effect of pore structure on catalytic behavior was investigated. The pore structure of the catalyst was found to affect the catalytic activity. Mesoporous Si-MCM41 supported SZ produced higher ether yields.

It is generally known that the pore structure of catalysts will influence the adsorption and catalytic activity. From what has been shown above, it is seen that SiO<sub>2</sub> is the best support for our acid catalysts. We, therefore, further investigated the effect of pore structure in the SZ/SiO<sub>2</sub> system. Three SiO<sub>2</sub> precursors with varying pore structure (fused SiO<sub>2</sub>, silica gel and Si-MCM41) were used to prepare supported sulfated zirconia catalysts and the results demonstrate that SZ/Si-MCM41 exhibits much high activity than that of other two catalysts. This effect can be attributed to the variation of pore size.

As has been shown in the last section, the catalytic behavior of SZ and supported SZ catalysts depends on preparation methods. Figure 14 presents the catalytic activity of SZ/Si-MCM41 with the variation of Zr(SO<sub>4</sub>)<sub>2</sub> loading. It is seen that SZ/Si-MCM41 shows the highest conversion activity at a Zr(SO<sub>4</sub>)<sub>2</sub> loading of 50%. The highest ether yield of ca. 30% is achieved at the loading of 40-50%.

### III. Future work.

The kinetic studies on the etherification reactions will be further studied using the most active catalysts developed in our previous investigations. The reaction mechanisms and kinetic models will be also developed. These catalysts will be tested in new reaction routes of alcohol coupling to produce ethers instead of reactions between alcohols and olefins. Catalysts with optimal composition for ether selectivity and yield will be developed by characterization /testing.

### References:

1. Liu, J., Wang S., Guin, J. A., *Fuel Processing Technology*, submitted.
2. Ancillotti, F., Mauri, M. M., Pescarollo, E., *J. Catal.* 46, 49-57 (1977).
3. Casey, W. J., Pietrzyk, D. J., *Anal. Chem.* 45, 1404-1409 (1973).
4. Linnekoshi, J. A., Paakkonen-Kiviranta, P., Krause, A.O., Rihko-struckmann, L. K., *Ind. Eng. Chem. Res.* 38, 4563-4570 (1999).
5. Wang S., Liu, J., and Guin, J. A., *J. Catal.*, submitted.

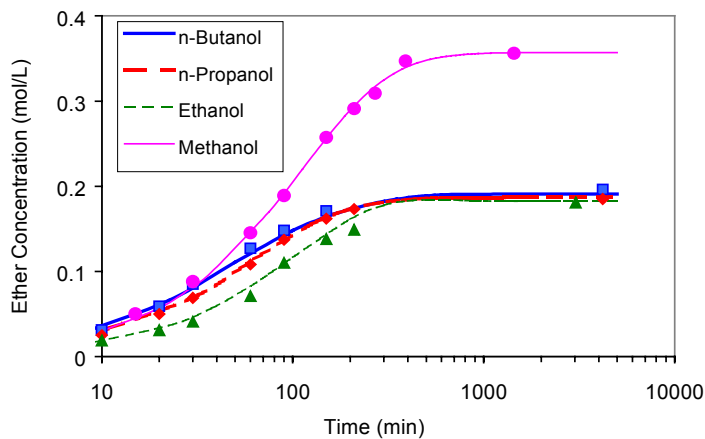


Figure 1. Concentration profiles of ethers for olefin etherification reactions with four different alcohols at 70°C.

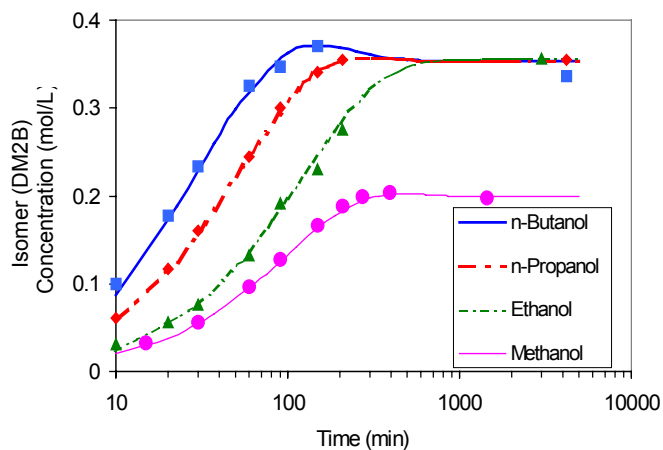


Figure 2. Concentration profiles of isomer DM2B for olefin etherification reactions with four different alcohols at 70°C.

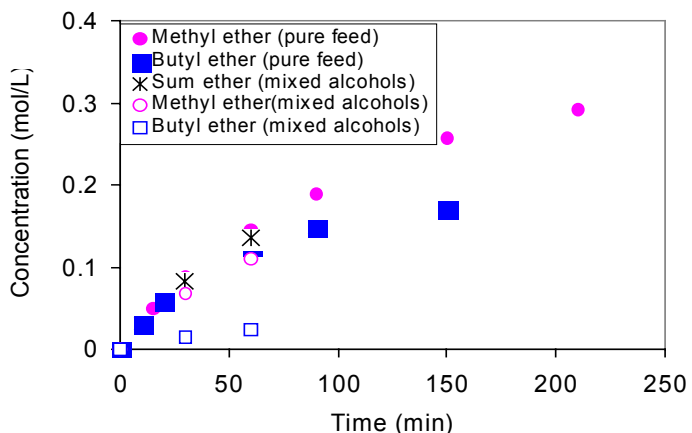


Figure 3. Comparison of ether concentrations for olefin etherification reactions with pure and binary equimolar alcohol mixtures.

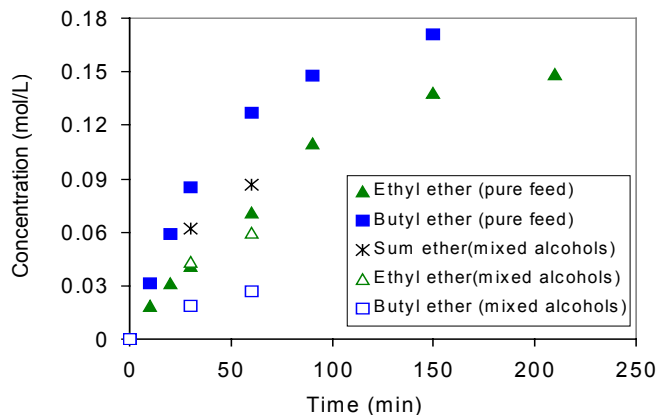


Figure 4. Comparison of ether concentrations for olefin etherification reactions with pure and binary equimolar alcohol mixtures.

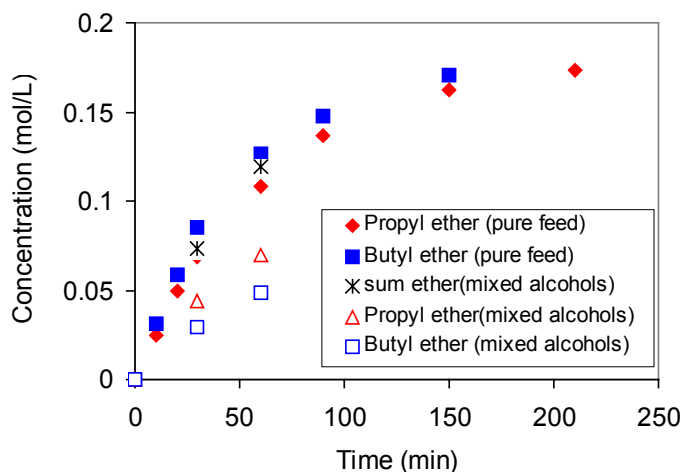


Figure 5. Comparison of ether concentrations for olefin etherification reactions with pure and binary equimolar alcohol mixtures.

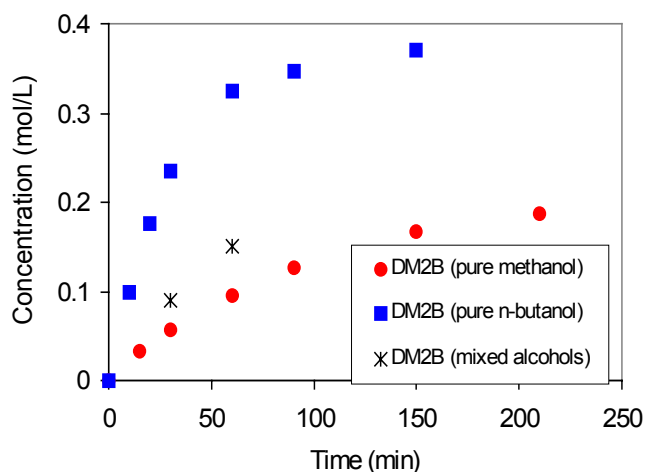


Figure 6. Comparison of isomer DM2B concentrations for olefin etherification reactions with pure and binary equimolar alcohol mixtures.



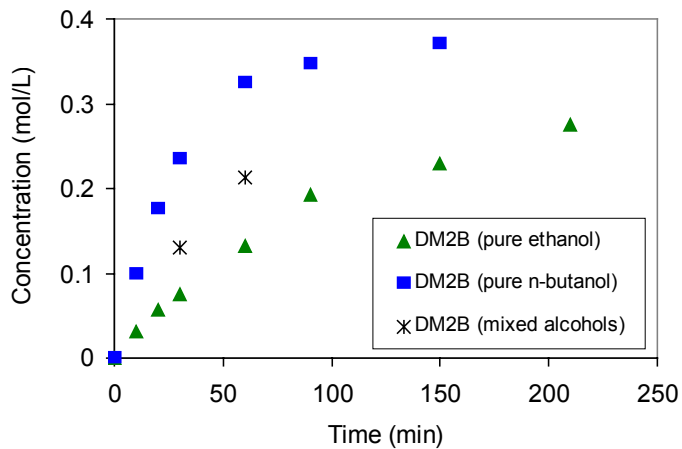


Figure 7. Comparison of isomer DM2B concentrations for olefin etherification reactions with pure and binary equimolar alcohol mixtures.

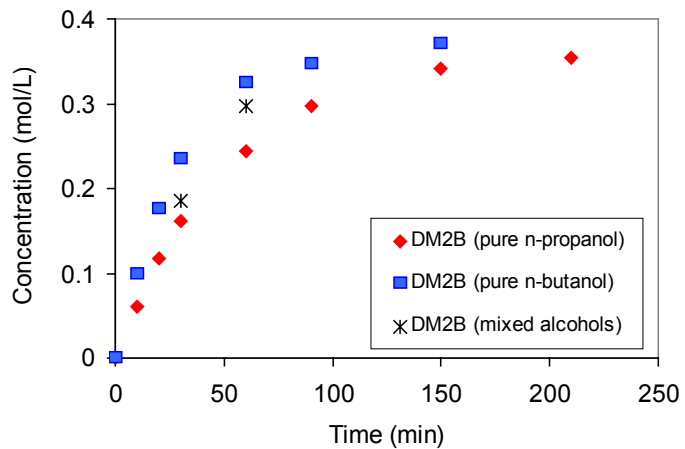


Figure 8. Comparison of isomer DM2B concentrations for olefin etherification reactions with pure and binary equimolar alcohol mixtures.

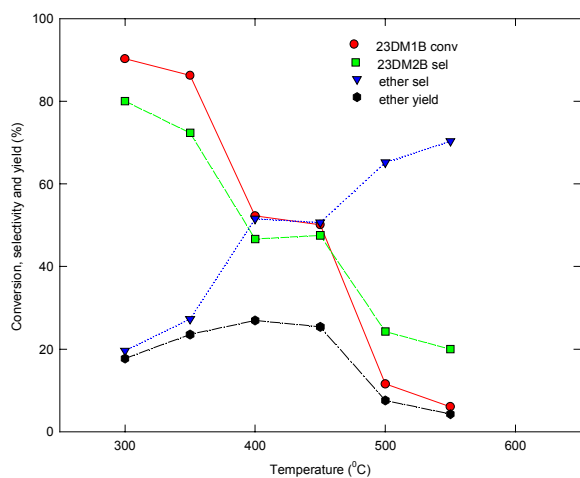


Figure 9. Effect of calcination temperature on activity of  $\text{SiO}_2\text{-H}_2\text{SO}_4$  catalysts.

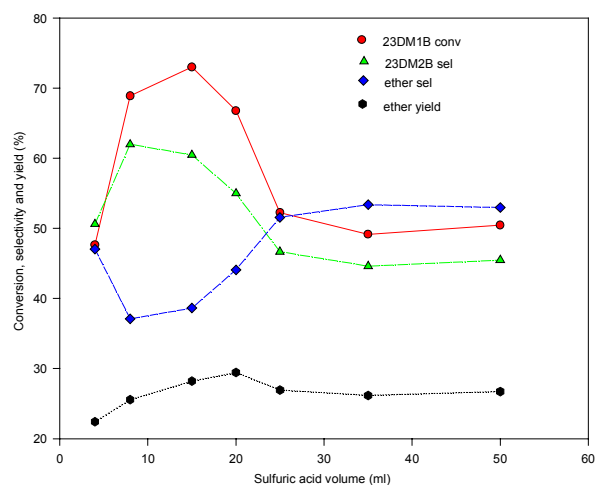


Figure 10. Effect of sulfuric acid volume used for treatment of  $\text{SiO}_2$  on activity of  $\text{SiO}_2\text{-H}_2\text{SO}_4$  catalysts.

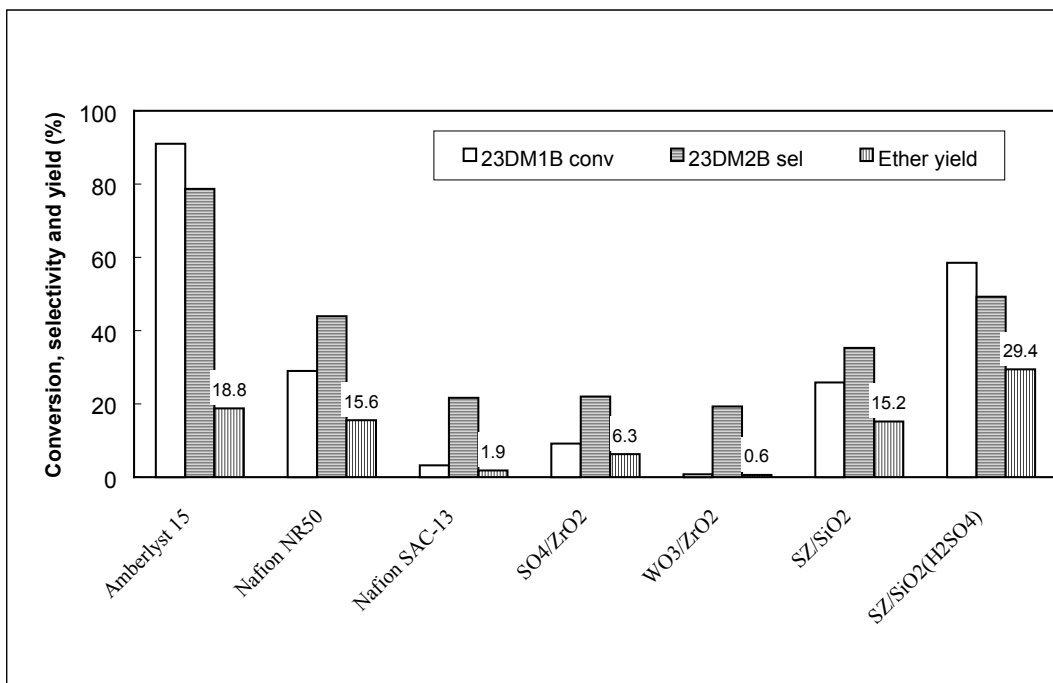


Figure 11. Catalytic activity over commercial ion exchange resin and prepared zirconia-based catalysts.

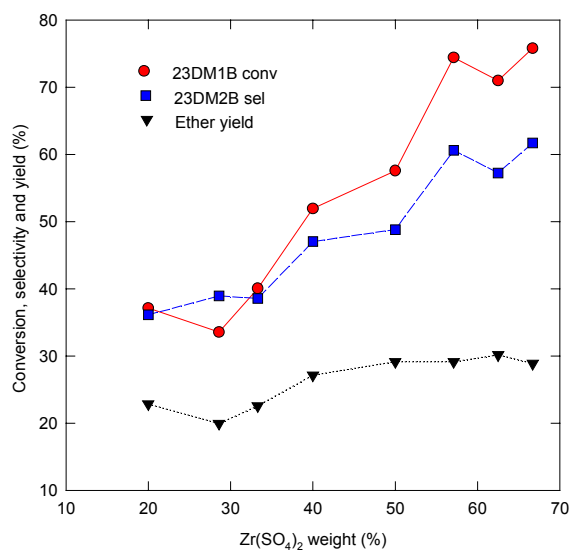


Figure 12. Effect of Zr(SO<sub>4</sub>)<sub>2</sub> content in SZ/SiO<sub>2</sub>(H<sub>2</sub>SO<sub>4</sub>) system on catalytic activity.

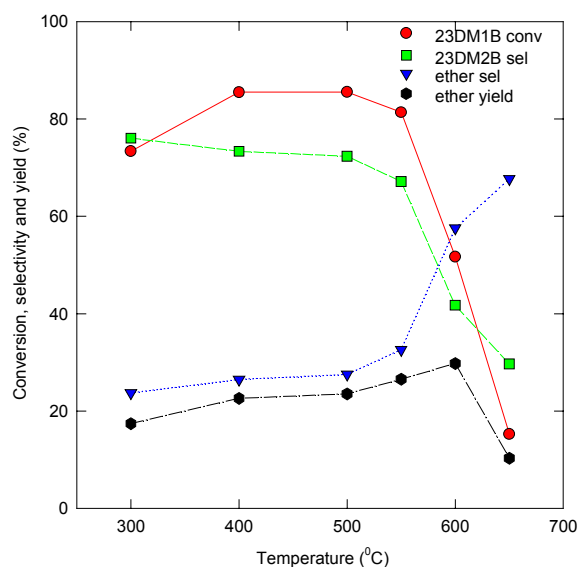
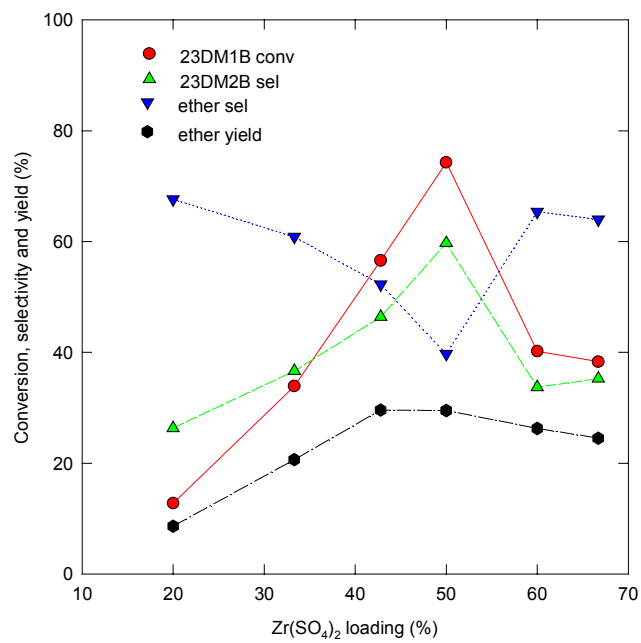


Figure 13. Effect of calcination temperature on activity of SZ/SiO<sub>2</sub>(H<sub>2</sub>SO<sub>4</sub>) catalysts.



**Figure 14. Effect of Zr(SO<sub>4</sub>)<sub>2</sub> loading in SZ/Si-MCM41 catalysts on catalytic activity.**