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Silica-supported sulfated zirconia: a new effective acid solid for etherification

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Silica-supported sulfated zirconia exhibits a comparable and even higher ether production than a reference acid resin (Amberlyst 15) giving an ether yield of 30% at 50% conversion.

Methyl *tert*-butyl ether (MTBE) has been the major gasoline additive in the past decade. However, its environmental consequences to drinking water have caused intense public attention in recent years.[1] Substantial quantities of unsaturated C_5 and C_6 compounds are present in the light gasoline produced in the fluid catalytic cracking units of refineries. Some of these compounds can be etherified with alcohols and possibly used to meet the demand for oxygenates and as a partial replacement for MTBE. Moreover, these higher ethers have lower vapor pressures and lower water solubilities compared to MTBE. Currently, ion exchange resins are the dominant catalysts for ether production. However, new catalysts could offer improvements over acid resins with respect to thermal stability, poor selectivity under certain conditions, and lack of regeneration ability. Several inorganic acid solids such as zeolites, sulfated zirconia, heteropolyoxoanions (HPA) and supported HPA catalysts have been evaluated for the production of MTBE.[2–5] Essayem *et al.* investigated etherification/esterification over two sulfated zirconia catalysts prepared by different methods and acid resins, but they found that sulfated zirconia showed faster deactivation.[6] No research has been thus far reported for the application of supported sulfated zirconia for etherification, though several researchers have reported the application of such catalysts in isomerization.[7–9] It is believed that unsupported sulfated zirconia suffers from the disadvantages of lower surface area and the very limited accessibility to the acid sites in liquid phase reactions with less polar solvents or in gas phase reactions. Therefore, development of well dispersed sulfated zirconia on supports with high surface areas is important for some acid-catalyzed reactions. This study reports preliminary results on the preparation of some inorganic acid solids, sulfated zirconia, tungstated zirconia, and supported sulfated zirconia, and their performance in the etherification of certain C_6 olefins with alcohols. These particular C_6 olefins, 2,3-dimethylbut-1-ene (23DM1B) or 2,3-dimethylbut-2-ene (23DM2B), were chosen on the basis of their potential for making oxygenated transportation fuel additives.[10]

A sulfated zirconia (SZ) was prepared by acid-treatment of $Zr(OH)_4$, obtained by precipitation of $ZrO(NO_3)_2$ solution with $NH_3{\cdot}H_2O$ at pH = 10, with 0.5 M H_2SO_4 solution, followed by evaporating and drying at 100 °C overnight and calcination at 600 °C for 2 h. A tungstated zirconia with 10 wt% WO_3 was prepared by impregnation of ammonium tungstate hydrate on $Zr(OH)_4$. Two silica-supported sulfated zirconia catalysts, referred to as SZ/SiO_2-S and SZ/SiO_2-N, were prepared by impregnation of 3 g of zirconium sulfate and 2.45 g $ZrO(NO_3)_2$ on 3 g of commercial silica gel support (S_{BET} = 650 $m^2\ g^{-1}$) in 0.5 M sulfuric acid solution, respectively, followed by calcination at 600 °C for 2 h. The third catalyst, SZ/SiO_2-NP, was prepared by precipitation of 2.45 g $ZrO(NO_3)_2$ on SiO_2 using $NH_3{\cdot}H_2O$ at pH = 10 under constant stirring, followed by sulfation in 0.5 M H_2SO_4 solution and calcination at 600 °C for 2 h. A commercial ion exchange resin, Amberlyst 15 (from Aldrich), was used as a reference catalyst. Two other commercial resins, Nafion NR50 and silica-supported Nafion SAC-13 (from Fluka and Aldrich, respectively), were also tested. Additionally, a zeolite sample H-ZSM-5, obtained from United Catalyst, was also tested.

The reactions were carried out at 80 °C for 2 h in a 25 ml stainless steel batch reactor with constant agitation under a pressure of 1.8 MPa of dried helium. The catalyst loading was 0.5 g in all the cases. Before reaction, all catalysts were dried overnight in an oven at 60 °C under vacuum. The reactants, consisting of an appropriate amount of alcohol (0.2 g methanol or 0.27 g ethanol) and 0.5 g 23DM1B with an alcohol : olefin molar ratio of *ca.* 1 : 1, were mixed with heptane (4 g) as a solvent. The products were analyzed in a Varian gas chromatograph equipped with a capillary column and FID.

Table 1 shows the results of 23DM1B etherification with methanol over the various laboratory-prepared and reference catalysts. In the reaction, 23DM2B and the ether are the major products. A small amount of 2,3-dimethylbutan-2-ol was also detected, probably due to the reaction between the olefins and a trace amount of water from the catalysts and reactant mixture. Amberlyst 15 is an active catalyst converting 23DM1B to 23DM2B and ether at an overall rate of 90%; however, this catalyst is non-selective for etherification, having instead a high (undesirable) isomerization selectivity of 80% and 19% ether yield. Nafion NR50 shows low activity and low isomerization selectivity, but an ether yield of about 16%. The silica-supported Nafion SAC-13 is less active than the unsupported Nafion NR50, a behavior which is not the same as in some other reactions, where Nafion SAC-13 exhibited higher activity than Nafion NR50 due to a high surface area and enhanced accessibility of the reactants to the acid sites.[11,12] HZSM-5 shows a similar activity to the Nafion NR50 but the highest isomerization selectivity (94%) among the all catalysts tested in this investigation and thus the lowest ether yield. For the laboratory-prepared solid acid catalysts, sulfated zirconia exhibits higher conversion, ether selectivity and yield than Nafion SAC-13, while tungstated zirconia is the least active catalyst with an isomerization selectivity similar to that of Nafion SAC-13 and SZ. SZ/SiO_2-S exhibits much higher conversion with a lower isomerization selectivity, and an ether yield of 30%, which is substantially higher than that over the reference Amberlyst 15. SZ/SiO_2-N shows 40% conversion and 64% ether selectivity, both higher than Nafion NR50, and an ether yield of 24%, which is also higher than that over

Table 1 Catalytic activity of various acid solids and commercial resins 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 NR50	29.0	44.0	53.9	15.6
Nafion SAC-13	3.2	21.7	58.9	1.9
HZSM-5	23.2	93.5	1.1	0.3
ZrO_2–WO_3	0.9	19.4	64.2	0.6
SZ	4.7	23.2	66.2	3.1
SZ/SiO_2-S	51.8	41.7	57.6	29.8
SZ/SiO_2-N	38.2	34.4	63.8	24.4
SZ/SiO_2-NP	21.2	28.7	67.4	14.3

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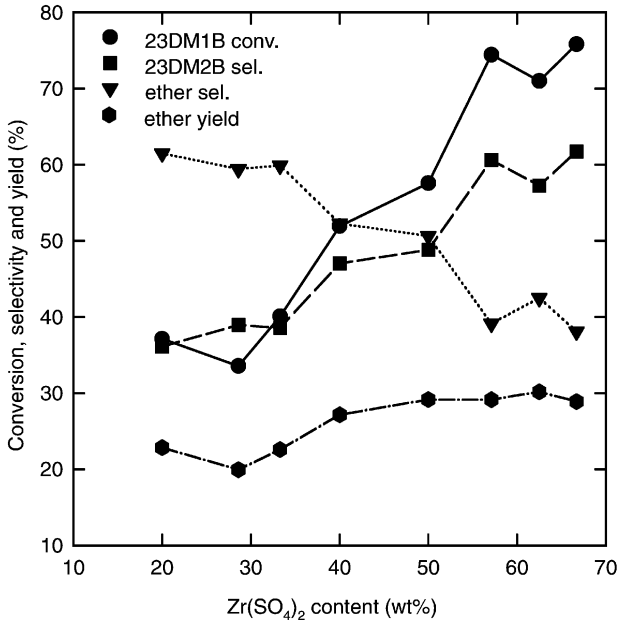

Fig. 1 Effect of $Zr(SO_4)_2$ loading of SZ/SiO_2-S catalysts on catalytic activity.

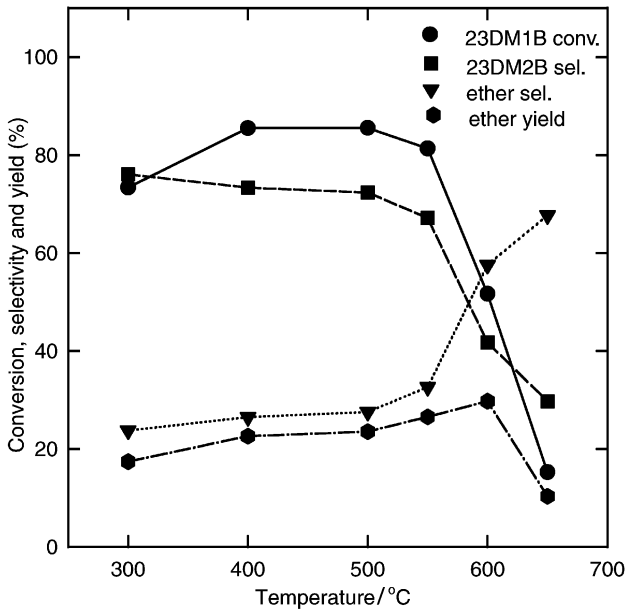

Fig. 2 Effect of calcination temperature on catalytic activity in SZ/SiO_2-S catalysts.

Amberlyst 15. SZ/SiO_2-NP exhibits a lower activity than the other two SiO_2-supported SZ catalysts, but the highest ether selectivity producing an ether yield of 14%, close to those over Amberlyst 15 and Nafion NR50. Therefore, SZ/SiO_2-S is the best catalyst in terms of ether production.

It is well known that etherification or isomerization of olefins generally occurs on acid sites. The acid content is thus an important factor influencing the catalytic activity. The surface areas of catalysts also influence the catalytic activity. Amberlyst 15 has an acid amount of 4.4 $meqH^+\ g^{-1}$ *vs.* 0.89 and 0.12 $meqH^+\ g^{-1}$ for Nafion NR50 and Nafion SAC-13, respectively, making an order: Amberlyst 15 > Nafion NR50 > Nafion SAC-13, which is in agreement with the order of activity. However, in consideration of activity per unit of acidity, the activity of the above catalysts shows a different order; Nafion NR50 > Nafion SAC-13 > Amberlyst 15, which suggests that the catalytic activity also depends on the nature of the acid site. SZ is believed to be a superacid solid, effective for acid-catalyzed reactions such as isomerization. Tungstated zirconia shows little activity probably due to a low acidity. Silica-supported sulfated zirconia could have a better dispersion of active sites for reactions and thus an improved catalytic activity. However, the catalytic behavior of these supported SZ catalysts depends on the preparation technique. Further research on the catalyst characterization is being carried out to elucidate the nature of the active sites responsible for etherification and isomerization.

The effect of varying the composition of $Zr(SO_4)_2$ in SZ/SiO_2-S was further investigated and the results are presented in Fig. 1. It is seen that the loading of $Zr(SO_4)_2$ in SZ/SiO_2-S greatly influences the catalytic activity and selectivity. Both the 23DM1B conversion and 23DM2B selectively generally increase as the $Zr(SO_4)_2$ content increases. The ether yield also increases with increasing $Zr(SO_4)_2$ loading and reaches a stable level of *ca.* 30% for $Zr(SO_4)_2$ exceeding 50 wt%.

Calcination temperature also exerts an influence on the catalytic behavior (Fig. 2). As shown, SZ/SiO_2-S catalysts calcined at 400–550 °C can give much higher conversions, over 80%, comparable to Amberlyst 15. When catalysts are calcined at higher temperatures over 600 °C, the selectivity to ether will be remarkably enhanced, although the overall conversion drops off. In terms of the ether yield, 600 °C is the optimal temperature at which the highest ether yield is achieved.

The catalytic activity of the etherification of 23DM1B with ethanol was also investigated over the resin catalysts and the inorganic acid solids. It was found that Amberlyst 15 is also an effective catalyst for this reaction, exhibiting similar conversion and selectivity to 23DM2B as for the etherification with methanol with an ether yield of 13%. Nafion NR50 and Nafion SAC-13 again are less active than Amberlyst 15, giving ether yields of 9% and 3%, respectively. Sulfated zirconia shows a lower activity than Amberlyst 15 with a conversion of 20% and 58% selectivity to ether but an ether yield of 12%, comparable to that of Amberlyst 15. The SZ/SiO_2-S exhibits 40% conversion and 48% ether selectivity, resulting in an ether yield of 18.4%, higher than that obtained over Amberlyst 15.

In summary, the commercial resin catalyst Amberlyst 15 is an effective but non-selective catalyst in the etherification of C_6 olefins with methanol and ethanol. Silica-supported SZ catalysts exhibit comparable and even higher ether yields than commercial resin catalysts such as Amberlyst 15 and are thus potential alternative catalysts, with the catalytic activity influenced by the zirconium precursor compounds and preparation technique, the ratio of SZ to silica, and calcination temperature.

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