Formation of Trimethylpentanes from Isobutane and 1-Butene Catalyzed by Sulfated Metal Oxides

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The gas-phase alkylation of 1-butene with isobutane was carried out over superacids of sulfated metal oxides, SO_4/Fe_2O_3, SO_4/Al_2O_3, SO_4/TiO_2, SO_4/SnO_2, and SO_4/ZrO_2, at 0 °C; SO_4/SnO_2 gave the highest yield of trimethylpentane (TMP). It was proved from relationship between the catalyst acidities and the yields of C_8 paraffins that the first intermediate species was a t-butyl cation formed on the superacidic Lewis site by abstraction of H^- followed by the alkylation with butenes to form TMP.

Alkylation of isobutane with butenes is an industrial process for the production of high octane gasoline, and two generally commercial plants are using sulfuric acid and hydrofluoric acid as acid catalysts. Due to the means of solving environmental problems, the search for alternative solid acids has been made, but no solid catalyst has reached industrial process. Efforts were focused attention on zeolite catalysts including a new high-silica zeolite, MCM-22.[1-7] Those results show that in spite of a high initial activity, catalysts rapidly deactivate with time-on-stream causing alkene oligomerization.

On the other hand, a solid superacid, sulfated zirconia (SO_4/ZrO_2), was examined in the reaction.[8-10] Althogh the catalyst was more selective to formation of trimethylpentanes than concentrated H_2SO_4 at low temperature, it deactivated quickly like other solid acids.[11] Besides the sulfated zirconia superacids were synthesized on the surface of oxides of Fe, Ti, Hf, Sn, Si, and Al by co-ordination of sulfate materials. In this work we performed a comparative study of sulfated metal oxides for the gas-phase alkylation of isobutane with 1-butene. The influence of various parameters affecting the alkylation was studied; in particular the relation between the acid strength and the formation of trimethylpentanes, most important in the products, was discussed.

Hydrogels of Zr, Fe, Sn, Al, and Ti were prepared from $ZrOCl_2$, $Fe(NO_3)_3$, $SnCl_4$, and isopropoxides of Al and Ti, respectively. The hydrogels were treated with sulfate ion by exposing 2 g of dried and powdered gels in 30 cm^3 of aqueous sulfuric acid on a glass filter for 1 h, followed by filtering, drying, and finally calcining in air for 3 h. The concentration of H_2SO_4 was 0.5 mol dm^{-3} for the gels of Fe, Ti, and Zr, and 3 mol dm^{-3} for those of Sn and Al; the calcination temperature was 500 °C for Fe, 525 °C for Ti, 550 °C for Sn, and 600 °C for Zr and Al. The prepared catalysts are indicated as SO_4/ZrO_2, SO_4/Fe_2O_3, SO_4/TiO_2, SO_4/Al_2O_3, and SO_4/SnO_2.

The alkylation was performed in a glass-made and closed recirculation reactor (300 cm^3). The catalyst was pretreated in vacuum at 200 °C for 1 h, and 50 Torr of isobutane was introduced into the reaction system at 0 °C to adsorb the reagent on the surface of catalyst for 5 min. After the evacuation, a mixture of isobutane (400 Torr) and 1-butene (40 Torr) was introduced to start the reaction. Samples were injected directly into an on-line GC for analysis using a 60 m capillary column (TC-1) with FID at 25-250 °C (18 °C/min). Conversions of isobutane and 1-butene and yield of products were calculated on the basis of mol fraction using propane, an impurity in the reactants, as an internal standard.

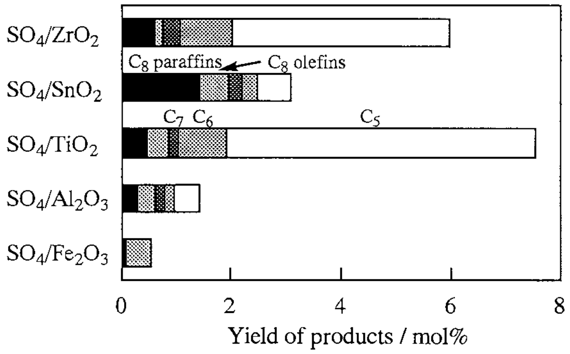

Figure 1. Yields of products over sulfated metal oxides.

The reaction was carried out over 0.2 g of sulfated metal oxides; yields of products are shown in Figure 1. The yields were quite high over SO_4/TiO_2 and SO_4/ZrO_2, but the chief product was pentanes (C_5) along with hexanes (C_6) and heptanes (C_7), produced by the cracking of C_8. On the other hand, SO_4/SnO_2 gave quite high yield of C_8 paraffins, though the whole yield was low compared with the former two. SO_4/Fe_2O_3, whose highest acid strength was $Ho=\sim-13$,[12] showed high selectivity for the formation of C_8 olefins, suggesting the dimerization of butene on week acid sites of superacidity. The acid strength of SO_4/SnO_2 is highest among those of the sulfated metal oxides.[12] This indicates that highly superacidic sites act as the formation of C_8 paraffins in the alkylation.

The product distribution formed on SO_4/SnO_2 showed that the selectivity for trimethylpentane (TMP) is large, more than 80% among octanes. The TMP isomers were identified by comparison with authentic samples; the most product is 2,2,4-TMP with 100.0 of the research octane number (RON) (28% selectivity in C_8 paraffins). A significant amount of 2,2,3-TMP with 109.6, highest in RON, is obtained (13%), though the formation catalyzed by mineral acids such as H_2SO_4 and HF is difficult.[11,13] Other TMP's, 2,3,3- and 2,3,4-TMP, were also sufficiently produced, their RON's being 106.1 and 102.7, respectively.

A relation between the acid strength of catalysts and the yield of C_8 paraffins was examined. The highest acid strength (H_{omax}) of sulfated metal oxides was determined by TPD using pyridine as well as color change method using the Hammett indicators.[12] Thus, the H_{omax} values in the literature were plotted with the yields of C_8 paraffins in Figure 1; a nearly linear relation was obtained as shown in Figure 2. The yield order of SO_4/SnO_2 > SO_4/ZrO_2 > SO_4/TiO_2 > SO_4/Al_2O_3 >

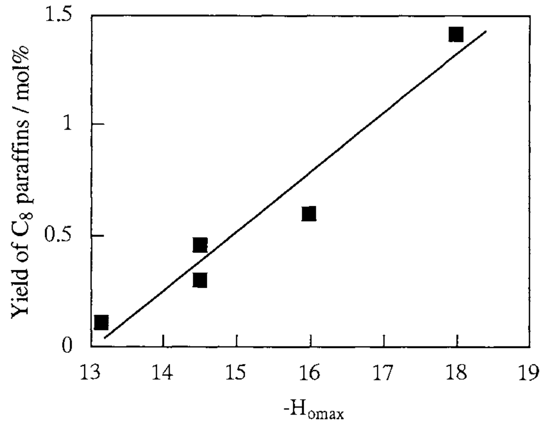

Figure 2. Relation between the yield of C_8 paraffins and H_{omax} of sulfated metal oxides.

SO_4/Fe_2O_3 is related to their highest acid strength values.

The catalytic activity and the surface acidity of sulfated metal oxides can be changed with the preparation procedures. The SO_4/ZrO_2 catalyst was varied with the drying temperature of the gel before sulfation along with the final calcination temperature of the sulfated matter, and thus prepared catalysts were denoted as CAT-1 to -6. These six materials were examined in the alkylation; as shown in Figure 3 the catalytic action was quite varied among them no matter what all the supports were zirconias. TPD of pyridine was also performed with them; several examples of profile are shown in Figure 4. The peak areas between 400 and 600 °C in the TPD profiles were estimated and plotted with their yields of C_8 paraffins as shown in Figure 5. A linear relation is observed, showing the significant relationship between the acidity and alkylation. It is indicated from the figure as well as the plot in Figure 2 that the alkylation to form C_8 paraffins is based on the catalytic action by highly superacidic sites as much as possible.

It can be indicated that the alkylation of isobutane with 1-butene to form C_8 alkylates depends on the activation of i-C_4. Butane is converted into the secondary butyl cation on Lewis acid sites of the SO_4/ZrO_2 catalyst followed by the formation of isobutane via the protonated cyclopropane intermediate.[14] The selectivity for C_8 paraffins was brought about by highly superacidic sites. Thus, it is reasonable that the first intermediate species is a t-butyl cation, thermodynamically most stable, formed on the superacidic Lewis site by abstraction of H^- followed by the alkylation with butenes. 2,2,3-TMP, highest in the RON value, is produced when the alkylated species directly accept H^- from the catalyst surface, but actually most of the H^- transfer occur after the methyl shift from 3- to 4-position, judging from the most product of 2,2,4-TMP.

In the alkylation to form TMP the reaction has been considered to be the alkylation of isobutane with olefins via the protonated olefins as an intermediate, but yields of the TMP products have not been satisfactory when catalyzed by solid acids such as zeolites and silica-aluminas in the heterogeneous system. In the present work it was proved that the reaction is the alkylation of olefins with isobutane via the t-butyl cation formed on highly superacidic sites to result in formation of TMP.

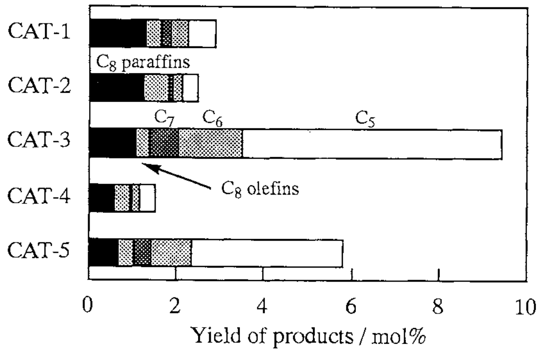

Figure 3. Yields of products over SO_4/ZrO_2 catalysts.

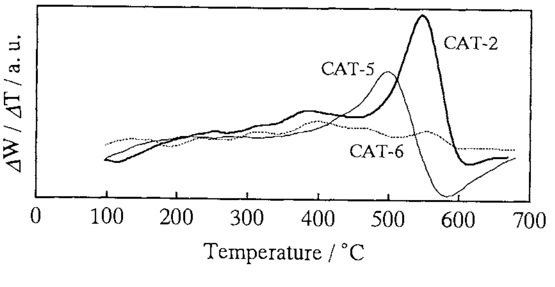

Figure 4. Pyridine TPD profiles of CAT-2, -5, and -6.

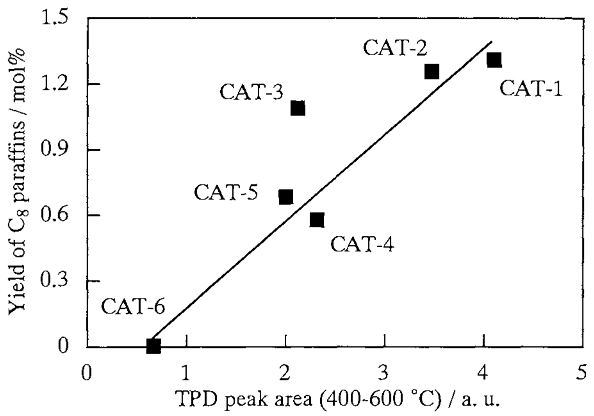

Figure 5. A plot of the peak areas between 400 and 600 °C in the TPD profiles of catalysts against the yields of C_8 paraffins.

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