The Preparation of Solid Superacid of Sulfated Tin Oxide with Acidity Higher Than Sulfated Zirconia

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A highly active solid superacid of sulfated tin oxide was prepared from tin oxide gel which was precipitated from $SnCl_4$ solution and washed with aqueous ammonium acetate solution. The sulfated tin oxide showed activity much higher than the sulfated zirconia, a well known solid superacid, for the skeletal isomerization of *n*-pentane, and its acid strength estimated by temperature-programmed desorption using argon was also higher than that of the latter.

Today, many studies have been reported concerning solid superacids of sulfated metal oxides, where sulfated zirconia (SO_4^{2-}/ZrO_2) is a typical example of those superacids and exhibits a high catalytic activity for the skeletal isomerization of saturated hydrocarbons, and so on.[1,2] Among the sulfated metal oxides, SO_4^{2-}/ZrO_2 is well known as one of the strongest solid superacids; its acid strength is lower than –16 in the Hammett function scale.[1] The preparation procedure has been also improved with very high reproducibility.[3]

Sulfated tin oxide (SO_4^{2-}/SnO_2) is one of the candidates with the strongest acidity on the surface. It has been reported that the acid strength is equal to that of SO_4^{2-}/ZrO_2 at least.[4–7] Nevertheless, papers concerning the SO_4^{2-}/SnO_2 catalyst have been quite few because of difficulty in the preparation, compared with the relative ease of preparation of the SO_4^{2-}/ZrO_2 matter, in particular owing to the difficulty in preparation of the oxide gels from the salts.

This study was aimed to improve the preparation procedure of SO_4^{2-}/SnO_2 for obtaining a highly active solid superacid, its catalytic activity for *n*-pentane isomerization being higher than that of SO_4^{2-}/ZrO_2. Temperature-programmed desorption (TPD) using argon[8] was employed to compare the acid strength of these two catalysts.

Tin oxide gel used as a precursor of SO_4^{2-}/SnO_2 was prepared by a method described below. One hundred grams of $SnCl_4{\cdot}nH_2O$ (Wako Pure Chemical) were dissolved in 3 dm^3 of distilled water followed by adding 25% NH_3 solution dropwise with stirring; the final pH of the solution was adjusted to 8. The precipitated product was collected by filtration and suspended in 4 dm^3 of distilled water or 4 dm^3 of solution containing 0.5–4% CH_3COONH_4. The precipitate was filtered by suction, dried at 373 K for more than 24 h, and finally ground.

The treatment with sulfuric acid was performed as follows. Tin oxide gel (2 g) was placed on a glass suction funnel, covered with 30 cm^3 of 3 mol dm^{-3} H_2SO_4, and allowed to stand for 1 h. After the sample was filtered and dried at 373 K for 2 h, it was calcined in air at 773 K for 3 h and stored in a sealed ampule until use. SO_4^{2-}/ZrO_2 for comparison was also prepared by a reported method.[3] This was calcined at 873 K in air for 3 h before use.

The relative acid strength was measured by TPD using Ar.[8] A sample (ca. 40 mg) was exposed to 6.7 kPa of Ar at room temperature, then cooled to 113 K by N_2 gas which was bubbled out of liquid N_2. After excess Ar was removed by evacuation, the Ar-TPD was performed in the temperature range from 113 to 253 K at the programmed rate of 2–5 K min^{-1}. Argon desorbed from the surface of solid acid was detected by an ionization gauge connected to the vacuum system. The acid strength was estimated as an activation energy of argon desorption.

Tin oxide gel prepared by the hydrolysis of $SnCl_4$ with ammonia water was obtained as a fine particle when it was washed with distilled water, but it was too small to collect by a conventional filter paper. The resulting weight of solid obtained was just 9.0 g (after drying) from 100 g of $SnCl_4{\cdot}nH_2O$ as a starting material. In contrast, the precipitate was obtained quantitatively (43.4 g in average) when it was washed with a solution containing CH_3COONH_4, showing a sharp contrast between a conventional washing using distilled water and this new procedure. The specific surface areas determined by the BET method were ca. 90 m^2 g^{-1} and ca. 20 m^2 g^{-1} for SO_4^{2-}/SnO_2 and SnO_2 samples, respectively; the areas of the sulfated oxides are much larger compared with those of the oxides without the sulfate treatment as observed with the oxides of Zr, Ti, and Fe.[1] The acetate concentration in washing solution showed small effect on the surface areas of SO_4^{2-}/SnO_2. The results indicate that washing with the acetate solution has desirable effects on the yield of the precipitate, but no effect on the surface area.

The present method of preparation was examined in an acid-catalyzed *n*-pentane isomerization. The interconversion between a linear alkane and the corresponding branched alkane is a characteristic reaction over solid superacids.[2] Figure 1 shows the changes of conversion and product composition with reaction time over the catalyst prepared from the oxide gel using the 4% acetate solution along with those of SO_4^{2-}/ZrO_2, whose reaction was performed at 273 K in a closed recirculation system.[9] Products were 2-methylbutane, isobutane, and hexanes. An induction period was observed with the composition change, the product being mainly 2-methylbutane in the induction period. After the period, increase of the activity was observed accompanying with the predominant formation of isobutane with small amount of hexanes. This reaction progress is just analogous to the case of a superacid of SO_4^{2-}/ZrO_2. The change of product composition expresses that the monomolecular reaction via pentyl cation intermediate is predominant in the induction period followed by changing to the bimolecular mechanism with the increase of the reaction rate.[9] Isobutane and hexanes are observed after the accumulation of intermediates for the bimolecular reaction. On the present SO_4^{2-}/SnO_2 catalyst, both of 2-methylbutane amount and total conversion were higher than those on the SO_4^{2-}/ZrO_2. The

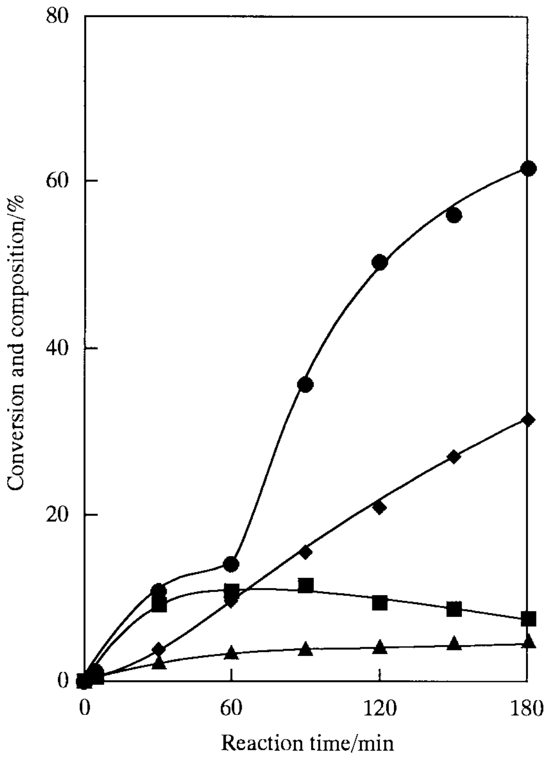

Figure 1. Changes of conversion and product composition in *n*-pentane isomerization. Conversion (●) and 2-methylbutane composition (■) on SO_4^{2-}/SnO_2, conversion (◆) and 2-methylbutane composition (▲) on SO_4^{2-}/ZrO_2.

formation of large amount of 2-methylbutane on SO_4^{2-}/SnO_2 indicates that the monomolecular reaction is more predominant.[9–11] Superacidity is required to form the pentyl cation by the abstraction of hydride on superacidic Lewis acid sites or by the addition of superacidic proton to C–H bond followed by the elimination of dihydrogen. Therefore, it can be expected that the high activity and 2-methylbutane selectivity of SO_4^{2-}/SnO_2 correspond to its high acid strength. The effect of acetate content in washing solution on the *n*-pentane isomerization activity of SO_4^{2-}/SnO_2 was examined to be small. It shows that the use of ammonium acetate solution for washing does not affect on the catalytic performance of the produced sulfated oxides.

The acid strength of the present catalyst prepared from the tin oxide gel using the 4% acetate solution, which showed the highest activity in this study, was compared with that of SO_4^{2-}/ZrO_2. Recently Ar-TPD was reported for evaluation of acid strength of solid superacids.[8] Argon is adsorbed on the surface of solid acids by an acid–base like interaction.[12] The activation energy of Ar desorption relates to the relative acid strength of solid acids and calculated by the following equation, $2\ \ln T_m - \ln\beta = E_d/RT_m$ + const., where T_m is the peak temperature of desorption, β is the temperature-programmed rate, R is gas constant, and E_d is the activation energy. Plots of $2\ \ln T_m - \ln\beta$ vs $1/T_m$ of SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2 are shown in Figure 2. From these plots, E_d from SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2 were calculated to be 10.6 kJ mol^{-1} and 9.3 kJ mol^{-1}, respectively. This result implies that the acid strength of SO_4^{2-}/SnO_2 is higher than that of SO_4^{2-}/ZrO_2.

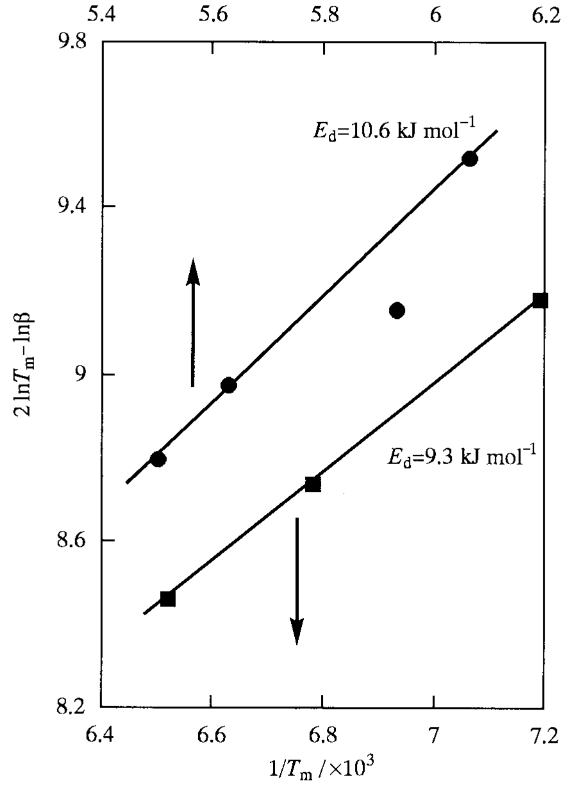

Figure 2. Plots of $2\ln T_m - \ln\beta$ vs $1/T_m$ on SO_4^{2-}/SnO_2 (●) and SO_4^{2-}/ZrO_2 (■) for calculation of the activation energy of Ar desorption.

In conclusion, It can be said that SO_4^{2-}/SnO_2 is a solid superacid with the highest acid strength among the reported solid superacids.

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