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Preparation of a Solid Superacid of Sulfated Tin Oxide with Acidity Higher Than That of Sulfated Zirconia and Its Applications to Aldol Condensation and Benzoylation[1]

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A highly active solid superacid of sulfated tin oxide was prepared from tin oxide gel, which was precipitated by the hydrolysis of $SnCl_4$ and washed with aqueous ammonium acetate solution, followed by exposure to aqueous sulfuric acid and calcining. Differencial thermal analysis suggested that the acetate ion remaining on the surface was replaced with sulfate ion. The acid strength of the sulfated tin oxide estimated by temperature-programmed desorption using argon was higher than that of sulfated zirconia, a well-known solid superacid, the activation energy of Ar desorption by the former being 10.6 kJ mol^{-1} in comparison with 9.3 kJ mol^{-1} by the latter. The sulfated tin oxide showed activities much higher than those of the sulfated zirconia for the skeletal isomerization of *n*-pentane, the Mukaiyama aldol condensation of 1-trimethylsilyloxy-1-cyclohexene with benzaldehyde, and the benzoylation of toluene with benzoic anhydride.

Introduction

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 other reactions.[2,3] Commonly, they have been prepared by the following procedures to generate superacidity: (i) preparation of amorphous metal oxide gels as precursors; (ii) treatment of the gels with sulfate ion by exposure to a H_2SO_4 solution or by impregnation with $(NH_4)_2SO_4$; (iii) calcination of the sulfated materials at a high temperature in air. 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 on the Hammett function scale.[2] The preparation procedure has also been improved with very high reproducibility.[4]

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.[5−7] The results of temperature-programmed desorption (TPD) of pyridine[8] and temperature-programmed reaction of adsorbed furan[3] indicate the possibility that SO_4^{2-}/SnO_2 has an acid strength higher than that of SO_4^{2-}/ZrO_2. Nevertheless, papers concerning the SO_4^{2-}/SnO_2 catalyst have been quite few[7,9] because of difficulty in preparation, compared with the relative ease of preparation of the SO_4^{2-}/ZrO_2 material, in particular owing to the difficulty in preparation of the oxide gels from its salts. Tin oxide gel prepared by the hydrolysis of $SnCl_4$ with ammonia water was obtained as fine particles after being washed with water, and a large part of the precipitates were passed through a conventional filter paper.

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 being higher than that of SO_4^{2-}/ZrO_2. Temperature-programmed desorption (TPD) using argon[10] was employed to compare the acid strength of these two catalysts. SO_4^{2-}/SnO_2 was applied to three acid-catalyzed reactions, skeletal isomerization of *n*-pentane, Mukaiyama aldol condensation, and Friedel−Crafts benzoylation of toluene with benzoic anhydride, to evaluate the catalytic performance.

Experimental Section

Tin oxide gel used as a precursor of SO_4^{2-}/SnO_2 was prepared by a method described below. A 100 g sample of $SnCl_4\cdot nH_2O$ (Wako Pure Chemical) was dissolved in 3 dm^3 of distilled water followed by addition of a 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.

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The sulfated tin oxide was obtained 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. SnO_2, which was not treated with sulfuric acid, was also obtained by calcination of the gel in air at 773 K as a reference sample.

Two kinds of SO_4^{2-}/ZrO_2 catalysts, one prepared by a reported method,[4] along with a commercial one (Wako Pure Chemical), were used as reference catalysts; they were calcined at 873 and 823 K, respectively, in air for 3 h before use. The former catalyst was denoted as SO_4^{2-}/ZrO_2-1 and the latter as SO_4^{2-}/ZrO_2-2.

The specific surface area was calculated by the BET method with the adsorption data of N_2 conducted in a conventional vacuum system. Thermogravimetric and differential thermal analyses (TGA and DTA) were carried out using a Rigaku model, at a programmed rate of 10 K min^{-1}.

The relative acid strength was measured by TPD using argon.[10] The solid acid (ca. 40 mg) was placed in a glass sample tube and pretreated in a vacuum at 473 K for 2 h. After the pretreatment, the sample was exposed to 6.7 kPa of Ar at room temperature and then cooled to 113 K by N_2 gas which was bubbled out of liquid N_2. The adsorption of Ar was carried out at 113 K for 10 min. Afterward, excess Ar was removed by evacuation at the same temperature. The final pressure of the system was lower than 5.0×10^{-3} Pa. The TPD of Ar (Ar-TPD) was performed in the temperature range from 113 to 253 K at the programmed rate of 2–5 K min^{-1}. The sample tube was heated by an electric heater regulated by a temperature controller. Argon desorbed from the surface of the solid acid was detected by an ionization gauge connected to the vacuum system. The acid strength was estimated as an activation energy of Ar desorption.

The skeletal isomerization of *n*-pentane was performed at 273 K in a closed recirculation system, whose volume was ca. 291 cm^3. After catalyst (0.8 g, 32–50 mesh) was set in a reactor and pretreated in a vacuum at 473 K for 3 h, 6.7 kPa of *n*-pentane was introduced into the reaction system. The products were analyzed by gas–liquid chromatography (GLC) using a 60 m capillary column of TC-1 (GL Science) operated at 313 K.

The Mukaiyama aldol condensation was carried out following the literature with a mixture of 1-trimethylsilyloxy-1-cyclohexene (3 mmol), benzaldehyde (3 mmol), and catalyst (100 mg) in dichloromethane (10 cm^3) with stirring at 273 K for 1 h under an Ar atmosphere.[11] After the catalyst was filtered off, the organic phase was worked up by adding dichloromethane, washing with water, and evaporating the solvent under reduced pressure. The yield and selectivity were analyzed by ^1H NMR of the residue, without further purification, in $CDCl_3$ with anisole as an internal standard.

The benzoylation of toluene was also carried out following the literature with a mixture of toluene (15 cm^3), benzoic anhydride (2 mmol), catalyst (500 mg), and tridecane (1 mmol) as an internal standard with stirring at 373 K for 4 h under an Ar atmosphere.[12] The products were analyzed by GLC using a 25 m capillary column of OV-1701 (GL Science).

Results and Discussion

Tin oxide gel prepared by the hydrolysis of $SnCl_4$ with ammonia water was obtained as fine particles when it was washed with distilled water, but they were too small to collect by a conventional filter paper, because a large part of the precipitates passed through the 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 starting material. In contrast, the precipitate was obtained quantitatively (43.4 g on 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. Figure 1 shows the effect of the acetate content in the washing solution on the surface area of calcined samples treated with sulfate ion and untreated. The specific surface areas were ca. 90 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.[2] The results indicate that washing with the acetate solution has no effect on the surface area of calcined tin oxides as well as the sulfated oxides. Ordinarily, the surface of the precipitate particles has a positive or negative charge in solution. There is a repulsive force between the precipitate particles with the same kind of charges. In the solution containing an electrolyte such as ammonium acetate, the surface charge is neutralized by the adsorption of ions, and thus the particles are condensed to be large and can be collected by filtration on a conventional filter paper. These condensed particles have no effect on the surface area of tin oxide as well as the sulfated oxide after calcination. As for other electrolytes for washing of the gel, ammonium sulfate was tried; although the surface area was not influenced, lowering of the catalytic activity was observed with the washing, in comparison with the opposite observations with washing with ammonium acetate.

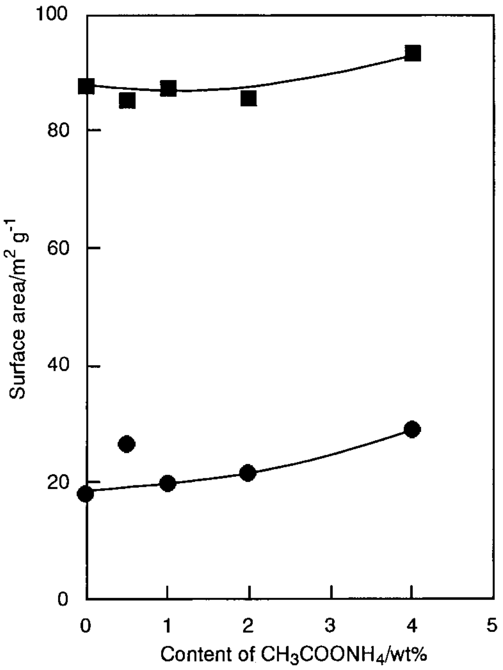

Figure 1. Effect of the CH_3COONH_4 content in the washing solution on the surface area of SO_4^{2-}/SnO_2 (■) and SnO_2 (●).

Figure 2 shows the DTA profiles of tin oxide gels washed with distilled water and an acetate solution in addition to the sample washed with the 4% acetate solution followed by treatment with sulfuric acid. Two exothermal peaks were observed around 530 and 610 K on the sample untreated with the acid. Both of them were attributed to exothermal reactions due to crystallization of the oxide. Although a significant change was

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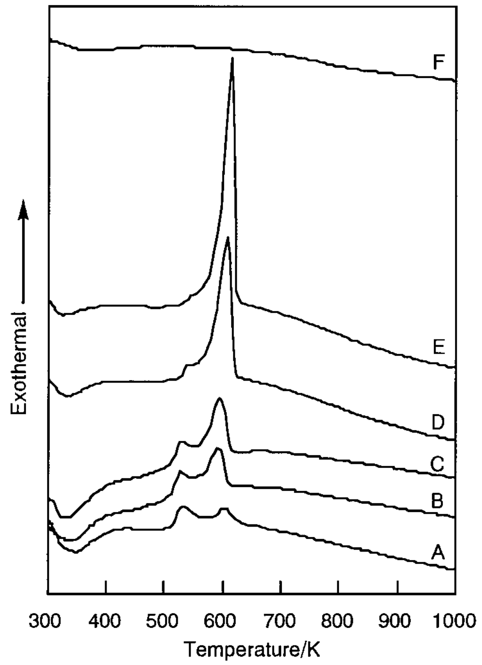

Figure 2. DTA profiles of tin oxide gels washed with distilled water (A) and with CH_3COONH_4 solution (0.5% (B), 1% (C), 2% (D), 4% (E)), and of the gel washed with 4% CH_3COONH_4 solution followed by treatment with sulfuric acid (F).

not observed in the former peak by washing with the acetate solution, the latter was enlarged with increasing acetate content. The calorimetric value of the latter peak, calculated on the basis of the peak area, was ca. 1.4 kJ g^{-1} on the sample washed with the 4% acetate solution. This value is too large to attribute to the heat of crystallization in comparison with that of zirconia (ca. 105 J g^{-1}).[4] Since the latter exothermal peak was accompanied by a weight loss in the TGA and the loss was larger when the acetate content in the washing solution was higher, it can be expected that a great part of the latter peak is due to the combustion of the remaining acetate ion on the oxide surface.

The exothermal peaks due to crystallization completely disappeared in the sulfate treatment as shown in Figure 2. The crystallization of tin oxide is inhibited by a strong interaction of the surface sulfate with the support,[2] and the crystallization occurs partially and gradually. Additionally, the remaining acetate ion was totally replaced with sulfate ion, because the exothermal peak due to the acetate combustion vanished. From this result, it can be speculated that large amounts of adsorption sites for sulfate ion are secured by acetate ion. It shows that the use of ammonium acetate solution for washing of the gel does not affect the catalytic performance of the sulfated oxides.

The present method of preparation was examined in three acid-catalyzed reactions. The interconversion between a linear alkane and the corresponding branched alkane is a characteristic reaction over solid superacids.[3,13] Figure 3 shows the effect of the acetate content in the washing solution on the activity of SO_4^{2-}/SnO_2 catalysts for isomerization of *n*-pentane at 273 K for 180 min. The samples prepared by washing the gels with the acetate solution showed activities approximately 2 times higher than that of the catalyst prepared using distilled water without any salt, though their product selectivities remained constant, isobutane and isopentane in a ratio of 7:1. It is noted that the use of basic ammonia salt raises the activity.

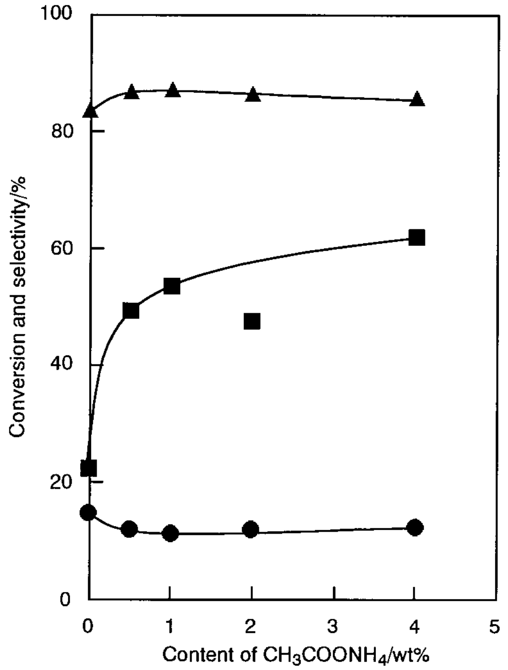

Figure 3. Effect of the CH_3COONH_4 content in the washing solution on the *n*-pentane isomerization activity and selectivity of SO_4^{2-}/SnO_2: conversion (■); isopentane (●); isobutane (▲). Reaction time 180 min.

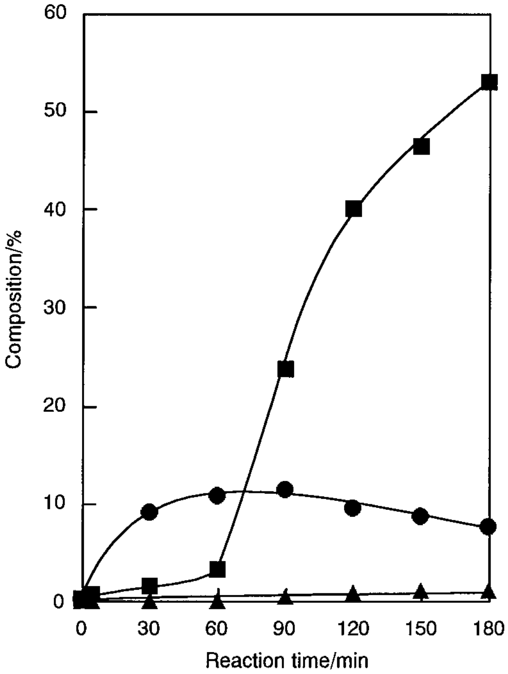

Figure 4. Change of the product composition in the skeletal isomerization of *n*-pentane at 273 K over SO_4^{2-}/SnO_2 prepared from SnO_2 gel washed with 4% CH_3COONH_4 solution: isopentane (●); isobutane (■); C_6 and C_7 alkanes (▲).

Figure 4 shows the changes of product composition with reaction time over the catalyst prepared from the oxide gel using the 4% acetate solution, whose reaction was performed at 273 K in a closed recirculation

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Table 1. Catalytic Activities in Aldol Condensation and Benzoylation

	aldol condensation[a]		benzoylation[b]	
catalyst	yield/ mol %	*syn*:*anti*	yield/ mmol (g of catalyst)$^{-1}$	*ortho*:*meta*:*para*
SO_4^{2-}/SnO_2	100	44:56	2.52	27:5:68
SO_4^{2-}/ZrO_2-2	52	33:67	2.37	37:3:60

[a] 1-Trimethylsilyloxy-1-cyclohexene (3 mmol), benzaldehyde (3 mmol), catalyst (100 mg), dichloromethane (10 cm^3), 273 K, 1 h. [b] Toluene (15 cm^3), benzoic anhydride (2 mmol), catalyst (500 mg), tridecane (internal standard) (1 mmol), 373 K, 4 h.

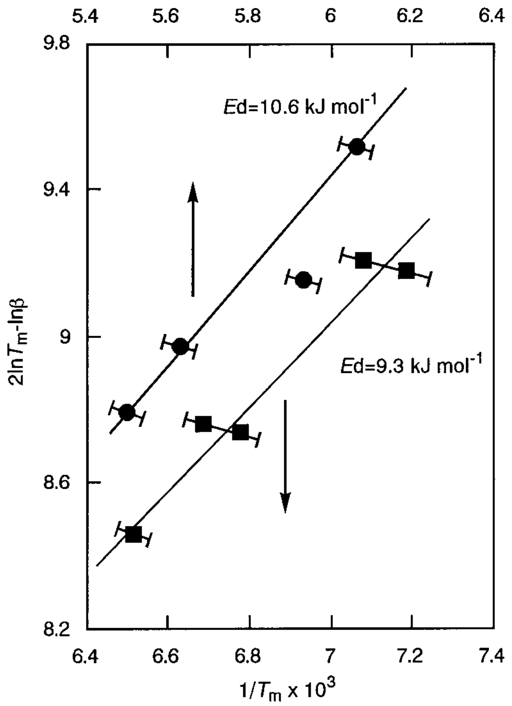
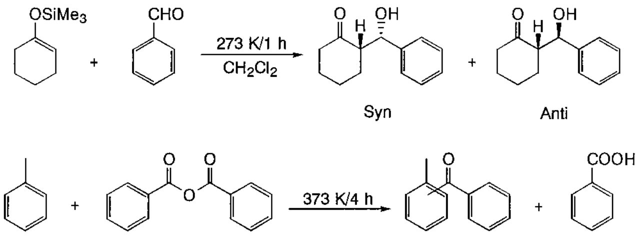


Figure 5. Plots of 2 ln $T_m - \ln \beta$ vs $1/T_m$ on SO_4^{2-}/SnO_2 (●) and SO_4^{2-}/ZrO_2-1 (■) for calculation of the activation energy of Ar desorption.

system.[13] Products were isopentane, isobutane, hexanes, and heptanes. An induction period was observed with the composition change, the product being mainly isopentane in the induction period. After the period, an increase of the activity was observed accompanied by the predominant formation of isobutane with small amounts of hexanes and heptanes. This reaction progress is just analogous to the case of a superacid of SO_4^{2-}/ZrO_2-1.[13] The change of product composition indicates that the monomolecular reaction via a pentyl cation intermediate is predominant in the induction period followed by a change to the bimolecular mechanism with the increase of the reaction rate.[13] Isobutane, hexanes, and heptanes are observed after the accumulation of intermediates for the bimolecular reaction.

On SO_4^{2-}/SnO_2, the isopentane amount and total conversion were 7.6% and 61.7% at 3 h, respectively. Both of them were higher than those on the prepared SO_4^{2-}/ZrO_2-1. In the case of the latter, the conversion of *n*-pentane was 31.2% with 4.8% of the highest isopentane selectivity under the same conditions as those in Figure 4. The formation of a large amount of isopentane on SO_4^{2-}/SnO_2 indicates that the monomolecular reaction via a pentyl cation intermediate is more predominant on the surface.[13-15] 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 a C−H bond followed by the elimination of dihydrogen. Therefore, it can be expected that the high activity and isopentane selectivity of SO_4^{2-}/SnO_2 correspond to its high acid strength. The effect of the acetate content in the washing solution on the *n*-pentane isomerization activity of SO_4^{2-}/SnO_2 was determined to be small. It shows that the use of ammonium acetate solution for washing does not affect the catalytic performance of the sulfated oxides.

Scheme 1. Mukaiyama Aldol Reaction of 1-Trimethylsilyloxy-1-cyclohexene with Aldehyde and Friedel−Crafts Benzoylation of Toluene with Benzoic Anhydride



Very recently Ar-TPD was reported for evaluation of the acid strength of solid superacids.[10] Ar is adsorbed on the surface of solid acids by an acid−base-like interaction,[16] and the activation energy of Ar desorption relates to the relative acid strength of solid acids. The activation energy of the present catalyst prepared from the tin oxide gel using the 4% acetate solution was compared with that of SO_4^{2-}/ZrO_2-1. The activation energy of Ar desorption is calculated by the following equation:[17]

$$2 \ln T_m - \ln \beta = \frac{E_d}{RT_m} + \text{constant}$$

Here, T_m is the peak temperature of desorption, β is the rate of temperature increase, and E_d is the activation energy. A plot of 2 ln $T_m - \ln \beta$ vs $1/T_m$ of the tin catalyst is shown in Figure 5 together with that of SO_4^{2-}/ZrO_2-1 for comparison. From these plots, E_d values were calculated to be 10.6 and 9.3 kJ mol^{-1} for SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2-1, respectively. This result implies that the acid strength of SO_4^{2-}/SnO_2 is higher than that of SO_4^{2-}/ZrO_2-1.

Sulfated tin oxide was applied to the organic reactions of large molecules catalyzed by superacidity, the Mukaiyama aldol reaction of 1-trimethylsilyloxy-1-cyclohexene with aldehyde and the Friedel−Crafts

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benzoylation of toluene with benzoic anhydride, shown in Scheme 1.

The Mukaiyama aldol condensation can be catalyzed by weak acids, such as acetic acid. However, a catalyst with higher acid strength showed higher activity.[18] The catalytic activities of SO_4^{2-}/SnO_2, prepared using the solution containing 4% acetate, for both reactions were compared with those of a commercial sulfated zirconia (SO_4^{2-}/ZrO_2-2); the results are summarized in Table 1. Among the solid superacids synthesized so far, SO_4^{2-}/ZrO_2 showed the highest acid strength ($H_o < -16$), and the SO_4^{2-}/ZrO_2-2 catalyst was highly effective for both reactions,[18] it being especially prepared as a catalyst suitable for the organic synthesis.[11,12]

Table 1 shows that the SO_4^{2-}/SnO_2 catalyst is higher in yield for both reactions, in particular for the aldol condensation, the quantitative reaction being achieved. The reaction of aldol afforded diastereoselectively alcohols with preferential *anti* selectivity as observed with SO_4^{2-}/ZrO_2-2, though the selectivity on SO_4^{2-}/SnO_2 was lower compared with that on SO_4^{2-}/ZrO_2-2; in general *anti* (*threo*) aldols are the preferred isomers under conventional Mukaiyama aldol reaction conditions. As for the products of *o*-, *m*-, and *p*-methylbenzophenones for the benzoylation, the predominant *para*-substitution was more or less similar to that by the SO_4^{2-}/ZrO_2-2 catalyst, this selectivity also being analogous to that of the usual and organic homogeneous reaction. The results in Table 1 indicate that SO_4^{2-}/SnO_2 is superior in superacidity to SO_4^{2-}/ZrO_2-2, along with their analogous catalytic action. This conclusion agrees with the observations determined by the Ar-TPD and the isomerization of *n*-pentane. SO_4^{2-}/SnO_2 shows greater acidity than any solid catalyst yet reported, though a very active catalyst of SO_4^{2-}/ZrO_2 is reported.[19]

Conclusion

A precursor of a highly active solid superacid of sulfated tin oxide was obtained from the precipitation of tin oxide gel, which was washed with aqueous solution containing CH_3COONH_4. The acid strength of the sulfated tin oxide estimated by Ar-TPD was higher than that of sulfated zirconia. It showed activities much higher than those of the sulfated zirconia for *n*-pentane isomerization, Mukaiyama aldol condensation of 1-trimethylsilyloxy-1-cyclohexene with benzaldehyde, and benzoylation of toluene with benzoic anhydride. Particularly the aldol condensation took place quantitatively.

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