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SYNTHESIS OF SOLID SUPERACID OF SILICA TREATED WITH SULFURYL CHLORIDE

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A solid superacid catalyst was synthesized from silica gel, which was obtained from the decomposition of $Si(OC_2H_5)_4$ with HNO_3 solution, by exposing to SO_2Cl_2 followed by calcination in air at 673 K. The catalytic activity for ethanol decomposition was higher than that of SiO_2-Al_2O_3.

Keywords: Solid superacid, silica gel, sulfated silica, ethanol

We have previously reported that solid superacid catalysts with an acid strength of up to $Ho \leqslant -16.04$ were obtained by exposing hydroxides or oxides of Fe, Ti, Zr [1], Hf [2], Al [3], and Sn [4], prior to the crystallization, to sulfate ion followed by calcination in air over 773 K. In our continuous interest in the possibility of creating the superacidic surface acidity on metal oxides, the activity enhancement of the oxides by sulfate addition was observed for SiO_2 by a preparation method different from the cases stated above; the activity for an acid-catalyzed reaction was higher than that of SiO_2-Al_2O_3 catalyst, whose acid strength was in the range of $-12.70 < Ho \leqslant -11.35$.

The catalyst was prepared as follows. Silica gel was obtained by hydrolyzing 100 ml of $Si(OC_2H_5)_4$ with 100 ml of distilled water and a few drops of HNO_3. They were mixed by stirring until the gel formation. The precipitate was obtained by evaporation of the excess water and ethanol, formed by hydrolysis of $Si(OC_2H_5)_4$, followed by drying at 373 K and powdering (20–32 mesh). The silica gel (3 g) was exposed to SO_2Cl_2 in a test tube (o.d. 30 mm) attached with a 3-way cock for 1 h followed by evacuating HCl evolved by the reaction of surface OH group with SO_2Cl_2 and excess SO_2Cl_2 in vacuum. The sample was calcined in a Pyrex tube in air and sealed in an ampoule until use.

Ethanol decomposition was selected as a test reaction to compare activity of the catalyst with that of SiO_2-Al_2O_3 (Syokubai Kogyo Ltd., 13 wt% Al_2O_3, heated at 773 K). The reaction was carried out in a microcatalytic pulse reactor (flow rate of He carrier gas 30 ml/min; pulse size 1.0 l; catalyst weight 20 mg). The

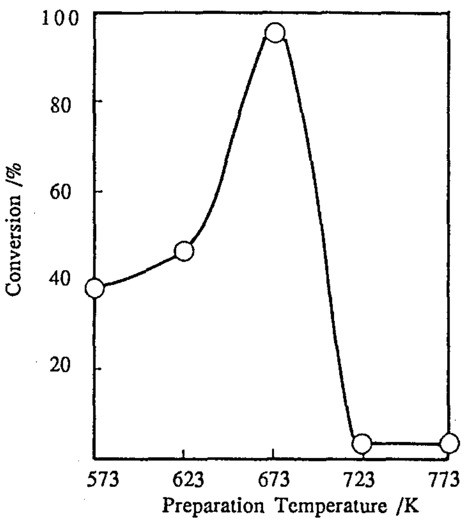


Fig. 1. Effect of preparation temperature on catalytic activity (2nd pulse data).

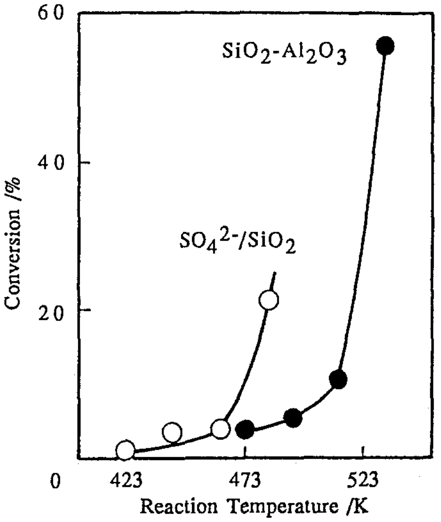


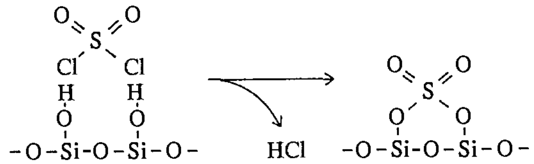
Fig. 2. Dependence of reaction temperature on catalytic activity (2nd pulse data).

catalysts were again heated at 523 K for 2 h in He flow before reaction. Effluent products were trapped at the end of the reaction tube by liq. N_2, then introduced into the gas chromatographic column for analysis (PEG-20M, 2m).

The calcination temperature dependence of catalytic activity for ethanol decomposition is shown in fig. 1. The products were predominantly ethylene with a small amount of diethyl ether. The maximum activity was observed with calcination at 673 K. Catalysts calcined at temperatures higher than 723 K were much lower in activities. Decomposition of sulfur materials on the surface was observed by TG analysis in the temperature range 673–723 K. IR spectra showed the catalysts to possess a bidentate sulfate ion coordinated to the metal as was observed in the case of other superacids [1–4]. The SO_3 content of the catalyst calcined at 673 K [SO_4^{2-}/SiO_2 (673 K)] determined by TGA was 3.9 wt%.

The comparison of catalytic activity of SO_4^{2-}/SiO_2 (673 K) with that of SiO_2-Al_2O_3 is shown in fig. 2. The ethanol decomposition activity of the former was higher than that of the latter in all reaction temperature range, the temperature difference between both catalysts to get the same conversion being ca. 40 K.

n-hexane conversion activity of both catalysts was examined in the pulse reactor (flow rate of He 20 ml/min; pulse size 0.1 1; catalyst weight 0.30 g; reaction temperature 643 K). The conversion of n-hexane was 1.4% (the 4th pulse data) for SO_4^{2-}/SiO_2; the activity was higher than that of SiO_2-Al_2O_3 (0.7%) under the same conditions. The product distribution was very different. Skeletal isomerization was mainly produced over SO_4^{2-}/SiO_2, the selectivity being 53%. In the case of SiO_2-Al_2O_3, the selectivity for skeletal isomers was 24%. Since the acid



Scheme 1. The formation mechanism of surface sulfate complex.

strength of SiO_2-Al_2O_3 is almost the same as that of 100% H_2SO_4, the present catalyst is concluded to be solid superacid.

The treatment with H_2SO_4 and the gelation using NH_3 were not effective to generate superacidity, the method being used for the general preparation of superacid catalysts [1–4]. The generation of superacid sites was explained by a bidentate sulfate complex on the surface of metal oxides, formed by the dehydration between $2H^+$ of H_2SO_4 and surface OH groups [1]. It seems that the complex could be formed by elimination of HCl from SO_2Cl_2 and the OH groups as shown in scheme 1 because of the strong bond of Si-O.

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