CHEMISTRY LETTERS, pp. 1027-1028, 1988.

Synthesis of the Solid Superacid of SO_4^{2-}/SnO_2 with Acid Strength of $Ho \leqq -16.04$

Hiromi MATSUHASHI, Makoto HINO,† and Kazushi ARATA
Hokkaido University of Education, Hachiman-cho, Hakodate 040
†Hakodate Technical College, Tokura-cho, Hakodate 042

A solid superacid catalyst with an acid strength of $Ho \leqq -16.04$ was synthesized from tin hydroxide, which was obtained from the solution with pH=10, by exposing to 3 $mol \cdot l^{-1}$ H_2SO_4 followed by calcination in air at 823 K; the catalyst was active for the skeletal isomerization of butane to isobutane at room temperature.

We have previously reported that solid superacid catalysts with an acid strength of up to $Ho \leqq -16.04$ were obtained by exposing hydroxides or oxides of Fe, Ti, Zr,$^{1)}$ and Hf,$^{2)}$ prior to the crystallization, to sulfate ion followed by calcination in air over 773 K. Tanabe et al. similarly applied this preparation method to tin oxide; the sulfate ion treatment was effective for increasing the catalytic activity of SnO_2 for cyclopentane isomerization, but the highest acid strength was $H_o \leqq -8.2$, whose value is not superacidic.$^{3)}$ In continuation of our interest in possibility of creating the superacidic surface acidity on SnO_2, the SnO_2 catalyst with an acid strength of $Ho \leqq -16.04$ was finally obtained by the different preparation method from the above stated cases.

The catalyst was prepared as follows. $Sn(OH)_4$ was obtained by hydrolyzing $SnCl_4 \cdot xH_2O$ with aqueous ammonium hydroxide; final pH of the solution was adjusted to be 10. The precipitate was washed, dried at 373 K for 24 h and powdered (32-60 mesh). The hydroxide (2 g) was exposed to 3 $mol \cdot l^{-1}$ H_2SO_4 (30 ml) for 30 min followed by filtering, drying at 373 K, and calcining in a Pyrex tube in air for 3 h.

The catalytic activities for the reaction of pentane (C_5) were examined and the results of the first pulse are shown in Table 1. The reaction was carried out in a microcatalytic pulse reactor (flow rate of He carrier gas 20 $ml \cdot min^{-1}$; pulse size 1.6 μl; catalyst 0.5 g). The catalyst was again heated at 523 K for 3 h in the He flow before reaction. Effluent products were directly introduced into a gas chromatographic column for analysis (VZ-7, 4m). The maximum activity was observed with calcination at 823 K [SO_4^{2-}/SnO_2(823 K)]. The products were isopentane (i-C_5), isobutane (i-C_4), and others (cracked materials smaller than C_3), large amounts of decomposed products being observed.

Catalysts [a) in Table 1] prepared from the tin hydroxides, which were obtained from the solution with pH 7, were much lower than those with pH 10 in activities, the former value being used for the general preparation of superacid catalysts.$^{1-3)}$ The maximum activity of the materials treated with sulfate ion

Table 1. Reaction of pentane over SO_4^{2-}/SnO_2 at 523 K

Calcination temp of catalyst/K	Products/%		
	i-C_5	i-C_4	Others
673	4.2	5.0	5.5
773	1.3	2.6	16.4
823	3.0	7.5	40.5
823$^{a)}$	0.6	0.5	7.2
873	0.8	2.1	16.9
873$^{a)}$	0.7	1.5	5.1

a) See text.

Table 2. Reaction of butane over SO_4^{2-}/SnO_2(823 K) at 303 K

Time	Products/%			
h	C_3	i-C_4	i-C_5	C_6
2	Trace	0.7	Trace	0.7
7	Trace	4.3	0.1	0.7
24	0.1	8.4	0.3	0.6
48	0.3	12.1	0.4	0.6
20$^{a)}$	0.3	28.6	1.1	1.8

a) Catalyst amount: 1.0 g.

of different concentrations was observed with 3 $mol \cdot l^{-1}$ concentration [the SO_3 content of SO_4^{2-}/SnO_2(823 K) determined by TGA: 5.2 wt%], though the material treated with <1 $mol \cdot l^{-1}$ concentration showed high activity for other superacids.[1,2] Tanabe et al. prepared the catalyst by immersing $Sn(OH)_4$, obtained from the solution with pH 8, in a solution of $(NH_4)_2SO_4$ followed by evaporating it to dryness and calcining at 773 K (the content of SO_4^{2-}: 2.9 wt%).[3]

The SiO_2-Al_2O_3 catalyst, whose acid strength was in the range of $-12.70 < H_0 \leqq -11.35$, was totally inactive even at temperature of 623 K. The acid strength of SO_4^{2-}/SnO_2(823 K) was estimated using the Hammett indicators to be $H_0 \leqq -16.04$, whose value is markedly superacidic; the catalyst in dried cyclohexane changed the basic form (colorless) of 1,3,5-trinitrobenzene (pKa=-16.04) to the conjugate acid form (yellow).

Reactions were carried out for butane in a recirculation reactor over SO_4^{2-}/SnO_2(823 K) [volume 170 ml; catalyst 0.3 g; butane 7.8 ml (NTP)]. The catalyst was heated at 373 K for 1.5 h at 10^{-3}-10^{-4} mmHg before reaction. The results are shown in Table 2. Propane (C_3), i-C_5, and hexane (C_6) were observed as products in addition to i-C_4, the main product, which was formed by the isomerization; the catalyst was active at room temperature.

The specific surface area of SO_4^{2-}/SnO_2(823 K) was 166 m^2/g, while that of SnO_2 without the sulfate treatment was only 28 m^2/g; the large increase in surface area was also observed on other superacids.[4,5] By XRD analysis the degree of crystallization of the former material was much lower than that of the latter. IR spectra showed the SO_4^{2-}/SnO_2 catalysts to possess a bidentate sulfate ion co-ordinated to the metal (987, 1041, 1153, 1211 cm^{-1}) as was observed in the case of other superacids,[1,4] though in the case of the Fe_2O_3 superacid the samples treated with high concentrations of sulfate ion such as 1.5 and 3 $mol \cdot l^{-1}$ showed the IR spectra of iron sulfate.[6]

References

1) K. Arata and M. Hino, Hyomen, 19, 75 (1981). 2) K. Arata and M. Hino, React. Kinet. Catal. Lett., 25, 143 (1984). 3) G. W. Wnag, H. Hattori, and K. Tanabe, Chem. Lett., 1983, 277. 4) T. Jin, M. Machida, T. Yamaguchi, and K. Tanabe, Inorg. Chem., 23, 4396 (1984); M. Hino, Ph. D. Thesis Hokkaido Univ. Sapporo (1982). 5) M. Hino, K. Arata, and K. Yabe, Shokubai, 22, 232 (1980).
6) M. Hino and K. Arata, Chem. Lett., 1979, 477.

(Received March 25, 1988)