CHEMISTRY LETTERS, pp. 971-972, 1989.

Synthesis of Solid Superacid of Molybdenum Oxide Supported on Zirconia and Its Catalytic Action[1)]

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A solid superacid catalyst was obtained by impregnating $Zr(OH)_4$ with molybdic acid followed by calcining in air at 750-800 °C. XRD showed that superacid sites were not created by impregnation of the molybdate on the crystallized oxide, but on the hydroxide; the material then converted to the crystalline form by calcination.

We have synthesized solid superacids by the addition of sulfate ion to oxides of Fe, Ti, Zr, Hf, and Sn.[2)] In continuation of our studies on superacids, we prepared a new superacid, not containing any sulfate ion but consisting of metal oxides, which was WO_3 supported on ZrO_2 with an acid strength of $H_0 \leqq -14.52$.[3)] This preparation method of catalyst was applied to other metal oxides, and molybdenum oxide supported on zirconia was found to show high surface acidity, much higher than SiO_2-Al_2O_3 which is well known as one of the solid catalysts with the highest surface acidity.

The catalyst was prepared as follows. $Zr(OH)_4$ was obtained by hydrolyzing $ZrOCl \cdot 8H_2O$ with aqueous ammonia, washing, drying at 100 °C, and powdering the precipitates. The hydroxide was impregnated with molybdic acid (H_2MoO_4) dissolved in ammonia water followed by evaporating water, drying, and calcining in air for 3 h. The concentration was 5 wt.% Mo metal based on the hydroxide.

Benzoylation of toluene with benzoic anhydride, which is an example of the Friedel-Crafts acylations, is generally catalyzed by strong acid, especially superacid. The reaction was carried out in liquid phase at reflux temperature (∿110 °C) for 3 h with a mixture of the anhydride (0.185 g), toluene (15 cm^3), and catalyst (0.5 g, 100 mesh) with stirring; the products were analyzed by GC using a 1 m column of Silicone SE-30 (140 °C) with isopropylbenzene as an internal standard. The results are shown in Table 1. The catalyst (MoO_3/ZrO_2) was quite effective for the benzoylation; high activities were observed on calcination at 750-800 °C. The isomer distribution of the product was 20% o-, 4% m-, and 76% p-methylbenzophenones in most cases. Other metal oxides as supports were also examined. The catalysts were prepared from $TiCl_4$, $Si(OC_2H_5)_4$, $Al(NO_3)_3$, and $Fe(NO_3)_3$ as starting materials in the same manner as the ZrO_2 catalyst; commercial $Mg(OH)_2$ was also used. All the materials were completely inactive except the case of slightly active TiO_2 calcined at 700 °C.

Reaction was carried out for hexane in a recirculation reactor over the catalyst calcined at 800 °C [MoO_3/ZrO_2(800 °C)] [volume 170 cm^3; catalyst 1.0 g

Table 1. Activities of MoO_3 supported on metal oxides for the benzoylation

Metal oxide	Temp of calcn./°C	Yield %
ZrO_2	600	14.5
	700	33.0
	750	45.6
	800	50.0
	850	28.5
	900	0
	700,[a] 800[a]	0
TiO_2	700	3.4
	800	0
SiO_2	700, 800	0
Al_2O_3	700, 800	0
Fe_2O_3	700, 800	0
MgO	700, 800	0

a) See text.

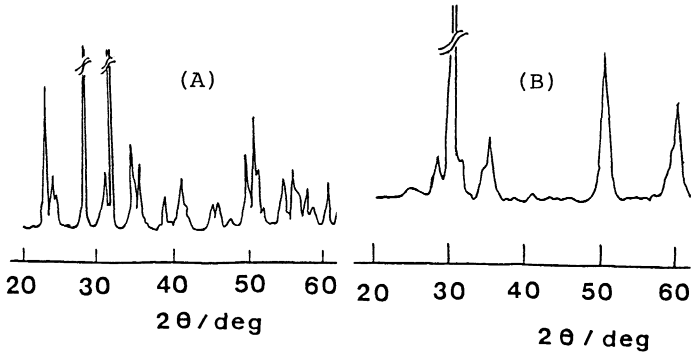

Fig. 1. XRD profiles of catalysts.
(A): See a) in Table 1 and text.
(B): MoO_3/ZrO_2(800 °C).

(32-60 mesh); hexane 7.8 cm^3 (NTP)]; the catalyst was again heated at 100 °C for 1 h in a vacuum before reaction. The catalyst converted hexane into 5.2% propane, 0.4% butane, 0.5% pentane, and 2.5% isopentane in yield at 50 °C for 24 h.

The SiO_2-Al_2O_3 catalyst, whose acid strength was in the range of $-12.70 < Ho \leq -11.35$, was totally inactive for both reactions under the same conditions. Since the present catalyst was itself colored (yellowish green), the acid strength was not estimated by the visual color change method of the Hammett indicators. The catalyst is considered to bear the surface acidity higher than Ho=-12.70 judging from the reaction results. Since the acid stronger than Ho=-12 is known as superacid, the present catalysts are concluded to be superacid.

Superacid sites were not created by impregnation of the molybdate on the crystallized oxide. Namely, the catalysts prepared by calcining $Zr(OH)_4$ at 700 °C to the crystallization (crystallization temperature of ZrO_2: 400 °C), impregnating with the molybdate and calcining at 700 and 800 °C were not active at all for the benzoylation [a) in Table 1]. The XRD pattern of the material prepared from the crystallized oxide was completely different from that prepared from the hydroxide as shown in Fig. 1; the former (A) showed the pattern of ZrO_2 to be monoclinic system, while the latter (B) was identified to be tetragonal.

The specific surface areas of MoO_3/ZrO_2 (700 °C) and MoO_3/ZrO_2 (800 °C) were 60 and 58 m^2/g, while those of the oxides without the molybdate treatment were 15 and 6 m^2/g, respectively; the large increase of area was also observed on a sulfate-treated superacid.[2] XPS spectra of Mo 3d and Zr 3d for MoO_3/ZrO_2(800 °C) were consistent with those for MoO_3 and ZrO_2, respectively.

References 1) Superacids by metal oxides, 3. For previous publication in the Series see Ref. 3. 2) M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., 1979, 1148; 1980, 851: Chem. Lett., 1979, 1259; K. Arata and M. Hino, React. Kinet. Catal. Lett., 1984, 25, 143; H. Matsuhashi, M. Hino, and K. Arata, Chem. Lett., 1988, 1027. 3) M. Hino and K. Arata, J. Chem. Soc., Chem. Commun., 1988, 1259; K. Arata and M. Hino, Proceed. 9th Int. Cong. Catal., p. 1727, Calgary, Canada, 1988.

(Received March 13, 1989)