Catalysis Letters 30 (1995) 25–30

Synthesis of highly active superacids of SO_4/ZrO_2 with Ir, Pt, Rh, Ru, Os, and Pd substances for reaction of butane[☆]

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Received 11 August 1994; accepted 1 November 1994

Highly acidic catalysts stronger than the SO_4/ZrO_2 superacid with an acid strength of $Ho \leqslant -16.04$ were obtained by kneading $Zr(OH)_4$ with ammonium sulfate together with chlorides of Ir, Pt, Rh, Ru, Os, and Pd followed by calcining in air at 600°C, the metal concentration being equivalent to Pt of 7.5 wt% based on the hydroxide. The catalysts with Ir and Pt materials were highest in activity for the skeletal isomerization of butane to isobutane. The present catalysts were not obtained by treating the crystallized oxide, ZrO_2 calcined at 700°C, but the amorphous form followed by calcination to the crystallization.

Keywords: superacid; solid superacid; zirconium oxide; platinum; iridium; rhodium; ruthenium; osmium; palladium; butane

Acids stronger than $Ho = -12$, which corresponds to the acid strength of 100% H_2SO_4, are known as superacids. Solid superacids with an acid strength of up to $Ho \leqslant -16.04$ have been prepared by addition of sulfate ions to oxides of Fe, Ti, Zr, Hf, Sn, Si, and Al [2,3]. Superacids by metal oxides with an acid strength of up to $Ho \leqslant -14.52$ were also synthesized in the same manner as those of the sulfate superacids by supporting oxides of Zr, Ti, Sn, and Fe with WO_3 or MoO_3 [1–4].

Among the superacids studied so far, sulfate-supported zirconia (SO_4/ZrO_2) is highest in acid strength ($Ho \leqslant -16.04$) and relatively easy to prepare, and thus it has been applied to various reactions. The SO_4/ZrO_2 system was recently used with

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[☆] Superacids by metal oxides, VI. For previous publication in this series see ref. [1].

platinum added for stabilizing the catalyst, which was reduced before use in most cases; usually less than 1 wt% of platinum on the surface was effective in preventing catalyst deactivation under hydrogen pressure: for example, hydroisomerization and hydrocracking of *n*-hexadecane [5], promotion by Pt and by adamantyl hydride transfer species for isomerization of alkanes [6], conversion of butane into isobutane [7], and dynamic modification of surface acid properties with molecular hydrogen for zirconium oxide promoted by platinum and sulfate ions [8,9].

Most researchers considered the metal state of platinum responsible for maintaining the catalyst activity [10–12], but there is controversy about the state of platinum on the sulfated zirconia to be the oxidic state [13]. However, nobody has described the intrinsic acidity of a platinum-doped solid superacid, $Pt/SO_4/ZrO_2$, thus less than 1 wt%, usually 0.5 wt%, of platinum being used. We discovered that the platinum-impregnated superacid showed pronounced activity for the acid-catalyzed reaction of butane without reducing it before use or in the absence of hydrogen, much higher than that of SO_4/ZrO_2 without platinum, and that impregnation of the great quantity gave a surprising effect. Here, we report new solid superacids of SO_4/ZrO_2 containing materials of platinum, iridium, rhodium, ruthenium, osmium, and palladium, that are much more active for isomerization of butane than any solid catalyst yet reported.

The catalyst was prepared as follows. $Zr(OH)_4$ was obtained by hydrolyzing $ZrOCl_2 \cdot 8H_2O$ with aqueous ammonia; the final pH of the solution was adjusted to be 8.0. The precipitate was washed with water, dried at 100°C for 24 h, and powdered below 100 mesh. The hydroxide was impregnated with aqueous hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Wako Pure Chemical, Ltd.) or osmium trichloride ($OsCl_3 \cdot 3H_2O$, Nakarai Chemicals, Ltd.) followed by evaporating water and drying at 100°C; the concentration was 0.5–10 wt% Pt based on the hydroxide and equivalent to 7.5 wt% Pt for the Os material. The dried material was then kneaded well with ammonium sulfate using a set of mortar and pestle without water; the quantity of $(NH_4)_2SO_4$ was 15 wt% (3.6 wt% S) based on Pt–ZrO_2. The kneaded material was pre-heated in a beaker at 150°C for 1.5 h followed by calcining 1 g of the sample in a quartz crucible at 600°C for 3 h and finally sealing in an ampoule until use.

The chlorides of Ir, Pt(II), Rh, Ru, and Pd used are insoluble in water, and thus the catalysts with those materials were all prepared by the kneading method without the impregnation step. After $Zr(OH)_4$ was kneaded well with $IrCl_3$ (Nakarai Chemicals), $PtCl_2$ (Nakarai), $RhCl_3$ (Nakarai), $RuCl_3$ (Wako Pure Chemicals), or $PdCl_2$ (Nakarai), ammonium sulfate was added, kneaded, and followed by the same procedures; the metal concentration was equivalent to Pt of 7.5 wt% based on $Zr(OH)_4$ (1.92×10^{-3} mol of the metal chlorides to 5 g of $Zr(OH)_4$).

Reactions for butane were carried out in a microcatalytic pulse reactor with a fixed-bed catalyst (flow rate of He carrier gas 20 ml/min; catalyst 0.05, 0.1 or 2.0 g; pulse size 0.05 ml). Gaseous reactants were introduced via a syringe and passed through the catalyst bed. The catalyst was again heated at 300°C for 1 h in the He flow before reaction. Effluent products were directly introduced into a gas chromatographic column for analysis (VZ-7, 6 m, 0–30°C). Conversions were taken as the average of the first to the fifth pulse value.

The reaction of butane (C_4) was carried out over the catalysts which were obtained by impregnating $Zr(OH)_4$ with hydrogen hexachloroplatinate (0.5 wt% Pt) followed by kneading with ammonium sulfate and then calcining in air at various temperatures; the results are shown in fig. 1 together with those of SO_4/ZrO_2 without Pt substance for comparison. The catalysts ($Pt–SO_4/ZrO_2$) were quite effective for the reaction; high activities were observed on calcination at 550–650°C. Propane (C_3) and pentane (C_5) were observed as products in addition to isobutane (i-C_4), the main product, which was formed from C_4 by skeletal isomerization.

Activities of the catalysts were compared with those of the SO_4/ZrO_2 materials with the highest acid strength of up to $Ho \leqslant -16.04$ among our synthesized superacids; the latter catalysts were prepared by exposing $Zr(OH)_4$ to 1 N H_2SO_4 followed by drying and calcining in air. In the absence of hydrogen or without any reduction before reaction the catalysts with Pt material were more active than the SO_4/ZrO_2 catalysts calcined at any temperature. For comparison of activities between both catalysts the conversions seem to be too high. Thus, the relative activity between the catalysts was examined in the reaction under milder conditions, at 140°C with 0.2 g catalyst; the conversions were 48.4 and 12.8% for the catalyst with Pt calcined at 600°C ($Pt–SO_4/ZrO_2$ (600°C)) and SO_4/ZrO_2 (600°C), respectively, the activity ratio being large.

The catalysts prepared by calcining $Zr(OH)_4$ at 700°C to crystallization, impregnating with the chloroplatinate and finally calcining with $(NH_4)_2SO_4$ at 450–600°C were not active for the reaction (fig. 1). Superacid sites for the reaction were not created by impregnation on the crystallized oxides, but on the amorphous form followed by calcination to crystallization.

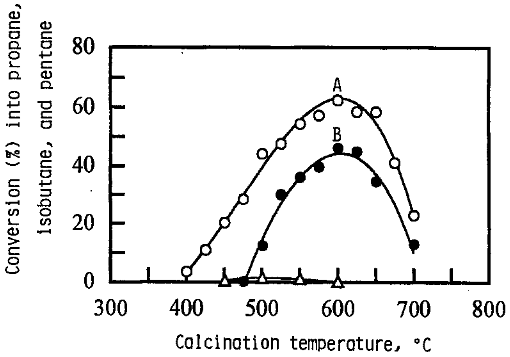

Fig. 1. Catalytic activities for reaction of butane at 180°C (catalyst 0.2 g). (○) SO_4/ZrO_2 with 0.5 wt% platinum. (●) SO_4/ZrO_2 without platinum. (△) SO_4/ZrO_2 prepared by calcining $Zr(OH)_4$ at 700°C for 3 h, impregnating with the platinate (0.5 wt% Pt), and calcining with $(NH_4)_2SO_4$. Yields: A: 25% C_3, 35% i-C_4, 3% C_5, B: 10% C_3, 34% i-C_4, 2% C_5.

Although an active component such as platinum has been usually present in low percentages, 0.1–0.5%, on various supports including SO_4/ZrO_2, the effect of modifying the proportion of platinum more than 0.5% in the catalyst was studied; the results over the catalysts calcined at 600°C are shown in table 1. The maximum activity was observed with 7.5 wt% (7.6 wt% after calcination at 600°C) under milder conditions, at 100 or 80°C with 0.1 g catalyst. This catalyst also gave sufficient conversion to isobutane at 50°C with the quite short contact time. Activity difference between the catalysts prepared from H_2PtCl_6 by the impregnation and from $PtCl_2$ by the kneading method was not observed.

The 7.5% Pt–SO_4/ZrO_2 catalyst, heat-treated at 600°C, also converted propane into butane and isobutane at 150°C (catalyst 0.2 g; pulse size 0.05 ml); yields were 0.7% C_4 and 0.4% i-C_4 in addition to trace amounts of methane, ethane, and pentanes in the fifth pulse.

Since a remarkable enhancement of activity by the Pt addition was observed, this preparation method of catalyst was applied to other metals, and the noble metals Ir, Rh, Ru, Os, and Pd were found to give high effectiveness. Their activity enhancement by the addition of metals equivalent to 7.5 wt% Pt was, however, too large to compare with the activity of the SO_4/ZrO_2 catalyst at a certain reaction temperature. Thus, the activity comparison was performed at different temperatures to get the same conversions among all the materials prepared; the results are shown in fig. 2. It is shown that all the materials with noble metals are much more active than the SO_4/ZrO_2 catalyst for the reaction of butane; Ir and Pt are highest in effectiveness, others being Rh, Ru, Os and Pd in order. The products over all the

Table 1
Activities of Pt–SO_4/ZrO_2 (600°C) catalysts with various amounts of Pt for the reaction of butane at 100°C[a]

Quantity of Pt (wt%)	Conversion (%)	Products (%)		
		C_3	i-C_4	C_5
0	0			
2	9.7	0.3	9.3	0.1
5	19.2	1.8	17.0	0.4
	9.4[b]	0.4	8.9	0.1
7.5	30.8	5.7	24.4	0.7
	12.8[b]	0.6	12.2	trace
	15.0[b,c]	1.0	13.8	0.2
	4.9[d]	trace	4.9	
10	18.4	1.7	16.3	0.4
	6.9[b]	0.3	6.5	0.1

[a] Catalyst: 0.1 g.
[b] Reactions at 80°C.
[c] Prepared from $PtCl_2$ by the kneading method.
[d] Reaction at 50°C.

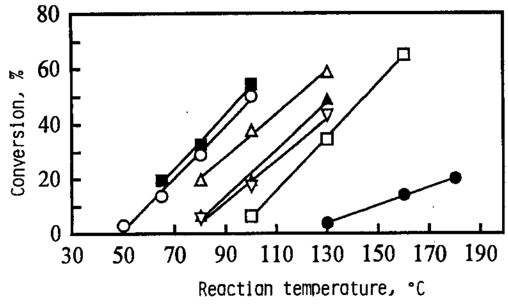

Fig. 2. Activities of SO_4/ZrO_2 with various metals, heat-treated at 600°C, for reaction of butane. Catalyst amount: 0.1 g. First pulse data. (■) Ir, (○) Pt, (△) Rh, (▲) Ru, (▽) Os, (□) Pd, (●), SO_4/ZrO_2 without metal.

catalysts were C_3, *i*-C_4, and C_5, and the selectivities were quite similar to those in table 1.

The present catalysts were themselves darkly colored; the acid strength was not estimated by the visual color change method using the Hammett indicators. The product selectivities from butane over the present catalysts were quite similar to those when catalyzed by superacids, and the activity enhancement by the metal addition was also observed with the cracking of ethylbenzene to benzene and ethene, one of the acid-catalyzed reactions. A continual loss of activity was observed with the pulse number. Since an acidity enhancement was observed with the sulfated ZrO_2 by the addition of Fe and Mn metals [14], we tried to determine the acid strength of 7.5 wt% Pt–SO_4/ZrO_2 from the temperature difference to get the same conversion. Isomerizations of butane and pentane were also reported to be probe reactions for estimating the superacidic strength [15].

The reaction of butane was carried out with a quite small portion of catalyst, 0.05 g, because of the large difference in activity between the present catalysts and the SO_4/ZrO_2 catalysts, whose acid strength was determined by the Hammett method to be $Ho = -16.04$ and -14.52 [2,3], the difference being 1.5. The SO_4/ZrO_2 sample with $Ho = -14.52$ was obtained by hydrolyzing $ZrO(NO_3)_2$ with aqueous ammonia followed by the same procedures and finally calcining at 650°C. As is shown in fig. 3, the temperature difference between both of the SO_4/ZrO_2 catalysts to show 10% conversion ($>90\%$ *i*-C_4 in selectivity) is 27°C. Since the 27°C is equivalent to a Ho value of 1.5, the temperature difference, 94°C, between Pt–SO_4/ZrO_2 and SO_4/ZrO_2 with $Ho = -16.04$ corresponds to values more than 4.5 for the Ho scale. Thus, the catalytic activity of the present catalyst for the reaction of butane corresponds to $Ho \leqslant -20.5$ in acidity on the assumption that the activity difference is due to difference in the Hammett acidity of the two catalysts.

Experiments using XPS were carried out in order to elucidate the surface property. The binding energy of Pt $4f_{7/2}$ in Pt–SO_4/ZrO_2 was 71.4 eV, which was coinci-

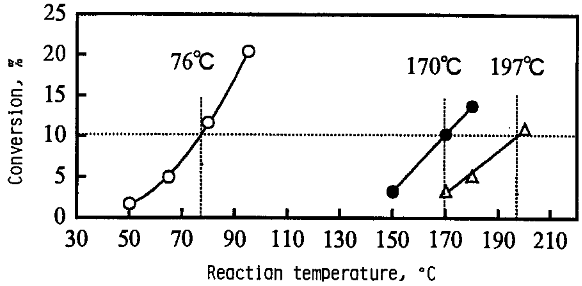

Fig. 3. Comparison of the activity of 7.5% Pt–SO_4/ZrO_2 (○) with those of SO_4/ZrO_2 prepared from $ZrOCl_2$ (●) and from $ZrO(NO_3)_2$ (△) Catalyst amount: 0.05 g. First pulse data.

dent with that of the Pt metal. However, no spectrum showing the metallic state was detected in the samples of Pd–, Rh–, and Ir–SO_4/ZrO_2; the binding energies were 337.0 eV for Pd $3d_{5/2}$, 308.9 eV for Rh $3d_{5/2}$, and 61.8 eV for Ir $4f_{7/2}$, close to those of PdO, Rh_2O_3, and IrO_2, respectively: the reference values for the metallic state; 335.0–335.6 eV for Pd, 306.1–307.4 eV for Rh, 60.3–61.0 eV for Ir. During air calcination, the Pt substance seems to be reduced by SO_2, originated from decomposition of the sulfate matter, but this action is unique to Pt, as suggested by Sayari and Dicko [11].

The specific surface area of all catalysts with 7.5% metals, heat-treated at 600°C, was 100–150 m^2/g, that of SO_4/ZrO_2 without metal being 102 m^2/g. It is not clear at this stage why impregnation of such great quantity of metal is effective.

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