Synthesis of a Highly Active Superacid of Platinum-supported Zirconia for Reaction of Butane

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A highly active superacid of 8 mass% Pt-supported ZrO_2 for the skeletal isomerization of butane to isobutane is obtained by impregnating zirconia gel with 0.5 mol dm^{-3} H_2SO_4 followed by drying, impregnating the sulfated gel with a solution of H_2PtCl_6, and finally calcining in air at 600 °C.

Among the superacids prepared by addition of sulfate ion to several kinds of metal oxides and by supporting the oxides with WO_3 or MoO_3,[1-3] the easily prepared sulfate-supported zirconia (SO_4–ZrO_2) exhibits the highest acid strength (Ho $\leq$ −16.04). The addition of platinum is known to stabilize the catalyst; usually 0.5 mass% of platinum on the surface is effective in preventing catalyst deactivation. There are two general procedures for the preparation of the Pt-doped superacid; one is an incipient wetness technique by impregnation of zirconia gel with 0.5 mol dm^{-3} H_2SO_4 followed by a second impregnation with a solution of H_2PtCl_6.[4-7] The second procedure is the opposite to the first, in that the first impregnation of the gel is with the platinum matter followed by sulfation of the platinum-doped zirconia.[8-10] Most researchers considered the role of platinum to maintain the catalyst activity as the metal state.[11,12]

We discovered that the platinum-impregnated superacid prepared by the impregnation of the zirconia gel with sulfuric acid followed by impregnation with a large quantity of platinum showed greater activity than any solid catalyst yet reported for the acid-catalysed isomerisation of butane without reducing the catalyst before use or in the absence of hydrogen.

Zirconia gel was obtained by hydrolysing $ZrOCl_2$ with aqueous ammonia to pH 8.0 followed by washing, drying at 100 °C for 24 h, and powdering to below 100 mesh.

Four sulfation methods were tried: (1s) exposure of samples (2 g) to 0.5 mol dm^{-3} H_2SO_4 (30 ml) on a filter paper followed by atmospheric drying; (2s) impregnation with an aqueous solution of ammonium sulfate (3.6 mass% S); (3s) kneading with ammonium sulfate using a mortar and pestle without water (15 mass% sulfate, 3.6 mass% S); and (4s) kneading with sulfur in the same manner as (3s) (5 mass%). The loading of platinum was carried out by (1p) impregnation with aqueous $H_2PtCl_6\cdot6H_2O$ followed by evaporating residual water and drying at 100 °C or (2p) kneading with $PtCl_2$ in the same manner as (3s). The concentration was 7.5 mass% Pt based on the gel (8 mass% after calcination). All samples were finally calcined in a quartz crucible at 600 °C for 3 h.

Reactions with butane were carried out in a microcatalytic pulse reactor with a fixed-bed catalyst [He carrier gas 20 ml min^{-1}; catalyst 0.05 g; pulse size 0.05 ml (gas)]: VZ-7, 6 m, 0–30 °C for GC analysis. The catalyst was again heated at 300 °C for 1 h in the He flow before reaction. Activities were compared with the first pulse value.

The reaction of butane was carried out with a small portion of catalyst at temperatures below 100 °C because of high activities. The results obtained by catalysts which were prepared by various methods are shown in Table 1. The catalysts exhibited high activity for the reaction with the short contact time in the absence of hydrogen or without any reduction before reaction. Table 1 shows how the preparation method controls the catalytic activity; the preparation method (1s)–(1p) is the most effective. No activity was observed with the opposite procedure, (1p)–(1s). Other preparations, (1s)–(2p), (1p)–(3s), and (1p)–(4s), were also acceptable, but those activities were much less than that with (1s)–(1p).

The addition of a large amount of platinum, 7–8 mass%, was very effective. For example, the catalysts prepared by the (1s)–

(1p) method with addition of 1.0, 2.0, 5.0, 7.5, 8.5 and 10.0 mass% Pt (based on the gel) gave conversions of 2, 6, 26, 40, 24 and 10%, respectively, at 60 °C; the maximum activity was also observed with 0.5 mol dm^{-3} of H_2SO_4. Propane and pentane were also observed as products in addition to the major product isobutane, formed by skeletal isomerization. In these examples, the selectivities were quite similar. We tried to determine the catalytic strength of these darkly coloured catalysts by temperature/conversion comparisons with the SO_4–ZrO_2 materials whose strength was determined by the visual colour change method using the Hammett indicators; the results are shown in Fig. 1. The product selectivities from butane over the present catalysts were quite similar to those when catalysed by superacids. A continual loss of activity was observed with the pulse number because of poisoning of the active sites. Isomerizations of butane and pentane were reported to be probe reactions for estimating the superacidic strength.[13]

The activities of catalysts prepared by the (1s)–(1p) and (1p)–(3s) methods were compared with those of the SO_4–ZrO_2 catalysts with Ho = −16.04 and −14.52,[1,2] the difference in Ho values being 1.5; the SO_4–ZrO_2 samples were obtained by hydrolysing $ZrOCl_2$ and $ZrO(NO_3)_2$, respectively, with ammonia followed by exposing to 0.5 mol dm^{-3} H_2SO_4 and calcination at 650 °C. The temperature difference to show 10% conversion (>90% isobutane selectivity) between the catalyst

Table 1 Activities of the catalysts prepared by various methods for the reaction of butane

Preparation method	T/°C	Conversion (%)	Products (%)		
			C_3H_8	i-C_4H_{10}	C_5H_{12}
(1s)–(1p)	60	40.0	5.2	33.9	0.9
	40	16.5	0.8	15.5	0.2
(1s)–(2p)	80	13.0	1.0	12.0	
(1p)–(1s)	80	3.2		3.2	
(1p)–(2s)	80	6.5	0.2	6.3	
(1p)–(2s)[a]	80	5.1	0.1	5.0	
(1p)–(3s)	80	11.6	0.7	10.8	0.1
(1p)–(4s)	80	14.4	1.1	13.1	0.2

[a] Prepared in one step.
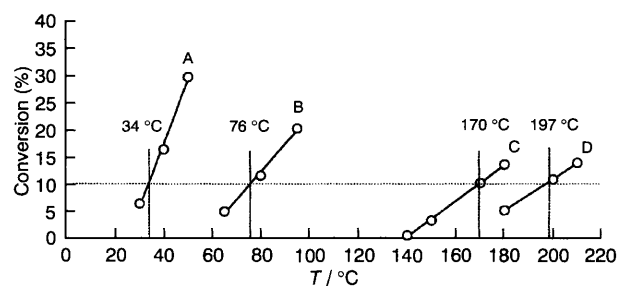

Fig. 1 Comparison of the activities of 8 mass% Pt-supported ZrO_2 prepared by the methods (1s)–(1p) (A) and (1p)–(3s) (B) with those of SO_4–ZrO_2 prepared from $ZrOCl_2$ (C) and from $ZrO(NO_3)_2$ (D)

(A) prepared by method (1s)–(1p) and SO_4–ZrO_2 (C) with Ho = −16.04 is 136 °C, and for the catalyst (B) prepared by method (1p)–(3s) being 94 °C; the catalytic activities correspond to Ho = −23.5 for (A) and −21 for (B) on the assumption that the activity difference is due to the Hammett acidity.

Experiments using XPS were carried out in order to elucidate the surface property of the sample prepared by method (1s)–(1p). The binding energy of Pt 4f7/2 was 73.7 eV, which was coincident with that of Pt^{4+}.[5] The specific surface area was 116 and 100 m^2 g^{-1} for the catalysts prepared by methods (1s)–(1p) and (1p)–(3s), respectively, close to that of SO_4–ZrO_2 without Pt.

The preparation method (1s)–(1p) leads to high dispersion of the Pt matter onto the support. The procedure (1p)–(1s) brings about removal of the platinum materials by the treatment with sulfuric acid, thus the (1p)–(3s) method is better. Pt ions produce complexes with ammonium ion, especially when Pt matter and ammonium sulfate are mixed in the liquid state to result in precipitation (Table 1).

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References

1 K. Arata, *Adv. Catal.*, 1990, **37**, 165.
2 K. Arata and M. Hino, *Mater. Chem. Phys.*, 1990, **26**, 213.
3 M. Hino and K. Arata, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1472.
4 F. Garin, D. Andriamasinoro, A. Abdulsamad and J. Sommer, *J. Catal.*, 1991, **131**, 199.
5 A. Sayari and A. Dicko, *J. Catal.*, 1994, **145**, 561.
6 K. Ebitani, J. Konishi and H. Hattori, *J. Catal.*, 1991, **130**, 257.
7 K. Ebitani, H. Konno, T. Tanaka and H. Hattori, *J. Catal.*, 1992, **135**, 60.
8 M. Y. Wen, I. Wender and J. W. Tierney, *Energy Fuels*, 1990, **4**, 372.
9 E. Iglesia, S. L. Soled and G. M. Kramer, *J. Catal.*, 1993, **144**, 238.
10 S. L. Soled, E. Iglesia and G. M. Kramer, in *Acid–Base Catalysis II*, ed. H. Hattori, M. Misono and Y. Ono, Kodansha, Tokyo, 1994; *Stud. Surf. Sci. Catal.*, vol. 90, Elsevier, Amsterdam–London–New York–Tokyo, 1994, pp. 531–536.
11 Z. Paal, M. Muhler and R. Schlogl, *J. Catal.*, 1993, **143**, 318.
12 J. Zhao, G. P. Huffman and B. H. Davis, *Catal. Lett.*, 1994, **24**, 385.
13 Z. Gao, J. Chen, W. Hua and Y. Tang, in *Acid–Base Catalysis II*, ed. H. Hattori, M. Misono and Y. Ono, Kodansha, Tokyo, 1994; *Stud. Surf. Sci. Catal.*, vol. 90, Elsevier, Amsterdam–London–New York–Tokyo, 1994, pp. 507–518.