Synthesis of Solid Superacid Catalyst with Acid Strength of $H_0 \leqslant -16.04$[1]

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Summary A solid superacid catalyst with an acid strength of $H_0 \leqslant -16{\cdot}04$, which was active for reactions of propane and butane, was obtained by exposing $Zr(OH)_4$, prepared by the hydrolyses of $ZrOCl_2$ and $ZrO(NO_3)_2$, to 1 N H_2SO_4 and then calcining in air at 575—650 °C.

WE have synthesized a solid superacid with an acid strength of $H_0 \leqslant -16{\cdot}04$, the strongest surface-acid system known, and which can be used at temperatures of up to 650 °C; this catalyst also showed a superacid strength of $H_0 \leqslant -13{\cdot}75$, with heat-treatment, even at 800 °C.

The catalyst was prepared as follows. $Zr(OH)_4$ was obtained by hydrolysing $ZrOCl_2{\cdot}8H_2O$ and $ZrO(NO_3)_2{\cdot}2H_2O$ with aqueous ammonia, washing, drying at 100 °C, and powdering the precipitates below a 100 mesh. The commercial hydroxide $Zr(OH)_4{\cdot}xH_2O$ (Nakarai Chemicals, Ltd.) was also used. The hydroxides (2 g) were exposed to 1 N H_2SO_4 (30 ml) on a filter paper followed by drying, calcining in a Pyrex tube in air for 3 h, and finally sealing in an ampoule until use. The catalysts thus prepared from $ZrOCl_2{\cdot}8H_2O$, $ZrO(NO_3)_2{\cdot}2H_2O$, and the commercial $Zr(OH)_4{\cdot}xH_2O$ are referred to as ZrO_2-I, -II, and -III, respectively.

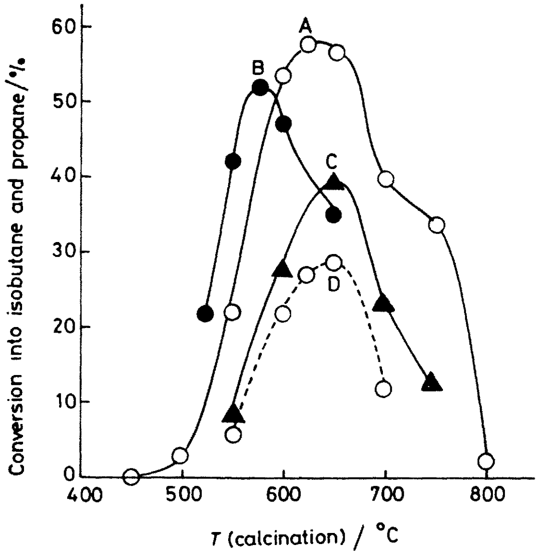

FIGURE. Reaction of butane over ZrO_2-I (○), ZrO_2-II (●), and ZrO_2-III (▲): solid lines, at 180 °C; dashed line, at 130 °C. Propane yields A (17%), B(10%), C(4%), D(0%).

The catalytic activities for the reaction of butane (C_4) were examined and the results are shown as a function of calcination temperature of the catalyst in the Figure. The reaction was carried out in a microcatalytic pulse reactor with a fixed-bed catalyst (flow rate of He carrier gas 10 ml min^{-1}; pulse size 0·05 ml; catalyst 0·3 g). The catalyst was again heated at 400 °C for 1·5 h in the He flow before reaction. Effluent products were directly introduced into a gas chromatographic column for analysis (Porapak R-2m, at 110 °C). Conversions were taken as the average from the first to the fifth pulse value. Since conversions increased until the fifth pulse for the reaction over ZrO_2-I at 130 °C, the average values from the sixth to the tenth pulse reaction are shown. The maximum activity was observed with calcination at 625—650 °C for ZrO_2-I, 575 °C for ZrO_2-II, and 650 °C for ZrO_2-III. The products were isobutane (i-C_4) and propane (C_3). Propane was observed as a minor material when conversions were >20% at 180 °C. Only isobutane was formed over ZrO_2-I at 130 °C.

The reaction of butane was carried out in a recirculation reactor at 25 °C over ZrO_2-I calcined at 650 °C, together with the catalyst treated at 500 °C for comparison [volume 170 ml; catalyst 0·3 g; butane 15 ml (normal temperature and pressure)]. The results are shown in Table 1. Pentane (C_5) and isopentane (i-C_5) were observed as products in addition to C_3 and i-C_4. The amount of butane produced after 48 h, 34·2%, is close to that of the equilibrium mixture of C_4 and i-C_4 at 25 °C, 27 and 73%, respectively.[2]

TABLE 1. Reaction of butane over ZrO_2-I at 25 °C.

T(calcination)/ °C	t/h	Product distribution/%[a]				
		C_3	C_4	i-C_4	C_5	i-C_5
500[b]	48	T[d]	90·5	9·5	0	0
650[b]	24	0·7	78·9	20·4	0	T
	48	1·3	59·7	37·7	T	1·3
650[c]	24	1·1	68·4	30·5	0	T
	48	4·8	34·2	57·8	T	3·2

[a] C_3, C_4, i-C_4, C_5, and i-C_5 indicate propane, butane, isobutane, pentane, and isopentane, respectively. [b] The catalyst was heated again in air at 500 °C for 1·5 h before reaction. [c] The catalyst was evacuated at 250 °C for 3 h at 10^{-2}—10^{-3} mmHg before the reaction. [d] T = Trace.

The catalyst ZrO-I, heat-treated at 650 °C, also converted propane into methane and ethane at 280 °C under pulse reaction conditions (carrier of He 10 ml min^{-1}; pulse size 0·05 ml; catalyst 0·6 g); yields of methane and ethane were 5·1 and 1·3% in the first pulse, 3·9 and 0·8% in the fifth pulse, and 3·7 and 0·8% in the tenth pulse reaction, respectively.

The acid strength of these catalysts was examined by a colour change method using Hammett indicators; the indicator is added to a powdered sample placed in sulphuryl chloride.[3] The results with the indicators *m*-nitrochlorobenzene (pK_a −13·16), 2,4-dinitrotoluene (−13·75), 2,4-dinitrofluorobenzene (−14·52), and 1,3,5-trinitrobenzene (−16·04) are shown in Table 2. The acid strengths of ZrO_2-I (650 °C) and ZrO_2-II (575 °C) are estimated to be $H_0 \leqslant -16{\cdot}04$, which is higher than $H_0 \leqslant -14{\cdot}52$ regarded as the strongest surface-acid known;[3] that for ZrO_2-III (650 °C) being $H_0 \leqslant -14{\cdot}52$. It is of considerable interest that the catalyst, even when heat-treated at quite a high temperature (800 °C), is still a superacid with an acid

TABLE 2. Measurement of the acid strength of the catalyst

Catalyst (T^a/°C)	pK_a Value of the Hammett indicator −13·16	−13·75	−14·52	−16·04
ZrO_2-I (500)	+[b]	+	±[c]	−[d]
ZrO_2-I (650)	+	+	+	+
ZrO_2-I (800)	+	±	−	−
ZrO_2-II (575)	+	+	+	+
ZrO_2-III (650)	+	+	+	−

[a] Calcination temperature. Acidic colour of the indicator was observed [b]distinctly, [c]slightly, and [d]was not observed on the surface.

strength higher than H_0 −13·75. The solid superacids SiO_2–Al_2O_3 and SbF_5–TiO_2–SiO_2, whose acid strengths are higher than that of 100% H_2SO_4 (H_0 −11·9)[4] are estimated to have strengths $-12{\cdot}70 < H_0 \leqslant -11{\cdot}35$[3] and $-14{\cdot}52 < H_0 \leqslant -13{\cdot}75$,[5] respectively.

X-Ray photoelectron and i.r. spectra showed the ZrO_2-I, -II, and -III catalysts to possess the bidentate sulphate ion co-ordinated to the metal. The existence of both Bronsted and Lewis acid sites was shown by the i.r. spectra of pyridine adsorbed on ZrO_2-I (650 °C). With regard to the crystalline structure, the sulphate-treated materials were very different from those not treated in this way. The catalysts ZrO_2-I (650 °C), ZrO_2-II (575 °C), and ZrO_2-III (650 °C) all showed the tetragonal *X*-ray pattern. Specific surface areas of the catalysts were much larger than those of the oxides which had not undergone the sulphate treatment.

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[1] For previous article in the series 'Solid Catalysts treated with Anions' see M. Hino and K. Arata, *Chem. Lett.*, 1980, 963.

[2] F. D. Rossini, 'Physical Chemistry of Hydrocarbons,' Academic Press, New York, 1950.

[3] M. Hino and K. Arata, *J. Chem. Soc., Chem. Commun.*, 1979, 1148.

[4] G. A. Olah, G. K. S. Prakash, and J. Sommer, *Science*, 1979, **206**, 13.

[5] K. Tanabe and H. Hattori, *Chem. Lett.*, 1976, 625.