Synthesis of Solid Superacid of Tungsten Oxide supported on Zirconia and its Catalytic Action for Reactions of Butane and Pentane

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A solid superacid catalyst with an acid strength of $H_0 \leqslant -14.52$ was obtained by impregnating $Zr(OH)_4$ or amorphous ZrO_2 with aqueous ammonium metatungstate followed by calcining in air at 800—850 °C (13 wt.% W); this catalyst was active for the isomerisations butane to isobutane at 50 °C, and pentane to isopentane at 30 °C.

We have synthesized solid superacids by supporting oxides of Fe, Ti, Zr, and Hf with sulphate ion;[1] the catalysts were sufficiently active in a heterogeneous system to facilitate reactions which are generally catalysed by strong acid: the skeletal isomerization of butanes and pentanes,[1,2] the acylation of aromatics with acetic and benzoic acids,[3] and the synthesis of esters from acids and alcohols.[4,5] We have now succeeded in synthesizing another type of superacid, not containing any sulphate ion but consisting of metal oxides, which can be used at temperatures of over 800 °C; this catalyst is more stable than the sulphate-treated materials.

The catalyst was prepared as follows. $Zr(OH)_4$ was obtained by hydrolysis of $ZrOCl{\cdot}8H_2O$ with aqueous ammonia, washing, drying at 100 °C, and powdering the precipitates (32—60 mesh). The hydroxide was impregnated with aqueous ammonium metatungstate $[(NH_4)_6(H_2W_{12}O_{40}){\cdot}nH_2O]$ followed by evaporating water, drying, and calcining in air for 3 h. The concentration was 15 wt.% W based on the hydroxide. Reactions were carried out in a microcatalytic pulse reactor using a stainless-steel tube with a fixed-bed catalyst (flow rate of He carrier gas 10 ml min^{-1}; catalyst 0.5 g; pulse size 1 μl). Liquid reactants were introduced *via* a syringe pump and passed through the catalyst bed. Effluent products were directly introduced into a gas chromatographic column for analysis (VZ-7, 4 m, 50 °C). Conversions were taken as the average of the first to the fifth pulse values.

The catalytic activities for the reaction of pentane (C_5) at 280 °C were examined and the results are shown in Table 1. The catalyst was again heated at 350 °C for 1.5 h in flowing He before reaction. Propane (C_3), butane (C_4), isobutane ($C_4{}^i$), and hexanes (C_6's) were observed as products in addition to isopentane ($C_5{}^i$), the chief product, which was formed from C_5 by skeletal isomerization. Carbon mass balances were conserved. The maximum activity was observed with calcination at the surprisingly high temperatures of 800—850 °C.

The SiO_2–Al_2O_3 catalyst, whose acid strength is in the range of $-12.70 < H_0 < -11.35$,[1] was totally inactive even at 350 °C. The acid strength of the catalyst heat-treated at 800 °C [WO_3–ZrO_2 (800 °C)] was determined by a colour change method using Hammett indicators, where the vapour of the indicators was adsorbed on the catalyst suface in a vacuum apparatus at room temperature. The catalyst changed distinctly from the basic form (colourless) of *m*-nitrochlorobenzene (pK_a −13.16), and 2,4-dinitrotoluene (−13.75), to the conjugate acid form (yellow), and slightly to the colour of 2,4-dinitrofluorobenzene (−14.52). Thus, the acid strength is estimated to be $H_0 < -14.52$, which is in the superacidic range.

Reactions were carried out for the less reactive butane in addition to pentane in a recirculation reactor over WO_3–ZrO_2 (800 °C) [volume 170 ml; catalyst 2.0 g; butane 7.8 ml (NTP)]. The catalyst was again heated at 100 °C for 1.5 h at 10^{-3}—

Table 1. Activities of WO_3–ZrO_2 catalysts for the reaction of pentane at 280 °C.

Calcination temp./°C	Products (wt. %)				Quantity of W (wt.%)
	C_3	$C_4 + C_4{}^i$	$C_5{}^i$	C_6's	
650	0.6	1.3	3.5	Trace	13.3
700	2.2	6.1	10.1	1.4	
800	3.3	9.7	13.1	1.7	12.5
800[a]	0.4	2.8	6.6	1.1	
850	3.2	9.1	13.3	1.9	
900	1.6	4.0	6.6	0.7	
950	0.2	0.4	2.6	Trace	12.9

[a] Reaction at 230 °C.

Table 2. Reactions of butane and pentane in a closed circulating reactor over WO_3–ZrO_2 (800 °C).

Reaction temp./°C	Time/h	Products (wt. %)			
		C_3	$C_4{}^i$	$C_5{}^i$	C_6's
50[a]	48	0.3	0.4		
100[a]	24	0.8	12.2	3.3[c]	
100[a]	48	2.1	20.0	3.4[c]	
30[b,e]	48	0.4	0.8[d]	1.8	0.2
50[b,e]	24	0.7	1.2[d]	1.7	0.2
100[b,e]	6	0.2	7.9[d]	7.3	0.9

[a, b] Reactant: [a] butane, [b] pentane. [c] $C_5 + C_5{}^i$. [d] $C_4 + C_4{}^i$.
[e] Catalyst amount: 1.0 g.

10^{-4} mmHg before reaction. The results are shown in Table 2. The catalyst was active for butane isomerisation at 50 °C and for pentane at 30 °C. The main product from C_4 was $C_4{}^i$, produced by skeletal isomerization; $C_5{}^i$ was predominantly formed from C_5.

The catalytic activities were found to depend greatly on the calcination temperature of the $Zr(OH)_4$ before impregnation. Differential thermal analysis and *X*-ray powder diffraction showed that superacid sites are not created (by impregnation) on the crystallized oxide (treated at >400 °C), but on the amorphous form which calcination then converts to the crystalline form; *i.e.* tungsten oxide combines with zirconium oxide to create superacid sites at the time when a tetragonal system is formed.

The surface properties were studied by *X*-ray photoelectron spectroscopy. The spectra of Zr 3d5/2 and O 1s for WO_3–ZrO_2 (800 °C) were consistent with those for ZrO_2: binding energies (B.E.) of 182.8 and 530.2 eV, respectively. The W 4f7/2 spectrum of WO_3–ZrO_2 was quite similar to that of WO_3, B.E. 36.2 and 35.9 eV, respectively.

The analogous superacid was also formed by the kneading method with tungstic acid (H_2WO_4) which is insoluble in water.

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