Reactions of Butane and Isobutane Catalysed by Titanium Oxide treated with Sulphate Ion. Solid Superacid Catalyst[1]

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Summary Solid superacid catalyst was obtained by exposing H_4TiO_4 to 1 N H_2SO_4 and then calcining in air at 500 °C; this catalyst was active for skeletal isomerizations of butane and isobutane.

Solid superacid has many advantages as a catalyst compared with liquid superacid. We have synthesized a solid superacid which can be used at temperatures up to 500 °C. The catalyst can be prepared with ease by treating H_4TiO_4 with sulphate ion followed by calcination, and is catalytically active for reactions of butane and isobutane which are generally catalysed by superacids such as SbF_5–HF[2] or SbF_5–SiO_2–Al_2O_3.[3]

A typical preparation of the catalysts was as follows. H_4TiO_4-I was obtained by dissolving titanium(IV) isopropoxide in aqueous nitric acid, hydrolysing with aqueous ammonia, washing the precipitate, and drying at 100 °C. H_4TiO_4-II was prepared by hydrolysing aqueous $TiCl_4$ with aqueous ammonia followed by washing and drying. The catalyst was treated with sulphate ion by pouring 1 N H_2SO_4 (30 ml) on to the dried titanium material (2 g) on a filter paper. The materials were dried and powdered below 100 mesh, calcined in a Pyrex tube in air at 500 °C for 3 h, and finally sealed in an ampoule until use. The catalysts thus prepared from H_4TiO_4-I and -II were referred to as TiO_2-I and -II, respectively. Each catalyst was again heated in air at 450 °C for 1·5 h before reaction. Reactions were carried out in a recirculation reactor of *ca.* 170 ml using 1·0 g of the catalyst and 7·8 ml (N.T.P.) of the hydrocarbon. The reaction products were analysed by g.l.c. using a 1 m column of Porapak R.

Both TiO_2-I and TiO_2-II catalysts‡ were active for the skeletal isomerization of butane at room temperature. Isobutane was produced in 4% yield after 24 h and in 8% yield after 48 h, together with trace amounts of propane. The results of the reactions of butane and isobutane at 50 °C are shown in the Table. Pentane, isopentane, and hexane were observed as products in addition to propane and the isomers of the reactants. For butane, the catalytic activity of TiO_2-I was higher than that of TiO_2-II, although the latter catalyst had a higher selectivity for skeletal isomerization, when isobutane was obtained in 93% yield after 48 h. The catalytic activity of TiO_2-I was lower for isobutane than for butane.

Since these catalysts were calcined at 500 °C and hence can be used for reactions up to 500 °C reactions were carried out at high temperatures under pulse reaction conditions (flow rate of He carrier gas, 3 ml min^{-1}; catalyst amount, 0·35 g; pulse size, 0·02 ml). Butane was converted into isobutane in 5% yield at 170 °C; in 13% yield at 200 °C, and to isobutane and propane in 25, and 5% yields, respectively, at 230 °C in the first pulse over TiO_3-I.

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‡ The sulphate-treated catalyst showed i.r. absorption bands at 980, 1040, 1140, and 1240 cm^{-1}, which are assigned to the bidentate sulphate ion co-ordinated to the metal (see ref. 1).

TABLE. Reaction of butane and isobutane over TiO_2-I at 50 °C.

Reactant	Time/h	Product distribution/%					
		Propane	Butane	Isobutane	Pentane	Isopentane	Hexane
Butane	6	1·0	95·8	3·1	0	0	0
	20	1·9	66·8	30·4	Trace	0·9	0
	48	5·8	31·3	59·4	Trace	3·5	Trace
	24[a]	Trace	90·4	9·6	0	0	0
	48[a]	0·7	77·0	21·5	Trace	0·8	0
Isobutane	24	Trace	3·0	97·0	Trace	Trace	0
	48	0·7	5·6	91·9	Trace	1·8	0
	96	1·2	8·5	85·1	0·7	4·5	Trace

[a] Reaction over TiO_2-II.

This catalyst also converted isobutane into butane in 4% yield at 140 °C and to butane and propane in 28 and 5% yields, respectively, at 170 °C in the first pulse.

SiO_2–Al_2O_3 (Shokubai Kasei Kogyo Ltd., 13% Al_2O_3, heat-treated at 500 °C), whose acid strength is in the range $-12{\cdot}70 < H_0 \leqslant -11{\cdot}35$,[1] was inactive for the reaction of butane at 50 °C and gave just 1·5% isobutane at 100 °C after 24 h. The acid strength of the present catalysts was examined by a colour change method using Hammett indicators,[4] when indicator is added to a powdered sample dissolved in solvent. TiO_2-I and -II in dried sulphuryl chloride changed the basic form (colourless) of 2,4-dinitrotoluene ($pK_a = -13{\cdot}75$) to the conjugate acid form (yellow), and also changed the colour of 2,4-dinitrofluorobenzene ($-14{\cdot}52$) slightly. Thus, the acid strength of the present superacid catalysts is estimated to be $-14{\cdot}52 \geqslant H_0$.

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[1] For previous article in the series 'Solid catalysts treated with anions' see M. Hino and K. Arata, *Chem. Letters*, 1979, 1259.

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