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THE SYNTHESIS OF SOLID SUPER ACIDS AND THE ACTIVITY FOR THE REACTIONS OF BUTANE AND ISOBUTANE

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Solid super acids such as SbF_5-TiO_2-SiO_2, SbF_5-TiO_2, and SbF_5-SiO_2-Al_2O_3 were synthesized, whose acid strengths were in the range of $-13.16 \geq H_0 > -14.52$. A SbF_5-TiO_2-SiO_2 showed the highest activity for the reaction of butane _at room temperature_. A SbF_5-TiO_2 was highly selective for the skeletal isomerization of butane, where 72 % of the products was isobutane.

Liquid super acids such as SbF_5-FSO_3H and SbF_5-HF whose acid strength is higher than that of 100 wt.% H_2SO_4 (H_0=-10.60) are known to catalyze the reactions of saturated hydrocarbons at room temperature.[1] The synthesis of solid super acids as catalysts has been desired because of easy separation of products from a reaction system and possibility of repeated use of catalyst. An attempt to support SbF_5 on graphite has been made, but a catalytic activity was not tested.[2] We have succeeded in synthesizing several solid super acids such as SbF_5-TiO_2-SiO_2 and SbF_5-SiO_2-Al_2O_3 whose acid strengths are $-13.16 \geq H_0 > -14.52$ and found that the solid super acids are catalytically active for the reactions of butane and isobutane at room temperature.

Solid super acids were prepared by contacting metal oxides put in a reaction tube made of pyrex glass with vapor of SbF_5 for 5-10 min at room temperature and evacuating for about 10 min at 50°C and repeating the above procedure in order to substitute the surface hydroxyl group by fluorine and to let SbF_5 adsorb on the substituted surface. The metal oxides were preliminarily evacuated _in situ_ at 500°C for 2 hr after calcined in air at 500°C for 1 hr. Silica gel, Al_2O_3, and TiO_2 were prepared by the hydrolysis of ethyl orthosilicate, aluminum isopropoxide, and titanium tetrachloride with aqueous NH_3 respectively, followed by washing thoroughly with distilled water and drying at 100°C. Titania-silica[3] was prepared by the hydrolysis of an aqueous solution of titanium tetrachloride and ethyl orthosilicate with aqueous NH_3 similarly as above. The composition of the binary oxide was 9:1 (molar ratio). Silica-alumina was an SL type (Al_2O_3:15 wt.%) of Shokubai Kasei Co.

The acid strengths of the solid super acids were determined by observing the color change of the following indicators on the surfaces: 2,4-dinitrofluorobenzene(pKa=-14.52), 2,4-dinitrotoluene (-13.75), m-nitrochlorobenzene(-13.16), and p-nitrochlorobenzene(-12.70). The vapor of an indicator was adsorbed on an oxide surface through a breakable seal at room temperature.

Reactions were carried out at 20°C by introducing about 5 ml (NTP) of butane or isobutane (Takachiho Shoji Co.,:99.7% purity) over 0.15g of a catalyst placed in about 30 ml of a reaction tube in a vacuum system. At an appropriate time, the tube was opened and the reaction products were analyzed by gas chromatography with a 6-m column of 30% propylene carbonate on Uniport C.

The results on the reaction of butane or isobutane are shown in Table I. For the reaction of butane, the catalytic activity of SbF_5-TiO_2-SiO_2 was highest, the reaction products being 58.1% of isobutane, 21.9 % of propane, 4.8% of isopentane and a small amount of higher paraffins. The lowest activity was found for SbF_5-Al_2O_3. A SbF_5-TiO_2 catalyst was highly selective for the skeletal isomerization of butane, where 72% of the products was isobutane. Silica-alumina, TiO_2-SiO_2 or SbF_5 alone was completely or almost inactive. The catalytic activities of SbF_5-SiO_2, SbF_5-Al_2O_3, and SbF_5-SiO_2-Al_2O_3 were lower for the reaction of isobutane than for the reaction of butane. This seems to be caused by the fact that the concentrations of butane and isobutane are 18 and 82%, respectively, in equilibrium of the mixture of butane and isobutane.

The SbF_5-TiO_2-SiO_2 which showed a high activity changed distinctly the basic form (colorless) of the indicators whose pKa values are -12.70 and -13.16 to the conjugate acid form (yellow) and slightly the color of the indicator (pKa=-13.75), but did not change the color of the indicator (pKa=-14.52). Thus, the acid strength of SbF_5-TiO_2-SiO_2 is estimated to be $-13.75 \geq H_0 > -14.52$. The acid strengths of SbF_5-TiO_2, SbF_5-SiO_2-TiO_2, and SbF_5-Al_2O_3 were in the range of $-13.16 \geq H_0 > -13.75$.

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Table I. Reaction of Butane and Isobutane over Solid Super Acids at 20°C

Catalyst	Reactant	Time hr	Distribution of Products, %							
			Propane	Butane	Isobutane	Pentane	Isopentane	2,2-DMB[b]	Hexanes[c]	Heptanes C_7
SiO_2-Al_2O_3	Butane	720	0	100	0	0	0	0	0	0
SbF_5-SiO_2		280	6.9	25.2	54.8	1.0	6.8	2.9	2.1	0
SbF_5-TiO_2		280	6.4	17.1	59.1	1.1	13.4	2.0	1.0	0
SbF_5-Al_2O_3		280	0.14	77.2	21.1	0.13	1.3	0.09	0	0
SbF_5-TiO_2-SiO_2		280	21.9	13.1	58.1	0.6	4.8	1.0	0.5	0
SbF_5-SiO_2-Al_2O_3		280	4.4	32.7	47.7	1.1	8.1	3.7	2.6	0
SbF_5-SiO_2-Al_2O_3		20	1.8	49.7	41.0	0.6	4.8	1.4	0.7	0
SiO_2-Al_2O_3	Isobutane	600	0	0	100	0	0	0	0	0
SiO_2-Al_2O_3		4[a]	0	0	99.9	0	<0.1	0	0	0
TiO_2-SiO_2		720	0	0	100	0	0	0	0	0
SbF_5		280	2.9	0.16	96.4	0	0.49	0	0	0
SbF_5-SiO_2		280	7.0	11.8	66.8	1.6	5.6	4.2	2.7	0.3
SbF_5-Al_2O_3		280	0.17	0.93	97.9	0.09	0.86	0	0	0
SbF_5-SiO_2-Al_2O_3		280	6.8	11.0	65.0	1.2	9.6	3.7	2.2	0.4
SbF_5-SiO_2-Al_2O_3		2	0.07	0.4	94.7	3.5	0.4	0.4	0.5	0

[a] Reacted at 200°C. [b] 2,2-Dimethyl butane. [c] 2,3-Dimethyl butane, 2-Methyl pentane, 3-Methyl pentane.

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