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Reaction of Butane to Isobutane Catalyzed by Iron Oxide Treated with Sulfate Ion. Solid Superacid Catalyst[1)]

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Solid acid catalysts were obtained by exposing $Fe(OH)_3$ or Fe_2O_3 to 0.1-0.5 N H_2SO_4 and then calcining in air at 500°C. $Fe(OH)_3$ used was prepared by hydrolyzing $FeCl_3$ or $Fe(NO_3)_3$ with ammonia, and Fe_2O_3 by decomposing $Fe(NO_3)_3$ at 200°C. These catalysts were active for the skeletal isomerization of butane at room temperature or 0°C.

In the previous paper,[2)] we reported that remarkable increases in the surface acidity and in the catalytic activity of Fe_2O_3 were caused by treatment with sulfate ion, followed by calcination, of $Fe(OH)_3$ or Fe_2O_3 prior to the crystallyzation. The sulfate-treated catalyst showed possibility of bearing the surface acidity higher than that of SiO_2-Al_2O_3, which is well known as one of the solid acid catalysts with the highest surface acidity.[3)] Thus in the present work, we studied the catalytic action for reactions of saturated hydrocarbons which are generally catalyzed by strong acid, especially superacid such as SbF_5-HF and SbF_5-FSO_3H[4)] or SbF_5-TiO_2-SiO_2 and SbF_5-SiO_2-Al_2O_3 (solid superacid),[5)] and found that the iron oxide catalyst treated with sulfate ion is active for the reaction of butane at room temperature or even at 0°C.

$Fe(OH)_3$-I and -II were prepared by hydrolyzing $Fe(NO_3)_3 \cdot 9H_2O$ and $FeCl_3$, respectively, with aqueous ammonium hydroxide, washing the precipitates and drying at 100°C. Fe_2O_3[6)] was prepared by thermally decomposing $Fe(NO_3)_3 \cdot 9H_2O$ at 200°C for 2-3 h. The treatment of catalyst with sulfate ion was performed by pouring 30 ml of 0.1 N [for $Fe(OH)_3$-II] or 0.5 N H_2SO_4 [for $Fe(OH)_3$-I and Fe_2O_3] to 2 g of the dried iron materials on a filter paper. After drying (without washing the treated materials with water),[7)] the materials were powdered below 100 mesh, calcined in a Pyrex glass tube in air at 500°C for 3 h and finally sealed in an ampoule until use. The catalysts thus prepared from $Fe(OH)_3$-I, $Fe(OH)_3$-II and Fe_2O_3 were referred to Fe_2O_3-I, -II and -III, respectively. Each catalyst held in the reactor was again heat-treated at 450°C for 1.5 h before reaction. Reactions were carried out at 25°C in a recirculation reactor having a volume of about 170 ml, 1.0 g of the catalyst and 7.8 ml (NTP) of butane being used. The reaction products were analyzed by gas chromatography with a 1-m column of Porapak R.

Figure 1 shows time courses of the isomerization of butane over the catalysts of Fe_2O_3-I, -II and -III at 25°C. The Fe_2O_3-I catalyst was quite active, and the catalytic activity was in the order of Fe_2O_3-I > Fe_2O_3-III > Fe_2O_3-II .[8,9)] Fe_2O_3-II was deactivated below 5 % of conversion, though the yield of isobutane increased with time over Fe_2O_3-I and -III. The product was just isobutane for every reaction. The Fe_2O_3-I catalyst was also active for the reaction even at 0°C. The reaction of isobutane was also performed over the Fe_2O_3-I catalyst under the same conditions, and the conversion to butane was 2.2 % at 25°C and 8.0 % at 40°C for 1 h.

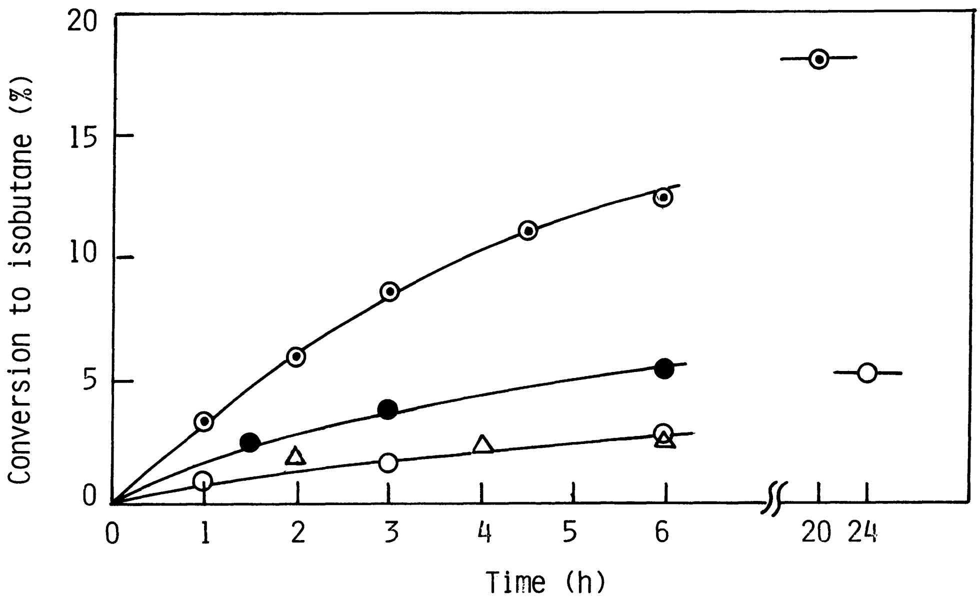

Fig. 1. Reaction of Butane at 25°C. Fe_2O_3-I (⊙), Fe_2O_3-II (△), Fe_2O_3-III (●), Fe_2O_3-I at 0°C (○).

SiO_2-Al_2O_3 (Shokubai Kasei Kogyo Ltd., 13 % Al_2O_3, heat-treated at 500°C) was totally inactive for the reaction of butane at room temperature and gave just 1.5 % isobutane at 100°C for 24 h. Acid strength of SiO_2-Al_2O_3 used was in the range of $-12.70 < Ho \leq -11.35$.[10] Consequently, the present catalysts which showed activities for the reaction of butane at room temperature are considered to bear the surface acidity higher than Ho=-12.70. Since the acid stronger than Ho=-10.6, which corresponds to the acid strength of 100 % H_2SO_4, is known as superacid,[11] the present catalysts are concluded to be solid superacid.

References and Notes

1) Solid catalyst treated with anion. Part III. Part II : M. Hino, S. Kobayashi, and K. Arata, J. Am. Chem. Soc., in press.
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6) DTA of Fe_2O_3 showed that this material crystallizes at 430°C.
7) Sulfate ion was all removed by washing the materials with water before calcination, though most of the ion could not be eliminated by that after calcination.
8) TGA data of the catalysts showed a weight decrease at 550-750°C, which was caused by the decomposition of sulfate adsorbed on the catalyst surface to form SO_3.[2] The SO_3 contents were 3.43, 3.02 and 3.40 wt % for Fe_2O_3-I, -II and -III, respectively.
9) Fe_2O_3-I showed IR absorption bands at 990, 1080, 1120 and 1200 cm^{-1}, which are assigned to the bidentate sulfate coordinated to metal elements.[2]
10) The catalyst changed the basic form (colorless) of indicator (p-nitrotoluene) whose pKa value is -11.35 to the conjugate acid form (yellow), but did not change the color of indicator of p-nitrochlorobenzene (pKa=-12.70). The indicators were adsorbed on the oxide surface in benzene.
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