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HIGHLY SELECTIVE ISOMERIZATION OF PENTANE WITH $AlBr_3$-METAL SULFATE MIXTURES

Yoshio ONO, Shigeharu SAKUMA, Tadashi TANABE,
and Nobumasa KITAJIMA
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

The mixtures of aluminum bromide and metal sulfate are found to be highly active and highly selective catalysts for the conversion of pentane to isopentane. For example, when 10 ml of pentane was shaked with the equimolar mixture of $AlBr_3$ and $Ti_2(SO_4)_3$ (7.5 mmol each) at 28°C for 3 hr, isopentane was obtained in a 86 % yield with the selectivity of > 99 %.

The isomerization of lower saturated hydrocarbons can be effectuated by aluminum halides with cocatalysts such as alkyl chloride, hydrogen halide or water. Because of the increased need of high octane branched paraffins, some modifications of Friedel-Crafts catalysts have been attempted recently to improve the catalysts. Magnotta et al.[1,2] prepared the catalyst with the "superacid character" by the reaction of $AlCl_3$ with sulfonic acid resin, and carried out the conversion of hexane and butane. Tanabe and Hattori[3] prepared "solid super acids" by supporting SbF_5 on oxides, especially on SiO_2-TiO_2, and carried out butane conversion. Ono et al.[4,5] have reported that the mixtures of aluminum chloride and a metal halide or a metal sulfate are effective catalysts for pentane conversion. In every case, however, the isomerization was accompanied by cracking and disproportionation of the hydrocarbons.

In this study, we have examined the catalytic activities of the mixtures of aluminum bromide with some metal salts for pentane isomerization, and found that they were highly active and highly selective catalysts for the isomerization.

Aluminum bromide was purified by sublimation from the eutectic of aluminum bromide and sodium bromide with a small amount of aluminum. Metal sulfates and cupric chloride were heated in vacuo at the tamperatures, at which water of crystallization was supposed to be completely removed. Titanium trichloride was obtained from Toho Titanium Co., and was supposed to have the composition of $TiCl_3 \cdot 1/3AlCl_3$. The catalysts were prepared by kneading the equimolar mixtures of $AlBr_3$ and a metal salt in a porcelain mortar in a nitrogen atmosphere.

The change in the liquid phase composition with time was examined in pentane conversion with $AlBr_3$-$CuSO_4$ mixture as a catalyst. Pentane (10 ml) and the equimolar mixtures of $AlBr_3$ and $CuSO_4$ (3.75 mmol each) were sealed in a glass ampule and shaked in a temperature controlled bath at 28°C. The liquid phase composition was determined by gas chromatography. The result is given in Fig. 1. After 4 hr, the liquid phase is composed of 21.8 % pentane, 77.0 % isopentane, 0.5 % isobutane, 0.7 % hexanes and trace of butane. Under the same conditions, $AlBr_3$ without $CuSO_4$ gives conversion of 8 % and $CuSO_4$ has no activity. Thus, the synergism of the two components are clear. The conversion follows approximately the first-order kinetics.

The catalytic activities of the mixtures of $AlBr_3$ with various metal salts are compared in Table 1. Pentane (10 ml) and the mixtures of $AlBr_3$ and a metal salt (7.5 mmol each) were shaked in a glass ampule at 28°C for 3 hr. The highest yield of isopentane (85.9 %) was obtained with $AlBr_3$-$Ti_2(SO_4)_3$. The mixtures of $AlBr_3$ with other metal sulfates are also highly active and the mixture $AlBr_3$-$TiCl_3$ is also active. It should be noted that the catalytic activities of $AlBr_3$-metal sulfate mixtures are much higher than those of corresponding mixtures of $AlCl_3$-metal sulfate. For example, the mixture of $AlBr_3$-$CuSO_4$ gives the 82.4 % conversion, while the mixture of $AlCl_3$-$CuSO_4$ gives the 20.8 % conversion under the same conditions. Another notable feature of the catalyst is that the selectivity to isopentane is extraordinarily high ($\geq$ 99 %) except the case of $AlBr_3$-$CuCl_2$ catalyst. It is known that the isomerization of saturated hydrocarbons by ordinary Friedel-Crafts catalysts is usually accompanied by side reactions such as cracking or disproportionation and the selectivities of the isomerization are low especially at high conversion.[6-8)]

Only in the case of isomerization with $AlBr_3$-$CuCl_2$ mixture, the selectivity to isopentane is low, though it is also highly active. The dependence of the selectivity on the metal salt suggests that metal sulfates or chlorides are not simply a support of $AlBr_3$, but they play some essential roles in the catalysis.

Table 1. Catalytic Activities of $AlBr_3$-Metal Salt Mixtures for Pentane Isomerization

Catalyst	Total Conversion (%)	Liquid Phase Composition (%)					Selectivity to isopentane (%)
		n-C_5	i-C_5	i-C_4	n-C_4	C_6	
$AlBr_3$-$Ti_2(SO_4)_3$	86.6	13.4	85.9	0.2	trace	0.5	99.2
$AlBr_3$-$CuSO_4$	82.4	17.6	81.5	0.3	trace	0.6	98.9
$AlBr_3$-$Fe_2(SO_4)_3$	71.8	28.2	71.3	0.1	trace	0.4	99.3
$AlBr_3$-$Al_2(SO_4)_3$	61.0	39.0	60.5	0.1	trace	0.4	99.2
$AlBr_3$-$NiSO_4$	60.1	39.9	59.7	0.1	trace	0.3	99.3
$AlBr_3$-$TiCl_3$	67.2	32.8	65.3	0.7	trace	1.2	97.2
$AlBr_3$-$CuCl_2$	94.5	5.5	23.7	40.6	2.9	27.3	25.1

Reaction time 3 hr at 28°C, Pentane 10 ml was shaked with $AlBr_3$-metal sulfate (7.5 mmol each)

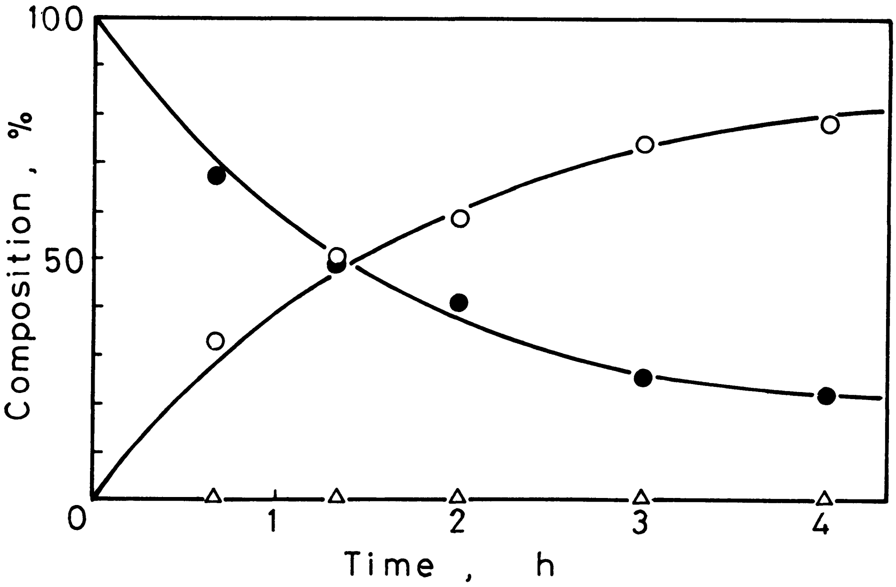

Fig. 1 Change in liquid phase composition with reaction time at 28.0°C.
Catalyst; $CuSO_4$ (3.75 mmol) + $AlBr_3$ (3.75 mmol)
(●) n-C_5, (○) i-C_5, (△) i-C_4 + C_6

The preliminary study revealed that the catalytically active species of $AlBr_3$-$CuSO_4$ system exist both in liquid phase and on the surface of sulfates. The studies on the mechanism of carbenium ion generation and on the nature of active species are now in progress.

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