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The Synergism of $AlCl_3$–$CuCl_2$ Mixtures in the Low-Temperature Conversion of Pentane

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The conversion of pentane has been studied with the mixtures of aluminum chloride and cupric chloride as catalysts at 28–44.5°C. In vapor-phase conversion the main product is isobutane, while in liquid-phase conversion the main product is isopentane at the early stage of the conversion. The mixture shows its highest activity with a composition of 40% $AlCl_3$. The catalytic activities of mixtures of aluminum chloride and other halides have been also examined, and a combination of aluminum chloride and titanium trichloride (AA) has been found most active.

INTRODUCTION

Isomerization of saturated hydrocarbons has assumed great importance in recent years because of the increased need for high-octane branched hydrocarbons. Friedel–Crafts catalysts such as a combination of aluminum chloride and hydrogen chloride are known to be effective for the isomerization (*1–3*). To improve the catalytic properties, some modifications of aluminum halide catalysts have been attempted recently. Lalancette *et al.* have reported that aluminum chloride intercalated in the lattice of graphite is a milder catalyst than aluminum chloride itself and gives less polysubstituted reaction products in the alkylation of aromatics (*4*). Magnotta *et al.* have reported that a catalyst synthesized from aluminum chloride and sulfonic acid resin has the catalytic character of super acid as shown by conversion data for cracking and isomerization of hexane at 85°C (*5, 6*). Schmerling and Vesely have claimed that mixtures of aluminum chloride and metal chloride have an activity for the conversion of cycloalkanes and paraffins at room temperature (*7*). Ono *et al.* have found that mixtures of aluminum halide with metal sulfate are more active than those of aluminum chloride and metal chloride (*8, 9*).

In this work, the synergetic effect of aluminum chloride–cupric chloride mixtures for the conversion of pentane has been studied. The catalytic activities of the mixtures of aluminum chloride and other metal halides have been also studied.

METHODS

Reagent and catalyst. Pentane from Kanto Chemical Co. Inc. was distilled and dried with sodium wire. Aluminum chloride and zirconium tetrachloride from Wako Pure Chemicals were purified by sublimation. Cupric chloride was used after evacuating anhydrous cupric chloride at 200°C. Two types of titanium chloride were obtained

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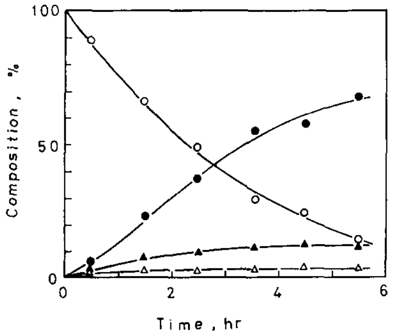

FIG. 1. Change in gas-phase composition with reaction time. Catalyst, $CuCl_2$ (7.5 mmol) + $AlCl_3$ (7.5 mmol); 44.5°C; pentane pressure, 150 Torr; (○) n-C_5, (▲) i-C_5, (●) i-C_4, (△) C_6.

from Toho Titanium Co. Titanium chloride (AA) is prepared by reduction of titanium tetrachloride by aluminum and is supposed to have the composition of $TiCl_3 \cdot \frac{1}{3} AlCl_3$, while titanium chloride (HA) is prepared by reduction of titanium tetrachloride by hydrogen. Hafnium chloride and tantalum chloride were used as received. The other metal halides were evacuated under vacuum to remove the water of crystallization and/or adsorbed water.

The catalysts were prepared by kneading the mixtures of aluminum chloride and a metal halide in a procelain mortar for 10 min in a nitrogen atmosphere.

Apparatus and procedure. The conversion of pentane was carried out both in vapor phase and in liquid phase. For vapor-phase conversion, the mixture catalyst was placed in a glass vessel attached to the constant-volume gas-circulation system (dead volume, 260 ml). The transfer of the catalyst to the glass vessel was done in a nitrogen atmosphere. After evacuating the circulation system, pentane of 150 Torr (1 Torr = 133.3 N m^{-2}) was introduced. A small amount of the gas was withdrawn periodically and analyzed by gas chromatography. For the liquid-phase conversion, the mixture catalyst and 10 ml of pentane were sealed in a glass ampoule and shaken in a temperature-controlled bath. The product mixture was analyzed by a gas chromatography with a hydrogen flame detector using a 6-m column packed with VZ 7 operating at 35°C.

RESULTS AND DISCUSSION

Vapor-phase conversion. Pentane of 150 mm Hg (2×10^4 N m^{-2}) was circulated over an equimolar mixture of aluminum chloride and cupric chloride (7.5 mmol each) at 44.5°C, and the vapor-phase composition was followed with time. A typical result is shown in Fig. 1. In 2 hr, the half of pentane is converted, and isobutane is the main product, isopentane and hexane isomers being minor products. During the run, a small pressure increase was observed, and the material balance was found satisfactory. When only 7.5 mmol of aluminum chloride is used as the catalyst under otherwise similar conditions, the total conversion of pentane is 2.4% in 3 hr. The activity may be caused by the presence of water, which cannot be removed by sublimation. Cupric chloride alone has no catalytic activity at all. Thus, the synergetic effect of the mixture is obvious.

The rate of pentane conversion was found to be first order with respect to pentane from the change in the molar fraction of pentane with the reaction time as well as from the dependence of the rate on the initial pressure of pentane:

$$-dP/dt = kP,$$

where P is the partial pressure of pentane and k is the first-order rate constant ($hours^{-1}$) for total amount of catalyst used. The temperature dependence of the constant gave an activation energy of 57 kJ mol^{-1}.

The effect of catalyst composition on activity is examined. The rate constants were determined from the change in the molar fraction of pentane with reaction time. Figure 2 shows the dependence of the amount of cupric chloride on the rate constant, k, with a fixed amount of aluminum chloride (7.5 mmol). The rate

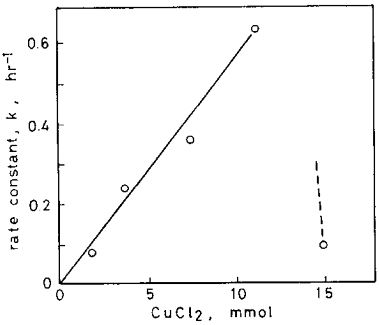

FIG. 2. Dependence of the rate constant, k, on the amount of $CuCl_2$. $AlCl_3$ (7.5 mmol), 44.5°C.

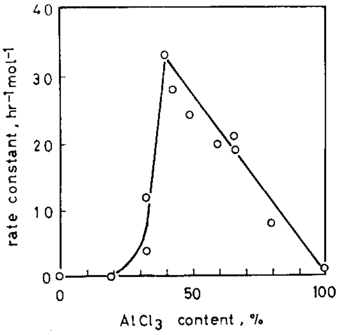

FIG. 4. Dependence of the rate constant on the composition of $AlCl_3$-$CuCl_2$ mixture; 44.5°C.

constant is proportional to the amount of cupric chloride up to 10 mmol, indicating that the active centers are on the surface of cupric chloride. However, the activity falls sharply with further increase of cupric chloride to a Cu/Al ratio of 2. Figure 3 shows the dependence of the amount of aluminum chloride on the rate constant, k, with a fixed amount of cupric chloride (7.5 mmol). Catalytic activity appears only when the amount of aluminum chloride is over 3.75 mmol (Cu/Al < 2) and does not depend on amount when the amount is over 4.5 mmol. The synergism of the mixture is clearly seen in Fig. 4, in which the data in Figs. 2 and 3 are gathered, and the rate constants, k, divided by the total moles of aluminum chloride and cupric chloride in the mixture, are plotted against the composition of the mixture. The activity increases with an increase in cupric chloride content up to 60%, but a further increase in cupric chloride content makes the mixture less active, and over 80%, the mixture shows no activity.

Conversion in liquid phase. The isomerization of pentane is carried out in liquid pentane with suspended catalyst in glass ampoules. A typical example of the change in the liquid-phase composition with time at 28°C is given in Fig. 5. In contrast with vapor-phase conversion, the main product is isopentane until a reaction time of 20 hr. Isobutane increases continuously and becomes main product after 20 hr. The conversion time curve shows that the reaction is first order with respect to pentane, and the rate constant is 0.073 hr⁻¹ at 28°C.

Catalytic activities of various $AlCl_3$-metal halide mixtures. The catalytic activities of

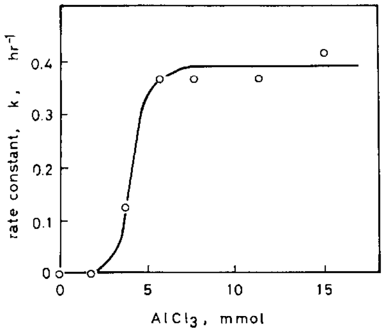

FIG. 3. Dependence of the rate constant, k, on the amount of $AlCl_3$. $CuCl_2$ (7.5 mmol), 44.5°C.

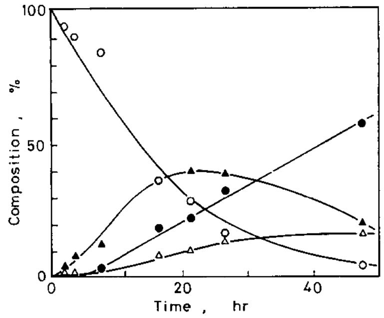

FIG. 5. Change in liquid-phase composition with reaction time. Catalyst, $CuCl_2$ (7.5 mmol) + $AlCl_3$ (7.5 mmol); pentane, 10 ml; 28°C; (○) n-C_5, (▲) i-C_5, (●) i-C_4, (△) C_6.

TABLE 1

Pentane Conversion with $AlCl_3$–Metal Chloride Mixtures[a]

Cocatalyst	Total conversion	Liquid-phase composition				
		n-C_5	iso-C_5	C_6	iso-C_4	n-C_4
$MnCl_2$	11.8	88.2	10.7	0.6	0.5	Trace
$CuCl_2$	11.4	88.6	8.9	1.1	1.4	Trace
$CoCl_2$	8.8	91.2	7.7	0.6	0.5	Trace
$NiCl_2$	6.7	93.3	5.6	0.7	0.4	Trace
$TiCl_3$ (AA)	31.3	68.7	29.7	0.8	0.8	0
$TiCl_3$ (HA)	0.5	99.1	0.5	0.3	0.1	0
VCl_3	6.9	93.1	5.6	0.5	0.8	Trace
$BiCl_3$	5.8	94.2	5.0	0.4	0.4	Trace
$FeCl_3$	3.2	96.8	2.6	0.4	0.2	0
$ZrCl_4$	0.8	99.2	0.2	0.6	Trace	0
$HfCl_5$	0.2	99.8	0.1	0.1	Trace	0
$TaCl_5$	2.4	97.6	2.1	0.2	0.1	0
$MoCl_5$	0.6	99.4	0.4	0.2	Trace	0
—	2.4	97.6	1.7	0.6	0.1	0

[a] Reaction time, 3 hr; temperature, 28°C; pentane, 10 ml; catalyst, $AlCl_3$ (7.5 mmol) + metal chloride (7.5 mmol) except $HfCl_4$ (5.4 mmol) and $TaCl_5$ (6.1 mmol).

the various mixtures of aluminum chloride and metal halides have been examined. Equimolar mixtures of aluminum chloride and metal chloride (7.5 mmol each) and 10 ml of pentane were sealed in glass ampoules and shaken for 3 hr at 28°C, and the liquid-phase compositions were determined by gas chromatography. The results are summarized in Table 1. It is found that a mixture of aluminum chloride and titanium chloride (AA) is most active, and the selectivity for isopentane is highest with this catalyst. The high activity of the $AlCl_3$–$TiCl_3$ (AA) catalyst may be related the fact that $TiCl_3$ (AA) occludes $AlCl_3$ with the composition $TiCl_3 \cdot \frac{1}{3}$ $AlCl_3$. In fact, it was confirmed that $TiCl_3$ (AA) alone has some catalytic activity for pentane conversion in the vapor phase. All the mixtures of aluminum chloride and divalent and trivalent chlorides except titanium chloride (HA) show synergetic phenomena. Mixtures of aluminum chloride and chlorides of tetra- or pentavalent metal cations, which are themselves known as active Friedel–Crafts catalysts, have no catalytic activity at all.

Reaction mechanism. The product distribution indicates that the carbonium ion mechanism is operative since the product distributions are very similar to ordinary Friedel–Crafts hydrocarbon conversion (*2, 3, 10, 11*). It is known that pure aluminum halides have no catalytic activity and requires a promotor or cocatalyst such as an alkyl halide or water. As for the present catalytic systems, the mechanism of carbonium ion generation is not clear yet. For example, it is not clear whether the active sites are Brønsted acid sites or Lewis acid sities.

The enhancement of the activity of aluminum chloride by cupric chloride has been reported in the alkylation of benzene by alkanes (*12*) and also in the polymerization of benzene (*13*). The 2:1 complex formation between aluminum chloride and various metal chlorides such as $CuCl_2$ (*14*), $MnCl_2$ (*15*), $NiCl_2$ (*15*), or $CoCl_2$ (*16*) in the gas phase have already been established and the presence of the complex $TiAl_2Cl_8$ in the liquid phase is known (*17*). It is also reported that the complexes between aluminum chloride and copper (II) compounds convert aromatic compounds into cation radicals under conditions in which aluminum chloride alone has no such capacity (*18*). This may indicate that the complex formation increases the Lewis acid strength of aluminum halides.

The synergetic effect of the mixture of aluminum chloride and cupric chloride may be caused by complex formation between the two components during kneading. The proportionality of the activity to the cupric chloride amount suggests that the complex is formed at the surface of cupric chloride powder between the exposed cupric chloride and aluminum chloride on it. However, it is not clear yet why the activity falls when the ratio of $CuCl_2$ to $AlCl_3$ is higher. The synergetic effect is probably not related to the chlorination properties of the metal halides, since mixtures of aluminum halide with metal sulfate are also very effective catalysts for pentane isomerization (*8, 9*).

The formation of butanes and hexanes

may be produced by the dimerization–decomposition mechanism (*19*, *20*). The greater extent of decomposition to isobutane in vapor-phase reactions than in liquid-phase reactions is probably due to the fact that the adsorbed products or intermediate ions are not easily desorbed from the surface to vapor phase, and the reactions proceed on the surface until isobutane is ultimately produced. In liquid-phase conversion, the products of the surface reactions are more easily desorbed to the hydrocarbon phase, and isopentane is obtained as a main product. The time course of the reaction indicates that isopentane once formed is readsorbed on the surface and undergoes further reactions to form isobutane and isohexanes.

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