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LOW TEMPERATURE CONVERSION OF PENTANE WITH ALUMINUM CHLORIDE-METAL SULFATE MIXTURES

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The mixtures of aluminum chloride and metal sulfate are found to be effective catalysts for the conversion of pentane at low temperatures. For example, when 10 ml of pentane was shaked with the equimolar mixture of $AlCl_3$ and $Ti_2(SO_4)_3$ (7.5 mmol each) at 28°C for 3 hr, the pentane conversion of 46 % was obtained with the selectivity to isopentane of 84 %. In the vapor phase conversion, however, the main product was found to be isobutane.

It has been known that the mixture of aluminum chloride and cupric chloride promotes carbonium ion reactions.[1,3] Schmerling and Vesely[1] have reported that benzene is alkylated by alkanes in the presence of the mixture, while Kovaic and Kyriakis[2] have reported that it is an effective catalyst for polymerization of benzene. In a previous work, we reported that the mixtures of aluminum chloride and metal chloride have catalytic activity for the conversion of pentane.[3] Here, we have examined the catalytic activities of the mixtures of aluminum chloride and metal salt and have found that aluminum chloride-metal sulfate mixtures are more effective catalysts for isomerization of pentane than aluminum chloride-metal chloride mixtures.

Catalysts were prepared by kneading a mixture of aluminum chloride and a dehydrated metal salt in a porcelain mortar in a nitrogen atmosphere. Aluminum chloride was purified by sublimation from the eutectic of aluminum chloride and sodium chloride with a small amount of aluminum powder. Metal salts were dehydrated under vacuum at the temperature, at which water of crystallization was supported to be completely removed.

Catalytic activities of various mixtures of aluminum chloride and copper salts for pentane conversion were examined. The equimolar mixture of aluminum chloride and a metal salt (7.5 mmol each) and 10 ml of pentane were sealed in a glass ampule, and shaked for 3 hr at 28°C. The liquid phase composition was analyzed by gas chromatography. The results are summarized in Table 1. Aluminum chloride alone gives the conversion of 2.4 %. Since perfectly anhydrous aluminum chloride is known to be inactive for hydrocarbon conversion,[4,5] aluminum chloride by the sublimation may still contain water as an impurity. The mixture of $AlCl_3$ with $CuSO_4$ (dehydrated at 350°C) is the most effective catalyst and its activity is twice higher than that of the mixture $AlCl_3$-$CuCl_2$. The mixtures $AlCl_3$-CuI, $AlCl_3$-$Cu_3(PO_4)_2$ show similar activities to $AlCl_3$-$CuCl_2$. The mixtures,

Table 1. Catalytic Activities of $AlCl_3$-Copper Compound Mixtures for Pentane Conversion

Copper Compound	Conversion (%)	Liquid Phase Composition (%)				
		n-C_5	i-C_5	C_6	i-C_4	n-C_5
—	2.4	97.6	1.7	0.6	0.1	0
$CuSO_4$	20.8	79.2	19.1	0.9	0.8	trace
$CuCl_2$	11.4	88.6	8.9	1.1	1.4	trace
$Cu_3(PO_4)_2$*	10.8	89.2	9.5	0.7	0.6	trace
CuI	10.7	89.3	9.9	0.4	0.4	trace
CuCl	7.8	92.2	5.8	1.0	1.0	trace
$CuBr_2$	7.0	93.0	5.7	0.8	0.5	trace
CuO	5.4	94.6	4.4	0.6	0.4	trace
$Cu(CH_3COO)_2$	0.8	99.2	trace	0.6	0	0
$Cu(HCOO)_2$	0.5	99.5	0.4	0.1	trace	0
$Cu(NO_3)_2$	-	99.9	trace	trace	0	0

Reaction time 3 hr, 28°C, Pentane 10 ml
Catalyst, $AlCl_3$ (7.5 mmol) + copper compound (7.5 mmol) except $Cu_3(PO_4)_2$* (4.1 mmol)

$AlCl_3$-$Cu(CH_3COO)_2$, $AlCl_3$-$Cu(HCOO)_2$, and $AlCl_3$-$Cu(NO_3)_2$ have an only negligible activity. The selectivity to isopentane is the highest with $AlCl_3$-$CuSO_4$. The dependence of the selectivity on the kind of cupric salt suggests that the cupric salts are not simple supports of aluminum chloride and play some decisive roles in the catalysis.

Since the mixture of $AlCl_3$ with $CuSO_4$ is found most effective for the pentane conversion among $AlCl_3$-copper salt mixtures, the catalytic activities of the mixtures of aluminum chloride with various metal sulfate were examined in a similar manner and the results are given in Table 2, which shows the most of metal sulfates are effective as a cocatalyst of aluminum chloride. Especially, the mixtures of $AlCl_3$ with $Ti_2(SO_4)_3$, $Fe_2(SO_4)_3$, $NiSO_4$, $CuSO_4$, $Al_2(SO_4)_3$, $FeSO_4$, and $CaSO_4$ are effective catalysts. They are more effective catalysts than the mixtures of $AlCl_3$ with the corresponding metal chlorides.[3)]

Conversion of pentane was examined also in gas phase with $AlCl_3$-$CuSO_4$ as a catalyst. The equimolar mixture of $AlCl_3$ and $CuSO_4$ (7.5 mmol each) was placed in a glass vessel attached to a gas circulation system (dead volume 260 ml). After evacuating the system, pentane of 150 Torr (= $2x10^4$ Nm^{-2}) was introduced and circulated over the catalyst mixture at 44.5°C. A small amount of gas was withdrawn periodically and was analyzed by gas chromatography. The change in gas phase composition with time is shown in Fig. 1. After 3 hr, the gas phase was composed of 10.9 % pentane, 12.5 % isopentane, 73.5 % isobutane, 2.2 % hexanes and 0.9 % butane. Thus, the main product in gas phase reaction is isobutane, instead of isopentane in liquid phase reaction. Butanes and hexanes may be produced by the dimerization-decomposition mechanism[6,7)] greater extent of decomposition to isobutane in gas phase reaction may be caused by the fact

Table 2. Catalytic Activities of $AlCl_3$-Metal Sulfate Mixtures for Pentane Conversion

Metal Sulfate	Conversion (%)	Liquid Phase Composition (%)				
		$n-C_5$	$i-C_5$	C_6	$i-C_4$	$n-C_4$
$Ti_2(SO_4)_3$	46.2	53.8	38.7	3.5	4.0	trace
$Fe_2(SO_4)_3$	29.1	70.9	20.6	3.9	4.7	trace
$NiSO_4$	25.2	74.8	20.2	2.3	2.7	trace
$CuSO_4$	20.8	79.2	19.1	0.9	0.8	trace
$MnSO_4$	17.2	82.8	15.9	0.7	0.6	trace
$FeSO_4$	16.2	83.8	14.5	0.8	0.9	trace
$Al_2(SO_4)_3$*	16.2	83.8	15.9	0.2	0.2	trace
$Zr(SO_4)_2$	15.7	84.3	13.0	1.5	1.2	0
$CoSO_4$	13.9	86.1	12.5	0.7	0.7	0
$MgSO_4$	13.5	86.5	12.5	0.3	0.7	trace
$CaSO_4$	11.4	88.6	10.8	0.3	0.3	0
$BaSO_4$**	11.2	88.8	10.2	0.5	0.5	0
$PdSO_4$	11.2	88.8	9.8	0.7	0.7	trace
$ZnSO_4$	9.4	90.6	8.3	0.6	0.5	trace
$SrSO_4$	7.6	92.4	7.1	0.3	0.2	trace
$Cr_2(SO_4)$	6.1	93.9	5.6	0.3	0.2	0
Na_2SO_4	2.2	97.8	1.9	0.2	0.1	0

Reaction time 3 hr, 28°C, Pentane = 10 ml
Catalyst, $AlCl_3$ (7.5 mmol) + metal sulfate (7.5 mmol) except $Al_2(SO_4)_3$* (5.8 mmol) and $PdSO_4$** (4.5 mmol)

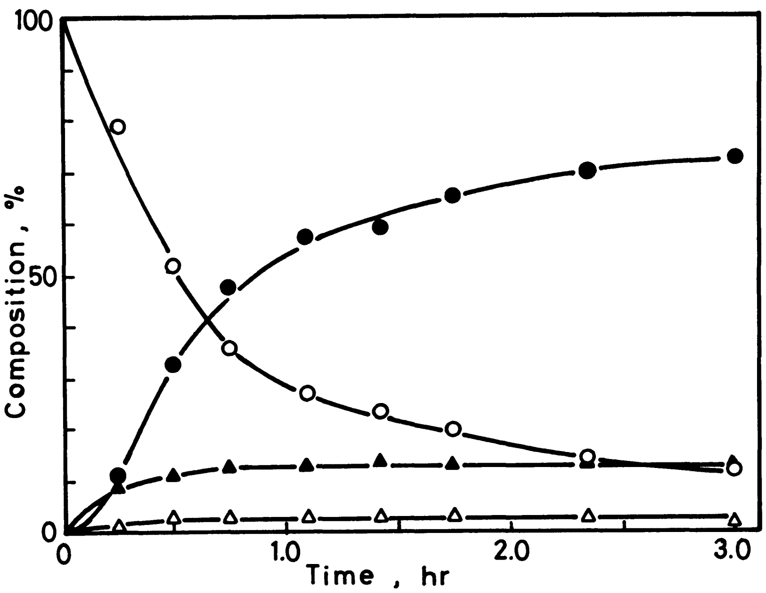

Fig. 1. Change in gas phase composition with reaction time at 44.5°C.
Catalyst; $CuSO_4$ (7.5 mmol) + $AlCl_3$ (7.5 mmol)
(○) $n-C_5$, (▲) $i-C_5$, (●) $i-C_4$, (△) C_6.

that the reaction product, pentane, or the reaction intermediates on the surface are less readily desorbed to gas phase than to hydrocarbon phase, and the dimerization-cracking reactions proceed on the surface until isobutane is ultimately formed. Under the same conditions, the reaction with $AlCl_3$-$CuCl_2$ mixture gave the total conversion of 49 %. As the liquid phase conversion, $AlCl_3$-$CuSO_4$ mixture is much higher activity than $AlCl_3$-$CuCl_2$ mixture.

In conclusion, the mixtures of aluminum chloride and metal sulfate were found to be effective catalyst for the isomerization of pentane near room temperature. The mechanistic features of the catalysis are now being investigated.

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References

1) L. Schmerling and J. A. Vesely, J. Org. Chem., 38, 312 (1973).
2) P. Kovaic and A. Kyriakis, J. Amer. Chem. Soc., 85, 454 (1963).
3) Y. Ono, T. Tanabe, and N. Kitajima, J. Catal., submitted.
4) A. L. Glasebrook, N. E. Phillips, and W. G. Lovell, J. Amer. Chem. Soc., 58, 1944 (1936).
5) R. C. Wackher and H. Pines, J. Amer. Chem. Soc., 68, 1642 (1946).
6) A. Schneider and R. M. Kennedy, J. Amer. Chem. Soc., 73, 5017 (1951).
7) D. A. McCaulay, J. Amer. Chem. Soc., 81, 6437 (1959).

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