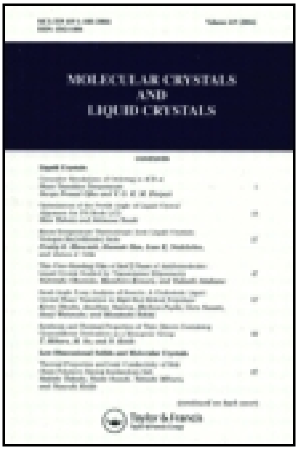

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Alkane Activation by Copper II Tetrachloroaluminate Intercalated in Graphite

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ALKANE ACTIVATION BY COPPER II TETRACHLOROALUMINATE INTERCALATED IN GRAPHITE

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Abstract Catalytic activity of the first stage graphite intercalation compound (GIC) in the form $C_{22}CuAl_2Cl_{8.5}$ has been studied for n-pentane conversion. The activity was compared with the noninserted heterocomplex. In the presence of copper II tetrachloroaluminate in a batch reactor at 27°C after 26 hours 46.6 mole% of n-pentane were converted. Under the same conditions with $CuAl_2Cl_8$-GIC the conversion was only 6.7 mol%. In a fixed-bed flow reactor system the temperature dependent activity of the intercalate reached a maximum n-pentane conversion at 88°C, but relatively rapid deactivation of the catalyst was observed.

INTRODUCTION

Strong Lewis acids intercalated in graphite are known to be active catalysts for hydrocarbon conversion[1]. For example $AlCl_3$- or $AlBr_3$-GIC's were used as catalysts for alkylation or transalkylation of aromatic hydrocarbons[2,3], and SbF_5-GIC was a very effective catalyst for isomerization of saturated hydrocarbons[4,5]. The main advantage of using this type of catalyst compared with a neat Lewis acid is that a reaction can be carried out in a flow reactor system with a fixed bed catalyst and that in the case of a batch-reactor, the liquid products can be easily separated from the catalyst.

Twenty years ago Schmerling and Vesely[6] reported that a mixture of $AlCl_3$ with $CuCl_2$ was an effective catalyst for aromatic hydrocarbon alkylation or for saturated hydrocarbon isomerization. The alkylation was found to proceed via oxidative carbocation formation by electron transfer involving cupric chloride. During the reaction cupric chloride was converted to cuprous chloride and hydrogen chloride was produced[6].

Kitajima investigated very extensively n-pentane isomerization in the presence of mixtures of various Friedel-Crafts catalysts with different metal chlorides or sulfates[8]. More careful studies of $AlCl_3$-$CuCl_2$ mixtures showed that the two chlorides formed a molecular crystalline heterocomplex the structure of which was determined by single crystal X-ray diffraction[8]. Based on the elementary and some spectral analyses, the formula of the heterocomplex was determined to be $Cu(AlCl_4)_2$[8]. It was found that the catalytic activity of this heterocomplex was about 20 times higher than that of a physical mixture of the components.

This heterocomplex was already known to be a product of the gas phase reaction between aluminum chloride and cupric chloride[7].

Two years ago Vangelisti and Polo reported the preparation of the first stage graphite intercalation compounds containing metal chloroaluminates. The heterocomplexes consisting of $AlCl_3$ and $CoCl_2$, $CuCl_2$ or $PdCl_2$, respectively, were intercalated from the gaseous or liquid phase. At 300°C, gaseous copper chloroaluminate reacts with graphite forming the first stage within four days, the formula of which ($C_{22}CuAl_2Cl_{8.5}$) was determined by elementary analysis[9,10].

In this paper we present some preliminary results on catalytic activity of $CuAl_2Cl_8$-GIC for n-pentane conversion. Since the catalyst lost activity during the course of the reaction we also investigated its structure and composition after reaction.

EXPERIMENTAL

Catalyst preparation

$CuAl_2Cl_8$. Copper chloroaluminate was obtained by heating a stoichiometric mixture of $AlCl_3$ and $CuCl_2$ for 24 h at 300°C. The complex was then crystallized at 195°C. The product consisted of green crystals, the homogeneity of which was verified by X-ray analysis.

$CuAl_2Cl_8$-GIC. At 300°C under chlorine pressure, gaseous $CuAl_2Cl_8$ reacts with graphite; after four days the first stage GIC was obtained. The GIC was investigated by means of chemical and radiocrystallographic analyses.

Procedures

Batch reactor system. The reaction setup consisted of a 25 cm^3 flask furnished with magnetic stirer and connected by a teflon tube (d = 1.2 mm) to a 600 cm^3 gas container. The reactor was loaded with 10 cm^3 of dry n-pentane and a given amount of catalyst. Reactions were carried out at ambient temperature and atmospheric pressure.

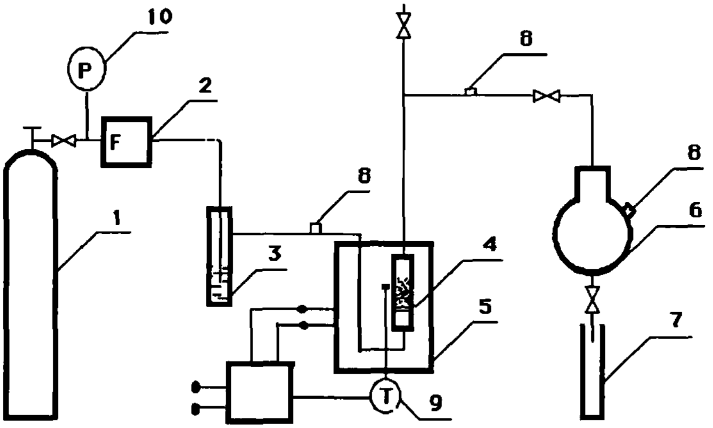


FIGURE 1 Experimental setup. 1-N_2 gas cylinder; 2-flow-meter ; 3-n-pentane evaporator; 4-reactor; 5-heating mantle; 6-gas container; 7-graduated cylinder; 8-gas sample ports; 9-thermocouple with heating regulator.

Flow reactor system (Fig.1). During flushing the reactor system with N_2, 660mg of the catalyst ($CuAl_2Cl_8$ -GIC) were introduced into the reactor (glass tube l=70mm, d=6mm with sintered glass partition), and 1.15 cm^3 (10 mmol) of n-pentane were poured into the evaporator. A mixture of nitrogen and n-pentane (about 60vol% n-pentane) was passed over the catalyst (flow rate 1.7$cm^3.mn^{-1}$) at a given temperature. The gas mixture after reaction was collected in the flask (gas container).

Analyses. Hydrocarbon mixtures in gas or liquid phase were analyzed by gas chromatography using a packed column DC200 with programmed temperature from 30°C to 120°C, rate of increase 10°C per minute. The catalyst was examined by X-ray diffraction using Mo Kα radiation.

RESULTS AND DISCUSSION

The catalytic activity of $CuAl_2Cl_8$-GIC was compared with the activity of the non-intercalated heterocomplex in n-pentane conversion. The experiments were carried out in a batch reactor at ambiant temperature (about 27°C) for 26 hours. The results are shown in Table 1.

TABLE 1 Product distribution (mol %) in the batch system.

Catalyst	i-C_4	n-C_4	i-C_5	n-C_5	C_6	C_7	C_8	C_9	C_{10}	n-C_5 (conver.)
$CuAl_2Cl_8$	16.1	0.05	17.6	53.4	6.1	1.9	1.8	1.1	0.8	46.6
$C_{22}CuAl_2Cl_8$	0.5	-	1.5	95.7	1.0	0.5	0.4	0.2	0.1	6.7

Catalyst : $CuAl_2Cl_8$ -0.391g; $C_{22}CuAl_2Cl_{8.5}$-0.594g; 27 hours at 27°C.

In the heterogeneous liquid-solid system under ambient conditions copper chloroaluminate was much more active than the heterocomplex-GIC giving 46.6% and 6.7% conversion rate, respectively. In agreement with previously reported observations[8] during the course of the reaction in the presence of $CuAl_2Cl_8$ the catalyst changed its color from yellow to greyish-white and formed a muddy phase on the bottom of the flask; this phase change excluded this catalyst from use in a flow reactor system.

The first series of experiments in the flow reactor system using $CuAl_2Cl_8$-GIC was done to determine the temperature influence on the process. The reaction was carried out at 50, 70, 88 and 95°C. The results of the experiments are shown in Table 2 and in Fig 2.

TABLE 2 n-Pentane conversion in flow system at different temperatures.

				Product distribution (mol %)						Convers. (mol %)
t (°C)	C_3	i-C_4	C_4	i-C_5	n-C_5	22DMB	2MP	3MP	n-C_6	n-C_5
50	0.0	1.8	0.0	2.6	93.6	0.0	1.9	0.1	0.0	6.4
70	0.0	5.7	0.1	3.9	89.0	0.1	1.1	0.1	0.1	11.0
88	0.0	17.7	0.2	6.0	73.8	0.2	0.8	9.7	0.1	26.2
95	0.1	4.7	0.6	1.3	92.6	0.0	0.5	0.0	0.0	7.4

22DMB-2,2-dimethyl butane; 2MP-2 methyl pentane; 3MP-3methyl pentane

With increasing temperature up to 88°C, the conversion of n-pentane increased reaching 26.2mol%. With further increase of temperature the conversion rate dropped to 7.4mol%.

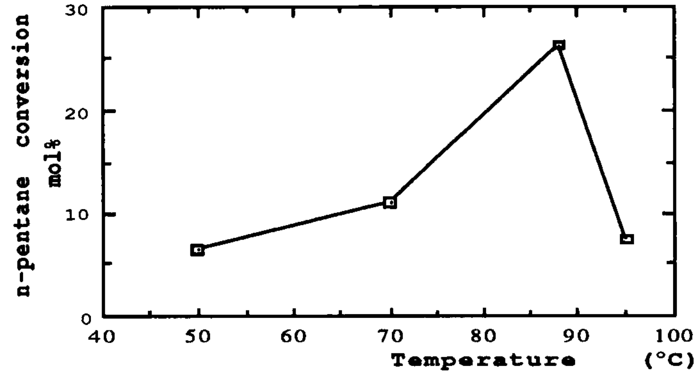


FIGURE 2 n-Pentane conversion versus reaction temperature in the flow system.

Such a behaviour of the catalyst at temperatures of about 100°C is in good agreement with thermogravimetric investigations which showed that $CuAl_2Cl_8$-GIC begins losing mass at 100°C as a consequence of dissociation[11]. In all the experiments the main products were isobutane and isopentane; also a substantial amount of hexane isomers was formed. At the same time no hydrocarbons smaller than C_4 were found (except 0.1%mol of C_3H_8 at 95°C). The product distribution indicates that the main reaction is dimerization of n-pentane and subsequent cracking of the dimer. Results of the gas sample analyses taken at given time intervals from a port situated just after the reactor showed a rapid decrease of the catalyst activity during the course of the reaction (Fig.3).

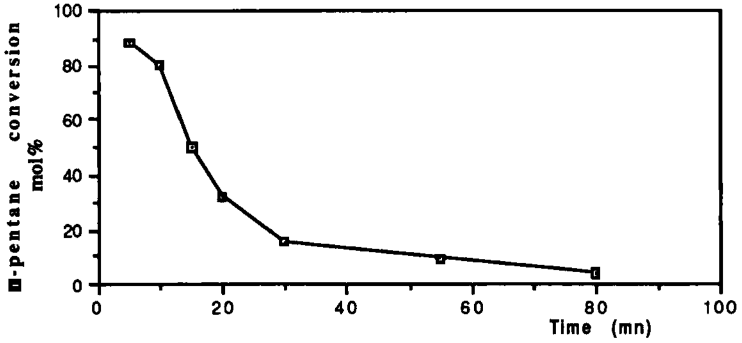


FIGURE 3 n-Pentane conversion versus time in the flow system at 88°C.

The muddy phase of the $CuAl_2Cl_8$ catalyst after n-pentane conversion was dried and then the resulting powder was subjected to radiocrystallographic analysis. The reflections indicate that the powder consists of orthorombic crystals (a=1.027nm, b=0.956nm and c=0.641nm) which is characteristic for $CuAlCl_4$. It means that copper changes the oxidation state from II to I during the reaction. The same analysis of the $CuAl_2Cl_8$-GIC catalyst after the reaction showed a mixture of stage 1 and 2 GIC with an overwhelming majority of stage 2 (Fig.4).

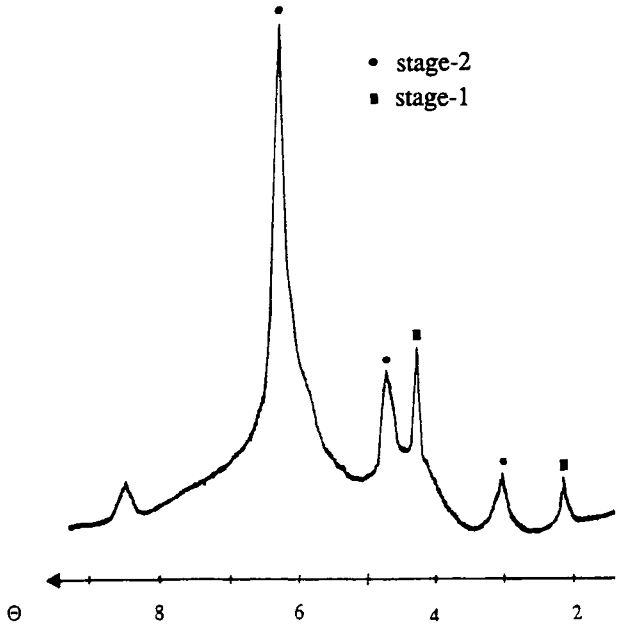
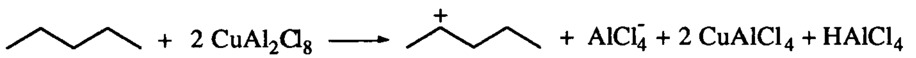
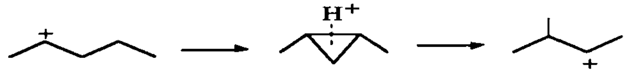


FIGURE 4 X-ray powder diffractogram of the used $CuAl_2Cl_8$-GIC after n-pentane conversion (Mo Kα.).

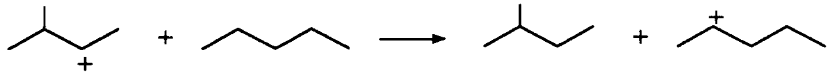
Based on this analysis it can be presumed that Cu(II) was reduced to Cu(I), the intercalate remaining in graphite as a mixture of $CuAlCl_4$ and $AlCl_3$. n-pentane was ionized by oxidation with copper involving electron transfer between hydrocarbon and copper(II):



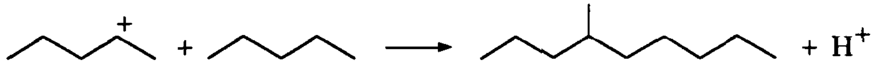
The secondary carbocation may undergo isomerization via a protonated cyclopropyl structure:



Hydride transfer from n-pentane leads to isopentane and a new secondary pentylcation:



Thereafter the main path of the reaction is the alkylation of the isopentyl carbocation by n-pentane or by pentene obtained by proton loss from the carbocartion:



The resulting C_{10} hydrocarbon (or carbocation) can then be cleaved protolytically (or by β-scission) forming butanes and hexanes. As no hydrogen was found in the gas mixture after the reaction, the formation of the carbocationic intermediates via C-H bond protolysis can be excluded.

CONCLUSION

The $CuAl_2Cl_8$ -GIC can be considered as a solid superacid since using this compound as an activating reagent, n-pentane undergoes isomerization, dimerization and cracking even at ambient temperature. However in agreement with previous investigations[6,8] the initial pentyl carbocation formation occurs at the expense of copper(II) reduction to copper(I).

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