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Isomerization of Pentane with $AlCl_3$–$CuSO_4$ Mixtures

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The isomerization of pentane over $AlCl_3$–$CuSO_4$ mixtures was studied in the temperature range of 5–23°C. The catalytic activity of the mixtures was found to be proportional to the amount of $CuSO_4$ and also to the specific surface area of the $CuSO_4$ used. The reaction did not continue when the solid was removed from the system. Thus, it was concluded that the active species were located on the surface of the $CuSO_4$. Traces of water added to the system have no influence on the reaction. The mixture has a strong acidity with $14.52 < H_o < -13.75$. Complex formation between the two components on the $CuSO_4$ surface was suggested.

INTRODUCTION

Mixtures of aluminum chloride and metal halides are known to promote the isomerization of alkanes at room temperature (*1*, *2*). Recently, it was reported that mixtures of aluminum chloride (or aluminum bromide) and metal sulfates have higher catalytic activity for the isomerization of pentane than the mixtures of aluminum chloride and the corresponding metal halides (*3*, *4*). In this work, the isomerization of pentane with $AlCl_3$–$CuSO_4$ mixtures was studied to clarify the cause of this synergetic effect.

METHODS

Materials. Aluminum chloride was obtained by sublimation from the eutectic of aluminum chloride (Wako Pure Chemical) and sodium chloride (10%) with a small amount of aluminum powder at 200°C. Anhydrous cupric sulfate was obtained by heating $CuSO_4 \cdot 5H_2O$ in air at 250–650°C for 3 h and then under vacuum at 250°C for 2 h. Pentane from Kanto Chemicals was distilled, dried with sodium wire, and kept under nitrogen.

Procedures. The catalysts were prepared by cogrinding aluminum chloride and cupric sulfate in a porcelain mortar for 10 min under nitrogen. In a typical run, an equimolar mixture (3.75 mmol each) of aluminum chloride and cupric sulfate dehydrated at 350°C and 10 ml of pentane were stirred under nitrogen in a flask at 23°C. Part of the liquid was periodically withdrawn by a microsyringe and analyzed by gas chromatography.

RESULTS AND DISCUSSION

Time course of the reaction. A typical time vs composition curve for the pentane isomerization is given in Fig. 1. Pentane (10 ml) was isomerized with an equimolar mixture (3.75 mmol each) of $AlCl_3$ and $CuSO_4$ at 23°C. The conversion of pentane increases linearly with time. Thus, the reaction is zero order with respect to pentane. The main product is isopentane, but the yields of hexanes (mainly 2,2- and 2,3-dimethylbutane) and isobutane increase with time. The pentane conversion reaches about 55% at a reaction time of 25 h.

During an investigation of the effect of temperature on rate, the rate remained zero order in the temperature range of 5–23°C. The rate plotted against the reciprocal of absolute temperature is shown in Fig. 2, which gives the apparent activation energy of 94 $kJ \cdot mol^{-1}$.

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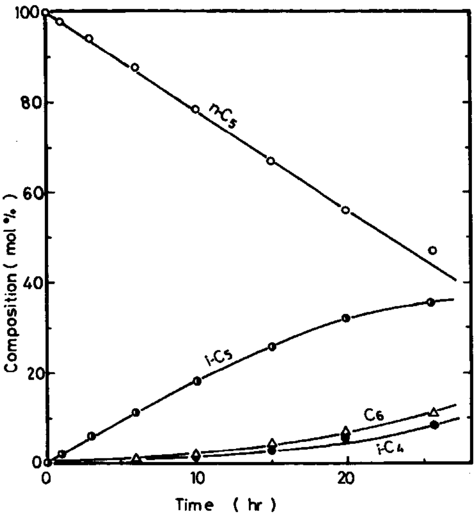

FIG. 1. Time course of pentane isomerization with $AlCl_3$–$CuSO_4$. $AlCl_3$–$CuSO_4$ 3.75 mmol each, n-C_5 10 ml, at 23°C.

Effect of dehydration temperature of $CuSO_4 \cdot 5H_2O$. As the anhydrous cupric sulfate was prepared by heating $CuSO_4 \cdot 5H_2O$ in air for 3 h at temperatures from 250 to 650°C, and then at 250°C under vacuum for 2 h, the effect of the temperature of dehydration in air was examined. The cupric sulfate (3.75 mmol) thus prepared was mixed with aluminum chloride (3.75 mmol) and used as a catalyst for the pentane isomerization. In Fig. 3, the rate is plotted as a function of the temperature at which the $CuSO_4 \cdot 5H_2O$ was heated. The rate was maximum for the mixture using cupric sulfate dehydrated at 350°C. Figure 3 also contains a plot of specific surface area for the cupric sulfate as a function of dehydration temperature. The same data can be used to draw Fig. 4, the rate per unit surface area of $CuSO_4$ plotted against the dehydration temperature. The rate per unit surface area of $CuSO_4$ depends only slightly on the dehydration temperature. Thus, it is clear that the rate of isomerization depends greatly, in fact almost proportionally, on the surface area of the $CuSO_4$, but not on the total moles of $CuSO_4$. This suggests that the catalytically active species are located on the surface of the cupric sulfate, but not on the surface of the $AlCl_3$, nor in the liquid phase. The result suggests also that the structural water remaining in $CuSO_4$, if any, does not play any decisive role in altering catalytic activity.

Effect of catalyst composition. The effect of composition of the mixture on the catalytic activity was also examined. Keeping the amount of aluminum chloride constant (3.75 mmol), the amount of cupric sulfate was varied. As shown in Fig. 5, aluminum chloride alone has only negligible activity and the activity of the mixture is proportional to the amount of cupric sulfate. This supports the conclusion that the active species are on the surface of the cupric sulfate.

When the amount of aluminum chloride was varied, using a fixed amount of cupric sulfate (3.75 or 1.88 mmol) the dependence of the rate on the aluminum chloride content was found to be rather complex as shown in Fig. 6. Thus, when the molar ratio of $AlCl_3$ to $CuSO_4$ is below 1/5, the mixtures show no activity, but the activity increases sharply at $AlCl_3/CuSO_4$ ratios of

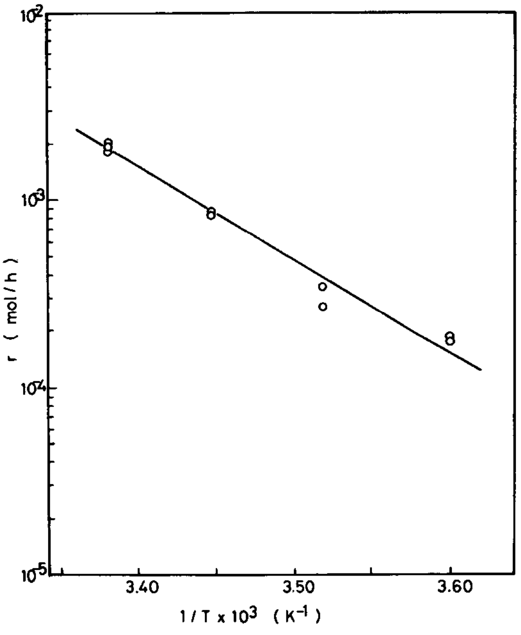

FIG. 2. Temperature dependence of the rate of pentane isomerization.

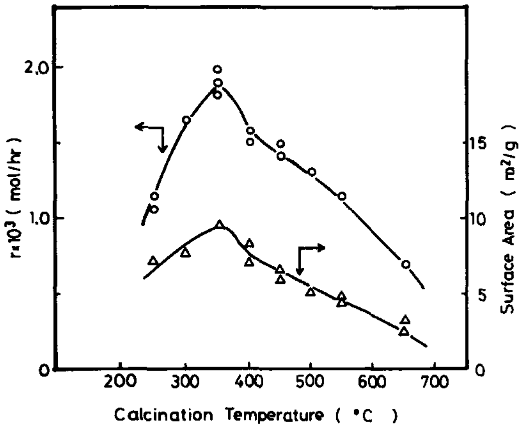

FIG. 3. Change in the catalytic activity of $AlCl_3$–$CuSO_4$ mixtures and in the surface area of anhydrous cupric sulfate as a function of the dehydration temperature for $CuSO_4 \cdot 5H_2O$.

1/2.5 or 1/3.0 and finally reaches constant at an $AlCl_3/CuSO_4$ ratio of 1/2. The constant rate depends on the amount of cupric sulfate, in agreement with the results described above. The reason why the mixture is entirely inactive with an $AlCl_3/CuSO_4$ ratio less than 1/5 is not clear at this moment.

Location of the active sites. The results described above suggest that the active species exist on the surface of the cupric sulfate. To confirm this, the following experiment was carried out. The reaction was started in the same way as the run in Fig. 1. After 10 h when the conversion of pentane reached 25%, the liquid phase was separated from the solid phase, and the change in the liquid-phase composition was monitored for another 10 h. No change in the liquid-phase composition was observed. This supports the conclusion that the active species exist on the solid surface, but not in the liquid phase. The result is a sharp contrast with that for the $AlBr_3$–$CuSO_4$ system, in which isomerization proceeds appreciably in the liquid phase (*4, 5*).

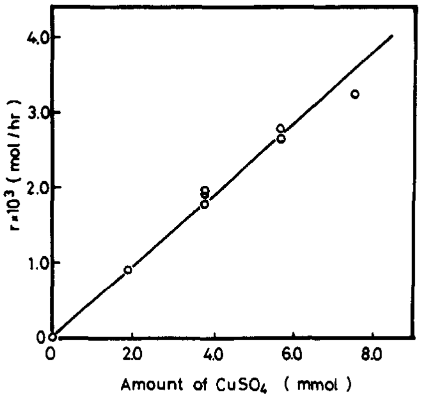

FIG. 5. Dependence of the catalytic activity for $AlCl_3$–$CuSO_4$ mixtures on the amount of $CuSO_4$. n-C_5 10 ml, $AlCl_3$ 3.75 mmol, at 23°C.

Influence of water. It is known that extremely pure aluminum halides have no

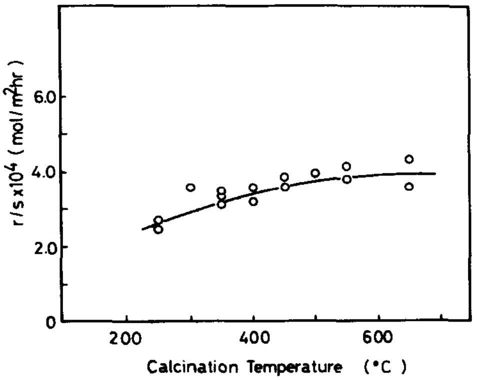

FIG. 4. Dependence of the catalytic activity for $AlCl_3$–$CuSO_4$ mixtures per unit surface area of $CuSO_4$ as a function of the dehydration temperature for $CuSO_4 \cdot 5H_2O$.

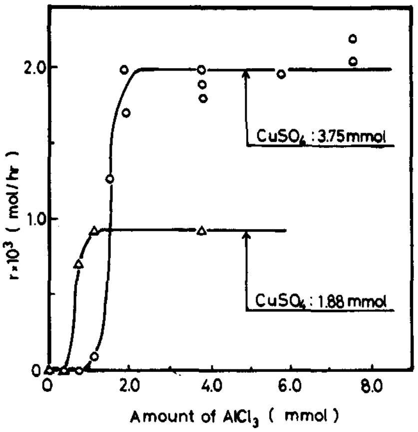

FIG. 6. Dependence of the catalytic activity for $AlCl_3$–$CuSO_4$ mixtures on the amount of $AlCl_3$. n-C_5 10 ml, $CuSO_4$ 3.75 mmol, at 23°C.

catalytic activity for alkane isomerization, but the presence of water as an impurity induces catalysis (*6, 7*), though the mechanism of this activation by water is not yet completely solved (*8*).

The effect of water on the catalytic activity of the $AlCl_3$–$CuSO_4$ mixture also was examined. The reaction was started with the usual equimolar mixture (3.75 mmol of each reagent). After several hours, water was added to the system, and the change in the reaction rate was monitored. In Fig. 7, the rate after water addition is plotted against the amount of water. A small amount of water (less than 3.75 mmol) has no effect on the reaction rate, while a larger amount (more than 7.5 mmol) retards the reaction. The effect of water on the isomerization with aluminum chloride was also examined in a similar manner. The aluminum chloride used has a negligible activity, but the addition of water to the system induces catalytic activity, in agreement with the results of previous workers (*6, 7*). These results show that water is not a necessary component for inducing catalytic activity in the $AlCl_3$–$CuSO_4$ system, and the active species in the system are essentially different from those in $AlCl_3$–H_2O system. Thus, cupric sulfate is not just a support of $AlCl_3$, but plays an essential role in forming the catalytically active species.

Acid strength of the mixture. To determine the acidic character of the mixture, the reflectance spectra were measured for several Hammett indicators adsorbed on the $AlCl_3$–$CuSO_4$ mixture. The equimolar mixture was packed into a quartz cell with flat surfaces and exposed to the vapor of substituted nitrobenzenes. The results are summarized in Table 1. The adsorption of *p*-chloronitrobenzene, *m*-chloronitrobenzene, and 2,4-dinitrotoluene on the mixture gave rise to the appearance of new bands at 384, 352, and 339 nm, respectively. These band positions are very close to the bands of the indicators in H_2SO_4–HSO_3F (*9*), showing that the solid mixture has an acidity of corresponding strength. The adsorption of 2,4-dinitrofluorobenzene did not yield a new band around 330 nm. Thus, the acid strength of the $AlCl_3$–$CuSO_4$ mixture is between Ho −14.52 and −13.75. Similarly, aluminum chloride alone has an acid strength between Ho −13.75 and −13.16, while cupric sulfate has no strong acid

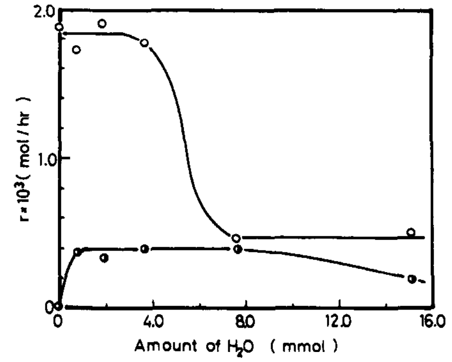

FIG. 7. Dependence of the catalytic activity for the $AlCl_3$–$CuSO_4$ mixture and $AlCl_3$ on the amount of water. (O) $AlCl_3$–$CuSO_4$ mixture, (◑) $AlCl_3$, *n*-C_5 10 ml, at 23°C.

TABLE 1

Wave Lengths for the Bands of Indicators Adsorbed on $AlCl_3$–$CuSO_4$, $AlCl_3$, and $CuSO_4$

Indicators pKa	*p*-Chloro-nitrobenzene −12.70	*m*-Chloro-nitrobenzene −13.16	2,4-Dinitro-toluene −13.75	2,4-DInitro-fluorobenzene −14.52
H_2SO_4–HSO_3F	386 nm	353 nm	339 nm	336 nm
$AlCl_3$–$CuSO_4$	384	352	339	—[a]
$AlCl_3$	375	350	—	—
$CuSO_4$	—	—	—	—

[a] The dashes indicate that no absorption bands were observed.

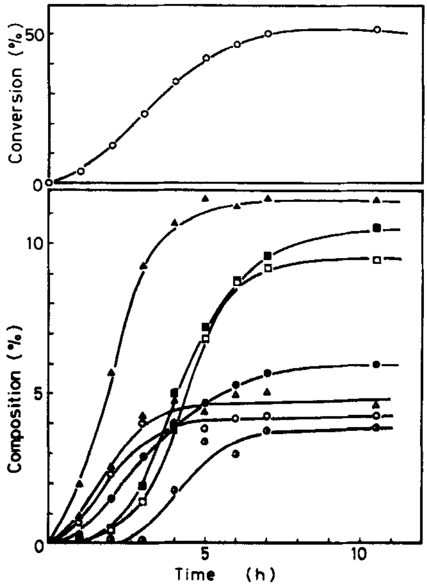

FIG. 8. Time course of hexane isomerization with $AlCl_3$–$CuSO_4$. $AlCl_3$–$CuSO_4$, 3.75 mmol each, n-C_5 10 ml, at 40°C. (●) 2,2-DMB,(○) 2,3-DMB, (▲) 2-MP, (△) 3-MP, (□) i-C_4, (■) i-C_5, (◑) C_7.

sites. Thus, the acid strength of aluminum halide increases on complexing with cupric sulfate.

Conversion of hexane. Hexane (10 ml) was stirred with an equimolar mixture of $AlCl_3$–$CuSO_4$ (3.75 mmol each) at 40°C. Figure 8 shows the change in liquid-phase composition with time. The conversion of hexane increases with time. About 10 mol of hexane per $AlCl_3$ or $CuSO_4$ was converted until the catalyst totally deactivated after 10 h. The most predominant product was 2-methylpentane, but the other hexane isomers were also formed. Isobutane and isopentane were also formed appreciably after 5 h. At 10 h when the reaction ceased, the selectivity to hexanes was 53%, and 2-methylpentane was the most predominant product (42% of the total hexanes).

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