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Adsorption Measurements during Catalytic Isomerization of Pentenes and 2-Methyl-1-pentene over KC_{24}

Susumu Tsuchiya,* Shinji Yamamoto, and Hayao Imamura
Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755
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The catalytic isomerization of pentenes over KC_{24} has been investigated. The double-bond-migration and the *cis-trans* isomerization took place over KC_{24}, but the skeletal isomerization was not observed. From the rates of reactions and the selectivity ratios, all six of the relative rate constants and the activation energies of reactions were determined. The reaction paths on the triangular graph calculated from the rate constants show the *cis*-convex type profile. The competitive isomerization of 1-pentene and 2-methyl-1-pentene has also been investigated. The rate of isomerization of 1-pentene was greater than that of 2-methyl-1-pentene, which can be explained on the basis that the amount of chemisorption of 1-pentene during the competitive reaction is greater than that of 2-methyl-1-pentene.

Great attention has been paid to all the characteristic properties of graphite intercalation compounds, and the catalytic properties of the compounds have been extensively investigated in various reactions.[1–2] In heterogeneous catalysis, adsorption plays an important role, and measuring the adsorption during the reaction has been fruitful in many investigations.[3] In this work, the interest has centered on the catalytic characteristics of KC_{24} for the isomerization of pentenes; the adsorption during the course of reaction was measured.

Experimental

Materials. The KC_{24} samples used as catalysts were prepared in the manner described elsewhere.[4] Graphite (1.25 g of Union Carbide Spectroscopic Grade powder) and 0.44 g of potassium metal were used for each preparation. The preparation vessel was heated in a electric heater for 24 h under *ca.* 10^{-3} Pa at 620 K to form KC_{24}, and then evacuated for 30 min. The X-ray diffraction data of the samples formed agreed quite well with those reported by Rüdorff and Schultze.[5] The color of the KC_{24} obtained was deep blue.

Pentenes used as the reactants were obtained from Tokyo Kasei Co., Ltd., and were purified by repeated distillation *in vacuo*. The purity was confirmed by gas chromatography to be more than 99%.

Helium (99.995%) and nitrogen (99.99%) were obtained from the Seitetsu Kagaku Co., Ltd.

Procedure. The apparatus used for the present study was essentially the same as that used previously.[6] A closed circulating system with greaseless stopcocks and with a U-shaped reactor, connected to a conventional vacuum line and a gas chromatograph, was used to follow the reaction. The volume of the reaction system corresponded to about 288 cm^3 at a reaction temperature of 373 K.

Known amounts of reactant and an inert gas, *e.g.* nitrogen, were introduced into the reaction system, and the reaction was started by circulating. The ambient pressure and the composition of circulating gas were measured at suitable time intervals by a gas chromatograph with a column of 2,4-dimethylsulfolane on Uniport C. Inert gases were useful for effective circulation and accurate analysis.

The amounts of adsorption were obtained from the material balance. When 1-pentene was the reactant, amounts of adsorption were estimated from the amount of 1-pentene introduced and the pressure and the composition of the circulating gas at the suitable time. The sum of pentenes adsorbed could only be estimated.

Before each run, the catalyst was evacuated under *ca.* 10^{-3} Pa for 3 h at 573 K, and helium was introduced into the reactor. The evacuation temperature was selected as about 50 K lower than the preparation temperature of the catalyst; care was taken to avoid changes of KC_{24}. The reactor was then cooled to the reaction temperature and evacuated for a few minutes. The experimental results were well reproducible.

Results and Discussion

Isomerization of Pentenes. The double-bond-migration and the *cis-trans* isomerization of pentenes took place over KC_{24}, of which BET surface area was 50 m^2/g. The graphite did not show any catalytic activity for the reaction under the same experimental conditions. No skeletal isomerization occurred. No gase-

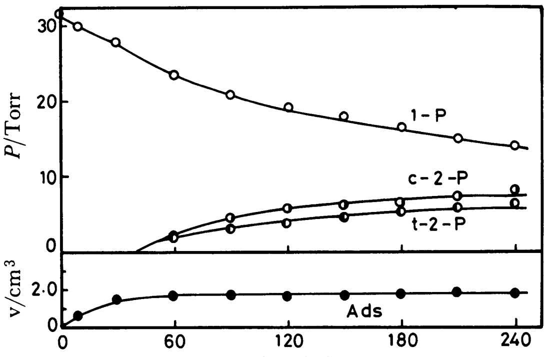


Fig. 1. Adsorption measurement during the isomerization of 1-pentene over KC_{24} at 440 K. (1 Torr = 133.322 Pa)

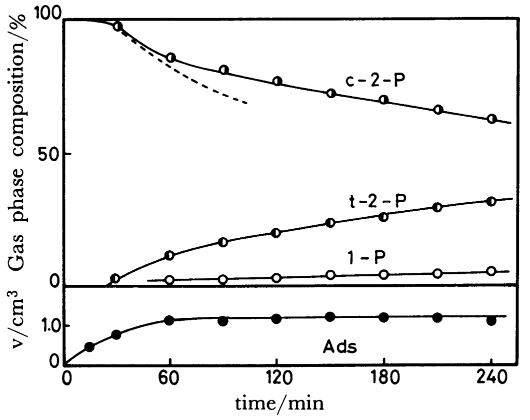


Fig. 2. Adsorption measurement during the isomerization of *cis*-2-pentene over KC_{24} at 513 K.

ous hydrocarbon other than pentenes was detected in the reaction mixtures under the present experimental conditions.

Figure 1 shows a typical result for the isomerization of 1-pentene over KC_{24} at 440 K, together with those of adsorption measurements. The adsorption measured appears to be chemical in nature, in view of the high adsorption temperature as 440 K. An induction period is observed at the initial stage of reaction. This may arise from the fact that at the initial stage the rate of adsorption of the reactant is much higher than that of desorption of the reactant as well as of the product. Accordingly, the decrease in the pressure of the reactant observed after the induction period is attributable to the progress of isomerization alone.

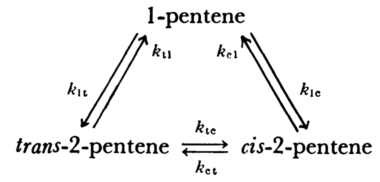
Figure 2 shows a typical result of the isomerization of *cis*-2-pentene over KC_{24} at 513 K. A similar induction period of the reaction is also observed. Instead of pressure, the composition in the gas phase is shown, as a function of time. The rate of the isomerization of *cis*-2-pentene is lower than that of 1-pentene (the broken line) under the same initial pressure.

The amounts of pentenes adsorbed appear to be almost constant; at the later stage of the reaction, the sums of the amount of reactant adsorbed and that of product adsorbed are constant. If the adsorption of reactant were the rate-determining step, the amounts of adsorption of reactant and of product would increase with increasing the pressure of product. If the desorption of product were the rate-determining step, the amounts of adsorption of reactant and of product would decrease with decreasing the pressure of reactant. In both cases, the sums of the adsorption of the reactant and product are not constant. The present result can be explained on the basis that the surface reaction is the rate-determining step. After the induction period the amount of reactant adsorbed depends on the ambient pressure of reactant, and will decrease with time. The rate of isomerization may be proportional to the amount of adsorbed reactant, since the surface reaction in the rate-determining step. Thus, the decrease in the rate of isomerization with its progress is explicable.

Ottmers *et al.*[7] reported that the catalytic activity of KC_n (n=8, 24, 36) for the isomerization of 1-pentene sharply declined with time on stream. The activity was estimated from the per pass conversion in the flow system. In the closed circulating system, a conversion is integrated with reaction time. Therefore, if the initial rapid decrease in catalytic activity actually takes place, the effect would be diluted. It was accordingly impossible in the present experiment to observe the clear deactivation process. As Ottmers *et al.*[7] suggested, the deactivation process might be due to traces of oxygen in the flow system.

The good reproducibility of the experimental results in the present work, however, suggests that the deactivation process during the course of the reaction, if it exists, is not permanent, and that the catalytic activity can be easily regenerated by evacuation.

The isomerization of pentenes was almost first order with respect to the pressure of reactant, ranging from 2×10^3 to 1.3×10^4 Pa, after the induction period. From the rates of reaction and the selectivity ratios: *cis/trans*, *trans*/1, and 1/*cis*, all six of the relative rate constants expressed by Scheme 1 and the activation energies of reaction were determined.



Scheme 1.

The relative rate constants at 440 K and the activation energies (bracketed) are shown in Fig. 3.

When the isomerization of 1-pentene takes place with the allyl anion mechanism, the initial *cis/trans* ratio is greater than unity.[8,9] The selectivity ratios obtained in the present study satisfy the condition of the allyl anion mechanism.

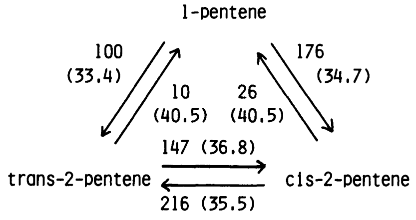


Fig. 3. Relative rate constants at 440 K and activation energies (kJ/mol) bracketed.

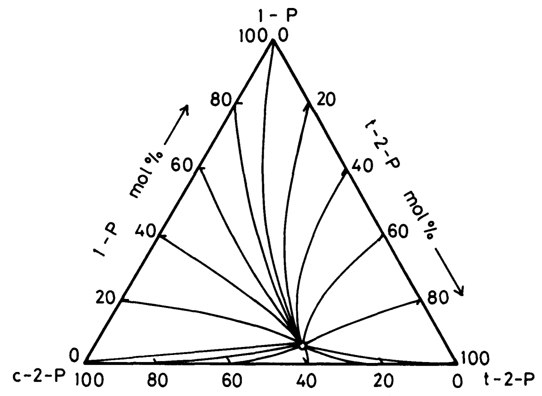


Fig. 4a. Reaction profile of isomerization of pentenes over KC_{24} at 440 K.

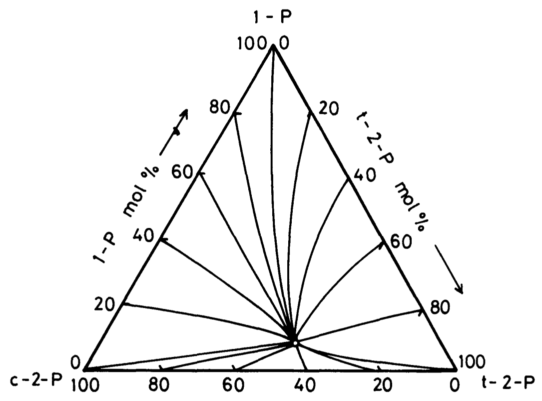


Fig. 4b. Reaction profile of isomerization of pentenes over KC_{24} at 513 K.

When the isomerization of pentenes proceeds, the composition of pentenes in the gas phase varies with time. The mol% of 1-pentene, *cis*-2-pentene, and *trans*-2-pentene corresponding to reaction time can be calculated from the relative rate constants, k_{ij}.[4,10,11] Figures 4a and 4b show the reaction paths calculated at 440 K and 513 K, respectively. These triangular graphs thus represent one of the catalytic characteristics of KC_{24} for the isomerization of pentenes. The curves, which originate from the left side of the triangle, bend in a convex manner to the left. The *cis*-convexity increased at a lower temperature, as shown in Fig. 4. These characteristics of pentenes are similar to those of butenes previously reported.[4]

Competitive Isomerization of 1-Pentene and 2-Methyl-1-Pentene. The reactivities of 1-pentene and 2-methyl-1-pentene have been studied. Figure 5 shows a typical result of the competitive isomerization of 1-pentene and 2-methyl-1-pentene over KC_{24} at 440 K. *cis*-2-Pentene, *trans*-2-pentene, and 2-methyl-2-pentene were observed as the products. The induction period is also observed both for 1-pentene and 2-methyl-1-pentene. The rate of adsorption of 1-pentene at initial state is larger than that of 2-methyl-1-pentene, which may be due to the structure effect of KC_{24}. 2-Methyl-1-pentene has a larger cross-sectional area than 1-pentene, and finds it more difficult to penetrate into the KC_{24} lattice. The amount of adsorption of 1-pentene at a later time is more than that of 2-methyl-1-pentene. The rate of isomerization of 1-pentene after the induction period is also more than that of 2-methyl-1-pentene. These results suggest that the higher rate of isomerization of 1-pentene than 2-methyl-1-pentene is due to either the larger rate of adsorption or the larger amount of adsorption of 1-pentene or both.

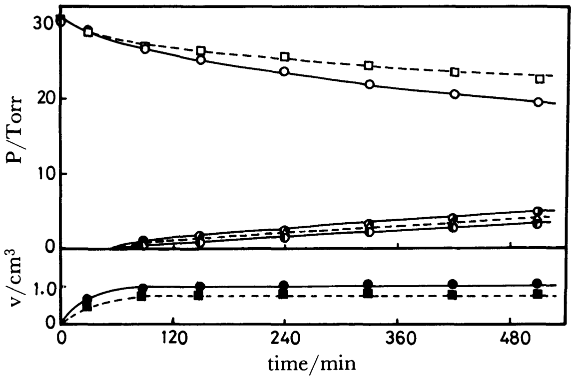


Fig. 5. Adsorption measurement during the competitive isomerization of 1-pentene and of 2-methyl-1-pentene over KC_{24} at 440 K.
Gaseous olefins: 1-pentene (-○-), 2-methyl-1-pentene (--□--), *cis*-2-pentene (-◑-), *trans*-2-pentene (-◐-), 2-methyl-2-pentene (--△--), Adsorbed olefins: *n*-pentenes adsorbed (-●-), methylpentenes adsorbed (--■--).

The degree of adsorption of 1-pentene in the presence of 2-methyl-1-pentene shown in Fig. 1 is less than that in the absence of 2-methyl-1-pentene shown in Fig. 5. This suggests that the adsorption of 1-pentene is disturbed by the presence of 2-methyl-1-pentene, and that 1-pentene is more strongly adsorbed on the same kind of sites than is 2-methyl-1-pentene in the competitive adsorption during the reaction.

Conclusion

The catalytic selectivity of KC_{24} for the isomerization of pentenes is similar to that of butenes. The initial *cis/trans* ratio can be explained on the basis that the reaction may proceed *via* an allyl anion mechanism. One of the catalytic characteristics is thus shown in Fig. 5. Competitive isomerization revealed that 1-pentene is more reactive than 2-methyl-1-pentene over KC_{24}. This fact can be explained on the basis that the rate and/or the amount of adsorption of 1-pentene during the competitive reaction are larger than those of 2-methyl-1-pentene.

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