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The Catalytic Isomerization of Butenes over a Graphite Oxide

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Synopsis. The relative rate constants and the activation energies of the isomerization of butenes over a graphite oxide have been measured, The reactivity of butenes and the selectivity ratios are in agreement with the characteristics of acid catalysts. The reaction profile shown on the triangular graph is of the rake-type.

Much attention has been paid to the characteristic properties of graphite oxide since Brodie first synthesized the compound.[1,2] Scarecely no study of its catalytic properties has, however, been reported so far. In this study, the isomerization of butenes, employed as a model reaction, has been investigated in order to explore its catalytic characteristics.

Experimental

Materials. The graphite oxide samples used as catalysts were prepared in a manner similar to that decribed previously.[3] The X-ray-diffraction data and the IR spectroscopic data of the sample formed agreed quite well with those reported by Alexanian.[4] The sample was dark brown.

The 1-butene, *cis*-, and *trans*-2-butene used as the reactans were obtained from the Tokyo Kasei Kogyo Co., Ltd.; their purity was confirmed by gas chromatography to be more than 99%. The nitrogen (99.99%) was obtained from the Seitetsu Kagaku Co., Ltd.

Procedure. A usual flow-type system with a by-pass at atmospheric pressure was employed to follow the reaction, nitrogen being used as the diluent. The graphite oxide, the catalyst, the BET surface area of which was 36 m^2/g, had been prepared beforehand; it was fixed in the system. The nitrogen stream with one of the butene isomers as a reactant was flowing only through the by-pass in the meantime; then it was diverted to flow through the reactor. The flowing rate of the nitrogen was *ca.* 15 cm^3/min, the amount of catalyst used being 0.39 g for each run. The [a butene isomer]/[nitrogen] ratio was 1/49. The reaction mixtures were analyzed by means of gas chromatography, with a column packing of 2,4-dimethylsulfolane on Uniport C. Before each run, the catalyst was evacuated at 353 K for 14 h. The experimental results were well reproducible.

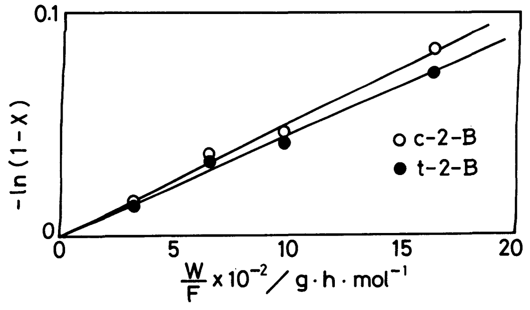

Fig. 1. First-order plots of isomerization of 1-butene over graphite oxide at 328 K.

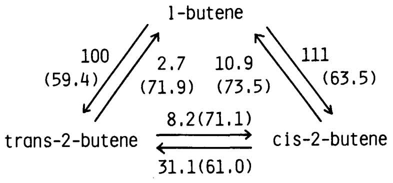

Fig. 2. Relative rate constants at 328 K and activation energies (kJ/mol) bracketed.

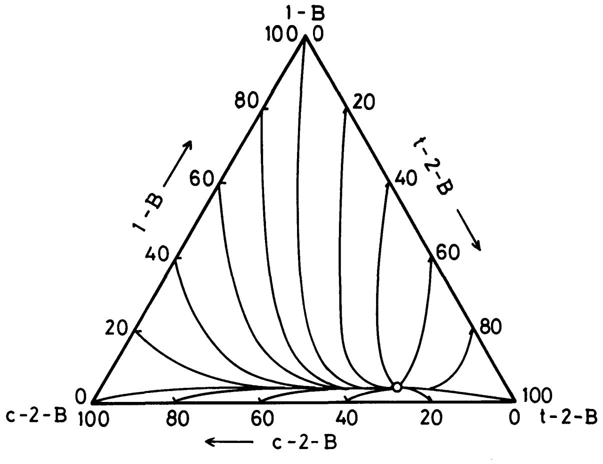

Fig. 3. Reaction profile of isomerization of butenes over graphite oxide at 328 K.

Results and Discussion

The double-bond migration and the cis-trans isomerization of butenes took place over graphite oxide. The skeletal isomerization could not be observed. No gaseous hydrocarbon other than the butenes could be detected in the reaction mixtures under the present experimental conditions. The graphite does not show any catalytic activity for a reaction under the same experimental conditions. In the initial stage the activity of a fresh catalyst was very high (the per-pass conversion was 85% at 323 K), but it decreased with time on stream. After about 200 min, the conversion became steady-state (with a per-pass conversion of *ca.* 8% at 323 K). Since the steady state continued a rather long time, all the kinetic studies were carried out in this state.

Figure 1 shows the first-order plots of the isomerization of 1-butene. From the rates of reaction and the selectivity ratios at different temperatures, all six of the relative rate constants and the activation energies of the reaction were determined in a manner similar to that described previously.[5] The results are shown in Fig. 2.

When the isomerization of butenes proceeds, the composition of the butenes in the gas phase may vary with the reaction time. The mol% of 1-butene, *cis*-, and *trans*-2-butene corresponding to the reaction time can be calculated from the relative rate constants, k_{ij}.[5—7] Figure 3 shows the reaction paths calculated at 328 K. The triangular graph thus represents one of the catalytic characteristics of graphite oxide for the isomerization of butenes. The time variable, *t*, is eliminated in the graph. When the reactants initially contain much more 1-butene than *cis*- or *trans*-2-butene, the curves corresponding to the reaction paths go downwards in an almost straight manner. This profile may be named the "rake-type," which is entirely different from that obtained in the isomerization over KC_8.[5)]

Graphite oxide is often called graphitic acid because of its acid character.[10)] The acid properties are caused by the acid-hydroxyl groups between the graphite layers, which can be observed by IR spectroscopy. The active sites of graphite oxide for the isomerization of butenes may therefore, have acid properties.

The following mechanisms for the isomerization of butenes have been proposed for different catalytic systems:[6)] (1) a hydride-addition mechanism for metals, (2) a carbenium-ion mechanism for acid catalysts, and (3) an allylic mechanism for basic catalysts. When the isomerization takes place with a carbenium-ion mechanism, (1) the order of the relative rate constants of the isomerization is 1-butene>*cis*-2-butene>*trans*-2-butene, and (2) the selectivity ratio, *cis/trans*, is about unity, while 1/*cis*-2- and 1/*trans*-2- are less than 3.0, usually less than 1.0.[8–9)] The reactivity of butenes as well as the selectivity ratios obtained in the present study are in agreement with a carbenium-ion mechanism for acid catalysts.

A large pulse of 1-butene (50 ml) was introduced into the flow system, where only carrier gas was flowing. The effluent stream was monitored by means of gas chromatography. The graphite-oxide catalyst (0.45 g) employed was at the steady state, as has been mentioned above. The flowing rate of the carrier gas was 8.6 cm^3/min. A large peak with tailing was observed, as is shown in the upper part in Fig. 4; the abscissa is the effluent time. The tailing continued more than 1 h. Since the active sites of graphite oxide may be the hydroxyl groups between the graphite layers, the reactant molecules must get into the space between the graphite layers and chemisorb on the sites for isomerization. The product admolecules then desorb from the sites and crawl out of the layer space. The tailing may correspond to the crawling-out-process.

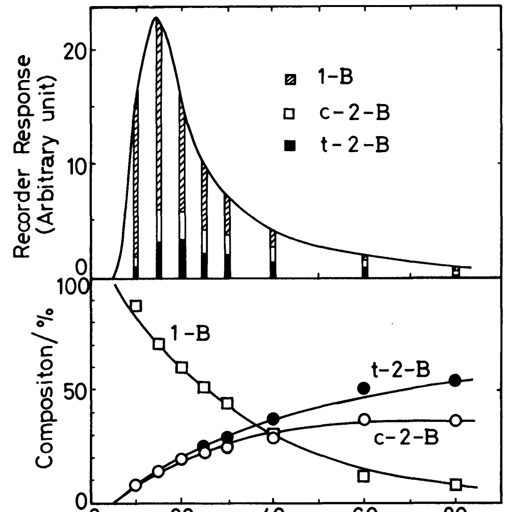

Fig. 4. Effluent peak and composition.
1-Butene (50 ml) was introduced over graphite oxide (0.45 g) at 298 K. Flowing rate of carrier gas was 8.6 cm^3/min.

The composition of the effluent gas was analyzed by means of gas chromatography. The analytical samples were taken out from the effluent at suitable time intervals. The results are shown in Fig. 4; the amounts of the individual butene isomers are shown in the upper part, while the compositions are shown in the lower part. In this case, the reaction time, the contact time, may correspond to the effluent time. The solid lines in the lower part represent the curves calculated from the relative first-order rate constants and the activation energies, the reaction time being assumed to be the effluent time. The points which represent the compositions experimentally obtained fall on the solid lines quite well. These results also support the idea that the isomerization reaction takes place between the graphite layers and proceeds by means of first-order kinetics.

It is, accordingly, concluded that the graphite oxide is a solid-acid catalyst and that it shows the rake-type profile for the isometization of butenes, which takes place between the graphite layers.

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