The Hydrogenation and Isomerization of Unsaturated Hydrocarbons over ZnO

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The catalytic reaction between unsaturated hydrocarbons and deuterium has been studied over several metal oxides, such as Cr_2O_3,[1] TiO_2[2] and ZnO,[3] and the main initial product in each case has been reported to be alkane-d_2. In this report, the reaction mechanism of propylene, butene, and 1,3-butadiene with deuterium was studied over ZnO. The adsorption during the course of the reaction was measured in order to study the working state of the surface. The mass and the microwave spectroscopic techniques were used to determine the deuterium content and distribution in the reactants and products.

The deuteration of propylene over ZnO proceeded readily at room temperature, and the catalytic exchange reaction between hydrogen atoms of propylene and deuterium took place simultaneously. The rate of the exchange reaction was considerably faster than that of the deuterium addition. The microwave spectroscopic measurements of propylene-d_1 demonstrated that, in the initial stage of the exchange reaction, propylene 3-d_1 predominated. As the reaction proceeded, three kinds of monodeuterio-propylene, 3-d_1, *cis*-1-d_1, and *trans*-1-d_1, were formed. However, propylene 2-d_1 was not observed during the reaction; this corresponds to the fact that the sixth hydrogen in propylene was not exchanged. These results suggest that the chemisorbed state of propylene is the π-allyl species.

The addition of deuterium to 1-butene over ZnO yielded only dideuterio-butane, and no exchange occurred in the hydrogen atoms of 1-butene in the initial stage of the reaction. During the course of the addition reaction, the isomerization of 1-butene proceeded simultaneously; this also occurred in the absence of deuterium, and the rate of isomerization was not affected by either the presence or absence of hydrogen in the ambient gas. The deuteration and isomerization of 1-butene seemingly proceed independently.

The deuteration of 1,3-butadiene over ZnO occurred easily at room temperature, and 1-butene was mainly produced (above 90%) until the 1,3-butadiene of the gas phase had been consumed; then butane started to be produced from 1-butene, accompanied by the isomerization described above. Only the dideuterio-1-butene was produced during the reaction; it was $H_2DC{-}CHD{-}CH{=}CH_2$ according to the microwave spectroscopy. On the other hand, hydrogen atoms of 1,3-butadiene did not exchange with deuterium molecules in the gas phase. When a mixed gas of 1,3-butadiene: H_2 : $D_2 = 1 : 1 : 1$ was introduced over ZnO, the main products were normal 1-butene and dideuterio-1-butene, while the amount of monodeuterio-1-butene was very small and was in proportion to the amount of HD in the gas phase.

The orders of the deuteration reaction of propylene, butene and 1,3-butadiene were all unity as to the partial pressure of deuterium and zero for the unsaturated hydrocarbons. The amounts of hydrocarbons and hydrogen chemisorbed during the hydrogenation were almost constant. In the case of 1-butene, the amounts of chemisorbed 1-butene and hydrogen were nearly half of their saturated amounts. The saturation value of the hydrogen chemisorption during the reaction between hydrogen and unsaturated hydrocarbons was in the following decreasing order: propylene, butene and butadiene, and the rates of the H_2–D_2 exchange reaction during the hydrogenation were retarded in the same order.

It can be seen from these experimental results that deuterium (or HD, H_2) participates in the addition process in a molecular form. To explain the experimental results, two alternative mechanisms may be considered. One of them is that dissociated deuterium atoms act in pairs on the surface, as if they were in a molecular form. In this case, the pair sites may be the zinc and oxygen ions on the surface, and the half-hydrogenated intermediate may be formed irreversibly. Secondly, the more probable mechanism is that deuteration proceeds by means of interaction between the chemisorbed hydrocarbons and the deuterium molecules in the ambient gas. The fact that the rate of deuteration is determined by the partial pressure of deuterium rather that by the amount of chemisorbed deuterium during the reaction favors the latter mechanism.

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