JOURNAL OF CATALYSIS **51**, 435–436 (1978)

Hydrogenation over Heterogeneous Alkali Metal Catalyst[1]

An important part of heterogeneous catalysis study deals with the nature of species formed at the reacting surface (*1*). An agent commonly employed is hydrogen which often undergoes dissociative chemisorption and enters into exchange and addition reactions. Much of this study has centered around the transition metals due to their high level of activity. We have extended this type of study to the heterogeneous alkali metal catalyst.

The behavior of hydrogen over alkali metal complexes has been extensively investigated by Ichikawa *et al.* (*2*). These catalysts are electron donor–acceptor (EDA) complexes of alkali metals with various aromatic compounds. These studies have elucidated the nature of exchange processes and hydrogenation reactions.

The nature of the reaction of ethylene with the surface of liquid potassium was studied by Parry and Pulham (*3*) who reported the dissociative chemisorption and self-hydrogenation of ethylene and postulated an ionic mechanism.

In our study the catalyst was formed by dispersing potassium (30%) on Harshaw 1401P γ-alumina. Passage of an H_2–D_2 mixture over this catalyst at 25°C with a 3-sec average contact time resulted in equilibration which is indicative of dissociative chemisorption of hydrogen on the surface metal atoms.

The chemisorbed hydrogen was found to add rapidly to ethylene and other olefins. To gain a better understanding of this reaction a mixture (mole part) consisting of H_2 (1.1), D_2 (1), and C_2H_4 (1.3) was monitored over this catalyst at 150°C with a 2-sec contact time. Mass spectrometric analysis of the product indicated the following distribution (mol%): H_2 (24), D_2 (2), HD (12), C_2H_6 (14), C_2H_5D (27), $C_2H_4D_2$ (14), $C_2H_3D_3$ (6), $C_2H_2D_4$ (2), and C_2HD_5 (t). In another experiment in which excess ethylene was treated with deuterium, 10 to 18 mol% of C_2H_3D was found in the reacted mixture. On the other hand, passage of D_2–C_2H_6 over this catalyst at 150°C did not yield any deuteroethanes.

The result of this study supports the following mechanism for the hydrogenation of ethylene over 30% K on alumina.

$$\begin{array}{lcl} & & H_2\,(g) \rightleftharpoons 2H\,(ads) \\ CH_2{=}CH_2\,(g) & \rightleftharpoons & CH_2{=}CH\,(ads) + H\,(ads) \\ & & \upharpoonleft\downharpoonright \\ & & CH{=}CH\,(ads) + H\,(ads) \\ CH_2{=}CH\,(ads) + 3H\,(ads) & \rightarrow & C_2H_6\,(g) \end{array}$$

This mechanism requires: (1) the reversible dissociative chemisorption of hydrogen and ethylene and (2) nonreversible hydrogenation of adsorbed ethylene species to ethane. The reversible nature of the chemisorption processes is supported by the formation C_2H_3D, $C_2H_3D_3$, $C_2H_2D_4$, and C_2HD_5.

The ionic mechanism postulated (*3*) for ethylene chemisorption may occur by one electron transfer process:

$$H_2C = CH_2 \xrightarrow{e^-} H_2C = \bar{C}H + H\,(ads)$$

$$H_2C = \bar{C}H + D\,(ads) \rightarrow H_2C = CHD + e^-$$

$$H_2C = \bar{C}H \xrightarrow{e^-} H\bar{C} = \bar{C}H + H\,(ads)$$

$$H\bar{C} = \bar{C}H \rightarrow \bar{C} \equiv \bar{C} + 2H\,(ads)$$

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[1] Contribution No. 595.

0021-9517/78/0513-0435$02.00/0

The data suggest a rapid equilibration of ionic intermediates followed by a slower hydrogenation reaction. In the case of higher olefins chemisorption should result in isomerization. This is shown in the hydrogenation of 1-butene where the products consisted of butane (65), *cis*-2-butene (14), and *trans*-2-butene (20).

It is also interesting to note that the nonionic mechanism proposed is, according to Dent and Kokes (*4*), the best approximation for ethylene hydrogenation over other metals and metal oxides.

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Received July 21, 1977