

The Nature of Adsorbed Olefin over Cobalt Oxide as Revealed by Competitive Hydrogenation

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Both individual and competitive hydrogenations of C₂ to C₄ olefins were carried out at 24°C over dehydrated surface of cobalt oxide. The kinetics is zero order in olefin and first order in hydrogen. The reactivity sequence of olefins are C'₂ ≈ C'₃ > C'₄. The rate of hydrogenation of propylene is, however, remarkably reduced in the presence of ethylene. Taking advantage of the zero-order kinetics in olefin, relative adsorption constants of olefins are obtained as C'₂:C'₃:C'₄ = 8.4:1:2.4, from which the following sequence of chemisorption force is derived after a possible correction for the physical interaction based on adsorption constants of paraffinic hydrocarbons.

$$C'_2 \gg C'_3 > C'_4$$

The nature of adsorbed olefin on the active site for the hydrogenation is concluded to be a π complex similar to silver nitrate-olefin complex.

INTRODUCTION

It has been known that some transition-metal oxides (1) such as Cr₂O₃ (2), Co₃O₄ (3) ZnO (4), and NiO (1) catalyze the hydrogenation of ethylene and the isotopic mixing in hydrogen (5) and in ethylene (6) at room temperature when the oxide surface is dehydrated at 400 to 500°C (6). The characteristic feature of the hydrogenation of ethylene over the oxide catalysts is preservation of molecular identity of hydrogen in the product ethane, that is, the reaction of C₂H₄ with D₂ results in C₂H₄D₂ as the main product. The nature of adsorbed olefin over these oxides is accordingly an important problem.

The adsorbed state of olefin over NiO (7) and Co₃O₄ (8) during oxidation reaction has been elucidated by means of a competitive oxidation method to be a π complex with some electrons donated to the oxide surface. However, the surface state of the oxide during oxidation should be substantially different from that during hydrogenation

because the oxide surface is hydrated by the product water vapor during the oxidation, while the hydrogenation is undertaken over the dehydrated surface.

As reported in the previous paper (3) the rate of hydrogenation of ethylene over Co₃O₄ is expressed by

$$\text{rate} = kP_{\text{C}_2\text{H}_4}^0 P_{\text{H}_2}^1 \quad (1)$$

These kinetics suggest that the active sites are occupied by adsorbed ethylene. Indeed, it was found that the rate of H₂-D₂ equilibration was effectively depressed by ethylene (3). This feature of the reaction appears suitable for the adsorption study by means of the competitive method. Thus it was decided to investigate the competitive hydrogenation of olefins over the dehydrated surface of cobalt oxide.

EXPERIMENTAL

The catalyst sample used was the one denoted as Co₃O₄ (III) in the previous paper (3) (45.6 g, total area 108 m²) and was ob-

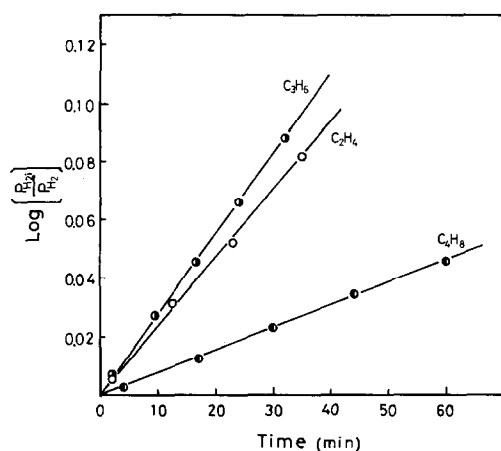


FIG. 1. First-order plots for the hydrogenation of single olefins.

tained by decomposition of cobaltic nitrate at 600°C. This catalyst was evacuated at 420°C and stabilized by an irreversible adsorption of hydrogen at room temperature. In this way the catalytic activity was stable during a run and between runs, except in the case of butene where a slight degradation of catalytic activity was observed between runs.

The hydrogenation runs were carried out in a closed circulating system following both pressure and composition of mixed olefins. Gas composition was intermittently analyzed by gas chromatography. All the runs were made at 24°C.

RESULTS

1. Hydrogenation of single olefin. The kinetics of hydrogenation as mentioned in the Introduction was reconfirmed with C₂ to C₄ olefins. Figure 1 shows the first-order plots with respect to hydrogen. Since the runs were made with excess hydrogen ($H_2/C_2 = 3.2$, $H_2/C_3 = 3.9$, $H_2/C_4 = 6.2$), Fig. 1 by itself is not convincing evidence for first-order dependence on hydrogen pressure. But these data are enough to demonstrate the zero-order dependence of olefin. The rate constants of hydrogenation are obtained from the slopes of these lines as follows.

Olefin	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈
$k \cdot 10^3 \text{ min}^{-1}$	2.34	2.75	0.77

It should be noted here that the isomerization of butene was extensive during the hydrogenation. Thus, although 1-butene was used as the starting olefin, the result obtained should be referred to as a *n*-butene mixture. The hydrogenation rate of the individual *n*-butene isomers could not be obtained in the present condition.

2. Competitive hydrogenation. Figure 2 shows the time course of the competitive hydrogenation of ethylene and propylene with a mole ratio of $H_2:C_2H_4:C_3H_6 = 5.9:1.1:1$. It is clear that ethylene is preferentially hydrogenated in the initial period

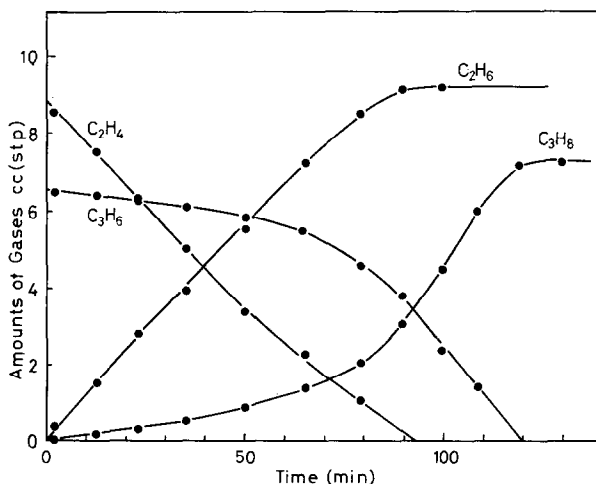


FIG. 2. Time course of competitive hydrogenation of ethylene and propylene.

and that the rate of hydrogenation of propylene increases with decrease in remaining ethylene, whereas the observed difference in the rates of single olefins is very slight. Thus it is qualitatively shown that ethylene is adsorbed more strongly than propylene.

3. Relative adsorption constants of olefins. Since the active sites on the oxide surface are occupied by olefin as pointed out in the Introduction, ethylene and propylene should compete for the active sites, with a relative extent of occupation depending on the individual adsorption constants, K_2 and K_3 . The zero-order kinetics in olefin may be modified in terms of Langmuir isotherm for the case of competitive reaction as follows;

$$-dP_2/dt = k_2 \frac{K_2 P_2}{K_2 P_2 + K_3 P_3} \cdot P_{H_2}, \quad (2)$$

$$-dP_3/dt = k_3 \frac{K_3 P_3}{K_2 P_2 + K_3 P_3} \cdot P_{H_2}, \quad (3)$$

where the subscripts 2 and 3 denote ethylene and propylene, respectively, and k is the rate constant of hydrogenation. Combining Eqs. (2) and (3), the following relation is derived;

$$dP_3/dP_2 = k_3 K_3 P_3 / k_2 K_2 P_2, \quad (4)$$

which can be integrated to;

$$\log (P_{3i}/P_3) = (k_3 K_3 / k_2 K_2) \log (P_{2i}/P_2), \quad (5)$$

where P_{2i} and P_{3i} denote the initial pressures. Figure 2 is replotted according to Eq. (5) as shown by solid circles in Fig. 3. A straight line is obtained as expected from Eq. (5). Another run of competitive reaction of ethylene and propylene is also plotted on Fig. 3 as shown by open circles. The reproducibility is satisfactory. A similar plot of the competitive reaction of propylene and 1-butene again gives a straight line as shown in Fig. 3. From the slopes of these lines, the following values are obtained, $k_3 K_3 / k_2 K_2 = 0.14$; and $k_4 K_4 / k_3 K_3 = 0.66$. With the known values of $k_3 / k_2 = 1.17$ and $k_4 / k_3 = 0.28$, the following relative values of adsorption constants are obtained: $K_2 : K_3 : K_4 = 8.4 : 1.0 : 2.4$.

4. Correction for the physical interaction. It has been shown for the adsorption of olefin over nickel oxide during oxidation that the adsorption force may be divided

into two parts, chemical and physical, and that the chemical interaction which is essentially a π -complex formation is sometimes masked by the physical interaction which increases in magnitude with the carbon number of the olefin. This kind of masking must be taking place in the present case, too. In this respect, the physical part of the adsorption force is estimated by the relative adsorption constants of corresponding saturated hydrocarbons to reveal the chemical interaction.

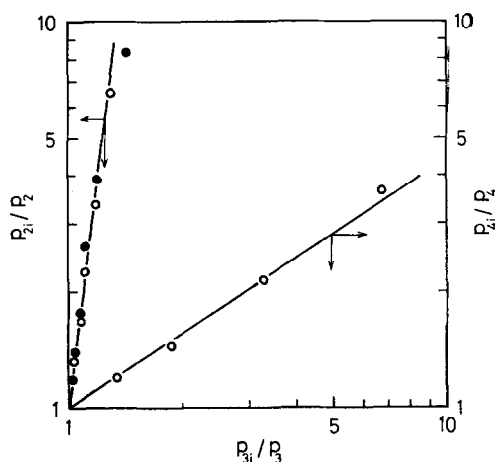


FIG. 3. Competitive hydrogenation of C₂-C₃ and C₃-C₄ olefins; plots according to Eq. (5).

The adsorption measurements of C₂ to C₄ paraffins were carried out by the static method at low pressures below 30 mm Hg and room temperature. The following relative adsorption constants K_p were estimated from inclination of the isotherm near the origin: $K_{p_2} : K_{p_3} : K_{p_4} = 1 : 2 : 9$. The adsorption constant increases with the carbon number of the hydrocarbon as expected. This effect is likely to be operative in the adsorption of olefin. If the relative values in K_p are applied to the olefin adsorption to subtract physical contribution, the following values of corrected relative adsorption constants (K') are obtained: $K'_2 : K'_3 : K'_4 = 31 : 2 : 1$. Thus the following sequence of chemical interaction between olefin and active site of hydrogenation may be assessed: $C'_2 \gg C'_3 > C'_4$.

DISCUSSION

The nature of the adsorption complex of olefin during oxidation has been elucidated by means of the competitive reaction method over nickel oxide (7), cobalt oxide (8), and palladium (9). Although the adsorption complexes over these catalysts can be considered as π complexes, they are classified into two types, types A and B. Type A complex, whose model is provided by silver nitrate (10) and palladium chloride (11) complexes, is found over palladium. This π complex is characterized by a reduction in stability when the number of alkyl substituents at the double-bonded carbon is increased. That is, the stability constant of Type A complex decreases from ethylene to propylene and to butene. Type B complex, whose model is provided by trinitrobenzene-olefin complex (12), is found over nickel oxide and cobalt oxide during oxidation. This π complex is characterized by a stability enhancement when the number of alkyl substituents at the double-bonded carbon is increased. That is, the stability constant of Type B complex increases from ethylene to butene, quite opposite to Type A.

The trend in the adsorption constants of olefins observed in this study during hydrogenation over the dehydrated surface of cobalt oxide suggests the adsorption complex to fall under Type A. As the adsorbed state of olefin over the same oxide is Type B during oxidation, it is realized that there is a striking difference in the adsorbed intermediates between hydrogenation and oxidation over cobalt oxide. The surface state of the oxide should be responsible for this difference.

It is accepted that the Type B complex is formed by electron donation from olefin. When this is the case, the adsorbent surface should act as an acceptor. Since the oxide surface is in a hydrated state during oxidation, there seems to be no direct interaction between adsorbed olefin and metal ion although the electron-accepting ability of surface oxygen should depend on electronegativity of metal ion. This seems to be the reason why the adsorbed state during ox-

idation takes Type B complex instead of Type A in which some extent of back donation of electron is admittedly involved (10).

On the other hand, in the case of hydrogenation, the oxide surface is in a dehydrated state having exposed metal ions. The active sites for the hydrogenation are those metal ions, possibly of low valence, as evidenced in the previous paper (3). Since the present method of competitive reaction is responsible only to the active site for the reaction, the adsorbed intermediate observed by this method reasonably involves a direct interaction with the exposed metal ion. In this way the change of adsorbed state of olefin on dehydration of cobalt oxide surface or from during oxidation to during hydrogenation can be understood as a transformation from Type B to Type A complex.

Since the surface concentration of exposed metal ion on the dehydrated surface of cobalt oxide is as low as $10^{12}/\text{cm}^2$ as reported in the previous paper, the oxide surface is mostly covered by oxide ion on which Type B complex can be formed. Indeed, two types of adsorbed ethylene are observed during hydrogenation as described in the previous paper (3). Type 1 adsorption is independent of ethylene pressure and very small in its amount. Type 2 adsorption is dependent on ethylene pressure and readily reversible. Since the rate of hydrogenation is zero order in ethylene, it is obvious that the Type 2 adsorption is not involved in the reaction path of hydrogenation. Thus the Type 1 adsorption has been ascribed to the metal ion, and the Type 2 to the oxide ion.

It is revealed by the present study that the Type 1 adsorption is a Type A π complex in nature. Although no evidence is available from the present study for the Type 2 adsorption, it is very likely that the Type B complex as observed during oxidation coexists with the Type A.

Dent and Kokes found a π -allyl species by means of infrared technique on zinc oxide (13) which is similar to cobalt oxide in its catalytic action in the hydrogenation of olefin as mentioned in the Introduction. However, the Type A nature of adsorbed

olefin over cobalt oxide is enough to rule out π -allyl species as the intermediate of hydrogenation over this oxide.

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