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

The transition metal oxides such as Co_3O_4, NiO, and Cr_2O_3 are known to be activated by evacuation at high temperature for catalytic reactions such as H_2–D_2 equilibration (*1*), hydrogenation of ethylene, and C_2H_4–C_2D_4 exchange (*2*). The adsorbed state of olefins over Co_3O_4 was previously studied by a competitive reaction method during hydrogenation (*3*) and also during oxidation (*4*) where the oxide surface was very likely hydrated. The adsorbed state during hydrogenation is significantly different from that during oxidation, giving an adsorption constant sequence of olefins. That is, during hydrogenation,

$$K_{C_2H_4} \gg K_{C_3H_6} > K_{C_4H_8},$$

and during oxidation,

$$K_{C_2H_4} < K_{C_3H_6} < K_{C_4H_8}.$$

Similar work was done over NiO during oxidation (*5*), giving an essentially identical results. Thus an analogous difference may be expected during hydrogenation. This was confirmed and is reported here.

The nickel oxide was obtained by thermal decomposition of a reagent grade nickel nitrate at about 600°C, pressed into tablets, and calcined at 600°C in air (12 g, total surface area 4.0 m^2).

After the air treatment, the oxide sample was evacuated at 400°C for 5 hr and then cooled *in vacuo* to 25°C at which 60 Torr of H_2 was introduced and kept there for 16 hr to stabilize the catalytic activity. The amount of H_2 irreversibly chemisorbed was 0.15 ml (STP)/g. The oxide sample thus stabilized by hydrogen was used for reactions. There was a gradual decrease of hydrogenation activity run by run, but the initial activity was recovered by heating the oxide sample at 400°C in circulating air with a liquid nitrogen trap. In this way the same sample was used repeatedly. The reaction temperature was fixed at 25°C. The apparatus employed was the same as before (*3*).

The ethylene hydrogenation on NiO was found to be poisoned by preadsorbed carbon monoxide with a fatal amount being 3×10^{13} molecules/cm^2, suggesting that the active site is the nickel ion exposed to the surface. Deuterogenation of *cis*-2-butene on NiO gave 69% butane-d_2 at 7.3% conversion, as is the case with Co_3O_4 (*6*). The kinetics of hydrogenation of olefins was found to conform to

$$r = kP_{\text{olefin}}{}^0 P_{H_2} \tag{1}$$

for olefin pressures above 30 Torr. The relative rate constants of ethylene, propylene, and isobutene were determined in individual hydrogenation runs as follows:

$$k_2 : k_3 : k_4 = 2.1 : 1.9 : 1.0.$$

The competitive hydrogenation of the C_2 to C_4 olefins was carried out in an olefin pressure range of 42 to 60 Torr, where the zero-order kinetics in olefin could be assumed. As derived in the previous paper (*3*), the relative adsorption constants (K) for olefins can be obtained by

$$\log (P_{3i}/P_3) = (k_3K_3/k_2K_2) \log (P_{2i}/P_2), \tag{2}$$

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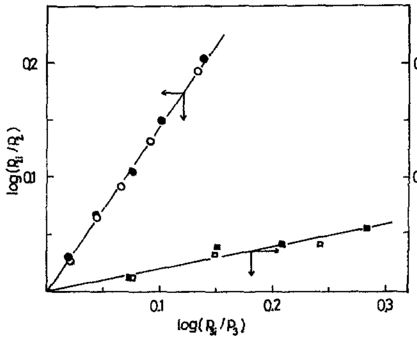

FIG. 1. Competitive hydrogenation of C_2–C_3 and C_3–C_4 olefins; plots according to Eq. (2). $P_{H_2} = 120$ Torr, $P_{olefin} = 40$ to 60 Torr.

where P_2 and P_3 denote the partial pressures of C_2 and C_3 olefins, and i the initial value.

The results of competitive runs are shown in Fig. 1 as plots according to Eq. (2), where circle and square, respectively, indicate the runs for C_2/C_3 and C_3/C_4, and open and solid marks indicate different runs. From the slopes of the two lines, the following values are obtained, $k_2K_2/k_3K_3 = 1.4$ and $k_3K_3/k_4K_4 = 5.1$. With the known relative values of rate constants, the relative values of adsorption constants are estimated to be

$$K_2:K_3:K_4 = 3.7:2.8:1.0.$$

In order to eliminate a difference caused by different molecular sizes, the adsorption constants of C_2 to C_4 paraffins were determined, as done in the previous study on Co_3O_4, as follows:

$$K_{P2}:K_{P3}:K_{P4} = 1.0:7.3:39.$$

If the relative values of K_P are applied to the olefin adsorption to subtract physical contribution, the following values of corrected relative adsorption constants are obtained:

$$K'_2:K'_3:K'_4 = 150:15:1,$$

which is in agreement, in nature, with the result on Co_3O_4:

$$K'_2:K'_3:K'_4 = 31:2:1.$$

The observed sequence of adsorption constants demonstrates that the strength of olefin chemisorption decreases as the number of alkyl substituents at the double-bonded carbon or the electron density at the double bond increases. This conforms to an olefin π-complex in which electrons are back-donated from nickel to olefin. Since this information originates in the adsorption of olefin during its hydrogenation, the olefin π-complex thus disclosed should be the adsorbed intermediate of the hydrogenation.

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