The Effect of Metallic Potassium Addition on Catalytic Properties of Nickel for Hydrogenation of Ethylene

YOSHIKO SHIGEHARA AND ATSUMU OZAKI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro-ku Tokyo Japan

Received June 19, 1973

Hydrogenation of ethylene on Ni-K catalyst has been studied and disclosed a nature different from simple nickel catalyst. Activity degradation with time and self-hydrogenation of ethylene was not found on the Ni-K catalyst. In order to monitor the behavior of hydrogen and ethylene on catalyst surfaces during the hydrogenation, the reaction of H_2 -D₂ mixture with ethylene, the reaction of H_2 with a mixture of C_2H_4 C_2D_4 and kinetic measurements were carried out. The rate of isotopic mixing in ethylene over the Ni-K catalyst is much slower either in the presence or in the absence of hydrogen. It is concluded that the dissociative adsorption of ethylene on nickel is effectively depressed by addition of potassium, resulting in a weaker inhibition of hydrogen chemisorption. In accordance with this conclusion, the reaction order in hydrogen is lower, H_2 -D₂ exchange reaction takes place even in the presence of ethylene.

I. INTRODUCTION

It is well known that a promoter can change remarkably the catalytic properties of a metal. The promoter effect in synthetic ammonia catalyst has been studied in this laboratory and the conclusion has been reached that ammonia synthesis is enhanced by an electron transfer from potassium oxide to iron (1). This recognition has led to discovery of a new catalyst system promoted by metallic alkali which is more electropositive than oxide (2). In view of this result, the effect of metallic alkali on the other catalytic properties of metals would be interesting and pertinent to be studied. It has been shown by Cimino, Boudart, and Taylor (3) that the addition of potassium oxide to iron or nickel reduces the extent of dissociation in the adsorbed species during hydrogenolysis of ethane. Thus it was decided to investigate the effect of metallic potassium on the catalytic properties of nickel for the hydrogenation of ethylene.

II. EXPERIMENTAL METHODS

Apparatus used in this study was a closed circulating system (about 140 ml) with a U-tube containing catalyst connected to a manometer and to a gas chromatograph which permitted analysis of the circulating gas at any time. Metallic potassium was placed in a side tube and transferred onto the catalyst by evaporation.

Materials. H_2 . Cylinder hydrogen was purified by passing it over a platinumasbestos catalyst at about 350°C and dried by use of a liquid nitrogen trap packed with alumina.

 C_2H_4 . Cylinder ethylene was condensed at liquid nitrogen temperature and distilled from -78°C. The distillation was repeated.

 D_2 . Deuterium, obtained by the electrolysis of D_2O was purified in a similar manner with that for H_2 .

 C_2D_4 . Tetradeuterio ethylene, obtained by deuteration of C_2D_2 over Girdler G-58

Copyright © 1973 by Academic Press, Inc. All rights of reproduction in any form reserved. catalyst, was purified by a gas chromatographic column of silica gel.

Ni. Nickel sample was obtained as follows, Nickel hydroxide, obtained by precipitating reagent grade nickel nitrate with ammonia solution, was decomposed to nickel oxide by calcination at 490°C. The oxide sample thus obtained was packed into a glass U-tube and treated with a hydrogen stream for 5 hr at 210°C, for 8 hr at 290°C and for 8 hr at 350°C. The surface area of the nickel sample thus obtained was 2.1 m²/g metal. In the case of pure nickel runs 76 mg of the sample was used.

Ni-K. Metallic potassium was adsorbed on the above nickel sample (275 mg) in an atmosphere of circulating helium and the circulation of helium was continued for 4 hr at 350°C to distribute the potassium. In this way the excess potassium was deposited on the glass wall outside of the reactor. The amount of adsorbed potassium was determined after the runs to be 0.3 wt %. This amount of potassium corresponds to one potassium atom over 5 Å^2 of nickel surface.

Analysis. The isotopic analyses of hydrogen, ethane and ethylene were made by mass spectrometry. The deuterium distributions in ethane and ethylene were calculated according to the data by Amenomiya and Pottie (4) with slight corrections characteristic of the mass spectrometer used. The usual correction was made for the natural abundance of ¹³C.

III. RESULTS

1. Degradation of Activity During Hydrogenation

It is known (5) that ethylene is irreversibly adsorbed on nickel. This irreversible adsorption causes degradation of catalytic activity of nickel. Indeed it was observed that the activity of pure nickel catalyst was decreased run by run even at -45 to -20° C. On the other hand, on the nickel-potassium catalyst, no such degradation was observed in repeated runs at -23° C. The initial amount of

ethylene introduced was recovered \mathbf{as} either ethylene or ethane after runs at -23° C by trapping with liquid nitrogen. These results suggest that the addition of potassium removes the irreversible adsorption of ethylene on nickel. It should be noted, however, that the catalytic activity was lowered when the nickel-potassium catalyst was allowed to stand in vacuum for about 10 min even at room temperature after pretreatment with hydrogen at 100°C. It seemed necessary to keep the catalyst in contact with hydrogen to avoid the degradation of catalytic activity, although the cause of degradation has not yet been identified. Thus the reaction was made immediately after quick evacuation of hydrogen at reaction temperature.

2. Behavior of Ethylene in the Absence of Hydrogen

It is known that ethylene is dissociated on a nickel surface in the absence of hydrogen at room temperature, resulting in self-hydrogenation (6). Neither such selfhydrogenation nor polymerization was detected over the nickel-potassium catalyst after contacts of ethylene for 19 min at -23° C, for 13 min at 0°C and for 53 min at room temperature. These results indicate that the dissociative adsorption of ethylene on nickel is suppressed by the addition of potassium.

3. Isotopic Mixing in Ethylene During Hydrogenation

Mixtures of C_2H_4 and C_2D_4 were hydrogenated with H_2 on Ni and Ni-K catalysts. The deuterium distributions both in ethane and ethylene are shown in Fig. 1a for Ni at -18.5 °C and in Fig. 1b for Ni-K at -23 °C. It is clear that the extent of isotopic mixing in ethylene is larger on Ni than Ni-K despite the lower conversion to ethane. It is accordingly concluded that the addition of potassium reduces the rate of isotopic mixing in ethylene on Ni catalyst.

4. Kinetics of Ethylene Hydrogenation

The kinetics of hydrogenation on Ni-K was examined at -23° C. Figure 2 shows



FIG. 1. Deuterium distribution in ethylene and ethane obtained by the reaction of C_2H_4 - C_2D_4 mixture with H_2 (a) on Ni at -18.50° C, 16% conversion, and (b) on Ni-K at -23° C 31% conversion: (---) initial ethylene; (O---) ethylene observed; (O--) ethane observed.

the variation of ethane formation rate with the extent of conversion of ethylene for a run with initial pressures of $P_{C_2H_4}$ 9.8 cm Hg and P_{H_2} 13.5 cm Hg. Since hydrogen was used in excess of ethylene, the observed small variation with the extent of conversion suggests a zero order dependence on $P_{C_2H_4}$. By changing $P_{C_2N_4}$ and P_{H_2} during another run, the zero order dependence on $P_{C_2H_4}$ was confirmed and



FIG. 2. Ethane formation rate with the extent of conversion of ethylene at -23° C on Ni-K: $P_{C_{2H_4}}$ (initial) = 9.8 cm Hg; P_{H_2} (initial) = 13.5 cm Hg; (Δ ---) the rate divided by { P_{H_2}/P_{H_2} (initial)}.

the order in $P_{\rm H_2}$ was determined to be about 0.4. The broken line in Fig. 2 represents the rate divided by $\{P_{\rm H_2}/P_{\rm H_2}$ (initial) $\}^{0.4}$.

5. The Isotopic Exchange of H_2 and D_2 in the Presence of Ethylene

It is to be noted that the well-known first order kinetics in hydrogen for the hydrogenation of ethylene over nickel at low temperature is not found with the Ni–K catalyst. It is known that the first order kinetics in hydrogen is explained by the rate determining chemisorption of hydrogen as evidenced by the drastic retardation of isotopic exchange between H_2 and D_2 during hydrogenation (7). In this respect the observed lower order kinetics in hydrogen seems to suggest that the adsorption of hydrogen is no longer rate determining over the Ni-K catalyst. Thus it would be interesting to examine the isotopic exchange of H_2 and D_2 during hydrogenation of ethylene. A 1:1 mixture of H_2 and D_2 premixed with ethylene in a ratio of $(H_2 + D_2)/C_2H_4 = 1.3$ was reacted over the Ni-K catalyst at -23° C for 10 min causing 10.7% conversion to ethane. The extent of isotopic mixing in hydrogen,

$$x = \{(HD) - (HD)_0\} / \{(HD)_e - (HD)_0\},\$$

during this period was 7.1%, whereas the value of x in the absence of ethylene was 33%. This result discloses that, although the rate of exchange is retarded by the presence of ethylene, isotopic mixing in hydrogen takes place over Ni-K catalyst in the presence of ethylene at as low as -23°C. Thus it appears that the chemisorption of hydrogen is not so much retarded by ethylene on the Ni-K catalyst as observed on the pure nickel catalyst.

6. Deuterium Isotope Effect

Since the reaction of H_2-D_2 mixture with C_2H_4 is a competitive reaction of H_2 and D_2 , the relative rates of protium and deuterium may be estimated by the value,

$$R = (2 - \tilde{d})/\tilde{d},$$

where \bar{d} is an averaged number of deu-

terium atoms in the product ethane. The isotopic distribution shown in Fig. 2 gives a value of $R = 2.1 \pm 0.1$, suggesting that protium is about twice as reactive as that of deuterium. This isotope effect was confirmed by separate runs with H₂ and D₂ (14 cm Hg) with C₂H₄ (5 cm Hg) at -23° C over the Ni-K, giving an isotope effect of $v_{\rm H}/v_{\rm D} = 2.0 \pm 0.2$.

IV. DISCUSSION

The present results obtained with the Ni-K catalyst disclose a nature different from the simple nickel catalyst. The absence of activity degradation with time, the absence of self-hydrogenation of ethylene and the lower rate of isotopic mixing in ethylene over the Ni-K catalyst all suggest that the dissociation of ethylene on nickel is suppressed by the addition of potassium, resulting a weaker inhibition of hydrogen chemisorption and thus the lower reaction order in hydrogen. This idea is in conformity with the faster isotopic mixing in hydrogen in the presence of ethylene over the Ni-K catalyst. It may be accordingly concluded that the addition of potassium reduces the extent of C-H dissociation of ethylene on nickel.

Since the potassium metal adsorbed on

nickel admittedly gives some electrons to the nickel surface, resulting in a reduction in the work function of nickel (8) the electron concentration in nickel should be increased by the addition of potassium. The reduced dissociation of ethylene as concluded above would be reasonable on such nickel surface of an increased electron concentration simply because the added electrons seem to reduce the extent of surface unsaturation.

References

- 1. AIKA, K., AND OZAKI, A., J. Catal. 13, 232 (1969).
- OZAKI, A., AIKA, K., AND MORIKAWA, Y., Prepr. Int. Congr. Catal., 5th (Miami) (1972);
 OZAKI, A., AIKA, K., AND HORI, F., Bull. Chem. Soc. Jap. 44, 3216 (1971).
- CIMINO, A., BOUDART, M., AND TAYLOR, H., J. Phys. Chem. 58, 796 (1954).
- 4. AMENOMIYA, Y., AND POTTIE, R., Can. J. Chem. 46, 1735 (1968).
- JENKINS, G. I., AND RIDEAL, E., J. Chem. Soc., London, 2490, 2496 (1955).
- 6. BEECK, O., Discuss. Faraday Soc. 8, 118 (1950).
- MATSUZAKI, I., Int. Congr. Catal., 2nd Pap. No. 53 (1960); J. Res. Inst. Catal. 7, 210 (1959).
- GERLACH, R. L., AND RHODIN, T. N., Surface Sci. 19, 403 (1970).