JOURNAL OF CATALYSIS **40**, 166–172 (1975)

Chemical Composition of the Catalyst Prepared by Reduction of Nickel Orthophosphate in Hydrogen and Catalytic Activity for Partial Hydrogenation of 1,3-Butadiene

F. NOZAKI AND R. ADACHI

Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba, Japan

Received March 4, 1975

The catalyst prepared by reduction of nickel orthophosphate in hydrogen at temperatures from 350 to 700°C has been investigated from a standpoint of structure–activity relationships.

The activity and the selectivity of catalyst varied in a characteristic way with the temperature of catalyst preparation. When the catalyst was prepared at low temperatures below 420°C, subsequent hydrogenation was rapid and gave 1-butene as the most abundant isomer. In this case, fine Ni^0 clusters were found to have an important role as an active site. Whereas, the catalyst prepared at high temperatures above 500°C was relatively weak in activity and gave *trans*-2-butene as the major product. In this case, dinickel phosphide, Ni_2P, served as an active site and the addition of small amounts of oxygen resulted in a significant increase in hydrogenation activity. A plausible interpretation for the variation of catalyst selectivity has been given by reference to the reaction model proposed by Siegel [*J. Catal.* **30**, 139 (1973)].

INTRODUCTION

Nickel compounds such as nickel sulfide, nickel phosphide or nickel arsenide are already known to have a different catalytic activity from metallic nickel and to be selective catalyst for partial hydrogenation of butadiene or acetylene to the corresponding olefin and for hydrogenation of nitrobenzene to aniline (*1–4*). There are a few reports in connection with nickel phosphide or nickel–phosphorus alloy catalyst (*5,6*), but the detail of activity–structure relationship is not completely understood. In this paper, we describe the correlation between the composition of material obtained by the reduction of nickel orthophosphate and its catalytic activity for hydrogenation of 1,3-butadiene.

EXPERIMENTAL METHODS

Catalyst Preparation

A stock of alumina-supported nickel phosphate catalyst containing 20%wt $Ni_3(PO_4)_2$ was prepared by the wet mixing method, which entailed the respective slurries of powdered nickel orthophosphate and alumina sol (Nissan Kagaku Inc., Alumina Sol Type 200), followed by drying at 110°C. The resulting solid masses were extruded to obtain the desired pellet size (ca. 2 mmϕ × 4 mm), and then calcined at 600°C for 2 hr in a stream of air. The alumina-supported catalyst was reduced with hydrogen at various temperatures before use for catalytic test.

Apparatus and Procedure for Catalytic Reaction

The hydrogenation reaction was carried out in a conventional closed circulation system of 390 ml, and pressure changes during reaction were measured manometrically. The reaction vessel contained the packed bed consisting of 2.0 g of the catalyst and small glass beads in the ratio of 1:5 by volume, thereby improving isothermal condition during the course of reaction. The catalyst was reduced again at 300°C under 200 mm Hg of hydrogen for 1 hr before being used. Butadiene (Tokyo Kasei Kogyo Co.) contained no detectable impurities by gas chromatographic analysis. Hydrogen was purified by passage over Pd–asbestos catalyst at 300°C and then dried.

Gas samples withdrawn from the gas-circulation system at regular time intervals were analyzed by using a gas chromatographic unit containing 12 m column of 30% wt dimethylsulforan supported on 40–60 mesh Chromosorb. The column was operated at room temperature with hydrogen as carrier gas.

Tests for Catalyst Composition

The reduction behaviors of $Ni_3(PO_4)_2$ in hydrogen were followed up by two methods, viz, reduction rate measurement during the course of temperature-programmed elevation and hydrogen consumption measurement as a function of time. The measurements were carried out by a similar gas-circulation system as used in the tests for catalytic reaction.

Both of ESR absorption and X-ray diffraction measurements served as a method of qualitative identification of the chemical composition of the catalysts. The ESR absorption measurements of the powdered catalyst samples were made with a JES-3X-type, *X*-band spectrometer (Japan Electron Optics Co.) operating at room temperature. The previously reduced samples in hydrogen at 400 or 650°C for 1 hr were evacuated for 1 hr at 400°C and 10^{-3} Torr in a quartz tube, and then reduced again with hydrogen at 400°C. The X-ray diffractograms were obtained at room temperature by using Ni-filtered iron radiation (Rigaku Denki Co., Geigerflex D-3F spectrometer). The measurements were made on the catalyst samples without alumina carrier, because of experimental convenience that X-ray diffraction was much more sensitive and defined than that of alumina-supported samples.

RESULTS AND DISCUSSION

Catalyst Activity and Selectivity

The temperature of catalyst preparation influenced remarkably both the activity and the selectivity. As shown in Fig. 1, the hydrogenation activity is beginning to emerge when the catalyst is reduced with hydrogen at temperatures near 350°C, and increases drastically with an increase in the reduction temperature, passes through a maximum at about 380°C, and then decreases. The catalyst activity remains almost constant at temperatures ranging from 500 to 650°C, and then virtually disappears above 700°C. The selectivity, S_1, for the partial hydrogenation to butene isomers exceeds 90%, even when the catalyst was prepared at low temperatures near 400°C. Further increase in selectivity S_1 is

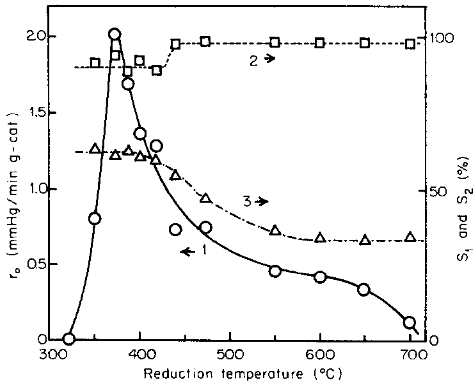


FIG. 1. Activity and selectivity as a function of the temperature of catalyst preparation. (1) Initial reaction rate, (2) Selectivity for partial hydrogenation to butene isomers $S_1 = C_4H_8/(C_4H_8 + C_4H_{10})$, (3) Selectivity to 1-butene $S_2 = 1\text{-}C_4H_8/(1\text{-}C_4H_8 + trans,cis\text{-}2\text{-}C_4H_8)$. Reaction temperature, 60°C; Initial hydrogen pressure, 225 mm Hg; initial butadiene pressure, 75 mm Hg; Time interval of catalyst reduction, 1 hr.

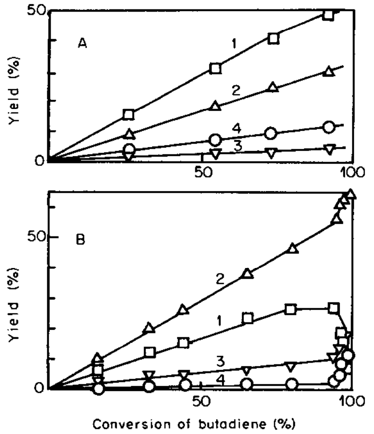


FIG. 2. Yield of the hydrogenated products as a function of butadiene conversion. (A) Catalyst prepared at 400°C; (B) catalyst prepared at 650°C; (1) $1\text{-}C_4H_8$; (2) *trans*-$2\text{-}C_4H_8$; (3) *cis*-$2\text{-}C_4H_8$; (4) C_4H_{10}.

achieved by preparing the catalyst at high temperature. As also shown in Fig. 1, the selectivity for the formation of 1-butene, S_2, was dependent largely on the temperature of catalyst preparation.

Figure 2 shows the detailed correlation between conversion of butadiene and yield of the hydrogenated products. Each of the products increases in yield linearly with butadiene conversion, except for the extreme case in which butadiene conversion approaches 100%. The isomerization of butene isomers owing to double bond migration was found to be rapid over these catalysts, when no butadiene coexisted. Thus, the data of Fig. 2 suggest that butene isomers produced are displaced from active site by butadiene before the isomerization takes place. It may be concluded that butene isomers are formed entirely by 1,2- and 1,4-addition of hydrogen at conditions where butadiene conversion is not very high. When the catalyst was prepared at low temperatures below 420°C, subsequent hydrogenation gave 1-butene as the most abundant isomer, whereas, the catalyst prepared at high temperatures above 500°C gave *trans*-2-butene as the major product.

Figure 3 indicates that the orders of reaction were appreciably influenced by the temperature of catalyst preparation. An elevation in the temperature while preparing the catalyst from 400 to 650°C results in a lowering of 1.0 to 0.8 order with respect to hydrogen and an increasing of 0.0 to 0.2 order with respect to butadiene. The variations in catalyst selectivity and in reaction order with a change of the temperature of catalyst preparation suggest either that chemical composition of the catalyst surface altered or that physical structure of the catalyst changed.

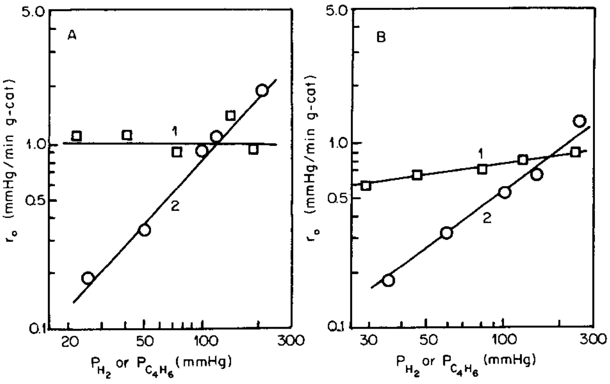


FIG. 3. Initial reaction rate as a function of butadiene and hydrogen pressure. (A) Catalyst prepared at 400°C; reaction temperature, 50°C; (B) catalyst prepared at 650°; reaction temperature, 80°C; (1) effect of butadiene pressure (P_{H_2} was kept at constant pressure of 130 mm Hg); (2) effect of hydrogen pressure ($P_{C_4H_6}$ was kept at constant pressure of 50 mm Hg).

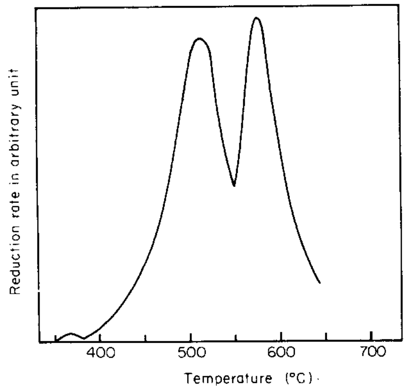


FIG. 4. Reduction rate of catalyst in hydrogen during the course of temperature-programmed elevation (temperature elevation speed, 5°C/min).

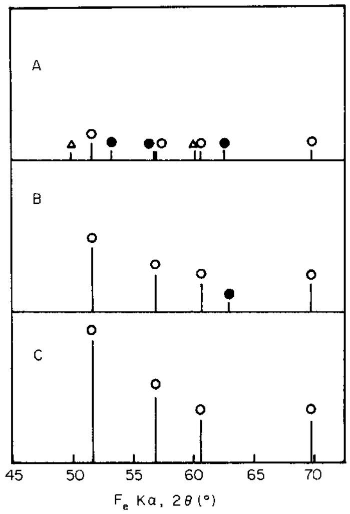


FIG. 6. X-Ray diffractograms. (A) after reduction at 500°C for 2 hr; (B) at 600°C for 1 hr; (C) at 700°C for 1 hr; (○) peak attributable to Ni_2P (Ref. ASTM card 3-0953); (△) Ni_7P_3 (Ref. ASTM card 3-1101), (●) unknown peak for assignment.

Catalyst Composition

The result of an experiment in which the temperature-programmed technique was applied to characterize the hydrogen reduction of $Ni_3(PO_4)_2$ is shown in Fig. 4. The curve depicts that reduction of $Ni_3(PO_4)_2$ in hydrogen consists of three distinct steps.

The results obtained from hydrogen consumption measurement are shown in Fig. 5. All of the pressure decrease vs time curves appear to level off within 10 hr. This suggests that the reduction continued over a period of 10 hr leads both the surface and the bulk of catalyst into the same degree of reduction being determined by temperature. The resulting correlation between the degree of reduction and the temperature was represented by line 8 in Fig. 5. Within the experimental error, the reduction of $Ni_3(PO_4)_2$ is considered complete at temperatures above 600°C.

The X-ray diffraction diagrams are shown in Fig. 6. The diffraction patterns of the samples prepared at 600 or 700°C (Fig. 6B and C) revealed the sample to consist mainly of Ni_2P. The diffractogram of the sample prepared at 500°C (Fig. 6A) was

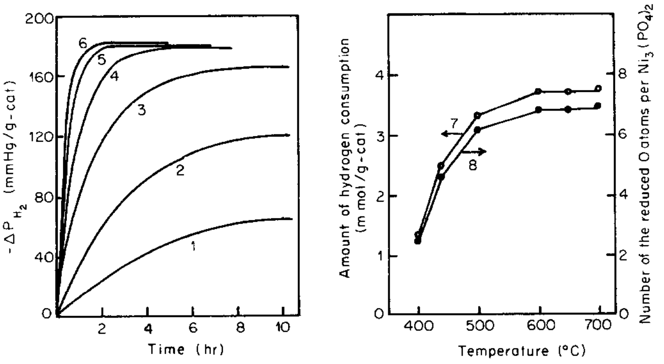
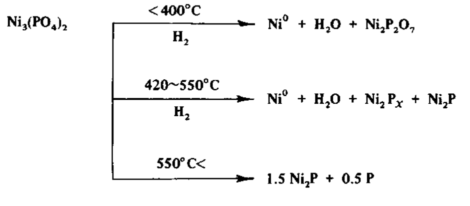


FIG. 5. Decrease in hydrogen pressure as a function of time and degree of reduction as a function of temperature. (1) 400°C; (2) 440°C; (3) 500°C; (4) 600°C; (5) 650°C; (6) 700°C; (7) amount of hydrogen consumption; (8) degree of reduction.

complicated and weak in signal intensity. And, it showed that various nickel phosphides and an unknown compound for assignment were present together with Ni_2P. All the samples prepared at temperatures below 450°C were amorphous and X ray diffraction analysis was invaluable in the identification of the catalyst composition.

The ESR absorption measurements gave the following observations: the alumina-supported $Ni_3(PO_4)_2$ sample showed none of the significant signals even after evacuation at 400°C. However, the broad single ESR signal ($g = 2.27$, $\Delta H_{msl} = 800$ G) appeared after reduction with hydrogen at 400°C. By reference to the established informations (*7–9*), the broad ESR signal was assigned to ferromagnetic resonance owing to Ni^0 species produced by reduction. The signal intensity increased with an increase in time interval of reduction at 400°C. The catalyst sample prepared at 650°C showed the weak single ESR signal ($g = 2.44$, $\Delta H_{msl} = 1500$ G). This similar ESR signal is presumably attributable to well-sintered clusters of Ni^0 species which still remain in the catalyst, even when it was prepared at the high temperature. However, the signal intensity was far less than that of the sample prepared at 400°C.

On the basis of the experimental results described above and the previous report on the thermal decomposition of nickel phosphate (*10*), we have speculated that the reduction of $Ni_3(PO_4)_2$ in hydrogen proceeds via the following three steps:



where Ni_2P_x is a variety of nickel phosphides other than Ni_2P that give $Ni_2P + P$ at elevated temperatures. This sequence of the reduction steps is consistent with informations described in the previous papers (*5,10,11*). In our present study, however, there is no direct evidence for the existence of such a compound as $Ni_2P_2O_7$ or Ni_2P_x. Consequently, it can only be said with certainty that Ni^0 clusters are formed at the low temperatures and Ni_2P is obtained at the high temperatures.

Catalyst Composition–Activity Relationship

From the results described above, it may be concluded that the hydrogenation with a faster reaction rate to the butene isomers consisting mainly of 1-C_4H_8 is attributed to fine clusters of Ni^0, whereas, the relatively slow hydrogenation leading mainly to trans-2-C_4H_8 formation is due to the catalytic action of Ni_2P surface. But, the ESR absorption measurement revealed that the catalyst prepared at the high temperature contains a slight amount of well-sintered Ni^0 cluster or Ni-phosphorus solid–solution. Thus, the difficult problem arises as to which of Ni^0 and Ni_2P play an important role as active site of the catalyst prepared at high temperatures. However, it was readily proved to be Ni_2P by the following experiment: the Ni^0-free catalyst showed a similar activity as before the treatment in which Ni^0 species were removed from the catalyst by extraction using 0.5 *N* HCl aqueous solution.

In order to make a further characterization of the catalyst surface, influences of oxygen addition on the hydrogenation reaction have been investigated. As shown in Fig. 7, the catalyst prepared at 400°C showed only a monotonically steep decrease in activity by addition of a very small amount of oxygen. In contrast, the catalyst prepared at 600°C increased drastically its activity with addition of oxygen at pressures ranging from 1 to 2 Torr, and then decreased. In the latter catalyst, a complete disappearance of catalytic activity was not encountered even at high oxygen pressures. This fact was distinct from

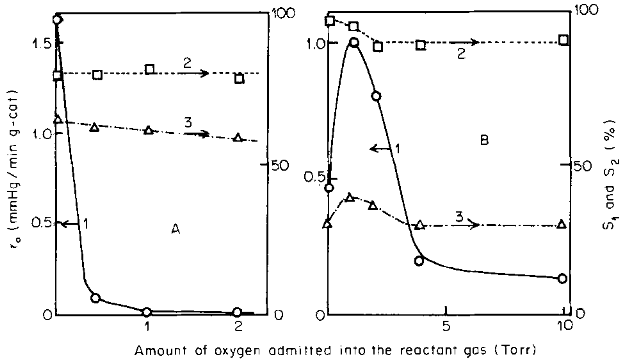


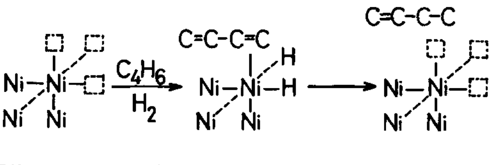
FIG. 7. Effect of oxygen addition on reaction rate. (A) Catalyst reduced at 400°C for 4 hr; (B) catalyst reduced at 600°C for 2 hr; (1) initial reaction rate; (2) selectivity for partial hydrogenation S_1; (3) selectivity to 1-butene S_2. Reaction temperature, 50°C for A and 60°C for B; initial hydrogen pressure, 145 mm Hg; initial butadiene pressure, 55 mm Hg.

the former catalyst. The exact mechanism on the enhancing of hydrogenation activity owing to oxygen addition is not yet clarified, however, in this section we wish to point out that there are two different types of sites responsible for activity and oxygen promotes the 1,4-addition of hydrogen to 1,3-C_4H_6 from Ni_2P.

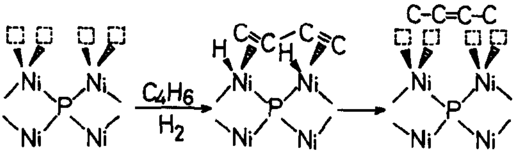
Selectivity for 1,2- and 1,4-Addition of Hydrogen

In the previous section, we noted that the selectivity for 1,2- and 1,4-addition of hydrogen is entirely dependent on difference in the chemical composition of catalyst surface. However, Joice *et al.* (*12*) and Phillipson *et al.* (*13*) have already pointed out that the selectivity of such metallic catalysts as Co or Ni for hydrogenation of butadiene varies extensively from 1,2-addition to 1,4-addition with the temperature of catalyst preparation, and that the change in selectivity is due unequivocally to the variation of physical characteristic of the metal surface. We have tried a similar experiment of the sintering effect on the selectivity, by using silica-supported nickel catalyst prepared in a separate batch. The results showed that changes in both the activity and the selectivity were quite analogous to those described in the previous papers (*12,13*). The other point to be additionally remarked here was the effect of oxygen addition on the catalyst activity, i.e., well-sintered nickel surface showed only a steep decrease in activity by addition of oxygen and such an enhanced activity as those obtained in the Ni_2P catalyst was not observed throughout experiment. Thus, we are led to the conclusion that the selectivity of the catalyst prepared from $Ni_3(PO_4)_2$ is directly dependent on the chemical composition of the catalyst surface.

It still remains to be investigated why 1,2- and 1,4-addition of hydrogen take place preferentially over the surface of Ni^0 and Ni_2P, respectively. It seems profitable to answer this question by way of applying the reaction model which has been recently proposed by Siegel (*14*). According to Siegel's model, Ni^0 surface in a not-sintered state gives mainly 1-C_4H_8, as is shown by the following scheme:



Whereas, the formation of 2-C_4H_8 over the Ni_2P surface is demonstrated by the model



By virtue of Siegel's model, it can be interpreted in the same way that the secondary hydrogenation of butene isomers to butane proceeds with difficulty over Ni_2P surface or well-sintered Ni surface, of which the vacant coordination numbers were considered to be less than 2. The fact that well-sintered Ni^0 surface behaved like Ni_2P surface, which prevailed in 1,4-addition, can be similarly understood. However, further experimental research is necessary to make clearer these postulations on reaction scheme and to characterize the Ni–P binary catalyst system.

REFERENCES

1. Kirkpartic, W. J., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal, Eds.), Vol. 3, p. 329. Academic Press, New York, 1951.
2. Takeuchi, A., Tanaka, K., and Miyahara, K., *Chem. Lett.* **171,** 411 (1974).
3. Morikawa, K., Shirasaki, T., and Okada, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 131. Academic Press, New York, 1969.
4. Johnson, M. M., Nowack, G. P., and Tabler, D. C., *J. Catal.* **27,** 397 (1972).
5. Sweeny, N. P., Rohrer, C. S., and Brown, O. W., *J. Amer. Chem. Soc.* **80,** 799 (1958).
6. Sada, S., *Kogyo Kagaku Zasshi* **71,** 957 (1968); *Kogyo Kagaku. Zasshi* **73,** 1074 (1970).
7. Yoshida, K., *in* "Butsusei Butsuri Gaku Koza" (K. Ariyama *et al.,* Eds.), Vol. 6, p. 179. Kyoritsu Shitsupan, Tokyo, 1958.
8. Misono, M., *Shokubai* **13,** 183 (1971).
9. Pichat, P., Vedrine, J. C., Gallezot, P., and Imelik, B., *J. Catal.* **32,** 190 (1974).
10. Viltange, M., *C. R. Acad. Sci.* **256,** 2816 (1963).
11. Hutter, P. J., *Ann. Chim. (Paris)* **8,** 450 (1953).
12. Joice, B. J., Rooney, P. B., and Wilson, G. R., *Discuss. Faraday Soc.* **41,** 223 (1966).
13. Phillipson, J. J., Wells, P. B., and Wilson, G. R., *J. Chem. Soc. A* 1351 (1969).
14. Siegel, S., *J. Catal.* **30,** 139 (1973).