

Hydrogenation Activity of Metal Phosphides and Promoting Effect of Oxygen

In previous papers (1, 2), we have reported on the catalytic activity of Ni_2P and the promoting effect of oxygen for the hydrogenation of butadiene to butene isomers. However, little is known about the basic nature of the other metal phosphides. In this report, we describe an experimental study in which the catalytic behavior of cobalt phosphide (Co_2P) and iron phosphide (FeP) has been compared with that of nickel phosphide (Ni_2P).

The method of catalyst preparation and the experimental procedure were similar to those previously reported (1, 2): the phosphide catalysts were prepared by reduction of metal phosphates in hydrogen and the catalytic tests on the hydrogenation of 1,3-butadiene to butene isomers were carried out in a conventional closed-circulation apparatus. Adsorption measurements of oxygen or hydrogen and investigations by ir spectroscopy were made to characterize the catalysts in the same manner as described in the previous papers (1, 2). The three phosphide catalysts supported on an alumina carrier, $\text{Ni}_2\text{P}-\text{Al}_2\text{O}_3$, $\text{Co}_2\text{P}-\text{Al}_2\text{O}_3$, and $\text{FeP}-\text{Al}_2\text{O}_3$, were obtained from alumina-supported $\text{Ni}_3(\text{PO}_4)_2$, $\text{Co}_3(\text{PO}_4)_2$, or FePO_4 by reduction in hydrogen at 600°C , respectively. In each catalyst, the metal phosphide content was adjusted to about 20 wt%. The chemical formula of metal phosphide, being contained in the catalysts as a main phosphide species, was identified as Ni_2P , Co_2P , or FeP by X-ray diffraction analysis of the respective powdered catalysts. As the simplified expression of alumina-supported phosphide catalyst, for example, $\text{Ni}_2\text{P}(20 \text{ wt}\%)-\text{Al}_2\text{O}_3$ is hereafter referred to simply as Ni_2P .

The surface areas of the catalysts used in this study were approximately $100 \text{ m}^2/\text{g}$ (Ni_2P), $95 \text{ m}^2/\text{g}$ (Co_2P), and $110 \text{ m}^2/\text{g}$ (FeP), respectively, as determined by the BET method using nitrogen as an adsorbate. The activity and selectivity of the catalysts both before and after oxygen treatment are shown in Fig. 1. In Fig. 1, the hydrogenation reaction was conducted with an initial pressure of 75 mm Hg butadiene and 225 mm Hg hydrogen, and the catalysts were pretreated with 3 mm Hg oxygen when oxygen effect was examined. Figure 1 indicates that the hydrogenation activity per unit mass of the catalysts drastically decreases in the order $\text{Ni}_2\text{P} > \text{Co}_2\text{P} > \text{FeP}$. The temperatures at which the activity for each of the catalysts becomes significant are considerably different in such a way that Co_2P or FeP catalyst is necessary to raise the temperature up to about 120 or 200°C , respectively. There is no remarkable difference in the BET surface area and in the adsorption amount of hydrogen or oxygen among the three catalysts, and accordingly it can be said that, even on the basis of unit area or unit site of the catalysts, the activity of Co_2P or FeP is extremely lower than that of Ni_2P . However, the following feature is common to the three catalysts: the addition of oxygen results in a significant increase in the catalyst activity, while it scarcely affects the catalyst selectivity. The fraction of butane formation is usually slight regardless of both the catalyst species and the pretreatment with oxygen, and the selectivity for the partial hydrogenation to butene isomers exceeds 90% throughout the experiments. As additional information on the selectivity, it should be noted that FeP

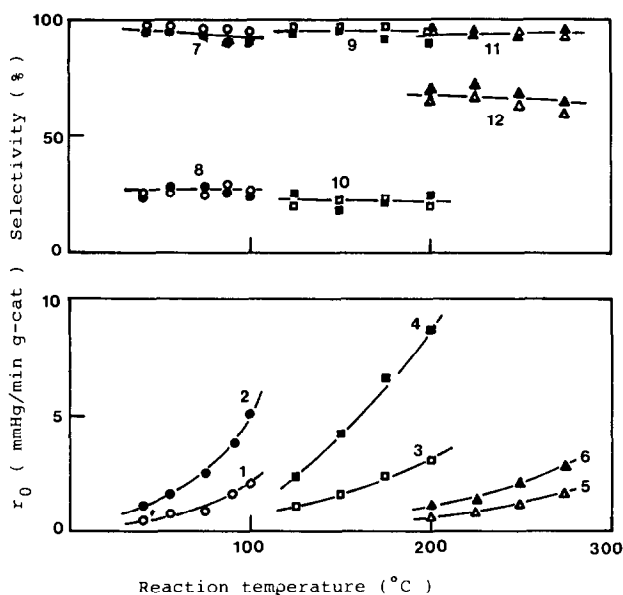


FIG. 1. Hydrogenation activity and selectivity of metal phosphide catalysts. Curves (1), (2), (7), and (8) are the data for Ni_2P catalyst; (3), (4), (9), and (10) for Co_2P catalyst; (5), (6), (11), and (12) for FeP catalyst. (1), (3), (5): Before catalysts were pretreated with oxygen; (2), (4), (6): after catalysts were pretreated with oxygen. (7), (9), (11): Selectivity for partial hydrogenation to butene isomers. $S_1 = \text{C}_4\text{H}_8/\text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10}$; (8), (10), (12): selectivity to 1-butene, $S_2 = 1\text{-C}_4\text{H}_8/1\text{-C}_4\text{H}_8 + \text{trans, cis-2-C}_4\text{H}_8$.

catalyst showed a high selectivity for 1,2-addition of hydrogen leading to 1- C_4H_8 formation, whereas Ni_2P or Co_2P catalyst promoted mainly 1,4-addition leading to 2- C_4H_8 formation. The reason for the varying selectivities among Ni_2P , Co_2P , and FeP is still unclear. Possibly this is due to their differences in the atomic Metal/P ratio of the catalyst surface, although there is no experimental evidence.

The dependence of the reaction rates on the partial pressure of C_4H_6 or H_2 was approximately expressed by the following equations: $r_{50^\circ\text{C}} = k' P_{\text{C}_4\text{H}_6}^{0.2} \cdot P_{\text{H}_2}^{0.8}$ (for Ni_2P catalyst), $r_{150^\circ\text{C}} = k'' P_{\text{C}_4\text{H}_6}^{0.0} \cdot P_{\text{H}_2}^{1.0}$ (for Co_2P catalyst), and $r_{200^\circ\text{C}} = k''' P_{\text{C}_4\text{H}_6}^{0.1} \cdot P_{\text{H}_2}^{0.9}$ (for FeP catalyst). The addition of oxygen had practically no influence upon the order in the power rate formula, although it increased remarkably the rate constant k' , k'' , or k''' . In order to elucidate a possible mechanism of the promoting effect of oxygen upon the catalyst activity, adsorption measurements of oxygen or hydrogen on the catalysts

were made. The results are shown in Table 1 and Fig. 2.

The adsorption isotherms, shown in Fig. 2, indicate that the adsorption amount of hydrogen is increased several or a few times by the preadsorption of oxygen. A comparison of Fig. 1 with Fig. 2 suggests

TABLE 1

Catalyst	Amount of Oxygen Adsorbed at 70°C, 4 mm Hg Oxygen Pressure	
	Total adsorption	Irreversible adsorption ^a
Ni_2P	3.3	1.9
Co_2P	2.1	1.5
FeP	9.2	6.5

^a (Total amount of oxygen adsorbed) - (Amount of oxygen adsorbed in the repeated adsorption process after the catalyst had been evacuated at 70°C for 30 min).

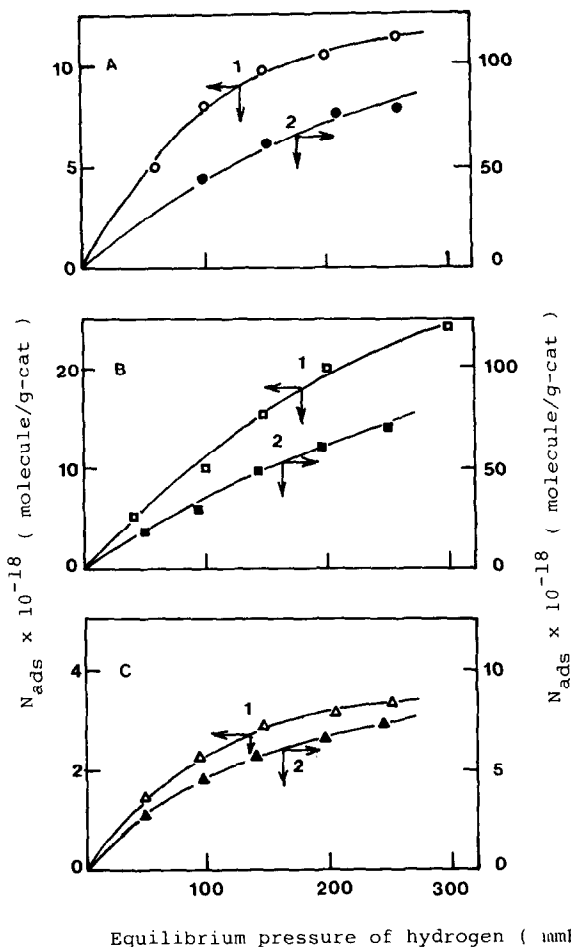


FIG. 2. Adsorption isotherm of hydrogen at 70°C. (A) Ni₂P catalyst; (B) Co₂P catalyst; (C) FeP catalyst. (1) Before catalyst was pretreated with oxygen; (2) after catalyst was pretreated with oxygen and then evacuated at 70°C.

that the promoting effect of oxygen upon the hydrogenation activity of the phosphide catalysts is believed to be caused by the increase in the hydrogen adsorption. The data of hydrogen adsorption obtained with the three phosphide catalysts both before and after oxygen treatment followed Langmuir-type expressions, in a similar way to that previously reported (2). However, it was not possible to draw any simplifying correlations among the values of the parameters of Langmuir expressions. In addition, the quantitative relationship between the oxygen and hydrogen adsorbed

was not simple and a specific stoichiometric correlation could not be derived from the adsorption data. These complicated situations are speculated to result from the variation of the atomic Metal/P ratio in the surface layers of the catalysts, depending upon the species of metal phosphides. In this paper, the discussion is limited to the qualitative interpretations of experimental results.

As additional information, it has been revealed that the addition of small amounts of H₂O to the phosphide catalysts results in some depression of the hydrogenation ac-

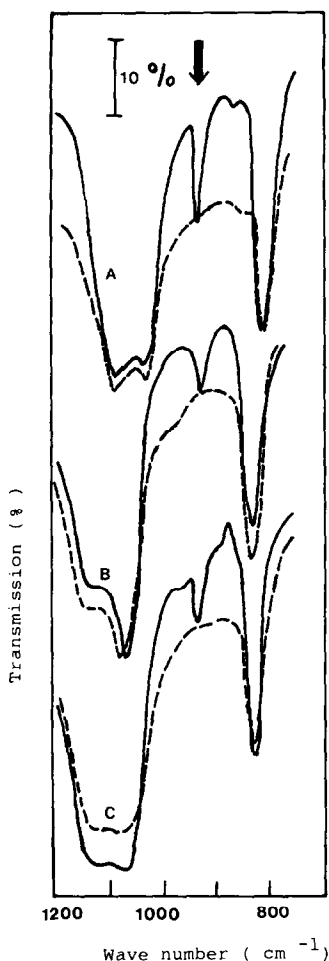


FIG. 3. Infrared spectra of (A) Ni₂P, (B) Co₂P, and (C) FeP catalyst. The spectrum shown by the broken line was recorded before addition of oxygen; the spectrum shown by the solid line was recorded after addition of oxygen. The arrow shows the appearance of a characteristic absorption peak in the range 940–950 cm⁻¹, after oxygen has been preadsorbed.

tivity rather than the promoting action. Therefore, the promoting effect of oxygen was not thought to be due to the formation of H₂O during the course of hydrogenation reaction.

The ir spectra of the catalysts and the samples after oxygen treatment were illustrated in Fig. 3. At this time Cab-O-Sil was used as a binder for making the ir sample disks, as described in the previous paper (2). In the range 940–950 cm⁻¹, the catalyst samples, after oxygen had been adsorbed, showed a new, single sharp peak. This characteristic absorption band was assigned to P–O stretching vibration, by reference to (3). Thus, the schematic adsorption of oxygen and hydrogen on various phosphide catalysts has been speculated to be similar to that previously reported (2), although structural analyses of the phosphide catalysts are incomplete and experimental evidence to support the argument is not sufficient.

In conclusion, the present study has been able to offer the experimental information concerning the hydrogenation activity of various phosphide catalysts and the nature of the effect of oxygen pretreatment.

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