

4. A. A. Pribylov, S. P. Vnukov, S. M. Kalashnikov, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1709 (1988).
5. M. M. Dubinin, *Dokl. Akad. Nauk SSSR*, 275, No. 6, 1442 (1984).
6. M. M. Dubinin and N. G. Zhukovskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, No. 5, 535 (1958).
7. A. Linares-Solano, F. Rodriguez-Reinoso, J. M. Martin-Martinez, and J. D. Lopez-Gonzales, *Adsorp. Sci. Technol.*, 1, No. 4, 317 (1984).
8. B. McEnaney, *J. Chem. Soc. Faraday Trans. 1*, 70, No. 1, 84 (1974).
9. S. Greg and K. Sing, in: *Adsorption, Surface Area, Porosity* [Russian translation], Mir, Moscow (1984).
10. O. N. Kabanova, T. S. Yakubov, and V. V. Serpinskiy, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1486 (1988).
11. M. M. Dubinin, K. M. Nikolaev, N. S. Polyakov, and N. I. Seregina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 1871 (1971).
12. M. M. Dubinin, K. M. Nikolaev, and N. S. Polyakov, in: *Kinetics and Dynamics of Physical Adsorption* [in Russian], Nauka, Moscow (1973).
13. M. M. Dubinin, K. M. Nikolaev, N. S. Polyakov, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1479 (1974).

SYNERGISM OF HYDROGENATING CAPACITY IN THE Ni-Pd/Al₂O₃ SYSTEM

A. A. Vedenyapin, N. G. Giorgadze, I. P. Murina, UDC 541.128:541.183:543.422.8:
 S. V. Yushin, G. O. Chivadze, B. K. Nefedov, 542.941.7
 and V. M. Akimov

In liquid-phase hydrogenation of ethyl acetoacetate on bimetallic Ni-Pd catalysts supported on Al₂O₃, the reaction rate increases sharply and passes through a maximum with an increase in the concentration of Pd. The change in the rate of hydrogenation with a change in the composition of the catalysts is not due to a change in the dispersion of the metallic phase in them or enrichment of their surface with one of the metals.

Synergistic effects are observed for processes on bimetallic catalysts [1]. The Ni-Pd system is one such system [2-4] for which this phenomenon has been manifested in hydrogenation reactions. The IR spectra of CO adsorbed on Ni-Pd/Al₂O₃ were studied in [5]. We investigated the behavior of these catalysts in hydrogenation of ethyl acetoacetate (EAA) in the present study [6].

EXPERIMENTAL

The catalysts (10 wt. % metal) were prepared by combined impregnation of γ -Al₂O₃ with aqueous solutions of NiNO₃·6H₂O and PdCl₂ with subsequent drying, annealing in an O₂ current at 450°C, and reduction of the catalysts in a H₂ current at the same temperature. The methods of hydrogenation of EAA and analysis of the catalyzate are described in [7]. Adsorption of O₂ on the catalysts was measured by the volumetric method at 25°C. The precision of the measurement was ±0.03 μ mole/g. Before the adsorption measurements, the samples were reduced directly in the setup and conditioned at 450°C and 10⁻³ Pa for 15 h, which degassed the sample [8]. The analysis of the composition of the surface of the catalysts was conducted with an Escalab-5 with a MgK α source of radiation. The x-ray phase analysis was conducted with a Dron-2 setup.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
 Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 1, pp. 11-13, January, 1990. Original article submitted December 22, 1988.

DISCUSSION OF RESULTS

The analysis of the products of hydrogenation of EAA showed that ethyl- β -hydroxybutyrate is the only product here. The activity of the catalysts referred to the total amount of g-atom of Ni and Pd in the metallic phase (V_{SP}). Note (Fig. 1) that V_{SP} passes through a maximum with an increase in [Pd]. The $Pd_{0.2}Ni_{0.8}$ catalyst was the most active. The reaction rate on it was 8.5 times higher than on Ni and 2.5 times higher than on Pd. The value of V_{SP} increases especially rapidly with an increase in the concentration of Pd in the region of low concentrations: addition of 0.5 at. % Pd to Ni causes an increase in V_{SP} by two times.

A similar phenomenon of synergism was observed in [2] in hydrogenation of ethylene on Ni-Pd films. Regardless of the temperature of film formation, there is distinct synergism in the series of mixed catalysts: the $Pd_{0.45}Ni_{0.55}$ catalyst is several times more active than Pd. The same effect is also found for disperse catalysts supported on SiO_2 [3, 4]. In discussing the causes of the synergistic effect, the following possibilities were examined: 1) The possibility of deviation of the system from the phase diagram, hypothesizing the formation of a continuous series of Ni-Pd solutions [9], and the appearance of structural defects as a result of this [2]; 2) the possibility of an increase in the dispersion of the metallic phase in going from the individual to the bimetallic catalyst [2]; 3) the possibility of enrichment of the surface of the bimetallic catalysts with palladium [2, 10-13]. Although it is understood that the last circumstance cannot be the cause of the increased activity of bimetallic catalysts in comparison to the Pd catalyst, it could be responsible for the rapid increase in the activity of Ni-Pd catalysts with an increase in [Pd] in the region of low concentrations, for example (Fig. 1); 4) the possibility of formation of clusters on the surface of Ni-Pd catalysts which are more active than the Ni and Pd active sites [4]. Real synergism is only possible in the last case, as the synergistic effect in the first three cases is essentially only apparent.

The Ni-Pd/ Al_2O_3 catalysts were studied by methods of XPA, XPES, and adsorption of O_2 was also measured. The x-ray phase analysis of Ni-Pd/ Al_2O_3 did not allow drawing any conclusions concerning the homogeneity of the metallic phase. The dispersion was estimated by the adsorption of O_2 (a_{O_2}). It was found that although the value of a_{O_2} is higher for Ni and $Pd_{0.03}Ni_{0.97}$ catalysts than for Pd, it is approximately the same for the most active $Pd_{0.20}Ni_{0.80}$ catalyst as for Pd (Table 1). It follows from the data reported that the high activity of the $Pd_{0.20}Ni_{0.80}$ catalyst in comparison to Pd cannot be due to an increase in the surface area of the active phase.

The XPES data reported in Table 1 show that the surface and bulk composition of the $Pd_{0.03}Ni_{0.97}$ catalyst almost coincide, which means the absence of enrichment of the surface of the metallic phase with Pd. At the same time, this enrichment is very marked for the $Pd_{0.20}Ni_{0.80}$ catalyst: the concentration of Pd on the surface is >1.5 times higher than in the bulk. Similar enrichment of the surface of the Ni-Pd system with Pd was observed in [2, 10, 12, 13] and is apparently due to differences in the heats of vaporization of Ni and Pd. The degree of enrichment is strongly dependent on the nature of the catalyst and the method of its preparation. Data are reported in [13] which indicate that for a concentration of Pd of 1 at. % it can be predominantly concentrated in the surface layer. At the same time,

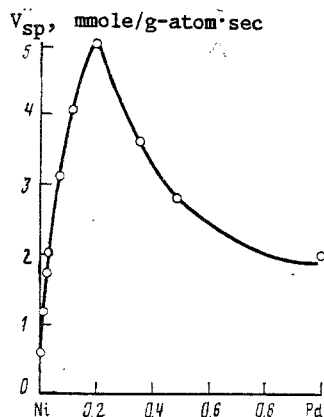


Fig. 1. Dependence of the activity of Ni-Pd/ Al_2O_3 catalysts on the concentration of Pd in it.

TABLE 1. Characteristics of Ni-Pd Catalysts

Composition of the catalyst	V_{sp} , $\frac{\text{mmole}}{\text{sec} \cdot \text{g-atom (Ni + Pd)}}$	α_{O_2} , $\frac{\mu\text{mole}}{\text{g}}$	Concentration of Pd on surface
Ni	0.6	154	0
$\text{Pd}_{0.03}\text{Ni}_{0.97}$	2.0	126	0.028
$\text{Pd}_{0.20}\text{Ni}_{0.80}$	5.1	85	0.33
Pd	2.0	81	1.00

it was shown in [12] that Pd is not redistributed between the bulk and the surface in the Ni-Pd/ Al_2O_3 catalyst up to 30 at. % Pd.

The comparison of the XPS data and the values of V_{sp} thus indicate that in the region of low concentrations of Pd (up to 3 at. %), the rapid increase in the activity of the bi-metallic catalysts with an increase in the concentration of Pd cannot be due to enrichment of the surface of the catalysts with Pd.

LITERATURE CITED

1. J. H. Sinfelt, Rev. Modern Phys., 51, 569 (1979).
2. R. L. Moss, D. Pope, and H. R. Gibbons, J. Catal., 46, 204 (1977).
3. R. L. Moss, D. Pope, and B. G. Davis, J. Catal., 62, 161 (1980).
4. D. Nizimeh and R. Frah, React. Kinet. Catal. Lett., 29, 121 (1985).
5. N. G. Giorgadze, M. D. Baturova, I. P. Murina, et al., Proceedings of the 1st Republic Conference on Asymmetric Reactions, Batumi (1986), p. 12.
6. A. A. Vedenyapin, T. I. Kuznetsova, and E. I. Klabunovskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 277 (1987).
7. A. A. Vedenyapin (Vedenjapin), B. G. Chankvetadze, and E. J. Klabunovski, React. Kinet. Catal. Lett., 24, 77 (1984).
8. P. C. Aben, J. Catal., 10, 224 (1968).
9. E. M. Savitskii, V. P. Polyakova, N. B. Gorina, and R. M. Roshan, Physical Metallurgy of Platinum Metals [in Russian], Metallurgiya, Moscow (1976).
10. V. Mintsa-Eya, L. Hilaire, R. Tonroude, et al., J. Catal., 76, 169 (1982).
11. R. L. Moss, D. Pope, and H. R. Gibbons, J. Catal., 55, 100 (1978).
12. T. Paryjczah, I. H. Farbotho, and I. J. Goralski, Catal., 88, 228 (1984).
13. L. Hilaire, Bull. Soc. Chim. Fr., 299 (1985).