Chemistry

A. B. Fasman, T. Kabiev,

1965

SovietRxiv

Abstract

Full Text

Chemistry

A. B. Fasman, T. Kabiev,
Academician of the Academy of Sciences of the Kazakh SSR D. V. Sokolsky, T. A. Yagudeev

Promotion of a Skeletal Nickel Catalyst by Oxygen-Containing Anions of Transition Metals

The activity of a skeletal nickel catalyst for the hydrogenation of unsaturated compounds in the liquid phase increases substantially as a result of treatment with solutions of salts of certain metals ($^{1-5}$). On the surface of the catalyst, in a hydrogen atmosphere, anions of elements of the platinum group are readily reduced and form intermetallic compounds of the Ni_3Pt type with nickel (^{5}). Recently it has also been found that the catalyst can be modified by adding salts of Cu^{2+}, Cd^{2+}, Fe^{2+}, CrO_4^{2-}, and WO_4^{2-} to the alkali solution used for decomposition of the Ni—Al alloy (^{6}).

In the present work we investigated the effect of additions of the anions VO_3^-, WO_4^{2-}, and MoO_4^{2-} on the activity of a skeletal nickel catalyst in the hydrogenation of unsaturated compounds with different types of bonds. Potassium salts of the indicated acids were introduced either into a 20% KOH solution intended for removal of aluminum from the initial Ni—Al (1 : 1) alloy, or into the reaction vessel before the start of saturation of the catalyst with hydrogen from the gas phase. In order to establish the mechanism of modification, the activity of catalysts prepared from Ni—Al—V, Ni—Al—W, and Ni—Al—Mo alloys with different contents of alloying additions was also studied.

The skeletal nickel catalyst was prepared by the method described in detail in the monograph (^{5}), and before the experiment it was saturated with hydrogen for one hour. Hydrogenation was carried out in a catalytic duck-shaped vessel with intensive stirring.

It is seen from Fig. 1 that leaching of the Ni—Al alloy in the presence of the VO_3^- anion leads to a 25% increase in the activity of the catalyst in the hydrogenation of potassium cinnamate. The magnitude of the shift of the catalyst potential $\Delta\varphi$ remains unchanged. Decomposition of the Ni—Al alloy in the presence of potassium metavanadate has no noticeable effect on the rate of reduction of potassium *o*-nitrophenolate under analogous conditions. Addition of KVO_3 to a 0.1 N KOH solution in which hydrogenation is carried out causes a sharp decrease in the rate of the process and a reduction in the values of $\Delta\varphi$. Alloying the Ni—Al alloy with metallic vanadium leads to a considerable increase in its activity, maximal at 10% V, relative to the sum Ni + V.

Fig. 1 and Fig. 2: graphs showing the effect of VO_3^- and WO_4^{2-} anions on hydrogenation rate and catalyst potential shift.

Figure 1: Fig. 1 and Fig. 2: graphs showing the effect of VO_3^- and WO_4^{2-} anions on hydrogenation rate and catalyst potential shift.

Leaching of the Ni—Al alloy in the presence of K_2WO_4 has an insignificant effect on the rate of hydrogenation of potassium cinnamate (Fig. 2) and is not at all reflected in the shape and position of the kinetic curves for reduction of *o*-nitrophenol. Introduction of potassium tungstate into the solvent proved effective, especially at 60°. In contrast to V, alloying of the Ni—Al alloy with metallic tungsten increases the activity of the catalyst by only 25-30%.

In contrast to salts of V and W, the anion MoO_4^{2-} suppresses the activity of the catalyst when introduced into the alkali used for decomposition of the starting alloy (Fig. 3). Addition to the solvent proves favorable at elevated temperatures. The absence of symmetry in the change in the activity of skeletal nickel upon alloying with metallic

molybdenum and treatment with solutions of K_2MoO_4 indicates substantially different forms of incorporation of molybdenum into the catalyst.

When the Ni—Al alloy is treated with solutions of caustic alkalis, intensive dissolution of aluminum occurs and the catalyst particles acquire

Fig. 1. Effect of the VO_3^- anion on the rate of hydrogenation of potassium crotonate in 0.1 N KOH and on the shift of the catalyst potential: 1, 2—during leaching of the Ni—Al alloy; 3, 4—during hydrogenation; 5—catalyst from the Ni—Al—V alloy; 1, 3, 5—20°; 2—40°; 4—60°.

Fig. 2. Effect of the WO_4^{2-} anion on the rate of hydrogenation of potassium crotonate in 0.1 N KOH and on the shift of the catalyst potential: 1, 2—during leaching of the Ni—Al alloy; 3, 4—during hydrogenation; 5—catalyst from the Ni—Al—W alloy; 1, 3, 5—20°; 2—40°; 3—60°.

a high negative potential. According to handbook data (7), the standard oxidation-reduction potential of the system

$$Al + 4OH^- = H_2AlO_3^- + H_2O + 3e^-$$

is −2.35 V. Since the standard potentials of the systems

$$6V + 33OH^- = 16H_2O + HV_6O_{17}^{3-} + 30e^-,$$

$$W + 8OH^- = WO_4^{2-} + 4H_2O + 6e^-,$$

Fig. 3

Figure 2: Fig. 3

$$\mathrm{Mo} + 8\mathrm{OH}^- = \mathrm{MoO}_4^{2-} + 4\mathrm{H}_2\mathrm{O} + 6\mathrm{e}^-$$

are, respectively, −1.15, −1.05, and −1.05 V, contact reduction of the anions should occur under these conditions.

During electrolysis of alkaline solutions of vanadates, in which, according to Dzhabarov and Gorbachev (8), only the VO_3^- form is present, an amphoteric jelly-like product is deposited at the cathode; the cation of this product contains V(IV), and the anion contains V(V) (9). Potassium was also found in the cathodic precipitate of vanadyl isopolyvanadates. The solubility of the precipitate increases with temperature and alkali concentration. On the other hand, at low V contents in the Ni—Al—V alloy it is practically completely leached out. Cathodic polarization of the alloy, occurring during dissolution of Al, not only does not hinder but even promotes oxidation of vanadium owing to loosening of the surface of the crystal lattice by atomic hydrogen (10). From the data presented it follows, as we believe, that the mechanism of promotion of a skeletal nickel catalyst by vanadium and its compounds

consists in the formation of phase surface oxides possessing, according to Balandin and Sokolova [11], a high value of $Q_{\mathrm{Me-H}}$.

Leaching of the Ni–Al alloy in the presence of the anion WO_4^{2-} should lead to cementation of metallic W [12-14], with simultaneous incorporation of its atoms into the newly formed Ni lattice. However, under the experimental conditions either no surface film of a nickel-based solid solution is formed at all, or, after complete removal of Al from the alloy, this phase dissolves again and has no effect on the activity of the catalyst.

Fig. 3. Influence of the MoO_4^{2-} anion on the rate of hydrogenation of cinnamic-acid potassium salt in 0.1 N KOH and on the shift of the catalyst potential: 1 –during leaching of the Ni–Al alloy; 2, 3 –during hydrogenation; 4 –catalyst prepared from a Ni–Al–Mo alloy; 1, 2, 4 –20°; 3 –60°.

Electrolysis of alkaline molybdate solutions is accompanied by formation at the cathode, according to some data [15], of the sesquioxide of molybdenum $Mo_2O_3 \cdot 3H_2O$, and according to other data [16], of the compound $Mo_2O_5 \cdot 2H_2O$, in which part of the molybdenum atoms are trivalent and part are hexavalent in the ratio

$$\mathrm{Mo}^{3+} : \mathrm{Mo}^{6+} = 1 : 2.$$

As follows from the results obtained, these oxides have a negative effect on the activity of the catalyst. Thus, the view expressed by us earlier [17] is once again confirmed: in the leached Ni—Al—Mo alloy, which possesses exceptionally high catalytic activity, the latter element is included in the composition of metallic phases.

The change in the hydrogenation rate upon addition of anions to the solution is associated with a change in the structure of the electrical double layer at the catalyst surface [5, 18, 19]. The anion VO_3^-, as follows from comparison of the kinetic and potential curves, is specifically adsorbed on nickel and screens the centers that activate the unsaturated compound. At high concentrations of KVO_3, poisoning also occurs of surface sites that activate molecular hydrogen.

Kazan State University
named after S. M. Kirov

Received
3 XII 1964

CITED LITERATURE

1. B. M. Bogoslovskii, Z. S. Kazakova, *Skeletal Catalysts, Their Properties and Use in Organic Chemistry*, Moscow, 1957.
2. Z. Csüros, J. Petró, *Acta chim. Acad. sci. hung.*, **20**, 129 (1959); **22**, 73 (1960).
3. Z. Csüros, J. Petró, S. Holly, *Acta chim. Acad. sci. hung.*, **29**, 449 (1961).
4. S. Nishimura, *Bull. Chem. Soc. Japan*, **32**, 63 (1959).
5. D. V. Sokol' skii, *Hydrogenation in Solutions*, Alma-Ata, 1962.
6. E. Takai, T. Yamanaka, *Scient. Papers Inst. Phys. and Chem. Res.*, **55**, 194 (1961).
7. V. Latimer, *Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, Moscow, 1954.
8. F. Z. Dzhabbarov, S. V. Gorbachev, *ZhFKh*, **9**, 2399 (1964).
9. A. S. Goncharenko, O. A. Suvorova, *ZhPKh*, **33**, 846 (1960); *Izv. AN KazSSR, Ser. Khim.*, issue 2, 46 (1962).
10. T. I. Kononchuk, I. B. Barmashev, et al., *Ukr. Khim. Zhurn.*, **26**, 25 (1960).
11. A. A. Balandin, N. P. Sokolova, *Izv. AN SSSR, Otd. Khim. Nauk*, No. 3, 398 (1960).

12. S. I. Sklyarenko, I. I. Lavrov, *Zhurn. Vsesoyuzn. Khim. Obshch. im. D. I. Mendeleeva*, **8**, 530 (1963).
13. K. Arte, I. Vatsek, *Tungsten and Molybdenum*, Moscow-Leningrad, 1964.
14. T. V. Frantsevich-Zabludovskaya, A. I. Zayats, *Proceedings of the IV Conference on Electrochemistry*, Publishing House of the Academy of Sciences of the USSR, 1959, p. 524.
15. A. G. Samartsev, E. I. Levitina, *ZhFKh*, **32**, 1023 (1958).
16. A. G. Goncharenko, *Tsvet. Met.*, No. 10, 60 (1963); *ZhPKh*, **37**, 915 (1964).
17. G. Kabil' ev, A. B. Fassman, et al., *DAN*, **159**, No. 5 (1964).
18. D. V. Sokol' skii, G. D. Zakumbaeva, *Tr. Inst. Khim. Nauk AN KazSSR*, **5**, 3 (1959).
19. G. D. Zakumbaeva, *Tr. Inst. Khim. Nauk AN KazSSR*, **8**, 73 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.