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# Chemistry

A. B. Fasman, T. Kabiev,

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**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 (<sup>1-5</sup>). 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<sub>3</sub>Pt type with nickel (<sup>5</sup>). Recently it has also been found that the catalyst can be modified by adding salts of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>2+</sup>, CrO<sub>4</sub><sup>2-</sup>, and WO<sub>4</sub><sup>2-</sup> to the alkali solution used for decomposition of the Ni—Al alloy (<sup>6</sup>).

In the present work we investigated the effect of additions of the anions VO<sub>3</sub><sup>-</sup>, WO<sub>4</sub><sup>2-</sup>, and MoO<sub>4</sub><sup>2-</sup> 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 (<sup>5</sup>), 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<sub>3</sub><sup>-</sup> 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<sub>3</sub> 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  $\text{VO}_3^-$  and  $\text{WO}_4^{2-}$  anions on hydrogenation rate and catalyst potential shift.

Figure 1: Fig. 1 and Fig. 2: graphs showing the effect of  $\text{VO}_3^-$  and  $\text{WO}_4^{2-}$  anions on hydrogenation rate and catalyst potential shift.

Leaching of the Ni—Al alloy in the presence of  $\text{K}_2\text{WO}_4$  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  $\text{MoO}_4^{2-}$  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  $\text{K}_2\text{MoO}_4$  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  $\text{VO}_3^-$  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  $\text{WO}_4^{2-}$  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



is  $-2.35$  V. Since the standard potentials of the systems

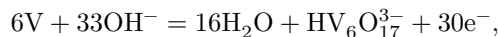


Fig. 3

Figure 2: Fig. 3



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

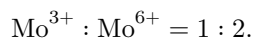
During electrolysis of alkaline solutions of vanadates, in which, according to Dzhubarov and Gorbachev (8), only the  $\text{VO}_3^-$  form is present, an amphoteric jelly-like product is deposited at the cathode; the cation of this product contains V(IV), and the anion contains V(V) (9). Potassium was 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  $Q_{\text{Me-H}}$ .

Leaching of the Ni—Al alloy in the presence of the anion  $\text{WO}_4^{2-}$  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  $\text{MoO}_4^{2-}$  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  $-20^\circ$ ; 3  $-60^\circ$ .

Electrolysis of alkaline molybdate solutions is accompanied by formation at the cathode, according to some data [15], of the sesquioxide of molybdenum  $\text{Mo}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , and according to other data [16], of the compound  $\text{Mo}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , in which part of the molybdenum atoms are trivalent and part are hexavalent in the ratio



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  $\text{VO}_3^-$ , 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  $\text{KVO}_3$ , poisoning also occurs of surface sites that activate molecular hydrogen.

Kazan State University  
named after S. M. Kirov

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