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Fig. 1

Figure 1: Fig. 1

Abstract**Full Text**

CHEMISTRY

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THE PROMOTION OF A SKELETON NICKEL CATALYST BY MOLYBDENUM

In recent years, the influence of additions of transition metals on the activity of a skeleton nickel catalyst has been investigated ever more widely (¹⁻⁷). It has been shown, in particular, that it increases appreciably when Mo is introduced into a Ni–Al alloy. Thus, Paul (¹) found that the rate of hydrogenation of safrole, furfural, and benzonitrile increases when 3–10% Mo is added to the initial alloy. Hadley (²) patented a highly active catalyst for the hydrogenation of glucose containing 0.5–5% Mo. Chores and Petro (⁴) showed that, depending on the degree of preliminary degassing, the activity of a catalyst prepared from an alloy with 2.3% Mo may double in comparison with skeleton Ni. On the other hand, in the hydrogenation of benzene in the gas phase (⁷), no promoting action of Mo was found. The works listed are not systematic, and they do not consider the mechanism of promotion.

Fig. 1. Kinetic and potential curves for the hydrogenation of *o*-nitrophenol (*a*), potassium maleate (*b*), and allyl alcohol (*c*). Temperature 20°. *a*, *b* –0.1 N KOH, catalyst 0.4 g; *c* –methanol, catalyst 0.2 g. 1 –skeleton Ni, 2 –Ni–Mo catalyst (10% Mo in the initial alloy).

In the present work, the influence of Mo additions to a Ni–Al alloy on the catalytic activity of skeleton nickel in the hydrogenation of *o*-nitrophenol, potassium maleate, and allyl alcohol was investigated. The total content of Ni and Mo in the alloys was 50 wt.%.

The experiments were carried out by the method described in (⁸), which made it possible to measure simultaneously the reaction rate and the catalyst potential. The catalysts were leached for 2 hr at a temperature of 95° with a 20% KOH solution. *o*-Nitrophenol and potassium maleate were hydrogenated in 0.1 N KOH solution, and allyl alcohol in methanol. Promotion of the skeleton nickel catalyst, as follows from the experimental data shown in Fig. 1, does not affect the shape of the kinetic curve, but

noticeably reduces the magnitude of the mixed potential (ΔE). In the hydrogenation of *o**-nitrophenol, potassium maleate, and allyl alcohol, the differences between ΔE for the promoted and nickel catalysts are, respectively, 30, 25, and 125 mV.

Alloying the Ni–Al alloy with Mo has a strong promoting effect on the activity of skeleton nickel, passing through a maximum when the Mo : Ni ratio is varied. A catalyst with the optimum promoter content (10% Mo in the initial alloy) is 3–3.5 times more active than skeleton Ni in the hydrogenation of *o*-nitrophenol and potassium maleate, and 1.5–2 times more active in the hydrogenation of allyl alcohol (Figs. 2 and 3). When the temperature is varied, the position of the activity maximum does not change. The favorable effect of Mo on the activity of a skeleton nickel catalyst was also observed by N. S. Samsonova and A. M. Pak in the hydrogenation of cottonseed oil and cinnamic acid.

In work ⁽⁹⁾ it was shown that *o*-nitrophenol and potassium maleate extract a considerable amount of hydrogen from skeleton Ni. Apparently, the main part of this hydrogen does not participate in the process of potential formation and is extracted from the deep layers of the catalyst ⁽¹⁰⁾. Similar phenomena have been noted by many investigators ^(4,8–10) and are observed in cases where the rate of reproduction of active hydrogen lags considerably behind the rate of removal of hydrogen from the catalyst surface by the substance being hydrogenated ⁽⁸⁾. Intensification of the process of reproducing active hydrogen should lead to a decrease in the degree of dehydrogenation of the catalyst. As can be seen from the data in Table 1, in the reduction of *o*-nitrophenol in the temperature range 20–40°, the amount of hydrogen extracted from the catalyst is a function of the promoter content and becomes minimal at 10% Mo in the initial alloy. With increasing temperature, the amount of hydrogen extracted increases markedly and ceases to depend on the Mo content.

Table 1

Volume of extracted hydrogen (ml)

Mo content in the alloy, wt. %	<i>o</i> -Nitrophenol at 20°	<i>o</i> -Nitrophenol at 40°	<i>o</i> -Nitrophenol at 60°	Potassium maleate at 20°	Mo content in the alloy, wt. %	<i>o</i> -Nitrophenol at 20°	<i>o</i> -Nitrophenol at 40°	<i>o</i> -Nitrophenol at 60°	Potassium maleate at 20°
0	49	70	73	14	15	23	42	58	5
3	35	45	63	8	18	23	48	55	4
5	25	39	58	4	21	25	52	45	4
8	21	32	50	—	25	—	50	52	3
10	18	25	55	5					

Figure 2

Figure 2: Figure 2

The promoting properties of Mo are also reflected in the dependence of the reaction-rate constant on temperature. In the hydrogenation of *o*-nitrophenol, introduction of Mo into the catalyst composition considerably lowers the temperature coefficient of the reaction (Fig. 4). The values of the activation energy in experiments with skeleton Ni and leached alloys containing 5; 10; 18 and 21% Mo are, respectively, 2.5; 1.5; 0.9; 1.5 and 2.2 kcal/mole. These experimental data indicate that the maximum activity of the promoted catalyst corresponds to the minimum value of the apparent activation energy.

The quantity ΔE is the algebraic sum of two terms⁽¹¹⁾—the mixed potential ΔE_1 , caused by removal of adsorbed hydrogen through the hydrogenation reaction, and ΔE_2 , reflecting the adsorption of unsatur—

* The kinetics and mechanism of hydrogenation of these compounds on skeleton Ni are discussed in detail in the monograph⁽⁸⁾.

of the compound being hydrogenated and of the reaction products. Under the condition $|\Delta E_2| \ll |\Delta E_1|$, the activation energy can be calculated from the magnitude of the potential shift⁽⁸⁾:

$$A = 23\Delta E + B, \quad (1)$$

where B is a constant.

Calculations based on equation (1) show that, in the hydrogenation of potassium maleate and allyl alcohol, introduction of Mo into the Ni–Al alloy also leads to a decrease in the activation energy. Thus, in the promotion of a skeletal nickel catalyst by molybdenum, the general regularity is a decrease in the activation energy of the catalytic hydrogenation reaction.

To study the effect of Mo on the stability of the catalyst, several successive portions of the unsaturated compound were hydrogenated on one and the same sample. After each experiment the catalyst was washed free of reaction products. It turned out that, in the reduction of *o*-nitrophenol, alloying the Ni–Al alloy leads to deterioration of stability (Table 2). This is probably due to the fact that, at deep shifts of the catalyst potential to the anodic side, the Mo present in the catalyst undergoes more intense corrosion in alkaline medium than Ni⁽¹²⁾. By contrast, in the hydrogenation of potassium maleate, promotion of Ni by molybdenum increases

Fig. 2. Dependence of the activity of the catalyst in the hydrogenation of *o*-nitrophenol on the Mo content in the starting alloy.

1 –20°, 2 –40°, 3 –60°.

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

Fig. 3. Dependence of the activity and magnitude of the catalyst potential shift in the hydrogenation of potassium maleate and allyl alcohol on the Mo content in the starting alloy. Temperature 20°. 1 –potassium maleate, 2 –allyl alcohol.

Fig. 4. Dependence of the rate constant of the hydrogenation reaction of *o*-nitrophenol on temperature. 1 –Ni, 2 –catalyst from an alloy with 3% Mo, 3 –5% Mo, 4 –8% Mo, 5 –10% Mo, 6 –15% Mo, 7 –18% Mo, 8 –21% Mo.

the stability of the catalyst. In the hydrogenation of five successive portions of the unsaturated compound, the activity of skeletal Ni decreased by a factor of 5, whereas that of the Ni–Mo catalyst after experiment No. 3 decreased threefold and subsequently remained practically constant.

Chemical analysis of the catalyst showed that the greater part of the Mo introduced into the initial alloy passes into solution during leaching. In catalysts obtained from alloys containing up to 8% Mo, no more than 10–15% of the initial amount remains, and at a content of 10–30% of the alloying component, up to 30% remains. In the leached catalysts the Mo : Ni ratio is, respectively, 0.6; 1.5; 6.5; 10.7; 17.5 and 41.5% for alloys with 3; 5; 10; 15; 21 and 25% Mo. It is not excluded that part of the Mo remaining in the catalyst is present in the form of oxides. A special communication will be devoted to consideration of the phase composition of the leached catalyst.

It is known that the heat of adsorption of atomic hydrogen on Mo is greater than on Ni (13), and alloying nickel alloys with Mo increases their activity in the ortho-para conversion of hydrogen by 1.5 orders of magnitude (14). A decrease in the amount of hydrogen extracted from the catalyst and a shift in the catalyst potential during hydrogenation indicate an increase in the bonding energy of hydrogen with the catalyst surface, as was observed, for example, during electrodeposition of Ni–Re alloys (15). The decrease in the magnitude of the activation energy and its passing through a minimum with increasing amount of promoter also indicates, as follows from multiplet theory, an increase in the value of the adsorption potential. It is known that Ni forms solid solutions with many metals (16), including Mo; in this case a change in its metalphysical properties is observed (17). In work (18) it was shown that these alloying components exert the same influence also in the presence of Al.

Table 2

Change in the hydrogenation rate (ml/min) in successive experiments

Mo content in the alloy, wt. %	Experiment No. 1	Experiment No. 2	Experiment No. 3
0	3.2	2	1
5	8	3.2	1.5
10	11	4.2	1.5

Thus, on the basis of the literature and experimental data, it may be assumed that the increase in the activity of a skeleton nickel catalyst upon alloying with molybdenum is associated with the formation of metallic compounds based on Ni, with a consequent increase in the energy of the bond between hydrogen and the catalyst and in the intensity of the process of reproduction of active hydrogen. Comparison of the results obtained with those described in the literature shows that the skeleton Ni–Mo catalyst has considerably greater activity and stability than Raney nickel in the hydrogenation of all the investigated unsaturated compounds with different types of bonds.

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