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Abstract

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INVESTIGATION OF THE CATALYTIC DECOMPOSITION OF HYDRAZINE ON NICKEL SULFIDE AND ON ITS SOLID SOLUTIONS

In recent years a number of experimental works have appeared that study the relation between the electronic characteristics of metal oxides and their catalytic (^{1,2}) and adsorption (^{3}) properties. Experimental works studying this relation for metal sulfides are as yet lacking.

A number of sulfides, for example the sulfides of Mn, V, W, Fe, Co, and Ni, are used in industry as catalysts for hydrogenation and dehydrogenation. Their principal advantage is their reduced poisoning by sulfur compounds, which has led to their use in the production of artificial liquid fuel from sulfur-containing raw material.

As a poisoning system, nickel sulfide was chosen, which, owing to the similarity of O and S in chemical respect, is analogous to the well-studied NiO, but differs sharply from it in electronic properties. According to Hauffe (^{4}), in the temperature range from 200 to 700° NiS possesses metallic conductivity. The relation of the electronic properties of NiS to catalytic properties has not previously been studied by anyone. By analogy with NiO it seemed of interest to determine how, in this case, additives of metal sulfides with valence different from 2 would affect the process. For this purpose Li_2S and In_2S_3 were introduced into NiS. Oxidation of CO with oxygen is unsuitable as a poisoning reaction for NiS, since, according to our preliminary data, the reaction does not proceed up to 350°, and according to literature data the formation of nickel sulfate begins already at 140°. For the same reason the decomposition of N_2O is unsuitable. We chose the decomposition of N_2H_4, which proceeds readily (^{5}), according to the equation

$$3N_2H_4 \to N_2 + 4NH_3 \quad (1)$$

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Fig. 2 and Fig. 3 graphs

Figure 1: Fig. 2 and Fig. 3 graphs

on metals and semiconductors. Experiments carried out by us showed (see Fig. 1) that this reaction proceeds at an appreciable rate on nickel oxide at room temperature, with Li_2O accelerating the reaction and In_2O_3 strongly retarding it. The character of the action of the additives differs from that observed for the same catalysts in the oxidation of CO at low temperatures.

Fig. 1. Kinetic isotherms of the decomposition of N_2H_4 at 22° C. $P_{\mathrm{N2H_4}} = 13.0$ mm: 1 –on NiO, 2 –on NiO (1 at.% Li), 3 –on NiO (1 at.% In)

For the experiments, chemically pure twice-distilled hydrazine was used. In a vacuum apparatus, N_2H_4 was purified from traces of dissolved air by repeated freezing with simultaneous pumping out of the gas evolved. After purification in vacuum, the vapor pressure of hydrazine corresponded to tabular data. The possible water content did not exceed 0.8%. Nickel sulfide was prepared by passing H_2S over nickel carbonate at 450°C for 10 hours. The solid solutions were obtained under the same conditions by sulfidizing mixtures of nickel carbonate with lithium carbonate or with indium nitrate, prepared in a definite proportion.

X-ray analysis, carried out by M. Ya. Kushnerev, showed that the obtained β-nickel sulfide has the usual hexagonal crystalline structure. When indium sulfide is dissolved, the lattice parameters of NiS increase somewhat; upon introduction of lithium, no regular changes in the parameters were observed.

The specific surface areas were determined by the BET method from equilibrium isotherms of the physical adsorption of krypton at the temperature of liquid nitrogen (−195°C). Dissolution of lithium sulfide decreased the specific surface area from 4.9 m^2/g for NiS to 3.5 m^2/g for NiS (1 at.% Li). The effect of dissolution

Fig. 2. Kinetic isotherms of the decomposition of N_2H_4 on NiS: 1 –at 60°C, 2 –at 75°C, 3 –at 100°C

Fig. 3. Dependence of the degree of conversion of N_2H_4 on the initial pressure on NiS at 75°C: 1, 2 –at $t = 5$ min.; 3 –at $t = 30$ min.; 4 –at $t = 50$ min.; 5 –at $t = 70$ min.

of indium sulfide in amounts corresponding to contents of 0.2 and 1 at.% In caused fluctuations in the specific surface area within $±$16%.

The resistance of a pellet pressed from nickel sulfide powder at a pressure of 4000 atm, measured by means of a bridge circuit at direct current, was only 1.2 ohm · cm. In the range of absolute temperatures from 78 to 573°K the resistance increases slightly with increasing temperature. Thus, in the temperature interval studied, nickel sulfide has metallic conductivity. Dissolution of lithium and indium sulfides in amounts corresponding to the content of one atomic per-

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Fig. 4

Figure 2: Fig. 4

cent of foreign atom in the nickel sulfide lattice has practically no effect on its resistivity. Measurement of the thermoelectromotive force showed that nickel sulfide is an electronic semiconductor.

Hydrazine decomposition was studied in a vacuum apparatus under static conditions. The catalyst was preliminarily conditioned for 1.5 hours at 400°C. Oxidation on Pd and passage through a palladium capillary showed that the products of hydrazine decomposition do not contain hydrogen and that on nickel sulfide the decomposition proceeds according to equation (1). The kinetics of hydrazine decomposition was investigated from the volume of nitrogen evolved during decomposition at an initial hydrazine pressure equal to 1 mm Hg.

As can be seen from Fig. 2, the kinetic isotherms of hydrazine decomposition on nickel sulfide at 60, 75, 100°C in the coordinates $\lg(-\Delta P_{\mathrm{N_2H_4}})$ and $\lg t$ are linear and obey the equation

$$-\Delta P_{\mathrm{N_2H_4}} = at^{1/n}, \tag{2}$$

where $n > 1$. Such kinetic isotherms are characteristic of processes proceeding with self-poisoning.

In Fig. 3 it can be seen that at $t = 5$ min the decomposition rate increases in proportion to the initial hydrazine pressure to the first power; at $t = 30; 50; 70$ min the rate increases in proportion to $P^{3/4}$. However, the kinetic isotherms of hydrazine decomposition obey neither first order nor simple fractional order. Investigation of the temperature dependence of hydrazine decomposition showed that in the temperature interval from 60 to 150°C the decomposition rate increases with increasing temperature, while above 150°C a decrease in the rate of hydrazine decomposition is observed. The observed kinetics of decomposition and the presence of a maximum in the rate as a function of temperature may be a consequence of poisoning by reaction products. Poisoning by nitrogen is unlikely; only ammonia remains.

Fig. 4. A –kinetic isotherms of decomposition of N_2H_4 at 75°C. 1 –on NiS; 2 –on NiS (0.2 at.% Li); 3 –on NiS (0.5 at.% Li); 4 –on NiS (1 at.% Li); 5 –on NiS (0.2 at.% In); 6 –on NiS (1 at.% In). B –dependence of the N_2H_4 decomposition rate on impurities at 75°C; $-\Delta P_{N_2H_4} = 0.03$ mm/m^2.

To test this hypothesis, an experiment was carried out in which a catalyst trained for 15 min at 100°C was brought into contact with ammonia at a pressure of about 1 mm Hg. The initial rate of hydrazine decomposition was thereby reduced by a factor of two. The kinetic curve of decomposition on NiS poisoned with ammonia corresponds to first order.

To determine the nature of the effect of adding Li_2S and In_2S_3 to NiS on hydrazine decomposition, solid solutions of nickel sulfide containing 0.2, 0.5, and 1 at.% Li, calculated relative to the sum of metal atoms, and solid solutions of nickel sulfide containing 0.2 and 1 at.% In were studied. The study showed that introducing lithium and indium into nickel sulfide samples does not change the direction or the kinetic equation of hydrazine decomposition.

Fig. 4A presents kinetic isotherms of decomposition at 75°C on nickel sulfide and its solid solutions. From Fig. 4A it is evident that dissolving lithium sulfide in an amount corresponding to 0.2 and 0.5 at.% lithium slightly increases the decomposition rate of N_2H_4; with a further increase in the content to 1 at.% Li, the decomposition rate becomes slightly lower than on the initial nickel sulfide. When indium sulfide is dissolved in an amount of 0.2 at.%, the initial decomposition rate does not change, but at high degrees of decomposition it proves to be lower than on the initial NiS sample. Increasing the indium content to 1 at.% has a similar effect, but somewhat stronger than 0.2 at.% In.

The dependence of the decomposition rate of N_2H_4 on the lithium and indium content is shown in Fig. 4B. At a lithium content of about 0.2 at.%, the decomposition rate is maximal. The dependence of the work function on additions of Li and In, measured by E. Kh. Enikeev on the same samples, also has a maximum at a content of 0.2 at.% Li. The form of the dependence of the work function on additions

is analogous to the dependence of the rate of hydrazine decomposition shown in Fig. 4B.

The dependence of the rate of decomposition of N_2H_4 on temperature is non-Arrhenius, which makes it difficult to determine the influence of Li and In on the activation energy of decomposition.

Discussion of Results

In the work described, a comparison was made of the influence of introducing analogous additives, including cations differing in charge magnitude from the cations of the parent compound, on the catalytic activity of nickel oxide and sulfide. In the first case Li_2O and In_2O_3 were introduced into the catalyst, and in the second Li_2S and In_2S_3. Both on NiO and on NiS (pure and with additives), decomposition proceeds in the direction characteristic of metals and semiconductors, with formation of N_2 and NH_3. On NiS the reaction is inhibited by the ammonia formed and has a rate optimum at $t \sim 150°C$. The effect of lithium and indium on the catalytic activity of nickel oxide is considerably stronger than on nickel sulfide, and in magnitude resembles the influence of the same oxides on the oxidation of CO, although the directions of the change in activity under the influence of Li^+ and In^{3+} for the decomposition of N_2H_4 and the oxidation of CO are opposite. The different sensitivity of NiO and NiS to analogous additives may be associated with the different character of their electrical conductivity—impurity semiconducting for NiO and quasimetallic for NiS.

It is possible that in other cases as well the sensitivity of degenerate semiconductors and semimetals to impurities that create electronic disorder will prove lower than that of impurity semiconductors. In this respect there is a definite correlation with the sharp influence of Me^+ and Me^{3+} on the electrical conductivity of the impurity semiconductor NiO and with the very low sensitivity of the electrical conductivity of NiS to the same additives.

In Fig. 4B, for the decomposition of N_2H_4 on NiS, a small maximum of activity is observed at a Li content of ~ 0.2 at. %. The difference of this preparation from the others is confirmed by its unusually large work-function value; however, since the properties of repeatedly prepared samples of the same composition were not studied, there is no certainty that the increased activity values and decreased work-function values were not due to some random properties of this preparation. Both pure nickel sulfide and nickel sulfide with additions of Li_2S and In_2S_3 in the range from 78°K to 700°K possess high electrical conductivity; the dependence of electrical conductivity on temperature has a metallic character. Investigation of the kinetics of decomposition of N_2H_4 showed that ammonia, formed during decomposition, exerts a strong inhibiting effect on the reaction.

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