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Abstract

Full Text

PHYSICAL CHEMISTRY

HUANG Yu-Mei, N. P. KEIER, and Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKII

CHEMICAL ADSORPTION ON PURE NiS AND NiS WITH ADDITIVES

In catalysis one has to deal with semiconductors (s.c.) having impurity, intrinsic, and degenerate conductivity (^{1}); meanwhile, the electronic theories of semiconductor catalysis and chemisorption usually consider only impurity semiconductors. The principal experimental works undertaken to test and substantiate the theory have also been carried out on them. This makes it interesting to include in the range of investigation semiconductors of other types. As one object, nickel sulfide was chosen; according to literature data (^{2}) and our measurements (^{3}), above 78°K it possesses degenerate conductivity that decreases with increasing temperature. NiS crystallizes in an atomic lattice and, chemically, is the closest analogue of the well-studied nickelous oxide, which is very sensitive to the action of additives. The present work sets forth the results of a study of the chemisorption of O_2 and C_2H_2 on NiS without additives and with additions of Li_2S and In_2S_3. On the semiconductors studied up to now, O_2 behaves as an acceptor, C_2H_2 as an electron donor. We found no data in the literature on the chemisorption of gases on NiS.

Fig. 1a –kinetics of oxygen adsorption on NiS: 1 –at 25°, 2 –at 45°, 3 –at 65°; **b** –isochrone of oxygen adsorption.

The method of preparing pure NiS and NiS with additives was described in a preceding article (^{3}). The presence of solid solutions was checked by X-ray diffraction. With increasing concentration of indium in the lattice, its parameters increase: a –from 3.4199 to 3.4219, c –from 5.3052 to 5.3064. The introduction of lithium into NiS had no effect on its parameters. It follows from this that In^{3+} forms solid solutions in NiS. Their formation for Li_2S has not been proved; however, the ease with which foreign cations enter the sulfide lattice makes this assumption probable. We note that for Li_2O in ZnO there is no change in the parameters either, although electrical-conductivity measurements

Figure 2

Figure 2: Figure 2

leave no doubt as to the existence of solid solutions. For $NiO—Li_2O$, at 1 at.% Li the change in the parameter lies at the limit of accuracy. When lithium sulfide and indium sulfide are dissolved in NiS, the specific resistance of nickel sulfide does not change appreciably, which is natural, taking into account the metallic character of the conductivity of this sulfide and the high concentration of current carriers in it. The values of the specific surface areas were determined by the BET method from krypton adsorption isotherms.

Adsorption was studied in a vacuum apparatus by the pressure-drop method. After it had decreased by 10% of the initial value, a new portion of gas was admitted,

the pressure was brought to the initial value, and this was repeated several times in the course of adsorption. The sulfide was protected from mercury vapor and grease by two U-shaped traps, one of which was sealed to the quartz reactor.

Oxygen adsorption. NiS and NiS–Li_2S were studied, with contents of 0.2, 0.5, and 1 at.% lithium cations, calculated relative to the sum of all cations, and solid solutions NiS–In_2S_3 containing 0.5 and 1 at.% indium cations. Oxygen adsorption was investigated in the temperature range 25-65°, in order to avoid oxidation of the sulfide, which is observed at higher temperatures. The catalyst was preliminarily degassed at 450° for 1.5 h at a pressure of 10^{-5} mm Hg.

Fig. 2. Oxygen adsorption at 65°:
1—on NiS, 2—on NiS (0.2 at.% Li), 3—on NiS (1 at.% Li), 4—on NiS (0.5 at.% In), 5—on NiS (1 at.% In)

Oxygen adsorption did not noticeably affect the electrical conductivity.

From Fig. 1a it can be seen that the kinetic isotherms of oxygen adsorption on NiS, except at the very beginning, obey equation (4)

$$q = At^{1/n}. \tag{1}$$

From Table 1 it is evident that the obtained values of $1/n$ and A increase with increasing temperature.

Figure 1b presents the kinetic isochore (4) of oxygen adsorption at constant time ($t = 30$ min) in the coordinates $\lg q_{t=\text{const}}$ and T. Since the points lie on a straight line, the isochore has the form

$$q = q_0 \cdot e^{\beta T}. \tag{2}$$

Equations (1) and (2) are characteristic of a heterogeneous surface with an exponential form of the distribution function (5) with respect to E and charge

$$\rho(E) = H \cdot e^{\alpha E}; \tag{3}$$

α and H, determined from the kinetic isotherms of adsorption (4), do not depend on T and are equal to: $\alpha \simeq 0.69{\cdot}10^{-3}$ (cal/mol)$^{-1}$, and $H \simeq 1.1{\cdot}10^{-7}$ (mol/cal)*.

Table 1

Dependence of A and $1/n$ for oxygen adsorption on NiS on temperature

Temp., °C	A, cm^3/m^2 • min^{-1}	$1/n$
65	$7.4 \cdot 10^{-3}$	0.47
45	$5.8 \cdot 10^{-3}$	0.44
25	$4.7 \cdot 10^{-3}$	0.40

In Fig. 2 the kinetic isotherms of oxygen adsorption on nickel sulfide and on its solid solutions are compared. It can be seen that both Li_2S and In_2S_3 introduced into NiS decrease the specific rate of oxygen adsorption, while the adsorption kinetics in all cases obey the same equation (1). In this case, the introduction of Li_2S and In_2S_3 into nickel sulfide, without changing the exponential type of the distribution function, changes the parameters α and H that characterize it. Within the limits of measurement error, the values of α and H do not depend on temperature. Table 2 presents the average values of these parameters for nickel sulfide and its solid solutions with lithium and indium sulfides.

From Table 2 it is evident that α increases slightly upon dissolution of indium sulfide in nickel sulfide and is almost unchanged upon dissolution of lithium sulfide. The value of H increases slightly upon dissolution of lithium sulfide and decreases substantially upon dissolution of indium sulfide. The preexponential the constant k_0 in the adsorption rate constant decreases upon dissolution of lithium sulfide and increases upon dissolution of indium sulfide. The change in H as a function of the distribution leads to the fact that the activation energies corresponding to a given surface coverage with adsorbed oxygen differ for these samples. They are slightly lower on the sample NiS (1 at.% Li) and somewhat higher on the sample NiS (1 at.% In) in comparison with NiS.

Table 2

Values of the parameters α and H, characterizing the distribution function over E and K_0 on sulfide and its solid solutions for oxygen adsorption

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* These figures are highly approximate, since the range of t over which linearity holds is insufficient for an accurate characterization of the distribution.

Figure 3 and Figure 4

Figure 3: Figure 3 and Figure 4

Sample	$\alpha \cdot 10^3$, cal/mol	$H \cdot 10^7$, mol/cal	$K_0 \cdot 10^{-3}$, $\min^{-1}$	Sample	$\alpha \cdot 10^3$, cal/mol	$H \cdot 10^7$, mol/cal	$K_0 \cdot 10^{-3}$, $\min^{-1}$
NiS	0.69	1.1	4.2	NiS (1 at.% Li)	0.71	1.8	0.2
NiS (0.2 at.% Li)	0.69	0.9	4.2	NiS (0.5 at.% In)	0.82	0.13	10.0
NiS (0.5 at.% Li)	0.71	1.3	1.0	NiS (1 at.% In)	0.81	0.07	29.0

Fig. 3. *a*—kinetics of acetylene adsorption on NiS: 1—at 100, 2—at 125°, 3—at 150°C; *b*—isostere of acetylene adsorption

Fig. 4. Adsorption of acetylene at 150°. 1—on NiS, 2—on NiS (0.2 at.% Li), 3—on NiS (1 at.% Li), 4—on NiS (0.2 at.% In), 5—on NiS (0.5 at.% In), 6—on NiS (1 at.% In)

The adsorption kinetics and the exponential isostere

$$q = q_0 \cdot e^{\beta T}$$

make it probable to assume that the cause of the change in the adsorption activation energy is associated with surface heterogeneity.

However, without experiments on the kinetics of isotopic exchange $(^{6-8})$ of adsorbed labeled molecules with molecules from the gas and without measuring the change in work function during adsorption, one cannot exclude changes in E due to interaction (repulsion) caused by charging.

The introduction of Li_2S into NiS leads to a decrease in the activation energy of oxygen adsorption at a given coverage. Dissolution of In_2S_3 in NiS increases the activation energy. Upon dissolution of Li_2S, the pre-exponential constant k_0 decreases, whereas upon dissolution of In_2S_3 the pre-exponential constant k_0 increases.

Adsorption of acetylene. The adsorption of acetylene at temperatures of 100, 125, and 150°C was measured on nickel sulfide and on NiS—Li_2S, with lithium contents of 0.2, 0.5, and 1 at.%, and on NiS—In_2S_3, with indium contents of 0.2, 0.5, and 1 at.%. The conditions for degassing the catalyst were the same as for oxygen adsorption. Acetylene adsorption likewise had no noticeable effect on the electrical conductivity of the samples. In Fig. 3a the kinetic isotherms of acetylene adsorption on NiS are presented in the coordinates $\lg q$ and

$\lg t$. It can be seen that they, just like the adsorption of oxygen, satisfy dependence (1).

Table 3 gives the values of $1/n$ and A, which increase as the temperature is raised.

In Fig. 3b an isostere for the adsorption of C_2H_2 on NiS is given in the coordinates $\lg q_{(t=\mathrm{const})}$ and temperature. In these coordinates the points of the isostere lie on a straight line. The isostere, as for oxygen adsorption, satisfies equation (2). This shows that the distribution function of active sites in this case also has the exponential form (3). The quantities α and H are practically independent of temperature.

Table 3

Temperature, °C	A, $cm^3/m^2 \cdot min^{-1}$	$1/n$
150	$1.1 \cdot 10^{-2}$	0.47
125	$7.2 \cdot 10^{-3}$	0.44
100	$4.5 \cdot 10^{-3}$	0.40

The dissolution of Li_2S and In_2S_3 in nickel sulfide does not change the character of the kinetic isotherms of acetylene adsorption.

Figure 4 presents the kinetic isotherms of acetylene adsorption on 1 m^2 of surface. The introduction of both Li_2S and In_2S_3 into NiS lowers the rate of acetylene adsorption. The introduction of Li_2S and In_2S_3 into NiS decreases the magnitude of A in equation (1). Upon dissolution of Li_2S in NiS, $1/n$ does not change; upon dissolution of In_2S_3 it increases, i.e., α increases. Table 4 gives the values of E, calculated for different coverages from the equation

$$E = RT\ln(t/t_0). \tag{4}$$

In all cases they increase.

Table 4

Values of the activation energies of adsorption of C_2H_2, kcal/mol (100—150° C)

Surface coverage, cm^3/m^2	NiS (1 at. % Li)	NiS (0.5 at. % Li)	NiS (0.2 at. % Li)	NiS	NiS (0.2 at. % In)	NiS (0.5 at. % In)	NiS (1 at. % In)
$6.3 \cdot 10^{-3}$	8.6	10.3	12.5	12.9	13.5	12.2	12.5
$7.9 \cdot 10^{-3}$	9.0	10.7	13.0	13.2	14.0	12.6	12.9
$1.0 \cdot 10^{-2}$	9.5	11.1	13.7	13.8	14.4	13.1	13.3
$1.3 \cdot 10^{-2}$	9.9	11.4	13.8	14.2	14.9	13.5	13.7
$1.6 \cdot 10^{-2}$	10.3	11.8	12.2	14.6	15.3	13.9	14.1
$2.0 \cdot 10^{-2}$	10.7	12.2	14.7	15.0	15.7	14.4	14.4
$2.5 \cdot 10^{-2}$	11.1	12.6	15.1	15.4	16.2	14.8	–

It follows from Table 4 that the introduction of Li_2S into NiS lowers the activation energy of adsorption at a given surface coverage, while the introduction of In_2S_3 has practically no effect on it.

The dependence of the activation energy on the degree of coverage obeys the equation

$$E_{\text{ads}} = 22.5 + 4.4 \lg q \text{ kcal/mol.}$$

The distribution function of active sites with respect to the activation energy of acetylene adsorption on NiS is equal to

$$\varphi(E_{\text{ads}}) = 0.25 \cdot 10^{-8} e^{0.55 \cdot 10^{-13} E_{\text{ads}}}.$$

Institute of Physical Chemistry
Academy of Sciences of the USSR

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