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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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N. P. KEIER and L. N. KUTSEVA

STUDY OF CHEMICAL ADSORPTION ON SOLID SOLUTIONS OF NICKEL OXIDE

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The electrical conductivity of nickel oxide can vary over wide limits when metal oxides whose valence differs from that of nickel are dissolved in its lattice ([1]). For the development of the theory of chemical adsorption on semiconductors, the study of it on systems differing in electronic properties is of special interest. We investigated the regularities of chemical adsorption of oxygen, adsorbed with capture of electrons, and also of the gases CO and C_2H_2, which are adsorbed with donation of electrons. The adsorption of these gases, as special measurements showed, was accompanied by a change in electrical conductivity in opposite directions. In the first case the electrical conductivity increased, while in the second it decreased.

Fig. 1. Dependence of the electrical conductivity of solid solutions of NiO with Li_2O and of the activation energy of electrical conductivity on the concentration of Li^+ cations in the NiO lattice

Nickel oxide was prepared by decomposition of nickel carbonate at 900° in air for 2.5 hr. Solid solutions were obtained under the same conditions by decomposition of mixtures of nickel carbonates and lithium carbonates prepared in a definite proportion.

With increasing concentration of the lithium cation in the lattice, its parameter decreases. Figure 1 shows the change in electrical conductivity and in the activation energy of electrical conductivity as a function of the concentration of the lithium cation in the nickel oxide lattice. The electrical conductivity was measured at room temperature in air.

Adsorption was studied in a vacuum apparatus by the pressure drop, which was recorded with a McLeod manometer. In order to eliminate the influence of pressure on the kinetics, it was lowered only within 10% of the initial value, then again brought to the original value by admitting gas from a large bulb with constant pressure. The catalyst was protected from lubricant vapors and mercury by two U-shaped traps, one of which was located on the quartz reactor (^{2}).

Oxygen adsorption

NiO and solid solutions NiO—Li_2O, containing 0.8 and 8.0% lithium cations calculated with respect to the sum of all cations, and NiO—Fe_2O_3 (1 at.% Fe) were investigated. Adsorption was studied in the temperature range 200—360°. Below 200° the rate of adsorption is low. Figure 2 shows kinetic isotherms of oxygen adsorption on 1 m^2 of surface. It can be

it can be seen that the adsorption rate increases when lithium oxide is dissolved in nickel oxide. The activation energies, calculated by Arrhenius' method from the ratio of adsorption rates at equal coverages, are given in Table 1. Increasing the content of lithium cations from 0.8 to 8.0% does not affect the adsorption.

The calculated values indicate a decrease in the activation energy of oxygen adsorption upon dissolution of lithium oxide and an increase in the activation energy of adsorption with increasing degree of surface coverage.

Fig. 2. Kinetic isotherms of oxygen adsorption, $P_0 = 0.44$ mm Hg.
1–$T = 360°$, NiO + 8 at. % Li^+; 2–$T = 360°$, NiO; 3–$T = 310°$, NiO + 8 at. % Li; 4–$T = 310°$, NiO; 5–$T = 210°$, NiO + 8 at. % Li; 6–$T = 210°$, NiO

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

On nickel oxide the kinetic isotherm satisfies this relationship, where $1/n$ varies proportionally with temperature. On the solid solution of lithium oxide in nickel oxide, the kinetic law of oxygen adsorption changes. In this case the following law holds:

$$q = A' \ln t. \tag{2}$$

This is a rare case in which this equation is obeyed in a study of adsorption over a wide time range at constant pressure. Dissolution of Fe_2O_3 lowers the rate of oxygen adsorption and increases the activation energy of adsorption.

Table 1

Values of the activation energies of oxygen adsorption, calculated from the Arrhenius equation (kcal/mole)

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

Coverage, cm^3/m^2	NiO	NiO (Li_2O)
0.005	30.0	–
0.010	40.0	–
0.020	–	18.0
0.030	–	24.0

Adsorption of carbon monoxide

Adsorption of CO proceeds at an appreciable rate even at room temperature. The adsorption rate decreases rapidly with increasing coverage; the maximum surface coverages are small: at room temperature, in 3 hours an amount of CO is adsorbed equal to 5.0% of the monolayer, calculated on the assumption that one Ni^{2+} cation can adsorb one CO molecule. In excess of the adsorbed gas, 10% of the absorbed CO is oxidized to CO_2 by oxygen from NiO. At 102°, in 3 hours an amount of CO is adsorbed equal to 5.0% surface coverage, and the amount of oxidized CO is 25% of that absorbed.

Dissolution of Li_2O in nickel oxide lowers the rate of CO adsorption and the degree of surface coverage (Fig. 3). Upon dissolution of 0.4 at. % Li, adsorption during the first minute amounts to 0.7% of the monolayer and then does not change up to 280°. Upon dissolution of Fe_2O_3 in NiO in an amount corresponding to a content of 1 at. % Fe, the rate of CO adsorption decreases (Fig. 3,4). When 1.2 at. % Fe from $Fe(NO_3)_3$ is introduced into a NiO sample containing 0.8 at. % Li, a partial restoration of its adsorption capacity with respect to CO is observed (Fig. 3,5).

Adsorption of acetylene

In contrast to CO, upon adsorption of C_2H_2 high surface coverages are reached in 3 hours: at 20°, 22%; at 79°, 53%; and at 116°, 68%.

Despite substantially higher degrees of surface coverage than in the case of CO, the same small amounts of dissolved lithium oxide have an inhibiting effect on the adsorption of acetylene (Fig. 4). Dissolution of 0.4 at.% lithium almost completely suppresses the adsorption of acetylene, up to 300°. Above 300°, measurements of adsorption are not meaningful, since in this temperature region side processes of oxidation and decomposition of C_2H_2 are observed.

Fig. 3. Kinetic isotherms of adsorption of carbon monoxide.
1 $-T = 20^\circ$, $P_0' = 0.096$ mm Hg, NiO;
2 $-T = 20^\circ$, $P_0 = 0.094$ mm Hg, NiO + 0.1 at.% Li;
3 $-T = 20^\circ$, $P_0 = 0.088$ mm Hg, NiO + 0.2 at.% Li;

4 –$T = 20°$, $P_0 = 0.092$ mm Hg, NiO + 0.82 at.% Li + 1.23 at.% Fe;
5 –$T = 20°$, $P_0 = 0.09$ mm Hg, NiO + 1 at.% Fe.

Fig. 4. Kinetic curves of adsorption of acetylene.
1 –$T = 80°$, NiO;
2 –$T = 80°$, NiO + 0.1 at.% Li;
3 –$T = 125°$, NiO + 0.2 at.% Li.

With the introduction of 0.2 at.% Li, the adsorption rate decreases so much that at room temperature it is practically absent, and at 125° in 3 hours it reaches only 13.5% of a monolayer.

The introduction of 0.1% Li slightly lowers the adsorption rate at low coverages. The coverage values in this case change only very slightly. The values of the activation energy of adsorption, calculated according to Arrhenius for identical degrees of surface coverage from the temperature dependence of the adsorption rate, indicate its increase upon dissolution of lithium oxide.

Adsorption of CO_2

The adsorption of carbon dioxide on nickel monoxide is small; at 26° on NiO it amounts to 2.4% of surface coverage, while on a solid solution of NiO with lithium oxide containing 8 at.% Li it is 3.5%. The kinetic isotherm of adsorption on the original nickel monoxide satisfies equation (1).

Discussion of the Results

The investigation showed that dissolution of lithium oxide in NiO lowers the adsorption rate of CO and acetylene and increases the adsorption rate of oxygen and CO_2. The first group includes gases that are electron donors, the adsorption of which is accompanied by transfer of an electron from the adsorbing molecule to the catalyst; the second group includes electron acceptors, which draw electrons from the catalyst according to the reactions:

$$\mathrm{CO} + \mathrm{Ni}^{3+} \to (\mathrm{CO})^{+}\mathrm{Ni}^{2+}, \tag{1}$$

$$\frac{1}{2}\mathrm{O}_2 + 2\mathrm{Ni}^{2+} \begin{cases} \mathrm{O}^{2-}(\mathrm{Ni}^{3+}) + \mathrm{Ni}^{3+} \\ \mathrm{O}^{-}(\mathrm{Ni}^{3+}) + \mathrm{Ni}^{2+}. \end{cases} \tag{2}$$

Nickel monoxide is a hole semiconductor, in which current transport is effected by electron exchange between Ni^{3+} and Ni^{2+}, loca-

located at lattice sites. Each surface cation Ni^{2+}, as a result of exchange with Ni^{3+} from the bulk, is converted for a certain time–which is the longer, the closer this site is to a Li^{+} cation–into a Ni^{3+} cation. The concentration of Ni^{3+} and the electrical conductivity can be increased by dissolving oxides of monovalent metals in the NiO lattice—in our case LiO_2, or excess oxygen (^{3}); in both cases black nickel oxide is obtained. It was found that increasing the concentration of Ni^{3+} in NiO by dissolving excess oxygen only slightly reduces the adsorption of CO and C_2H_2 per unit surface area, although in electrical conductivity the specimen corresponded to nickel oxide containing 0.9 at.% Li. This fact leads to the supposition that the retardation of the adsorption of CO and C_2H_2 upon dissolution of Li_2O in NiO is connected with the presence of Li^+ cations on the surface. This supposition removes the contradiction between the increase in the concentration of Ni^{3+} cations, which are adsorption centers for CO and C_2H_2, and the decrease in the rate of adsorption of these gases upon dissolution of Li_2O in NiO. The influence of Li^+ cations on the surrounding Ni^{2+} cations is connected with the fact that, at the lattice sites in which they are located, the charge of neighboring oxygen ions is not compensated. Cations with an anomalous charge create a strong electrostatic field that changes the work function of the electron at the surrounding cation sites. The transition of Ni^{2+} to Ni^{3+} at sites neighboring Li^+ should be facilitated, which leads to a decrease in the activation energy of oxygen adsorption on Ni^{2+} cations near Li^+. Conversely, Li^+ cations will influence the reactivity of Ni^{3+} cations located at neighboring lattice sites. As a result of interaction between them, their ability to undergo reaction (1) decreases. It follows from the experimental data that the Li^+ cation affects several nearest cation sites. The farther the lattice site is removed from the Li^+ cation, the more readily adsorption of CO and C_2H_2 proceeds on Ni^{3+} cations.

The nonuniformity of the active surface of nickel oxide, established by isotope methods (^{4}), is thereby explained.

The decrease in the rate of CO adsorption upon dissolution of Fe_2O_3 is associated with a decrease in the concentration of Ni^{3+} cations. When Fe_2O_3 is dissolved in NiO with Li_2O, the Fe^{3+} cations are located at the sites nearest to Li^+, shielding their influence. At a ratio of Li^+ to Fe^{3+} cations of $1 : 1$, the adsorption capacity is not restored. An excess of Fe^{3+} cations of about $1 : 1.2$ is required for the adsorption capacity of NiO containing 0.8 at.% Li to be partially restored.

There is complete similarity in the influence of dissolved lithium and iron oxides in NiO on the chemical adsorption of carbon monoxide and its catalytic oxidation, studied previously (^{5}). We have attempted to explain the complex dependences obtained in the study of the catalytic and chemisorption properties of solid solutions of NiO that differ in electronic structure. It is quite likely that other explanations of these data are also possible. Further investigation will promote an unambiguous interpretation of the results of studies of solid oxide solutions differing in electronic structure, which is necessary for constructing a theory of the active surface and of catalysis on semiconductors.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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