INVESTIGATION OF THE CHEMICAL ADSORPTION OF GASES ON NICKELOUS OXIDE AND OF ITS SOLID SOLUTIONS WITH LITHIUM OXIDE

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For the development of the theory of chemical adsorption and to elucidate the nature of the active surface, it was of interest to investigate chemical adsorption on solid solutions of oxides differing in their electronic properties. The electrical conductivity of nickeloous oxide can be altered over a wide range by dissolving in its lattice oxides of metals having a different valence from nickel [1]. There is no data in the literature on chemical adsorption by such semiconducting systems.

EXPERIMENTAL

We have investigated the laws for the chemical adsorption of different gases (O₂, CO, CO₂ and C₂H₅) on nickeloous oxide and its solid solutions with lithium oxide, and also on ternary systems of nickeloous oxide, lithium oxide and ferric oxide. Nickeloous oxide was prepared by decomposing nickeloous oxide, lithium oxide and ferric oxide. Nickeloous oxide was prepared by decomposing nickel carbonate by heating in air at 900° for 2.5 hours. Solid solutions were obtained, under the same conditions, by decomposing a mixture of the carbonates of nickel and lithium. In the case of ternary systems (NiO, Li₂O, Fe₂O₃), the catalyst was additionally impregnated with ferric nitrate, after which it was dried and calcined as usual. The existence of solid solutions was checked by x-ray diffraction. The lattice parameter decreased with increasing concentration of the lithium cation.

Values of the specific surfaces were determined by the BET method, from the equilibrium isotherms for the physical adsorption of krypton at the temperature of liquid nitrogen (-195°). Solution of lithium oxide decreased the value of the specific surface from 1 m²/g (for NiO) to 0.3 m²/g (for NiO with 8 at.% of Li). Adsorption was investigated in a vacuum apparatus of the usual type by the decrease in pressure, which was registered by a McLeod gauge. To avoid the effect of pressure on the kinetics, it was only reduced by 10% of the original, and then brought back to the initial value by addition of gas from a large bulb at constant pressure. The catalyst was protected from oil and mercury vapors by two U-shaped traps, one of which was joined to the quartz reactor [2]. Adsorption of gases was carried out on granulated catalyst, which was degassed before the experiment, at 550° for 5 hours in the case of oxygen adsorption (10 g of catalyst), and at 500° for 1.5 hours in the case of CO and C₂H₅ (1 g of catalyst).

Adsorption of Oxygen. The adsorption of oxygen was investigated in the temperature range 200-360°, at a pressure of 0.09 mm, on NiO and solid solutions of Li₂O in NiO, containing 0.2, 0.4, 0.8 and 8.0 at.% of Li, expressed as a percentage of the total cations. Kinetic isotherms for oxygen adsorption are shown in Fig. 1. The initial rate of adsorption of oxygen increased when a small amount of lithium oxide was dissolved in the nickeloous oxide, reached a maximum with 0.8 at.% of Li, and then decreased for the sample containing 8 at.% of Li. The increase in rate of adsorption when lithium oxide was dissolved in the NiO led to a higher degree of coverage of the surface. The maximum coverage of the surface of NiO containing 0.8 at.% of Li was 27% of a monolayer, compared with 18% for NiO alone, reckoning that adsorption took place on Ni⁶⁺ cations and was accompanied by dissociation of O₂ into atoms.
Adsorption activation energies, calculated by the Arrhenius method from the ratios of the rates of adsorption for the same coverage, decreased with increasing amounts of dissolved lithium oxide; they increased slightly for the initial parts of the isotherms with increasing lithium content. For the two extreme samples, NiO and NiO with 8 at. % Li, oxygen adsorption was investigated over the temperature range 200-360°C at an oxygen pressure of 0.4 mm. On the original nickelous oxide the kinetic isotherms satisfied the relation

\[ q = A t^{1/n}, \]  

(1)

where \(1/n\) altered with temperature (Fig. 2,a). On solid solutions of lithium oxide in nickelous oxide, the kinetic law of oxygen adsorption changed (Fig. 2,b) to

\[ q = A' \log t. \]  

(2)

The rule of constancy of displacement with coordinates \(RT, \log t\) was not fulfilled. Activation energies for oxygen adsorption, found from the kinetic isotherms, were lower for samples containing 8 at. % Li. It should be noted that the activation energies found were only correct for a narrow temperature range (300-360°C).

We also investigated solid solutions of NiO with Fe₂O₃, prepared with a calculated 1 at. % of iron. The rate of adsorption was considerably less in this case, than on the original NiO, and the coverage achieved in the same time was two orders of magnitude less. The activation energy for oxygen adsorption increased rapidly with increasing coverage of the surface.

Adsorption of Carbon Monoxide. Adsorption of CO took place with considerable speed even at room temperature; the rate of adsorption decreased sharply as adsorption occurred, although the degree of coverage was small; after 3 hours at room temperature, the volume of CO adsorbed was 5% of the filled surface, calculated on the assumption that one Ni²⁺ cation was capable of holding one CO molecule. Up to 10% of the adsorbed CO was oxidized to CO₂ by oxygen from the nickelous oxide. No considerable increase in the adsorption rate was found at higher temperatures up to 100°C, and this was attributed to the increased desorption rate with rising temperature. The total quantity of gas adsorbed also altered little. The kinetic curve for CO adsorption gave a straight line when plotted with log-log coordinates \(\log q_{CO}\) and \(\log t\). Dissolution of Li₂O in the nickelous oxide reduced the rate of adsorption and the degree of coverage of the surface. With 0.8 at.% of dissolved Li, there was no significant adsorption, or oxidation of CO by oxygen in the contact material, up to 280°C.

When ferric oxide, as well as lithium oxide, was dissolved in the nickelous oxide, a partial restoration of the adsorptive capacity for carbon monoxide was observed. When 0.8 at.% of lithium and 1.2 at.% of Fe (from Fe(NO₃)₃) were dissolved in the NIO, the adsorption of CO was measurable, but was below that for pure nickelous oxide (Fig. 3, curve 4). With equal concentrations of lithium and iron, 0.8 at. %, there was no adsorption of CO.

Adsorption of Acetylene. Acetylene adsorption was investigated over the temperature range 20 to 150°C. Adsorption of acetylene, as opposed to that of carbon monoxide, gave a high surface coverage after 3 hours. It was 22% at 20°C, 53% at 79°C and 68% at 116°C.

In spite of the almost 20-fold greater coverage as compared with CO, the same quantity of dissolved lithium oxide had an inhibiting effect on the adsorption of acetylene (Fig. 4). The presence of 0.4 at% of dissolved Li completely suppressed the adsorption of acetylene up to 300°C. Measurements above this temperature had no significance because secondary processes occurred. With the introduction of 0.2 at.% Li, the rate of adsorption was reduced to the extent that there was practically no adsorption at room temperature, only 13.5% at 125°C and 14.5% at 150°C. The introduction of 0.1% Li slightly reduced the adsorption rate at low coverages. The extent of coverage altered very slightly. The adsorption activation energy, calculated by the Arrhenius method, for the same degree