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CHEMICAL ADSORPTION AND CATALYTIC OXIDATION OF CO ON ZnO AND ITS SOLID SOLUTIONS DIFFERING IN THEIR ELECTRICAL CONDUCTIVITY

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One of the principal tasks of the electronic approach in catalysis is to establish the connection between the electronic characteristics of semiconductors and their catalytic properties. The present work is a continuation of an investigation of oxide systems with controllable electronic properties ([1]-[4]). Zinc oxide and its solid solutions with lithium and gallium oxide were studied, differing in electrical conductivity by many orders of magnitude (see Table 2). In parallel with catalytic activity, the chemical adsorption of the reaction components was studied, which makes it possible to judge the changes occurring on the active surface when the electrical characteristics of the preparations are varied and makes the interpretation of the physical nature of the relation between electrical conductivity and catalytic activity more unambiguous.

Table 1

Specific surface areas of the tested samples

Sample	Specific surface area, m^2/g
ZnO (6 h and 30 h)	1.5
ZnO (0.5 at. % Li)	0.2
ZnO (0.7 at. % Li)	0.2
ZnO (0.9 at. % Li)	0.2
ZnO (1.2 at. % Li)	0.1
ZnO (1.0 at. % Ga)	1.7

Zinc oxide was prepared by decomposing zinc carbonate in air at 850° for 6 h. Solid solutions with lithium oxide were obtained under the same conditions by decomposing zinc carbonate impregnated with a solution containing the calculated amount of lithium carbonate. Solid solutions with gallium oxide were prepared from zinc carbonate impregnated with a solution of gallium nitrate. In this case calcination at 850° was continued for 30 h. The specific surface areas of the preparations, found by the BET method from krypton adsorption isotherms at a temperature of −195°, are presented in Table 1.

Dissolution of lithium oxide sharply decreases the magnitude of the specific surface area. Table 2 presents data on the electrical conductivity of samples annealed in vacuum at 350°, obtained at 25°, and the activation energies of electrical conductivity.

The catalytic reaction was studied in a vacuum apparatus under static conditions on a stoichiometric mixture at a pressure not exceeding 2 mm Hg. The CO_2 formed was frozen out in a liquid-nitrogen trap. Before the experiment the catalyst was degassed at 500°. Adsorption was studied under analogous conditions from the pressure drop, which did not exceed 10% of the initial value. The catalyst was protected from mercury vapors and grease by a system of traps immersed in liquid nitrogen, one of which was on the quartz reactor, preventing grease vapors from the ground joint, by means of which the reactor was connected to the apparatus, from entering.

Catalytic activity. The oxidation reaction of CO proceeds at a measurable rate only at temperatures above 250°. The kinetic-

tion rate for all samples corresponds to first order. Figure 1 gives the temperature dependence of the rate constant for CO oxidation on the samples studied. It is seen from the figure that dissolving lithium oxide

Table 2

Electrical conductivity and activation energy of electrical conductivity of ZnO and its solid solutions

Sample	σ $(\Omega \cdot \mathrm{cm})^{-1}$ (25°)	σ_0 $(\Omega \cdot \mathrm{cm})^{-1}$	E_0, kcal/mol
ZnO (1 at. % Ga)	$6.3 \cdot 10^{-4}$	$3.3 \cdot 10^{-3}$	2
ZnO	$1.6 \cdot 10^{-5}$	$6.8 \cdot 10^{-2}$	10
ZnO (0.5 at. % Li)	$2.5 \cdot 10^{-7}$	$3.0 \cdot 10^{-2}$	14
ZnO (0.9 at. % Li)	$4.5 \cdot 10^{-9}$	$3.4 \cdot 10^{-2}$	19
ZnO (1.2 at. % Li)	$4.5 \cdot 10^{-10}$	$1.9 \cdot 10^{-2}$	21

up to 0.5 at. % Li has a weak effect on the rate constant; with further increase in lithium oxide content it decreases sharply, and its measurement becomes possible only in the region of higher temperatures. As the lithium oxide content increases, the activation energy and the pre-exponential constant in the rate constant increase. In this case the dependence $E = E_0 + \gamma \lg k_0$ is observed (Fig. 2).

Fig. 1. Dependence of the catalytic activity of ZnO and its solid solutions with respect to the CO oxidation reaction. 1 –ZnO (pure), 2 –ZnO (0.5 at. % Li), 3 –ZnO (0.7 at. % Li), 4 –ZnO (0.9 at. % Li), 5 –ZnO (1.2 at. % Li), 6 –Zn (1 at. % Ga)

Figure 1: Fig. 1. Dependence of the catalytic activity of ZnO and its solid solutions with respect to the CO oxidation reaction. 1 –ZnO (pure), 2 –ZnO (0.5 at. % Li), 3 –ZnO (0.7 at. % Li), 4 –ZnO (0.9 at. % Li), 5 –ZnO (1.2 at. % Li), 6 –Zn (1 at. % Ga)

Table 3 presents the values of the activation energy of oxidation and the pre-exponential constants in the rate constant. Dissolving gallium oxide slightly lowers the activation energy of CO oxidation, but at the same time strongly lowers the pre-exponential constant in the rate constant. On the whole, the oxidation rate in the temperature range measured decreases.

Adsorption measurements. a) **Oxygen adsorption** lowers the electrical conductivity of all samples, which indicates a decrease in the concentration of free electrons accompanying adsorption. Adsorption was measured in the temperature range from 300 to 500°. Dissolving lithium oxide very strongly increases the rate of oxygen adsorption, this acceleration at a content of 0.5 at. % Li being considerably stronger than at 1.2 at. % Li. Figure 3 presents kinetic adsorption isotherms at 400° on ZnO, ZnO (0.5 at. % Li), and ZnO (1.2 at. % Li). In all cases

Fig. 1. Dependence of the catalytic activity of ZnO and its solid solutions with respect to the CO oxidation reaction. 1 –ZnO (pure), 2 –ZnO (0.5 at. % Li), 3 –ZnO (0.7 at. % Li), 4–ZnO (0.9 at. % Li), 5 –ZnO (1.2 at. % Li), 6 –Zn (1 at. % Ga)

Table 3

Rate constants, activation energies, and pre-exponential constants in the rate constant for CO oxidation

Sample	K ($t = 368°$), $(\text{min} \cdot \text{m}^2)^{-1}$	K_0, $(\text{min} \cdot \text{m}^2)^{-1}$	E, kcal/mol
ZnO	$1.5 \cdot 10^{-1}$	$2.4 \cdot 10^{4}$	16.6
ZnO (0.5 at. % Li)	$1.9 \cdot 10^{-1}$	$5.7 \cdot 10^{5}$	19.3
ZnO (0.7 at. % Li)	$0.8 \cdot 10^{-1}$	$2.9 \cdot 10^{6}$	23.0
ZnO (0.9 at. % Li)	$0.9 \cdot 10^{-3}$	$1.1 \cdot 10^{8}$	28.0
ZnO (1.2 at. % Li)	$2.2 \cdot 10^{-4}$	$9.1 \cdot 10^{9}$	40.6

Fig. 2

Figure 2: Fig. 2

Sample	K ($t = 368°$), $(\mathrm{min} \cdot \mathrm{m}^2)^{-1}$	K_0, $(\mathrm{min} \cdot \mathrm{m}^2)^{-1}$	E, kcal/mol
ZnO (1 at. % Ga)	$6.9 \cdot 10^{-2}$	$6.6 \cdot 10^{2}$	18.8

adsorption remains below the corresponding monolayer. The increase in rate is associated with a decrease in the activation energy of adsorption from 36 kcal/mol at a coverage of 0.01 $\mathrm{cm}^3/\mathrm{m}^2$ for ZnO to 7 kcal/mol for ZnO containing 1.25 at.% Li, and still lower for the sample containing 0.5 at.% Li. The degree of surface coverage in the adsorption of oxygen by dissociation reaches, for the ZnO sample (0.5 at.%), in the region of maximum coverage, 40% of the Zn^{2+} cations on the surface. This value is 16 times higher than on ZnO and 4 times higher than on ZnO (1.2 at.% Li).

Fig. 2

b) **Adsorption of CO** was measured on ZnO and its solid solutions containing 0.5 and 1.25% Li. From the literature, two types of CO adsorption on ZnO are known: reversible adsorption, occurring at low temperatures, and irreversible adsorption at higher temperatures (^{5}). We investigated CO adsorption in the temperature interval from 0 to 300°. At room temperature, CO adsorption proceeds at a high rate. Part of the gas is adsorbed reversibly and can be removed from the surface by evacuation.

With an increase in temperature from room temperature and above, the measured rate of gas uptake decreases, and at 200° it becomes negligibly small, which is associated with the high rate of desorption. Above 250° the adsorption rate begins to increase, but under these conditions adsorption is accompanied by a slow process of CO oxidation by the oxygen of zinc oxide. At 300°, the oxidized CO amounts to 23% of that absorbed.

These two kinds of adsorption affect the electrical conductivity differently. CO adsorption at room temperature, despite the higher degrees of surface coverage, causes no change in electrical conductivity. CO adsorption at 340° increases the electrical conductivity.

Dissolution of lithium oxide in amounts of 0.5 and 1.25 at.% completely suppresses both the CO adsorption that occurs at room temperature and the adsorption that occurs at higher temperatures.

Discussion of results. The strong influence of lithium oxide dissolution on the catalytic properties is connected with a change in the active surface, which we can judge on the basis of studying the chemical adsorption of the reaction

Fig. 3

Figure 3: Fig. 3

components. The decrease in activation energy cannot be explained by a change in the level of the chemical potential of the electrons, since upon dissolution of lithium oxide it decreases; according to Hauffe and Stown (^{6}), this should have led to a decrease in the heats of adsorption and to an increase in the activation energy of O_2 adsorption by virtue of the Brønsted rule. For adsorption of CO —an electron donor—the opposite dependence should have been observed. The absence of a relation in the change of the oxygen adsorption rate with the concentration of free electrons indicates that free electrons cannot be the adsorption centers for oxygen. The commonality of the results with those obtained for the influence on the chemical adsorption of oxygen of dissolving lithium oxide in nickel oxide may be regarded as evidence of a similar mechanism of its influence in these oxides, which belong to different classes of semiconductors. The electrical conductivity of ZnO is associated with the presence of excess zinc in interstitial sites, which is readily ionized with donation of electrons to the conduction band. Upon dissolution of lithium oxide in ZnO, a substitutional solid solution is formed, in which part of the cation sites Zn^{2+} is occupied by Li^+ cations. The lowered charge

Fig. 3. Adsorption of oxygen at 400°. 1 —on ZnO, 2 —on ZnO (0.5 at.% Li), 3 —on ZnO (1.2 at.% Li)

is compensated by the presence of cations in interstices ($Zn^+_{\text{interst.}}$). The combination of cations [$Li^+Zn^+_{\text{interst.}}$] is an electron acceptor. As a result of electron exchange this acceptor can accept an electron, which will correspond to the formation of neutral zinc ($Zn^0_{\text{interst.}}$) near a lithium cation. When ($Li^+Zn^0_{\text{interst.}}$) is formed, the charge of the oxygen ions surrounding it is uncompensated. This should lead to the creation around it of a strong electrostatic field, lowering the work function of electrons in neighboring cation sites. The consequence of this should be a decrease in the activation energy of adsorption of electron-acceptor gases at neighboring cation sites when electrons are present in them. With increasing lithium concentration, the concentration of free electrons decreases; under this hypothesis the number of active centers for oxygen adsorption should pass through a maximum, which is indeed observed experimentally.

The adsorption of CO decreases with increasing concentration of lithium oxide, which indicates a different nature of its active centers. The most probable centers may be donor local levels ($Zn^0_{\text{interst.}}$), free of electrons, whose activity decreases with increasing dissolved lithium. Transfer of an electron to this cation ($Zn^+_{\text{interst.}}$) or to the neighboring Zn^{+2} is energetically favorable, since it restores the local disturbance of neutrality in the given site.

Comparison of the adsorption data with the results obtained for the oxidation of CO leads to the conclusion that the oxidation rate cannot be determined either by oxygen adsorption or by CO adsorption, since the former increases strongly at a content of 0.5 at.% Li, while the latter is absent. The activation energy of CO oxidation increases with increasing lithium concentration, but at the same time the constant K_0 also increases strongly. Such a dependence indicates that oxygen adsorption, while not being the process limiting the oxidation rate, exerts a substantial influence on the stage that determines the oxidation rate. This may be either CO adsorption or the interaction of adsorbed oxygen with CO from the gas phase. In the latter case, the increase in the activation energy of this interaction with increasing lithium concentration leads to a decrease in the reaction rate.

Experiment showed that oxygen adsorbed on a ZnO sample (0.5 at.% Li) reacts at a high rate with CO from the gas phase with the formation of CO_2.

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Note: Figure translations are in progress. See original paper for figures.