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Abstract

Full Text

PHYSICAL CHEMISTRY

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STUDY OF THE REACTION OF HOMOMOLECULAR OXYGEN EXCHANGE ON ZnO AND NiO AT ROOM TEMPERATURE

The reaction of homomolecular oxygen exchange, $O_2^{16} + O_2^{18} = 2O^{16}O^{18}$, on the surface of solid oxides is a convenient model reaction for studying the reactivity of oxygen. In the studies known up to the present time ($^{1-6}$), this reaction has usually been investigated at relatively high temperatures (above 200°), at which isotopic exchange of the oxide oxygen with oxygen of the gas phase also proceeds, i.e., under conditions of an equilibrium oxygen content in the near-surface layer of the oxide. As a rule, the rates of homomolecular oxygen exchange on the oxide surface and of isotopic exchange of surface oxygen with the gas phase are then close or even equal. In the region of lower temperatures, the reaction of homomolecular oxygen exchange on most of the oxides studied has not been observed. Only on MgO was Winter (^{3}) able to detect homomolecular exchange at room temperature, when isotopic exchange between the oxygen of MgO and the oxygen of the gas phase was not observed. Therefore the results of the work of Barry and Stone (^{7}), who observed homomolecular oxygen exchange on a series of ZnO preparations at low temperatures (from room temperature to the temperature of liquid nitrogen), are of great interest. Other authors (^{1,3}) did not observe exchange on ZnO at these temperatures.

Fig. 1. Kinetics of the reaction of homomolecular oxygen exchange on ZnO; $t = 25^\circ$, $P_{O2} = 40$ mm Hg (series II)

The purpose of the present work is to investigate the possibility of the oxygen-exchange reaction proceeding at room temperature on various types of oxides. ZnO—a semiconductor of the n-type—and NiO—a semiconductor of the p-type—were chosen as the objects of study.

Fig. 2. Kinetics of the reaction of homomolecular oxygen exchange on NiO;
$t = 25^\circ$, $P_{O_2} = 40$ mm Hg.

Figure 2: Fig. 2. Kinetics of the reaction of homomolecular oxygen exchange on NiO; $t = 25^\circ$, $P_{O_2} = 40$ mm Hg.

ZnO of "for phosphors" grade and NiO obtained by decomposition of Ni_2CO_3 of "analytical grade" purity were studied. The samples studied were heated, respectively, at 850° for 6 h and at 800° for 3 h in air; subsequently they were rapidly cooled to room temperature and then pressed into tablets. The specific surface area of ZnO was 1.27 m^2/g, and that of NiO was 5.5 m^2/g.

The apparatus and the method for calculating the rate of the exchange reaction were analogous to those described in ([1,2]). Before the experiment the samples were conditioned at 400° for 8 h in vacuum. At the end of conditioning the vacuum was $5 \cdot 10^{-5}$ mm Hg. Oxygen was admitted into the system at the temperature of the experiment. In the study of the exchange reaction on ZnO at room temperature, 4 series of experiments were carried out, with 5-6 experiments in each. In the first three series, between experiments the gas was pumped out in less than 1 min to 5 mm···

mm Hg, and in the last series—to 10^{-3}–10^{-4} mm Hg. Between series the specimen was trained in vacuum at 400°C for 3-8 h.

As a result of the experiment it was found that, at room temperature, exchange on ZnO can proceed at a very high rate, exceeding the exchange rate at high temperatures. Figure 1 presents typical kinetic dependences obtained in processing the results of the first series of experiments. The numbers on the graph indicate the sequence in which the experiments were carried out. Processing of the data from the other series of experiments gives analogous straight lines. It follows from Fig. 1 that, although during each experiment (the duration of the experiments was from 2 to 28 min) the reaction is well described by a first-order equation (1), from experiment to experiment the reaction rate decreases, i.e., ZnO is deactivated with time under the action of the oxygen atmosphere. The freshly trained specimen had such high activity that exchange proceeded practically instantaneously to equilibrium. But already after 2-2.5 min the exchange rate decreases to measurable values, and after 5 h it becomes immeasurably small. The activity of ZnO with respect to homomolecular oxygen exchange is completely restored by subsequent training of the specimen in vacuum at 400° for 3-8 h. The reproducibility of the results obtained at the same holding time in oxygen in different series of experiments is good.

Fig. 2. Kinetics of the reaction of homomolecular oxygen exchange on NiO; $t = 25^\circ$, $P_{O_2} = 40$ mm Hg.

Comparison of the decrease in activity with time from the results of the first three and the last series of experiments (Fig. 3) shows that pumping out oxygen between experiments to 10^{-3}–10^{-4} mm Hg at room temperature does not

Fig. 3. Relative change in rate with time

Figure 3: Fig. 3. Relative change in rate with time

restore the activity of ZnO, but only somewhat reduces the rate of deactivation. In studies of homomolecular oxygen exchange on the same ZnO samples in the high-temperature region, no decrease in activity with time of exposure in oxygen was observed. As far as can be judged from the graphs given in the work of Barry and Stone (7), the ZnO specimens used by them were not deactivated with time.

Table 1

Activity of the specimens at low and high temperatures

Specimen	Parameter	25	425	450	475	500
ZnO	°C	25	425	450	475	500
ZnO	$K \cdot 10^5$	341—0.1	0.6	2.2	5.6	13.3

Specimen	Parameter	25	275	300	325	350
NiO	°C	25	275	300	325	350
NiO	$K \cdot 10^5$	74.7—23.1	0.17	0.23	0.81	2.7

The results of the study of the reaction of homomolecular oxygen exchange at room temperature on nickel oxide are presented in the form of kinetic curves in Fig. 2. It follows from the figure that on NiO as well, at room temperature, homomolecular oxygen exchange proceeds at a very high rate. With time the exchange rate on NiO decreases somewhat (Fig. 3), but, in contrast to ZnO, the decrease in rate is insignificant (approximately by a factor of 3 over 27 h). An analogous effect was observed in the study of homomolecular oxygen exchange on the same NiO specimens in the high-temperature region (275—350°).

The results of comparing the catalytic properties of the investigated preparations at 25° and at high temperatures are given in Table 1. From the data of Table 1 it is evident that on ZnO the initial exchange rate at 25°, measured 2 min after admitting oxygen into the system, is 26 times greater than the exchange rate on the same preparation at 500°, while on NiO the exchange rate at 25° is 28 times greater than the exchange rate at 350°. At the same time, the initial rate of homomolecular exchange at room temperature on ZnO is 5 times greater than the exchange rate on NiO, whereas in the high-temperature region NiO is a more active catalyst with respect to the reaction of homomolecular oxygen exchange than ZnO. In Table 1, K is expressed in g-mol O_2/m^2 h.

Fig. 3. Relative change in rate with time

Thus, the results obtained show that both on ZnO and on NiO two temperature regions are observed for the occurrence of the reaction of homomolecular oxygen exchange. When the oxides are heated in vacuum during the process of conditioning the preparations, adsorbed oxygen is removed, which may also be accompanied by removal of oxygen from the surface layer of the oxide. In ZnO this conditioning promotes a greater deviation from stoichiometry in the surface layer of the oxide, an increase in the amount of excess zinc; in NiO, on the contrary, conditioning brings the system closer to stoichiometry through removal of excess oxygen. The fact that oxides conditioned at high temperature in vacuum possess, at room temperature, increased catalytic activity with respect to homomolecular oxygen exchange apparently indicates that the catalytic properties of ZnO are connected with the presence of excess zinc, and those of NiO with Ni^{+2} ions of the lattice. The loss of activity in an oxygen atmosphere may be explained for ZnO by the reverse process of approach to stoichiometry at the expense of oxygen from the gas phase, which leads to a decrease in the amount of excess zinc. Probably, in ZnO this process proceeds rather rapidly even at room temperature: in 5 h the exchange rate decreases from an immeasurably large value to an immeasurably small one. In the case of NiO the decrease in activity is associated with an increase in the amount of excess oxygen in the surface layer.

The possibility is not excluded that the increased activity at room temperature is connected with metallic Ni in NiO ([9]) and metallic zinc in ZnO. Thus, for example, it is known ([8]) that ZnO is prone to decomposition at high temperatures. Therefore, at the temperature of preparation a considerable amount of interstitial zinc may dissolve in the oxide. Rapid cooling (freezing of the equilibrium) makes it difficult for interstitial zinc, nonequilibrium at other temperatures, to separate out. However, this zinc may precipitate in the form of a new phase at dislocations, grain boundaries, and other structural defects during conditioning of the preparation in vacuum. Therefore the exchange reaction may also be associated with this new zinc phase, and the decay may be associated with its low-temperature oxidation.

Carrying out homomolecular exchange at high temperatures immediately restores the state of the oxide surface disturbed by conditioning,

which explains the comparatively low exchange rates at high temperatures. In going from high temperatures to low ones, in this case the exchange rate decreases, and exchange at low temperatures cannot be observed on samples kept in an oxygen atmosphere at high temperatures. The coincidence of the rate of homomolecular exchange at high temperatures with the rate of isotopic exchange of surface oxygen with oxygen of the gas phase indicates that, in this case, the adsorbed oxygen does not differ from lattice oxygen.

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