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Abstract

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ON THE ISOTOPIC EXCHANGE OF OXYGEN IN THE SYSTEM γ-ALUMINA–MOLECULAR OXYGEN

In principle, two cases of homomolecular oxygen exchange on oxides are possible –with and without the participation of the oxygen of the oxide. The first case is realized on all oxides at sufficiently high temperatures; in this case, if the oxygen content in the surface layer of the oxide is at equilibrium, the observed homomolecular oxygen exchange is, as a rule, a consequence of isotopic exchange of molecular oxygen with the oxygen of the oxide ($^{1-3}$). Cases of the second type have so far been investigated only rarely (^{2,4,5}). In these cases, homomolecular exchange occurs at lower temperatures on samples preliminarily deoxygenated at high temperatures and characterized by a nonequilibrium oxygen content in the surface layer. Samples treated in this way possess appreciable activity with respect to homomolecular exchange, which is unstable and decreases as the sample remains in the presence of oxygen. Deactivation, as a rule, proceeds the faster the higher the temperature.

In the present work, homomolecular exchange of oxygen on γ-alumina was investigated in the low-temperature and high-temperature regions, as well as the relation between homomolecular exchange and isotopic exchange with the oxygen of the oxide.

Active alumina was prepared by thermal decomposition of the hydroxide obtained by precipitation with ammonia from a solution of an aluminum nitrate salt; after decomposition of the hydroxide, Al_2O_3 was calcined for 10 hours in air at a temperature of 700°. The samples prepared in this way had a specific surface area of 124 m^2/g and were the γ-modification.*

The heavy oxygen used for studying exchange contained 34.6 at. % O^{18} and was carefully purified of water vapor and hydrogen; for homomolecular exchange a nonequilibrium mixture in a 1:1 ratio of heavy oxygen of the indicated concentration and oxygen of natural isotopic composition was used. Exchange was studied by a static circulating method with periodic mass-spectrometric analysis (^{1,3}). The rates of homomolecular exchange and of isotopic exchange with the oxygen of the oxide were characterized by the quantities K and R, expressed in molecules $O_2/\mathrm{sec}\cdot\mathrm{cm}^2$ and determined by the equations (^{1,3})

$$K = \frac{2.3 N_\Gamma \lg G}{S\tau}, \qquad \text{where} \quad G = \frac{C_{34}^* - C_{34}}{C_{34}^* - C_{34}^0},$$

$$R = \frac{2.3 N_\Gamma N_s \lg H}{S(N_\Gamma + N_s)\tau}, \qquad \text{where} \qquad H = \frac{C_{18}^* - C_{18}}{C_{18}^* - C_{18}^0}.$$

On freshly prepared samples of γ-Al_2O_3, homomolecular exchange is not observed at temperatures below 350°. After preliminary evacuation at a sufficiently high temperature, the samples show appreciable activity at low temperatures (measurements of the activity with respect to homomolecular exchange were carried out over a fairly broad in-temperature range—from −78 to 350°), the greater the higher the temperature and the longer the time of the preliminary treatment, and it decreases noticeably as the sample remains in an oxygen atmosphere. The dependence of the initial activity on the temperature of the preliminary treatment is illustrated in Fig. 1, which presents the change of $\lg G$ with the exchange time for a sample successively degassed at temperatures of 350, 400, 450, and 500° for 5 h. Treatment at a temperature below 350° does not lead to activation, whereas treatment at a temperature above 600° leads to an immeasurably high activity (the very first sample, taken 2 min after the start of the experiment, has a practically equilibrium composition, which corresponds to $K > 10^{12}$ molecules $O_2/\mathrm{s} \cdot \mathrm{cm}^2$). Samples activated at 350° have a low initial activity and are completely deactivated after approximately an hour. Subsequent treatment of such a deactivated sample with oxygen at 660° in a system with a trap cooled by liquid nitrogen leads to the appearance of a very high activity ($K = 9 \cdot 10^9$ molecules $O_2/\mathrm{s} \cdot \mathrm{cm}^2$).

(Figure: Fig. 1)

Fig. 1. Dependence of $\lg G$ on the exchange time at $t = 25°$ and $P_{O_2} = 10$ mm Hg (sample charge 5 g). Temperature of preliminary treatment in vacuum: 1 −350°, 2 −400°, 3 −450°, 4 −500°.

The data given below illustrate the rate of decrease of the activity of a sample preliminarily degassed at 660° for 18 h, during successive experiments on homomolecular exchange at 20° and an oxygen pressure $P_{O_2} = 10$ mm Hg. Between experiments the sample was kept under the same conditions.

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	Time of residence of the sample in oxygen						
	0	1 h	1 day	2 days	3 days	4 days	8 days
K, O_2/s·cm^2	$5.1 \cdot 10^{11}$	$4.3 \cdot 10^{10}$	$2.9 \cdot 10^{10}$	$2.9 \cdot 10^{10}$	$1.5 \cdot 10^{10}$	$1.5 \cdot 10^{10}$	$1.5 \cdot 10^{10}$

At first the activity falls very rapidly, changing noticeably during the experiment, but after only a few hours the decrease becomes very slow, and after two days the activity remains practically stable.

When a γ-Al_2O_3 sample is treated, after evacuation at high temperature, with oxygen at the same temperature, the time required to reach a stable activity is substantially shortened and the difference between the initial and stable activities decreases. The dependence of the activity of a sample, preliminarily treated for 6 h at 600° in vacuum and then for 2 h at the same temperature and an oxygen pressure of 10 mm Hg, on the residence time in oxygen at room temperature and at the same oxygen pressure is illustrated by the data given below. The experiments were carried out at $t = 25°$ and $P_{O_2} = 10$ mm Hg.

	Time of residence of the sample in oxygen					
	immediately after treatment	1 h	2 h	1 day	2 days	3 days
K, O_2/s·cm^2	$2 \cdot 10^{10}$	$3.1 \cdot 10^9$	$2.5 \cdot 10^9$	$1.55 \cdot 10^9$	$1.5 \cdot 10^9$	$1.5 \cdot 10^9$

It was precisely this preliminary treatment that was adopted in the study of the temperature dependence of the rates of homomolecular and isotopic exchange of molecular oxygen with the oxygen of the oxide. The results of these experiments are presented in Fig. 2.

The isotopic exchange of molecular oxygen with the oxygen of the oxide becomes noticeable at a temperature of about 350°, coinciding with the minimum activation temperature of γ-Al_2O_3 for low-temperature homomolecular exchange of oxygen. The activation energy of isotopic exchange in the temperature range from 425 to 475° is 40 kcal/mole.

The temperature dependence of the rate of homomolecular exchange is not monotonic: at a temperature of about 150° a minimum is observed, apparently associated with different mechanisms of oxygen exchange. The presence of a minimum in the temperature dependence was previously found for the amount of adsorbed oxygen on certain oxides (chromium oxide (6), zinc oxide (4, 7)), and Barri and Stoun (4, 7) observed a minimum in the rate of chemisorption of oxygen on zinc oxide when the temperature was varied.

Fig. 2. Dependence of $\lg K$ and $\lg R$ on temperature. The experiments were carried out at $P_{O2} = 10$ mm Hg. Homomolecular exchange was studied on two samples (*a*, *b*); for the study of isotopic exchange (*v*), a fresh sample was used at each temperature. The numbers in the figure denote the sequence in which the experiments were carried out on one and the same sample.

The dependence of the rate of isotopic and homomolecular exchange on the oxygen pressure was determined at temperatures of −78, 25, 300, and 450°. At all temperatures except −78°, the order with respect to oxygen is equal to unity; at −78° it is less than unity.

From the results presented it is seen that the rate of homomolecular exchange on the investigated samples of γ-$\mathrm{Al_2O_3}$ is significantly greater than the rate of isotopic exchange of molecular oxygen with the oxygen of the oxide (by approximately two orders of magnitude). In the low-temperature region, γ-$\mathrm{Al_2O_3}$ treated in the manner indicated has appreciable and practically stable activity with respect to the homomolecular exchange of oxygen.

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