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Isotopic Exchange between Molecular Oxygen and Oxides of Rare-Earth Elements

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Recently, considerable attention has been devoted to the study of the catalytic properties of compounds of rare-earth elements (r.e.e.). Such a study is of interest both from the standpoint of the practical use of r.e.e. compounds as catalysts, since at present these elements can be obtained in considerable quantities, and from the standpoint of the theory of catalysis, since certain properties of r.e.e. compounds are determined by the structure of the deeply lying $4f$-shell.

There are indications in the literature of the possibility of using r.e.e. oxides as oxidation catalysts; however, systematic data on this question are lacking. The present work was undertaken with the aim of a systematic investigation of the mobility of oxygen in r.e.e. oxides, which, as was shown in a number of works by Boreskov and his coworkers ([1,2]) and by Winter ([3,4,5]), is related in a definite way to the catalytic activity of oxides in oxidation reactions. The study was carried out by the method of isotopic exchange of r.e.e. oxides with molecular oxygen according to a circulation-static procedure (an apparatus similar to that described in work ([2])). The r.e.e. oxides were prepared by precipitating hydroxides from nitrate solutions at pH 9 and subsequently calcining the hydroxides obtained at 600° in air for 6 hours. The powders obtained were tableted at a pressure of 4500 atm and crushed into grains 1.5–3 mm in size. The purity of all the r.e.e. oxides investigated was 99.8%. Oxygen was obtained by electrolysis of water enriched with O^{18}. Analysis of gas samples was carried out on an MI-1305 mass spectrometer.*

Before the experiment, a weighed portion of oxide (1 g) was subjected to pretreatment under vacuum at 500° for 6 hours. The residual pressure at the end of the pretreatment in all experiments was $4 \cdot 10^{-5}$ mm Hg. All experiments were carried out at an oxygen pressure of 40 mm Hg. The amount of gas in the apparatus circuit at this pressure was 0.0489 g.

The mobility of oxygen in the oxides investigated was compared according to the rates of exchange with O_2 and according to the number of monolayers of oxide oxygen, X_S, that had attained the isotopic composition of the gas phase by a certain moment of time, which was calculated from the experimental data by the equation:

$$X_S = \frac{C_{18}^0 - C_{18}^n}{\lambda_S \left(C_{18}^n - 0.2\right)}, \tag{1}$$

where C_{18}^0 is the fraction of O^{18} in the gas at the initial moment, at.%; C_{18}^n is the fraction of O^{18} in the n-th gas sample, at.%; 0.2 is the fraction of O^{18} in natural oxygen, at.%; λ_S is the ratio of the amounts of oxygen in the surface layer of the oxide and in the gas

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(when calculating λ_S, the amount of oxygen in 1 m^2 of surface was taken as equal to $0.34 \cdot 10^{-3}$ g) ([2]). The initial rate of exchange of the oxide with O_2, R_0, is a characteristic of the mobility of the most reactive oxygen of the oxide. Calculation of R_0 for the exchange of all the oxides studied, with the exception of CeO_2, was carried out using tangents to the kinetic curves at the initial moment of time according to the general equation for exchange kinetics in molecular oxygen–oxide systems:

$$R = -\frac{2.3N}{S\tau} \frac{\lg(1-F)}{(1+\lambda)}, \tag{2}$$

where N is the amount of oxygen in the oxide (g); λ is the ratio of the amount of oxygen in the oxide to that in the gas; S is the surface area of the sample (m^2); F is the degree of exchange; τ is time (min); R is the exchange rate (g $O_2/m^2 \cdot$ min). The exchange of CeO_2 with molecular oxygen is completely described by equation (2). Figure 1 shows the dependence of R_0 at a temperature of 370° on the atomic number of the rare-earth element. Table 1 gives some physicochemical characteristics of the oxides studied and the dependence of X_S on the exchange time at 370°. The specific surface area of the oxides was measured by a gas-chromatographic single-point method after training ([6]). X-ray structural investigation of the samples was carried out at room temperature. The apparent activation energies of exchange of the various oxides with O_2 were estimated from the dependence of $\lg R_0$ on $1/T$, shown in Fig. 2.

In considering the kinetic data of Table 1 and Fig. 1, attention is drawn to the periodicity in the change of the mobility characteristics of oxide oxygen in the series from lanthanum to lutetium. The oxides Pr_6O_{11} and Tb_4O_7 have the maximum activity with respect to the exchange reaction with O_2, while an intermediate minimum of activity falls at Sm_2O_3. The investigation carried out on the influence of training in vacuum and in oxygen on the mobility of oxygen of the rare-earth elements showed that the latter increases upon removal of part of the oxygen from the surface layer of the oxides during vacuum training. The available data on homomolecular

Fig. 1. Dependence of the initial exchange rate R_0 on the atomic number of the rare-earth element at 370°.

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Fig. 2. Dependence of lg R_0 on 1/T for exchange of the rare-earth oxides studied with O_2: 1–La_2O_3; 2–CeO_2; 3–Pr_6O_{11}; 4–Nd_2O_3; 5–Sm_2O_3; 6–Gd_2O_3; 7–Tb_4O_7; 8–Dy_2O_3; 9–Ho_2O_3; 10–Er_2O_3; 11–Tu_2O_3; 12–Yb_2O_3

Figure 2: Fig. 2. Dependence of lg R_0 on 1/T for exchange of the rare-earth oxides studied with O_2: 1–La_2O_3; 2–CeO_2; 3–Pr_6O_{11}; 4–Nd_2O_3; 5–Sm_2O_3; 6 –Gd_2O_3; 7–Tb_4O_7; 8–Dy_2O_3; 9–Ho_2O_3; 10–Er_2O_3; 11–Tu_2O_3; 12–Yb_2O_3

Table 1

Some characteristics of the investigated rare-earth oxides and the kinetics of exchange with oxygen at 370° **and** $P_{O_2} = 40$ **mm Hg (sample weight 1 g)**

Oxide	Structural form	Specific surface area, m^2/g	Time, min: 1	Time, min: 3	Time, min: 5	Time, min: 10	Time, min: 20	Time, min: 30	Apparent activation energy, kcal/mol
La_2O_3	C	28	–	–	0.152	0.357	0.572	0.894	23
CeO_2	C	29	0.34	0.71	1.105	2.21	4.7	7.4	16
Pr_6O_{11}	C	32	3.55	5.85	6.88	9.66	–	11.17	14
Nd_2O_3	C	26	1.405	2.51	3.56	5.08	7.13	7.53	13
Sm_2O_3	C	42	0.41	–	1.14	1.60	2.18	2.26	12
Gd_2O_3	C	31	0.63	1.37	2.01	3.39	4.44	5.97	23
Tb_4O_7	C	49	–	3.36	–	5.33	6.66	7.08	22
Dy_2O_3	C	49	0.40	0.74	1.05	1.85	2.25	2.69	29
Ho_2O_3	C	46	0.18	0.32	0.53	0.83	1.33	1.70	22
Er_2O_3	C	21	0.27	0.53	0.70	1.21	1.92	2.41	16
Tm_2O_3	–	22	0.05	0.16	0.39	0.68	1.25	1.85	–
Yb_2O_3	C	34	0.12	0.27	0.46	0.82	1.27	1.73	25
Lu_2O_3	–	20	0.07	0.29	0.47	0.91	1.76	2.42	–

exchange of oxygen on some oxides treated in vacuum and in oxygen. The mobility of oxygen in the family of lanthanide oxides, apparently, depends on the presence in the latter of variable valence (the ability to form nonstoichiometric oxides).

As is known, in periodic dependence on the atomic number such properties of the rare-earth elements as magnetic susceptibility and valence change.

Fig. 2. Dependence of lg R_0 on $1/T$ for exchange of the rare-earth oxides studied with O_2:

1–La_2O_3; 2–CeO_2; 3–Pr_6O_{11}; 4–Nd_2O_3; 5–Sm_2O_3; 6–Gd_2O_3; 7–Tb_4O_7; 8–Dy_2O_3; 9–Ho_2O_3; 10–Er_2O_3; 11–Tu_2O_3; 12–Yb_2O_3.

According to modern concepts, the periodicity of these properties is associated with the electronic structure of the rare-earth elements. On the basis of the data obtained one may suppose that the periodic character of the change in the mobility of oxygen in rare-earth oxides is also associated with the electronic structure of the latter. There is no absolute parallelism between the change in the characteristics of oxygen mobility as a function of atomic number and the change in the magnetic susceptibility of the rare-earth elements, nor would it be easy to expect it, since, undoubtedly, the ability of rare-earth oxides to undergo exchange, apart from the electronic structure of the elements forming them, is connected with a number of properties of the oxides, such as the type of conductivity, lattice parameters, degree of dispersion, etc. In addition, the presence of impurities may be of great importance. It is interesting to note, however, that the oxides whose magnetic susceptibility is close to the maximum possess the maximum mobility of oxygen, while the intermediate minimum of mobility falls on samarium oxide, the element whose magnetic susceptibility is minimal.

This regularity is expressed more clearly at high degrees of exchange (cf. columns 1, 10, and 30 min in Table 1). One reason for this is the nonequivalence of the surface and bulk oxygen of the oxides; another may be a change in the stoichiometry in the surface layer of the oxides during the course of exchange.

The minimum of the apparent activation energy of exchange with O_2 falls on samarium oxide. On the whole, the oxides of the cerium subgroup are characterized by lower activation energies than the oxides of the yttrium subgroup. It should be noted at once, however, that the accuracy of these quantities is not high, since their determination is associated with drawing tangents to the kinetic curves at the initial moment of time. Evidently, more exact characteristics of the reactivity of the surface oxygen of rare-earth oxides can be provided by a study of the reaction of homomolecular oxygen exchange. Such a study is being carried out at the present time.

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