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Kinetics and Mechanism of Hydrogen Oxidation over Lanthanum–Cerium Oxide Catalyst Using Deuterium and Oxygen-18

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The kinetics of oxidation of stoichiometric mixtures of hydrogen and oxygen with different isotope compositions was studied on La_2O_3 doped with CeO_2 (ratio La/Ce = 99) in the temperature range between 250 and 400°C. It was found that during the oxidation the rate constant of $H_2 + D_2 = 2HD$ exchange is equal to the rate of the oxidation under all experimental conditions. $^{16}O_2 + {}^{18}O_2 = 2{}^{16}O^{18}O$ exchange and exchange of ^{18}O between gas and catalyst did not occur during oxidation. The data obtained led to the conclusion that the limiting step of the oxidation reaction is the interaction between hydrogen in molecular form and adsorbed oxygen.

INTRODUCTION

The role played by the oxygen of oxide catalysts in catalytic oxidation reactions presents a problem of great concern for the theory of heterogeneous catalysis. A substantial body of experimental data obtained with ^{18}O is available. These data show the surface oxygen of oxides to exhibit mobility within the temperature range characteristic of heterogeneous catalytic oxidation. Most of these data are summed up in reviews (*1*, *2*, *4*). These data give evidence in favor of an oxidation–reduction scheme. According to it, catalysis of oxidation reactions by oxide catalysts proceeds via oxidation–reduction of the catalyst surface (*5*, *6*). This scheme suggests active participation of the catalyst surface oxygen in oxidation reactions. The correlation dependence between the catalytic activity of oxides and their thermodynamic characteristics (*7*, *9*) or oxygen binding energy with oxides (*2*, *9*) is also evidence which supports this scheme. On the other hand, in a number of recent publications (*10*, *11*, *12*) it has been shown by EPR that there are paramagnetic oxygen forms in quite high concentration on the oxide surface. These, in the authors' opinion, may play an important role in oxidation catalysis.

At present, the involvement of the surface oxygen of a catalyst in the reaction proceeding on it can be regarded as strictly proved only for the simplest reactions: homomolecular oxygen exchange (*2*) and the exchange $^{12}C^{16}O + {}^{13}C^{18}O = {}^{12}C^{18}O + {}^{13}C^{16}O$ (*3*). As for oxidation reactions the complication is due, in the first place, to the fact that the substance to be oxidized may significantly affect the surface properties of oxides. For instance, hydrogen and oxygen are known to affect mutually their chemisorption over oxide catalysts (see, for example (*13*)).

One might think it possible to obtain some valuable information by using the tracer technique in studying, for instance, the isotopic composition of the products resulting from the reaction, with the starting oxygen and catalyst of different ^{18}O content. However, no unequivocal conclusions could be drawn from such experiments (*14*, *15*) since water and carbon dioxide have been shown to exchange their oxygen with that of oxides (*1*, *16*, *17*), i.e., oxygen with ^{18}O content other than that of the starting oxygen could be introduced into the reaction product not as a result of the reaction itself but as a result of exchange between its products and the catalyst.

The objective of this work was to elucidate the mechanism of catalytic hydrogen oxidation by a kinetic method in combination with the study of two isotopic exchange reactions, viz., $^{16}O_2 + {}^{18}O_2 = {}^{16}O^{18}O$ and $H_2 + D_2 = 2HD$.

Since these reactions may have some common stages with that of hydrogen oxidation proceeding simultaneously, one might think it possible to obtain some data concerning the mechanism of the latter and, in particular, about the role of the oxygen of oxides.

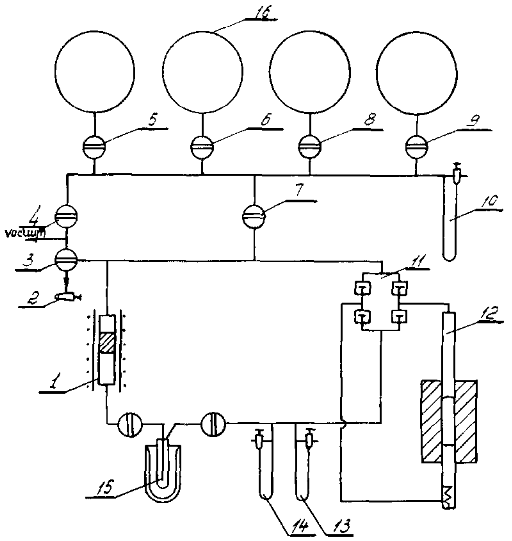


FIG. 1. Schematic representation of the vacuum unit to study the reactions of isotope exchange and hydrogen oxidation: (1) catalytic reaction vessel, (2) ampoule for gas sampling from the circulation loop of the unit; 3-tap for collecting gas samples; (4, 5, 6, 7, 8, 9) taps; (10) U-shaped mercury manometer; (11) nonreturn flap; (12) circulation pump; (13) differential manometer; (14) U-shaped mercury manometer; (15) trap; (16) flasks for the storage of gases.

EXPERIMENTAL METHODS

Apparatus. A high vacuum constant volume circulatory unit was used in the experiments. It is shown schematically in Fig. 1. A quartz reaction vessel (*1*) was fitted with a coil to preheat the reaction mixture. The temperature in the catalyst bed was maintained constant with an accuracy of ±1°C while pretreating the catalyst and studying the isotopic exchange reactions and with an accuracy of ±2°C in studying the hydrogen oxidation reaction. Gas circulation (ca. 600 liters/hr) was provided by a glass electromagnetic pump (12); water resulting from oxidation was frozen out in a trap (15) cooled with liquid nitrogen. The loop included a U-shaped manometer (14) to measure gas pressure and a differential manometer (13) filled with silicone oil to control pressure constancy during hydrogen oxidation (see below). The vacuum facilities afforded a vacuum of ca. 10^{-6} Torr.

Isotopic composition of gases was determined by using an omegatron.

Materials used. Lanthanum-cerium oxide catalyst was prepared by coprecipitation of the hydroxides from a mixture of lanthanum and cerium nitrate solutions (ratio La/Ce = 99). Precipitation was carried out with ammonium hydroxide up to pH 9. The resulting precipitate was washed to free it from NO_3^- ions and heated in air at 600°C for 6 hr. Pelleted forms of catalyst (4 mm in diameter, 5 mm thick) were used.

Oxygen was prepared by electrolysis of water of natural isotopic composition or enriched in ^{18}O. Oxygen was frozen out in a trap cooled with liquid nitrogen. Noncondensing admixtures together with some oxygen were pumped out. Gas from the trap was passed through an aerosol filter into flasks for storage.

Cylinder hydrogen and deuterium 99 atom % purified in a trap with NaA zeolite at temperature of liquid nitrogen were employed.

Hydrogen–oxygen stoichiometric mixtures of different isotopic composition were prepared by electrolysis of natural water, $D_2{}^{16}O$ (99% mole D_2O) and $H_2{}^{18}O$ (40% mole $H_2{}^{18}O$). The mixture was freed from water and alkali by passing through a trap with an aerosol filter at the temperature of liquid nitrogen. A working mixture of gases resulting from electrolysis of heavy hydrogen and heavy oxygen water ratio 1:1, was prepared to study $^{16}O_2 + {}^{18}O_2 = 2{}^{16}O{}^{18}O$ and $H_2 + D_2 = 2HD$ reactions, during hydrogen oxidation.

Procedure. The circulatory method was used to study the reaction of isotopic exchange of individual gases. Fresh samples of the catalyst, pretreated *in vacuo* (10^{-5} Torr) at 400°C for 5 hr, were used in each experiment when studying the heterogenous exchange of ^{18}O and the reaction $H_2 + D_2 = 2HD$. The homomolecular oxygen exchange was studied over a catalyst sample with an ^{18}O content equal to that in the gas (20 atom %). In the latter case the catalyst sample was pretreated *in vacuo* as above and then it was treated many times by a nonequilibrium mixture of $^{16}O_2$ and $^{18}O_2$ molecules at 400°C and 10 Torr. Then, hydrogen oxidation kinetics were studied over the same sample of the catalyst. The following experimental procedure (*18*) was used in this case: reaction mixture from the known volume limited by the taps (4, 7, 5–9) was fed into the loop through tap 7 so that the pressure in the loop was kept constant. Pressure constancy was controlled by the differential manometer (13). The reaction rate was determined from the changes of pressure in that known volume. The reading of the mercury manometer (10) was recorded every 15–30 sec. Figure 2 illustrates the experimental data obtained by studying the oxidation rate as a function of pressure in the reaction mixture at 250°C. During oxidation, pressure was maintained constant with an accuracy not lower than ±0.7 Torr.

When working with the hydrogen–oxygen mixture with a nonequilibrium content of nonsymmetric HD and $^{16}O^{18}O$ molecules, the ^{18}O content in the gas phase was equal to that in the catalyst (20 atom %). Experiments with the mixtures obtained by electrolysis of heavy hydrogen water and by electrolysis of water enriched in ^{18}O (40 atom %) were carried out over the same sample of the catalyst. Isotopic composition of the reaction mixtures and their HD and $^{16}O^{18}O$ molecule content were checked by mass spectrometry, gas samples being collected from the circulation loop in the course of the experiment.

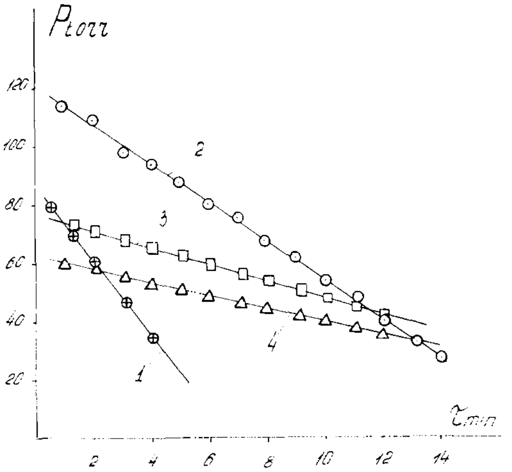


FIG. 2. Rate of oxidation of stoichiometric mixture 2 $(0.5D_2 + 0.5H_2) + (0.8{}^{16}O + 0.2{}^{18}O)_2$ as a function of pressure in the loop at 250°C: (1) 40; (2) 20; (3) 12; (4) 7 Torr: The ordinate is the pressure of the reacting mixture as followed on the manometer (10).

RESULTS

Oxygen homomolecular exchange kinetics were studied in the temperature range 300–400°C, with an oxygen pressure from 8 to 42 Torr. The experimental data were treated with the first order equation against $^{16}O^{18}O$ molecule concentration. The rate constant values were reproduced with an accuracy not lower than ±10%. Table 1 presents the rate constant values of homomolecular exchange reactions at various temperatures and oxygen pressures. The activation energy of homomolecular exchange is estimated from the temperature dependence of the rate constants whilst the order of the reaction is found from the dependence of the constants on oxygen pressure. These values are also presented in Table 1.

The initial rate of isotope exchange between the catalyst and molecular oxygen, which was calculated by using the first order equation from the experimental data at 400°C and 10 Torr, is 74×10^{11} atoms/cm² sec.

TABLE 1

RATE CONSTANTS OF $^{16}O_2 + {}^{18}O_2 = 2{}^{16}O{}^{18}O$ REACTION AS A FUNCTION OF THE TEMPERATURE AND OXYGEN PRESSURE

Temp (°C)	Pressure (Torr)	Rate constants (atoms × 10^{-11}/cm² sec)	Activation energy (kcal/mole)	Order with respect to oxygen
400	10	79		
370	10	44		
350	10	36	15 ± 1.5	
340	10	19		
300	10	11		
400	42	420		
400	36	360		
400	29	290		1 ± 0.1
400	10	79		
400	8	71		

The method of determining the catalyst activity in hydrogen oxidation used in this work is a variety of the nongradient method and allows a direct measurement of the rate of the hydrogen catalytic oxidation reaction (*18*). With the stationary state over the catalyst being the same at constant pressure the data on rate temperature dependence can be used to calculate the activation energy of the reaction. The values of the hydrogen oxidation rate at various temperatures and pressures of stoichiometric mixtures of different isotope composition are given in Table 2. These allow us to conclude that the rate of the catalytic oxidation within the accuracy range of the method used (±15%) does not depend on the isotopic composition of the mixture. The activation energies of catalytic oxidation for all the mixtures under

TABLE 2

HYDROGEN OXIDATION REACTION RATE AS A FUNCTION OF TEMPERATURE AND PRESSURE OF STOICHIOMETRIC MIXTURE FOR MIXTURES OF VARIOUS ISOTOPIC COMPOSITIONS

		Oxidation rate (atoms + 10^{-11}/cm² sec)				
t(°C)	Pressure (Torr)	$2H_2 + {}^{18}O_2$	$2D_2 + {}^{16}O_2$	$2(H_2 + D_2) + (0.8\,{}^{16}O + 0.2\,{}^{18}O)_2$	Activation energy (kcal/mole)	Overall reaction order
400	20	275	268	—		
370	20	—	—	240		
350	20	188	180	2	8 ± 2	
320	20	—	—	167		
300	20	117	101	—		
250	20	43	36	47		
350	40	300	290	—		
350	20	168	180	—		1 ± 0.15
350	10	94	87			
350	5	36	54			
250	40	—	—	90		
250	20	43	36	46		
250	12	—	—	20		
250	7	—	—	87		

study is the same and equal to 8 ± 2 kcal/mole. The catalytic oxidation rate at constant temperature is proportional to the overall pressure of the stoichiometric mixture. It should be pointed out that in the experiments with stoichiometric mixtures of hydrogen and oxygen the catalyst activity from one run to another was well reproducible; whereas the attempts to determine the reaction order with respect to either hydrogen or oxygen, that is the attempts to carry out the reaction in excess of one of these components, failed. No reproducible results were obtained.

By comparing the data of Tables 1 and 2 it follows that the oxygen exchange rate constant is 4–5 times lower than the rate of oxidation at maximum temperature and under a pressure equal to that of the oxygen in stoichiometric mixtures; at low temperature this difference increases. The activation energy of oxygen homomolecular exchange in the temperature range under consideration is about twice as high as that of hydrogen catalytic oxidation.

The reaction $H_2 + D_2 = 2HD$ at 300–400°C over the La/Ce catalyst proceeded at such a high rate that its kinetic characteristics could not be measured.

Next, the results obtained studying isotope exchange in the course of the oxidation reaction are considered. Table 3 presents some data obtained when working with the mixture of nonequilibrium content of HD and $^{16}O^{18}O$ molecules. Table 3 shows that the ionic current ratios of masses 3 and 4 corresponding to HD and D_2 molecules and those of masses 34 and 36 corresponding to $^{16}O^{18}O$ and $^{18}O^{18}O$ molecules are constant in the course of the experiment within experimental error (±0, 10). It is obvious from consideration of the data in Table 3 that for oxygen, the relationship between different isotope molecules does not change and corresponds to that of the starting mixture. As for hydrogen a sharp shift of this relationship towards equilibrium is observed. However, the mixture does not attain equilibrium in the temperature range studied. Attention should be drawn to the fact that the relationship between different isotope molecules of hydrogen that is established in the reaction mixture during oxidation does not depend on temperature and pressure of working mixture.

TABLE 3

RATIOS OF IONIC CURRENT OF MASSES 3 AND 4 (J_3/J_4), 34 AND 36 (J_{34}/J_{36}) DURING OXIDATION OF MIXTURE 2 $(0.5D_2 + 0.5H_2) + (0.8\ ^{16}O + 0.2\ ^{18}O)_2$

In starting mixture $(J_3/J_4)^\circ = 0.6$, $(J_{34}/J_{36})^\circ = 2.6$. Equilibrium values $(J_3/J_4)^* = 1.9$ and $(J_{34}/J_{36})^* = 9.5$.

Condition of experiment	Time taken from beginning of experiment (min)	$\frac{J_3}{J_4}$	$\frac{J_{34}}{J_{36}}$
370°C	5	1.03	2.7
20 Torr			
350°C	5	1.05	2.6
10 Torr	10	1.03	2.7
320°C	5	1.15	2.6
20 Torr	11	1.02	2.5
	15	1.03	2.6
250°C	5	1.02	2.7
40 Torr	10	1.18	2.7
250°C	10	1.12	2.6
20 Torr	20	1.02	2.6
	30	1.01	2.6
250°C	5	1.0	2.6
12 Torr	10	1.06	2.6
	40	0.97	2.6

It should be recalled that the data in Table 3 were obtained when working with the mixture whose ^{18}O content was equal to that in the catalyst, i.e., these data do not afford a conclusion concerning the exchange between oxygen of the reaction mixture and that of the catalyst. To verify the possibility of the latter reaction occurring during oxidation we have carried out experiments with $2D_2 + {}^{16}O_2$ mixture and a catalyst sample "heavy" with oxygen and with $2H_2 + {}^{18}O_2$ mixture and a catalyst sample with a smaller ^{18}O content. These experiments gave negative results: during hydrogen oxidation no isotope exchange between oxygen in gas phase and that of the catalyst was observed. This suggests that the isotopic content of the resulting water should correspond to that of the reaction mixture. But isotope analysis of the water carried out in one of the experiments over "heavy" catalyst has shown the ^{18}O content in the water resulting from oxidation of small amounts of hydrogen to be close to that of the catalyst rather than to that of the reaction mixture. As already mentioned in the beginning, this may be accounted for by the ease of isotope exchange between the resulting water and the catalyst under the conditions of catalysis.

Discussion

Before discussing the results, let us sum up the main observations as follows:

1. The rate of hydrogen catalytic oxidation in the temperature range studied is higher than that of oxygen homomolecular exchange in the absence of H_2 and lower than that of HD-exchange in the absence of O_2.
2. The oxidation rate does not depend on the isotopic composition of the reaction mixture.
3. In the course of the reaction of hydrogen oxidation the relationship between various isotopic molecules of oxygen does not change and is the same as that in the starting mixture.
4. During the oxidation reaction HD molecules appear in the system, the stationary concentration of the molecules being independent of temperature and lower than that of equilibrium.

Heterogeneous catalytic oxidation of hydrogen proceeds through a number of stages, the most important being:

a. interaction between oxygen and the catalyst;

b. interaction between hydrogen and the catalyst;

c. surface reaction between hydrogen and oxygen.

Each of these stages falls into a number of elementary steps. For example, a molecule of oxygen introduced into the surface has been shown to undergo a number of transformations:

$$O_2(\text{gas}) \rightleftarrows O_2(\text{ads}) \rightleftarrows 2O^-(\text{ads}) \rightleftarrows 2O^{2-}(\text{s}),$$

the last one being its transformation into the oxide surface layer to form the oxygen surface ion O^{2-} (s).

By studying oxygen homomolecular exchange and HD-exchange kinetics one can obtain information concerning the rate of the limiting stages of oxygen and hydrogen interaction with catalyst in the absence of the second component of the oxidation reaction.

In considering the relationship between the hydrogen oxidation rate and the rates of these reactions, there appears, at first glance, to be a discrepancy: the rate of oxygen transformation is lower than that of the slowest step of oxidation reaction. This may be accounted for in the following way. For the reaction of oxygen isotope exchange to proceed, oxygen should undergo all the transformations similar to those considered above both in forward and reverse direction; whereas hydrogen and oxygen interaction evidently precedes the limiting stage of the oxygen transformation. As evidenced by most of the data on isotope exchange in the O_2-oxides systems, desorption is the limiting stage of the exchange (*2–4*). From the present data, one may conclude that, during hydrogen oxidation over the catalyst studied, hydrogen interacts with oxygen at one of the adsorption stages of the latter and the rate of further transformation is higher than that of oxygen desorption. The oxidation rate can be determined by:

a. The rate of oxygen transformation before interaction with hydrogen.

b. The rate of hydrogen and oxygen interaction or by the rate of further transformations of the products resulting from this interaction.

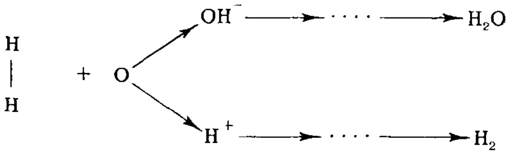
c. The rate of hydrogen transformation; if we take into account that HD-exchange rate in the absence of O_2 over the catalyst studied is considerably higher than that of oxidation the latter possibility seems to be unlikely. However, it may be the case because during hydrogen oxidation the rate of the exchange $H_2 + D_2 = 2HD$ becomes slower. It may be due to poisoning of the catalyst by O_2 or by the products of oxidation.

Let us next analyze the data obtained when working with the mixture with the nonequilibrium content of $^{16}O^{18}O$ and HD molecules. Consider the material balance of HD:

Its content in the starting mixture did not exceed a few percent and further may be neglected. Thus, the only source of HD molecules is the reaction of hydrogen and deuterium rearrangement, which proceeds simultaneously with hydrogen oxidation. Designate the rate of this reaction as W. Since no kinetic isotope effect was observed in the system one may write $W = K\ (C^*_{\mathrm{HD}} - C_{\mathrm{HD}})$, where K is the rate constant of the first order reaction, C^*_{HD} is the HD mole fraction under equilibrium, C_{HD} is the HD mole fraction during the oxidation reaction. HD molecules were withdrawn from the circulation loop only as a result of chemical reaction of oxidation proceeding in the system. Designate its rate as ω. If the latter is expressed as the number of hydrogen molecules entering the reaction in unit time, then the rate at which HD molecules are withdrawn from the system is obviously equal to ωC_{HD}. In the stationary state the inlet rate is equal to that of outlet and

$$K = \frac{\omega C_{\mathrm{HD}}}{C^*_{\mathrm{HD}} - C_{\mathrm{HD}}}.$$

From the experimental data obtained, it follows that the HD mole fraction during oxidation is ~ 0.25. The HD equilibrium concentration for the mixture used is ~ 0.5. Hence, $C_{\mathrm{HD}}/(C^*_{\mathrm{HD}} - C_{\mathrm{HD}}) \cong 1$. Thus, the rearrangement rate of hydrogen atoms in molecules (equal to HD-exchange rate constant) is equal to that of hydrogen catalytic oxidation. Since this equality is valid in the whole temperature and pressure range under study, one may conclude that the limiting step of these reactions is that of interaction between hydrogen and oxygen, hydrogen entering into the reaction in its molecular form, for example, according to the scheme:



Further transformations cannot limit the oxidation reaction, otherwise one should assume the most unlikely coincidence of temperature dependences of transformation of such different intermediates as OH^- and H^+. Similar considerations enable us to conclude that hydrogen or oxygen transformations preceding the stage of interaction between hydrogen and oxygen cannot be the limiting stage of hydrogen oxidation.

From the consideration of material balance of $^{16}O^{18}O$ molecules during oxidation, it follows that the rate of the reaction $^{16}O_2 + {}^{18}O_2 = 2\,{}^{16}O^{18}O$ is equal to zero. No oxygen isotope exchange between the phases has been observed either. As indicated by these data, oxygen enters the oxidation reaction in a form other than $O_{(s)}{}^{2-}$. One may assume that there is a small number of very active sites on the catalyst surface at which occur alternate reduction of $O_{(s)}{}^{2-}$ to H_2O and reoxidation of the surface by O_2 from gas phase. But such sites must also possess very high activity in reaction $^{16}O_2 + {}^{18}O_2 = 2\,{}^{16}O^{18}O$ and if $O_{(s)}{}^{2-}$ ion were the active form of oxidation, isotopic exchange between oxygen molecules should be observed in the system, because oxygen transformations do not limit the oxidation reaction.

CONCLUSION

1. The interaction between molecular hydrogen and oxygen has been shown to be the limiting stage of hydrogen oxidation reaction over lanthanum-cerium oxide catalyst.

2. The surface oxygen of the catalyst does not play an important role in the reaction of hydrogen oxidation.

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