JOURNAL OF CATALYSIS 28, 230–235 (1973)

Studies of Isotopic Exchange in Molecular Oxygen on Silica-Supported Vanadium Pentoxide at Low Temperatures

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Received April 7, 1972

The isotopic oxygen exchange reaction has been investigated on partially reduced silica-supported vanadium pentoxide between +20 and −140°C. The reaction occurs readily in this temperature range with an apparent activation energy of $E = 0.5$–1.0 kcal/mole. The reaction is suggested to occur according to the scheme: ${}^{16}O^-_{ads} + {}^{18}O^{18}O_{gas} \rightleftharpoons ({}^{16}O^{18}O^{18})^-_{ads} \rightleftharpoons {}^{18}O^-_{ads} + {}^{16}O^{18}O_{gas}$. Active intermediates are formed on the surface of the catalysts during the oxygen chemisorption. It is concluded that O^-_{ads} and $O_3{}^-{}_{ads}$ anion-radicals are active intermediates in the oxygen exchange reaction at low temperatures.

INTRODUCTION

At low temperatures isotopic exchange in molecular oxygen $O^{16}O^{16} + O^{18}O^{18} \rightleftharpoons 2O^{16}O^{18}$ has been studied over a number of oxides: ZnO, NiO, γ-Al_2O_3, rare earth oxides, etc. (*1*, *2*). This reaction is the simplest one in which molecular oxygen participates. Its study may give information about the nature of the oxygen intermediates adsorbed on the surface of oxide catalysts. For instance, hypotheses about dissociative oxygen adsorption during isotopic exchange and the formation of either three or four-membered oxygen complexes have been proposed. However, the real mechanism of the reaction is still unknown. Another interesting feature of this reaction is the small activation energy (usually less than 5 kcal/mole) and the high reaction rate even at low temperatures.

In the present work the low temperature isotopic oxygen exchange has been studied on slightly reduced silica-supported vanadium pentoxide. This catalyst was chosen because the properties of paramagnetic oxygen radicals $O_2{}^-$ and O^- adsorbed on reduced V_2O_5/SiO_2 have been studied in detail in our laboratory by Shvets, Vorotinzev and Kazansky (*3*, *4*). It thus seemed interesting to try to discover whether these species do act as intermediates in the isotopic exchange reaction.

EXPERIMENTAL METHODS

The apparatus used in this work allowed measurements of both the kinetics of isotopic exchange and the ESR spectra of adsorbed oxygen species for the same sample. The kinetics of isotopic exchange were studied in a static system at an oxygen pressure of 0.2–0.3 Torr. The nonequilibrium mixture of oxygen isotopes used in this study contained 13% at O^{18}. Isotopic analysis was carried out using a quadrupole mass spectrometer with a pressure in the ion chamber of $\sim 2.10^{-7}$ Torr. During the experiment the oxygen pressure above the sample did not change more than 2%. The rates of isotopic exchange in molecular oxygen were calculated from the following equation (*5*):

$$k_e = -\frac{N_0}{\tau \cdot s} \ln \frac{C_{34}{}^* - C_{34}{}^t}{C_{34}{}^* - C_{34}{}^0},$$

where N_g is the total number of oxygen molecules in the gas phase, τ = time, s = surface area of V_2O_5 on the silica gel (the surface area of V_2O_5 on silica gel was calculated with assumption of a monolayer coverage and was about 10 m²/g), C_{34}^*, C_{34}^0, C_{34}^t = the concentrations of $^{16}O^{18}O$ at equilibrium, at the beginning and at time t, respectively. The kinetics of exchange were well described by this equation in all our experiments.

The V_2O_5/SiO_2 samples were prepared as described previously (*3*). The catalyst samples (~80 mg) were placed in ampoules for ESR measurements and heated in oxygen (100 Torr) for an hour at 500°C. They were then evacuated to 10^{-5} Torr and reduced in hydrogen (30–40 Torr) for 15 min and finally pumped off at 500°C to 10^{-5} Torr. The vanadium contents in the catalysts were either 1 or 2.4% by weight.

ESR spectra were taken using an X-band spectrometer.

RESULTS AND DISCUSSION

The oxidized silica-supported vanadium pentoxide does not catalyze isotopic exchange at room temperature. After reduction in hydrogen or *in vacuo* at 500°C the exchange occurs with a high rate at room temperature and below while the activity slowly decreases (Fig. 1). After the same treatment silica gel without vanadium pentoxide does not catalyze isotopic exchange. The addition of H_2 and CO to the reaction mixture at any moment completely inhibits the exchange reaction. The activity, however, is restored to the initial value after the catalyst has been reduced *in vacuo* or in hydrogen at 500°C. The exchange rate depends slightly on temperature with apparent activation energy of E = 0.5–1.0 kcal/mole in the range +20 to −140°C.

After the addition of oxygen to partially reduced V_2O_5/SiO_2 at room temperature and below a transfer of electrons from V^{4+} ions to oxygen molecules occurs (*3*, *4*). As a result anion-radicals O^- and O_2^- ($\sim10^{17}$ g^{-1}) are formed (Fig. 2a). At room temperature the concentration of O^- and O_2^- slowly decreases. The O_2^- concentration decreases more rapidly during the first 15 hr after the addition of oxygen and then remains constant (see Fig. 1). After

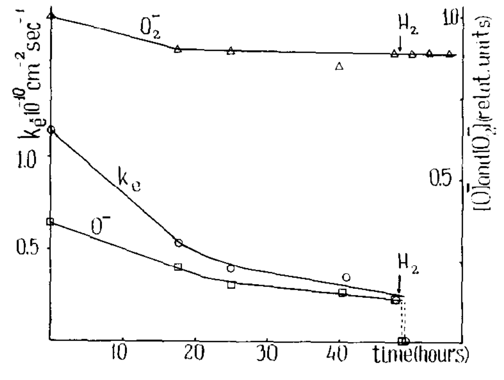

FIG. 1. Effect of hydrogen addition on the rate of isotopic exchange (K_e) and the concentrations of O^- and O_2^- at 20°C. The moment of injection of H_2 (p = 20 Torr) into the ampoule is marked by the arrows.

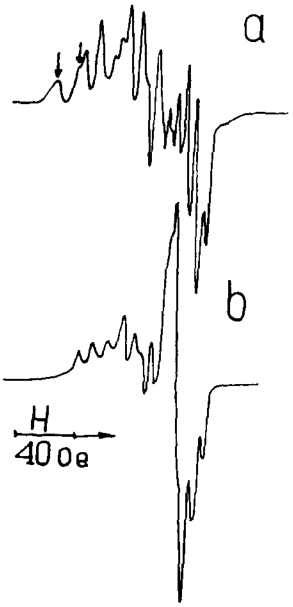

FIG. 2. (a) ESR spectra of O^- and O_2^- on V_2O_5/SiO_2 formed by the room temperature reaction of O_2 with V^{4+} ions. The nonoverlapping lines of O^- are marked by the arrows. (b) Spectrum of the same sample after adsorption of a small amount of O_2 at −196°C. Spectra were recorded at −196°C.

addition of H_2 or CO to the catalysts O^- ions disappear from the ESR spectra and the isotopic exchange rate drops drastically. At the same time the concentration of O_2^- ions remains unchanged (Fig. 1).

Addition of H_2 at room temperature to the reduced samples before the oxygen treatment, followed by evacuation, affects neither the exchange rate nor the O^- and O_2^- ion concentration. This fact means that the active centers on which isotopic exchange proceeds are formed only after the addition of oxygen to the reduced V_2O_5/SiO_2. Thus the inhibiting effect of H_2 or CO is only apparent after such active centers have been formed.

From the results shown in Fig. 1 one may conclude that the anion-radicals O_2^- do not take part as active intermediates in isotopic exchange. On the other hand alteration of the O^- concentration does lead to a change in the exchange rate (Fig. 1). Therefore, isotopic exchange may proceed according to a mechanism involving O^- and possibly the formation of O_3^- as an intermediate:

$$ {}^{16}O_{ads}^- + {}^{18}O^{18}O_{gas} \rightleftharpoons ({}^{16}O^{18}O^{18}O)_{ads}^- \rightleftharpoons {}^{18}O_{ads}^- + {}^{16}O^{18}O_{gas}. \quad (1) $$

Since O_3^- is a paramagnetic species, an attempt was made to detect it by ESR. However, at room temperature no new signals are observed after the addition of O_2 to the sample containing adsorbed anion-radicals O^- and O_2^-. On the other hand, adsorption of a small amount of oxygen, which does not lead to considerable line broadening at −196°C, results in the disappearance of lines belonging to O^- and the appearance of a new signal without hyperfine structure (Figs. 2b). A similar but more intense signal is obtained after the addition of oxygen to the samples containing only adsorbed O^- (Fig. 3b).* A weak signal belonging to O_2^- is simultaneously observed. The spectrum in Fig. 3c is the result of subtraction of the spectrum of anion-radicals O_2^- from the spectrum in Fig. 3b. The g-values of the new signal are $g_\parallel \cong 2.017$ and $g_\perp = 2.001$. Addition of oxygen at −196°C to the samples containing only $O_2^-{}_{ads}$ does not result in the appearance of any new ESR signals.

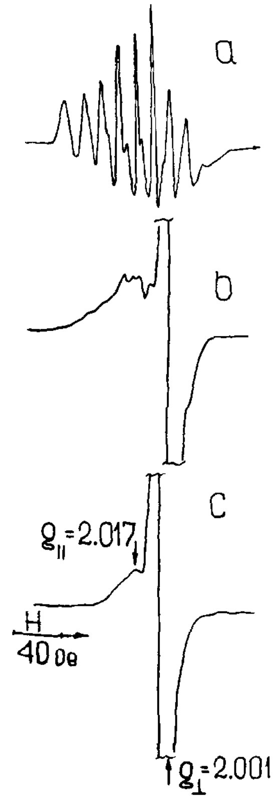

FIG. 3. (a) ESR spectrum of O^- on V_2O_5/SiO_2 formed by the room temperature reaction of N_2O with V^{4+} ions. (b) Spectrum of the same sample after adsorption of a small amount of O_2 at −196°C. (c) Spectrum obtained as a result of subtracting the O_2^- spectrum from the spectrum (b). Spectra (a) and (b) were recorded at −196°C.

The intensity of ESR signals (Figs. 2b and 3b) does not change between −196 and −150°C for a long time. Increasing the temperature from −140 to +20°C with simultaneous evacuation of the excess oxygen results in the disappearance of this signal and the original spectrum of O^- (Fig. 2a) is completely restored. Repeated addition of oxygen at −196°C again results in the disappearance of the O^- spectrum and the spectrum in Fig. 2b is ob-

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* In these samples anion-radicals O^- were obtained by adsorption of N_2O at room temperature (*4*).

served. These procedures can be repeated many times.

It is thus clear that the disappearance of O^- and the appearance of a new signal when oxygen is present at low temperatures is connected with formation of O_3^- which decomposes when temperature is elevated. At room temperature the concentration of these species is probably too small for ESR detection.

It should be noted that the *g*-values of adsorbed O_3^- obtained from Fig. 3c differ from that reported for O_3^- on the surface of MgO (*6*). This discrepancy is probably due to the difference in binding mode of these radicals with the surface adsorption centers in both cases.

O_3^- anion-radicals have an essentially different reactivity from O^-. It has been shown earlier (*4*) that O^- radicals react rapidly with H_2 even at −196°C. For example, at $p_{H_2} = 5$ Torr the concentration of O^- decreases to one-fifth after 3 min. The rate of isotopic exchange for this sample measured at room temperature also decreases to about one-fifth of the original value. On the other hand, anion-radicals O_3^- are stable in a hydrogen atmosphere (5 Torr) at −196°C and their concentration does not change appreciably for several minutes. In this case hydrogen does not affect the isotopic exchange rate either. (The concentration of O_2^- remains constant in all these experiments.) Undoubtedly these experiments confirm the conclusion that isotopic exchange proceeds via the formation of O_3^- as intermediates.

If the isotopic exchange reaction really proceeds according to scheme (1), the heterophase equilibration must be observed during the reaction, i.e., O^-_{ads} should be enriched by ^{18}O and at the same time the concentration of ^{18}O in the gas phase should decrease. However, in the experiments described above no such changes have been found since the amount of O^-_{ads} on the surface of the sample was two orders of magnitude smaller than that of oxygen molecules in the gas phase. Thus special experiments were performed to try to discover a heterophase equilibration with a larger amount of sample (1.0 g) but still using the same system. The procedure was as follows. Oxygen (p = 20–40 Torr) of natural isotopic composition was admitted to partially reduced V_2O_5/SiO_2 and after exposure for 1 hr evacuated to 10^{-6} Torr. The equilibrated mixture of oxygen isotopes ($p \approx 0.3$ Torr) containing 39% at. ^{18}O was then added and the sample was kept under oxygen for 1 hr followed by evacuation to 10^{-6} Torr. Then the oxygen of natural isotopic composition was added (p = 0.2 Torr) and the content of ^{18}O in the gas phase was analyzed after certain time intervals. The results given in Table 1 (sample A) show that the ^{18}O content in the gas phase increases.

TABLE 1

THE HETEROPHASE EQUILIBRATION ON V_2O_5/SiO_2, CONTAINING ADSORBED O^- AND O_2^-

V_2O_5/SiO_2 with adsorbed O^- and O_2^- (sample A)[a]		V_2O_5/SiO_2 with adsorbed O_2^- (sample B)[a]	
Time (min)	% ^{18}O ± 0.05	Time (min)	% ^{18}O ± 0.05
0	0.2	0	0.2
1	0.4	1	0.3
2	0.8	2	0.7
4	1.1	4	0.8
8	1.4	8	1.1
15	1.6	15	1.3
26	1.8	26	1.4
36	2.0	33	1.4
46	2.1	45	1.6
50	2.1	50	1.6

[a] Samples containing 2.5 % V_2O_5 by wt were used.

Similar experiments were carried out with another sample (sample B), containing only anion-radicals O_2^- (O^- ions were eliminated by hydrogen treatment at room temperature). The data are shown in Table 1.

The data of Table 1 demonstrate that the heterophase equilibration takes place both on sample A and on sample B, but to a smaller degree on sample B than on sample A. Since, as shown above, the homophase exchange on the samples of V_2O_5/SiO_2 containing only $O^-_{2\,ads}$ did not proceed, it seems that the heterophase equilibration on sample B is due to following reactions:

$$({}^{16}O^{16}O)_{ads}^{-} + {}^{18}O^{18}O_{gas} \rightleftarrows ({}^{18}O^{18}O)_{ads}^{-} + {}^{16}O^{16}O_{gas},$$

$$({}^{16}O^{16}O)_{ads}^{-} + {}^{18}O^{16}O_{gas} \rightleftarrows ({}^{18}O^{16}O)_{ads}^{-} + {}^{16}O^{16}O_{gas}. \quad (2)$$

These reactions result in the replacement of $({}^{16}O^{18}O)^{-}_{ads}$ by oxygen molecules of the other isotopic composition without dissociation of O–O bonds.

On sample A both reactions (1) and (2) proceed and therefore the final content of ^{18}O in the gas phase is greater than that for sample B. The percentage ^{18}O in the gas phase corresponds approximately to the ratio of O^- and O_2^- on the V_2O_5/SiO_2 surface ($[O^-]/[O_2^-] \approx 1{:}3$) determined from ESR spectra. It should be emphasized that no change in the ^{18}O content of the gas phase was observed over the surface V_2O_5/SiO_2 in the absence of O^- and O_2^- species. All these results may be considered as support for the reaction mechanism proposed above.

It is of interest to discuss probable reasons for the small activation energy of the isotopic exchange reaction. In Fig. 4a the energy level diagram for the formation and decomposition of O_3^- ions, based upon literature data (7), is shown. In the gas phase the heat of formation of the ozone molecule from an oxygen atom and O_2 is 1.1 eV. Since the electron affinity of the O atom is 1.5 eV and that of O_3 is 2.9 eV, the heat of formation of O_3^- from O_2 and O^- is 2.5 eV. This value is high enough to prevent the decomposition of O_3^- at low temperatures and thus it is reasonable to expect that the isotopic exchange reaction would proceed with a very low rate. Probably the main thing which may facilitate the decomposition of O_3^- species on the surface is the much greater chemisorption heat (Q_1) for O^- ions as compared to that (Q_2) for O_3^-. In this case the heat of formation for O_3^- adsorbed ions (and consequently the activation energy of their decomposition) decreases strongly (Fig. 4b) and so the isotopic exchange reaction may occur even at low temperatures.

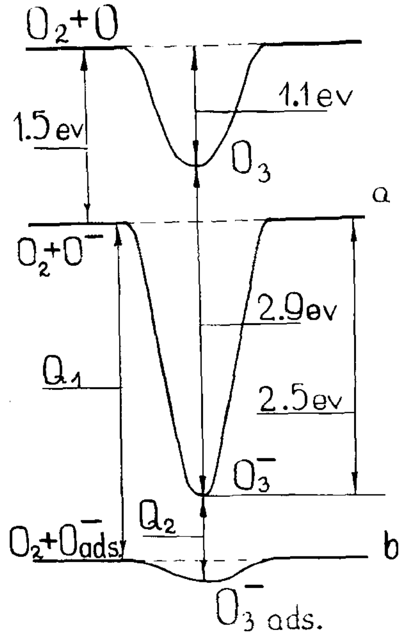

FIG. 4. Energy level diagram for the formation of O_3^- ions: (a) in the gas phase and (b) on the surface.

Thus the results of the simultaneous study of the kinetics of oxygen isotopic exchange on V_2O_5/SiO_2 and ESR investigation of the oxygen intermediates during the reaction at low temperatures strongly suggest that this reaction proceeds through the formation and dissociation of anion-radicals O_3^-. We suggest that in order to act as intermediates O_3^- species have to satisfy certain demands. First of all, it is necessary that O–O bonds in the O_3^- complexes must be equivalent and secondly these complexes have to dissociate easily under the conditions of reaction.

ACKNOWLEDGMENTS

The authors are indebted to Dr. G. V. Antoshin for helpful discussions and to Dr. M. F. O'Connor for his help in translation.

REFERENCES

1. BORESKOV, G. K., AND KASATKINA, L. A., *Usp. Khim.* **37**, 1462 (1968).
2. NOVAKOVA, J., *Catal. Rev.* **4**, 77 (1970).
3. SHVETS, V. A., VOROTINZEV, V. M., AND KAZANSKY, V. B., *J. Catal.* **15**, 214 (1969).
4. SHVETS, V. A., VOROTINZEV, V. M., AND KAZANSKY, V. B., *Kinet. Katal.* **10**, 356 (1969).
5. MUZIKANTOV, V. S., POPOVSKY, V. V., AND BORESKOV, G. K., *Kinet. Katal.* **5**, 624 (1964).

6. TENCH, A. J., AND LAWSON, T., *Chem. Phys. Lett.* **7**, 459 (1970). WILLIAMSON, W. B., LUNSFORD, J. H., AND NACCACHE, C., *Chem. Phys. Lett.* **9**, 33 (1971).
7. VEDENEEV, V. I., GURVICH, L. V., KONDRATIEV, V. N., MEDVEDEV, V. A., AND FRANKEVICH, E. L., "Energies of Bond Dissociation, Ionization Potentials and Affinities to Electron," Academy of Science Issue, Moscow, 1962.