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# ESR Study of Electron Transfer to Oxygen Adsorbed on Supported Catalysts Containing Molybdenum and Vanadium

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Paramagnetic species which appeared upon low-temperature adsorption of oxygen on the surface of partially reduced Mo/MgO, V/MgO, $Mo/Al_2O_3$, and $V/Al_2O_3$ catalysts were studied. The results show that on chemisorption a transfer of electron from the supported atoms to molecules $O_2$ take place and that the appearing $O_2^-$ species are stabilized on the ions of host lattices or on supported ions depending upon the temperature of the experiments.

Study of complex formation at the surface of transition metal solid oxides, specifically that accompanied with charge transfer, lead to certain hypotheses on the mechanism of redox reactions catalyzed by these oxides (*1*). It is often believed that redox reactions involve two metal atoms at the crystal surface. Either these atoms change their valence in the course of adsorption, or there occurs electron transfer through the catalyst crystalline lattice.

Adsorption on transition metal ions in low concentrations, supported by an inert matrix, seemed to be most convenient for investigation of electron transfer on an individual atom, since it ruled out charge transfer through the oxide lattice. Mo and V ions on MgO and $\gamma$-$Al_2O_3$ were chosen for such investigation.

Complex signals exhibited by transition metal ions in different valence and coordination states were observed earlier in ESR spectra of partially reduced Mo/MgO, V/MgO, $Mo/Al_2O_3$ and $V/Al_2O_3$ samples (*2-4*). For instance, a spectrum of $Mo^{5+}$ ions from the molybdenum bulk and signals from at least two forms of surface molybdenum (*3*) are exhibited by the Mo/MgO sample; the V/MgO sample shows $V^{2+}$, $VO^{2+}$, $V^{4+}$ signals, a part of vanadium ions being stabilized as pairs ($VO^{2+} \ldots V^{5+}$) (*4*). Certain other forms of transition metal ions are seemingly not observed by the ESR technique.

This investigation concerns oxygen adsorption on MgO and $\gamma$-$Al_2O_3$ with Mo and V ions.

## EXPERIMENTAL METHODS

Samples of MgO and $\gamma$-$Al_2O_3$ were prepared from hydroxides precipitated with ammonia from nitrates, with subsequent decomposition at 500°C in air, and sintering at 1000–1100°C in air for 1–2 hr. The surfaces obtained appeared to be 57 and 55 $m^2/g$, respectively. The V and Mo ions were deposited by impregnation of the adsorbents with aqueous solutions of ammonia salts. The samples were dried at 80–90°C and sintered in air at 550–600°C. The concentration of $V^{5+}$ ions calculated for the initial surface was $(1 \div 10)10^{13}$ ions/cm$^2$ and that of $Mo^{6+}$ was $(0.1 \div 10)10^{13}$ ions/cm$^2$. Thermovacuum treatment of the samples was carried out for 4 to 12 hr at 500–520°C and $P < 10^{-5}$ Torr. Then a part of the samples was reduced with hydrogen at the same temperature and $P_{H_2} = 50$ Torr, and the samples were degassed for 1 hr. The ESR spectra were obtained at 77°K using the EPR-2M spectrometer with $\lambda = 3.2$ cm. Fast cooling was ensured by introducing He at $P = 40$ Torr. Oxygen was adsorbed from dry air, or else electrolytic $O_2$ was used. The hydrogen used was electrolytic. The $g$-factors were determined relative to the HFS components of $Mn^{2+}$ impurity ions or to the F-center signals in quartz.

## RESULTS AND DISCUSSION

Adsorption of oxygen on Mo/MgO and Mo/$Al_2O_3$ at 25°C results in the appearance of anisotropic ESR signals with $g_1 = 2.070$; $g_2 = 2.009$; $g_3 = 2.001$; and $g_{\parallel} = 2.035$; $g_{\perp} = 2.009$ for MgO and $Al_2O_3$, respectively (Fig. 1). The signal intensity increases with the concentration of Mo ions and with degree of reduction of samples. After adsorption of oxygen the surface $Mo^{5+}$ signal intensity essentially increases for both catalyst. This seems to be accounted for either by predominant oxidation of low-valence Mo ions to $Mo^{5+}$ or by interaction of $O_2$ with paired $M^{5+} \ldots Mo^{5+}$ ions.

A similar anisotropic signal with $g_1 = 2.070$; $g_2 = 2.009$; and $g_3 = 2.001$; as well as weaker anisotropic lines with $g_{\parallel} = 2.080$ and $g_{\perp} = 2.009$, are observed for V/MgO under the same conditions. The species exhibiting these signals are stable up to 150°C both supports. Heating of the samples to a temperature over 150°C results in disappearance of the oxygen signal and in weakening of the surface molybdenum signals.

The parameters of the signal appearing upon adsorption of oxygen on V/MgO and Mo/MgO virtually coincide with those of the $O_2^-$ radical anion obtained by Lunsford and Jayne (*5*) for samples of pure magnesium oxide irradiated with X-rays. A signal from adsorbed $O_2^-$ radical ions resembling that from Mo/$Al_2O_3$ obtained here was observed earlier upon adsorption of $O_2$ on $Al_2O_3$ under $^{60}Co$ irradiation (*6*).

It was assumed from the value of the $g$-factor anisotropy (*5, 6*) that $O_2^-$ stabilized on 2- and 3-charged cations of MgO and $Al_2O_3$ respectively, since $\Delta_g = g_{\parallel} - g_e$ for $O_2^-$ must decrease linearly with the relevant cation charge (*7, 8*). This leads to the conclusion that the signals appearing upon adsorption of oxygen on V/MgO, Mo/MgO, and Mo/$Al_2O_3$ at 25°C are due to the $O_2^-$ radical ions on $Mg^{2+}$ and $Al^{3+}$. (With V/$Al_2O_3$ a decrease in the V(IV) signal was only observed under these conditions, and no new lines appeared.)

The regularity observed in (*7, 8*) was observed both for adsorption of oxygen on individual oxides (*4, 5, 9*) and for supported cations of a charge close to or the same as that of the support cations (*10, 11*), and it cannot be said a priori whether this regularity will hold for adsorption of

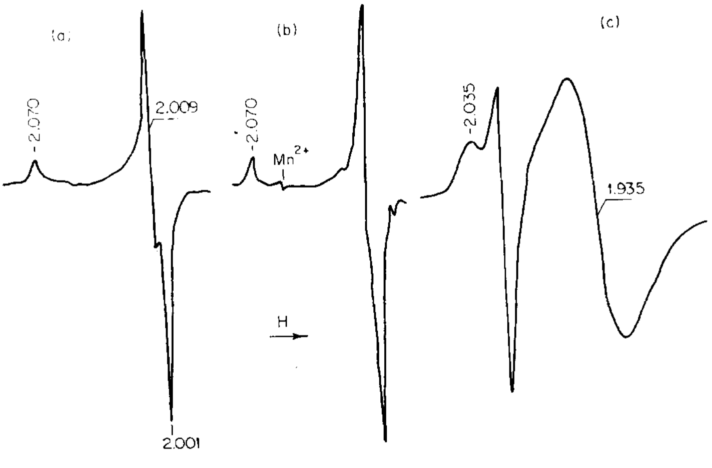


FIG. 1. Adsorption of $O_2$ on Mo/MgO, V/MgO, and Mo/$Al_2O_3$ at 25°C: spectra of $O_2^-$ on: Mo/MgO (a); V/MgO (b); and Mo/$Al_2O_3$ (c).

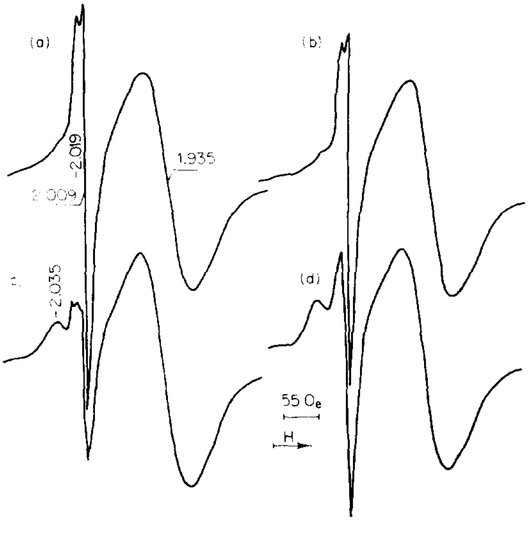
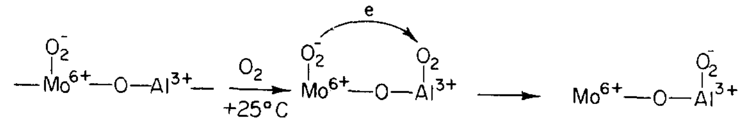


FIG. 2. Adsorption of $O_2$ on $Mo/Al_2O_3$: initial spectrum of $O_2^-$ adsorbed at 77°K (a); spectrum of the same sample after heating in vacuum up to 25°C (b); after heating in air up to 25°C (c); heating in $O_2$ to 100°C.

$O_2$ on all supported systems. It might fail in the case of impurity ions of a valence essentially different from that of the lattice ion, due to the effect of the support field. For instance, Lunsford and Jayne (*5*) ascribes the small change in the $g$-factor anisotropy of the $O_2^-$ radical ion when passing from ZnO to MgO to the effect of the support field. From this standpoint the results in (*10*, *11*) are not characteristic in view of the close charges of supported ions and of the lattice cations. However, the regularity holds for adsorption of $O_2$ on zeolites with cations of different valences (*7*, *12*).

The possibility of determining the site of $O_2^-$ stabilization on the cation of host lattice or on an impurity ion from the $g$-factor anisotropy was found in investigating adsorption at 77°K. Under these conditions (Fig. 2a) signals with $g_\parallel = 2.019$ and $g_\perp = 2.008$ are exhibited by $Mo/Al_2O_3$ (the same but considerably weaker signals were observed at room temperature) and signals with $g_\parallel = 2.035$ and $g_\perp = 2.009$ were absent. The $g$-factor anisotropy for these signals is that of the $O_2^-$ radical ion on a cation of a +5 or +6 charge. A similar signal was obtained (*13*) for adsorption of $O_2$ at 25°C on $Mo/SiO_2$ and $Mo/Al_2O_3$ samples at a considerable surface coverage with Mo ions (at a 5 to 10 wt % of molybdenum). This form of adsorbed oxygen is stable in He up to 100°C. However, on admission of oxygen at 25°C the signal intensity decreases and there appears a new line with $g_\parallel = 2.035$ and $g_\perp = 2.009$ due to the radical anion $O_2^-$ on $Al^{3+}$ (Fig. 2c). The narrow signal disappears only after heating of the sample in oxygen to 100°C. The intensity of the molybdenum surface ion signals remains unchanged. It seems that at room temperature $O_2^-$ stabilized on $Mo^{6+}$ is capable of transferring its electron to the adsorbed neutral oxygen molecule that becomes stabilized on $Al^{3+}$ in the form of $O_2^-$. A possible scheme of this process is:



$$\overset{O_2^-}{\overset{|}{-Mo^{6+}}}-O-Al^{3+}- \xrightarrow[+25°C]{O_2} \overset{O_2^-}{\overset{|}{Mo^{6+}}}-O-\overset{O_2}{\overset{|}{Al^{3+}}} \longrightarrow Mo^{6+}-O-\overset{O_2^-}{\overset{|}{Al^{3+}}}$$

Things are considerably more complicated with adsorption of $O_2$ on V/MgO and Mo/MgO at 77°K. It results in appearance of a signal form $O_2^-$ on $Mg^{2+}$ (Fig. 3), its intensity is considerably higher than with adsorption of $O_2$ at 25°C. The lines with $g_\parallel = 2.080$ and $g_\parallel = 2.090$ also are considerably more intensive (oxygen stabilized on different facets of the MgO crystal might be responsible for these lines). There is an additional complex anisotropic signal from oxygen with $g_1 = 2.026$, $g_2 = 2.009$, and $g_3 = 2.003$ (Fig. 4), no HFS from $^{51}V$ nuclei being observed. Admission of $H_2$ at 77°K brings no change in the spectrum. Adsorbed radical ions $O^-$ rapidly disappear at 77°K in the presence of oxygen (*14*).

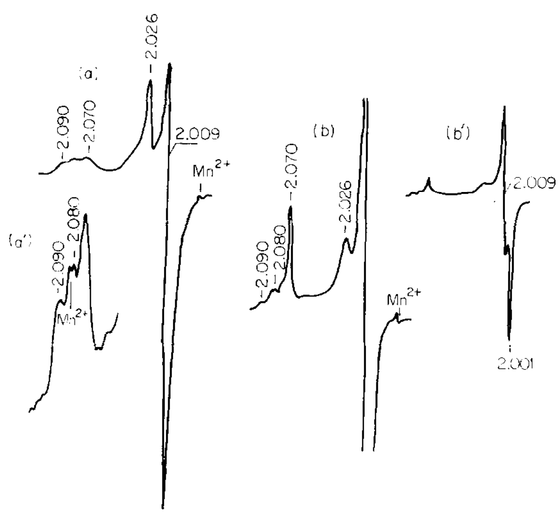


FIG. 3. Adsorption of $O_2$ on Mo/MgO and V/MgO at 77°K: $O_2^-$ on Mo/MgO (b); scale enlarged for the $g_\parallel$ region (b′); $O_2^-$ on V/MgO (a); scale enlarged for the $g_\perp$ region (a′).

Thus, all signals observed upon oxygen adsorption seem to be due to various forms of $O_2^-$.

However, the $g$-factor anisotropy for a signal with $g_\parallel = 2.026$ cannot be used for location of the stabilization site, it can only be stated that this radical ion does not stabilize on $Mg^{2+}$. At the same time this radical seems to be connected with the donor ion, since heating of samples in vacuum to room temperature leads to disappearance of adsorbed oxygen which is responsible for this line and, in the case of Mo/MgO, to restoration of the signal from Mo(V) surface ions. Maybe the bonding with the donor ion is not direct here, but is realized through the lattice oxygen. A pair of impurity ions (Mo or V) might represent the adsorption center too, and then the HFS from $^{51}V$ nuclei can be absent in the case of V/MgO. The possibility of $O_2$ adsorption on paired centers has not been treated theoretically and it is not clear at present what will be the HF splitting accounted for by interaction of $O_2^-$ with two $^{51}V$ nuclei.

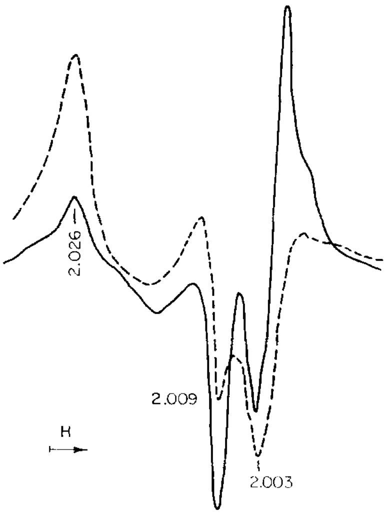


FIG. 4. Signal from the unstable form of $O_2^-$ on Mo/MgO and V/MgO was obtained by substracting the spectra observed after heating in vacuum to 25°C the samples with adsorbed oxygen from the spectra in Fig. 3a and b. (—) V/MgO; (..) Mo/MgO.

Note that the $O_2^-/Mg^{2+}$ signal intensity also decreases upon heating to room temperature, i.e., a part of $O_2^-$ adsorbed at 77°K might stabilize on $Mg^{2+}$ close to the supported ions. Consequently, distortion of the lattice would weaken the $O_2^-$–$Mg^{2+}$ bond and heating would result in desorption of oxygen from these centers with reduction of Mo (or V) ions to +5 (+4).

In this way, electron transfer with adsorption of oxygen on MgO might occur with participation of lattice ions adjacent to the adsorbed one.

The $Al_2O_3$ adsorption of $O_2$ at 77°K results in lesser intensity of V(IV) signals and in appearance of a weak signal with $g_\parallel = 2.024$ and $g_\perp = 2.008$ that superposes on one of the HFS components of V(IV) ions (Fig. 5). On heating to room temperature in vacuum, this signal disappears and the initial V(IV) signal intensity is not restored, probably due to dissociation of oxygen yielding nonparamagnetic species. Since the parameters of this signal are close to those of the "narrow" signal from oxygen on V/MgO, their nature may be the same.

Thus, adsorption of $O_2$ on Mo/MgO, $Mo/Al_2O_3$, V/MgO at room temperature results in formation of $O_2^-$ radical anions stabilized on the support lattice cations. It was found for $Mo/Al_2O_3$ that at 77°K

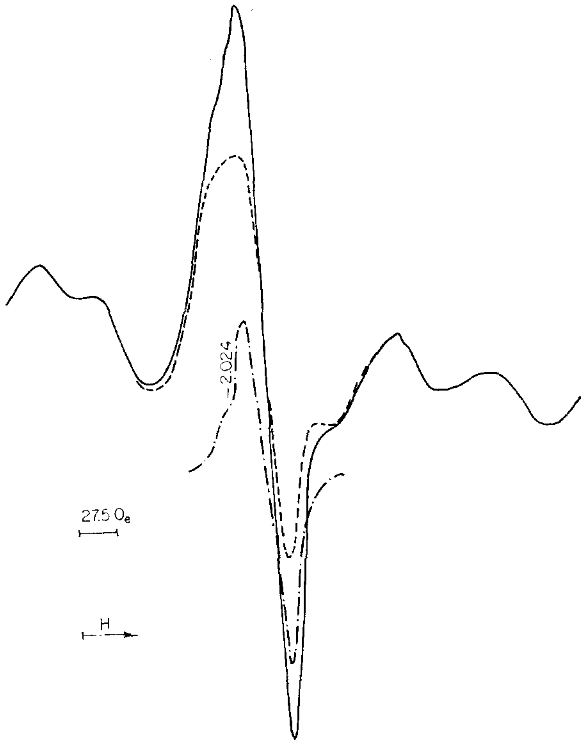


FIG. 5. Adsorption of $O_2$ on $V/Al_2O_3$ at 77°K: (—) summary spectrum of V(IV) ions and $O_2^-$; (. .) sample after heating to 25°C; (— ·) to the result of subtracting the latter from the former.

oxygen is adsorbed in the form of $O_2^-$ bonded with the supported ions. This form is stable up to 100°C in an inert medium such as He, and converts to the form $O_2^-$ on $Al^{3+}$ in an oxygen medium.

Low-temperature adsorption of oxygen on Mo/MgO and V/MgO results in stabilization on $O_2$ on the support lattice ions. It follows from thermal stability of this species that a part of radical anions $O_2^-$ are desorbed by heating in the form of $O_2$ and restore the amount of initial donor ions. It is suggested that the desorbing $O_2^-$ is that bonded with $Mg^{2+}$ ions adjacent to donor ions. Complex anisotropic signals (Fig. 3) stable at low temperature only were observed for both systems, along with the above-mentioned signals. These might be due to $O_2^-$ stabilized either on oxygen lattice ions adjacent to the supported donor ions or on the donor ions as such. It is not clear whether this form is an intermediate in the formation of $O_2^-$ stabilized on $Mg^{2+}$.

Adsorption of oxygen on $V/Al_2O_3$ both at 77°K and at room temperature does not result in formation of $O_2^-$ stabilized on the support lattice cations, but only in oxidation of donor ions.

The results obtained are evidence of electron transfer from supported donor ions to molecules of oxygen adsorbed on the support. This process might be due to migration of electrons over adsorbed oxygen molecules and/or to participation of the support lattice ions.

## REFERENCES

1. KRYLOV, O. V., Problemy *Kinet. Katal.* **13,** 141 (1968).
2. SPIRIDONOV, K. N., PARIISKII, G. B., AND KRYLOV, O. V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, in press.
3. SPIRIDONOV, K. N., PARIISKII, G. B., AND KRYLOV, O. V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, **11,** 2646 (1970).
4. SPIRIDONOV, K. N., PARIISKII, G. B., AND KRYLOV, O. V., *Kinet. Katal.*, in press.

5. LUNSFORD, J. H., AND JAYNE, J. P., *J. Chem. Phys.* **44**, 1487 (1966).
6. GEZALOV, A. A., ZHABROVA, G. M., NIKISHA, V. V., PARIISKII, G. B., AND SPIRIDONOV, K. N., *Kinet. Katal.* **9**, 462, 1968.
7. KASAI, P. H., *J. Chem. Phys.* **43**, 3322 (1965).
8. MIKHEIKIN, I. D., MASHCHENKO, A. I., AND KAZANSKII, V. B., *Kinet. Katal.* **8**, 1363 (1967).
9. VAN HOOF, J. H. C., AND VAN HELDEN, J. F., *J. Catal.* **8**, 199 (1967).
10. SHVETS, V. A., SARYCHEV, M. E., AND KAZANSKII, V. B., *J. Catal.* **11**, 378 (1968).
11. TARANAO, K., YOSHIDA, S., ISHIDA, S., AND DOI, Y., *Bull. Chem. Soc. Jap.* **42**, 1161 (1969).
12. WANG, K. M., AND LUNSFORD, J. H., *J. Phys. Chem.* **74**, 1514 (1970).
13. DUFUX, M., Thesis, Lyon, Institute de Catalyse, CNRS, 1968.
14. SHVETS, V. A., VOROTYNTSEV, V. M., AND KAZANSKII, V. B., *Kinet. Katal.* **10**, 356 (1969).