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Oxygen Anion–Radicals Adsorbed on Supported Oxide Catalysts Containing Ti, V and Mo Ions

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By ESR technique the formation of adsorbed O_2^- and O^- on Ti/SiO_2, V/SiO_2, Mo/SiO_2, $V/\gamma\text{-}Al_2O_3$, $V\text{-}K/SiO_2$, V/ZrO_2, V/MgO has been studied. The properties of adsorbed radicals are determined by valence state and coordination of surface transition metal ions. The very high reactivity of adsorbed O^- is discovered.

Supported oxide catalysts containing transition metal ions are known to be widely used in oxidation of organic substances with molecular oxygen. Therefore it seems interesting to study the state of the oxygen adsorbed on their surface.

The ESR measurements (*1–7*) have shown that the oxygen adsorption on *n*-semiconducting oxides and radiation chemisorption on dielectrics results in formation of the O_2^- adsorbed radicals. This technique appears to be attractive also for the studies of the state of the oxygen adsorbed on the surface of supported oxide catalysts. The investigation of such systems, in particular at a low concentration of a supported transition metal oxide, seems to be more advantageous than that of unsupported oxides since this permits one simultaneously to follow both the change of the valence state of the adsorption centers and the formation of the adsorbed oxygen radicals. Moreover, the structure of the adsorption centers of many supported transition metal oxides has been studied in some detail by spectroscopy, facilitating the interpretation of experimental results. Finally, the study of oxygen adsorption by catalysts on various supports reveals the dependence of formation of adsorbed oxygen radicals on coordination of transition metal surface ions.

This paper is concerned with the discussion of the experimental results, reported in part earlier (*8–14*), on the ESR studies of oxygen radicals adsorbed on the surface of partially reduced transition metal oxides supported on various carriers. An attempt has been made to study the influence on their formation and properties of both the nature of transition metal ions and that of the support. For this purpose partially reduced titanium, vanadium and molybdenum oxides supported on silica gel and vanadium pentoxide supported on SiO_2, $\gamma\text{-}Al_3O_2$, ZrO_2 and MgO have been used.

EXPERIMENTAL

The supported V- and Mo-containing samples were prepared by impregnation of appropriate supports by aqueous NH_4VO_3 and $(NH_4)_2MoO_4$ solutions. The Ti-containing samples were prepared by impregnation of silica gel by $TiCl_4$ hydrochloride solution. The samples were dried at 70–80°C and calcined in air for several hours at 500°C. Silica gel ($S = 500$ m^2/g), γ — Al_2O_3 ($S = 200$ m^2/g), ZrO_2 ($S = 30$ m^{2}g), and MgO ($S = 50$ m^2/g) were used as supports.

Before studying the adsorption of various molecules the samples were placed into 5 mm diameter quartz ampoules, heated for 1 hr in oxygen at 500°C, reduced with hydrogen for 20–30 min at 500°, and evacuated to 10^{-4}–10^{-5} Torr at the same temperature. Unless otherwise stated the ESR spectra were measured in the same ampoules at liquid-nitrogen temperature with a GES-3 BS-Q "GEOL" instrument in the X-band.

RESULTS AND DISCUSSION

a. O_2 and N_2O adsorption on TiO_2, MoO_3 and V_2O_5 supported on silica gel

After reduction of the samples their ESR spectra showed signals of paramagnetic Ti^{3+}, V^{4+}, and Mo^{5+} ions (*9–12, 15*). A V_2O_5 on silica gel catalyst containing 0.2–6 wt % of vanadium showed V^{4+} signals only at liquid nitrogen temperature. No V^{4+} signals were observed at room temperature due to fast spin-lattice relaxation. Therefore one may conclude that these ions are tetrahedrally coordinated. In MoO_3 on silica gel catalysts containing 0.2–6 wt % of Mo, two kinds of Mo^{5+} ions were formed: those in tetrahedral coordination observed only at liquid-nitrogen temperature, and molybdenyl $(Mo{=}O)^{3+}$ ions in a square-pyramidal coordination observed at any temperature.

The state of Ti^{3+} ions in Ti/SiO_2 system depends on the amount of titanium dioxide. With small amounts of titanium (0.2%) most of Ti^{3+} ions are in tetrahedral coordination. Its increase results in the appearance of Ti^{3+} ions of square-pyramidal coordination which prevail if titanium content exceeds 2 wt %. The coordination of surface transition metal ions in these systems is discussed in more detail (*9–12, 15*).

O_2 adsorption at room temperature on all of these partially reduced catalysts results in decreasing the intensity of ESR spectra of Ti^{3+}, V^{4+} and Mo^{5+} ions. Simultaneously there appear new intense narrower anisotropic lines at $g > 2$. As in the case of *n*-semiconductors this effect can be explained by electron transfer from surface transition metal ions to the adsorbed O_2 molecules which are known to be electron acceptors. The parameters of new signals are in accordance with those predicted for the adsorbed O_2^- anion-radicals (*16, 17*).

Let us consider each system separately.

Ti/SiO_2. The ESR spectrum of O_2^- anion-radicals formed on a Ti/SiO_2 catalysts containing 2% of titanium is an anisotropic line with three *g*-tensor values: $g_1 = 2.020 \pm 0.001$; $g_2 = 2.009 \pm 0.001$; $g_3 = 2.003 \pm 0.001$ (Fig. 1a). The form of the spectrum and its parameters are in good agreement with those for the O_2^- radicals formed on the unsupported titanium dioxide (*1, 2*). The O_2 adsorption at room temperature on a samples containing 0.2% of titanium produces a similar ESR signal, but with a different g_1 value ($g_1 = 2.026$; $g_2 = 2.009$; $g_3 = 2.003$) (Fig. 1b). Samples containing a mean amount of titanium (0.7%) produce both of these signals observable after oxygen adsorption.

The *g*-tensor parameters of the adsorbed O_2^- anion-radicals are known to depend on the electric charge of the adsorption center and symmetry of its electric field, a low

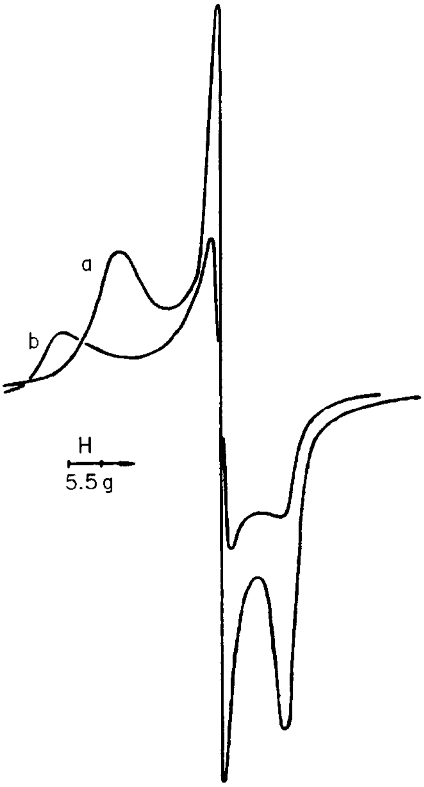

FIG. 1. ESR spectra of O_2^- anion-radicals adsorbed on Ti/SiO_2 samples containing a-2 wt %; b-0. 2 wt % of titanium.

field g-tensor value (g_1) being more sensitive to these characteristics (*16*, *17*). For the O_2^- anion-radicals stabilized on the positively charged centers with formal electric charge +1 the g_1 value is in the range of 2.07–2.14; with formal electric charge +2 it is about 2.05–2.07; and with charge +3 and higher it is smaller than 2.03. So far as the differences in the g_1 values of the O_2^- anion–radical ESR spectra arising after the oxygen adsorption on the samples of high and low titanium content are small, they seem to be due rather to the symmetry than to the different charge of the adsorption centers. The ESR signals with $g_1 = 2.026$ are likely to be produced by the O_2^- radicals adsorbed on the tetrahedrally coordinated titanium ions which are formed at a low concentration of the supported oxide. The ESR signals with $g_1 = 2.020$ are produced by the radicals adsorbed on titanium ions in a square-pyramidal coordination prevailing at higher concentration.

Essentially the same two types of O_2^- were observed on rutile and anatase in (*2*, *18*). We believe that this could be attributed to the similar structure of adsorption centers in supported and unsupported systems.

In order to verify if atomic O^- anion-radicals can form on the partially reduced Ti-containing samples we have studied the adsorption on this catalyst of N_2O molecules and their light induced dissociation. The N_2O adsorption at room temperature does not give rise to any new ESR signals, but the intensity of the Ti^{3+} spectra decreases. Irradiation of the samples with a mercury lamp at room temperature gives rise to a weak signal of the O_2^- anion–radicals. The N_2O adsorption at —78°C and subsequent irradiation of the samples at liquid-nitrogen temperature for 2–3 min with unfiltered uv-light give rise to an intense signal shown in Fig. 2a. This is a sum of a signal from O_2^- and an asymmetric line, with $g_\parallel = 2.011 \pm 0.001$ and $g_\perp = 2.002 \pm 0.001$. So far as this line disappears after the sample has been heated to —78°C it can be obtained after subtraction of the O_2^- signal, which does not change upon heating the samples (Fig. 2b), from the original spectrum (Fig. 2a, dotted line).

One can suggest that the signal shown in this figure is produced by the adsorbed O^- anion–radicals resulting from the following reactions:

$$N_2O \xrightarrow{h\nu} N_2 + O$$
$$O + Ti^{3+} \rightarrow [Ti^{4+}O^-]$$

Simultaneous formation of the adsorbed O_2^- radicals is likely due to the secondary reactions:

$$O + O \rightarrow O_2$$
$$O_2 + Ti^{3+} \rightarrow [Ti^{4+}O_2^-]$$

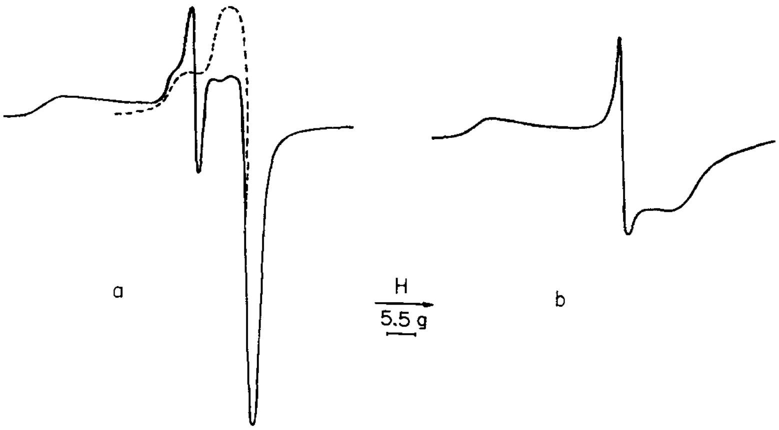

FIG. 2. ESR spectra of anion-radicals adsorbed on Ti/SiO_2: a-sum of O_2^- and O^- radicals; dotted line-O^- radicals; b-O_2^- radicals.

The adsorbed O^- radicals disappear upon heating the sample. This can be accounted for by their further transformation into the diamagnetic double-negatively charged oxygen of the oxide lattice.

V/SiO_2. Adsorption of a small amount of oxygen at —196°C on the surface of partially reduced V/SiO_2 samples (0.2–6% of V) gives rise to a complex signal with well-resolved hyperfine structure from ^{51}V nuclei. The detailed analysis of the spectrum (*9, 14*) gives the following parameters: $g_1 = 2.023$; $g_2 = 2.011$; $g_3 = 2.004$; $A_1 = 9.7$ gauss; $A_2 = 6.8$ gauss; $A_3 = 5.9$ gauss.

The g-tensor values and the conditions under which the signal was obtained allow the conclusion that it is produced by the adsorbed O_2^- anion–radicals. The hyperfine structure clearly indicates that the adsorption centers involve vanadium ions and the number of its components (eight) indicates that the adsorption proceeds on the isolated V^{4+} ions, i.e., according to the scheme:

$$V^{4+}_{tetr} + O_2 \rightarrow [V^{5+}O_2^-]$$

The calculation reported in (*19*) based on the values of the hyperfine splittings and values of g-tensor components shows the bond in the adsorbed complex to be partially covalent. This results from the partial transfer of both unpaired electron and electron pair of the O_2^- ion-radical to vacant orbitals of V^{5+} ion.

It should be noted that the adsorption of large amounts of oxygen at —196° gives rise to the dipole–dipole broadening of the components of the ESR spectra from the adsorbed O_2^- radicals. As a result the lines of the hyperfine structure in the high field part of the spectrum become overlapping. This may produce an impression that there is an additional singlet as has been assumed by the authors of (*20*). It should be pointed out that in contrast to the Ti/SiO_2 system that of V/SiO_2 produces the adsorbed O_2^- radicals of only one kind within the concentration range of vanadium 0.2–6 wt %.

On heating the V/SiO_2 samples with the oxygen adsorbed at —196 up to —78°C or higher the intensity of the ESR signal from the adsorbed O_2^- radicals decreases and additional lines appear. The adsorption of oxygen at —78° or at room temperature results in simultaneous formation of both O_2^- anion-radicals and paramagnetic oxygen species which are responsible for the second signal. If O_2 is adsorbed at a temperature as high as 350°C for 2–3 min only the latter is observable. This octet should be of the following parameters $g_\perp = 2.026$; $A_\perp = 14$ gauss. But we failed to determine $g_\parallel$ and $A_\parallel$. It seems however that $g_\perp > g_\parallel$ and $A_\perp \geqslant A_\parallel$, so far as one of the parallel components is observed at higher magnetic field (*9, 14*). The signal under discussion is assumed to be produced by the adsorbed O^- anion-radicals since its parameters are in good agreement with those predicted and experimentally observed for O^- stabilized in matrices (*21, 22*). This assumption is also supported by the fact that the same signal arises upon the adsorption of N_2O on V/SiO_2 at room or higher temperatures and a pressure of 10–50 Torr; the N_2O molecules decomposing according to:

$$N_2O + V^{4+} \rightarrow N_2 + [O^-V^{5+}].$$

Finally, the suggested interpretation of the ESR spectra is supported by the mutual transformations of the adsorbed O_2^- and O^- radicals at elevated temperatures.

The sequence of the formation of various adsorbed oxygen species during oxidation of the partially reduced V/SiO_2 could be presented as follows:

$$O^2_{gas} \rightarrow O^2_{ads} \rightarrow O_2^- \rightarrow 2O^- \rightarrow 2O^- ,$$

where O^{2-} is the oxygen of the oxide lattice. According to this scheme, the formation of the O_2^- anion-radicals would precede that of O^-. Therefore at low temperature the species stabilized on the surface would largely be O_2^- anion-radicals. At elevated temperature they would transform into the adsorbed O^- anion-radicals. These conclusions are in accordance with the above experimental data.

It should be emphasized that the O^-

radicals adsorbed on V/SiO_2 show not only high thermal stability but also high reactivity. As has been pointed out it was possible to observe their ESR spectra at temperatures as high as 300°C (*9*), *i.e.*, under conditions close to those of catalytic oxidation on vanadium catalysts. They instantly disappear, however, in the presence of hydrogen, methane and carbon monoxide at room temperature or even at lower temperatures. The O^- anion-radicals retain their high reactivity at temperatures as low as 77°K. At hydrogen pressure of 5.5 Torr they completely disappear in about 1.5 min. In the case of the reaction of the adsorbed O^- radicals with carbon monoxide at room temperature the formation of CO_2 was detected chromatographically (*23*). The high thermal stability of the O^- radicals on V/SiO_2 and their high reactivity shows that they could be involved as active intermediates in catalytic oxidation.

Mo/SiO_2. The adsorption of O_2 and N_2O on Mo/SiO_2 is similar to that on V/SiO_2 catalysts. The only difference is that the ESR spectra of the adsorbed oxygen species do not show hyperfine structure. Fig. 3a shows the ESR spectrum of the adsorbed O_2^- radicals with $g_1 = 2.018$; $g_2 = 2.010$; $g_3 = 2.004$. This was observed upon the adsorption of O_2 on the prereduced sample either at −196°C or at room temperature. Its parameters are in agreement with those reported in (*24*). The ESR spectrum from the tetrahedrally coordinated Mo^{5+} ions after oxygen adsorption decreases while that of the adsorbed O_2^- radicals appears but the amount of Mo^{5+} ions which form the molybdenyl bond with the oxygen of the catalyst lattice remains unchanged. Therefore one may conclude that the O_2^- anion–radicals would arise on the surface of the supported Mo/SiO_2 catalysts only in the coordination sphere of the tetrahedrally coordinated molybdenum ions.

The adsorption of N_2O at 100°C 10–50 Torr pressure gives rise to the ESR signal which is shown in Fig. 3b with $g_1 = 2.020$ and $g_2 = 2.006$. This is assigned to the adsorbed O^- anion–radicals. In the atmosphere of hydrogen at −196°C the intensity of this signal decreases. The intensity of the spectrum of O_2^- however does not change even at room temperature. Thus the reactivity of O^- and O_2^- adsorbed on Mo/SiO_2 is different in the same way as in the case of supported vanadium, the former being much more active.

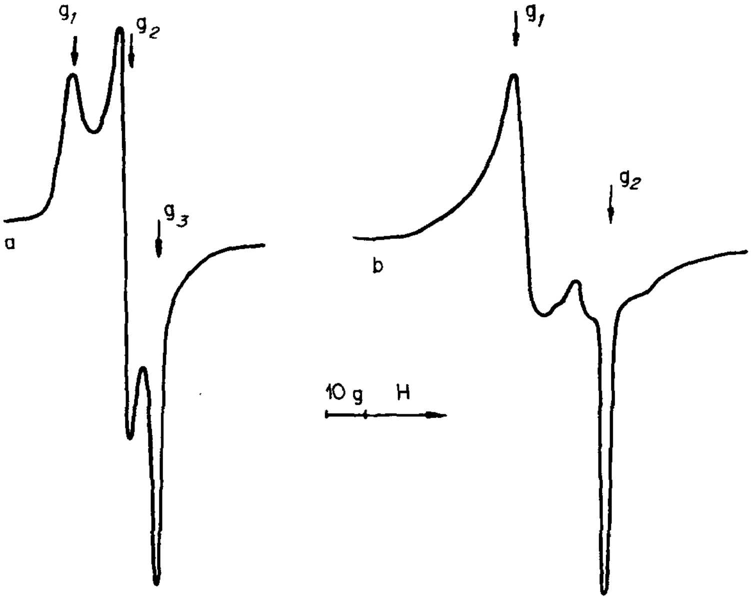

FIG. 3. ESR spectra of anion-radicals adsorbed on Mo/SiO_2: a-O_2^- radicals; b-O^- radicals.

b. Coordination effect of vanadium surface ions on the formation of adsorbed oxygen radicals

On supported V/SiO_2 catalysts, adsorbed oxygen anion–radicals are formed due to electron transfer from tetrahedrally coordinated V^{4+} ions to the O_2 molecules. It seemed interesting to establish if oxygen radicals could form upon the adsorption of O_2 on vanadium surface ions in other coordinations. Therefore we studied oxygen adsorption on γ-Al_2O_3, ZrO_2 and MgO supported vanadium catalysts and on K_2O doped V/SiO samples. In some experiments the coordinations of vanadium surface ions was changed also by adsorption of polar molecules.

The reduction and thermovacuum treatment of V/γ-Al_2O_3; V/ZrO_2; V/MgO and V–K/SiO_2 gives rise to formation of V^{4+} ions in the same way as in the case of silica gel. However, their coordination state is not tetrahedral. On γ-Al_2O_3 it is either a square-pyramid or an octahedron shortened due to formation of the vanadyl bond (*15*). A similar situation holds for K_2O doped vanadium catalysts (*23*). On the surface of ZrO_2 and MgO the coordination may be more complicated but most likely it would also be that of a shortened octahedron, however, more distorted (*13*).

Another difference between silica gel and other supports consists in the distribution of transition metal ions. On SiO_2 all of them are on the surface insofar as their ESR spectra are changed after adsorption of polar molecules (*10–12, 15*). For γ-Al_2O_3, ZrO_2 and MgO supported systems, solid solutions seem to be formed and adsorption of water or ammonia has almost no influence on ESR of V^{4+} (*10, 13, 15*). Properties of these systems with respect to oxygen free radical stabilization are also different.

The adsorption of O_2 on the partially reduced V/γ-Al_2O_3 (0.2–10 wt % of V) or V–K/SiO_2 (0.2–5 wt % of V; V:K = 1:1) in the temperature range of $-196 - +300$°C does not result in the formation of the O_2^- anion–radicals, nor were the O^- anion-radicals formed on these catalysts upon the adsorption of N_2O. This is likely to be accounted for by the fact that there are no tetrahedrally coordinated V^{4+} ions in these systems, but only vanadyl complexes $(V{=}O)^{2+}$ which are unable to donate electrons to oxygen.

This conclusion was confirmed independently in experiments where the tetrahedral coordination of the vanadium ions in the silica supported catalysts was brought to octahedral by adsorption of H_2O and NH_3 molecules at room temperature. This gave rise to the changes of ESR spectra of V^{4+} which corresponded to the transition from the tetrahedral to vanadyl configuration (*10, 15*). Oxygen adsorption on such $(V{=}O)^{2+}$ complexes does not result in O_2^- or O^- anion–radical formation. Moreover, if water or ammonia is adsorbed after oxygen then the already formed oxygen-containing $[V^{5+}O_2^-]$ and $[V^{5+}O^-]$ charge transfer complexes are destroyed and V^{4+} ions regenerated, however not in tetrahedral but in vanadyl coordination. The surface reaction in this case may be represented as follows:

$$V^{4+}_{tetr} + O_2 \rightarrow [V^{5+}O_2^-];$$

$$[V^{5+}O_2^-] + H_2O \rightarrow V^{4+}_{sq\,pyr} + O_2.$$

Upon adsorption of O_2 at room temperature on partially reduced V/ZrO_2 and V/MgO catalysts (1 wt % of V), the intensity of V^{4+} ESR signals decreases and simultaneously there appear new lines from the adsorbed O_2^- anion–radicals. If they are formed on V/ZrO_2 catalysts they do not show hyperfine splitting from V nuclei and have the following parameters: $g_1 = 2.032$; $g_2 = 2.009$; $g_3 = 2.003$. For V/MgO several types of adsorbed O_2^- are formed. None of them shows hyperfine splitting and they have g_1 value about 2.07–2.09. These g-tensor parameters are in agreement with those of O_2^- adsorbed on the surface of pure supports (*1, 3, 13*). The interesting feature is that if oxygen is adsorbed on pure ZrO_2 the intensity of the O_2^- ESR signal is two orders of magnitude lower than for V/ZrO_2, whereas for pure MgO the adsorbed O_2^- anion–radicals are formed only upon ultraviolet irradiation (*3*). Thus, the presence of V^{4+} ions on these supports would considerably facilitate the electron transfer to the adsorbed O_2 molecules.

The absence of hyperfine splitting and coincidence of *g*-tensor parameters of O_2^- for vanadium-containing systems with those for pure supports provides evidence that these species would stabilize not in the vanadyl complex coordination sphere, but on the defects characteristic of the surface of pure supports, such as Mg^{2+} or Zr^{4+} cations. On the other hand the decrease in the intensity of the ESR spectra from the V^{4+} ions upon oxygen adsorption provides evidence for the possibility of electron transfer from the transition metal ions via the MgO and ZrO_2 lattice to the stabilizing centers of the O_2^- anion–radicals. It should be pointed out that the same phenomenon was observed in (*25*) for the partially reduced molybdenum oxide supported on Al_2O_3. The mechanism of this effect is not completely clear, but it seems quite reasonable that even in the case of such insulating oxides as MgO and γ-Al_2O_3 the orbitals of the supported transition metal ions and those of the support cations would largely overlap. As a result surface energy bands are formed that may result in electron transfer characteristic of semiconducting solids.

CONCLUSIONS

The experimental data obtained in the present paper allow conclusions concerning different factors affecting the formation of the O_2^- and O^- anion–radicals adsorbed on the surface of the supported oxide catalysts.

The valence state of the transition metal surface ions and their reducing properties are primarily responsible for electron transfer from the adsorption center to the adsorbed molecules. For example, in the series of the isoelectronic ions with configuration $3d^1$-Ti^{3+}, V^{4+}, Cr^{5+}, the O_2^- anion–radicals are formed only for titanium and vanadium ions due to their reducing properties. No O_2^- anion–radicals are formed in the case of tetrahedral Cr^{5+} ions (*26*) that are known to have oxidizing properties.

The surface reducing properties of the catalysts are also responsible for the thermal stability of the adsorbed radicals. The O^- anion–radicals adsorbed on the surface of supported titanium catalysts are stable only at low temperature because Ti^{3+} ions readily give off their electrons to the oxygen radicals reducing them to the diamagnetic lattice O^{2-} ions. The O^- anion–radicals on the surface of the supported vanadium catalysts are much more thermally stable and can survive temperatures as high as 300°C due to poorer reducing properties of V^{4+} ions.

Another factor affecting the formation of the adsorbed oxygen radicals is the coordination of the transition metal surface ions for which, in the first place, the crystalline structure of a support is responsible. In the case of the silica gel supported catalysts with tetrahedrally coordinated titanium, vanadium, and molybdenium ions, the electron transfer can readily proceed within the first coordination sphere of the adsorption centers. For $(V{=}O)^{2+}$ and $(Mo{=}O)^{3+}$ complexes the adsorbed anion–radicals of oxygen would not stabilize in the first coordination sphere. Yet, if the electron transfer through the support lattice is possible, then anion–radicals stabilized on the support cations would form.

It should be pointed out that in the case of unsupported TiO_2, V_2O_5 and MoO_3, it is only for TiO_2 that the O_2^- anion–radicals are formed (*1*, *2*). On the surface of the partially reduced V_2O_5 and MoO_3, no O_2^- and O^- anion–radicals have been found in this study, nor was it reported in (*5*) for MoO_3, although V^{4+} and Mo^{5+} ions are formed in these systems. The different behavior of the supported and non-supported vanadium and molybdenium oxides could be accounted for by different coordination states of V^{4+} and Mo^{5+} ions on their surfaces.

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