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Selective Photoreduction of Molybdenum Ions Supported on Silica

B. N. SHELIMOV, A. N. PERSHIN, AND V. B. KAZANSKY

N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, USSR

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The photoreduction of Mo^{6+} ions supported on a silica gel surface in the atmosphere of H_2 or CO has been investigated at 77 or 300°K. A selective photoreduction of Mo^{6+} to Mo^{5+} in H_2 occurs under uv irradiation with $320 < \lambda < 350$ nm. On the basis of EPR data it appears that at 77°K Mo^{5+} ions in distorted tetrahedral coordination are predominently formed ($g_1 = 1.811$, $g_2 = 1.929$, and $g_3 = 1.952$). After warming the samples to 300°K or after exposure to H_2O or C_2H_4 at this temperature a rearrangement of the first coordination sphere of Mo^{5+} ions takes place and they get a distorted octahedral coordination characterized by an EPR signal with $g_\parallel = 1.891$ and $g_\perp = 1.961$. Photoreduction of Mo^{6+}/SiO_2 in CO under uv light with $\lambda \leq 340$ nm differs markedly from that in H_2 and results mainly in the formation of tetravalent Mo^{4+} ions which exhibit high reducing properties. Mo^{4+} ions on photoreduced samples are oxidized by N_2O, CO_2, and H_2O molecules at −150, 100, and ≥150°C, respectively. After NO admission at 77°K on Mo^{4+}/SiO_2 an EPR signal with $g_\parallel = 2.075$ and $g_\perp = 1.996$, $a_\parallel^N \simeq 0$, $a_\perp^N = 15$ Oe appears which is tentatively assigned to a $Mo^{6+} \ldots NO^{2-}$ complex involving a two-electron transfer for the Mo^{4+} ion into NO π^* orbitals. It is suggested further that at room temperature this complex reacts with another NO molecule giving rise to N_2O formation. Conceivable reaction schemes of photoreduction processes in H_2 and CO are discussed. It is concluded that photoreduction differs considerably from the thermal reduction process both from viewpoints of the selectivity and the chemical properties of reduced molybdenum ions.

INTRODUCTION

Study of the valence state and coordination of molybdenum ions supported on oxide catalysts is of considerable importance for understanding catalytic reactions such as oxidation, olefin metathesis, and some others occurring on these catalysts. In a number of papers (*1–4*) dedicated to the study of this problem it has been shown using spectroscopic methods that high-temperature (400–600°C) reduction of Mo^{6+}/SiO_2 in the atmosphere of H_2, CO, or hydrocarbons usually leads to the formation of molybdenum ions in different coordination and valence states (Mo^{5+}, Mo^{4+}, Mo^{3+}). Therefore it was thought interesting to study the reduction of Mo^{6+}/SiO_2 catalysts under milder conditions, namely, under uv irradiation at room or lower temperatures. One might expect that under these conditions reduction of Mo^{6+} ions would proceed more selectively.

EXPERIMENTAL

Sample preparation. As a supporting material for Mo^{6+} ions a high-purity silica gel, prepared by hydrolysis of $SiCl_4$ (*5*), was used. The samples of Mo^{6+}/SiO_2 were obtained by impregnating the gel with an aqueous solution of ammonium paramolybdate, drying at 100°C, and calcinating at 500°C in air. The molybdenum content was 1% by weight.

Catalyst treatment and irradiation. Before photoreduction the samples were heated in quartz tubes for EPR measurements under vacuum (~10^{-4} Torr) for 1 hr at 600°C and then in oxygen (p = 50 Torr) for another hour at the same temperature. The catalyst was then cooled down to 100°C and evacuated. Irradiation by uv light was performed *in situ* in H_2 (D_2) or CO atmosphere at pressures of 5–10 Torr. The uv source was a high-pressure mercury lamp, model DRSh-1000, equipped with a

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water filter. In some experiments glass filters BS-4 or BS-5 cutting wavelengths shorter than 320 or 340 nm respectively were used. To provide a more uniform irradiation the powder samples were shaken during irradiation using a mechanical microvibrator.

Gaseous reactants. H_2 and D_2 were purified by diffusion through a red-hot (~800°C) palladium capillary. Oxygen from a cylinder was at first condensed in a liquid-nitrogen trap. Then the liquid nitrogen was slowly warmed up and the middle boiling fraction was collected. N_2O was purified by conventional freeze–pump–thaw cycles. CO was freed from oxygen contamination by passing through a column filled by silica gel-supported Cr^{2+}. NO was obtained by HNO_3 decomposition by Cu wire. Then it was submitted to purification from H_2O, N_2O, and NO_2 by passing in series through the traps cooled down by dry ice in acetone and liquid oxygen.

Spectrometers. EPR spectra were recorded with an X-band spectrometer EPR-3 or a K-band (12 mm) JES-3BS-Q (JEOL) spectrometer at 77 or 300°K. Optical spectra were measured with a SP-700 Pye-Unicam instrument supplied with a diffusion reflectance attachment. An analysis of gaseous products was performed by a quadrupole mass spectrometer, model UTI 100C (UTHE Technology International).

RESULTS

A. Photoreduction in hydrogen. Irradiation of Mo^{6+}/SiO_2 samples at 77°K by light with $320 < \lambda < 350$ nm in D_2 atmosphere leads to the formation of Mo^{5+} ions whose EPR spectrum is shown in Fig. 1a. After warming the sample up to room temperature the intensity of the signal with g_1 =

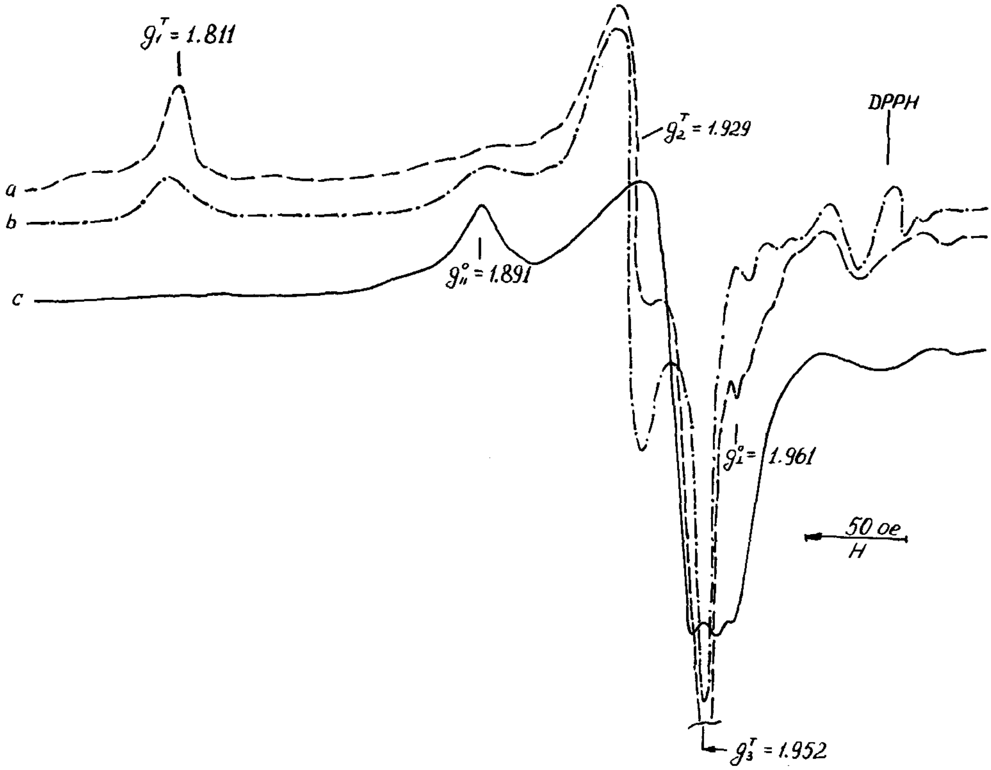


FIG. 1. X-Band EPR spectra of Mo^{5+} ions. (a) After irradiation of Mo^{6+}/SiO_2 in D_2 at 77°K (recorded at 77°K); (b) after warming the sample to 300°K (recorded at 77°K); (c) the same as (b) but recorded at 300°K.

1.811, g_2 = 1.929, and g_3 = 1.952 (signal A) decreases, and a new signal with $g_\parallel$ = 1.891 and $g_\perp$ = 1.961 (signal B) appears (Fig. 1b). Lines in the lower field part of the spectra are due to $^{95}Mo^{5+}$ and $^{97}Mo^{5+}$ ions (natural abundance of ~24%) having a nuclear spin of 5/2.

The spectrum with the same g values is observed after uv irradiation of Mo^{6+}/SiO_2 in H_2 at room temperature; however, in this case g-tensor components are split into doublets (Figs. 2a and b) due to hyperfine interaction of the Mo^{5+} d electron with the neighboring proton. The hyperfine splitting constants are equal to 15 and 19 Oe for signals A and B, respectively. The temperature behavior of signals A and B is different; the former is not seen at room temperature (Figs. 1c and 2b), whereas the latter is.

TABLE 1

EPR g and a Values for $^{95}Mo^{5+}$ Ions

	g_1	g_2	g_3	a_1 (Oe)	a_2 (Oe)	a_3 (Oe)
Signal A	1.811	1.929	1.952	82 ± 3	30 ± 3	30 ± 3
Signal B	$g_\parallel$ = 1.891	$g_\perp$ = 1.961		$a_\parallel$ = 98 ± 5	$a_\perp$ = 43 ± 3	

In order to determine the hyperfine splitting constants on the molybdenum nucleus a Mo^{6+}/SiO_2 sample enriched by ^{95}Mo isotope (98 at.%) was used. Signal A, obtained after uv irradiation of this sample in D_2 atmosphere at 77°K, is presented in Fig. 3. Both g and a values for ^{95}Mo signals A and B are listed in Table 1.

The number of Mo^{5+} ions produced by photoreduction in H_2 was calculated by integration of the EPR spectra as well as by measurement of the oxygen amounts consumed during the reoxidation of photoreduced samples at 400–500°C. In the last case it was accepted that one oxygen molecule oxidizes four Mo^{5+} ions. The results of both sets of experiments are summarized in

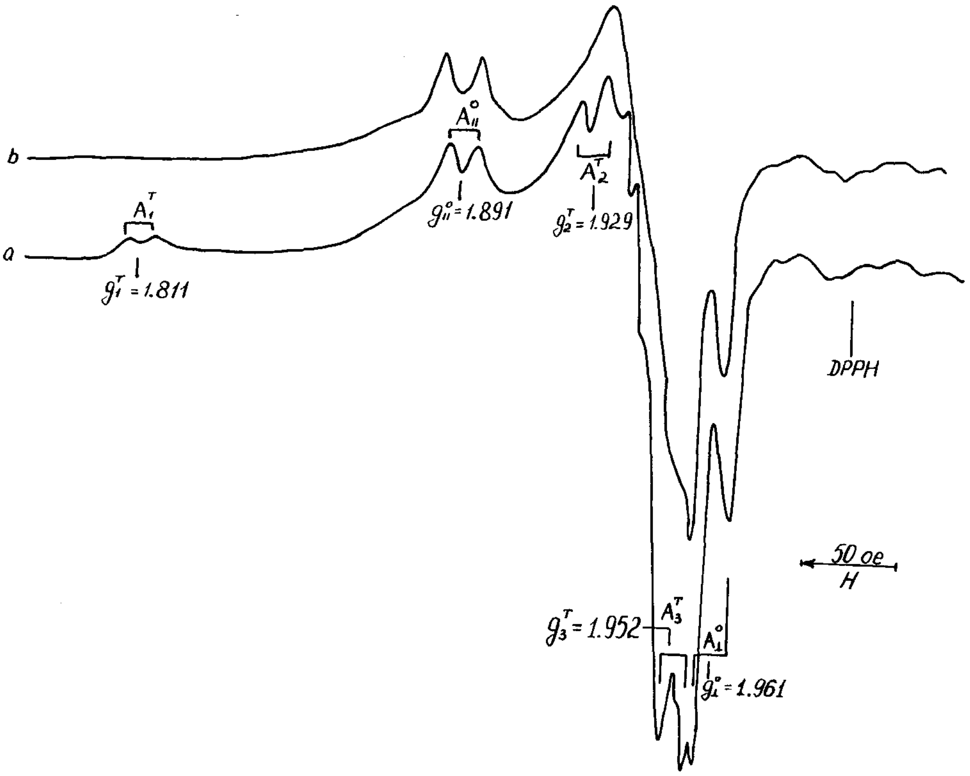


FIG. 2. X-Band EPR spectra of Mo^{5+} ions. (a) after irradiation of Mo^{6+}/SiO_2 in H_2 at 300°K (recorded at 77°K); (b) the same as (a) but recorded at 300°K.

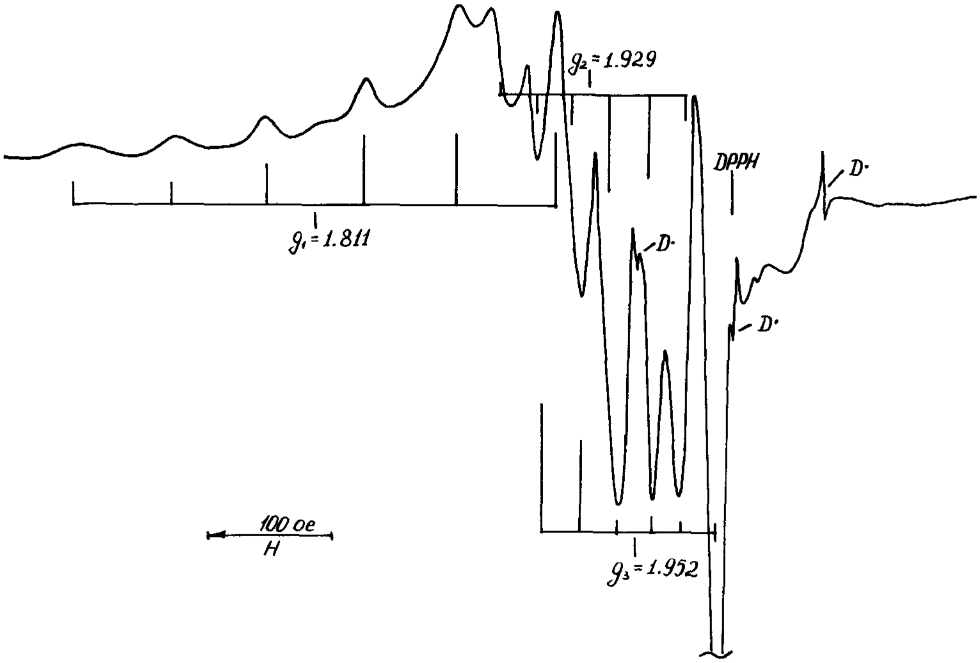


FIG. 3. X-Band EPR spectrum of $^{95}Mo^{5+}$ ions after photoreduction of $^{95}Mo^{6+}/SiO_2$ in D_2 at 77°K (recorded at 77°K).

Table 2, showing that the Mo^{5+} concentrations determined by the different ways coincide within the experimental errors. It should be noted that the reduction degrees of Table 2 are apparently not the highest possible ones, since no attempt was made to get a maximum Mo^{5+} concentration by prolonged irradiation of a Mo^{6+}/SiO_2 sample with filtered light. Furthermore, photoreduction was found to proceed much faster when unfiltered light of the mercury lamp was used. For example, in one experiment the reduction degree of about 30% was already achieved after uv irradiation for 3 hr.

TABLE 2

Reduction Degrees of Mo^{6+}/SiO_2 in H_2 as a Function of Irradiation Time

Irradiation time (hr)	Mo^{5+} concn, from EPR spectra (g^{-1})	Mo^{5+} concn, by reoxidation (g^{-1})	Reduction degrees of Mo^{6+} ions (%)
2	$1.21 \pm 0.12 \times 10^{18}$	$1.4 \pm 0.2 \times 10^{18}$	2
5	$6.5 \pm 0.6 \times 10^{18}$	$8.2 \pm 1.6 \times 10^{18}$	10

After exposure of photoreduced samples to water vapor at room temperature signal A disappears, and g values of signal B are slightly changed, becoming $g_{\parallel} = 1.895$, $g_{\perp} = 1.952$. The proton hyperfine splitting is no longer seen in the spectra. Analogous changes in the EPR spectra take place after C_2H_4 admission ($p = 5$ Torr) at room temperature.

N_2O adsorption at room temperature does not give rise to any appreciable changes in the EPR spectra. However, N_2O decomposition followed by N_2 evolution in the gas phase is found to occur at temperatures higher than 100°C. It is accompanied by disappearance of the Mo^{5+} signals.

B. Photoreduction in carbon monoxide. Irradiation of Mo^{6+}/SiO_2 samples at room temperature in CO atmosphere by light with $\lambda \leq 350$ nm results in CO_2 evolution in the gas phase. In a series of experiments an average valence state of photoreduced molybdenum ions (x) was determined using the equation

$$x = 6 - 2N_{CO_2}/N_{Mo^{6+}},$$

where N_{CO_2} is the number of CO_2 molecules evolved and $N_{Mo^{6+}}$ is the total number of molybdenum ions in the sample (see Table 3). The average valence state of Mo ions calculated from the series of three experiments is found to be 3.9.

Thus, the photoreduction in CO differs considerably from that in H_2, where, as described above, mainly Mo^{5+} ions are produced. This difference is further confirmed by spectroscopic data.

After photoreduction in CO the samples show an EPR signal of relatively low intensity with $g_\parallel = 1.875$ and $g_\perp = 1.947$ characteristic of Mo^{5+} ions in octahedral coordination. The number of Mo^{5+} ions estimated from EPR spectra is approximately 100 times smaller than the number of CO_2 molecules formed during photoreduction. Neither CO desorption at 100°C nor H_2O or NH_3 adsorption at room temperature results in any appreciable increase in the intensity of Mo^{5+} EPR signals.

Carbon monoxide molecules are rather strongly bonded to the surface on photoreduced samples and cannot be removed by outgassing at room temperature. The complete CO desorption occurs only at temperatures higher than 100°C. After CO removal the samples display a green color. In Fig. 4a a diffusion reflectance spectrum of such a "green sample" is presented. CO adsorption at 20°C causes a remarkable change in the spectrum (Fig. 4b). Note that samples photoreduced in CO which were not outgassed at 100°C give very similar spectra.

TABLE 3

Average Valence State of Molybdenum Ions Formed after Mo^{6+}/SiO_2 Irradiation in CO by Unfiltered uv Light

Run number	Irradi-time (hr)	Number of CO_2 molecules evolved	Total number of Mo ions in sample	Average valence state of Mo ions
1	4	6.2×10^{17}	6.0×10^{17}	3.92
2	3.5	6.5×10^{17}	6.0×10^{17}	3.90
3	3.5	1.4×10^{19}	1.3×10^{19}	3.92

After photoreduction and CO desorption at 100°C "green samples" show very high reducing properties. Several examples are given below.

(1) Adsorbed N_2O is reduced by Mo^{4+} ions at temperatures as low as −120°C, resulting in N_2 evolution in the gas phase.

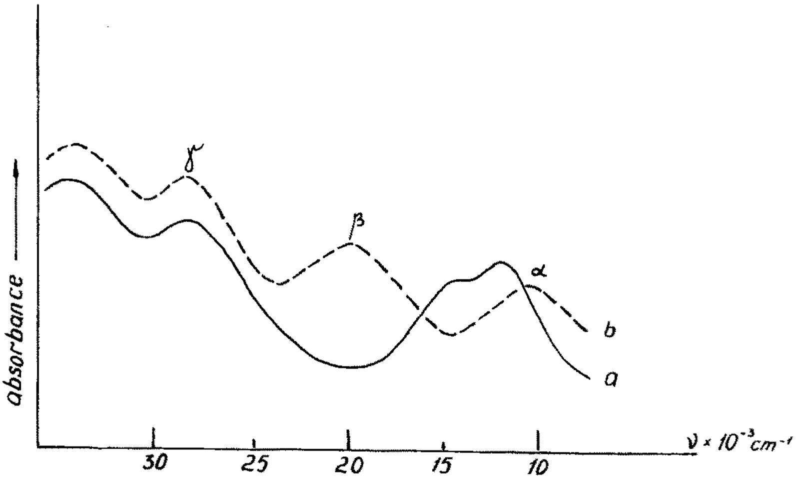


FIG. 4. Optical spectra of samples of Mo^{6+}/SiO_2 photoreduced in Co after (a) CO desorption at 100°C; (b) CO adsorption at 20°C.

The number of N_2 molecules is equal to that of CO_2 molecules formed during photoreduction. The EPR spectrum is not changed; however, the green color disappears.

(2) CO_2 decomposition with CO formation proceeds with a considerable rate already at 90°C. No change in the EPR spectra is observed. The number of CO molecules evolved approximately corresponds to that of CO_2 formed during photoreduction.

(3) H_2O is reduced at tempertures higher than 150°C. Simultaneously hydrogen is evolved in the gas phase. The intensity of Mo^{5+} EPR signals increases 4–5 times.

The green color vanishes after reactions (2) and (3) are completed.

(4) After NO admission at 77°K a new EPR signal with $g_{\parallel} = 2.075$ and $g_{\perp} = 1.996$ appears. Its intensity drastically increases (more than 100 times) after the sample is taken out of the liquid-nitrogen bath and kept at room temperature for 10–15 sec (Fig. 5). There is also a remarkable increase in intensity of the EPR signal after uv irradiation of the sample, containing adsorbed NO, at 77°K. However, it is not clear whether this effect is linked to a photoreaction or to a small temperature rise during the irradiation.

By integration of the EPR spectra the intensity of this signal was estimated to be $\sim 2 \cdot 10^{19}\ g^{-1}$ or ~30% of the total molybdenum ion content in the sample. As seen from Fig. 5 the perpendicular component of the g tensor consists of three hyperfine lines separated by 15 ± 1 Oe, owing to interaction of an unpaired electron with the ^{14}N ($I = 1$) nucleus. Both keeping the sample at room temperature for 30 min and oxygen adsorption at this temperature destroy this EPR signal.

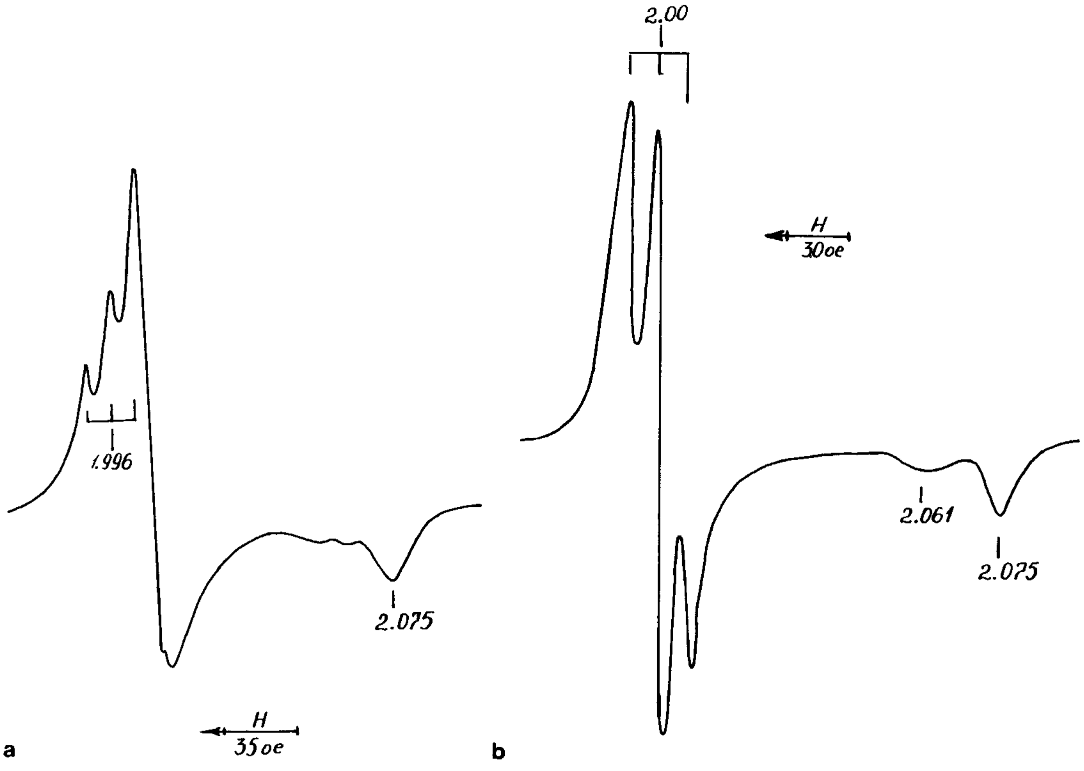


FIG. 5. EPR spectra of samples of Mo^{6+}/SiO_2 photoreduced in CO after NO adsorption: (a) X-band; (b) K-band. The spectra were recorded at 77°K.

N_2O and small amounts of N_2 are found to be the products of NO interaction with photoreduced Mo/SiO_2 samples at room temperature and the N_2O/N_2 ratio depends on the amount of NO adsorbed.

DISCUSSION

Photoreduction in hydrogen. Let us first discuss coordination states of Mo^{5+} ions formed by photoreduction in H_2. Signal B g values are characteristic of Mo^{5+} ions in distorted octahedral coordination. Similar EPR signals were detected (*2*) after high-temperature reduction of the Mo^{6+}/SiO_2 system in hydrogen.

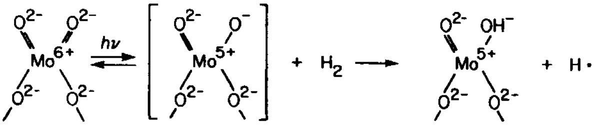
As far as we know, signal A with a much higher g-value anisotropy was not observed earlier on Mo^{6+}/SiO_2 catalysts. On the other hand, it is well-known that transition metal ions such as V^{4+}, Cr^{5+}, etc., on silica gel support very often occupy positions inside the oxygen tetrahedra. The crystal field theory gives the following ratio for d^1-transition metal ions in C_{2v}-distorted tetrahedral coordination (*6*):

$$\frac{g_e - g_\parallel}{g_e - g_\perp} = \frac{\Delta g_\parallel}{\Delta g_\perp} = 4.$$

For signal A, $\Delta g_\parallel/\Delta g_\perp$ is equal to 3.12 (if one accepts $g_\parallel = g_1$, $g_\perp = g_2 + g_3/2$); this value is rather close to the theoretical one. Therefore it seems reasonable to assign signal A to Mo^{5+} ions in distorted tetrahedral coordination.

This interpretation is confirmed by the disappearance of signal A after H_2O and C_2H_4 adsorption, indicating the coordinative unsaturated state of Mo^{5+} ions responsible for this signal. Furthermore, the absence of signal A in EPR spectra at room temperature is also characteristic of d^1 ions in tetrahedral coordination and is linked to the short spin–lattice relaxation time at this temperature. Earlier (*7*), similar behavior for Cr^{5+} and V^{4+} supported on silica gel was reported.

Photoreduction of Mo^{6+}/SiO_2 probably occurs according to the scheme which is similar to that proposed earlier (*8*) for V^{5+} ions:



(1)

At the first step under uv light corresponding to the charge transfer band of $[MoO_4]^{2-}$ complexes there is an electron transfer from the O^{2-} anion to Mo^{6+} ion giving rise to a short-lived electronically excited complex $[(MoO_4)^{2-}]^*$. The latter was shown to reveal chemical reactivity very similar to that of the adsorbed O^- anion radicals, and it readily reacts with hydrogen molecules even at 77°K. As it follows from the experiments where irradiation was carried out by filtered light, the lowest photon energy required for reaction (1) corresponds to the long-wavelength border of the charge transfer band in the optical spectra of $Mo^{6+} \ldots O^{2-}$ complexes.

Scheme (1) is evidenced by the presence of proton hyperfine splitting in Mo^{5+} EPR spectra owing to delocalization of the unpaired d electron onto σ-orbital of the neighboring OH group.

According to this scheme OD groups must be formed under irradiation in D_2. However, in this case hyperfine splitting becomes 6.5 times smaller and therefore it cannot be seen in the EPR spectra.

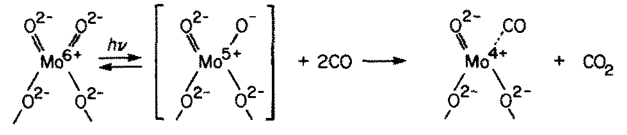
It follows from Fig. 1 that the major part of Mo^{5+} ions produced by uv irradiation at 77°K is in tetrahedral coordination. Since at such low temperature a rearrangement of the first coordination sphere of Mo^{5+} ions seems to be unlikely, it is reasonable to assume that in original samples Mo^{6+} ions would also occupy positions in the center of oxygen tetrahedra. After warming the samples, which were submitted to irradiation at 77°K, to room temperature or after H_2O and C_2H_4 adsorption a rearrangement of the first coordination sphere of Mo^{5+} ions takes place and they get octahedral coordination. Signal B corresponds to these Mo^{5+} ions. No chemical reaction occurs under these conditions. On the contrary, N_2O interacts with Mo^{5+} ions at $\sim 100°C$ in the following way:

$$2\ Mo^{5+} + N_2O \rightarrow 2\ Mo^{6+} + O^{2-} + N_2.$$

It has been shown earlier (*1*, *4*) that N_2O admission on Mo^{6+}/SiO_2 samples previously reduced in H_2 at high temperatures results in appearance of O^- species in EPR spectra. However, on photoreduced samples no O^- could be detected after N_2O treament in similar conditions.

B. Photoreduction in carbon monoxide. Photoreduction in CO differs markedly from that in H_2. The data of Table 3 show that mainly Mo^{4+} ions are produced. An alternative explanation, namely, formation of equal amounts of Mo^{3+} and Mo^{5+} ions, can apparently be ruled out because no Mo^{3+} EPR signal is detected and the number of Mo^{5+} ions formed corresponds only to about 1% of CO_2 molecules evolved. One might suggest further that a certain fraction of Mo^{5+} ions formed would not be detected by EPR at 77°K, since they are in a regular tetrahedral coordination and as a consequence are characterized by a very short spin–lattice relaxation time, T_1. However, as no change in EPR spectra of Mo^{5+} ions was found to occur after H_2O or NH_3 adsorption at room temperature this suggestion cannot be taken into account. Note that Mo^{4+} ions (electron configuration d^2) in polycrystalline powder samples have never been observed by EPR.

The formation of Mo^{4+} during photoreduction in CO can be presented in the following way:



(2)

The first step, electron transfer from the O^{2-} anion to the Mo^{6+} ion, was discussed earlier. The excited complex $[(MoO_4)^{2-}]^*$ then interacts with CO molecules giving rise to CO_2 formation and to the transfer of one more electron to the Mo^{5+} ion. Thus, reaction (2) is in fact a two-electron-transfer process which proceeds under uv light.

As discussed above, in original samples Mo^{6+} ions are predominantly in tetrahedral coordination. One may conclude from scheme (2) that photoreduction in CO might have been accompanied by removal of one ligand from the first coordination sphere of the Mo ion. Apparently this site is replaced by a CO molecule and consequently tetrahedral coordination of Mo^{4+} ions is restored. Generally speaking, the CO desorption at 100°C would lower the complex symmetry. However, the presence of molybdenum ions on the silica gel surface characterized by coordination number less than four seems to be unlikely. Therefore it is reasonable to assume that after CO removal a rearrangement of the first coordination sphere of the Mo^{4+} ion occurs and a coordination close to tetrahedral coordination is restored. The Mo–O bond formed as a result of such reconstruction is rather weak and can be easily broken by CO adsorption.

Based upon these considerations let us now examine optical spectra of Mo^{4+}/SiO_2 photoreduced in CO.

The literature data concerning optical spectra of Mo^{4+} ions are not numerous and mainly refer to the octahedral halide complexes. For $[MoCl_6]^{2-}$ the adsorption band with maximum at 21,510 cm^{-1} has been assigned to the $^3T_{1g} \rightarrow {}^3T_{2g}$ transition while two other bands at 25,640 and 27,780 cm^{-1} have been ascribed to the $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ and $^3T_{1g} \rightarrow {}^3A_{2g}$ transitions, respectively (*9*). Later (*10*), where adsorption spectra as well as that of magnetic circular dichroism of a $Cs_2ZrCl_6 : Mo^{4+}$ single crystal have been studied, it has been supposed that the absorption bands in 26,000- and 28,000-cm^{-1} region are due to charge transfer transitions.

What concerns oxide catalysts, the optical data, are less reliable. In a number of papers (*2, 11, 12*), reduced surface molybdenum ions (Mo^{3+}, Mo^{4+}, Mo^{5+}) supported on γ-Al_2O_3, MgO, and SiO_2 have been investigated using diffuse reflectance optical spectroscopy. The reduced ions have been produced by thermal reduction in H_2 or CO at 400–600°C. Under these conditions Mo ions in various valence states and coordinations are usually formed, and therefore assignment of absorption bands in optical spectra is rather ambiguous owing to the bands overlapping. In (*12*) the absorption band at 20,000 cm^{-1} has been assigned to the $^3T_1 \rightarrow {}^3T_2$ transition of octahedral Mo^{4+} ions on the basis of the correlation between optical spectra of Mo^{6+}/γ-Al_2O_3 reduced in H_2 and that of MoO_2 where Mo^{4+} ions are known to be localized in distorted oxygen octahedra.

As far as we know there are no literature data on the optical spectra of Mo^{4+} ions in tetrahedral coordination. Therefore we start with some theoretical predictions for *d–d* transitions of d^2 ions.

According to the crystal field theory (*13*) the ground state of d^2 ions in fields of tetrahedral symmetry is characterized by $^3A_2$ term.

There exist three spin-allowed *d–d* transitions, namely, $^3A_2 \rightarrow {}^3T_2$, $^3A_2 \rightarrow {}^3T_1$, $^3A_2 \rightarrow {}^3T_1$ (3*P*). It seems to be likely that three absorption bands in the spectrum in Fig. 4b labeled α, β, and γ at 10,000, 20,000, and 27,000 cm^{-1} are due to these transitions. The absorption bands at shorter wavelengths in the spectra, presented in Fig. 4a, are attributed to the charge transfer transitions; they will not be discussed further. It follows from the crystal field theory of d^2 ions that the frequency corresponding to the longest wavelength transition is equal to the crystal field parameter, 10 *Dq*; in the case under consideration $10(Dq) \simeq 10{,}000$ cm^{-1}. Since $(Dq)_{\text{tetr.}} = 4/9(Dq)_{\text{oct.}}$, the value of $10(Dq)_{\text{tetr.}} = 10{,}000$ cm^{-1} agrees well with that of $10(Dq)_{\text{oct.}} = 20{,}000$–$21{,}500$ cm^{-1} for the Mo^{4+} octahedral complexes with oxygen (*12*) or chlorine (*9*) ligands.

Changes in the spectrum of tetrahedral Mo^{4+} caused by CO desorption at 100°C (Fig. 4a) can be tentatively attributed to an essential symmetry distortion of the oxygen tetrahedron. However, an unambiguous assignment of the three absorption bands in the spectrum of Fig. 4a requires further investigation.

As far as we know, very high reducing properties of Mo^{4+} ions in photoreduced samples are unique. Apparently CO_2 reduction by Mo^{4+} at 100°C occurs in the following way:

$$Mo^{4+} + CO_2 \rightarrow Mo^{6+} + O^{2-} + CO.$$

This reaction can explain CO evolution in the gas phase as well as the absence of surface paramagnetic species after the reaction is completed.

In a similar way, but at much lower temperatures, N_2O reduction proceeds:

$$Mo^{4+} + N_2O \rightarrow Mo^{6+} + O^{2-} + N_2.$$

H_2O reduction at temperatures as high as 500°C accompanied by H_2 formation has been observed (*14*) over catalysts containing Cr^{2+} ions. On photoreduced Mo^{4+}/SiO_2 samples this process takes place with appreciable rates at lower temperatures (150°C); it can be described by the following scheme:

$$Mo^{4+} + H_2O \rightarrow Mo^{5+} + OH^- + \frac{1}{2}H_2.$$

Mo^{5+} ions produced in this reaction are observed by EPR.

An interaction of NO with Mo^{4+} ions should be discussed in more detail. It is seen from the lineshape of the spectra shown in Fig. 5. that they are due to a species with $S = \frac{1}{2}$. The hyperfine splitting of $g_\perp$ into three lines means that only one NO molecule enters the complex under study. Comparison of the g values for the observed EPR signals ($g_\perp \simeq 2.0$, $g_\parallel > 2.0023$) with the data of (*15, 16*) reveals that they cannot be attributed to adsorbed NO molecules.

Following Refs. (*17, 19*), where an interaction of surface ions Cr^{2+} (d^4), Fe^{2+} (d^6), and Ni^{2+} (d^8) has been studied by EPR, one may suggest that an electron transfer from a NO π^* orbital to a Mo^{4+} d orbital could occur with the formation of a d^3 low-spin configuration. As stated above, in this case symmetry of a complex formed in such a way would be close to tetrahedral coordination. Then, according to the molecular orbital diagrams, calculated in Ref. (*20*) by the Wolfsberg–Helmholz method for nitrosyl complexes of various symmetries, the lowest energy state for C_{3v} or C_s symmetry will be either double generated ($e(x^2 - y^2, xy)$) or quasi-generated ($a''(xy)$ and $a'(x^2 - y^2)$), respectively. In both cases detection of any EPR low-spin signal ($S = \frac{1}{2}$) especially at room temperture is unlikely. Furthermore, none of the molecular orbitals discussed above have any NO π^*-orbital contribution; therefore no hyperfine splitting on ^{14}N could be expected in EPR spectra. Also g values of the signal in Fig. 5 do not agree with those expected for Mo^{3+} (d^3) ions, since the latter must be characterized by $g_{av} < g_e = 2.0023$. Thus, the suggestion about an electron transfer from the NO molecule to the Mo^{4+} ion should apparently be ruled out.

On the other hand, taking into account the high reducing properties of Mo^{4+} ions one may assume donation of two electrons from the Mo^{4+} d orbital into NO π^* orbitals with the formation of species which can be formlaly written as NO^{2-}. These species are isoelectronic to O_2^-, and so Kanzig and Cohen's formula (*21*) may be applied for g-value calculations. According to this formula one may obtain for NO^{2-} $g_\perp \simeq 2.0$ and $g_\parallel > 2.0$; these values are consistent with our experimental findings. The isotropic hyperfine splitting constant on ^{14}N $a_{iso} = 2a_\perp + a_\parallel/3$ and the anisotropic constant are equal to 10 and 5 Oe respectively. Taking into account the anisotropic splitting constant on ^{14}N $2\beta = 34$ Oe (*22*) one can find that the unpaired electron orbital in NO^{2-} to an appreciable extent (~30%) consists of nitrogen p orbital.

Certainly, the description of Mo^{4+} interaction with NO based upon an ionic model is only a rough approximation, since the Mo^{4+}–NO bond as well as that in other nitrosyl complexes has a covalent character. Therefore one must take into account not only a transfer of electron density from the Mo^{4+} ion into the NO π^* orbital but as well as a reverse process, namely, back donation from filled NO orbitals into the d orbital of the Mo ion. Nevertheless, even this rough model explains well the observed g values of EPR spectra.

N_2O formation as a result of NO and Mo^{4+} interaction probably proceeds via a $Mo^{6+}NO^{2-}$ complex:

$$Mo^{6+}NO^{2-} + NO \rightarrow N_2O + Mo^{6+} + O^{2-}.$$

Appearance of a small amount of N_2 is apparently due to a byproduct reaction:

$$Mo^{4+} + N_2O \rightarrow N_2 + Mo^{6+} + O^{2-}$$

which was shown to occur already at −150°C.

CONCLUSIONS

The data presented in this paper show quite clearly that low-temperature photoreduction of Mo^{6+}/SiO_2 in H_2 and CO differs considerably from the thermal reduction. On one hand, photoreduction is a much more selective process leading either to the formation of Mo^{5+} ions or under certain conditions to the practically complete conversion of Mo^{6+} to Mo^{4+} ions. On the other hand, Mo^{4+} ions formed during photoreduction reveal unusually high reducing properties. For example, it has never been reported in the literature that thermally reduced molybdenum–silica catalysts are able to dissociate CO_2 and H_2O molecules or to form NO^{2-} species by interaction with NO. The oxidation temperatures of these samples by N_2O is about 200° higher than that for photoreduced samples. The exact reasons for such great differences in properties of the surface Mo^{4+} ions, produced in different ways, are not yet clear and can be the subject of a further investigation.

However, it is likely that this difference may arise from lower coordination states of molybdenum ions in a photoreduced system. In this case oxygen vacancies near Mo ions produced by the low-temperature photoreduction process are conserved whereas in high-temperature reduction they are easily eliminated by rearrangements of the first coordination sphere of Mo ions.

REFERENCES

1. Vorotyntzev, V. M., Shvetz, V. A., and Kazansky, V. B., *Kinet. Katal.* **12,** 1249 (1971).
2. Che, M., Figeras, F., Forisier, M., McAteer, J., Perrin, M., Portefaix, J. L., and Praliaud, H., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bonds, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 261. The Chemical Society, London, 1977.
3. Vaghi, A., Castellan, A., Bart, J. C. J., and Giordano, N., *J. Catal.* **42,** 381 (1976).
4. Ward, M. B., Lin, M. J., and Lunsford, J. H., *J. Catal.* **50,** 306 (1977).
5. Sourin, S. A., Shelimov, B. N., and Kazansky, V. B.; *Khim. Vys. Energ.* **6,** 120 (1972).
6. Alexandrov, I. V., Mikheikin, I. D., and Kazansky, V. B., *Kinet. Katal.* **6,** 120 (1972).
7. van Reijen, L. L., and Cossee, P., *Disc. Faraday Soc.* **41,** 277 (1966).
8. Sourin, S. A., Shouklov, A. D., Shelimov, B. N., and Kazansky, V. B., *Khim. Vys. Energ.* **11,** 147 (1977).
9. Allen, E. A., Brisdon, B. J., Edwards, D. A., Fowles, G. W. A., and Williams, R. G., *J. Chem. Soc.,* 4649 (1963).
10. Collingwood, J. C., Shwartz, R. W., Shatz, P. N., and Patterson, H. H., *Mol. Phys.* **27,** 129 (1974).
11. Asmolov, G. N., and Krylov, O. V., *Kinet. Katal.* **13,** 204 (1975).
12. Giordano, N., Castellan, A., Bart, J. C. J., Vaghi, A., and Campadelli, F., *J. Catal.* **37,** 204 (1975).
13. Sviridov, D. T., Sviridova, P. K., and Smirnov, Yu. F., "Optical Spectra of Transition Metal Ions in Crystals." Nauka Pub., Moscow, 1976.
14. Przevalskaja, L. K., Ssvetz, V. A., and Kazansky. V. B., *Kinet. Katal.* **5,** 1310 (1970).
15. Primet, M., Che, M., Naccache, C., Mathieu, M.-V., and Imelik, B., *J. Chim. Phys. Physicochim. Biol.* **67,** 1629 (1970).
16. Kasai, P. H., and Bishop, R. J., *J. Amer. Chem. Soc.* **94,** 5560 (1972).
17. Jermyn, J. H., Johnson, T. J., Vansant, E. F., and Lunsford, J. H., *J. Phys. Chem.* **77,** 2964 (1973).
18. Naccache, C., and Ben Taarit, Y., *J. Chem. Soc. Faraday Trans. I* **69,** 1475 (1973).
19. Przevalskaja, L. K., Shvetz, V. A., and Kazansky, V. B., *Kinet. Katal.* **20,** 1005 (1979).
20. Mingos, D. M. P., *Inorg. Chem.* **12,** 1209 (1973).
21. Kanzig, W., and Cohen, M. M., *Phys. Rev. Lett.* **3,** 509 (1959).
22. Atkins, P. W., and Symons, M. C. R., "The Structure of Inorganic Radicals." Elsevier, Amsterdam/New York, 1967.