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LETTER TO THE EDITORS

EPR Study of the Coordination Sphere of Mo^{5+} Ions in UV-Irradiated Silica-Supported Molybdenum Catalysts

The determination of the number of coordination vacancies existing at transition metal cations at the surface of bulk or supported oxides is of great interest in relation to the adsorption and catalytic properties of such systems (*1*). In the case of paramagnetic cations, we have developed a method consisting of the recording of their first and third derivative EPR spectra after adsorption of ^{13}CO, (^{13}C, $I = 1/2$). In this way, the ^{13}C superhyperfine structure which is normally observed permits the determination of the number of CO molecules bonded to the metal center (*2, 3*).

In a recent EPR work published in this journal, Seyedmonir and Howe (*4*) have reported the formation of a CO adduct of the tetrahedral Mo^{5+}–OH^- species formed by UV-irradiation at 20 K of a MoO_3/SiO_2 catalyst in the presence of H_2. In that work, although the structure of such an adduct could not be derived unambiguously on the basis of the g tensor values, the coordination of the Mo^{5+} ion by two CO molecules was suggested. This would be in agreement with our previous results with thermally reduced V_2O_5/SiO_2 (*3*) and MoO_3/SiO_2 (*5*) catalysts, where the coordination of, respectively, V^{4+} and Mo^{5+} tetrahedral centers by two CO molecules was proved by means of the combined use of ^{13}CO and third derivative EPR spectra. In the present work, using this approach, we have studied the structure of these Mo^{5+} ions photochemically generated on MoO_3/SiO_2 catalysts and concluded that only one CO molecule is bonded to the paramagnetic ion.

The supported molybdenum catalyst used here has been prepared by impregnating the silica with an ammonium paramolybdate solution according to a procedure previously described (*6*). Analysis of the sample gave ca. 2% Mo by weight and a surface area of 450 $m^2\,g^{-1}$. A similar method has been used for preparing the ^{95}Mo-enriched sample. In this case the labeled ammonium paramolybdate solution was obtained by dissolving $^{95}MoO_3$ (97% ^{95}Mo, A.E.R.E., Harwell, UK) in concentrated ammonia solutions (*7*). The resulting solids were heated at 773 K, first under vacuum for 3 h and then under 100 Torr oxygen for 2 h. Finally, they were outgassed for 30 min at 298 K. After this standard treatment the samples were white, free from water or any other contaminant, and did not develop any EPR signal.

The gases (O_2, H_2, D_2, and CO) were supplied by L'Air Liquide (France) and used without further purification. The 90% ^{13}C-enriched carbon monoxide was supplied by C.E.A. (France).

UV-irradiation for 30 min at 77 K under H_2 or D_2 (30 Torr) was carried out through a Dewar vessel made of Pyrex and filled with liquid nitrogen. For this purpose, the samples were placed in the same quartz tubes used for EPR recording. These could be attached via grease-free stopcocks to a conventional vacuum system. Prior to CO adsorption at 77 K on these UV-irradiated samples, H_2 or D_2 was outgassed at this temperature. The carbon monoxide was passed through a liquid nitrogen trap just before use.

The EPR spectra were recorded at 77 K on a Varian (Model E-3) spectrometer working at 9.3 GHz (*X*-band) with 100 kHz field modulation. Third derivative curves (*3*) were obtained with a subharmonic genera-

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TABLE 1

EPR Parameters of $(Mo = O)^{3+}$ Species in Different Systems

System	g tensor			^{95}Mo A tensor (G)			^{1}H tensor (G)			^{13}C A tensor (G)			Ref.
	g_1	g_2	g_3	A_1	A_2	A_3	A_1	A_2	A_3	A_1	A_2	A_3	
MoO_3/SiO_2–UV	1.952	1.929	1.811	30	30	82	15	15	15				This work
MoO_3/SiO_2–UV–CO	1.965	1.941	1.891	41	36	95	22.5	17	17	6.5			This work
MoO_3/SiO_2–UV	1.954	1.933	1.813				11	15	14				*(4)*
MoO_3/SiO_2–UV–CO	1.969	1.944	1.898				20	20	20				*(4)*
$[NH_3Pr](Mo_7O_{24})\,3H_2O$	1.935	1.924	1.899	34	38	84	13.8	10.2	9.2				*(10a)*
MoO_3/SiO_2–H_2 (773 K)	1.944	1.844	1.892	44	44	29							*(6)*

Note. NH_3Pr: isopropylammonium.

tor accessory (Telmore instruments) using multiple field modulation. The g factors were measured relative to the DPPH sample ($g = 2.0036$). The magnetic field increases from left to right in all the figures.

The MoO_3/SiO_2 samples UV-irradiated in H_2 or D_2 developed spectra similar to those previously described by Shelimov *et al.* *(8)* and Seyedmonir and Howe *(4, 9)* and attributed by these authors *(4, 8)* to a tetrahedrally coordinated Mo^{5+}–OH^- species. The magnetic parameters obtained in our case are shown in Table 1. When CO (20 Torr) was adsorbed on the samples, the spectra shown in Fig. 1 were recorded, depending on whether UV-irradiation was carried out in H_2 or D_2. Worth noting in Fig. 1b is the appearance at g_1 and g_2 of a well-defined hyperfine structure due to the hyperfine interaction of the unpaired electron with the ^{1}H of a OH^- group attached to molybdenum *(4, 8)*. Figure 2 shows the equivalent spectrum obtained using the $^{95}MoO_3/SiO_2$ catalyst and D_2. The magnetic parameters of this center involving CO, reported in Table 1, are also in good agreement with the values previously reported by Seyedmonir and Howe *(4)* for a similar species.

When instead of ^{12}CO, ^{13}C-enriched CO was used, the spectra shown in Fig. 3 were recorded. In the first derivative mode, the spectrum exhibits a much broader shape as compared to its equivalent in Fig. 1b, a fact that is expected because of the superposition of the ^{13}C hyperfine structure. The use of the third derivative technique *(2, 3, 5)* provides a much better defined spectrum (Fig. 3b) characterized by two peaks centered at the positions of the ^{1}H hyperfine peaks at g_1 and g_2 in the spectrum of the sample UV-irradiated in H_2 (Fig. 1a). The measured superhyperfine splitting constant

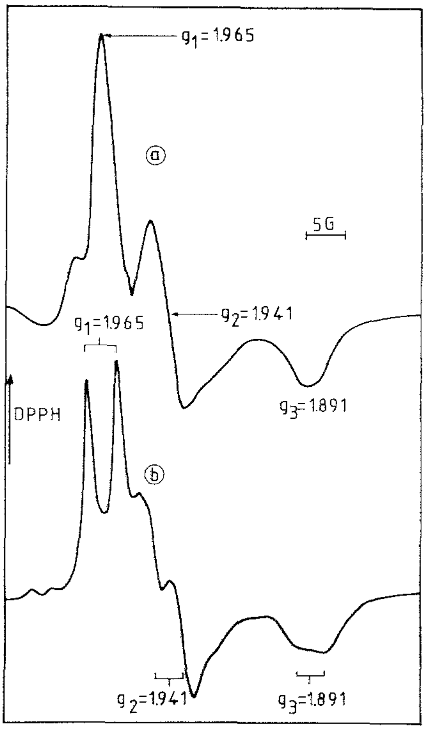


FIG. 1. First derivative EPR spectra at 77 K after the adsorption of ^{12}CO on the MoO_3/SiO_2 sample UV-irradiated at 77 K under D_2 (a) and H_2 (b).

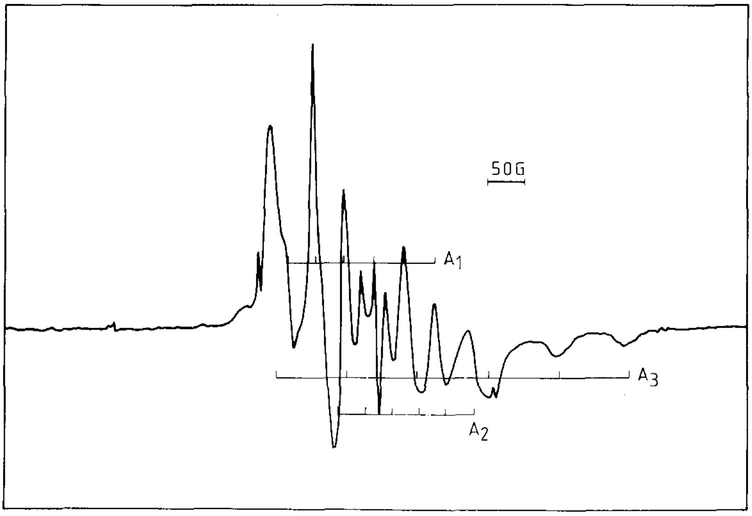


FIG. 2. First derivative EPR spectrum at 77 K after the adsorption of ^{12}CO on the $^{95}MoO_3/SiO_2$ sample UV-irradiated at 77 K under D_2.

was ca. 6.5 G, similar to that obtained on thermally activated V_2O_5/SiO_2 (*3*) and MoO_3/SiO_2 (*5*) catalysts (ca. 7 G), and much smaller than that measured for Ni^+ centers (ca. 30 G) in Ni/SiO_2 (*2*). This difference in the superhyperfine splitting constants is mainly due to different ground state *d* orbitals, i.e., xy for V_2O_5/SiO_2 and MoO_3/SiO_2 systems and x^2–y^2 or z^2 for Ni/SiO_2 catalysts (*2, 3, 5*).

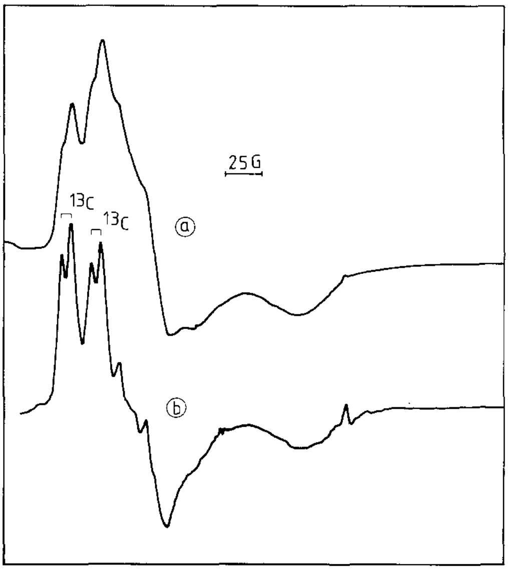
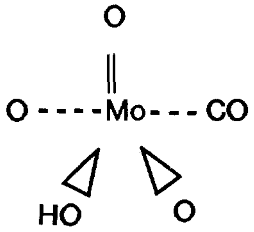


FIG. 3. EPR spectra at 77 K after the adsorption of ^{13}CO on the MoO_3/SiO_2 sample UV-irradiated at 77 K under H_2: (a) first derivative spectrum, (b) third derivative spectrum.

According to previous considerations (*2, 3, 5*) a ^{13}C superhyperfine pattern formed by two peaks can be explained if one CO molecule is directly bonded to the paramagnetic center. On this basis, and taking into account the *g* and *A* parameters of this species, the following structure can be proposed:



This structure does not present any symmetry axis, accounting for the orthorhombic character of the *g* tensor. The proposed molybdenyl bond along the *z* axis is consistent with the *g* and *A* values of this species, which are similar to those found in the literature for molybdenum ions with such structure (see values reported in Table 1). It also agrees with the small value of the ^{13}C superhyperfine splitting which, as discussed previously (5), is the result of a poor overlap between the orbitals of the CO and the d_{xy} orbital of Mo^{5+} in which, for molybdenyl structures, the unpaired electron is located.

In relation to the proposed structure, it is also interesting that when O_2 was adsorbed under a 10^{-1} Torr pressure at 77 K onto the sample with the CO–Mo^{5+} species, no electron transfer of the type $Mo^{5+} + O_2 \rightarrow Mo^{6+} - O_2^-$ was observed, indicating that no available coordination position exists at the Mo^{5+} center (*11*).

These findings contrast with previous results showing that at room temperature two CO molecules can coordinate the tetrahedral Mo^{5+} or V^{4+} centers obtained by heating MoO_3/SiO_2 or V_2O_5/SiO_2 catalysts in H_2 at 773 K (*3*, *5*). The main differences between these and the present adsorption experiments are the temperature of adsorption, 77 K in the present case, and the method of reduction which, for thermally reduced samples, proceeds through the formation of oxygen vacancies within the lattice of the molybdenum oxide (i.e., $Mo\text{-}O + H_2 \rightarrow Mo\text{-}\square + H_2O$). The absence of such vacancies in the photochemically reduced sample would explain why the surface relaxation of the lattice ions around the tetrahedral Mo^{5+} centers is partially prevented, enabling thus only a small rearrangement to occur with admission of an extra ligand in their coordination sphere.

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