Electron Paramagnetic Resonance Study of the Reactivity toward Carbon Monoxide and Oxygen of O⁻ Ions Adsorbed on Silica-supported Molybdenum Catalysts

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Using the e.p.r. technique, the reaction at 77 K of an O⁻ radical, formed by N_2O adsorption on reduced MoO_3/SiO_2 samples, with CO or ¹³CO was followed, and it was possible to detect a CO_2^- radical ($g_1 = 2.0029$, $g_2 = 2.0016$, $g_3 = 1.9974$, $A_1 = 199$ G, $A_2 = 240$ G, $A_3 = 207$ G) which was stable at room temperature. This species reacted with O_2 at 77 K to give rise to a radical of the type $(O_2COO)^-$ ($g_1 = 2.0486$, $g_2 = 2.0078$, $G_3 = 2.0026$, $A_{1C} = 0$G, $A_{2C} = 4.8$ G, $A_{3C} = 6$ G, $A_{3O_I} = 104$ G, $A_{3O_{II}} = 40$ G). At 150 K, it disappeared irreversibly, generating an O_3^- radical ($g_1 = 2.0175$, $g_2 = 2.0097$, $g_3 = 2.0040$, $A_{3O_I} = 80$ G, $A_{3O_{II}} = 70$ G) similar to that formed by direct adsorption of oxygen on reduced MoO_3/SiO_2.

Because of their possible role as intermediates in catalytic reactions, oxygen anion radicals have been widely studied. The mononuclear oxygen species adsorbed on oxide surfaces have been recently reviewed,[1] and the experimental results show that the O⁻ species in particular is very reactive. The O⁻ ion adsorbed on molybdenum catalysts was first reported by Shvets and Kazansky,[2] and confirmed using ¹⁷O-enriched N_2O by Ben Taarit and Lunsford.[3] These O⁻ ions react with hydrogen,[4] ethene,[5,6] propene and but-l-ene[6] and carbon monoxide.[4,7]

In the present work we have investigated the reactivity of O⁻ adsorbed on MoO_3/SiO_2 toward carbon monoxide and oxygen. Evidence is presented for the formation of a CO_4^--type radical. These results are related to the findings of Ben Taarit *et al.*[8] and Shvets *et al.*,[9] who were able to stabilize the same type of radical on MgO and Cr/SiO_2 catalysts, respectively.

EXPERIMENTAL

The supported molybdenum catalyst was prepared by impregnation of silica with ammonium paramolybdate according to a procedure described earlier.[10] Analysis of the sample gave *ca.* 2% Mo by weight with a surface area of 450 m² g⁻¹. The solid was activated at 773 K first under 20 Torr‡ oxygen for 3 h, then under 200 Torr hydrogen for 30 min, and was finally outgassed *in vacuo* (10⁻⁵ Torr) at 773 K for 1 h. The adsorption and pressure measurements were carried out in a conventional volumetric apparatus to which the e.p.r. tubes could be attached *via* grease-free stopcocks.

The gases (N_2O, CO and O_2) were supplied by l'Air Liquide (France). 70% ¹⁷O-enriched oxygen and 90% ¹³C-enriched carbon monoxide were supplied by CEA (France). Prior to adsorption, N_2O was purified by the freeze–pump–thaw technique, while O_2 and CO were used without further purification and passed through a liquid-nitrogen trap before adsorption.

‡ 1 Torr = 101 325/760 Pa.

The O^- radicals were obtained by adsorbing N_2O at 300 K under 30 Torr and heating the catalyst to 360 K for 30 min. This procedure gave the highest concentration of O^- ions. The adsorptions of CO and O_2 under 30 and 10^{-1} Torr, respectively, were performed at 77 K.

The e.p.r. spectra were obtained on a Varian (model E-3) spectrometer working at 9.3 GHz (X band) with 100 kHz field-modulation and supplied with a variable-temperature accessory. The values of the g tensor were measured relative to a DPPH sample ($g = 2.0036$). The magnetic field increases from left to right in all the figures.

RESULTS AND DISCUSSION

THE O^- ION

The activation treatment led to several types of Mo^{5+} ions, some of which have been described previously.[10-12] The situation is complex and a detailed investigation will be given elsewhere.[13]

The adsorption of N_2O under 30 Torr at room temperature did not generate a new e.p.r. signal. To produce O^- ions it was necessary to heat the sample at 360 K for 30 min. Thus an e.p.r. species was formed with $g_\perp = 2.0198$ and $g_\parallel = 2.0050$, consistent with the formation of O^- ions.[1]

CO ADSORPTION

Adsorption of carbon monoxide under 30 Torr at 77 K did not cause any change in the O^- spectrum. On heating the sample at 140 K, the O^- signal disappeared to give rise to a spectrum characterized by $g_1 = 2.0029$, $g_2 = 2.0016$ and $g_3 = 1.9974$ (fig. 1). In the present case, the g tensor alone can be used to identify the radical[14] and this signal can be assigned to CO_2^-, in agreement with Kazusaka and Lunsford who reported a g tensor with $g_\perp = 2.0020$ and $g_\parallel = 1.9976$ for the same system.[7] Using ^{13}C-enriched carbon monoxide led to the spectrum of fig. 2 composed of the CO_2^- radical, O^- radical and the Mo^{5+} ion. The following ^{13}C hyperfine tensor was obtained: $A_1 = 199$ G, $A_2 = 240$ G and $A_3 = 207$ G.

CO_2^- was stable at room temperature on MoO_3/SiO_2. The magnetic parameters of adsorbed CO_2^- ions are in good agreement with earlier measurements performed either on a surface (MgO)[15] or in a solid (calcite).[16] Using the same procedure as that followed by Mériaudeau et al.[15] an OCO angle of ca. 124° can be derived for CO_2^- on MoO_3/SiO_2. This angle is smaller than that found in solids[16] or on MgO,[15] and this might be related to the non-flat surface site produced by the presence of surface molybdenyl ions with a short Mo=O bond.[12] A similar explanation has been given for the non-equivalence of oxygen nuclei in O_2^- adsorbed on MoO_3/SiO_2 catalysts.[14] In the present case it is interesting that the carbon atom of CO_2^- achieves nearly sp^2 hybridization.

CO_4^--TYPE ION

After the formation of CO_2^- on MoO_3/SiO_2, the excess of carbon monoxide was pumped off at 77 K and $^{16}O_2$ admitted under 10^{-1} Torr at 77 K. The CO_2^- signal disappeared, leading to a new e.p.r. spectrum with the following g-tensor components (fig. 3): $g_1 = 2.0486$, $g_2 = 2.0078$ and $g_3 = 2.0026$.

When $^{16}O_2$ was adsorbed onto ^{13}C-enriched CO_2^- under the same conditions, it was possible to observe a hyperfine tensor due to ^{13}C which was measured as $A_{1C} \approx 0$ G, $A_{2C} \approx 4.8$ G and $A_{3C} = 6$ G.

Adsorption of ^{17}O-enriched oxygen onto CO_2^- generated the spectrum depicted in fig. 4, where the peaks marked with an asterisk probably correspond to $^{17}O_2^-$ formed in small concentrations on adsorbing ^{17}O-enriched oxygen onto sites not occupied by CO_2^-. Only the low-field part of the spectrum is given.

Analysis of the hyperfine structure following a method[17] described earlier indicates that there are two oxygen nuclei in the species and that these are non-equivalent. The [17]O hyperfine tensor components are measured as $A_{3O_I} = 104$ G and $A_{3O_{II}} = 40$ G, where O_I and O_{II} refer to the two non-equivalent oxygen nuclei. Only the hyperfine component centred around $g_3 = 2.0026$ could be resolved.

The detection in the spectra of hyperfine structures due to ^{13}C and [17]O shows that the corresponding radical probably comes from an addition reaction to form a CO_4^--type radical according to

$$O_2 + CO_2^- \rightarrow O_2{-}CO_2^-. \tag{1}$$

This is in agreement with previous results which are summarized in table 1.

Note that the oxygen nuclei of this species which are non-equivalent are very similar
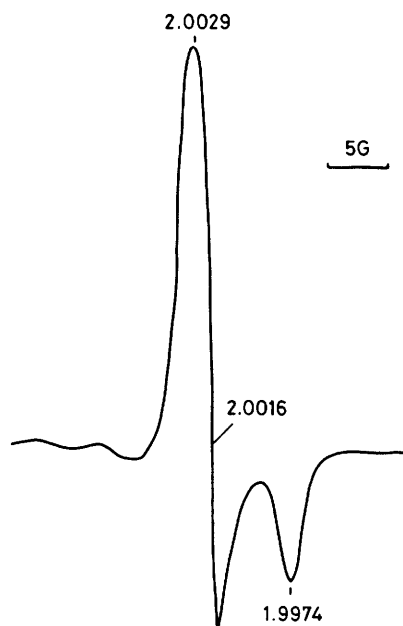

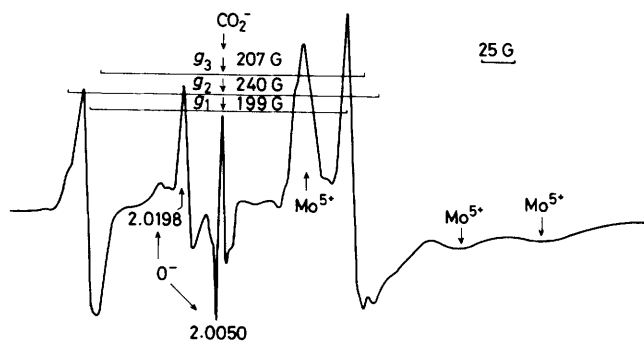FIG. 1.—E.p.r. spectrum at 77 K of CO_2^-, formed by reacting O^- with CO, adsorbed on MoO_3/SiO_2.

FIG. 2.—E.p.r. spectrum at 77 K of 90% ^{13}C-enriched CO_2^-, formed by reacting O^- with CO, adsorbed on MoO_3/SiO_2. The spectrum has been obtained when only a fraction of O^- ions have reacted. The values 207, 240 and 199 G refer to the hyperfine tensor (see text).

in nature to peroxy radicals attached to a polymeric chain. Thus for peroxy radicals on polytetrafluoroethylene (PTFE) the ^{17}O hyperfine tensor was measured as $A_{3O_I} = 107$ G and $A_{3O_{II}} = 46$ G,[18] very close to the values observed for CO_4^-.

Thus a reasonable structure for CO_4^- is

$$\begin{array}{c} O \diagdown \\ \qquad C - O_{II} \diagdown \\ O \diagup \qquad\qquad O_I \end{array}$$
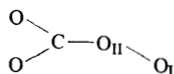
where O_I is the oxygen atom further from the carbon.

FORMATION OF O_2^- FROM CO_4^-

The CO_4^- species was stable up to 150 K, at which temperature it was irreversibly transformed into a species which did not show any ^{13}C hyperfine structure. The corresponding g tensor was measured as $g_1 = 2.0175$, $g_2 = 2.0097$ and $g_3 = 2.0040$.
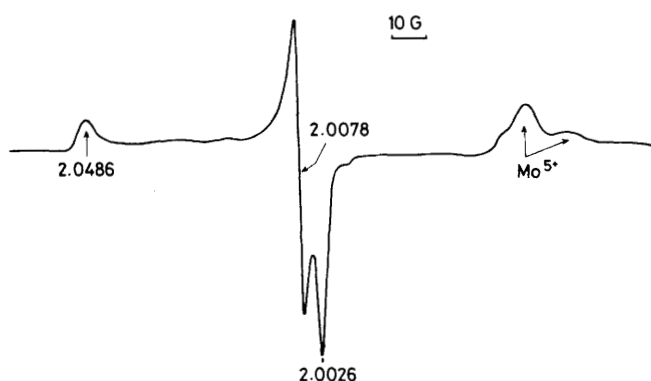

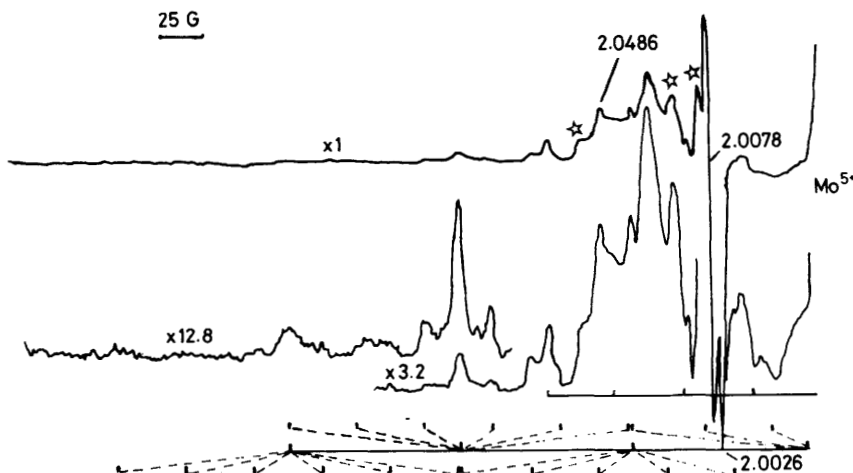FIG. 3.—E.p.r. spectrum at 77 K of $(O_2CO_2)^-$, formed by reacting CO_2^- with O_2, adsorbed on MoO_3/SiO_2.

FIG. 4.—E.p.r. spectrum at 77 K of $(O_2CO_2)^-$, formed by reacting CO_2^- with 70% ^{17}O-enriched O_2, adsorbed on MoO_3/SiO_2. Only the low-field part of the spectrum is given. The peaks marked with an asterisk correspond to $^{17}O_2^-$ (see text).

TABLE 1.—E.P.R. PARAMETERS FOR $(O_2-CO_2)^-$ IONS ADSORBED ON SURFACES

system	g_1	g_2	g_3	A_{1_C}/G	A_{2_C}/G	A_{3_C}/G	A_{3O_I}/G	$A_{3O_{II}}/G$
MgO^a	2.040	2.0072	2.0015	—	3.5	2.8	100	50
Cr/SiO_2^b	2.046	2.006	2.001	—	4.0	4.7	98	42
MoO_3/SiO_2^c	2.0486	2.0078	2.0026	—	4.8	6	104	40

^{a} Ref. (8); ^{b} ref. (9); ^{c} this work.

When ^{17}O-enriched oxygen was used under the same conditions to form a CO_4^--type ion, the increase in temperature above 150 K led to a hyperfine structure which was consistent with two non-equivalent oxygen nuclei. The hyperfine tensor was measured as $A_{3O_I} = 80$ G and $A_{3O_{II}} = 70$ G. Only the hyperfine component centred around $g_3 = 2.0026$ could be resolved. A similar signal can be obtained by direct adsorption of O_2 on a reduced MoO_3/SiO_2 sample, and this has been assigned to O_2^- bound to Mo^{6+}.[19]
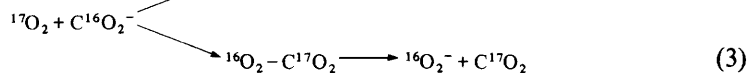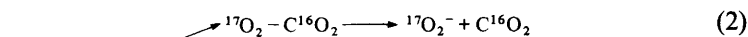
Despite the similarity of the non-equivalence of the two oxygen nuclei in $O_2C-O_{II}-O_I^-$ and in peroxy radicals on PTFE their stabilities were very different, since the latter were stable up to 573 K.[20]

Spin-density measurements performed as described by Mériaudeau et al.[15] indicate 5% on C, 26% and 69% on the two oxygen nuclei O_{II} and O_I, respectively, leaving ca. 0% on the two oxygen nuclei belonging to CO_2.

The e.p.r. spectra of the $(CO_2-O_2)^-$ ions adsorbed on MgO reported by Ben Taarit et al.[8] have recently been discussed by Schlick and Kevan.[21] These authors have shown that some $(CO_2-O_2)^-$ ions retain some mobility on the oxide surface, giving rise to additional features superimposed on the e.p.r. spectra of the immobile $(CO_2-O_2)^-$ ions.

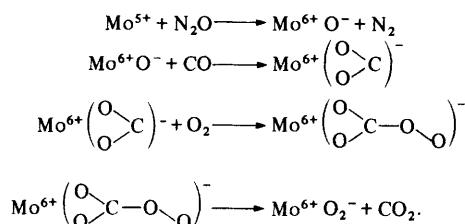In the present work we have not observed any of these additional features, so that the $(CO_2-O_2)^-$ ions can be considered as trapped on the surface. The only possible adsorption sites are the supported Mo^{6+} ions or Si^{4+} ions of the support. The choice between these two possible sites can be made by considering the g_3 component of the O_2^- produced by the decomposition of $(CO_2-O_2)^-$. This component indicates that the O_2^- are adsorbed on Mo^{6+}, as shown earlier.[19] It is thus reasonable to assume that the parent $(CO_2-O_2)^-$ radicals were also adsorbed on Mo^{6+}. This is also consistent with the Mo^{6+} adsorption site for the initial O^- ion, whose e.p.r. spectrum exhibits weak hyperfine structure due to Mo nuclei with $I = \frac{5}{2}$ (natural abundance ca. 25%).

A study of the thermal decomposition of $(CO_2-O_2)^-$ confirms that its formation indeed arises according to reaction (1) and that the spin-density measurements are correct. In fact from the two following possible mechanisms

$$^{17}O_2 + C^{16}O_2^- \begin{cases} {}^{17}O_2 - C^{16}O_2 \longrightarrow {}^{17}O_2^- + C^{16}O_2 & (2) \\ {}^{16}O_2 - C^{17}O_2 \longrightarrow {}^{16}O_2^- + C^{17}O_2 & (3) \end{cases}$$

only reaction (2) is supported by the experimental results, since ^{17}O hyperfine lines are indeed detected in the e.p.r. spectrum of O_2^- resulting from the decomposition of $(CO_2-OO)^-$ ions prepared by reacting $C^{16}O_2^-$ with $^{17}O_2$. Furthermore, the intensities of the O_2^- lines are those expected from oxygen labelled with 70% ^{17}O.

The previous results support the following mechanism for CO oxidation onto MoO_3/SiO_2:

$$Mo^{5+} + N_2O \longrightarrow Mo^{6+} O^- + N_2$$

$$Mo^{6+}O^- + CO \longrightarrow Mo^{6+} \begin{pmatrix} O \\ O \end{pmatrix} C \Bigg)^-$$

$$Mo^{6+} \begin{pmatrix} O \\ O \end{pmatrix} C \Bigg)^- + O_2 \longrightarrow Mo^{6+} \begin{pmatrix} O \\ O \end{pmatrix} C - O \begin{matrix} O \end{matrix} \Bigg)^-$$

$$Mo^{6+} \begin{pmatrix} O \\ O \end{pmatrix} C - O \begin{matrix} O \end{matrix} \Bigg)^- \longrightarrow Mo^{6+} O_2^- + CO_2.$$

The O^{2-} surface ions play no role. This mechanism is in agreement with those proposed earlier for V_2O_5/SiO_2[22] and Cr/SiO_2[9] catalysts.

Note that the $(O_2COO)^-$ ion belongs to the class 'B' of adsorbed species formed by secondary reactions.[14] At present only a few cases of such adsorbed species are known.

Finally, we have found that the stability of the $(O_2COO)^-$ ion is very sensitive to the chosen preparation conditions. In this work we have found that it was not stable above 150 K on impregnated samples. This prevented us from studying the exchange reactions between $(O_2COO)^-$ and gas-phase oxygen. We are thus trying to increase the stability of the $(O_2COO)^-$ ion in order to investigate the exchange reaction.

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