

## ESR Study of CO Adsorption on Thoria

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Electron spin resonance (ESR) study of  $^{12}\text{CO}$  and  $^{13}\text{CO}$  adsorbed on thoria between 25 and 300°C shows that part of the adsorbate exists in the form of a paramagnetic axial radical, the unpaired electron of which is located in a  $\pi$  orbital.

Two types of adsorbed CO are detected by ESR, for which the unpaired electron is, respectively, 33 and 15% on the carbon atom. These observations are consistent with the previous hypothesis of a positively charged CO adsorbate on thoria.

### I. INTRODUCTION

Electron spin resonance (ESR) spectroscopy has proved to be a powerful tool in the characterization of adsorbed species, but has been comparatively more used for oxygen (1) than for other adsorbates. In the course of a thorough study of carbon monoxide oxidation on thoria, ESR has been employed for the detection of oxygen species (2). The present work is devoted to an ESR study of carbon monoxide adsorption on  $\text{ThO}_2$  and of the reactivity of the adsorbed species towards oxygen. More specifically, our aim is to check the existence of a positively charged CO species, which has been supposed to be an intermediary of catalytic oxidation of CO since our early work on this catalysis (3).

Brey and co-workers (4) have lately reported on the ESR study of CO adsorption on thoria. According to them, this adsorption gives rise to five different signals, depending on the conditions of adsorption and of spectrum recording. The assignment of one of these species, called *D* in their publication, could be  $\text{CO}^+$ , although this interpretation does not seem convincing to the authors. We deemed it valuable to re-investigate these results while operating in the actual conditions of our own previous experiments in order, not only to detect paramagnetic forms of adsorbed CO, but

also to follow their transformation under the influence of adsorbed oxygen. Moreover, we considered that the use of  $^{13}\text{CO}$  should allow us to derive hyperfine constants and to obtain some insight into the electronic structure of CO adsorbate.

### II. EXPERIMENTAL METHODS

Thoria has been prepared by thorium oxalate decomposition, and its surface has been standardized by heating in oxygen at 500°C for 8 hr, followed by degassing at  $10^{-5}$  Torr and 500°C for 16 hr. The specific area is then about 30  $\text{m}^2/\text{g}$ .

Subsequent surface reduction by hydrogen, according to a procedure described in Ref. (2) did not change the ESR signals given by CO adsorption, so that this hydrogen treatment was not used in the experiments reported below.

Electron spin resonance measurements have been carried out with Varian spectrometers, either of E 3 type for the X band, or of V 4502 type for the Q band. The 90% enriched  $^{13}\text{CO}$  from Merck Canada was used without further purification.

### III. RESULTS

#### A. $^{12}\text{CO}$ Adsorption

When CO, under a pressure of 120 Torr, is contacted with thoria at 25°C, the

solid progressively and reversibly assumes a yellow shade. The ESR spectrum recorded in this partial pressure of CO and at this temperature of 25°C gives the signal shown in Fig. 1, with  $g$  values of  $g_{\parallel} = 1.981$  and  $g_{\perp} = 1.998$ . We shall call this signal I; it is typical of paramagnetic species with axial symmetry. The width of the line corresponding to  $g_{\perp}$  can be due to an insufficient resolution. Passage from  $X$  band to  $Q$  band does not improve the resolution; however, the width of the line is strongly increased (about four times). When CO is contacted with thoria at 250°C and 120 Torr, the number of paramagnetic species responsible for signal I increases (Fig. 2b). After 100 min, the number of paramagnetic species, as determined by comparison with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , is about  $5 \times 10^{17}$  species/g. The gravimetric curve (Fig. 2a) gives an overall amount of CO adsorbed at the same time equal to  $2.66 \text{ mg g}^{-1}$  of adsorbent, i.e.,  $57 \times 10^{18}$  molecules  $\text{g}^{-1}$ .

The shape of signal I is maintained for higher adsorption and recording temperatures (up to 300°C), and pressures lower than 120 Torr, but, of course, the number of detected spins depends on these parameters. It is worth noting that when  $\text{CO}_2$  is adsorbed on thoria before CO adsorption, according to the following procedure at 25°C—

- (i)  $\text{CO}_2$  adsorption at 50 Torr,
- (ii) evacuation down to  $10^{-5}$  Torr,
- (iii) CO adsorption at 120 Torr—

the solid remains white, and no ESR signal is observed. Conversely, when the same procedure is applied when oxygen is pre-

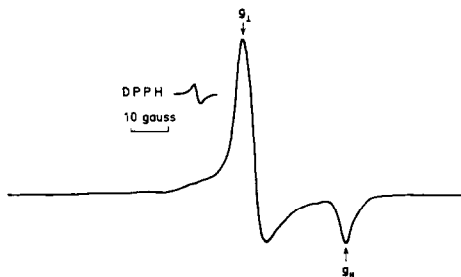


FIG. 1. Electron spin resonance spectrum of  $^{12}\text{CO}$  adsorbed on thoria at 25°C and 120 Torr pressure. Recording at 25°C,  $X$  band.

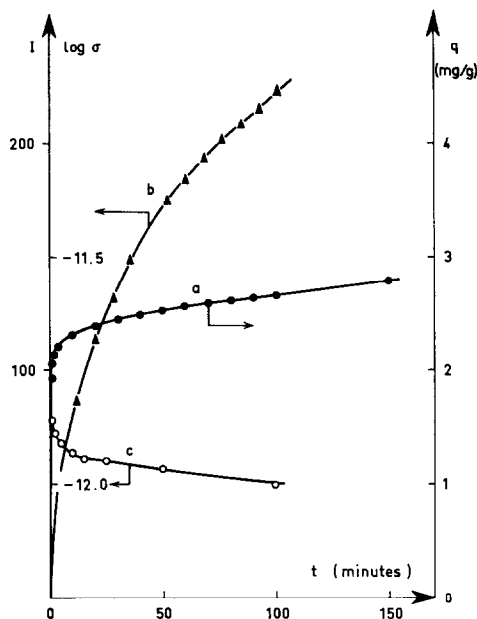


FIG. 2. Comparison of (a) the overall amount of CO adsorbed on  $p$ -type thoria at 250°C and 120 Torr pressure, (b) the amount of paramagnetic CO species, and (c) the variation of electrical conductivity vs time. a—gravimetric curve; b—ESR signal amplitude  $I$  (arbitrary units); c—variation of the logarithm of conductivity.

adsorbed at 1 Torr pressure, then signal I is observed again.

### B. $^{13}\text{CO}$ Adsorption

$^{13}\text{CO}$  has been adsorbed on thoria at 20 Torr at room temperature (spectrum shape is identical at higher temperature). The experimental results are compared to those obtained with  $^{12}\text{CO}$  in Fig. 3 ( $X$  band) and Fig. 4 ( $Q$  band). They show two values of the hyperfine splitting  $A_{\parallel}$  and one of the hyperfine splitting  $A_{\perp}$ ; hence it appears that two CO adsorbates are involved.

### C. Oxygen Adsorption on Preadsorbed CO

The procedure is as follows:

- (i) CO adsorption at 120 Torr and 25°C;
- (ii) evacuation down to  $10^{-5}$  Torr at 25°C;
- (iii)  $\text{O}_2$  adsorption at  $10^{-1}$  Torr.

(a) If the latter adsorption takes place at 77°K, signal I keeps about the same

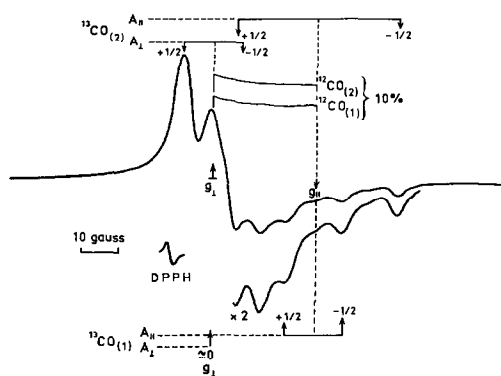


FIG. 3. Electron spin resonance spectrum of  $^{13}\text{CO}$  adsorbed on thoria at  $25^\circ\text{C}$ . Recording at  $25^\circ\text{C}$ , X band.

intensity, whereas another signal II immediately develops, with the following  $g$  values:

(II)  $g_1 = 2.019$ ,  $g_2 = 2.007$ ,  $g_3 = 2.002$ . If the sample is kept at  $77^\circ\text{K}$  during 30 min, signal II remains unaltered and I slowly diminishes, whereas a signal III appears, characterized by the following  $g$  values:

(III)  $g_1 = 2.040\text{--}2.050$ ,  $g_2 = 2.0094$ ,  $g_3 = 2.004$ .

(b) If oxygen adsorption takes place at  $25^\circ\text{C}$ , the triplets II and III appear simul-

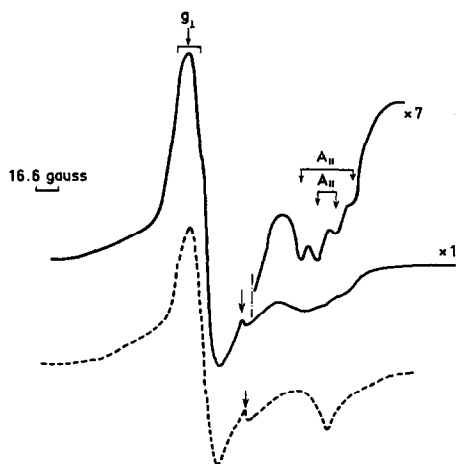


FIG. 4. Comparison of ESR spectra of  $^{12}\text{CO}$  (dashed line) and of  $^{13}\text{CO}$  (solid line) adsorbed on thoria at  $25^\circ\text{C}$ . Recording at  $25^\circ\text{C}$ , Q band. (The weak line indicated with an arrow and appearing only in Q band recording remains unidentified.)

taneously and are accompanied by an asymmetric signal that we shall denote as IV, the amplitude of which slowly increases with time, whereas that of I slowly decreases and that of II rapidly decreases.

If thoria is then progressively heated from  $25$  to  $250^\circ\text{C}$  (all the ESR spectra being recorded at  $25^\circ\text{C}$ ), the amplitude of all the signals decreases, and at  $250^\circ\text{C}$  only signal IV remains, with  $g$  values equal to:

(IV)  $g_{\perp} = 2.0018$ ,  $g_{\parallel} = 1.990$ .

At  $250^\circ\text{C}$ , this signal itself is strongly reduced, and its lifetime is short. It should be noted that the same signal is obtained by oxygen adsorption at  $250^\circ\text{C}$  on a solid on which CO has been previously adsorbed at  $250^\circ\text{C}$ , but its short lifetime does not allow its systematic study.

No hyperfine coupling could be detected in signal IV by using  $^{13}\text{CO}$ , owing to the weakness of this signal. Likewise, it has not been possible, by adsorbing  $\text{O}_2$  after  $^{13}\text{CO}$ , to detect any reactivity difference between the two types of adsorbed CO.

#### IV. INTERPRETATION AND DISCUSSION

##### A. ESR Spectrum of Adsorbed CO

In Table I, we have collected the  $g$  values which may be attributed to adsorbed CO. First, the signal denoted by A in Ref. (4) seems to be similar to our signal II, which is undoubtedly due to oxygen. This assignment is consistent with the transient existence of the signal A observed in Ref. (4). Experiments at  $77$  and  $298^\circ\text{K}$  using  $^{17}\text{O}_2$  as adsorbate undoubtedly showed that triplets II and III are due to  $\text{O}_2^-$  species (5): signal III corresponds to  $\text{O}_2^-$  proper ( $A_3 \approx 74$  G,  $A_1 \approx A_2 \approx 0$ ) and II is most probably due to an  $\text{O}_2^-$  adsorbate, but with  $A_{3(1)} \approx 95$  G and  $A_{3(2)} \approx 65$  G, i.e., with two nonequivalent oxygen atoms. It is noteworthy that oxygen adsorption under a pressure as low as  $10^{-1}$  Torr does not give rise to an  $\text{O}_2^-$  spectrum when the solid has not been pretreated with CO. Detection of  $\text{O}_2^-$  on an originally bare surface requires much greater oxygen pressures (2).

Signal IV in the present work has  $g$  values close to those of the signal called E in Ref. (4), so that its assignment could be

TABLE 1

Adsorbent	Adsorbate	$g_x$	$g_y$	$g_z$	Reference
MgO	CO	2.0021	2.0021	2.0055	(6)
SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	CO	2.0020	2.0020	2.0065	(7)
H-Y type zeolite	CO <sup>+</sup>	2.0005	2.0005	2.0045	(8)
ThO <sub>2</sub>	CO "A"	2.004	2.009	2.020	(4)
	CO "B"	1.980	1.992	1.997	
	CO "C"	1.982	1.998	1.998	
	CO "D" (CO <sup>+</sup> ?)	2.008	2.013	2.013	
ThO <sub>2</sub>	CO (signal I)	1.981	1.998	1.998	(This work)

the same, i.e., a CO<sub>2</sub><sup>-</sup> species. However, in our case, its stability seems much smaller than for species E in the previous work, and no hyperfine structure due to the <sup>13</sup>C nucleus was observed, so that the precise interpretation of signal IV deserves further study.

Finally, the only signal that we can ascribe to a CO species is the axially symmetric signal I, which is the same as the signal called C in Ref. (4). The question then arises to look closer firstly at its electronic distribution, as indicated by the hyperfine structure, and secondly at its formation kinetics and reactivity.

### B. Nature of Adsorbed CO Species

We have observed two values of the hyperfine splitting  $A_{\parallel}$  and one of the hyperfine splitting  $A_{\perp}$ . This observation can be accounted for by the existence of two types of CO adsorbates, without mutual interaction, and corresponding to the following  $A$  tensors:

	$A_{\perp}$ (G)	$A_{\parallel}$ (G)
CO <sub>(1)</sub>	0	14
CO <sub>(2)</sub>	14	44

It should then be possible to derive from these constants some information on the electronic distribution in the corresponding adsorbates. If we introduce

$$a_{\text{iso}} = \frac{2A_{\perp} + A_{\parallel}}{3},$$

we may write

$$a_{\text{iso}} = A_0 c_{2s}^2,$$

where  $c_{2s}^2$  is the spin density on the 2s orbital of <sup>13</sup>C atom and  $A_0$  is a constant which has been calculated equal to 1110.8 G (10).

Conversely, it is possible to calculate the spin density on the 2p orbital, by using the dipolar tensor (6):

$$A = a_{\text{iso}} + \begin{vmatrix} -b & & \\ & -b & \\ & & 2b \end{vmatrix}.$$

Thus, the  $p$  character of the orbital is given by

$$c_{2p}^2 = \frac{b}{B_0}$$

with a value of  $B_0$  which has been evaluated equal to 32.4 G (10). The following values of  $c_{2s}^2$  and  $c_{2p}^2$  are found according to these derivations:

	$c_{2s}^2$	$c_{2p}^2$	$c_{2s}^2 + c_{2p}^2$
(CO $s_1$ )	$4 \times 10^{-3}$	0.14	0.15
(CO $s_2$ )	$2 \times 10^{-2}$	0.31	0.33

It can be concluded that the electron responsible for the paramagnetism is, for either type, on an orbital of marked  $p$  character, and spends, respectively, 15 and 33% of its time around the carbon atom.

The question then arises as to how this electronic distribution can be realized by bonding of a CO molecule with a surface site. In interpreting results somewhat similar to our own, Lunsford and Jayne (6) supposed that this bonding resulted from the transfer of two electrons from the carbon  $\sigma$  orbital to the site, and the back

transfer of one electron from the site to the antibonding  $\pi$  orbital of CO, and they likened this process to a metal carbonyl formation. It must be recalled that, in our case, no such formation of metal-CO bonds could have been detected by ir spectroscopy (11), which, on the contrary, supports the formation of bonds between CO and surface oxygen ions. However, the overall amount of adsorbed CO being higher than the amount of paramagnetic adsorbate by a factor of 100, the sensitivity of the ir technique would not have been sufficient to detect a carbonyl bonding type for the latter. The fact that the ir spectrum of adsorbed CO is not modified at 250°C by an oxygen introduction at 30 Torr pressure (11), whereas the ESR spectrum of CO radical vanishes at the same temperature in the presence of oxygen at  $10^{-1}$  Torr pressure, can be explained by a difference in reactivity between adsorbates, the paramagnetic one being more reactive than the others.

Taking into account the marked change of electrical conductivity during CO chemisorption (Fig. 2), we suppose that the electronic exchange between CO and the surface results in the formation of slightly positive CO adsorbates and a surface becoming, *as a whole* and to a depth of a few atomic layers, negative. This creates energy band curvature in the vicinity of the surface, and accounts for the change of electrical conductivity. Figure 2 shows that the formation of the paramagnetic CO species is slower than the overall adsorption of CO, as measured by gravimetry, under given conditions of temperature and pressure. Besides, ESR confirms that CO<sub>2</sub> is an inhibitor of CO adsorption whereas oxygen is not, which is in accordance with our previous findings concerning the adsorption sites (9). The observation according to which oxygen adsorption under the paramagnetic charged form O<sub>2</sub><sup>-</sup> is enhanced by

the presence of preadsorbed CO is a direct consequence of the electronic theory of adsorption (12).

## V. CONCLUSION

It has been shown that when CO is adsorbed on thoria between 25 and 300°C, part of the CO exists in the form of a positively charged axial radical. The unpaired electron is located on a  $\pi$  orbital. Two adsorption types are detected by ESR, for which the unpaired electron is, respectively, 33% and 15% on the carbon atom. These observations are consistent with what was previously known on CO chemisorption on thoria.

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