$$CpV(CO)_4 + bpy \xrightarrow{xylene} V(bpy)_3 + \text{unidentified products} \quad (3)$$

presence of bpy leads to the formation of unidentifiable products.

The structure of **2** consists of discrete *cis*-($\eta^5$-$C_5H_5$)V(CO)$_2$·bpy molecules possessing an imposed crystallographic *Cm* symmetry (Figure 2). The vanadium lies on the mirror plane bisecting the C3–C3′ and C16–C16′ bonds. The coordination geometry around the metal center is square pyramidal with the two nitrogen atoms from bpy and two carbon atoms from the carbonyls on the basal plane and the centroid of $\eta^5$-bonded Cp ring on the apex. The vanadium lies at 0.898 (1) Å from the basal plane, which is perfectly planar for symmetry requirements. Bond distances and angles in the vanadium coordination sphere are in agreement with the corresponding ones observed in complex **1**, the V–N distance being 2.138 (4) Å. All bond distances and angles within the Cp ring and bpy are as expected.

Complex **2** does not display any special spectroscopic features. Two intense absorptions are present in the IR spectrum ($\nu(CO)_{sym}$ 1843 cm$^{-1}$; $\nu(CO)_{asym}$ 1780 cm$^{-1}$), as expected for a *cis*-dicarbonyl transition-metal derivative. The Cp resonances are present as singlets in the $^1$H NMR (4.80 ppm) and $^{13}$C NMR (96.55 ppm) spectra, and the resonances of the coordinated bpy are as expected for an ABCD spin system. No resonances attributable to carbonyl groups have been observed in the $^{13}$C NMR spectrum.

Attempts to utilize **1** for oxidative-addition reactions with a diverse range of substrates such as $CO_2$, $CO_2$-like molecules, azobenzene, diazoalkanes, and organic azides have led to the formation of CpV(CO)$_4$ as the main product. We believe that the low affinity for CO of the mono(cyclopentadienylvanadium(III)) derivatives formed during the oxidative-addition reactions is responsible for such a failure. In other words, for each molecule of 1 that undergoes oxidative addition, three molecules of CO are released. Fast reaction of **1** with CO leads to the unreactive CpV(CO)$_4$ in 75% yield. Efforts to isolate other species from the reaction mixtures have been unsuccessful so far.

**Acknowledgment.** This work has been supported by the University of Groningen and the University of Parma. We are indebted to Bart Hessen for recording and discussing the NMR spectra.

**Registry No.** **1**, 111635-23-5; **2**, 99620-52-7; **3**, 111635-24-6; CpV(CO)$_4$, 12108-04-2; CpV(CO)$_3$PPh$_3$, 12213-09-1; CpV(CO)$_3$dppe, 73557-87-6; CpV(CO)$_3$dppm, 73574-37-5; CpV(CO)$_3$L (L = cyclohexyl isocyanide), 103903-19-1.

**Supplementary Material Available:** Details of the structure solutions and refinements with references and listings of coordinates for hydrogen atoms (Table SI) and thermal parameters (Table SII) for **1**, thermal parameters for **2** (Table SIII), and nonessential bond lengths and angles for both **1** and **2** (Tables SIV and SV) (6 pages); tables of calculated and observed structure factors for both structure determinations (8 pages). Ordering information is given on any current masthead page.

---

(13) Herzog, S. *Z. Anorg. Allg. Chem.* **1958**, *294*, 155.

---

Contribution from the Istituto di Chimica Fisica, Universita di Torino, Corso M. D'Azeglio 48, 10125 Turin, Italy,
and Departamento de Quimica Inorganica, Universidad de Oviedo, 33071 Oviedo, Spain

# Infrared Characterization of Group VI ($6^1$) Metal Carbonyls Adsorbed onto $\gamma$-Alumina

Adriano Zecchina,*[†] Estrella Escalona Platero,[‡] and Carlos Otero Arean[‡]

*Received March 27, 1987*

The interactions of Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$ with highly dehydroxylated $\gamma$-Al$_2$O$_3$ have been studied by the use of IR spectra, which show both a reversible adsorption and progressive room-temperature loss of CO. Adsorption of the three metal hexacarbonyls occurs via O-bonding between a CO ligand and different Lewis acid sites present at the $\gamma$-Al$_2$O$_3$ surface. These sites are as follows (in order of decreasing Lewis acid strength): (i) defective sites representing less than 1% of the surface cations; (ii) bulk tetrahedral Al$^{3+}$ ions emerging on the surface; (iii) bulk octahedral Al$^{3+}$ ions emerging on the surface. The sum of the last two types corresponds roughly to the total number of surface cations. Comparison of the IR spectra of the adsorbed metal carbonyls with the spectra of the homogeneous analogues formed by interaction in solution with Lewis acceptors of similar strength allowed full assignment of the IR spectra of adsorbed species and showed the close similarity between heterogeneous and homogeneous O-bonded carbonyl adducts. The major fraction of adsorbed hexacarbonyls is removed by pumping at room temperature. However, a small fraction (in the order Mo(CO)$_6$ > Cr(CO)$_6$ > W(CO)$_6$) undergoes reversible decarbonylation, giving a subcarbonyl species still O-bonded to the Lewis acid centers of the metal oxide support.

## Introduction

Deposition of metal carbonyls on high surface area metal oxides can provide a convenient means to investigate ligand substitution reactions[2] and catalytic behavior.[3] Reactions catalyzed by supported group VI metal carbonyls, such as olefin metathesis and hydrogenation and Fischer–Tropsch synthesis, have recently been investigated.[4–8] A related approach is to use the immobilized carbonyls as precursor materials for the preparation of highly dispersed transition metals and to use metallic clusters for heterogeneous catalysis.[9–15] In all of these contexts, characterization of the supported metal carbonyl is a prime requirement to understand the subsequent chemical processes.

Transition aluminas[16] are among the most extensively used catalyst supports. $\gamma$-Alumina, which belongs to this group, shows a spinel-type lattice where Al$^{3+}$ ions occupy tetrahedral and octahedral interstices in a cubic close-packed array of oxide ions. The structure of the oxide surface is not entirely clear,[17–19] particularly because relaxation of the underlying oxide structure gives

---

[†] Universita di Torino.
[‡] Universidad de Oviedo.

(1) The periodic group notion in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)
(2) Zecchina, A. *Mater. Chem. Phys.* **1985**, *13*, 379.
(3) (a) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109. (b) Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1977**, *15*, 189.
(4) Davie, E. S.; Whan, D. A.; Kemball, C. *J. Catal.* **1972**, *24*, 272.
(5) Smith, J.; Howe, R. F.; Whan, D. A. *J. Catal.* **1974**, *34*, 191.
(6) Brenner, A. *J. Mol. Catal.* **1979**, *5*, 157.
(7) Thomas, T. J.; Brenner, A. *J. Mol. Catal.* **1983**, *18*, 197.
(8) Sivasonker, S.; Yesodharan, E. P.; Sudhakar, C.; Brenner, A. *J. Catal.* **1984**, *87*, 514.
(9) Brenner, A.; Hucul, D. A.; Hardwick, S. J. *Inorg. Chem.* **1979**, *18*, 1478.
(10) Ugo, R.; Psaro, R.; Zanderighi, G. M.; Basset, J. M.; Theolier, A.; Smith, A. K. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. 3, p 579.

0020-1669/88/1327-0102$01.50/0

rise to ill-defined surface reconstruction. However, it is known that $Al^{3+}$ ions with various types of coordinatively unsaturated environment are exposed. This, together with the presence of some remaining hydroxide ions, confers on the alumina surface an acid–base character. Lewis acid centers are of particular relevance to metal carbonyl adsorption. They have been evidenced through the interaction of the oxide surface with bases such as ammonia and pyridine.[17,20–24] Surface acidity of $\gamma$-alumina is also manifested by weak chemisorption of CO that shows evidence for the presence of several types of Lewis sites of different strength.[25–27] On highly dehydroxylated $\gamma$-$Al_2O_3$ the most abundant sites are bulk tetrahedral and bulk octahedral $Al^{3+}$ ions emerging on the surface. Highly acidic sites with defective character are also present, although in a much smaller concentration.

Previous IR studies of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ adsorbed on $\gamma$-$Al_2O_3$ have been reported by Howe[28] and Kazusaka.[29] $W(CO)_6$ supported on $\eta$-alumina was studied by Bilhou et al.,[30] also by means of IR spectroscopy. These authors, however, interpreted their spectra on the basis of only one type of adsorption site. In the present paper we report detailed IR spectra that indicate the presence of two major families of metal carbonyl anchoring sites on the surface of highly dehydroxylated $\gamma$-alumina, in agreement with the above-mentioned CO adsorption studies.[25–27]

## Experimental Section

Mesoporous $\gamma$-alumina with a BET surface area of 170 $m^2\ g^{-1}$ has been prepared by thermolysis, at 1173 K, of ammonium alum (Koch-Light 99.97%). X-ray diffraction[31] showed this material to have a spinel-type defective lattice with $2^2/_3$ cation vacancies on the octahedral sites. This corresponds to the unit-cell structural notation $Al_8(Al_{13\,1/3}\square_{2\,2/3})O_{32}$, where parentheses enclose the octahedral cation sites. In the bulk material, 8 $Al^{3+}$ ions (per unit cell) are tetrahedrally coordinated and the remaining $13^1/_3$ are octahedrally coordinated to oxide ions.

Samples of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were obtained from Strem Chemical Co.

A specially designed IR cell allowed activation of the $\gamma$-alumina sample prior to dosification of increasing amounts of each metal carbonyl by vacuum sublimation at room temperature (ca. 298 K). For activation, the $\gamma$-alumina in the form of a self-supporting compressed disk was fired for 20 min at 1073 K under a dynamic vacuum (residual pressure $10^{-5}$ Torr). In order to eliminate residual sulfate impurities, the sample was then reduced three times in hydrogen at 1073 K (10 min), as fully described in ref 27. IR transmission spectra were recorded by using a Perkin-Elmer 580B spectrometer equipped with a data station that allowed difference spectra to be taken.

**Table I.** IR Frequencies ($cm^{-1}$) of Cr, Mo, and W Carbonyls Adsorbed onto $\gamma$-$Al_2O_3$

| bands | $Cr(CO)_6$ | $Mo(CO)_6$ | $W(CO)_6$ |
|---|---|---|---|
| A1 | 2142 (w) | 2145 (w) | 2140 (w) |
| A2 | 2090 (w) | 2090 (w) | 2080 (w) |
| A3 | 2040 (s) | 2040 (s) | 2030 (s) |
| A4 | 1770–1780 (m) | 1760–1770 (m) | 1755–1770 (m) |
| B1 | 2130 (w) | 2132 (w) | 2130 (w) |
| B2 | 2075 (w) | 2070 (sh) | 2060 (sh) |
| B3 | 2000 (s) | 2000 (s) | 1995 (s) |
| B4 | 1850–1875 (m) | 1835–1860 (m) | 1825–1845 (m) |
| D | 1670 (w) | 1670 (w) | 1670 (w) |
| C1 | 2075 (vw) | 2080 (w) | |
| C2 | 2010 (sh) | 2010 (m) | |
| C3 | 1922 (w) | 1925 (m) | |
| C4 | 1605 (w) | 1620–1600 (m) | |
| E | 1530 (w) | 1520 (w) | |

**Scheme I**

$$M(CO)_6 + Al^{3+}_{surf} \longrightarrow (CO)_5M-CO\cdots Al^{3+}_{surf}$$

## Results

The blank IR spectrum showed the $\gamma$-alumina to be highly transparent in the CO stretching region and presented only very weak OH bands in the 3800–3650-$cm^{-1}$ region. These were not significantly affected on subsequent metal carbonyl deposition.

Difference spectra (blank subtracted) of an alumina sample containing increasing amounts of adsorbed $Cr(CO)_6$ are presented in Figure 1a. Parts b and c of Figure 1 show the effect of progressive outgassing at room temperature and of CO admission after the last outgassing step. Corresponding spectra for $Mo(CO)_6$ and $W(CO)_6$ are available as supplementary material. They all show the same general features, which were also observed in a parallel experiment conducted (for $Cr(CO)_6$) on a commerical $\gamma$-alumina (SCS100 Rhone-Poulenc). This material, however, was abandoned because of its higher optical density in the CO stretching region.

As can be immediately observed, the IR spectra are essentially the superposition of two quartets of bands (A1–A4 and B1–B4) (Table I). The components of each quartet grow in a parallel way when the coverage is increased (Figure 1a). A further, much less intense and broader component (labeled D) is observed in the low-frequency side of the A4 band and is centered at about 1670 $cm^{-1}$. Desorption at room temperature (Figure 1b) leads to a gradual disappearance of quartets B1–B4 and A1–A4 and provides further support for the correlation of bands within each quartet. These two experiments clearly demonstrate that the two quartets belong to two well-defined slightly different species (A and B).

It is most noticeable that in adsorption, the A1–A4 quartet is predominant during the initial adsorption stages while B1–B4 predominates at the highest coverages. In desorption, the B1–B4 quartet is the first one to disappear, A1–A4 being more resistant. This shows that the adsorption energy of the A species is greater than that of B. For the $Cr(CO)_6/\gamma$-$Al_2O_3$ system, Figure 1b shows that progressive reduction of the B and A quartets upon outgassing is accompanied by the parallel growth of a new quartet, C (Table I). The C2, C3, and C4 components of this quartet are clearly seen in Figure 1b. Component C1 is inferred from a comparison between spectra of similar intensities in adsorption and desorption. The $Mo(CO)_6/\gamma$-$Al_2O_3$ system showed the same general behavior. However, the C1–C4 quartet was not observed for $W(CO)_6/\gamma$-$Al_2O_3$.

In the $Cr(CO)_6/\gamma$-$Al_2O_3$ system a very weak component at about 1530 $cm^{-1}$ (labeled E in Figure 1b) also appears upon desorption. A similar band cannot be excluded on $Mo(CO)_6/\gamma$-$Al_2O_3$.

---

(11) Guglielminotti, E.; Zecchina, A.; Boccuzzi, F.; Borello, E. In *Growth and Properties of Metal Clusters*; Bourdon, J., Ed.; Elsevier: Amsterdam, 1983; p 165.

(12) Guglielminotti, E.; Zecchina, A. *J. Chem. Phys.* **1981**, *78*, 891.

(13) Hucul, D. A.; Brenner, A. *J. Chem. Soc., Chem. Commun.* **1982**, 830.

(14) Zanderighi, G. M.; Dossi, C.; Ugo, R.; Psaro, R.; Theolier, A.; Choplin, A.; D'ornelas, L.; Basset, J. M. *J. Organomet. Chem.* **1985**, *296*, 127.

(15) You-Sing, Y.; Howe, R. F. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2887.

(16) Lippens, B. C.; Steggerda, J. J. In *Physical and Chemical Aspects of Adsorbents and Catalysts*; Linsen, B. G., Ed.; Academic: New York, 1970; Chapter 4.

(17) Maciver, B. S.; Tobin, H. H.; Barth, R. T. *J. Catal.* **1963**, *2*, 485.

(18) Peri, J. B. *J. Phys. Chem.* **1965**, *69*, 220.

(19) Knözinger, H.; Ratnasamy, P. *Catal. Rev.* **1978**, *17*, 31.

(20) Fripiat, J. J.; Léonard, A.; Uytterhoeven, J. B. *J. Phys. Chem.* **1965**, *69*, 3274.

(21) Peri, J. B. *J. Phys. Chem.* **1965**, *69*, 231.

(22) Knözinger, H. *Adv. Catal.* **1976**, *25*, 184.

(23) Morterra, C.; Chiorino, A.; Ghiotti, G.; Garrone, E. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 271.

(24) Zecchina, A.; Garrone, E.; Guglielminotti, E. *Catalysis*; Specialist Periodical Reports; Royal Society of Chemistry: London, 1983; pp 109–113.

(25) Della Gatta, G.; Fubini, B.; Ghiotti, G.; Morterra, C. *J. Catal.* **1976**, *43*, 90.

(26) Tsyganenko, A. A.; Denisenko, L. A.; Zverev, S. M.; Filimonov, V. N. *J. Catal.* **1985**, *94*, 10.

(27) Zecchina, A.; Escalona Platero, E.; Otero Areán, C. *J. Catal.*, in press.

(28) Howe, R. F. *Inorg. Chem.* **1976**, *15*, 486.

(29) Kazusaka, A.; Howe, R. F. *J. Mol. Catal.* **1980**, *9*, 183, 199.

(30) Bilhou, J. L.; Theolier, A.; Basset, J. M. *J. Mol. Catal.* **1977/1978**, *3*, 245.

(31) Escalona Platero, E.; Rubio González, J. M.; Otero Areán, C. *Thermochim. Acta* **1986**, *102*, 303.

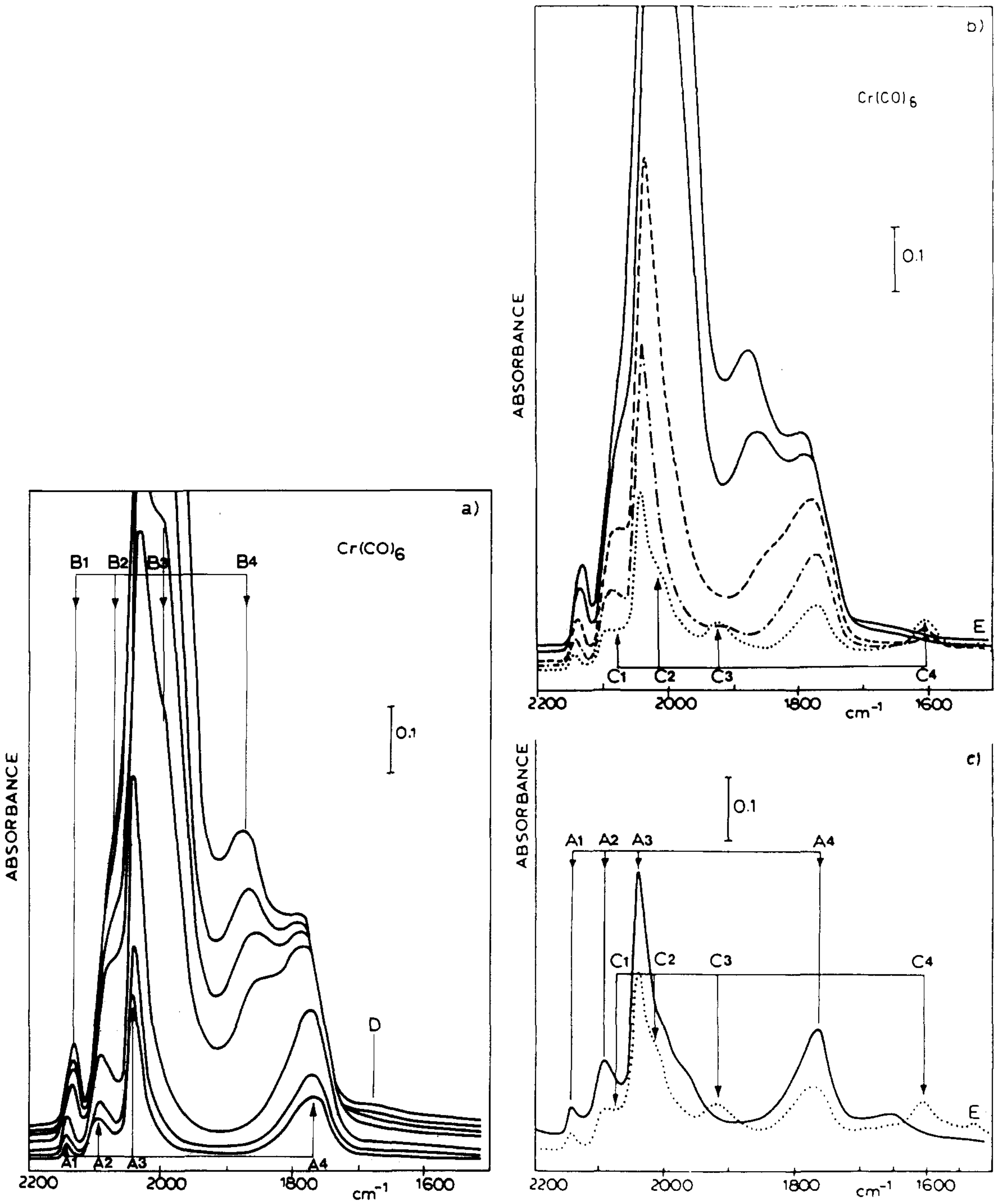


**Figure 1.** (a) IR spectra of $Cr(CO)_6$ on $\gamma$-$Al_2O_3$ at increasing dose. (b) IR spectra of adsorbed $Cr(CO)_6$ at increasing outgassing time at room temperature. (c) Effect of dosing with 40 Torr of CO after the last outgassing step.

In order to investigate whether the C1–C4 bands (which are intensified by desorption) belong to a partially decarbonylated species, CO was dosed (at room temperature) following the last desorption step. The effect on the IR spectra is shown in Figure 1c. The following was observed: (i) In the $Cr(CO)_6/\gamma$-$Al_2O_3$ and $Mo(CO)_6/\gamma$-$Al_2O_3$ systems the C3 and C4 components readily disappear upon dosing CO. The fate of the C1 and C2 components is less clear, because of their weakness and proximity to the A2, A3, B2, and B3 components; however, they probably disappear as well. (ii) Disappearance of the C1–C4 quartet (upon dosing with CO) is accompanied by the simultaneous growth of the A1–A4 quartets for $Cr(CO)_6/\gamma$-$Al_2O_3$ and $Mo(CO)_6/\gamma$-$Al_2O_3$ and also of the B1–B4 quartet for $Mo(CO)_6/\gamma$-$Al_2O_3$. (iii) The D bands are restored. For the $W(CO)_6/\gamma$-$Al_2O_3$ system this was the main effect observed upon dosing with CO, together with some intensification of very weak shoulders at about 1960 and 2000 $cm^{-1}$. Two weak shoulders, at about 1965 and 2000 $cm^{-1}$, are also seen in the $Cr(CO)_6/\gamma$-$Al_2O_3$ system (Figure 1c).

## Discussion

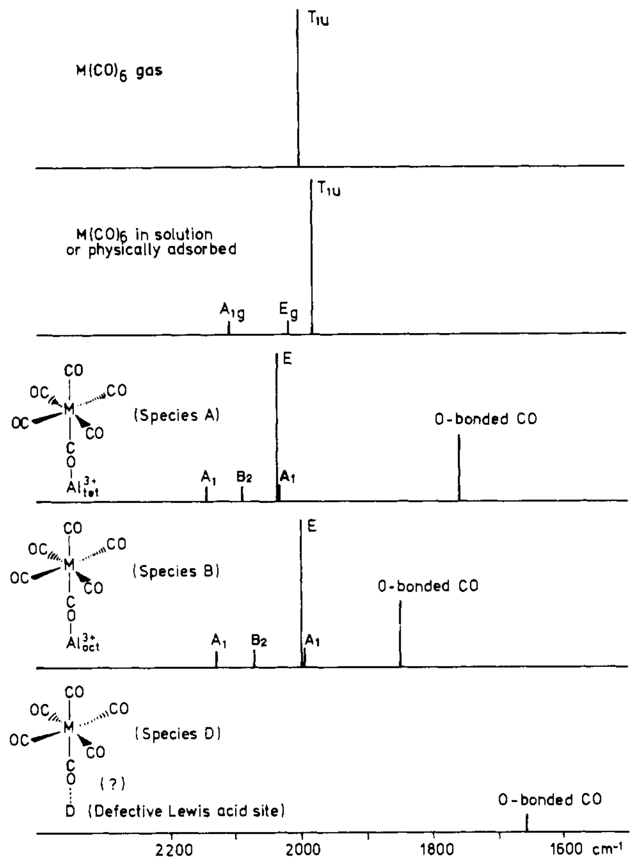
**(a) Assignment of the IR Spectrum in Terms of Metal Carbonyls O-Bonded to $Al^{3+}$ Surface Ions.** Extensive literature[19,25,26] on the nature of the active alumina surface and recent IR spectra of CO adsorbed on $\gamma$-$Al_2O_3$[27] allow one to conclude that the surface of highly dehydroxylated $\gamma$-$Al_2O_3$ presents three main types of Lewis acid sites: defective, tetrahedral, and octahedral, their relative acid strength being in the order defective > tetrahedral > octahedral.

It is well documented[32] that CO groups in metal carbonyls exhibit a distinct basicity at the carbonyl oxygen. In view of this fact, and of the presence of Lewis acid sites on the alumina surface, it is inferred that metal hexacarbonyl–$Al_2O_3$ interaction should be essentially of the donor–acceptor type with formation of O-

---

[32] Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219 and references therein.

**Scheme II**



bonded surface compounds, according to Scheme I.

On the basis of the previous considerations three different coordinated species are foreseen. However, as the defective sites represent only 0.6% of the total,[25] carbonyl molecules adsorbed on them should provide only minor contributions to the overall IR spectrum.

In the gaseous phase the octahedral $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ molecules are characterized[33] by a single IR-active CO stretching mode of $T_{1u}$ symmetry at $\sim$2000 cm$^{-1}$ (Scheme II). The $A_{1g}$ and $E_g$ modes, being only Raman active, are not observed. In solution, the $A_{1g}$ and $E_g$ modes become slightly active. Consequently, three bands, two of them weak (2112–2118 and 2018–2010 cm$^{-1}$) and the other one very strong (1984–1976 cm$^{-1}$), are observed,[33] as illustrated in Scheme II. If the interaction between $M(CO)_6$ (M = Cr, Mo, W) and the $\gamma$-$Al_2O_3$ surface is a simple physical adsorption, three peaks should appear with frequencies and intensities not substantially different from those reported above (because the adsorption process would essentially involve weak dispersion forces).

It is a matter of fact that the IR spectrum of $M(CO)_6$ on $\gamma$-$Al_2O_3$ is dominated by two quartets, A1–A4 and B1–B4, which are different in number of bands, intensity, and frequency from those corresponding to the metal carbonyls in a condensed phase. Therefore, although partially reversible to outgassing at room temperature, the IR spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ on $\gamma$-$Al_2O_3$ cannot be explained in terms of physically adsorbed species. We should therefore consider the spectroscopic consequences of the anchoring of the $M(CO)_6$ molecule to Lewis acid sites (mainly $Al^{3+}{}_{tet}$ and $Al^{3+}{}_{oct}$) via the oxygen atom of a carbonyl group, as hypothesized in Scheme I. The most likely structures have $C_{4v}$ symmetry, as illustrated in Scheme II. The CO groups O-bonded to $Al^{3+}$ Lewis acid sites should have stretching frequencies several hundred wavenumbers lower than that of the gaseous molecule[32] and fall in the 1900–1600-cm$^{-1}$ region. Figure 1a shows that two peaks, A4 and B4, belonging to two different surface species fall in this region. We assign them to the stretching vibrations of terminal carbonyls O-bonded to $Al^{3+}{}_{tet}$ (A4) and $Al^{3+}{}_{oct}$ (B4) surface cations. The agreement with the frequency values reported in the literature for similar adducts is excellent.[32] The stretching frequency of CO bonded to $Al^{3+}{}_{tet}$ is lower than that of CO bonded to $Al^{3+}{}_{oct}$. This is in agreement with the stronger acceptor character (Lewis acidity) of the $Al^{3+}{}_{tet}$ sites.

The normal modes of the five unperturbed carbonyls have $2A_1$, $B_2$, and E symmetries.[33] Although only the $2A_1$ and the E modes are expected to be IR active, it is a matter of fact that in many complexes with X–$M(CO)_5$ structure, the $B_2$ mode is also observed by IR spectroscopy.[33] The frequencies of the four modes are usually in the order $\nu(A_1)_1 > \nu(B_2) > \nu(E) \gtrsim \nu(A_1)_2$, with the E mode showing the highest intensity and the $(A_1)_2$ band appearing as a shoulder of the main E peak. On this basis, we assign the A1–A3 bands (two of them weak and one very strong) to the $(A_1)_1$, $B_2$, and E modes (Scheme II and Figure 1) of the $M(CO)_5$ moiety, the remaining $(A_1)_2$ mode being probably obscured by the much stronger adjacent E band. In this respect we notice that the E peak is always asymmetric in the low-frequency side. In comparison with the $A_{1g}$, $E_g$, and $T_{1u}$ modes of the free carbonyls, the A1–A3 and B1–B3 bands (Table I) are shifted to higher frequencies (the largest shift corresponding to the A1–A3 components). This result agrees with the surface structures hypothesized in Scheme II. It is well-known that O-coordination of terminal carbonyls to Lewis acid centers causes not only a decrease of the stretching frequency of the directly perturbed carbonyl but also an increase of the stretching frequency of the remaining carbonylic groups not directly involved in O-bonding.[32] It is worth mentioning that the larger the downward shift of the O-bonded carbonyl, the larger the upward shift of the remaining frequencies. The analogy between homogeneous and heterogeneous adducts is evident: adsorption of $M(CO)_6$ on $\gamma$-$Al_2O_3$ is mainly governed by the Lewis acid character of the exposed $Al^{3+}$ sites.

On the basis of the previous considerations, we can now advance the hypothesis that the D peak (Figure 1a) is associated with surface carbonyls anchored to the highly acidic defective sites. In favor of this hypothesis we have the following: (i) the frequency of the perturbed carbonyl is further lowered, in agreement with the higher acidity of these sites; (ii) the observed intensity of the peak is always very small, in agreement with the very low concentration of defective surface sites. As in the previous cases, other IR bands of the same surface species should also be present. However, because of the small concentration together with the fact that they should fall in the same region of the A1–A3 and B1–B3 bands, they probably cannot be observed.

Parts a and b of Figure 1 show that the frequency of some components of the A1–A4 and B1–B4 quartets changes with the degree of coverage ($\theta$). In particular, as $\theta$ increases, the following can be observed: (i) the A4 and A3 components of quartet A move upward and downward, respectively; (ii) similarly, B4 shifts upward (nothing definite can be said about B3, because it appears as a shoulder on A3).

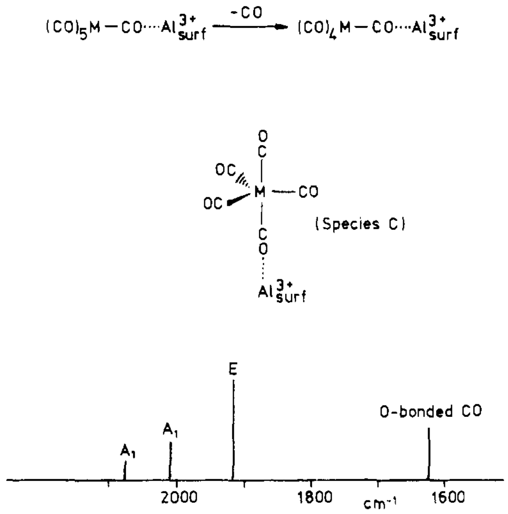
The behavior of the A4 and A3 components of quartet A clearly indicates that the strength of the O-bonding to tetrahedral centers gradually decreases as $\theta$ is increased. A similar behavior has been observed for CO adsorbed on $\gamma$-$Al_2O_3$. The strength of the $Al^{3+}{}_{tet}$–CO interaction was found to decrease with increasing $\theta$, as revealed by the gradual downward shift of the CO stretching frequency.[27] This can be explained in terms of $\sigma$-donation from the carbonyl group (or CO molecule) to the adsorbing center. The donated charge is dissipated through the solid and increases the electron density at adjacent (and also more distant) $Al^{3+}{}_{tet}$ sites. Incoming $M(CO)_6$ molecules find surface sites with decreased electron-accepting capacity; hence, the strength of O-bonding decreases. This explains (i) the upward shift of the A4 band and (ii) the downward shift of the A3 band. Through-solid induction effects of the same type have been found, and fully discussed, for several diatomic molecules adsorbed on metal oxides.[34-36] What

---

(33) Braterman, P. S. *Metal Carbonyl Spectra*; Academic: London, 1975.

(34) Escalona Platero, E.; Scarano, D.; Spoto, G.; Zecchina, A. *Faraday Discuss. Chem. Soc.* **1985**, *80*, 183.

**Scheme III**



is relevant here is the more complex nature of the adsorbed molecule and the fact that the effect is also felt by the remaining CO ligands, not directly involved in $\sigma$-bonding to the metal oxide surface.

The same explanation holds for the behavior of the B4 band corresponding to $M(CO)_6$ adsorbed on $Al^{3+}{}_{oct}$ sites. However, in this case the behavior of the B3 partner cannot be observed with accuracy.

**(b) Formation of Decarbonylated Species upon Room-Temperature Outgassing.** Inspection of Figure 1b shows that prolonged room-temperature outgassing causes total disappearance of the B1–B4 quartet, along with progressive diminution of the intensity of the A1–A4 quartet. This is readily explained in terms of partial desorption of the adsorbed carbonyl, which is most keenly felt by the B species (adsorbed on the weaker $Al^{3+}{}_{oct}$ sites). For the $Cr(CO)_6/\gamma\text{-}Al_2O_3$ and $Mo(CO)_6/\gamma\text{-}Al_2O_3$ systems, formation of a new quartet of bands, C1–C4, was observed in the last outgassing steps (Figure 1b). Subsequent admission of CO (Figure 1c) brings about destruction of the C1–C4 bands and parallel increase of the A1–A4 quartet. We therefore conclude that the C1–C4 bands belong to partially decarbonylated species originating from A upon loss of CO. This result is not unexpected. In fact, it is well-known that O-bonding of metal carbonyls to strong Lewis acids in homogeneous phase favors CO elimination.[37–39] The C1–C4 bands are thus assigned to subcarbonylic species formed according to Scheme III. In favor of this interpretation, the following arguments can be put forward: (i) the observed frequencies of the C1–C3 bands are all shifted to lower values with respect to those of the parent O-coordinated hexacarbonyls, in agreement with literature data which show that the stretching frequencies of mononuclear subcarbonyls are lower than those corresponding to the fully coordinated compound;[40,41] (ii) the C4 band, which can be assigned to the stretching mode of a surface O-bonded CO group, appears at a frequency lower than the A4 band, as expected from the higher basicity of CO groups in subcarbonylic entities.[33]

A brief consideration was given to the possibility that the C4 band at low frequency could arrive from a subcarbonyl species containing a bridging CO group, such as $M_2(CO)_{10}(\mu\text{-}CO)\cdots Al^{3+}(surf)$. Indeed, bridging CO groups are known to be more basic than terminal ones.[32,42,43] However, at the present, we believe a dimeric species to be less likely than the monomeric subcarbonyl of Scheme III for the following reasons: (i) the C1–C4 bands are only observed during the last outgassing steps (i.e. at low coverage) where the A (and B) species are likely to be isolated and distant from one another; hence, dimerization would be unlikely; (ii) the fast, and apparently nonactivated, transformation of C into A (and to a lesser extent B) species upon addition of CO is better explained on the basis of Scheme III. In conclusion, the main decarbonylation products formed during room-temperature outgassing appear to be mononuclear subcarbonylic species attached to Lewis acid centers of $\gamma$-alumina by O-bonding through a CO group. The tendency to give such species is in the order $Mo(CO)_6 > Cr(CO)_6$. It is noteworthy that this sequence of reactivity is similar to that observed for the same metal carbonyls under photochemical conditions.[40,41] IR spectra did not give any clear indication of formation of subcarbonylic species in the $W(CO)_6/\gamma\text{-}Al_2O_3$ system.

It is not possible to establish from the present IR investigation the number of CO groups remaining in the subcarbonylic species, which could depend on outgassing time and temperature. For the $Mo(CO)_6$/alumina system it has been reported[44] that outgassing at 373 K leads to $Mo(CO)_3$.

Parts b and c of Figure 1 show that species D is also destroyed by room-temperature outgassing and is restored upon admission of CO. Such behavior suggests that species D also undergoes decarbonylation. Parts b and c of Figure 1 show that, on prolonged outgassing, a weak band (E) appears at about 1530 $cm^{-1}$. Such a low-frequency probably indicates subcarbonylic species O-bonded to strong Lewis acid sites. They could well be the subcarbonyls formed from species D. This would explain why, upon CO admission, the E band disappears and band D is regenerated.

**Acknowledgment.** E.E.P. thanks the Spanish Ministry of Education for the award of a grant under the "Plan de Formaciõn de Personal Investigador".

**Registry No.** $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Al_2O_3$, 1344-28-1.

**Supplementary Material Available:** IR spectra of $Mo(CO)_6$ and $W(CO)_6$ on $\gamma\text{-}Al_2O_3$ at increasing dose and of adsorbed $Mo(CO)_6$ and $W(CO)_6$ at increasing outgassing time at room temperature, also showing the effect of dosing with 40 Torr of CO after the last outgassing step (3 pages). Ordering information is given on any current masthead page.

---

(35) Zecchina, A.; Scarano, D.; Garrone, E. *Surf. Sci.* **1985**, *165*, 492.

(36) Escalona Platero, E.; Coluccia, S.; Zecchina, A. *Surf. Sci.* **1986**, *171*, 465 and references therein.

(37) Alich, A.; Nelson, N. J.; Shriver, D. F. *J. Chem. Soc., Chem. Commun.* **1971**, 254.

(38) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

(39) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

(40) Poliakoff, M.; Weitz, E. *Adv. Organomet. Chem.* **1986**, *25*, 277.

(41) Graham, M. A.; Poliakoff, M.; Turnes, J. J. *J. Chem. Soc. A* **1971**, 2939.

(42) Alich, A.; Nelson, N. J.; Strope, D.; Shriver, D. F. *Inorg. Chem.* **1972**, *11*, 2976.

(43) Shriver, D. F. *J. Organomet. Chem.* **1975**, *94*, 259.

(44) Burwell, R. L., Jr.; Brenner, A. In *Catalysis Heterogeneous and Homogeneous*; Delmon, B., Jannes, G., Eds.; Elsevier: Amsterdam, 1975; p 157.