## Spectroscopic Investigation of the Interaction of $Co_2(CO)_8$ with MgO and SiO<sub>2</sub>

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 $Co_{9}(CO)_{8}$ , when absorbed in the gas phase, in vacuo, on fully dehydrated MgO, forms a variety of carbonyl clusters both neutral and ionic. These clusters disintegrate into monometallic species upon dosing with either CO or NH<sub>3</sub>, resulting in Co(CO)<sup>-</sup><sub>4</sub> and Co<sup>2+</sup>(CO)<sub>n</sub> (n = 2 or 3) with CO and  $Co(CO)_4^-$  and  $Co^{2+}(NH_3)_6$  with  $NH_3$ , respectively. The negatively charged species are formed via several routes, including disproportionation and nucleophilic attack by O<sup>2-</sup> on the carbonyl groups of different cobalt carbonyl clusters. These effects are attributed to the strongly basic nature of the highly dehydroxylated magnesia used in the present investigation. Diffuse reflectance and e.s.r. spectral studies performed in similar conditions on magnesia confirm all these transformations. The results on a highly dehydrated SiO<sub>2</sub> surface are quite different:  $Co_2(CO)_8$  is mostly adsorbed without appreciable chemical modification, giving two isomers containing linear and bridged CO. Only by removing CO by outgassing at the beam temperature, is the total transformation into Co<sub>4</sub>(CO)<sub>12</sub> and possibly  $Co_6(CO)_{12}$  observed.

Cluster chemistry is a rapidly developing field, and clusters have a valid contribution in providing plausible models of metal surfaces. Work on clusters is in its early stage, and  $Co_2(CO)_8$  is one of the few metal carbonyl clusters used in industrial catalysis because it readily gives catalytic intermediates, *i.e.* coordinatively unsaturated cobalt carbonyl derivatives.<sup>1-3</sup>

The interaction of  $Co_2(CO)_8$  in vacuo with silica (Cabosil), outgassed at 673 K, was studied by Schneider *et al.*<sup>4</sup> the immediate formation of  $Co_4(CO)_{12}$  by surface-catalysed decarbonylation of  $Co_2(CO)_8$  was reported. The fully hydrated SiO<sub>2</sub> surface contains *ca.* 5 OH per 100 Å<sup>2.5</sup> Dehydration at 673 K causes the elimination of only 2 OH per 100 Å<sup>2</sup>. Consequently, as *ca.* 60% of the surface hydroxyls are still present on the surface outgassed at 673 K,<sup>5</sup> the observed catalysed decarbonylation could be associated with the presence of silanols (as hypothesized by the same authors).<sup>4</sup> Gopal and Watters<sup>6</sup> have studied the interaction of  $Co_2(CO)_8$  with MgO: they concluded that the  $Co_2(CO)_8$  undergoes a series of transformations with the formation of coordinatively saturated and unsaturated compounds. The magnesia which they used had been treated at 673 K, and therefore a non-negligible number of OH groups (20% of the monolayer capacity) was still present on the surface.<sup>7</sup> Iwasawa *et al.*<sup>8</sup> supported  $Co_2(CO)_8$  on silica by a dry-mixing method and observed the formation of an abundant amount of  $[Co(CO)_3]_n$  surface species. The formation of these oxidized species could be due to the preparation procedure adopted (the dry mixing was apparently carried out in air).

In order to separate the role of adsorbed water from that of the free surface in determining the surface transformations of adsorbed carbonyls, Guglielminotti *et al.*<sup>9</sup> made a preliminary investigation on the adsorption of  $Co_2(CO)_8$  on totally dehydrated MgO. In the present study we report a more extensive investigation of the interaction

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of  $Co_2(CO)_8$ , in vacuo, with MgO outgassed at 1073 K and at  $10^{-5}$  Torr (1 Torr = 133  $N m^{-2}$ ), *i.e.* characterized by a fully dehydroxylated surface (as monitored by the total absence of OH groups) and with a surface area of 180 m<sup>2</sup> g<sup>-1.9</sup> The effect of CO and NH<sub>3</sub> over the resulting species was also investigated. Diffuse reflectance spectra (d.s.r.) and electron spin resonance (e.s.r.) studies were also performed along the similar lines to provide supporting evidence for the i.r. assignments. In addition, the adsorption of  $Co_2(CO)_8$ , in vacuo, on silica which had been outgassed at 1100 K (the highly dehydroxylated form) and the effect of pumping over the species formed in this way are reported.

## Experimental

The MgO was obtained by vacuum decomposition of Mg(OH)<sub>2</sub> following a procedure described elsewhere<sup>9</sup> and the surface was then cleaned of adsorbed impurities at 1073 K and at  $10^{-5}$  Torr for a few hours. The specific surface area of the sample treated in this way was typically 180 m<sup>2</sup> g<sup>-1</sup>. Silica (Aerosil, Degussa, specific surface area 370 m<sup>2</sup> g<sup>-1</sup>) was outgassed at 1100 K for several hours in order to remove most of the hydroxyl groups (only ca. 1 OH per 100 Å<sup>2</sup> was left on the surface).<sup>5</sup> The CO and NH<sub>3</sub> used in this experiment were of high-purity grade (Matheson). Co<sub>2</sub>(CO)<sub>8</sub> was obtained from ICN Labs.

Infrared studies were carried out on a PE 580B IR instrument equipped with a data station, using a low-path (0.7 cm) i.r. cell and thin (0.01-0.02 cm) wafers of silica and magnesia, containing ca. 15-20 mg cm<sup>-2</sup> of powder. The diffuse reflectance spectra were recorded from 200 to 1900 nm on a Varian Cary 2390 instrument, equipped with a diffuse reflectance attachment and a data station. E.s.r. studies were performed on a Varian E109 instrument operating in the X-band mode (9.4 GHz). Varian pitch (g =2.0029) was used as a reference.

The adsorption of  $Co_2(CO)_8$  from the gas phase on fully dehydrated MgO is a highly irreversible process with a high sticking probability. Consequently the  $Co_{s}(CO)_{s}$  vapour is adsorbed immediately on the MgO pellet with the formation of reddish-brown penetration front which moves progressively from the external to the internal part of the pellet. The front divides the white cobalt-free part of the pellet from the coloured one, where the coverage is constant and near or equal to the maximum value. As already shown for the systems<sup>10</sup> where this phenomenon occurs, the i.r. spectra do not change qualitatively with the amount adsorbed, only the intensity being effected by the change in coverage. The same phenomenon does not occur (or it occurs to much lower extent) on silica.

## **Results and Discussion**

## Transformation of Co<sub>2</sub>(CO)<sub>8</sub> on the SiO<sub>2</sub> Surface

Fig. 1(a) shows the i.r. spectra obtained when  $Co_2(CO)_8$  is dosed on SiO<sub>2</sub> in a vacuum through gas-phase sublimation (the different curves correspond to increasing doses). The first small dose gives a doublet at 2080-2065 cm<sup>-1</sup> and a less intense but broader peak at 1870 cm<sup>-1</sup>. Successive doses cause the formation of several bands in the range 2100-2000 cm<sup>-1</sup> (2032, 2045, 2057 and 2072 cm<sup>-1</sup>). Besides these bands, a broad peak in the region of 1860 cm<sup>-1</sup> grows in parallel with a shoulder at 1970 cm<sup>-1</sup>. By comparing these bands with the data shown in scheme 1, we can conclude that the first dose (corresponding to ca. 0.1 mol per 100 Å<sup>2</sup>; vide infra) is totally transformed into  $Co_4(CO)_{12}$  by surface decarbonylation (in fact the doublet is readily assigned to the two tetrameric species adsorbed on slightly different sites; vide infra). The successive doses give both the bridged and linear  $Co_{2}(CO)_{8}$  species (the last one monitored by the peak



Fig. 1. (a) Infrared spectra (2200–1700 cm<sup>-1</sup>) of increasing doses of Co<sub>2</sub>(CO)<sub>8</sub> adsorbed through gas-phase sublimation on silica (Aerosil: specific surface area 370 m<sup>2</sup> g<sup>-1</sup>) previously outgassed under high vacuum (10<sup>-5</sup> Torr) at 1073 K. The most intense spectrum corresponds to 0.5 molecules of Co<sub>2</sub>(CO)<sub>8</sub> per 100 Å<sup>2</sup>. (b) Effect of 15 min outgassing, at the i.r. beam temperature and under high dynamic vacuum (10<sup>-5</sup>), on the i.r. spectrum of adsorbed Co<sub>2</sub>(CO)<sub>8</sub>.

at 2032 cm<sup>-1</sup>). When these species are subjected to evacuation at the infrared beam temperature, the spectrum is modified according to fig. 1(*b*). The bands at 2032 and 2045 cm<sup>-1</sup> and the shoulder at 1970 cm<sup>-1</sup> disappear and new bands appear at 2120, 2108, 2080, 2065 and 1870 cm<sup>-1</sup>. [The peak at 1870 cm<sup>-1</sup> is slightly shifted towards the positive side with respect to that in fig. 1(*a*) and is increased in intensity.] The presence of two doublets at 2120–2100 and 2080–2065 cm<sup>-1</sup> together with the broad peak at 1870 cm<sup>-1</sup> indicates that two forms of Co<sub>4</sub>(CO)<sub>12</sub> adsorbed on slightly different sites are becoming the predominant species present on the surface. From the known extinction coefficient of the bridged carbonylic species<sup>15</sup> of Co<sub>4</sub>(CO)<sub>12</sub> it is possible to conclude that the Co<sub>4</sub>(CO)<sub>12</sub> coverage (broken curve) is still very low (*ca*. 0.5 molecule per 100 Å<sup>2</sup>). The presence of a small amount of Co<sub>6</sub>(CO)<sub>16</sub> cannot be excluded: in fact, upon evacuation a weak shoulder at 1780 cm<sup>-1</sup> grows which can be assigned to Co<sub>6</sub> clusters.

We can describe the effect of evacuation in the following way:

$$\operatorname{Co}_2(\operatorname{CO})_8(\operatorname{ads}) \to \operatorname{Co}_4(\operatorname{CO})_{12} \to \operatorname{Co}_6(\operatorname{CO})_{16}.$$
 (1)

Schneider *et al.*<sup>4</sup> reported that a fast and complete decarbonylation process occurs *in* vacuo when  $\text{Co}_2(\text{CO})_8$  is dosed on  $\text{SiO}_2$  outgassed at 673 K. In our case only the first dose (0.1 molecule per 100 Å<sup>2</sup>) is quickly decarbonylated. Extensive decarbonylation occurs on subsequent doses only by prolonged outgassing at the i.r. beam temperature. We think that the smaller decarbonylating activity observed in our case is closely related to the lower concentration of residual OH groups which, as proposed by Schneider *et al.*,<sup>4</sup> are acting as catalytic centres.

A detailed examination of the data illustrated in scheme 1 and fig. 1(a) and (b)

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indicates that for clustered cobalt carbonylic compounds (both in solution or in the adsorbed state) and for dispersed cobalt particles, the following conclusions can be drawn: (1) the linear carbonyls absorb in the 2120–2000 cm<sup>-1</sup> range; (2) the bridged carbonyls absorb in the 1900–1800 cm<sup>-1</sup> range; (3) in the 2000–1900 cm<sup>-1</sup> interval, no substantial absorption occurs. Observations (1)–(3) are well known and fairly obvious: however, they must be borne in mind because they will be useful in discussing the results of the  $Co_2(CO)_8$ –MgO system.

## Transformation of Co<sub>2</sub>(CO)<sub>8</sub> on MgO

In fig. 2 the i.r. spectra of increasing doses of  $Co_2(CO)_8$  on MgO, in vacuum, *i.e.* through gas-phase sublimation, are illustrated. The spectrum is very complex: however, the relative intensity of the components does not change much with coverage, as expected for a highly irreversible adsorption process. Bands and shoulders are observed at: 2112(vw), 2090(sh), 2070(sh), 2038(vs), 1960(sh), 1935(sh), 1870(s), 1820(m), 1760(w), 1675(m), 1615(m), 1520(br, w), 1380(w), 1320(m), 1280(w), 1240(w), 1180(vw), 980(vbr), 930(w) and 850(w) cm<sup>-1</sup>.

With respect to the spectra of  $Co_2(CO)_8$  adsorbed on  $SiO_2$ , the most important differences are: (1) the presence of non-negligible absorptions in the region 2000–1900 cm<sup>-1</sup> [a region which is totally clear for the  $SiO_2-Co_2(CO)_8$  system]; (2) the presence of a strong and broad absorption tail at frequencies as low as 1700 cm<sup>-1</sup> (well documented in the strongest i.r. spectra of fig. 2) which is totally absent on  $SiO_2$ ; (3) the presence of discrete bands at frequencies lower than 1700 cm<sup>-1</sup> (1675, 1615, 1520, 1380, 1320, 1280, 1240, 1180, 980, 930 and 850 cm<sup>-1</sup>) which can be partially ascribed to carbonate-like species. Without entering into details of the assignments, we can briefly say that, as for the  $SiO_2/Co_2(CO)_8$  system, many of the bands observed in the 2120–1800 cm<sup>-1</sup> interval (particularly the strong and complex peak centred at 2038 cm<sup>-1</sup>) can be explained on the basis of the stretching frequencies of a variety of neutral carbonyl clusters [Co<sub>2</sub>(CO)<sub>8</sub>,

 $Co_4(CO)_{12}$ ,  $Co_6(CO)_{16}$  etc.] and even of CO adsorbed on small metallic cobalt particles (see scheme 1). This fact suggests that an extensive release of CO is immediately occurring upon contact of  $Co_2(CO)_8$  with the totally dehydrated MgO surface, with subsequent clustering, following reaction (1). This conclusion is proved by simultaneous measurements of the pressure, which show that a gaseous product is immediately released. CO abstraction in this case is favoured by the capacity of highly dehydrated MgO to adsorb CO strongly to give complex dimeric and polymeric structures described earlier.<sup>16</sup> A weak shoulder at 2100 cm<sup>-1</sup> and a peak at 1380 cm<sup>-1</sup> coincide with the vibrational modes of the dimeric structures observed on the CO–MgO system.<sup>16</sup>



However, the large spectral differences described in points (1)–(3) show that, unlike the  $\text{Co}_2(\text{CO})_8$ –SiO<sub>2</sub> system, negatively charged entities like those illustrated in scheme 2 must also be taken into consideration. In fact, negatively charged carbonyl compounds show strong bands in the 2000–1900 and 1700–1600 cm<sup>-1</sup> regions.

In the inset of fig. 2, the u.v.-visible-near-i.r. reflectance spectrum of  $Co_2(CO)_8$ (measured at maximum coverage) absorbed on MgO under the same conditions described before is reported. Several broad absorptions are observed at 37300, 26600, 18600 and 14800(sh) cm<sup>-1</sup>, and when these bands are compared with the data shown in scheme 3 (where the spectra of several neutral and negatively charged carbonylic complexes are reported) the following conclusions can be deduced: (1) the complex adsorption at frequencies  $\geq 25000 \text{ cm}^{-1}$  can be explained on the basis of a mixture of neutral carbonylic clusters  $[Co_2(CO)_8, Co_4(CO)_{12} \text{ and } Co_6(CO)_{16}]$ ,  $Co_n$  polymers and small cobalt particles; (2) the band at 19000 cm<sup>-1</sup> and the tail extending to lower frequencies find a closer analogy among the polynuclear carbonylic anionic species.

It is evident that both the i.r. and reflectance experiments lead to the same (general) conclusion: the absorption of  $Co_2(CO)_8$ , on MgO, *in vacuo*, occurs with loss of CO with the formation of both larger neutral clusters (and possibly metallic particles) and negatively charged carbonylic species. This conclusion totally differentiates the surface chemistry of highly dehydrated SiO<sub>2</sub> and MgO towards the adsorption of Co<sub>2</sub>(CO)<sub>8</sub>.

The formation of negatively charged cobalt carbonylic species from  $\text{Co}_2(\text{CO})_8$  and other neutral clusters is well known in homogeneous chemistry.<sup>25</sup> It is useful to summarize briefly the main mechanisms leading to the formation of mononuclear and polynuclear negative species under homogeneous conditions.





Fig. 2. Infrared spectrum (2000–900 cm<sup>-1</sup>) of increasing doses of  $Co_2(CO)_8$  adsorbed through gasphase sublimation on MgO (180 m<sup>2</sup> g<sup>-1</sup>) fully dehydroxylated at 1073 K under high vacuum (10<sup>-5</sup> Torr). The most intense spectrum corresponds to *ca*.  $60 \times 10^{-2}$  per 100 Å<sup>2</sup> cobalt atoms as determined *via* the spectroscopic method described in the text.

## Mononuclear Negative Species $[Co(CO)_4^{-1}]$

(1) Reaction of cobalt carbonyls with a Lewis base B:

$$3Co_2(CO)_8 + 12B \rightarrow 2(CoB_6)^{2+} + 4Co(CO)_4^- + 2CO$$
 (2*a*)

$$3Co_4(CO)_{12} + 24B \rightarrow 4(CoB_6)^{2+} + 8Co(CO)_4^- + 4CO$$
 (2b)

(and equivalent reactions involving higher nuclearity clusters).

These reactions occur with a release of CO and they involve disproportionation of zerovalent clusters with the simultaneous formation of both  $Co^{2+}$  and  $Co^{-}$ . The stoichiometry of the positively charged complexes could be different with respect to what has been stated previously: in the presence of CO and an insufficient number of B molecules,  $Co^{2+}$  complexes with formulae  $Co(CO)_x B_y^{2+}$  could also be formed.

(2) Reaction with a Brønsted base:

$$8Co_2(CO)_8 + 8CO + 32OH^- \rightarrow 16Co(CO)_4^- + 8CO_3^{2-} + 16H_2O.$$
 (3)

According to this equation  $\text{Co}_2(\text{CO})_8$  is transformed into  $\text{Co}(\text{CO})_4^-$  and  $\text{CO}_3^{2-}$  (only in the presence of CO); in other words  $\text{Co}^0$  is reduced to  $\text{Co}^-$  while CO is oxidized to  $\text{CO}_3^{2-}$ .

(3) Reaction with a Brønsted base and disproportion:

$$11Co_{2}(CO)_{8} + 32OH^{-} \rightarrow 2Co^{2+} + 20Co(CO)_{4}^{-} + 8CO_{3}^{2-} + 16H_{2}O.$$
(4)

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This reaction can be considered as a mixture of reactions (2) and (3) and is not accompanied by the release or consumption of CO. However, in the presence of a CO atmosphere, the Co<sup>2+</sup> ions could form Co<sup>2+</sup>(CO)<sub>x</sub> complexes.

## Polynuclear Negative Species

Reaction between  $Co_2(CO)_8$  and  $Co(CO)_4^-$ :

$$2Co_2(CO)_8 + 2Co(CO)_4^- \rightarrow Co_6(CO)_{15}^{2-} + 9CO$$
 (5)

This reaction occurs with release of CO. Similar reactions can be hypothesized between  $Co(CO)_4^-$  and higher cobalt carbonyl clusters formed *via* reaction (1). It is most noticeable that the direction of these relations can be reversed easily by increasing the CO pressure.

The fully dehydroxylated MgO surface contains a large variety of surface  $O^{2^-}$  species in different coordination states (five-fold, four-fold or three-fold coordinated).<sup>26</sup> These  $O^{2^-}$  species possess basic properties and can act as Lewis bases or behave like OH<sup>-</sup> anions.

If we consider the heterogeneous analogues for the reactions (2)–(4), the possible equations are as follows:

$$3Co_2(CO)_8 + 2O^{2-} \rightarrow 2Co^{2+}O^{2-} + 4Co(CO)_4^- + 8CO$$
 (2*a'*)

$$3Co_4(CO)_{12} + 4O^{2-} \rightarrow 4Co^{2+}O^{2-} + 8Co(CO)_4^- + 4CO$$
 (2b')

(and equivalent reactions involving higher-nuclearity clusters).

The reactivity of surface  $O^{2^-}$  is in the order: five-fold < four-fold < three-fold.<sup>16, 26, 27</sup> The four-fold and three-fold coordinated  $O^{2^-}$  ions are formed by dehydration at temperatures > 773 K.<sup>16, 26, 27</sup> Consequently, we think that the higher complexity of the i.r. spectra of  $Co_2(CO)_8$  adsorbed on MgO dehydrated at 1073 K in respect to that dehydrated at 673 K<sup>6</sup> can be mainly ascribed to the more abundant participation of lowcoordinated oxygen ions in CO abstraction and disproportionation. In presence of CO

gas  $(CO)_{r}Co^{2+}O^{2-}$  complexes could be formed. However, the stoichiometry of the surface positive complexes,  $(CO)_x Co^{2+}O^{2-}$ , cannot be predicted a priori because the number and nature of the ligands depend very much upon the CO pressure and upon the location of the  $Co^{2+}$  ions on the surface [e.g. on the surface each  $Co^{2+}$  ion is in contact with more than one  $O^{2-}$ , in contrast to the scheme shown in reaction (2a')].

The surface analogues of reactions (3) and (4) involving  $O^{2-}$  are as follows:

$$8Co_2(CO)_8 + 8CO + 16O^{2-} \rightarrow 16Co(CO)_4^- + 8CO_3^{2-}$$
 (3')

$$11Co_2(CO)_8 + 16O^{2-} \rightarrow 2Co^{2+} + 20Co(CO)_4^- + 8CO_3^{2-}.$$
 (4')

[In the presence of CO gas  $Co^{2+}(CO)_x$  complexes could be formed.]

Both the reactions (3') and (4'), if occurring at the surface, lead to the formation of  $CO_3^{2-}$  adsorbed groups. As we have definite proof of the formation of a small amount of such species in our present experiment, we infer that the reactions (2') and/or (4')must also have occurred on the MgO surface.

It is evident that if reactions (2')-(4') are operating simultaneously, the incoming  $Co_{2}(CO)_{4}$  can react with preformed  $Co(CO)_{4}^{-}$  (ads) to give a variety of negatively charged carbonyl clusters.

All the previous considerations suggest that the adsorption of  $Co_{2}(CO)_{2}$  on fully dehydrated MgO leads to a variety of species both neutral and negatively charged, and all these species can be partially transformed into one other by changing the external conditions (e.g. the pressure of CO). An overall scheme is shown in scheme 4.

$$\operatorname{Co}_{2}(\operatorname{CO})_{8_{9}} \neq \operatorname{Co}_{2}(\operatorname{CO})_{8ads} \xrightarrow{-\operatorname{CO}}_{+\operatorname{CO}} \operatorname{Co}_{4}(\operatorname{CO})_{12} \rightleftharpoons \operatorname{Co}_{n}(\operatorname{CO})_{m}$$

$$\xrightarrow{-}_{+\operatorname{CO}} \xrightarrow{-}_{+\operatorname{CO}} \xrightarrow{-}_{+\operatorname{$$

According to Indovina et al.,<sup>28</sup> the  $Co^{2+}(CO)_x$  complexes should be e.s.r.-active. Furthermore, it is not excluded that as a result of the interaction of  $Co(CO)_{4}^{-}$  with neutral clusters, other paramagnetic structures of the type  $Co_{\nu}(CO)_{x}^{-}$  can also be formed.<sup>18</sup> In conclusion, the adsorption of  $Co_2(CO)_8$  in vacuo on MgO could lead to the formation of paramagnetic species with a subsequent appearance of e.s.r. activity. To observe these species we have performed e.s.r. experiments, keeping all the experimental conditions as described earlier.

A very broad e.s.r. signal centred at g = 2.006 is detected. The signal breadth is probably associated with spin-spin interactions occurring in the reddish-brown adsorbed layer, which (for the reasons already discussed in the experimental section) is always highly concentrated. Unfortunately the signal breadth prevents a detailed interpretation of the spectrum. However, it must be stressed that both the  $Co^{2+}(CO)_3^{28}$  and  $\operatorname{Co}_{v}(\operatorname{CO})_{x}^{-18}$  species or a mixture of the two are consistent with the observed spectrum.

Scheme 4 suggests that the relative proportion of low- and high-nuclearity neutral and



Fig. 3. Infrared spectra (2000–900 cm<sup>-1</sup>) of increasing coverages of  $Co_2(CO)_8$  adsorbed through gas-phase sublimation in presence of 40 Torr of CO, on MgO (180 m<sup>2</sup> g<sup>-1</sup>) fully dehydroxylated at 1073 K under high vacuum (10<sup>-5</sup> Torr).

charged species should be governed by the amount of adsorbed  $\text{Co}_2(\text{CO})_8$  and by the CO pressure. In particular, high CO pressures should favour low nuclearity complexes like  $\text{Co}_2(\text{CO})_8$ (ads) and  $\text{Co}(\text{CO})_4^-$ , while *in vacuo* the clustered systems should be predominant (in agreement with the results illustrated in fig. 1).

The reliability of the network of reactions illustrated in scheme 4 for describing the interaction of  $\text{Co}_2(\text{CO})_8$  with MgO is further reinforced by the results shown in fig. 3 and 4.

In fig. 3 the i.r. spectra of  $Co_2(CO)_8$  adsorbed at increasing coverages in the presence of 40 Torr<sup>†</sup> of CO are shown. These spectra are very different from those reported in fig. 2. The first spectrum is simply that of CO adsorbed initially on MgO.<sup>16</sup> The other spectra are mainly due to the superimposition of two families of carbonyls,  $Co^{2+}(CO)_3$ [or less probably  $Co^{2+}(CO)_2$ ] and  $Co(CO)_4^-$  (see fig. 3 and 4). As demonstrated in previous papers,<sup>16</sup> the spectra of  $Co(CO)_4^-$  absorbed at the surface of MgO (and hence with a symmetry lower than  $T_d$ ) consists of a quartet of bands in the 2100–1800 cm<sup>-1</sup> range. While the first peak [deriving from the i.r.-inactive mode of the free  $Co(CO)_4^$ molecule in  $T_d$  symmetry] is weak and fairly fixed in frequency (2030 cm<sup>-1</sup>), the remaining three modes [coming from the triply degenerate mode of the free  $Co(CO)_4^-$  ion by a splitting caused by the interaction with the surface] are strong and variable in the 2000–1800 cm<sup>-1</sup> range. (Their separation depends upon the distortion introduced by the

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<sup>† 1</sup> Torr = 101325/760 Pa.



Fig. 4. Effect of dosing CO (40 Torr) (broken line) on  $Co_2(CO)_8$  preadsorbed on MgO through gas-phase sublimation in vacuum (full line).

interaction with the surface.) The spectra of  $Co(CO)_3^{2+}$  on an MgO-CoO solid solution<sup>29</sup> consists of a doublet of peaks in the 2100-2040 cm<sup>-1</sup> range, with the low-frequency component (corresponding to the degenerate asymmetric stretching mode of the three carbonyls) being three times more intense than the high-frequency one. On this basis we conclude that the two peaks at 2097 and 2040 cm<sup>-1</sup> are associated with  $Co(CO)_3^{2+}$  species, while the peaks at 1975, 1862 and 1818 cm<sup>-1</sup> are due to the  $Co(CO)_4^{-}$  entity (as shown in fig. 3 and 4). The i.r. spectra of these species obscure those of the residual neutral clusters. The shoulders at 1950 and 1780 cm<sup>-1</sup> could be due to the residual clustered anionic compounds. Also in this case the presence of the  $CO_3^{2-}$  species is well documented.

In the inset of fig. 3 the reflectance spectra in the u.v.-visible-near-i.r. range corresponding to the first and last spectra are shown. From these spectra the following comments can be made: (1) the first spectrum is typical of CO adsorbed on MgO and does not require further comment because it has been discussed in detail in an earlier paper;<sup>27</sup> (2) the difference between the spectrum shown in the inset of fig. 2 and the strongest spectrum of the inset of fig. 3 (which corresponds to the most intense i.r. spectrum) can be explained in terms of different distributions of neutral and negatively charged carbonylic species. In presence of CO, lower-nuclearity species (in agreement with i.r. assignments) are predominant; consequently the absorbance in the lower-frequency range of the reflectance spectrum is definitely smaller.

From all these experiments the following conclusions are drawn: in the presence of CO the formation of high-nuclearity clusters (both neutral and negatively charged) is



**Fig. 5.** Effect of dosing NH<sub>3</sub> on Co<sub>2</sub>(CO)<sub>8</sub> preadsorbed on MgO through gas-phase sublimation. (----) Initial spectrum; (----) after dosing with 2 Torr NH<sub>3</sub>; (----): after dosing with 6 Torr of NH<sub>3</sub>.

depressed, and the primary disproportionation reaction leading to  $Co^{3+}(CO)_3$  and  $Co(CO)_4^-$  mononuclear products is dominating.

The role of CO in the gas phase, to shift the equilibria towards the low-nuclearity compounds as described in scheme 4, is further proved by the experiment shown in fig. 4, where the effect of dosing CO on the i.r. and reflectance spectra (inset) of  $Co_2(CO)_8$  absorbed *in vacuo* is illustrated. The i.r. spectra of the  $Co(CO)_4^-$  species grow at the expense of the absorption centred at 2000–2100 cm<sup>-1</sup> [associated with terminal CO of adsorbed  $Co_2(CO)_8$ ,  $Co_4(CO)_{12}$  and other clusters]. Meanwhile, in the reflectance spectra the low-frequency absorption associated with high-nuclearity clusters (both neutral and negatively charged) is heavily eroded.

In the inset the dotted broken curve shows the difference spectrum. Upon CO contact, two main bands, one centred at  $25000 \text{ cm}^{-1}$  and the second at  $15000 \text{ cm}^{-1}$ , are eroded. On the basis of scheme 4, we believe that the disappearance of the two peaks corresponds to the destruction of zerovalent and negatively charged clusters, respectively.

# Transformation of $Co_2(CO)_8$ Adsorption Products in the Presence of Coadsorbed Base (NH<sub>3</sub>)

If, on vacuum adsorbed  $Co_2(CO)_8$ , NH<sub>3</sub> is dosed at two different pressures (2 and 6 Torr), the spectrum in the range 2150–1700 cm<sup>-1</sup> changes abruptly as shown in fig. 5.

The absorption at  $2100-2000 \text{ cm}^{-1}$  disappears and a new (very complex) one appears at lower frequency (2000-1800 cm<sup>-1</sup>).

 $NH_a$  is a Lewis base. Therefore reaction (2) should readily occur between adsorbed neutral carbonyls  $[Co_2(CO)_8(ads) etc.]$  and adsorbed NH<sub>3</sub>, leading to the extensive formation of  $Co(CO)_4^-$  and  $Co(NH_3)_6^{2+}$ . The main peak (which is generally associated with terminal CO in zerovalent clusters) totally disappears, while a quartet of new bands in the 2030–1750 cm<sup>-1</sup> interval clearly associated with  $Co(CO)_4^-$  is produced. When the NH<sub>3</sub> pressure is increased, the three low-frequency bands coalesce into a single absorption at 1900 cm<sup>-1</sup> typical of  $Co(CO)_4^-$  in a nearly tetrahedral situation.<sup>19</sup> (This is because the Co<sup>2+</sup> and Mg<sup>2+</sup> ions are completely solvated by NH<sub>3</sub>, and consequently tight surface cation-anion pairs are not formed in these conditions.<sup>19</sup>)

This experiment clearly shows that the same type of reaction, well known in homogeneous conditions, also occurs on the surface via the intervention of extra bases coming from the gas phase.

As the extinction coefficient of the  $Co(CO)_{4}^{-}$  anion with  $T_{d}$  symmetry in solvents with high solvation power is known,<sup>30</sup> we can infer via a purely spectroscopic method that the number of  $Co(CO)_4^-$  groups (assumed to be uniformly distributed on the whole MgO surface) is ca.  $15 \times 10^{-2}$  per 100 Å<sup>2</sup>. As a consequence we can also deduce that the total amount of Co atoms responsible for the full-line spectrum of fig. 5 is ca.  $21 \times 10^{-2}$  per 100 Å<sup>2</sup>. In fact the concentration in the sample is not uniform (for the reasons briefly summarized in the experimental section), and consequently in the external layers it is certainly larger. However, an accurate figure for the dependence of the concentration upon the distance of the pellet from the surface cannot be given.

This research was carried out with financial support from the Ministero Pubblica Istruzione, Progetti di rilevante interesse nazionale (Italy). M.R. thanks the 'Third World Academy of Sciences', ICTP, Trieste, Italy for awarding a grant for this research.

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Paper 7/1689; Received 21st September, 1987