

## The Effect of Particle Size in the Adsorption of Carbon Monoxide on Iridium: An Infrared Investigation

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The effect of a varying particle size on the infrared absorption band frequency of CO adsorbed on Ir/Al<sub>2</sub>O<sub>3</sub> has been investigated. The experimentally observed increase of the frequency with increasing particle size is ascribed to a weaker electron exchange of CO with the metal. This picture is confirmed by hydrogen and carbon monoxide adsorption measurements. By use of the isotopic dilution method, other possible effects, such as a varying dipole-dipole coupling, an electronic influence of the carrier, or electronic structure changes due to a varying metal particle size, could be discarded as possible explanations.

### INTRODUCTION

It is a well established but so far a little understood fact that catalytic reactions may or may not be structure sensitive (1). Structure-sensitive reactions show pronounced variations in rate and product distribution upon varying particle size (2) or with different exposed crystallographic planes (3). These variations may be quite fundamental and of practical importance.

Several reasons can in principle be held responsible for a particle size effect in the catalytic and adsorptive behaviour of metals:

1. The electronic band structure (reflected inter alia by the ionization potential and the electron affinity) may for small particles be different from that of the bulk metal.

2. Small particles contain a higher percentage of coordinatively unsaturated atoms in their surface. This may change the local geometric and/or electronic structure of the surface.

3. Small particles may be influenced by the support (e.g., by an often postulated electron transfer) more strongly than large particles.

4. If the contact with the support is formed by an oxidized form of the metal,

this may affect the electronic structure and chemical behaviour more strongly in the case of small particles.

A very sensitive method to investigate the properties of finely dispersed metals is ir transmission spectroscopy, applied to the adsorption of gases like CO or NO. The frequency of the ir absorption band of these molecules can be an important source of information on the electronic and geometric aspects of the chemisorption bonding. The following factors have been identified as being important contributions to the absorption band frequency of, e.g., CO:

- (i) *Chemical bonding.* The formation of molecular orbitals which can be visualized (4-6) as a "direct donation" from the non-bonding 5σ orbital of CO into unfilled metal orbitals (which increases the frequency), accompanied by a "back-donation" of electrons from the metal orbitals (usually of *d*-character) into the anti-bonding 2π-orbital of CO (which decreases the frequency). Upon adsorption of CO on zero-valent Group 8 metals the latter effect is generally regarded as being most important for the position of the ir absorption band. The resultant net decrease of the frequency (or "red shift") is further regarded as the major, though not the sole, reason for the experimentally observed absorption band fre-

quencies in the region below  $2100\text{ cm}^{-1}$ , i.e., well below the gas-phase value of  $2143\text{ cm}^{-1}$ .

(ii) *Vibrational interaction with the metal.* Apart from the chemical bonding, the interaction with the metal comprises also the interaction with the image dipole (7) and a flow of electrons to and from the metal due to the compressing and stretching of the C–O bond (8). These effects may influence the frequency and the intensity of the absorption band.

(iii) *Mutual interaction of the CO dipoles.* The so-called dipole–dipole coupling leads to an increase of the frequency (or a “blue shift”) with decreasing mutual distance, or increasing surface coverage  $\Theta(\text{CO})$ . Actually, the whole upward shift of  $\nu(\text{CO})$  with  $\Theta$  on a metal like Pt could be explained by this effect (9); with metals such as Ir (10) or Pd (11) other effects may also play a role (a competition for  $d$  electrons (4) is frequently mentioned in this respect).

Any change in the chemical bonding will thus most probably be reflected by an ir frequency shift. However, the reverse statement is not necessarily true. The shift can also have other reasons. It is therefore important to be able to separate electronic (i.e., chemical bonding) effects from “geometric” (i.e., coupling) ones. By doing so we can also gain more insight into the possible particle size effects, listed above under (1)–(4). This separation has been proved possible by the isotopic dilution method in which the dipole–dipole coupling effect is eliminated by diluting  $^{12}\text{CO}$  by  $^{13}\text{CO}$ : there is no coupling between two species with a sufficiently different absorption band frequency (8, 9, 12, 13). The frequency of the (pseudo) isolated molecule can then be found by extrapolating to infinite dilution of  $^{12}\text{CO}$  in  $^{13}\text{CO}$ . Once the coupling effect has been eliminated a more reliable discussion of the various effects is possible (14).

#### EXPERIMENTAL

Ir/Al<sub>2</sub>O<sub>3</sub> (with ca. 10 wt% metal) has been prepared by homogeneous precipitation

with urea (15). Iridium was obtained from a solution of (NH<sub>4</sub>)<sub>2</sub>IrCl<sub>6</sub> in water. The average particle size was below the detection limit of X-ray diffraction line broadening, from which we infer that particles had a diameter smaller than 25 Å. This sample will be arbitrarily designated below as “20 Å.” The average particle size could be increased by sintering under flowing hydrogen at a temperature of ~750 K. By this procedure, samples with an average particle size (determined by X-ray diffraction) of 30, 50, and 170 Å could be prepared. The preparation of the Ir/SiO<sub>2</sub> samples (16) as well as the *in situ* treatment of all powders and the way the ir experiments were carried out, have been described elsewhere (14). Oxidation was performed under flowing oxygen at ~470 K for at least 30 min, and the subsequent reduction under flowing hydrogen at ~620 K for at least 2 hr.

Hydrogen and carbon monoxide adsorption measurements were performed with a glass vacuum system. The ultimate pressure in the adsorption cell was about  $10^{-6}$  Torr. Pressure measurements were made with a Baratron pressure meter Type 170 (MKS Instruments). The sample weights were 0.05 g for the “20-Å” sample and 0.25 g for the “170-Å” sample. Both samples were pretreated under oxygen (~200 mbar) at 473 K for 1 h, followed by a reduction under flowing hydrogen at 573 K for at least 3 h and evacuation at 673 K for at least 5 h. Between consecutive hydrogen adsorption experiments the samples were again evacuated at 673 K. Pressure measurements were performed at 293 K. Each uptake point was measured after 15 min. Gas doses were admitted up to an equilibrium pressure of 0.5 Torr.

The isotherms  $N_A = f(P_{\text{eq}})$  were plotted as linearized Langmuir isotherms:

$$\frac{P_{\text{eq}}}{N_A} = \frac{P_{\text{eq}}}{N_M} + C$$

in which  $N_A$  is the number of adsorbed molecules at a certain pressure,  $N_M$  is the number of adsorbed molecules at full coverage,

and  $C$  is a constant. The slope of the curve  $P_{\text{eq}}/N_A$  vs.  $P_{\text{eq}}$  is  $N_M^{-1}$ .

This value is used in the determination of specific surface area.

#### RESULTS

Adsorption of CO on the Ir/Al<sub>2</sub>O<sub>3</sub> (20 Å) sample produced the ir spectrum shown in Fig. 1, with a major band at 2050 cm<sup>-1</sup> and a high-frequency shoulder at 2075 cm<sup>-1</sup>. The data for the 170-Å sample (the largest particle size used in this study) are also presented. The data for the samples with the intermediate size (not shown in Fig. 1) offer the following picture. Upon increasing the particle size, the integrated absorption band intensity becomes smaller and the ratio of band intensities changes in favour of the high frequency band. For the sample with largest particles, the high frequency band clearly dominates the spectrum.

The effect of isotopic dilution on these spectra can be seen in Figs. 2 and 3. A peculiar phenomenon is immediately obvious. At all isotopic ratios the spectra reveal only one set of bands attributable to <sup>12</sup>CO. This band shifts to lower frequencies with increasing <sup>13</sup>CO content (reduced dipole-dipole coupling) but does not lose any intensity. This is caused by the so-called

intensity transfer from the low-frequency (<sup>13</sup>CO-like) to the high-frequency (<sup>12</sup>CO-like) band. This is a metal-dependent phenomenon: it is present on all metals, but to a different degree.

Evidently on iridium the transfer is particularly strong (10), in contrast to Pt or Cu (17). A convenient consequence of this effect is that it is easy to follow the <sup>12</sup>CO-like band over a broad range of isotopic ratios. The essential results of the experiments with <sup>12</sup>CO/<sup>13</sup>CO mixtures are collected in Fig. 4. The curve obtained by ir reflection experiments on evaporated iridium films (10) is also shown. In Fig. 5 comparable results with Ir/SiO<sub>2</sub> samples are presented. Two conclusions are obvious: the dipole-dipole coupling is essentially the same with all forms of iridium investigated here, while both Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> can be considered as having no influence.

It has been shown by several authors (18) that the ions of some metals (Cu, Ni, Pd) reveal upon CO adsorption an ir absorption band at higher frequencies than the zero-valent metals. Therefore, when "doublets" as in Fig. 1 are observed it is necessary to pay attention to a proper assignment of the bands with regard to the degree of reduction, in particular to the high-frequency

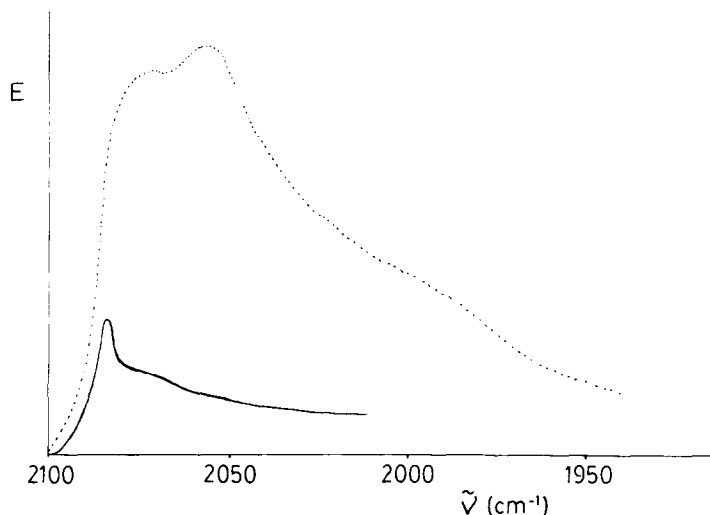


FIG. 1. Infrared spectra of CO adsorbed on Ir/Al<sub>2</sub>O<sub>3</sub> (20 Å) (dotted curve) and Ir/Al<sub>2</sub>O<sub>3</sub> (170 Å) (solid curve). The absorption band of the 170-Å sample is four times enlarged to make the comparison easier.

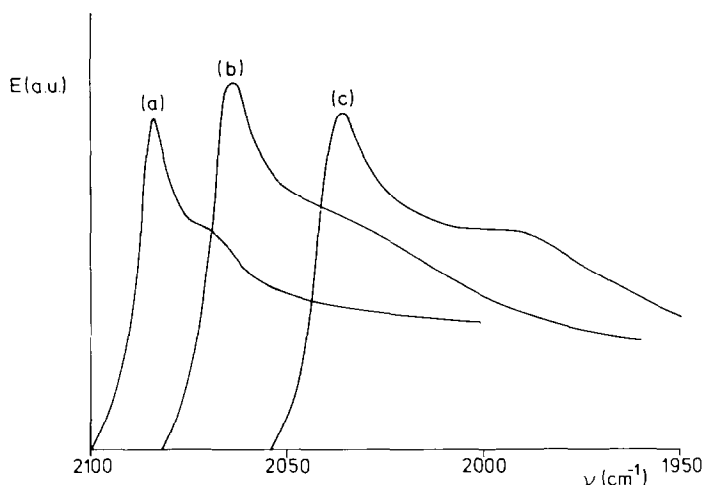


FIG. 2. Infrared spectra of CO adsorbed on Ir/Al<sub>2</sub>O<sub>3</sub> (170 Å). (a) Pure <sup>12</sup>CO. (b) <sup>12</sup>CO/<sup>13</sup>CO, 55/45. (c) <sup>12</sup>CO/<sup>13</sup>CO, 10/90.

band (or shoulder). A simple way to check a possible role of adsorbent ions, or the effect of ions in the sense of Point (4) in the list of effects in the Introduction, is to oxidize the samples without a subsequent reduction and to study the spectra of adsorbed CO.

The effect of this pretreatment can be seen in Fig. 6 for the 20-Å sample. After

oxidation only one rather symmetric band remains at 2085  $\text{cm}^{-1}$  with an integrated absorption band intensity of about one-third compared to that of the reduced sample. For the 170-Å sample a practically identical band at the same frequency was obtained. In the case of oxidized catalysts the particle size has obviously no effect on  $\nu(\text{CO})$ . The question now is whether this band is identi-

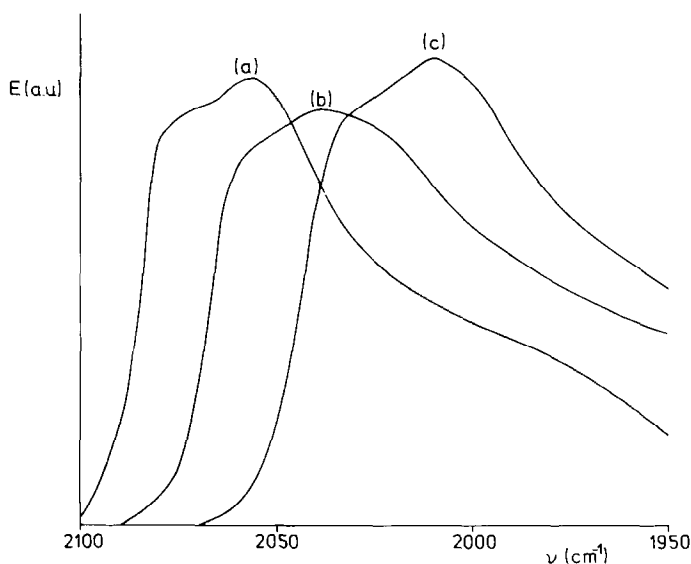


FIG. 3. Infrared spectra of CO adsorbed on Ir/Al<sub>2</sub>O<sub>3</sub> (20 Å). (a) Pure <sup>12</sup>CO. (b) <sup>12</sup>CO/<sup>13</sup>CO, 55/45. (c) <sup>12</sup>CO/<sup>13</sup>CO, 10/90.

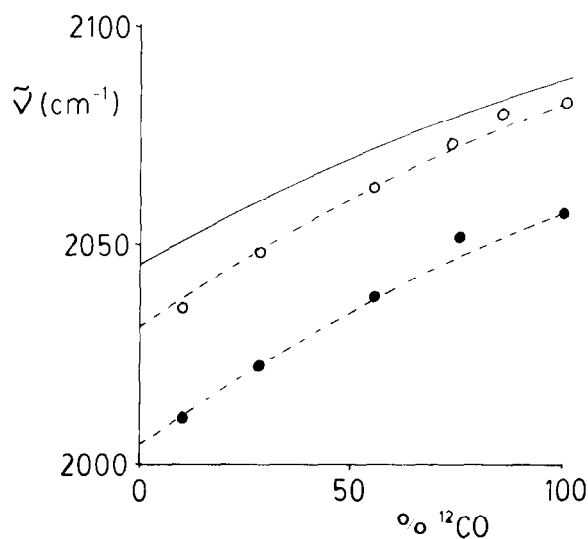


FIG. 4. Wavenumber of the high-frequency band of  $^{12}\text{CO}/^{13}\text{CO}$  mixtures as a function of isotopic composition. —, Ir-film (Ref. (10)).  $\circ$ , Ir/ $\text{Al}_2\text{O}_3$  (170 Å).  $\bullet$ , Ir/ $\text{Al}_2\text{O}_3$  (20 Å).

cal with the one which appears as a high-frequency band after reduction. To obtain more information on this question we performed isotopic dilution experiments with the oxidized powder. In Fig. 7 the characteristic features observed in these experiments are shown. No other bands in the region 2500–1200  $\text{cm}^{-1}$  could be detected. A striking result is the total absence of any

transfer of intensity. A clear and concentration-proportional low-frequency ( $^{13}\text{CO}$ -like) band can be observed. The pretreatment with oxygen has evidently perturbed the metal structure, a perturbation which prevents the intensity transfer.

In Fig. 8 all the results on reduced and oxidized Ir/ $\text{Al}_2\text{O}_3$  samples are collected. The dipole-dipole coupling on oxidized

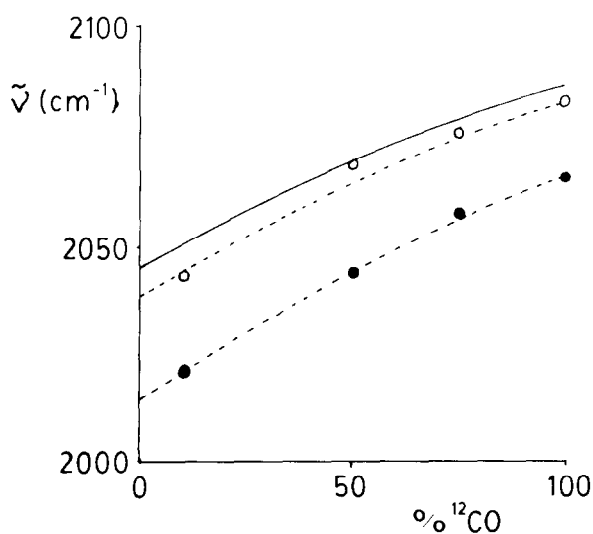


FIG. 5. Wavenumber of the high-frequency band of  $^{12}\text{CO}/^{13}\text{CO}$  mixtures as a function of isotopic composition. —, Ir-film (Ref. (10)).  $\circ$ , Ir/ $\text{SiO}_2$  (120 Å).  $\bullet$ , Ir/ $\text{SiO}_2$  (30 Å).

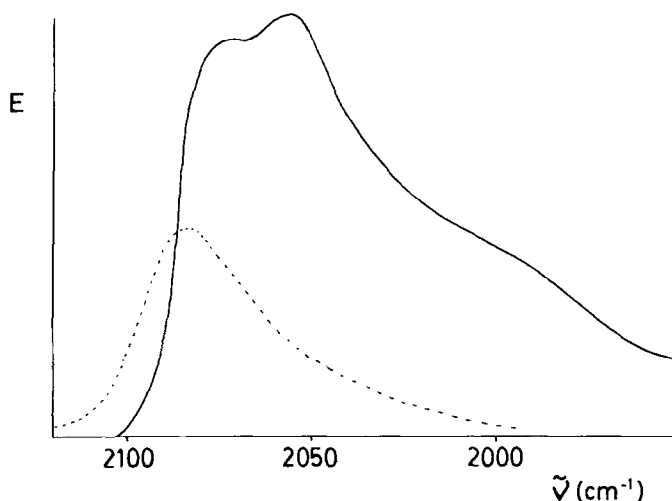


FIG. 6. Infrared spectra of CO adsorbed on Ir/Al<sub>2</sub>O<sub>3</sub> (20 Å). Dependence on pretreatment: solid curve, reduced; dashed curve, oxidized.

iridium is clearly much smaller than with the same samples after reduction. Obviously, the surface coverage of CO on oxidized iridium is likewise smaller. Two conclusions are possible now, both very essential for the discussion which follows:

(a) oxidation disturbs the metal structure and thus the intensity transfer,

(b) the high-frequency band on reduced samples reveals a strong dipole-dipole coupling and intensity transfer and therefore

cannot be ascribed to CO on incompletely reduced iridium.

The results of the adsorption measurements are collected in Table 1. As can be seen, the amount of adsorbed hydrogen is consistently higher than that of carbon monoxide. This is in compliance with data available for adsorption of hydrogen (19) and carbon monoxide (20) on palladium, according to which the  $N_M(\text{H}_{\text{ads}})/N_M(\text{CO}_{\text{ads}})$  ratio should be around 1.5 or slightly lower.

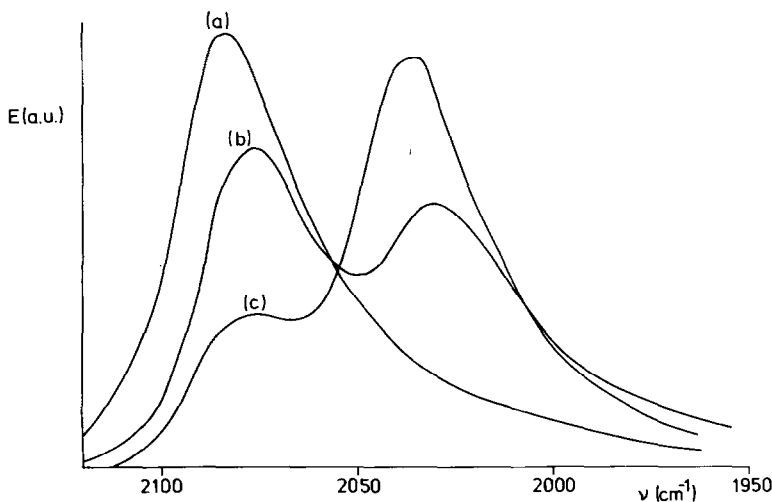


FIG. 7. Infrared spectra of CO adsorbed on Ir/Al<sub>2</sub>O<sub>3</sub> (20 Å). Oxidized sample without reduction after oxidation. (a) Pure <sup>12</sup>CO. (b) <sup>12</sup>CO/<sup>13</sup>CO, 55/45, (c) <sup>12</sup>CO/<sup>13</sup>CO, 28/72.

TABLE 1

Hydrogen and Carbon Monoxide Adsorption Measurements; Infrared Absorption Band Intensities

Sample	$d_H^a$ (Å)	H/Ir	CO/Ir	$I_{CO}^b$ ( $\text{cm}^{-1}$ )	$\overline{\epsilon}_{\text{mol}}^c$ ( $\times 10^{-6} \text{ cm}^{-1} \text{ mol}^{-1}$ )	$A_T^d$ ( $\times 10^{-7} \text{ cm} \text{ mol}^{-1}$ )
Ir/Al <sub>2</sub> O <sub>3</sub> (20 Å)	20 ± 2	0.52 ± 0.05	0.45 ± 0.03	150 ± 25	13 ± 1	6.8 ± 0.5
Ir/Al <sub>2</sub> O <sub>3</sub> (170 Å)	100 ± 10	0.12 ± 0.02	0.08 ± 0.01	4.5 ± 0.5	2.1 ± 0.2	1.1 ± 0.1

<sup>a</sup> Particle size determined by hydrogen adsorption measurements.

<sup>b</sup> Intensity of the ir absorption band of adsorbed CO  $\int E_\nu d\nu$  in which  $E = \log T_{\text{back}}/T_{\text{ads}}$ , where  $T$  stands for transmission and  $T_{\text{back}}$  for the background  $T$ .

<sup>c</sup>  $\overline{\epsilon}_{\text{mol}} = I_{CO}/n_{CO}$  in which  $n_{CO}$  is the number of adsorbed CO molecules according to CO adsorption measurements.

<sup>d</sup>  $A_T = \frac{1}{C} \int E_\nu d\nu$  (see Ref. (29)).

Small particles of Ir might be accommodating more CO than the smooth monocrystal planes so that the ratios (see Table 1) found here are not surprising. In determining the metal surface area and the average particle size, the data on the hydrogen adsorption are preferred.

The magnitude to be compared is  $\overline{\epsilon}_{\text{mol}} = I/n_{CO}$ , where  $n_{CO}$  is the amount (in moles) of CO adsorbed, as calculated according to the independent (*ex situ*) adsorption measurements. When according to Vannice and Twu (21) the absorbance  $A_T$  is calculated, the values of the last entry in Table 1 result.

## DISCUSSION

Although Ir has been less studied than other metals, there are several papers which deal with CO adsorption on this metal, either in the form of well-sintered films (10, 22) or as supported small particles (23, 24).

The effect of particle size on the ir spectrum of adsorbed CO or NO has not been reported very frequently. Nevertheless, some data have accumulated already, as can be seen from Table 2. The agreement between the various authors is not particularly good. However, this is not uncommon with data (as in Refs. (23–29)) obtained by ir transmission spectroscopy (30) and can be ascribed most probably to differences in preparation. Moreover, without a proper determination of the extent of dipole–dipole coupling with the isotopic dilution method, band assignment may be difficult or even impossible. For example, the interpretation of McVicker *et al.* (24) of the bands of CO on Ir/Al<sub>2</sub>O<sub>3</sub> (see Table 2) in terms of dicarbonyl species (Ir(CO)<sub>2</sub>) seems questionable because of the absence of an asymmetric vibration of this species, which has been shown to exist on Rh/Al<sub>2</sub>O<sub>3</sub> (31).

Our results concerning the particle size

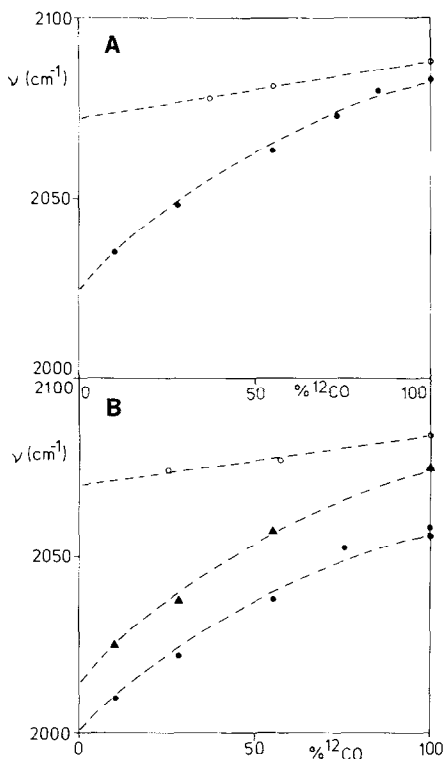


FIG. 8. Wavenumbers of the high-frequency band of the <sup>12</sup>CO/<sup>13</sup>CO mixtures as a function of isotopic composition. (A) Ir/Al<sub>2</sub>O<sub>3</sub> (170 Å); ○, oxidized; ●, reduced. (B) Ir/Al<sub>2</sub>O<sub>3</sub> (20 Å); ○, oxidized; ▲, reduced (high-frequency shoulder); ●, reduced (main band).

TABLE 2  
Particle Size Effects on the Infrared Absorption  
Band of Adsorbed CO<sup>a</sup>

Sample	Particle size	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )	$\nu(\text{CO}) = f(\text{size})$	Reference
Ni/Al <sub>2</sub> O <sub>3</sub>	1.5% Ni	2045	Increasing	28
	10% Ni	2080		
Ni/SiO <sub>2</sub>	20 Å	2075	?	25
	21 Å	2057		
	70 Å	2057		
	214 Å	2075		
Ni/SiO <sub>2</sub>	25 Å	2077	Decreasing	26
	96 Å	2045		
Pt/Al <sub>2</sub> O <sub>3</sub>	10 Å	2077	Increasing	27
	120 Å	2093		
Pt/SiO <sub>2</sub>	20 Å	2075	Increasing	Unpublished results
	150 Å	2085		
Ir/SiO <sub>2</sub>	8 Å	2048	Increasing	25
	100 Å	2078		
Ir/Al <sub>2</sub> O <sub>3</sub>	<6 Å	2060	Decreasing	24
	~50 Å (?)	2020		
Ir/SiO <sub>2</sub>	30 Å	2065	Increasing	16, 29, this paper
	120 Å	2080		
Ir/Al <sub>2</sub> O <sub>3</sub>	20 Å	2055	Increasing	This paper
	170 Å	2075		

<sup>a</sup> Only the summit type of adsorption (2000–2100  $\text{cm}^{-1}$ ) is considered.

effect (see Table 2) agree with most of the literature data: an increase of the particle size leads to a (new) band at a *higher* frequency which becomes dominating for a particle size larger than 100 Å.

The question to be solved concerns the interpretation of the bands in Fig. 1. Do the two bands for the (20 Å) sample originate from a difference in electronic interaction between CO and the metal (i.e., a difference in bonding) or are they caused by a different extent of dipole–dipole coupling between CO molecules adsorbed on high- and low-index planes respectively? Still another possibility is that both effects exist and operate always together.

The isotopic dilution method can provide information on the relative importance of these two effects: upon increasing the content of <sup>12</sup>CO in the adsorption layer, all bands shift parallel to each other as can be seen in Figs. 3 and 8, and the conclusion is then obvious: the dipole–dipole coupling is the same for both bands and the difference between them should be primarily looked

for in a different electronic interaction with the metal on, e.g., two types of sites.

Any electronic influence of the carrier can probably be neglected in view of the very close similarity of the results obtained on Ir/Al<sub>2</sub>O<sub>3</sub> and Ir/SiO<sub>2</sub> with transmission spectroscopy and on evaporated iridium films with reflection spectroscopy (see Figs. 3 and 4).

As mentioned above a difference in electronic interaction might have been caused by a difference in the degree of reduction of the metal. Therefore, we have performed experiments with the same samples pretreated with oxygen. As can be seen in Fig. 6, the effect of this pretreatment on the band position is rather small (probably this excludes as a possibility the formation of a real ionic oxide structure). The question now was whether the single band observed after the oxygen pretreatment was the same as the high-frequency band after reduction. As stated already in the Results section, the isotopic dilution experiments supply conclusive evidence that this is *not* the case. After pretreatment with oxygen, the dipole–dipole coupling clearly is much smaller than after reduction (see Fig. 8). The similarity of the frequencies is therefore coincidental only. The “real”  $\nu(\text{CO})$  wavenumbers, free of the coupling effect, can be found on the left side of Fig. 8 and they differ considerably, being 2075 and 2030  $\text{cm}^{-1}$  on oxidized and reduced Ir, respectively. The interpretation of the band after oxidation seems now to be possible. The band is much smaller than that observed after reduction (see Fig. 6) and it displays much less dipole–dipole coupling (see Fig. 8). Obviously oxygen occupies sites which would have been otherwise occupied by CO on the reduced samples. At the same time, oxygen has the effect of increasing the wavenumber of the absorption band of coadsorbed CO by about 45  $\text{cm}^{-1}$ . These experiments do not indicate whether this latter effect is caused by the coadsorbed oxygen or by oxygen incorporated in the metal. The reason for the frequency



increase could be the influence of oxygen on the iridium *s*-electrons, which are responsible for a considerable part of binding in any case. One cannot speculate here as with Pt (14) on the increase of  $\nu(\text{CO})$  due to a compression of the CO domains on the surface with oxygen, since in that case not only the frequency but also the  $\bar{\nu} = f(^{12}\text{CO})$  shift should be higher. Obviously, iridium adsorbs (and perhaps also absorbs) oxygen much more strongly than does platinum. Additional information on the state of iridium after oxidation can be obtained from the transfer of intensity from the low- to the high-frequency band upon adsorption of isotopic mixtures. On reduced iridium this transfer is very pronounced as can be seen in Figs. 2 and 3. However, on oxidized iridium it is completely absent, as can be seen in Fig. 7. In this regard there is also no difference between small and large particles. A comparable loss of intensity transfer has been observed upon alloying Pt with Cu (17). Although the mechanism of this transfer is not established yet, it seems probable that it is a "through-the-metal" effect. A second metal (like copper) or a coadsorbate (like oxygen) can therefore "perturb" the metal structure, thereby impeding the intensity transfer. On platinum, however, oxygen did not inhibit the intensity transfer (14), which indicates again that the interaction between iridium and oxygen is much stronger.

However, let us now return to the original question: why is  $\nu(\text{CO})$  dependent on the particle size? One possibility to consider is a change in the electronic structure of the metal particles upon decreasing particle size. Several reports exist (32) which mention an increase of the ionization potential (I.P.) and the electron affinity (E.A.), from the value of the work function of the metal, upon decreasing particle size. These effects should cause a decreased back-donation (I.P.) as well as an increased direction donation (E.A.) with decreasing particle size. Both effects would increase the frequency. However, this is just opposite to

what is experimentally found, which excludes this possibility as a major factor.

An inspection of the available literature on small particles, stepped surfaces, and metal clusters reveals that two phenomena may be considered as possible explanations.

1. Small particles expose more low coordinated atoms which show a higher population of the almost filled orbitals and may reveal a higher density of states  $N(E)$  (33) in the relevant region of energies (i.e., around the Fermi energy). Both of these factors may lead to an increased back-donation on the Group 8 metals. Unfortunately, a more exact analysis is not possible at the moment.

2. It is known that the back-donation increases sharply with a shortening of the CO-metal distance (see Fig. 3 in Ref. (5)). A slight reduction of this distance would suffice already to explain the frequency difference in  $\nu(\text{CO})$  for small and big particles.

The validity of these points is supported by a comparison of the ir absorption band intensities. It has been stated earlier (21) that an increased adsorption bond strength, probably accompanied by an increased electron exchange, leads to a larger extinction coefficient and thus a larger integrated ir absorption band intensity. We have indeed observed a strong increase of the area of the ir absorption band of adsorbed CO upon decreasing particle size (see Fig. 1). However, the absorption band increases also because of a larger amount of surface metal atoms. Therefore, we have compared the absorption band areas of both samples, normalized by means of the adsorption data. The results are collected in Table 1. Upon decreasing particle size the number of surface metal atoms increases by a factor of 5, but the ir absorption band by a factor of 30. This additional increase can be caused then by an increase of the average extinction coefficient, reflected by the value of  $\bar{\epsilon}_{\text{mol}}$  in Table 2. This is not uncommon: comparable differences have been

found for different adsorption sites on Pt (21), Pd (34), and Rh (31).

In conclusion we can now suggest a tentative explanation of Fig. 1: on the (20 Å) sample the band at 2050  $\text{cm}^{-1}$  represents the (summit-type) adsorption of CO on "low-coordinate" sites (edges, corners, etc.); the high-frequency shoulder at 2075  $\text{cm}^{-1}$  as well as the single band at 2080  $\text{cm}^{-1}$  of the (170 Å) sample represents summit type adsorption on "high-coordinate" sites (planes). The small variations (5–10  $\text{cm}^{-1}$ ) of one band may be caused by differences in extent of dipole–dipole coupling. Upon decreasing the particle size, the number of CO molecules with stronger interaction with the metal increases and will ultimately predominate.

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