JOURNAL OF CATALYSIS 88, 273–282 (1984)

Electronic Transfer and Ligand Effects in the Infrared Spectra of Adsorbed Carbon Monoxide

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Received September 19, 1983

Adsorption of carbon monoxide at low coverages on alumina-supported platinum leads to a heterogeneous distribution of the CO molecules on the metal particles. Heating in a closed system between 200 and 300°C allows a redispersion of the CO layer over the platinum crystallites. Isotopic dilution experiments using ^{12}CO–^{13}CO mixtures show that the CO molecules are free of dipole–dipole coupling after the redispersive treatment. Subsequent adsorption of electron donor (or acceptor) compounds leads to a shift in the νCO frequency of adsorbed CO which is interpreted in terms of electron transfer between the second adsorbate and the metal.

INTRODUCTION

The adsorption of carbon monoxide on unsupported and supported transition metals has been extensively studied by infrared spectroscopy (*1*) and the CO stretching frequency has been found to be very sensitive to the metal surface coverage. Coadsorption of CO with several molecules was also investigated. As far as unsaturated hydrocarbons (benzene, ethylene) (*2–4*) or Lewis bases (ammonia, pyridine) (*5*) are concerned, the adsorption of these molecules on a metal surface precovered by CO shifts the νCO band toward lower wavenumbers (red shift). Two types of interpretation have been proposed to explain the changes in the position of the νCO band:

(i) In the model proposed by Blyholder (*6, 7*), binding to the metal populates the antibonding orbitals of CO leading to a decrease in the bond order of the carbon–oxygen bond and a lowering of the νCO frequency. The coverage-dependent frequency shift would be caused by the decrease of the population of the CO $2\Pi^*$ orbitals due to a competition for the *d* electrons of the metal. The adsorption of electron donor compounds increases the electron density at the metal resulting in an additional transfer of metal *d* electrons to $2\Pi^*$ orbitals of CO and a lowering of the νCO frequency (*2*).

(ii) In the electrodynamic model, the shift observed by changing the CO coverage is consistent with dipole–dipole coupling between chemisorbed species (*8*). It has been found that the full frequency shift observed with increasing the CO coverage on platinum is attributable to coupling (*9, 10*). According to Stoop *et al.* (*4*) the adsorption of donor compounds like C_2H_4 causes the separation of the CO dipoles; thus the dipole–dipole coupling between adjacent CO molecules decreases, leading to a red shift in the νCO frequency although there is no change in the C–O bond strength. From photoelectron spectroscopy measurements, it was found that the O (1*s*) binding energy in the nondissociative adsorption of CO on metals decreases as the heat of adsorption increases (*11*). The backdonation CO → metal was assumed to be the major contribution to the metal–CO bond. The presence of sulfur on metals (*12*) or metallic clusters (*13*) strongly modifies the forms of chemisorbed CO as well as its reactivity. These changes were also explained by using the Blyholder–Dewar–Chatt model for the CO bonding.

The latter interpretation is consistent

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with the formation of islands during the adsorption of CO on the metal (*10, 15*); the breaking-up of CO islands by adsorption of donor compounds would be at the origin of the red shift observed (*4*).

In the present paper, adsorption of CO on alumina-supported platinum was performed; experimental conditions in which the clustering of the CO molecules can be avoided have been carefully determined. Then adsorption of various compounds on CO-covered samples has been performed in order to follow the influence of the ligand effect on the frequency of adsorbed CO.

EXPERIMENTAL

The Pt/Al_2O_3 sample was prepared by impregnation of alumina (Oxide C from Degussa, 200 m^2/g) with an aqueous solution of hexachloroplatinic acid in order to obtain a concentration of 5 wt% of platinum. The reduction was achieved according to the following procedure: desorption at 500°C for 1 h, treatment at the same temperature under 200 Torr hydrogen pressure for 12 h, then evacuation at 500°C for 2 h to remove adsorbed hydrogen. The dispersion of the metallic phase measured by adsorption of oxygen or hydrogen was equal to 50%, i.e., platinum exhibits a mean particle size of 20 Å.

The sample was compressed under 4 tons cm^{-2} pressure to obtain a disk 18 mm in diameter (weight comprised between 20 and 30 mg). The reduction procedure was performed *in situ* in an ir cell previously described (*14*). Adsorption of CO at a given coverage was achieved by introducing a known pressure of carbon monoxide contained in a calibrated vessel.

The isotopic dilution method was used to determine the extent of the dipole–dipole coupling on the position of the CO frequency (*4, 7, 9*). Mixtures of ^{12}CO–^{13}CO with different isotopic concentrations were contacted with the sample of supported catalyst. By increasing the concentration of ^{13}CO in the mixture, the ^{12}CO molecules adsorbed on platinum were progressively substituted by ^{13}CO molecules; the interactions of the CO layer with the surface remain unchanged since the bondings of ^{12}CO and ^{13}CO molecules with the metal are identical. On the contrary the dipole–dipole coupling between the ^{12}CO vibrators decreases with the amount of ^{13}CO molecules in the adsorbed layer since the ^{12}CO species are diluted by ^{13}CO molecules. In addition ^{12}CO dipoles do not couple with the ^{13}CO dipoles. By using various ^{12}CO–^{13}CO mixtures and by extrapolating the $\nu^{12}CO$ frequency to zero coverage in adsorbed ^{12}CO, it is possible to find the $\nu^{12}CO$ frequency of singleton ^{12}CO, i.e., free of dipole–dipole coupling. Thus various mixtures ^{12}CO–^{13}CO have been prepared and their composition was checked using a quadrupole mass spectrometer (Supavac V.G.)

To prevent pollution by water, the various adsorbates were stored in vessels containing 4A molecular sieves dehydrated by vacuum treatment at 350°C prior to use.

Infrared spectra were recorded at room temperature using either a Perkin–Elmer 580 Spectrometer or a Fourier transform spectrometer (Bruker IFS 110). In each case, the spectral resolution was better than 2 cm^{-1} in the spectral range 4000–1000 cm^{-1}.

RESULTS AND DISCUSSION

1. *Adsorption of ^{12}CO and of ^{12}CO–^{13}CO Mixtures*

(*a*) *Effect of the CO coverage on the νCO frequency.* The reduced Pt/Al_2O_3 sample was contacted at room temperature with a few Torr CO pressure, then evacuated at 25°C. The ir spectrum showed two νCO bands, one at 2080 cm^{-1} (linear species Pt–CO), the other of weak intensity at 1845 cm^{-1} (bridged species Pt_2CO). The intensity of the 2080-cm^{-1} band was about 20 times larger than that of the 1845-cm^{-1} band. To a first approximation, we shall neglect the contribution of bridged species toward that of linear groups and we shall consider that

CO adsorption on platinum occurs only in the linear form.

The fully CO-covered sample was then heated under vacuum step by step at increasing temperature. Infrared spectra were recorded for each temperature of desorption. If we assume that the θ_{CO} coverage was equal to unity after desorption at 25°C, the CO coverage for higher temperatures of evacuation can be determined by dividing the optical density of the νCO band (after evacuation at higher temperatures) by that of the CO band observed after room temperature desorption.

The frequency of the νCO band as a function of the coverage (or the temperature of desorption) is plotted in Fig. 1. The νCO frequency decreases continuously when the CO coverage diminishes to reach a pseudo plateau for low values of CO coverage. Extrapolation of this curve to $\theta_{CO} = 0$ gave the frequency of the isolated CO molecule, i.e., $\nu CO = 2052\ cm^{-1}$.

(*b*) *Adsorption of* ^{12}CO–^{13}CO *mixtures.* The change of νCO vs θ_{CO} has been previously explained by a competition of the metal *d* electrons in populating the $2\Pi^*$ orbitals of CO (*6, 7*). Other authors attribute this shift to changes in dipole–dipole coupling between adsorbed ^{12}CO molecules (*4, 8, 9*). As previously mentioned, the use of ^{12}CO–^{13}CO mixtures allow us to measure the extent of coupling since the coverage of the metal remains constant whatever the isotopic composition of the mixture. The main effect will be the separation of the ^{12}CO dipoles by ^{13}CO dipoles, and since they do not vibrate at the same frequency ($\Delta\nu = 50\ cm^{-1}$), the coupling is not operative.

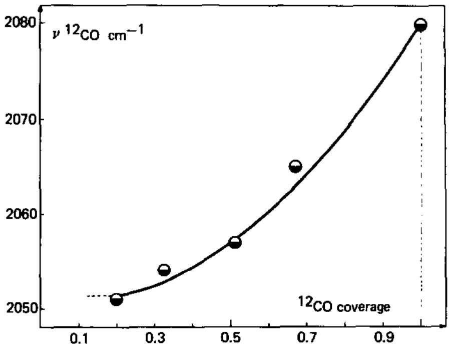


FIG. 1. Change of $\nu^{12}CO$ frequency with CO coverage. Various coverages were obtained by desorption at increasing temperatures of the Pt/Al_2O_3 sample fully covered by CO at 25°C.

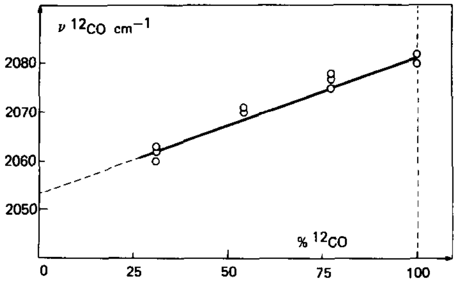


FIG. 2. $\nu^{12}CO$ frequency as a function of isotopic composition for ^{12}CO–^{13}CO mixtures adsorbed on Pt/Al_2O_3.

Adsorption of ^{12}CO–^{13}CO mixtures was performed at 25°C on the 5% Pt/Al_2O_3 samples. After 10 min of contact, the cell was evacuated at room temperature and ir spectra were recorded. Due to the transfer of intensity already observed by other authors (*4, 8*) we shall consider only the $\nu^{12}CO$ band which is observable over the whole range of isotopic compositions. The evolution of the $\nu^{12}CO$ frequency due to the linear form as a function of the isotopic composition of the gas phase is given in Fig. 2. The $\nu^{12}CO$ frequency is shifted toward lower wavenumbers when the ^{12}CO concentration decreases. Extrapolation of $\nu^{12}CO$ to infinite dilution of ^{12}CO in ^{12}CO–^{13}CO mixtures gives a frequency around $2053\ cm^{-1}$.

Such extrapolation gives the frequency of the singleton vibrator, since the dipole–dipole interaction has been suppressed. Note that this frequency is indeed very close to that deduced from desorption experiments (preceding paragraph).

(*c*) *Adsorption of* ^{12}CO *below full coverage.* In previous papers (*2, 3*), adsorption of CO at low coverages was used as a probe to follow the interactions of a second adsorbate with the metal surface. It has been postulated that this procedure can lead to a clustering of the CO molecules or to the formation of islands. In addition, the formation of doublets in the spectrum of CO adsorbed on Pt has been observed at 2070 and 2049 cm^{-1} (*15*).

Small amounts of ^{12}CO have been adsorbed at 25°C on the Pt/Al_2O_3 samples in order to reach a coverage of platinum close to 10%. The $\nu^{12}CO$ frequency of the linear form was found at 2072 cm^{-1}. By comparison of the data plotted in Fig. 1, the position of the νCO band suggests a local θ_{CO} coverage of 85%. This unexpected result may be explained in two possible ways:

(i) there is a clustering of the CO layer leading to a more compressed layer than that expected for the θ_{CO} postulated;

(ii) the first platinum particles are almost saturated by CO whereas the other crystallites are practically free of carbon monoxide.

The second explanation supposes a distribution of νCO frequencies since the CO molecules are not identical over all the platinum particles. Since the νCO band at 2072 cm^{-1} is symmetrically shaped we favor the first hypothesis to account for this high frequency, i.e., clustering of the CO molecules on the metal particles. Whatever the right explanation, the CO molecules are dispersed in a heterogeneous manner on the platinum crystallites.

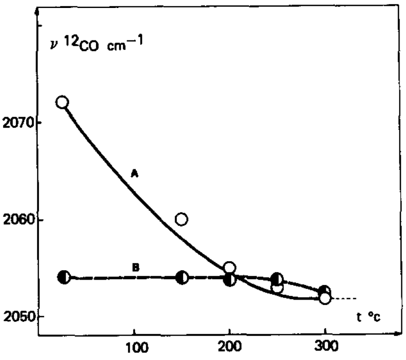


FIG. 3. Change of the $\nu^{12}CO$ frequency of ^{12}CO adsorbed at low coverage on Pt/Al_2O_3. Curve A: adsorption of CO at 25°C (θ_{CO} = 0.1), then evacuation at increasing temperatures. Curve B: adsorption of CO at 25°C (θ_{CO} = 0.1), heating in a closed system for 1 h at 300°C, then evacuation at increasing temperatures.

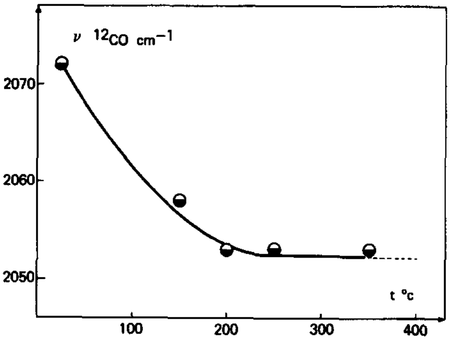


FIG. 4. Adsorption of ^{12}CO on Pt/Al_2O_3 at 25°C (θ_{CO} = 0.1), then heating in a closed system at increasing temperatures.

Treatments of the partly covered CO sample at increasing temperature under vacuum led to a shift of the νCO band toward lower wavenumbers, as shown in Fig. 3A. The change is similar to that of the sample fully covered by CO. The extrapolation of $\nu^{12}CO$ to $\theta_{CO} = 0$ gave a frequency of 2052 cm^{-1}; this value is identical to the values found for desorption experiments and for the adsorption of ^{12}CO–^{13}CO mixtures.

In another experiment, the Pt/Al_2O_3 sample with $\theta_{CO} = 0.1$ was heated in a closed system at increasing temperatures and ir spectra were recorded at 25°C. Figure 4 shows that the νCO frequency decreased when the temperature was increased to 200°C; the νCO frequency then remained constant even after heating at 350°C. As in the previous cases, the frequency limit was equal at 2053 cm^{-1}. No decrease in the νCO absorption intensity could be observed.

In a final experiment, the Pt/Al_2O_3 sample was covered by CO to obtain a theoretical coverage $\theta_{CO} = 0.1$; the catalyst was then heated in a closed system at 300°C for 1 h and cooled to room temperature. After recording its ir spectrum, the sample so obtained was treated under vacuum step by step at higher temperatures and ir spectra were registered after each temperature of desorption. Figure 3B shows the change of the νCO frequency as a function of the temperature of vacuum treatment. In contrast with Fig. 3A, the νCO frequency remained constant at 2054 cm^{-1} throughout the entire temperature range. After desorption at 300°C, a small shift in the νCO band gave the value (2052 cm^{-1}) already observed for the singleton CO.

(*d*) *Discussion.* On our Pt/Al_2O_3 sample at full CO coverage, the νCO frequency is equal to 2080 cm^{-1}, and progressive elimination of adsorbed CO shifts the νCO band to a frequency limit which has been found to be 2052 cm^{-1}. The frequency shift dependent on coverage is then 28 cm^{-1} and might be at the present time interpreted as the sum of two effects, viz., competition of metal *d* electrons for the back-donation and variations in the coupling of the ^{12}CO dipoles.

Following the pioneering work of Hammaker *et al.* (*8*), various theoretical and experimental papers have been published with the aim of measuring the extent of the dipole–dipole coupling on the νCO frequency of carbon monoxide adsorbed on metals. Mahan and Lucas (*16*) found that the dipole interactions provide a frequency shift of about 10 cm^{-1}. Scheffler (*17*), reexamining the theory of dipole–dipole interactions, concluded that the shift of the νCO frequency can be totally explained by a dipole–dipole coupling mechanism. Experimental study of CO adsorption on Pt(111) ribbon led to the conclusion that the full 35-cm^{-1} frequency shift with increasing the CO coverage is attributable to coupling (*9*). More recently, similar conclusions have been obtained in the case of platinum supported on alumina or on silica (*4, 10*).

In the present work, isotopic dilution experiments show that the νCO frequency extrapolated at infinite dilution of ^{12}CO ($\nu CO = 2052$ cm^{-1}) is exactly the frequency limit observed during the thermal desorption of CO. Since the platinum coverage by CO remains constant during the isotopic dilution experiments, the identical nature of the two $\nu^{12}CO$ frequencies observed in the two cases shows that the 28-cm^{-1} shift can be totally explained by the decrease of the dipole–dipole coupling due to the separation of the CO dipoles: the distance between adsorbed ^{12}CO molecules increases either by desorption or by dilution with ^{13}CO molecules. This conclusion is in complete agreement with the recent papers devoted to this subject (*4, 9, 10, 15, 18*) and stresses the importance of dipole–dipole coupling in the spectra of CO adsorbed on metal.

For the Pt/Al_2O_3 samples used in the present study, a νCO frequency close to 2052 cm^{-1} will be typical of adsorbed molecules free of dipole–dipole coupling or isolated CO molecules (singleton).

Adsorption of CO on Pt/Al_2O_3 for a theoretical $\theta_{CO} = 0.1$ produces a νCO frequency (2072 cm^{-1}) which is not in accordance with the frequency deduced from Fig. 1: a $\nu^{12}CO$ band at 2052 cm^{-1} is expected for such a low CO coverage. Similar results have already been observed for CO adsorption–desorption experiments on Pt/SiO_2 (*15*). Heating in a closed system between 200 and 300°C shifts the νCO band to the value predicted from Fig. 1. In addition, desorptions at increasing temperatures do not affect the position of the νCO band; in the absence of the heating in a closed system the CO frequency continuously shifts with the temperature of desorption until the frequency of the singleton (2052 cm^{-1}) is reached.

The high frequency observed (2072 cm^{-1}) is in accordance with a heterogeneous dispersion of the CO molecules over the platinum particles. The formation of CO islands already postulated (*4, 10*) is at the origin of this too high frequency since the CO molecules are more compressed than in the case of $\theta_{CO} = 0.1$. Heating in a closed system results in a redispersion of the CO molecules over the whole metallic phase. The observed νCO frequency (2052 or 2054 cm^{-1}) is the frequency of the CO singleton, i.e., when there is no dipole–dipole coupling between adsorbed CO molecules after the redispersive treatment at 300°C and the CO molecules can be considered as isolated.

2. *Interactions with Other Adsorbates*

Stoop *et al.* (*4*) concluded that the red shift observed during the coadsorption of CO and C_2H_4 on platinum must be attributed mainly to a dilution effect of the CO molecules by the fragments of olefinic species which reduces the dipole–dipole coupling between CO molecules. In their experimental procedure, C_2H_4 was adsorbed at 60°C prior to the adsorption of CO and it is not possible to exclude a partial desorption of adsorbed C_2H_4 when the sample is subsequently contacted with CO.

In the preceding part of this paper, we have shown that room temperature CO adsorption for $\theta_{CO} = 0.1$ followed by heating at 300°C allows a homogeneous redispersion over all the crystallites with a νCO frequency (2052 cm^{-1}) characteristic of isolated CO molecules.

If now the adsorption of a second adsorbate on such samples shifts the νCO frequency toward lower wavenumbers it will not be possible to postulate a separation of the CO dipoles since they are already isolated; in such a case a ligand effect will be at the origin of the νCO shift.

In the following, we shall refer by sample A to a 5% Pt/Al_2O_3 solid reduced by hydrogen and contacted with CO at 25°C, in order to obtain a theoretical θ_{CO} equal to 0.1, and then heated in a closed system for 1 h in order to achieve the redispersion of the CO layer. Sample A exhibits the singleton νCO frequency at 2052 cm^{-1}.

(*a*) *Adsorption of ethylene.* Infrared spectra resulting from the interaction of C_2H_4 with sample A were reported in Fig. 5. Introduction of C_2H_4 at 25°C under 45 Torr pressure causes a shift of the νCO band from 2052 to 2015 cm^{-1}. Evacuation of the gas phase at room temperature hardly affects the position of the νCO band. Introduction of hydrogen at 25°C leads to the formation of gaseous or weakly adsorbed ethane while the νCO band recovers its original frequency (2052 cm^{-1}).

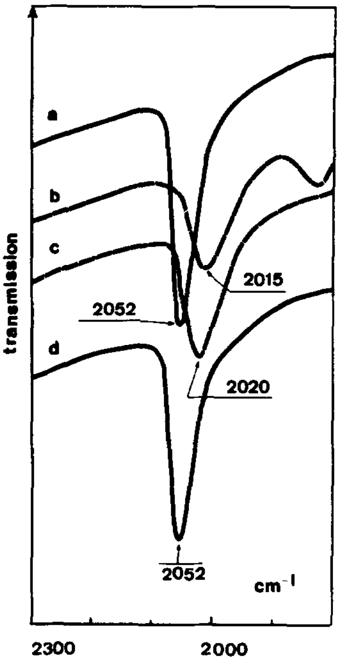


FIG. 5. Adsorption of C_2H_4 on sample A. (a) $\theta_{CO} = 0.1$, heating in a closed system for 1 h at 300°C, then (b) introduction of 45 Torr C_2H_4, (c) evacuation at 25°C, (d) introduction of 200 Torr H_2 at 25°C followed by an evacuation at the same temperature.

(*b*) *Adsorption of ammonia.* Introduction of ammonia (pressure = 20 Torr) on sample A at 25°C (Fig. 6) shifts the νCO band from 2052 to 1985 cm^{-1}. Prolonged evacuation at room temperature gives a νCO band at 1995 cm^{-1}. Evacuation at higher temperature allows the determination of the thermal stability of ammonia adsorbed on platinum. From the spectra shown in Fig. 6, it can be concluded that ammonia is no longer adsorbed on platinum after vacuum treatments between 200 and 300°C since in this temperature range the νCO band has the frequency of the initial sample (sample A).

(*c*) *Adsorption of benzene.* Irreversible adsorption at 25°C of benzene on sample A produces a shift of the νCO band from 2052 to 2010 cm^{-1} (Fig. 7).

Small bands at 3080, 3060, 3040, and 1480 cm^{-1} were also observed and attributed to C_6H_6 mainly adsorbed on the support. Introduction of 200 Torr hydrogen pressure fully restores the νCO frequency and leads to the formation of weakly adsorbed cyclo-

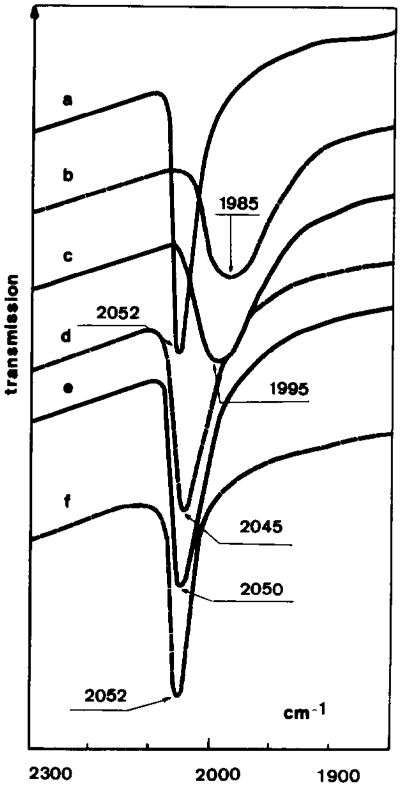


FIG. 6. Adsorption of ammonia on sample A. (a) Sample A, then (b) introduction of NH_3 (10 Torr pressure) followed by a desorption at 25°C for 5 min, (c) evacuation for 2.5 h at 25°C, (d) evacuation for 2 h at 100°C, (e) evacuation for 2 h at 200°C, (f) evacuation for 1 h at 300°C.

hexane detected by absorptions at 2920, 2850, and 1450 cm^{-1}. Evacuation at room temperature removed cyclohexane; at the same time the νCO band shifted to 2008 cm^{-1} whereas the weak bands at 1480 cm^{-1} and between 3100 and 3000 cm^{-1} were observed again. A second introduction of hydrogen at 25°C shifted the νCO band to 2052 cm^{-1} and led to the formation of cyclohexane. The cycle hydrogenation–desorption can be repeated several times; the same picture was observed for the shifts of the νCO band.

(*d*) *Adsorption of Oxygen.* Adsorption of CO at full coverage on Pt/Al_2O_3 gave the νCO bands at 2080 and 1845 cm^{-1}. Introduction of oxygen at the same temperature (Fig. 8) caused the disappearance of the 1845-cm^{-1} band, a decrease of the intensity of the 2080-cm^{-1} band and the formation of bands at 1650, 1450, and 1230 cm^{-1} attributed to hydrogenocarbonate groups resulting from the interaction of CO_2 with the hydroxyl groups of alumina (*19*). By increasing the time of the reaction of oxygen with adsorbed CO, the intensity of the 2080-cm^{-1} band decreased and its position was progressively shifted toward higher wavenumbers, whereas the bands due to HCO_3^- groups grew. The νCO band was progressively shifted from 2080 to 2095 cm^{-1} during the oxidation process. After heating at 50°C, CO adsorbed on platinum gave only a band at 2120 cm^{-1}.

(*e*) *Discussion.* Interaction of electron donor compounds with a partly CO covered platinum surface shifts the νCO frequency

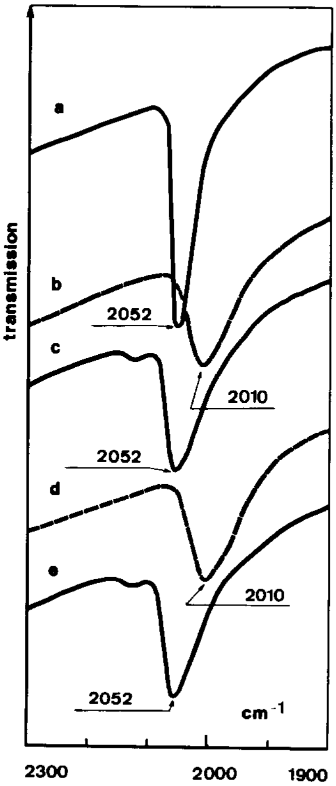


FIG. 7. Adsorption of benzene on sample A. (a) Sample A. (b) C_6H_6 irreversibly adsorbed at 25°C on sample A, then (c) introduction of H_2 at 25°C (200 Torr pressure), (d) evacuation at 25°C, (e) introduction of 200 Torr H_2 at 25°C on the previous sample.

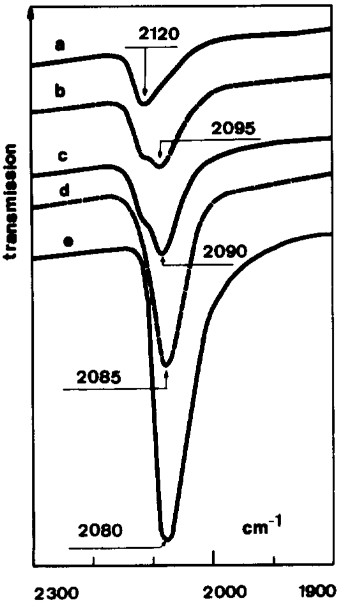


FIG. 8. Interaction O_2–CO with Pt/Al_2O_3. (a) Pt/Al_2O_3 sample fully covered by CO at 25°C, then introduction of 100 Torr O_2 at 25°C, (b) for 10 min, (c) for 1.5 h, (d) for 3 h, (e) heating under O_2 at 50°C for 1 h.

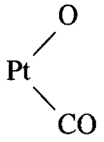
toward lower wavenumbers. The extent of this shift depends on the electron donor molecule, being 32 cm $^{-1}$ for C_2H_4, 42 cm^{-1} for C_6H_6, and 67 cm^{-1} for NH_3. These changes in νCO frequency cannot be explained by a separation of the ^{12}CO dipoles caused by the second adsorbate (*4*) since isotopic dilution experiments have shown that the CO molecules are already isolated after the redispersive treatment. Thus an electron transfer from the second adsorbate toward platinum must be at the origin of the full shift in the νCO frequency.

As far as C_2H_4 and C_6H_6 molecules were concerned, these compounds can be chemisorbed on platinum with the formation of σ- or Π-bonded species. As already discussed in previous papers (*2, 3, 20*), Π-bonded unsaturated hydrocarbons are the only species able to take into account an increase in the electron density of the metal particles. In addition the frequency shift larger for C_6H_6 than for C_2H_4 is in accordance with the values reported for the ionization potentials of the two molecules (10.5 eV for C_2H_4 and 9.24 eV for C_6H_6) (*21*). Thus the electron transfer associated with the formation of a Π-complex is larger for C_6H_6 than for C_2H_4. Both Π-complexes are hydrogenated into saturated hydrocarbons by hydrogen treatment at room temperature while the νCO frequency recovers its initial value. It has been checked that hydrogen adsorption does not change the frequency of CO adsorbed on platinum. Cyclohexane is readily dehydrogenated into benzene at 25°C when hydrogen in excess is eliminated. The aromatic compound is adsorbed again on platinum and the νCO band is shifted at the frequency initially encountered for C_6H_6 adsorbed on Pt. Dehydrogenation of ethane does not occur on platinum at room temperature.

The large frequency shift observed after NH_3 adsorption ($\Delta\nu$ = 67 cm^{-1}) shows that the electron transfer is greater than with the previous hydrocarbons and suggests a strong bond between platinum and ammonia. NH_3 remains adsorbed on Pt until 300°C since at this temperature of evacuation the νCO band possesses the frequency of isolated molecules. The frequency shift is larger than the shift previously observed in Ref. (*2*) (25 cm^{-1}) where CO was chemisorbed in the form of islands. Isolated CO molecules on platinum particles can accommodate more NH_3 molecules than in the case of CO islands. The ratio $NH_{3\,ads}/CO_{ads}$ is then larger in the former case and consequently the number of electrons back-donated to one CO molecule increases, leading to a larger red shift.

Adsorption of oxygen on a fully CO-covered platinum surface produces a shift of the CO band toward higher wavenumbers. At full coverage, i.e., the most compressed CO layer, the νCO frequency is equal to 2080 cm^{-1}. When the oxidation of CO occurs at 25°C, the CO band is progressively shifted to 2095 cm^{-1}. Similar studies performed on Pt(111) ribbon (*22*) or on Pt/SiO_2 (*18*) have shown that islands of adsorbed oxygen atoms form and the oxidation reaction is limited to the boundaries between adsorbed oxygen and CO. In such a case, when the CO oxidation occurs the formation of smaller and smaller CO islands surrounded by oxygen adatoms is expected. Because of the coexistence of CO islands and oxygen islands, the νCO frequency is not too much affected until enough carbon monoxide is oxidized into CO_2. The blue shift observed ($\Delta\nu$ = 15 cm^{-1}) cannot be explained by a compression of the CO layer (*4*) since the starting surface is fully covered by CO. It must be attributed to an electronic effect of adsorbed oxygen atoms surrounding the CO islands, which decreases the electron density of platinum when the oxygen coverage becomes important.

Finally, after oxidation at 50°C, the band at 2120 cm^{-1} has been previously assigned to species like



with an oxygen atom and a CO molecule bonded to the same site (*2*). It can also be attributed to small CO islands completely surrounded by a layer of oxygen atoms.

The argument that oxygen adsorption could not compress CO islands may not be valid for fairly small islands. It would be very interesting to look at the spectra of coadsorbed oxygen and $^{13}CO/^{12}CO$ mixtures. Unfortunately adsorbed oxygen atoms are progressively removed from the surface by $^{12}CO_2$ and $^{13}CO_2$ formation.

CONCLUSIONS

Adsorption of carbon monoxide at low coverages on alumina-supported platinum leads to a heterogeneous distribution of the CO molecules over the metal particles. The formation of CO islands (clustering of CO molecules) seems to be at the origin of this heterogeneity. Heating in a closed system at 300°C allows a redistribution of the CO molecules over all the metal particles. From isotopic dilution results as well as from desorption experiments, it can be concluded that the CO molecules so redistributed are isolated, i.e., there is no dipole–dipole coupling between adsorbed CO molecules.

Chemisorption of electron donor compounds (C_2H_4, C_6H_6, NH_3) was performed on the redispersed CO layer. In every case a decrease of the νCO frequency was observed; this ir shift is suppressed by hydrogenation or vacuum treatments. The shift of the νCO frequency cannot be explained by a decrease of the dipole–dipole coupling. Chemisorption on platinum of electron donor compounds produces an electron transfer toward platinum which increases the extent of the backdonation Pt–CO. On the contrary, the adsorption of electron acceptor compounds shifts the νCO frequency toward higher wavenumbers because of an electron transfer from the metal to the adsorbate.

The results obtained in the present work show that the bonding of an adsorbate with a metal is dependent on the presence of other species adsorbed on the surface. Ligand effects are then observed on metal surfaces as for organometallic compounds.

ACKNOWLEDGMENT

The author expresses his gratitude to Mr. T. Decamp for his help in infrared measurements.

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