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RESEARCH NOTE

Comparison of the Coverage of the Linear CO Species on Pt/Al_2O_3 Measured under Adsorption Equilibrium Conditions by Using FTIR and Mass Spectroscopy

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There is controversy in the literature about the relationship between the IR band area (denoted by A) of the adsorbed CO species (i.e., linear (denoted by L) and bridged (denoted by B) CO species) on noble-metal-containing solids (supported metal catalysts and single crystals) and the coverage (denoted by θ) of the surface by CO. Usually, a straight line is observed at low coverages ($\theta < 0.5$) but various profiles are observed at high coverages. This constitutes a limitation on performing quantitative analysis using FTIR spectroscopy. Several explanations for the various profiles for the curves $A = f(\theta)$ (i.e., dipole–dipole coupling, nonadsorption equilibrium) have been suggested. In the present study we show that this also may be due to the fact that the coverage values involve the amounts of several adsorbed CO species. The coverages (denoted by θ_L) of the L species adsorbed on a 2.9% Pt/Al_2O_3 catalyst are determined at several adsorption temperatures (adsorption equilibrium, T_a range 300–740 K, $P_a \approx 10^3$ Pa) by using two analytical methods: FTIR and mass spectroscopy. It is shown that at high adsorption temperatures ($T_a > 550$ K) the two analytical methods give the same coverage values in the range $\theta = 1$–0.6. This leads to the conclusion (a) that there is a proportionality between the IR band area of the L species and its amount on the Pt surface and (b) that quantitative studies involving the L species can be performed by using FTIR spectroscopy (i.e., determination of the heats of adsorption of the L species at several coverages). © 2000 Academic Press

I. INTRODUCTION

The adsorption of CO at 300 K on supported platinum catalysts exhibits a strong IR band at 2070 ± 10 cm^{-1} associated with a weak and broad IR band at ≈1850 ± 10 cm^{-1} (1–3) ascribed to the linear (denoted by L) and bridged (denoted by B) CO species, respectively. We have recently reported (4) that the change in the IR band of the L species can be studied during CO adsorption (1%CO/He, 1 atm total pressure, flow rate 200 cm^3/min) at several temperatures T_a, in the range 300–800 K. These FTIR spectra were used to determine the change in the coverage θ_L of the L species with T_a, at the fixed adsorption pressure $P_a = 10^3$ Pa. The curve $\theta_L = f(T_a)$ provided the heats of adsorption of the linear CO species at various coverages using an adsorption model that assumed (a) immobile adsorbed CO species and (b) a linear decrease in the heat of adsorption with the increase in the coverage (4). In another study (5), using several CO partial pressures, we have shown that the heats of adsorption of the linear CO species, measured by the above procedure, were in good agreement with the isosteric heats of adsorption. This was considered proof that the various assumptions included in the adsorption model were justified. However, to obtain these curves $\theta_L = f(T_a)$ at a given adsorption pressure P_a, it was assumed that the IR band area of the L species (denoted by A_L) was proportional to its amount on the surface and that this proportionality was not modified by a change in the adsorption temperature. However, there is controversy in the literature concerning these assumptions for the IR bands of the adsorbed CO species on noble-metal-containing solids (denoted by NM-CS or Pt-CS).

For instance, on a Pd/SiO_2 solid, Hicks *et al.* (6) observed that the IR band area (denoted by A) of the adsorbed CO species varied linearly with the amount of CO adsorbed at the surface in the CO/Pd_s ratio range 0–1.1. Cavanagh and Yates observed a similar result for the gem dicarbonyl CO species formed on Rh/Al_2O_3 catalysts (7). Rasband and Hecker (8) showed that the IR absorption coefficients for both L and B species were not significantly modified by the dispersion (100 to 22%) and the adsorption temperature (range 323–473 K) on supported Rh/SiO_2 solids. Srinivas and Chuang (9) determined (with an experimental uncertainty of 20%) the IR absorption coefficient for

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the L and B species formed on Rh/SiO_2; these values were further used for the determination of the coverage of each adsorbed species during the hydroformylation of propylene. However, several studies on various NM-CS indicate that the curves $A = f(\theta)$ (for the L or B species) are only linear for a limited range of coverages (mainly $\theta < \approx 0.6$), while higher θ values lead to various distinct profiles. For instance, Winslow and Bell (10) on a Ru/SiO_2 solid observed that the curve $A_L = f(\theta)$ increased linearly for $\theta < \approx 0.5$ and that at $\theta > 0.5$ the curve increased more slowly. These observations were similar to those reported by other authors on Pt/SiO_2, Ru(001), Pt(111), and Pt(100) (10, and references therein). Kuhn *et al.* (11) observed similar results on Pd/Ta(110) for the IR band of the L species. On Ru(001), Pfnur *et al.* (12) observed that $A_L = f(\theta)$ increased linearly for $\theta < 1/3$ and then decreased. He *et al.* (13) observed a similar results on Ru(0001) using HRELS spectroscopy. On Pt(111), Shigeishi and King (14) observed that the curve $A_L = f(\theta)$ increases linearly for $\theta < \theta_c$ ($\theta_c \approx 1/3$) and then remained constant. Ortega *et al.* (15) observed a similar result for the B species on Pd(100) but here the linear relationship ceased at $\theta_c \approx 0.5$. These authors (15) showed that θ_c increased slightly with decreasing adsorption temperature ($T_a < 300$ K). Moreover, Shigeishi and King (14) also observed that the curves $A_L = f(\theta)$ were not identical when the measurements were performed during either an adsorption (increasing coverage) or a desorption (decreasing coverage) procedure. This clearly showed that several parameters must be considered in interpreting the curves, such as (14) the presence of other adsorbed CO species, the dipole–dipole coupling, the absence of equilibrium adsorption, and the island formation (in particular, for $T_a < 300$ K). The involvement of defects or steps is also to be considered (16). Dipole–dipole coupling is a factor in the explanation of the shift to the higher wavenumbers of the IR bands of the adsorbed CO species on NM-CS with an increase in coverage (14, 11). However, Ortega *et al.* (15) showed that other effects (i.e., chemical) must also be taken into account in explaining certain results, in particular, with labeled CO.

It must be noted that in the studies referenced above, θ refers mainly to the total amount of CO adsorbed and rarely to the coverage of the specific adsorbed species characterized by the A values. The involvement of a second adsorbed species in the high coverage values may explain the deviation from a straight line for the curves $A = f(\theta)$. The values of θ are obtained either by volumetric measurements (supported metal catalysts) or by a TPD procedure (single crystals). Usually, it is assumed that the total amount of adsorbed CO quantifies the specific adsorbed species because a strong IR band (i.e., ≈ 2070 cm^{-1} for the L species on Pt-CS) associated with very weak IR bands ascribed to minor adsorbed species (i.e., ≈ 1850 cm^{-1} for the multibound CO species of Pt-CS) is often observed by IR spectroscopy. However, on supported Pt catalysts, Vannice and Twu (17) determined the extinction coefficients ε_L and ε_B of L and B species, respectively, using a procedure (volumetric method) involving both hydrogen and CO chemisorption. Assuming reasonable H/Pt_s and CO/Pt_s ratios, they determined that $\varepsilon_L/\varepsilon_B = 13$. This means that the B species can be present on the surface in significant amounts, even with a weak IR band. This also leads to the conclusion that on Pt-CS the possibility that the curves $A_L = f(\theta)$ found in the literature data are obtained with θ values involving both L and B species cannot be ruled out. On single crystals the amounts of adsorbed CO species are mainly determined using a TPD procedure. This method makes it possible to quantify the adsorbed species with respect to their activation energies of desorption (usually equal to the heat of adsorption for the CO/noble metal system). At first sight, this analytical method seems well adapted for determination of the amounts of specific adsorbed species (i.e., L and B species) by measuring the amount of CO desorbed in each TPD peak. However, the situation is more complex, in particular, for Pt-CS. For instance, after adsorption of CO at $T_a < 300$ K on Pt-CS (mono crystals, film, supported Pt catalysts) numerous studies (18–21, 22 and references therein) indicate two TPD peaks at $T_{M1} \approx 400$ K and $T_{M2} \approx 500$ K. At low total coverages, only the T_{M2} peak is observed while the T_{M1} peak appears and increases at high total coverage. Several studies show that the heat of adsorption of the L species is higher than that of the B species (22, 23–25). Usually, the high and low TPD peaks are not assigned to L and B species but to adsorbed species on steps and terraces (26, 27). Using IRAS spectroscopy, Xu and Yates (27, 28) have shown on Pt(335) that four adsorbed CO species were formed according to the coverage values: two L species and two B species adsorbed on steps and terraces. The TPD spectra only indicated the T_{M2} peak at low coverage ($\theta < 0.29$) while the T_{M1} peak appeared and increased at high coverages (27). These authors concluded that the T_{M2} peak involved L and B species on steps while the T_{M1} peak corresponded to L and B species on terraces, according to the following order of stability (and order of appearance on the surface): L on step > B on step > L on terrace > B on terrace. Moreover, they showed (26) that the adsorption of CO on Pt(112) led to the same TPD results but that the two linear CO species were not resolved by IRAS spectroscopy, while the intensities of the IR bands of the B species were very weak. These results show that a TPD procedure is not an unambiguous method of determining the amounts of L and B on a Pt surface. Finally, on Pt-CS it can be considered that the curve $A_L = f(\theta)$ links a parameter characteristic of the L species (A_L) to a second parameter, θ, which involves both L and B species. This situation (also likely on other NM-CS) may explain some particular profiles of the curves $A = f(\theta)$.

In agreement with certain data in the literature (22 and references therein), we have shown that the heats of adsorption of the L species on Pt sites are significantly higher, whatever the coverages, than those of multibonded species (B and 3-fold-coordinated CO species denoted by 3FC). This means that, at low coverages of the surface, only the L species is adsorbed while L, B, and 3FC species contribute θ values at high coverages. The consequence is that the experimental curve $A_L = f(\theta)$ is a straight line at low coverage ($\theta = \theta_L$) until the value θ_c, at which the slope then decreases progressively due to the appearance of the B/3FC species on the Pt surface. The $A_L = f(\theta)$ profile is determined by the heats of adsorption of the various adsorbed species and their respective amounts on the surface. For instance, if the two adsorbed species are present on the surface with strongly different heats of adsorption, a plateau can be obtained after θ_c. Note that the decrease in the A values at high coverage as observed on Ru monocrystals (12, 13) cannot be explained by the presence of several adsorbed species with different heats of adsorption. To evaluate the possibility of performing quantitative studies using the IR band of the L species on the Pt solid, it is necessary to correlate A_L to θ_L (coverage of the L species) by determining the amount of the L species on the surface. This is the objective of the present paper, considering the L species formed on a 2.9% Pt/Al_2O_3 catalyst.

We have observed (4, 5, 22) that the adsorption of CO (1% CO/He mixture) at 300 K leads to a strong IR band at 2070 cm^{-1} and a weak one at 1850 cm^{-1} ascribed to L and B/3FC species, respectively. The increase in T_a leads to a progressive decrease in the IR band intensity of the B species which disappears at $T_a > \approx 550$ K (at 550 K the IR band area is decreased by 90% from its values at 300 K (22)). This means that the volumetric measurements of the adsorption of CO on the 2.9% Pt/Al_2O_3 at $T_a > \approx 550$ K concern only the L species. This permits us to compare the coverage of the L species at $T_a > 550$ K obtained using FTIR spectroscopy (assuming a proportionality between the IR band area and the amount of L species on the surface) to the coverage obtained via a volumetric method with a mass spectrometer as the detector. An agreement between the two curves must be considered as proof (a) that there is a proportionality between the intensity of the IR bands of the L species and the amount of the L species on the surface and (b) that quantitative FTIR studies involving the IR band of the L species can be reasonably performed.

II. EXPERIMENTAL

The 2.9% Pt/Al_2O_3 solid was prepared by the incipient wetness method using an aqueous solution of H_2PtCl_6 according to a procedure described previously (4). The amounts of adsorbed CO on the reduced solid at various adsorption temperatures were obtained with an analytical system used for transient experiments described previously (29) using a mass spectrometer as the detector. Mainly, various valves allowed us to perform switches between regulated gas flows (1 atm total pressure), which passed through a catalyst (powder) contained in a quartz microreactor. A quadrupole mass spectrometer permitted the determination of the composition (molar fraction) of the gas mixture at the outlet of the reactor during a switch, after a calibration procedure. Before each adsorption, the catalyst was pretreated according to the following procedure: He(713 K, 10 min) → O_2(713 K, 10 min) → He(713 K, 10 min) → H_2(713 K, 20 min) → He(713 K, 5 min) → He(adsorption temperature, T_a). However, the first pretreatment of the fresh catalyst was slightly different: He(300 K) → He(473 K) → He(473 K, 60 min) → H_2(473 K) → H_2(713 K) → H_2(713 K, 20 min) → He(713 K, 5 min) → He(300 K) → adsorption of CO. A 2%CO/3%Ar/He mixture was used for the CO adsorption. The FTIR results have been described in detail previously (4, 5). Mass and FTIR spectroscopy studies were performed on separated analytical systems.

III. RESULTS AND DISCUSSION

Figure 1 shows the composition of the gas mixture at the outlet of the reactor during the switch He → 2%CO/3%Ar/He, performed at $T_a = 300$ K with the fresh solid. Curve a shows the evolution of Ar, which is not adsorbed (mixing curve for Ar). This curve indicates the beginning of the CO adsorption. Curve b, which corresponds to the absence of CO adsorption (mixing curve for CO), is obtained from curve a (curve b = $2/3^*$ curve a). Curve c indicates the molar fraction of CO at the outlet of the reactor as a function of the duration of the adsorption. The total CO uptake $QA_{CO}(T_a) = 125$ μmol/g is determined (for given gas molar flow rate F and weight of catalyst W)

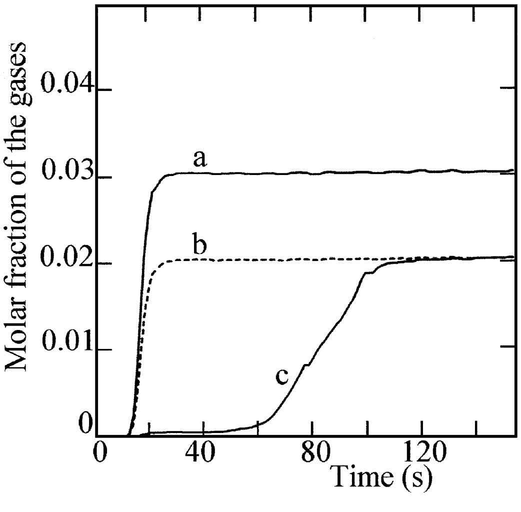

FIG. 1. Composition of the gas mixtures during the adsorption of 2% CO/3% Ar/He on the Pt/Al_2O_3 solid at 300 K: (a) Ar; (b) CO without adsorption; (c) CO during adsorption.

by

$$\int_0^{t_a} (\text{curve.b} - \text{curve.c}) \cdot \frac{F}{W}\, dt,$$

where t_a is the duration of the adsorption. This amount corresponds to irreversibly adsorbed CO species because, after the experiment in Fig. 1, the desorption in He at 300 K for 1 min followed by the readsorption of CO leads to an experimental CO curve that overlaps the mixing curve for CO (curve b in Fig. 1). The rapid adsorption of CO (no slow step) is in agreement with the previous FTIR observations, which indicated that the intensities of the IR bands of the linear and bridged CO species were constant after $\approx$30 s on stream with a 1% CO/He mixture (4, 5). The amount of CO adsorbed at 300 K leads to a Pt dispersion of 85%, assuming the ratio CO/Pt$\,=\,$1. A progressive decrease in the total CO uptake at 300 K is observed after the first two adsorption/pretreatment cycles due to aging of the solid. For instance, after the first cycle, the amount of CO adsorbed is 95 μmol/g. The next cycle leads to 81 μmol/g. The adsorption of CO at 713 K followed by pretreatment leads to a CO uptake at 300 K of 72 μmol/g. Two following adsorption at T_a/pretreatment cycles do not lead to a significant difference in the amount of CO adsorbed at 300 K ("stabilized" solid). However, the decrease in the CO uptake at 300 K slowly continues, leading to 63 μmol/g after 10 adsorption/pretreatment cycles. Experiments similar to that shown in Fig. 1 were performed at several adsorption temperatures T_a on a stabilized solid. For $T_a < 573$ K, the results were similar to those observed at 300 K but the CO uptake changed (see below). For $T_a > 573$ K, CO$_2$ and H$_2$ were detected during CO adsorption as shown in Fig. 2 for $T_a = 713$ K. H$_2$ production (curve d) comes from the hydroxyl groups of the alumina support. At high temperatures, it is known that CO can form formate groups ($CO + OH_{ads} \rightarrow HCOO_{ads}$) on the metallic oxides (8 and references therein). The formate species is not stable and decomposes either by the reverse reaction or through the production of $CO_2 + \frac{1}{2}H_2$. This reaction contributes to CO$_2$ production in Fig. 2 (curve e). Moreover, CO$_2$ production can also be linked to the disproportionation of CO: $2CO \rightarrow C_{ads} + CO_2$.

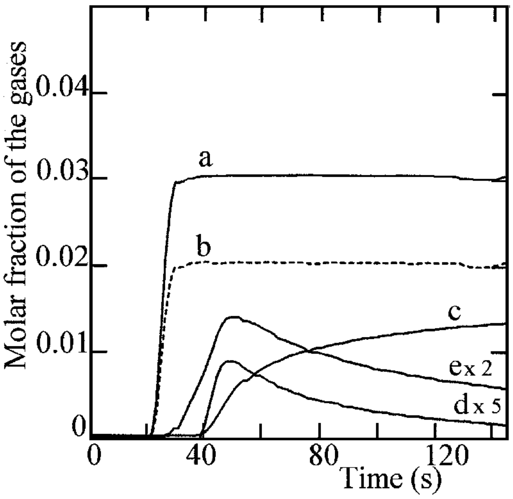

FIG. 2. Composition of the gas mixtures during adsorption of 2% CO/3% Ar/He on the Pt/Al$_2$O$_3$ solid at 713 K: (a) Ar; (b) CO without adsorption; (c) CO in the course of the adsorption; (d) H$_2$ formation; (e) CO$_2$ formation.

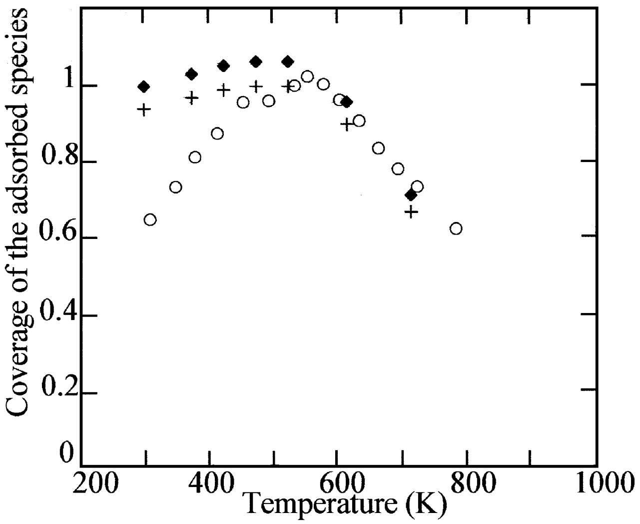

FIG. 3. Coverage on the adsorbed CO species on the Pt/Al$_2$O$_3$ solid: ◆, (a) from the total CO uptake; ○, (b) from the intensity of the IR band of the linear CO species; +, (c) curve a after correction (see the text).

The amount of CO adsorbed at 713 K, QA_{CO}(713 K), is obtained using a carbon mass balance. The total amount of CO that has disappeared after a given time of adsorption, t_a (due to the CO adsorption and the two reactions cited above), is determined as in Fig. 1: $QT_{CO} =$ 132 μmol/g. The amounts of H$_2$ and CO$_2$ formed during t_a are determined by integrating curves d and e in Fig. 2: $Q_{H_2} =$ 8 μmol/g and $Q_{CO_2} = 50$ μmol/g, respectively. The amount of CO$_2$ linked to the decomposition of the formate species is given by $QF_{CO_2} = 2^* Q_{H_2}$ and the amount of CO$_2$ linked to the disproportionation reaction is given by $QD_{CO_2} = Q_{CO_2} - QF_{CO_2}$. The quantity of CO adsorbed at 713 K is given by $QA_{CO}(713\text{ K}) = QT_{CO} - QF_{CO_2} - 2^* QD_{CO_2} = QT_{CO} - 2(Q_{CO_2} - Q_{H_2}) = 48$ μmol/g. Note that in the present procedure we have not taken into account the adsorption of CO and/or CO$_2$ on the alumina support because the FTIR spectra have shown that IR bands for carbonate and/or formate species on the support were very weak for times of adsorption lower than 2 min. The above procedure was applied for $T_a > 573$ K. The coverage $\theta(T_a)$ of the adsorbed CO species at various temperatures T_a was obtained by the ratio $\theta(T_a) = QA_{CO}(T_a)/QA_{CO}(300\text{ K})$. To take into account the slow aging of the catalyst, each adsorption temperature T_a was preceded by the determination of QA_{CO}(300 K) followed by a pretreatment of the solid. Curve a in Fig. 3 gives the experimental curve $\theta(T_a)$ according to that procedure. Note that the coverage increases from 1 to 1.1 between 300 and ≈420 K, then stays constant until ≈520 K, and finally decreases progressively. This profile can be compared to that (curve b, Fig. 3), previously obtained from the changes of the IR band area of the linear CO species with T_a (4, 5). We have suggested that the increasing section of curve b, between 300 and 473 K, was due to a restructuring of the CO/Pt surface during adsorption. We have also shown (4, 5) that the IR band area remains constant during cool down of the solid in CO/He after adsorption at $T_a = 450$ K (irreversible modifications of the CO/Pt surface system). The coverages in curve b were obtained using $\theta = A(T_a)/A(550\text{ K})$. To compare the values of the coverage obtained from the two experimental procedures (FTIR and mass spectrometry studies), we applied a multiplying factor to curve a in Fig. 3 to obtain $\theta(550\text{ K}) = 1$. This led to curve c, which can be compared to curve b taking into account previous results. We indicated above that the increase in T_a from 300 to 550 K led to the increase in the IR band of the linear CO species while that of multibonded CO species (B and 3FC) decreased (4, 5, 22) and was not detected for $T_a > \approx 550$ K (22). However, the cooling of the sample in CO/He from $T_a > 550$ to 300 K led to the detection of the IR bands of the multibonded CO species, indicating that their decrease during the heating stage was due to their low heats of adsorption (22) and not to the poisoning of the surface (i.e., carbon deposition). Comparison of curves b and c in Fig. 3 shows good agreement between the two experimental procedures for $T_a > \approx 500$ K, because measurements by the two analytical methods concern only the L species and the curves correspond to $A_L = f(\theta_L)$. This agreement indicates that the assumption used in (4, 5) is verified: A_L is proportional to the amount of L species on the surface in the present coverage range. We indicated in the Introduction that several factors have been proposed to explain that the curves $A = f(\theta)$ were linear only for $\theta < 0.5$. In particular, Shigeishi and King (14) considered the nonequilibrium adsorption and island formation at low adsorption temperatures. The present procedure using adsorption equilibrium conditions at $T_a > 550$ K discards the eventual influence of theses effects. The dipole–dipole coupling involved in the shift of the IR band of the L species to lower wavenumbers with a decrease in the coverage is also suggested to explain the profile of the curves $A = f(\theta)$ at high coverages. On the present Pt/Al_2O_3 solid, this shift has been observed (4, 5) for the IR band of the L species for $T_a > 550$. However, the good agreement between curves c and b in Fig. 3 leads to the conclusion that if dipole–dipole coupling decreases the A values at high coverages, its effect is lower than the accuracy of the two analytical methods used in the present study. We have shown (4, 5) that the profiles of curves b and c in Fig. 3 for $T_a > 500$ K are in agreement with the adsorption model, considering that the L species is immobile while its heat of adsorption decreased linearly with the increase in the coverage from $E_0 = 206$ kJ/mol at $\theta = 0$ to $E_1 = 115$ kJ/mol at $\theta = 1$, in agreement with certain data in the literature (4, 5). Indeed, this agreement cannot be obtained with a curve $A_L = f(\theta_L)$, significantly different from a straight line.

Now, for $T_a < 450$ K, curves b and c in Fig. 2 show that there is a significant difference between the evolution of the coverage determined by the two analytical methods. This is probably due to the contribution of the bridged CO species to the data obtained with the mass spectrometer. Curve b only involves the IR band of the linear CO species and the increasing section for $T_a < \approx 500$ K is attributed to a restructuring of the CO/Pt surface system (4, 5). Curve c in Fig. 3 involves the total CO uptake (multibonded and linear CO species). It can be considered that the total CO uptake does not vary strongly from 300 to 450 K in curve c, because the increase in the amount of linear CO on the surface (restructuring of the CO/Pt surface system) is probably compensated by the decrease in the quantity of the multibonded CO species (low heat of adsorption). This explanation infers that the IR absorption extinction coefficient of the bridged CO species is significantly lower than that of the linear CO species. This is also in agreement with the study of Vannice and Twu (17), who have determined a ratio $\varepsilon_L/\varepsilon_B$ of 13.

IV. CONCLUSION

The good agreement between the coverage values of the linear CO species adsorbed on Pt/Al_2O_3 species, obtained at $T_a > 550$ K either by FTIR spectroscopy or by mass spectrometry (volumetric method), (a) validates the assumption made previously (4, 5) to exploit quantitatively the FTIR spectra (the IR absorption extinction coefficient of the L species was assumed constant both with the coverage and with the adsorption temperature) and (b) shows that the mass spectrometry procedure constitutes an alternative method for determination of the coverage of the adsorbed CO species at various adsorption temperatures. However, the procedure using the FTIR spectra is simpler because the measurements are performed using a single pretreatment/CO adsorption cycle while the mass spectrometer necessitates several cycles. Moreover, we have shown that an accurate analysis of the data obtained with the mass spectrometer necessitates that one use FTIR spectroscopy to prove that a single adsorbed species is present on the Pt surface during the volumetric measurements.

Finally, it seems that the assumption that the area of the IR band of an adsorbed CO species on NM-CS is proportional to its amount on the surface is reasonable, at least under adsorption equilibrium conditions. We have shown that previous experimental curves $A = f(\theta)$, significantly different from a straight line, must be at least partially reconsidered, taking into account the presence of several CO species with different heats of adsorption in addition to other explanations (14).

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