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Heat of Adsorption of Carbon Monoxide on Various Pd-Containing Solids Using *in Situ* Infrared Spectroscopy at High Temperatures

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The FTIR spectra of the adsorbed CO species (linear and bridged species) formed on five Pd-supported solids are recorded at various adsorption temperatures, T_a, in the range 300–800 K. These spectra are used to determine for each solid the individual coverage θ of the two adsorbed CO species as a function of T_a. The curves $\theta = f(T_a)$ observed on four solids are in good agreement with an adsorption model assuming a linear decrease in the heat of adsorption with an increase in coverage. This permits the determination of the heat of adsorption of each species at various coverages. The results observed on the various solids allow us to correlate the variation of the heats of adsorption with some parameters involved in the preparation of the solids, such as (a) the composition of the support and (b) the nature of the salt used as a precursor of the metallic phase (with and without chlorine). It is shown that the heat of adsorption of the linear CO species (varying from 54 kJ/mol at $\theta = 1$ to 92 kJ/mol at $\theta = 0$) is independent of the parameters studied. The heat of adsorption of the bridged CO species is significantly modified by the nature of the salt precursor of the metallic phase. The presence of chlorine leads to a clear decrease in the heat of adsorption at high coverages ($\theta > 0.5$) compared with the solids without chlorine, but at low coverages this difference disappears (i.e., on two 1.4% Pd/20% CeO_2/Al_2O_3 solids, the heat of adsorption of the bridged CO species varies from $\approx$100 kJ/mol at $\theta = 1$ to $\approx$170 kJ/mol at $\theta = 0$ on the Cl-free solid and from 80 kJ/mol to 170 kJ/mol on the Cl-containing solid). © 2000 Academic Press

Key Words: **carbon monoxide; palladium catalysts; preparation methods; FTIR; heat of adsorption; adsorption model.**

I. INTRODUCTION

The characterization of the adsorbed species formed on noble metals during a catalytic reaction, in particular those involving CO (i.e., CO/H_2, CO/O_2, CO/NO), is the objective of numerous studies in catalysis. The adsorption of CO on the metal, which constitutes the initial step of these reactions, has been widely studied by various analytical methods adapted to the physical nature of the metal-containing solid (monocrystals, model particles, and supported metal catalysts). Among the parameters which can be determined to characterize the adsorption of CO, some appear to be fundamental, such as (a) the number of adsorbed CO species formed, (b) their chemical structures (linear, bridged/multibound), and (c) their heats of adsorption as a function of the coverage. FTIR spectroscopy has been proven to be a powerful tool to obtain experimental data on the above characterizations on supported metal solids as well as on monocrystals. For instance, in the case of palladium monocrystals, infrared reflection–absorption spectroscopy (IRAS) has shown that bridged CO species are mainly formed, associated with a lower concentration of the linear CO species (1, 2 and references therein) while on model Pd particles deposited on a monocrystal of Ta(110) only the linear CO species is detected (3). FTIR spectroscopy (transmission mode) has been extensively used to characterize the adsorbed CO species formed on Pd-supported catalysts (4–11 and references therein): Al_2O_3 (4, 5), SiO_2 (6–8), TiO_2 (9), MgO (10), and La_2O_3 (11). These studies have shown that whatever the support, the linear CO species as well as the bridged CO species are formed on the dispersed palladium particles. The IRAS method allowed us to record the IR spectra at high temperatures (1000 K in (2)), and in the presence of the gas-phase CO, the isosteric heat of adsorption has been determined using the change of the intensities of the IR bands according to T_a and P_a, the adsorption temperature and pressure respectively (2, 3). The adsorption temperatures used with monocrystals such as 1000 K were rarely reproduced with supported metal catalysts during an FTIR analysis. In previous works (12, 13), we showed that an experimental procedure can be developed to record the FTIR spectra (transmission mode) of the adsorbed CO species on supported metal catalysts in the presence of the gas-phase CO (CO/He mixture, 1 atm total pressure) and at temperatures in the range 300–900 K. This allows us (a) to follow, at a constant partial pressure of CO, the change of the intensities of the IR bands of the adsorbed CO species on supported metal solids up to $T_a = 840$ K, (b) to determine the coverage of

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each adsorbed CO species with T_a, and (c) to determine the evolution of the heats of adsorption of each adsorbed species with the decrease in coverage. The heats of adsorption determined, on Pt-containing solids (12) and on a 1.4% Pd/Al_2O_3 solid (13), were in good agreement with the literature data on monocrystals as well as on supported metal catalysts (measured by microcalorimetry).

In the present study the procedure is used to determine how the heats of adsorption of the linear and the bridged CO species formed on Pd-supported solids evolve due to the modification of some parameters involved in the solid preparation, such as (a) the nature of the support (Al_2O_3, CeO_2/Al_2O_3, and La_2O_3/CeO_2/Al_2O_3) and (b) the salt precursor of the metal particles (with and without chlorine). The supports are similar to those mainly used for the preparation of three-way exhaust gas catalysts.

II. EXPERIMENTAL

(a) Catalysts

Several Pd-containing solids have been prepared by impregnation of various supports.

Alumina support. A 1.4% Pd (Cl-f)/Al_2O_3 solid (in wt%, Cl-f = chlorine-free solid) was prepared according to the following procedure: γ-alumina from Condea was slowly introduced in an aqueous solution of $Pd(NH_3)_4(NO_3)_2$ (the final solution/alumina weight ratio is around 5). After 24 h of agitation at room temperature, the suspension was slowly heated to evaporate the solvent. The powder was then treated in air for 4 h at 393 K followed by 2 h at 773 K. A 1.4% Pd(Cl)/Al_2O_3 solid (Cl = chlorine-containing solid) was prepared according to the following procedure: γ-alumina from Degussa was impregnated by the incipient wetness method by using an H_2PdCl_4 solution. This solution was obtained according to Refs. (14 and 15) by dissolving $PdCl_2$ in concentrated HCl, evaporating to near dryness, and diluting with distilled water before a new evaporating step. This cycle was repeated twice before the impregnation of the support. After drying for 12 h at room temperature and 24 h at 373 K, the solid was treated for 3 h in air at 773 K (heating rate 2 K/min).

CeO_2/Al_2O_3 support. A 1.4% Pd(Cl-f)/20% CeO_2/Al_2O_3 solid was prepared as follows: alumina (γ-Al_2O_3, from Condea) was impregnated with an aqueous solution of cerium acetate (solution/alumina weight ratio $\approx$ 5). The solvent was slowly evaporated and the powder was dried for 12 h at room temperature and then for 4 h at 393 K before a treatment in air for 2 h at 773 K. After this treatment, the powder was impregnated using an aqueous solution of $Pd(NO_3)_2$ according to the above procedure using $Pd(NH_3)_4(NO_3)_2$. After drying for 12 h at room temperature and then for 24 h at 373 K, the solid was treated at 773 K in air for 2 h. A 1.4% Pd(Cl)/20% CeO_2/Al_2O_3 solid was prepared using alumina (γ-Al_2O_3, from Degussa) which was impregnated with an aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich) by the incipient wetness method. After drying for 12 h at room temperature and then for 24 h at 373 K, the solid was treated at 773 K in air for 2 h (heating rate 5 K/min). The noble metal was impregnated (incipient wetness method) on the 20% CeO_2/Al_2O_3 powder with an aqueous solution of H_2PdCl_4. After drying for 12 h at room temperature and then for 24 h at 373 K the solid was treated at 773 K in air for 3 h.

CeO_2/La_2O_3/Al_2O_3 support. A CeO_2/Al_2O_3 solid was prepared using a cerium acetate solution and the γ-alumina from Condea. After the final treatment in air at 773 K for 2 h, the powder was impregnated with an aqueous solution of lanthanum acetate. After drying, the solid was treated in air for 2 h at 773 K. The powder was then impregnated with an aqueous solution of H_2PdCl_4. After drying, the solid was treated for 2 h at 773 K in air. The composition of the solid was 1.96% Pd/16% La_2O_3/56% CeO_2/Al_2O_3.

For the FTIR studies of the adsorbed species, the powders were compressed to form a disk ($\Phi = 1.8$ cm, weight 40–90 mg) which was placed in the sample holder of the IR cell briefly described below. Before the adsorption of CO (using a 1% CO/He mixture), the solids were treated *in situ* (1 atm total pressure, 150 cm^3/min) according to the following procedure: oxygen ($T = 713$ K, $t = 30$ min) → helium ($T = 713$ K, $t = 30$ min) → hydrogen ($T = 713$ K, $t = 1$ h) → hydrogen (adsorption temperature) → helium (10 min) → 1% CO/He.

(b) High-Temperature IR Cell

The FTIR spectra of the CO species adsorbed on the prepared solids, in the presence of the CO/He mixture, were recorded with a Nicolet Protégé FTIR spectrometer by using a small internal volume stainless steel IR cell described elsewhere (12). The disks of solids were placed between two CaF_2 windows 2.2 mm apart. This small volume increases the ratio between the incoming signal due to the adsorbed species and the signal due to the gas-phase species. This cell allows *in situ* treatments at atmospheric pressure, with a gas flow rate in the range 150–2000 cm^3/min, and temperatures in the range 300–900 K.

(c) Catalyst Characterization

The palladium dispersion was determined using the amount of CO adsorbed (μmol/g of catalyst) at 300 K on the reduced solids. This amount was measured with a quadrupole mass spectrometer according to a procedure previously described (12). In particular, the analytical system permitted the determination of the modification of the composition of a gas mixture at the outlet of a quartz microreactor during a switch between two controlled flows of gas at 1 atm total pressure (i.e., He → x% CO/y% Ar/He).

For the determination of the dispersion we assumed a CO/Pd_s ratio equal to 1 as considered by Rieck and Bell (16) and Chou and Vannice (17). The dispersion values (see below) were similar to those found in the literature on Pd-containing solids with similar metal loading and reduction temperatures. For instance, on the 1.4% Pd(Cl-f)/Al_2O_3 solid the amount of chemisorbed CO was 32 μmol/g of catalyst, leading to a dispersion of 24%. This value is in agreement with those measured in (17) on 1.8% and 2.3% Pd/Al_2O_3 after reduction at 673 K, 27% and 30% respectively, and with 27% measured on 1.9% Pd/Al_2O_3 (18). The Pd dispersion values on the other solids are 27%, 27%, 25%, and 19% for Pd(Cl)/Al_2O_3, Pd(Cl-f)/CeO_2/Al_2O_3, Pd(Cl)/CeO_2/Al_2O_3, and Pd/La_2O_3/CeO_2/Al_2O_3 respectively. The chlorine content of the Cl-containing catalysts (capillary electrophoresis) indicates that less than $\approx$15% of the chlorine from the precursor remains on the catalysts after the pretreatment. This value is in agreement with that ($\approx$7%) determined by Kondarides *et al.* (19) on Rh(Cl)/CeO_2 solid and the authors have shown that this remaining Cl is mainly adsorbed on the CeO_2 support.

III. RESULTS AND DISCUSSION

(a) FTIR Spectra after Adsorption of CO at 300 K on a Selection of Solids

Figure 1 compares the FTIR spectra recorded at 300 K after the adsorption of CO (1% CO/He) at 300 K on the following reduced solids: 1.4% Pd(Cl-f)/Al_2O_3 (spectrum a), 1.4% Pd(Cl)/20% CeO_2/Al_2O_3 (spectrum b), and 1.9% Pd/16% La_2O_3/56% CeO_2/Al_2O_3 (spectrum c). These three solids have been selected because their FTIR spectra after adsorption of CO are representative of the other solids. There is an aging of the solids during three consecutive cycles, pretreatment/adsorption of CO at high temperatures, leading to (a) a decrease in the IR band intensities and (b) some slight modifications of the profiles of the IR bands. This has been described in more details for the 1.4% Pd(Cl-f)/Al_2O_3 solid (13). The spectra in Fig. 1 are obtained on stabilized solids (after three consecutive cycles) and with pellets of similar weights (range 70–80 mg). Thus the semiquantitative comparison of the intensities of the FTIR bands confirms that the Pd dispersions of the solids are not strongly different. It can be observed that the solids lead to the formation of a linear CO species (IR bands above 2000 cm^{-1}) and of a bridged CO species (IR bands below 2000 cm^{-1}). The positions of the IR band of the linear CO species, denoted L, are 2072 cm^{-1} for Pd(Cl-f)/Al_2O_3 (spectrum a) and 2090 cm^{-1} for Pd(Cl)/CeO_2/Al_2O_3 (spectrum b) and Pd/La_2O_3/CeO_2/Al_2O_3 (spectrum c). These values are in agreement with the literature data on Pd-supported catalysts (4–13). The differences observed in the positions of the IR bands of the L species, according to the solid considered, indicate some interactions between the Pd sites and the components of the solids, in particular the presence of chlorine. It has been observed (20) that the treatment of a Pt/Al_2O_3 solid with HCl leads to a shift of the linear CO species from 2065 to 2075 cm^{-1}. This shift was assigned to the electron acceptor properties of Cl which decreases the back donation of the platinum to the antibonding orbital of CO. The presence of oxygen also leads to a shift of the linear IR band to higher wavenumbers (16). In a recent study (19) on the influence of residual chlorine on the chemisorptive properties of CO on a 0.5% Rh/CeO_2 catalyst, the authors note, among several effects, that the IR band of the L species on Rh^0 is situated at 2070 cm^{-1} on a Cl-containing solid and at 2056 cm^{-1} on a Cl-free solid. In Fig. 1, the shift of the linear CO species from 2072 cm^{-1} on Pd(Cl-f)/Al_2O_3 to 2090 cm^{-1} on the other solids can be attributed to the presence of residual chlorine on the Pd particles. It can also be considered that oxygen is involved via the decoration of the particles by some fragments of the support (MO_x; M = Ce, La). One of the objectives of the present study is to determine if there is a correlation bewteen the heat of adsorption of the linear CO species and the position of the IR band at 300 K.

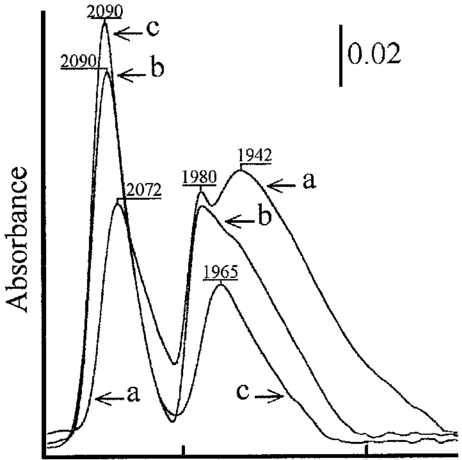

FIG. 1. FTIR spectra after adsorption of 1% CO/He at 300 K on reduced solids: (a) Pd(Cl-f)/Al_2O_3, (b) Pd(Cl)/CeO_2/Al_2O_3, and (c) Pd/La_2O_3/CeO_2/Al_2O_3.

The IR bands of the bridged CO species are more strongly influenced by the preparation and composition of the Pd-containing solids. For the Pd(Cl-f)/Al_2O_3 solid, two IR bands are detected at 1980 and 1942 cm^{-1}. These IR bands can be ascribed according to the literature (see (13) and references therein) to two species, denoted B_1 (1980 cm^{-1}) and B_2 (1942 cm^{-1}) and situated on Pd(100) or on Pd(110) and on Pd(111) respectively. On 1.4% Pd(Cl)/20% CeO_2/Al_2O_3 the IR band at 1942 cm^{-1} is detected as a shoulder of the IR band of the B_1 species (1983 cm^{-1}), indicating either a specific orientation of the particles or a higher sensitivity of the Pd(111) planes to residual chlorine and/or to decoration. On the Pd/La_2O_3/CeO_2/Al_2O_3 solid a single well-defined IR band is detected at 1965 cm^{-1}. This IR band is similar (position and profile) to that observed at room temperature on the reduced Pd(Cl-f)/Al_2O_3 catalyst after adsorption of CO at high temperatures (13) when the surface of the Pd particles is probably modified by the carbon deposition (and maybe by the oxygen adsorption) due to the dissociation/disproportionation reaction of CO. The same IR band has been observed by Hicks *et al.* (11) on a 1.9% Pd/La_2O_3 catalyst prepared with H_2PdCl_4. In particular, the authors note the absence of a low-frequency shoulder by comparison with a 2% Pd/SiO_2 catalyst. On this solid, the FTIR spectrum indicates the formation of the B_1 and B_2 species characterized by two IR bands at 1975 and 1920 cm^{-1} respectively. On the Pd/La_2O_3 solids, the authors considered that patches of partially reduced support material, LaO_x, transferred to the surface of the Pd crystallites during the preparation, explain the differences of chemisorption properties between the two solids. For this reason the authors consider that the IR band at 1965 cm^{-1} corresponds to the B_1 species in interaction with LaO_x fragments (the B_2 species is not formed on the La_2O_3 support). It can be considered that the position and the profile of the IR band of the B species on spectrum c in Fig. 1 are due to MO_x fragments in interaction with the B_1 species (shift of the IR band) and to the disappearance of the sites adsorbing the B_2 species. However, it cannot be excluded that some preparation methods create Pd particles with specific exposed planes leading to several IR bands for the B species. Hereafter, an IR band at $\approx$1960 cm^{-1} is assigned to a bridged species referred to as B_3 whatever the reason for its presence: specific oriented planes due to the solid preparation or modifications of the sites giving the B_1 and B_2 species by some interactions with MO_x fragments or adsorbed C (or adsorbed O). The changes of the intensities of the IR bands of the L and B_i ($i = 1, 2, 3$) species in Fig. 1 with T_a are used to determine for each species their coverages at various temperatures and their respective heats of adsorption as a function of the coverage.

(b) *Heats of Adsorption of the Linear and Bridged CO Species on the Pd/Al_2O_3 Solids*

The results observed on 1.4% Pd(Cl-f)/Al_2O_3 have been described in detail in (13) and are briefly summarized below to facilitate the comparison with the other Pd-containing solids. Figure 2 gives for a stabilized solid the change of the FTIR spectra recorded at various temperatures during the adsorption of CO using a 1% CO/He mixture. The IR band of the linear CO species is constant between 300 and 323 K and then progressively decreases with T_a alongside a shift to a lower wavenumber (2072 cm^{-1} at 300 K and 2042 cm^{-1} at 628 K). The IR band of the B_1 species shifts to lower wavenumbers between 300 and 428 K but the area of the two IR bands remains constant (the IR band of the B_1 species shifts and overlaps that of the B_2 species). For temperatures higher than 428 K, the single broad IR band of the bridged species decreases progressively and shifts to lower wavenumbers (1939 cm^{-1} at 428 K and 1900 cm^{-1} at 688 K). We showed in (13) that during the CO adsorption at temperatures higher than 450 K, the disproportionation reaction leads to the deposition of C (and maybe to the adsorption of oxygen) on the Pd particles associated with the adsorption of various carbonate species on the support (via the formation of CO_2). However, it has been observed by the comparison of the intensities of the IR bands at 300 K before and after adsorption of CO at high temperatures that the number of adsorption sites of the Pd surface was not strongly modified by the reaction. The coverage, θ, of each species, L and B (B_1 and B_2 are not differentiated), at T_a can be obtained from the results of Fig. 2, using the ratio between the IR band area at T_a and the highest IR band area of their respective IR bands (accuracy, $\theta \pm 0.02$). Figure 3 gives the change of the coverages of the L (curve a) and of the B species (both B_1 and B_2, curve b) as a function of T_a. In (13) we have shown that the almost constant coverage of the linear CO species above 573 K was probably due to the presence of a linear adsorbed CO species (denoted L_2) with a heat of adsorption higher than 165 kJ/mol. The coverage of the linear CO species with a lower heat of adsorption (denoted L_1) is obtained by subtracting the intensity of the IR band recorded 717 K from that recorded at lower temperatures before the determination of the coverages (Fig. 3c).

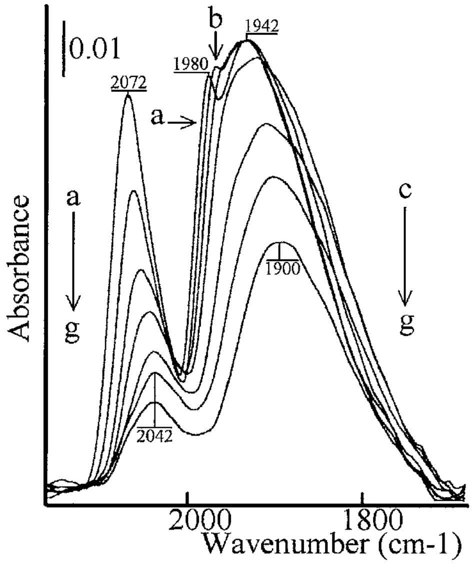

FIG. 2. Infrared spectra taken during the adsorption of CO (1% CO/He) at various temperatures on the reduced Pd(Cl-f)/Al_2O_3 solid: (a) 300 K, (b) 368 K, (c) 428 K, (d) 488 K, (e) 568 K, (f) 628 K, and (g) 688 K.

We have also shown in (13) that the profiles of curves a and b do not correspond to Langmuir's model of

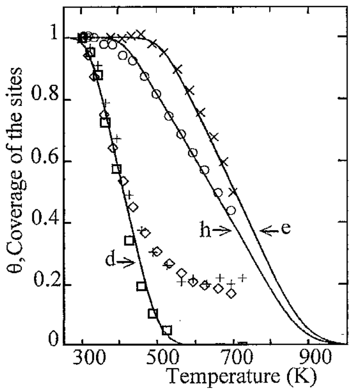

FIG. 3. Change of the coverages of the linear and bridged CO species with the adsorption temperature on the Pd/Al_2O_3 solids: +, (a) and ×, (b) respectively experimental data for L and B on Pd(Cl-f)/Al_2O_3; □, (c) experimental data for L after correction (see the text); (d) and (e) respectively L and B on Pd(Cl-f)/Al_2O_3 according to expression [1]; ◇, (f) and ○, (g) respectively experimental data for L and B on Pd(Cl)/Al_2O_3; and (h) B on Pd(Cl)/Al_2O_3 according to expression [1].

adsorption,

$$\theta = \frac{LP_a}{1 + LP_a}, \qquad [0]$$

where L is the adsorption coefficient and P_a the adsorption pressure. The curves are in agreement with a model assuming a linear increase in the heat of adsorption of each adsorbed species (linear and bridged) with a decrease in coverage (12, 13). The coverage of the sites according to this adsorption model is given by (12, 13) and references therein:

$$\theta = \frac{RT_a}{\Delta E} \ln\left(\frac{1 + L_0 P_a}{1 + L_1 P_a}\right). \qquad [1]$$

L_0 and L_1 are the adsorption coefficients at $\theta = 0$ and $\theta = 1$ respectively, given by the statistical thermodynamics assuming the loss of three degrees of translation,

$$L = \frac{h^3}{k(2\pi mk)^{3/2}} \frac{1}{T_a^{5/2}} \exp\left(\frac{E_d - E_a}{RT_a}\right), \qquad [2]$$

where in [1] and [2] h is Planck's constant, k is Bolztmann's constant, m is the weight of the CO molecule, T_a is the adsorption temperature, E_d and E_a are the activation energies of desorption and adsorption respectively, while $E_d - E_a$ is the heat of adsorption, and ΔE is the difference of the heats of adsorption at $\theta = 0$ (E_0) and $\theta = 1$ (E_1). Curve d in Fig. 3 gives the change of the coverage of the L species according to expression [1] with the following values: $E_0 = 92$ kJ/mol and $E_1 = 54$ kJ/mol in order to obtain the best fit of the experimental curve c. Note the agreement between the adsorption model and the experimental data. The accuracy on the E values is $E_i \pm 5$ kJ/mol. There are very few studies on the heat of adsorption of the L species on monocrystals and/or model particles. After adsorption of CO on a Pd/Ta(110) solid (Pd deposited onto the crystal by evaporation), Kuhn *et al.* (3) observed IRAS spectra with a single IR band situated between 2096 cm^{-1} at high coverage and 2053 cm^{-1} at low coverage. The isosteric heat of adsorption at low coverage of the corresponding adsorbed species is 92 kJ/mol (3), in agreement with our value (92 kJ/mol) and the value (88 kJ/mol) found by Zhao and Gomer on Pd/W(110) (21). Expression [1] fits also the experimental data of the B species, using $E_0 = 168$ kJ/mol and $E_1 = 92$ kJ/mol (curve e). These values are clearly higher than those of the L species and are in agreement with the literature data on various Pd-containing solids: monocrystals, model particles, and Pd-supported catalysts (13 and references therein). In particular, Yeo *et al.* (22) have determined the heat of adsorption of CO on Pd(100) at several coverages using single-crystal adsorption calorimetry (SCAC). They observed that the heat of adsorption varies linearly with the coverage from 169 kJ/mol at $\theta \approx 0$ to 70 kJ/mol at $\theta = 0.7$. For $\theta > 0.7$ the heat of adsorption is constant. The relationship between the heat of adsorption and the coverage as well as the heat of adsorption at low coverage are in very good agreement with the results obtained in the present study. For the B species, it can be noted that an adsorption model assuming a single adsorbed species fits an experimental result involving two species (B_1 and B_2). This indicates that the two species have similar heats of adsorption as described in the literature on monocrystals. In particular, Conrad *et al.* (23) have observed that the heats of adsorption of CO (B species) at low coverage are in the range 142–152 kJ/mol on Pd(111), -(100), -(311), and -(210), while the value is 167 kJ/mol on Pd(110). In the next part of this study, the above procedure is used to determine if the heats of adsorption of the L and B_i species on the various Pd-containing solids are influenced by the nature of the support and by the salt precursor of the metallic phase.

Spectra a and b in Fig. 4 are obtained after adsorption of CO (1% CO/He mixture) at 300 K on Pd(Cl-f)/Al_2O_3 and Pd(Cl)/Al_2O_3 respectively, after the first pretreatment. The preparation method of the solids leads to the following differences: (a) on Pd(Cl)/Al_2O_3 a single broad IR band is detected at 1938 cm^{-1} assigned to the B_2 species observed on Pd(Cl-f)/Al_2O_3, and (b) the IR band of the L species is situated at a higher wavenumber (2090 cm^{-1}) than on Pd(Cl-f)/Al_2O_3 (2080 cm^{-1}). This shift can be attributed to the presence of residual chlorine on the palladium surface (19, 20). The absence of the B_1 species on Pd(Cl)/Al_2O_3 can be due either to the specific effect of the residual chlorine on the Pd(100) plane or to a difference in the morphology of the Pd particles due to the preparation method. Spectra c and d in Fig. 4 are recorded on the reduced Pd(Cl)/Al_2O_3 solid, after respectively one and two cycles of pretreatment/adsorption of CO at high temperatures. The decrease in the IR band intensities with the number of cycles is similar to that observed on Pd(Cl-f)/Al_2O_3 (13). This indicates an

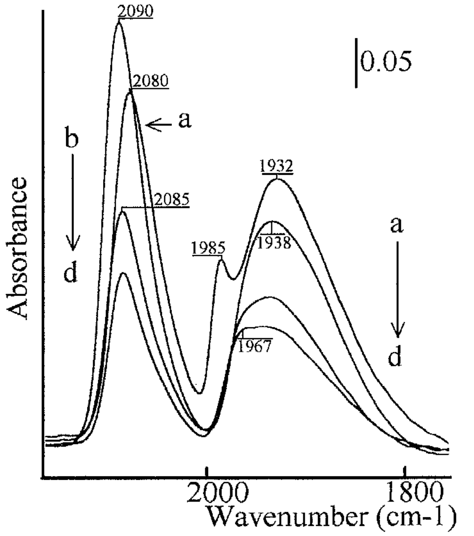

FIG. 4. Infrared spectra after adsorption of CO at 300 K on the reduced Pd/Al_2O_3 solids: (a) first reduction on the Cl-free solid (with a multiplying factor of 2.3), (b) first reduction on the Cl-containing solid, (c) and (d) after one and two cycles pretreatment/adsorption of CO at 700 K, respectively.

aging of the catalyst which leads to the shift of the IR band of the L species from 2090 to 2085 cm^{-1} and to the detection of a shoulder at 1967 cm^{-1}. Both effects can be interpreted either by a reconstruction of the palladium particles during the adsorption of CO or by the progressive removal of chlorine during the cycles. After three cycles there is no more change in the spectra between two consecutive experiments.

Figure 5 shows the IR bands of the adsorbed CO species on the stabilized $Pd(Cl)/Al_2O_3$ solid as a function of T_a using the 1% CO/He mixture. The spectra are similar to those observed on $Pd(Cl\text{-}f)/Al_2O_3$ (Fig. 2). The IR band of the L species decreases at a temperature lower than that of the B species and shifts to lower wavenumbers (2085 cm^{-1} at 300 K, 2078 cm^{-1} at 359 K, 2068 cm^{-1} at 436 K, 2050 cm^{-1} at 563 K, and 2045 cm^{-1} at 693 K). The IR bands of the B species become sharper with an increase in T_a with a maximum at 1960 cm^{-1} at 436 K but without a major change of the IR band area. For higher temperatures, the IR band shifts to lower wavenumbers (1939 cm^{-1} at 563 K and 1900 cm^{-1} at 693 K) and its intensity decreases. The comparison of the FTIR spectra recorded after adsorption of CO at 300 K before and after adsorption at 693 K (not shown) followed by cooling down of the sample to 300 K in 1% CO/He indicates that the position of the IR band of the L species is not modified but its intensity is decreased by 20%. After the heating in CO, the IR band of the B species is sharper with a maximum at 1962 cm^{-1} and its intensity is decreased by 20%. These observations are similar to those made on $Pd(Cl\text{-}f)/Al_2O_3$ (13) and indicate a decrease in the numbers of palladium sites adsorbing the L and B species, probably associated with the dissociation/disproportionation reaction of CO. However, the decrease in the number of sites adsorbing the L species is observed for $T_a > 468$ K while that of the sites adsorbing the B species is observed for $T_a > 643$ K.

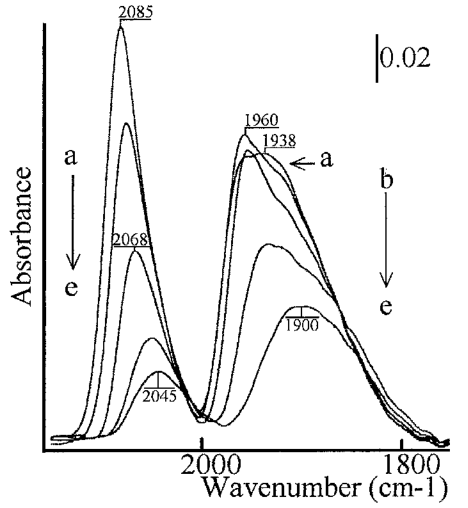

FIG. 5. Infrared spectra taken during the adsorption of CO (1% CO/He) at various temperatures on the reduced $Pd(Cl)/Al_2O_3$ solid: (a) 300 K, (b) 359 K, (c) 436 K, (d) 563 K, and (e) 693 K.

Curves f and g in Fig. 3 provide for the $Pd(Cl)/Al_2O_3$ solid the changes, with T_a, of the coverages of the L and B species respectively. In a wide range of temperatures curve f is superimposed onto curve a obtained with 1.4% $Pd(Cl\text{-}f)/Al_2O_3$. The decrease in coverage at high temperatures (curve f) is linked to the decrease in the number of superficial sites as indicated above. Curves f and a show that there is no difference in the heat of adsorption of the L species on the two solids, even if the positions of the IR bands at 300 K are different due to the presence of residual chlorine. In (13) we showed that the heats of adsorption of the L_1 species were not influenced by the shift of its IR band from 2072 to 2090 cm^{-1} due to the presence of oxygen on the surface. Curves g and b in Fig. 3 are clearly different and indicate a significant decrease in the heat of adsorption of the B species on the Cl-containing solid. However, the difference between curves g and b is related to the value of θ: the difference is larger at high coverages. Curve h in Fig. 3 is obtained using in expression [1] $E_0 = 168$ kJ/mol and $E_1 = 75$ kJ/mol. These values can be compared with that on $Pd(Cl\text{-}f)/Al_2O_3$: 168 and 92 kJ/mol respectively. This shows that at low coverages, the heats of adsorption are equal and that the difference (−17 kJ/mol) is maximum at $\theta \approx 1$.

The following conclusions can be derived from the above results on the Pd/Al_2O_3 solids: (a) residual chlorine leads to a shift of the IR band of the L species from 2072 to 2085 cm^{-1} (after stabilization of the solids) but has no influence on the heat of adsorption exhibited by the L_1 and L_2 species whatever the coverage, and (b) the residual chlorine leads to a modification of the profile of the IR bands of the B

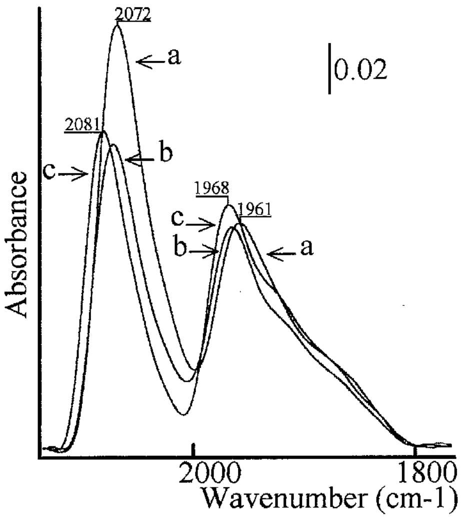

FIG. 6. Infrared spectra after adsorption of CO at 300 K on the reduced Pd(Cl-f)/CeO_2/Al_2O_3 solid: (a) first reduction, (b) after the first cycle pretreatment/adsorption, and (c) after the second cycle.

species (modification of the B_1/B_2 ratio) and to a significant decrease (≈ -20 kJ/mol) in the heat of adsorption of the B species at high coverage.

(c) Heats of Adsorption of the Linear and Bridged CO Species on Pd/CeO_2/Al_2O_3

The adsorption of 1% CO/He at 300 K on the reduced Pd(Cl-f)/CeO_2/Al_2O_3 (spectrum a, Fig. 6) leads to the appearance of an IR band at 2072 cm^{-1} identical to that detected on Pd(Cl-f)/Al_2O_3 (Fig. 1) corresponding to the L species and to an IR band at 1961 cm^{-1} identical to that observed on Pd/$CeO_2/La_2O_3/Al_2O_3$ (spectrum c, Fig. 1) and ascribed to a bridged species B_3. The aging phenomenon developed by the number of cycles of pretreatment/adsorption of CO at high temperature leads to a slight change of the FTIR spectra (spectra b and c in Fig. 6). The IR band of the L species decreases after the first cycle and shifts to 2074 cm^{-1}. Another shift to 2081 cm^{-1} is recorded after the second cycle. The intensity of the IR band of the B_3 species is not affected but a shift is recorded after the first cycle from 1961 to 1968 cm^{-1}. Figure 7 shows for a stabilized solid the change of the FTIR spectra with T_a using the 1% CO/He mixture. The IR band of the L species shifts progressively with increases in temperature (2081 cm^{-1} at 300 K, 2060 cm^{-1} at 430 K, 2052 cm^{-1} at 548 K, and 2026 cm^{-1} associated with a shoulder at 2055 cm^{-1} at 715 K). The shoulder observed at 715 K supports our previous interpretation about the presence of an L_2 species (with a heat of adsorption higher than 165 kJ/mol) which dominates the spectra at high temperatures while the L_1 species dominates the spectra at low temperatures. It is the L_1 species which gives the shoulder at 2055 cm^{-1} in spectrum d. The IR band of the B species shifts from 1968 cm^{-1} at 300 K to 1959 cm^{-1} at 430 K without a significant modification of its intensity. For higher temperatures, the intensity decreases and the position shifts to lower wavenumbers (1942 cm^{-1} at 548 K and 1900 cm^{-1} at 715 K). The comparison of the FTIR spectra recorded at room temperature on Pd(Cl- f)/CeO_2/Al_2O_3 before and after interaction of CO at 715 K followed by cooling down of the sample to room temperature in 1% CO/He indicates that the intensities of both IR bands are not strongly modified (decreases of around 10% for the IR bands of the L and B species) and that they shift to higher wavenumbers: from 2081 to 2090 cm^{-1} for the L species and from 1968 to 1974 cm^{-1} for the B_3 species. The shift of the linear IR band is similar to that observed on Pd(Cl-f)/Al_2O_3 (13) and seems to be associated with the presence of carbon and/or oxygen at the surface linked to the dissociation/disproportionation reaction of CO (13).

Curves c and d in Fig. 8 give the change of the coverage of the L and B species on Pd(Cl-f)/CeO_2/Al_2O_3 using the experimental data of Fig. 7. It can be observed that the two curves are superimposed with that determined on Pd(Cl-f)/Al_2O_3 (Figs. 8a and 8b). This shows that for the two Cl-free solids, the heats of adsorption of the L and B species are not modified by the nature of the support: Al_2O_3 and 20% CeO_2/Al_2O_3. In particular, curves b and d in Fig. 8 are in good agreement with expression [1] using $E_0 = 168$ kJ/mol and $E_1 = 92$ kJ/mol (Fig. 8h). This means that the differences in the position of the IR bands of the L and B species (after adsorption of CO at 300 K) between the two solids (Fig. 4) exert no significant influences on their respective heats of adsorption. In particular, this indicates that the B_1, B_2, and B_3 species have similar heats of adsorption. Note that the lowest coverage of the L species is higher on Pd(Cl-f)/CeO_2/Al_2O_3 than on Pd(Cl-f)/Al_2O_3

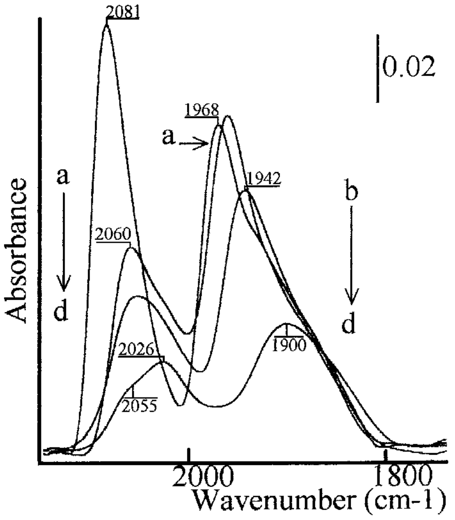

FIG. 7. Infrared spectra taken during the adsorption of CO (1% CO/He) at various temperatures on the reduced Pd(Cl-f)/CeO_2/Al_2O_3 solid: (a) 300 K, (b) 430 K, (c) 548 K, and (d) 715 K.

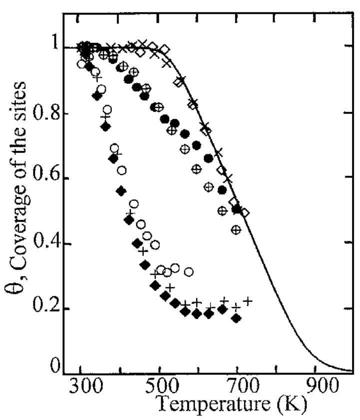

FIG. 8. Change of the coverages of the linear and bridged CO species with the adsorption temperature on Pd(Cl-f)/Al_2O_3 and Pd/CeO_2/Al_2O_3: +, (a) and ×, (b) respectively experimental data for the L and B on Pd(Cl-f)/Al_2O_3; ○, (c) and ◇, (d) respectively experimental data for the L and B on Pd(Cl-f)/CeO_2/Al_2O_3; ◆, (e) and ●, (f) experimental data for the L and B species on Pd(Cl)/CeO_2/Al_2O_3; ⊕, (g) experimental data for the B species on Pd(Cl)/Al_2O_3; and —, (h) B species according to expression [1].

because the concentration of the L_2 species is probably higher on the CeO_2/Al_2O_3 support (see spectrum d in Fig. 7). The same experiments described above have been performed on the Pd(Cl)/CeO_2/Al_2O_3 solid.

Spectrum a in Fig. 9 is recorded after adsorption of CO at 300 K on the stabilized Pd(Cl)/CeO_2/Al_2O_3 solid (two cycles). An IR band is detected at 2090 cm^{-1} (L species) associated with an IR band at 1985 cm^{-1} (B_1 species) with a shoulder at 1946 cm^{-1} (B_2 species). On a fresh solid, an IR band is detected at 1960 cm^{-1} with a profile similar to that recorded on Pd(Cl)/Al_2O_3 (spectrum b, Fig. 4). Figure 9 shows the changes of the IR bands with T_a using the 1% CO/He mixture. The IR band of the L species shifts to lower wavenumbers (2090 cm^{-1} at 300 K, 2083 cm^{-1} at 383 K, 2074 cm^{-1} at 443 K, 2067 cm^{-1} at 488 K, 2057 cm^{-1} at 563 K, and 2051 cm^{-1} at 693 K) and its intensity decreases progressively. The IR band of the B species (a) increases slightly and becomes sharper between 300 K and 343 K, (b) shifts to 1975 cm^{-1} without a change of its intensity from 343 to 383 K, and (c) decreases progressively and shifts to lower wavenumbers for temperatures higher than 383 K (1967 cm^{-1} at 443 K, 1962 cm^{-1} at 488 K, 1948 cm^{-1} at 563 K, and 1911 cm^{-1} at 693 K). The FTIR spectra at 300 K before and after adsorption of CO at 693 K followed by cooling of the sample to 300 K in 1% CO/He indicate that the intensities of the IR bands of the L species and B species are not modified by the interaction of CO at high temperatures but a shift of the IR band of the L species to 2095 cm^{-1} is observed. However, a significant difference is observed with the other solids. After adsorption at 693 K followed by cooling of the sample to 300 K, a small IR band is detected at 2160 cm^{-1} which can be attributed to the adsorption of CO on $Pd^{\delta+}$ sites (18, 24) with probably $\delta = 2$ (24). This confirms that the dissociation/disproportionation reaction of CO at high temperatures leaves some adsorbed oxygen on the palladium surface leading to a shift of the L species to higher wavenumbers (on the various solids used) and to the formation of a cationic site able to adsorb CO on the present solid. Using the results of Fig. 9, curves e and f in Fig. 8 provide the change with T_a of the coverages of the L and B species respectively. Curve e is superimposed onto that obtained for the L species on the other studied Pd-containing solids (Figs. 8a and 8b). This indicates that the heats of adsorption of the L species (L_1 and L_2) are not significantly modified by the presence of residual chlorine nor by the nature of the support (Al_2O_3 and CeO_2/Al_2O_3). Another conclusion is that the heat of adsorption of the L species is independant of the position of its IR band after adsorption of CO at 300 K (2072 cm^{-1} on Pd(Cl-f)/Al_2O_3, 2085 cm^{-1} Pd(Cl)/Al_2O_3, 2081 cm^{-1} on Pd(Cl-f)/CeO_2/Al_2O_3, and 2090 cm^{-1} on Pd(Cl)/CeO_2/Al_2O_3).

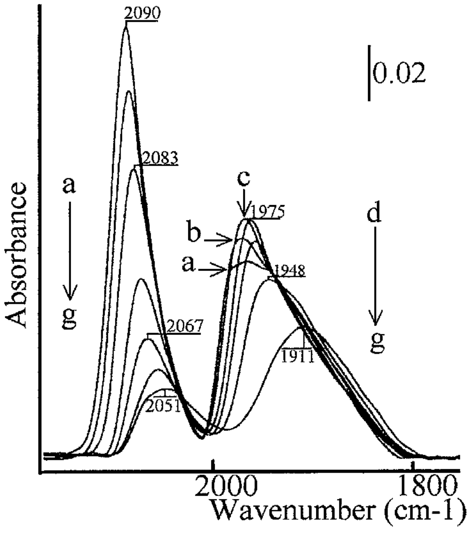

FIG. 9. Infrared spectra taken during the adsorption of 1% CO/He at various temperatures on the reduced Pd(Cl)/CeO_2/Al_2O_3 solid: (a) 300 K, (b) 343 K, (c) 383 K, (d) 443 K, (e) 488 K, (f) 563 K, and (g) 693 K.

Curve f in Fig. 8 shows that at a given adsorption temperature, the coverage of the B species on Pd(Cl)/CeO_2/Al_2O_3 is lower than that on Pd(Cl-f)/CeO_2/Al_2O_3 and is similar to that observed on Pd(Cl)/Al_2O_3 (Fig. 8g). It appears that as on the Al_2O_3 support the heat of adsorption decreases in the presence of Cl. However, curve f reveals a Z-shaped profile between $\theta = 0.8$ and $\theta = 0.6$ which cannot be fit by expression [1] assuming a linear decrease in the heat of adsorption with an increase in coverage. Note that the repeatability of curve f has been verified by several experiments on a stabilized solid. The relationship between the heat of adsorption of the B species and the coverage is represented by curve c in Fig. 10. The curves in Fig. 10 are obtained as in (12) considering (a) the experimental values of θ at T_a, (b) the Langmuir model (expression [0]), and (c) the adsorption

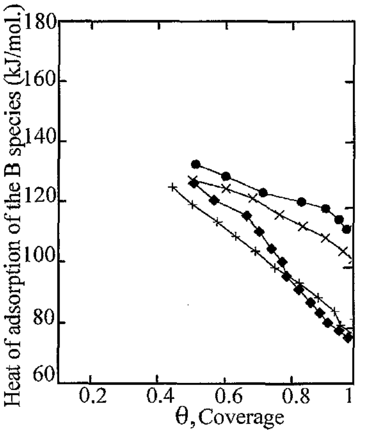

FIG. 10. Change of the heat of adsorption of the B species with the coverage on various Pd-containing solids: ×, (a) Pd(Cl-f)/Al_2O_3;+, (b) Pd(Cl)/Al_2O_3; ◆, (d) Pd(Cl)/CeO_2/Al_2O_3; and ●, (e) Pd(Cl)/La_2O_3/CeO_2/Al_2O_3.

coefficient l given by expression [2] but assuming that the heat of adsorption changes with the coverage. As expected Pd(Cl-f)/Al_2O_3 (curve a) and Pd(Cl)/Al_2O_3 (curve b) give two straight lines which converge at low θ values. Curve d reveals a different profile for the Pd(Cl)/CeO_2/Al_2O_3 solid. A jump of around 20 kJ/mol in the heat of adsorption of the B species is observed between $\theta = 0.8$ and $\theta = 0.6$. For $\theta > 0.8$ and $\theta < 0.6$ a linear relationship is observed similar to those for Pd(Cl-f)/Al_2O_3 and Pd(Cl)/Al_2O_3 respectively. Figure 10 shows that the larger difference between the heats of adsorption of the B species on the Cl-containing and Cl-free solids is observed at $\theta \approx 1$ and that all the solids show a similar heat of adsorption for low θ values (i.e., on the two Pd/Al_2O_3 solids the differences are $\approx$25 kJ/mol at $\theta \approx 1$ and 8 kJ/mol at $\theta \approx 0.5$).

The above results show that the heat of adsorption of the L species is independent of the nature of the support (Al_2O_3 and 20% CeO_2/Al_2O_3) and of the salt precursor of the metallic phase (with and without chlorine) even if this parameter affects the position of the IR band of the L species at 300 K. For the Cl-free solids, the heat of adsorption of the B species is independent of the nature of the support. The presence of residual chlorine leads for the two supports to a decreases in the heat of adsorption of the B species at high coverages. This difference decreases with decreases in coverage and tends to 0 at $\theta = 0$.

(d) Heats of Adsorption of the Linear and Bridged CO Species on 1.96% Pd/16% La_2O_3/56% CeO_2/Al_2O_3

On the fresh reduced solid, the adsorption of CO at 300 K gives a spectrum (not shown) with two IR bands at 2096 cm^{-1} (L_1 species) and 1965 cm^{-1} (B_3 species). After a single cycle adsorption of CO/pretreatment a decrease (by $\approx$15%) in the intensity of the IR band of the L species which shifts to 2090 cm^{-1}. The intensity decreases again (by $\approx$10%) after a second cycle but without any shift. The position of the IR band of the L species is in agreement with that observed on the other Cl-containing Pd solids. The IR band of the B species decreases with the number of cycles ($\approx$5% after the first and the second cycle) but without any shift. Figure 11 shows the FTIR spectra recorded at various adsorption temperatures on a pretreated stabilized solid. The increase in T_a leads to a progressive decrease in the intensity of the IR band of the L species and to a shift to lower wavenumbers (i.e., 2091 cm^{-1} at 300 K, 2086 cm^{-1} at 368 K, 2076 cm^{-1} at 455 K, 2057 cm^{-1} at 546 K, and 2050 cm^{-1} at 723 K) according to a linear relationship in a wide range of temperatures. The change of the IR band of the B species is more complex: (a) between 300 and 445 K the intensity increases slightly without modifications of the position, and (b) for higher temperatures the IR band shifts to lower wavenumbers (1962 cm^{-1} at 445 K, 1948 cm^{-1} at 545 K, and 1906 cm^{-1} at 723 K) and its intensity decreases progressively. If after heating at 445 K the solid is cooled down to 373 K in CO/He, the intensity of the bridged CO species remains constant. This means that the initial increase in the IR band is due to an irreversible modification of the adsorbed CO/surface system. Figure 12 compares the FTIR spectra recorded at room temperature before and after heating of the sample in CO at 723 K. It can be observed that the intensities of the IR band of the B species are similar on the two spectra with a small shift to higher wavenumbers (1969 cm^{-1}). However, taking into account the initial increase in the IR band with T_a, spectra a and b indicate that there is a slight decrease in the number of sites adsorbing the B species. The position of the IR band of the L species is sightly affected (2087 cm^{-1}) by the

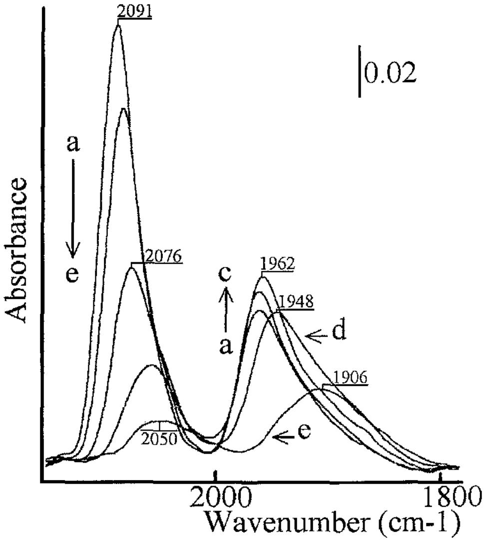

FIG. 11. Infrared spectra taken during the adsorption of 1% CO/He at various temperatures on Pd/La_2O_3/CeO_2/Al_2O_3: (a) 300 K, (b) 368 K, (c) 455 K, (d) 545 K, and (e) 723 K.

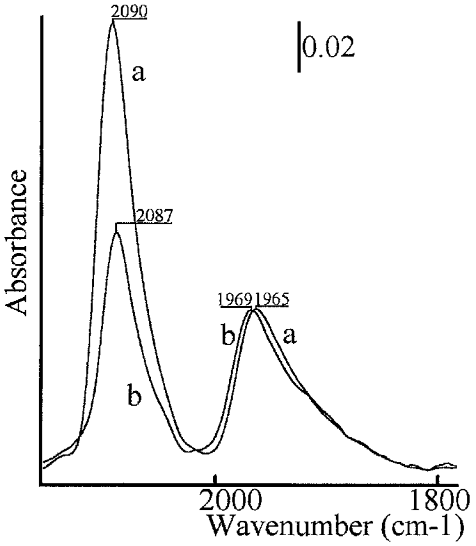

FIG. 12. Infrared spectra after adsorption of 1% CO/He at 300 K on Pd/La_2O_3/CeO_2/Al_2O_3: (a) on the reduced solid, and (b) after heating at 723 K and cooling to 300 K in 1% CO/He.

adsorption at high temperatures but its intensity is significantly decreased. However, for $T_a < 473$ K, the intensity of the IR band of the linear species is not modified after cooling of the sample to room temperature. The changes of the two IR bands with T_a are probably linked to the dissociation/disproportionation reaction of CO. It must be noted that on Pd/La_2O_3 solids, Rieck and Bell (25) have observed that the presence of LaO_x moieties on the Pd particles facilitated the dissociation of CO and this was an argument to explain the very rapid formation of CH_4, from CO/H_2, on these solids compared with Pd/SiO_2 catalysts. This is in good agreement with the fact that it is on the La_2O_3-containing solid that we observe the stronger decrease in the sites forming the L species after the adsorption of CO at high temperatures.

Figure 13 gives the evolution of coverages of the L and B species (curves c and d) with T_a. The full coverage ($\theta = 1$) of the sites is determined by the IR band area at 300 and 474 K for the L and B species respectively. In a wide range of temperatures, curve c is superimposed onto that (Fig. 13a) obtained with Pd(Cl-f)/Al_2O_3. At high temperatures the difference between curves a and c is due to the decrease in the number of sites adsorbing the L species on Pd(Cl)/La_2O_3/CeO_2/Al_2O_3 as shown in Fig. 12. Curves a and c indicate that the heats of adsorption of the L_1 and L_2 species on the present solid evolve with the coverage as on the other Pd-containing solids. This confirms that the heats of adsorption of the L species are not significantly influenced by the nature of the support nor by the nature of the salt precursor of the metallic phase. For the bridged CO species, curve d in Fig. 13 is similar to that observed on Pd(Cl-f)/Al_2O_3 (Fig. 13b). The increasing section of curve d for $T_a < 550$ K corresponds to the increase in the intensity of the IR band observed in Fig. 11. The profile of curve d for $T_a > 550$ K is in agreement with an adsorption model assuming a linear increase in the heat of adsorption with decrease in coverage. Using $E_0 = 168$ kJ/mol and $E_1 = 105$ kJ/mol in expression [1], curve e in Fig. 13 is obtained in agreement with the experimental data. Note that the value of the heat of adsorption of the B species at low coverage (168 kJ/mol) is the same as that found on the other solids while the value at high coverages is higher than that determined on the other Cl-containing solids (see also Fig. 10d). The first remark confirms that whatever the Pd-containing solid, the heat of adsorption of the B species tends to the same value at low coverage ($E_0 \approx 170$ kJ/mol). The second remark shows that the use of $PdCl_2$ as salt precursor of the Pd particles does not have the same effect on the all solids. There are some other factors linked to the preparation method of the La_2O_3-containing solid which may influence the heat of adsorption of the B species at high coverages. It can be considered that the level of residual chlorine on the Pd particles of the present solid is very low. The position of the L species at 2091 cm^{-1} may be due not to the presence of residual chlorine but to the decoration of the particles by LaO_x fragments as suggested by Rieck and Bell (25). It can be considered that it is the presence of the LaO_x fragments which leads to a low level of Cl on the Pd surface and which explains the value of the heat of adsorption of the B species at high coverages.

(e) Effects of the Preparation Method of the Solids on the Heats of Adsorption of CO

Table 1 summarizes the heats of adsorption of the L and B species on the various solids at low and high coverages. Taking into account that the heats of adsorption of the L and B species (at low coverage) on 1.4% Pd(Cl-f)/Al_2O_3

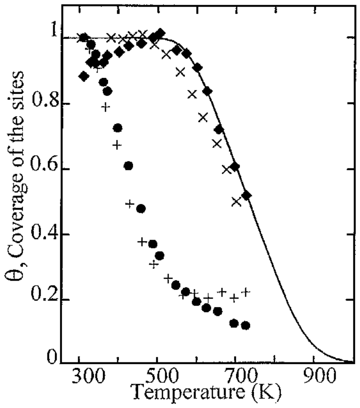

FIG. 13. Change of the coverages of the linear and bridged CO species with the adsorption temperature on Pd(Cl-f)/Al_2O_3 and Pd/La_2O_3/CeO_2/Al_2O_3: +, (a) and ×, (b) respectively experimental data for L and B on Pd(Cl-f)/Al_2O_3; ● (c) and ◆, (d) respectively experimental data for L and B on Pd(Cl)/La_2O_3/CeO_2/Al_2O_3; and —, (e) coverage according to expression [1] (see the text).

TABLE 1

Heats of Adsorption of the Adsorbed CO Species on the Various Pd-Containing Solids at Low (E_0) and High (E_1) Coverage

Sample	Linear CO species: L_1		Bridged CO species:[a] B_i	
	E_0 (kJ/mol)	E_1 (kJ/mol)	E_0 (kJ/mol)	E_1 (kJ/mol)
Pd(Cl-f)/Al_2O_3	92	54	168	92
Pd(Cl)/Al_2O_3	92	54	168	75
Pd(Cl-f)/CeO_2/Al_2O_3	92	54	168	92
Pd(Cl)/CeO_2/Al_2O_3	92	54	168	75
Pd(Cl)/La_2O_3/CeO_2/Al_2O_3	92	54	168	105

[a] The various bridged species are not differentiated.

are in agreement with the literature data on Pd monocrystals as well as supported model particles (see above and (13)), this solid is used as a reference to evaluate the effects of the preparation method of the other solids on the heats of adsorption of the two adsorbed species. There are very few studies in the literature dedicated to the effect of the preparation method of Pd-supported solids on the heat of adsorption of CO. On monocrystals and supported model particles the TPD technique makes it possible to determine the activation energies of desorption of several adsorbed species (equal to the heats of adsorption of CO taking into account that the adsorption of CO is not activated). However, there are some difficulties linked to this technique with conventional catalysts. In particular, it has been shown that it is difficult to achieve experimental conditions to prevent the influence of chemical (readsorption) and physical (diffusion) phenomena on the TPD spectra (26, 27). This explains that the heats of adsorption of CO on Pd-supported catalysts are preferentially determined by microcalorimetric methods (17, 28) at room temperature. With these experimental conditions, the L and B species are formed simultaneously and the heat of adsorption determined is an average between those of the two species. This means that the values depend of the L/B ratio which is a function of the particle sizes (6): at high dispersion the proportion of the L species increases. The main objective of the studies in the published literature on Pd-supported catalysts was to determine if and how the particle size affects the heat of adsorption. Chou and Vannice (17) using several Pd-supported solids (on SiO_2, Al_2O_3, SiO_2/Al_2O_3, TiO_2) have shown that the heat of adsorption of CO is roughly constant (≈ 96 kJ/mol) for particle sizes higher than 5 nm and sharply increases for lower particles. A similar result was obtained by Henry *et al.* (29) on Pd clusters formed on MgO(100) but with the heat of adsorption changing at 3 nm. The increase in the heat of adsorption for particle size lower than 3–5 nm can be interpreted taking into account our results and those in the literature. The linear CO species is considered to be formed on the low coordinated Pd atoms and it has been shown that the proportion of the L species toward the B species increases with dispersion (6). We have shown (Table 1) that on the Pd particles there are (a) a linear CO species denoted L_1 with a heat of adsorption (varying from 92 kJ/mol at $\theta \approx 0$ to 54 kJ/mol at $\theta \approx 1$) lower than that of the B species, and (b) a linear CO species denoted L_2 with a heat of adsorption higher than 165 kJ/mol. To interpret the results of Ref. (17 and 29) (the increase in the heat of adsorption with a decrease in particle size) it must be considered that for particle sizes lower than 3–5 nm, it is the L_2/L_1 ratio which increases (13). Note that Voogt *et al.* (30) using ellipsometry spectroscopy with model Pd particles supported on SiO_2 found that the particle sizes (in the range 1.5–9 nm) have no effect on the heat of adsorption of CO. This is not contradictory with the results of (17, 29) because under the experimental conditions of (30) (low pressures of CO) mainly the B species are studied. The results of (30) indicate probably that the heat of adsorption of the B species is independent of the Pd particle size. The above comments show that the results of the present study which give the heat of adsorption of each type of adsorbed species cannot be significantly influenced by the dispersion of the Pd particles.

The first conclusion of the present study is that the heat of adsorption of the L_1 species, varying from 92 kJ/mol at $\theta \approx 0$ to 54 kJ/mol at $\theta \approx 1$, is independent (in the limit of the accuracy ±5 kJ/mol) of the parameters involved in the preparation of the solids (Table 1) such as (a) the composition of the support (i.e., Al_2O_3 (two origins), CeO_2/Al_2O_3, and $La_2O_3/CeO_2/Al_2O_3$), (b) the nature of the salt precursors of the support, (c) the nature of the salt precursor of the metallic phase (with and without chlorine), and (d) the mode of impregnation of Pd on the support (see Figs. 3, 8, and 13). The above conclusion also seems to be valid for the L_2 species. However, for this species it has been shown only that the heat of adsorption does not decrease (an increase cannot be detected). Another conclusion is that the heat of adsorption of the L_1 species is independent of the position of the IR band at 300 K, although this position is influenced by some parameters of the preparation such as the presence of residual chlorine and/or the decoration of the particles. We have found no data in the literature on the heat of adsorption of the L species on supported Pd catalysts to confirm or to contradict our conclusions. However, the heat of adsorption at low coverage (92 kJ/mol) is equal to that found on model Pd particles deposited on Ta(110) (3) (which form only an L species) and on W (21). In this last study the authors determine the heats of adsorption of CO at low (87 kJ/mol) and high coverages (50 kJ/mol), both values in agreement with our results. Taking into account the differences in the preparation of the various solids (present solids, (3) and (4)) it can only be concluded that the heat of adsorption of the L species is almost independent of the method of preparation of the Pd-supported solids.

At the opposite of the L species, the heat of adsorption of the B species is influenced by some of the parameters involved in the preparation of the Pd-supported solids. However, the higher difference observed (Fig. 13) at $\theta = 1$ is 30 kJ/mol, between the values for Pd(Cl)/CeO_2/Al_2O_3 solid (75 kJ/mol) and the La_2O_3-containing solid (105 kJ/mol). On four Pd-containing solids studied the heat of adsorption of the B species increases with the decrease in θ according to a linear relationship. On the Pd(Cl)/CeO_2/Al_2O_3 solid a jump in the heat of adsorption is detected between $\theta = 0.6$ and $\theta = 0.8$. Moreover, on the various solids the values converge to $\approx$170 kJ/mol at $\theta \approx 0$. This leads to the following conclusion: the heat of adsorption of the B species at $\theta \approx 0$ is not influenced by the parameters involved in the preparation of the solid (nature of the support, precusor salts, . . .) and corresponds to that determined on monocrystals. Some correlated conclusions are (a) the heat of adsorption at low coverage is not a function of the position of the IR band of the B species at 300 K (around 1980 cm^{-1} for B_1, 1965 cm^{-1} for B_3, and 1940 cm^{-1} for B_2), and (b) if some parameters of the preparations (i.e., residual chlorine) have an effect on the heat of adsorption of the B species at high coverages, their influences disappear at low coverage. Some data of the literature seem to support the above conclusions. It has been observed (31) that whatever the nature of the support of several Pd-containing catalysts, the position of the IR band of the B species shifts to lower wavenumbers when the coverage decreases and tends toward the same value (singletones) around 1900 cm^{-1} ($\pm$10/15 cm^{-1}) (1985 cm^{-1} in (31) and 1910 cm^{-1} in (32)). This value is close to that observed on monocrystals (31). It is considered that the singletone may vary slightly according to the particle size (31). Taking into account this last remark, some authors (31) conclude that "singletones of appropriate carbonyl types for Pd, (Rh and Pt), are close to those for monocrystals and, in fact, are independent of the support and preparations conditions." This conclusion is in full agreement with our observations on the heat of adsorption of the B species at low coverage. Note that on the Pd-containing solids of the present study, the position of the IR band of the B species at $\theta \approx 0.5$, around 1900 cm^{-1} (the higher value is 1911 cm^{-1} on Pd(Cl)/CeO_2/Al_2O_3), is in agreement with that observed at a lower coverage in (29, 31).

At high coverage of the sites, the heat of adsorption of the B species is influenced by the preparation method. Thus, we have observed (Fig. 8) that the presence of chlorine on two supports (Al_2O_3 and CeO_2/Al_2O_3) decreases the heat of adsorption at $\theta \approx 1$. This effect was also observed by Chou and Vannice (17), using a microcalorimetry method, but was not commented on by the authors. Under their experimental conditions, the heat of adsorption of CO (B and L species are not differentiated) is determined at high coverages of the B species with nevertheless a contribution of the heat of adsorption of the L species (13). The authors (17) have used several Pd-supported catalysts prepared with different supports (SiO_2, Al_2O_3, SiO_2/Al_2O_3, and TiO_2) and precursors (with and without chlorine). Their main objectives were to study the effects of the particle size and the nature of the support on the heat of adsorption of CO. We have noted above their conclusions on the particle size effect and our results. However, even though these authors did not consider the effects of residual chlorine, their results (Table 3 in (17)) show that, whatever the particle size and the support, all the solids prepared with a chlorine precursor ($PdCl_2$) exhibit a heat of adsorption significantly lower than that determined on solids prepared with a precursor without chlorine. For instance, a 1.95% Pd (Cl)/SiO_2/Al_2O_3 solid prepared with $PdCl_2$ with a particle size in the range 3.2–3.9 nm leads to a heat of adsorption of around 22 kcal/mol while a 0.98% Pd(Cl-f)/SiO_2/Al_2O_3 solid with a particle size of 2.5 nm leads to a heat of adsorption of 32 kcal/mol. A 0.36% Pd(Cl)/Al_2O_3 solid with a particle size of 1.8 nm leads to a heat of adsorption of 23.5 kcal/mol while a 0.32% Pd(Cl-f)/Al_2O_3 solid with a particle size of 2.3 nm leads to a heat of adsorption of 32.5 kcal/mol. A 2.03% Pd(Cl)/TiO_2 solid with a particle size of 3.6 nm leads to a heat of adsorption of 23.8 kcal/mol and a 1.88% Pd(Cl-f)/TiO_2 with a particle size of 6.9 nm gives a heat of adsorption of 30.4 kcal/mol. Thus, the results of (17) reveal that whatever the Pd particle size and the nature of the support, the precursor with chlorine leads to a heat of adsorption of CO lower than that determined with the solids prepared without chlorine. The difference, around 8 kcal/mol, is in agreement with that determined in the present study for the B species at high coverages (30 kJ/mol) on the Al_2O_3 and CeO_2/Al_2O_3 supports. The above discussion leads to the conclusion that the presence of residual chlorine on the Pd particles decreases the heat of adsorption of the B species at high coverages. Note that it has been observed that the presence of alkali metal on Pd/SiO_2 increases slighlty (10 kJ/mol) the heat of adsorption of CO (28). In the present study an exception to the above conclusion has been found with the Pd/LaO_3/CeO_2/Al_2O_3 solid prepared with $PdCl_2$: the heat of adsorption of the B species at $\theta = 1$ is close to that on a solid prepared without chlorine. In this respect there are some other factors which eliminate the effect of Cl. We suggest that the decoration of the particles with LaO_x fragments (25) may lead to a decrease in the level of the residual chlorine on the Pd particles and to a heat of adsorption of the B species similar to those of the solids prepared without any chlorine.

Concerning the influence of the support on the heat of adsorption, it can be concluded that at low coverages of the L and B species the nature of the support (Al_2O_3, CeO_2/Al_2O_3, and La_2O_3/CeO_2/Al_2O_3) has no effects. At high coverages for the same precursor (with or without chlorine) the heats of adsorption of the L and B species are not influenced by the nature of the support (Al_2O_3 and CeO_2/Al_2O_3). These conclusions agree (a) with those of Chou and Vannice (17) who conclude that "there is no evidence that the heat of adsorption is noticeably affected by the supports (SiO_2, Al_2O_3, SiO_2/Al_2O_3, and TiO_2) used to prepare the catalyst" and (b) with those of Henry *et al.* on Pd model particles deposited on MgO and mica (29).

The above conclusions deserve two comments. The first is that the rate of a given reaction, involving CO, on the Pd-containing solids depends on the coverage of the CO species. The present study shows that only the coverage of the B species can be affected by the presence of residual chlorine on the Al_2O_3 and CeO_2/Al_2O_3 supports. However, the ratio between the coverages on two solids (without and with chlorine) is not higher than $\approx$1.2 at $\approx$510 K (Figs. 3 and 8). This means that a higher increase in the rate of a catalytic reaction must involve a factor other than the heat of adsorption. The second comment is that there is no correlation between the heats of adsorption of the L and B species and the positions of their IR bands at 300 K. This also agrees with the study of the influence of the alkali metal on Pd/SiO_2 solids (28), which indeed showed that the IR bands of the L and B species were strongly affected (decrease of $\approx 30\ cm^{-1}$ of the IR band of the L species and of more than $100\ cm^{-1}$ for the IR band of the B species) but that the heat of adsorption is only slightly modified (increase of 10 kJ/mol).

CONCLUSIONS

The evolutions of the FTIR spectra recorded on five Pd-supported solids with the adsorption temperature of CO have been used for the determination of the heats of adsorption of the linear (denoted L) and of the bridged (denoted B) CO species as a function of the coverage of each species. The comparison between the various solids has made it possible for us to study the influence on the heat of adsorption of some parameters involved in the preparation of the solids, such as (a) the nature of the support (Al_2O_3, CeO_2/Al_2O_3, and $La_2O_3/CeO_2/Al_2O_3$), (b) the precursor of the support, and (c) the precursor of the metallic phase (with and without chlorine).

The heat of adsorption of an L_1 species varies with the coverage from 92 kJ/mol at $\theta = 0$ to 54 kJ/mol at $\theta = 1$ according to a linear relationship. A second L_2 species is present in lower concentration than the L_1 species on the Pd surface and its heat of adsorption is higher than 165 kJ/mol. The heats of adsorption of the two species are independent of the method of preparation of the solids.

The heat of adsorption of the B species on a Pd(Cl-f)/Al_2O_3 solid varies with the coverage from 168 kJ/mol at $\theta = 0$ to 92 kJ/mol at $\theta = 1$. It has been shown that some parameters of the preparation influence the heat of adsorption of the B species at high coverages, but all the solids lead to the same heat of adsorption at low coverages. The presence of residual chlorine decreases the heat of adsorption at $\theta = 1$ of around 20–30 kJ/mol. However, in the presence of La_2O_3, the effect of Cl is not observed and this is probably linked to the formation of an LaO_x fragment on the palladium particles.

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