

Research Note

# Heats of adsorption of the linear CO species on Pt/Al<sub>2</sub>O<sub>3</sub> using infrared spectroscopy: impact of the Pt dispersion

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Received 24 July 2002; revised 20 November 2002; accepted 2 December 2002

## Abstract

In previous studies, it has been shown that the heats of adsorption at several coverages of each adsorbed CO species (linear, bridged, and threefold coordinated) on a 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst can be obtained from the change in the IR band area of each adsorbed CO species with the adsorption temperature  $T_a$  (in the 300–800 K range) at a constant CO partial pressure  $P_a$ . In the present study, this procedure is used to reveal the eventual impact of the Pt dispersion (range 0.44–0.75) on the heats of adsorption of the linear CO species adsorbed on several Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. It is shown that the Pt dispersion has no strong impact on this parameter at several coverage values.

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## 1. Introduction

To improve the understanding of the CO adsorption on supported metal catalysts an effort must be performed to characterize each adsorbed CO species (i.e., linear and multibound). We have previously shown [1] that the heats of adsorption of each CO species (linear, bridged, and threefold coordinated CO species, denoted by L, B, and 3FC, respectively) adsorbed on a 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst can be determined using an analytical procedure called adsorption equilibrium infrared spectroscopy (AEIR) [2]. The evolution of the IR band intensities of each CO species with the adsorption temperature  $T_a$  at a given partial CO pressure  $P_a$  allows us to determine for each CO species (a) the evolution of their coverages with  $T_a$  and (b) their heats of adsorption at several coverages [1,2]. It has been observed [1,2] that the heats of adsorption (denoted  $E_\theta$ ) of the three adsorbed CO species linearly decrease with the increase in their coverage (denoted  $\theta$ ): (a) from  $E_{L_0} = 206$  kJ/mol to  $E_{L_1} = 115$  kJ/mol for the L species; (b) from  $E_{B_0} = 94$  kJ/mol to  $E_{B_1} = 45$  kJ/mol for the B species, and (c) from  $E_{3FC_0} = 135$  kJ/mol to  $E_{3FC_1} = 104$  kJ/mol for the 3FC species. The AEIR method allows us to study easily how the heats of adsorption of specific adsorbed CO species are modified

by parameters involved in the catalyst preparation such as the salt precursor of the metal particles [3]. In the present study, the AEIR method is used to reveal the impact of the Pt dispersion on the heat of adsorption of the L CO species. This species which dominates the CO adsorption on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts is involved in the CO/O<sub>2</sub> reaction [4–6].

## 2. Experimental

Several  $x\%$  Pt/Al<sub>2</sub>O<sub>3</sub> catalysts ( $x = 0.1, 1.2, \text{ or } 2.9$  in wt%) were prepared by the incipient wetness method. Alumina (Degussa  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, BET area 100 m<sup>2</sup>/g) was impregnated using an appropriate amount of aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> ·  $x$ H<sub>2</sub>O (Aldrich). After drying at 373 K, the powder is treated in air at 713 K as previously described [1,2,4–6]. Before CO adsorption the catalysts were pretreated and reduced according to the following procedure: He (713 K, 10 min) → O<sub>2</sub> (713 K, 10 min) → He (713 K, 10 min) → H<sub>2</sub> (713 K, 30 min) → He (713 K, 5 min) → He (300 K). The Pt dispersions of the different catalysts were determined using CO chemisorption at room temperature with an analytical system described elsewhere [5] using a quadrupole mass spectrometer as the detector. It permitted the determination of the composition (molar fractions, denoted MF) of the gas mixture (flow rate  $\approx 100$  cm<sup>3</sup>/min, total pressure = 1 atm) at the outlet of a quartz microreactor after a calibration procedure. The CO adsorption at 300 K is performed accord-

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ing to a switch He  $\rightarrow$  1% CO/2% Ar/He mixture. For the FTIR study the catalyst was compressed to form a disk ( $\Phi = 1.8$  cm) that was placed in the sample holder of a small internal volume stainless steel IR cell (transmission mode) described elsewhere [7]. This IR cell enabled in situ treatments (293–900 K) of the solid, at atmospheric pressure, with a gas flow rate in the range of 150–2000 cm<sup>3</sup>/min. The experimental procedure of the AEIR method consisted of introducing at  $T_a = 300$  K a 1% CO/He mixture (total pressure = 1 atm, flow rate = 200 cm<sup>3</sup>/min) on the reduced catalyst and then  $T_a$  was slowly increased ( $\approx 5$ –10 K/min) to 700 K while the FTIR spectra of the adsorbed species were periodically recorded. The AEIR procedure imposed that the evolutions of a specific IR band with the increase in  $T_a$  were only due to the adsorption equilibrium and not to the overlaps of different processes such as adsorption equilibrium and disappearance of the Pt sites by sintering or poisoning. In a previous study [1,2], it has been observed that the first increase in  $T_a$  with 1% CO/He on a fresh catalyst led to a decrease of the number of Pt sites. Then the cycles that followed CO adsorption at high temperatures/reduction did not strongly modify the Pt dispersion and the solid was considered stabilized. The experiments performed in the present study have been obtained on a stabilized solid after two increases in  $T_a$  with 1% CO/He followed by the reduction procedure.

### 3. Results and discussion

#### 3.1. Determination of the Pt dispersion

The dispersion has been measured according to the procedure previously described [5,8]. The total CO uptake (irreversible and reversible CO species) at 300 K; QTCO, is obtained from the evolutions of the MFs of Ar and CO during a switch He  $\rightarrow$  1% CO/2% CO/He on the stabilized 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> solid. The amount of reversible CO species at 300 K; QrCO = 4  $\mu$ mol/g<sub>cat</sub>, ascribed to B CO species [1,5] is determined from readsorption experiments according to 1% CO/2% Ar/He  $\rightarrow$  He  $\rightarrow$  1% CO/2% Ar/He [5]. The adsorption of CO on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts mainly leads to the L CO species on Pt sites [1] justifying the ratio; CO/Pt<sub>s</sub> = 1, for the determination of the dispersion as recently considered by Fanson et al. [9]. Moreover, it has been shown that O<sub>2</sub> and H<sub>2</sub> adsorption at 300 K gives similar dispersion values (O/Pt<sub>s</sub> = 1 and H/Pt<sub>s</sub> = 1) for the 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> [5]. The dispersion  $D$  and the average particle sizes  $d$  ( $d$  (nm)  $\approx 1.1/D$  similar to [10]) of the different stabilized catalysts are listed in Table 1. The modification of the Pt dispersion during the stabilization pretreatment of the 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst has been studied in detail [8]. We have used hydrogen chemisorption (1% H<sub>2</sub>/2% Ar/He) to confirm the Pt dispersion on 1.2% Pt/Al<sub>2</sub>O<sub>3</sub> without observing significant differences with CO chemisorption.

Table 1

Pt dispersions, average Pt particle sizes, and heats of adsorption of the L CO species on stabilized Pt/Al<sub>2</sub>O<sub>3</sub> catalysts

| Catalyst                               | Dispersion | Particle diameter (nm) | Heats of adsorption (kJ/mol) |              |
|--|------------|------------------------|------------------------------|--------------|
|  |            |                        | $\theta = 0$                 | $\theta = 1$ |
| 2.9% Pt/Al <sub>2</sub> O <sub>3</sub> | 0.44       | 2.5                    | 206                          | 115          |
| 1.2% Pt/Al <sub>2</sub> O <sub>3</sub> | 0.65       | 1.7                    | 220                          | 106          |
| 0.1% Pt/Al <sub>2</sub> O <sub>3</sub> | 0.75       | 1.4                    | 210                          | 100          |

#### 3.2. Impact of $D$ on the IR spectra of the adsorbed CO species

Fig. 1 shows the IR spectra obtained at 300 K after adsorption of 1% CO/He on the different solids. The increase in the dispersion leads to a red shift of the IR band of the L CO species: 2073, 2066, and 2054 cm<sup>-1</sup> for  $D = 0.44$  (2.9% Pt/Al<sub>2</sub>O<sub>3</sub>),  $D = 0.65$  (1.2% Pt/Al<sub>2</sub>O<sub>3</sub>), and  $D = 0.75$  (0.1% Pt/Al<sub>2</sub>O<sub>3</sub>), respectively. These observations are similar to those of Fanson et al. [9] on platinum supported silica: 2076, 2065, and 2058 cm<sup>-1</sup> for  $D = 0.60$  (3% Pt/SiO<sub>2</sub>),  $D = 0.90$  (0.6% Pt/SiO<sub>2</sub>), and  $D = 0.99$  (0.05% Pt/SiO<sub>2</sub>), respectively. The authors [8] explained this shift considering the Blyholder's model [11] for the bonding of CO molecules to metal surfaces. For small Pt particles the average number of Pt–Pt bonds per Pt atom is less than that in the larger particles and a higher metal electron density is available for back bonding into the  $2\pi^*$  orbital of adsorbed CO molecules [8]. This leads to a decrease in the C–O bond strength and a resulting decrease in the CO stretching frequency.

Fig. 1 shows that the IR band of the L CO species dominates the CO adsorption while those of the multibound CO species in the range 2000–1750 cm<sup>-1</sup> are very weak

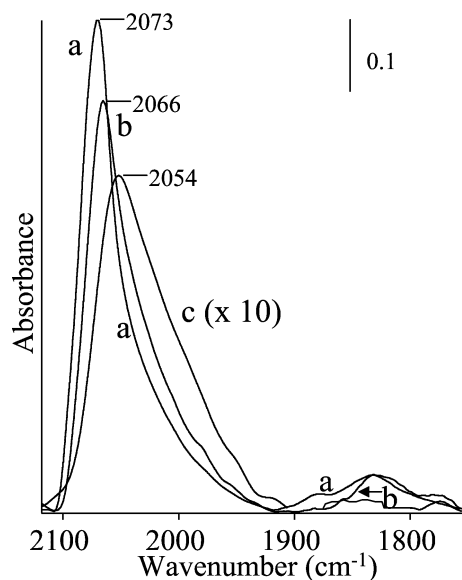


Fig. 1. FTIR spectra recorded at 300 K on reduced stabilized solids with the 1% CO/He mixture: (a) 2.9% Pt/Al<sub>2</sub>O<sub>3</sub>; (b) 1.2% Pt/Al<sub>2</sub>O<sub>3</sub>; (c) 0.1% Pt/Al<sub>2</sub>O<sub>3</sub>.

(not detected on 0.1% Pt/Al<sub>2</sub>O<sub>3</sub>). This explains that the impact of the dispersion has only been studied on the heat of adsorption of the L CO species.

### 3.3. Evolutions of the IR band of the L CO species with $T_a$

These evolutions for a constant CO partial pressure  $P_a$  (1% CO/He) on the stabilized 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst have been described in detail [1,2,12]. However, to facilitate our presentation the results are briefly summarized here. The increase in  $T_a$  with 1% CO/He leads to the increase in the intensity of the IR band for  $T_a \lesssim 400$  K alongside a shift to 2067 cm<sup>-1</sup> at 398 K. This shift is associated to the detection of a shoulder at 2086 cm<sup>-1</sup>. This has been tentatively ascribed to the reconstruction of the CO/Pt surface system in the course of the CO adsorption. For  $T_a > 400$  K, it is observed [1,12] that (a) the shoulder shifts (2080 cm<sup>-1</sup> at 564 K and 2068 cm<sup>-1</sup> at 715 K); (b) the main IR band also shifts to lower wavenumbers (2059 cm<sup>-1</sup> at 564 K and 2052 cm<sup>-1</sup> at 715 K); (c) the IR band area (the shoulder and the main IR band are not differentiated) is constant between  $\approx 440$  K and  $\approx 600$  K; and (d) the IR band area decreases for  $T_a > 600$  K.

The evolution of the IR band of the L CO species for the stabilized 1.2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with 1% CO/He leads to similar observations (Fig. 2): (a) the main IR band at 2066 cm<sup>-1</sup> at 300 K shifts to lower wavenumbers: 2056 cm<sup>-1</sup> at 493 K (Fig. 2d) and 2047 cm<sup>-1</sup> at 693 K (Fig. 2g); (b) a shoulder at 2080 cm<sup>-1</sup> is detected at 373 K (Fig. 2b); (c) this shoulder shifts to lower wavenumbers with the increase in  $T_a$  (2064 cm<sup>-1</sup> at 693 K, Fig. 2g); and (d) the IR band area (the shoulder and the main IR band are not differentiated) increases for  $T_a < 480$  K, then remains constant for  $480 \text{ K} < T_a \lesssim 580 \text{ K}$ , and finally

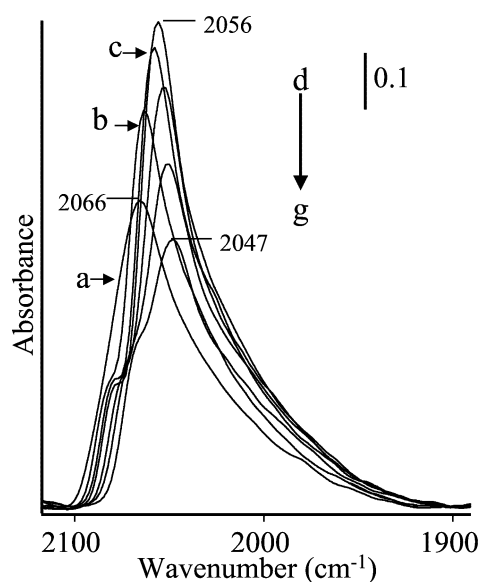


Fig. 2. Evolution of the IR band of the L CO species with  $T_a$  using the 1% CO/He mixture for 1.2% Pt/Al<sub>2</sub>O<sub>3</sub>: (a)–(g)  $T_a = 300, 373, 443, 493, 603, 648, 693$  K.

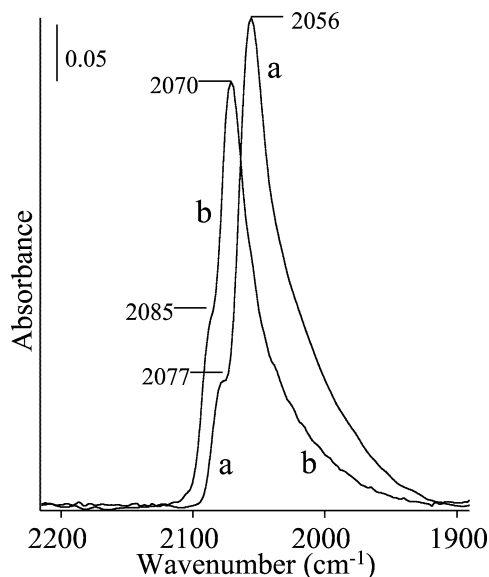


Fig. 3. Comparison of the FTIR spectra of the L CO species on 1.2% Pt/Al<sub>2</sub>O<sub>3</sub> before and after heating at 693 K in 1% CO/He: (a) at 483 K before heating and (b) at 323 K after heating.

decreases for higher temperatures. The increase in the IR band intensity and the detection of the shoulder at 383 K show that the Pt surface is modified by the CO adsorption at high temperatures as observed on 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> [1,2,12]. It must be noted that, if after adsorption at 480 K, the catalyst is cooled in the presence of 1% CO/He, the IR band area remains constant (result not shown), indicating that the modification of the surface during the heating stage in CO is irreversible as previously observed on 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> [1,2,12]. However, at the difference of the 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst [1,7,12], cooling of the solid in 1% CO/He after heating at 693 K reveals a decrease by  $\approx 25\%$  (Fig. 3) in the IR band area of the L CO species. This is possibly linked to the poisoning of the Pt surface by the carbon deposition coming from the disproportionation reaction;  $2\text{CO} \rightarrow \text{C}_{\text{ads}} + \text{CO}_2$ , detected at high adsorption temperatures using a mass spectrometer [8]. On 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> this reaction is also detected but its impact on the IR band intensity of the L CO species before and after heating to 713 K is limited [1,7,12].

On the stabilized 0.1% Pt/Al<sub>2</sub>O<sub>3</sub> solid, the evolutions of the IR spectra during the increase in  $T_a$  with 1% CO/He (Fig. 4) are similar to those on the other Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. However, it can be observed that there is no shoulder at  $\approx 2080$  cm<sup>-1</sup> on this solid. The IR band of the L CO species shifts to lower wavenumbers: 2054, 2048, and 2040 cm<sup>-1</sup> at 300, 471, and 698 K, respectively. The IR band area (a) increases for  $T_a < 473$  K, (b) is constant between 473 and 540 K, and (c) finally decreases for  $T_a > 540$  K. Similar to the 1.2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst the comparison of the IR band area at  $T_a < 470$  K before and after heating to 700 K reveals a decrease by 25% probably due to the CO disproportionation.

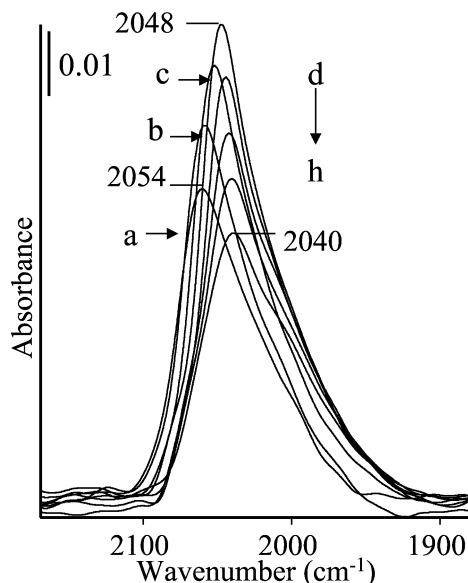


Fig. 4. Evolution of the IR band of the L CO species with  $T_a$  using the 1% CO/He mixture for 0.1% Pt/Al<sub>2</sub>O<sub>3</sub>: (a)–(h)  $T_a = 321, 368, 418, 471, 573, 623, 673, 698$  K.

The presence or the absence of the shoulder at 2080 cm<sup>-1</sup> during the CO adsorption is a parameter which differentiates the three solids. In a previous study on Pt/Al<sub>2</sub>O<sub>3</sub> [12] and according to Anderson and Rochester [13] this shoulder has been tentatively attributed to L CO species adsorbed on platinum atoms existing in small mats or arrays, possibly strongly interacting with the alumina support. However, this explanation is not in agreement with the absence of the shoulder on the solid with the highest dispersion (Fig. 4). In a recent study [9] the authors suggested, considering an early work of Herz and Shinouskis [14], that this IR band is linked to Pt<sup>δ+</sup> site due to the presence of residual chlorine. The absence of the shoulder on 0.1% Pt/Al<sub>2</sub>O<sub>3</sub> is possibly linked to the low amount of Cl introduced during preparation.

### 3.4. Heats of adsorption of the L CO species and Pt dispersion

In the AEIR method, the coverage of a specific CO species on several supported metal catalysts (i.e., Pt [1,2,7,12], Pd [15–17], Cu [18], Ru [19]) is obtained using the ratio between its IR band area at  $T_a$  and its highest IR band area considering as shown in [8,20] that (a) the intensity of the IR band is proportional to the amount of the adsorbed CO species on the metal surface; and (b) the IR absorption extinction coefficient is independent of  $T_a$ . Curve a in Fig. 5 provides for  $T_a \geq 400$  K the change in the coverage  $\theta_L$  of the Pt site by the L CO species with  $T_a$  for the stabilized 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> [1,2] solid. Fig. 5a shows that  $\theta_L$  is constant between  $\approx 520$  and  $\approx 600$  K and then decreases in a straight line in a wide range of temperatures.

The heats of adsorption of a specific adsorbed CO species at several coverages are determined comparing the experimental curves  $\theta_L = f(T_a)$  to theoretical curves

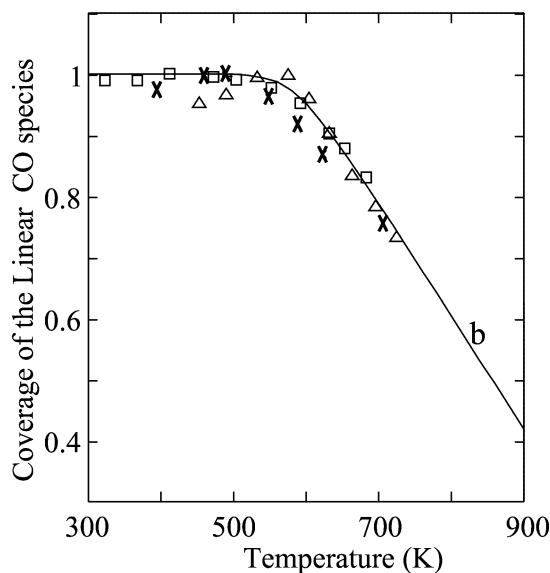


Fig. 5. Evolution of the coverage of the L CO species with  $T_a$  for  $P_a = 1000$  Pa:  $\Delta$ , (a) experimental data for 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> (heating stage); (b) theoretical curve according to the adsorption model (see the text for more details);  $\square$ , (c) experimental data for 1.2% Pt/Al<sub>2</sub>O<sub>3</sub> (cooling stage);  $\times$ , (d) experimental data for 0.1% Pt/Al<sub>2</sub>O<sub>3</sub> (cooling stage). Note that (a), (c), and (d) are experimental data points.

obtained from an adsorption model [1–7,12,15–19]. This model assumes that (a) the adsorbed species are localized and (b) the heat of adsorption linearly decreases with the increase in  $\theta$ . According to assumption (a), the statistical thermodynamics [21,22] gives the adsorption coefficient  $K$  (ratio of the rate constant of adsorption and desorption)

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

where  $h$  is Planck's constant,  $k$  is Boltzmann's constant,  $m$  is the mass of the molecule ( $28 \times 10^{-3}$  kg/( $6.02 \times 10^{23}$ )),  $T_a$  is the adsorption temperature,  $E_d$  and  $E_a$  are the activation energies of desorption and adsorption respectively, and  $E_d - E_a$  is the heat of adsorption (denoted by  $E$ ). Assumption (b) leads to an expression of the coverage for an adsorbed species given by [12,15–19] and references therein

$$\theta = \frac{RT_a}{\Delta E} \ln\left(\frac{1 + K_0 P_a}{1 + K_1 P_a}\right), \quad (2)$$

where  $\Delta E$  is the difference in the heats of adsorption at  $\theta = 0$  ( $E_0$ ) and  $\theta = 1$  ( $E_1$ ),  $K_0$  and  $K_1$  are the adsorption coefficients at  $\theta = 0$  and  $\theta = 1$ , respectively, and  $T_a$  and  $P_a$  are the adsorption temperature and pressure, respectively. For the determination of  $E_1$  and  $E_0$  we only have to find the values to be used in (1) and (2) to obtain the best fit between the experimental and the theoretical values of the coverage [1,2,7,12]. For instance, curve b in Fig. 5 which overlaps curve a is obtained by using in expressions (1) and (2)  $E_0 = 206$  kJ/mol and  $E_1 = 115$  kJ/mol with an accuracy of  $\pm 5$  kJ/mol [1,2,12]. In previous studies, it has been shown that these values are in good agreement (a) with the isosteric

heats of adsorption [12] and (b) with certain data in the literature on Pt-containing solids [1,7,12] and references therein.

The experimental curves  $\theta_L = f(T_a)$  for the stabilized 1.2% Pt/Al<sub>2</sub>O<sub>3</sub> and 0.1% Pt/Al<sub>2</sub>O<sub>3</sub> catalysts are shown Figs. 5c and 5d, respectively, using the FTIR spectra recorded during the cooling stage in 1% CO/He (to prevent the impact of the C deposition on the IR band area). The values of the heats of adsorption at high and low coverage to fit the experimental data (see Table 1) are very close to those found on the 2.9% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst [1,2,12]; roughly whatever the Pt dispersion  $E_{L_0} = 212 \pm 8$  kJ/mol and  $E_{L_1} = 105 \pm 5$  kJ/mol. This indicates that the Pt dispersion does not have a strong impact on the heat of adsorption of L CO species although it affects its IR band position (Fig. 1). In a previous study [23] on a 0.5% Pt/ZrO<sub>2</sub> solid with a low Pt dispersion ( $D = 0.05$ ), it has been observed using the AEIR method that  $E_{L_0} = 195$  and  $E_{L_1} = 96$  kJ/mol. These values are not very different from those on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with higher Pt dispersions confirming the above conclusion. Moreover,  $E_{L_0} = 212 \pm 8$  kJ/mol for  $D$  in the 0.44–0.75 range are close to that found at a low coverage by Yeo et al. [24] on Pt(100) using single crystal microcalorimetry, 225 kJ/mol. This also confirms that the Pt dispersion has a limited impact on the heat of adsorption of the L CO species. The  $E_{L_0}$  value also agrees with theoretical calculations for the adsorption of the L CO species on Pt clusters: Liao et al. [25] determined 185 kJ/mol at low coverage on a Pt<sub>10</sub> while Curulla et al. [26] on Pt<sub>40</sub> found 192 and 199 kJ/mol on center and corner atoms, respectively. In a recent study Podkolzin et al. [27] showed using microcalorimetric measurements at high temperatures under adsorption equilibrium conditions that the heat of adsorption of CO on 5.6% Pt/SiO<sub>2</sub> ( $D = 0.62$ ) at a low coverage is at least 190–180 kJ/mol in agreement with DFT calculations for linear CO species on Pt<sub>13</sub> clusters, 217 kJ/mol. It seems clear from the present study and the data in the literature that the Pt dispersion has a very limited impact on the heat of adsorption of the L CO species at low coverage. In addition, the AEIR method leads to the conclusion that this is also true for high coverage values. This agrees with Sen and Vannice's [28] study on the impact of Pt crystallite sizes of Pt/SiO<sub>2</sub> catalysts on the integral heat of adsorption of CO at 300 K using a microcalorimetric method. They showed that there is no significant variation of this parameter,  $123 \pm 16$  kJ/mol in the 1.3 to 22 nm particle size range. Note that this value is probably the average of the heats of adsorption of the various adsorbed CO species even if the L CO species dominates the adsorption (Fig. 1). Similar results have been obtained by Sharma et al. [29] on 1.22%, 3.55%, and 7.18% Pt/SiO<sub>2</sub>. The authors determined an average value of  $140 \pm 3$  kJ/mol for dispersion values in the range 0.51–0.76.

Some catalytic reactions are structure sensitive: their rates (i.e. turnover number) depend on the crystallite size [30] as observed by Zafiris and Gorte [31] for the CO/O<sub>2</sub> reaction on Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001). This must be due to the modifications of the kinetic parameters of the surface elementary steps in-

involved in the reaction as studied in [4–6]. By kinetic modeling, Zafiris and Gorte [31] concluded that the activation energy of the reaction which decreases by 44 kJ/mol from 164 to 120 kJ/mol for  $d = 1.7$  nm and  $d = 14$  nm respectively is equal to the heat of adsorption of CO. The present study reveals that it is not the change in the heat of adsorption of the L CO species (the plausible adsorbed intermediate species of the CO/O<sub>2</sub> reaction [4–6]) which can be used to explain the impact of  $D$  on the rate of the CO/O<sub>2</sub> reaction. However, the kinetic modeling which supports the conclusion in [31] is based on a formal mechanism which does not consider the nature of the adsorbed CO species (i.e., L or B) involved in the CO/O<sub>2</sub> reaction. For instance, it can be noted that in [31] TPD experiments after CO adsorption revealed a strong CO peak at  $\approx 410$  K associated to a smaller peak at 510 K on large Pt particles while on 1.7 nm Pt particles a strong peak at 510 K with a weak shoulder at 410 K was observed. This is interpreted mainly considering differences in the repulsive interaction between CO neighboring molecules with the particle size. However, this can be also interpreted by the modification with  $D$  of the proportion of two adsorbed CO species with different activation energies of desorption such as L (highest energy) and B (lowest energy). In a forthcoming paper in line with previous studies ([4–6], Bourane and Bianchi, submitted for publication), it is shown that the Pt dispersion (in the 0.44–0.75 range) affects the kinetic parameters of some surface elementary steps of the CO/O<sub>2</sub> reaction on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts showing that the reaction can be structure sensitive in agreement with [31]. However, it is not the modification of the heat of adsorption of the L CO species (the CO adsorbed intermediate species of the CO/O<sub>2</sub> reaction) which can be involved in the explanation.

#### 4. Conclusion

In the present study, the AEIR method [2] has been used to determine the impact of the Pt dispersion on the heat of adsorption of the L CO species on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. The evolution of its coverage  $\theta_L$  with  $T_a$  has been obtained from the change in the intensity of its characteristic IR band. The comparison of the experimental curves  $\theta_L = f(T_a)$  with those obtained from an adsorption model allows us to determine the heats of adsorption of the L CO species at several coverages. It has been shown that the Pt dispersion  $D$  in the 0.44–0.75 range does not affect significantly the heats of adsorption of the L CO species which linearly decrease with the increase in  $\theta_L$  from  $212 \pm 8$  kJ/mol at  $\theta_L = 0$  to  $108 \pm 7$  kJ/mol at  $\theta_L = 1$ .

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