

# Heats of Adsorption of the Linear CO Species Adsorbed on a Ir/Al<sub>2</sub>O<sub>3</sub> Catalyst Using in Situ FTIR Spectroscopy under Adsorption Equilibrium

Abdenmour Bourane, Mostafa Nawdali, and Daniel Bianchi\*

Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 5634, Université Claude Bernard, Lyon-I, Bat. 303, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France

Received: October 8, 2001; In Final Form: December 14, 2001

The adsorption of CO on a reduced 1% Ir/Al<sub>2</sub>O<sub>3</sub> catalyst has been studied by using Fourier transform infrared spectroscopy (FTIR) at two constant CO partial pressures  $P_a$  (200 and 2000 Pa) in the adsorption temperature (denoted by  $T_a$ ) range of 300–740 K. At 300 K, it is observed a strong IR band at 2044 cm<sup>-1</sup> ascribed to linear CO species (denoted by L) associated to weak shoulders at  $\approx 2080$  and  $\approx 2000$  cm<sup>-1</sup>. The FTIR spectra show how the coverage  $\theta_L$  of the L CO species evolves with  $T_a$  for the two  $P_a$  values. At  $T_a > 580$  K, the curves  $\theta_L = f(T_a)$  are in very good agreement with an adsorption model based on Temkin's approximations indicating that the heat of adsorption linearly increases with the decrease in  $\theta_L$  from  $E_1$  to  $E_0$  at  $\theta_L = 1$  and 0, respectively. This allows us to evaluate the ratio  $E_0/(E_0 - E_1) \approx 2.1$  and then  $E_0 - E_1 \approx 115$  kJ/mol. Moreover, it is shown that, in the  $T_a$  range of 300–740 K, the curves  $\theta_L = f(T_a)$  for the two CO partial pressures are in very good agreement with an adsorption model considering the following: (a) an immobile adsorbed species and (b) a linear decrease in the heat of adsorption with the increase in  $\theta_L$  from  $E_0 = 225$  kJ/mol at  $\theta_L = 0$  to  $E_1 = 115$  kJ/mol at  $\theta_L = 1$ . Finally the two isobars are used to determine the isosteric heats of adsorption at several coverages in the range of 1–0.8 from the Clausius–Clapeyron equation. A good agreement is observed with the values determined using the adsorption model and this validates the various assumptions involved in the model. The heat of adsorption values are compared to the literature data on single crystals and supported Ir catalysts. Moreover, it is shown that the heat of adsorption values allow us to quantify several quantitative data found in the literature on the stability of the L CO species on Ir-containing solids either in a vacuum or in an inert gas.

## 1. Introduction

The heats of adsorption of the adsorbed species (denoted by  $E$ ) and their evolution with the coverage  $\theta$  (denoted  $E_\theta$  with  $0 \leq \theta \leq 1$ ) constitute a fundamental characterization of the CO/metal system because the  $E_\theta$  values quantify the coverage of the sites under adsorption equilibrium. This parameter is rarely studied on supported metal catalysts as compared to the amount and the nature of the adsorbed CO species due to experimental difficulties using, for instance, temperature programmed desorption (TPD)<sup>1,2</sup> or microcalorimetric methods.<sup>3–5</sup> We have previously shown that an IR cell in transmission mode enables the study of the adsorbed CO species on supported metal catalysts at the adsorption equilibrium in wide pressure and temperature ranges.<sup>6</sup> This allows us to determine the evolution of the coverage  $\theta$  of each adsorbed CO species (i.e., Linear and Bridged CO species denoted by L and B, respectively) with the adsorption temperature  $T_a$  for several adsorption pressures  $P_a$ . The curves  $\theta = f(T_a)$  permit us to determine the isosteric heats of adsorption of CO at several coverages.<sup>7,8</sup> Moreover, it has been shown<sup>7,8</sup> that these values are in good agreement with those obtained from an adsorption model which assumes (a) an immobile adsorbed CO species and (b) a linearly decrease in  $E_\theta$  with the increase in  $\theta$ . This last procedure (denoted by AEIR: adsorption equilibrium infrared spectroscopy<sup>9</sup>) which is very simple (a single isobar) and accurate ( $\pm 5$  kJ/mol) has been used to determine the heats of adsorption of L and/or

B CO species on several supported (on alumina) metal catalysts such as Pt,<sup>6,7,10</sup> Cu<sup>+</sup> and Cu<sup>0</sup>,<sup>8</sup> Pd,<sup>11,12</sup> Rh,<sup>13</sup> and Ru.<sup>14</sup> Other supports have been also used such as CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub><sup>12</sup> and ZrO<sub>2</sub>.<sup>15</sup> This procedure is used in the present study to determine the heats of adsorption of the L CO species adsorbed on 1% Ir/Al<sub>2</sub>O<sub>3</sub> at several coverages. To our knowledge it is the first time that these parameters are determined on a supported Ir catalyst. This allows us to quantify some qualitative literature data on the stability of the L CO species on Ir-containing solids during isothermal desorption.

## 2. Experimental Section

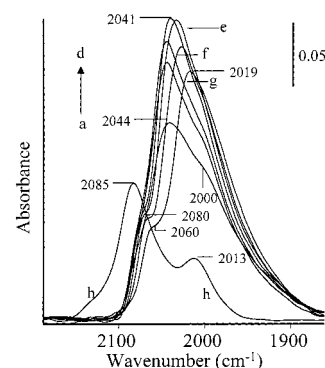
A 1% Ir/Al<sub>2</sub>O<sub>3</sub> (in wt %) catalyst was prepared using the incipient wetness method. Alumina (Degussa C  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was impregnated with an appropriate amount of an aqueous solution of IrCl<sub>3</sub>·3H<sub>2</sub>O. After drying for 24 h at room temperature and then for 12 h at 383 K, the solid was treated in air 12 h at 623 K leading to a BET area of 100 m<sup>2</sup>/g. For the FTIR study, the catalyst was compressed to form a disk ( $\Phi = 1.8$  cm,  $m = 40$ – $90$  mg) which was placed in the sample holder of a small internal volume stainless steel IR cell described elsewhere<sup>6</sup> allowing 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 amounts of adsorbed CO were determined by a volumetric method according to a procedure previously described using a mass spectrometer as a detector.<sup>16,17</sup> Mainly the composition (molar fraction) of the gas mixture at the outlet of a quartz microreactor containing the catalyst was determined

\* To whom correspondence should be addressed. E-mail: daniel.bianchi@univ-lyon1.fr.

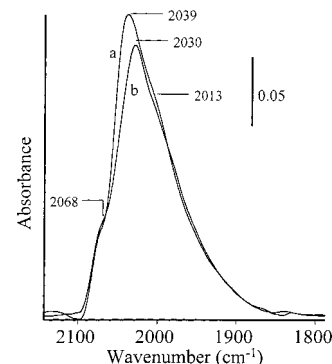
during switches between regulated gas flows such as  $\text{He} \rightarrow x\% \text{CO}/y\% \text{Ar}/\text{He}$  (1 atm,  $100 \text{ cm}^3/\text{min}$ ,  $x$  and  $y$  in the range of 0.5–4) to determine for instance the amount of adsorbed CO.<sup>16,17</sup> Before the first CO adsorption at 300 K, the solid was treated in situ according to  $\text{He}$ , 298 K  $\rightarrow$   $\text{He}$ , 383 K  $\rightarrow$   $\text{H}_2$ , 383 K (1 h)  $\rightarrow$   $\text{H}_2$ , 523 K, (1 h)  $\rightarrow$   $\text{H}_2$ , 713 K (2 h). We have used a high reduction temperature to stabilize the Ir dispersion which is strongly dependent on the pretreatment temperature.<sup>18</sup> This stabilization was a necessity for our analytical procedure because the variation of the intensity of the IR bands of the adsorbed CO species must only be due to the adsorption equilibrium. After this treatment the metallic dispersion determined with the mass spectrometer<sup>16,17</sup> by the irreversible CO chemisorption at 300 K (26  $\mu\text{mol CO/g}$  of catalyst) was  $D \approx 0.5$  using a ratio  $\text{CO}/\text{Ir} = 1$ . This value was in good agreement with those of McVicker et al.<sup>18</sup> on 1% Ir/ $\eta\text{-Al}_2\text{O}_3$  prepared with  $\text{IrCl}_3$  ( $D = 0.67$  and 0.56 after reduction at 748 and 773 K respectively) and of Alexeev and Gates<sup>19</sup> on 1% Ir/ $\gamma\text{-Al}_2\text{O}_3$  prepared from  $\text{Ir}_4\text{CO}_{12}$  after treatment in  $\text{O}_2$  at 573 K before reduction at 673 K:  $D = 0.39$  (without the oxygen pretreatment the dispersion was  $D = 0.78$ ). For the FTIR studies, the same pellet of catalyst was used for several experiments and before each CO adsorption at 300 K the solid was treated as follows (total pressure = 1 atm, flow rate =  $200 \text{ cm}^3/\text{min}$ ):  $\text{He}$ , 713 K  $\rightarrow$   $\text{O}_2$ , 713 K (10 min)  $\rightarrow$   $\text{He}$ , 713 K (10 min)  $\rightarrow$   $\text{H}_2$ , 713 K (1 h) then the solid was cooled to 300 K either in  $\text{H}_2$  or in  $\text{He}$  after 10 min in  $\text{He}$  at 713 K. After adsorption of 2% CO/ $\text{He}$  at 300 K the adsorption temperature  $T_a$  was increased (5–10 K/min) up to 720 K while the FTIR spectra of the adsorbed species were periodically recorded. After the highest adsorption temperature, the solid was cooled to a temperature  $T$  in the presence of 2% CO/ $\text{He}$  and the spectrum was compared to that recorded at a similar temperature in the course of the heating stage. This enabled the detection of the modifications of the catalyst during the CO adsorption at high temperatures such as the poisoning of the surface by the carbon deposition coming from the dissociation/disproportionation reaction of CO:  $2 \text{CO} \rightarrow \text{C}_{\text{ads}} + \text{CO}_2$ . We have observed a decrease in the intensity of the IR bands of the adsorbed CO species after adsorption at 300 K during the three first cycles adsorption of CO at high temperatures/pretreatment, then the solid was stabilized and the dispersion was  $D \approx 0.2$ . The heat of adsorption of the L CO species was determined on stabilized solids.

### 3. Results

**3.1. Adsorption of CO on 1% Ir/ $\text{Al}_2\text{O}_3$  at Several Adsorption Temperatures.** Figure 1 gives the FTIR spectra (Figure 1a–g) recorded on the 1% Ir/ $\text{Al}_2\text{O}_3$  catalyst reduced at 713 K and cooled in  $\text{H}_2$  to 300 K in the course of the adsorption with 2% CO/ $\text{He}$  in the 300–720 K range. At 300 K (Figure 1a), a strong IR band at  $2044 \text{ cm}^{-1}$  is observed (Figure 1a) associated to weak shoulders at  $\approx 2080$  and  $2000 \text{ cm}^{-1}$ . The main IR band at  $2044 \text{ cm}^{-1}$  is ascribed to L CO species (see discussion section).<sup>18–27</sup> Cooling of the sample in helium from 713 to 300 K (after 10 min in  $\text{He}$  at 713 K) leads to a strongly different spectrum (Figure 1h) with two IR bands at 2085 and  $2013 \text{ cm}^{-1}$ . Similar spectra have been observed by Solymosi et al.<sup>26</sup> on 1% Ir/ $\text{Al}_2\text{O}_3$  treated in helium after reduction and by Alexeev et al.<sup>28</sup> after decarbonylation in helium at 573 K of  $\text{Ir}_4\text{CO}_{12}$  supported on  $\text{Al}_2\text{O}_3$ . The two IR bands are assigned to gem dicarbonyl CO species (denoted by G) but the nature of the Ir sites ( $\text{Ir}^0$ ,  $\text{Ir}^{1+}$ , small clusters such as  $\text{Ir}_4$  and  $\text{Ir}_6$ ) is debated.<sup>25,26,28</sup> The small shoulders observed at 2080 and  $2000 \text{ cm}^{-1}$  in Figure 1a probably are due to the presence of a very small amount of

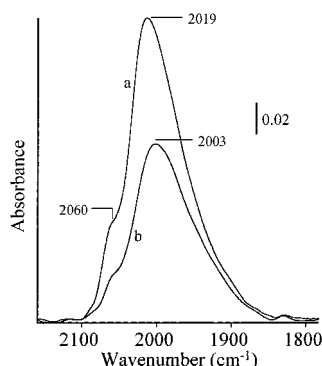


**Figure 1.** FTIR spectra recorded on a reduced 1% Ir/ $\text{Al}_2\text{O}_3$  in the course of the CO adsorption at various temperatures with an adsorption pressure  $P_a = 2000 \text{ Pa}$ : (a) 300 K, (b) 409 K, (c) 438 K, (d) 529 K, (e) 584 K, (f) 643 K, (g) 715 K, and (h). Adsorption of CO at 300 K on a solid treated in helium at 713 K after reduction.



**Figure 2.** Comparison of the FTIR spectra at 510 K on 1% Ir/ $\text{Al}_2\text{O}_3$  before and after heating at 713 K: (a) before and (b) after heating.

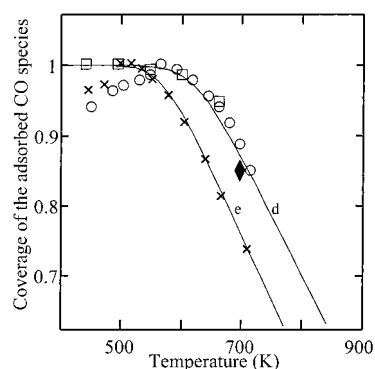
G CO species. Solymosi et al.<sup>26</sup> consider that a disruptive CO chemisorption on large Ir particles may produce the G CO species. The increase in  $T_a$  (Figure 1, curves b–d) leads to the increase in the intensity of the IR band of the L CO species for  $T_a < 500 \text{ K}$  alongside a slight shift to  $2041 \text{ cm}^{-1}$  at 529 K. For higher temperatures the IR band of the L species shifts to lower wavenumbers 2033 and  $2019 \text{ cm}^{-1}$  at 584 and 715 K, respectively, and its intensity decreases. This shift leads to the clear detection of a shoulder at  $2060 \text{ cm}^{-1}$  at 715 K. The results in Figure 1 show that the Ir surface is modified during the CO adsorption at  $T_a < 550 \text{ K}$  (increase in the intensity of the IR band of the L species). If after the heating from 300 to 550 K, the catalyst is cooled in the presence of 2% CO/ $\text{He}$ , the IR band area remains constant, indicating that the modification of the Ir surface is irreversible. Similar processes have been observed on other supported metal catalysts and we have suggested that they are due to the reconstruction of the metal surface by comparison with single-crystal studies.<sup>6–14</sup> On the present catalyst the conversion of G CO species to L CO species also may contribute to the increase in the intensity of the IR band of the L CO species. Figure 2 compares the FTIR spectra at  $\approx 520 \text{ K}$  before heating (spectrum a) to 713 K and after cooling (spectrum b) from 713 K in 2% CO/ $\text{He}$ . It can be observed that the treatment at high temperatures has a very small impact on the intensities of the IR spectra. The CO adsorption is not strongly disturbed by the CO dissociation/disproportionation reaction at high temperatures. Weak IR bands at 1587 and  $1392 \text{ cm}^{-1}$  (not shown) are detected for  $T_a > 530 \text{ K}$ , attributed to adsorbed carbonate species on the  $\text{Al}_2\text{O}_3$  support probably due to the  $\text{CO}_2$  coming from the CO disproportionation.



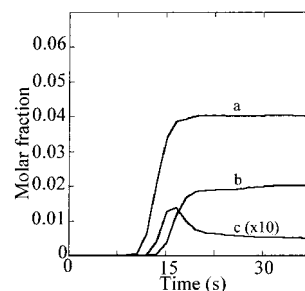
**Figure 3.** Comparison of the FTIR spectra on 1% Ir/Al<sub>2</sub>O<sub>3</sub> at 713 K for two CO partial pressures: (a) in the presence of 2% CO/He and (b) in the presence of 0.2% CO/He.

We have performed similar FTIR experiments using a 0.2% CO/He mixture ( $P_a = 200$  Pa) and the evolutions of the IR spectra with the increase in  $T_a$  qualitatively were similar to that described in Figure 1. However, for  $T_a > 550$  K, the intensity of the IR band of the L CO species for the same  $T_a$  value was lower with  $P_a = 200$  Pa than with  $P_a = 2000$  Pa as shown in Figure 3 for  $T_a = 713$  K. The lower intensity of the IR band in Figure 3b is due to the modification of the adsorption equilibrium with  $P_a$ . Note that (a) the position of the IR band is lower with the 0.2% CO/He mixture (2003 cm<sup>-1</sup>) than with 2% CO/He (2019 cm<sup>-1</sup>) due to a decrease in the coverage and (b) the intensity of the shoulder at 2060 cm<sup>-1</sup> also is affected by the CO partial pressure indicating that it characterizes an adsorbed CO species which has a heat of adsorption similar to the L CO species.

**3.2. Coverage of the L CO Species at Several Adsorption Temperatures.** The change in the coverage  $\theta_L$  of the L CO species with  $T_a$  in the presence of the 2% CO/He mixture can be obtained, as previously achieved on other supported metal catalysts using the ratio  $\theta = A/A_M$  with  $A$  the IR band area at  $T_a$  and  $A_M$  the highest IR band area and assuming: (a) a linear relationship between the intensity of the IR band and the quantity of the linear CO species on the surface and (b) that the IR absorption extinction coefficient is independent of the adsorption temperature. We have shown that these assumptions are valid for the L CO species adsorbed on Pt<sup>16</sup> and Cu.<sup>17</sup> The determination of  $\theta_L$  on Ir/Al<sub>2</sub>O<sub>3</sub> can be determined without any difficulties because the IR band of the L CO species dominates the IR spectra in Figure 1 (the shoulders are not differentiated). Figure 4 shows (curve a) the evolution of the coverage of the L species with  $T_a$  for  $P_a = 2000$  Pa using the spectra in Figure 1. The coverage  $\theta \pm 0.02$  is obtained using as  $A_M$  the IR band area at  $\approx 570$  K. The increasing section of curve a for  $T_a < 570$  K corresponds to the increase in the IR band of the L species due to the reconstruction of the CO/Ir particles system (increase in the number of sites). For  $T_a > 600$  K the decrease in the IR band is due to the adsorption equilibrium. Curve b in Figure 4 shows the evolution of the coverage during the cooling of the sample in 2% CO/He from 650 K. Curve b indicates that the reconstruction is irreversible and that the coverage remains 1 for  $T_a < 570$  K. The above coverage values are determined assuming that the IR band area of the L CO species (denoted by  $A$ ) linearly varies with the coverage as observed on Pt<sup>16</sup> and Cu.<sup>17</sup> However, Lyons et al.<sup>20</sup> have observed on Ir(110) that  $A$  only linearly varies with the coverage  $\theta$  of the single-crystal surface in the range of 0–0.45 while  $A$  remains constant for  $\theta > 0.45$ . Considering these observations we have determined the



**Figure 4.** Evolution of the coverage of the linear CO species with the adsorption temperature: O, (a) experimental data for  $P_a = 2000$  Pa during the heating stage; □, (b) experimental data during the cooling stage from 650 K; ×, (c) experimental data for  $P_a = 200$  Pa during the heating stage; (d) and (e) theoretical coverage according to the adsorption model with  $E_1 = 115$  kJ/mol and  $E_0 = 225$  kJ/mol for  $P_a = 2000$  Pa and  $P_a = 200$  Pa respectively; ♦, coverage determined by a volumetric method.



**Figure 5.** Composition of the gas mixtures during adsorption of 2% CO/3%Ar/He on 1% Ir/Al<sub>2</sub>O<sub>3</sub> at 713 K: (a) Ar, (b) CO, and (c) CO<sub>2</sub>.

coverage of the L CO species at high temperature from the amount of CO adsorbed at two adsorption temperatures using a volumetric method with a mass spectrometer as a detector.<sup>16,17</sup> For instance, Figure 5 shows the evolution of the molar fractions of the gas at the outlet of the quartz reactor during a switch He  $\rightarrow$  2%CO/4%Ar/He performed at 713 K. The argon signal (Figure 5, curve a) permits to determine the beginning of the CO adsorption and the mixing curve for CO without adsorption (mixing curve = (2/4)curve a). At 713 K there is a small production of CO<sub>2</sub> (curve c) probably due to the CO disproportionation reaction. The total amount of CO consumed (adsorption and disproportionation reaction) during the CO adsorption is obtained from

$$Q_{CO} = \int_0^{t_a} (\text{curve a} \times 2/4 - \text{curve b}) \frac{F}{W} dt = 11.3 \mu\text{molCO/g}$$

where  $t_a$  is the duration of the adsorption,  $F$  the gas molar flow rate, and  $W$  the weight of catalyst. The CO<sub>2</sub> production is obtained from  $Q_{CO_2} = \int_0^{t_a} \text{curve c} \times \frac{F}{W} dt = 1.1 \mu\text{mol CO}_2/\text{g}$ . The amount of CO adsorbed is  $Q_{CO_{ads}}(713 \text{ K}) = Q_{CO} - 2Q_{CO_2} = 8.9 \mu\text{mol/g}$ . A similar experiment has been performed at 548 K (maximum in the IR band of the L CO species). At this temperature the CO<sub>2</sub> production is very small and the adsorption of CO is 10.3  $\mu\text{mol/g}$ . Considering that this quantity corresponds to the full coverage of the Ir surface by the L CO species, then the coverage of the surface at 713 K is  $\theta = (8.9/10.3) = 0.86$  in good agreement with the value found using the FTIR data (see the “♦” symbol in Figure 4). This validates the assumption of the linear relationship between the IR band area of the L CO



species and its amount on the surface. The discrepancy between the present results and those on Ir(110) can be explained by the following remark. Lyons et al.<sup>20</sup> have studied the shift of the IR band of the L CO species with the coverage of the Ir(110) surface. They observe that the IR band roughly linearly shifts from 2001  $\text{cm}^{-1}$  at  $\theta = 0.007$  to 2086  $\text{cm}^{-1}$  at  $\theta = 0.87$ . The point of interest is that the authors observe that  $A$  linearly varies with  $\theta$  in the range of 0–0.45 while in parallel the IR band shifts from 2001 to  $\approx 2050$   $\text{cm}^{-1}$  (see Figures 3 and 4 in ref 20). The  $A$  value remains constant with the increase in  $\theta$  while the IR band shifts from 2050 to 2086  $\text{cm}^{-1}$ . It is remarkable that on the present 1% Ir/Al<sub>2</sub>O<sub>3</sub> catalyst the highest position of the IR band is 2044  $\text{cm}^{-1}$  at full coverage (Figure 1). This corresponds to that where Lyons et al.<sup>20</sup> observe that the linear relationship between  $A$  and  $\theta$  ceases on Ir(110). Considering that the position of the IR band is an indication of the interaction between adsorbed molecules (dipole–dipole coupling), it seems that on the supported Ir particles the interactions at full coverage of the surface are limited (2044  $\text{cm}^{-1}$ ) as compared to that on the Ir(110) surface. This probably explains the linear relationship between  $A$  and  $\theta$  on the present Ir/Al<sub>2</sub>O<sub>3</sub> catalyst in the range of 0–1.

Curve c in Figure 4 gives the change in the coverage  $\theta$  with  $T_a$  for  $P_a = 200$  Pa. A profile similar to curve a is observed, but for  $T_a > 550$  K the coverage is lower in curve c due to the adsorption equilibrium. In the discussion section, the two isobars in Figure 4 are used for the determination of the relationship between the heat of adsorption of the linear CO species and its coverage using several exploitation methods.

**3.3. Stability of the L CO Species during Isothermal Desorption.** The stability of the L CO species during helium treatment (200  $\text{cm}^3/\text{min}$ ) has been studied at several desorption temperatures  $T_d$ . At  $T_d = 310$  K, there is no desorption even after 30 min in He. For  $T_d = 378$  K, the coverage slightly decreases to a pseudo stationary value of 0.93 after 10 min in helium. The increase in  $T_d$  decrease progressively this value. However, for  $T_d > 473$  K, a fraction of the L CO species is converted into G CO species (very stable adsorbed species) and the strong overlap of the IR bands does not allow us to evaluate the coverage of the L CO species.

## 4. Discussion

The curves in Figure 4 are used to determine the heats of adsorption of the L CO species on Ir/Al<sub>2</sub>O<sub>3</sub> at several coverages. However, in a first step the assignment of the IR bands observed in Figures 1 and 2 are discussed.

### 4.1. Assignment of the IR Bands to Specific CO Species.

The adsorption of CO on Ir single crystals gives a single IR in the range 2000–2100  $\text{cm}^{-1}$  assigned to a linear CO species (on-top site). The exact position of the IR band depends on the coverage. For instance, at 300 K on Ir(110) the IR band shifts from 2001 to 2086  $\text{cm}^{-1}$  for  $\theta = 0.07$  and 0.87, respectively, due to dipole–dipole interactions and competition for back-donation of metallic electrons.<sup>20</sup> Marinova and Chakarov<sup>21</sup> describe similar observations at 170 K on Ir(111) and Ir(110). The nature of the single crystal slightly affects the position of the IR band at low coverage (2001  $\text{cm}^{-1}$  on Ir(110)<sup>21,23</sup> and  $\approx 2025$   $\text{cm}^{-1}$  on Ir(111)<sup>21,23</sup> and Ir(100)<sup>22</sup>) as well as at high coverage (2090  $\text{cm}^{-1}$  on Ir(111),<sup>23</sup> 2086  $\text{cm}^{-1}$  on Ir(110),<sup>20</sup> 2075 and 2068  $\text{cm}^{-1}$  on (5 × 1) and (1 × 1) reconstructed Ir(100)<sup>22</sup>). The adsorption of CO at 300 K on Ir film gives a similar IR band observed at 2010  $\text{cm}^{-1}$  at low coverage and 2093  $\text{cm}^{-1}$  at saturation coverages.<sup>24</sup> There are no IR bands below 2000  $\text{cm}^{-1}$  due to bridged CO species on the various Ir single-crystal

surfaces. Lyons et al.<sup>20</sup> consider that the presence of three TPD peaks at high coverage on Ir(110) is not due to the formation of several adsorbed CO species (i.e., L and B CO species) but to a change in the repulsive interaction between the L CO species. Adsorption of CO on reduced Ir-supported catalysts also leads to a strong IR band at  $2060 \pm 10$   $\text{cm}^{-1}$  at full coverage.<sup>18,19,25–29</sup> These IR bands are assigned in agreement with single-crystal studies to a L CO species on Ir<sup>o</sup> sites.<sup>18,19,25–29</sup> Toolenaar et al.<sup>30</sup> have suggested that the position of the IR band at high coverage is affected by the particle size due to the presence of several sites: an IR band at  $\approx 2050$   $\text{cm}^{-1}$  represents a L CO species adsorbed on low-coordinated sites (edges and corners) while an IR band at  $\approx 2080$   $\text{cm}^{-1}$  corresponds to high-coordinated sites (planes). Due to the above studies, the main IR band at 2044  $\text{cm}^{-1}$  observed at 300 K in Figure 1 is ascribed to a L CO species on Ir<sup>o</sup> sites. The position may indicate an adsorption on low coordinated Ir sites.<sup>30</sup> The shift to lower wavenumbers observed in Figure 1 with the increase in  $T_a$  is ascribed to the decrease in the coverage of the L CO species as observed on single crystals.<sup>20,21</sup> Tanaka et al.<sup>25</sup> have observed on Ir/Al<sub>2</sub>O<sub>3</sub> a similar shift from 2063 to 1992  $\text{cm}^{-1}$  studying the change in the IR band with the desorption temperature in the range of 300–573 K.

The main difference between single-crystal studies and supported Ir catalysts is the presence of G CO species (either alone or in the presence of L CO species) leading to two IR bands in the ranges 2100–2080 and 2035–2010  $\text{cm}^{-1}$  respectively.<sup>25–27</sup> The ratio between the intensities of the IR bands of the L and G CO species depends on several parameters such as the metal loading, the nature of the support and the reduction temperature.<sup>26</sup> Helium treatment at  $T \leq 673$  K after reduction in H<sub>2</sub> of 1% Ir/Al<sub>2</sub>O<sub>3</sub> only leads to G CO species after adsorption of CO at 300 K.<sup>26</sup> The decarbonylation in helium at 573 K of Ir<sub>4</sub>CO<sub>12</sub> impregnated on Al<sub>2</sub>O<sub>3</sub> leads to Ir<sub>4</sub> clusters which only form G CO species after adsorption of CO at 300 K<sup>19</sup> while the decarbonylation in H<sub>2</sub> leads to Ir aggregates ( $\approx 50$  atoms) which form the L CO species.<sup>28</sup> The two IR bands observed in Figure 1h are similar to those observed 1% Ir/Al<sub>2</sub>O<sub>3</sub> solids<sup>19,26</sup> treated in helium at high temperatures and are assigned to G CO species. The two weak shoulders observed at 2080 and 2000  $\text{cm}^{-1}$  in Figure 1a–c are probably due to the presence of small amount of G CO species maybe formed by the disruptive CO chemisorption.<sup>26</sup> However, increasing  $T_a$  seems to eliminate those adsorbed species probably by transformation into Ir<sup>o</sup> sites adsorbing the L CO species. The shoulder observed at 2060  $\text{cm}^{-1}$  at high adsorption temperature is maybe due to another L CO species on different Ir sites<sup>30</sup> formed during the reconstruction of the surface. However, stable G CO species with IR bands at  $\approx 2075$  and  $\approx 2000$   $\text{cm}^{-1}$  are observed at high temperatures on Ir containing solids<sup>19,25</sup> and the IR band at 2060  $\text{cm}^{-1}$  is maybe associated to those species (in that case in Figure 1 the second IR band is overlapped by the strong IR band of the L CO species).

Finally in the present experimental conditions whatever the adsorption temperature it must be considered that the reduced Ir particles mainly adsorb CO as a L CO species. This explains that we neglect the contribution of the minor adsorbed CO species to the IR band area to determine the coverage of the L CO species in Figure 4.

**4.2. Heats of Adsorption of the L CO Species as a Function of the Coverage.** The two curves a and c in Figure 4 are very similar to those previously observed on other supported metal catalysts for the L and/or B CO species.<sup>6–14</sup> We have shown that their profiles are due to a linear decrease in the heat of

adsorption  $E_\theta$  with the increase in the coverage of the adsorbed species  $\theta$ . This assumption provides an expression of the coverage given by (refs 6–14 and references therein):

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

where  $\Delta E$  is the difference in the heats of adsorption at  $\theta = 0$  ( $E_0$ ) and  $\theta = 1$  ( $E_1$ ), and  $K_0$  and  $K_1$  are the adsorption coefficients at  $\theta = 0$  and  $\theta = 1$ , respectively. This expression leads to the Temkin equation assuming  $(K_0 P_a) \gg 1$  and  $(K_1 P_a) \ll 1$  in expression 1:

$$\theta = \frac{RT_a}{\Delta E} \ln(K_0 P_a) \quad (2)$$

Considering an expression of the adsorption coefficient such as  $K_0 = C \exp(E_0/RT_a)$  (the preexponential factor  $C$  is assumed independent of  $T_a$ ) expression 2 leads to expression 3:

$$\theta = \left[ \frac{R}{\Delta E} \ln(C P_a) \right] T_a + \frac{E_0}{\Delta E} \quad (3)$$

This shows that, at a given partial pressure  $P_a$ ,  $\theta$  varies with  $T_a$  according to a straight line (Temkin's approximations correspond to the decreasing linear fraction of the isobar as observed in Figure 4). Expression 3 shows that the linear section of the isobar must intercept the  $\theta$  axis ( $T_a = 0$  K in expression 3), in  $E_0/\Delta E$  independently of the adsorption pressure  $P_a$ . Curves a and c in Figure 4 lead to  $E_0/\Delta E \approx 2.07$ , which indicates that there is an important difference between  $E_0$  and  $E_1$ . Moreover, expression 2 shows that, at a constant temperature  $T_a$ ,  $\theta = f(\ln P_a)$  is a straight line ( $K_0$  only depends on  $T$ ) with a slope ( $RT_a/\Delta E$ ). From the two curves a and c in Figure 4, this slope has been estimated for several  $T_a$  values leading to  $\Delta E \approx 115$  kJ/mol. This indicates that  $E_0 \approx 238$  kJ/mol and  $E_1 \approx 123$  kJ/mol.

The  $E_0$  and  $E_1$  values can be obtained without the above approximations considering that the L CO species is immobile and that the adsorption coefficient is provided by the statistical thermodynamics assuming the loss of three degrees of translation (see refs 31 and 32):

$$K = \frac{h^3}{(2\pi mk)^{3/2}} \frac{1}{T_a^{5/2}} \exp \left( \frac{E_d - E_a}{R \times T_a} \right) \quad (4)$$

where  $h$  is Planck's constant,  $k$  is Boltzmann's constant, and  $m$  is the mass of the molecule,  $E_d$  and  $E_a$  are the activation energies of desorption and adsorption respectively, while  $E_d - E_a$  is the heat of adsorption. This allows us to determine  $E_0$  and  $E_1$  by considering the following: (a) the experimental curves a and c in Figure 4, (b) the theoretical coverage provided by expression 1, and (c) the adsorption coefficient from expression 4. It is only required to find  $E_1$  and  $E_0$  leading to theoretical curves  $\theta_L = f(T_a)$  in agreement with the experimental data. Curves d and e in Figure 4 are obtained using  $E_1 = 115$  kJ/mol and  $E_0 = 225$  kJ/mol with  $P_a = 2000$  Pa and  $P_a = 200$  Pa, respectively. A good agreement is observed between theoretical and experimental curves for the two CO partial pressures. The determination of  $E_\theta$  using this procedure is very accurate because a modification of few kJ/mol ( $\leq 5$  kJ/mol) of  $E_0$  and/or  $E_1$  gives theoretical curves significantly different from the experimental data. It is this set of values (not strongly different than that found with Temkin's approximations) which is compared to the data in the literature.

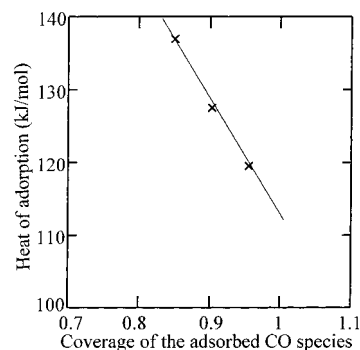


Figure 6. Isosteric heats of adsorption from the Clausius–Clapeyron equation using curves a and c in Figure 4.

Finally, with the Clausius–Clapeyron equation, the two experimental isobars in Figure 4 (curves a and c) can be used to determine the isosteric heats of adsorption  $\Delta H$  at several coverages from the plots of  $\ln P_a = f(1/T_a)$  at constant coverage. It can be observed in Figure 6 that the curve  $\Delta H = f(\theta)$  is a straight line in the studied coverage range and that the  $\Delta H$  values are in reasonable agreement with the  $E_\theta$  values (i.e.,  $\Delta H_\theta = 128$  kJ/mol and  $E_\theta = 126$  kJ/mol at  $\theta_L = 0.9$ ). This supports the basic assumptions of the adsorption model. Note that the  $\Delta H_\theta$  values are significantly influenced by experimental uncertainties. For instance, considering  $T_a \pm 2$  K leads to an uncertainty on  $\Delta H$  of  $\approx \pm 8$  kJ/mol.

Note that we have indicated that a shoulder at  $2060 \text{ cm}^{-1}$  (Figure 1) is detected at high adsorption temperatures. Figure 3 shows that its IR band intensity is dependent on the adsorption partial pressure similarly to the intensity of the main IR band. This clearly indicates that the heats of adsorption of the two CO species are similar.

**4.3. Comparison of the Heat of Adsorption of the L CO Species with the Data in the Literature.** The comparison mainly concerns the data obtained on Ir single crystals because we have found very few studies on supported Ir catalysts.

Comrie and Weinberg<sup>33,34</sup> have determined the isosteric heat of adsorption of CO on Ir(111) at  $\theta = 1/3$  using LEED spectroscopy:  $146 \pm 4$  kJ/mol. The values have been confirmed by a TPD experiment using a preexponential factor of  $2.4 \times 10^{14} \text{ s}^{-1}$ : 150 kJ/mol.<sup>35</sup> For the same coverage we determine 190 kJ/mol. Moreover, at lower coverages the authors have estimated with some approximations due to the analytical procedure that the heat of adsorption is in excess of 188 kJ/mol.<sup>33</sup> A similar (184 kJ/mol) value was previously determined by Agreev and Ionov.<sup>36</sup> Hagen et al.<sup>37</sup> by using LEED have also determined the isosteric heat of adsorption at  $\theta = 1/3$  on Ir(111) and on a stepped surface Ir(S)-[6(111)  $\times$  (100)]. They have determined  $163 \pm 12$  kJ/mol on the two surfaces in better agreement with our values (190 kJ/mol). Recently, Sushchikh et al.<sup>38</sup> have studied using FTIR the rate of desorption of the L CO species on Ir(111) at a constant temperature in the range of 380–450 K either in a vacuum or during a switch  $^{12}\text{C}^{16}\text{O} \rightarrow ^{13}\text{C}^{18}\text{O}$  with the total pressure maintained constant in the range of  $10^{-9}$ – $10^{-5}$  mbar. The interest in the second procedure is that the total coverage of the Ir surface is constant during the desorption of the L  $^{12}\text{C}^{16}\text{O}$  species and the adsorption of the L  $^{13}\text{C}^{18}\text{O}$  species. This leads to a constant activation energy of desorption during the experiments while using a classical isothermal desorption this parameter increases with the decrease in  $\theta$ .<sup>38</sup> From these experiments the authors determine the evolution in the activation energy of desorption  $E_d(\theta)$  of the L CO species with the coverage  $\theta$  using a preexponential factor of  $2 \times 10^{15} \text{ s}^{-1}$ . At  $\theta \approx 0$  the heat of adsorption is  $\approx 180$  kJ/

mol then a sharp decrease is observed to  $\approx 165$  kJ/mol at  $\theta \approx 0.04$ . These values are attributed to L CO species desorbing from step sites. For  $\theta > 0.04$ ,  $E_d(\theta)$  roughly linearly decreases (slight change in the slope at  $\theta = 1/3$ ) to  $\approx 110$  kJ/mol at 0.7 due to repulsive dipole–dipole interactions. The linear relationship between  $E_d$  and  $\theta$  observed by Shushchikh et al.<sup>38</sup> in the  $\theta$  range of 0.004–0.7 is in very good agreement with the relationship used in our adsorption model. Note that  $E_d = 110$  kJ/mol observed at high coverage<sup>38</sup> is in good agreement with  $E_1 = 115$  kJ/mol determined on the present Ir/Al<sub>2</sub>O<sub>3</sub> catalyst. Moreover, the authors show that L CO species on step sites have  $E_d$  values significantly higher than on terrace sites and this agrees with  $E_0 = 225$  kJ/mol determined on the present supported Ir particles where sites of different nature (steps, corners) may adsorb the L CO species.

The present values reasonably agree with those on single crystals in particular with refs 37 and 38. At first sight, it can be considered as surprising that the heat of adsorption of the L CO species on supported Ir particles does not strongly differ from that on single crystals. However, Lee et al.<sup>39</sup> have underscored the fact that the heats of adsorption of simple molecules such as CO and NO on Pt are not strongly affected by the nature of the surface (stepped or kinked surfaces, closely packed planes). They suggest that reconstruction of the surface during the adsorption leads to surface atoms having the same coordination number that on Pt(111) whatever the initial surface. This is maybe valid on other noble metal surfaces such as Ir. Finally, it must be noted that Ducker and Bonzel<sup>40</sup> studying the adsorption of CO on Ir and Pt by yttrium M $\zeta$  photoemission conclude that the heats of adsorption of CO on Pt and Ir are similar. This is in very good agreement with the heats of adsorption values of the L CO species (which is the main adsorbed CO species on Pt and Ir) determined with our procedure: on Pt/Al<sub>2</sub>O<sub>3</sub><sup>6,7,9</sup> ( $E_1 = 110$  kJ/mol and  $E_0 = 206$  kJ/mol) and on Ir/Al<sub>2</sub>O<sub>3</sub> ( $E_1 = 115$  kJ/mol and  $E_0 = 225$  kJ/mol).

We have found a single study on the heat of adsorption of CO on supported Ir catalysts. This is maybe linked to the fact that several processes may overlap the adsorption of CO such as those linked to the formation of the G CO species.<sup>26,27</sup> However, Gelin et al.<sup>27</sup> by using a differential calorimetric method have determined a heat of adsorption of CO on Ir/NaY zeolithe and Ir/SiO<sub>2</sub> of  $\approx 145$  kJ/mol at low coverage. This value significantly differs from that found in the present study at low coverage 225 kJ/mol. However, on Ir/NaY and Ir/SiO<sub>2</sub>,<sup>27</sup> adsorption of CO leads to the formation of L and G CO species and the calorimetric signal is probably an overlap of several surface processes while with the present procedure only the heat of adsorption of the L CO species is determined.

#### 4.4. Heats of Adsorption and Stability of the L CO Species.

We have shown above that there is very few literature data on the heat of adsorption of the L CO species on supported Ir catalysts to establish a comparison with our values. However, some experimental data on the stability of the L CO species adsorbed on Ir-containing solids during desorption in a vacuum or in an inert gas at high temperatures support our values. For instance, Tanaka et al.<sup>25</sup> indicate on Ir/SiO<sub>2</sub> and Ir/Al<sub>2</sub>O<sub>3</sub> that the IR band of the L species at  $\approx 2065$  cm<sup>-1</sup> very progressively decreases in intensity and shifts to lower wavenumbers during successive treatments (1 h) in a vacuum at several temperatures in the range of 373–623 K. The estimated coverages (see Figures 5 and 8 in ref 25) after 1 h of desorption are  $\approx 1$ , 0.8, 0.5, 0.4, and 0.1 at 373, 423, 523, 573, and 623 K, respectively. Similar observations have been made by Mc Vicker et al.<sup>18</sup> on

Ir/Al<sub>2</sub>O<sub>3</sub>: after 0.5 h at 523 K the coverage decreases to 0.85. Alexeev and Gates<sup>28</sup> have followed the change in the IR band intensity of the L CO species at 2058 cm<sup>-1</sup> with the increase in the temperature in helium. There is no indication of the duration of the desorption. However, the IR band is not strongly affected between 300 and 383 K and then decreases progressively ( $\theta \approx 0.32$  at 573 K) and is still detected at 530 K. Shushchikh et al.<sup>38</sup> have observed similar data on Ir(111): the coverage is  $\approx 0.1$  after  $\approx 2$  min at 460 K and  $\approx 0.3$  after 7 min at 390 K. The above studies clearly show that during the desorption of the L CO species the coverage evolves to pseudo stationary values for each desorption temperature. This indicates that the activation energy of desorption must strongly increase with the decrease in the coverage as observed in the present study and in ref 38. The theoretical evolution of the coverage of the L CO species at a constant desorption temperature can be estimated considering a first kinetic order for the desorption of the L CO species:

$$\frac{-d\theta}{dt} = \frac{kT}{h} \exp\left(-\frac{E_d(\theta)}{RT}\right) \theta \quad (5)$$

where  $E_d(\theta)$  is the activation energy of desorption at  $\theta$  assumed equal to the heat of adsorption. Simple calculations similar to those performed in a previous study<sup>8</sup> considering that the activation energy of desorption linearly varies from 115 kJ/mol at  $\theta = 0$  to 225 kJ/mol at  $\theta = 1$  indicate that the L CO species does not desorb at 300 K as experimentally observed. For higher temperatures, due to the increase in the activation energy with the decrease in the coverage the coverage sharply decrease in the first second and then more slowly to a pseudo stationary value. At 378 K, this value is stationary of 0.92 after 10 min at 378 K as experimentally observed. After 1 h of desorption, the coverages are 0.88, 0.73, 0.44, 0.3, and 0.16 at 373, 423, 523, 573, and 673 K, respectively. These values are in reasonable agreement with the data of Tanaka et al.<sup>25</sup> Note that assuming that the heat of adsorption is 150 kJ/mol<sup>27</sup> at  $\theta \approx 0$  and 115 kJ/mol at  $\theta = 1$  it is found that the coverages are 0.03 and 0 after 1 h of desorption at 423 and 523 K, respectively. These values are clearly lower than that found in the literature<sup>25</sup> on supported Ir catalysts.

## 5. Conclusions

This study on the adsorption of CO on a 1% Ir/Al<sub>2</sub>O<sub>3</sub> catalyst has shown that the IR spectra of the L CO species recorded under adsorption equilibrium in the adsorption temperature range of 300–720 K can be used to determine the evolution of its coverage with  $T_a$  for two constant partial pressures of CO (200 and 2000 Pa). The curves  $\theta = f(T_a)$  allow us to determine the evolution of the heat of adsorption  $E_\theta$  of this species with its coverage using an adsorption model which considers: (a) a linear decrease in  $E_\theta$  with the increase in  $\theta_L$  and (b) an immobile adsorbed species. This model fits very well the experimental data with  $E_0 = 225$  kJ/mol and  $E_1 = 115$  kJ/mol at  $\theta = 0$  and  $\theta = 1$ , respectively. These values are in reasonable agreement with certain studies on Ir single crystals and with the isosteric heat of adsorption.

Moreover, these values provides a quantitative explanation of qualitative literature data on the stability of the L CO species during a desorption at high temperatures.

**Acknowledgment.** We acknowledge with pleasure FAU-RECIA, Bois sur Pré, Bavans, France, for its financial support and the M.E.R.T (Ministère de l'Education Nationale, de la



Recherche et de la Technologie) for the research fellowship of A.B. Thanks are also due to May Elias and François Leotoing, students at the CPE-Lyon School for their contributions to preliminary studies.

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