

Heats of Adsorption of Linear CO Species Adsorbed on the Au^o and Ti^{+δ} Sites of a 1% Au/TiO₂ Catalyst Using in Situ FTIR Spectroscopy under Adsorption Equilibrium

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Abstract: The heats of adsorption of two linear CO species adsorbed on the Au^o particles (denoted L_{Au^o}) and on the Ti^{+δ} sites (denoted L_{Ti^{+δ}}) of a 1% Au/TiO₂ catalyst are determined as the function of their respective coverage by using the AEIR procedure (adsorption equilibrium infrared spectroscopy) previously developed. Mainly, the evolutions of the IR band area of each adsorbed species (2184 cm⁻¹ for L_{Ti^{+δ}} and at 2110 cm⁻¹ for L_{Au^o}) as a function of the adsorption temperature T_a , at a constant CO adsorption pressure P_{CO} , provide the evolutions of the coverages $\theta_{L_{Ti^{+\delta}}}$ and $\theta_{L_{Au^o}}$ of each adsorbed CO species with T_a in isobar conditions that give the individual heats of adsorption. It is shown that they linearly vary from 74 to 47 kJ/mol for L_{Au^o} and from 50 to 40 kJ/mol for L_{Ti^{+δ}} at coverages 0 and 1, respectively. These values are consistent with literature data on model Au particles and TiO₂. In particular, it is shown that the mathematical formalism supporting the AEIR procedure can be applied to literature data on Au-containing solids (single crystals and model particles).

1. Introduction

The evolutions of the heats of adsorption of the adsorbed species (denoted by E) with their coverage θ (denoted by $E_\theta = f(\theta)$ with $0 \leq \theta \leq 1$) constitute fundamental characterizations of the gas/solid interactions because the E_θ values (a) quantify the coverage of the sites under adsorption equilibrium and (b) contribute to the coverage of the active surface during a catalytic reaction. However, this parameter is rarely studied on supported metal catalysts as compared to the amount (i.e., volumetric measurements) and the nature (i.e., FTIR spectroscopy) of the adsorbed species due to experimental difficulties using, for instance, temperature programmed desorption^{1,2} or microcalorimetric methods.^{3–5} We have previously shown that the evolutions of the IR bands of each adsorbed species with the adsorption temperature $T_a > 300$ K at a constant partial pressure P_a may allow one to determine the evolution of the coverage θ of each adsorbed species with T_a .^{6–14} The curves $\theta = f(T_a)$

provide $E_\theta = f(\theta)$ for each adsorbed species according to different mathematical formalisms: Clausius–Clapeyron equation and adsorption models.^{6–14} This analytical procedure (denoted by AEIR: adsorption equilibrium infrared spectroscopy)^{8,12} has been used to determine the heats of adsorption of linear (denoted by L), bridged, and three-fold coordinated adsorbed CO species on several metal-supported (on alumina) catalysts such as Pt,^{6–9} Cu⁺ and Cu^o,¹⁰ Pd,¹¹ Rh,¹³ and Ru.¹⁴ In the present study, one of the advantages of the AEIR method is used to determine the individual heats of adsorption of two L CO species adsorbed on the Au^o particles and on the Ti^{+δ} sites of a 1% Au/TiO₂ catalyst. The AEIR procedure is particularly useful due to the fact that the two adsorbed CO species have similar heats of adsorption. Recent literature data on the high performances of Au-containing solids, in particular Au/TiO₂, for the CO/O₂ reaction at low temperatures and the selective CO oxidation in the presence of hydrogen^{15–19} justify the interest for the determination of the heats of adsorption of the adsorbed CO species on Au-containing catalysts to quantify the coverage of the Au surface.

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2. Experimental Section

A 1% Au/TiO₂ catalyst has been prepared according to the classical deposition-precipitation method²⁰ using the procedure described by Ruth et al.²¹ with TiO₂ P25 from Degussa.^{21,22} In the absence of light, 5 g of TiO₂ is introduced in an appropriated amount of aqueous solution (350 cm³) of H₂AuCl₄·4H₂O (Aldrich) heated at 343 K and adjusted to pH = 7 by addition of a NaOH solution. The suspension is stirred for 1 h before decanting off the liquid. The solid was washed several times with distilled water to remove Na⁺ and Cl⁻ ions. The presence of Cl⁻ in the filtrate was followed by precipitation of AgCl. After drying at 353 K during 12 h, the solid is heated (2 K/min) in air at 673 K during 5 h. A 1% Au/TiO₂ solid prepared according to this procedure showed high performances for the CO/O₂ oxidation at low temperatures.²¹ The deposition-precipitation method for Au/TiO₂ led to a mean diameter of gold particles in the range of 3–5 nm for a similar (a) Au loading and (b) pretreatment procedure at ~673 K.^{18,20} For the FTIR study, the solid (either Au/TiO₂ or pure TiO₂) 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 in transmission mode described elsewhere.⁶ It permitted in-situ treatments of the solid in the temperature range of 293–900 K, with a controlled gas flow rate (in the range of 150–2000 cm³/min, at atmospheric pressure) selected using different valves. The AEIR method imposed that the evolutions of the IR band intensities of a specific adsorbed CO species during the increase in T_a were mainly due to the adsorption equilibrium. To prevent the contribution of the sintering of the Au particles to the measurements, the solid was stabilized before CO adsorption by oxidation/reduction cycles as follows: He, 298 K → He, 673 K → O₂, 673 K (10 min) → He, 673 K (10 min) → H₂, 673 K (10 min) → He, 673 K (10 min) → He, 300 K. After the pretreatment procedure, the CO adsorption at 300 K was performed according to He → $x\%$ CO/He with $x = 1, 2, 5, 8, 10, 15, \text{ and } 20$. The same sample of solid was used for several experiments, and it was treated as above before each CO adsorption. The AEIR procedure was applied with $x = 1$ and 10 on Au/TiO₂ and 20 on pure TiO₂ as follows: after adsorption equilibrium at 300 K, the adsorption temperature T_a was increased (~10 K/min) at a constant CO partial pressure, while the IR spectra were recorded periodically. After the highest adsorption temperature, the solid was cooled (without any oxidation/reduction pretreatment) in the presence of CO, and the spectra were compared to those recorded at similar temperatures 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 reconstruction and eventual poisoning of the surface by C deposition.

3. Results and Discussion

3.1. FTIR Spectra of CO Adsorbed on 1% Au/TiO₂. Figure 1 shows the FTIR spectra after adsorption of 1% CO/He on the reduced 1% Au/TiO₂ solid. Two IR bands are observed at 2184 and 2115 cm⁻¹ ascribed to linear CO species adsorbed on Ti⁺_δ cations (denoted L_{Ti+δ}) with probably $\delta = 4$,^{23,24} and Au⁰ sites^{24–28} of the Au particles (denoted L_{Au⁰}), respectively.

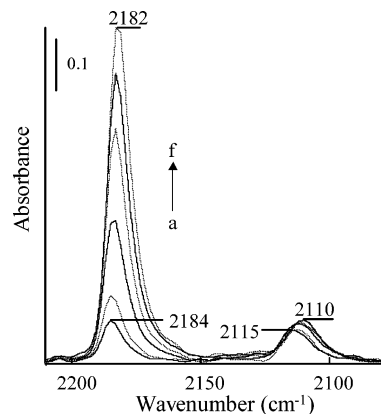


Figure 1. Evolution of the FTIR spectra of the adsorbed CO species on 1% Au/TiO₂ at 300 K with the CO partial pressure: (a–f) $P_{\text{CO}} = 1, 2, 5, 10, 15, 20$ in kPa, respectively.

Adsorption of CO on Au single crystals leads to a similar IR band at ~2110 cm⁻¹ at high coverage on Au(110)^{29,30} and Au-(332),³¹ while it shifts to higher wavenumber at low coverage.^{30,31} On a single crystal, there is a reconstruction of the Au surface under CO, while C deposition is observed for long adsorption duration at 300 K.²⁹ On model Au particles deposited on a TiO₂ film, Meier and Goodman³² have observed that the position of the IR band is dependent on the particle size in the range of 1.8–3.1 nm (blue-shifts of ~4 cm⁻¹). A desorption in helium after adsorption at 300 K leads to the rapid (<1 min) disappearance of the two IR bands, indicating weakly adsorbed CO species. Spectra a–f in Figure 1 show the evolution of the IR bands with the increase in the CO partial pressure P_{CO} . It can be observed that the IR band of the L_{Ti+δ} CO species increases associated with a shift to 2182 cm⁻¹, while that of the L_{Au⁰} species increases and shifts to 2110 cm⁻¹ for $P_{\text{CO}} \leq 15$ kPa due to the increase in the coverage of the Au⁰ sites as observed on single crystals.^{29,30} For $P_{\text{CO}} \geq 15$ kPa, the IR band area of the L_{Au⁰} species is not modified, indicating the full coverage of the Au⁰ sites, while that of the L_{Ti+δ} CO species continues to increase (the coverage of the Ti⁺_δ sites is <1 for $P_{\text{CO}} = 20$ kPa). Note that with the present Au loading and pretreatment procedure, the IR band intensity of the L_{Ti+δ} species is higher than that of the L_{Au⁰}.

Figure 2 shows the evolution of the IR bands during the increase in T_a for 10% CO/He. It can be observed that the intensities of the two IR bands progressively decrease and at $T_a = 407$ K that of the L_{Ti+δ} is no more detected while that of L_{Au⁰} is still present and detected at 2115 cm⁻¹. This clearly indicates that the heat of adsorption of the L CO species on Au⁰ is slightly higher than that of the L_{Ti+δ} CO species. Figure 3 compares the IR bands at 307 K before (Figure 3a) and after (Figure 3b) adsorption to 441 K in 10% CO/He. It can be observed that the IR bands are not significantly modified by the adsorption at high temperatures. The surface reconstruction of the Au particles^{29,33} has no impact probably due to their small particle sizes, while the eventual C deposition²⁹ does not

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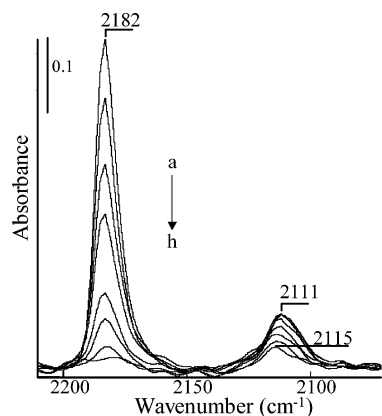


Figure 2. Evolution of the FTIR spectra of the adsorbed CO species on 1% Au/TiO₂ at a constant partial pressure $P_{\text{CO}} = 10$ kPa with the adsorption temperature: (a–h) $T_a = 307, 313, 323, 353, 364, 392, 407$ K, respectively.

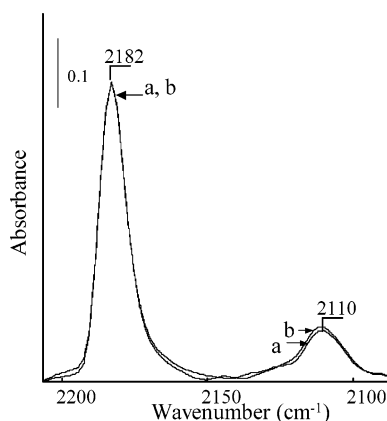


Figure 3. Comparison of the IR bands before (a) and after (b) adsorption at 441 K with $P_{\text{CO}} = 10$ kPa.

decrease the number of Au^o sites probably because of the storage of the carbonaceous species on the TiO₂ support at the proximity of the Au particles. On the pure TiO₂ support pretreated as the 1% Au/TiO₂ solid, the adsorption of CO leads to the detection of the IR band for the L_{Ti+δ} CO species at 2184 cm⁻¹ at 300 K, and its evolution with T_a (not shown) at a constant CO partial pressure <20 kPa is similar to that in Figure 2.

3.2. Evolution of the Coverage of the L_{Ti+δ} and L_{Au^o} Species with T_a in Isobar Conditions. In previous work, it has been shown that the IR band area of each L CO species adsorbed on the metallic sites of Pt,³⁴ Cu,³⁵ and Ir³⁶ supported on Al₂O₃ is proportional to the amount of each L CO species on the surface. These observations have been a priori extended for each adsorbed CO species on the surface of metal particles supported on metal oxide supports. The coverage of a specific adsorbed X CO species at an adsorption temperature T_a is determined according to $\theta_X = A(T_a)/A_M$, where $A(T_a)$ and A_M are the IR band area at T_a and the highest IR band area of the X CO species. For the L_{Au^o} species, the increase in P_{CO} at 300 K from 15 to 20 kPa does not change the IR band area, indicating the full coverage of the Au^o sites: A_M is the IR band area of the L_{Au^o} CO species at 300 K for $P_{\text{CO}} = 15$ kPa. This allows us to determine the evolutions of its coverage $\theta_{\text{L}_{\text{Au}^{\text{o}}}}$ with

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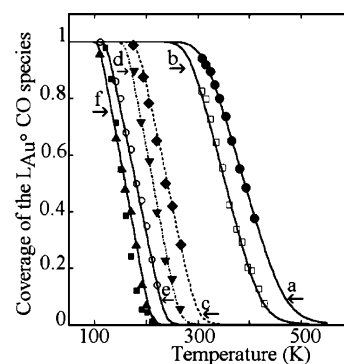


Figure 4. Experimental and theoretical evolutions of the coverage of the L_{Au^o} CO species on several Au-containing solids in isobar conditions (see the text for more details): ●, □ experimental data and a, b theoretical curves (expressions 2 and 3) for $P_{\text{CO}} = 10$ and 1 kPa, respectively, for 1% Au/TiO₂; ◆, ▼ experimental data from ref 32, and c, b theoretical curves (expressions 2 and 3) for $P_{\text{CO}} = 0.32$ and $5.9 \cdot 10^{-3}$ Pa, respectively, for Au model particles on TiO₂; ○, ▲ experimental data from ref 30, and e, f theoretical curves (expressions 2 and 3) for $P_{\text{CO}} = 1.3 \cdot 10^{-3}$ and $1.3 \cdot 10^{-5}$ Pa, respectively, for Au(110); ■, experimental data on Au(110) from ref 38.

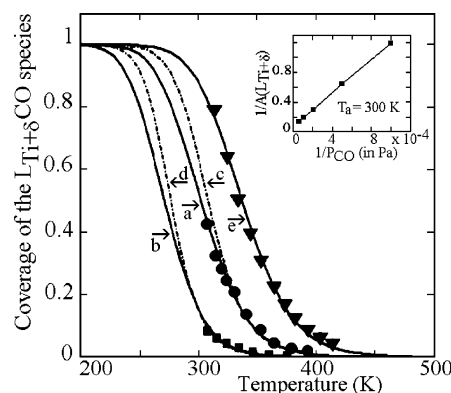


Figure 5. Experimental and theoretical evolutions of the coverage of the L_{Ti+δ} species on 1% Au/TiO₂ and TiO₂ (see the text for more details): ●, ■ experimental data and a, b theoretical curves (expressions 2 and 3) for $P_{\text{CO}} = 10$ and 1 kPa, respectively, on Au/TiO₂; c and d theoretical curves (expressions 1 and 3) for $P_{\text{CO}} = 10$ and 1 kPa, respectively, on Au/TiO₂; ▼, e experimental data and theoretical curves (expressions 2 and 3) for the pure TiO₂ support for $P_{\text{CO}} = 20$ kPa. Inset: Determination of the A_M value assuming the Langmuir model on Au/TiO₂.

T_a for two CO partial pressures as shown in Figure 4: curves □ and ● for $P_{\text{CO}} = 1$ and 10 kPa, respectively. The IR band area of the L_{Ti+δ} CO species increases between 15 and 20 kPa, indicating that the full coverage of the sites is not obtained at $P_{\text{CO}} = 20$ kPa. For the determination of the A_M value, it is assumed that the adsorption of L_{Ti+δ} CO corresponds to the Langmuir model. This is a priori justified by the fact that the surface concentration of the Ti^{+δ} sites is small, limiting the interaction between L_{Ti+δ} CO species. The Langmuir adsorption model gives:

$$\theta_{\text{L}_{\text{Ti}+\delta}} = \frac{A(T_a)}{A_M} = \frac{K_{\text{L}_{\text{Ti}+\delta}} P_{\text{CO}}}{1 + K_{\text{L}_{\text{Ti}+\delta}} P_{\text{CO}}} \quad (1)$$

where $K_{\text{L}_{\text{Ti}+\delta}}$ is the adsorption coefficient of the L_{Ti+δ} CO species at T_a . Expression 1 shows that $(1/A(T_a)) = f(1/P_{\text{CO}})$ at a constant adsorption temperature must be a straight line providing A_M and $K_{\text{L}_{\text{Ti}+\delta}}$ as shown in the inset of Figure 5 for the L_{Ti+δ} CO species on Au/TiO₂ at $T_a = 300$ K. This provides A_M that allows us to determine the evolution of the coverage

$\theta_{L_{Ti+\delta}}$ at two CO partial pressures as shown in Figure 5: curves ■ and ● for $P_{CO} = 1$ and 10 kPa, respectively. The experimental data in Figures 4 and 5 are used to measure the heats of adsorption of the two adsorbed CO species at several coverages. Curve ▼ in Figure 5 gives the evolution of the coverage of the $L_{Ti+\delta}$ CO species on the pure TiO_2 support for $P_{CO} = 20$ kPa.

3.3. Heats of Adsorption of the L_{Au° and $L_{Ti+\delta}$ CO Species on 1% Au/ TiO_2 . The experimental curves in Figures 4 and 5 are very similar to those previously observed on other supported metal catalysts for the L and/or B CO species.^{6–14} It has been shown that their profiles are due to a linear decrease in E_θ with the increase in the coverage θ of each adsorbed CO species leading to the generalized expression of the Temkin's model.^{6–14}

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

where ΔE 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. The E_0 and E_1 values are obtained considering that the adsorbed CO species are localized and that the adsorption coefficients are provided by the statistical thermodynamics.^{6–14}

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

where h is Planck's constant, k is Boltzmann's constant, m is the mass of the molecule, E_d and E_a are the activation energies of desorption and adsorption, respectively, while $E = E_d - E_a$ is the heat of adsorption depending of the coverage θ . The E_0 and E_1 values are those leading to theoretical curves $\theta_x = f(T_a)$ (from expressions 2 and 3) in agreement with the experimental data. For instance, the curves a and b in Figure 4 are obtained for $E_0(L_{Au^\circ}) = 74$, and $E_1(L_{Au^\circ}) = 47$ kJ/mol that correspond to the heats of adsorption of the L_{Au° CO species. The choice of the E_0 and E_1 values is limited in a short range (± 3 kJ/mol); otherwise the theoretical and experimental curves are different. Similarly, curves a and b in Figure 5 are obtained for $E_0(L_{Ti+\delta}) = 50$, and $E_1(L_{Ti+\delta}) = 40$ kJ/mol for the $L_{Ti+\delta}$ CO species. The small difference between those two values indicates that the Temkin's adsorption model for the $L_{Ti+\delta}$ CO species can be reasonably approximated to the Langmuir model as confirmed by curves c and d obtained using expressions 1 and 3 with a constant heat of adsorption: $E_L = 46$ kJ/mol. This supports the determination of A_M for this adsorbed CO species (inset of Figure 5). The heats of adsorption of the L_{Au° and $L_{Ti+\delta}$ CO species are very similar, and this shows the difficulties that can be encountered by using classical procedures such as TPD and microcalorimetry that may provide an average of their values. For $L_{Ti+\delta}$ CO species on the pure TiO_2 support, the best agreement between the experimental data and the theoretical curve (Figure 5e) is obtained from expressions 2 and 3 for $E_0 = 54$ and $E_1 = 44$ kJ/mol, showing that the Au particles have a very small impact on the heats of adsorption of the $L_{Ti+\delta}$ CO species considering the experimental uncertainties.

3.4. Comparison of the Heats of Adsorption of the L_{Au° Species to Literature Data. This comparison mainly concerns literature data on single crystals and model particles on TiO_2 due to the very small number of studies on Au-supported solids. Several studies provide the isosteric heats of adsorption of CO

from the Clausius–Clapeyron equation using experimental data (from different analytical methods) recorded under adsorption equilibrium. These experimental conditions are similar to those of the present study, and this allows us to perform a comparison between the isosteric heats of adsorption and the E_θ values from expressions 2 and 3. The practice of measurements of the isosteric heats of adsorption^{7,10,36} reveals that the values are significantly affected by experimental uncertainties, and this is also the situation on Au single crystals.^{30,32,38} However, these measurements show that the heats of adsorption of L_{Au° on Au single crystals are slightly lower than those of the present study. On Au(100), McElhiney and Pritchard³⁷ have determined the following by using surface potential (denoted SP) measurements: 58 ± 3 kJ/mol at low coverage decreasing progressively with the increase in θ . The same analytical method has been used by Ruggiero and Hollins²⁵ for the adsorption of CO on Au(332): 55 ± 3 kJ/mol at low coverages. This value remains constant during the increase in the coverage (until a SP = 125 mV) and then decreases roughly linearly to 20 kJ/mol. In recent work, Gottfield et al.³⁸ have measured the isosteric heats of adsorption of CO on Au(110)–(1 × 2) by using the work function: 59 ± 2 kJ/mol at low coverages progressively decreasing (roughly linearly) with the increase in θ to 35 kJ/mol at full coverage. Meier et al.³⁰ have determined the isosteric heats of adsorption by using the IR band intensity (IRAS) of the L_{Au° species on Au(110)–(1 × 2) (this is a procedure very similar to the present AEIR method): 46 kJ/mol at low coverage and 33 kJ/mol at coverage >0.19 . Moreover, Meier and Goodman³² have used the same experimental approach to measure the isosteric heats of adsorption of the L_{Au° species on Au metal clusters deposited on a TiO_2 film. They observed that this parameter varies at low coverage with the cluster sizes (diameter): 75, 68, 53, and 45 kJ/mol on 2.6, 1.6, 3.1 nm, and bulk, respectively. It can be observed that the values for 2.6 and 1.6 nm are in very good agreement with the present study. Moreover, for the 2.6 nm size, the author noted a roughly linear decrease with the coverage to 61 kJ/mol at high coverages, a value moderately higher than $E_1 = 45$ kJ/mol considering the uncertainties of the experimental procedures. These comparisons clearly show that the present E_θ values for the L_{Au° CO species on the Au° particles supported on TiO_2 are consistent with the isosteric heats of adsorption³² on model Au particles on a TiO_2 film. This seems to confirm the view of Meier and Goodman³² that the heat of adsorption of the L_{Au° CO species is slightly higher on the supported Au° cluster than on Au single crystals. Note that this difference is not linked to a shift in the IR band of the L_{Au° species that is situated at ~ 2110 cm^{-1} at high coverage, regardless of the Au-containing solid.

To our knowledge, there are few reports on others Au-containing solids. By microcalorimetry, Gupta et al.^{39,40} indicated that the heats of adsorption of CO on Au powder are in the range of 20–50 kJ/mol and in the range of 60–100 kJ/mol on Au/ Fe_2O_3 . These values are consistent with the view that the heats of adsorption of CO on Au are higher on small particles. The values on Au/ Fe_2O_3 are different than those of the present study, maybe due to the impact of the Fe_2O_3 support.

3.5. Application of the Present Adsorption Model to Literature Data on Au-Containing Solids. The isosteric heat

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of adsorption measurements constitute tedious experiments leading to values significantly affected by experimental uncertainties. This explains that we have adopted^{6–14} the mathematical formalism leading to expressions 2 and 3 for the exploitation of the experimental data in the AEIR approach. This strongly simplifies the experimental procedure: a single isobar provides the parameters of interest, while the experimental uncertainties have a limited impact. Expressions 2 and 3 are linked to a specific adsorption model: mainly the generalized Temkin's model and localized adsorbed species. There are several approximations on the partition functions that are involved in the final form of the adsorption coefficient. However, it has been shown that they have a very limited impact on the E_θ values.⁴¹ The literature data on the isosteric heats of adsorption of CO on Au single crystals and Au clusters, by using various analytical procedures, offer a quasi unique situation to compare the E_θ values obtained according to either the Clausius–Clapeyron equation or expressions 2 and 3 considering independent experimental data. There are several available experimental data in the literature to apply our formalism similarly to Figures 4 and 5. For instance, on Au clusters, Meier et al.³² provide the isothermal evolution (10 adsorption temperatures) of the IRAS band intensity of the L_{Au° CO species under adsorption equilibrium as a function of the adsorption partial pressure (12 low P_{CO} values). These data allow one to deduce the evolution of the intensity of the IRAS band in isobar conditions. We select the data in Figure 11 of ref 32 for the 0.125 MLE Au/TiO₂ sample because a constant IR band intensity is observed for $P_{CO} > 0.32$ Pa at the lower adsorption temperature ($T_a = 175$ K), allowing one to consider that the Au^o sites are fully covered under those experimental conditions. This provides the A_M value needed to determine the coverage of the Au^o sites adsorbing the L_{Au° CO species. This leads to curves \blacklozenge and \blacktriangledown in Figure 4 for two CO partial pressures in Figure 11 of ref 32: $\ln(P_{CO}/\text{Torr}) = -6$ (0.32 Pa) and -10 (5.9×10^{-3} Pa). Curves c and d are obtained from expressions 2 and 3 considering $E_0 = 70$ and $E_1 = 41$ kJ/mol. It can be observed that there is a very good agreement between experimental data and theoretical curves for the two CO partial pressures and that the E_0 and E_1 values are (a) very consistent with those measured on the present 1% Au/TiO₂ catalyst while P_{CO} and T_a are strongly different in the two studies ($P_{CO} < 0.5$ Pa and T_a in the range of 175–265 K in ref 32 and $P_{CO} > 1$ kPa and T_a in the range of 300–415 K in the present study) and (b) in reasonable agreement with the isosteric heats of adsorption.³² A similar comparison is performed using the IRAS experimental data on Au(110) (see Figure 3 in ref 30 with 15 T_a and 8 P_{CO} values). At the lower adsorption temperature, $T_a = 100$ K, the intensity of the IRAS band is roughly constant in the range 2×10^{-6} – 4×10^{-3} Pa, and this value is used as A_M . Curves \circ and \blacktriangle in Figure 4 are obtained for two P_{CO} values in Figure 3 of ref 30: $\ln(P_{CO}/\text{Torr}) = -11.5$ (1.3×10^{-3} Pa) and -16.1 (1.3×10^{-5} Pa). Curves e and f that overlap the experimental data are obtained considering expressions 2 and 3 with $E_0 = 65$ and $E_1 = 32$ kJ/mol that can be compared to 46 and 34 kJ/mol extrapolated from the isosteric heat of adsorption measurements (see Figure 5 in ref 30). The comparison with

the E_0 and E_1 values used for curves c and d on Au clusters on TiO₂ (Figure 4e and 4f) confirms the conclusion of Meier and Goodmann³² that the heats of adsorption of L_{Au° on Au particles are slightly higher than those on Au single crystals. A similar comparison can be performed considering the experimental data (work function) of Gooftfried et al.³⁸ (see Figure 12 in ref 38) on Au(110). However, at the lower adsorption temperature, $T = 120$ K, the highest CO pressure indicated does not correspond to the saturation coverage. By extrapolating the 120 K isotherm, it can be reasonably considered that the full coverage corresponds to $\theta \approx 0.5$ (by using the total surface of Au(110)) which corresponds to a coverage of 1 in the definition of the coverage linked to expressions 2 and 3 (by using a given number of sites). Curve \blacksquare in Figure 4 provides the isobar at 10^{-6} mbar from Figure 12 in ref 38. As expected, this curve is overlapped with that obtained from the experimental data of ref 30. However, the profile is slightly different, and the theoretical curve (not shown) from expressions 2 and 3 is obtained using $E_0 = 57$ and $E_1 = 35$ kJ/mol that are equal to the isosteric heats of adsorption determined by the authors at low and high coverages.³⁸

These comparisons between the isosteric heats of adsorption and the values obtained by using the mathematical formalism involved in the AEIR procedure considering independent experimental data (a) provide a very good support to the adsorption model and the approximations involved in expressions 2 and 3 and (b) show that the AEIR approach strongly simplifies the experimental procedures (a single isobar can be used: the fitting of two isobars such as in Figures 4a and 4b with the same E_0 and E_1 values reinforces the procedure). The use of a single isobar for metal-supported catalysts is particularly interesting for following the evolutions of the heats of adsorption by changing, for instance, a specific parameter in the catalyst preparation (natures of the precursors and of the support, pretreatment procedure, dispersion). One of the interests of the determination of $E_\theta = f(\theta)$ for the L_{Au° CO species in relationship with the performances of Au-containing solids in the CO/O₂ reaction at low temperatures is that this parameter participates in the coverage of the gold particles during the reaction. The comparison of the heats of adsorption of the L_{Au° CO species on various Au-containing solids (single crystals, model particles, and supported catalysts) shows that this parameter is moderately affected by the mean gold particle size: it can be roughly estimated that it is decreased by ~ 15 kJ/mol between small and large particles (single crystal). Expressions 2 and 3 indicate that this modification decreases the coverage of the L_{Au° species by a factor of ~ 0.44 (coverage on large particles/coverage on small particles) at 300 K for $P_{CO} = 1$ kPa. Assuming that the turnover frequency (TOF) of the CO/O₂ reaction is proportional to this coverage, this shows that a modification of the TOF with the particle size by a factor significantly different must be related to the change of other kinetic parameters (i.e., the oxygen coverage and the rate constant of the Langmuir–Hinshelwood elementary step).

3.6. Comparison of the Heats of Adsorption of the $L_{Ti+\delta}$ Species to Literature Data. Bolis et al.⁴² have studied by microcalorimetry the heats of adsorption of CO on TiO₂ powders in parallel to the FTIR characterization of the adsorbed CO

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species. On a pure anatase sample dehydrated at 403 K, they observed a single IR band at 2184 cm^{-1} (corresponding to that observed in the present study) ascribed to a linear CO species (denoted A). For a pretreatment in a vacuum at $T > 473\text{ K}$, a second IR band at 2203 cm^{-1} is observed ascribed to a second linear CO species (denoted B). The A and B species are attributed⁴² to the CO adsorption on Ti^{4+} on terraces and steps, respectively (5 and 4 coordinated Ti^{4+}). The heat of adsorption of the A CO species is 52 kJ/mol ,⁴² in very good agreement with the values used in Figure 5 for TiO_2 and Au/TiO_2 , while that of the B CO species is 69 kJ/mol . Moreover, the authors⁴² show that the isotherm at $T = 303\text{ K}$ for the A CO species is different from the Langmuir adsorption model. This observation is consistent with the fact that we observed that the E_θ slightly varies with the coverage of the $\text{L}_{\text{Ti}+\delta}$ CO species. Raup and Dumesic⁴³ have measured by a TPD procedure (assuming a preexponential factor of 10^{13} s^{-1}) the heats of adsorption of CO on TiO_2 (formed by oxidation of a Ti foil) as a function of the reduced state of the surface. They determine 49 kJ/mol on the most reduced state in very good agreement with the present study and 44 kJ/mol for the most-oxidized surface. On TiO_2 -(110), Linsebigler et al.⁴⁴ have determined by a TPD procedure a value of 42 kJ/mol at low coverages on the oxidized surface with a decrease by 9 kJ/mol at a coverage of 0.68 ML. Moreover, the CO binding energy was enhanced by 12% after reduction of the surface by annealing at 900 K : 47 kJ/mol at low coverage that is consistent with $E_0 = 50\text{ kJ/mol}$ in the present study. Bowker et al.⁴⁵ have measured the adsorption of CO on TiO_2 (110) in the presence of Pd nanoparticles by using a thermal molecular beam. The fitting of experimental data according to a kinetic modeling provides 38 kJ/mol that is consistent with $E_1 = 40\text{ kJ/mol}$. Several theoretical calculations^{46–48} of the heats of adsorption of CO on TiO_2 provide values in the range of $40\text{--}78\text{ kJ/mol}$ that are consistent with

the experimental data. It must be noted that Sorescu and Yates⁴⁷ determine 46 kJ/mol at half coverage that is in good agreement with 45 kJ/mol determined in the present study. Finally, it appears that the AEIR procedure provides heat of adsorption values for the adsorption of CO on TiO_2 (in the presence and in the absence of Au° particles) in reasonable agreement with literature data on TiO_2 -containing solids.

4. Conclusions

The AEIR procedure has been applied to determine the individual heats of adsorption at several coverages of the two linear CO species adsorbed on the Au° and $\text{Ti}^{+\delta}$ sites (denoted $\text{L}_{\text{Au}^\circ}$ and $\text{L}_{\text{Ti}+\delta}$) of a reduced 1% Au/TiO_2 catalyst. The adsorbed species are characterized by two IR bands at 2183 and 2110 cm^{-1} for the $\text{L}_{\text{Ti}+\delta}$ and $\text{L}_{\text{Au}^\circ}$ CO species, respectively. The heats of adsorption of the two species linearly vary with their respective coverages from 74 to 46 kJ/mol at coverages 0 and 1, respectively, for $\text{L}_{\text{Au}^\circ}$ CO species and from 50 to 40 kJ/mol at coverages 0 and 1 for the $\text{L}_{\text{Ti}+\delta}$ CO species. These values are consistent with literature data on different Au° - and TiO_2 -containing solids. In particular, the E_θ values obtained according to the present procedure for the $\text{L}_{\text{Au}^\circ}$ CO species are in good agreement with the isosteric heats of adsorption of CO on Au model particles on TiO_2 . It has been shown that the mathematical formalism of the AEIR method can be applied to these experimental data, providing heat of adsorption values similar to those of the isosteric method. This constitutes a new support to the measurement of the heats of adsorption using the AEIR method that strongly simplifies the experimental procedure as compared to the isosteric heats of adsorption.

The adsorption of CO on 1% Au/TiO_2 confirms the advantages of the AEIR procedure that provides the individual heats of adsorption at several coverages of two adsorbed CO species having similar binding energies.

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