

Heats of adsorption and activation energies of surface processes measured by infrared spectroscopy

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Abstract

The temperature-programmed adsorption equilibrium of CO at 4 kPa on Pd/SiO₂ and of CO₂ at 101.3 kPa on γ -Ga₂O₃ was studied by infrared spectroscopy between 298 and 723 K. The relative coverage (θ) evolution of each adsorbed species as a function of the adsorption temperature was measured by normalizing the IR absorption bands. The Temkin's model was used to fit the experimental data of θ versus temperature of each surface species and to obtain the initial ($\theta=0$) and final ($\theta=1$) isobaric heats of adsorption of linear and bridged CO adsorbed on palladium, and of HCO₃⁻ (bicarbonate), b-CO₃²⁻ (bidentate carbonate), br-CO₃²⁻ (bridged carbonate) and CO₂⁻ (carboxylate) on gallium oxide. The reactive adsorption of CO (101.3 kPa) on gallium oxide was also studied. CO reacts with surface OH groups to give formate species from 448 K. These formate species are further decomposed to CO₂(g) and Ga–H species from 573 K onwards. The whole process was modeled by considering the rate of reaction for each elementary step. Thus, the activation energy of the reactive adsorption of CO and of the formate decomposition on Ga₂O₃ was calculated. The calculated kinetic parameters are discussed and compared to those reported in the literature.

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1. Introduction

Heats of adsorption and activation energies of chemisorbed species participating in surface reactions on solid catalysts are required parameters to perform a microkinetic modeling, i.e., to correlate the elementary reaction steps with the performance of a catalyst [1].

Classically, adsorption microcalorimetry and adsorption isotherms over a temperature range are the methods used for determining heats of adsorption [2]. Microcalorimetry allows to measure differential heats of adsorption as a function of the surface species coverage and, thus, average integral heats can be derived. Then, the Clausius–Clapeyron equation can be applied to a series of isotherms recorded at different temperatures to give the isosteric heat (enthalpy) of adsorption.

In addition, elementary kinetic parameters are frequently measured by temperature-programmed experiments, that is, measures taken under transient conditions, which consist in a controlled perturbation to the gas/solid system and the measurement of a signal generated from the gas phase or the surface. For

instance, temperature-programmed desorption (TPD) methods permit the determination of the desorption activation energies, which can be equal to the heat of adsorption whenever the adsorption process is not activated.

However, these techniques present experimental difficulties such as: (i) the presence of several co-adsorbed species on the surface, (ii) possible parallel reactions, (iii) mass and heat transfer phenomena and (iv) readsorption of the products. In this respect, Gorte [3] and Gorte and Demmin [4] established a series of criteria allowing to set the experimental conditions, particularly in regard to TPD, where the influence of factors such as diffusion, lag time and readsorption over the measurement could be minimized.

Some of the above-mentioned problems can be overcome by carrying out adsorption experiments under equilibrium conditions because, among other considerations, the theoretical modeling of the recorded experimental data becomes simplified [5]. Consequently, some authors have proposed to use variable-temperature infrared spectroscopy to measure heats of adsorption for different surface species [5–8]. The infrared spectra are used to follow the evolution of the coverage of a particular surface species as a function of the adsorption temperature at a constant pressure of the adsorbed gas, and a suitable model is then used to calculate the heat of adsorption.

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Bianchi et al. have been successful in using variable-temperature infrared spectroscopy to measure the isobaric heats of adsorption of individual, linear and bridged CO species on several metal supported catalysts, such as Pt/Al₂O₃ [9–12], Cu/Al₂O₃ [5,13,14], Ru/Al₂O₃ [15], Pd/Al₂O₃ [16,17], Pd/CeO₂/Al₂O₃ and Pd/La₂O₃/Al₂O₃ [17], Pt/Ru/CeO₂/Al₂O₃ [8,17], Ir/Al₂O₃ [18], Pt/ZrO₂ [19] and Au/TiO₂ [20]. However, as far as we know, this approach has been seldom applied to the study of the adsorption and/or reactive adsorption over the surface of metal oxides [7,19].

Here we explore the use of this approach to study two cases: (i) the temperature-programmed equilibrium adsorption of CO and CO₂ on Pd/SiO₂ and γ -Ga₂O₃, respectively and (ii) the temperature-programmed reactive adsorption of CO on γ -Ga₂O₃.

2. Experimental

2.1. Materials

Pd/SiO₂ (2 wt.% Pd) was obtained by ion exchange of Pd(II) acetate (Sigma, 99.97%) onto silica (Davison 59; BET surface area = 301 m²/g) at pH 11 in NH₄OH(aq) [21]. The exchanged material was washed at the same pH, and dried at 423 K. The resulting diammine palladium complex was then calcined in flowing air (200 cm³/min), by heating from 298 to 673 K (2 h) at 2 K/min to obtain dispersed PdO on the surface. The PdO/SiO₂ was reduced in a 5% (v/v) H₂/Ar mixture (200 cm³/min), heating from 298 to 723 K (2 h) at 2 K/min. Finally, the catalyst was passivated at 298 K by flowing O₂/Ar mixtures (200 cm³/min) with increasing O₂ content, from 0.1 to 5% (v/v). The Pd metal dispersion, measured by the double isotherm of hydrogen chemisorption at 293 K, was 58%. γ -Ga₂O₃ was obtained from Ga(NO₃)₃·xH₂O (Strem, 99.99 wt.% Ga) as previously described [22–24]. The presence of a single crystallographic phase was verified by XRD (Shimadzu model XD-D1 diffractometer; Cu K α radiation). The specific surface area of the γ -gallia polymorph was 105 m²/g, measured by the BET isotherm (N₂, 77 K) in a Micromeritics Accusorb 2001E unit.

2.2. In situ FTIR spectroscopy

Temperature-programmed experiments were performed by employing self-supported wafers of 13 mm in diameter, pressing 10 mg of Pd/SiO₂ or 30 mg of γ -Ga₂O₃ at 5 t/cm². A heated IR cell made in Pyrex glass with water cooled NaCl windows, which was attached to a conventional high-vacuum system (base pressure = 1.33 × 10⁻⁴ Pa) equipped with a manifold for gas flow, was used for the in situ experiments.

Samples were pretreated in situ with O₂ (100 cm³/min, 5 K/min) at 723 K and cooled under vacuum to room temperature (RT). Additionally, the Pd/SiO₂ catalyst was further reduced in H₂ (100 cm³/min, 5 K/min) at 723 K (30 min) and again cooled down under vacuum to 298 K. It was verified that this activation protocol does not change the morphology of the employed solids.

To study the adsorption of CO over Pd/SiO₂, this catalyst was exposed to flowing CO (4%)/N₂ (100 cm³/min) at 298 K and heated to 723 K (5 K/min). The adsorption of pure CO₂ or CO on calcined γ -Ga₂O₃ was performed under flow of each gas (100 cm³/min) from 298 to 723 K (5 K/min) at 101.3 kPa.

A Shimadzu 8210 FTIR spectrometer with a DGTS detector was used in the transmission mode; spectra were acquired every 25 K at 4 cm⁻¹, averaging 25–100 scans. When needed, background correction of the spectra was achieved by subtracting the spectra of the pretreated wafers at each temperature. A Lorentzian sum function was used to fit the overlapping bands and to measure peak areas and/or intensities [25].

All the gases used in this study were high purity grade and were further purified as follows: H₂ (AGA, 99.999%), N₂ (AGA, 99.998%) and CO₂ (AGA, 99.996%) were passed through MnO/Al₂O₃ and molecular sieve (3 Å, Fisher Co.) traps to eliminate oxygen and water impurities, respectively; CO (AGA Research grade, 99.99%) and O₂ (AGA, 99.999%) were passed through molecular sieve (3 Å, Fisher Co.) and Ascarite traps to remove water and carbon dioxide, respectively.

3. Results and discussion

3.1. Surface coverage and heats of adsorption of CO species on Pd/SiO₂

Fig. 1 shows the temperature-variable infrared spectra taken in the 298–723 K temperature range, under flow of CO (4%)/N₂. The IR band initially centered at 2090 cm⁻¹ is assigned to linear or on-top CO (CO_L), which down shifts due to coverage decrease at increasing temperature. The broad and overlapped bands at 1975 and 1925–1900 cm⁻¹ correspond to bridged-bonded CO [CO_B on (1 0 0) planes and particle edges] and hollow-bonded CO [CO_H on (1 1 1) planes], respectively [26–29]. As it can be seen in the spectra, the absorbance of the CO_B species decreases monotonically and down shifts, while the CO_H band slightly

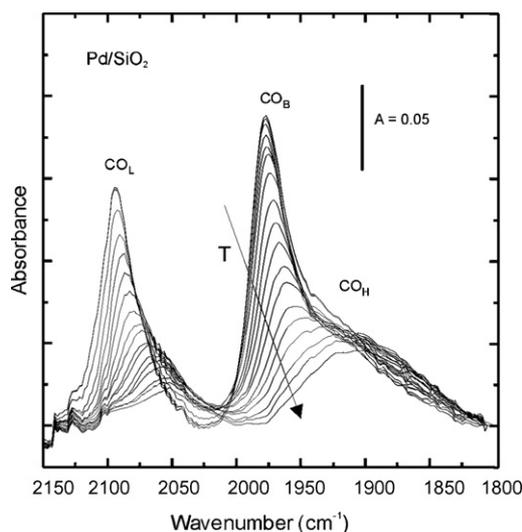


Fig. 1. Infrared spectra during the temperature-programmed adsorption of CO (4kPa) on Pd/SiO₂, between 298 and 723 K (the arrow indicates spectra at increasing temperature).

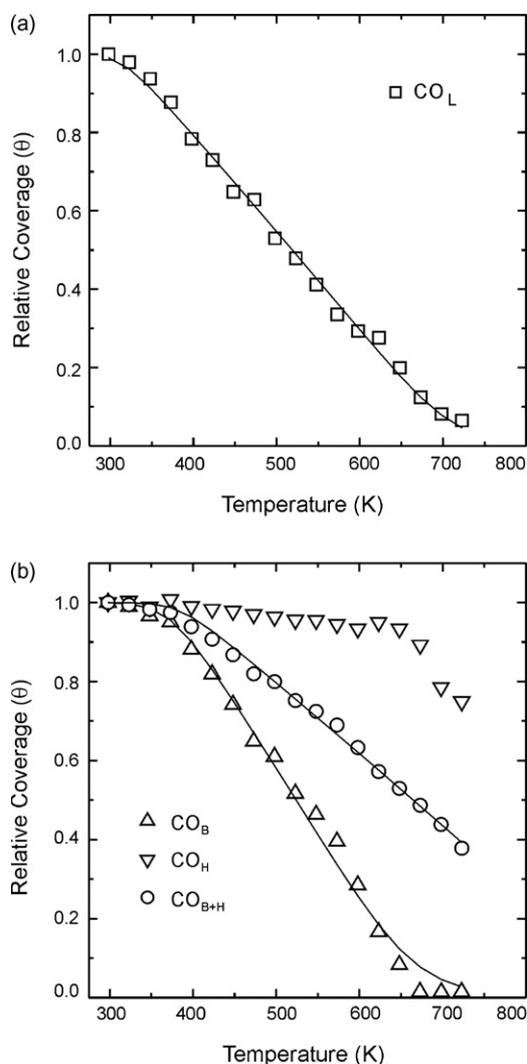


Fig. 2. Thermal evolution of the: (a) CO_L , and (b) CO_B , CO_H and CO_{B+H} relative coverages on Pd/SiO₂ at increasing temperature. Full lines correspond to the simulation using the Temkin's model.

reduces its intensity between 550 and 673 K due to its higher heat of adsorption as compared to the other CO adsorbed species [26]. This last observation is in agreement with the detection of CO_H species on Pd monocrystals at temperatures higher than 700 K, by IRAS [26,30].

The evolution of the relative surface coverage (θ) of linear-, bridged- and hollow-bonded CO on Pd/SiO₂ (θ_L , θ_B and θ_H , respectively) as a function of the adsorption temperature is shown in Fig. 2. For comparison purposes (see below) the θ_{B+H} , which corresponds to CO_{B+H} ($=\text{CO}_B + \text{CO}_H$), is also included.

The relative coverage of CO was determined as the ratio between the integrated absorbance of each IR band (or pair of bands for the case of CO_{B+H}) at each adsorption temperature (Fig. 1) and the highest IR band area at 298 K. That is, we assumed that: (a) the intensity of the IR bands are proportional to the amount of the CO species on the surface, (b) the IR absorption coefficients are independent of the adsorption temperature and, also, that (c) the system is in equilibrium at each temperature. The first two assumptions, (a) and (b), can be sustained by

comparing the coverage of the CO adsorbed species obtained using FTIR with mass spectroscopy data. To this end, in an additional experiment we measured the CO coverage by mass spectrometry, following the procedure described by Bourane et al. [31], and a fairly good agreement was achieved as compared to infrared relative coverages determined from integrated peak areas. Moreover, it can be theoretically shown that the transition probability between two vibrational states is independent of the temperature, as long as the re-population of the vibrational states of higher energy does not occur upon increasing the temperature [32]. Since CO adsorption on Pd is considered a non-activated process (the activation energy of adsorption is close to zero), a new equilibrium can be reached in $\sim 10^{-2}$ s for a temperature perturbation equal to 10 K [5]. Then, under our experimental conditions (that is, for a heating rate of 5 K/min) the adsorption equilibrium is reached almost instantaneously, which satisfies point (c).

Based on the previous assumptions, the thermal evolutions of θ_L and θ_B and at a constant CO pressure (4 kPa) were used to determine the heats of adsorption of CO_L and CO_B species, respectively. Temkin's model produced the best fitting, in agreement with previous results on palladium catalysts [16,17]. This model assumes that the heat of adsorption decreases linearly with the increase of the coverage. So:

$$\theta = \frac{RT}{\Delta E} \ln \left(\frac{1 + L_0 P}{1 + L_1 P} \right) \quad (1)$$

where T and P stand for the adsorption temperature and pressure, respectively, ΔE stands for the difference between the heat of adsorption at $\theta = 0$ (E_0) and the one at $\theta = 1$ (E_1); and L_0 and L_1 stand for the adsorption coefficients at $\theta = 0$ and 1, respectively.

The adsorption coefficients (L_θ) were estimated by statistical thermodynamics assuming that the CO adsorbed species is localized (loss of three translational degrees of freedom) [5,15–17]:

$$L_\theta = \frac{h^3}{k(2\pi mk)^{3/2}} \frac{1}{T^{5/2}} \exp \left(\frac{E_\theta}{RT} \right) \quad (2)$$

where h is the Planck's constant, k the Boltzmann's constant, m the weight of the adsorbate and E_θ is the heat of adsorption at $\theta = 0$ or $\theta = 1$.

The best fits of the experimental CO coverages as a function of the adsorption temperature are shown in Fig. 2 (full lines) for the following heats of adsorption: $E_0 = 125$ kJ/mol and $E_1 = 49$ kJ/mol for CO_L and $E_0 = 98$ kJ/mol and $E_1 = 51$ kJ/mol for CO_B . We also calculated the overall heat of adsorption (E_0 and E_1) for CO_B plus CO_H (that is, CO_{B+H}) in order to compare our results with those reported in the literature (it is clear from Fig. 2b, though, that thermodynamic data cannot – and should not – be computed for CO_H due to the narrow range of θ_H variation). Table 1 shows a fair agreement between the different E_θ values for the CO_L and CO_{B+H} adsorptions over supported palladium crystallites. The differences can be ascribed to the different supports and metal particle sizes.

Table 1
Heats of adsorption of bonded CO on palladium particles supported on different metal oxides, calculated by the variable-temperature infrared adsorption approach

Catalyst	CO _L		CO _B		CO _{B+H}		Reference
	E ₀ (kJ/mol)	E ₁ (kJ/mol)	E ₀ (kJ/mol)	E ₁ (kJ/mol)	E ₀ (kJ/mol)	E ₁ (kJ/mol)	
Pd/Al ₂ O ₃	92	54	–	–	168	92	[16,17]
Pd/(Cl)Al ₂ O ₃	92	54	–	–	168	75	[17]
Pd/CeO ₂ /Al ₂ O ₃	92	54	–	–	168	92	[17]
Pd/La ₂ O ₃ /CeO ₂ /Al ₂ O ₃	92	54	–	–	168	92	[17]
Pd/SiO ₂	125	49	98	51	168	62	This work

3.2. Coverage and heats of adsorption of CO₂ adsorbed on γ -Ga₂O₃

Upon exposure of the γ -gallia polymorph at 323 K to increasing CO₂ pressure, up to atmospheric pressure (101.3 kPa), several signals readily evolved in the 2000–1000 cm⁻¹ region. The absorbance of these bands reached a saturation plateau at approximately 600 Torr of CO₂ (not shown) [24]. The infrared spectra collected during the temperature-programmed adsorption of CO₂ (at 101.3 kPa) on γ -Ga₂O₃ are reported in Fig. 3. All these bands followed the same, reverse evolution after decreasing the temperature from 723 to 300 K under flowing pure CO₂, which suggests that all carbonaceous species are reversibly adsorbed on Ga₂O₃.

For the assignment of the IR signals of the carbonaceous surface species chemisorbed onto Ga₂O₃, it is appropriate to examine the following features [23,24]: (i) their frequency position and its comparison with reported IR signals of carbonates adsorbed over other metal oxides, (ii) the width of the $\Delta\nu_3$ -band splitting of the CO₃²⁻ anion (that is, the $\Delta\nu_3 = \nu_{as} - \nu_s$ of the CO₃ stretching modes) due to the loss of its D_{3h} symmetry by chemisorption and (iii) the thermal stability of each signal.

Accordingly, the IR signals in the 2000–1000 cm⁻¹ region were assigned to the following surface species: bicarbonate, HCO₃⁻ [$\nu_{as}(\text{CO}) = 1630 \text{ cm}^{-1}$, $\nu_s(\text{CO}) = 1430 \text{ cm}^{-1}$,

$\delta(\text{OH}) = 1225 \text{ cm}^{-1}$]; bidentate carbonate, b-CO₃²⁻ [$\nu_{as}(\text{CO}) = 1587 \text{ cm}^{-1}$, $\nu_s(\text{CO}) = 1325 \text{ cm}^{-1}$]; polydentate carbonate, p-CO₃²⁻ [$\nu_{as}(\text{CO}) = 1460 \text{ cm}^{-1}$, $\nu_s(\text{CO}) = 1410 \text{ cm}^{-1}$]; bridged carbonate, br-CO₃²⁻ [$\nu_{as}(\text{CO}) = 1750 \text{ cm}^{-1}$, $\nu_s(\text{CO}) = 1170 \text{ cm}^{-1}$]; and carboxylate, CO₂⁻ [$\nu_{as}(\text{CO}) = 1680 \text{ cm}^{-1}$, $\nu_s(\text{CO}) = 1280 \text{ cm}^{-1}$]. More details about these assignments can be found in Refs. [23,24].

The relative coverage of the carbonate species during the temperature-programmed adsorption experiment (298–723 K) of CO₂ are plotted in Fig. 4, taking into account the same assumptions made regarding the CO adsorption on Pd [former items (a–c)], but for CO₂ now. The coverage of HCO₃⁻, b-CO₃²⁻, br-CO₃²⁻ and CO₂⁻ decreased monotonically during the adsorption of CO₂ at increasing temperature, while the concentration of p-CO₃²⁻ remained almost constant (not shown in Fig. 4). It is worth noticing that the same evolution of the coverage of the carbonate groups was obtained during the cooling process of the sample in the IR cell from 723 to 298 K under flowing CO₂ at 101.3 kPa, which confirms that the adsorption of CO₂ on gallia also satisfied the adsorption equilibrium condition.

The experimental data were first adjusted using the Langmuir's adsorption model, which assumes that the heat of adsorption is independent of the coverage. However, the Langmuir's model did not provide a successful fitting for the CO₂ adsorption data on gallia. Then, the thermal evolution of the coverage of each surface carbonate species was predicted by

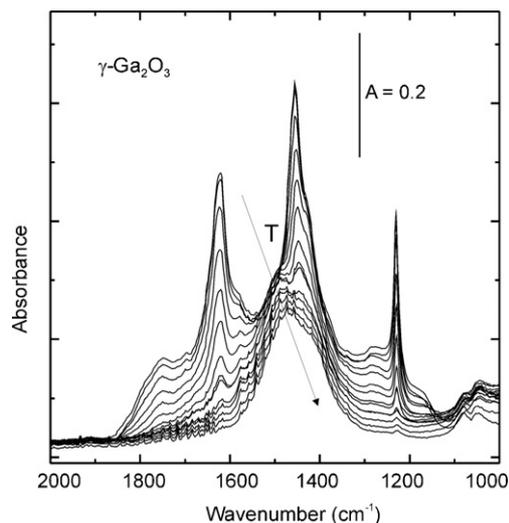


Fig. 3. Infrared spectra during the temperature-programmed adsorption of CO₂ (101.3 kPa) on γ -Ga₂O₃, between 298 and 723 K (the arrow indicates spectra at increasing temperature).

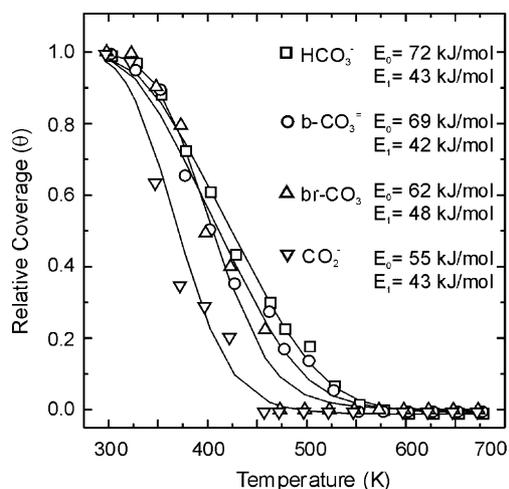


Fig. 4. Thermal evolution of the relative coverages of carbonate and bicarbonate species on γ -Ga₂O₃ (except for p-CO₃²⁻) at increasing temperature. Full lines correspond to the simulation using the Temkin's model.

using the Temkin's model, and the best fit is depicted in Fig. 4.

Unfortunately, neither E_0 nor E_1 of individual surface carbonate groups have been reported, as far as we know, in the open literature. Petre et al. [33] reported an initial global heat of adsorption of CO_2 over Ga_2O_3 equal to 115 kJ/mol measured by microcalorimetry. This value is higher than the E_0 determined in this work ($E_0 = 55\text{--}72$ kJ/mol, see Fig. 4). Nevertheless, it is clear that initial heat of adsorption reported by Petre et al. [33] is an average, overall value, i.e., the result of the adsorption of several surface species, including the p-CO_3^{2-} group. Fig. 3 shows that the p-CO_3^{2-} coverage slightly changed along the adsorption ramp (see also Fig. 9 in Ref. [24]). Then, it is not possible to calculate any heat of adsorption for this species. Yet, for a surface species whose coverage does not change appreciably throughout the temperature range used here, we can still make an estimation of the lower expected value of the initial adsorption heat. Hence, $E_0 > 200$ kJ/mol is predicted for p-CO_3^{2-} species. Therefore, the average value for the initial heat of adsorption of all carbonate species over Ga_2O_3 might be closed to the one reported by Petre et al. [33].

3.3. Reactive adsorption of CO on $\gamma\text{-Ga}_2\text{O}_3$

We have shown in the previous section that variable-temperature infrared spectroscopy can be used to measure heats of adsorption of carbonate species on gallium oxide, because the adsorption process is reversible and can be considered under equilibrium condition at each temperature. However, this approach can be further employed when the adsorbate reacts irreversibly with a solid surface, as is the case of CO adsorption on gallium oxide.

CO chemisorbs on $\gamma\text{-Ga}_2\text{O}_3$ from 448 K (Fig. 5) by reacting with surface OH ($3800\text{--}3000\text{ cm}^{-1}$) groups to produce formate

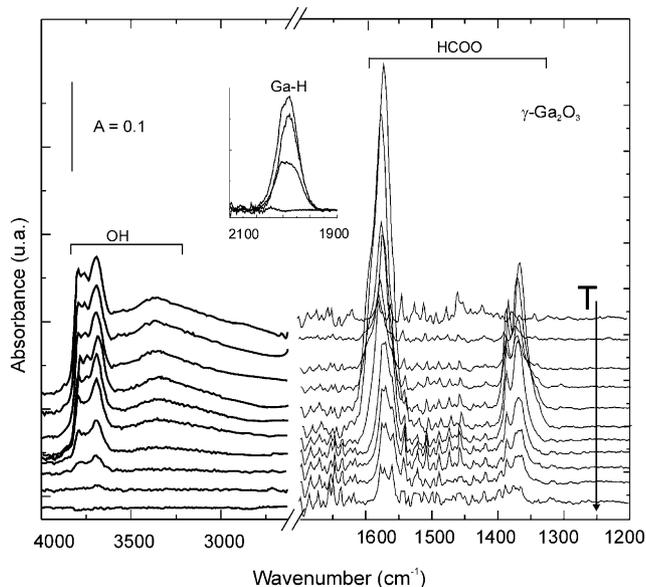


Fig. 5. Infrared spectra during the temperature-programmed reactive adsorption of CO (101.3 kPa) on $\gamma\text{-Ga}_2\text{O}_3$, between 298 and 723 K (the arrow indicates spectra at increasing temperature).

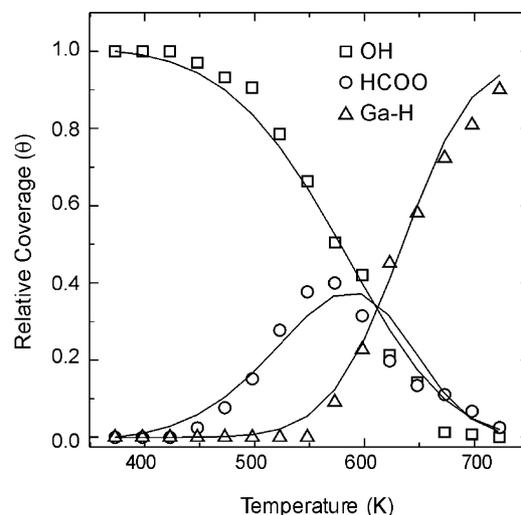
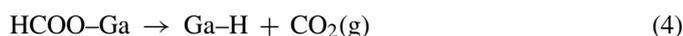


Fig. 6. Thermal evolution of the relative coverages of OH, HCOO and Ga-H species on $\gamma\text{-Ga}_2\text{O}_3$ at increasing temperature. Full lines correspond to the simulation (see text).

species (HCOO) [$\nu_{\text{as}}(\text{COO}) = 1580\text{ cm}^{-1}$, $\delta(\text{CH}) = 1386\text{ cm}^{-1}$, $\nu_{\text{s}}(\text{COO}) = 1372\text{ cm}^{-1}$] [23]. From 573 K onwards HCOO decomposes into Ga-H surface species [$\nu(\text{Ga-H}) = 1990\text{ cm}^{-1}$] [22] and $\text{CO}_2(\text{g})$. Considering that the adsorption of CO proceeds according to an Eley-Rideal mechanism, the following pathway for the reactive adsorption of CO on gallia can be proposed:



In the same direction, Haneda et al. proposed the HCOO formation and the subsequent release of $\text{CO}_2(\text{g})$ for the CO adsorption on $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$, using FTIR and mass spectrometry [34]. Furthermore, the complete removal of OH surface group was verified over the surface of our sample in additional CO_2 and/or CO adsorption experiments and after the absence of any bicarbonate and/or formate group formation.

Fig. 6 shows the normalized coverage of OH, HCOO and Ga-H surface groups. These relative coverages were calculated assuming that the total concentration of said surface species was equal to the initial concentration of OH groups [i.e., $\theta(\text{OH}) + \theta(\text{HCOO}) + \theta(\text{Ga-H}) = 1$].

According to the above reaction mechanism, the reactive adsorption of CO on $\gamma\text{-Ga}_2\text{O}_3$ can be described by the following differential equations:

$$\frac{d\theta(\text{OH})}{dT} = -\frac{A_1}{\beta} T^{-3/2} \theta(\text{OH}) P_{\text{CO}} \exp\left(-\frac{E_{a1}}{RT}\right) \quad (5)$$

$$\frac{d\theta(\text{HCOO})}{dT} = \frac{A_1}{\beta} T^{-3/2} \theta(\text{OH}) P_{\text{CO}} \exp\left(-\frac{E_{a1}}{RT}\right) - \frac{A_2}{\beta} T \theta(\text{HCOO}) \exp\left(-\frac{E_{a2}}{RT}\right) \quad (6)$$

$$\frac{d\theta(\text{GaH})}{dT} = \frac{A_2}{\beta} T \theta(\text{HCOO}) \exp\left(-\frac{E_{a2}}{RT}\right) \quad (7)$$

where A_i stands for the Arrhenius pre-exponential factor (not a function of the temperature for localized surface species [2,35]), E_{ai} for activation energy of reaction i ($i = 1$ or 2), and β stands for the heating rate.

This system of differential equations was numerically integrated (fourth order Runge–Kutta) and the error between the model and the experimental data was minimized with A_i and E_{ai} as parameters (Down-Simplex). Full lines in Fig. 6 represent the best fits of the experimental data with $A_1 = 1.95 \times 10^5 \text{ K}^{3/2}/\text{s Pa}$, $E_{a1} = 35 \text{ kJ/mol}$ and $A_2 = 3.27 \times 10^4 (\text{K s})^{-1}$, $E_{a2} = 103 \text{ kJ/mol}$.

The calculated pre-exponential factors are in the same order of magnitude than the expected ones for adsorption and decomposition/desorption processes of gases on metal surfaces [2]. A comparison of the activation energy for formate formation is not possible at the moment, because the results reported in the literature usually deal with the synthesis of formate from CO_2 and H, instead of CO and OH [36–38]. Nevertheless, the kinetic of the synthesis and decomposition of formate species have been studied on copper single crystals [36,37] and on copper supported catalysts [37,38] due to the importance of this intermediate on the water gas shift reaction: Yatsu et al. [37] reported an activation energy for the formate decomposition on copper equal to 115.7 kJ/mol , which is in reasonable agreement with the value of E_{a2} calculated in this work.

4. Conclusions

In situ variable-temperature infrared spectroscopy was employed to follow the relative coverage of different surface species generated by adsorption of CO over a Pd/SiO₂ catalyst and of CO₂ and CO over $\gamma\text{-Ga}_2\text{O}_3$. Under equilibrium reversible adsorption, the individual heats of adsorption of CO on Pd and CO₂ on $\gamma\text{-Ga}_2\text{O}_3$, leading to the formation of different surfaces species in each case, were calculated using the Temkin's adsorption model.

The variable-temperature infrared spectroscopy strategy was also used to study the reaction of CO with OH groups on the surface of $\gamma\text{-Ga}_2\text{O}_3$. The thermal evolution of OH, HCOO and Ga–H species was successfully simulated considering the system of differential equations that describe the elementary reaction steps, by using the pre-exponential factors and the activation energies as fitting parameters.

In general, the calculated values of different kinetic parameters for both reversible (CO and CO₂ on Pd/SiO₂ and Ga₂O₃, respectively) and reactive adsorption (CO on Ga₂O₃) following the variable-temperature infrared spectroscopy approach were in good agreement with those reported employing other classical methods.

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