Impact of the Residual Chlorine on the Heat of Adsorption of the Linear CO Species on Cu/Al₂O₃ Catalysts

Salim Derrouiche, Vincent Perrichon, and Daniel Bianchi*

Laboratoire d'Application de la Chimie à l'Environnement (LACE), UMR 5634, Université Claude Bernard, Lyon-1, Bat. 305, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France

The adsorption of CO at several adsorption temperatures (T_a) in the range of 300–550 K on several reduced ≈5 wt % Cu/Al₂O₃ solids, with and without residual chlorine, is studied by FTIR spectroscopy. Whatever the solid, the main adsorbed species is a linear (denoted by L) CO species adsorbed on Cu° sites. On the Cl-free solids, the L CO species is detected at 2095 cm⁻¹, while the presence of Cl leads to a shift to higher wavenumbers. The evolution of the coverage θ_L of the L CO species with the adsorption temperature for a constant CO partial pressure ($P_{CO} = 1$ kPa) allows us to determine the heat of adsorption of the L CO species as a function of the coverage on the various Cu-containing solids by using the AEIR method. It is shown that the presence of residual Cl has no impact on the heat of adsorption at low coverages (82 kJ/mol), while it decreases slightly the heat of adsorption at high coverages from 57 to 45 kJ/mol.

1. Introduction

In the gas–solid heterogeneous catalysis, numerous studies concern the influence of the preparation parameters on the catalyst properties. On supported metal catalysts, one of these parameters is the nature of the precursor of the metallic phase, i.e., with or without chlorine. The detrimental impact of residual Cl on the performances of metal-supported catalysts in catalytic oxidation reactions is well-documented,[1–4] even if there is a discussion of the causes of this influence. The nature of the precursor may have an impact either on the preparation steps of the catalyst (i.e., metal dispersion) or on the reactivity of the adsorbed species (i.e., electronic effect). For instance, it is well-known that the presence of Cl may significantly affect the position of the IR band of the linear (denoted by L) CO species on various supported metal catalysts. Usually, the IR band shifts to higher wavenumbers in the presence of Cl such as from 2065 to 2075 cm⁻¹ on Pt/Al₂O₃,[5] from 2056 to 2070 cm⁻¹ on Rh/CeO₂,[6] from 2072 to 2090 cm⁻¹ on Pd/Al₂O₃,[7] and from 2031 to 2078 cm⁻¹ on 5% Ru/SiO₂.[8] These shifts are assigned to the electron acceptor properties of Cl which decrease the extent of back-donation of metal to the antibonding orbital of CO.[5] It is of interest to know if the presence of Cl also modifies the reactivity of the catalyst for a selected simple molecule such as CO, O₂, or H₂. On Pd-containing solids, we have studied the influence of Cl on the heat of adsorption of the L and bridged (denoted by B) CO species.[11] This parameter is one of those which control the coverage of an adsorbed species during a catalytic reaction. We have observed using a new analytical procedure (denoted by AEIR[9,10]) that the heat of adsorption of the B CO species on Pd particles, which linearly varies with its coverage from 168 to 92 kJ/mol when $\theta = 0$ and 1, respectively, on Cl-free solids,[11] slightly decreases by ≈15–20 kJ/mol at high coverages on Cl-containing catalysts[11] but is not modified at low coverages. A similar conclusion has been reached for the L CO species adsorbed on Ru/Al₂O₃ catalysts:[12] on the Cl-free solid, the heat of adsorption linearly varies with its coverage θ from 175 to 115 kJ/mol when $\theta = 0$ and 1, respectively, and

from 175 to 105 kJ/mol when $\theta = 0$ and 1, respectively, on the Cl-containing solid. This means that on Pd and Ru catalysts, if a catalytic reaction involving CO is strongly modified by the presence of Cl, it is not a change in the heats of adsorption of the L and/or B CO species which can been used as an explanation. From these previous studies,[7,11,12] it seems that the residual chlorine only slightly affects the heat of adsorption of the adsorbed CO species at high coverages while the positions of the IR band are significantly affected. On Pd and Ru, whatever the coverage, the adsorbed CO species are strongly adsorbed, and this may be the cause of the slight impact of the residual Cl on the heats of adsorption at high coverages. On a reduced Cu/Al₂O₃ catalyst, it has been shown that the heats of adsorption of the L CO species are significantly lower (weakly adsorbed CO species) than those of the adsorbed species on Pd and Ru: $E_0 = 82$ kJ/mol when $\theta = 0$ to $E_1 = 57$ kJ/mol when $\theta = 1$.[13] This offers the opportunity to study if there is a stronger impact of the residual Cl on the heats of adsorption of weakly adsorbed CO species.

2. Experimental Section

Catalysts. Several Cu/Al₂O₃ catalysts with and without chlorine have been prepared according to various methods.

Solids without Chlorine. A 4.7 wt % Cu(Cl-f)/Al₂O₃(R) solid has been prepared by the incipient wetness method using Cu-(NO₃)₂·3H₂O and γ-Al₂O₃ (BET area of 110 m²/g) without any Cl from Rhodia [reference 531P; the main impurities were Na₂O (570 ppm), Fe₂O₃ (300 ppm), CaO (280 ppm), and SiO₂ (170 ppm)]. The solid was slowly dried in air at 300 K over the course of 48 h, and then it was treated according to the following procedure (denoted by P1) which was used for the various preparations. After 12 h in air at 383 K, the solid was treated in an O₂ flow (6 L/h) at 673 K for 6 h (heating rate of 1 K/min), and then after a purge under N₂, the solid was reduced in an H₂ flow (7 L/h) at 773 K over the course of 6 h. The solid was cooled in H₂ to 300 K, and after a purge in N₂, it was stored in a glass flask before being used.

A 5.1% Cu(Cl-f)/Al₂O₃(R) solid has been prepared by wet impregnation according to the following procedure. Ten grams

of Rhodia alumina was introduced in 80 cm^3 of water contained in a 250 cm^3 flask of a rotary evaporator. After homogenization for 30 min at 80 °C, a solution containing the appropriated amount of Cu(NO$_3$)$_2$·3H$_2$O in 80 cm^3 of H$_2$O was introduced. After homogenization for 1 h, the solvent was evaporated at 80 °C in a vacuum. After the solid had been crushed, the powder was treated according to procedure P1. This solid was similar (new preparation) to that (with 4.7 wt % Cu) used in a previous study.[13]

Solids with Chlorine. A 4.7 wt % Cu(Cl)/Al$_2$O$_3$(D) solid has been prepared by the incipient wetness method as described above using γ-Al$_2$O$_3$ (BET area of 100 m^2/g) from Degussa (Oxid C) with a chlorine content of $\leq$5000 ppm.

Two 4.7 wt % Cu(Cl-x)/Al$_2$O$_3$(R) solids (x = 500 or 5000, which denotes the amount of Cl in parts per million on the support) have been prepared by the same method using the prechlorinated Rhodia Al$_2$O$_3$ prepared according to the following procedure. Ten grams of alumina was impregnated by the incipient wetness method with an HCl solution to obtain 5000 ppm of Cl (x). Then the solid was dried at room temperature and then at 383 K before a treatment in O$_2$ (6 L/h) at 673 K. This chlorinated alumina was used for the preparation of the Cu/Al$_2$O$_3$ catalyst. A similar preparation has been made with an x of 500 ppm. The elemental Cl analysis after the calcination and reduction pretreatments indicates significantly smaller amounts on Cl than the preparation at 1500 ppm for an x of 5000.

Analytical Procedure. For the FTIR study, the catalyst was compressed to form a disk (Φ = 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,[14] 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^3/min. Before the adsorption of CO, the solid was treated in situ (200 cm^3/min) according to the following procedure: He at 298 K → He at 713 K → O$_2$, 713 K (0.5 h) → He at 713 K (0.5 h) → H$_2$ at 713 K (0.5 h) → He at 713 K (0.5 h) → He at 300 K → CO adsorption. The CO adsorption was performed according to the following procedure: pretreated solid → He at 300 K → x% CO/He (total pressure = 100 kPa, flow rate = 200 cm^3/min, x = 1 or 10) → increase in T_a (5−10 K/min) up to a T_a of <713 K. The FTIR spectra of the adsorbed species were recorded periodically. After the highest adsorption temperature was reached, the solid was cooled in the presence of x% CO/He and the spectra were compared to those recorded in the course of the heating stage to reveal an eventual modification of the catalyst during the CO adsorption at high temperatures. In the study presented here, the weights of the catalyst pellets were similar, allowing semiquantitative comparisons.

3. Results and Discussion

3.1. Heats of Adsorption of the L CO Species on Solid Cl-Free Cu/Al$_2$O$_3$ Determined by Using the AEIR Method. The evolution of the FTIR spectra recorded during the increase in T_a with a 1% CO/He mixture on 5.1 wt % Cu(Cl-f)/Al$_2$O$_3$-(R) was identical to that described in detail previously.[13] Those recorded on the 4.7 wt % Cu(Cl-f)/Al$_2$O$_3$(R) solid are similar. Briefly, the introduction of the 1% CO/He mixture at 300 K (Figures 1a and 2a) leads to the detection of a strong IR band at 2095 cm^{-1} alongside a weak shoulder in the range of 2080−2060 cm^{-1} ascribed to linear CO species on Cu°.[13] There are no IR bands above 2100 cm^{-1}, indicating the absence of Cu$^{\delta+}$ sites on the surface.[13] The successive 1% CO/He → 5% CO/He → 10% CO/He switches do not modify the intensity of the IR band, proving a full coverage of the sites at the lower CO
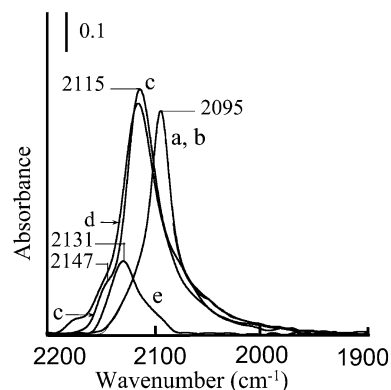

Figure 1. FTIR spectra after adsorption of a 1% CO/He mixture at 300 K on the various Cu/Al$_2$O$_3$ solids after reduction in H$_2$: (a) 4.7 wt % Cu(Cl-f)/Al$_2$O$_3$(R), (b) after (a) heating to 460 K and cooling to 300 K in CO/He, (c) 4.7 wt % Cu(Cl)/Al$_2$O$_3$(D), (d) 4.7 wt % Cu(Cl-500)/Al$_2$O$_3$(R), and (e) 4.7 wt % Cu(Cl-5000)/Al$_2$O$_3$(R).
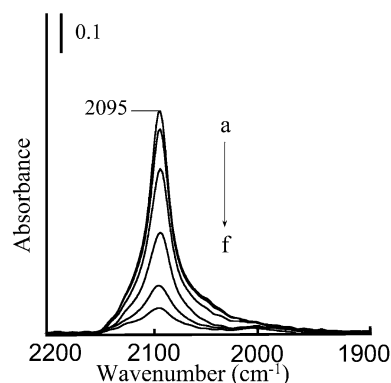

Figure 2. FTIR spectra recorded on the reduced 4.7 wt % Cu(Cl-f)/Al$_2$O$_3$(R) solid over the course of the CO adsorption (P_a = 1000 Pa) at various temperatures: (a) 300, (b) 323, (c) 353, (d) 393, (e) 434, and (f) 460 K.

partial pressure (1 kPa). A 1% CO/He → He switch leads to the progressive decrease in the intensity with time on stream without any shift of the IR band. The increase in T_a with the 1% CO/He mixture progressively decreases the intensity of the IR band (Figure 2a−f) without any significant shift of the position of the IR band which disappears at $\approx$520 K (T_a). After the sample had been cooled in a 1% CO/He mixture, the FTIR spectrum recorded at 300 K overlapped that recorded before the increase in T_a (Figure 1b). This indicates that there are no significant modifications of the Cu surface in the course of the adsorption at high temperatures. From the evolution of the IR band intensities with T_a at a constant partial pressure of CO, the AEIR method allows us to determine the heat of adsorption of the L CO species. The change in the coverage θ_L of the Cu° sites by the L species in the presence of the 1% CO/He mixture as a function of T_a is obtained using the ratio A/A_M (θ), where A is the IR band area at T_a and A_M the greatest IR band area (at 300 K). It has been shown that there is a linear relationship between the IR band area and the amount of L species on the surface.[15] Curve a in Figure 3 shows the evolution of θ with T_a for the 1% CO/He mixture. These experimental points are compared in the AEIR procedure[5,6] to the curve obtained from an adsorption model built with two main assumptions.

(1) The adsorbed CO species are localized, and their adsorption coefficient K is given by the statistical thermodynamics:

$$K = \frac{h^3}{k(2\pi mk)^{3/2}} \frac{1}{T_a^{5/2}} \exp\left(\frac{E_d - E_a}{RT_a}\right) \qquad (1)$$
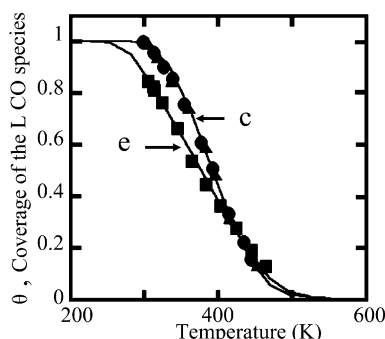
Figure 3. Evolution of the coverage of the linear CO species on Cu°
according to the adsorption temperature T_a for a 1% CO/He mixture:
▲ (a) and ● (b), experimental data on 4.7 wt % Cu(Cl-f)/Al$_2$O$_3$(R)
during the heating and cooling stages, respectively; (c) theoretical
coverage for an E_0 of 82 kJ/mol and an E_1 of 57 kJ/mol (■); (d)
experimental data on 4.7 wt % Cu(Cl)/Al$_2$O$_3$(D); and (e) theoretical
coverage for an E_0 of 82 kJ/mol and an E_1 of 45 kJ/mol.

where h is Planck's constant, k is Bolztmann's constant, m is
the mass of the molecule, E_d and E_a are the activation energies
of desorption and adsorption, respectively, and $E_d - E_a$ equals
the heat of adsorption (denoted by E_θ with θ being the value of
the coverage).

(2) The heat of adsorption linearly varies with the coverage
θ

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

where K_0 and K_1 are the adsorption coefficients when $\theta = 0$
and 1, respectively, and ΔE is the difference in the heat of
adsorptions E_0 and E_1.

To evaluate E_1 and E_0, we have only to determine the
numerical values which lead to the best agreement between the
experimental and theoretical curves. For instance, curve c in
Figure 3 is obtained using an E_0 of 82 kJ/mol at $\theta_L = 0$ to an
E_1 of 57 kJ/mol at $\theta_L = 1$ with an accuracy of approximately
± 2 kJ/mol (E_0 and E_1 values of greater than 2 or less than -2
kJ/mol give theoretical curves clearly different from the exper-
imental curve). These values are identical (a) to those previously
determined for a 4.7 wt % Cu(Cl-f)/Al$_2$O$_3$(R) solid prepared
by wet impregnation[13] and (b) to those determined on the present
4.7 wt % Cu(Cl-f)/Al$_2$O$_3$(R) solid. They agree with the fact that
the IR band intensity of the L species adsorbed on Cu°
progressively decreases during an isothermal desorption at 300
K[13] as observed by other authors.[16] Clearly, there is no impact
of the preparation method (incipient wetness or wet impregna-
tion[13] method) on the heats of adsorption of the L CO species
on Cu° for the Cl-free solids. Moreover, we have previously
shown[13] that the E_0 and E_1 values as well as the linear increase
in E_θ with the decrease in θ are in reasonable agreement with
the isosteric heat of adsorption at several coverages obtained
by using the Clausius−Clapeyron equation. This strongly
supports the mathematical procedure using eqs 1 and 2.

**3.2. Heats of Adsorption of the L CO Species on Cl-
Containing Cu/Al$_2$O$_3$ Solids.** Spectrum c in Figure 1 shows
the IR band recorded at 300 K with the 1% CO/He mixture on
reduced 4.7 wt % Cu(Cl)/Al$_2$O$_3$(D). The comparison with Figure
1a reveals a shift of the IR band of the L CO species on Cu° to
higher wavenumbers for the Cl-containing support (2115 cm^{-1}).
Figure 1d recorded after adsorption of the 1% CO/He mixture
on the reduced 4.7 wt % Cu(Cl-500)/Al$_2$O$_3$(R) solid shows that
the introduction of Cl on the Cl-free Al$_2$O$_3$ support leads to a
shift of the IR band of the L CO species from 2095 cm^{-1} (Cl-
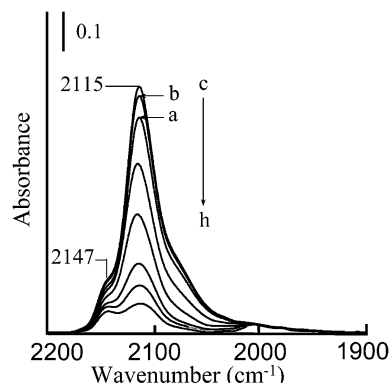

Figure 4. FTIR spectra recorded on the reduced 4.7 wt % Cu(Cl)/
Al$_2$O$_3$(D) solid over the course of the CO adsorption at various
temperatures: (a−c) 300 K with x% CO/He mixtures (x = 1, 2.5, and
5, respectively) and (d−h) in a 1% CO/He mixture at T_a values of
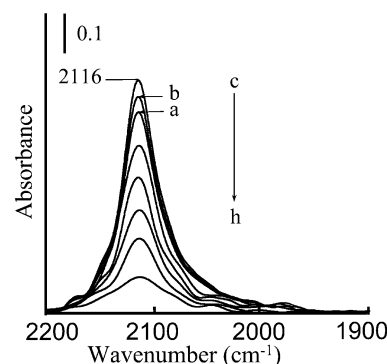343, 383, 423, 443, and 463 K, respectively.

Figure 5. FTIR spectra recorded on the reduced 4.7 wt % Cu(Cl-
500)/Al2O3(R) solid over the course of the CO adsorption at various
temperatures: (a−c) 300 K with x% CO/He mixtures (x = 1, 2.5, and
5, respectively) and (d−h) in a 1% CO/He mixture at T_a values of
330, 371, 395, 421, and 450 K, respectively.

free Al$_2$O$_3$) to 2115 cm^{-1}, and Figure 1e shows that this shift
is larger for 4.7 wt % Cu(Cl-5000)/Al$_2$O$_3$(R) (2131 cm^{-1}) while
the intensity of the IR band is significantly decreased as
compared to spectra a and c. Clearly, Figure 1 indicates that
the presence of residual Cl leads to a shift of the IR band of the
L CO species on Cu° to higher wavenumbers, in agreement
with the explanation of the impact of Cl based on its electron
acceptor properties.[5] These shifts in the position of the IR band
of the L CO species comprise the single indication that there is
an interaction between Cl and the Cu° sites because it is difficult
to quantify the amounts of Cl on the Al$_2$O$_3$ support and on the
Cu° particles. At the opposite of the Cl-free solids, spectra a−c
in Figure 4 indicate that the IR band intensity of the L CO
species on the 4.7 wt % Cu(Cl)/Al$_2$O$_3$(D) solid increases at 300
K with the increase in the CO partial pressure according to the
1% CO/He → 2.5% CO/He → 5% CO/He program (the intensity
remains constant for a P_{CO} of ≥5 kPa). The 4.7 wt % Cu(Cl-
x)/Al$_2$O$_3$(R) solid leads to the same observations as shown in
Figure 5a−c for an x of 500. Clearly, on the Cl-containing solids
for a P_{CO} of 1 kPa, the coverage at the equilibrium is less than
1 at 300 K. This indicates that the heat of adsorption of the L
CO species at high coverages is lower than on the Cl-free solids.
Figure 4 shows the change in the IR band intensity of the L
CO species on the 4.7 wt % Cu(Cl)/Al$_2$O$_3$(D) solid during the
increases in T_a. The observations are qualitatively similar to
those on the Cl-free solids, and the intensity of the IR band of
the L CO species progressively decreases with the increase in
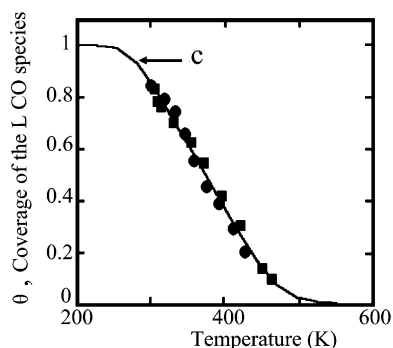T_a. This leads to better detection of a small IR band at 2147

Figure 6. Evolution of the coverage of the linear CO species on Cu° according to the adsorption temperature T_a for a 1% CO/He mixture on 4.7 wt % Cu(Cl-x)/Al$_2$O$_3$(R): ■ (a) and ● (b), experimental data during the heating stage for x values of 500 and 5000, respectively; and (c) theoretical coverage for an E_0 of 84 kJ/mol and an E_1 of 45 kJ/mol.

cm^{-1} (Figure 4f,g) which is detected as a shoulder at 300 K (Figure 4a). This IR band is usually ascribed[17,18] to an L CO species adsorbed on isolated Cu$^+$ sites on the alumina surface [an L CO species on Cu$^+$ sites on the surface of CuO$_x$ particles gives an IR band (see ref 13 and references therein) at 2120 cm^{-1}]. The fact that the intensity decrease of this IR band with T_a is smaller than that of the IR band at 2115 cm^{-1} indicates that the heat of adsorption of this species is higher than that of the L CO species on Cu°. As for Cl-free solids, cooling the sample to 300 K leads to an IR band identical to that before the heating stage (result not shown). Figure 3d shows the evolution of the coverage of the L CO species on the 4.7 wt % Cu(Cl)/Al$_2$O$_3$(D) solid for a 1% CO/He mixture. Curve e is obtained from the adsorption model using an E_0 of 82 kJ/mol and an E_1 of 45 kJ/mol.

The evolutions of the IR band of the L CO species on Cu° during the increase in T_a with the 1% CO/He mixture on the 4.7% Cu(Cl-x)/Al$_2$O$_3$(R) solids are similar to that on the 4.7% Cu(Cl)/Al$_2$O$_3$(D) solid as shown in Figure 5 for an x of 500. Curves a and b in Figure 6 give the experimental data for $\theta = f(T_a)$ for x values of 500 and 5000, respectively, while curve c corresponds to the theoretical coverage using an E_0 of ≈83 kJ/mol and an E_1 of 45 kJ/mol.

As for adsorbed CO species on Pd and Ru supported on Al$_2$O$_3$, it appears that the presence of residual chlorine on Cu/Al$_2$O$_3$ leads to a slight decrease from 57 to 45 kJ/mol in the heat of adsorption of the L CO species on Cu° at high coverages, but it does not modify significantly the heat of adsorption at low coverages (≈82 kJ/mol). Finally, whatever the heat of adsorption of the adsorbed CO species (strongly adsorbed CO species on Pd° and Ru° and weakly adsorbed CO species on Cu°), the impact of Cl is very similar: it decreases slightly the heat of adsorption of the adsorbed CO species at high coverages. The impact of Cl on this parameter on metal-supported catalysts is rarely studied. However, in the discussion of a previous study[7] on Pd-containing catalysts, it has been shown that the slight decrease in the heat of adsorption of CO in the presence of Cl revealed by the AEIR method is in good agreement with the microcalorimetric measurements of Chou and Vannice[19] on Pd-supported catalysts. The decrease in the heats of adsorption of CO observed on Pd-, Ru-, and Cu-containing catalysts leads to the conclusion that if a catalytic reaction involving the adsorbed CO species (i.e., CO/O$_2$) is strongly modified (a factor of more than 2) by the presence of Cl, it is not due to the change in the

heats of adsorption of these species which only leads to a decrease in the CO coverage of ≈10−20%. For the oxidation reactions, the modification of the catalytic activity is probably due to the impact of Cl on the heats of adsorption of the oxygen species. For instance, on Ag/Al$_2$O$_3$ catalysts, Badani and Vannice[20] have observed by microcalorimetry an increase in the heat of adsorption of O$_2$ in the presence of residual Cl associated with a decrease in the amount of O$_2$ chemisorbed.

4. Conclusion

This study on the adsorption of CO on Cl-free and Cl-containing Cu/Al$_2$O$_3$ catalysts by using FTIR spectroscopy has shown that the presence of residual Cl leads to a shift of the IR band of the linear CO species (main adsorbed CO species) at 300 K from 2095 to 2115 cm^{-1} or from 2095 to 2131 cm^{-1} for a low or high Cl content, respectively. These shifts are in agreement with the explanation based on the electroacceptor properties of Cl. However, the measurements of the heats of adsorption of the L CO species at different coverages (denoted E_θ) by using the AEIR method have shown that this parameter is not affected by Cl at low coverages ($E_0 \approx 82$ kJ/mol), while E_1 decreases slightly at high coverages from 57 to ≈45 kJ/mol. This corresponds to a decrease from 1 to ≈0.85 in the coverage of the L CO species at 300 K with a CO partial pressure P_{CO} of 1 kPa. Finally, there is a strong similitude in the impact of Cl on the heats of adsorption of adsorbed CO species on Pd,[7] Ru,[12] and Cu; independent of the E_θ values, Cl only decreases the heat of adsorption at high coverages by ≈10−20 kJ/mol.

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