A Semiempirical Quantum Approach to the Formation of Carbon Dioxide Adsorbates on Pt(100) and Pt(111) Cluster Surfaces

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The geometries and binding energies of CO₂ adsorbates on Pt(100) and Pt(111) cluster surfaces were calculated by means of an improved version of the extended Hückel molecular orbital method. The polarization of the surface by an applied electric potential and coadsorption of H atoms were included in the model. For simulated applied potentials in the range −1.0 to 1.0 V, CO₂ coordination geometries (side-on, formate) involving two adsorbate atoms bonded to the surface are favored, regardless of the surface topology and the presence of coadsorbed H atoms. In agreement with experiment, larger binding energies are always calculated for the Pt(100) cluster surface.

1. Introduction

Reactions of CO₂ yielding energy-enriched products, most of them carbon monoxide derivatives such as formaldehyde, formic acid, and carbon monoxide have been studied on several metal electrodes in both aqueous and nonaqueous media.1−4 The distribution of reaction products depends on the nature of the electrode, the composition of the solution, and other operational conditions.1,5−7

The adsorption of CO₂ on metal electrocatalysts8 is favored when H-adatoms are present on the electrode, as it appears that the formation of CO₂-containing adsorbates, usually denoted as reduced CO₂ adsorbates, requires the simultaneous interaction of CO₂ and H-adatoms. Some of these adsorbates can be detected by anodic stripping voltammetry.

The role of H-adatoms in the formation of reduced CO₂ adsorbates has been studied combining spectroelectrochemical and voltammetric techniques on faceted and polycrystalline Pt and Rh electrodes in aqueous sulfuric acid. For (100)- and (111)-faceted Pt electrodes in acid solutions, two main anodic stripping current peaks have been recorded, which have been related to a weakly and a strongly CO₂ adsorbate. The electrooxidation current peak ratio for these adsorbates depends on the potential sweep rate and solution composition.8

The formation of reduced CO₂ adsorbates on Pt from aqueous environments is a surface-structure sensitive reaction, as demonstrated using different types of electrodes.3,4,9 Thus, in contrast to Pt(111),10,11 the activity of Pt(100) for this process is relatively high. This crystallographic-face-dependent CO₂ adsorption on Pt can be related to the difference in the electronic characteristics of the electroadsorptive sites and their relative distribution.

The complete anodic stripping of reduced CO₂ adsorbates from Pt has been mainly related to the electrooxidation of CO- and CHO-type adsorbates to CO₂,13,12 Photoelectron spectroscopy has provided interesting results for the formation of both reduced CO₂ adsorbates and their decomposition products, such as formate species on Fe and Ni.13,14

Moreover, EMIRS (electrochemical modulated infrared spectroscopy)15 data have shown the presence of either HCO- or HCO₂⁻ adsorbates, whereas from SNIFTIRS (subtractively normalized interfacial Fourier transform infrared spectroscopy)16 data, the formation of linear, bridge, and multibonded CO adsorbates on Pt in CO₂-saturated aqueous acid solution has been confirmed. Otherwise, in situ infrared spectra of CO and CO₂ adsorbates on Pt electrodes are different.16,17 as the C−O
stretched frequency resulting from CO adsorbates corresponds to a stronger bond than that resulting from reduced CO₂ adsorbates. Furthermore, it has been proposed that CO adsorbates formed from CO₂ reduction products may result from the decomposition of a more reactive species such as formate. Therefore, reduced CO₂ adsorbates on Pt(111) and Pt(100) cluster surfaces at different simulated electric potentials, calculated from a modified Bates model, has been chosen. This model appears as an adequate approach for providing relevant information that helps the understanding of the much more complex situation prevailing at the electrochemical interface. This work is focused, hence, on the possible geometries and binding energies of reduced CO₂ adsorbates on Pt(111) and Pt(100) cluster surfaces at different simulated electric potentials, calculated from a modified version of the extended Hückel molecular orbital method. Besides the complications associated with the experimental system, mainly related to the definition of the adsorbate when a simulated electric potential is applied. The relative influences of the negative applied potential and H adsorption on CO₂ sticking to Pt are then compared. The model allows us to identify the different species that are likely involved in the reduced CO₂ adsorbate formation. The results derived from these calculations are useful, as a first approximation, to discriminate among possible adsorbates and intermediate species involved in either thermal or electrochemical reduction of CO₂ and oxidation of reduced CO₂ adsorbates.

2. Details on the Calculation

2.1. The Calculation Procedure. The extended Hückel molecular orbital (EHMO) method is the simplest calculation procedure that can be used to describe the valence electronic structure, bonding energy, and chemical properties of relatively large transition metal clusters involved in adsorption problems. Despite its simplicity, it is still the choice when dealing with large systems and high atomic numbers. It has been developed by Hoffmann to study the structural and electronic properties of systems at a frozen geometry. Improvements of this method, mainly related to the addition of two-body electrostatic terms, have made it capable of optimizing the geometry of the adsorbed ensemble within certain limits. In this framework, the energy of the system, $E_t$, is expressed as

$$E_t = E_{EHMO} + \sum_{\mu} b^\mu \text{VSIP}_\mu + E_R$$

where $E_t$ stands for the binding energy of the system, calculated as the difference between the noncorrected EHMO total energy ($E_{EHMO}$) and the addition of the mono-electronic terms that describe the constituents of the system as being infinitely separated and corrected by repulsion. The second term is calculated for the $\mu$th atomic orbital, by means of the occupation number ($b^\mu$) and the valence state ionization potential (VSIP$_\mu$), which, in absolute value, equals the diagonal terms of the Hamiltonian (VSIP = $\text{H}_{\mu\mu}$). The correction implies the addition of an electrostatic repulsion energy term ($E_R$) that is evaluated from the contribution of the electrostatic repulsion energies between atoms A and B ($E_{AB}$),

$$E_R = \sum_A \sum_B E_{AB}$$

Among the different approaches that have been developed for computing $E_{AB}$, we prefer to calculate it as the energy difference between the Coulombic interaction of A and B separated by a distance $R_{AB}$ and the arithmetic mean of $A-B$ and $B-A$ attractive interaction energies.26–27

$$E_{AB} = Z_A Z_B |R_{AB}^{-1/2} Z_A \int \rho_B(r)|/r - R_{AB}| \rho_A(r)|/r - R_{AB}|\, dr$$

where $Z_r$, $R_r$, and $\rho_r$ are the nuclear charge, position, and electron density of atom $i$ ($i = A, B$), $B$ being more electronegative than A. Besides, a distance-dependent exponential factor is also included to correct the off-diagonal EHMO matrix elements, which are calculated by the empirical weighted Wolfsberg–Helmholz formula applied to the diagonal Hamiltonian and overlap matrix terms

$$H_{\mu\nu} = 1/2 K_{AB} (H_{\mu\mu} + H_{\nu\nu}) S_{\mu\nu}$$

where $\mu$ and $\nu$ are the $\mu$th and the $\nu$th orbitals of atoms A and B, respectively.

$K_{AB}$ and $\delta$ are adjustable empirical parameters such as 1.4 $\leq (1 + \kappa) \leq 2.5$ and 0.0 $\leq \delta \leq 0.1$ nm. They are related by the equation

$$K_{AB} = 1 + \kappa \exp[-\delta (R_{AB} - r_s)]$$

$K_{AB}$ is the EHMO K parameter used in the off-diagonal Hamiltonian matrix elements, and $r_s$ is the sum of atomic radii of A and B. Other energy matrix elements are kept as in the conventional EHMO methodology.

2.2. The Model. The preceding calculation procedure was extended to describe the interaction of CO₂ with Pt(111) and Pt(100) cluster surfaces considering the influence of a simulated electric potential and the coadsorption of H-atoms. High-spin bilayer Pt₅₃ clusters ($N = 25, 32$), with d bands filled with at least one electron per d orbital, were used to model the Pt(111) and Pt(100) cluster surfaces, respectively (Figure 1). Clusters were geometrically built, keeping constant the Pt–Pt bond length at 0.277 nm, in

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multiplicity of the adsorbed ensemble results from interactions with the close shell CO2 molecule.

Coordination of the CO2 molecule with the Pt surface may involve one or two atoms of the adsorbate and one, two, or more atoms of the substrate. When coordination through a single atom from the adsorbate is considered, the occupation of different Pt adsorption sites defines several adsorption configurations on each Pt cluster, i.e., linear on-top (1-fold), bridge (2-fold), and hollow (higher coordinated sites). Hollow sites are associated with a 5-fold coordination of the adsorbate on Pt(100) (four Pt atoms of the topmost layer and one Pt atom from the underlying layer). For Pt(111), either three or four Pt atoms may define either the (3−1)- or (3−3)-hollow coordination site, depending on the local symmetry of the adsorbate. For each case, the coordination through either the C or the O atom is considered (Figure 2). When two adsorbate atoms are involved in the coordination, two adsorbed species are distinguished, namely, the formate species, which is bound directly through two O atoms

agreement with the interatomic distance of bulk Pt. The multiplicity of the adsorbed ensemble results from interactions with the close shell CO2 molecule.

Coordination of the CO2 molecule with the Pt surface may involve one or two atoms of the adsorbate and one, two, or more atoms of the substrate. When coordination through a single atom from the adsorbate is considered, the occupation of different Pt adsorption sites defines several adsorption configurations on each Pt cluster, i.e., linear on-top (1-fold), bridge (2-fold), and hollow (higher coordinated sites). Hollow sites are associated with a 5-fold coordination of the adsorbate on Pt(100) (four Pt atoms of the topmost layer and one Pt atom from the underlying layer). For Pt(111), either three or four Pt atoms may define either the (3−1)- or (3−3)-hollow coordination site, depending on the local symmetry of the adsorbate. For each case, the coordination through either the C or the O atom is considered (Figure 2). When two adsorbate atoms are involved in the coordination, two adsorbed species are distinguished, namely, the formate species, which is bound directly through two O atoms

Figure 1. Scheme of the clusters used to model (a) Pt(111) and (b) Pt(100).

Figure 2. Linear coordination of a CO2 molecule with a Pt(100) cluster surface (a) bonded through the O atom and (b) bonded through the C atom.

Figure 3. Adsorbate geometries resulting from a two-atom CO2 coordination on a Pt(100) surface: (a) formate adsorbate; (b) side-on CO2 adsorbate.

Table 1. EHMO Calculation: Optimized Parameters Based on Pt–O Bond

| atomic orbital | VSIP, eV | $\zeta_0^b$ | $\zeta_0^c$ | $c_1^c$ | $c_2^c$ |
|----------------|---------|-------------|-------------|---------|---------|
| Pt 5d          | 12.83   | 4.0950      | 1.8600      | 0.7980  | 0.3520  |
| Pt 6s          | 9.32    | 1.9830      |             |         |         |
| Pt 6p          | 5.72    | 1.3440      |             |         |         |
| C 2s           | 21.85   | 2.1600      |             |         |         |
| C 2p           | 11.85   | 2.0750      |             |         |         |
| O 2s           | 27.96   | 2.5640      |             |         |         |
| O 2p           | 12.16   | 2.7640      |             |         |         |
| H 1s           | 13.50   | 1.3000      |             |         |         |

$^a$ VSIP = valence state ionization potential. $^b$ $\zeta_0$ = orbital exponents of the base generating functions. $^c$ $c_1$ = linear coefficients of the double zeta Pt d-orbitals.

Table 2. EHMO Calculation: Optimized Parameters Based on Pt–C Bond

| atomic orbital | VSIP, eV | $\zeta_0^b$ | $\zeta_0^c$ | $c_1^c$ | $c_2^c$ |
|----------------|---------|-------------|-------------|---------|---------|
| Pt 5d          | 13.33   | 4.8950      | 2.3600      | 1.2980  | 0.8520  |
| Pt 6s          | 9.82    | 2.4830      |             |         |         |
| Pt 6p          | 7.22    | 2.8440      |             |         |         |
| C 2s           | 22.35   | 2.8600      |             |         |         |
| C 2p           | 12.35   | 2.5790      |             |         |         |
| O 2s           | 28.46   | 3.0640      |             |         |         |
| O 2p           | 12.66   | 2.7640      |             |         |         |
| H 1s           | 14.00   | 1.8000      |             |         |         |

$^a$ VSIP = valence state ionization potential. $^b$ $\zeta_0$ = orbital exponents of the base generating functions. $^c$ $c_1$ = linear coefficients of the double zeta Pt d-orbitals.

(Equilibrium VSIP values are evaluated in the way previously proposed by Anderson.23 To consider the polarization of the substrate surface by the CO2 molecule, the VSIP and Slater exponents are changed until the calculated charges on the atoms for the diatomic bond are close to those predicted by the electronegativity difference resulting from the Pauling’s ionicity relationship.34 This approach has been extensively applied to the study of electrochemical systems.35-40

Coordination of CO2 through either the C or O atom would imply a different polarization of the surface. Different values of VSIP and Slater orbital exponents define, hence, the reference potential of the CO2−Pt system for coordinations through the C atom (Table 1) and the O atom (Table 2). Values $\delta_{AB}$ = 1.75 and $\delta$ = 0.035 render an appropriate description of the equilibrium distances and associated energies with the set of param-

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eters assembled in Tables 1 and 2. When coordination is accomplished through both the C and O atoms simultaneously, the polarization induced by the O atom has been considered in the calculations, as it always renders the most stable structures. For CO$_2$ and H coadsorption, both species also contribute to modify the electronic density of the Pt surface and, accordingly, the VSIP. Because experimental data on the formation and characteristics of the stable structure of the CO$_2$-H coadsorbate on Pt are not perfectly known, we have chosen a model that considers the influence of H atoms interacting with adsorbed CO$_2$ and the surface polarized, thence, by the latter. In this way, the surface polarization induced by the CO$_2$ molecule and H atom is taken into account by comparing the CO$_2$ and CO$_2$H adsorption without further changes in the physical model.

The applied electric potential is simulated by changing the Fermi energy level of Pt, either decreasing or increasing the absolute value of VSIP, from the reference value taken as the potential of zero charge (pzc) of Pt (Table 1), leading to a negative or a positive metal surface charge, respectively. Considering the accuracy of the results obtained in previous investigations, the correlation between the VSIP shift and the simulated electric potential has been set as 1 (1 V = 1 eV).

The geometry of reduced CO$_2$ adsorbates has been fully optimized to minimum energy in each case. This implies the simultaneous modification of bond lengths and planar and dihedral angles. Thus, the C–O(1) distance ($r_{O(1)C}$) (Figures 2–4) has been varied stepwise in 0.001 nm until minimum energy was attained. For each fixed value of

Figure 4. Different CO$_2$H adsorbate configurations on a Pt(100) surface: (a) H–C atom coordination; (b) H–O(2) atom coordination; (c) H–O(1) atom coordination; (d) hydrogenated formate adsorbate resulting from bending the O(1)–C–O(2) angle toward a neighbor Pt atom; (e) side on H–O(2)CO adsorbate resulting from bending the O(1)–C–O(2) angle toward a neighbor Pt atom; (f) side on H–O(1)CO adsorbate resulting from bending the O(1)–C–O(2) angle toward a neighbor Pt atom; (g) hydrogenated formate adsorbate with the H atom bound to one O atom.
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The equilibrium C–O bond length, \( r_{CO} = 0.118 \text{ nm} \), calculated for free CO\(_2\) is close to the experimental value,\(^{28}\) that is, 0.120 nm, whereas the calculated dissociation energy is 5.6963 eV, a figure that exceeds published data by 1.6 eV.\(^{29}\) However, despite this difference, the optimized geometry resulting from the calculation is very accurate. As the semiempirical method is limited for energy value calculations because of their large dependence on the parametrization, attention is focused on the calculated geometries.

\[ BE = E_{T,PtN,X} - E_{T,PtN} - E_{T,X} \]  

for the molecule bound to Pt through either the C or O atom, considering for each case the on-top (1-fold), bridge (2-fold), and hollow (multi)-coordination.

In contrast to the adsorption of CO\(_2\) on Pt through the C atom, which always results in a positive value of BE, that is, no stable adsorbate is formed, the adsorption through the O atom leads to stable CO\(_2\) adsorbates.

The geometric characteristics and BE values for stable O-bonded adsorbates are assembled in Table 3. These data show that the linear (on-top) CO\(_2\) adsorption is favored on both Pt(111) and Pt(100) cluster surfaces at the reference potential, as earlier reported by Anderson et al.\(^{44}\)

For both Pt(100) and Pt(111) cluster surfaces, the on-top adsorption of CO\(_2\) implies the stretching of the O(1)–C bond by 0.03 nm (Figure 2), resulting in a strained C–O(1) single bond.\(^{29}\) With this stretched bond length fixed, configurations with a tilting of the O(1)–C–O(2) planar angle between 0° and 30° define isoenergetic adsorbates. This result is in agreement with the ab initio calculations about the interaction of CO\(_2\) with a single transition metal atom recently reported by Jeung.\(^{33}\)

A molecular orbital analysis shows that both the \( \sigma \) and \( \pi \) orbitals of the on-top CO\(_2\) adsorbate are involved in bonding interactions with the d atomic orbitals of adjacent Pt atoms. Then, the CO\(_2\) adsorption bond on both Pt(100) and Pt(111) cluster surfaces can be described as a charge transfer from CO\(_2\) to the Pt cluster, involving a \( \sigma \)-bond reinforced by a \( \pi \)-type Pt(1)–O(1) bond delocalized toward the adjacent O(1)–C bond. However, although an electron transfer from CO\(_2\) to Pt(1) occurs, the Pt atom remains positively charged, as the transferred electron charge is spread throughout the entire Pt cluster. In this case, the O(2) atom is scarcely involved in the adsorption bond, its coordination being mainly related to the extended \( \pi \)-type interaction. Hence, according to the bond distances (Table 3), the O(1)–C bond changes from a double to a single bond because of charge donation. It should be noted that ab initio calculations which describe the CO\(_2\)–Pt adsorption interaction defining the metal side by a single Pt atom,\(^{33}\) also found an ionic character of the bond but a charge transfer from Pt to CO\(_2\). These results are affected to some extent by the absence of Pt interacting atoms, which, without the application of embedding techniques, precludes the spreading of charge over the metal cluster.

The bridge CO\(_2\) adsorbate on both Pt(100) and Pt(111) cluster surfaces involves two Pt atoms interacting with the CO\(_2\) molecule. As the Pt–O bond length is larger

\[ \delta \]  

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Table 4. Binding Energy (BE) Values at Different Simulated Electric Potentials for Adsorbates Resulting from One Atom CO2 Coordination on Pt(111) and Pt(100)

| Pt(100) | Pt(111) |
|-----------------|-----------------|
| potential | on-top | bridge | hollow | side-on | formate |
| 1.0   | +0.3946 | +0.4359 | 1.5634 | 1.3452 | -5.6775 | -4.5757 |
| 0.8   | +0.3878 | +0.4167 | 1.3467 | 1.0347 | -5.0131 | -4.0341 |
| 0.6   | +0.4247 | +0.4178 | 1.1378 | 0.8734 | -4.8751 | -3.7757 |
| 0.4   | +0.5467 | +0.5194 | 0.8543 | 0.5523 | -4.1254 | -2.9872 |
| 0.2   | +0.6154 | +0.5137 | 0.2043 | 0.2189 | -3.6732 | -2.5261 |
| 0.1   | +0.7416 | +0.1679 | 0.0559 | 0.0086 | -3.0184 | -1.4674 |
| -0.2  | -1.2159 | -1.0490 | 0.3016 | -3.8681 | -2.1649 |
| -0.4  | -1.3886 | -1.2450 | 0.2413 | -4.1516 | -2.7251 |
| -0.6  | -2.3526 | -2.2119 | -0.0191 | -4.4452 | -3.6267 |
| -0.8  | -3.8020 | -3.8476 | -0.4543 | -4.8983 | -2.4331 |
| -1.0  | -4.1600 | -4.3519 | -0.8980 | -5.0844 | -2.5662 |
|-----------------|-----------------|
| potential | on-top | bridge | hollow | side-on | formate |
| 1.0   | -0.3946 | -0.4359 | 1.5634 | 1.3452 | -5.6775 | -4.5757 |
| 0.8   | -0.3878 | -0.4167 | 1.3467 | 1.0347 | -5.0131 | -4.0341 |
| 0.6   | -0.4247 | -0.4178 | 1.1378 | 0.8734 | -4.8751 | -3.7757 |
| 0.4   | -0.5467 | -0.5194 | 0.8543 | 0.5523 | -4.1254 | -2.9872 |
| 0.2   | -0.6154 | -0.5137 | 0.2043 | 0.2189 | -3.6732 | -2.5261 |
| 0.1   | -0.7416 | -0.1679 | 0.0559 | 0.0086 | -3.0184 | -1.4674 |
| -0.2  | -1.2159 | -1.0490 | 0.3016 | -3.8681 | -2.1649 |
| -0.4  | -1.3886 | -1.2450 | 0.2413 | -4.1516 | -2.7251 |
| -0.6  | -2.3526 | -2.2119 | -0.0191 | -4.4452 | -3.6267 |
| -0.8  | -3.8020 | -3.8476 | -0.4543 | -4.8983 | -2.4331 |
| -1.0  | -4.1600 | -4.3519 | -0.8980 | -5.0844 | -2.5662 |

3.1.2. CO2 Coordination through Two Adsorbate Atoms. When the adsorption of CO2 on Pt involves two adsorbate atoms, two species can be formed, namely, a formate adsorbed species that is bound directly through two O atoms (Figure 3a) and a side-on CO2 species that is bound through the C and one O atom (Figure 3b). Formate adsorbates have been experimentally detected on metal surfaces by means of spectroscopic techniques, whereas the existence of side-on adsorbates has been concluded from infrared emission spectroscopy during hydrocarbon oxidations on Pt.

Binding energy data for formate and side-on CO2 adsorbates on the Pt(100) and Pt(111) cluster surfaces are assembled in Table 3. For both adsorbates, the BE values depend on the applied potential, defining minimum stabilization at 0 V. However, regardless of the simulated potential, side-on CO2 adsorbates become the most stable ones on both Pt cluster surfaces. Data assembled in Table 4 show that the stabilization of the side-on CO2 adsorbate on Pt(100) is always substantially higher than that on Pt(111), and the corresponding BE differences decrease as the applied potential is negatively shifted.

As previously mentioned, the greatest stability of the adsorbates at 1.0 V is due to a charge transfer from CO2 to Pt, which results in a charge on the molecule that is around +0.36 for the Pt(111) surface and +0.6 for the Pt(100) surface. The reverse charge-transfer process is responsible of the stabilization at ~1.0 V. This is reflected in a negative charge for the adsorption of CO2 on Pt which is again larger for Pt(100) (−0.53) than for Pt(111) (−0.17). These figures justify, also, the larger stabilization on the Pt(100) surfaces.

3.2. The Interaction of a Single CO2 Molecule with the Pt(111) and Pt(100) Cluster Surface in the Presence of H Atoms. The influence of a H atom of the environment on the stabilization of CO2 adsorbates has been extensively discussed in relation to the mechanism of CO2 electrooxidation on Pt. Therefore, the calculation procedure previously described was extended to determine the geometry and BE values of the most likely adsorbates that might result from the coadsorption of CO2 and H on Pt(100) and Pt(111) cluster surfaces. In this way, the occupation of on-top, bridge, and hollow sites by H and on-top, bridge, hollow, side-on, and formate sites by CO2 have been considered simultaneously, to compare the binding energies of the different resulting CO2-H adsorbates as well as their evolution under the influence of an applied electric potential. In all the cases, full geometry optimizations were performed in order to find out the characteristics of the most stable adsorbed structures. The results from these calculations are assembled, for the uncharged surfaces, in Table 5.

Coadsorption of hydrogen with formate species define the most stable structures on both Pt surfaces, followed by the system associated with the on-top coordination of both adsorbates. For these, most stable structures, the coordination of H with a Pt atom adjacent to CO2 has been compared with the direct coordination to either the C or O atoms of the adsorbed CO2 molecule (Figure 4). For both the formate and the on-top linear CO2-H coordination, the direct bonding of H to the C atom of the adsorbed molecule stabilizes the system relative to the adjacent adsorption of both species. In the case of formate, the system is stabilized in 1.0 eV on Pt(100) and 0.6 eV on Pt(111) by hydrogen migration to the C atom of the CO2 molecule, whereas for the case of linear coordination the

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Coordination of the H atom to the O atoms of the adsorbed CO$_2$ molecule leads to less stable structures than those defined by direct H–Pt interaction (Figure 4b,d). Furthermore, the bending of either the Pt(1)–O(1)–C or O(1)–C–O(2) angles in the H–O(2)CO adsorbate would result in a hydrogenated side-on CO$_2$ adsorbate (Figure 4e). The values of AE strongly depend on the adsorbate configuration are AE = 0.20 eV for Pt(100) and AE = 0.22 eV for Pt(111). These values of AE decrease to zero (−0.2 V downward) when the simulated electric potential is shifted negatively. Similarly, the bending of the Pt(1)–O(1)0.17 eV for Pt(111). These values of AE decrease to zero (−0.3 V downward) as the simulated electric potential is negatively shifted.

Values of BE and their dependence on the simulated electric potential for the different adsorbates can be seen in Table 7. The stability of these adsorbates decreases from −1.0 to 0 V and then increases again from 0 to 1.0 V, although the greatest stability is observed at −1.0 V. The explanation for the potential dependence of BE values was already discussed in section 3.1.2.

Summarizing, when H atoms are considered in the definition of the electrochemical interface, the coordination of a H atom with the CO$_2$ adsorbate leads to the formation of formate adsorbates, on both Pt(100) and Pt(111) cluster surfaces over the potential range covering from the reference potential downward. Hydrogen coordination may imply the direct attachment to the C atom of an adsorbed formate species or the bending of a linearly bonded C-hydrogenated CO$_2$ one. This fact suggests that formate species are the most likely adsorbed intermediates formed in the electrochemical reaction of CO$_2$ on Pt.

### 4. Conclusions

According to our calculations, CO$_2$ adsorption on Pt(100) and Pt(111) surfaces implies the simultaneous coordination of two atoms of the molecule, to give side-on and formate configurations. This result might be valid in the experimental potential range including the pzc (potential of zero charge) and the H-adatom potential region. Among these configurations, and regardless the simulated potential, side-on CO$_2$ adsorbates become the most stable ones on both Pt surfaces. In agreement with experiment, larger BE are always calculated for the Pt(100) cluster surface.

When H-atoms are also considered in the definition of the electrochemical interface, formate adsorbates become the most stable ones. Because it appears that the formation of CO$_2$-containing adsorbates requires the simultaneous interaction of CO$_2$ and H adatoms, our system is stabilized in 1.5 and 1.7 eV respectively, for the uncharged surface, as concluded from data shown in Table 6. Moreover, for the latter, a formate adsorbate is formed by bending the Pt(1)–O(1)–C angle (Figure 4d). At the reference potential, this process requires an activation energy that is AE = 0.04 eV for Pt(100) and AE = 0.08 eV for Pt(111). These values of AE become zero when the simulated electric potential is lower than −0.4 eV for both Pt surfaces.

### Table 5. Values of BE for CO$_2$ and H Adsorbates on Pt(111) and Pt(100) at the Reference Potential

| H-atom | CO$_2$ | BE/eV | H-atom | CO$_2$ | BE/eV |
|--------|--------|-------|--------|--------|-------|
| on-top | on-top | −3.0129 | on-top | on-top | −2.4560 |
| on-top | bridge | −2.8567 | bridge | bridge | −2.2324 |
| hollow | on-top | −1.9786 | hollow | (3−3) | −1.0954 |
| formate | hollow | −5.5589 | hollow | (3−1) | −1.0002 |
| side-on | side-on | −2.6651 | formate | side-on | −3.4254 |
| bridge | bridge | −2.9029 | bridge | bridge | −2.3456 |
| hollow | hollow | −1.6723 | hollow | (3−3) | −0.9456 |
| formate | formate | −3.4577 | bridge | hollow | (3−1) | −0.8751 |
| side-on | side-on | −2.3197 | bridge | formate | −3.3278 |
| hollow | on-top | −1.7531 | hollow | (3−1) | −1.5623 |
| hollow | bridge | −1.5673 | bridge | bridge | −1.1211 |
| hollow | hollow | −0.3489 | hollow | (3−1) | −0.3632 |
| hollow | hollow | −2.0146 | hollow | (3−1) | −1.1455 |
| hollow | side-on | −1.8831 | hollow | (3−1) | −1.9433 |
| hollow | side-on | −1.6723 | hollow | (3−3) | −1.7675 |
| hollow | side-on | −1.2378 | hollow | side-on | −1.2378 |
| hollow | bridged | −0.9684 | hollow | side-on | −0.9684 |
| hollow | formate | 0.0123 | hollow | side-on | 0.0123 |
| hollow | formate | 0.1029 | hollow | side-on | 0.1029 |
| hollow | side-on | 0.4099 | hollow | side-on | 0.4099 |

$^a$ where H–CO$_2$(f) refers to H bound to C atom of formate species, H–OCO(f) refers to H bound to one O atom of formate species, H–CO$_2$(t) refers to H bound to C atom of on-top species (Figure 4a), H–O(2)CO(t) refers to H bound to the O(2) atom of on-top species (Figure 4b), H–O(1)CO(t) refers to H bound to one O(1) atom of on-top species (Figure 4c).

### Table 6. Values of BE for CO$_2$.H Adsorbates on Pt(111) and Pt(100) Surfaces at the Reference Potential

| H-atom | CO$_2$ | BE/eV | H-atom | CO$_2$ | BE/eV |
|--------|--------|-------|--------|--------|-------|
| on-top | on-top | −3.0129 | on-top | on-top | −2.4560 |
| H–CO$_2$(f) | 4.5782 | H–CO$_2$(f) | 4.1233 |
| H–O(2)CO(t) | 2.8431 | H–O(2)CO(t) | 2.2143 |
| H–O(1)CO(t) | 2.9973 | H–O(1)CO(t) | 2.2241 |
| formate | 3.5589 | formate | 3.4254 |
| O–HOCO | 3.1192 | O–HOCO | 3.0637 |
| H–CO$_2$(t) | 3.5435 | H–CO$_2$(t) | 3.2138 |

### Table 7. Values of BE for Adsorbates Resulting from CO$_2$ and H on Pt(111) and Pt(100) Surfaces at Different Simulated Electric Potentials (V)

| pot. | H–CO$_2$(f) | H–CO$_2$(f) |
|------|-------------|-------------|
| 1.0  | −4.8563     | −4.8563     |
| 0.8  | −4.6751     | −4.6432     |
| 0.6  | −4.3242     | −4.3242     |
| 0.4  | −4.0875     | −3.9654     |
| 0.2  | −3.7456     | −3.6543     |
| 0.1  | −3.5589     | −3.5431     |
| 0.00 | −3.4544     | −3.4323     |
| 0.0  | −4.8244     | −4.7654     |
| −0.6 | −5.3675     | −5.3675     |
| −0.8 | −5.7365     | −5.7365     |
| −1.0 | −5.7452     | −5.7452     |
calculations suggest that hydrogenated formate species are the most likely adsorbates formed in the electroformation of reduced CO₂ on Pt.

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