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Modeling of high-pressure CO dissociation on Pt(1 0 0) and Pt(1 1 1)

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Abstract

We present DFT calculations of the Boudouard reaction occurring under pressure over a platinum surface. The adsorbed CO molecules dissociate the O atom reacting with a CO molecule from the second layer while the carbon atom is stabilized by adsorption at the hollow site. In case of coadsorption with O_2, the carbon atom is better stabilized, forming another CO_2 molecule. Then the reaction takes place at lower pressure.

Keywords: DFT; CO; Platinum; Boudouard; High pressure

1. Introduction

Observations of the structures of adsorption were predominantly obtained by spectroscopic measurements requiring ultra-high-vacuum conditions whereas reacting conditions are made under pressure. In parallel, most of the quantum chemistry simulations up to now correspond to the ideal conditions of vacuum. The cluster approaches usually mimic the interaction with a single adsorbate. The periodic approaches usually consider the first layer of adsorbate on a slab deprived of interacting gas molecules above. Recently, sum frequency generation (SFG) spectroscopy allows observing the adsorption in high-pressure conditions since the gas phase molecules do not contribute to the SFG signal. The role of pressure has been shown to allow the CO dissociation on the platinum surfaces. The carbon deposition by CO dissociation is an important step for the onset of ignition, and the carbon oxide covered platinum surface is a better CO oxidation catalyst than platinum [1]. This reaction occurs when CO still coexists with O_2 on the surface under 40 Torr (5.3 kPa) of CO, 100 Torr (13.3 kPa)of O_2 and 630 Torr (84 kPa) of He; it is better on the Pt(1 0 0) surface than on the Pt(1 1 1) surface [1,2].

The dissociation is the Boudouard reaction:

$$2CO \rightarrow C + CO_2$$

This reaction also takes place on Rh(1 1 1) at elevated pressure over 10 mbar [3]. It does not occur at low pressure.

A possible explanation lies on the roughness of the surface. If a surface Pt atom has an incomplete coordination, it may form a metal carbonyl resembling $Ni(CO)_4$ by adsorbing several CO molecules. However, the stability of the CO ligands in coordination chemistry is an argument against initiating CO dissociation.

In this paper, we propose a model for the simulation of high-pressure condition and show that pressure indeed facilitates the Boudouard reaction. A first idea to mimic the increase of pressure is to go to high coverage and to adsorb two CO on the same surface atoms. Highest coverage reported is around 1 ($\theta = 1.09$ for Pt(1 1 0) [4], where the lateral interactions between the CO molecules impose both perpendicular and tilted molecules as also observed for high coverage ($\theta = 0.75$) for CO/MgO) [5]. First tests soon suggest rejecting a search for an interaction between adsorbed molecules: at very high coverage (more than one CO adsorbed per surface Pt), the CO molecules are very close to each other and condense forming polymers or condensed layers. This might occur for the first layer generating graphite. It does not make sense forming chains in the upper layers. We thus took a different approach by considering the interaction between adsorbed molecules and gas molecules with a geometry constraint. The Boudouard reaction imposes considering a reaction between two molecules. We have simplified the description imposing a collinear approach: one molecule is adsorbed (C-down) and the other (also C-down) lies in the gas phase above it so that the geometry favors a C–O interaction between the two molecules. The pressure is introduced by imposing a third layer of inert molecules at a fixed distance to the surface. Decreasing this distance corresponds to

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increasing the pressure. We naturally chose CO molecules to play this role. After studying the condition for $\theta = 1$, we analyze the situation at lower coverage and with O_2 coadsorbed.

2. Model and computational details

We represent the adsorption of three collinear CO molecules on a top and hollow site of a fixed Pt bilayer. The unit cell in the surface direction is the primitive (1 0 0) cell of the platinum atom, the Pt–Pt distance being fixed at 2.77 Å; the length of the third vector that repeats the whole system has been chosen equal to 15 Å. The external CO molecule is fixed, oriented C-down and the two others are optimized, being forced to remain collinear as represented in Fig. 1. The fixed distance, here called FD, from the C3 atom of the external CO to the surface varies from 9 to 7 Å (hollow site) or 7.5 Å (top site), reducing the interval available for the two other molecules and simulating an increase of the pressure. Since the CO bond length is 1.2 Å, the average distance between the CO molecules or between the CO molecule and the surface is originally 2.2 Å, avoiding excessive interaction; it next decreases to 1.7 Å where the molecules are forced to interact. When the reaction takes place on top, we allowed the C1 atom, once detached from O1, to move in plane so that it can reach the hollow site that is the best site for atomic adsorption. To study the coadsorption effect with O, we have chosen the adsorption at a hollow position of the (1 0 0) surface. We have used the 3 × 1 unit cell shown in Fig. 2. Two O atoms are bridging two parallel Pt–Pt bonds adjacent to the adsorption site.

We have carried out spin-polarized ab initio periodic calculations with the Vienna ab initio Simulation Package code [6–8] (VASP 4.4.4). In the VASP program, the Kohn–Sham equations are solved with the generalized gradient approximation (GGA) proposed by Perdew et al. [9,10]. Ultrasoft pseudopotentials have been used [11,12] together with plane wave basis sets. Since our approach is qualitative rather than quantitative, we used a limited model (two layers for the slab) and the less time consuming potentials; the cutoff of plane waves is 270 eV. The integrations in the Brillouin zone are performed on a grid of 5 × 5 × 1 for the geometry. The adsorption energies have been defined relative to two references:

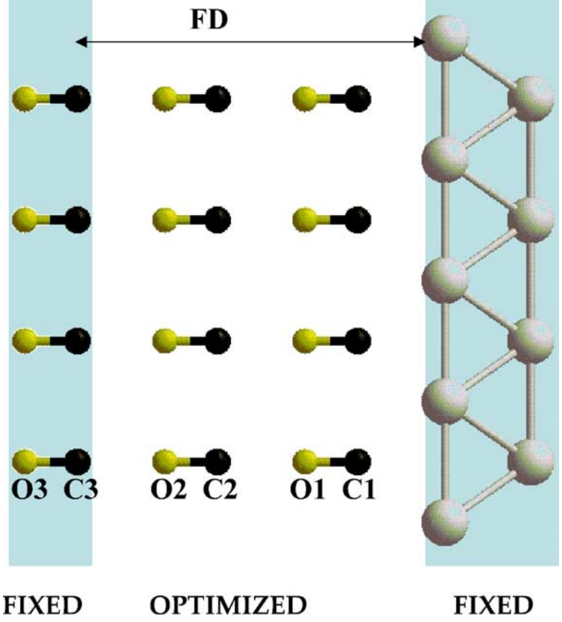

Fig. 1. The model used in the calculations. The four atoms O1, C1, O2 and C2 are optimized under the constraint of a fixed interval between the surface and C3 (FD distance). The CO molecules are separated by equivalent distances in the initial geometry.

$$BE_1 = E(\text{covered slab}) - [E(\text{naked slab}) + 3E(\text{CO})]$$

$$BE_2 = E(\text{covered slab}) - [E(\text{naked slab}) + E(3\text{CO})]$$

The first refers to independent molecules and shows the destabilization associated with the compression and the stabilization due to the reaction and the atomic adsorption of C1. For BE_2, in the reference energy, $E(3\text{CO})$, the 3CO molecules are collinear in the gas phase with the same

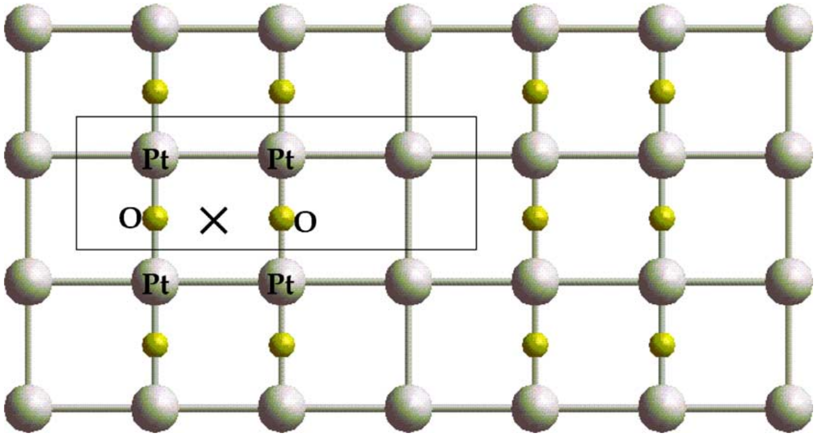

Fig. 2. The unit cell for the coadsorption with two O atoms. The cross indicates the axis on the hollow site where the CO molecules are located.

density as under adsorption (the CO distance has been fixed at 1.2 Å and the intermolecular distance between the collinear CO fixing the cell vector in the direction normal to the surface is such that the global density is preserved); the reference energy takes into account the interaction of a molecule with the other in the *z*-axis and with the translated molecules from the complete layer. This repulsion is part of BE_1 (referred to independent CO molecules) and is eliminated for BE_2, which focus more clearly on the stabilization due to the interaction with the metal for a given CO distribution.

3. Boudouard reaction on Pt(1 0 0) for a CO coverage $\theta = 1$

Table 1 displays the result of optimization for FD values ranging from 8.4 to 7 Å. The decrease of FD expresses the increase in pressure. For the approach above the hollow site, three distinct CO molecules are clearly distinguished for FD larger than 7.5 Å. One is close to the surface, bound by four Pt–C bonds that slightly strengthen with decreasing FD. The bond distance decreases from 2.22 to 2.13 Å. The two gaps between the CO molecules decrease from 2.46 to 2.1 Å. The geometry corresponds to that shown in Fig. 1. The increase of the pressure is accompanied by a destabilization of the system. At 7.0 Å from the surface, the optimization process spontaneously leads to a CO_2 molecule. The C2 atom is bound to its two neighboring oxygen atoms, O1 and O2. The CO_2 molecule is isolated from its neighbors. The geometry then corresponds to that shown in Fig. 3. The process is accompanied by a stabilization of the energy. The C1 atom settles at the hollow site, bound to five Pt atoms, including the Pt–C bond with an atom from the sublayer.

For the approach above the top site, three distinct CO molecules are also clearly observed for FD larger than 7.8 Å. This distance is larger than for the hollow case since the Pt–C1 bond is now vertical. The two gaps between the CO molecules decrease from 2.5 to 1.8 Å and the energy rises. The Pt–C1 bond is compressed to 1.69 Å. And this too short distance explains the rise in energy. At 7.5 Å from the surface, the optimization process spontaneously leads to a Pt–COCO moiety that is not very stable. The C1 atom at the top site is not well located. We then allowed this carbon atom

Table 1
Energy and geometrical parameters for different FD values

FD[a]	BE_1 (eV)	BE_2 (eV)	Pt–C1 (Å)	C1–O1 (Å)	O1–C2 (Å)	C2–O2 (Å)	O2–C3 (Å)	*n*/*V*	Structure
(1 0 0) hollow site									
8.4	0.69	−4.95	2.22	1.25	2.44	1.21	2.46	67.62	2CO
8.0	1.28	−6.13	2.19	1.25	2.27	1.21	2.30	70.56	2CO
7.5	2.54	−6.91	2.13	1.25	2.08	1.20	2.13	74.62	2CO
7.0	2.17	−9.14	1.98	2.02	1.26	1.24	2.22	79.17	CO_2
(1 0 0) top site									
9.0	–	–	2.15	1.21	2.52	1.30	1.78	63.64	2CO
8.4	1.56	−4.08	2.65	1.21	2.10	1.20	2.14	67.62	2CO
8.0	3.21	−4.20	1.71	1.20	1.91	1.19	1.99	70.56	2CO
7.8	4.28	−3.94	1.69	1.20	1.82	1.20	1.89	72.13	2CO
7.5	4.84	−4.61	1.73	1.28	1.26	1.23	1.99	74.62	CO_2
7.5[b]	1.23	−8.22	2.17	2.71	1.22	1.22	2.32	74.62	CO_2
(1 1 1) hollow site									
9.0	0.29	−3.58	2.10	1.24	2.56	1.22	2.62	73.49	2CO
8.0	3.77	−3.34	2.04	1.23	2.12	1.20	2.18	81.48	2CO
7.5	2.71	−5.52	1.94	1.39	1.33	1.28	2.41	86.16	CO_2
7.0	3.48	−7.83	1.92	1.36	1.27	1.24	2.06	91.42	CO_2
(1 1 1) top site									
9.0	0.76	−3.11	1.80	1.21	2.35	1.21	2.42	73.49	2CO
8.0[c]	3.51	−3.60	1.71	1.20	1.93	1.19	1.97	81.48	2CO
7.8	3.77	−4.06	1.75	1.16	2.18	1.35	1.36	83.29	2CO
7.5[b]	1.91	−7.09	1.95	2.36	1.22	1.22	2.23	86.16	CO_2

Except for C1 when indicated, the atoms are forced to remain collinear. For BE_1, the reference energies are $E(1\,0\,0) + 3E(\mathrm{CO}) = -50.71$ eV and $E(1\,1\,1) + 3E(\mathrm{CO}) = -50.93$ eV. For BE_2, the reference energy is $E(1\,0\,0) + E(3\mathrm{CO})$ or $E(1\,1\,1) + E(3\mathrm{CO})$, the 3CO being collinear in the gas phase with the same density as under adsorption (the cell vector in the direction *Z* is FD + 1.2 Å for the 3CO cell; the CO distance has been fixed at 1.2 Å; the distance between the collinear molecules is $(\mathrm{FD} - 2.4)/3$).

[a] We do not provide the value for FD = 9 Å for the (1 0 0) face because the interaction of the fixed molecule with the bottom of the slab after translation becomes significant. Since these atoms are in fixed positions, such interaction does not influence the optimization of the CO molecules allowed to move.

[b] The C1 atom is optimized and moves to the hollow position.

[c] The C1 atom is optimized but remains at a top position. *n*/*V* is the number of CO moles per liter. The volume, V (m^3), occupied by the CO molecules is the product of the surface of the unit cell per (FD + 1.2); $n/V = (3 \times 10^{-3})/VN$ (*N* is the Avogadro number). The last column indicates the structure (reactant: 2CO or product: CO_2 formation). This property appears clearly from the C1–O1 distance (short for the reactant, long for the product) and the O1–C2 distance (the opposite).

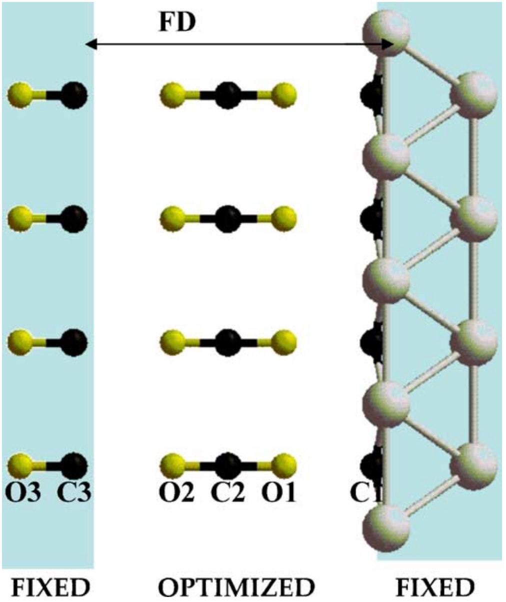

Fig. 3. Final geometry for short FD distances. The four atoms O1, C1, O2 and C2 are optimized under the constraint of a fixed interval between the surface and C3 (FD distance). The Boudouard reaction occurs spontaneously for short FD values: the C1–O1 distance elongates and the O1–C2 distance is shortened.

to move in the plane and obtained stabilization by 3.6 eV with the migration of the C1 atom to the hollow position. The resulting system is very similar to the final one obtained with the CO above the hollow position.

The binding energies, BE_1, referred to the Pt slab and three independent CO molecules, are displayed in the second column of Table 1. All the values are endothermic due to the CO CO repulsion. The positive values increase when FD decreases and after passing a barrier decrease when CO_2 is formed. The repulsion is more pronounced on the top site than on the hollow site as long as the C1 atom remains collinear. It drops when this atom is shifted to the hollow position.

4. The (1 1 1) face

Similar trends are observed for the (1 1 1) orientation. When the molecules are constrained to remain above the top site, the energy rises up to FD =7.8 Å. It decreases for FD =7.5 Å with the CO_2 formation when the C1 is allowed to move to the hollow site. On the hollow site, in the region FD =7.0–7.5 Å, the CO_2 molecule is formed but remains strongly bound to C1. The C1–O1 distance remains short and the CO_2 molecule is not really free. This is again the Pt–COCO moiety that would require exiting from the collinearity with a shift parallel to the surface of the C1 atom. The CO_2 molecule has to move away from the C atom. The Boudouard reaction seems more difficult in these conditions. The energy barrier is higher than for the (1 0 0) surface. The coverage on the surface, per surface unit is also larger by a factor $2/\sqrt{3}$ and the model is thus associated with a larger number of CO moles per liter (see last column of Table 1).

5. Low coverage and coadsorption with oxygen

Our model is simplified and the n/V values from Table 1 correspond to excessive high pressures ($n/V = 79.17$ would imply a pressure of 1800 bars at room temperature). The periodicity in our model implies that the Boudouard reaction occurs simultaneously at all sites whereas in an ignition process it would occur once at a unique site. In our model, the platinum atoms were kept at fixed positions whereas their mobility may contribute to facilitate the reaction. Finally, O_2 and He are present in the experiments whereas the gas phase in our model is completely filled by CO molecules.

Table 2 displays the results for the adsorption on Pt(1 0 0) at the hollow site for a decreased coverage ($\theta = 1/3$). The binding energies are larger than for $\theta = 1$. (The removal of the repulsion between parallel COs makes BE_1 negative; this repulsion was excessive at $\theta = 1$ and BE_1 values were positive in Table 1.) The reaction occurs at smaller pressure (higher FD values).

Table 3 displays the results for the coadsorption with two atomic oxygen atoms; the position of these atoms is fully optimized. Without CO molecules, the O atoms are bridging two Pt atoms (Fig. 3). For FD = 9 Å, the Boudouard reaction does not occur between the collinear molecules; however, the C1 atom binds to the coadsorbed O atoms, forming a CO_3 moiety. At FD = 8.7 Å, a large value corresponding to a small pressure, the Boudouard reaction takes place between the collinear CO molecules. The energy is strongly

Table 2
Energy and geometrical parameters for different FD values for the adsorption of three collinear CO molecules at the hollow site of the Pt(1 0 0) surface

FD	BE_1 (eV)	Pt–C1 (Å)	C1–O1 (Å)	O1–C2 (Å)	C2–O2 (Å)	O2–C3 (Å)	h_{C1}	Structure
(1 0 0) hollow site, $\Theta = 1/3$								
8.4	−0.46	2.213	1.259	2.64	1.215	2.452	1.031	2CO
8.0	−0.11	2.180	2.92	1.224	1.225	2.645	0.956	CO_2
7.5	−0.56	1.965	2.606	1.228	1.225	2.288	0.153	CO_2
7.0	−0.31	1.959	2.33	1.217	1.215	2.27	−0.032	CO_2

The unit cell is 3 × 1. h_{C1} is the distance of C1 to the top layer of the surface. When $h_{C1} = 0$, the Pt–C1 distance is 1.96 Å remains reasonable and thus C1 can pass below the top layer for short FDs (negative h_{C1} values).

Table 3

Energy and geometrical parameters for different FD values for the adsorption of three collinear CO molecules at the hollow site of the Pt(1 0 0) surface in the presence of two coadsorbed O atoms

FD	BE_1 (eV)	Pt–C1 (C1–O_{ads})	C1–O1 (Å)	O1–C2 (Å)	C2–O2 (Å)	O2–C3 (Å)	h_{C1}	$h_{O_{ads}}$ ($\Delta \times O$)	Structure
Co-adsorbed with 2O, $\Theta = 1/3$									
9.0	0.106	2.001 (1.378)	1.251	2.130	1.205	2.193	2.222	1.585 (1.222)	2CO
8.7	−1.287	2.492 (1.299)	2.466	1.209	1.219	2.264	1.542	2.041 (1.199)	CO_2
8.4	0.445	1.959 (3.044)	3.247	1.225	1.229	2.673	+0.025	1.105 (2.846)	CO_2
8.0	0.509	1.959	2.921	1.225	1.223	2.645	−0.015	1.105 (2.824)	CO_2
7.5	3.11	1.969	2.806	1.179	1.193	2.120	0.203	1.631 (2.625)	CO_2
7.0	4.10	1.997	2.33	1.217	1.215	2.27	0.388	1.409 (2.625)	CO_2
Reference								1.390 (1.386)	

The unit cell is 3 × 1. The labels of the atoms are still those used in Figs. 1 and 3. ($\Delta \times O$) is the distance of O_{ads} to the axis bearing the CO molecules. h_{C1} and $h_{O_{ads}}$ are the distances of C1 and O_{ads} to the surface.

stabilized. Simultaneously with the reaction, another CO_2 molecule is made by the C1 atom and the two neighboring O atoms. This molecule deviates from linearity; its location, symmetric and compressed between the surface and the CO_2 that is perpendicular to the surface is not very comfortable and thus, if a shift were allowed, this molecule would migrate on the surface and desorb. The symmetry of our calculation prevents any asymmetrical shift of the system and forbids this desorption. It is suggested from this result that the coadsorbed O atom helps ignition by lowering the pressure. This is in agreement with the experiment showing that increasing O_2 pressure makes the ignition easier. The coadsorption with O is then important for two reasons: it facilitates the reaction and it avoids that the saturation of the surface site by C atoms could block the reaction. The addition of O_2 can rapidly oxidize the surface C atoms to CO_2 restoring the naked surface Pt sites and allowing a large turnover. Above ignition the surface is rapidly covered by O_2 [13].

Our calculations at lower FDs lead to the same picture as without O coadsorption: the C1 atom is trapped at the hollow site. The O atoms starting to interact with the O1 atom move to the hollow position on each side. This situation, in a dynamic process occurring after the reactive situation (FD = 8.7 Å), is not very realistic.

6. Conclusions

We have proposed one model to simulate the local role of the pressure. A fixed layer of molecules is introduced at decreasing distances from the surface, compressing the spacing between them. This model is of course an idealization. Pressure can be simulated by a Gibbs free expression. Recently DFT total energies have been introduced in $G(T, p)$ expressions to determine the adsorption of O_2 on a metal-oxide surface [14]. Such approaches should provide a more realistic description of the covering of the surface by the oxygen atoms. At the moment however, no simple modeling can be built for a more complex system involving the reactivity of several molecules. The Boudouard reaction implies the reaction between two CO molecules that are in minority in the gas mixture. The CO adsorption is weak and interaction between coadsorbed CO molecules is unlikely, increasing the coverage leading to prohibitive energy cost. Besides, the ignition process is compatible with the occurrence of favorable approaches with low probability. It cannot be simplified to the oxidation of a single CO by adsorbed oxygen atoms.

This model is general; the layer of inert CO molecules that has been used in this paper can be replaced by a layer of rare gas atoms when the interacting gas molecules are more complicated.

Our model demonstrates the influence of the pressure on the CO dissociation. The constraint in a small volume forces the CO molecules from the first adsorbate layer to interact with those of the second one. This occurs at one end of the chain where the C1 atom that is isolated in the fragmentation process is stabilized by adsorption. Considering the binding energies, BE_1, it is easier at the hollow site for the (1 0 0) surface since the C1 atom settles at the best site for atomic adsorption. For the top site, this atom has to move to the hollow position. The reaction is easier at lower coverage. The Boudouard reaction can also occur on the (1 1 1) surface; it however seems to be more difficult, requiring higher temperature and pressure, as experimentally observed by McCrea et al. [1] who found that a temperature over 620 K was necessary. The role of the Pt surface is mainly to stabilize the atomic carbon generated by the Boudouard reaction. In the presence of two coadsorbed O atoms, the C1 atom is more effectively coupled with them, forming another CO_2 molecule, and this mechanism takes place at lower pressure.

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