Surface Science 606 (2012) 490–495

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

# $CO_2$ adsorption on calcium oxide: An atomic-scale simulation study

R. Besson [a,*], M. Rocha Vargas [b,c], L. Favergeon [b]

[a] Unité Matériaux et Transformations, CNRS UMR 8207, Université de sciences et technologies de Lille, F-59655 Villeneuve d'Ascq, France
[b] Laboratoire des Procédés en Milieux Granulaires – CNRS FRE 3312, Centre SPIN – Ecole Nationale Supérieure des Mines de Saint-Etienne, France
[c] Departamento de Engenharia Quimica, Instituto Superior Técnico, Av. Rovisco Pais n°1, 1049–001 Lisboa, Portugal

ARTICLE INFO

*Article history:*
Received 29 August 2011
Accepted 10 November 2011
Available online 18 November 2011

*Keywords:*
Density functional calculations
Carbon dioxide adsorption
Thermodynamic modelling

ABSTRACT

We present a detailed study of $CO_2$ adsorption on CaO, by means of atomic-scale simulations relying on Density Functional Theory. Combining ab initio thermodynamics of the $CO_2$ gas phase and a thorough analysis of its interaction with the oxide, we build an orientation-sensitive adsorption model, which demonstrates that low coverage by the gas is expected in a wide range of working conditions, including the domain of stability of $CaCO_3$ calcite. Investigation of the interactions between the adsorbed molecules reinforces this conclusion. Our work thus provides a strong hint that calcite nucleation should occur by a localised mechanism, discarding the possibility of collective surface transformation.



## 1. Introduction

Reducing the amount of $CO_2$ emitted by power plants or large industrial combustion sources is an important environmental and scientific issue. To this aim, CaO-based sorbents allow separation and capture of $CO_2$ from fuels and flue gases as well as $CO_2$ capture from ambient air [1], thus offering a possible route towards the desired stabilization of $CO_2$ concentration in the atmosphere. The process consists of a series of cycles where CaO is transformed into $CaCO_3$ in a carbonation reactor, and then calcination of $CaCO_3$ in a decarbonation reactor allows to regenerate the sorbent and to produce a concentrated stream of $CO_2$ suitable for disposal. However, a major practical difficulty stems from the significant degradation of performance in $CO_2$ capture [2,3] when increasing the number of carbonation/decarbonation cycles, and several studies have already been carried out in order to explain this detrimental effect. In this context, while the $CaCO_3$ decarbonation reaction has been extensively studied [4–8], only few works deal with a comprehensive understanding of CaO carbonation, whereas this process may have important consequences, not only for the capture of environmental $CO_2$, but also for various other issues such as CaO-containing minerals in underground locations or biogenic $CaCO_3$ formation. Bathia et al. [9] have proposed a mechanism of growth in elementary steps for CaO carbonation, but without inferring a rate law satisfactorily modelling the reaction trends. Rouchon et al. [10] have performed a kinetic study in order to precise the link between the carbonation rate and the porosity structure of the CaO aggregates. They have shown that the reaction involves a slow surface nucleation process followed by the growth of the nuclei, the hypothesis of nucleation being supported by the observation of an induction period at the beginning of the reaction. During solid–gas reactions, the nucleation process often involves several elementary steps. In the case of CaO carbonation, the first step should consist of the adsorption of $CO_2$ molecules on the CaO surface, and it is therefore of primary interest to reach a better understanding of this phenomenon.

Only few works have studied the interaction of $CO_2$ with CaO surfaces. Voigts et al [11] have used Metastable Induced Electron Spectroscopy (MIES) together with Ultraviolet and X-ray Photoelectron Spectroscopy data (UPS and XPS) to investigate the adsorption of $CO_2$ on CaO films under ultrahigh vacuum conditions. This study suggests that no $CO_2$ dissociation occurs on the CaO (100) surface, and that the O–C–O bonding angle decreases to about 130°, in agreement with prior studies [12,13]. The MIES spectra led to the assumption that the whole CaO surface is covered with $CO_2$, the XPS data showing the formation of $CO_3^{2-}$ complexes throughout the (100) surface. As part of an experimental and theoretical work on the same system [14], Density Functional Theory (DFT) simulations allowed to conclude that the most stable adsorption configuration of $CO_2$ occurs, as expected, via the C atom which is adsorbed on O sites of CaO, therefore confirming the existence of $CO_3^{2-}$ complexes. No adsorption takes place via the O atoms or on Ca sites. The calculations were performed on $Ca_xO_x$ clusters, taking into account that adsorption may occur either on terrace, edge or corner sites. This study also allowed to acknowledge that the molecule may be linked to the cluster with an angle of either 0° or 45°, with respect to the <100> atomic rows within the (100) surface.

In this context, the present work is devoted to a thorough atomic-scale analysis of $CO_2$ adsorption on the surface of CaO. Its main purpose will be to investigate issues that have been generally overlooked in previous studies, in particular the way of using atomic-scale energy calculations in order to achieve a quantitative assessment of the

* Corresponding author.
*E-mail address:* Remy.Besson@univ-lille1.fr (R. Besson).

0039-6028/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2011.11.016

adsorption properties. To this aim, we will consider with special detail the thermodynamic modeling of adsorption. As a second original feature, attention will be paid to the role of interactions between adsorbed molecules, an intricate task seldom investigated at the atomic scale. Whereas efficient available empirical potentials for CaO [15] and $CaCO_3$ [16,17] might *a priori* be convenient tools for our goal, this would require to design additional empirical interactions between the oxide and the gas. Due to this severe practical difficulty, ab initio calculations based on DFT were preferred in this work, with pseudopotentials ensuring the required transferability to various environments (gas and adsorption). After a preliminary part dealing with the thermodynamics of $CO_2$ gas and a comparison of CaO clean surfaces, we focus on the elaboration of an adsorption model following two successive steps: (i) adsorption considering non-interacting adsorbed $CO_2$ molecules and (ii) role of lateral interactions between molecules. Our work finally provides arguments related to the practically important issue of carbonate nucleation.

## 2. Methodological background

### 2.1. Ab initio calculations

The required DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP) [18,19], using the Projector Augmented Wave (PAW) method. The Generalized Gradient Approximation (GGA) was employed with the Perdew-Burke-Ernzerhof (PBE) functional [20,21]. The plane wave expansions of Kohn–Sham orbitals were truncated at a cut-off energy of 600 eV. With a $4\times4\times4$ k-mesh for a CaO unit cell, these values were found sufficient throughout to ensure the convergence of total energies within 1 meV. $atom^{-1}$. All bulk calculations included relaxations for ionic positions as well as lattice vectors, while surface calculations were performed keeping fixed supercell (SC) dimensions within the surface plane. In presence of adsorbed $CO_2$, special attention had to be paid to the realistic determination of the optimal height of the molecule above the surface plane, since slight variations for the initial value of this parameter were found to lead to significantly different energies.

### 2.2. Modeling of $CO_2$ gas

In the pressure and temperature ranges considered here (see Section 3.3), the $CO_2$ gas phase may reasonably be considered as perfect. The partition function for a gas with N identical non-interacting molecules is $Z = z^N/N!$, where $z = z_0\,\zeta(\beta)$ is the partition function of a single molecule. Here, $\zeta(\beta)$ is the partition function for the internal structure of the molecule and $z_0$ the partition function of its translational movement:

$$z_0 = V\left(\frac{m}{\beta 2\pi\hbar^2}\right)^{3/2} \tag{1}$$

where $\beta = 1/k_BT$, $V$ is the volume of the gas, $m$ the mass of the $CO_2$ molecule and $\hbar$ the reduced Planck constant. The partition function associated with the internal structure of the molecule is $\zeta(\beta) = \zeta_e\,\zeta_r\,\zeta_v$, where $\zeta_e$, $\zeta_r$ and $\zeta_v$ are the electronic, rotational and vibrational partition functions. The first two terms are given by $\zeta_e = g_0 e^{\beta\varepsilon_0}$ and $\zeta_r = 2I/\sigma\hbar\beta$, where $\varepsilon_0$ is the ground-state energy of the molecule, $g_0$ its degeneracy, $\sigma$ a symmetry factor (2 for a linear symmetrical molecule), and $I$ the moment of inertia. The vibrational part is:

$$\zeta_v = \prod_{i=1}^{4}\frac{1}{2sh(\beta\,\hbar\,\omega_i/2)} \tag{2}$$

$\{\omega_i\}$ being the four vibrational frequencies of the molecule (one degenerate bending mode and two stretching modes). The $CO_2$ vibration frequencies were deduced from the ab initio analysis of the force constants, the latter being determined by applying displacements on the equilibrium configurations of the molecule. The magnitude of the displacements was selected as 0.1 Å, ensuring the required linear behavior of the atomic forces.

From the free energy $F = -\frac{1}{\beta}\,ln\,Z$, the chemical potential for the $CO_2$ gas is readily obtained:

$$\mu_{CO_2} = \frac{\partial F}{\partial N} = -\frac{1}{\beta}ln\frac{z}{N} = -\frac{1}{\beta}\ln\left[\frac{\zeta(\beta)}{\beta P}\left(\frac{2\pi\beta\hbar^2}{m}\right)^{3/2}\right] \tag{3}$$

### 2.3. Adsorption models

Models describing the adsorption of $CO_2$ on CaO are most conveniently built using the grand canonical (GC) framework [22], namely by considering the equilibrium between the atoms adsorbed on the surface and a reservoir of particles and energy (surrounding gas) which imposes a given temperature and $CO_2$ chemical potential. In the present case, this requires taking into account (i) the two non-equivalent orientations of adsorbed $CO_2$, and (ii) the twofold symmetry degeneracy of these orientations. In the following, type 1 (resp. type 2) therefore refers to $CO_2$ orientations of 0° or 90° (resp. 45° or 135°). Neglecting first the lateral interactions between the adsorbed molecules (Independent Point Defect Approximation IPDA) leads to a simple additive form for the energy of the solid–gas system:

$$E_a^{IPDA}(N_1, N_2) = E_{ref} + E_1^{GC}N_1 + E_2^{GC}N_2 \tag{4}$$

with $E_{ref}$ the reference energy of the clean surface, $(N_1, N_2)$ the numbers of particles adsorbed for both types of orientations and $(E_1^{GC}, E_2^{GC})$ the corresponding GC energies. In the GC formalism, the equilibrium is characterized by the minimum, with respect to $(N_1, N_2)$, of the partial GC partition function:

$$\tilde{Z}^{GC} = \Omega(N_1, N_2)e^{-\beta\left(E_a-(N_1+N_2)\mu_{CO_2}\right)} \tag{5}$$

with $\Omega(N_1, N_2) = 2^{N_1}2^{N_2}\,C_{N_s}^{N_1}C_{N_s-N_1}^{N_2}$, the number of microscopic states, accounting for the degeneracy of each type of orientation. Under the assumption of non-interacting adsorbed molecules, the surface coverage $\theta_i = N_i/N_s$ ($N_s$ = total number of available surface sites) is thus given by:

$$\frac{\theta_1}{2(1-\theta_1-\theta_2)} = e^{-\beta\left(E_1^{GC}-\mu_{CO_2}\right)} \qquad \frac{\theta_2}{2(1-\theta_1-\theta_2)} = e^{-\beta\left(E_2^{GC}-\mu_{CO_2}\right)} \tag{6}$$

Modeling the interactions between the adsorbed molecules is an extremely intricate task since, strictly speaking, the latter are configuration-dependent. In order to preserve tractability and realistic modelling, we thus adopted a correction term for the energy of the adsorbed molecules:

$$E_a(N_1, N_2) = E_a^{IPDA}(N_1, N_2) + N\delta E^{IPDA}(\theta_1, \theta_2) \tag{7}$$

where $\delta E^{IPDA}(\theta_1, \theta_2)$ describes the deviation from IPDA and $N = N_s/2$ the number of sites on the surface. Modifying accordingly the GC partition, Eq. (5), as:

$$\tilde{Z}^{GC} = \tilde{Z}^{GC}(IPDA)e^{-\beta N\delta E^{IPDA}(\theta_1,\,\theta_2)} \tag{8}$$

leads to the interaction-dependent coverage rates as solutions of the following non linear system of equations (i = 1 or 2):

$$\frac{\theta_i}{2(1-\theta_1-\theta_2)} = e^{-\beta\left(E_i^{GC}-\mu_{CO_2}+\frac{1}{2}\frac{\partial\delta E^{IPDA}}{\partial\theta_i}\right)} \tag{9}$$