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# $CO_2$ adsorption on (0 0 1) surfaces of metal monoxides with rock-salt structure

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ABSTRACT

The adsorption of $CO_2$ on isostructural metal monoxides of rock-salt structure (CaO–NiO) is investigated by DFT to probe the surface properties. The nature of adsorption varies with M. Adsorption is found particularly large on TiO, VO and CrO which can be easily oxidized; it is then accompanied by an electron transfer leading to the formation of $CO_2^{2-}$ adsorbed on a lattice oxygen atom.



## 1. Introduction

The (0 0 1) surface of metal monoxide with the rock-salt structure is stable and simple for modeling, presenting in each direction an alternation of ions of opposite charge. Such surfaces are classified of type I according to Tasker [1]; they are stable and do not undergo large relaxations. This paper probes the $CO_2$ adsorption modes on the perfect (0 0 1) terraces, investigating properties of different metal monoxides MO (CaO–NiO). On MgO(0 0 1) which is, for model studies, the most popular metal oxide having the rock-salt structure, $CO_2$ adsorption is weak and involves surface cations. On different oxides, $CO_2$ adsorption may be strong leading to carbonates whose formation implies surface oxygen [2]. To understand such a large difference in surface behavior, we have here investigated a series of metal oxides with the same structure, (the (0 0 1) surface of a rock-salt monoxide) varying the nature of the cation along the first period of the Mendeleev table. Calcium is the most electropositive atom in the series and Ni the least one. Thus, this tests a wide range of cations with different acidities.

$CO_2$ is an amphoteric compound able to behave either as an acid molecule when the carbon atoms bind to surface oxygen atoms or as a weak base when it binds to the surface cations through the electron pairs of the oxygen atoms. Although $CO_2$ is often considered as a probe molecule testing the basic sites of the surfaces [3], it often binds to the exposed cations [4–8] with a weak adsorption compared to stronger bases. A systematic study can thus check both properties; however, the picture for adsorption reveals immediately more complexity than this simple project; indeed $CO_2$ can also bind simultaneously to several vicinal surface atoms and, when the cations are not in their highest oxidation state, an electron transfer can be involved in the adsorption process.

On clean and anhydrous MgO(0 0 1) surfaces, $CO_2$ binds to two adjacent surface cations. $CO_2$ adsorbs parallel to the surface binding to two adjacent $Mg^{2+}$ cations (see mode FLAT Fig. 1); however since the interaction is weak, the $CO_2$ geometry is not distorted. The adsorption energy (calculated by DFT, to be compared with values for other metal oxides from this contribution) is 0.126 eV; the Mg–O distance is large, 2.71 Å and the $CO_2$ molecule is linear with a CO distance of 1.175 Å). The Mg electronegativity (1.2 according to Pauling) is larger than that of Ca (1.1) but smaller than those of the metal atoms from the other monoxides (1.3–1.8). We expect then the surface acidity of MgO to be larger than that of CaO but weaker than those of all the other oxides. MgO also represents a case where cations have no valence electrons, $Mg^{2+}$ being the highest oxidation states for Mg; the adsorption is controlled by acid–base properties and no formal charge transfer occurs (redox mechanism). The MgO band structure is then characterized by the presence of a large gap, an acid–base control being the easiest way to preserve the existence of this gap. The width of the gap is associated with a large stability and a poor reactivity if nothing (solvent) is perturbing the system (UHV conditions). Frontier orbitals are well separated, making the surface oxygen atom poorly basic and the cations poorly acidic. The surface acidity prevails over the basicity [7,9–11].

The molecular adsorption of $CO_2$ at the cation sites seems very general for surfaces of low indices in metal oxides such as MgO and $TiO_2$ whose metal is in the highest oxidation state; indeed, we do

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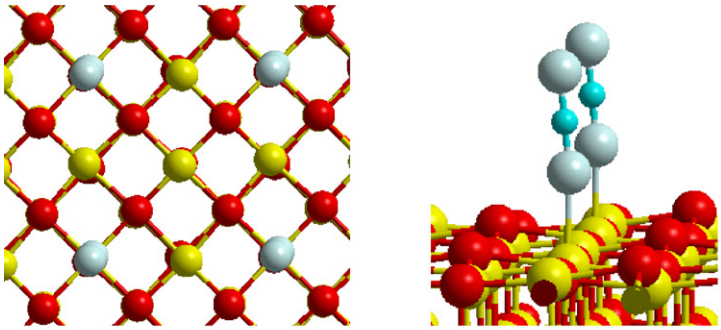
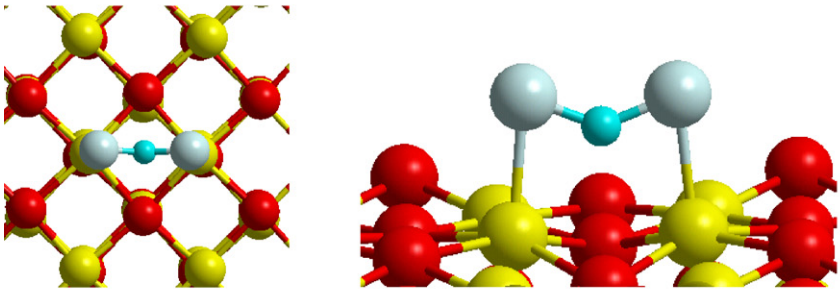
(A) mode VERT

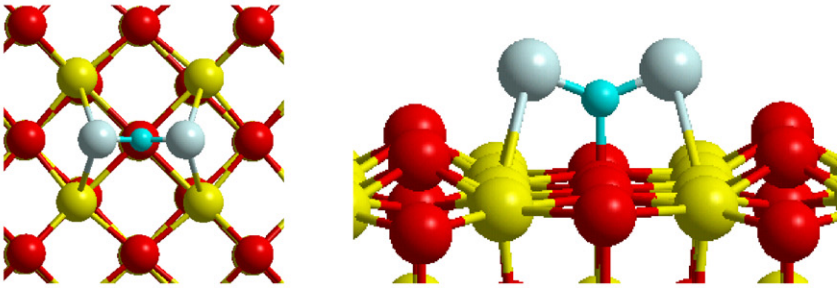


(B) FLAT



| monoxide | ScO | TiO | VO | CrO |
|---|---|---|---|---|
| O-C-O angle | 132°0 | 134°7 | 136°7 | 135°2 |

(C) mode BA1



(D) mode BA2

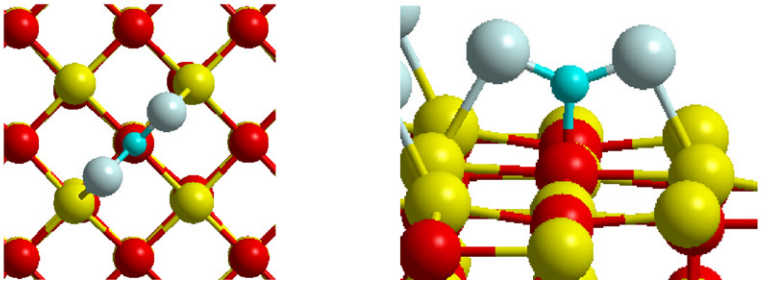


**Fig. 1.** Models for $CO_2$ adsorption on metal oxides (top and side views). (A) Mode VERT: vertical. (B) FLAT above two metal cations. (C) BA1: C on top of O, oriented along the OOO rows. (D) BA2: C on top of O, oriented along the OMO rows; there are two M-O interactions. Color code for the oxide and metals—yellow, oxygen—red, $CO_2$—light blue, carbon—small sphere, oxygen—large sphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

not find on terraces of these metal oxides many examples of binding through the C atom only. The interaction with surface oxide anions, $O^{2-}$, leads to carbonates and is involved in catalytic reactions [6,12]. This does not happen on terraces. The monodentate and bidentate modes are found on the edge and corner sites of MgO, where the coordination of O decreases, making it more reactive [13]. For the extreme cases where the surface oxygen are expected to be basic, the unidentate mode ($CO_2$ binding through the acid center, C, to a surface oxygen) does not clearly result from this single interaction. For CaO, analyzed in this paper, the interaction (O to Ca) also contributes binding (see hereafter). In the case of $Cs_2O$ ($CdCl_2$-type structure) where the $Cs^+$ cation is the most electropositive one and where the surface oxygen atoms are the most basic, Neurock and co-workers [14] have found a "bridge" adsorption mode where $CO_2$ binding appears to be both acid and base, two bonds being made, involving C and O at the same time. Recently, we have found that $CO_2$ strongly binds to a $LaMnO_3$ perovskite surface [2] generating a carbonate species. In these cases, the adsorption energy is large, cumulating several interactions, acidic and basic.

In this paper investigating the adsorption of $CO_2$ on a series of metal oxide having the rock-salt structure (CaO–NiO), we compare different adsorption modes according to the nature of $M^{2+}$ cations. The choice of this series implies that some cations are not in the highest oxidation state, allowing possibilities of reducing $CO_2$ and forming CO. The adsorption modes are displayed in Fig. 1. In VERT and FLAT, $CO_2$ binds to one (VERT: vertical) or two (FLAT: on two adjacent) cations, testing the surface acidity. In BA1 and BA2, $CO_2$ is centered above a surface oxygen, testing mainly the basic surface sites; according to its orientation, it does not interact with the surface cations (mode BA1), or it does with two of them (BA2). Finally, the mode DISS (not shown) corresponds to the dissociation into O/M and OC/M which implies the formal electron transfer of two electrons from the surface (redox process). We have only considered adsorption on adjacent M cations. Diffusion may favor more distant locations.

## 2. The metal oxides

We considered the series of MO oxides (CaO–NiO) varying the cation along the first period of the transition metals from the Mendeleev table. CaO has been already studied by Jensen et al. [13] who found rather large adsorption energies involving the oxygen site (modes BA1 and BA2). The basicity of the surface oxygen is explained by the large cell parameter of CaO that makes O poorly coordinated and more reactive (small Madelung stabilization).

The $M^{2+}$ cations (M = Sc, Ni) have valence d electrons while $Mg^{2+}$ or $Ca^{2+}$ do not; the monoxides are then metallic or semiconducting, the gap being underestimated by the use of the Perdew–Wang functional [15]. Concerning adsorption, redox mechanisms are possible which could modify the adsorption modes (strength and site).

We did not find experimental evidence for the existence of scandium monoxide. According to the calculations with the VASP program, the cohesive energy is reasonable, but it has not been compared with alternative structures. We have included this oxide to be able to discuss of a continuous series.

Titanium, vanadium, iron, cobalt and nickel monoxides are known with the rock-salt structure even though other structures also exist: BCC for FeO [16] *Fm*3*m* for VO [17]; below the Curie temperature, NiO exists in rhombohedral form and CoO in tetragonal form [18]. Rock-salt TiO, NbO (isoelectronic to VO) structures belong to the family of compounds called "hard refractory metals". These structures accumulate a large percentage of vacancies [19–21]. The chromium monoxide has been stabilized as film [22] with a good crystallinity even though bulk does not exist. MnO also exists and has been studied as support for Fe catalyst [23,24]. CoO and NiO are magnetic insulators [25]. We have not considered, CuO and ZnO since they have different structures. ZnO is known with the rock salt B1 structure only at a pressure of about 9 GPa; the hexagonal B4–ZnO could then transform to the rock-salt structure (see [26] and [27]).

**Table 1**
DFT results for the rock-salt structures of metal monoxides

| | $\mu_B$ | Bader charges | $E_{MO}$ | $d$(MO) |
|---|---|---|---|---|
| M in MO | | | | |
| Ca | 0 | 2.000 | 1.98 | 2.369 |
| Sc | 0 | 1.906 | 2.18 | 2.245 |
| Ti | 0 | 1.5355 | 2.18 | 2.129 |
| V | 1 | 1.668 | 1.87 | 2.113 |
| Cr | 4 | 1.511 | 1.53 | 2.194 |
| Mn | 5 | 1.4965 | 1.46 | 2.232 |
| Fe | 4 | 1.438 | 1.56 | 2.143 |
| Co | 3 | 1.315 | 1.50 | 2.117 |
| Ni | 1.66 | 1.127 | 1.45 | 2.085 |

$\mu_B$: number of unpaired electrons per cation. $E_{MO}$: bonding energy per M–O bond (in eV—1/6th of the cohesive energy per MO); this represents the binding energy (eV) of a MO bond *w* respect to atoms. $d$(MO): distance in Å.

Along the period, the cohesive energy referred to the atoms decreases from CaO to NiO (see Table 1 and Fig. 2). There are modulations and ScO–TiO and FeO represent maxima while MnO represents a minimum. $Mn^{2+}$ is in a high spin state which does not favor binding. The lattice parameters also decrease from CaO to NiO (see Table 1). That for MnO is a maximum.

Except for MgO and CaO, there are few studies on adsorption on isostructural compounds [28,29]. They mostly concern NiO that represents a difficult challenge to theory [30]. The adsorption is then weak and a correct description necessitates including the dynamic correlation beyond the difficulty for DFT of describing the gap. To our knowledge none of these studies include $CO_2$. In spite of these difficulties, we have included NiO to complete our systematic study; it then represents an extreme case of small binding energies.

## 3. Models of surface and details of calculations

We have performed periodic calculations using the VASP4.6-26 program [31–33], a plane wave basis set (kinetic energy cut-off at 396 eV) and ultrasoft pseudopotentials [34,35] for the electron–ion interactions. Spin-polarized calculations have been done using the

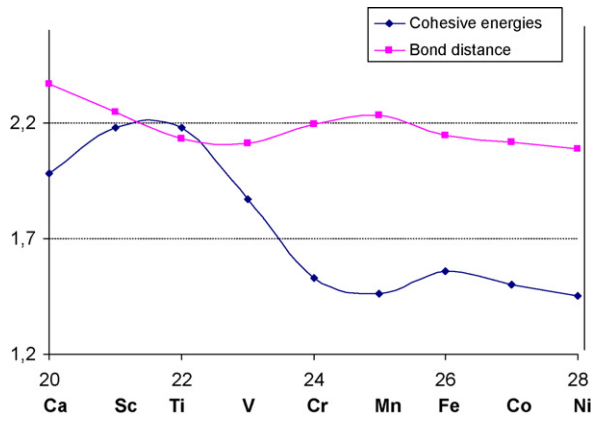



**Fig. 2.** Cohesive energies and MO distances vs. atomic numbers for M as calculated from DFT calculations. The *y*-axis indicates eV for cohesive energies and Å for MO distances. The two curves are correlated, varying in opposite directions.

**Table 2**
Adsorption energies (eV) for the different modes

| Predominant interaction | VERT<br>Cation site | FLAT<br>Cation site | BA1<br>Cation + anion | BA2<br>Cation + anion | DISS |
|---|---|---|---|---|---|
| Ca | 0.104 | 0.26 | 1.245 | 1.225 | −4.91** (−5.67) |
| Sc | 0.261 | 2.09 | −0.187 | 0.129 | 0.538 |
| Ti | 0.119 | 1.337 | 0.520 | 0.534 | 2.062 |
| V | 0.166 | 1.491* (1.418) | −0.872 | 0.269* (−0.208) | 2.275* (0.166) |
| Cr | 0.029 | 0.798* (−0.151)<br>*0.491* (*0.413**) | −0.76 | −0.57* (−0.23) | −0.181* (−2.121) |
| Mn | 0.055 | 0.101 | 0.101 | 0.120 | −1.859 |
| Fe | −0.03 | 0.088 | −0.25 | 0.468 | −1.261 (−0.98**) |
| Co | 0.205 | 0.281 | −0.48 | 0.261 | −1.205** (−1.195) |
| Ni | 0.02 | 0.055 | 0.03 | 0.38 physisorption *0.088 chemisorption* | −1.893 |

The highest values are underlined. When the spin states of the covered surface are the same than in the bare surface (i.e. the sum, $\sum\mu_B$ of the spins of the cations ($\mu_B$ from Table 1)) there is no special indication. When it differs, the variation of spin state is indicated by one or two stars). A single star (*) corresponds to a global number of unpaired electron equal to ($\sum\mu_B - 2$) and two stars (**) to ($\sum\mu_B + 2$); this two cases correspond to a transfer of two electrons from the metal cation to the adsorbate (see text). When $CO_2$ is bent, the position of C relative to O is down (toward the surface as shown in Fig. 1). For CrO, the opposite orientation (C up) is a secondary minimum; adsorption energies are indicated in italics). For MnO, all the adsorptions occurring without dissociation correspond to physisorption, for NiO, the adsorption modes of lowest energy correspond to a physisorption, even though for BA2, an adsorption mode with $CO_2$ closer to the surface is a secondary minimum.

generalized gradient approximation with the Perdew–Wang functional [15]. The atoms within the supercell are relaxed until the energy difference between two subsequent steps is smaller than 0.001 eV. The calculations have been performed sampling the Brillouin zone in a 5×5×1 Monkhorst-Pack set.

We started by the optimization of the ideal bulk, with rock-salt structures without defects. The spin states are indicated in Table 1 ($\mu_B$ is the difference between the number of spin alpha and beta per metal) together with charges, energies and geometrical results. The electronic structure of the metal oxides (M = Sc–Ni) is often calculated metallic or weakly semiconducting. However, the spin states of the cations is well defined and associated with an electron count for M(+II). The number of odd electrons ($\mu_B$) is 0 for ScO ($d^1$ antiferromagnetic) and TiO ($d^2$), 1 for VO ($d^3$), 3 for CoO ($d^7$), 4 for CrO ($d^4$) and FeO ($d^6$) and 5 for MnO ($d^5$). CoO and NiO are magnetic insulators. For CoO, $\mu_B$ = 3 is slightly less than the experimental values, 3.35–3.8, (see Ref. [25]) but clearly corresponds to a high spin configuration for $Co^{2+}$ ($t^5_{2g}\ e^2_g$). The spin state for NiO (1.66 $\mu_B$) deviates from integers; it is smaller than found in Ref. [18] and close to the value from [25]. The antiferromagnetic state is slightly more stable than the ferromagnetic state [25].

We have considered a three-layer slab and a $P2\times2$ unit cell. The volume of the cell is kept fixed and the position of all the atoms is optimized. The translation vector normal to the surface is 19 Å and thus the vacuum distance between successive slabs is larger than 15 Å. For the majority of the surface calculation, the number of unpaired electrons per cation was imposed similar to that obtained in a spin-polarized calculation of the bulk monoxide as displayed in Table 1. For NiO, since the magnetization number of the bulk is not an integer, we have optimized this value in each case. In cases of two electron transfers, the spin state varies. Indeed, the electron transfer removes unpaired electrons when the number of valence electrons ($n$) of the cations is less than five and removes two electrons from the upper pairs when $n$ is over 5. The global number of unpaired electrons has been modified accordingly; this is then specified in text and in Table 2.

The adsorption energy has been calculated as

$$E_{ads} = E_{surface} + E_{CO_2} - E_{CO_2+surface}$$

where $E_{surface}$ represents the energy of surface of reference, $E_{CO_2}$ is the energy of $CO_2$ and $E_{CO_2+surface}$ that of the adsorption system. A positive value of $E_{ads}$ indicates an exothermic process.

### 3.1. Adsorption on M sites (VERT and FLAT modes)

The acidic property of the cation depends on the energy level of the CB that is influenced by several factors: (i) the electronegativity of the metal (the reactivity should increase from CaO to NiO), (ii) the repulsion with the valence electrons of the metal (the reactivity should decrease when the d orbital perpendicular to the surface becomes populated, this should occur for $Mn^{2+}$ which has five electrons) and (iii) the strength of the MO binding in the metal monoxide (for MnO the orbitals localized on Mn should be less antibonding).

When $CO_2$ is on top of M (VERT mode), the chemisorption energy increases from CaO to VO in agreement with (i) and (ii) (see Table 2 and Fig. 3). The value for ScO presents an anomalous large value. Then, it drops. The calculated value for MnO is very weak due to the occupancy of all the d orbitals of the cation in the highest spin state. The weak cohesive energy of MnO also reveals the low reactivity of $Mn^{2+}$. The adsorption corresponds to a physisorption and we have not found stable chemisorption for the VERT and FLAT modes. Beyond MnO, the adsorption values are weak due to a further increase of electronegativity; that for CoO is the highest. For the largest interaction in the VERT mode, $CO_2$/VO, the $CO_2$ geometry is unchanged relative to the molecule and the V–O distance, 2.17 Å is in the same range as the V–O distance of VO bulk

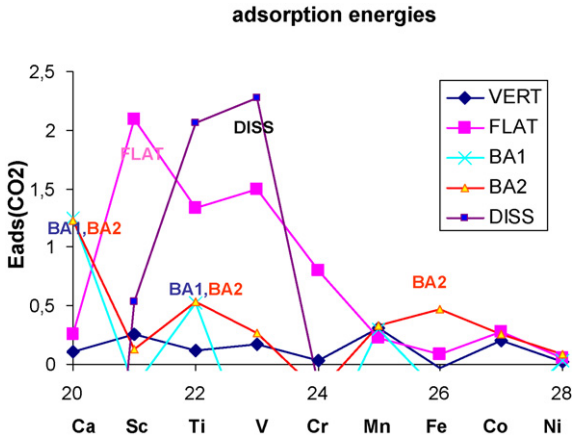



**Fig. 3.** Energy of $CO_2$ adsorption in the different modes. Only positive (exothermic) values are shown.

(2.11 Å). The molecule slightly deviates from the direction normal to the surface (V–O–C = 162°).

In the bridging mode on two adjacent cations (FLAT mode), two M–O bonds being made, we can anticipate a doubling of the chemisorption energy. This is the case for CaO. For all the other cases, the calculated values are much larger and something different happens. The $CO_2$ geometry no longer remains that of the molecule. The C–O distances are in the range of 1.26–1.28 Å and the molecule is bent with an angle of 133–137°. The adsorbed species corresponds to a negatively charge species resulting from an electron transfer from the oxide to $CO_2$. In the case of VO, the sum of the Bader charges for $CO_2$ represents a net charge of 1.125 e. The FLAT adsorption mode is not controlled by the acidity of the cation but also depends on redox properties, on the availability of electron transfer from the cations which are not in the highest oxidation state. The electron donation from the surface cations is weak for $Mn^{2+}$ where the stabilization of five electrons of same spin is important. It is weak for metal monoxides with M at the right-hand side of the period (more important for CoO where $Co^{2+}$ is more easily oxidized to $Co^{3+}$).

The geometry of the $CO_2$ unit is rather that of a $CO_2^{2-}$ species. Such electron count is still compatible with an acidic carbon atom since the negative charges are localized on the O atoms while C has an oxidation number of +II. To account for the coupling of two electrons, we modified the total number of unpaired electrons by two units in the case of high spin states. This leads to decrease the number of unpaired electrons by two up to MnO and to decrease it by two beyond: 10 instead 12 for the VO surface (the cell contains 12 M atoms) 46 instead of 48 for the CrO surface, 50 instead of 48 for the FeO surface and 38 instead of 36 for the CoO surface. In these cases, except for CoO, this allows a larger heat of adsorption.

For ScO–CrO, $CO_2$ is bent (O–C–O ∼135° see Fig. 1) and the C atom is oriented toward the surface. If the surface atom were kept at the bulk positions, the C would be above the middle of a MOMO square, at equal distances to M and O. The surface relaxation distorts the square and shortens the M–M diagonal, involved in the bonding; the two M atoms move up, out of the plane, isolating from the other surface atoms. The motion for the O is the opposite: they move down and the OO is elongated. The C atoms then interact more with the metal than with the O atoms. This is the reason to have the C down. Since the $CO_2$ is negatively charged, this additional interaction is stabilizing. CrO behaves like VO and TiO when we assume that two electrons are paired. The preservation of the number of electrons for the Cr (48 e) leads to the opposite orientation with C up instead of down as shown in Fig. 4. In this case, the distortion of the CrOCrO square at the surface site brings the O atoms closer and moves away the Cr atoms. This orientation, though less stable, offers perhaps more opportunity for a reaction implying C and a molecule from the gas phase. It is also interesting to note that the central C atom is isolobal to a carbene species. When it is up, the electrons are not coupled. On the contrary, when it is down, the stabilizing interaction with the surface imposes a coupling and a lowering of the total spin.

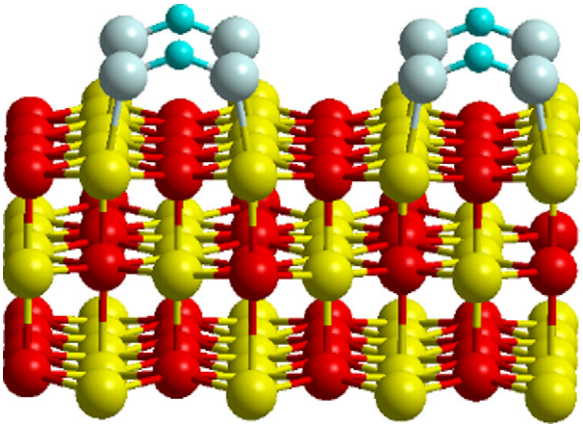


**Fig. 4.** Adsorption on CrO with the C atom "up" (FLAT mode). Compared with the FLAT mode of lowest energy (C atom "down"—see Fig. 1), the distance from C to the surface plane is larger than that from O to the surface. (For interpretation of the references to colour in the artwork, the reader is referred to the web version of the article.)

### 3.2. Adsorption on O sites (BA1 and BA2 modes)

Considering $CO_2$ adsorption through the C atom allows testing the basicity of the surface. Except CaO, TiO and FeO, the series of monoxide with a rock-salt structure is not favorable to this mode for two reasons: it requires a poorly coordinated oxygen at the adsorption site whereas on (0 0 1) terraces the coordination of the surface oxygen remains high (five) making the O dianion stable and poorly basic; it requires the metal from the metal oxide to be in a high oxidation state. These two factors are not independent; when the ratio of O atoms vs. M is large (dioxides or trioxides), the O coordination decreases and O atoms are more basic than in the monoxide.

For the adsorption modes BA1 and BA2, the carbon atom is on top of a surface oxygen atom and $CO_2$ is parallel to the surface. There are two orientations for $CO_2$. In mode BA1, $CO_2$ is parallel to the OO rows and the O atoms from $CO_2$ are not oriented toward the surface cations. On the contrary, in mode BA2, $CO_2$ is parallel to the OMO rows and the O atoms from $CO_2$ interact with two surface cations (the OM distances are slightly shorter than the OM distances inside the bulk structures). The mode BA1 may thus be seen a pure top-adsorption over O testing only the basic site of the surface (unidentate) whereas, the mode BA2 involves three interactions, the difference in energy between the modes BA1 and BA2 revealing the interaction with the cations. Excepting on CaO, the mode BA2 is more favorable in energy that the mode BA1; for ScO, VO, CrO, FeO and CoO, the adsorption energy for BA1 mode is negative (endothermic adsorption). This shows that the surfaces of the monoxides are predominantly acidic.

CaO is the exception appearing as a basic surface; this is due, as mentioned above, to the large cell parameter of CaO that makes O poorly coordinated and more reactive (small Madelung stabilization). BA1 and BA2 represent the largest adsorption energy, BA1 being slightly larger than BA2. This is due to the large cationic radius of $Ca^{2+}$ that allows interacting with the four surface oxygen atoms close by. In BA1, the four Ca–O distances, 2.57 Å, remain close to the Ca–O 2.37 Å of the bulk crystal. For the other cations, the difference is larger and such interaction becomes negligible as stated above as a general rule. In these two modes, the C–$O_{surf}$ distance (1.41–1.44 Å) is small and comparable to a typical C–O single bond. The moiety $CO_2$+$O^{2-}$ therefore could be thought as a carbonate species, $CO_3^{2-}$, strongly attached to the surface.

Though most often not competitive with the FLAT mode, the BA2 mode corresponds to a strong binding (chemisorption). The two M–O interactions appear to be the driving force for this adsorption mode. The M–O distances are indeed slightly smaller than the M–O distances inside the MO bulk structures (given in Table 1). The role of the CO interaction varies in the series. In Table 2, the difference in energy between BA2 and FLAT is often large. In a first approach, the adsorption with the FLAT mode is due to two M–O binding and the extra energy for the BA2 mode can be then attributed to the C–O interaction. It is a stabilizing interaction only for MnO and FeO. However in all cases, the distance from the C atom to the surface oxygen is that typical of a C–O single bond, ∼1.43 Å or slightly higher. Most of the calculated C–O distances are in the range of 1.43–1.57 Å. The $CO_2$ molecule is bent and the bond

**Table 3**
Vibrational frequencies calculated for chemisorption ($CO_2$/VO) and physisorption ($CO_2$/MnO)

| $CO_2$ molecule | Physisorption on MnO | Mode BA2 on VO (CrO) | Mode FLAT on VO (CrO) | NaOCONa model | $CO_2^{2-}$ |
|---|---|---|---|---|---|
| 2363 | 2331 | 1636 (1744) | 1675 (1646) | 1678 | 1999 |
| 1336 | 1286 | 1190 (1172) | 1187 (1178) | 1084 | 1135 |
| 640 × 2 | 617–578 | 763 (703) | 703 (674) | 544 | 525 |

Model corresponds molecules, having $CO_2^{2-}$ complexed by two Na + counter-ion optimized in a W shape ($d_{CO}$ = 1.25 Å, $d_{ONa}$ = 2.31 Å and O–C–O = 137°).

lengths differ from that of the molecule, 1.175 Å; the CO distances and O–C–O angle of $CO_2$ are ~1.26 Å and 130–135°.

The chemisorption energy for the mode BA2 which is large for TiO drops for CrO and rises again for MnO and FeO. Similar curves, presenting two maxima, are found for the cohesive energies of the metal bulk [36,37] and for the adsorption of M/MgO [38]. There is a shift, from Mn to Cr, from Ni to Fe which can be associated to the fact that for the metal monoxides, we consider ions instead of atoms. The adsorption on FeO is not the largest from Table 2; however relative to the FLAT mode, the BA2 mode prevails.

As for the FLAT mode, when the geometry of the unit is close to that of a $CO_2^{2-}$ species we have modified the total number of unpaired electrons by two units as discussed in the previous section. This improves in the cases of VO and CrO the binding energy of $CO_2$ for the same reasons as for the FLAT mode.

The adsorption for the BA1 and BA2 modes singularize the atoms belonging to the rows where adsorption takes place. The uncovered surface oxygen atoms that pertain to the same rows rise above the average surface plane.

### 3.3. Adsorption with dissociation, reduction of $CO_2$

We also investigated the coadsorption of O and CO. CO is vertical, C oriented down above a cation, O being on top of an adjacent cation. Considering O in the oxidation state (+II), there is an electron transfer from the metal cations that should not be in the highest oxidation state for the stoichiometric monoxide. Again, we have modified the total number of electrons to account for the pairing of electrons when O is adsorbed. For TiO and VO, the $CO_2$ decomposition is strongly exothermic. The $CO_2$ adsorption with the A mode is strong for these oxides and already involves the electron transfer to reduce the O atom. Starting from there, the $CO_2$ decomposition is exothermic. The reaction path however implies the migration of C (initially bridging two cations in the mode FLAT) to a single surface cation. It will be studied in a forthcoming study.

### 3.4. Consequences of the redox process

As explained above, the clearest evidence for an electron transfer from the metal cation to $CO_2$ is the variation of the number of unpaired electrons ($\mu_B$). Several observations corroborate this analysis. The geometry of $CO_2^{2-}$ (C–O distances of 1.21 Å, O–C–O angle of 153°) imposes vibrational frequencies that differ from those of the linear $CO_2$ molecule. These parameters become 1.25 Å and 137° in a small model where $CO_2^{2-}$ is bound to counter-ions (2 $Na^+$). For strong chemisorption, ($CO_2$/VO mode FLAT) they become 1.26 Å and 137°.

In Table 3, the frequencies for the modes BA2 and FLAT on VO and CrO (strong chemisorption) resemble those calculated for the anion alone, or associated with $Ca^{2+}$ or two $Na^+$ (see Section 3). On the contrary, for MnO (physisorption) they remain close to that of the $CO_2$ molecule.

The Bader analysis show a transfer of about 1 e, inferior to 2, the value for the formal transfer of an electron pair, but significant: the total value for $CO_2$/VO (mode FLAT) is 1.125 e. For $CO_2$/MnO (physisorption in modes BA2 and VERT) it is 0.041 and 0.033 e

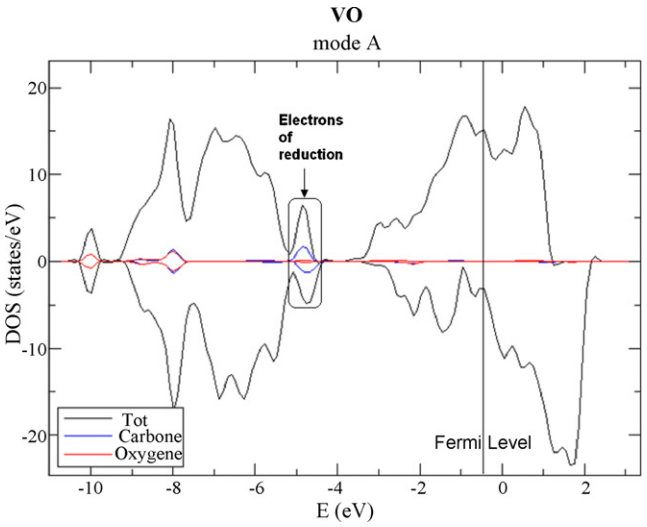



**Fig. 5.** DOS for $CO_2$/VO FLAT mode. At the right hand side of the 2p(O) levels (from −9 eV to −5 eV) and clearly below the DOS for the electrons of the vanadium cations (above −3 eV), a peak associated to the electrons of reduction is shown with a significant contribution on the carbon atom. The oxidation state of the carbon atom of $CO_2$ varies from +IV to +II with the electron transfer. The Bader analysis also shows an increase (from 0 for the gas-phase, all the density (8 e) being on the O atoms, to 1.125 e under adsorption). (For interpretation of the references to colour in the artwork, the reader is referred to the web version of the article.)

respectively (all the density (8 e) being on the O atoms as for the gas phase).

Finally, the DOS analysis of $CO_2$/VO (mode FLAT) shown in Fig. 5 clearly shows a reduction of the carbon atom of $CO_2$ (a band at the right hand side of the 2p(O) band above −5 eV; the oxidation state of this atom varies from +IV to +II with the electron transfer.

## 4. Conclusion

$CO_2$ adsorption on rock-salt monoxide strongly differ from those on MgO(0 0 1). Comparing different monoxides with similar structures, we hoped to emphasize simple trends for adsorption. The situation obtained remains however complex with the coexistence of several interactions and with the electron transfers occurring. Some conclusions however emerge. For the acid–base control, the interaction with the cations is more important than that with the anions. CaO is the exception where the C–O binding is strong, leading to the formation of a carbonate bound by several bonds to the surface. When the metal of the monoxide has d electrons, the adsorption involves an electron transfer to $CO_2$ that then behaves as $CO_2^{2-}$. This transfer is seen by a modification of the spin state, by the local geometry and by the vibration analyses. This reduced species $O^{2-}$–$C^{2+}$–$O^{2-}$ is potentially reactive with a central carbon isolobal to a carbene. The FLAT mode is the most favorable one at the left hand side of the periodic table (ScO–VO) and leads to strong adsorption. This is also in this region (ScO–VO) that dissociation into CO+O is favorable (see Fig. 3). In mode BA2, $CO_2$ does not bind to the surface oxygen of perfect surfaces without also strongly binding to the cations. The binding to surface oxygen

therefore needs the presence of undercoordinated O atoms, at edge or corner sites or at defect sites. MnO appears singular, the physisorption being stronger than the chemisorption. The poor reactivity of MnO is related to the high spin state of $Mn^{2+}$. At the right hand side of the periodic table (FeO–NiO), the BA2 mode becomes very favorable. FeO is the monoxide for which this mode is the most selective.

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