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**Lewis Acido-Basic Interactions Between CO₂ and MgO
Surface: DFT and DRIFT Approaches**

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Lewis acido-basic interactions between CO₂ and MgO surface: DFT and DRIFT approaches

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Abstract

Combined experimental infrared (IR) and theoretical approaches have been carried out in an attempt to specify the actual structure of the CO₂ species adsorbed on the magnesium oxide surface. The interaction of CO₂ with regular sites of the MgO(100), (111) and (110) surfaces as well as MgO(100) defect sites (steps, corners, kinks and di-vacancies) has been investigated by mean of Density Functional Theory study. Theoretical IR frequencies compared with IR experiments show distinguishable carbonate species, adsorbed on different planes and defects, vibrating in different IR-frequency ranges. In addition, by mean of thermodynamic model, the stability of carbonates as a function of temperature have been calculated and compared to the experiment. Analyzing the nature of basic sites, the results show that the most active site versus CO₂, which is a Lewis acid, is not the same that the strongest site for the deprotonating adsorption of Br onsted acids. The present work revisits and improves the understanding of carbonate species that could exist on the magnesium oxide surface and gives a picture of the accessible planes of magnesium oxide as well as their surface Lewis basicity.

Keywords: MgO(111), MgO(110),MgO(100), defects, charge density difference, thermodynamic calculation, Lewis basicity, Infra-red.

1. Introduction

Due to environmental questions, the interest for developing the use of basic catalysts is increasing [1-2]. One of the main drawbacks of these basic catalysts is that they are naturally polluted by water and carbon dioxide forming, by the way of an acid-base reaction, hydroxyl and carbonate groups on the catalyst surface. These adsorbates are usually considered as poisons of the reactivity even if they can be desorbed at specific temperatures depending on their nature and local environment [3]. In order to understand the catalytic properties of the basic catalysts linked to the pretreatment conditions, it is important to be able to characterize the adsorbates remaining on the surface before the catalytic reaction and, as a consequence, to know which basic sites are available after the thermal treatment.

Such an attempt has already been made with hydroxyl groups of magnesium oxide [4-5] which is a well-known basic catalyst involved in numerous studies of industrial interest [3, 6-9]. The aim of this paper is to investigate, by a mixed experimental-theoretical approach, the nature of the carbonates formed by interaction with CO_2 on MgO surface defects and their stability upon thermal treatment. As CO_2 is a Lewis acid while H_2O or methanol used in previous studies are Brønsted acidic molecules, the discussion of the results will involve a comparison between Lewis and Brønsted basic properties of MgO.

Infra-Red spectroscopy is one of the more informative techniques for the characterisation of adsorbed molecules [10], as carbonate species, formed on MgO surfaces [11-19]. The literature describes the carbonates present on MgO surface as monodentates or bidentates, but their detailed pictures have been unclear so far and the interpretation of IR band spectra and their attributions in connection to specific adsorbed species are questions which are far from being resolved [2]. In this work, using DRIFT spectroscopy we have followed, for different temperature ranges, the interaction of CO_2 with MgO powder sample, prepared by precipitation. The originality of the pre-treatment operated here resides in covering the surface

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3 previously cleaned up from hydroxyl and carbonates groups by different amounts of CO₂. In
4
5 addition, we have attempted to specify adsorbed CO₂ species by ab-initio DFT method. The
6
7 theoretical investigation of CO₂ interactions with MgO surface has often concerned (100) flat
8
9 surface [20-22], step and corner defects [20, 22-23]. Due to their lower stability compared to
10
11 the (100) surface, the (110) [24] and (111) [23] lattice planes have attracted much less
12
13 attention. Nevertheless, as the adsorption of molecules such as water or CO₂ can modify the
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15 relative stabilities of the lattice planes [25], this work presents results obtained on all these
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17 surfaces and also includes kinks and divacancies which can be formed on the (100) surface.
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22 In the following the configuration and energetic stability as well as electronic structures of
23
24 the different carbonate species which could be formed over MgO support are investigated
25
26 using DFT calculations. In addition by mean of thermodynamic model, the stabilities of
27
28 carbonates are drawn as a function of temperature. Thus the comparison of DFT calculated
29
30 frequencies and measured IR data leads to a detailed description of the surface state
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32 depending on the temperature treatment.
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2. Experimental and Computational details

2.1. Materials and experiments

2.1.1. Preparation of the catalyst: $\text{Mg}(\text{OH})_2$ was obtained from $\text{Mg}(\text{NO}_3)_2$ (Aldrich, 99.99%) solution using ammonium hydroxide (Aldrich, 99%) (8 mol.L^{-1}) as precipitating agent. Thus, the latter was added to a magnesium nitrate solution (1 mol.L^{-1}) and the pH value adjusted to 10 at 303 K. After stirring for 30 min, the precipitate was washed several times with deionized water, and then filtered. The hydroxide sample was finally treated in vacuum (10^{-6} Torr) up to 1273 K (ramp 1 K.min^{-1}) and maintained at this temperature for 2 h.

2.1.2. Thermal treatments: Figure 1 reports the different steps of the thermal treatments of the magnesium oxide sample. During the pre-treatment phase, the sample is “cleaned up” 2h at 1023 K under nitrogen flow (Air Liquide, U nitrogen >99.995% pure) ($20 \text{ cm}^3.\text{min}^{-1}$), then cooled down to 323 K. During the treatment phase, the sample is first contacted with carbon dioxide (Air Liquide, Alphagaz, >99.9% pure) diluted in nitrogen (5% in a $20 \text{ cm}^3.\text{min}^{-1}$.flow) for 15 min. Then, it is once again heated at intermediate temperature ($473 \text{ K} < \text{temp} < 1073 \text{ K}$) in a nitrogen flow ($20 \text{ cm}^3.\text{min}^{-1}$) for 2 h. In the following, only the final temperature “temp” that determines the degree of carbonatation of the sample will be indicated.

Insert Figure 1

2.1.3. Spectroscopic measurement: DRIFT spectra were recorded on a Brüker IFS 66 V spectrometer in the $4000\text{--}600 \text{ cm}^{-1}$ range (4 cm^{-1} resolution, 256 scans/spectrum) using a Thermo Spectra-Tech high temperature cell. All spectra were converted into Kubelka–Munk

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2
3 units after subtraction of the spectrum recorded on dehydrated KBr sample. All spectra are
4
5 recorded in situ after the pretreatment procedure described in section 2.1.2 and the cooling
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7 down of the sample to 333K. Finally, Raman spectra were recorded on a Model HL5R of
8
9 Kaiser Optical System Inc. in the the 3450–100 cm^{-1} range (4 cm^{-1} resolution). It is equipped
10
11 with a high-powered near-IR laser diode working at 785 nm.
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15 16 **2.2. Computational details**

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20 **2.2.1. Methods.** All calculations were performed using *ab-initio* plane-wave pseudopotential
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22 approach as implemented in VASP [26-27]. The generalized gradient approximation
23
24 exchange-correlation functional of Perdew and Wang PW91 [28] was chosen to perform the
25
26 periodic DFT calculations with reliable accuracy on the convergence criterions. The one
27
28 electron wave function was developed on a basis set of plane waves and the interaction
29
30 between the core and the valence electrons is described by the projector augmented waves
31
32 (PAW) approach [29]. The selected description of the oxygen atomic core allows a good
33
34 convergence on the energy for a cutoff of 400 eV. The convergence criterion for the
35
36 electronic self-consistent cycle was fixed to 10^{-6} eV per supercell. Geometry optimizations
37
38 were performed within a conjugate-gradient algorithm until the convergence criterion on
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40 forces (10^{-2} eV.Å $^{-1}$) was reached. A dipolar correction along the perpendicular to the slab was
41
42 applied in order to remove the effect of electrostatic interaction between the slab and its
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44 periodic images along the z axis. The adsorption energy of carbonates on the MgO surfaces
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46 was calculated as:
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$$52 \quad E_{\text{ads}}(\text{OK}) = E_{\text{CO}_2/\text{surf}} - (E_{\text{surf}} + E_{\text{CO}_2\text{free}}) \quad \text{eq. 1}$$

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54
55 Where E_{surf} represents the energy of bare surface, $E_{\text{CO}_2\text{free}}$ is the energy of CO_2 gas and
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57 $E_{\text{CO}_2/\text{surf}}$ that of the adsorbed system.
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3 Vibrational spectra were calculated for selected surface species within the harmonic
4 approximation. In addition to CO₂ molecules, magnesium and oxygen surface atoms in direct
5 interaction with adsorbed species were allowed to relax. The Hessian matrix was computed by
6 the finite difference method followed by a diagonalization procedure. The eigenvalues of the
7 resulting matrix lead to the frequency values. The assignment of the vibrational modes is done
8 by inspection of the corresponding eigenvectors. Free carbon dioxide molecule is used as a
9 reference in order to estimate the systematic deviation between experimental and calculated
10 ν_{CO} values. The DFT calculated vibration frequencies for free CO₂ are 2366 (2349),
11 1318(1340) and 637(667) cm⁻¹ (experimental frequencies [30] are indicated in parenthesis).
12 As the average of calculated frequencies fit quite well the average experimental values, no
13 empirical scaling factors were applied to the DFT reported frequencies.
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32 **2.2.2. Surfaces.**

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34 The computed models representing MgO (100) irregularities such as monatomic steps (S1),
35 diatomic steps (S2), corners (C3), divacancies (D), and kinks (K), used in this work, were the
36 same ones that were already considered by C. Chizallet and H. Petitjean et al. regarding the
37 interaction of water [4-5] and methanol molecules [31]. The MgO (100) terrace (T) involving
38 five coordinated oxygen ions (O²⁻_{5C}) was modelled by considering a slab formed by 5 layers
39 where only the 3 topmost ones were allowed to relax during optimization process. Each layer
40 was formed by 8 MgO pairs and was separated from the other by optimized distance of 2.13 Å.
41 The MgO (110) surface consists of alternating rows of Mg and O ions. The slab was formed
42 by 6 layers and only the 4 topmost layers were allowed to relax. The rows were 6 dMg-O of
43 length and were separated by optimized distance of 3.01 Å.
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51 The MgO (111) surface was modelled by repeated slab of 12 layers. Because we are
52 interested here into the formation of carbonate species by interaction of CO₂ with the oxide
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3 surface, we have limited our investigation to the oxygen terminated rocksalt (111) surface
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5 model. The central 6 atomic layers (including 3 Mg and 3 O layers) were kept fixed in the
6
7 structure optimization process and the other top most layers were free to relax. To avoid
8
9 artificial surface-surface interactions, the vacuum between the repeated slabs was fixed to 20
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11 Å. We have tested that our optimized properties as surface atomic distances and inter-planar
12
13 distances between O and Mg close-packed (111) planes are in line with previous reliable
14
15 models used in the literature [32-33].
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19 The Brillouin zone integrations are performed on a Monkhorst-Pack 2x1x1 k point mesh for
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21 (100) surface and defects and 2x2x1 k point mesh for (110) and (111) surfaces. For MgO
22
23 (100), (110) and (111) surfaces, we have checked that the calculated average surface energies
24
25 for each surface orientation are comparable to literature values [34-36]. As expected, the
26
27 calculated surface energy for the (111) facet was found to be relatively high (5.3 J.m^{-2} (4.16
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29 J.m^{-2} [34])) compared to (110) facet (2.2 J.m^{-2} (2.18 J.m^{-2} [34])) and (100) facet (1.73 J.m^{-2}
30
31 (1.29 J.m^{-2} [34])). This difference reflect well the instability of the polar terminated surface
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33 compared to the (100) one.
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40 41 **2.2.3. Thermodynamic**

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43 In order to study the adsorption phase diagram of CO_2 molecule on the different considered
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45 surfaces, a model of atomistic thermodynamics was developed. This model was inspired from
46
47 the one developed by D. Loffreda et al. [37] for a realistic description of adsorption
48
49 thermodynamics of multifunctional molecules on metal surfaces.
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52
53 The Gibbs free adsorption energy depends on the adsorption internal energy and on the
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55 vibrational entropy change during the adsorption process. Thus, for an accurate description of
56
57 the free Gibbs energy, the vibrational contributions of the initial (bare surface and gas phase)
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and final system (adsorbed system) should be included in the formalism. In this work the Gibbs free adsorption energy was calculated as follows:

$$\Delta G_{ads} = \Delta E_{ads} + \Delta E_0 + T(\Delta S_{vib} + \Delta S_{trans,rot} + S_{config}) - kT \ln(P/P_0) \quad \text{eq. 2}$$

Where ΔE_{ads} is the adsorption energy calculated from DFT (see eq. 1), ΔE_0 is the zero point energy (ZPE) change during adsorption process and ΔS_{vib} , $\Delta S_{trans,rot}$ are the vibrational and transitional, rotational entropy changes, respectively. The calculated vibrational properties in carbonated systems included the interacting molecule and all top-most surface atoms. Similarly for decarbonated systems the first surface layer was considered.

When several adsorption sites (N_{site}) are available on the surface, an additional term called configurational or positional entropy, S_{config} is included in the formalism. It defines the logarithm of all possible arrangements of the molecule on the surface. Its value is given by the equation 3.

$$S_{config} = -k \ln \left[\frac{N_{site}!}{(N_{site} - N_{ads})! N_{ads}!} \right] \quad \text{eq. 3}$$

Finally, ΔS_{vib} is derived from the reduced vibrational partition functions Q^{vib} of adsorbate system, gas phase and surfaces (eq. 4) and $\Delta S_{trans,rot}$ is calculated (eq. 5) on the basis of the transitional partition function of the adsorbate system Q_{ads}^{trans} and the gas phase Q_{gas}^{trans} as well as the rotational partition function of gas phase Q_{gas}^{rot} .

$$\Delta S_{vib} = -k \ln \left(\frac{Q_{ads}^{vib}}{Q_{surf}^{vib} Q_{gas}^{vib}} \right) \quad \text{eq. 4}$$

$$\Delta S_{trans,rot} = -k \ln \left(\frac{Q_{ads}^{trans}}{Q_{gas}^{trans} Q_{gas}^{rot}} \right) \quad \text{eq. 5}$$

3. Results and discussion

3.1. Experimental IR data

The effect of the pretreatment (1023 K, 2h under N₂) on the adsorbed species over MgO surface is shown by the comparison of the DRIFT spectra of the initial sample and of the treated one (Figure 2). The considered high temperature process cleans up the surface from almost all hydroxides and carbonates. The IR spectra (black line) shows a weak remaining absorption band at 3750 cm⁻¹ which is attributed to strongly bounded hydroxides [5], and some carbonates with IR bands at 1657 and 1329 cm⁻¹.

Insert Figure 2

After the addition of CO₂, DRIFT data show strong modifications in the IR range 1800- 1000 cm⁻¹. Figure 3 gathers the set of IR spectra obtained after the surface treatments at temperatures *temp* = 523 K, 673 K, 873 K. As expected, the spectra show the formation of carbonate species the amount of which decreases upon the successive thermal treatments. After the treatment at 873 K, the obtained spectra show the same absorption in the 1000 – 2000 cm⁻¹ range as the one recorded after the pre-treatment at 1023 K. In addition, the successive thermal treatments (*temp*) do not affect the recorded high frequencies (> 2000 cm⁻¹) on magnesium dioxide surface. In the lower frequency ranges, the absorptions are always very high due to the bulk infrared absorption of MgO with a lateral phonon frequency at 800 cm⁻¹ [38].

Insert Figure 3

According to the literature, adsorption of carbonate species leads to the splitting of the ν_3 stretching vibration band of the free ion, located at 1415 cm⁻¹, and gives different contributions depending on the geometry of the adsorbed ion [2,13]. The carbonate ν_3

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3 stretching mode is split to $\nu_{3\text{high}}$ and $\nu_{3\text{low}}$ contributions. Generally a consensus is gained that
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5 the more coordinated the carbonate ion the more split the two contributions. In addition the
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7 average $\Delta\nu$ for each species has also been determined [13]. As reported in Table 1, which
8
9 summarizes the IR results from numerous experimental studies, the vibrational frequency
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11 bands recorded on magnesium oxide surfaces have been assigned either to monodentate,
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13 bidentate or hydrogen carbonate species [11-12, 14-16, 18]. This table also evidences many
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15 discrepancies relative to the IR values assigned to different carbonate species, which may be
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17 due to the different states of the MgO surfaces obtained after the thermal treatment such as
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19 hydration state, morphology etc...
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26 Insert Table 1
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29 In this work (see figure 3), MgO surface is almost free of residual adsorbates. Therefore no
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31 hydrogen carbonate can be found on the surface even at $temp = 523$ K (no contribution at
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33 1220 cm^{-1}). Comparing the position of our recorded spectra with IR attributions reported in
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35 Table 1, one can assign, “at first sight”, all the identified bands in the range of $1370\text{--}1590\text{ cm}^{-1}$
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37 to monodentate species and those in the ranges of $1270\text{--}1390\text{ cm}^{-1}$ and $1620\text{--}1710\text{ cm}^{-1}$ to
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39 bidentate species. Moreover, two minor contributions located at 1252 and 1275 cm^{-1} do not
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41 change with the thermal treatment and can be linked to the small amount of silicon which is a
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43 residual impurity in the sample. This attribution of the carbonate bands goes on line with the
44
45 evolution of the spectra with $temp$: the most stable species are reported as bidentate [11] and
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47 are the only ones remaining on MgO surface after a treatment at 873 K, giving contributions
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49 at 1661 cm^{-1} and 1321 cm^{-1} . Nevertheless, for each carbonate species, several contributions
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51 are obtained. For instance, in the infrared range attributed to bidentate species, two bands at
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53 1680 and 1651 cm^{-1} (split bands at 1321 and 1304 cm^{-1}) can be attributed to two different
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55 bidentate species. The same analysis can be made with the monodentate species. These
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3 different contributions are probably linked to the carbonate formation on different MgO
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5 defects. Because in catalytic applications these defects may behave differently [39-41] it is
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7 important to know which of them are poisoned by carbonates as a function of the thermal
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9 treatment process. Modelling is thus necessary to calculate the theoretical position of the IR
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11 band linked to carbonates species depending on their topological environment.
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18 **3.2. Computational results**

19 **3.2.1. On the nomenclature of carbonates**

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22 The earlier work of Fukuda and Tanabe [11] described the carbonates as “bidentate” or
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24 “unidentate” for the carbonate linked with only one magnesium ion, and “bridging” for the
25
26 one bonded with two magnesium ions (see scheme 1). Busca and Lorenzelli [13] added some
27
28 complexity to this model by considering “polydentate” species. The improvement in the
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30 description of the carbonates by the way of computational methods allows us to give a more
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32 precise description of the carbonates. Those carbonate should be given an unambiguous name.
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34 We propose that the carbonates should be ranked by the number of oxygen atoms making
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36 connection with the surface (ionic or covalent bonds), such connections being the bonds that
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38 lengths are less or equal to the Mg-O bond length in the bulk magnesium oxide ($\approx 2.1 \text{ \AA}$). Let
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40 us add that a thorough description of the nature of carbonate bonds will be evaluated through
41
42 DFT electronic analysis. Thus, mono-, di- and tri-dentate carbonates refer, from now on, to
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44 carbonate species in which one, two and three oxygen atoms are connected to the surface,
45
46 respectively. In addition among a general type of carbonate species, for example bidentate,
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48 distinctions will be made considering the type of plan or surface defect on which the
49
50 interaction occurs. The carbonates will be named by the combination of a letter for each type
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52 (M : monodentate, B : bidentate, T : tridentate) and of the name of defect or plane. For
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3 instance, T-S1 will refer to a tridentate carbonate formed on a S1 step, and M-(111) will
4
5 refers to a monodentate carbonate on a (111) plane.
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8 Inset scheme 1
9

10 11 **3.2.2. CO₂ species adsorbed on MgO(100) surface** 12 13

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15 In table 2 are reported geometric and energetic parameters as well as ν_{CO} frequencies of all
16
17 optimized configurations of CO₂ species adsorbed on the MgO (100) plane and its various
18
19 defects (mono (S1) and diatomic steps (S2), corner (C3), kink (K) and divacancy (D)).
20
21 Comparisons with available values from the literature are also considered [14, 20, 22-24].
22
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24
25 Inset Table 2
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28
29 *Adsorption on the flat surface:* The low calculated adsorption energy (-0.09 eV) for linear
30
31 CO₂ molecule on flat (100) terraces T confirms that five coordinated O²⁻_{5C} ions of MgO
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33 surface are totally unreactive for the formation of carbonates in agreement with literature data
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35 [21, 42].
36
37

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39 *Adsorption on surface defects:* DFT calculations of CO₂ interactions with four and three
40
41 coordinated oxygen ions (O²⁻_{4C} and O²⁻_{3C}), involved in the defects of the MgO(100) plan,
42
43 show largely more stable adsorbed carbonate species compared with flat MgO(100), (Table
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45 2). Pacchioni has investigated the interaction of CO₂ on regular and defect sites of the
46
47 MgO(100) surface by mean of *ab-initio* cluster model SCF calculations [42]. He explained
48
49 that because of the considerably large Madelung potential of a surface five coordinated
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51 oxygen ion (O²⁻_{5C} site) compared to the lower coordinated site as the four coordinated O²⁻_{4C}
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53 sites, the electron cloud of the O²⁻_{4C} ion is more spatially diffuse and can easily overlap with
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55 the CO₂ empty orbitals interacting with the surface.
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Inset Figure 4

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3 DFT optimizations predict that CO₂ molecule adsorbs with energy values of -2.26 and -2.16 eV
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5 on the S1 and S2 step systems, respectively (Figures 4.a and 4.b). The molecule interacts with
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7 O²⁻_{4C} ions with an average d_{C-O} distance of 1.37 Å and assumes an orientation “parallel” to the
8
9 edge which allows a direct electrostatic interaction of its O atoms with the Mg²⁺_{4C} cations of
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11 the surface. The O-C-O angle is predicted to be of about 130°. These results are in line with
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13 those of Olsbye and co-workers [20] who have called a similar configuration of adsorbed
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15 carbonate species as “monodentate”. Nevertheless, as in a such configuration the carbonate
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17 species form three connections (short bonds < 2.10 Å) with the MgO surface (one O²⁻ is
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19 already inserted in the magnesium oxide network (Oβ) and two Mg²⁺ are linked to the
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21 oxygen ions (Oα) of CO₂). Thus we propose (see section 3.2.1) to call them as tridentate
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23 carbonates (T-S1 and T-S2).
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29 One way in which one can gain further insight into the molecule/surface interactions as well
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31 as the character of the bonding from the results of the DFT calculations is to investigate the
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33 change in the electron density distribution in the surface as a result of the adsorbate bonding.
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35 This can be reached by calculating the difference charge electron density obtained by
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37 subtracting from the charge electron density of the adsorbed carbonate system both the charge
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39 electron density of the clean MgO surface and that of an isolated CO₂. The atomic positions of
40
41 the clean surface and of the isolated gas are taken to be the same as those of the relaxed
42
43 adsorbate system [43]. Figure 5 depicts the *charge density difference* of computed carbonate
44
45 species graphically represented [44] by isosurface contours. These 3D visualizations reveal
46
47 that all relevant chemical changes are suffered by the O valence of carbonates. Concerning the
48
49 T-S1 configuration, there is clearly evidence of three connections occurring between
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51 carbonate and the edge of the MgO step. The electron charge appearing into O2p orbitals
52
53 pointing towards Mg²⁺_{4C} cations indicates the formation of two polar covalent bonding. The
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3 third connection is the ionic one between ($O\beta$) and the magnesium cations of the oxide
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5 network.
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8 Insert Figure 5
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12 In order to investigate the effect of coverage on the surface interactions of carbonates we
13 report in table 3 the calculated adsorption energies of carbonates with increasing coverage.
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15 With respect to the adsorption energy of single T-S1 (S1 surface includes 3 adsorption sites),
16
17 the adsorption of a second and a third carbonate is lowered by 1.01 and 1.94 eV, respectively
18
19 (the adsorption energies are calculated by considering the surface already adsorbing CO_2
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21 molecules). Because of the strong repulsive interaction between oxygen carbonates, the
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23 second adsorbed T-S1, which has a similar geometry, adopts an orientation shifted with
24
25 regard to the first carbonate. In that conformation (see figure 6), one magnesium ion of the
26
27 edge is connected to two carbonates and so tries to reach the MgO bulk octahedral geometry.
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29 The calculated Hessian matrix (table 2) of the adsorbed tridentate species indicates
30
31 wavenumbers of 1603 cm^{-1} (T-S1), 1639 cm^{-1} (T-S2) and 1300 cm^{-1} (T-S1), 1287 cm^{-1} (T-S2)
32
33 for ν_{3h} and ν_{3l} , respectively. As shown in table 3, these later frequencies are affected by the
34
35 presence of the second and the third neighbouring carbonate surface ($\theta = 2/3$ and $\theta = 1$ ML).
36
37 Thus, compared to the case of isolated carbonate, the calculated vibrations vary by less than
38
39 100 cm^{-1} for $\theta = 2/3$ ML and highly change for the monolayer coverage. The split between low
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41 and high frequencies grows when the coverage increases, due to the coupling between the
42
43 adsorbed carbonates sharing a Mg^{2+} cation. Similar results were also observed for CO_2
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45 adsorbed on ZnO surface [45].
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55 Insert table 3 and Figure 6
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58 Considering these results, the experimental bands (Figures 2 and 3) observed around 1660 and
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60 1320 cm^{-1} , that remain clearly visible whether the considered temperature, can be attributed to

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3 single tridentate species strongly attached on the steps defects of the magnesium oxide
4 surface.
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8 The modelled corner, kink and divacancy systems (Figure 4.c, 4.d, 4.e) involve a three
9 coordinated ion O^{2-}_{3C} which interacts directly with the adsorbed CO_2 molecule. On this sites,
10 the adsorption energy of carbonate species are found to be lower than on the four coordinated
11 sites. The analysis of the distances between $O\alpha$ and the surface (table 2) show that carbonates
12 are doubly bounded to the surface through the network oxygen ($O\beta$) and one oxygen atom
13 ($O\alpha$) from CO_2 . The bond character of these bidentate carbonates (B-C3, B-K and B-D) can
14 be analysed from the *charge density difference* graphic represented in figure 5. On the kink
15 (the same trend is observed for divacancy (not represented)), the adsorption does not strongly
16 modify the slab. The electron rich zones appearing into $O2p$ orbitals indicate only one polar
17 covalent bond between ($O\alpha$) from CO_2 and Mg^{2+}_{4C} . The electron rich zone around the third
18 oxygen atom, the ($O\gamma$) of the carbonate molecule, is orientated out of the plane and thus, that
19 oxygen does not make any connection with the surface. On the corner, the interaction of B-C3
20 induces a strong modification on the substrate. The surface oxygen atom ($O\beta$) is strongly
21 displaced in order to insure the double connection of carbonate species with the surface. IR
22 ν_{CO} ($\nu_{3h} - \nu_{3l}$) frequencies of carbonates adsorbed on corners, kinks and divacancies, are
23 calculated to be of $1727-1198\text{ cm}^{-1}$ (B-C3), $1679-1125\text{ cm}^{-1}$ (B-K) and $1649-1149\text{ cm}^{-1}$ (B-D),
24 respectively. These resulted values can predict that the experimental band observed at 1680
25 cm^{-1} on the sample treated at $temp = 523$ and 673 K is the signature of bidentate carbonate
26 species adsorbed on corner, kink and/or divacancie defects. The ν_{3l} band frequencies are out
27 of the range of this study. As there is only one adsorption site, the effect of coverage is not
28 considered here.
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57 Finally, it remains the question of the observed IR bands between 1350 and 1600 cm^{-1}
58 (namely located at 1516 cm^{-1} , 1423 cm^{-1} and 1367 cm^{-1}) for the sample treated at $temp = 523$
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3 and 673 K which cannot be explained by the presence of carbonate species on the MgO (100)
4 defects. Moreover, Yanagisawa et al. [14] have already considered the adsorption of CO₂ on
5 cubic crystallites of the MgO smoke, which exhibit well-defined (100) facets, and they have
6 not observe any IR adsorption between 1350 and 1600 cm⁻¹. This means that the recorded IR
7 frequencies on our samples would results from different adsorption configurations on other
8 crystallographic planes even if they are known to be less stable in vacuum conditions
9 compared to the (100) plane. In fact, several theoretical [34, 46-47] and experimental [48]
10 studies have shown the change in the stability of surface orientations after the addition of
11 adsorbates such as water. As IR spectroscopy showed that, in our conditions, few OH groups
12 remain on the surface, we investigate, in the following section, the adsorption configurations
13 and properties of CO₂ on faceted (110) and (111) MgO.
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30 **3.2.3. CO₂ species adsorbed on MgO(111) and (110) surfaces**

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34 In figures 4f and 4g are reported the configurations of carbonate species formed over the
35 modelled MgO(111) and (110) surfaces, respectively. As shown in table 2, the most
36 energetically stable species (-2.75 eV) is formed over the MgO (110) surface. Over this plan,
37 the orientations as well as the geometry of carbonates are similar to T-S1 and T-S2; thus, this
38 carbonate is called tridentate T-110. Therefore, while the *charge density difference* graphic
39 (figure 5) show similar isosurface shape of the electron rich zones of tridentate species, the
40 adsorption is energetically favourable, by 0.49 eV, on the (110) than on the stepped (100).
41 The vibrational frequency calculations of T-110 indicate values at 1559 and 1331 cm⁻¹ for the
42 $\nu_{\text{CO}_{3\text{h}}}$ and $\nu_{\text{CO}_{3\text{l}}}$, respectively. This carbonate type may correspond to the species vibrating
43 around 1510 and 1360 cm⁻¹ on our sample treated at *temp* = 523 and 673 K.
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3 As for the stepped (100) surface, in presence of neighbouring carbonates the ν_{CO} strongly
4 vary and the split between low and high frequencies of T-110 grows as the coverage increases
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8 (Table 3).
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10 Over the (111) surface terminated by oxygen atoms, the carbonate lies to the surface through
11 a single connection. Thus, the carbonates adsorbs as monodentate species on the MgO(111)
12 surface. In spite of the short $d_{\text{C-O}(\beta)}$ bond distance of 1.31 Å, which is the same than for the
13 tridentate configuration, the small O-C-O angle of 115° illustrate the repulsive interactions
14 that undergoes between the oxygen atoms (O_γ) and the surface (Figure 4g). These repulsive
15 interactions can clearly be attested in figure 5 by the *charge density difference* on M-111
16 configuration that evidences the low electron density between (O_γ) and the surface. This may
17 explains the low energetic stability of these species. In addition, as the carbonate presents a
18 symmetry close to D_{3h} , the split between $\nu_{\text{CO}_{3h}}$ and $\nu_{\text{CO}_{3l}}$ is very low: 1440 and 1378 cm^{-1}
19 (1415 cm^{-1} for the free carbonate [49]). These values are smaller than the frequency values
20 calculated by Allen et al [23] who predicted a vibrational frequencies for adsorbed carbonates
21 on MgO(111) surface in the ranges of 1440 – 1459 and 1572 – 1631 cm^{-1} . This is probably
22 due to the empirical method used by these authors. In this work, the resulted monodentate
23 carbonate, with weekly degenerated IR-band, could be attributed to the species vibrating at
24 1423 cm^{-1} on the DRIFT spectra for the sample treated at $temp = 523$ and 673 K.
25 Nevertheless, the low bonding energy of -0.8 eV is not consistent with the persistence of the
26 IR bands for high temperature treatments. This point will be discussed in the next section. In
27 table 3 are also reported the adsorption energies and ν_{CO} frequency values of carbonate M-
28 111 for increasing coverage. The high coverage was not reached because of the strong
29 repulsive interactions occurring between surface/carbonates and carbonate/carbonate species.
30 Thus, as depicted in table 3, for coverage of 3/4 monolayer the adsorption is highly
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3 endothermic and the calculated frequency values are highly different from those of single
4 carbonate calculations.
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10 11 **3.2.4. Adsorption thermodynamics** 12

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15 In order to get a more precise picture of the respective stabilities of adsorbed carbon dioxide
16 on different plans and defects and more particularly, to determine the temperature of
17 desorption of the different adsorbed carbonates, the Gibbs free adsorption energy diagram was
18 plotted for each considered system (see figure 7). The partial pressure is set to 0.001 Pa and
19 desorption is presumed to occur when the Gibbs free adsorption energy becomes positive.
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27 Insert Figure 7
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29 As reported in figure 7, Gibbs free adsorption energies of carbonates follow the same linear
30 trend. On the (100) plan, bidentate carbonate species which populate the corners, kinks and
31 divacancies are predicted to leave the MgO support for temperature range of 722-822 K.
32 Tridentate carbonates formed on the Mg(100) steps would desorb at higher temperature and
33 remain on the surface for temperatures as high as 908 K. This is in agreement with the
34 assignment we made for the IR bands recorded at $temp = 873$ K to highly adsorbed tridentate
35 species
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46 The same kind of tridentate species is also strongly adsorbed on (110) surface thus should not
47 disappear at $temp < 1200$ K. But experimentally, it is shown that the corresponding IR bands
48 (1516 and 1367 cm^{-1}) disappear from the spectrum at $673 < temp < 873$ K. We suppose that
49 this contradiction may be explained considering the well known stability of the (100) surface
50 compared to the (110): surface recombination may thus occur at $temp < 873$ K, leading to the
51 disappearance of the (110) plane and to the desorption of these species at lower temperature
52 than predicted by our thermodynamic calculations. Moreover, the surface reconstruction of
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3 the (110) planes into reconstructed stepped (100) surface [50] may also explain the
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5 enhancement of the IR-adsorption at 1321 cm^{-1} assigned to T-S1. Let us add that this
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7 reconstruction phenomenon should be confirmed by an appropriate kinetic study.
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10 Finally, on the (111) surface, the desorption of monodentate carbonates is predicted to occur
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12 at 314 K. Regarding this result, the IR band observed at 1440 cm^{-1} for temperature as high as
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14 $temp = 673\text{ K}$ can not be attributed to the monodentate species. Du and co-workers have
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16 attributed similar infrared recorded bands of $\nu_{\text{CO}_{3\text{h}}} = 1445\text{ cm}^{-1}$ and $\nu_{\text{CO}_{3\text{l}}} = 1375\text{ cm}^{-1}$ to
17
18 bulk-like carbonates which could desorb at high temperature [19]. Mekhemer et al. [17] have
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20 reported similar suggestion. In order to characterize such carbonates, we have performed
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22 Raman spectra on a sample treated at 673 K. Nevertheless, no absorption band at 1100 cm^{-1} ,
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24 characteristic of the ν_1 Raman active bulk carbonates [51-52] was observed on this sample. As
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26 bulk carbonates can be present but their amount may be under the detection limit of the
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28 Raman spectrometer, a conclusion on that point is difficult to be made.
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3.3. New insights on basicity characterization

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35 As underlined in the introduction, in order to study the catalysis, we need to know the nature
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37 of the basic sites available after the pretreatment step. For that purpose, the data obtained in
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39 this study on carbonates species, giving their nature, localisation, desorption temperature and
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41 IR vibration bands (calculated and experimentally detected) are summed up in Table 4. The
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43 new nomenclature of these species is also reported in order to take into account not only their
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45 mono-, bi- or tri-dentate character but also the topology of their adsorption site.
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52 Insert Table 4
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54 Moreover, the literature dealing with basic catalysts reactivity shows that the characterization
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56 of the basic sites is a key point for the interpretation of the catalytic results. One of the most
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58 popular method to determine these basic properties is CO_2 TPD that consists in following the
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60 progressive desorption of pre-adsorbed CO_2 with increasing temperature (see as an example,

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3 Hattori's review [53]). An attempt to discuss the relevance of this method has already been
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5 made [54] underlining that CO₂ adsorption probes the Lewis basic character of the surface
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7 whereas Brønsted basicity is mainly involved in catalytic reaction. Let us remind that Lewis
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9 basicity is the ability of the surface to give an electronic pair to a Lewis acid molecule while
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11 Brønsted basicity is, according to Brønsted definition [55], the ability to deprotonate a
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13 molecule. It implies that all Lewis bases are also Brønsted bases and reciprocally. But we
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15 demonstrate here, in the particular case of oxides ions, that the strength scale is different
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17 depending on the nature of the considered basicity.
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22 This demonstration is made from the comparison of the deprotonating adsorption energy of
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24 water (a Brønsted acid) and the formation of the Lewis adducts of CO₂ (a Lewis acid) on
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26 MgO (100) plane defects. Using similar theoretical approach, C. Chizallet and co-workers
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28 have established the desorption temperature of H₂O from the MgO (100) defects. According
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30 to these authors water leaves S1, K, D and C3 defects at temperatures of 620K, 805K, 1110K
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32 and 740K, respectively [4]. Thus, it can be seen that the strongest interaction between water
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34 and the surface is achieved on kinks and divacancies whereas the most stabilizing sites for
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36 CO₂ adsorption are predicted here to be the steps. By consequence, direct correlation between
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38 the information obtained by CO₂ TPD and a reaction which first step is a deprotonation has to
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40 be made very cautiously.
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46 **4. Conclusion**

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48 Attribution of the IR bands of the carbonates adsorbed on MgO is a very important tool to
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50 identify the nature of the active basic sites available after a pretreatment. DFT calculations
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52 combined with the DRIFT measurement on MgO sample after peculiar pretreatments allow us
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54 to give a new assignment to these IR bands considering the adsorption on (100) defects and
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56 (110) and (111) planes. These attributions are confirmed by the thermodynamic calculations
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58 of the stability of all carbonate species. Moreover, these results give a new tool to identify the
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3 crystallographic plane and defects by analysing the formation of IR-band when absorbing the
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5 CO₂ on it. Results show that the strongest basic site versus CO₂, which is a Lewis acid, is not
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7 the same that the strongest basic site for the deprotonating adsorption of Brønsted acids. Thus,
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9 even of the same nature, Lewis and Brønsted basic sites differ by their basicity strength scale.
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11 This conclusion should have consequences on the use of CO₂ TPD, when it has to be
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13 correlated with kinetic studies of basic Brønsted reactivity.
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32 Equipement National de Calcul Intensif).
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Tables:

Table 1: Review of the literature experimental attributions of IR-bands assigned to carbonates and hydrogen carbonates species adsorbed on MgO

Hydrogen carbonates:

ν_2	ν_3	ν_4	Work references
1655 – 1658	1405 – 1419	1220 – 1223	[16]
	1480	1250	[15]
1650	1510,1408	1220	[18]

Carbonates:

species	$\nu_{3\text{high}}$	$\nu_{3\text{low}}$	ν_1	Work references
Monodentate	1510 – 1550	1390 – 1410	1035 – 1050	[16]
	1550	1410	1050	[11]
	1520	1370	1060	[12]
	1590,1510	1415		[15]
Bidentate		1385,1335		[15]
	1659, 1626	1329, 1273	1024, 947	[14]
	1665 – 1710	1325 – 1330	1005 – 1030	[16]
	1670, 1630	1270		[12]
	1670, 1630	1315, 1280	1000,850 950,830	[11]

Table 2: Geometric (distances (Å) and angles (degrees °)), energetic (E_{ads} (eV)) and frequency values (ν_{CO} (cm^{-1})) of optimized CO_2 species adsorbed on the (100) plan and its defects as well as the (110) and (111) surfaces. Values in brackets are reported from the literature

	E_{ads} (eV)	O(α)-Mg (Å)	O(α)-C (Å)	O(β)-C (Å)	O(γ)-C (Å)	OCO (degree)	$\nu_{3\text{h}}$ (cm^{-1})	$\nu_{3\text{l}}$ (cm^{-1})
Terrace (T)	-0.09	2.70	1.18			177.8	2346	1308
Monoatomic step (S1)	-2.26	2.10	1.28	1.36	-	129.9	1603	1300
Diatomic step (S2)	-2.16 (-1.58) ^a (-2.16) ^b	2.09 (2.14) ^b (2.08) ^c	1.27 (1.25) ^a (1.26) ^b (1.26) ^c	1.38 (1.38) ^a (1.37) ^b (1.38) ^c	-	130.6 (130.6) ^a (131) ^b	1639 (1784) ^a (1606) ^c	1287 (1288) ^a (1237) ^c
Corner (C3)	-1.53 (-1.18) ^a (-1.87) ^b	1.95 (1.97) ^b	1.31 (1.29) ^b (1.29) ^c	1.40 (1.42) ^b (1.40) ^c	1.24 (1.21) ^a (1.22) ^b	126.9 (129) ^a (128) ^b	1727 (1778) ^b	1198 (1243) ^b
Kink (K)	-2.02	2.04	1.34	1.37	1.23	125.8	1679	1125
Divacancy (D)	-1.97	2.05	1.33	1.37	1.24	125.9	1649	1149
(110)	-2.75 -2.16 ^d	2.08	1.28	1.34	-	128.9	1559	1331
(111)	-0.79 (0.28) ^d (-3.97) ^f		1.31	1.31	-	115.8	1440 (1572- 1631) ^f	1378 (1440 - 1459) ^f

Ref. ^a[20], ^b[22], ^c[14], ^d[24], ^f[23]

Table 3 : Calculated DFT adsorption energies (eV) and ν_{3h} and ν_{3l} IR vibrations (cm^{-1}) for different coverage of carbonate species adsorbed on MgO(100) steps and MgO (110) and (111) surfaces. Values in brackets are reported from the literature

	Coverage ML	E_{ads} (eV)	ν_{3h} (cm^{-1})	ν_{3l} (cm^{-1})
S1 (3 sites)	1/3	-2.26	1603	1300
	2/3	-1.25	1691, 1626 (1588-1638) ^G	1284, 1259 (1520-1564) ^G
	1	-0.32	1754, 1710, 1657	1260, 1255, 1248
S2 (3 sites)	1/3	-2.16	1639	1287
	2/3	-0.90	1728, 1691	1280, 1262
	1	+0.93	1824, 1775, 1695	1284, 1235, 1224
(110) (9 sites)	1/9	-2.75	1559	1331
	1/3	-2.49	1554, 1552, 1525	1316, 1302, 1301
	2/3	-0.93	1688, 1687, 1660, 1609, 1608, 1594	1287, 1272, 1271, 1254, 1253, 1250
	1	+2,70	1796, 1795, 1759, 1759, 1743, 1742, 1742, 1721, 1720	1270, 1258, 1258, 1252, 1252, 1251, 1251, 1246, 1246
(111) (9 sites)	1/4	-0.85	1440	1378
	2/4	-0,34	1523, 1463	1399, 1236
	3/4	+0,10	1850, 1824, 1789	1161, 1077, 1034

Ref. ^G[43]

Table 4 : Summary of experimental and theoretical data: Nomenclature, Desorption temperatures (K), and frequencies of all computed carbonate species adsorbed over MgO support.

Face	Type of carbonate	Type of defect	Nomenclature	experimental data			DFT Calculations		
				Desorption on DRIFT spectra	ν_{3h} DRIFT	ν_{3l} DRIFT	T (K) for $\Delta G_{ads}=0$	ν_{3h} DFT	ν_{3l} DFT
(100)	Bidentate	Corner	B-C3	873 > T > 673 K	1680	Out of range	722	1650-1730	1125-1200
		Kink	B-K	873 > T > 673 K			822		
		Divacancy	B-D	873 > T > 673 K			812		
	Tridentate	Step	T-S1 T-S2	T > 873 K	1651	1304	908	1600-1650	1280-1300
(110)	Tridentate		T-110	873 > T > 673 K	1516	1347	1212	1560	1330
(111)	Mono dentate		M-111	873 > T > 673 K			314	1440	1378

Scheme 1: Description of the carbonate species adsorbed on magnesium oxide according to the literature and as revisited in this study

Described as	Monodentate [2], unidentate [6]	Bridging [2,6]	Bidentate [2,6]	Polydentate [2] monodentate [15]
Our description	Monodentate	Bidentate	Bidentate	Tridentate

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3 **Figure captions:**
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9 **Figure 1:** The different steps of thermal treatment of the MgO sample.
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13 **Figure 2:** DRIFT spectra of the adsorbed species over magnesium oxide before (red line) and
14 after (black line) pre-treatment at 1023 K (arbitral unit for absorbance)
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20 **Figure 3:** Recorded DRIFT spectra of the adsorbed species over magnesium oxide after CO₂
21 adsorption under inert gas for different *temp* treatments (arbitral unit for absorbance)
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27 **Figure 4:** Optimized configurations of adsorbed carbonates over MgO(100) defects and
28 MgO(110) and (111) surfaces. Red, gray and blue balls represent Oxygen, Magnesium and
29 Carbon atoms, respectively. O_β is the oxygen of the carbonate inserted in the magnesium
30 oxide network, O_α is the oxygen coming from CO₂ bonded to magnesium cation and O_γ is the
31 oxygen which doesn't make connection with the surface.
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41 **Figure 5:** 3D visualization of the *charge density difference* of tridentate (T-S1 and T-110),
42 bidentate (B-C3 and B-K) and mondentate (M-111) carbonate species. Pertinent isosurface
43 values = $-3.7 \cdot 10^{-2} \text{ e}/\text{\AA}^3$ for T-S1 and T-110; $-20 \cdot 10^{-2} \text{ e}/\text{\AA}^3$ for B-C3 and B-K; $12 \cdot 10^{-2}$ for M-
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49 111.
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51 **Figure 6 :** Minimum energy configuration of the adsorption of two carbonates over the
52 stepped MgO(100) defects; As the S1 has 3 adsorption sites on the edge, the coverage is
53 supposed to be 2/3 ML.
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3 **Figure 7** : Gibbs free energy diagrams (kJ/mol) at a constant pressure ($P_{\text{CO}_2} = 0.001 \text{ Pa}$) as a
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5 function of temperature K for adsorbed carbonates on different MgO surfaces and defects.
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Figures

Figure 1

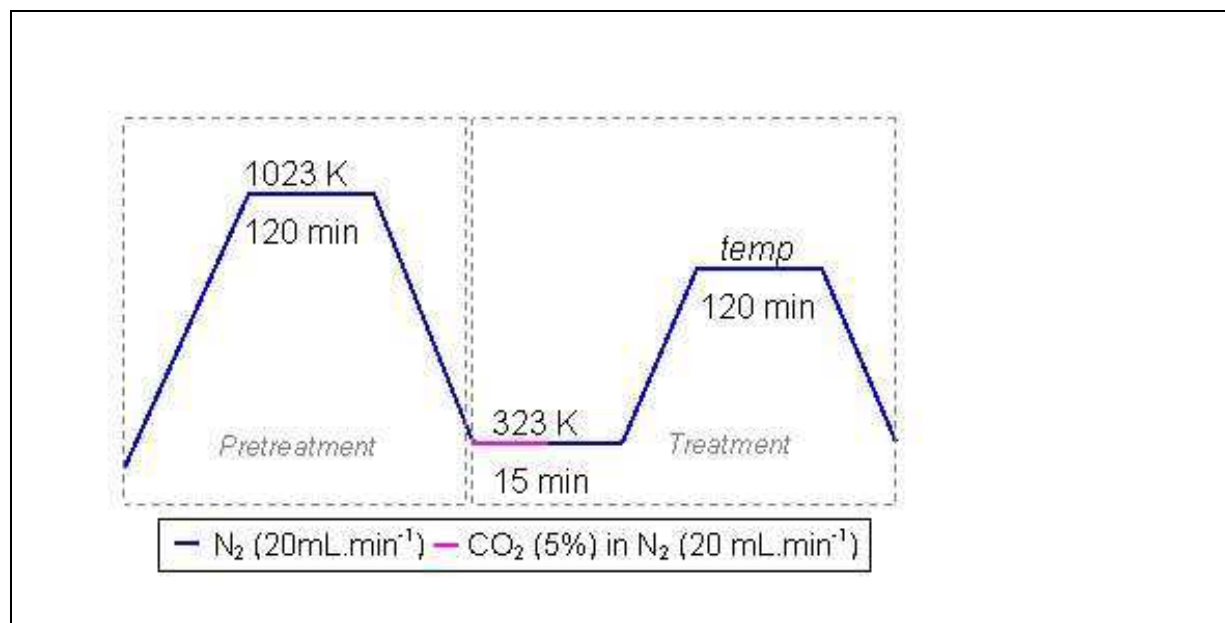


Figure 2

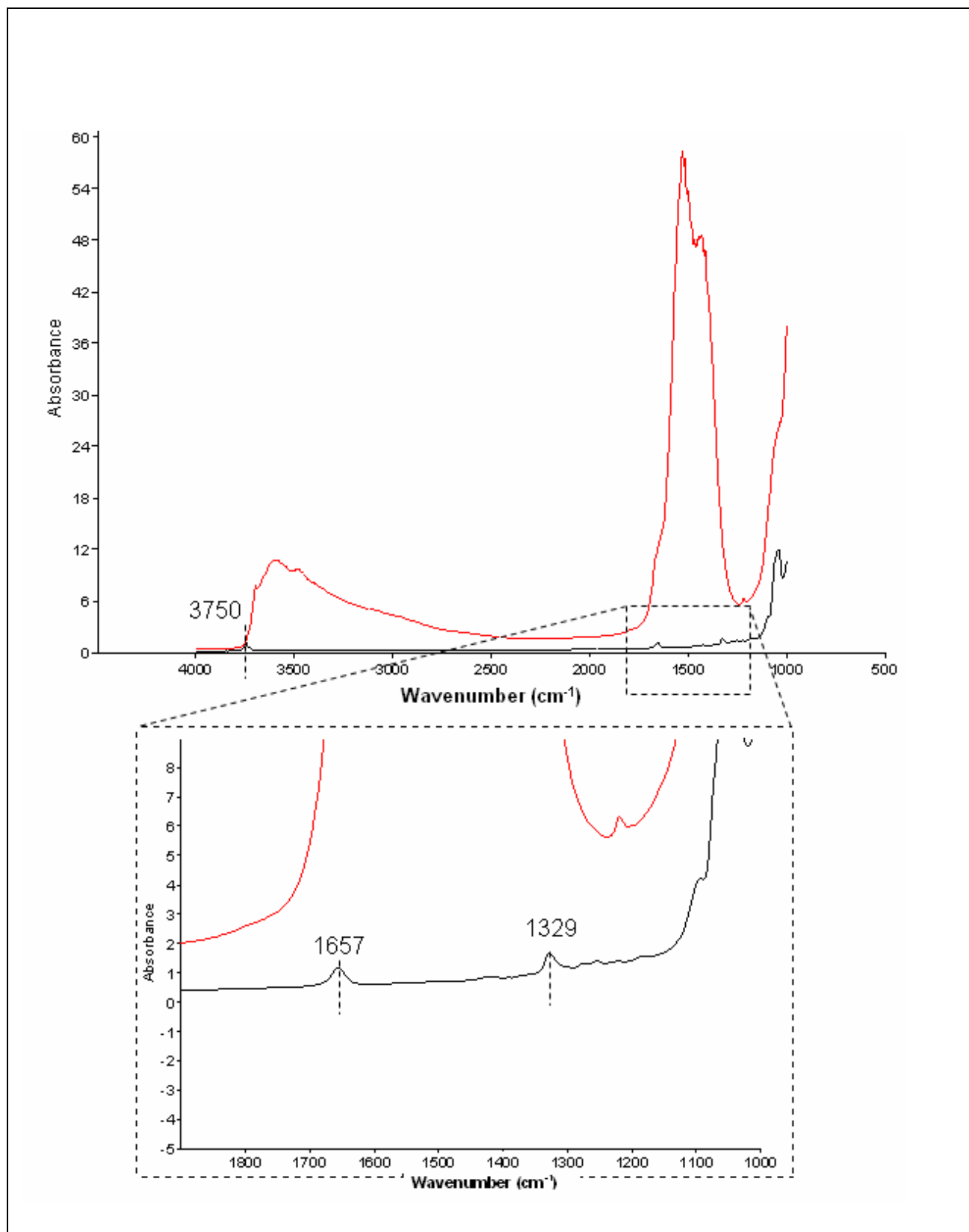


Figure 3

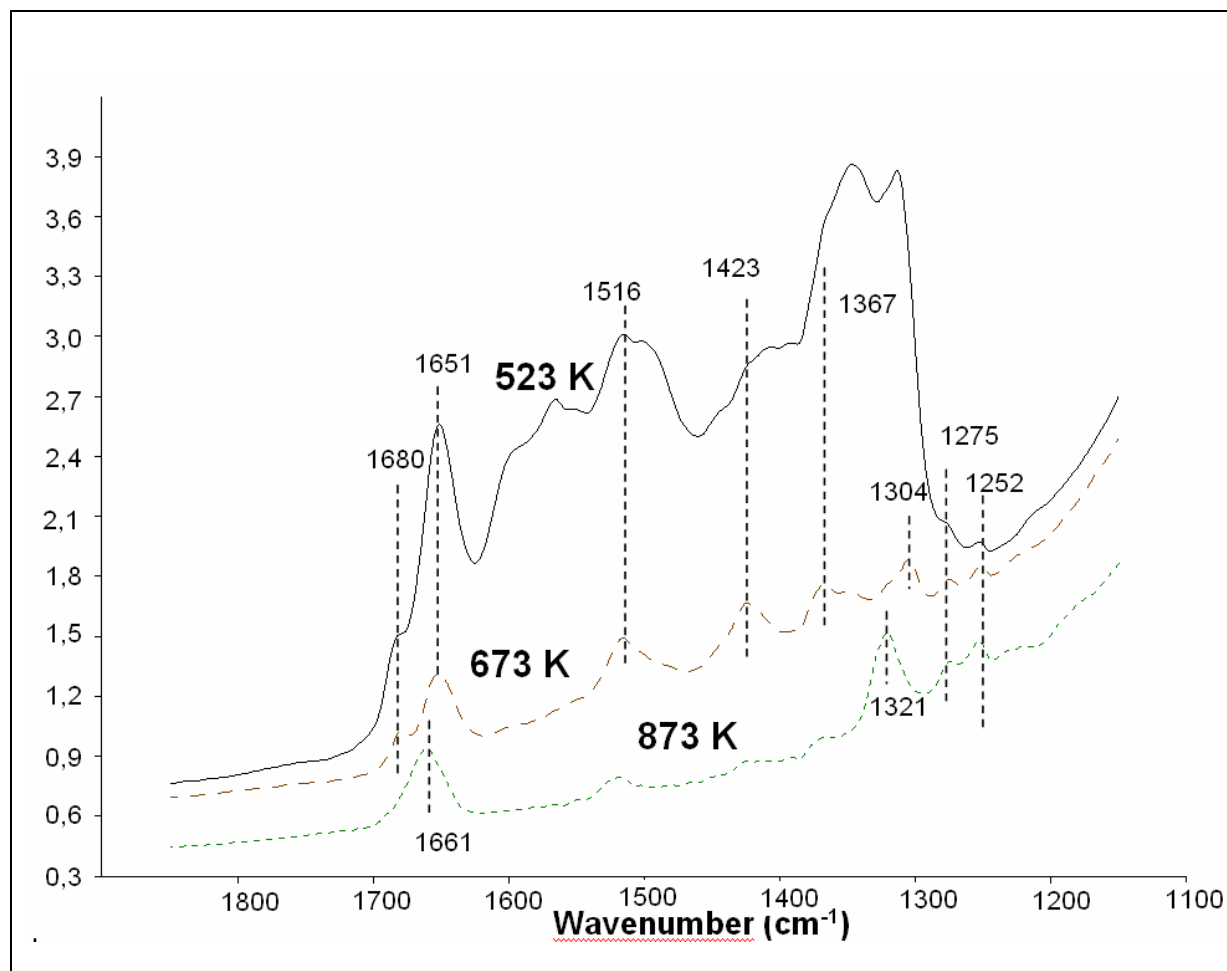


Figure 4

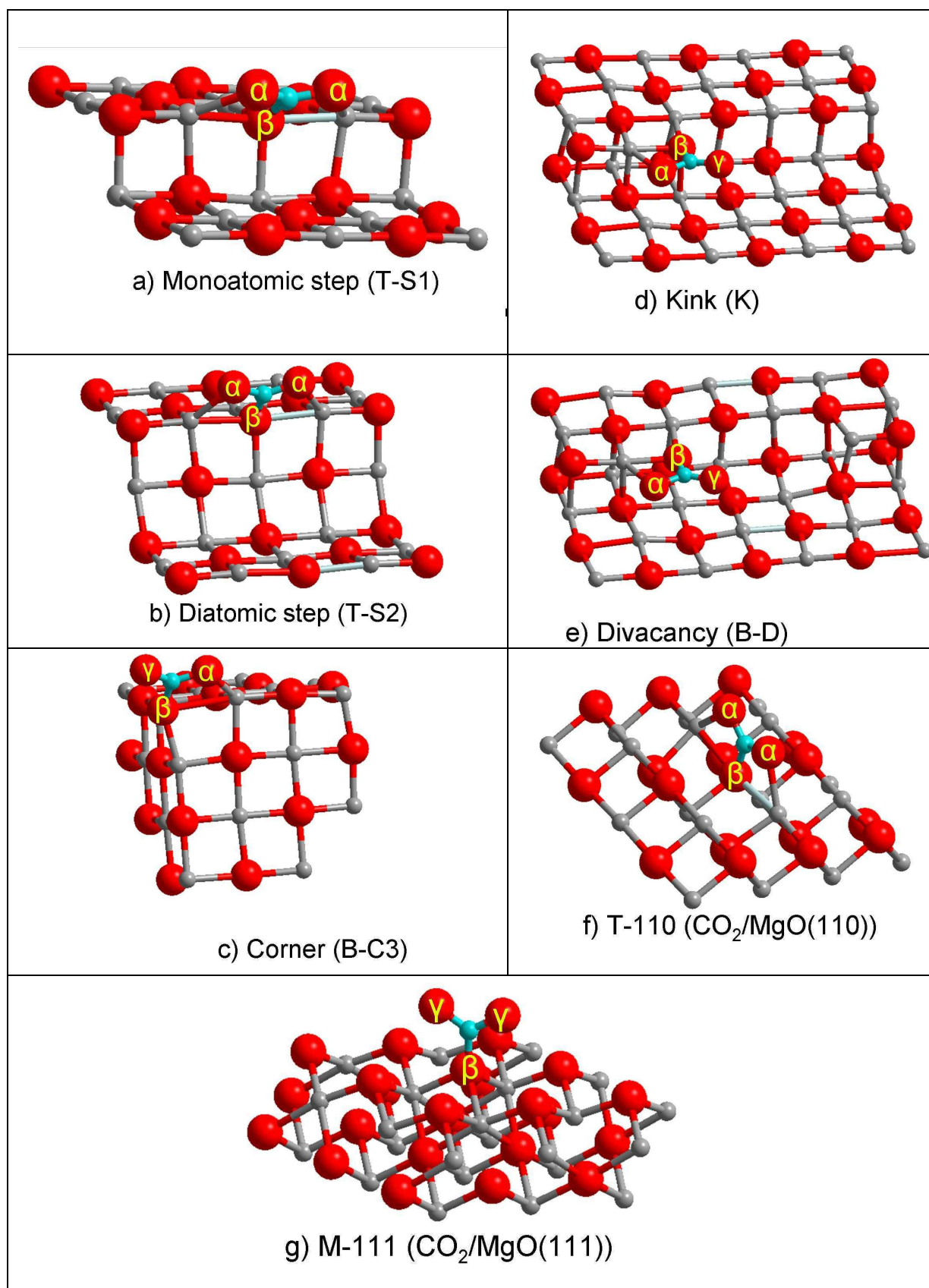


Figure 5

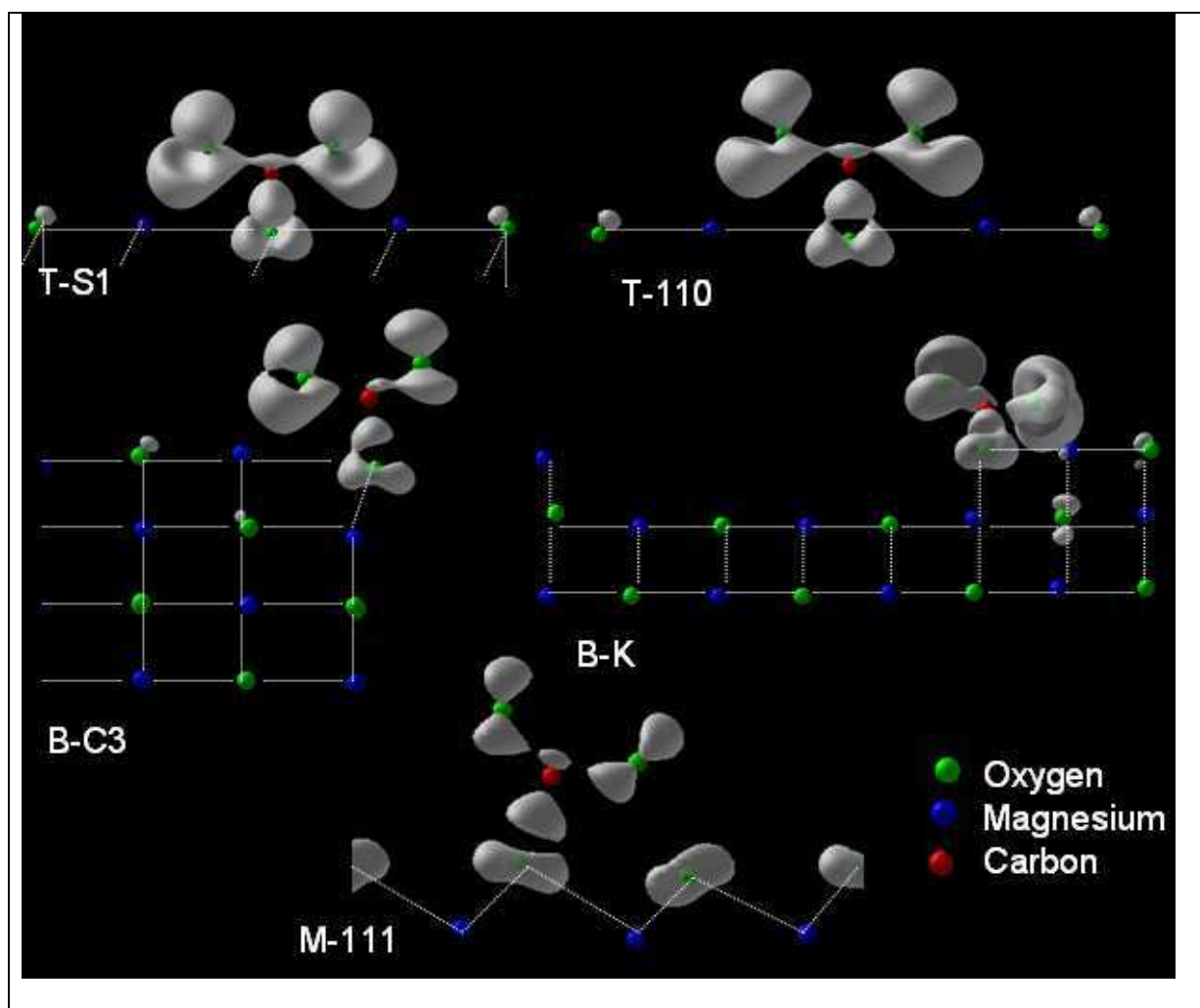


Figure 6

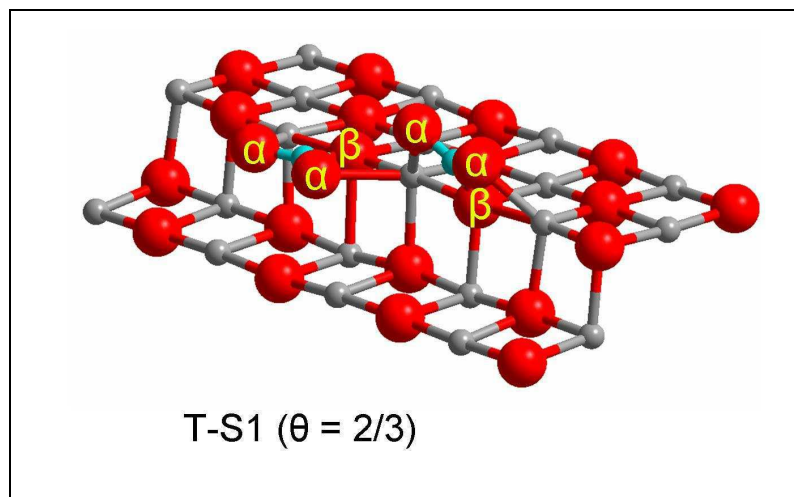
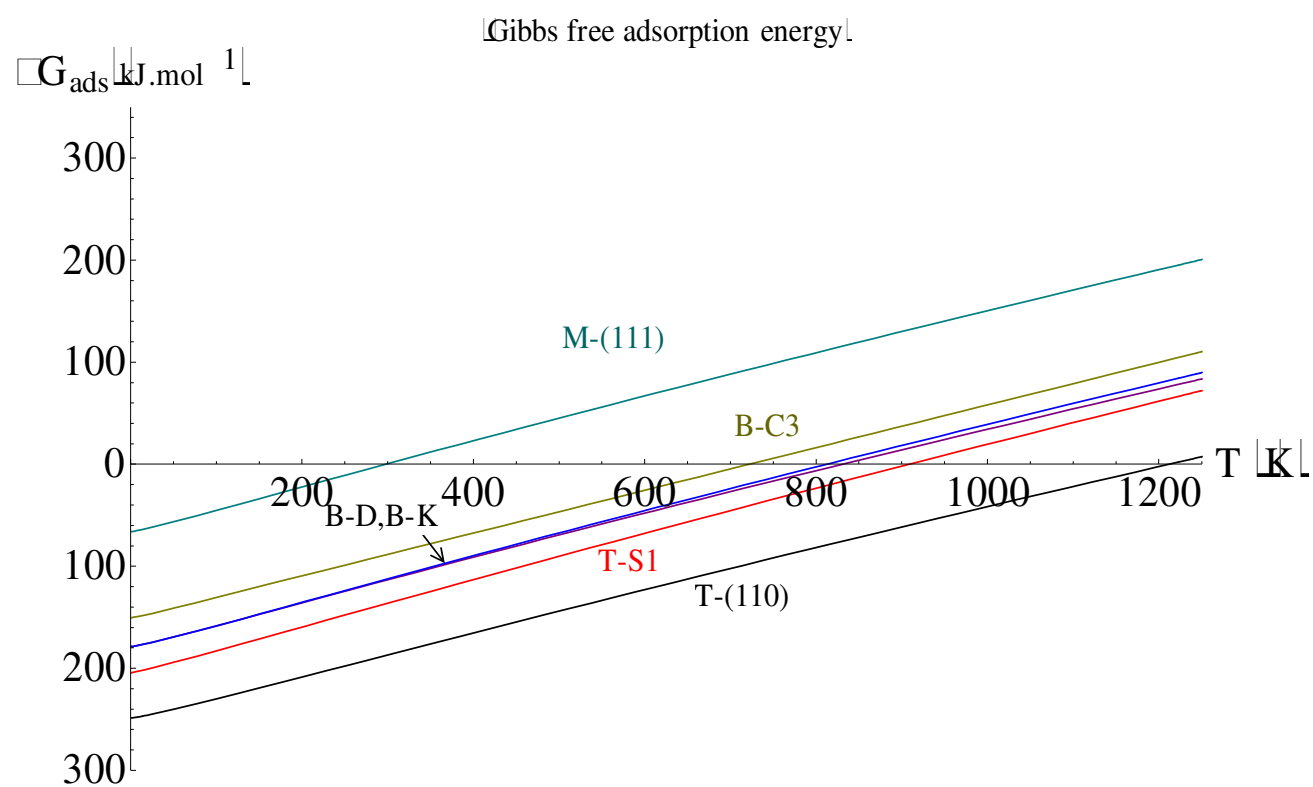


Figure 7



The graphic for the TOC

