



Oxide clusters as source of the third oxygen atom for the formation of carbonates in alkaline earth dehydrated zeolites

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ABSTRACT

In our paper, we show that carbonates can be formed with almost no energetic barrier from CO₂ and metal-oxide binuclear MO_xM species (M = Mg, Ca, Sr, Ba, with X = 1–4, depending on the cation) in alkaline earth zeolites, mordenite (MOR) and phillipsite (PHI), on the basis of quantum mechanical density functional theory (DFT) calculations at both isolated cluster and 3D periodic levels. The participation of MO_xM species (X = 1 and 3) explains the source of the third O atom in CO₃ species in dehydrated zeolites, on the basis of a good agreement between the calculated and experimental positions of the asymmetric and symmetric CO₃ vibration bands, of the ratio of their intensities, and of the weak dependence *versus* the cation and framework type. The reaction of formation of dimethylcarbonate from CaCO₃Ca in the 8-membered (8R) ring of MOR and methanol has also been considered, suggesting the carbonate activity as the source of CO₂ at elevated temperatures.

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1. Introduction

The origin of the chemisorbed forms of CO₂ is a key question for modeling its possible chemical mechanisms of activation. In the case of zeolite frameworks, there is, to our best knowledge, still no clear answer about a microscopic model of CO₂ chemisorption for all classes of cation-exchanged zeolite form, involving transition metal, alkaline, and alkaline earth zeolites (AEZ). The CO₂ chemisorbed moiety can correspond to various carbonate species from a negligibly weak coordinated to the strongly coordinated toward one or more zeolite framework atoms. For simplicity, below in the article, we will use the term “carbonate” for all CO₃ moieties independently of their coordination number. Even if numerous assignments of IR spectroscopic data have already been published for those materials [1–6], a final explanation about the carbonate formation remains indeed ambiguous.

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Early studies [1,2] mentioned differences between CO₂ adsorbed in the Mg form and in the other AEZ. However, this difference was later denied by the work of Jacobs et al. [3] who registered similar IR bands of carbonates, in particular, in CaX zeolite. The influence of the cation type was shown in Ref. [4] regarding rather moderate variations of the most intense IR band positions. Additionally, weak or at least non-clear dependences of the zeolite framework type (the MgETS-10 zeolite) for similar strong bands manifested at 1620 and 1380 cm⁻¹ were noticed in Ref. [6]. A strong doublet at 1665 and 1325 cm⁻¹, conserved in the spectra up to 500 °C, was assigned to carbonate species similar to the one over an MgO surface [7], while a less stable doublet at 1620/1370 cm⁻¹ disappears when the temperature rises above 200 °C over MgO. Starting from the assignment available in Ref. [8], the higher and lower frequencies of the CO₃ group were attributed to symmetric and asymmetric carbonate vibrations, respectively [3,4]. A ratio of the higher/lower band intensities was published in Ref. [4]. Going forward, we should note that our assignment of the symmetric and asymmetric carbonate vibrations for the lower and higher branches is inverted *versus* the conventional interpretation [3,4].

An important chemical problem behind our assignment proposed here just above is the origin of the third O atom in the CO₃ species. In hydrated forms, it is obvious that the water oxygen can be involved in the CO₃ formation. For dehydrated zeolites,

two possibilities were discussed in the literature [3,6]. Either the framework O atoms or the oxo-species can be the source of the third O for the carbonates. On the one hand, the similarity between the various O types denied the suggestion about the participation of the framework oxygens in the carbonate structure [6]. On the other hand, some of us recently considered CO oxidation on binuclear MO_xM clusters ($X = 2-3$) in AEZ at both the isolated cluster [9,10] and periodic [11] calculation levels. It was shown that the products of CO oxidation transform *via* a barrierless reaction profile to carbonates. The present work actually adds evidence for the hypothesis about the oxo-species as the source of O for carbonates. Till now, to our knowledge, no theoretical study proposed a clear explanation of the experimental data obtained so far. The assignment of the carbonate frequencies could thus help to understand the carbonate formation mechanism. The comparison of the IR bands is therefore the main goal of this paper. More precisely, we optimized the structure of the products of the interaction between the MO_xM species ($M = \text{Mg, Ca, Sr, Ba, with } X = 1-4$) and CO_2 and calculated the respective frequencies at both the isolated cluster and periodic DFT levels.

2. Computational details

First, we applied the isolated cluster approach, considering Gaussian 03 [12], to check the possibility of carbonate formation over an isolated cation or cluster, as well as to further calculate the frequencies and intensities of the carbonate species in an 8-membered ring (8R) as found in mordenite (MOR) and in a fragment that includes two 6R and 4R windows (6R + 4R) with one common Si–O–Si moiety for zeolite Y. Initial chemical compositions of the cluster models (without carbonate species) are $\text{MAl}_2\text{Si}_6\text{O}_8\text{H}_{16}$ and $\text{MAl}_2\text{Si}_6\text{O}_9\text{H}_{14}$ for 8R and 6R + 4R, respectively, where M is the AE cation. Two Al atoms are present in both 8R and 6R + 4R models as in our previous work [9–11]. Most of the results were obtained at the B3LYP/6-31G* level, while a higher MP2/6-31G* level was applied in some cases. To determine the reaction coordinate for CO_2 or carbonate reaction with methanol (see Section 4), we applied the QST3 algorithm as supplied with Gaussian 03 considering the optimized geometries of both the reagents and products.

Second, for the periodic approach, we optimized the cell parameters and the geometries of the $\text{MO}_x\text{M}(\text{MOR})$ and $\text{MO}_x\text{M}(\text{PHI})$ moieties ($M = \text{Mg, Ca, with } X = 1-4$) using VASP [13]. The projector augmented wave (PAW) method [14] was used to describe the electron–ion interactions, and a plane-wave basis set was employed for the valence electrons. The plane-wave cutoff was set to 500 eV. Results were obtained with the PBE and PW91 generalized gradient approximation (GGA) functionals [15]. The Brillouin zone sampling was restricted to the Γ -point. The chemical composition of the unit cell is $\text{MAl}_2\text{Si}_{46}\text{O}_{96}$ for MMOR and $\text{M}_2\text{Al}_4\text{Si}_{12}\text{O}_{32}$ for MPHI. The compositions including the MO_xM moieties correspond to $(\text{MO}_x\text{M})\text{Al}_2\text{Si}_{46}\text{O}_{96}$ and $(\text{MO}_x\text{M})_2\text{Al}_4\text{Si}_{12}\text{O}_{32}$, respectively. The optimized cell parameters are given in Table 1. After optimization of the $\text{MO}_x\text{M}(\text{MOR})$ moiety, we added CO_2 and performed the optimization of the entire systems. Vibrational frequencies were calculated using the finite difference method as implemented in VASP. Small displacements (0.015 Å) of the atoms from the $\text{MCO}_3\text{M}(\text{MOR})$ species were used to estimate the numerical Hessian matrix. The rest of the zeolite atoms were kept fixed at their equilibrium positions. As any theoretical approach results in frequency values shifted relative to the experimental data, we scaled all frequencies by fitting one band position ν_{cal} to the experimental ν_{exp} value and then recalculated the positions of the other bands multiplying them by $(\nu_{\text{exp}}/\nu_{\text{cal}})$. Regarding that the frequencies obtained with B3LYP are pretty similar to the experimental ones, we

Table 1

Unit cell parameters (a, b, c , in Å, α, β, γ , in degrees) and cell volumes (in Å³) of MOR and PHI type zeolites as optimized at (PW91) level.

	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Volume
CaOCa(MOR)	13.73	13.70	15.06	90.33	90.11	83.46	2813.5
CaO ₂ Ca(MOR)	13.74	13.71	15.08	90.29	90.10	83.36	2821.6
CaO ₃ Ca(MOR)	13.72	13.67	15.05	90.38	90.10	83.65	2804.9
CaO ₄ Ca(MOR)	13.70	13.63	15.04	90.44	90.04	85.23	2799.1
MgOMg(MOR)	13.76	13.72	15.11	90.52	89.96	83.49	2834.1
SrOSr(MOR)	13.77	13.74	15.10	90.32	90.07	83.50	2838.7
BaOBa(MOR)	13.78	13.74	15.10	90.28	90.08	83.52	2840.6
MgOMg(PHI)	9.70	13.93	8.90	90.00	124.21	90.00	994.0

rescaled only the frequencies calculated at the periodic level with PW91. In order to check the accuracy of the projected densities of states (PDOS) of the CaO_3Ca and $\text{CaOCa} + \text{O}_2$ complexes in MOR, we considered different (2, 2, 2) and (3, 3, 3) sets of shrinking factors. The *s*-, *p*-, and *d*-orbitals for selected Ca, Al, and O atoms were projected in both the singlet and triplet states that possess similar (CaO_3Ca) or essentially different ($\text{CaOCa} + \text{O}_2$) relative stability. Visualization at both cluster and periodic theoretical levels was realized with the MOLDRAW code [16].

3. Results

3.1. Consideration of the framework oxygen for the carbonate formation

To test the possibility of carbonate formation involving a framework oxygen of the zeolite cationic form without any MO_xM species, a series of optimization was performed considering one M cation with both 8R and (6R + 4R) cluster models for all $M = \text{Mg, Ca, Sr, and Ba}$. More precisely, we looked for a geometry in which the carbonate is formed with a third O atom of the framework owing to a partial weakening of its binding to the neighbor T atoms. No carbonate structure could be obtained. Only a linear CO_2 geometry with a maximal distortion of 169.8° was observed for the Mg(8R) cluster in MOR (Fig. 1). The weakness of CO_2 interaction with the framework oxygen in alkali form zeolites was already discussed [17]. The authors concluded as well that carbonate formation should not be observed in regards of the weak interaction between CO_2 and the framework oxygen in this type of zeolites.

3.2. Consideration of the oxygen of metal oxide species for the carbonate formation

3.2.1. Isolated cluster approach

We next studied the reactions between CO_2 and the MO_xM species. The Ca cluster geometries were already described in details

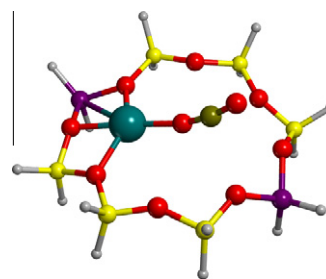


Fig. 1. Optimized structure of the product of CO_2 interaction with the Mg(8R) moiety in MOR, as calculated at the B3LYP/6-31G* level. The color code is O in red, Si in yellow, Al in violet, Ca in blue, C in brown, and H in gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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