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Ceramic hydration with expansion. The structure and reaction of water layers on magnesium oxide. A cyclic cluster study

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MgO hydration is an expansive process. It is used in cement to compensate for shrinkage, but it can be harmful at higher concentrations. In this quantum-chemical study, the first steps of the hydration of MgO have been explored. The semiempirical MO method MSINDO with the cyclic cluster model, including long-range electrostatic interactions, has been applied to investigate water adsorption on the (001) surface of MgO. Both molecular adsorption and dissociative adsorption have been found to occur. The latter is stabilized by hydrogen bonding from neighbouring water molecules and surface oxygen. Several energy minima exist for the experimentally low temperature $p(3\times2)$ monolayer H_2O observed on the MgO (001) surface which consists of a mixture of dissociated and molecular water. One third of the water molecules were dissociated, which is consistent with previous DFT studies. A stable fully hydroxylated MgO (001) surface with OH bridging two Mg ions and the hydrogen bound to the surface oxygen was discovered. This structure appears to promote the expansive, topotactic nucleation of brucite on the MgO (001) surface.

Key words: *magnesium oxide; brucite; water; hydration; adsorption*

1. Introduction

The hydration of magnesium oxide provides an interesting example for studying the surface structure and chemical reactions of ceramic oxides. Its simple crystallographic and electronic structure makes MgO known by its mineral name, periclase, a prototype for investigating the surface chemistry of ceramics, and in particular, for ceramic hydration. The final product of MgO hydration is $Mg(OH)_2$, brucite, which is

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a layered mineral of hexagonal symmetry with the crystallographic space group $P\vec{3}m1$. The relation

$$\mathrm{MO}\{Fm\overline{3}m\} + \mathrm{H_2O} \rightarrow \mathrm{M(OH)_2}\ \{P\overline{3}m1\} \tag{1}$$

holds not only for M = Mg but for a whole group of divalent metals: Mg, Ca, Mn, Fe, Co, Ni, and Cd. Their oxides MO have a rock-salt structure and their hydroxides $M(OH)_2$ have brucite structure. Thus the hydration of MgO can be considered as representative of the whole group. A particular feature of the hydration is the volume expansion associated with the reaction. The MgO hydration increases the solid volume by a factor of 2.2.

The expansion associated with periclase hydration is significant for ceramics engineering in at least two aspects. Although it is useful it can also be hazardous.

1. The long-term expansion produced by periclase hydration compensates in part for the thermal and autogenous shrinkage in concrete. Because of its high durability, concrete made from Portland slag cement which has a slight expansion is used for huge dam constructions. Much research has been carried out to achieve shrinkage -compensating cement by increasing the amount of MgO and determining the proper hydration conditions. Due to the heat produced by cement hydration, the temperature in an uncooled mass of concrete may reach more than 50 °C. Without appropriate and costly temperature-controlling measures the tensile thermal stress caused by mass concrete shrinkage during the cooling may exceed the tensile strength and the concrete may crack. The cooling generally lasts six months or more. The amount and rate of shrinkage compensating MgO expansion has to be controlled in practice by adjusting the calcinating conditions of MgO, its fineness, the amount in the cement and other parameters [1, 2].

2. However, periclase is generally regarded as a harmful component in cement because of its very slow hydration with significant volume expansion, which generates unsoundness in concrete and even causes cracking (Fig. 1). Up to 2 weight per cent of magnesium oxide is incorporated into clinker phases by building magnesium ions into the crystal lattice [3]. Excess MgO exists in industrially produced Portland cement clinkers as primary or secondary periclase at room temperature. The permitted limit for the total MgO content for Portland cement is 5% by mass in Germany, 6% in USA.

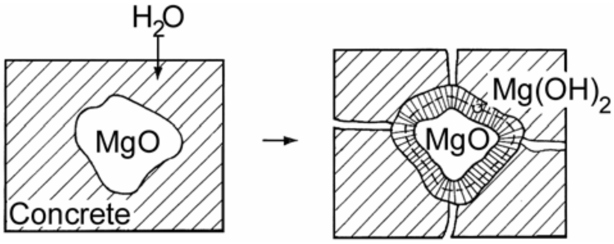

Fig. 1. Scheme of MgO hydration with volume expansion in concrete

Furthermore, the MgO hydration has to be considered in the processing of widely used industrial products such as fused periclase, refractory (chemically inert) magnesia and calcinated (chemically active) magnesia.

In view of the wide range of applications an understanding of the hydration process of MgO at an atomic and nanometer scale is desirable. This paper describes the quantum-chemical modelling of the magnesia hydration on a scale ranging from the atom to the nanometer cluster.

2. Quantum chemical modelling. MSINDO CCM

In this work, the semiempirical molecular orbital method MSINDO [4] is used. This method is based on the intermediate neglect of the differential overlap (INDO) approximation. This reduces the total number of integrals for a n-electron system to n^2 compared to n^4 in the case of ab initio Hartree–Fock calculations, or n^3 for calculations based on the density-functional theory (DFT). The remaining two-centre integrals are Coulomb integrals of the form $(\mu_I\mu_I|\nu_J\nu_J)$ with basis function μ_I on atom I and ν_J on atom J, nuclear attraction integrals $-(\mu_I|Z_J/r_{IJ}|\mu_I)$, overlap integrals $S_{\mu\nu}$ and the two-centre one-electron integrals $L_{\mu\nu}$ and $\Delta H_{\mu\nu}$ for the kinetic energy and the orthogonalization correction, respectively [5]. The striking feature of MSINDO is the use of a symmetrically orthogonalized valence basis with 6-31G and 6-31G* quality. The atomic basis set is augmented by 2p functions on hydrogen to account for hydrogen bonding. Core electrons are included by Zerner's pseudopotential [6].

The cyclic cluster model (CCM) [7] implemented in MSINDO has been applied to investigate the first steps of the reaction (Eq. 1) with M = Mg. Since the Coulomb interactions in these systems with partial ionic character decrease slowly, large clusters are considered and the effects of long-range electrostatic interactions are calculated [8] based on the Ewald summation technique. Within the CCM, the interactions of each atom with all other atoms of its Wigner–Seitz cell are calculated. To retain the proper symmetry, weighting factors are used for the interaction integrals with atoms at the border of the Wigner-Seitz cells. The deficiencies of the free cluster model, such as the loss of local symmetry and the occurrence of boundary effects at the borders of free clusters are overcome by employing the CCM [7]. The dimension of the Coulomb matrix **G**, the density matrix **P** and the Fock matrix **F** is given only by the basis functions of the original cluster atoms I in MSINDO CCM.

The work involved the exploration of a multidimensional potential energy surface and considered the interplay between several competing interactions: substrate–water, water–water–hydrogen bonding, partial and complete dissociation of water, surface hydroxylation as well as covalent, ionic, and dispersive interactions. This complexity of the pertinent bulk and surface phases precluded the systematic application of the more common ab initio or DFT methods. The method MSINDO has been successfully used to study the bulk and surface properties of various oxides [9–12] and provided the theoretical framework to systematically explore the energetic, structural and elastic properties of the MgO–water system with models containing up to 1000 atoms.

In all the simulations, the magnesium oxide surface was modelled by a $Mg_{96}O_{96}$ slab containing four layers of (001) crystal planes with 48 atoms each, of which the bottom three were fixed in the optimized bulk structure, while the water molecules were optimized together with a relaxation of the atoms of the first layer of MgO. In this way, structures denoted as "relaxed" were obtained. In order to determine the effects of surface relaxation all atoms of the MgO slab were fixed at their optimized bulk positions while the positions of the adsorbed water molecules were optimized. These structures were denoted as "unrelaxed".

3. Results and discussion

3.1. Energetics of MgO

The binding energy E_B per MgO unit for the perfect crystal was calculated using cyclic clusters of increasing size. The results for E_B show fast convergence to the bulk limit with increasing cluster size. The Madelung term does converge rapidly in CCM due to the cubic symmetry of MgO. The result of E_B^{CCM} = 1023 kJ/mol is close to the experimental value of 990 kJ/mol [13]. The same rapid convergence occurs also for the lattice parameter a of MgO in the cyclic cluster model. In principle, the same trends are found for the (001) surface energy and the (001) surface relaxation energy. The surface energy E_s was calculated using the equation:

$$E_s = \frac{E_{2D} - E_{3D}}{n_s} \tag{2}$$

The converged value of E_s is 76 kJ/mol, compared to the experimental range of 55–63 kJ/mol [14]. E_{3D} denotes the energy of the optimized periodic bulk structure, in three dimensions. E_{2D} is the energy of the slab model obtained by using the same cluster and geometry as for the calculation of E_{3D} but with the periodicity in only two dimensions in the (001) plane. n_s is the number of MgO units in the surface.

3.2. Adsorption of water on MgO (001) and surface hydroxylation

All theoretical models agree that dissociative water adsorption occurs at surface defects such as steps, kinks or vacancies. Systematic optimization of the geometry of the water monolayer adsorbed on MgO (001) using MSINDO CCM yields several types of stable structures including physisorbed structures with undissociated water molecules; chemisorbed structures with a part of the water molecules dissociated due to lateral hydrogen bonding; and structures with a fully hydroxylated surface. In Table 1 the results for the adsorption energies of various configurations of water monolayers on MgO (001) are given. The adsorption energy E_{ads} per water molecule was calculated for a cluster adsorbate structure of n water molecules on MgO according to:

$$E_{\text{ads}} = \frac{E_{\text{MgO/water}} - E_{\text{MgO}} - nE_{\text{water}}}{n} \tag{3}$$

Table 1. Adsorption energy [kJ/mol] per H_2O molecule of different monolayer structures

Structure	Remarks	Unrelaxed	Relaxed	Experimental
$p(3\times2)$				–85 [16]
A	No dissociation	–60		
B	1/3 dissociated	–79	–111	
C	1/3 dissociated	–72	–100	
(1×2)				–
D	Dissociated OH bridge	– 69		
(1×1)				–
E	No dissociation	– 6	– 6	
F	Dissociated OH on top of Mg	–24	–24	
G	Dissociated OH bridge		–99	

Polarization infrared spectroscopy detected a stable ordered H_2O MgO (001) adsorbate at temperatures between 185 and 220 K [15]. Diffraction indicated its $p(3\times2)$ symmetry and its adsorption energy was measured as –85 kJ/mol [16]. The model calculations found the lowest energy minimum for the $p(3\times2)$ structure consisting of a mixture of dissociated and molecular water, one third of the molecules being dissociated. OH is stabilized by three hydrogen bonds, one from the dissociated proton and two from undissociated water molecules (Fig. 2, structure **B**). Less stable is the physisorbed $p(3\times2)$ structure **A** on the unrelaxed MgO(001) surface. A complete network of hydrogen bonds connects the undissociated water molecules. Upon surface relaxation, structure **A** forms a chemisorbed layer with one third of the molecules dissociated. In the similar $p(3\times2)$, structure **C**, with the second lowest energy, one third of the molecules are also dissociated. OH is again stabilized by three hydrogen bonds, but in this case from three undissociated water molecules.

Both the physisorbed and chemisorbed states of water on MgO (001) have recently been reported in theoretical studies by DFT [17, 18] and spectroscopic work [19]. According to earlier DFT work, water chemisorption on MgO(001) involves a reconstruction and protonation to form a stable (111) hydroxyl surface [20]. Experimentally, using x-ray standing waves, a (1×1) H_2O overlayer on MgO (001) at 300 K was observed and a fully hydroxylated surface was postulated [21, 22]. In contrast, the fully hydroxylated surface with OH placed over the Mg ion was found to be unstable by correlation corrected periodic Hartree–Fock calculations [23] and self-consistent tight-binding studies of embedded clusters [24], in accordance with DFT based molecular dynamics calculations [25].

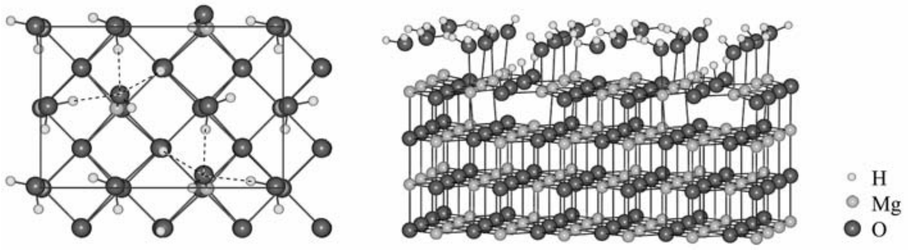

Fig. 2. Most stable structure **B** of the water monolayer on MgO (001). One third of the water molecules dissociated, $p(3\times2)$ symmetry. OH stabilized by three hydrogen bonds. (see Table 1). Top view, section (left). Side view (right)

In a more complete study of the potential energy surface this result was confirmed for the on-top adsorption of OH (structure **F**), but a stable fully hydroxylated MgO (001) surface was discovered. The OH group is placed in a bridging position over two Mg ions and the hydrogen atom is bound to the surface oxygen, the adsorption energy being $E_{\mathrm{ads}} = -99$ kJ/mol (Fig. 3, structure **G**). This (1×1) structure is consistent with diffraction measurements at 300 K. It is slightly less stable than the $p(3\times2)$ structure **B**, with only one third of the water molecules dissociated, and $E_{\mathrm{ads}} = -111$ kJ/mol. The (2×1), structure **D**, consists of a completely dissociated water monolayer characterized by a tilted OH group, bridging the Mg ions, with antiparallel ordering of OH chains (antiferroelectric order). The (1×1), structure **E**, is an undissociated monolayer.

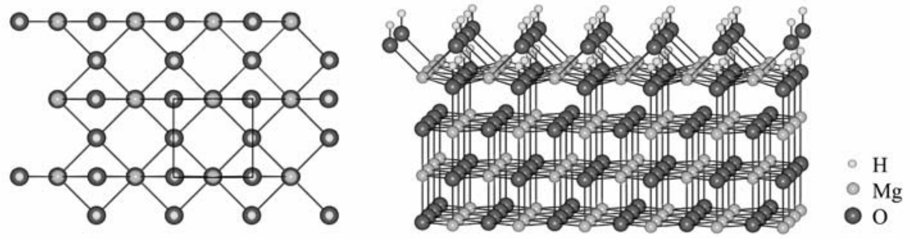

Fig. 3. Fully hydroxylated MgO (001) surface with (1×1) symmetry, with relaxation of the first layer of the MgO cluster. (see Table 1, structure **G**). Top view, section (left). Side view (right)

This fully hydroxylated structure **G** promotes the topotactic nucleation and growth of brucite. The (111) planes of the reactant periclase are typically observed parallel to the (0001) planes of the product brucite [26]. The development of brucite-like layers from the MgO (001) surface occurs perpendicularly to the brucite [0001] axis (Fig. 4). This reaction, including the elastic behaviour, will be modelled in a subsequent study based on the results obtained for the MgO surface hydration.

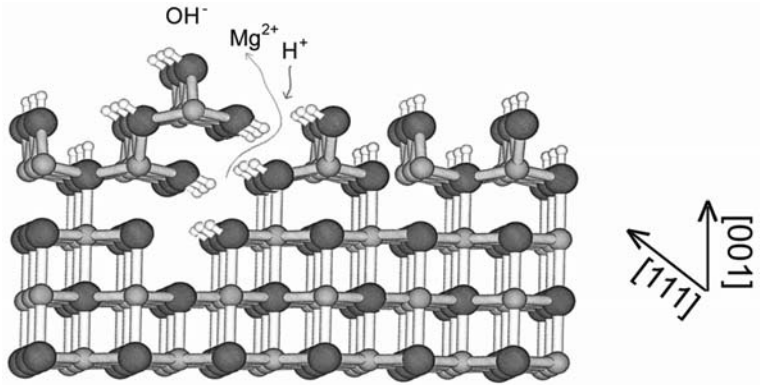

Fig. 4. Schematic picture of the expansive,
topotactic nucleation of brucite on the MgO (001) surface

4. Summary and conclusions

The cyclic cluster model with the Madelung potential implemented in the semiempirical SCF-MO method MSINDO is applied in a study of the periclase hydration.

The calculations reveal several types of stable water monolayer structures on MgO (001) including special physisorbed species. These form a hydrogen-bonded network of undissociated water molecules and chemisorbed water with part of the water molecules dissociated, mainly due to lateral interactions. A stable fully hydroxylated MgO (001) surface with OH bridging two Mg ions and hydrogen bound to the surface oxygen was discovered. This structure promotes the expansive, topotactic nucleation of brucite and provides the basis for future studies of periclase to brucite transformation reactions including the elastic behaviour of the product.

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