A First-Principles Study on the Hydration Behavior of (MgO)\(_n\) Clusters and the Effect Mechanism of Anti-Hydration Agents

Yu Gao \(^1\), Long Dong \(^1\), Liang Huang \(^1\,*\), Zhong Huang \(^1\), Faliang Li \(^1\), Haijun Zhang \(^1\,*\) and Shaowei Zhang \(^2\)

\(^1\) The State Key Laboratory of Refractories and Metallurgy, College of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China; gaoyu@wust.edu.cn (Y.G.); dl18797318871@163.com (L.D.); huangzhong@wust.edu.cn (Z.H.); lfliang@wust.edu.cn (F.L.)

\(^2\) College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, UK; sw-zhang2004@yahoo.co.uk

* Correspondence: huangliang1986@wust.edu.cn (L.H.); zhanghaijun@wust.edu.cn (H.Z.)

Abstract: Magnesia-based refractory is widely used in high-temperature industries; its easy hydration is, however, a key concern in refractory processing. Understanding the hydration mechanism of MgO will help in solving its hydration problem. Herein, the hydration behavior of (MgO)\(_n\) \((n = 1–6)\) at the molecular level and the effect mechanisms of several anti-hydration agents on the hydration of (MgO)\(_4\) were investigated with first-principles calculations. The results indicated that the following: (1) The smaller the (MgO)\(_n\) cluster size, the more favorable the hydration of MgO and the tendency to convert into Mg(OH)\(_2\) crystal; (2) Anti-hydration agents can coordinate with the unsaturated Mg atom of (MgO)\(_4\) to form a bond, increasing the coordination number of Mg, thus reducing its activity when reacting with H\(_2\)O; (3) The greater the number of −COOH groups and the longer the chain length in the anti-hydration agents, the better its effect of inhibiting the hydration of MgO. These findings could enhance the understanding of the mechanism of hydration of MgO and provide theoretical guidance for the design of novel anti-hydration agents.

Keywords: MgO hydration; clusters; mechanism of hydration; anti-hydration agents; first-principles calculations

1. Introduction

Magnesia or magnesium oxide (MgO) is an important refractory raw material with the combined characteristics of high fire resistance and excellent alkaline stability. Magnesia refractory is widely used in key parts such as the converter, ladle and tundish, which are of great significance for smelting clean steel [1–5]. However, the hydration of magnesium oxide can cause cracks due to the density mismatch between magnesium oxide \((\rho = 3.5 \text{ g/cm}^3)\) and its hydroxide \((\rho = 2.4 \text{ g/cm}^3)\), which damages the integrity of the material and limits its industrial application as a refractory material [6]. At present, the mechanism of the hydration of MgO at the molecular level is still not clear, which restricts the solutions to the hydration problem of MgO [7–11]. Therefore, it is necessary to study the initial adsorption behavior of water molecules on magnesium oxide at the molecular scale [12–16].

In order to fundamentally solve the hydration problem of MgO, researchers have carried out a large number of experimental studies on hydration resistance. In the study of Chen et al., oleic acid and stearic acid were used as hydration-resistant modifiers to significantly improve the hydration resistance of magnesia refractories due to the formation of insoluble films on the surface of MgO particles [17]. Similarly, Salomão and Pandolfelli evaluated how the presence of different anti-hydration agents influences the kinetics of the MgO hydration reaction. They found that citric acid can be adsorbed on the magnesia surface, building up an insoluble magnesium citrate protective coating and inhibiting the magnesia hydration [18–20]. The effects of propionic acid, acetic acid and formic acid on the hydration of magnesia were also investigated by T. dos Santos Jr. et al. [21], who reported
that the hydration degree of magnesia increased according to the following sequence: propionic acid > acetic acid > formic acid > distilled water. Therefore, carboxylic acids, such as citric, malic and acetic acid, are demonstrated to influence the hydration behavior of MgO, but their mechanisms of action are not fully understood.

As an effective means by which to investigate the interface reaction, first-principles calculations can supplement the experimental explanation, so it has attracted increased attention from researchers in recent years. A cluster is considered as a bridge between molecular and crystal structures, which can be used as pre-nucleation clusters leading to the formation of minerals [22]. Clusters can also be regarded as the transitional forms between atoms and bulk, and their fundamental properties depend vitally on the cluster size [23]. Thus, the interface between magnesium oxide and water or anti-hydration agents can be extracted at the cluster level to model the interaction between them. Although the reaction interface at clusters is small, it could essentially reflect the hydration process of magnesium oxide [24].

In this study, the hydration behavior of (MgO)n clusters (n = 1–6) was systematically investigated with first-principles calculations. The influences of the boric acid (BA), oxalic-acid (OA), tartaric-acid (TA), citric-acid (CA) and ISOBAM-104 (IB-104, CAS No. 52032-17-4, an amide-ammonium salt type of copolymer of isobutylene and maleic-anhydride developed by KURARAY, whose full name is poly(isobutylene-alt-maleic acid, ammonium salt)-co-(isobutylene-alt-maleic anhydride)) on the hydration of (MgO)4 clusters were evaluated, and the effect mechanism of anti-hydration agents was discussed.

2. Calculation Methods

All the calculations were carried out using density functional theory embedded in the DMol³ package (BIOVIA company, San Diego, CA, USA) [25]. Generalized gradient approximation (GGA) coupled with the Perdew-Burke-Ernzerhof (PBE) mixed exchange-correlation functional was adopted [26]. A double numerical basis set with polarization functions (DNP) was established to describe the valence electrons, and an all-electron treatment was used to perform full optimization of the investigated cluster model without symmetry constraints [27]. The convergence accuracy was set as fine quality with the tolerance for a total optimization energy of 1.0 × 10⁻⁵ Ha, maximum force of 2 × 10⁻³ Ha/Å, and maximum displacement of 5 × 10⁻³ Å, respectively. For the self-consistent calculation, the SCF density convergence was 1.0 × 10⁻⁶ e/Å³ and smearing was set to 5.0 × 10⁻³ Ha.

The lowest energy and ground-state configuration of (MgO)n (n = 1–6) clusters were determined with reference to the existing literature [28–33]. The water molecules or anti-hydration agents (AA) were placed near the (MgO)n (n = 1–6) clusters by gradually increasing their amounts. Next, the assumed [(MgO)n], [(MgO)n·H2O], and [(MgO)n·mAA·(n-m)H2O] (n = 1–6, m ≤ n) structures were optimized. The COSMO solvation model (solvent is water, ε = 78.54) was used to simulate the solvent effect of free water in solution.

The average reaction energy (E_avg) per MgO unit between (MgO)n clusters and the water molecules is given by

\[
E_{\text{avg}} = \left( E_{(\text{MgO})_n\cdot\text{nH}_2\text{O}} - (E_{(\text{MgO})_n} + E_{\text{H}_2\text{O}}) \right) / n,
\]

where n is the number of water molecules in the optimized cluster, \( E_{(\text{MgO})_n} \) is the total energy of the optimized (MgO)n cluster, \( E_{\text{H}_2\text{O}} \) is the total energy of the water molecule, and \( E_{(\text{MgO})_n\cdot\text{nH}_2\text{O}} \) is the total energy of the optimized (MgO)n·H2O cluster.

Similarly, the average Gibbs free energy change (ΔG_avg) per MgO unit between (MgO)n cluster and the water molecules is given by

\[
\Delta G_{\text{avg}} = \left( G_{(\text{MgO})_n\cdot\text{nH}_2\text{O}} - (G_{(\text{MgO})_n} + G_{\text{H}_2\text{O}}) \right) / n,
\]

where \( G_{(\text{MgO})_n} \) is the free energy of the optimized (MgO)n clusters, \( G_{\text{H}_2\text{O}} \) is the free energy of a water molecule, and \( G_{(\text{MgO})_n\cdot\text{nH}_2\text{O}} \) is the free energy of the optimized (MgO)n·H2O clusters. The free energy (G) values are obtained with a vibrational analysis.
Negative values of $\Delta G$ indicate that the addition of one water molecule to the cluster is thermodynamically favorable, i.e., spontaneous.

The stepwise hydration reaction energy and Gibbs free energy change ($\Delta G$) are defined as

$$
\Delta E = E_{(\text{MgO})_n-m\text{H}_2\text{O}} - (E_{(\text{MgO})_n-(m-1)\text{H}_2\text{O}} + E_{\text{H}_2\text{O}}), \quad (0 < m \leq n)
$$

(3)

$$
\Delta G = G_{(\text{MgO})_n-m\text{H}_2\text{O}} - (G_{(\text{MgO})_n-(m-1)\text{H}_2\text{O}} + G_{\text{H}_2\text{O}}), \quad (0 < m \leq n)
$$

(4)

The average reaction energy and Gibbs free energy change ($\Delta G$) for (MgO)$_n$·nH$_2$O clusters conversion to Mg(OH)$_2$ crystal were defined as

$$
\Delta E = \frac{[E_{n\text{Mg(OH)}_2} - E_{(\text{MgO})_n-n\text{H}_2\text{O}}]}{n},
$$

(5)

$$
\Delta G = \frac{[G_{n\text{Mg(OH)}_2} - G_{(\text{MgO})_n-n\text{H}_2\text{O}}]}{n},
$$

(6)

The energy change caused by the addition of one anti-hydration agent or water molecule to the cluster is defined as

$$
\Delta E = \frac{E_{(\text{MgO})_n-x\text{AA}} - (E_{(\text{MgO})_n-(x-1)\text{AA}} + E_{\text{AA}})}{(0 < x \leq n)}
$$

(7)

$$
\Delta E = \frac{E_{(\text{MgO})_n-x\text{AA}-y\text{H}_2\text{O}} - (E_{(\text{MgO})_n-x\text{AA}-(y-1)\text{H}_2\text{O}} + E_{\text{H}_2\text{O}})}{(0 < x + y \leq n)}
$$

(8)

3. Results
3.1. Hydration Mechanism of (MgO)$_n$·nH$_2$O Clusters

The optimized geometries of (MgO)$_n$ (n = 1–6) and (MgO)$_n$·nH$_2$O clusters are shown in Figure 1, which are consistent with previous reports [28–33]. In the hydration reaction process, one (MgO)$_n$ can react with H$_2$O to form the corresponding hydration products-(MgO)$_n$·nH$_2$O. The average reaction energy ($E_{\text{avg}}$) per MgO unit between (MgO)$_n$ clusters and n H$_2$O molecules is plotted in Figure 1a. It was found that the reaction of (MgO)$_n$ clusters with H$_2$O is exothermic and the released heat per MgO unit decreased with an increase in cluster size. The average Gibbs free energy change ($\Delta G_{\text{avg}}$) per MgO unit of the reaction between (MgO)$_n$ clusters and H$_2$O molecules (as shown in Figure 1b) was negative at room temperature (300 K) and at an elevated temperature (625 K), further demonstrating that (MgO)$_n$ clusters were able to easily react with H$_2$O. The smaller the (MgO)$_n$ cluster size, the more favorable the reaction between (MgO)$_n$ clusters and H$_2$O. The possible reason is that the smaller the (MgO)$_n$ cluster size, the smaller the coordination number of the Mg atom, resulting in increased activity to dissociate the water.
The tendency for the conversion of hydration products – (MgO)_n·nH_2O to Mg(OH)_2 crystal was also investigated, as shown in Figure 2. The results showed that the conversion of (MgO)_n·nH_2O into Mg(OH)_2 crystal was also an exothermic reaction. Generally, the released heat per MgO unit decreased with an increase in the (MgO)_n·nH_2O cluster size when it was converted into a Mg(OH)_2 crystal, except for (MgO)_4·4H_2O. The Gibbs free energy change per MgO unit for the conversion of (MgO)_n·nH_2O to Mg(OH)_2 crystal at different cluster sizes were negative at room temperature (300 K) and at an elevated temperature (625 K). It indicated that the hydrated (MgO)_n·nH_2O clusters tend to be transformed into Mg(OH)_2 crystals spontaneously. Among them, (MgO)_4·4H_2O clusters show a tendency to form Mg(OH)_2 crystals more easily from the point of view of reaction energy and Gibbs free energy change. One possible reason is that the (MgO)_4 cluster helps to maintain the cube structure, which is closer to the MgO crystal structure than other clusters in terms of crystal structure. Therefore, (MgO)_4 cluster can better reflect the hydration behavior of MgO. The above results indicated that the smaller the (MgO)_n cluster size, the more favorable the hydration of MgO and the trend to convert into Mg(OH)_2 crystal, which is consistent with the fact that the rate of the hydration reaction increases as the crystallinity of the MgO decreases (i.e., smaller mean crystallite size) [34].

![Figure 2](image-url)  
(a) The reaction energy and (b) Gibbs free energy change for conversion of (MgO)_n·nH_2O clusters into Mg(OH)_2 crystals.

Taking (MgO)_4 clusters as an example, its stepwise reaction with the H_2O molecule was also studied in detail to expound the hydration characteristics of MgO, as shown in Figure 3. As the reaction progressed, a great deal of heat was released at each step, and the reaction energies were −165.0, −163.2, −173.9 and −200.6 kJ/mol, respectively. The Gibbs free energy changes of each step at 300 K were −119.1, −120.4, −134.3 and −152.9 kJ/mol, respectively. Although the Gibbs free energy change at 625 K moved towards a positive direction, it was still less than zero. The reaction energy for the conversion of (MgO)_4·4H_2O to Mg(OH)_2 was −425.1 kJ/mol, and Gibbs free energy changes were −488.9 kJ/mol at 300 K and −372.6 kJ/mol at 625 K, respectively. These results show that (MgO)_4 clusters were easily and gradually hydrated and transformed into Mg(OH)_2 crystals at room temperature (300 K) and at an elevated temperature (625 K).
with a dissociation adsorption energy of –265.82 kJ/mol, indicating that the (MgO)$^4$ which is slightly more positive than adsorption energy of the first H$_2$O (MgO)$^4$·BA, and the dissociation adsorption energy changed from –130.25 kJ/mol to –139.96 kJ/mol to –129.67 kJ/mol. When the second boric acid was adsorbed on the (MgO)$^4$·BA cluster, the –OH of boric acid also dissociated to form a Mg–OH and O–H bond with a dissociation adsorption energy of –265.82 kJ/mol, indicating that the (MgO)$^4$·BA cluster preferentially adsorbs the second boric acid instead of the second H$_2$O. When the (MgO)$^4$ cluster adsorbed two or more boric acid molecules, the H$_2$O was only adsorbed in its molecular form and no longer dissociated on (MgO)$^4$·(BA)$_n$ (n = 2–4). Nevertheless, (MgO)$^4$·(BA)$_n$ preferentially adsorbed another H$_2$O instead of a boric acid molecule after (MgO)$^4$ adsorbed two or more boric acid molecules, because the absolute value of boric acid’s adsorption energies was smaller than that of H$_2$O’s. Therefore, increasing the amount of boric acid can retard the hydration of (MgO)$^4$ but cannot completely inhibit its hydration.

3.2. Effect Mechanism of Anti-Hydration Agents on Hydration of (MgO)$^4$ Cluster

The previous study suggested that the hydration of magnesium oxide could be inhibited by the addition of various additives to a certain degree [17–21,35]. To investigate the potential of boric acid (BA), oxalic acid (OA), tartaric acid (TA), citric acid (CA) and ISOBAM-104 (IB-104) as anti-hydration agents, the effect of these molecules on the hydration of (MgO)$^4$ cluster was investigated.

Without the addition of an anti-hydration agent, the first H$_2$O was dissociated spontaneously on the (MgO)$^4$ clusters to form Mg–OH and an O–H bond, because the unsaturated Mg ion of (MgO)$^4$ had an empty orbital, and the oxygen atom of H$_2$O contained lone pairs of electrons for donation. The reaction between the first H$_2$O and (MgO)$^4$ cluster to form (MgO)$^4$·H$_2$O occurred as an exothermic reaction that released –139.96 kJ/mol of energy. The reaction energies were 134.3 and 130.25 kJ/mol, and Gibbs free energy changes were 163.2, 173.9 and 200.6 kJ/mol, respectively. The reaction heats (a) and reaction free energy for the stepwise hydration of (MgO)$^4$.

3.2.1. Effect Mechanism of Boric Acid on Hydration of (MgO)$^4$ Cluster

The previous study suggested that the hydration of magnesium oxide could be inhibited by the addition of various additives to a certain degree [17–21,35]. To investigate the potential of boric acid (BA), oxalic acid (OA), tartaric acid (TA), citric acid (CA) and ISOBAM-104 (IB-104) as anti-hydration agents, the effect of these molecules on the hydration of (MgO)$^4$ cluster was investigated.

Without the addition of an anti-hydration agent, the first H$_2$O was dissociated spontaneously on the (MgO)$^4$ clusters to form Mg–OH and an O–H bond, because the unsaturated Mg ion of (MgO)$^4$ had an empty orbital, and the oxygen atom of H$_2$O contained lone pairs of electrons for donation. The reaction between the first H$_2$O and (MgO)$^4$ cluster to form (MgO)$^4$·H$_2$O occurred as an exothermic reaction that released –139.96 kJ/mol of energy.

3.2.2. Effect Mechanism of Anti-Hydration Agents on Hydration of (MgO)$^4$ Cluster

The effect of the addition of boric acid content on the hydration reaction of the (MgO)$^4$ cluster was investigated, as shown in Figure 4. When first boric acid molecule was adsorbed on the (MgO)$^4$ cluster, the –OH of boric acid dissociated to form a Mg–OH and O–H bond on the (MgO)$^4$ cluster. The dissociation adsorption energy was –130.25 kJ/mol, which is slightly more positive than adsorption energy of the first H$_2$O on the (MgO)$^4$ cluster, indicating that a small amount of boric acid cannot inhibit the initial hydration of (MgO)$^4$. After the (MgO)$^4$ cluster adsorbed one boric acid, the second H$_2$O was adsorbed and dissociated on (MgO)$^4$·BA, and the dissociation adsorption energy changed from –139.96 kJ/mol to –129.67 kJ/mol. When the second boric acid was adsorbed on the (MgO)$^4$·BA cluster, the –OH of boric acid also dissociated to form a Mg–OH and O–H bond with a dissociation adsorption energy of –265.82 kJ/mol, indicating that the (MgO)$^4$·BA cluster preferentially adsorbs the second boric acid instead of the second H$_2$O. When the (MgO)$^4$ cluster adsorbed two or more boric acid molecules, the H$_2$O was only adsorbed in its molecular form and no longer dissociated on (MgO)$^4$·(BA)$_n$ (n = 2–4). Nevertheless, (MgO)$^4$·(BA)$_n$ preferentially adsorbed another H$_2$O instead of a boric acid molecule after (MgO)$^4$ adsorbed two or more boric acid molecules, because the absolute value of boric acid’s adsorption energies was smaller than that of H$_2$O’s. Therefore, increasing the amount of boric acid can retard the hydration of (MgO)$^4$ but cannot completely inhibit its hydration.
3.2.2. Effect Mechanism of Oxalic Acid on Hydration of (MgO)$_4$ Cluster

The effect of the addition of oxalic acid on the hydration reaction of the (MgO)$_4$ cluster was investigated, as shown in Figure 5. When the first oxalic acid molecule was adsorbed on the (MgO)$_4$ cluster, the –OH of oxalic acid also dissociated to form Mg–OH and an O–H bond on the (MgO)$_4$ cluster. However, its dissociation adsorption energy was $-233.75$ kJ/mol, which is much smaller than the adsorption energy of the first H$_2$O on the (MgO)$_4$ cluster, indicating that the oxalic acid was preferentially adsorbed on the (MgO)$_4$ clusters and inhibited the initial hydration of (MgO)$_4$. Similarly, the (MgO)$_4$·OA clusters will preferentially adsorb the second oxalic acid instead of the second H$_2$O. When two or more oxalic acid molecules were adsorbed on the (MgO)$_4$ clusters, H$_2$O was no longer dissociated on (MgO)$_4$·OA clusters, but instead adsorbed in the form of molecules. Meanwhile, the absolute value of oxalic acid’s adsorption energies was larger than that of H$_2$O’s, suggesting that (MgO)$_4$·(OA)$_n$ preferentially adsorbs another oxalic acid instead of the H$_2$O molecule after (MgO)$_4$ adsorbing two or more oxalic acid molecules. It showed that an appropriate amount of oxalic acid can protect (MgO)$_4$ clusters and inhibit their hydration. With an increase in the adsorption amount of oxalic acid, the hydration-inhibition effect is improved.

Figure 5. Optimized structures and relative energies of (MgO)$_4$·(OA)$_n$ (n = 0–4) and (MgO)$_4$·(OA)$_n$·H$_2$O (n = 0–4). [Legend: red, O atoms; Green, Mg atoms; white, and H atoms; Gray, C atoms.]. The black arrow represents the preferred reaction path.
3.2.3. Effect Mechanism of Tartaric Acid, Citric Acid and ISOBAM-104 on Hydration of (MgO)\textsubscript{4} Cluster

The effect of the use of tartaric acid, citric acid or ISOBAM-104 as the anti-hydration agent (AA) and its content on the hydration reaction of the (MgO)\textsubscript{4} cluster was also investigated, as shown in Figures 6–8. A similar phenomenon to oxalic acid was observed. The first tartaric acid, citric acid or ISOBAM-104 preferentially adsorbed on the (MgO)\textsubscript{4} clusters and inhibited the initial hydration of (MgO)\textsubscript{4}. Nevertheless, when only one tartaric acid, citric acid or ISOBAM-104 molecule was adsorbed on the (MgO)\textsubscript{4} clusters, H\textsubscript{2}O was no longer dissociated on (MgO)\textsubscript{4}·(AA)\textsubscript{n} (n = 2–4), but adsorbed in the form of a molecule, indicating that acid, citric acid or ISOBAM-104 has a better ability to inhibit the initial hydration of (MgO)\textsubscript{4}. Meanwhile, the adsorption energies also suggested that (MgO)\textsubscript{4}·(AA)\textsubscript{n} preferentially adsorbs another tartaric acid, citric acid or ISOBAM-104 instead of an H\textsubscript{2}O molecule after (MgO)\textsubscript{4} by adsorbing one or more anti-hydration agent molecules. It is worth mentioning that the affinity of citric acid or ISOBAM-104 to MgO was stronger than that of H\textsubscript{2}O molecule. The results showed that a small amount of tartaric acid, citric acid or ISOBAM-104 can protect (MgO)\textsubscript{4} clusters and inhibit their hydration. With the increase in the adsorption amount of tartaric acid, citric acid or ISOBAM-104, the hydration inhibition effect obviously improved.

![Figure 6.](image1)

**Figure 6.** Optimized structures and relative energies of (MgO)\textsubscript{4}·(TA)\textsubscript{n} (n = 0–4) and (MgO)\textsubscript{4}·(TA)\textsubscript{n}·H\textsubscript{2}O (n = 0–4). [Legend: red, O atoms; green, Mg atoms; white, H atoms; gray, C atoms.]. The black arrow represents the preferred reaction path.

![Figure 7.](image2)

**Figure 7.** Optimized structures and relative energies of (MgO)\textsubscript{4}·(CA)\textsubscript{n} (n = 0–4) and (MgO)\textsubscript{4}·(CA)\textsubscript{n}·H\textsubscript{2}O (n = 0–4). [Legend: red, O atoms; green, Mg atoms; white, H atoms; gray, C atoms.]. The black arrow represents the preferred reaction path.
Figure 7. Optimized structures and relative energies of \((\text{MgO})_4\cdot(\text{CA})_n\) (\(n = 0\)−4) and \((\text{MgO})_4\cdot(\text{CA})_n\cdot\text{H}_2\text{O}\) (\(n = 0\)−4). [Legend: red, O atoms; green, Mg atoms; white, H atoms; gray, C atoms; blue, N atoms.]. The black arrow represents the preferred reaction path.

Figure 8. Optimized structures and relative energies of \((\text{MgO})_4\cdot(\text{IB-104})_n\) (\(n = 0\)−4) and \((\text{MgO})_4\cdot(\text{IB-104})_n\cdot\text{H}_2\text{O}\) (\(n = 0\)−4). [Legend: red, O atoms; green, Mg atoms; white, H atoms; gray, C atoms; blue, N atoms.]. The black arrow represents the preferred reaction path.

4. Discussion

The thermodynamic data of the reaction between \((\text{MgO})_n\) clusters and \(\text{H}_2\text{O}\) molecules demonstrated that the smaller the size of MgO, the more easily it is hydrated. The hydrated \((\text{MgO})_n\cdot\text{nH}_2\text{O}\) clusters show a tendency to convert to \(\text{Mg(OH)}_2\) crystals, among which \((\text{MgO})_4\cdot\text{4H}_2\text{O}\) is easier to convert to \(\text{Mg(OH)}_2\) crystals from the point of view of reaction energy and reaction free energy. Each hydration step of the \((\text{MgO})_4\) clusters releases a lot of heat, and the reaction free energy is negative at 300 K and 625 K, indicating that \((\text{MgO})_4\) clusters are easily hydrated step by step, and the hydrated \((\text{MgO})_4\cdot\text{4H}_2\text{O}\) tends to transform into \(\text{Mg(OH)}_2\) crystals.

Different kinds of anti-hydration agents and \(\text{H}_2\text{O}\) are competitively adsorbed on \((\text{MgO})_n\) clusters. Even the amount of adsorbed boric acid molecules increased to more than two and the \((\text{MgO})_4\cdot(\text{BA})_n\) preferentially adsorbed another \(\text{H}_2\text{O}\) instead of a boric acid molecule, suggesting that boric acid could not completely inhibit the initial hydration of \((\text{MgO})_4\) clusters. By increasing the adsorption amount of oxalic acid to two or more, the \(\text{H}_2\text{O}\) was adsorbed on the \((\text{MgO})_4\) cluster in the form of a molecule, and the adsorption of another oxalic acid molecule was more favorable than the adsorption of the \(\text{H}_2\text{O}\) molecule. After only one molecule of tartaric acid, citric acid or ISOBAM-104 was adsorbed on the
(MgO)\textsubscript{4} cluster, H\textsubscript{2}O was adsorbed in the form of a molecule instead of the occurrence of dissociation. With the increase in the adsorption amount, the adsorption energy of tartaric acid, citric acid or ISOBAM-104 was found to be more negative than that of H\textsubscript{2}O, indicating the preferential adsorption of tartaric acid, citric acid or ISOBAM-104. These results indicated the following: (1) the inhibition effect of boric acid on (MgO)\textsubscript{4} hydration was not obvious because borate is a weak ligand; (2) the adequate amount of oxalic acid could protect the (MgO)\textsubscript{4} cluster and inhibit its hydration to some extent; (3) the tartaric acid, citric acid or ISOBAM-104 had a good inhibition effect on (MgO)\textsubscript{4} hydration. By increasing the dosage of tartaric acid, citric acid or ISOBAM-104, the inhibition effect would improve. At pH\textless{}5, the hydration rate was proportional to the proton concentration [35]. On one hand, the dissociation of a water molecule is related to the deprotonation of bound water, meaning that the deprotonation of water at an acidic pH is unfavorable, whereas it is favorable at a neutral (water) or slightly basic pH (boric acid). On the other hand, the formation of an O-H bond (formed by releasing of H\textsuperscript{+} species) is favored when the acidity coefficient (pKa) of organic acid is stronger [36]. At a pH < 5, the rate-controlling step was proton attack [MgO + 2H\textsuperscript{+} \rightarrow Mg\textsuperscript{2+} + H\textsubscript{2}O] and depended on the concentration of Mg\textsuperscript{2+} [35]. In this situation, the strong bonding energy (adsorption energy) between the ligand of the anti-hydration agent can chelate Mg\textsuperscript{2+} and suppress the formation of Mg(OH)\textsubscript{2}. Simply, suitable organic acids could have a high chemical affinity to bind to Mg ions and protect them from hydration. Once a certain supersaturation threshold is reached, the “unwanted” Mg(OH)\textsubscript{2} formation can be avoided.

By analyzing the molecular structure of the anti-hydration agents, we found the following: (1) the greater the number of \texttt{−COOH} groups in the anti-hydration agent, the more easily it bonds with the unsaturated Mg atom of the (MgO)\textsubscript{4} cluster; (2) the greater the molecular weight of the anti-hydration agent, the better its protective effect is on the (MgO)\textsubscript{4} cluster; thus, it can better inhibit the hydration of MgO. When tartaric acid, citric acid or ISOBAM-104 is used as the anti-hydration agent, it can hinder the spontaneous dissociation of H\textsubscript{2}O on (MgO)\textsubscript{4} and even if initially only one anti-hydration agent molecule is adsorbed, it can inhibit the hydration of MgO. The calculation results are consistent with Li and Pandolfelli’s experimental results demonstrating that tartaric acid and citric acid could inhibit the hydration of MgO to a certain extent, although citric acid is more effective than tartaric acid [18,37]. However, as of yet, there is no report describing the effect of ISOBAM-104 as an anti-hydration agent. Therefore, the use of ISOBAM-104 to modify MgO-containing materials in the future is expected to improve their hydration resistance.

5. Conclusions

In this work, the hydration behavior of (MgO)\textsubscript{n} clusters (n = 1–6) and the effect mechanism of anti-hydration agents on the hydration of (MgO)\textsubscript{4} clusters were studied with first-principles calculations. The thermodynamic data of the reaction between (MgO)\textsubscript{n} clusters and H\textsubscript{2}O molecules demonstrate that the smaller the size of MgO, the more easily it is hydrated. Each hydration step of (MgO)\textsubscript{4} clusters releases a considerable amount of heat, and the reaction free energy is negative at 300 K and 625 K, indicating that the (MgO)\textsubscript{4} cluster can easily be hydrated step by step. The hydrated (MgO)\textsubscript{n}·nH\textsubscript{2}O clusters show a tendency to convert to Mg(OH)\textsubscript{2} crystals, among which (MgO)\textsubscript{4}·4H\textsubscript{2}O is easier to convert to Mg(OH)\textsubscript{2} crystals from the point of view of reaction heat and reaction free energy. Different kinds of anti-hydration agents and H\textsubscript{2}O are competitively adsorbed on (MgO)\textsubscript{4} clusters. The adsorption energies show that tartaric acid, citric acid or poly[(isobutylene-alt-maleic acid, ammonium salt)-co-(isobutylene-alt-maleic anhydride)] (ISOBAM-104) could protect the (MgO)\textsubscript{4} cluster and has a better inhibitory effect on the hydration of (MgO)\textsubscript{4} clusters, and the inhibition effect improves with increased amounts of anti-hydration agents. The greater the number of \texttt{−COOH} groups in the anti-hydration agents, the more easily it bonds with unsaturated Mg\textsuperscript{2+} on the (MgO)\textsubscript{4} clusters; and the
greater the molecular weight of the anti-hydration agents, the better the protective effect on the (MgO)₃₉ cluster; thus it can better inhibit the hydration of MgO.

This study not only reveals the hydration mechanism behavior of MgO at the molecular level and the effect mechanism of anti-hydration agents on its hydration, but it also serves as indispensable knowledge for future experimental approaches.

**Author Contributions:** Conceptualization, L.H., H.Z. and S.Z.; investigation, Y.G. and L.D.; data analysis, Z.H. and F.L.; writing—original draft preparation, Y.G. and L.D.; writing—review and editing, L.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by National Natural Science Foundation of China (grant number 51702241); the Special Project of Central Government for Local Science and Technology Development of Hubei Province (grant number 2019ZYGD076), and Open Foundation of State Key Laboratory of Advanced Refractories (grant number SKLAR202002). We also acknowledge the support by High-Performance Computing Center of Wuhan University of Science and Technology.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** All data generated in this study are available from the corresponding author (L.H., huangliang1986@wust.edu.cn) without restriction.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Shahraki, A.; Ghasemi-Kahrizsangi, S.; Nemati, A. Performance improvement of MgO–CaO refractories by the addition of nano-sized Al₂O₃. *Mater. Chem. Phys.* 2017, 198, 354–359. [CrossRef]
2. Ghasemi-Kahrizsangi, S.; Dehsheikh, H.G.; Boroujerdia, M. Effect of micro and nano-Al₂O₃ addition on the microstructure and properties of MgO–C refractory ceramic composite. *Mater. Chem. Phys.* 2017, 189, 230–236. [CrossRef]
3. Dehsheikh, H.G.; Ghasemi-Kahrizsangi, S. Performance improvement of MgO–C refractory bricks by the addition of Nano-ZrSiO₄. *Mater. Chem. Phys.* 2017, 202, 369–376. [CrossRef]
4. Ghasemi-Kahrizsangi, S.; Dehsheikh, H.G.; Karamian, E.; Boroujerdia, M.; Payandeh, K. Effect of MgAl₂O₄ nanoparticles addition on the densification and properties of MgO–CaO refractories. *Ceram. Int.* 2017, 43, 5014–5019. [CrossRef]
5. Ghasemi-Kahrizsangi, S.; Sedeh, M.B.; Dehsheikh, H.G.; Shahraki, A.; Farooghi, M. Densification and properties of ZrO₂ nanoparticles added magnesia–doloma refractories. *Ceram. Int.* 2016, 42, 15658–15663. [CrossRef]
6. Cai, M.; Liang, Y.; Yin, Y.; Nie, J. Effect of citric acid on the hydration process of colloidal silica-bonded magnesia gunning materials. *Ceram. Int.* 2019, 45, 1514–15159. [CrossRef]
7. Kurosawa, R.; Takeuchi, M.; Ryu, J. Fourier-transform infrared and X-ray diffraction analyses of the hydration reaction of pure magnesium oxide and chemically modified magnesium oxide. *RSC Adv.* 2021, 11, 24292–24311. [CrossRef]
8. Huang, L.; Yang, Z.; Wang, S. Influence of calcination temperature on the structure and hydration of MgO. *Constr. Build. Mater.* 2020, 262, 120776. [CrossRef]
9. Shab, V.; Scott, A. Hydration and microstructural characteristics of MgO in the presence of metakaolin and silica fume. *Cem. Concr. Compos.* 2021, 121, 104068. [CrossRef]
10. He, J.; Zheng, W.; Bai, W.; Hu, T.; He, J.; Song, X. Effect of reactive MgO on hydration and properties of alkali-activated slag pastes with different activators. *Constr. Build. Mater.* 2021, 271, 121608. [CrossRef]
11. Warnuz, K.; Madej, D. Effect of the particle size on the reactivity of MgO–Al₂O₃ hydrating mixtures: A long-term kinetic investigation of hydrotalcite synthesis. *Appl. Clay Sci.* 2021, 211, 106196. [CrossRef]
12. Li, X.; Zhang, C.; Wang, J.; Huang, H.; Wang, S. Atomic-level insights into nano-salt droplets wetting on the MgO surface using molecular dynamics simulations. *Corros. Sci.* 2020, 167, 108549. [CrossRef]
13. Da Silva Alvim, R.; Borges, L., Jr.; Leitão, A.A. Proton migration on perfect, vacant, and doped MgO (001) surfaces: Role of dissociation residual groups. *J. Phys. Chem. C* 2018, 122, 21841–21853. [CrossRef]
14. Oncak, M.; Wlodarczyk, R.; Sauer, J. Water on the MgO (001) surface: Surface reconstruction and ion solvation. *J. Phys. Chem. Lett.* 2015, 6, 2310–2314. [CrossRef][PubMed]
15. Alessio, M.; Usvyat, D.; Sauer, J. Chemically accurate adsorption energies: CO and H₂O on the MgO (001) surface. *J. Chem. Theory Comput.* 2018, 15, 1329–1344. [CrossRef]
16. Souza, T.M.; Braulio, M.A.L.; Luz, A.P.; Bonadip, P.; Pandolfelli, V.C. Systemic analysis of MgO hydration effects on alumina–magnesia refractory castables. *Ceram. Int.* 2012, 38, 3969–3976. [CrossRef]
17. Chen, S.J.; Lu, P.G.; Chen, G.R.; Cheng, J.J. Improved hydration resistance of synthesized magnesia–calcia clinker by surface modification. *J. Am. Ceram. Soc.* 2004, 87, 2164–2167. [CrossRef]
18. Amaral, L.F.; Oliveira, I.R.; Bonadia, P.; Salomao, R.; Pandolfelli, V.C. Chelants to inhibit magnesia (MgO) hydration. Ceram. Int. 2011, 37, 1537–1542. [CrossRef]

19. Nouri-Khezrabad, M.; Luz, A.P.; Golestani-Fard, F.; Rezaie, H.R.; Pandolfelli, V.C. Citric acid role and its migration effects in nano-bonded refractory castables. Ceram. Int. 2014, 40, 14523–14527. [CrossRef]

20. Salomão, R.; Pandolfelli, V.C. Citric acid as anti-hydration additive for magnesia containing refractory castables. Ceram. Int. 2011, 37, 1839–1842. [CrossRef]

21. Dos Santos, T., Jr.; dos Santos, J.; Luz, A.P.; Pagliosa, C.; Pandolfelli, V.C. Kinetic control of MgO hydration in refractory castables by using carboxylic acids. J. Eur. Ceram. Soc. 2014, 38, 2152–2163. [CrossRef]

22. Xing, X.D.; Hermann, A.; Kuang, X.Y.; Ju, M.; Lu, C.; Jin, Y.Y.; Xia, X.X.; Maroulis, G. Insights into the geometries, electronic and magnetic properties of neutral and charged palladium clusters. Sci. Rep. 2016, 6, 19656. [CrossRef] [PubMed]

23. Ju, M.; Lv, J.; Kuang, X.Y.; Ding, L.P.; Lu, C.; Wng, J.J.; Jin, Y.Y.; Maroulis, G. Systematic theoretical investigation of geometries, stabilities and magnetic properties of iron oxide clusters (FeO)\(^n\)\(^\mu\) (\(n = 1–8\), \(\mu = 0, \pm 1\)): Insights and perspectives. RSC Adv. 2015, 5, 6560–6570. [CrossRef]

24. Zhao, Z.; Li, Z.; Shi, T.T.; Qi, J.L.; Wang, Q. Calculation on the CO\(_2\) influences on the structure, stability of (MgO)\(_m\) (\(m = 1–6\)) clusters. Phase Transit. 2018, 91, 1223–1231. [CrossRef]

25. Delley, B. From molecules to solids with the DMol\(^3\) approach. J. Chem. Phys. 2000, 113, 7756–7764. [CrossRef]

26. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865. [CrossRef]

27. Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. J. Chem. Phys. 1990, 92, 508–517. [CrossRef]

28. Malliavin, M.J.; Coudray, C. Ab initio calculations on (MgO)\(_n\), (CaO)\(_n\), and (NaCl)\(_n\) clusters (n = 1–6). J. Chem. Phys. 1997, 106, 2323–2330. [CrossRef]

29. Bawa, F.; Panas, I. Competing pathways for MgO, CaO, SrO, and BaO nanocluster growth. Phys. Chem. Chem. Phys. 2002, 4, 103–108. [CrossRef]

30. De la Puente, E.; Aguado, A.; Ayuela, A.; Lopez, J.M. Structural and electronic properties of small neutral (MgO)\(_n\) clusters. Phys. Rev. B 1997, 56, 7607. [CrossRef]

31. Hong, L.; Wang, H.L.; Cheng, J.G.; Tang, L.L.; Zhao, J.J. Lowest-energy structures of (MgO)\(_n\) (n = 2–7) clusters from a topological method and first-principles calculations. Comput. Theor. Chem. 2012, 980, 62–67. [CrossRef]

32. Dong, R.B.; Chen, X.S.; Wang, X.F.; Lu, W. Structural transition of hexagonal tube to rocksalt for (MgO)\(_{3n}\), 2 ≤ n ≤ 10. J. Chem. Phys. 2008, 129, 044705. [CrossRef] [PubMed]

33. Jain, A.; Kumar, V.; Sluiter, M.; Kawazoe, Y. First principles studies of magnesium oxide clusters by parallelized Tohoku University Mixed-Basis program TOMBO. Comput. Mater. Sci. 2006, 36, 171–175. [CrossRef]

34. Nguyen, N.Y.T.; Grelling, N.; Wetteland, C.L.; Rosario, R.; Liu, H. Antimicrobial activities and mechanisms of magnesium oxide nanoparticles (nMgO) against pathogenic bacteria, yeasts, and biofilms. Sci. Rep. 2018, 8, 16260. [CrossRef] [PubMed]

35. Fruhwirth, O.; Herzog, G.W.; Hollerer, I.; Rachetti, A. Dissolution and hydration kinetics of MgO. Surf. Technol. 1985, 24, 301–317. [CrossRef]

36. Maiti, S.; Ghosh, S.; Ghosh, A. Elucidating the secondary effect in the Lewis acid mediated anodic shift of electrochemical oxidation of a Cu (II) complex with a N\(_2\)O\(_2\) donor unsymmetrical ligand. Dalton Trans. 2019, 48, 14898–14913. [CrossRef]

37. Li, Z.G.; Ji, Z.S.; Jiang, L.L.; Yu, S.W. Effect of additives on the properties of magnesium oxy sulfate cement. J. Intell. Fuzzy Syst. 2017, 33, 3021–3025. [CrossRef]