Study of Thermal Stability of Hydrotalcite and Carbon Dioxide Adsorption Behavior on Hydrotalcite-Derived Mixed Oxides Using Atomistic Simulations

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ABSTRACT: Hydrotalcites (HTlcs) or layered double hydroxides (LDHs) have been used in a wide range of applications such as catalysis, electrochemical sensors, wastewater treatment, and carbon dioxide (CO₂) capture. In the current study, molecular dynamics simulation was employed to investigate carbon dioxide adsorption behavior on amorphous layered double oxides (LDOs) derived from LDHs at elevated temperatures. The thermal stability of LDHs was first examined by heating the sample up to T = 1700 K. Radial distribution functions confirmed the structural evolution upon heating and the obtained structures were in good agreement with experiments, where periclase was confirmed to be the stable phase in the recrystallized mixed oxides above T = 1200 K. Further, CO₂ adsorption was studied as a function of amorphous HTlc-derived oxide composition, where static and dynamic atomistic measures have been employed to characterize the CO₂ adsorption behavior. The simulation results showed that the CO₂ dynamic residence time on LDH-derived LDOs was sensitive to the Mg/Al molar ratio and the average amount of residence time of CO₂ on the surface of LDOs reached maximum when the Mg/Al molar ratio was equal to 3.0. Meanwhile, the activation energy for diffusion also showed local maximum when the Mg/Al molar ratio was 3.0, suggesting that this particular ratio of Mg/Al mixed oxides possessed the highest CO₂ adsorption capacity. This is consistent with experimental results. Examination of the binding between CO₂ and mixed oxides revealed that both magnesium and oxygen in amorphous LDOs contributed to CO₂ adsorption. Further analysis suggested that the interaction between Mg—O and O(LDO)—C were the most important interactions for the physisorption of CO₂ on amorphous surface and different CO₂ adsorption behavior on different Mg/Al molar ratio surfaces was directly related to their amorphous local structure.

1. INTRODUCTION

Increasing emission of greenhouse gases such as CH₄, N₂O, and CO₂ is a major concern that modern industries are facing all over the world. A robust near-linear relationship between CO₂ emissions and global warming has been established through climate modeling studies. One of the main sources of CO₂ emission is fossil fueled power plants. Pre-combustion CO₂ capture is one of the CO₂ capture and storage (CCS) technologies that involve separating CO₂ from hydrogen-rich atmospheres and fast adsorption and desorption kinetics. The solid CO₂ adsorbents can be divided into three major categories according to their working temperature: low-temperature adsorbents (<473 K), such as carbon-based and zeolite-based adsorbents; intermediate temperature adsorbents (473–673 K), such as layered double hydroxide (LDH)-based and magnesium oxides (MgO)-based adsorbents; and high-temperature adsorbents (>673 K), such as calcium oxides (CaO)-based and silicate-based adsorbents. Among various solid CO₂ adsorbents, LDHs have been recognized as one of the candidate materials for carbon dioxide adsorption in the intermediate temperature regime. LDHs consist of positively charged brucite-like layers with interlayer space containing charge-compensating anions. The general formula for LDHs are [M²⁺₋ₓM³⁺ₓ(OH)₂]₀ₓ₋ₓ⁺ₓAₓ/n⁺ₓ·nH₂O, where M²⁺ is divalent cation (Mg²⁺), some of which are substituted by trivalent cation M³⁺ (Al³⁺), A is an anion (OH⁻, CO₃²⁻, Cl⁻, NO₃⁻) and x is normally in the range of 0.2–0.4.

The structural changes of LDHs during thermal treatment have been experimentally investigated in the previous studies. Using in situ techniques to study the thermal evolution of Mg/Al LDHs, Yang et al. suggested that Mg/Al LDHs first dehydrated between 343 and 463 K while the remaining was the layered structure, then dehydroxylated and transformed into an amorphous phase between 463 and 678 K, and finally lost anions in the temperature range of 678–853 K. It is well accepted that LDHs does not possess appreciable CO₂ capture capacity because of the limited space between the layers. However, the CO₂ adsorption capacity increases significantly within the temperature range of 473–673 K with LDHs gradually losing their compensating anions and OH⁻ and transforming into amorphous mixed oxides. Although the structure has been labeled as amorphous oxide, diffraction
CO2 materials strengthened CO2 capture dramatically. Using M3+ determined the CO2 adsorption capacity. Hutson and et al.18 However, it is noted that both experiments were condition for CO2 adsorption at 303 and 333 K when the Mg/Al molar ratio is between 3.0 and 3.5. Sharma et al.23 had also adopted a series of Mg–Al–CO3 LDHs (M = Al, Fe, Ga, Mn) and demonstrated that it was the optimal parameter determining the CO2 adsorption capacity. Reddy et al.22 found that Mg–Al–CO3 had the highest CO2 capture capacity after calcination at around 673 K. Gao et al.18 conducted a study on the effect of Mg/Al ratio on CO2 capture capacity of amorphous mixed oxide at 673 K. They demonstrated that CO2 capture capacity was the highest when the Mg/Al molar ratio is between 3.0 and 3.5. Sharma et al.23 had also adopted a series of Mg–Al–CO3 LDH samples with varied Mg/Al ratio and concluded that it was the optimal condition for CO2 adsorption at 303 and 333 K when the Mg/Al molar ratio is 1.7, which is different from the results of Gao et al.18 However, it is noted that both experiments were performed in different temperature regions. Nevertheless, the previous studies suggest that the Mg/Al molar ratio is a key parameter determining the CO2 adsorption capacity of the LDH-derived mixed oxides. Recent studies suggested that CO2 uptake capacity of LDH-derived mixed oxides changed with increasing temperature. Marta et al.24 found a decrease in CO2 uptake of Mg–Al–CO3 LDH-derived mixed oxide as the adsorption temperature increased from 323 to 373 K. Moreover, different adsorption sites exhibited different CO2 adsorption capacity. Majority of adsorption sites corresponded to physisorption, and some were chemisorption sites. As a result, the available surface area could be another controlling factor for adsorption.

In the current paper, we present the investigation of a series of MD simulations on the thermal stability of Mg–Al–Cl LDH and CO2 adsorption behavior on LDH-derived oxides. First, we built a series of LDH structure models with six different Mg/Al ratios, that is, 1.0, 1.7, 2.2, 3.0, 3.7, and 4.5. The structural evolution of LDHs containing Mg and Al in the ratio 3.0 during thermal treatment from 300 to 1700 K were then characterized utilizing the radial distribution function (RDF) and XRD. We found that the layered structure of LDHs collapsed at 800 K, where the amorphous LDOs formed. The amorphous structure recrystallized to become oxides, and periclase was observed to be the main phase when temperature reached 1200 K. The oxide structure finally turned to liquid when it was heated up to 1700 K. The atomic local structure of amorphous LDOs was further investigated using Voronoi tessellation and neighbor analysis. Finally, we performed GCMC simulation to examine the static CO2 adsorption behavior on the surface of amorphous LDOs, and it showed similar density distribution at six different Mg/Al molar ratios. To further examine the dynamic adsorption behavior of CO2 on different Mg/Al molar ratios, we calculated the residence time of CO2 on the surface of amorphous oxides determined through dynamic adsorption analyses. We found that the average amount time for CO2 adsorption reached maximum when the Mg/Al molar ratio was 3.0. The CO2 diffusion calculation also suggested that the diffusion barrier for the Mg/Al molar ratio of 3.0 was highest. We further analyzed the partial RDF of Mg2+–O2−, O2− (LDO)–C or Al3+–O2− pairs. It showed that the binding of Mg2+ and O2− were predominant in CO2 adsorption and different CO2 adsorption behavior on different Mg/Al molar ratio surfaces was directly related to their amorphous local structure.

2. SIMULATION METHOD

2.1. Force Field Parameters. The CLAYFF force field39 using empirically derived interaction parameters have been recently employed extensively to model clay minerals, including LDHs.40 In this study, both nonbonded (van der
Waals and Coulombic) and bonded (bond, angle) interactions were applied. The CLAYFF atom type for Mg and Al are octahedral magnesium (mgo) and octahedral aluminum (ao). Oxygen’s partial charges vary from −0.95 for hydroxyl oxygen (oh), to −1.1808 for bridging oxygen with octahedral substitution (obos). Aqueous chloride ion with a partial charge of −1.0 was intercalated into the interlayer region for charge balancing. Zhu et al. have developed a flexible model for CO2 that allows for intramolecular bond stretching and angle bending. Cygan et al. optimized the force field parameters for CO2 to improve the accuracy of symmetrical bond stretch frequency. These force field parameters along with partial charges acquired from a previous study on CO2 adsorption on montmorillonite were used to model CO2.

2.2. Simulation Details. Classical MD simulation was carried out using LAMMPS, developed at the Sandia National Laboratories. An atomic configuration of the simulation cell of Mg3Al1-LDH, containing chlorine intercalated into interlayer region for charge balancing, is illustrated in Figure 1. The simulation cell consisted of 4465 atoms with a dimension of approximately 3.7 nm × 6.4 nm × 2.3 nm. Crystallographic directions of [100], [010], and [001] were oriented along the X-, Y-, and Z-directions, respectively. In the MD simulations, periodic boundary conditions were applied in three dimensions of the system. The time step was 1 fs. After initial construction of the models, energy minimization was conducted until the force and energy tolerance were below 10−5 kcal/(mol Å) and 10−5 kcal/mol, respectively. In the current study, continuous heating was first performed from 300 to 800 K with a heating rate of 2.5 × 1011 K/s to investigate the layer structure collapse of LDHs. Pressure was set to be zero in all dimensions using the Parrinello–Rahman method and Nose–Hoover thermostat was used to control the temperature. As reported in previous experimental studies that after complete collapse of layered structure of LDHs between 623 and 873 K, the LDHs become disordered oxide mixtures, suggesting hydrogen atoms and intercalated ions are no longer existing in the oxides. Following the experimental observation, we manually removed hydrogen atoms, ions, and some of the oxygen atoms to maintain charge neutral after the layered structure of LDHs collapsed at 800 K in the simulation. Then, the simulation was relaxed at 900 K for 2 ns to form amorphous LDOs and further re-heated to 2000 K at the same heating rate. Because some kinetic processes may not reach equilibrium during the continuous heating, isothermal heating for an extended period of time was also performed at the temperatures of interest (e.g., T = 300, 700, 800, 900, 1200, and 1700 K) to ensure a better equilibrium. The typical simulation time was 2 ns, and the atomic configurations were dumped every 2 ps for data storage and analysis during isothermal treatment.

To obtain the amorphous LDOs at room temperature to further examine CO2 adsorption behavior, the amorphous LDOs at T = 900 K were then cooled down to 300 K with a cooling rate of 2.0 × 1011 K/s through an NPT ensemble. The structure was further equilibrated at 300 K through an NVT ensemble with two free surfaces in Z-direction for 2 ns. To study the CO2 adsorption on amorphous LDOs, different numbers of CO2 were added into the vacuum gap between the two free surfaces, and the CO2 adsorption simulation was performed for 2 ns in the NVT ensemble.

Voronoi tessellation was applied to investigate the local packing and the coordination number of atoms of the amorphous LDOs. A Voronoi diagram is a partitioning of a volume into regions based on distances from a reference point to others in a specific subset of the volume. For each set of points, there is a corresponding region consisting of all points closer to that seed than to any other, and the region is called a Voronoi cell. It is noted that the number of faces of a Voronoi cell is equal to the coordination number.

2.3. CO2 Static Adsorption Simulations. The static adsorption of CO2 on amorphous LDOs was studied using GCMC simulations. After equilibrating the amorphous LDO configurations at 300 K, a vacuum gap of 5 nm was added to the Z-direction to build two free surfaces parallel to the XY plane. The adsorption isotherms were then calculated through series of fixed pressure GCMC simulations at 300 K. During each fixed pressure GCMC simulation, CO2 were randomly created in and deleted from the framework. Molecules within the framework were also randomly translated and rotated with maximum amplitudes of 1 Å and 5°, respectively. The configuration that results from one of these steps is accepted.
or rejected according to the Metropolis criterion. Initial $1 \times 10^6$ steps were used to equilibrate the system, followed by $2 \times 10^6$ steps of the production run from which the average loading and energy were calculated.

The amount of the adsorbed CO$_2$ (surface excess) at each pressure was obtained from the difference between the average loading of CO$_2$ in the presence and absence of the adsorbent (LDOs). The latter was calculated through GCMC simulation of an empty box having the same volume as accessible to the gas molecules in the presence of the adsorbent. The GCMC simulations of the empty boxes were also used to build the equation of state of the CO$_2$ model used in this study. On the basis of the calculated equation of state, the pressure of 50 bar was chosen for adsorption dynamics analysis. The most stable configurations (having the lowest potential energy) resulted from GCMC simulations at 50 bar were also saved for further MD simulations. All GCMC simulations were performed using sorption module in the Materials Studio 8.0 software package.

3. RESULTS AND DISCUSSION

3.1. Structural Evolution of LDH upon Heating. Figure 2 shows the potential energy ($E_{\text{potential}}$) as a function of temperature over a temperature range from 300 to 900 K for a Mg–Al–Cl-LDH with Mg/Al ratio of 3.0. Evidently, there is an abrupt jump in the potential energy around 800 K, which indicates that the layered structure of the LDH begins to collapse and transforms into an amorphous state. The inset shows the corresponding RDFs between all species from 300 to 800 K. The RDF at 300 K shows a typical pattern of crystalline structure including a sharp peak centered at $\sim 2.1$ Å and peaks at other interatomic distances. The RDFs do not exhibit significant changes with increasing temperature from 300 to 700 K, which indicates that the Mg/Al-LDH retains its layered crystalline structure. However, at 800 K the original sharp peak at $\sim 2.1$ Å becomes significantly weakened, suggesting that the original layered crystalline structure starts to collapse.

When temperature was higher than 700 K, LDHs began to dehydroxylate and bonds between atoms were gradually broken, as indicated by the previous study. Figure 3 supports such observation as the average bond distances of Mg–O increase abruptly when temperature is higher than 700 K, suggesting that magnesium oxide is transformed from a crystalline structure into an amorphous state. The result is consistent with the bond distance in layered mineral brucite Mg(OH)$_2$ calculated by D’Arco et al. In general, crystalline phases have higher density and shorter average bond lengths than those of liquids. However, Gutiérrrez et al. investigated the structural properties of liquid Al$_2$O$_3$ using MD and demonstrated that the liquid phase of Al$_2$O$_3$ was indeed denser than the crystalline phase and possessed larger fraction of tetrahedral coordinated Al, suggesting that the bond length of Al–O was longer in the crystalline phase than in the amorphous state. In the current study, the Al atoms substitute Mg atoms in the LDHs structure that cause the Al–O bond length in LHDs longer than that in Al$_2$O$_3$ crystal. Hence, we should expect a drop in Al–O bond length as the structure transfers to the amorphous state. As expected, the average Al–O bond distance shown in Figure 3 exhibits an abrupt drop when the temperature is higher than 700 K, which confirms this structural change.

After the layer structure of LDHs collapsed, we removed hydroxyl and anions and then continued to maintain the system at 900 K for 2 ns to form amorphous LDOs and then to heat to 2000 K to examine structural change in LDOs. Figure 4 shows the change in potential energy of LDOs by increasing the temperature from 900 to 1700 K. With increasing temperature, the potential energy of amorphous LDOs continuously increases between 900 and 1700 K. However, there exists an abrupt drop at 1200 K, which manifests another phase transformation. RDF diagrams in the inset of Figure 4 show a typical amorphous structure with two broad peaks centered on 2 and 2.8 Å at 900 K. This indicates that LDH transforms to an amorphous structure. However, the RDF at 1200 K shows four distinct broad peaks centered on $\sim$ 2, 3, 4.8, and 6.6 Å, indicating the emerging of crystalline structure of LDOs. The sharp jump in potential energy around 1700 K suggests a first-order phase transformation, in which the LDOs melt to the liquid state. The RDF at 1700 K indicates that the structure has transformed back to amorphous (i.e., melting of the LDOs).

To further examine the structural evolution of LDH, XRD patterns were calculated at different temperatures. Figure 5 summarizes these patterns. They indicate that the thermal evolution involves three stages. In the first stage, which is from 300 to 700 K, XRD patterns show sharp peaks implying that there is no significant change of layered structure in LDH. The XRD pattern of LDH from simulation indeed agrees very well with experimental observations. However, the layered
structure of LDH begins to collapse and transforms into an amorphous structure at 800 K (the second stage), as no obvious peaks appeared. With further temperature increase, two broad peaks centered at $2\theta \approx 30^\circ$ and $2\theta \approx 60^\circ$ at 900 K manifests the formation of amorphous LDOs. The two peaks centered at $2\theta \approx 42.8^\circ$ and $62.0^\circ$−$62.4^\circ$ at 1200 K indicate that amorphous LDOs recrystallize. This is in agreement with previous observations,57,58 which indicate that periclase (MgO) is the main observed phase in Mg3Al1-LDH-derived mixed oxides (see the inset). In the third stage, crystalline LDOs melt and return to an amorphous structure at 1700 K.

### 3.2. Local Structure of Amorphous LDOs.

We cooled down the amorphous LDOs from 900 to 300 K using a cooling rate of $2 \times 10^{11}$ K/s. The structure of amorphous LDOs was then maintained at 300 K for another 2 ns. The atomic configuration of amorphous LDO is illustrated in Figure 6a. To examine the structure of amorphous LDO at 300 K, the local structure of each atom, especially its coordination number in the simulation cell, was determined. In the current study, the coordination number is defined as the number of oxygen atoms surrounding a central atom (Mg here) in the first neighbor. Voronoi tessellation has been applied to calculate the coordination number of magnesium with different Mg/Al molar ratios, as shown in Figure 6b. The coordination number of magnesium atom is close to 6 when the Mg/Al molar ratio is 3.0, which means that each magnesium atom is surrounded by 6 atoms on average. However, the coordination number of magnesium is close to 5 when the Mg/Al molar ratio is other than 3.0. The percentage of coordination number of 5 is close to 100 percent for Mg/Al molar ratios of 1.7 and 2.2 and it is near 70% for an Mg/Al molar ratio of 3.7. In other words, the coordination number of magnesium is the highest when the Mg/Al molar ratio is 3.0. The inset of Figure 6b shows the probability of finding oxygen in Mg2+ for four different molar ratios. Most magnesium atoms are surrounded by five oxygen atoms when the Mg/Al molar ratio is 3.0. However, most magnesium atoms are surrounded by four oxygen atoms when the Mg/Al molar ratio is 1.7, 2.2 or 3.7. It can be concluded that the structure of amorphous LDOs at 300 K varies with the Mg/Al molar ratio and the magnesium atoms of amorphous LDOs tend to bind with more atoms, especially oxygen atoms when the Mg/Al molar ratio is 3.0.

### 3.3. CO2 Adsorption Behavior on Amorphous LDOs.

To examine CO2 adsorption behavior as a function of amorphous oxide composition, amorphous LDO models with six different Mg/Al molar ratios were employed, that is, Mg/Al = 1.0, 1.7, 2.2, 3.0, 3.7, and 4.5. The CO2 adsorption behavior of LDH-derived amorphous LDOs was investigated at room temperature using two different approaches: static and dynamic adsorption analysis. Static adsorption analysis was performed using GCMC simulations, whereas MD simulations were used to study the dynamics of CO2 adsorption on LDOs. In GCMC simulations, the pressure range of adsorption isotherms was assigned according to the equation of state of the CO2 model used in this study (see Figure 7). In fact, we have performed multiple simulations at different pressures based on this calculated equation of state, and the pressure of 50 bar was chosen for MD simulations and adsorption dynamics analysis. Choosing such a high pressure enabled us to access better statistics while ensuring that CO2 would still behave as a gas.

#### 3.3.1. Static Adsorption Analysis.

To calculate the amount of adsorbed CO2 on the surface of LDOs, two sets of GCMC simulations were required. In the first set, the ensemble averaged mass of CO2 in the presence of LDO adsorbents, $\langle m_{\text{tot}} \rangle$, was calculated at different pressures based on this calculated equation of state, and the pressure of 50 bar was chosen for MD simulations and adsorption dynamics analysis. Choosing such a high pressure enabled us to access better statistics while ensuring that CO2 would still behave as a gas.
The excess CO2 adsorption per surface area $m_{\text{ex}}$ is then calculated as

$$m_{\text{ex}} = \frac{(\langle m_{\text{tot}} \rangle - \langle m_0 \rangle)}{2A} \quad (1)$$

where $A$ is the area of the free surfaces of LDOs. Calculated adsorption isotherms are shown in Figure 8.

As mentioned before, the most stable configurations resulted from GCMC simulations at 50 bar were used as the initial configuration of NVT simulation at 300 K. These NVT simulations were used to calculate the density profile of CO2 and further dynamic adsorption analysis. Figure 9 shows a sample of configurations resulted from GCMC and the density profile calculated from the MD simulations.

The accumulation of the CO2 molecules near the LDO surfaces can be recognized in both atomic configuration and density profiles shown in Figure 9. Two distinct peaks which emerge near the LDO surfaces in the density profiles are the confirmation that CO2 molecules formed multiple adsorption layers consistent with the shape of the adsorption isotherms shown in Figure 8. Formation of the second adsorption layer is due to the high pressure (50 bar) at which the density profiles were calculated. The position of peaks in the density profiles is used to define the adsorption region for the dynamic adsorption analysis. Similar to adsorption isotherms, density profiles of LDOs with different Mg/Al ratios do not show significant differences.

3.3.2. Dynamic Adsorption Analysis. For the dynamic CO2 adsorption, we used the definition proposed by Impey et al., which was first employed to calculate the residence time of adsorbed water molecules and has been used extensively to study the hydration behavior of ions, surfaces, and nanostructures. Following our previous work, we use a simplified version of this quantity defined as

$$\tau_i(t) = \sum (P_i(t_0, t)) \Delta t \quad (2)$$

where $\tau_i(t)$ is the $i$th CO2 residence time within a distance criterion for adsorption at $t$, $P_i(t_{0}, t)$ is a parameter of the $i$th CO2 molecule which takes values of 0 or 1. $P_i(t_{0}, t)$ equals to 1 if CO2 molecules are marked as adsorbed on the surface of amorphous LDOs at $t_0$ and $t$, and it has not left out of the specific distance for any continuous period between $t_0$ and $t$. Under other circumstances, it takes a value of 0. $\Delta t$ is the time interval at which the observation is made to check adsorption of the $i$th CO2. In this definition, $t_0$ is updated if a CO2 molecule leaves the adsorption layer and comes back to it. This means that each CO2 molecule has multiple residence times, and we can calculate the number of adsorbed CO2 within a specific time window. Figure 10 shows the typical semilog plot of residence time versus amount of adsorbed CO2 for LDO with Mg/Al = 3.0 at $P = 50$ bar. Dynamic adsorption analysis performed in lower pressure show similar trends; thus, we present only the results corresponding to $P = 50$ bar to avoid redundancy. As mentioned before, using the highest pressure at which CO2 acts as a good gas also enables us to access to better statistics.

Previous study suggests that individual CO2 molecules could reside near the defects on the surface for an extended period of time, and majority of CO2 molecules would dynamically visit and leave the surface, which makes the residence time of CO2 a dynamic value. A cutoff distance of 9 Å has been used to define a CO2 as adsorbed on the surface for all six samples with different Mg/Al ratios. This value is chosen according to density profile of CO2 near the oxide surface (see Figure 9b). Three distinctive regions can be recognized in the residence time diagram of CO2 molecules in Figure 10. In region I, there are a few number of CO2 molecules with relatively long residence times for more than 600 ps. In region III, CO2 molecules visit the adsorption layer with high frequency but
stay in this layer for short periods of time. None of these two regions in the semilog plot shows linear relationship. In region II, the residence time versus amount of CO₂ in semilog plot follows linear relationship; phenomenologically, we can express the residence time as follows.

\[ \tau \approx e^{-n/\langle n \rangle} \] (3)

where \( \tau \) represents the residence time, \( n \) is the number of adsorbed molecules, and \( \langle n \rangle \) is the average number of molecules adsorbed on the surface. We believe that the region II represents the steady-state adsorption behavior of CO₂ on the surface.

To compare CO₂ adsorption behavior between different Mg/Al molar ratios, the number of average adsorbed CO₂ in region II was rescaled by the surface area of each composition, as shown in the inset of Figure 10. This inset clearly shows that the dynamic adsorption behavior of CO₂ molecules on the LDH-derived amorphous LDOs is sensitive to the Mg/Al molar ratio. Overall, with the increasing Al content, the amount of average adsorbed CO₂ increases and reaches maximum when the Mg/Al molar ratio is equal to 3.0. Gao et al. also investigated the effect of the Mg/Al molar ratio on CO₂ adsorption at high temperatures, and our observations here agree well with their experimental results. It is worth mentioning that CO₂ adsorption simulations in this study were performed at room temperature, and the adsorption of CO₂ at high temperatures deserves further investigation.

3.4. CO₂ Diffusion. The other related dynamic property of CO₂ adsorption is the diffusion of molecules on the surface. The mean square displacement (MSD) of CO₂ was calculated for all CO₂ molecules within a specified time interval \( \Delta t \). The MSD was then defined as

\[ \text{MSD} = \frac{1}{N} \sum_{n=1}^{N} [r_n(t_0 + \Delta t) - r_n(t_0)]^2 \] (4)

where \( N \) is the total number of atoms and \( r(t_0) \) is the position of the atom at \( t_0 \). The MSD of carbon dioxide was calculated at
five different temperatures from 240 to 350 K for each composition, and four representative MSD for Mg/Al molar ratio of 3.0 are shown in Figure 11a.

The slope of MSD versus time intervals is proportional to the diffusion coefficient $D$, and the temperature dependence of the diffusion coefficients can be well approximated by

$$D = D_0 e^{-Q/RT}$$

where $D_0$ is pre-exponential factor and $Q$ is the activation energy for diffusion. Figure 11b shows the Arrhenius temperature dependence of diffusion coefficients along with the activation energy for diffusion. The activation energy for diffusion obtained in the current study falls into the same ballpark of previous studies. The inset shows that activation energy of CO$_2$ diffusion as a function of LDO composition, and it suggests that Mg/Al molar ratio of 3.0 possesses the highest diffusion barrier. The result is consistent with the results of the dynamic CO$_2$ adsorption analysis (see the inset of Figure 10).

3.5. Correlation between Structure and Dynamics Adsorption Behavior. Both dynamic adsorption behavior and diffusion coefficient data point to the direction that the Mg/Al molar ratio of 3.0 possesses the highest CO$_2$ adsorption capacity. How does this dynamic property relate to the amorphous LDO composition? We further investigated the binding arrangement between CO$_2$ and amorphous LDOs to examine the potential correlation. Bolognini et al. demonstrated that the chemical reaction between CO$_2$ and Mg$^{2+}$–O$_2^-$ or Al$^{3+}$–O$_2^-$ pairs was a key parameter for CO$_2$ adsorption, and Yong and Rodrigues concluded that increasing the aluminum content strongly affected CO$_2$ adsorption because of larger partial charge of Al. Unfortunately, in the MD simulation, we can only observe physisorption; therefore, we examine the binding arrangement between CO$_2$ molecules and atoms on the surface. In the

Figure 12. Partial RDFs of CO$_2$ and amorphous LDO, (a) Mg/Al molar ratio of 1.0 (b) Mg/Al molar ratio of 1.7 (c) Mg/Al molar ratio of 2.2, (d) Mg/Al molar ratio of 3.0, (e) Mg/Al molar ratio of 3.7, and (f) Mg/Al molar ratio of 4.5. Mg–O and Al–O represent the respective binding arrangement between CO$_2$ and magnesium and aluminum in the amorphous LDO, respectively, O(LDO)–C represents the binding arrangement between CO$_2$ and oxygen in the amorphous LDO.
current study, only heterocharges of amorphous LDO are considered, such as Mg$^{2+}$−O, Al$^{3+}$−O, and O$^{2−}$−C, because homocharges will possess repulsive force between CO$_2$ molecules and amorphous LDO. Mg−O, Al−O, and O−(LDO)−C binding lengths are studied, as they interact through relatively strong Columbic interaction, and the RDF of atoms has been rescaled as follows:

$$g^*(r) = g(r) \times N_{pairs}$$  \hspace{1cm} (6)

where $N_{pairs}$ is the number of pairs of atoms where one atom is from each of two selections. Here, the $N_{pairs}$ for partial RDF is the product of number of atoms of amorphous LDO (Mg, Al or O) and O or C of CO$_2$ molecules.

Figure 12 shows the rescaled partial RDF of atoms on the surface of amorphous LDO with different Mg/Al molar ratios. The pair RDF of Al−O indicates that the binding length of Al−O is the longest, suggesting that aluminum atoms on the surface of amorphous LDO possess weak interaction. It is also noticed that the binding length of Mg−O is the shortest, which indicates that magnesium atoms on the amorphous surface are mainly bound with the CO$_2$ in the first adsorption layer. Figure 13 shows the integrated $g^*(r)$ of Mg$^{2+}$, which is related to the coordination number on the surface, in amorphous LDO in six different Mg/Al molar ratios. It reveals that the binding between Mg$^{2+}$ or O$^{2−}$ and CO$_2$ is relatively high for Mg/Al molar ratio = 3.0. This is also related to the fact that the Mg in the bulk amorphous LDOs with a Mg/Al molar ratio of 3.0 have higher coordination number and are on the surface, and they tend to bind with more atoms, as suggested in Figure 6b. It shows that the integrated $g^*(r)$ between Mg$^{2+}$ on the surface and the first CO$_2$ adsorption layer is the most predominant, whereas the binding fraction of Al−O is negligible, which is consistent with the results of partial RDF.

**4. CONCLUSIONS**

MD simulations were performed to investigate the structural change of LDHs during the thermal treatment and CO$_2$ adsorption behavior on LDOs. The layered structure of LDHs began to collapse at ~800 K. The hydroxyl groups and anions were removed after structural collapse, and amorphous LDOs were obtained. Amorphous LDOs recrystallized at 1200 K and retained their crystalline structure between 1200 and 1700 K. The crystalline structure of LDOs at 1200 K is close to that of periclase. With the increasing temperature, LDOs melt to a liquid at 1700 K. The static and dynamic CO$_2$ adsorption behavior of the amorphous LDHs with different Mg/Al ratios was studied. We showed that most of the CO$_2$ molecules were captured within 9 Å from the surface and fewer CO$_2$ molecules moved freely in the free space above the surface of amorphous LDOs. Among the six different Mg/Al molar ratios used (1.0, 1.7, 2.2, 3.0, 3.7, and 4.5), a higher CO$_2$ diffusion barrier was found when the Mg/Al molar ratio was 3.0. The amount of adsorbed CO$_2$ on amorphous LDOs was also the highest at the same molar ratio, which was in agreement with previous experimental studies. As reported in Gao et al., the CO$_2$ adsorption capacity when Mg/Al ratio is 3.0 is approximately 30% higher than that in ratio 1.7. However, the ratio at 3.0 is only about 15% higher than that in ratio 1.7 in current simulation study, and this discrepancy could be attributed to the fact that the classical MD simulation deals only with interactions such as columbic, van der Waals forces between molecules, that is, physisorption, while both physisorption and chemisorption could be important in experiments. The partial RDF of atoms on the surface of amorphous LDO suggests that magnesium atoms contribute to the first-layer CO$_2$ capture. The binding arrangement between CO$_2$ molecules and amorphous LDO surface indicates the binding between magnesium and oxygen predominant in CO$_2$ adsorption. A relatively higher integrated $g^*(r)$ of Mg−O and O(LDO)−C when the Mg/Al molar ratio is 3.0 indicates that magnesium atoms incline to attract more of surrounding atoms, especially oxygen. This result is supported by the fact that the $g^*(r)$ of Mg−O is also highest at the same ratio. It can be concluded that the CO$_2$ capture capacity of amorphous LDOs is closely related to the Mg/Al molar ratio because of the high value of $g^*(r)$. This study describes a promising simulation method to investigate the characteristics of LDHs and LDH-derived amorphous LDOs and the results provide molecular-scale insight into the structural and dynamical origins of the interactions of CO$_2$ with LDHs. This can be helpful to design LDOs structures with optimal CO$_2$ capture capacities.

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**Notes**
The authors declare no competing financial interest.

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