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ABSTRACT

We have performed first-principles density functional theory calculations, incorporated with van der Waals interactions, to study CO2 adsorption and diffusion in nanoporous solid – OMS-2 (Octahedral Molecular Sieve). We found the charge, type, and mobility of a cation, accommodated in a porous OMS-2 material for structural stability, can affect not only the OMS-2 structural features but also CO2 sorption performance. This paper targets K+, Na+, and Ba2+ cations. First-principles energetics and electronic structure calculations indicate that Ba2+ has the strongest interaction with the OMS-2 porous surface due to valence electrons donation to the OMS-2 and molecular orbital hybridization. However, the Ba-doped OMS-2 has the worst CO2 uptake capacity. We also found evidence of sorption hysteresis in the K- and Na-doped OMS-2 materials.

I. Introduction

The capture and storage of carbon dioxide from fossil fuel power plant emissions are important tasks that scientists are facing today [1]. Research has shown that adsorption of CO2 onto solids can be an effective method for selectively separating CO2 from flue gases [2-7]. This method has a lower parasitic energy than current aqueous technologies and could potentially replace them [6,8-11]. Porous solids, including zeolite membranes, molecular sieves, and metal organic frameworks are preferential for gas adsorption because of their high surface areas [4-7,12-18]. These materials can have a variety of pore geometries and sizes which can affect the CO2 adsorption and desorption properties [6,19-22]. There is also the potential for further “tuning” of the properties by chemical substitution making these great candidates for ‘materials-by-design’ applications [5,6,9,18]. Extensive computational studies confirm the need to explore the structural behavior of CO2 with an analysis of relative van der Waals (vdW) bonding for metal organic framework candidates [2,6,17,18,23,24]. However, many of these materials experience hysteresis in their adsorption and desorption processes which increase the parasitic energy. Understanding the mechanism behind this hysteresis is necessary for advancing these materials into industrial applications.

Manganese dioxide α-MnO2, referred to as OMS-2, is a nanoporous octahedral molecular sieve (OMS) that experiences CO2 hysteresis [21,22,25]. The framework of the OMS-2 structure is made up of edge-sharing MnO6 octahedra that form relatively small (1×1) and large (2×2) tunnels. These tunnels act as one-dimensional “traps” where CO2 adsorption and molecular sieving processes can occur[2]. The OMS-2 structure requires the presence of cations inside the large (2×2) tunnels that act as a means of structural support. Common dopants for this system
include K\(^+\), Ba\(^{2+}\), Na\(^+\), and Pb\(^{4+}\) [21,22,25]. Previously, we found that adding K\(^+\) ions to the (2×2) tunnels leads to hysteresis looping in the adsorption and desorption isotherms [26]. The onset of hysteresis only occurs at experimental partial pressures exceeding 7 bar (700 kPa). This study revealed the importance of understanding the CO\(_2\) sorption mechanism and the physical factors involved.

Density functional theory (DFT) calculations with van der Waals forces revealed CO\(_2\) sorption on K-doped OMS-2, known as cryptomelane [27]. We investigated the diffusion of CO\(_2\) through the (2×2) tunnel and found that the K\(^+\) dopant acts as a ‘gate keeper’ blocking the path of the CO\(_2\) molecules. When the concentration of CO\(_2\) is increased (>7 bar pressure), the activation energy barrier for the CO\(_2\) to bypass K\(^+\) reduces significantly. This allows the CO\(_2\) to become trapped behind K\(^+\), hindering desorption. More recently, we compared the sorption behavior of Ba-doped OMS-2, known as hollandite, to the results from cryptomelane [9]. The higher-charge cation Ba\(^{2+}\) was found to perform worse in the CO\(_2\) sorption than the lower-charge cation K\(^+\). This could be attributed to the stronger binding energy of Ba\(^{2+}\) with the OMS-2 porous surface.

In further studying the cation effect, this paper compares K\(^+\), Na\(^+\), and Ba\(^{2+}\) cations in the OMS-2, including their structural features, interactions with the pore surface, and CO\(_2\) adsorption and diffusion mechanisms. These studies identify key factors controlling CO\(_2\) uptake capacity and help develop high-performance porous solids for carbon capture and storage.

II. Computational Methods

The Vienna ab-initio Software Package (VASP)[28] was performed within density functional theory (DFT) to conduct all structural, energetic, and electronic structure calculations. The spin-polarized generalized gradient approximation (GGA) was used within the Perdew Burke Ernzerhoff formalism revised for solid systems (PBEsol)[29]. The plane-wave basis sets were expanded using projector-augmented wave (PAW) pseudopotentials[30,31] to a cutoff energy of 400eV. To account for the d-orbitals of Mn, the GGA+U approach of Liechtenstein et al [32] was employed, where an effective on-site Coulomb potential (U) of 2.8eV and an exchange potential (J) of 1.2eV were applied to the system. The Brillouin zone integration was performed on a 6x6x6 Monkhorst-Pack mesh. To account for Fermi surface broadening, a Gaussian smearing value of 0.05eV was applied. The Mn atoms have an antiferromagnetic interaction with magnetic moments of ±4 \(\mu_B\) [33,34] All relaxations of the unit cell along the \(a\) axis. The 1x3x1 supercell was found to be energetically favorable and was used to elongate the tunnels formed by the edge-sharing MnO\(_6\) octahedra. We used the cell of X\(_{Mn_24O_48}\) (i.e. X\(_{0.04MnO_2}\)), where X = K, Na, or Ba, and varied CO\(_2\) concentration in the cell to provide insight into the CO\(_2\) sorption mechanism.

III. Results and Discussion

K\(^+\), Na\(^+\), and Ba\(^{2+}\) Cations

The equilibrium parameters of undoped 1x3x1 \(\alpha\)-MnO\(_2\) supercell (i.e. with no cation) are \(a = 9.702 \text{ Å}, b = 2.856 \text{ Å},\) and \(c = 9.685 \text{ Å}\). In order to accommodate the cations and CO\(_2\) molecules in the (2×2) tunnel, we tripled the unit cell along the \(b\) axis. The 1x3x1 supercell was found to be energetically favorable and was used to elongate the tunnels formed by the edge-sharing MnO\(_6\) octahedra. We used the cell of X\(_{Mn_24O_48}\) (i.e. X\(_{0.04MnO_2}\)), where X = K, Na, or Ba, and varied CO\(_2\) concentration in the cell to provide insight into the CO\(_2\) sorption mechanism.
cation is Site A, which neighbors with eight oxygen atoms. The α-MnO₂ cell volume increase in the presence of K⁺ and Ba²⁺ causes the slightly longer distances between the cation and its closest Mn and O than those for Na⁺ (Table 1).

To analyze the cation – α-MnO₂ interaction, the binding energy $E_b$ of a cation is defined as:

$$E_b = \frac{E_{\text{tot, doped}} - E_{\text{tot, undoped}} - nE_{\text{dopant}}}{n}$$

where $E_{\text{tot, doped}}$ and $E_{\text{tot, undoped}}$ are the total energy of Mn₂₄O₄₈ doped with and without a cation, respectively. $E_{\text{dopant}}$ is the energy of an individual K, Na, or Ba atom, and $n$ is the number of cations in the cell.[9,34] $E_b$ between cation and α-MnO₂ is 4.48eV/K⁺, 4.18 eV/Na⁺, and 8.34eV/Ba²⁺, indicating a strong interaction. Ba²⁺ donates more valence electrons to α-MnO₂, leading to much higher $E_b$ than that of K⁺ and Na⁺. Interestingly, the same-charged cations K⁺ and Na⁺ also have slightly different $E_b$.

It is worth noting that during synthesis of these compounds, H₂O molecules can be found to coordinate with the cation and hinder CO₂ adsorption uptake [26,34]. However, in a previous experimental study of K-doped OMS-2, it has been shown that upon heating to 150°C, the H₂O can be removed without affecting the K⁺ dopant [34]. This is likely due to the difference in binding energy between the H₂O molecule (0.39 eV) and the K⁺ dopant (> 4 eV) in α-MnO₂ [34]. Given that the other cations investigated in this study have similar or greater binding energies than K⁺, it is reasonable to assume the same ease of H₂O removal from their compounds as well.

Adding a cation to α-MnO₂ also reduces Mn⁴⁺ to Mn³⁺.[34,38] Our calculations showed that each donated electron is shared by several Mn, resulting in non-integer charges on the Mn. We calculated the electronic structures of undoped and doped α-MnO₂ and compared them to provide detailed insight into the cation effect on the molecular orbitals of the α-MnO₂. Fig 2(a) – (c) shows the DOS (density of states) of α-MnO₂ doped with K, Na, and Ba, compared with the DOS of K, Na, and Ba individually. The Fermi energy is zero in each case. Undoped α-MnO₂ is a semiconductor with a band gap of 1.33 eV (see the DOS of undoped α-MnO₂ in Fig 2(d)). In the presence of a cation, the conduction band of α-MnO₂ is shifted below the Fermi energy at zero due to the accumulated electrons from the cation, leading to the n-type conduction and the ionic characteristics of the cation – α-MnO₂ bonds. For K and Ba doping, molecular orbital hybridization also occurs on the higher energy level between -13 eV and -12 eV, indicating the covalent characteristics of the cation – α-MnO₂ bonds. This feature explains the binding energy, $E_b$, difference for K⁺ and Na⁺ in α-MnO₂. Fig 2(d) combines the DOS curves of doped and undoped α-MnO₂. Cation doping can minimize the band gap of α-MnO₂. Ba doping provides the calculated band gap of 1.14 eV, smaller than 1.29 eV with K doping. Experimentally, the band gap for cryptomelane, i.e. α-MnO₂ with K⁺, is 1.32 eV [39], agreeing well with our calculations.

CO₂ Sorption

CO₂ adsorption in the OMS-2 tunnel more greatly affects the structure of α-MnO₂ than cation doping does. Table 2 shows that this effect is larger for the K- and Ba-doped systems with cell volume increases of 1.00% and 0.97%, respectively. The Na-doped system is the least affected with a cell volume increase of only 0.63%. However, the CO₂ adsorption enlarges the volume change by three times more than the cation-doped system without CO₂.

Cations are distributed along the OMS-2 (2x2) tunnel. When CO₂ diffuses in the tunnel and encounters a cation, there are three possible scenarios (Fig. 3). For different cations, we estimated an activation energy barrier for each scenario. The lower activation energy barrier represented the more favorable scenario for the cation.

- Scenario I: CO₂ does not continue diffusing, and it remains in a stable position.
- Scenario II: CO₂ continues diffusing, and it can bypass a cation.
- Scenario III: CO₂ continues diffusing, and it can push a cation away.

With a low concentration of CO₂ in the K-doped OMS-2 (averagely KMn₂₄O₄₈ with one CO₂ molecule), CO₂ is kinetically trapped in a position away from a K⁺ cation with the equilibrium distance of 3.0Å. Due to a high activation energy barrier of ~6eV/CO₂, CO₂ remains in the equilibrium position without further diffusion (Scenario I,
Fig 3(a)). As the concentration of CO$_2$ increases, the activation energy barrier minimizes to 0.13 eV/CO$_2$ [26], smaller than a diffusion energy barrier of 0.37 eV for a K$^+$ cation. These computational results suggest Scenario II (Fig 3(b)), where CO$_2$ bypasses a K$^+$ cation to further diffuse along the OMS-2 tunnel when CO$_2$ has a high concentration (averagely KMn$_{24}$O$_{48}$ with two or more than two CO$_2$ molecules). The reduction in activation energy barrier indicates that at elevated CO$_2$ partial pressures, the transition state becomes more energetically favorable [26].

In the Ba-doped OMS-2, the activation energy barrier for CO$_2$ diffusion decreases from 6.87 eV/CO$_2$ to 1.02 eV/CO$_2$ due to the CO$_2$ concentration increase, but the barrier is still higher than that in the K-doped OMS-2. It is not low enough to be overcome. Thus, CO$_2$ is stuck in the optimum position with a distance of ~3Å (Scenario I). No further diffusion occurs. This mechanism suggests worse CO$_2$ uptake performance of the Ba-doped OMS-2.

Table 3 summarizes different CO$_2$ sorption mechanisms in the OMS-2 with K, Na, and Ba doping. Scenario I occurs in all three cases. After adsorption, CO$_2$ is thermally activated to diffuse in the OMS-2 tunnel until it encounters a cation. For a K$^+$ cation, CO$_2$ bypasses it to further diffuse along the OMS-2 tunnel (Scenario II). For a Na$^+$ cation, CO$_2$ continues diffusing by pushing the cation (Scenario III). These scenarios are illustrated in Figure 3. For a Ba$^{2+}$ cation, CO$_2$ remains in an optimum position with no further diffusion. These mechanisms suggest a sorption hysteresis. The phenomenon of sorption hysteresis commonly occurs in gas molecule adsorption and desorption isotherms. This indicates that the path to adsorption of gas molecules by a porous host differs from that of desorption.

Even though it has the worst CO$_2$ uptake capacity, the Ba-doped OMS-2 is expected to have the smallest hysteresis. Upon desorption (e.g., a pressure decrease) CO$_2$ can easily exit the OMS-2 tunnel. In contrast, CO$_2$ can diffuse farther in the OMS-2 tunnel by passing through a K$^+$ cation and pushing a Na$^+$ cation. These mechanisms require a
longer time to vacuum CO\textsubscript{2} in the OMS-2 tunnel, yielding the phenomenon of sorption hysteresis. The Na-doped OMS-2 should have a slightly smaller hysteresis than the K-doped OMS-2. In Scenario II, upon desorption CO\textsubscript{2} has to pass through the K\textsuperscript{+} cation in reverse. This action costs an energy penalty and requires more time than the Na\textsuperscript{+} cation case, where CO\textsubscript{2} can directly exit the tunnel with no need to pass any Na\textsuperscript{+} cation. The computational prediction has been validated by our experiment, which will be published in another experimental paper soon. Our results suggest that the charge, size and mobility of cation accommodated in a porous material control the CO\textsubscript{2} uptake capacity and sorption hysteresis.

\section*{IV. Conclusions}

We have performed first-principles quantum mechanical simulations, based on density functional theory incorporated with van der Waals interaction (DFT+vdW), to study cation effects on the OMS-2 structure and CO\textsubscript{2} sorption. K\textsuperscript{+}, Na\textsuperscript{+}, and Ba\textsuperscript{2+} cations have to be accommodated in the OMS-2 tunnel for structural stability. The charge and type of the cation affect the OMS-2 structure where the K\textsuperscript{+} and Ba\textsuperscript{2+} cations lead to a cell volume increase while the Na\textsuperscript{+} cation decreases the cell volume. Conversely, the like-charge K\textsuperscript{+} and Na\textsuperscript{+} cations have the smaller binding energies with the porous surface of the OMS-2 than the higher-charged Ba\textsuperscript{2+} cation. Besides the charge and type, cation mobility is also found to control the CO\textsubscript{2} uptake capacity and sorption mechanism of OMS-2. The diffusion of adsorbed CO\textsubscript{2} is hindered by the cations, which act as ‘gatekeepers’ blocking the CO\textsubscript{2} diffusion. It traps CO\textsubscript{2} within the OMS-2 leading to a sorption hysteresis. After adsorption, CO\textsubscript{2} diffuses until it encounters a cation. Three possible mechanisms occur, depending on an activation energy barrier for further CO\textsubscript{2} diffusion and cation mobility. Scenario I involves CO\textsubscript{2} becoming kinetically trapped in an equilibrium position with no further diffusion. Scenario II is that CO\textsubscript{2} bypasses the cation to further diffuse along the OMS-2 tunnel. Scenario III is that CO\textsubscript{2} continues diffusing by pushing the cation away. In all three cation cases, Scenario I occurs. In the K- and Na-doped OMS-2, CO\textsubscript{2} can diffuse further through Scenarios II and III, respectively. These mechanisms also suggest that the Ba-doped OMS-2 should have the smallest sorption hysteresis, followed by the Na-doped OMS-2, and finally the K-doped OMS-2. Our studies provide detailed insights into the interactions between cations and OMS-2 and the CO\textsubscript{2} sorption performance of OMS-2. The results reveal that CO\textsubscript{2} uptake capacity and sorption hysteresis can be optimized by changing the cations accommodated in the porous materials, which is important to develop effective and efficient CO\textsubscript{2} capture and storage materials.

\section*{Acknowledgments}

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Table 1. Effect of cation on the structural features of α-MnO2, including lattice parameters (Å) and cell volume (Å³).

<table>
<thead>
<tr>
<th></th>
<th>Cell Parameters, (a, b, c) (Å)</th>
<th>Volume (Å³)</th>
<th>Bond length (Å)</th>
<th>Cation-Mn</th>
<th>Cation-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mn(<em>{24})O(</em>{48})</td>
<td>9.702 8.568 9.685</td>
<td>805.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>With Cation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(^+)</td>
<td>9.702 8.554 9.731</td>
<td>807.48</td>
<td>3.57</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>Na(^+)</td>
<td>9.678 8.555 9.706</td>
<td>803.63</td>
<td>3.55</td>
<td>2.82</td>
<td></td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>9.713 8.542 9.735</td>
<td>807.64</td>
<td>3.59</td>
<td>2.83</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Effect of CO\(_2\) sorption on the structural features of α-MnO2, including lattice parameters (Å) and cell volume (Å³)

<table>
<thead>
<tr>
<th></th>
<th>Cell Parameters, (a, b, c) (Å)</th>
<th>Volume (Å³)</th>
<th>Volume Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mn(<em>{24})O(</em>{48})</td>
<td>9.702 8.568 9.685</td>
<td>805.04</td>
<td>--</td>
</tr>
<tr>
<td>With Cation and CO(_2) Adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KMn(<em>{24})O(</em>{48})+CO(_2)</td>
<td>9.797 8.545 9.712</td>
<td>813.06</td>
<td>1.00%</td>
</tr>
<tr>
<td>NaMn(<em>{24})O(</em>{48})+CO(_2)</td>
<td>9.735 8.557 9.725</td>
<td>810.13</td>
<td>0.63%</td>
</tr>
<tr>
<td>BaMn(<em>{24})O(</em>{48})+CO(_2)</td>
<td>9.747 8.536 9.769</td>
<td>812.83</td>
<td>0.97%</td>
</tr>
</tbody>
</table>

Table 3. Summary of three CO\(_2\) diffusion mechanisms for corresponding cations

<table>
<thead>
<tr>
<th></th>
<th>Scenario I</th>
<th>Scenario II</th>
<th>Scenario III</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-doped OMS-2</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-doped OMS-2</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Ba-doped OMS-2</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

Fig. 1 Different views of a crystal structure of α-MnO2, where Mn is purple, and O is red. The (2×2) tunnel is along the \(b\) axis. Sites A and B are two high-symmetry positions.
Fig. 2 Density of states (DOS) for doped and undoped $\alpha$-MnO$_2$. (a)-(c) DOS projected on $\alpha$-MnO$_2$, K, Na, and Ba individually; and (d) DOS comparison before and after doping in $\alpha$-MnO$_2$.

Fig. 3 Three possible diffusion mechanisms for CO$_2$ in an OMS-2 (2×2) tunnel: red, O; black, C; green, cation (K$^+$, Na$^+$, or Ba$^{2+}$); red cross, corresponding CO$_2$ position; red arrow, diffusion direction. For clarity, yellow walls highlight the location of the MnO$_2$ (tunnel walls). (a) CO$_2$ remains an optimum distance from the cation (Scenario I); (b) CO$_2$ bypasses a cation while the cation shifts towards the porous surface (Scenario II), the insert depicts the transition state in the OMS-2 tunnel where the CO$_2$ molecule sits alongside the cation and the O-C-O angle is distorted to 134.5° (foreground atoms removed for clarity); and (c) CO$_2$ pushes a cation to diffuse (Scenario III). There is an activation energy barrier associated with the formation of the transition state in Scenario II and a diffusion energy barrier for the CO$_2$ to push the cation in Scenario III.
References