Ab Initio Thermodynamic Study of the CO₂ Capture Properties of Potassium Carbonate Sesquihydrate, K₂CO₃·1.5H₂O

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ABSTRACT: By combining density functional theory and lattice phonon dynamics, the thermodynamic properties of CO₂ absorption/desorption reactions with dehydrated potassium carbonates through K₂CO₃·1.5H₂O + CO₂ = 2KHCO₃ + 0.5H₂O(g) are analyzed. The energy change and the chemical potential of this reaction have been calculated and used to evaluate its thermodynamic properties and phase transitions. The results indicate that the K₂CO₃·1.5H₂O can only be applied for postcombustion CO₂ capture technology at temperatures lower than its phase transition temperature, which depends on the CO₂ pressure and the steam pressure with the best range being P(H₂O) ≤ 1.0 bar. Above the phase transition temperature, the sorbent will be regenerated into anhydrous K₂CO₃. If the steam pressure P(H₂O) is much greater than 1.0 bar, it is possible to use the K₂CO₃·1.5H₂O sorbent for precombustion CO₂ capture technology. Compared to anhydrous K₂CO₃, K₂CO₃·1.5H₂O requires less energy for regeneration.

I. INTRODUCTION

Since the burning of fossil fuels is the main energy source for the world economy, carbon dioxide, a major product from fossil fuel combustion, is released into the atmosphere in large quantities and may cause global climate change.¹–⁵ In order to solve this environmental problem, there is a need to reduce CO₂ emissions through capture and sequestration while maintaining acceptable energy costs.⁶–⁹ During the past few decades, many efforts have been devoted to new technologies for CO₂ capture, sequestration, and utilization.⁴,¹⁰ Among them, capture is economically the key step, and the use of sorbents to remove CO₂ from large point sources is a feasible capture technology. Inorganic solid sorbent materials have been proposed for capture of CO₂ through a reversible chemical transformation.¹¹⁻¹³

Solid sorbents containing alkali and alkaline earth metals have been reported in the literature.¹⁴⁻¹⁸ Their oxides, hydroxides, and carbonates/bicarbonates attract more attention from researchers because of their high CO₂ absorption capacities and moderate working temperatures.¹⁰,¹⁴,¹⁹,²⁰ Experimental evidence also shows that mixtures of hydroxides with oxides could improve the CO₂ absorption performance.¹⁴ Since alkali metal bicarbonates can be decomposed into carbonates releasing CO₂ and H₂O within a relatively small temperature range (for example, NaHCO₃ at 70–250 °C), carbonate/bicarbonate conversions can be used for CO₂ capture under postcombustion conditions.¹⁰⁻¹⁵,¹⁷,¹⁹,²¹–²⁶ Generally, a fluidized-bed or transport reactor is imagined for the postcombustion CO₂ capture by alkali metal carbonates.²²,²⁷⁻³⁰ The flue gas enters the carbonation reactor to react with carbonate/bicarbonate is used. Then the loaded sorbents are transferred into the regeneration reactor to release CO₂ and regenerate the sorbent in the temperature range 100–200 °C. Lee et al.¹¹⁻¹⁵,²³,³¹ and Zhao et al.²²,²⁷,²⁹,³²,³³ investigated pure K₂CO₃ and potassium-based sorbents (K₂CO₃/TiO₂, K₂CO₃/Al₂O₃, K₂CO₃/MgO, K₂CO₃/ZrO₂, etc.) to capture CO₂ through the overall reaction K₂CO₃ + CO₂ + H₂O = 2KHCO₃. Their results indicated that the global carbonation rate for Na₂CO₃/K₂CO₃ was rather slow. The results measured by Lee et al.¹¹,²³,²⁸ showed that, within 100 min, the carbonation conversion rate of the potassium-based sorbents reached 80% while for sodium-based sorbents it only reached 65%.²¹ Hirano et al.³⁴ and Hayashi et al.³⁵ reported that the formation of active species K₂CO₃·1.5H₂O plays an important role in the CO₂ capture capacity and that a vapor pretreatment process substantially improved the CO₂ capture capacity.¹⁴ The experimental results showed that the CO₂ capture capacity could be enhanced due to the conversion of the K₂CO₃ phase

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to the K$_2$CO$_3$.15H$_2$O phase through the K$_2$H$_2$(CO$_3$)$_3$.15H$_2$O phase during pretreatment with sufficient water vapor.\textsuperscript{14} Shigemoto and Yanagihara\textsuperscript{25} proposed potassium carbonate supported on an activated carbon as an efficient sorbent to recover CO$_2$ from moist flue gas through the reaction K$_2$CO$_3$.15H$_2$O + CO$_2$ = 2KHCO$_3$ + 0.5H$_2$O. However, by using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) measurements to obtain the characteristics of potassium-based sorbents for CO$_2$ capture, Zhao et al.\textsuperscript{22} found that the carbonation reactivity of K$_2$CO$_3$.15H$_2$O and K$_2$CO$_3$ (in monoclinic structure and dehydrated from K$_2$CO$_3$.15H$_2$O) was weak, but K$_2$CO$_3$ (in hexagonal structure) calcined from KHCOn showed excellent carbonation capacity and reproducibility.

Although the thermodynamic properties of K$_2$CO$_3$ are well-known either from databases\textsuperscript{36,45} or from our first-principles calculations,\textsuperscript{17,18,38} in the literature, there is a lack of thermodynamic data for K$_2$CO$_3$.15H$_2$O. In order to evaluate the CO$_2$ capture performance of K$_2$CO$_3$.15H$_2$O and to compare with the corresponding anhydrous K$_2$CO$_3$, in this study we apply our previous approach\textsuperscript{16,39,40} to explore the electronic and lattice dynamic properties of K$_2$CO$_3$.15H$_2$O crystal. Then, based on the calculated energetic properties, we will calculate the thermodynamic properties of CO$_2$ capture reactions by K$_2$CO$_3$.15H$_2$O and K$_2$CO$_3$ to find the optimal working conditions for achieving maximum capture capacity.

The rest of this paper is organized as follows: section II briefly describes the theoretical method employed. Section III presents the results of the electronic structural and phonon properties of K$_2$CO$_3$.15H$_2$O compared with the corresponding anhydrous K$_2$CO$_3$. Based on those properties, the thermodynamic properties of reactions of these carbonates in capturing CO$_2$ are evaluated and their corresponding working conditions are fully analyzed. Section IV contains a brief summary and conclusions.

II. THEORETICAL METHODS

The complete description of our computational methodology can be found in our previous studies.\textsuperscript{16–18,38–42} Here, we limit ourselves to provide only the main aspects relevant for the current study. When applying hydrated and dehydrated potassium carbonates as solid CO$_2$ absorbents, we have the following reactions:

K$_2$CO$_3$.15H$_2$O + CO$_2$ $\xleftrightarrow{T,P}$ 2KHCO$_3$ + 0.5H$_2$O(g) \hspace{1cm} (R1)

and

K$_2$CO$_3$ + H$_2$O(g) + CO$_2$ $\xleftrightarrow{T,P}$ 2KHCO$_3$ \hspace{1cm} (R2)

Assuming the difference between the chemical potentials of solid phases (K$_2$CO$_3$, KCO$_3$.15H$_2$O, and KHCO$_3$) can be approximated by the differences in their electronic energies ($\Delta E_{\text{DFT}}$) and their entropies ($\Delta S_{\text{PH}}$) and harmonic free energies ($\Delta F_{\text{PH}}$), we can obtain the temperature- and pressure-dependent chemical potential ($\Delta \mu$) for the above reactions:

\[ \Delta \mu(T, P) = \Delta \mu^0(T) - RT \ln \left( \frac{P_{\text{CO}}}{P_0} \left( \frac{P_{\text{H}_2\text{O}}}{P_0} \right)^{0.5} \right) \]

where

\[ \Delta \mu^0(T) = \Delta E_{\text{DFT}} + \Delta F_{\text{PH}}(T) - G_{\text{CO}_2}(T) - n_0G_{\text{H}_2\text{O}}(T) \]

and

\[ \Delta E_{\text{DFT}} = \Delta \mu^0(T) - T(\Delta S_{\text{PH}}(T) - S_{\text{CO}_2}(T)) - n_0S_{\text{H}_2\text{O}}(T) \]

As described in our previous study,\textsuperscript{16,38–41} the zero-point energies, the free energies, and the entropies of the gas phases of CO$_2$ ($E_{\text{g}(\text{CO}_2)}$, $G_{\text{CO}_2}(T)$, and $S_{\text{CO}_2}(T)$) and H$_2$O(g) ($E_{\text{g}(\text{H}_2\text{O})}$, $G_{\text{H}_2\text{O}}(T)$, and $S_{\text{H}_2\text{O}}(T)$) can be obtained by standard statistical mechanics and accurately evaluated using the Shomate equation.\textsuperscript{37} In eq 2, $\Delta E_{\text{DFT}}$ is the total energy change of the reactants and products calculated by density functional theory (DFT). In this work, the Vienna Ab initio Simulation Package (VASP)$^{43,44}$ was employed to calculate the electronic structures of the solid materials involved in this study. All calculations have been done using the projector augmented wave (PAW) pseudopotentials and the PW91 exchange-correlation functional.\textsuperscript{45} This computational level was shown to provide an accurate description of oxide systems.\textsuperscript{16,17,40,46} Plane wave basis sets were used with a cutoff energy of 500 eV and a kinetic energy cutoff for augmentation charges of 605.4 eV. The k-point sampling grids of $n_1 \times n_2 \times n_3$ were determined consistent to a spacing of about 0.028 Å$^{-1}$ along the axes of the reciprocal unit cells. The corresponding k-points sets that we used in our calculations is $4 \times 3 \times 6$ for K$_2$CO$_3$.15H$_2$O. The valence electrons contain the outer s and p orbitals of H, C, and O atoms, and the outer s, p, and d orbitals of K. During the calculations, all atoms in the cell as well as the lattice dimensions and angles were relaxed to the equilibrium configurations. For band structure and phonon dispersion calculations, the symbols and coordinates of the high symmetry points in the first Brillouin zone of the crystals are taken from Bradley and Cracknell’s definitions.\textsuperscript{48}

In eqs 2 and 3, the zero-point energies ($E_{\text{ZP}}$), entropies ($S_{\text{PH}}$), and harmonic free energies ($F_{\text{g}}$) excluding the zero-point energy which was already counted in the term $\Delta E_{\text{DFT}}$ of solids were calculated by the PHONON software package,\textsuperscript{49} in which the direct method is applied following the formula derived by Parlinski et al.\textsuperscript{50} to combine ab initio DFT with lattice phonon dynamics calculations. In the phonon calculations, a $1 \times 1 \times 2$ supercell is created for K$_2$CO$_3$.15H$_2$O from its optimized unit cell that is calculated through DFT. Based on the partition function carried out with the phonon dispersions and phonon densities of states, their thermodynamic properties, such as internal energy, free energy, entropy, and heat capacity, can be evaluated under different temperature and pressure conditions that are used in eq 1 to calculate the chemical potentials for reactions R1 and R2, which are further used to evaluate their CO$_2$ capture properties as presented in section III.C.
III. RESULTS AND DISCUSSION

III.A. Electronic Structural Properties of K₂CO₃·1.5H₂O.
The original synthesis and crystal structure of potassium carbonate sesquihydrate, K₂CO₃·1.5H₂O, was first reported by Hunter and Jeffrey⁵¹ and further redetermined by Skakle et al.⁵² It is monoclinic with space group C₂/c (No. 15), and its crystal structure is shown in Figure 1a. From it one can see that the CO₃²⁻ groups are connected with H₂O by hydrogen bonding to form a chain structure along (010). O1 of CO₃²⁻ is not involved in the hydrogen bonding. One water molecule (O4 in Figure 1) participates in hydrogen bonds bridging between O3 atoms of two symmetry-related CO₃²⁻ anions, whereas the other water (O5 in Figure 1) acts as a donor to both O2 and O3 as shown in Figure 1b.⁵² The K atoms are located within the hydrogen-bonded chains with K−O bond lengths around 2.74−3.05 Å.

In Table 1 we summarize the optimized crystal structure parameters of K₂CO₃·1.5H₂O. For comparison, we also list the optimized data for anhydrous K₂CO₃³⁸ and KHCO₃¹⁸ in Table 1. As one can see, the optimized crystal constants along the a-axis and c-axis are increased by about 3.1 and 1.9% compared to experiment whereas the b-axis dimension is decreased 0.5%. Overall, the optimized crystal structure and volume of K₂CO₃·1.5H₂O are in good agreement with the experimental measurements. In Table 2, we summarize the calculated bond lengths and bond angles as well as the experimentally measured data. The optimized bond lengths and angles in the CO₃²⁻ anion are very close to the measured data. As pointed out by Ireta et al.,⁵³ the accuracy of DFT for describing hydrogen bonds depends on the bond directionality and, for better accuracy, the hydrogen bond angle should be larger than 130°. As shown in Table 2, the hydrogen bond angles in our K₂CO₃·1.5H₂O calculation are larger than 167° (close to linear), so the hydrogen bonds should be well described by the DFT method we have used. For the hydrogen bonding (Ow−H···O′) in K₂CO₃·1.5H₂O, although the calculated bond lengths of Ow−O′ (Ow refers to O of H₂O, O′ refers to O2 and O3 of CO₃²⁻) are close to experiment, the bond lengths of Ow−H and H···O′ have a larger discrepancy. A likely reason is that the H position in the XRD measurement was not precisely determined, as the experimentally reported H−O lengths are substantially shorter than expected for a water molecule.

The calculated band structure of K₂CO₃·1.5H₂O is shown in Figure 2. The bandwidths and gaps are listed in Table 3. Comparing with the band structure of anhydrous K₂CO₃³⁸ similarities are observed in that both are insulator materials and have direct band gaps with values of 4.298 and 3.697 eV for K₂CO₃·1.5H₂O and K₂CO₃, respectively. They have several valence bands (VBs), and in both solids around −12 eV the p electrons of K form a single band. However, as described below, K₂CO₃·1.5H₂O has its own special electronic structures. However, as described in our previous work,³⁹−⁴¹,⁴⁶ due to the DFT approximations, which underestimate the unoccupied orbital energies, our calculated band gap is usually smaller than the experimental measurements. Although there is no experimental band gap available for crystalline K₂CO₃·1.5H₂O, it is expected that the real band gap should be larger than our predicted value.

Figure 3 shows the calculated total density of states (TDOS) and partial density of states (PDOS) projected onto the H, C, O, and K contributions for K₂CO₃·1.5H₂O. For comparison, the TDOS of anhydrous K₂CO₃ is also plotted in Figure 3.³⁸ The s orbital of O contributes to the second lowest energy VB₆ by interacting with the p orbital of C, while its p orbitals mainly contribute to VB₁ and VB₂. The p orbital of K forms a single valence band (VB₅) while its s, p, and d orbitals also are involved in other VBs and the conduction band interacting with Figure 1. (a) Crystal structure of K₂CO₃·1.5H₂O; (b) hydrogen-bonded chains formed from water and carbonate groups. The biggest balls in red stand for O, the smallest balls in white stand for H, medium-size balls in gray stand for C, and medium-size balls in purple stand for K. The hydrogen bonds are in yellow.

The s orbital of O contributes to the second lowest energy VB₆ by interacting with the p orbital of C, while its p orbitals mainly contribute to VB₁ and VB₂. The p orbital of K forms a single valence band (VB₅) while its s, p, and d orbitals also are involved in other VBs and the conduction band interacting with...
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Space Group</th>
<th>Lattice Const (Å)</th>
<th>Atomic Fractional Coord</th>
<th>Lattice Const and Deviations (%)</th>
<th>Atomic Fractional Coord</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃·1.5H₂O</td>
<td>C12/c1 (No. 15)</td>
<td>a = 11.8175, b = 13.7466, c = 7.1093, β = 120.769°</td>
<td>K: (0.0000, 0.38193, 0.25000) C: (0.1929, 0.17350, 0.15183) O: (0.10641, 0.22728, 0.15315)</td>
<td>a = 12.17844 (3.05), b = 13.67275 (−0.54), c = 7.23472 (1.89), β = 120.5247° (−0.2)</td>
<td>K: (0.0000, 0.38210, 0.25000) C: (0.19381, 0.17052, 0.15174) O: (0.08221, 0.31998, −0.27315)</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>P12/a1 (No. 14)</td>
<td>a = 15.1725, b = 5.6283, c = 3.7110, β = 104.631°</td>
<td>K: (0.16533, 0.02177, 0.29533) C: (0.11967, 0.5150, −0.14363) O: (0.19329, 0.52915, 0.09482)</td>
<td>a = 15.45481 (1.86), b = 5.71536 (1.52), c = 3.76864 (1.55), β = 105.878° (1.19)</td>
<td>K: (0.16530, 0.02299, 0.28726) C: (0.11977, 0.51419, −0.14585) O: (0.19443, 0.52683, 0.08663)</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>P12/c1 (No. 14)</td>
<td>a = 5.63961, b = 9.8312, c = 6.83407, β = 98.703°</td>
<td>K: (0.2418, 0.0831, 0.2148)</td>
<td>a = 5.76055 (2.14), b = 9.90478 (0.75), c = 7.18110 (5.08), β = 97.295° (−1.42)</td>
<td>K: (0.24109, 0.08186, 0.19586) C: (0.2455, 0.4174, 0.2489) O: (0.07368, 0.0430, 0.2014)</td>
</tr>
</tbody>
</table>

*Taken from ref 38. †Taken from refs 17 and 18.
the s and p orbitals of C and O. From Figure 3, it can be seen that the O of H₂O (denoted as Ow in Figure 1 and Tables 1 and 2) is different from the O of CO₃²⁻: the s orbital of Ow interacting with s and p orbitals of H forms the band VB₇ in Figure 2 with lowest energy, while its p orbitals interact with orbitals of H, C, and O to form other valence bands (VB₂−VB₄). The s orbital of H also interacts with the p orbitals of O of CO₃²⁻ to form hydrogen bonds.

### III.B. Dynamic Phonon Properties

As shown in Table 1, for K₂CO₃·1.5H₂O there are eight formula units (f.u.) in its unit cell, but its primitive cell has only 4 f.u. with a total of 42 atoms. Therefore, there are 126 phonon modes in K₂CO₃·1.5H₂O. The calculated phonon dispersion of K₂CO₃·1.5H₂O is shown in Figure 4a. Along the wave vector L−A there is one soft mode that corresponds to the displacements of one type of O in CO₃²⁻.

The calculated phonon densities of states of K₂CO₃·1.5H₂O, K₂CO₃, and KHCO₃ are shown in Figure 4b. Compared to anhydrous K₂CO₃, K₂CO₃·1.5H₂O has several extra peaks which corresponds to H (88−95 THz) and O (45−55 THz) of H₂O-related vibrations. In KHCO₃, the HCO₃⁻ moieties form hydrogen-bound dimers (HCO₃⁻)$_2$ which are separated by K$^+$ ions. As shown in Figure 1, for K₂CO₃·1.5H₂O through the hydrogen bonding, CO₃²⁻ anions are linked into the chain structure with a H₂O linker. Obviously, from Figure 4b, the hydrogen bonding in K₂CO₃·1.5H₂O is weaker than that in

### Table 2. Calculated Bond Lengths and Hydrogen-Bonding Geometry

<table>
<thead>
<tr>
<th>R(C−O₁)</th>
<th>R(C−O₂)</th>
<th>R(C−O₃)</th>
<th>∠(O₁−C−O₂)</th>
<th>∠(O₁−C−O₃)</th>
<th>∠(O₂−C−O₃)</th>
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<tbody>
<tr>
<td>1.289 (1.266)</td>
<td>1.310 (1.288)</td>
<td>1.312 (1.296)</td>
<td>120.5 (120.3)</td>
<td>119.4 (119.7)</td>
<td>120.1 (119.8)</td>
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</table>

<table>
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<tr>
<th>O₆−H−O′</th>
<th>R(O₆−H)</th>
<th>R(H−O)</th>
<th>R(O₆−O)′</th>
<th>∠(O₆−H−O′)</th>
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</thead>
<tbody>
<tr>
<td>008 (0.77)</td>
<td>1.658 (1.93)</td>
<td>2.652 (2.686)</td>
<td>167.90</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>O₅−H₅A−O₂</th>
<th>R(O₅−H₅A)</th>
<th>R(H₅A−O₂)</th>
<th>R(O₅−O₂)+</th>
<th>∠(O₅−H₅A−O₂)</th>
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<tbody>
<tr>
<td>001 (0.69)</td>
<td>1.662 (2.03)</td>
<td>2.659 (2.670)</td>
<td>173.27</td>
<td></td>
</tr>
</tbody>
</table>

"Bond lengths are in angstroms (Å) and bond angles are in degrees. b Taken from ref 51. c Taken from ref 52.

### Table 3. DFT Calculated Energies ($E_{DFT}$), Band Gap, Zero-Point Energy ($E_{ZP}$), and Entropy (S) Calculated from Phonon and Available Experimental Data

<table>
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<tr>
<th>compound</th>
<th>space group</th>
<th>$E_{DFT}$ (eV/f.u.)</th>
<th>band gap (eV)</th>
<th>$E_{ZP}$ (eV/f.u.)</th>
<th>phonon (T = 300 K)</th>
<th>expt&quot; (T = 298.15 K)</th>
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<tr>
<td>K₂CO₃·1.5H₂O</td>
<td>C12/c1 (No. 15)</td>
<td>−59.494 83</td>
<td>4.298 (direct)</td>
<td>1.492 22</td>
<td>217.386</td>
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<tr>
<td>KHCO₃</td>
<td>P12/c/a1 (No. 14)</td>
<td>−37.886 04</td>
<td>4.967 (direct)</td>
<td>0.760 68</td>
<td>122.406</td>
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<tr>
<td>K₂CO₃</td>
<td>P12/c/a1 (No. 14)</td>
<td>−36.904 80</td>
<td>3.697 (direct)</td>
<td>0.457 33</td>
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<tr>
<td>CO₂ molecule</td>
<td>P1</td>
<td>−22.994 09</td>
<td>0.315 98</td>
<td>0.585 41</td>
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<td>H₂O molecule</td>
<td>P1</td>
<td>−14.272 67</td>
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</table>

"Taken from HSC Chemistry Package. b Taken from refs 18 and 38. c Taken from refs 17 and 38.

Figure 2. Calculated electronic band structure of K₂CO₃·1.5H₂O. The Fermi level is set as relative zero.

Figure 3. Calculated total density of states (TDOS) and projected partial density of states (PDOS) of K₂CO₃·1.5H₂O. For comparison, the TDOS of K₂CO₃ (No. 14) is also plotted in the TDOS figure.
KHCO₃ because the latter has lower frequency of H vibration (peak within 75–85 THz).

The calculated phonon free energy of K₂CO₃·1.5H₂O versus temperature is shown in Figure 5a, from which the zero-point energies (\(E_{ZP}\)) can be obtained and are listed in Table 3. In order to compare their properties for capturing CO₂, the thermodynamic properties of anhydrous K₂CO₃ and KHCO₃ are also shown in Figure 5. The zero-point energies of these solids are significant and must be included in predicting their thermodynamic properties (eq 2). With increasing temperature, the free energy of K₂CO₃·1.5H₂O decreases faster than those of anhydrous K₂CO₃ and KHCO₃. Figure 5b shows the calculated entropies of these solids versus the temperature. Obviously, at 0 K, their entropies are zero and increase with increasing temperature. Because the structure of K₂CO₃·1.5H₂O has a larger configuration entropy than K₂CO₃ and KHCO₃, its entropy is higher over the temperature range. Our previous results on other solids indicated that with our approach the calculated entropy of solids is quite close to the experimentally measured values.¹⁶,¹⁷,³⁹ Although in the literature there are no experimental data available for K₂CO₃·1.5H₂O, our calculated entropy should be consistent with the experimentally measured value. By including these free energies and entropies at different temperatures in eqs 1–3, the thermodynamic properties of the reactions of K₂CO₃·1.5H₂O and anhydrous K₂CO₃ capturing CO₂ can be evaluated as described in section III.C.

## III.C. Capabilities of K₂CO₃·1.5H₂O To Capture CO₂

According to eq 3, the calculated heats of reaction (enthalpy change) for reactions R1 and R2 versus temperature are plotted in Figure 6a. Obviously, along the temperature range, the anhydrous K₂CO₃ capture of CO₂ can release more reaction heat than the hydrated K₂CO₃·1.5H₂O. This means the interaction of K₂CO₃ with CO₂ is much stronger than that of K₂CO₃·1.5H₂O, and during the regeneration stage, more energy is required to regenerate K₂CO₃. With \(P_{CO_2} = 1\) bar, Figure 6b shows the calculated Gibbs free energy of these two reactions versus temperature. The slope of the free energy versus temperature for the reaction K₂CO₃ + H₂O(g) + CO₂ = 2KHCO₃ is larger than that of K₂CO₃·1.5H₂O + CO₂ = 2KHCO₃ + 0.5H₂O(g). This indicates that the driving force for K₂CO₃ to capture a CO₂ is larger than that of K₂CO₃·1.5H₂O, and the energy needed to reverse the \(\Delta G > 0\) for reaction R2 is larger than that for the forward reaction.

By examining eq 1, for the reaction of K₂CO₃·1.5H₂O capturing CO₂, we can explore the relationship among the chemical potential (\(\Delta \mu(T,P)\)), temperature, and CO₂ pressure (\(P_{CO_2}\)) at several fixed values of \(P_{H_2O}\). This kind of relationship for reactions R1 and R2 is shown in Figure 7 as a contour plot in a two-dimensional representation. The lines in Figure 7...
indicate conditions at which $\Delta \mu (T, P) = 0$. Near these lines is a good region for energy-efficient absorption and desorption because of the minimal energy costs at the given temperature and pressure. Above these lines in Figure 7 ($\Delta \mu (T, P) < 0$), the solids $K_2CO_3 \cdot 1.5H_2O$ and $K_2CO_3$ are respectively favored to absorb $CO_2$ and to form $KHCO_3$, while below these lines ($\Delta \mu (T, P) < 0$) $K_2CO_3$ is favored to release $CO_2$, regenerating the solid sorbent.

From Figure 7 one can see that at each fixed $P_{H_2O}$ these two lines of the reactions for $K_2CO_3 \cdot 1.5H_2O$ and $K_2CO_3 \cdot 1.5H_2O$ capturing $CO_2$ cross at a transition temperature ($T_{tr}$), which means that at this temperature there is a phase transition $K_2CO_3 \cdot 1.5H_2O \leftrightarrow K_2CO_3 + 1.5H_2O$ happening. Obviously, at each fixed $P_{H_2O}$ the $T_{tr}$ is fixed and does not depend on $P_{CO_2}$ as shown with vertical lines in Figure 7. Therefore, in Figure 7 the phase diagram has three regions corresponding to three solid phases: the region below $T_{tr}$ and under the line is $K_2CO_3 \cdot 1.5H_2O$, the region above $T_{tr}$ and under the line is $K_2CO_3$, while the rest of the region above the lines is the $KHCO_3$ phase. In other words, below $T_{tr}$ only reaction R1 can happen and only $K_2CO_3 \cdot 1.5H_2O$ could be regenerated, while above $T_{tr}$ reaction R2 can happen and anhydrous $K_2CO_3$ could be regenerated.

As shown in Figure 7 and eq 1, $\Delta \mu (T, P)$ is dependent not only on temperature but also on gas pressure ($P_{CO_2}$). For reaction $R1 \quad P_{gas} = P_{CO_2}/(P_{H_2O}P_0)^{1/2}$, while for reaction $R2 \quad P_{gas} = P_{CO_2}P_{H_2O}/P_0^2$, where $P_0 = 1$ bar is the reference pressure. Even with the same $P_{CO_2}$, $P_{H_2O}$ plays a different role in reactions $R1$ and $R2$. The behavior can be discussed in more detail by setting $P_{H_2O}$ at several values giving different scenarios as shown in Figure 7.

(i) The first scenario is $P_{H_2O} = 1.0$ bar, which corresponds to the saturation pressure of water vapor at 100 °C. In this case, the $P_{gas}$ values for reactions $R1$ and $R2$ are the same and equal $P_{CO_2}$. From Figure 7, these two lines cross at $T_{tr1} = 445$ K (172 °C), which means above this temperature ($T_{tr1}$) the hydrated $K_2CO_3 \cdot 1.5H_2O$ will be dehydrated to $K_2CO_3$ through the phase transition reaction of $K_2CO_3 \cdot 1.5H_2O \leftrightarrow K_2CO_3 + 1.5H_2O$, which agrees with the experimental findings that hydrates of $K_2CO_3 \cdot 1.5H_2O$ can be stable up to 153 °C at ambient atmosphere condition.51 As one can see from Figure 7, both of these reactions are thermodynamically favorable over a wide range of temperature and $P_{CO_2}$, which means that under this temperature range the absorption of $CO_2$ is thermodynamically favored by $K_2CO_3$ and $K_2CO_3 \cdot 1.5H_2O$.

However, as a $CO_2$ solid sorbent, it should not only be easy to absorb $CO_2$ in the capture cycle but also be easy to release the $CO_2$ during the regeneration cycle. The operating conditions for absorption/desorption processes depend on their use in a pre- or a postcombustion application. The U.S. Department of Energy (DOE) programmatic goal for postcombustion and oxy-combustion $CO_2$ capture is to capture at least 90% of the $CO_2$ produced by a plant with the cost in electricity increasing no more than 35%, whereas the goal in the case of precombustion $CO_2$ capture is to capture at least 90% of the $CO_2$ produced with the cost in electricity increasing no more than 10%.54–56 Under precombustion conditions, after the water gas shift reactor, the gas stream mainly contains $CO_2$, $H_2O$, and $H_2$. The partial $CO_2$ pressure could be as high as 20–
Table 4. Calculated Thermodynamic Properties of Reactions of CO₂ Captured by Hydrated and Dehydrated Potassium Carbonates (in kJ/mol): Highest Temperature for Carbonates Capturing CO₂ at Precombustion (T₁) (P_{H₂O} = 20 bar) and Postcombustion (T₂) (P_{CO₂} = 0.1 bar) Conditions and Phase Transition Temperature (T_u) of K₂CO₃·1.5H₂O into K₂CO₃

<table>
<thead>
<tr>
<th>reaction</th>
<th>CO₂ (wt %)</th>
<th>ΔE_{gas}</th>
<th>ΔE_{298}</th>
<th>ΔH(T = 300 K)</th>
<th>ΔG(T = 300 K)</th>
<th>T₁ (K)</th>
<th>T₂ (K)</th>
<th>T_u (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃·1.5H₂O + CO₂ = 2KHCOS + 0.5H₂O(g)</td>
<td>26.88</td>
<td>-40.474</td>
<td>-0.737</td>
<td>-40.678</td>
<td>-12.820</td>
<td>580b</td>
<td>370b</td>
<td>445b</td>
</tr>
<tr>
<td>K₂CO₃ + CO₂ + H₂O(g) = 2KHCOS</td>
<td>31.84</td>
<td>-154.429</td>
<td>18.293</td>
<td>-141.728</td>
<td>-46.281</td>
<td>490b</td>
<td>420b</td>
<td>445b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-142.854</td>
<td>-44.716</td>
<td></td>
<td>455b</td>
<td>395b</td>
<td>515d</td>
</tr>
</tbody>
</table>

*Calculated by HSC Chemistry package.*

30 bar, and the temperature is around 313–573 K. To minimize the energy consumption, the ideal sorbents should work in these pressure and temperature ranges to separate CO₂ from H₂. The temperature denoted T₁ and listed in Table 4 is the temperature above which the sorbent solids cannot absorb CO₂ and will start to release CO₂. This indicates that, during the capture cycle, the operating temperature should be lower than T₁, whereas the temperature may be higher than T₁ (depending on the desired CO₂ pressure) during the regeneration cycle. Under postcombustion conditions, the gas stream mainly contains CO₂ and N₂, the partial pressure of CO₂ is in the range 0.1–0.2 bar, and the temperature range (T₂) is quite different. Currently, in postcombustion CO₂ capture technology, the amine-based solvents and carbon- and zeolite-based solid sorbents (including metal organic framework) capture CO₂ within a lower temperature range (>200 °C), while oxides (CaO, Na₂O, etc.) and salts (Li₄SiO₄, Li₂ZrO₂, etc.) capture CO₂ usually within a higher temperature range (>400 °C). The turnover temperatures (denoted as T₁ and T₂) for pre- and postcombustion capture by K₂CO₃·1.5H₂O and K₂CO₃, as well as their phase transition temperatures (T_u), are listed in Table 4. For K₂CO₃·1.5H₂O, T₁ and T₂ are 580 and 370 K, respectively. As discussed above and shown in Figure 6, K₂CO₃·1.5H₂O can only be stable below T_{tr1} = 445 K. Since its T₁ > T_{tr1}, K₂CO₃·1.5H₂O cannot be used for precombustion CO₂ capture technology, but can be applied to postcombustion CO₂ capture technology because its T₂ < T_{tr1}. As shown in Figure 7, K₂CO₃ could be used for both post- and precombustion CO₂ capture technologies. However, if the operating temperature for the regeneration step is lower than T_{tr2}, KHCO₃ will be first regenerated into K₂CO₃·1.5H₂O, not K₂CO₃. When the operating temperature is higher than T_{tr2}, KHCO₃ will be first regenerated into K₂CO₃, not K₂CO₃·1.5H₂O, regardless of whether the initial solid sorbent is K₂CO₃·1.5H₂O or K₂CO₃.

(ii) The second scenario for showing the role of P_{H₂O} in reactions R1 and R2 is when P_{H₂O} < 1.0 bar, which corresponds to the saturation pressure of water vapor below 100 °C. Here we only discuss one example with P_{H₂O} = 0.1 bar, which corresponds to the saturation pressure of water vapor at around 47 °C. In this case, the gas pressure (P_{gas}) is different for reactions R1 and R2: P_{gas}^{R1} = P_{CO₂}/(P_{H₂O}P_{O₂})^{1/2} and P_{gas}^{R2} = P_{gas}^{R1}P_{H₂O}/P_{O₂}. From this one can see that, with decreasing P_{H₂O}, P_{gas}^{R1} < P_{gas}^{R2}, under the same P_{gas}. Therefore, compared with case i, with black lines in Figure 7, in this case (red lines) the Δμ = 0 curve of reaction R1 for K₂CO₃·1.5H₂O capturing CO₂ shifted down while the Δμ = 0 curve of reaction R2 for K₂CO₃ capturing CO₂ moved up. Hence, it can be expected that the phase transition temperature (T_u) of K₂CO₃·1.5H₂O into K₂CO₃ could be lower when P_{H₂O} is decreased. Indeed, from Figure 7, the calculated T_u is 395 K, which is lower than T_{tr1} = 445 K. At T_u = 395 K, the corresponding CO₂ pressure is about 0.1 bar, which matches the postcombustion CO₂ pressure condition. Therefore, although it is not suitable for precombustion CO₂ capture since its T₁ = 665 K > T_u = 395 K compared to case i, K₂CO₃·1.5H₂O may still be used for postcombustion CO₂ capture technology with lower operating temperature (≤395 K, when P_{H₂O} ≤ 0.1 bar) as its T₂ = 395 K ≈ T_u. By increasing P_{H₂O} from 0.1 to 1 bar (Figure 7), T_u could reach T_{tr1}. Again, similar to case i shown in Figure 7, if the regeneration operating temperature is higher than T_u, only anhydrous K₂CO₃ can be obtained. As shown in Table 4, the corresponding T₁ and T₂ for K₂CO₃ are 455 and 395 K, respectively. This means that under this steam pressure K₂CO₃ is only suitable for precombustion CO₂ capture while K₂CO₃·1.5H₂O could be used for postcombustion CO₂ capture technology. If one expects to regenerate K₂CO₃·1.5H₂O, the operating regeneration temperature must be lower than T_u. In other words, case ii serves as the low end for the steam pressure, which means that, in order to use K₂CO₃·1.5H₂O as CO₂ sorbent, the steam pressure should be higher than 0.1 bar.

(iii) The last scenario is when P_{H₂O} > 1.0 bar, which corresponds to the saturation pressure of water vapor above 100 °C. Here we also discuss one example of P_{H₂O} = 10 bar. In this case, P_{gas}^{R1} is also different for reactions R1 and R2: P_{gas}^{R1} = P_{CO₂}/(P_{H₂O}P_{O₂})^{1/2} and P_{gas}^{R2} = P_{gas}^{R1}P_{H₂O}/P_{O₂}. With increasing P_{H₂O}, P_{gas}^{R1} is greater than P_{gas}^{R2} under the same P_{gas}. Compared with cases i and ii, it can be expected that the phase transition temperature of K₂CO₃·1.5H₂O into K₂CO₃ could be higher when P_{H₂O} was increased, because the Δμ = 0 curve of reaction R1 for K₂CO₃·1.5H₂O capturing CO₂ moved up while the Δμ = 0 curve of reaction R2 for K₂CO₃ capturing CO₂ shifted down as shown by the green lines in Figure 7. Indeed, T_u = 515 K is greater than T_{tr1} = 445 K. Compared to case i, when K₂CO₃·1.5H₂O is used for postcombustion CO₂ capture technology, its highest absorption temperature is around T₃ = 335 K and its regeneration temperature range is 335–515 K. Above T_u = 515 K, the regenerated solid is anhydrous K₂CO₃, not K₂CO₃·1.5H₂O. When K₂CO₃·1.5H₂O is used as sorbent for precombustion CO₂ capture technology, its highest absorption temperature is around T₃ = 510 K and its regeneration temperature range is very narrow with 510–515 K.
K if we want to obtain a high pressure of CO₂ (≈20 bar as before the capture). Above $T_{tr3} = 515$ K, instead of regenerating $K_2CO_3$·1.5H₂O anhydrous $K_2CO_3$ will be obtained. Below $T_{tr3} = 515$ K, regenerating $K_2CO_3$·1.5H₂O is possible, but with low released CO₂ pressure. In conclusion, at high steam pressure (at least >1.0 bar), $K_2CO_3$·1.5H₂O could be used as CO₂ sorbent for both post- and precombustion CO₂ capture technologies. Overall, from Figure 7 one can see that decreasing $P_{H_2O}$ will enhance the ability of $K_2CO_3$·1.5H₂O to capture CO₂ and move its turnover temperature higher because, as shown in reaction R1, H₂O is on the product side. For the case of anhydrous $K_2CO_3$, decreasing $P_{H_2O}$ will weaken its capacity for CO₂ capture and move its turnover temperature lower as listed in Table 4 because, as shown in reaction R2, H₂O is on the reactant side. The phase transition temperature of $K_2CO_3$·1.5H₂O into $K_2CO_3$ increases with increase of the steam pressure $P_{H_2O}$. In order to use $K_2CO_3$·1.5H₂O as an efficient CO₂ sorbent in postcombustion capture technology, the best steam pressure range should be less than 1.0 bar, while in precombustion CO₂ capture technology, the best steam pressure range should be greater than 1.0 bar.

IV. CONCLUSIONS

By combining density functional theory and phonon lattice dynamics, the electronic structural and phonon properties of $K_2CO_3$·1.5H₂O were investigated. The optimized structure of this solid is in good agreement with experimental measurements. $K_2CO_3$·1.5H₂O has a direct band gap of 4.298 eV. Similar to $K_2CO_3$, the $p$ orbital of K forms a single valence band. Different from the O of CO₃²⁻, the $s$ orbital of O₆ in H₂O interacts with $s$ and $p$ orbitals of O to form other valence bands. The hydrogen bond in $K_2CO_3$·1.5H₂O is formed by interacting the $s$ orbital of H with $p$ orbitals of O of CO₃²⁻.

The phonon dispersions and phonon density of states for $K_2CO_3$·1.5H₂O were calculated by the direct method. Among its 126 phonon modes, one soft mode along the wave vector $\mathbf{q} = \mathbf{L} - \mathbf{A}$ was found and corresponded to one type of O displacement.

From the calculated thermodynamic properties of $K_2CO_3$·1.5H₂O and $K_2CO_3$ reacting with CO₂ through reactions $K_2CO_3$·1.5H₂O + CO₂ = 2KHCΟ₃ + 0.5H₂O(g) and $K_2CO_3$ + H₂O(g) + CO₂ = 2KHCΟ₃, it was found that the $K_2CO_3$·1.5H₂O is better applied for postcombustion CO₂ capture technology at a temperature lower than its phase transition temperature which depends on the CO₂ pressure and the steam pressure ($P_{H_2O} \leq 1.0$ bar). When $P_{H_2O} > 1.0$ bar, it is possible to use $K_2CO_3$·1.5H₂O sorbent for precombustion CO₂ capture. Above the phase transition temperature, the sorbent will be regenerated into anhydrous $K_2CO_3$. Compared to $K_2CO_3$, $K_2CO_3$·1.5H₂O requires less energy for regeneration.

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