International Journal of Clean Coal and Energy, **2012, 1, 1-11**
http://dx.doi.org/10.4236/ijcce.2012.11001 Published Online February 2012 (http://www.SciRP.org/journal/ijcce)

Efficient Theoretical Screening of Solid Sorbents for CO_2 Capture Applications*

Yuhua Duan, David Luebke, Henry Pennline
National Energy Technology Laboratory, United States Department of Energy, Pittsburgh, USA
Email: yuhua.duan@netl.doe.gov

Received December 15, 2011; revised January 28, 2012; accepted February 13, 2012

ABSTRACT

By combining thermodynamic database mining with first principles density functional theory and phonon lattice dynamics calculations, a theoretical screening methodology to identify the most promising CO_2 sorbent candidates from the vast array of possible solid materials has been proposed and validated. The *ab initio* thermodynamic technique has the advantage of allowing identification of thermodynamic properties of CO_2 capture reactions without any experimental input beyond crystallographic structural information of the solid phases involved. For a given solid, the first step is to attempt to extract thermodynamic properties from thermodynamic databases and the available literatures. If the thermodynamic properties of the compound of interest are unknown, an *ab initio* thermodynamic approach is used to calculate them. These properties expressed conveniently as chemical potentials and heat of reactions, which obtained either from databases or from calculations, are further used for computing the thermodynamic reaction equilibrium properties of the CO_2 absorption/desorption cycles. Only those solid materials for which lower capture energy costs are predicted at the desired process conditions are selected as CO_2 sorbent candidates and are further considered for experimental validations. Solid sorbents containing alkali and alkaline earth metals have been reported in several previous studies to be good candidates for CO_2 sorbent applications due to their high CO_2 absorption capacity at moderate working temperatures. In addition to introducing our computational screening procedure, in this presentation we will summarize our results for solid systems composed by alkali and alkaline earth metal oxides, hydroxides, and carbonates/bicarbonates to validate our methodology. Additionally, applications of our computational method to mixed solid systems of Li_2O with SiO_2/ZrO_2 with different mixing ratios, our preliminary results showed that increasing the Li_2O/SiO_2 ratio in lithium silicates increases their corresponding turnover temperatures for CO_2 capture reactions. Overall these theoretical predictions are found to be in good agreement with available experimental findings.

Keywords: *Ab Initio* Thermodynamics; CO_2 Sorbent and Capture Technology; DFT and Phonon Lattice Dynamics

1. Introduction

Carbon dioxide is one of the major combustion products which once released into the air can contribute to the global climate warming effects [1-3]. In order to mitigate the global climate change, we must stop emitting CO_2 into the atmosphere by separating and capturing CO_2 from coal combustion and gasification plants and sequestering the CO_2 underground. Current technologies for capturing CO_2 including solvent-based (amines) and CaO-based materials are still too energy intensive. Hence, there is critical need for new materials that can capture and release CO_2 reversibly with acceptable energy costs. Accordingly, solid sorbent materials have been proposed for capturing CO_2 through a reversible chemical transformation and most of them result in the formation of carbonate products. Solid sorbents containing alkali and alkaline earth metals have been reported in several previous studies to be good candidates for CO_2 sorbent applications due to their high CO_2 absorption capacity at moderate working temperatures [4-6].

To achieve such goals, one of these new methods considered at National Energy Technology Laboratory (NETL) is based on the use of regenerable solid sorbents. In this case sorbents such as alkaline earth metal oxides or hydroxides are used to absorb CO_2 at warm temperatures typically ranging from 100˚C - 300˚C [7,8]. The key phenomenon used in these processes is transformation of the oxide or hydroxide materials to a carbonate upon CO_2 absorption. Regeneration of the sorbent can be obtained, if necessary, in a subsequent step represented by the reverse transformation from the carbonate phase to the oxide or hydroxide phases. The efficiencies of these processes are highly dependent on identification of the

*The original manuscript of this paper was initially included in the Proceedings of 28th Annual International Pittsburgh Coal Conference, September 12-15, 2011, Pittsburgh, PA.

Copyright © 2012 SciRes.

optimum temperature and pressure conditions at which absorption, respectively regeneration are performed. In the case of high-performance sorbents, both these two mechanistic steps are optimized in order to achieve minimal energetic and operational costs.

Optimization of the sorbent material can be obtained starting from the analysis of their intrinsic atomistic structure and of their transformations upon interaction with CO_2. Particularly important is to identify the corresponding thermodynamic and kinetic characteristics of the sorbent material of interest. For this purpose scientists at NETL have developed a multi-step computational methodology based on combined use of first principles calculations combined with lattice phonon dynamics to describe the thermodynamic properties of CO_2 capture reactions by solid sorbents [4,9-15]. This methodology has been used to screen different classes of solid compounds and has as major objective identification of the optimum candidate materials that can be further subjected to experimental testing. The advantage of this proposed method is that it allows identification of the thermodynamic properties of the CO_2 capture reaction as a function of temperature and pressure conditions with- out any experimental input, excepting the crystallographic structural information of the solid phases involved. Such thermodynamics information is essential to guide experimental groups at NETL in development of highly optimized CO_2 sorbents. For a given database of solid materials, our screening scheme allows identification of a short list of promising candidates of CO_2 sorbents with optimal energy usages, which can be further evaluated by our experimental research groups.

In this work, we summarize our progress on development of novel screening scheme to indentify most promising candidates for CO_2 sorbents. The remainder of this report is organized as follows: In the second section we briefly describe the screening method we developed. In the third section, we provide validation results of our computational method for the case of alkali and alkaline metal compounds. Then, we present the preliminary results on CO_2 capture reactions by lithium related salts. The main conclusions are summarized in the last section.

2. Screening Methodology

2.1. *Ab Initio* Thermodynamics Approach

The complete description of the computational methodology can be found in our previous papers [4,9-15]. Here, we limit ourselves to provide only the main aspects relevant for the current study. The CO_2 capture reactions by solids in the presence of water vapors can be expressed generically in the form

$$Solid\_A + n_1\mathrm{CO_2} \leftrightarrow Solid\_B + \left[Solid\_C\right] \pm n_2\left[\mathrm{H_2O}\right] \tag{1}$$

where the terms given in [···] are optional and n_1 and n_2 are the numbers of moles of CO_2 and H_2O involved in the capture reactions. We treat the gas phase species CO_2 and H_2O as ideal gases. By assuming that the difference between the chemical potentials ($\Delta\mu^o$) of the solid phases of *A*, *B* (and *C*) can be approximated by the difference in their electronic energies (ΔE^o), obtained directly from first-principles DFT calculations, and the vibrational free energy of the phonons and by ignoring the PV contribution terms for solids, the variation of the chemical potential ($\Delta\mu$) for capture reaction with temperature and pressure can be written as

$$\Delta\mu(T,P) = \Delta\mu^0(T) - RT\ln\frac{P_{\mathrm{CO_2}}^{n_1}}{P_{\mathrm{H_2O}}^{\pm n_2}} \tag{2}$$

where $\Delta\mu^0(T)$ is the standard chemical potential changes between reactants and products. If these thermodynamical data are available in the thermodynamic database or literature, we can direct apply them into above equation. If these data are not available, they can be calculated using the *ab initio* thermodynamic approach based on the following approximation.

$$\begin{aligned}\Delta\mu^0(T) \approx \Delta E^{DFT} + \Delta E_{ZP} + \Delta F^{PH}(T) \\ - n_1 G_{\mathrm{CO_2}}(T) \pm n_2 G_{\mathrm{H_2O}}(T)\end{aligned} \tag{3}$$

Here, ΔE_{ZP} is the zero point energy difference between the reactants and products and can be obtained directly from phonon calculations. The ΔF^{PH} is the phonon free energy change between the solids of products and reactants. If the capture reaction does not involve H_2O, then the P_{H_2O} in above equations is set to P_0, which is the standard state reference pressure of 1 bar, and the G_{H_2O} term is not present. The "+" and "–" signs correspond to the cases when H_2O is a product, respectively a reactant, in the general reaction. The free energies of CO_2 (G_{CO_2}) and H_2O (G_{H_2O}) can be obtained from standard statistical mechanics. The enthalpy change for the reaction (1), $\Delta H^{cal}(T)$, can be derived from above equations as

$$\begin{aligned}&\Delta H^{cal}(T) \\ &= \Delta\mu^0(T) + T\left(\Delta S_{PH}(T) - n_1 S_{\mathrm{CO_2}}(T) \pm n_2 S_{\mathrm{H_2O}}\right)\end{aligned} \tag{4}$$

In Equation (3), ΔE^{DFT} is the total energy change of the reactants and products calculated by DFT. In this work, the Vienna *Ab-initio* Simulation Package (VASP) [16,17] 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) pseudo-potentials and the PW91 exchange-correlation functional [18]. This computational level was shown to provide an accurate description of oxide systems [13-14,19]. 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 $n_1 \times n_2 \times n_3$, obtained using the Monkhorst-Pack

Copyright © 2012 SciRes.

method [20], were used for these bulk calculations, where n_1, n_2, and n_3 were determined consistent to a spacing of about 0.028 Å^{-1} along the axes of the reciprocal unit cells. In Equations (3) and (4), the zero point-energies (E_{ZP}), entropies (S_{PH}), and harmonic free energies (F^{PH}, excluding zero-point energy which was already counted into the term ΔE_{ZP}) of solids were calculated by the PHONON software package [21] in which the direct method is applied following the formula derived by Parlinski *et al.* [22] to combine *ab initio* DFT with lattice phonon dynamics calculations.

As an optimal 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 regeneration cycle. The operating conditions for absorption/desorption processes depend on their use as in a preor a post-combustion application. The US Department of Energy (DOE) programmatic goal for post-combustion 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 pre-combustion CO_2 capture is to capture at least 90% of the CO_2 produced with the cost in electricity increasing no more than 10% [23-24]. Under pre-combustion 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 to 30 bar and the temperature (T_1) is around 313 - 573 K. To minimize the energy consumption, the ideal sorbents should work in these ranges of pressure and temperature in order to separate CO_2 from H_2. For post-combustion conditions, the gas stream mainly contains CO_2 and N_2, the partial pressure of CO_2 is in the range 0.1 to 0.2 bar, and the temperature range (T_2) is quite different. Currently, in post-combustion CO_2 capture technology, the amine-based solvents, carbon- and zeolite-based solid sorbents (including metal organic framework) capture CO_2 within a lower temperature range (<200˚C) [25], while oxides (such as CaO, Na_2O, etc.) and salts (such as Li_4SiO_4, Li_2ZrO_3, etc.) capture CO_2 usually within a higher temperature range (>400˚C) [9-13]. Based on Equation (2), the working conditions of each solid capturing CO_2 can be evaluated and used for determining its suitability as CO_2 sorbent.

In this study, the thermodynamic database HSC Chemistry [26] and Factsage [27] packages were employed to search for the available thermodynamic properties of solids.

2.2. Screening Scheme

Figure 1 shows the schematic of our screening methodology. For a given solid databank, this methodology includes four main screening steps (or filters) which allow identification of the most promising candidates [13].

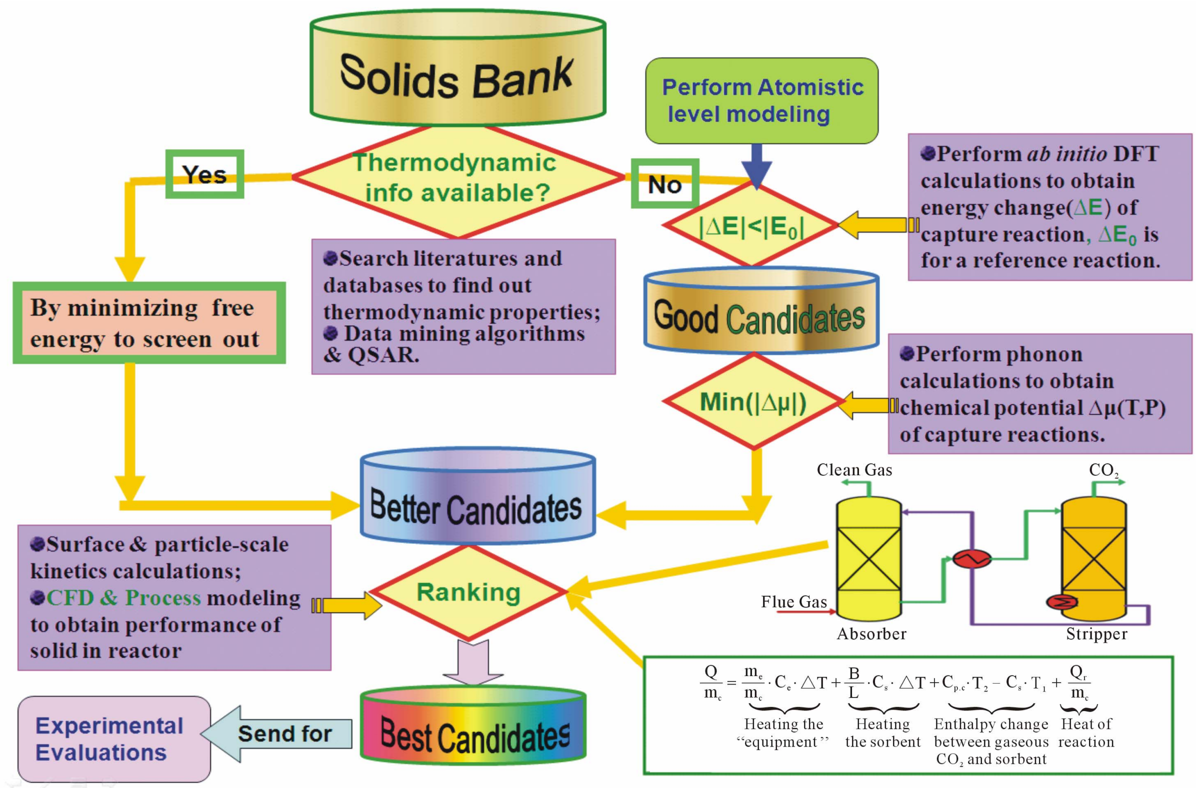


Figure 1. Schematic of our screening methodology.

***Step* 1:** For each solid in the data bank, we first conduct basic screening based on acquisition of general data, such as the wt% of absorbed CO_2 in the assumption of a complete reaction, the materials safety and cost, *etc.* We also include where available the thermodynamic data from literature and from general thermodynamic databases, such as HSC Chemistry, Factsage, *etc*. If the necessary data for evaluation of the thermodynamic properties exists, then the use of DFT calculations is not necessary and the optimal candidates can be obtained by minimizing their known free energies based on the operating conditions. Otherwise, if the material passes basic screening, but no thermodynamic data are available, then continue to the next step.

***Step* 2:** Perform DFT calculations for all compounds in the candidate reaction with this solid. If $|\Delta E^{DFT} - \Delta E_{ref}|/n_1 < 20$ kJ/mol, where n_1 is CO_2 molar number in capture reaction, and ΔE_{ref} is the DFT energy change for the reference capture reaction (e.g. $CaO + CO_2 = CaCO_3$), we add this compound to the list of good candidates. Other- wise, we go back to *Step* 1 and pick another solid.

***Step* 3:** Perform phonon calculations for reactant and product solids to obtain the corresponding zero point energies and the phonon free energies for the list of good candidates. Specify the target operating conditions (temperature, partial pressures of CO_2 and H_2O) and compute the change in chemical potential for the reaction, namely $\Delta\mu(T, P)$ from above equations. If $\Delta\mu(T, P)$ is close to zero (e.g. $|\Delta\mu(T, P)| < 5$ kJ/mol) at the operating conditions, then we select this reaction as a member of the "better" list. Only a short list of compounds will likely be left after application of *Step* 3.

***Step* 4:** Additional modeling could be performed to rank the remaining short list of better candidates both obtained from database searching and *ab initio* thermodynamic calculations as shown in **Figure 1**. One is the kinetics of the capture reactions, which could be done by transport and diffusion calculations as well as using experimental measurements. Another necessary and doable modeling task is the behavior of the solid in the reactor, which can be done by computational fluid dynamics (CFD) methods based on finite element method (FEM) approach and process modeling to estimate the overall costs [28]. These simulations are currently underway. Application of these screening filters will ensure that only the most promising candidates will be identified for the final experimental testing.

This screening methodology provides a path for evaluating materials for which experimental thermodynamic data are unavailable. One area where this approach could be used to great advantage is in evaluating mixtures and doped materials, where thermodynamic data are generally not available but for which the crystallographic structure is known or can be easily determined. Based on the above screening methodology, we have screened hundreds of solid compounds and found some promising candidates for CO_2 sorbents. Here, in this work we summarize the results obtained by applying the screening methodology to several classes of solid materials.

3. Results and Discussions

3.1. Applications to Alkali and Alkaline Earth Metal Oxides and Hydroxides [4,12-14]

The thermodynamic data for these oxides, hydroxides and corresponding carbonates and bicarbonates are available in thermodynamic databases, in order to validate our theoretical approach, we also made the *ab initio* thermodynamic calculations for these known crystals. **Table 1** shows the calculated thermodynamic properties of these reactions accompanying with experimental data obtained from HSC Chemistry database [27].

As an example, **Figure 2** shows the heats of reactions for alkali and alkaline earth metal oxides capture CO_2. From it, one can see that, except for $BeO + CO_2 \rightarrow BeCO_3$ reaction, overall, the calculated results are in good agreement with HSC experimental data. These findings indicate that our theoretical approach can predict the right thermodynamic properties of various solid reacting with CO_2 if the right crystal structure of solids is known or is easy to be determined. The larger discrepancy observed for $BeO/BeCO_3$ system is due to lack of the crystal structure information of $BeCO_3$. As the only one input property of the solid in the *ab initio* thermodynamics calculations, this indicates that in order to obtain reliable results the crystal structure must be known or can be easily predicted correctly.

Table 1 listed the calculated DFT energy changes and

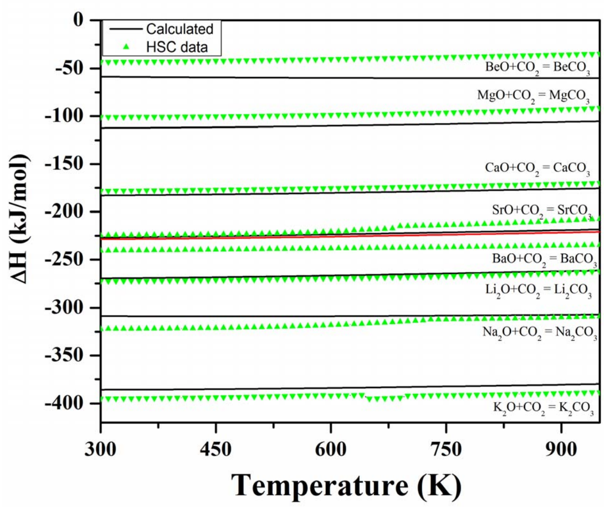


Figure 2. The calculated (solid line) and HSC data (dot line) heat of reaction for alkali and alkaline earth oxides reacting with CO_2 to form carbonates [13,14].

Table 1. The calculated and experimental thermodynamic properties of reactions of CO_2 captured by alkali and alkaline-earth oxides and hydroxides [13,14].

Reactions	CO_2 wt%	Calculated thermodynamic properties at T = 300 K			Thermodynamic data at T = 300 K	
		ΔE^{DFT} (kJ/mol)	ΔH^{cal} (kJ/mol)	ΔG^{cal} (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
$Li_2O + CO_2 = Li_2CO_3$	147.28	−204.7859	−226.731	−179.261	−224.643	−176.290
$Na_2O + CO_2 = Na_2CO_3$	71.01	−284.7066	−308.572	−258.100	−322.153	−277.155
$K_2O + CO_2 = K_2CO_3$	46.72	−363.4242	−385.508	−335.698	−394.785	−349.084
$BeO + CO_2 = BeCO_3$	129.35	−33.0514	−58.514	−0.8976	−43.090	1.665
$MgO + CO_2 = MgCO_3$	**109.19**	**−92.5092**	**−112.254**	**−58.867**	**−100.891**	**−48.206**
$CaO + CO_2 = CaCO_3$	**78.48**	**−161.7445**	**−176.751**	**−129.523**	**−178.166**	**−130.127**
$SrO + CO_2 = SrCO_3$	42.47	−207.3441	−228.490	−178.591	−240.494	−188.850
$BaO + CO_2 = BaCO_3$	28.70	−248.2164	−269.536	−218.095	−272.491	−220.394
$Li_2O + 2CO_2 + H_2O = 2LiHCO_3$	285.04	−273.0209	−285.961	−142.695	−311.043	−189.930
$Na_2O + 2CO_2 + H_2O = 2NaHCO_3$	142.02	−426.5613	−436.196	−290.639	−457.494	−311.281
$K_2O + 2CO_2 + H_2O = 2KHCO_3$	93.44	−517.8530	−539.023	−382.926	−537.639	−393.799
$Li_2CO_3 + CO_2 + H_2O = 2LiHCO_3$	59.56	−68.2349	−85.429	10.366	−86.400	−13.640
$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3$	**41.52**	**−141.8547**	**−153.824**	**−58.739**	**−135.341**	**−34.126**
$K_2CO_3 + CO_2 + H_2O = 2KHCO_3$	**31.84**	**−154.4288**	**−175.852**	**−55.970**	**−142.854**	**−44.716**
$2LiOH + CO_2 = Li_2CO_3 + H_2O(g)$	**91.88**	**−76.6589**	**−98.623**	**−97.134**	**−94.567**	**−88.442**
$LiOH + CO_2 = LiHCO_3$	183.77	−72.4469	−92.026	−43.384		
$2NaOH + CO_2 = Na_2CO_3 + H_2O(g)$	55.02	−108.6058	−134.416	−127.313	−127.510	−122.984
$NaOH + CO_2 = NaHCO_3$	**110.03**	**−158.3597**	**−177.250**	**−126.155**	**−131.426**	**−78.555**
$2KOH + CO_2 = K_2CO_3 + H_2O(g)$	39.22	−136.6990	−154.110	−157.036	−150.711	−141.079
$KOH + CO_2 = KHCO_3$	**78.44**	**−145.5639**	**−156.116**	**−97.638**	**−146.782**	**−92.897**
$Be(OH)_2 + CO_2 = BeCO_3 + H_2O(g)$	102.28	120.0110	88.238	92.326	8.579	16.532
$Mg(OH)_2 + CO_2 = MgCO_3 + H_2O(g)$	**75.46**	**−8.6502**	**−32.687**	**−26.177**	**−19.665**	**−12.762**
$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O(g)$	**59.40**	**−57.9497**	**−80.212**	**−76.610**	**−69.035**	**−64.033**
$Sr(OH)_2 + CO_2 + SrCO_3 + H_2O(g)$	**36.18**	**−85.7463**	**−111.059**	**−106.685**	**−105.424**	**−97.990**
$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O(g)$	25.68	−112.0479	−121.733	−115.686	−121.733	−115.686

thermodynamic properties of reactions of these oxides and hydroxides capture CO_2. Among the 25 CO_2 capture reactions indicated in this table, after applying the first filter (*Steps* 1 and 2), only 10 reactions satisfied our selection criteria and are worth to be considered for third screening step (filter two). After applying the second filter on these 10 reactions, as summarized in **Figure 3**, we found that only $MgO(Mg(OH)_2)/MgCO_3$, $Na_2CO_3/NaHCO_3$, $K_2CO_3/KHCO_3$ are promising candidates for CO_2 sorbents in either post-combustion or pre-combustion CO_2 capture technologies [7,8,10]. These results are in good agreement with the experimental facts, which means our screening methodology is reliable and could be used to identify promising solid CO_2 sorbents by predicting the thermodynamic properties of solids reacting with CO_2 [14].

Based on Equation (2), **Figure 4** gives the calculated relationships of the chemical potential $\Delta\mu(T,P)$ with temperature and CO_2 pressure for reactions $M_2CO_3 + CO_2 + H_2O = 2MHCO_3$ (M = Na, K), $MgO + CO_2 = MgCO_3$, and $Mg(OH)_2 + CO_2 = MgCO_3 + H_2O$. From **Figure 4**, one can see that $Na_2CO_3/NaHCO_3$ and $K_2CO_3/KHCO_3$

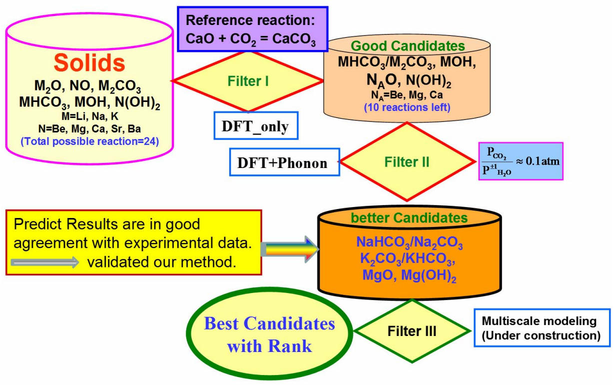


Figure 3. Schematic screening results of alkali and alkaline metal oxides, hydroxides and bicarbonates.

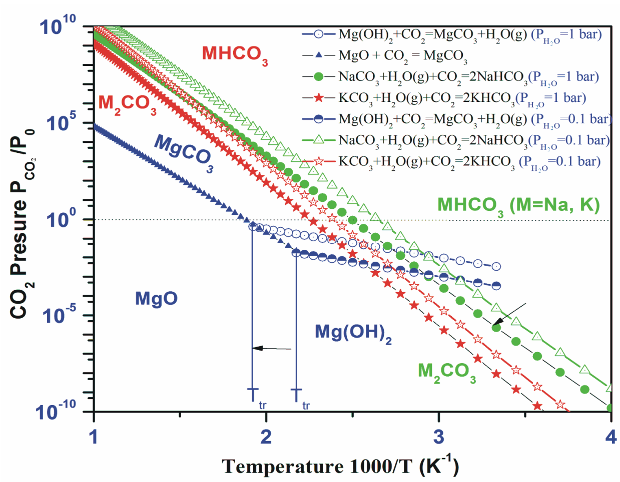


Figure 4. The calculated chemical potentials ($\Delta\mu$) versus CO_2 pressure P_{CO_2}/P_0 and temperatures for the reactions of MgO, $Mg(OH)_2$, and alkali metal carbonates capturing CO_2 at fixed P_{H_2O} = 1.0 bar and 0.1 bar [13,14]. Only the curve with $\Delta\mu$ = 0 for each reaction is shown explicitly.

can capture CO_2 at low temperature range (400 - 500 K) when CO_2 pressure is around 0.1 bar (post-combustion) or 20 - 30 bar (pre-combustion) [10, 14]. We have examined the effect of H_2O on the reaction thermodynamics and have found that our modeling approach can be used to account for partial pressures of CO_2 and H_2O and the temperature. We found that formation of bicarbonates from the alkali metal oxides results in a lower sorbent regeneration temperature and that formation of bicarbonate from the carbonates, by addition of CO_2 and H_2O, reduces the CO_2 capturing temperature even further. Indeed, as shown in **Figure 4**, we predict that Na_2CO_3 and K_2CO_3 have turnover temperatures for CO_2 capture through bicarbonate formation that are suitable for operation under both pre- and post-combustion conditions. When the steam pressure (P_{H_2O}) increases as shown in **Figure 4**, at the same temperature, the P_{CO_2} is decreased because both CO_2 and H_2O are on the reactant sides.

As one can see from **Figure 4**, our results show that MgO could be used for both pre- and post-combustion capture technologies due to its low regenerating temperature (T_2 = 540 K for post-combustion conditions and T_1 = 690 K for pre-combustion conditions) which are close to experimental findings. However, $Mg(OH)_2$ can only be used for post-combustion capture technologies with a turnover T_2 = 600 K because its turnover temperature (T_1) is very high, outside the temperature range of interest for pre-combustion applications.

Among the list of alkaline-earth metal oxides and hydroxides analyzed in **Table 1**, comparing with CaO, only MgO and $Mg(OH)_2$ are found to be good sorbents for CO_2 capture. Upon absorption of CO_2 both of MgO and $Mg(OH)_2$ can form $MgCO_3$. However, the regeneration conditions of the original systems can take place at different conditions as indicated in **Figure 4**. In this case we present the calculated phase diagram of MgO-$Mg(OH)_2$-$MgCO_3$ system at different CO_2 pressures and at two fixed P_{H_2O} values (0.1 and 1.0 bar). From **Figure 4** it can be seen that when H_2O is present and at low temperatures, $MgCO_3$ can release CO_2 to form $Mg(OH)_2$ instead of forming MgO. For example, at P_{H_2O} = 0.1 bar, only for temperatures under the transition temperature (T_{tr}) 460 K, $MgCO_3$ can be regenerated to form $Mg(OH)_2$. By the increase in the H_2O pressure, the transition temperature is increased. As shown in **Figure 4**, when P_{H_2O} is increased to 1.0 bar from 0.1 bar, the corresponding T_{tr} = 520 K. Above T_{tr}, $MgCO_3$ is regenerated to MgO. Therefore, when water is present in the sorption/desorption cycle, no matter whether the initial sorbent is MgO or $Mg(OH)_2$, and for temperatures below T_{tr}, the CO_2 capture reaction is dominated by the process $Mg(OH)_2 + CO_2 \leftrightarrow MgCO_3 + H_2O(g)$, whereas above T_{tr} the CO_2 capture reaction is given by $MgO + CO_2 \leftrightarrow MgCO_3$. The reason is that between MgO and $Mg(OH)_2$, there is a phase transition reaction $MgO + H_2O(g) = Mg(OH)_2$ happening at the transition temperature T_{tr}. Obviously, by controlling the H_2O pressure as shown in **Figure 4**, the CO_2 capture temperature (*T* swing) can be adjusted because the CO_2 is a reactant while H_2O is a product. However, adding more water in the sorbent system will require more energy due to its sensible heat. These results are in good agreement with the experimental measurements [8].

3.2. Applications to Mixture of Solids [9-11,15]

Lithium silicate (Li_4SiO_4) and zirconate (Li_2ZrO_3) have been proposed experimentally as promising high-temperature CO_2 sorbents [29-35]. And our previous theoretical studies confirmed these findings [9-11]. However, with different ratios of Li_2O/SiO_2 and Li_2O/ZrO_2, one can get different lithium salt compounds as shown in **Table 2**. We performed first filter (*Steps* 1 and 2) on these lithium salts. The absorbed CO_2 molar and weight

Copyright © 2012 SciRes.

Table 2. The mole and weight percentages of CO_2 capture by lithium silicates and zirconates, and the calculated energy change (ΔE^{DFT}) of the absorption reactions.

Reaction	Absorb CO_2		ΔE^{DFT} (eV)
	mol/mole	wt%	
$Li_2O + CO_2 \leftrightarrow Li_2CO_3$	1	147.28	−2.11386
$Li_8SiO_6 + CO_2 \leftrightarrow Li_2CO_3 + Li_2O + Li_4SiO_4$	1	24.50	−1.99333
$Li_8SiO_6 + 2CO_2 \leftrightarrow 2Li_2CO_3 + Li_4SiO_4$	2	49.01	−4.11576
$Li_8SiO_6 + 3CO_2 \leftrightarrow 3Li_2CO_3 + Li_2SiO_3$	3	73.51	−5.65692
$Li_8SiO_6 + 4CO_2 \leftrightarrow 4Li_2CO_3 + SiO_2$	4	98.01	−6.44485
γ-$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3$	1	36.72	−1.52239
γ-$Li_4SiO_4 + 2CO_2 \leftrightarrow 2Li_2CO_3 + SiO_2$	2	73.44	−2.31032
$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3$	**1**	**36.72**	**−1.54116**
$Li_4SiO_4 + 2CO_2 \leftrightarrow 2Li_2CO_3 + SiO_2$	2	73.44	−2.32908
$Li_6Si_2O_7 + CO_2 \leftrightarrow Li_2CO_3 + 2Li_2SiO_3$	1	20.98	−1.71488
$Li_6Si_2O_7 + 2CO_2 \leftrightarrow 2Li_2CO_3 + Li_2SiO_3 + SiO_2$	2	41.95	−2.50281
$Li_6Si_2O_7 + 3CO_2 \leftrightarrow 3Li_2CO_3 + 2SiO_2$	3	62.93	−3.29073
$Li_2SiO_3 + CO_2 \leftrightarrow Li_2CO_3 + SiO_2$	**1**	**48.92**	**−0.78793**
$Li_2Si_2O_5 + CO_2 \leftrightarrow Li_2CO_3 + 2SiO_2$	**1**	**29.33**	**−0.70450**
meta−$Li_2Si_2O_5 + CO_2 \leftrightarrow Li_2CO_3 + 2SiO_2$	**1**	**29.33**	**−0.93127**
$Li_2Si_3O_7 + CO_2 \leftrightarrow Li_2CO_3 + 3SiO_2$	**1**	**20.94**	**−0.67324**
$SiO_2 + CO_2 \leftrightarrow Li_2SiO_3$	1	73.38	7.20670
$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2$	**1**	**28.78**	**−1.47803**
$Li_6Zr_2O_7 + CO_2 \leftrightarrow Li_2CO_3 + 2Li_2ZrO_3$	1	13.09	−1.80877
$Li_6Zr_2O_7 + 2CO_2 \leftrightarrow 2Li_2CO_3 + Li_2ZrO_3 + ZrO_2$	2	26.19	−3.32639
$Li_6Zr_2O_7 + 3CO_2 \leftrightarrow 3Li_2CO_3 + 2ZrO_2$	3	39.28	−4.84401
$Li_2MgSiO_4 + CO_2 \leftrightarrow Li_2CO_3 + MgSiO_3$	**1**	**33.79**	**−1.05955**
$Li_2MnSiO_4 + CO_2 \leftrightarrow Li_2CO_3 + MnSiO_3$	**1**	27.37	**0.23571**
$Li_2FeSiO_4 + CO_2 \leftrightarrow Li_2CO_3 + FeSiO_3$	**1**	27.21	**−0.74047**
$Li_2CoSiO_4 + CO_2 \leftrightarrow Li_2CO_3 + CoSiO_3$	**1**	26.70	**−0.55828**
$Li_2ZnSiO_4 + CO_2 \leftrightarrow Li_2CO_3 + ZnSiO_3$	**1**	25.70	**−0.36963**
$Li_2CdSiO_4 + CO_2 \leftrightarrow Li_2CO_3 + CdSiO_3$	1	20.17	0.12937
$Li_2Rb_2SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Rb_2SiO_3$	1	15.91	11.1380
$Li_2TiSiO_5 + CO_2 \leftrightarrow Li_2CO_3 + TiSiO_4$	1	25.93	0.34016
$Li_2VSiO_5 + CO_2 \leftrightarrow Li_2CO_3 + VSiO_4$	1	25.47	0.51246

percentages as well as the calculated DFT energy differences for the capture reactions are also listed in **Table 2**.

Figure 5 shows the free energy changes of CO_2 capture reactions by some lithium silicates as obtained from HSC Chemistry database. From **Table 2** and **Figure 5**, one can see that comparing with Li_2O, Li_4SiO_4, and Li_2ZrO_3, the Li_2SiO_3, $Li_2Si_2O_5$, and $Li_2Si_2O_7$ are better CO_2 solid sorbent candidates because they require less free energy to reverse the CO_2 capture reactions and have lower regenerating temperatures. Our calculations show

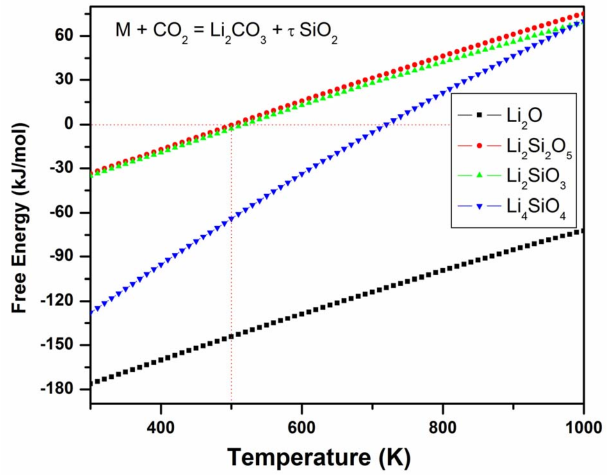
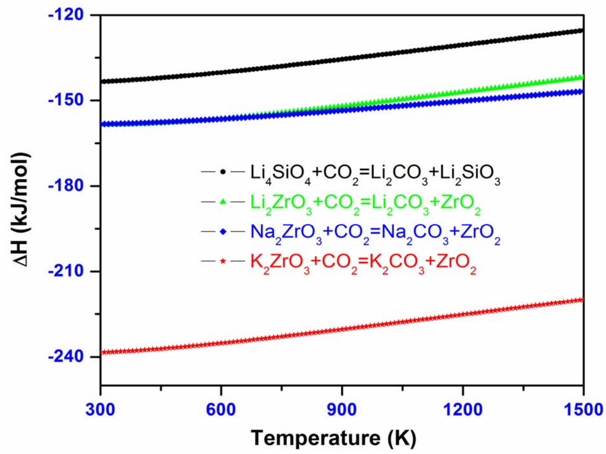


Figure 5. The Gibbs free energy changes of some lithium silicates capture CO_2 reactions from HSC Chemistry database [26].

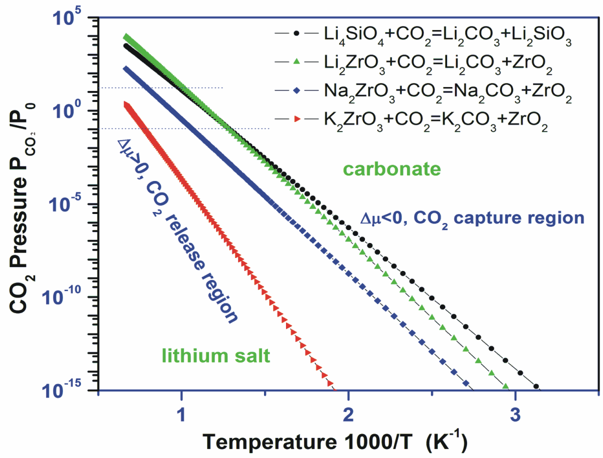
that although pure Li_2O can absorb CO_2 efficiently, it is not a good solid sorbent for CO_2 capture because the reverse reaction, corresponding to Li_2CO_3 releasing CO_2, can only occur at very low CO_2 pressure and/or at very high temperature [12]. SiO_2 does not interact with CO_2 at normal conditions. Therefore, it can be concluded that when a lithium silicate compound with the ratio of Li_2O/SiO_2 is less or equal to 1.0, it could have better CO_2 capture performance than Li_4SiO_4, because its regeneration can occur at low temperature and hence require less regeneration heat. Further calculations (*Steps* 3 and 4) and analysis on these lithium silicates capture CO_2 properties are underway.

Figure 6(a) summarizes our calculated heats of reactions (ΔH) for four alkali metal silicate and zirconates [9-11]. From **Figure 6(a)** and **Table 2**, one can see that the K_2ZrO_3 capture CO_2 has a larger ΔH than the other three solids. Li_4SiO_4 has a relative small ΔH while along a large temperature range the Li_2ZrO_3 and Na_2ZrO_3 have similar ΔH. Therefore, K_2ZrO_3 is not a good candidate as CO_2 sorbent because it needs more heat to regenerate. Among these four solids, Li_4SiO_4 is the best choice. These results are in good agreement with available experimental measurements [29-35].

According to Equation (2), the calculated relationships of $\Delta\mu$ with CO_2 pressure and temperature for these four solids are shown in **Figure 6(b)**. The line in **Figure 6(b)** indicates that for each reaction, $\Delta\mu(T, P)$ is approaching zero. The region close to the line is favorable for the absorption and desorption because of the minimal energy costs at a given temperature and pressure. Above the line, the solid (Li_4SiO_4, M_2ZrO_3 (M = Li, Na, K)) is favorable to absorb CO_2 and to form Li_2CO_3, while below the line the Li_2CO_3 is favorable to release CO_2 and to regenerate lithium silicate solids. The calculated thermodynamic



(a)



(b)

Figure 6. The calculated thermodynamic properties of some alkali metal silicate and zirconates capture CO_2 [9-11]. (a) The heat of reactions; (b) The contour plotting of calculated chemical potentials ($\Delta\mu$) versus CO_2 pressures and temperatures of the sorbents capture CO_2 reactions. Y-axis plotted in logarithm scale. Only $\Delta\mu = 0$ curve is shown explicitly. For each reaction, above its $\Delta\mu = 0$ curve, their $\Delta\mu < 0$, which means the sorbents absorb CO_2 and the reaction goes forward, whereas below the $\Delta\mu = 0$ curve, their $\Delta\mu > 0$, which means the CO_2 start to release and the reaction goes backward to regenerate the sorbents.

properties of these solids are also summarized in **Table 3**.

From **Figure 6(b)** and **Table 3** one can see that these solids capture CO_2 up to higher temperatures ($T_1 > 1000$ K) compared with desired pre-combustion condition (313 - 573 K). Therefore, they are not good sorbents for capturing CO_2 in pre-combustion technology. However, some of them could be used for high-temperature post-combustion CO_2 capture technology with T_2 = 1285 K, 925 K, 780 K, 880 K, and 770 K for K_2ZrO_3, Na_2ZrO_3, Li_2ZrO_3 and Li_4SiO_4 respectively. Obviously, compared

Copyright © 2012 SciRes.

Table 3. The summary of the calculated energy change ΔE^{DFT}, the zero-point energy changes ΔE_{ZP} and the thermodynamic properties (ΔH, ΔG) of the CO_2 capture reactions by alkali metal silicates and zirconates. (unit: kJ/mol) [9,11-13]. The turnover temperatures (T_1 and T_2) of the reactions of CO_2 capture by solids under the conditions of pre-combustion (P_{CO_2} = 20 bar) and post-combustion (P_{CO_2} = 0.1 bar) are also listed.

Reaction	ΔE^{DFT}	ΔE_{ZP}	ΔH (T = 300 K)	ΔG (T = 300 K)	Turnover T (K)	
					T_1	T_2
$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3$	−148.704	5.971	−143.548	−93.972	1010	770
$Li_2ZrO_3 + CO_2 \leftrightarrow Li_2CO_3 + ZrO_2$	−146.648	11.311	−158.562 −162.69[a]	−103.845 −113.18[a]	1000	780
$K_2ZrO_3 + CO_2 \leftrightarrow K_2CO_3 + ZrO_2$	−223.158	5.813	−238.490	−187.884	hT[b]	1285
$Na_2ZrO_3 + CO_2 \leftrightarrow Na_2CO_3 + ZrO_2$	−140.862	2.236	−158.327 −151.403[a]	−114.121 −105.252[a]	1275	925

[a]from HSC-Chemistry database package[16]; [b]hT means the temperature is higher than our temperature range (1500 K).

to CaO, the T_2 of K_2ZrO_3 is still too high to be used for post-combustion technology. This may be part of the reason that there is no experimental work found in the literature for pure K_2ZrO_3 capturing CO_2. Therefore, Li_4SiO_4, Na_2ZrO_3, and Li_2ZrO_3 are good candidates for CO_2 sorbents working at high temperature.

Although Li_4SiO_4 and Li_2ZrO_3 have similar turnover temperature T_2 as shown in **Table 3**, from **Figure 6(a)** one can see that the reaction heat of Li_2ZrO_3 capture CO_2 is about 20 kJ/mol lower than that of Li_4SiO_4. This indicates that more heat is needed for regenerating Li_2ZrO_3 from Li_2CO_3 and ZrO_2. Therefore, as a CO_2 sorbent, the Li_4SiO_4 is thermodynamically better than Li_2ZrO_3 despite they may have different kinetics behaviours [36].

4. Conclusions

By combining thermodynamic database searching with first principles density functional theory and phonon lattice dynamics calculations, from vast of solid materials, we proposed a theoretical screening methodology to identify most promising candidates for CO_2 sorbents. The thermodynamic properties of solid materials are obtained and used for computing the thermodynamic reaction equilibrium properties of CO_2 absorption/desorption cycle based on the chemical potential and heat of reaction analysis. According to the pre- and post-combustion technologies and conditions in power-plants, based on our calculated thermodynamic properties of reactions for each solid capturing CO_2 varying with temperatures and pressures, only those solid materials, which result in lower energy cost in the capture and regeneration process and could work at desired conditions of CO_2 pressure and temperature, will be selected as promised candidates of CO_2 sorbents and further be considered for experimental validations. Compared to experimental thermodynamic data for known systems, our results show that this screening methodology can predict the thermodynamic properties for sorbents capture CO_2 reactions and there- fore can be used for screening out good CO_2 solid sorbents from vast of solid materials which thermodynamic data are unknown.

5. Acknowledgements

One of us (YD) thanks Drs. D. C. Sorescu, J. K. Johnson, B. Zhang, Y. Soong, R. Siriwardane and G. Richards for fruitful discussions.

REFERENCES

[1] D. Aaron and C. Tsouris, "Separation of CO_2 from Flue Gas: A Review," *Separation Science and Technology*, Vol. 40, No. 1-3, 2005, pp. 321-348. doi:10.1081/SS-200042244

[2] M. R. Allen, D. J. Frame, C. Huntingford, C. D. Jones, J. A. Lowe, M. Meinshausen and N. Meinshausen, "Warming Caused by Cumulative Carbon Emissions towards the Trillionth Tonne," *Nature*, Vol. 458, No. 7242, 2009, pp. 1163-1166. doi:10.1038/nature08019

[3] R. S. Haszeldine, "Carbon Capture and Storage: How Green Can Black Be?" *Science*, Vol. 325, No. 5948, 2009, pp. 1647-1652. doi:10.1126/science.1172246

[4] Y. Duan, "Computational Screening of Solid Materials for CO_2 Capture," 2011. http://www.netl.doe.gov/publications/proceedings/11/co2cture/Posters/Poster-Duan-NETL-ComputationalScreening.pdf

[5] C. M. White, B. R. Strazisar, E. J. Granite, J. S. Hoffman and H. W. Pennline, "Separation and Capture of CO_2 from Large Stationary Sources and Sequestration in Geological Formations-Coalbeds and Deep Saline Aquifers," *Journal of the Air & Waste Management Association*, Vol. 53, 2003, pp. 645-715.

[6] J. C. Abanades, E. J. Anthony, J. Wang and J. E. Oakey, "Fluidized Bed Combustion Systems Integrating CO_2 Capture with CaO," *Environmental Science & Technology*, Vol. 39, No. 8, 2005, pp. 2861-2866. doi:10.1021/es0496221

Copyright © 2012 SciRes.

[7] R. Siriwardane, J. Poston, K. Chaudhari, A. Zinn, T. Simonyi and C. Robinson, "Chemical-Looping Combustion of Simulated Synthesis Gas Using Nickel Oxide Oxygen Carrier Supported on Bentonite," *Energy & Fuels*, Vol. 21, No. 3, 2007, pp. 1582-1591. doi:10.1021/ef0604947

[8] R. V. Siriwardane and R. W. Stevens, "Novel Regenerable Magnesium Hydroxide Sorbents for CO_2 Capture at Warm Gas Temperatures," *Industrial & Engineering Chemistry Research*, Vol. 48, No. 4, 2009, pp. 2135-2141. doi:10.1021/ie8011598

[9] Y. Duan, "Electronic Structural and Phonon Properties of Lithium Zirconates and Their Capabilities of CO_2 Capture: A First-Principle Density Functional Approach," *Journal of Renewable and Sustainable Energy*, Vol. 3, No. 1, 2011, Article ID: 013102. doi:10.1063/1.3529427

[10] Y. Duan, "A First-Principles Density Functional Theory Study of the Electronic Structural and Thermodynamic Properties of M_2ZrO_3 and M_2CO_3 (M=Na, K) and Their Capabilities of CO_2 Capture," *Journal of Renewable and Sustainable Energy*, Vol. 4, No. 1, 2012, Article ID: 013109. doi:10.1063/1.3683519

[11] Y. Duan and K. Parlinski, "Density Functional Theory Study of the Structural, Electronic, Lattice Dynamical, and Thermodynamic Properties of Li_4SiO_4 and Its Capability for CO_2 Capture," *Physical Review B*, Vol. 84, No. 10, 2011, Article ID: 104113. doi:10.1103/PhysRevB.84.104113

[12] Y. Duan and D. C. Sorescu, "Density Functional Theory Studies of the Structural, Electronic, and Phonon Properties of Li_2O and Li_2CO_3: Application to CO_2 Capture Reaction," *Physical Review B*, Vol. 79, No. 1, 2009, Article ID: 014301. doi:10.1103/PhysRevB.79.014301

[13] Y. Duan and D. C. Sorescu, "CO_2 Capture Properties of Alkaline Earth Metal Oxides and Hydroxides: A Combined Density Functional Theory and Lattice Phonon Dynamics Study," *Journal of Chemical Physics*, Vol. 133, No. 7, 2010, Article ID: 074508. doi:10.1063/1.3473043

[14] Y. Duan, B. Zhang, D. C. Sorescu and J. K. Johnson, "CO_2 Capture Properties of M-C-O-H (M = Li, Na, K) Systems: A Combined Density Functional Theory and Lattice Phonon Dynamics Study," *Journal of Solid State Chemistry*, Vol. 184, No. 2, 2011, pp. 304-311. doi:10.1016/j.jssc.2010.12.005

[15] B. Zhang, Y. Duan and J. K. Johnson, "First-Principles Density Functional Theory Study of CO_2 Capture with Transition Metal Oxides and Hydroxides," *Journal of Chemical Physics*, Vol. 136, No. 6, 2012, Article ID: 064516. doi:10.1063/1.3684901

[16] G. Kresse and J. Hafner, "*Ab Initio* Molecular-Dynamics for Liquid-Metals," *Physical Review B*, Vol. 47, No. 1, 1993, pp. 558-561. doi:10.1103/PhysRevB.47.558

[17] G. Kresse and J. Furthmuller, "Efficient Iterative Schemes for *Ab Initio* Total-Energy Calculations Using a Plane-Wave Basis Set," *Physical Review B*, Vol. 54, No. 16, 1996, pp. 11169-11186. doi:10.1103/PhysRevB.54.11169

[18] J. P. Perdew and Y. Wang, "Accurate and Simple Analytic Representation of the Electron-Gas Correlation-Energy," *Physical Review B*, Vol. 45, No. 23, 1992, pp. 13244-13249. doi:10.1103/PhysRevB.45.13244

[19] Y. Duan, "Electronic Properties and Stabilities of Bulk and Low-Index Surfaces of SnO in Comparison with SnO_2: A First-Principle Density Functional Approach with an Empirical Correction of van der Waals Interactions," *Physical Review B*, Vol. 77, No. 4, 2008, Article ID: 045332. doi:10.1103/PhysRevB.77.045332

[20] H. J. Monkhorst and J. D. Pack, "Special Points for Brillouin-Zone Integrations," *Physical Review B*, Vol. 13, No. 12, 1976, pp. 5188-5192. doi:10.1103/PhysRevB.13.5188

[21] K. Parlinski, "PHONON Software," 2006. http://wolf.ifj.edu.pl/phonon/

[22] K. Parlinski, Z. Q. Li and Y. Kawazoe, "First-Principles Determination of the Soft Mode in Cubic ZrO_2," *Physical Review Letters*, Vol. 78, No. 21, 1997, pp. 4063-4066. doi:10.1103/PhysRevLett.78.4063

[23] National Energy Technilogy Laboratory, "Cost and Performance Baseline for Fossil Energy Plants," 2007. http://www.netl.doe.gov/energy-analyses/baseline_studies.html

[24] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, "Advancesn in CO_2 Capture Technology—The US Department of Energy's Carbon Sequestration Program," *International Journal of Greenhouse Gas Control*, Vol. 2, No. 1, 2008, pp. 9-20. doi:10.1016/S1750-5836(07)00094-1

[25] Q. Wang, J. Luo, Z. Zhong and A. Borgna, "CO_2 Capture by Solid Adsorbents and Their Applications: Current Status and New Trends," *Energy & Environmental Science*, Vol. 4, No. 1, 2011, pp. 42-55.

[26] Software HSC Chemistry, "Pori: Outotec Research Oy," 2006. www.outotec.com/hsc

[27] Factsage, www.factsage.com

[28] H. W. Pennline, J. S. Hoffman, M. L. Gray, R. V. Siriwardane, D. J. Fauth and G. A. Richards, "NETL In-House Postcombustion Sorbent-Based Carbon Dioxide Capture Research," *Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting*, Pittsburgh, 24-26 March 2009.

[29] K. Essaki, K. Nakagawa, M. Kato and H. Uemoto, "CO_2 Absorption by Lithium Silicate at Room Temperature," *Journal of Chemical Engineering of Japan*, Vol. 37, No. 6, 2004, pp. 772-777. doi:10.1252/jcej.37.772

[30] M. Kato and K. Nakagawa, "New Series of Lithium Containing Complex Oxides, Lithium Silicates, for Application as a High Temperature CO_2 Absorbent," *Journal of the Ceramic Society of Japan*, Vol. 109, No. 11, 2001, pp. 911-914. doi:10.2109/jcersj.109.1275_911

[31] K. Nakagawa and T. Ohashi, "A Novel Method of CO_2 Capture from High Temperature Gases," *Journal of the Electrochemical Society*, Vol. 145, No. 4, 1998, pp. 1344-1346. doi:10.1149/1.1838462

[32] K. Nakagawa and T. Ohashi, "A Reversible Change between Lithium Zirconate and Zirconia in Molten Carbonate," *Electrochemistry*, Vol. 67, No. 6, 1999, pp. 618-621.

[33] M. Olivares-Marin, T. C. Drage and M. M. Maroto-Valer, "Novel Lithium-Based Sorbents from Fly Ashes for CO_2

Copyright © 2012 SciRes.

Capture at High Temperatures," *International Journal of Greenhouse Gas Control*, Vol. 4, No. 4, 2010, pp. 623-629.

[34] R. Rodriguez-Mosqueda and H. Pfeiffer, "Thermokinetic Analysis of the CO_2 Chemisorption on Li_4SiO_4 by Using Different Gas Flow Rates and Particle Sizes," *Journal of Physical Chemistry A*, Vol. 114, No. 13, 2010, pp. 4535-4541. doi:10.1021/jp911491t

[35] R. Xiong, J. Ida and Y. S. Lin, "Kinetics of Carbon Dioxide Sorption on Potassium-Doped Lithium Zirconate," *Chemical Engineering Science*, Vol. 58, No. 19, 2003, pp. 4377-4385. doi:10.1016/S0009-2509(03)00319-1

[36] A. Lopez-Ortiz, N. G. P. Rivera, A. R. Rojas and D. L. Gutierrez, "Novel Carbon Dioxide Solid Acceptors Using Sodium Containing Oxides," *Separation Science and Technology*, Vol. 39, No. 15, 2004, pp. 3559-3572. doi:10.1081/SS-200036766