

EFFICIENT THEORETICAL SCREENING OF SOLID SORBENTS FOR CO₂ CAPTURE APPLICATIONS

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ABSTRACT

Carbon dioxide is a major combustion product of coal, which once released into the air can contribute to global climate change. Current CO₂ capture technologies for power generation processes including amine solvents and CaO-based sorbent materials require very energy intensive regeneration steps which result in significantly decreased efficiency. Hence, there is a critical need for new materials that can capture and release CO₂ reversibly with acceptable energy costs if CO₂ is to be captured and sequestered economically. Inorganic sorbents are one such class of materials which typically capture CO₂ through the reversible formation of carbonates. 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 CO₂ sorbent candidates from the vast array of possible solid materials has been proposed and validated. The *ab initio* thermodynamic technique has the advantage of identifying thermodynamic properties of CO₂ 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 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, either from databases or from calculations, are further used for computing the thermodynamic reaction equilibrium properties of the CO₂ absorption/desorption cycle based on the chemical potential and heat of reaction. Only those solid materials for which lower capture energy costs are predicted at the desired process conditions are selected as CO₂ sorbent candidates and 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 CO₂ sorbent applications due to their high CO₂ absorption capacity at moderate working temperatures. In addition to introducing our selection process in this presentation, we will present our results for solid systems of alkali and alkaline metal oxides, hydroxides and carbonates/bicarbonates to validate our methodology. Additionally, applications of our computational method to mixed solid systems of Li₂O and SiO₂ with different mixing ratios, we showed that increasing the Li₂O/SiO₂ ratio in lithium silicates increases their corresponding turnover temperatures for CO₂ capture reactions. These theoretical predictions are in good agreement with available experimental findings.

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I. 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 global climate change, we must stop emitting CO₂ into the atmosphere by separating and capturing CO₂ from coal combustion and gasification plants and sequestering that CO₂ underground. Current technologies for capturing CO₂ 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 CO₂ reversibly with acceptable energy costs. One approach to solving such environmental problems is to capture and sequester the CO₂.^{2,3} Accordingly, solid sorbent materials have been proposed for capturing CO₂ 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 CO₂ sorbent applications due to their high CO₂ absorption capacity at moderate working temperatures.⁴⁻⁶

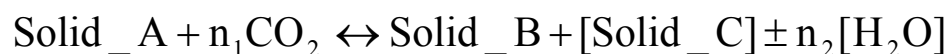
Currently, there is a critical need for development of new materials that can capture and release CO₂ reversibly with acceptable energy and operating costs. One of these new methods considered at NETL is based on the use of regenerable solid sorbents. In this case sorbents such as alkaline earth metal oxides or hydroxides are used to absorb CO₂ at warm temperatures typically ranging from ~100-300 °C. The key phenomenon used in these processes is transformation of the oxide or hydroxide materials to a carbonate upon CO₂ 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 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 CO₂. 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 CO₂ capture reactions by solid sorbents.

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. Recently, we proposed a theoretical methodology to identify promising solid sorbent candidates for CO₂ capture by combining thermodynamic database searching with *ab initio* thermodynamics calculated based on first-principles density functional theory (DFT) and lattice phonon dynamics.⁶⁻¹⁴ The advantage of this proposed method is that it allows identification of the thermodynamic properties of the CO₂ capture reaction as a function of temperature and pressure conditions without 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 CO₂ sorbents. For a given database of solid materials, from our screening scheme, a short list of promising candidates of CO₂ sorbents can be identified with optimal energy usages and can be further evaluated by our experimental research groups.

II. Our Screening Methodology

The complete description of the computational methodology can be found in our previous papers.⁶⁻¹¹ Here, we limit ourselves to provide only the main aspects relevant for the current study. The CO₂ capture reactions by solids in the presence of water vapors can be expressed generically in the form



where the terms given in [...] are optional and n_1 and n_2 are the numbers of moles of CO₂ and H₂O involved in the capture reactions. We treat the gas phase species CO₂ and H₂O as ideal gases. By assuming that the difference between the chemical potentials ($\Delta\mu^0$) of the solid phases of A, B (and C) can be approximated by the difference in their electronic energies (ΔE^0), obtained directly from 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

$$\Delta \mu (T, P) = \Delta \mu^0 (T) - RT \ln \frac{P_{\text{CO}_2}^{n_1}}{P_{\text{H}_2\text{O}}^{\pm n_2}}$$

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, with *ab initio* thermodynamic approach, we can calculate them based on the following approximation.

$$\Delta\mu^0(T) \approx \Delta E^{\text{DFT}} + \Delta E_{\text{ZP}} + \Delta F^{\text{PH}}(T) - n_1 G_{\text{CO}_2}(T) \pm n_2 G_{\text{H}_2\text{O}}(T) - \Delta H_0$$

Here, ΔE_{ZP} is the zero point energy difference between the reactants and products and can be obtained directly from phonon calculations. ΔH_0 is an empirical correction constant, and ΔE^{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 $P_{\text{H}_2\text{O}}$ in above equations is set to P_0 , which is the standard state reference pressure of 1 bar, and the $G_{\text{H}_2\text{O}}$ 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 ($G_{\text{H}_2\text{O}}$) can be obtained from standard statistical mechanics.

Figure 1 shows the schematic of our screening methodology. For a given solid databank, this methodology includes four main screening steps (or filters) to identify the most promising candidates:

Step I: 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 the complete reaction, materials safety, materials cost, *etc.* We also include where available the thermodynamic data from literature and from general software package, 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 better candidates can be obtained by minimizing their known free energies based on the operating conditions. Otherwise, if the material passes basic screening, continue to the next step.

Step II: Perform DFT calculations for all compounds in the candidate reaction with this solid. If $|\Delta E^{\text{DFT}} - \Delta E_{\text{ref}}|/n_1 < 20 \text{ kJ/mol}$, 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.* $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$), we add this compound to the list of good candidates. Otherwise, we go back to *step 1* and pick another solid.

Step III: 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.

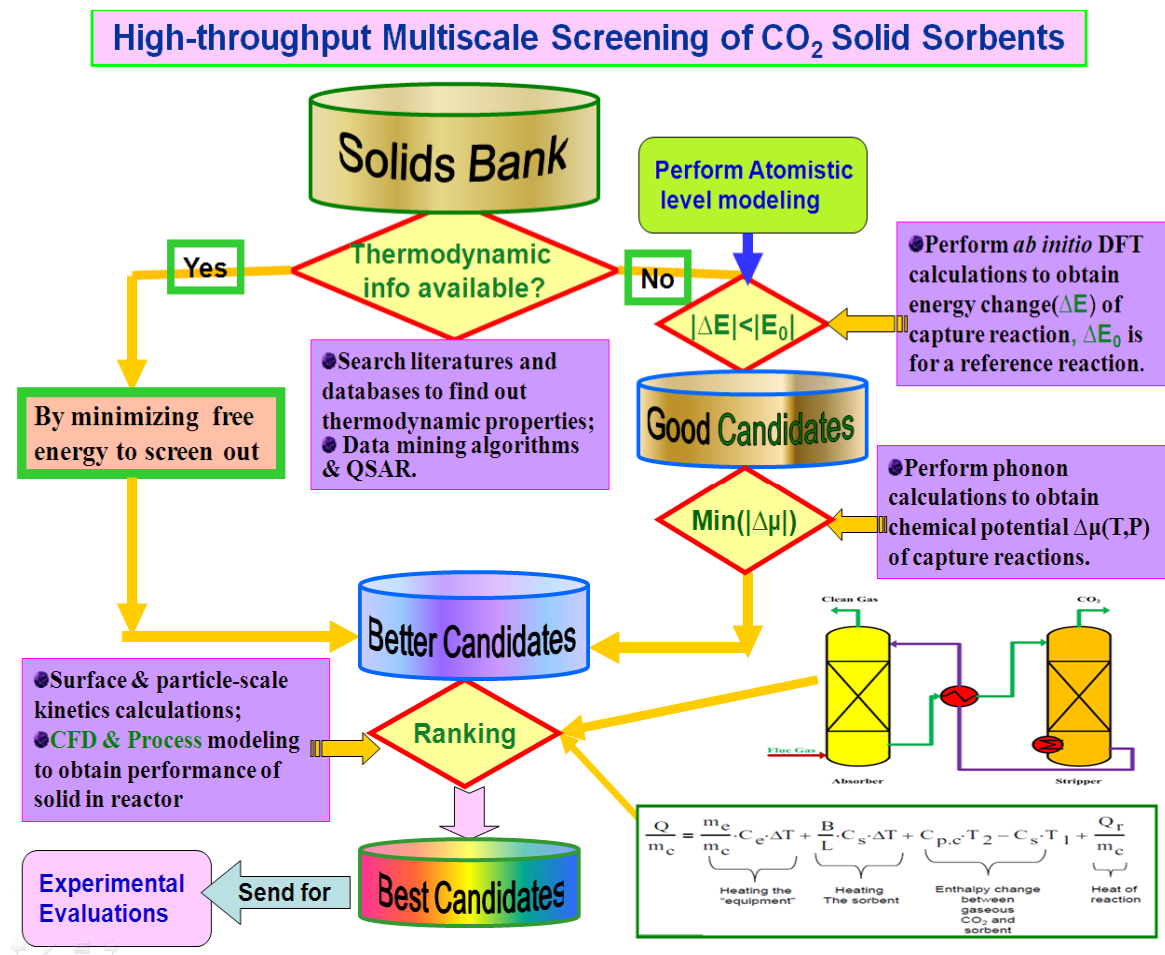


Figure 1. Schematic of our screening methodology

Step IV: 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 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. 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.

III. Results and Discussions

Based on the above screening methodology, we have screened hundreds of solid compounds and found some promising candidates for CO₂ sorbents. Here, we show several examples. In our study, the thermodynamic database we use is HSC Chemistry¹⁵ and Factsage¹⁶ packages. The DFT calculations were done by VASP package¹⁷, and the Phonon package¹⁸ was employed to conduct phonon calculations.

3.1 Applications to alkali and alkaline earth metal oxides and hydroxides^{6,8,10}

We applied our methodology to alkali and alkaline-earth metal oxides and hydroxides. Since 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.

As an example, Figure 2 shows the heat of reaction for alkali and alkaline earth metal oxides capture CO₂. From it, one can see that, except for BeO+CO₂→BeCO₃ reaction, overall, the calculated results are in good agreement with HSC experimental data. The larger discrepancy in BeO/BeCO₃ system is due to lack of the crystal structure of BeCO₃. Which means our theoretical approach can predict the right thermodynamic properties of solid reacting with CO₂ if the right crystal structure of solids is known.

After applying our screening steps(filters), among these oxides and hydroxides, we found that only MgO/Mg(OH)₂, Na₂CO₃/NaHCO₃, K₂CO₃/KHCO₃ are promising candidates for CO₂ sorbents which could be used for post-combustion and pre-combustion CO₂ capture technologies.^{7,8,10} Figure 3 gives the calculated relationships of chemical potential $\Delta\mu(T,P)$ with temperature and CO₂ pressure for reactions $M_2CO_3+CO_2+H_2O=2MHCO_3$, where M=Li, Na, K. Figure 4 shows the calculated phase diagram of MgO-Mg(OH)₂-MgCO₃.

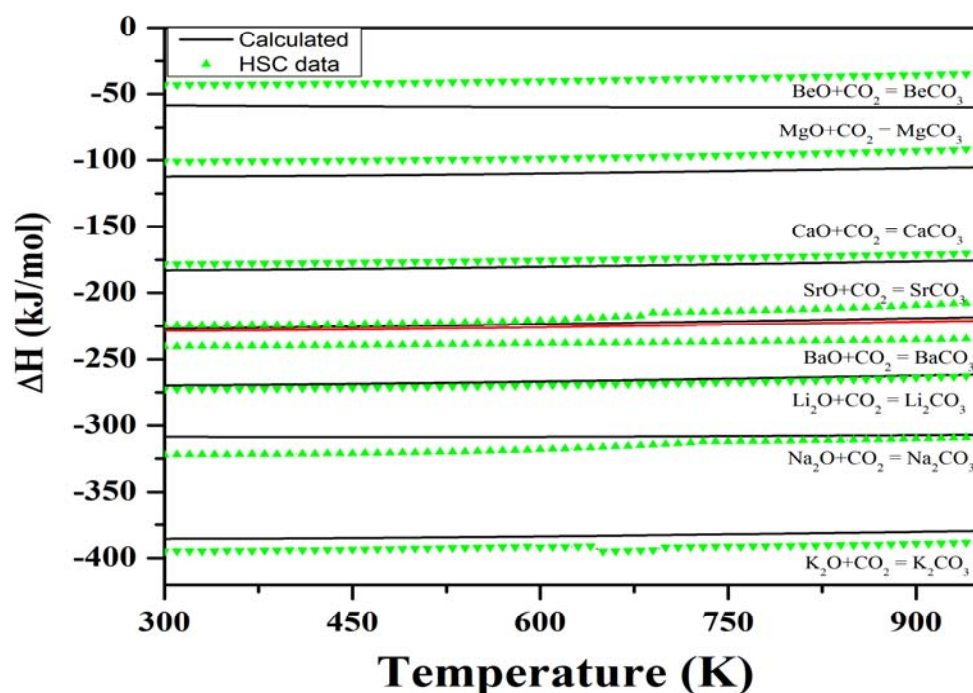


Figure 2. The calculated (solid line) and HSC data (dot line) heat of reaction for alkali and alkaline earth oxides reacting with CO_2 to form carbonates.

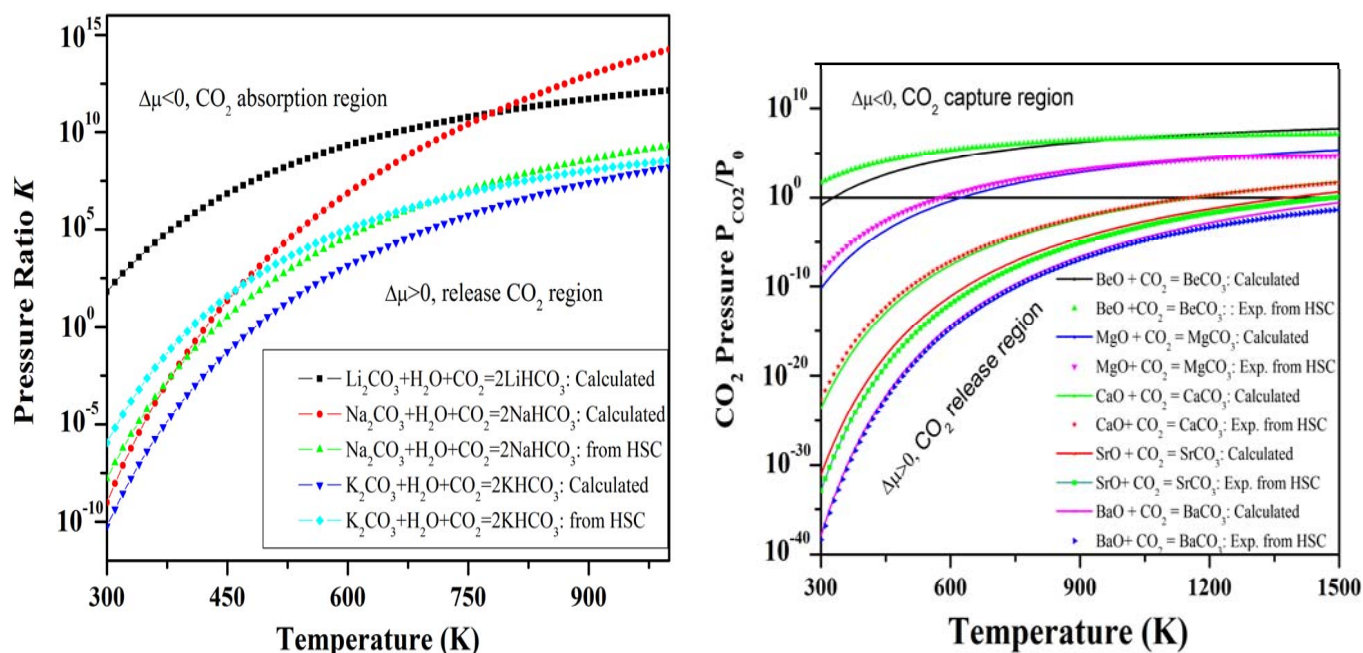


Figure 3. The calculated chemical potentials versus pressure ratio $K = P_{\text{CO}_2}P_{\text{H}_2\text{O}}/P_0^2$ and temperatures for the reactions of alkali metal carbonates capturing CO_2 to form bicarbonates.

From Figure 3, we can see that $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ and $\text{K}_2\text{CO}_3/\text{KHCO}_3$ can capture CO_2 at low temperature range (400~500K) when CO_2 pressure is around 0.1bar (post-combustion) or 20~30 bar (pre-combustion). 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, 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.

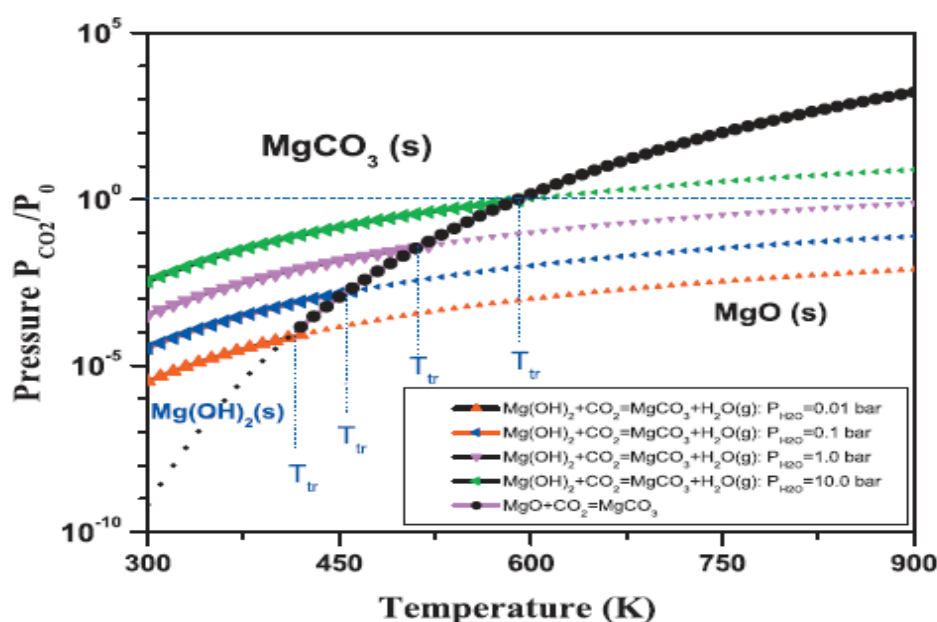


Figure 4. The calculated phase diagram of MgO - Mg(OH)_2 - MgCO_3 system versus the CO_2 pressure at fixed $P_{\text{H}_2\text{O}} = 0.01, 0.1, 1.0$ and 10.0 bar. For each $P_{\text{H}_2\text{O}}$, only Mg(OH)_2 can be regenerated from MgCO_3 for temperatures under the transition values (T_{tr}). Above T_{tr} values only MgO can be obtained.

Our results show that MgO could be used for both pre- and post-combustion capture technologies due to its low regenerating temperature ($T_2=560$ K for post-combustion conditions and $T_1=720$ 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 $T_2=720$ 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 this study, comparing

with CaO, only MgO and Mg(OH)₂ are found to be good sorbents for CO₂ capture. Upon absorption of CO₂ both of these two systems can form MgCO₃. 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-MgCO₃ system at different CO₂ pressures and under several fixed P_{H2O} values (0.01, 0.1, 1.0, and 10.0 bar respectively). From Fig.4 it can be seen that when H₂O is present and at low temperatures, MgCO₃ can release CO₂ to form Mg(OH)₂ instead of forming MgO. For example, at P_{H2O}=0.01 bar, only for temperatures under the transition temperature (T_{tr}) 420 K, MgCO₃ can be regenerated to form Mg(OH)₂. By the increase in the H₂O pressure, the transition temperature is increased. As shown in Fig.4, when P_{H2O} is increased to 10 bar, the corresponding T_{tr} = 600K. Above T_{tr}, MgCO₃ 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 CO₂ capture reaction is dominated by the process Mg(OH)₂+CO₂↔MgCO₃+ H₂O(g), whereas above T_{tr} the CO₂ capture reaction is given by MgO+CO₂ ↔MgCO₃. The reason is that between MgO and Mg(OH)₂, there is a phase transition reaction MgO+H₂O(g)= Mg(OH)₂ happening at the transition temperature T_{tr}. Obviously, by controlling the pressure of H₂O as shown in Fig.4, the capture CO₂ temperature (T swing) can be adjusted. However, more water in the sorbent system will cost more energy due to its sensible heat, there should be a trade-off to balance them in the practical technology.

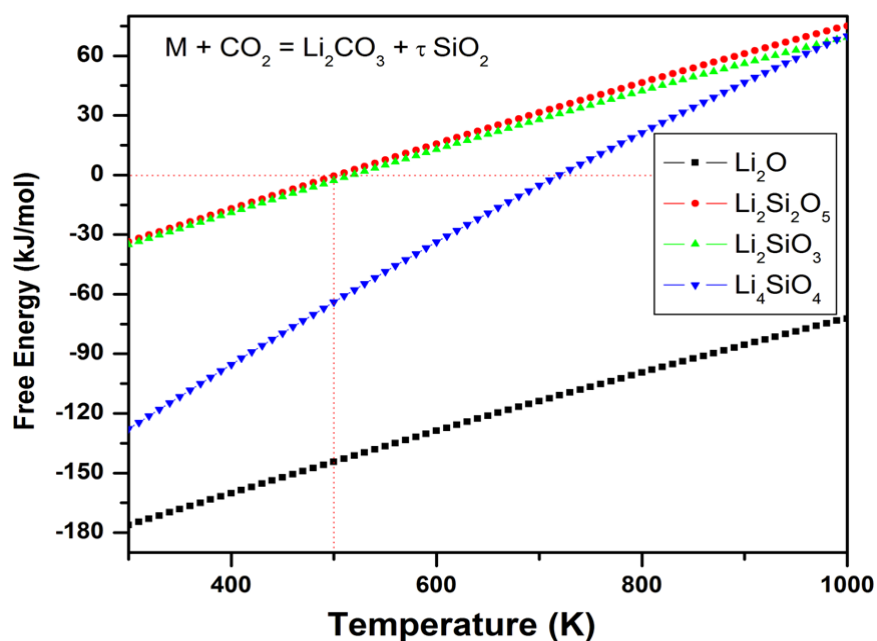


Figure 5. The free energy changes of some lithium silicates capture CO₂ reactions from HSC Chemistry database.

3.2 Applications to mixture of solids

With different ratio of $\text{Li}_2\text{O}/\text{SiO}_2$ and $\text{Li}_2\text{O}/\text{ZrO}_2$, we can get different compounds as shown in Table 1. In Table 1, the absorbed CO_2 molar and weight percentage as well as the calculated DFT energy differences for the capture reactions are also listed.

Figure 5 shows the free energy changes of reactions of some lithium silicates capture CO_2 , obtained from HSC Chemistry database. Figure 6 shows the calculated chemical potential of the CO_2 capture reactions by Li_2ZrO_3 and $\text{Li}_6\text{Zr}_2\text{O}_7$.

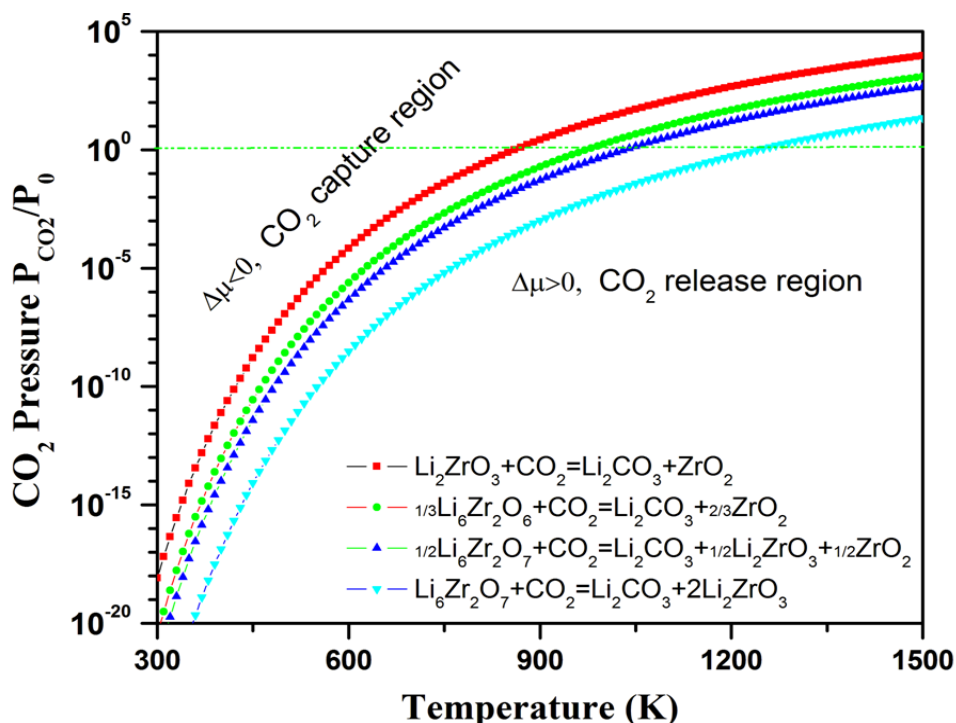


Figure 6. The contour plotting of calculated chemical potentials versus CO_2 pressures and temperatures of the lithium zirconates capture CO_2 reactions. Y-axis plotted in logarithm scale. Only $\Delta\mu=0$ curve is shown explicitly. For each reaction, above its $\Delta\mu=0$ curve, their $\Delta\mu<0$, which means the lithium zirconates 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.

From Table 1 and Figure 5, one can see that comparing with Li_2O , Li_4SiO_4 and Li_2ZrO_3 , the Li_2SiO_3 , $\text{Li}_2\text{Si}_2\text{O}_5$, and $\text{Li}_2\text{Si}_2\text{O}_7$ are better solid sorbent candidates for CO_2 sorbent at higher temperature. Our calculations show 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. SiO_2 does not

interact with CO₂ at normal conditions. Therefore, it can be concluded that when a lithium silicate compound with the ratio of Li₂O/SiO₂ is less or equal to 1.0, it could have better CO₂ capture performance than Li₄SiO₄, because its regeneration can occur at low temperature and hence require less regeneration heat. Further analysis on these lithium silicates capture CO₂ properties are under the way.

Table 1. The mole and weight percentages of CO₂ capture by lithium silicates and zirconates, and the calculated free energy change (ΔE^0) of the absorption reactions.

reaction	absorb CO ₂		ΔE^0 (eV)
	Mol/mole	Wt%	
Li ₂ O + CO ₂ ↔ Li ₂ CO ₃	1	147.28	-2.11386
Li ₈ SiO ₆ + CO ₂ ↔ Li ₂ CO ₃ + Li ₂ O + Li ₄ SiO ₄	1	24.50	-1.99333
Li ₈ SiO ₆ + 2CO ₂ ↔ 2Li ₂ CO ₃ + Li ₄ SiO ₄	2	49.01	-4.11576
Li ₈ SiO ₆ + 3CO ₂ ↔ 3Li ₂ CO ₃ + Li ₂ SiO ₃	3	73.51	-5.65692
Li ₈ SiO ₆ + 4CO ₂ ↔ 4Li ₂ CO ₃ + SiO ₂	4	98.01	-6.44485
γ-Li ₄ SiO ₄ + CO ₂ ↔ Li ₂ CO ₃ + Li ₂ SiO ₃	1	36.72	-1.52239
γ-Li ₄ SiO ₄ + 2CO ₂ ↔ 2Li ₂ CO ₃ + SiO ₂	2	73.44	-2.31032
Li ₄ SiO ₄ + CO ₂ ↔ Li ₂ CO ₃ + Li ₂ SiO ₃	1	36.72	-1.54116
Li ₄ SiO ₄ + 2CO ₂ ↔ 2Li ₂ CO ₃ + SiO ₂	2	73.44	-2.32908
Li ₆ Si ₂ O ₇ + CO ₂ ↔ Li ₂ CO ₃ + 2Li ₂ SiO ₃	1	20.98	-1.71488
Li ₆ Si ₂ O ₇ + 2CO ₂ ↔ 2Li ₂ CO ₃ + Li ₂ SiO ₃ + SiO ₂	2	41.95	-2.50281
Li ₆ Si ₂ O ₇ + 3CO ₂ ↔ 3Li ₂ CO ₃ + 2SiO ₂	3	62.93	-3.29073
Li ₂ SiO ₃ + CO ₂ ↔ Li ₂ CO ₃ + SiO ₂	1	48.92	-0.78793
Li ₂ Si ₂ O ₅ + CO ₂ ↔ Li ₂ CO ₃ + 2SiO ₂	1	29.33	-0.70450
meta-Li ₂ Si ₂ O ₅ + CO ₂ ↔ Li ₂ CO ₃ + 2SiO ₂	1	29.33	-0.93127
Li ₂ Si ₃ O ₇ + CO ₂ ↔ Li ₂ CO ₃ + 3SiO ₂	1	20.94	-0.67324
Li ₂ ZrO ₃ + CO ₂ ↔ Li ₂ CO ₃ + ZrO ₂	1	28.75	-1.51762
Li ₆ Zr ₂ O ₇ + CO ₂ ↔ Li ₂ CO ₃ + 2Li ₂ ZrO ₃	1	13.09	-1.80877
Li ₆ Zr ₂ O ₇ + 2CO ₂ ↔ 2Li ₂ CO ₃ + Li ₂ ZrO ₃ + ZrO ₂	2	26.19	-3.32639
Li ₆ Zr ₂ O ₇ + 3CO ₂ ↔ 3Li ₂ CO ₃ + 2ZrO ₂	3	39.28	-4.84401

From Figure 6 and Table 1, one can see that these two lithium zirconates capture CO_2 up to higher temperatures ($T_1 > 1000\text{K}$) compared with desired pre-combustion condition ($673\sim 723\text{K}$). Therefore, they are not good sorbents for capturing CO_2 in pre-combustion technology. However, they could be used for high-temperature post-combustion CO_2 capture with $T_2 = 780\text{K}$, 880K for Li_2ZrO_3 and $\text{Li}_6\text{Zr}_2\text{O}_7$ respectively, as experimental results indicate that Li_2ZrO_3 reacts immediately with ambient CO_2 ($P_{\text{CO}_2} = 1\text{ bar}$) in the range of 723K to 823K and products react and return reversibly to lithium zirconate at temperatures above 873K .

From Fig.6, one can see that during the first half cycle of absorbing CO_2 , the $\text{Li}_6\text{Zr}_2\text{O}_7$ can be fully converted into ZrO_2 and Li_2CO_3 because the partial reactions do not gain any energetic advantage. Interestingly, during the second half cycle of capturing, when the Li_2CO_3 and the ZrO_2 reacts each other to release CO_2 and regenerate the sorbent back, only Li_2ZrO_3 can be regenerated. As shown in Fig.6, the reaction curve of Li_2ZrO_3 capturing CO_2 is always higher than the other three curves of $\text{Li}_6\text{Zr}_2\text{O}_7$ reacting with CO_2 . Therefore, the regeneration first forms Li_2ZrO_3 , not $\text{Li}_6\text{Zr}_2\text{O}_7$. The $\text{Li}_6\text{Zr}_2\text{O}_7$ only can be formed either at low CO_2 pressure (T fixed) or at high temperature (P_{CO_2} fixed) through Li_2ZrO_3 further reacting with Li_2CO_3 and ZrO_2 . In other words, no matter what the initial solid is Li_2ZrO_3 or $\text{Li}_6\text{Zr}_2\text{O}_7$, after first sorption/desorption cycle, the following cycle only is for the reaction $\text{Li}_2\text{ZrO}_3 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{ZrO}_2$ and there is no $\text{Li}_6\text{Zr}_2\text{O}_7$ left in the system. This is in good agreement with the experimental findings as that the hexa-lithium zirconate ($\text{Li}_6\text{Zr}_2\text{O}_7$) absorbed four times more CO_2 than Li_2ZrO_3 , and its CO_2 sorption rate is faster than Li_2ZrO_3 at short times, but after long times, their capture behaviors became similar. This result indicates that there is no advantage to use $\text{Li}_6\text{Zr}_2\text{O}_7$ over Li_2ZrO_3 as CO_2 sorbent because they have the same functionality after the first cycle.

From Table 1 and Fig. 6, one can see that the reverse reaction is not just to dissociate Li_2CO_3 but also to regenerate Li_2ZrO_3 from Li_2O by reacting with ZrO_2 which involves net energy gain, and lay down the conditions for $\Delta\mu > 0$ compared with the case of Li_2O . In other words, the presence of ZrO_2 can destabilize the stable phase of Li_2CO_3 and make the reverse reaction to release CO_2 less energy required.

As described above and shown in Fig.7, all of these reactions are thermodynamically favorable over a quite wide range of temperatures ($< 1000\text{K}$) and P_{CO_2} , which means that under this temperature range the CO_2 is thermodynamically favored by M_2ZrO_3 ($\text{M} = \text{Li, Na, K}$). But as a CO_2 solid sorbent, the sorbent should not only be easy to absorb CO_2 in the first half cycle but also be easy

to release the CO₂ from products (M₂CO₃ and ZrO₂ for example) in the second half cycle. The operating conditions for absorption/desorption processes are depending on the pre- and post-combustion technologies.

Table II. The weight percentage of CO₂ capture, the calculated energy change ΔE^{DFT} , the zero-point energy changes ΔE_{ZP} and the thermodynamic properties (ΔH , ΔG) of the CO₂ capture reactions by alkali metal zirconates. (unit: kJ/mol). The turnover temperatures (T_1 and T_2) of the reactions of CO₂ 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	absorbing CO ₂ Wt%	ΔE^{DFT}	ΔE_{ZP}	ΔH (T=300K)	ΔG (T=300K)	Turnover T (K)	
						T_1	T_2
$\text{K}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{K}_2\text{CO}_3 + \text{ZrO}_2$	20.24	-223.158	5.813	-238.490	-187.884	hT ^b	1285
$\text{Na}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{Na}_2\text{CO}_3 + \text{ZrO}_2$	23.76	-140.862	2.236	-158.327 -151.403 ^a	-114.121 -105.252 ^a	1275	925
$\text{Li}_2\text{ZrO}_3 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{CO}_3 + \text{ZrO}_2$	28.75	-146.648	11.31 1	-158.562 -162.69 ^a	-103.845 -113.18 ^a	1000	780

^a from HSC-Chemistry database package¹⁶

^b hT means the temperature is higher than our temperature range (1500 K)

The Department of Energy (DOE) programmatic goal for post-combustion and oxy-combustion CO₂ capture is to capture at least 90% CO₂ with the cost in electricity no more than 35%, whereas in the case of pre-combustion CO₂ capture is to capture at least 90% CO₂ with the cost in electricity no more than 10%. Under pre-combustion conditions, after water-gas shifting, the gas stream mainly contains CO₂, H₂O and H₂. The partial CO₂ pressure is around 20~25 bar and the temperature is around 473~623K. To minimize the energy consumption, the ideal sorbents should work at these pressure and temperature ranges to separate CO₂ from H₂. This temperature, denoted T_1 , is listed in Table II, and is the temperature above which the M₂ZrO₃ cannot absorb CO₂ anymore and will start to release CO₂. This indicates that, during the first half cycle to capture CO₂, the operating temperature should be lower than T_1 , whereas the operating temperature may be higher than T_1 (depending on the desired obtained CO₂ pressure) during the second half cycle of sorbents

regeneration to release CO₂. For post-combustion conditions, the gas stream mainly contains CO₂ and N₂, the partial pressure of CO₂ is around 0.1~0.2 bar, and the temperature range is quite different. The turnover temperatures (denoted as T_2) for post-combustion capture by these zirconates are also listed in Table II.

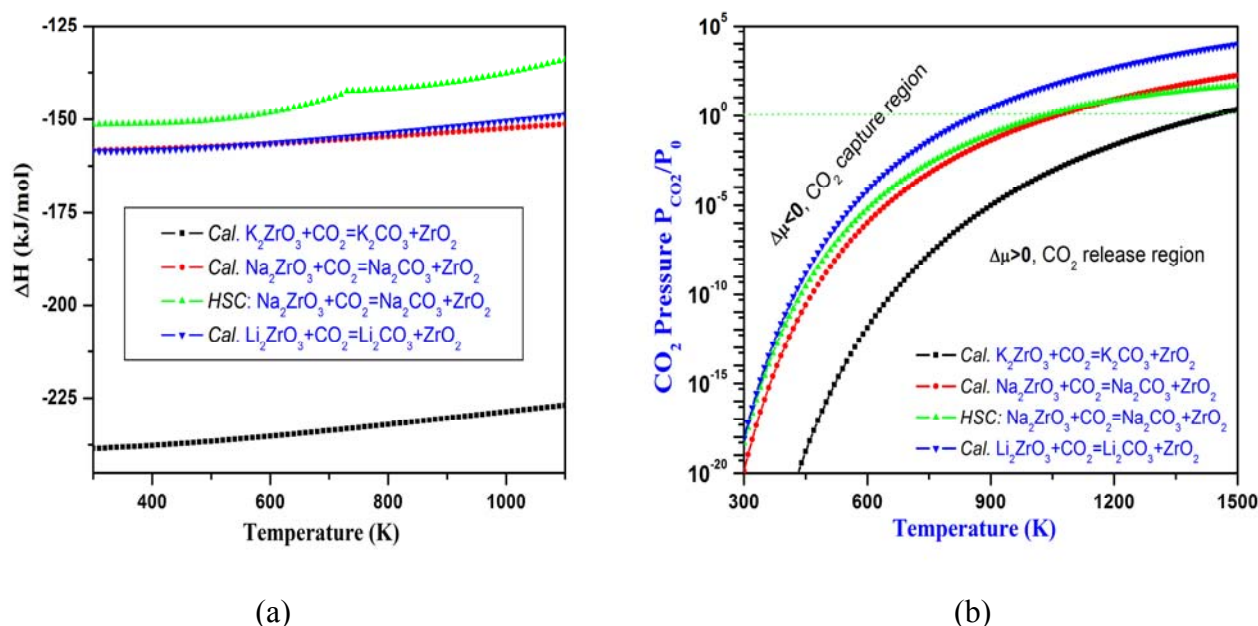


Figure 7. The calculated thermodynamic properties of the reactions of M_2ZrO_3 ($\text{M}=\text{K}, \text{Na}, \text{Li}$) capturing CO₂: (a) the heat of reaction versus temperature. For the case of Na_2ZrO_3 , the data from HSC package are also presented in this figure. The discontinuity of HSC data at 723K indicates solid-solid phase transition of the product Na_2CO_3 ; (b) The contour plotting of calculated chemical potentials versus CO₂ pressures and temperatures of the 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 alkali metal zirconates absorb CO₂ and the reaction goes forward, whereas below the $\Delta\mu=0$ curve, their $\Delta\mu>0$, which means the CO₂ start to release and the reaction goes backward to regenerate the sorbents.

From Table II and Fig.7(b), one can see that these three zirconates capture CO₂ up to higher temperatures ($T_1>1000\text{K}$) compared with desired pre-combustion condition (473~623K). Therefore they are not good sorbents for capturing CO₂ in pre-combustion technology. However, they could be used for high-temperature post-combustion CO₂ capture with $T_2=1285\text{K}$, 925 K, 780K for K_2ZrO_3 , Na_2ZrO_3 and Li_2ZrO_3 respectively. Obviously, compared 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, Na_2ZrO_3 and Li_2ZrO_3 are good candidates for CO_2 sorbents working at high temperature.

From Table II and Fig. 7(b) one can see that the reverse reaction is not just to dissociate M_2CO_3 but also to regenerate M_2ZrO_3 from M_2O by reacting with ZrO_2 which involves net energy gain, and lay down the conditions for $\Delta\mu > 0$ compared with the case of M_2O ($\text{M}=\text{K}, \text{Na}, \text{Li}$). In other words, the presence of ZrO_2 can destabilize the stable phase of M_2CO_3 and make the reverse reaction to release CO_2 less energy required.

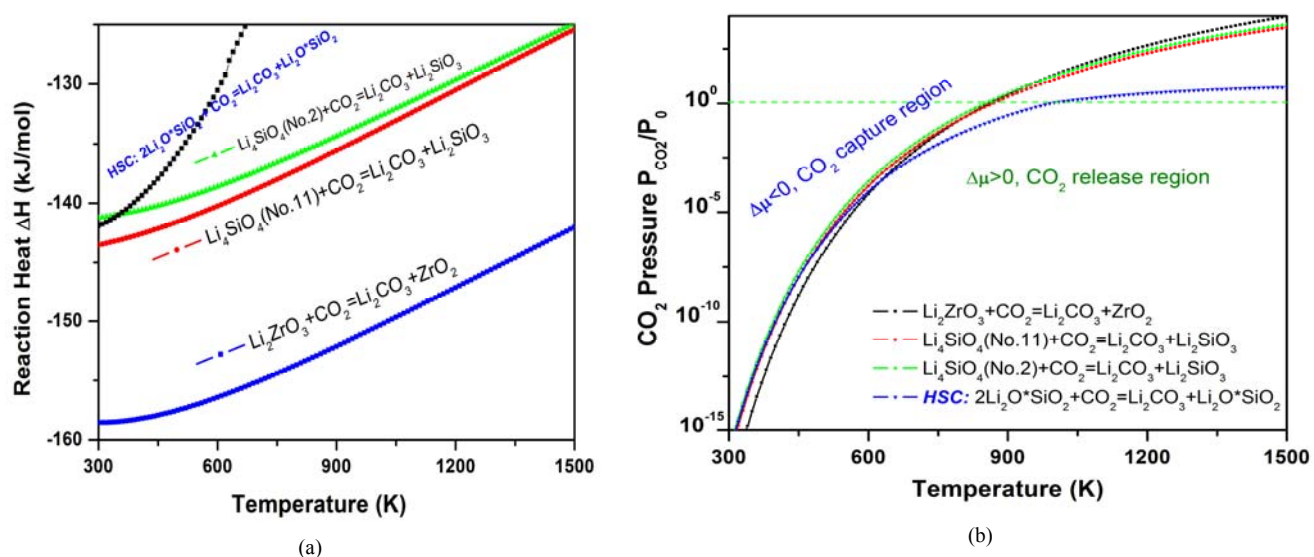


Figure 8. The calculated thermodynamic properties of the reactions of lithium silicate capturing CO_2 . For comparison, the data of lithium zirconate is also plotted in the figure. The data of $\text{Li}_2\text{O} \cdot \text{SiO}_2$ and $2\text{Li}_2\text{O} \cdot \text{SiO}_2$ from HSC are also presented in the figure. (a) The heat of reaction versus temperature; (b) The contour plotting of calculated chemical potential ($\Delta\mu$) versus temperature and the CO_2 pressure (P plotted in logarithmic scale) for the CO_2 capture reactions. 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.

One can see from Fig.8(a) that the calculated heat of reactions for both phases of Li_4SiO_4 are quite close to each other with less than 3 kJ/mol difference. At low temperature ($T < 400\text{K}$), the calculated heat of reaction is very close to the value obtained from HSC Chemistry database. However, with the increase in temperature, the discrepancy between the calculated and HSC data become larger. There are two main reasons for such large discrepancy at higher temperatures: (1) Since our calculations are based on the assumption that except for CO_2 all materials are perfect

crystalline solids and their low-temperature structures were used to represent the structures among the whole temperature range, as discussed in our previous work, a large discrepancy is possible and indicated that reasonable caution should be exercised in the use of these data at high temperature. To resolve such an issue, the correct structure at different temperatures should be used in the calculation. However, for most materials, such structure at each temperature keeps unknown experimentally. (2) Another reason is on the experimental related measurement. Experimentally, the Li_4SiO_4 and Li_2SiO_3 were synthesized by mixing Li_2CO_3 and SiO_2 with 2:1 and 1:1 molar ratio and heat treated at high temperature. Therefore, the experimental samples may not be the exactly perfect crystalline Li_4SiO_4 and Li_2SiO_3 . Instead, they may be in the mixed forms, such as $2\text{Li}_2\text{O} \cdot \text{SiO}_2$ and $\text{Li}_2\text{O} \cdot \text{SiO}_2$ as denoted from HSC Chemistry database. Obviously, such mismatched structure of the material can also created some discrepancies. Compared to Li_4SiO_4 , from Fig.8(a) one can see that the reaction heat of Li_2ZrO_3 capture CO_2 is about 20 kJ/mol lower, indicating that more heat is needed for regenerating Li_2ZrO_3 back from Li_2CO_3 and ZrO_2 .

The relationship among the chemical potential ($\Delta\mu(T,P)$), temperature, and the CO_2 pressure (P_{CO_2}) is shown in Fig.8(b). The line in Fig.8(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 , Li_2ZrO_3) 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 back. Although Li_2SiO_3 could absorb CO_2 to further reduce to SiO_2 and Li_2CO_3 , experimental results showed that the kinetic behavior of CO_2 absorption on Li_2SiO_3 is much slower than that on Li_4SiO_4 . Therefore, upon capturing CO_2 , the Li_4SiO_4 only forms Li_2SiO_3 , but it doesn't further decompose to SiO_2 .

IV. 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 CO₂ varying with temperatures and pressures, only those solid materials, which result lower energy cost in the capture and regeneration process and could work at desired conditions of CO₂ pressure and temperature, will be selected as promised candidates of CO₂ 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 CO₂ reactions and therefore can be used for screening out good CO₂ solid sorbents from vast of solid materials which thermodynamic data are unknown.

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