



# Ab initio thermodynamic approach to identify mixed solid sorbents for CO<sub>2</sub> capture technology

Yuhua Duan \*

National Energy Technology Laboratory, United States Department of Energy, Pittsburgh, PA, USA

Because the current technologies for capturing CO<sub>2</sub> are still too energy intensive, new materials must be developed that can capture CO<sub>2</sub> reversibly with acceptable energy costs. At a given CO<sub>2</sub> pressure, the turnover temperature ( $T_t$ ) of the reaction of an individual solid that can capture CO<sub>2</sub> is fixed. Such  $T_t$  may be outside the operating temperature range ( $\Delta T_o$ ) for a practical capture technology. To adjust  $T_t$  to fit the practical  $\Delta T_o$ , in this study, three scenarios of mixing schemes are explored by combining thermodynamic database mining with first principles density functional theory (DFT) and phonon lattice dynamics calculations. Our calculated results demonstrate that by mixing different types of solids, it's possible to shift  $T_t$  to the range of practical operating temperature conditions. According to the requirements imposed by the pre- and post- combustion technologies and based on our calculated thermodynamic properties for the CO<sub>2</sub> capture reactions by the mixed solids of interest, we were able to identify the mixing ratios of two or more solids to form new sorbent materials for which lower capture energy costs are expected at the desired pressure and temperature conditions.

**Keywords:** CO<sub>2</sub> capture, mixed solid sorbent, *ab initio* thermodynamics, turnover temperature shift, mixing ratio

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### \*Correspondence:

Yuhua Duan  
yuhua.duan@netl.doe.gov

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## INTRODUCTION

Today, fossil fuels are still the main energy sources for the world's economy. One consequence of the use of these fuels is the emission of huge quantities of CO<sub>2</sub> into the atmosphere, creating environmental problems such as climate change (White et al., 2003; Aaron and Tsouris, 2005; Allen et al., 2009; Haszeldine, 2009; Li et al., 2013). To mitigate such problems, CO<sub>2</sub> emissions into the atmosphere must be reduced by being captured and stored (Ochoa-Fernandez et al., 2005; Pfeiffer and Bosch, 2005; Li et al., 2013). Current technologies for capturing CO<sub>2</sub>, including solvent-based (amines) and CaO-based materials, are still too energy intensive. Hence, development of new materials that can capture and release CO<sub>2</sub> reversibly with acceptable energy costs are critical. In particular, solid oxide sorbent materials have been proposed for capturing CO<sub>2</sub> through a reversible chemical transformation leading primarily to formation of carbonate products. Solid sorbents containing alkali and alkaline earth metals have been reported in previous studies to be promising candidates for CO<sub>2</sub> sorbent applications due to their high CO<sub>2</sub> absorption capacity at moderate working temperatures (Duan and Sorescu, 2009, 2010; Duan et al., 2012a).

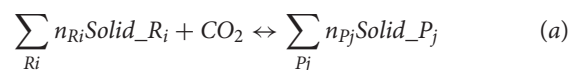
During the past few years, NETL developed a theoretical methodology to identify promising solid sorbent candidates for CO<sub>2</sub> capture by combining thermodynamic database searching with *ab initio* thermodynamics obtained based on the first-principles density functional theory (DFT) and lattice phonon dynamics (Duan and Sorescu, 2009, 2010; Duan and Parlinski, 2011; Duan et al., 2011, 2012a,b,c; Zhang et al., 2012). As shown in **Figure 1**, the primary outcome of our

screening scheme is a list of promising CO<sub>2</sub> sorbents with optimal energy usage. After screening a given material databank, we selected only a short list of candidates for further experimental validations.

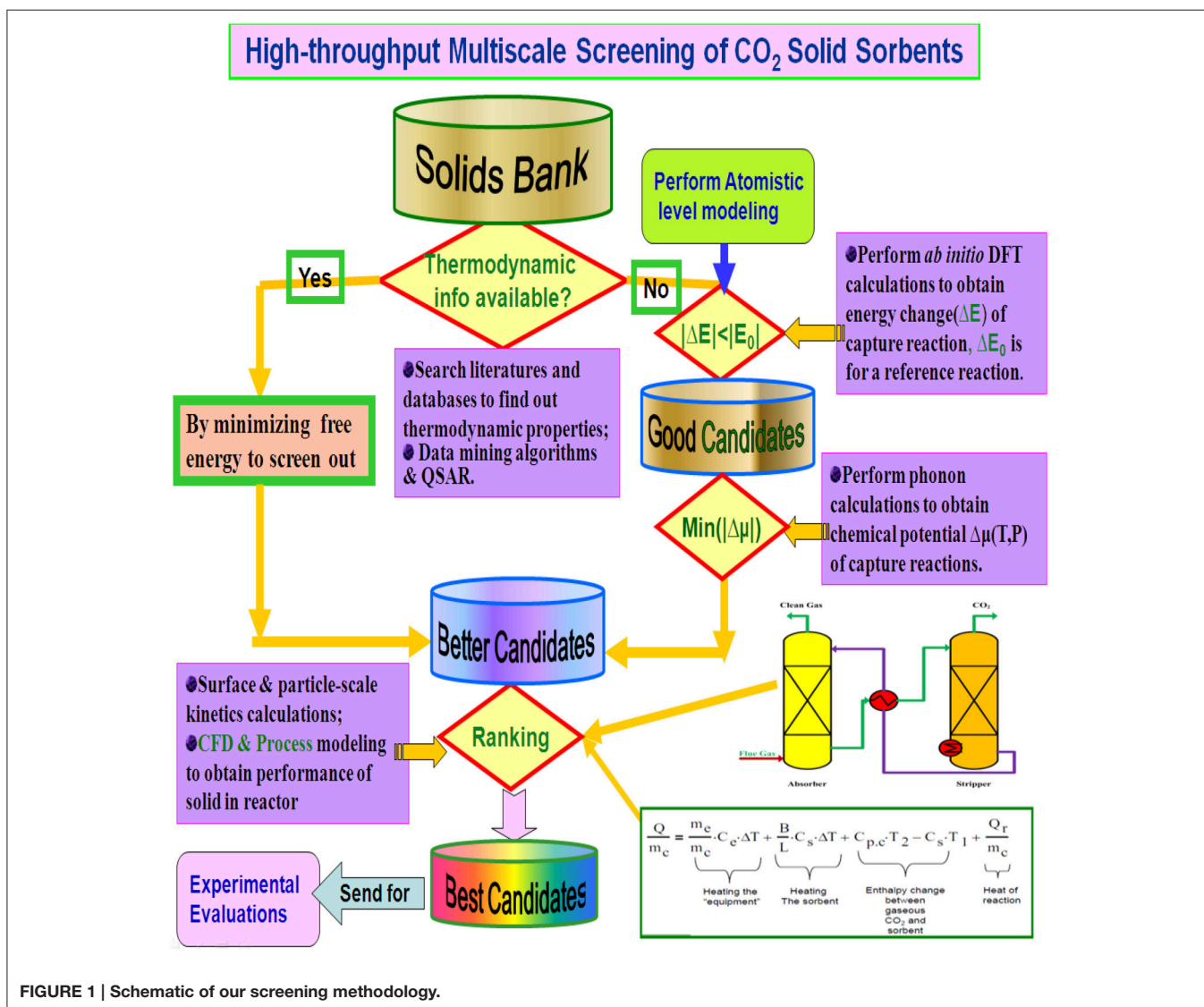
A practical CO<sub>2</sub> capture technology has optimal operating conditions, such as the absorption/desorption of CO<sub>2</sub> at the necessary pressure and operating temperature range ( $\Delta T_o$ ). As a good sorbent, its CO<sub>2</sub> capture/release temperature should fit into such a range. However, at a given CO<sub>2</sub> pressure, the turnover temperature ( $T_t$ ) of an individual solid capture CO<sub>2</sub> reaction is fixed. Such  $T_t$  may be outside the operating temperature range ( $\Delta T_o$ ) for a particular capture technology. In order to adjust  $T_t$  to fit the practical  $\Delta T_o$ , its corresponding thermodynamic property must be changed by changing its structure by reacting (mixing) it with other materials or doping it with other elements. In this study, we demonstrate that by mixing different types of solids in three scenarios, it's possible to shift  $T_t$  to the range of practical operating conditions.

## CALCULATION METHODS FOR MIXED SOLID SORBENTS

A complete description of the computational methodology together with relevant applications can be found in our previous publications (Duan and Sorescu, 2009, 2010; Duan, 2011; Duan and Parlinski, 2011; Duan et al., 2011, 2012a,b,c; Zhang et al., 2012). The CO<sub>2</sub> capture reactions of solids can be expressed generically in the form (for convenient description, we normalized the reaction to 1 mole of CO<sub>2</sub>)



where  $n_{R_i}$ ,  $n_{P_j}$  are the numbers of moles of reactants ( $R_i$ ) and products ( $P_j$ ) involved in the capture reactions. As discussed in the following section, the reactants  $R_i$  can simply be mixed solids or a newly formed solid by mixing different kinds of solids with



certain mixing ratios. We treat the gas phase CO<sub>2</sub> as an ideal gas. By assuming that the difference between the chemical potentials ( $\Delta\mu^0$ ) of the solid phases of reactants ( $R_i$ ) and products ( $P_j$ ) can be approximated by the difference in their total energies ( $\Delta E^{\text{DFT}}$ ), obtained directly from DFT calculations, and their vibrational free energies of phonons dynamics and by ignoring the PV contribution terms for solids, the variation of the Gibbs free energy ( $\Delta G$ ) for reaction (a) with temperature and CO<sub>2</sub> pressure can be written as (Duan and Sorescu, 2009, 2010; Duan, 2011; Duan and Parlinski, 2011; Duan et al., 2011, 2012a,b,c; Zhang et al., 2012)

$$\Delta G(T, P) = \Delta\mu^0(T) - RT \ln \frac{P_{\text{CO}_2}}{P_0} \quad (1)$$

where

$$\Delta\mu^0(T) \approx \Delta E^{\text{DFT}} + \Delta E_{\text{ZP}} + \Delta F^{\text{PH}}(T) - G_{\text{CO}_2}^0(T) \quad (2)$$

Here,  $\Delta E^{\text{DFT}}$  is the DFT energy difference between the reactants and products of reaction (a),  $\Delta E_{\text{ZP}}$  is the zero point energy difference between the reactants and products and can be obtained directly from phonon calculations.  $\Delta F^{\text{PH}}$  is the phonon free energy change excluding zero-point energy (which is already counted into the  $\Delta E_{\text{ZP}}$  term) between the solids of products and reactants.  $P_{\text{CO}_2}$  is the partial pressure of CO<sub>2</sub> in the gas phase and  $P_0$  is the standard state reference pressure taken to be 1 bar. The heat of reaction [ $\Delta H^{\text{cal}}(T)$ ] can be evaluated through the following equation

$$\Delta H^{\text{cal}}(T) = \Delta\mu^0(T) + T[\Delta S_{\text{PH}}(T) - S_{\text{CO}_2}(T)] \quad (3)$$

where  $\Delta S_{\text{PH}}(T)$  is the difference of entropies between product solids and reactant solids. The free energy of CO<sub>2</sub> ( $G_{\text{CO}_2}^0$ ) can be obtained from standard statistical mechanics (Duan and Sorescu, 2009, 2010; Zhang et al., 2012), and its entropy ( $S_{\text{CO}_2}$ ) can be found in the empirical thermodynamic databases (Chase, 1998). Equation (1) provides the relationships of Gibbs free energy change of reaction (a) vs. temperature and CO<sub>2</sub> pressure. Obviously, when set  $\Delta G = 0$ , the P-T relationship (van't Hoff plot) is obtained to determine the  $T_t$ :

$$T_t = \frac{\Delta\mu^0(T)}{R \ln \frac{P_{\text{CO}_2}}{P_0}} \quad (4)$$

Based on this equation, at giving CO<sub>2</sub> pressure  $P_{\text{CO}_2}$ , the  $T_t$  can be determined for each CO<sub>2</sub> capture reaction.

## RESULTS AND DISCUSSION

For a given CO<sub>2</sub> capture process, its optimal working conditions [CO<sub>2</sub> pressures of pre- and after-capture, absorption/desorption temperature range ( $\Delta T_0$ ), etc.] were fixed. However, at a given CO<sub>2</sub> pressure, the  $T_t$  of an individual solid capture CO<sub>2</sub> reaction is also fixed. Such  $T_t$  may be outside the operating temperature range  $\Delta T_0$  for a particular capture technology. To adjust  $T_t$  to fit the practical working range through reversible chemical

transformations, the chemical properties (such as structure, phase, etc.) of solids must be modified to change the  $\Delta G(T, P)$  in Equation (1). If we want to increase the  $T_t$  to a higher temperature range, the  $\Delta G(T, P)$  should be more negative. To achieve it, we can either destabilize the reactants (sorbents), stabilize the products, or do both. Conversely, if we want to decrease  $T_t$  to a lower temperature range, the  $\Delta G(T, P)$  should be less negative, which can either stabilize the reactant (sorbents), destabilize the products, or do both. In other words, mixing stabilizer/destabilizer with a solid could change the thermodynamic properties of their CO<sub>2</sub> capture reactions to shift  $T_t$ . Some mixing examples are given in **Table 1**. As one can see that the mixed sorbent could be a new formed solid (e.g., lithium silicates) or just a simple mixture (e.g., MgO + Na<sub>2</sub>CO<sub>3</sub>) to change the chemical properties of reactants and products. Depending on the main captor *A* and the direction of  $T_t$  shifts, a different mixed solid *B* and mixing ratio could be determined. Although one can mix any number of solids to form a new CO<sub>2</sub> sorbent, to focus on exploring the nature of mixtures, here we restrict ourselves with cases of two and three mixed solids.

As shown in **Table 1**, as effective main CO<sub>2</sub> captors through chemical reactions to form carbonates, alkali and alkaline earth metal oxides are of interest due to their ease in reacting with CO<sub>2</sub> and low costs. The problem is that they can strongly react with CO<sub>2</sub> to form carbonates, but their  $T_t$  are very high, and they can only be regenerated at very high temperatures, which are unsuitable for many CO<sub>2</sub> capture technologies. Hence, mixing with other solids to shift their  $T_t$  becomes important for their suitability as CO<sub>2</sub> sorbents. Generally, when we mix two solids *A* and *B* to form a new sorbent *C*, the  $T_t$  of the new system ( $T_C$ ) is located between the *A* and *B* ( $T_A, T_B$ ). Here, it was assumed that *A* is a strong CO<sub>2</sub> sorbent, while *B* is a weak CO<sub>2</sub> sorbent and  $T_A > T_B$ . Also, we assumed that the desired operating temperature  $T_0$  is between  $T_A$  and  $T_B$  ( $T_A > T_0 > T_B$ ). Depending on the properties of *A* and *B*, as shown in **Table 1**, we typically have three scenarios to synthesize the mixing sorbent *C*.

### $T_A \gg T_B$ and the *A* Component is Key to Capturing CO<sub>2</sub>

In this case, by mixing *B* into *A*, a new solid *C* is formed. Because *B* is not involved in the CO<sub>2</sub> capture, it serves as a stabilizer to stabilize *A* to form solid *C*, and the reaction possesses lower energy than *A* and *B* individually. Therefore, the energy state of reactant is lower than pure *A*. The  $\Delta\mu^0$  in Equation (2) will become higher (less negative). According to Equation (4), the corresponding  $T_C$  should be lower than  $T_A$ . In other words, the mixed sorbent *B* shifts  $T_A$  to a lower temperature range. The amount of shifted temperature depends on the mixing ratio.

An example of this case is represented by Li<sub>2</sub>O. As we know, Li<sub>2</sub>O is a very strong CO<sub>2</sub> sorbent that forms Li<sub>2</sub>CO<sub>3</sub>. However, its regeneration from Li<sub>2</sub>CO<sub>3</sub> can only occur at very high temperatures ( $T_A > 1000$  K). In order to move its  $T_A$  to lower temperatures, one can mix in some weak CO<sub>2</sub> sorbents (such as SiO<sub>2</sub>, ZrO<sub>2</sub>). With different mixing ratios of Li<sub>2</sub>O/SiO<sub>2</sub> (or ZrO<sub>2</sub>), different stable lithium silicates (or zirconates) can be formed, such as Li<sub>8</sub>SiO<sub>6</sub>, Li<sub>4</sub>SiO<sub>4</sub>, Li<sub>6</sub>Si<sub>2</sub>O<sub>7</sub>, Li<sub>2</sub>SiO<sub>3</sub>, Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>Si<sub>3</sub>O<sub>7</sub>; Li<sub>8</sub>ZrO<sub>6</sub>, Li<sub>6</sub>Zr<sub>2</sub>O<sub>7</sub>, Li<sub>2</sub>ZrO<sub>3</sub>, etc. The crystal structures

**TABLE 1 |** Mixing schemes and examples of mixed solids and their effects on CO<sub>2</sub> capture.

Main captor A	Mixed solids B (one or more)	Newly formed sorbent C	Examples of CO <sub>2</sub> capture reaction	Effect on CO <sub>2</sub> capture capacity and operating T	References
N <sub>2</sub> O, N = Li, Na, K MO, M = Mg, Ca	SiO <sub>2</sub> , TiO <sub>2</sub> , ZrO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , MeO (Me: transition metal) Two solids mixing with different ratios	Lithium silicates, lithium zirconates, calcium aluminum oxides	Li <sub>4</sub> SiO <sub>4</sub> + CO <sub>2</sub> = Li <sub>2</sub> CO <sub>3</sub> + Li <sub>2</sub> SiO <sub>3</sub> Li <sub>2</sub> ZrO <sub>3</sub> + CO <sub>2</sub> = Li <sub>2</sub> CO <sub>3</sub> + ZrO <sub>2</sub> <sup>1</sup> / <sub>12</sub> Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> + CO <sub>2</sub> = CaCO <sub>3</sub> + <sup>7</sup> / <sub>12</sub> Al <sub>2</sub> O <sub>3</sub>	(1) B stabilizes A, but does not capture CO <sub>2</sub> (2) Compared to pure N <sub>2</sub> O, the T <sub>t</sub> shifts to low-T range (3) The maximum CO <sub>2</sub> capture capacity decreases with increasing solid B	Duan and Sorescu, 2009; Duan, 2011, 2012, 2013; Duan and Parlinski, 2011; Duan et al., 2013
MO, M = Mg, Ca	N <sub>2</sub> O or N <sub>2</sub> CO <sub>3</sub> , N = Li, Na, K Two solids mixing with different ratios	MO + N <sub>2</sub> O MO + N <sub>2</sub> CO <sub>3</sub> MgO + CaCO <sub>3</sub>	MgO + Na <sub>2</sub> CO <sub>3</sub> + CO <sub>2</sub> = Na <sub>2</sub> Mg(CO <sub>3</sub> ) <sub>2</sub> MgO + CaCO <sub>3</sub> + CO <sub>2</sub> = MgCa(CO <sub>3</sub> ) <sub>2</sub>	(1) N <sub>2</sub> O (or N <sub>2</sub> CO <sub>3</sub> ) stabilizes the product to form double salt and does not capture CO <sub>2</sub> in the ΔT <sub>o</sub> range (2) Compared to pure MO, the T <sub>t</sub> shifts to high-T range (3) The maximum CO <sub>2</sub> capture capacity decreases with B	Zhang et al., 2013, 2014; Duan et al., 2014
N <sub>2</sub> O, N = Li, Na, K	SiO <sub>2</sub> + MeO Three solids mixing with different ratios	Li <sub>2</sub> MeSiO <sub>4</sub> (Me = Fe, Co, Ni, Mg, Mn, Zn, etc.)	Li <sub>2</sub> MeSiO <sub>4</sub> + CO <sub>2</sub> = Li <sub>2</sub> CO <sub>3</sub> + MeSiO <sub>3</sub>	(1) B stabilizes both A and product. The final effect depends on the bonding strength of MeO with A and SiO <sub>2</sub> (2) The T <sub>t</sub> may shift to low-T and high-T range (3) The maximum CO <sub>2</sub> capture capacity decreases with B	
N <sub>2</sub> O, N = Li, Na, K	N <sub>2</sub> O + SiO <sub>2</sub> N <sub>2</sub> O + ZrO <sub>2</sub> MO + SiO <sub>2</sub> Three solids mixing with different ratios	Li <sub>2-x</sub> Na <sub>x</sub> ZrO <sub>3</sub> Li <sub>2-x</sub> K <sub>x</sub> ZrO <sub>3</sub> Li <sub>4-x</sub> Na <sub>x</sub> SiO <sub>4</sub> They also can be treated as doped materials	Li <sub>2-x</sub> N <sub>x</sub> ZrO <sub>3</sub> + CO <sub>2</sub> = ZrO <sub>2</sub> + (2-x)/2 Li <sub>2</sub> CO <sub>3</sub> + x/2 N <sub>2</sub> CO <sub>3</sub> Li <sub>4-x</sub> N <sub>x</sub> SiO <sub>4</sub> + CO <sub>2</sub> = (2-x)/2 Li <sub>2</sub> CO <sub>3</sub> + x/2 N <sub>2</sub> CO <sub>3</sub> + Li <sub>2</sub> SiO <sub>3</sub>	(1) B stabilizes A and a portion of B (N <sub>2</sub> O) also involved in CO <sub>2</sub> capture (2) T <sub>t</sub> may shift to low-T range (3) The maximum CO <sub>2</sub> capture capacity decreases with weaker portion of B (SiO <sub>2</sub> , ZrO <sub>2</sub> , etc.)	Duan, 2014; Duan and Lekse, 2015; Duan et al., 2015

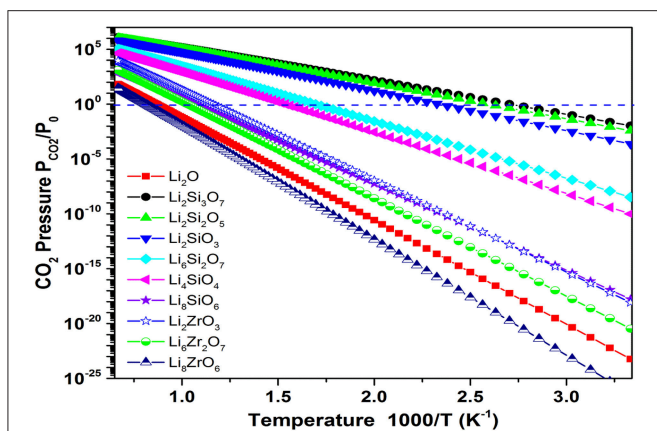
of these lithium silicates and zirconates can be found in the literature. By performing *ab initio* thermodynamic property calculations on these solids capturing CO<sub>2</sub> reactions (Duan and Sorescu, 2009; Duan, 2011, 2012, 2013; Duan and Parlinski, 2011; Duan et al., 2013), **Figure 2** shows the calculated relationships of Gibbs free energy (ΔG), P<sub>CO<sub>2</sub></sub>, and T of the CO<sub>2</sub> capture reactions by the mixed Li<sub>2</sub>O/SiO<sub>2</sub> and Li<sub>2</sub>O/ZrO<sub>2</sub> solids with different mixing ratios. **Figure 3** shows the turnover temperatures and the CO<sub>2</sub> capture capacities of Li<sub>2</sub>O/SiO<sub>2</sub> and Li<sub>2</sub>O/ZrO<sub>2</sub> mixtures vs. the ratio of Li<sub>2</sub>O/SiO<sub>2</sub> or Li<sub>2</sub>O/ZrO<sub>2</sub> (Duan and Sorescu, 2009, 2010; Duan, 2011, 2012, 2013; Duan and Parlinski, 2011; Duan et al., 2012a; Duan and Lekse, 2015).

From **Figures 2, 3**, one can see that after mixing SiO<sub>2</sub> (or ZrO<sub>2</sub>) in Li<sub>2</sub>O with different Li<sub>2</sub>O/SiO<sub>2</sub> (or Li<sub>2</sub>O/ZrO<sub>2</sub>) ratios, the T<sub>C</sub> of the newly formed C compound (silicate or zirconate) is lower than T<sub>A</sub> of pure Li<sub>2</sub>O and could be close to the ΔT<sub>o</sub> range to fit the practical needs. Although SiO<sub>2</sub> and ZrO<sub>2</sub> do not capture CO<sub>2</sub>, they can exothermically react with Li<sub>2</sub>O to form silicates and zirconates (as shown in **Figure 2**). Such reactions bring the energy levels of sorbents (reactants) down to more negative values, but do not affect the products (carbonates).

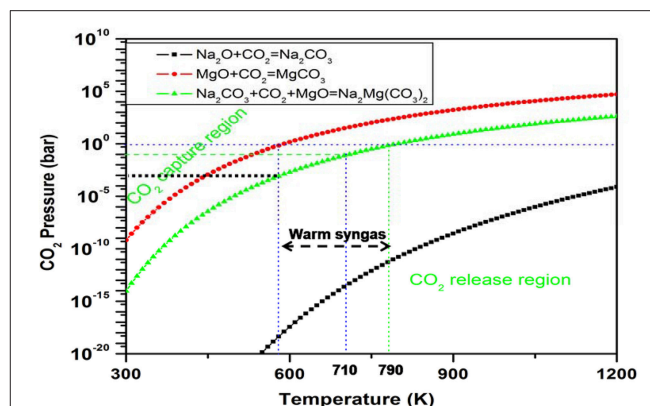
Therefore, the heat of reaction and free energy change of the CO<sub>2</sub> capture reactions by these lithium silicates and zirconates will be increased to less negative values compared to pure Li<sub>2</sub>O reacting with CO<sub>2</sub>, and in turn, the turnover temperatures are shifted to a lower temperature range. When the SiO<sub>2</sub>/Li<sub>2</sub>O or ZrO<sub>2</sub>/Li<sub>2</sub>O ratios are increased by adding more SiO<sub>2</sub> or ZrO<sub>2</sub> into Li<sub>2</sub>O, as shown in **Figures 2, 3**, the turnover temperatures of mixed sorbents (T<sub>t</sub>) are shifted to a lower temperature range. Therefore, by controlling the mixing ratio, it is possible to move the CO<sub>2</sub> capture temperature down to the range required by certain capture technology.

### T<sub>A</sub> >> T<sub>B</sub> and B Component is Key to Capturing CO<sub>2</sub>

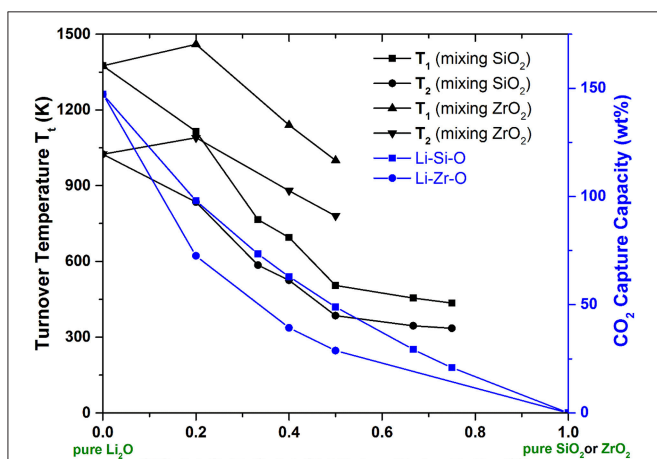
Opposite to the previous case, in this case, we want to increase the T<sub>t</sub>. Because T<sub>B</sub> is lower than T<sub>O</sub>, mixing A into B will increase the turnover temperature T<sub>C</sub> of the C solid to a value closer to T<sub>O</sub>. In this way, A will either destabilize solid B or stabilize the captured products. For example, pure MgO has a very high theoretical CO<sub>2</sub> capture capacity. However, its T<sub>t</sub> (250°C) is lower than the required temperature range of 300–470°C used in warm gas



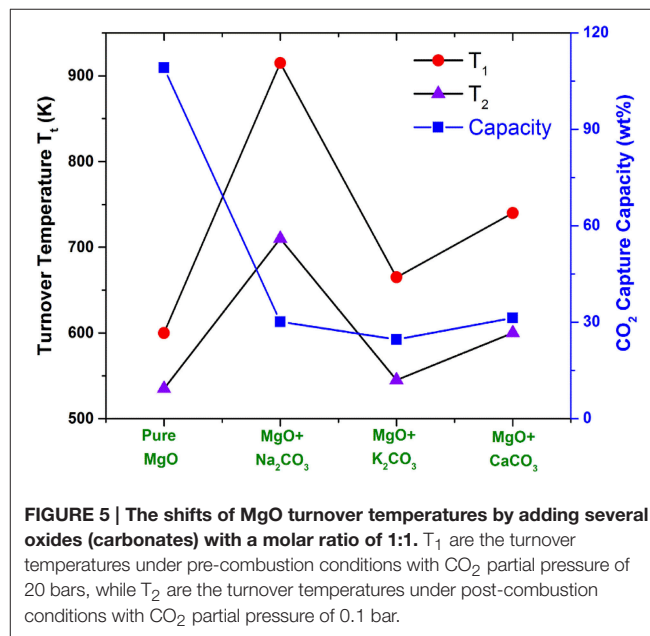
**FIGURE 2 |** Plots of the calculated free energy vs. CO<sub>2</sub> pressures and temperatures for the CO<sub>2</sub> capture reaction by Li<sub>2</sub>O+SiO<sub>2</sub> or Li<sub>2</sub>O+ZrO<sub>2</sub> mixtures. Y-axis plotted in logarithm scale. The line shows  $\Delta G(T, P) = 0$ . For each reaction, above its  $\Delta G(T, P) = 0$  curve, its  $\Delta G < 0$ , which means the solids absorb CO<sub>2</sub> and the reaction goes forward, whereas below the  $\Delta G(T, P) = 0$  curve, its  $\Delta G > 0$ , which means the CO<sub>2</sub> starts to release and the reaction goes backward to regenerate the sorbents.



**FIGURE 4 |** Plots of the calculated free energy vs. CO<sub>2</sub> pressures and temperatures for the CO<sub>2</sub> capture reaction by MgO + Na<sub>2</sub>CO<sub>3</sub> (or Na<sub>2</sub>O) to form the double salt Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>. Y-axis plotted in logarithm scale. The line shows  $\Delta G(T, P) = 0$ . For each reaction, above its  $\Delta G(T, P) = 0$  curve, its  $\Delta G < 0$ , which means the solids absorb CO<sub>2</sub> and the reaction goes forward, whereas below the  $\Delta G(T, P) = 0$  curve, its  $\Delta G > 0$ , which means the CO<sub>2</sub> starts to release and the reaction goes backward to regenerate the sorbents.



**FIGURE 3 |** The calculated turnover temperatures and CO<sub>2</sub> capture capacity vs. molar percentage of SiO<sub>2</sub> or ZrO<sub>2</sub> in the lithium silicates or zirconates. T<sub>1</sub> are the turnover temperatures under pre-combustion conditions with CO<sub>2</sub> partial pressure at 20 bars, while T<sub>2</sub> are the turnover temperatures under post-combustion conditions with CO<sub>2</sub> partial pressure at 0.1 bar.



**FIGURE 5 |** The shifts of MgO turnover temperatures by adding several oxides (carbonates) with a molar ratio of 1:1. T<sub>1</sub> are the turnover temperatures under pre-combustion conditions with CO<sub>2</sub> partial pressure of 20 bars, while T<sub>2</sub> are the turnover temperatures under post-combustion conditions with CO<sub>2</sub> partial pressure of 0.1 bar.

clean up technology and its practical CO<sub>2</sub> capacity is very low. Therefore, pure MgO cannot be used directly as a CO<sub>2</sub> sorbent in such capture technology (Zhang et al., 2013, 2014; Chi et al., 2014). **Figure 4** shows an example of mixing Na<sub>2</sub>O (or Na<sub>2</sub>CO<sub>3</sub>) with MgO to move the  $\Delta G(T, P) = 0$  curve of MgO (red line in **Figure 4**) to a higher temperature range (green line in **Figure 4**).

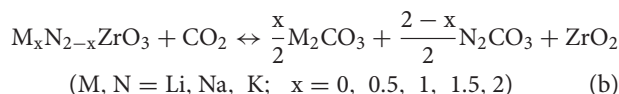
One can see that in **Figure 4**, Na<sub>2</sub>O (or Na<sub>2</sub>CO<sub>3</sub>) does not react with the reactant MgO directly, but it reacts exothermically with the carbonate MgCO<sub>3</sub> to form the double salt Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> and, hence, stabilizes the product. Therefore, the heat of reaction and free energy change of CO<sub>2</sub> capture reaction by MgO +

Na<sub>2</sub>CO<sub>3</sub> are lower (more negative) compared with pure MgO reacting with CO<sub>2</sub>. According to Equations (1) and (4), the T<sub>t</sub> of the Na<sub>2</sub>CO<sub>3</sub>-promoted MgO sorbent capturing CO<sub>2</sub> is higher than that of pure MgO. **Figure 5** shows the changes of MgO turnover temperatures by adding different oxides or carbonates. Generally, by mixing alkali metal oxides, M<sub>2</sub>O (M = Na, K, Cs, Ca) or their carbonates (M<sub>2</sub>CO<sub>3</sub>) into MgO, the corresponding newly formed mixing systems have higher turnover temperatures, making them useful as CO<sub>2</sub> sorbents through the reaction MgO + CO<sub>2</sub> + M<sub>2</sub>CO<sub>3</sub> = M<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> (Zhang et al., 2013; Duan et al., 2014).

From **Figure 5**, one can see that, in these CO<sub>2</sub> capture reactions, the Na<sub>2</sub>CO<sub>3</sub>-promoted MgO possesses a larger T<sub>t</sub> shift to a higher temperature range than the K<sub>2</sub>CO<sub>3</sub> + MgO and CaCO<sub>3</sub> + MgO do. Because the desired T<sub>t</sub> of the mixture is lower than the dissociation temperature of promoters (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>), during the CO<sub>2</sub> capture sorption process, these promoters act as stabilizers to react with MgCO<sub>3</sub> to form a double salt, while during the CO<sub>2</sub> desorption, the double salt dissociates to MgO and the promoter.

## Both A and B are Active for CO<sub>2</sub> Capture

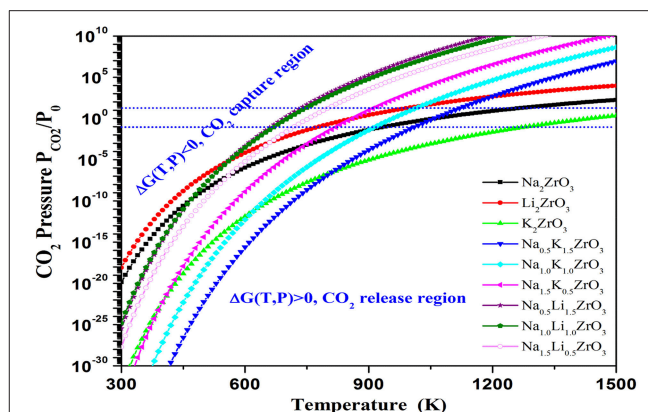
In this case, we want both A and B components active to capture CO<sub>2</sub>, and the CO<sub>2</sub> capture capacity of the mixture is the summation of those of A and B. As we know, another potential advantage of mixing solids is to increase the surface area of the solids to have a faster reaction rate. Such a mixing scenario does not show too much advantage in shifting the capture temperature, but it may enhance the kinetics of the capture process and eventually make the mixtures more efficient for capturing CO<sub>2</sub>. Although, up to now, no such report has appeared in literature, we think such an attempt is worthwhile, and we are working on several doped systems. Here we show a case of Li-/K- doped Na<sub>2</sub>ZrO<sub>3</sub> capture for CO<sub>2</sub> through the following reaction (b): (Duan, 2014; Duan and Lekse, 2015; Duan et al., 2015)



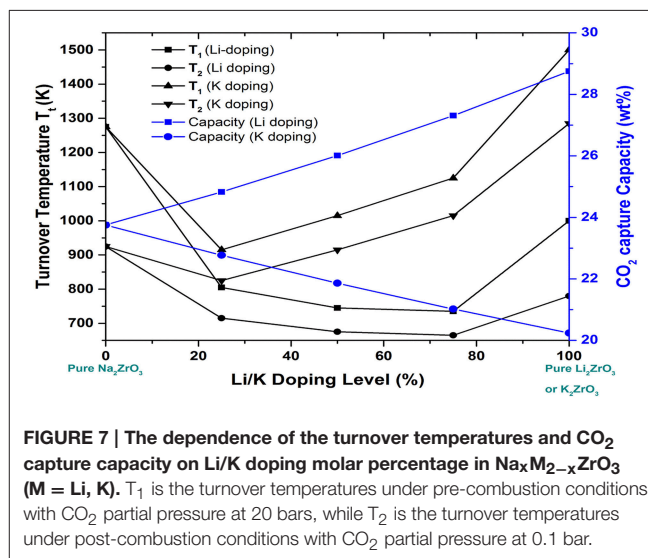
**Figure 6** demonstrated the calculated relationships among the Gibbs free energy change, CO<sub>2</sub> pressure and temperature for CO<sub>2</sub> capture reactions by Na<sub>2-x</sub>M<sub>x</sub>ZrO<sub>3</sub> (M = Li, K, x = 0.0, 0.5, 1.0, 1.5, 2.0). **Figure 7** showed the dependence of T<sub>t</sub> and CO<sub>2</sub> capture capacity on Li/K doping molar percentage in Na<sub>x</sub>M<sub>2-x</sub>ZrO<sub>3</sub> (M = Li, K). One can see from **Figure 6** that when Na<sub>2</sub>ZrO<sub>3</sub> is doped with a different molar ratio of Li or K, the thermodynamic properties of the doped systems are quite different from pure Na<sub>2</sub>ZrO<sub>3</sub>.

Based on the calculated relationships among the Gibbs free energy change, CO<sub>2</sub> pressure and temperature for CO<sub>2</sub> capture reactions by Na<sub>2-x</sub>M<sub>x</sub>ZrO<sub>3</sub> are shown in **Figure 6**. Compared to pure Na<sub>2</sub>ZrO<sub>3</sub>, overall, the Li- and K-doped mixtures Na<sub>2-x</sub>M<sub>x</sub>ZrO<sub>3</sub> have lower T<sub>t</sub>, shown in **Figure 7**. The calculated results show that the shift in T<sub>t</sub> depends not only on the doping element, but also on the doping level. As one can see from **Figure 7**, the Li-doped systems have larger T<sub>t</sub> decreases than the K-doped systems. When increasing the Li-doping level x, the T<sub>t</sub> of the corresponding mixture Na<sub>2-x</sub>Li<sub>x</sub>ZrO<sub>3</sub> decreases further to a low temperature range. However, in the case of K-doped systems Na<sub>2-x</sub>K<sub>x</sub>ZrO<sub>3</sub>—although initial doping of K into Na<sub>2</sub>ZrO<sub>3</sub> can shift its T<sub>t</sub> to a lower temperature range—further increasing the K-doping level x results in an increase in T<sub>t</sub>. Therefore, compared to K-doping, lithium inclusion into Na<sub>2</sub>ZrO<sub>3</sub> structure has a larger influence on its CO<sub>2</sub> capture performance.

All of these obtained results may be of great interest in the development of specific CO<sub>2</sub> capture applications. As shown in



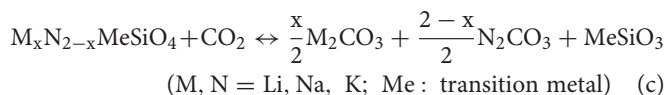
**FIGURE 6 |** The contour plotting of calculated Gibbs free energy vs. CO<sub>2</sub> pressures and temperatures of the CO<sub>2</sub> capture reactions by Na<sub>x</sub>M<sub>2-x</sub>ZrO<sub>3</sub> and M<sub>2</sub>ZrO<sub>3</sub> (M = Li, Na, K, x = 0, 0.5, 1.0, 1.5, 2.0) through reaction Na<sub>x</sub>M<sub>2-x</sub>ZrO<sub>3</sub> + CO<sub>2</sub> = x/2Na<sub>2</sub>CO<sub>3</sub> + (2-x)/2M<sub>2</sub>CO<sub>3</sub> + ZrO<sub>2</sub>. Y-axis plotted in logarithm scale. The line shows ΔG(T, P) = 0. For each reaction, above its ΔG(T, P) = 0 curve, its ΔG < 0, which means the solids absorb CO<sub>2</sub> and the reaction goes forward, whereas below the ΔG(T, P) = 0 curve, its ΔG > 0, which means the CO<sub>2</sub> starts to release and the reaction goes backward to regenerate the sorbents.



**FIGURE 7 |** The dependence of the turnover temperatures and CO<sub>2</sub> capture capacity on Li/K doping molar percentage in Na<sub>x</sub>M<sub>2-x</sub>ZrO<sub>3</sub> (M = Li, K). T<sub>1</sub> is the turnover temperatures under pre-combustion conditions with CO<sub>2</sub> partial pressure at 20 bars, while T<sub>2</sub> is the turnover temperatures under post-combustion conditions with CO<sub>2</sub> partial pressure at 0.1 bar.

**Figures 6, 7**, the Na<sub>2-x</sub>Li<sub>x</sub>ZrO<sub>3</sub> and Na<sub>2-x</sub>K<sub>x</sub>ZrO<sub>3</sub> compositions can produce modifications in the CO<sub>2</sub> capture temperatures, which may be used in the design of a specific composition, depending on the temperature range that industry requires. These results have identified that the capture of CO<sub>2</sub> in zirconate materials is not simply a matter of a substitutional element but also the doping level. This insight will need to be considered during future sorbent development. The obtained results have also demonstrated that computational methods can be used to accurately predict aspects of CO<sub>2</sub> capture and have the potential to drive future work by leading to researchers identifying and designing the most promising candidate materials.

In addition, the Na<sub>2-x</sub>M<sub>x</sub>ZrO<sub>3</sub> materials can be stoichiometrically regarded as a mixture of three oxides: Na<sub>2</sub>O, M<sub>2</sub>O, and ZrO<sub>2</sub> in the ratio (2-x):x:1. These results provide ways that mixing/doping more than two oxides to form new sorbents that can fit the industrial needs to capture CO<sub>2</sub> with better performances and proper working conditions. More complicated doping systems, such as N<sub>2-x</sub>M<sub>x</sub>MeSiO<sub>4</sub> (N, M = Li, Na, K; Me = Fe, Co, Ni, Mn, Zn, Mg, etc.), can be regarded as a mixture of four oxides: N<sub>2</sub>O, M<sub>2</sub>O, MeO, SiO<sub>2</sub> in the ratio (2-x):x:1:1. Their CO<sub>2</sub> capture reactions could be written as:



By analyzing their CO<sub>2</sub> capture behaviors with different doping/mixing ratios, researchers will draw more general conclusions. Analysis of the results is underway and will appear in future reports.

From the mixing systems mentioned, one can see that after mixing/doping solid *B* into *A*, the theoretical maximum of CO<sub>2</sub> capture capacity of the mixture is decreased compared with pure *A* or *B*. However, it does not mean the practical CO<sub>2</sub> capacity will be decreased. The CO<sub>2</sub> capacity of solid sorbents should be above 3 mole CO<sub>2</sub> per kilogram solid (~15 wt. %) to meet the industrial requirements and have a chance of providing energy reductions of 30–50% or more compared to the optimum aqueous-monoethanolamine(MEA)-based process (Gray et al., 2008). As shown in **Figures 3, 5, 7**, the theoretical CO<sub>2</sub> weight percentage maxima of all these mixtures are greater than this minimum requirement (>15 wt. %). Therefore, from the CO<sub>2</sub> capture capacity point of view, all of these systems could meet this criterion to be used as CO<sub>2</sub> sorbents. In addition, after mixing another solid, the structure of the sorbent is changed, and more active sites could be contacted by CO<sub>2</sub> to enhance the capture kinetics, and in turn, to increase its practical capture capacity.

## CONCLUSIONS

At a given CO<sub>2</sub> pressure, the T<sub>t</sub> of an individual solid capture CO<sub>2</sub> reaction is fixed. Such T<sub>t</sub> may be outside the operating temperature range (ΔT<sub>o</sub>) for a practical capture technology. To adjust T<sub>t</sub> to fit the practical ΔT<sub>o</sub>, in this study, by combining thermodynamic database mining with first principles DFT and phonon lattice dynamics calculations, our calculated results demonstrate that by mixing different types of solids, it is possible to shift T<sub>t</sub> to the range of practical operating temperature conditions.

The obtained results showed that by changing the mixing ratio of solid *A* and solid *B* to form mixed solid *C*, it is possible to shift T<sub>t</sub> of the newly formed solid *C* to fit the practical CO<sub>2</sub> capture technologies. In this study, we investigated three scenarios of mixing schemes: (i) T<sub>A</sub> >> T<sub>B</sub>, and the *A* component is the key component for capturing CO<sub>2</sub>. In this case, because T<sub>A</sub> is higher than T<sub>o</sub>, mixing *B* into *A* will decrease the turnover T<sub>A</sub> of the *A* solid to values closer to T<sub>o</sub>. For example, Li<sub>2</sub>O is a very strong

CO<sub>2</sub> sorbent that forms Li<sub>2</sub>CO<sub>3</sub>. However, its regeneration from Li<sub>2</sub>CO<sub>3</sub> only can occur at very high temperatures (T<sub>A</sub>). To move its T<sub>A</sub> to lower temperatures, Li<sub>2</sub>O can be mixed with some weak CO<sub>2</sub> sorbents (such as SiO<sub>2</sub>, ZrO<sub>2</sub>). Our results showed that, in this way, the turnover T<sub>t</sub> and the theoretical CO<sub>2</sub> capture capacity of mixtures decrease as the ratios of Li<sub>2</sub>O/SiO<sub>2</sub> or Li<sub>2</sub>O/ZrO<sub>2</sub> decrease. (ii) T<sub>A</sub> >> T<sub>B</sub> and *B* component is the key part to capturing CO<sub>2</sub>. In this case, because T<sub>B</sub> is lower than T<sub>o</sub>, mixing *A* into *B* will increase the T<sub>B</sub> of the *B* solid to values closer to T<sub>o</sub>. For example, pure MgO (as *B* component) has a very high theoretical CO<sub>2</sub> capture capacity. However, its T<sub>B</sub> (250°C) is lower than the required temperature range of 300–470°C used in warm gas clean up technology. The obtained results showed that by mixing alkali metal oxides M<sub>2</sub>O (M = Na, K, Cs, Ca) or their carbonates (M<sub>2</sub>CO<sub>3</sub>) into MgO, the corresponding newly formed mixed systems have higher turnover temperatures by forming double salts through the reactions MgO + CO<sub>2</sub> + M<sub>2</sub>CO<sub>3</sub> = M<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>. (iii) Both *A* and *B* components are active to capture CO<sub>2</sub>. In this case, the CO<sub>2</sub> capacity of the mixture is the summation of those of *A* and *B*. Li<sub>2</sub>MSiO<sub>4</sub> (M = Mg, Ca, etc.) and M<sub>2-x</sub>N<sub>x</sub>ZrO<sub>3</sub> (M, N = Li, Na, K) belong to this category. Those doped systems can be treated as the mixing of three solids (Li<sub>2</sub>O:MO:SiO<sub>2</sub>, M<sub>2</sub>O:N<sub>2</sub>O:ZrO<sub>2</sub>). This study summarized the results of Na<sub>2-x</sub>M<sub>x</sub>ZrO<sub>3</sub> (M = Li, Na, K, x = 0, 0.5, 1, 1.5, 2) doped sorbents. The results showed that when capturing CO<sub>2</sub>, the K-/Li- doped Na<sub>2</sub>ZrO<sub>3</sub> have lower T<sub>t</sub> compared to pure Na<sub>2</sub>ZrO<sub>3</sub>.

The obtained results can be used to provide insights for designing new CO<sub>2</sub> sorbents. Therefore, although one single material taken in isolation might not be an optimal CO<sub>2</sub> sorbent to fit the particular needs to operate at specific temperature and pressure conditions, by mixing or doping two or more materials to form a new solid, the calculated results showed that it is possible to synthesize new CO<sub>2</sub> sorbent formulations that can fit the industrial needs. Our results also show that computational modeling can play a decisive role for identifying materials with optimal performance.

It should be pointed out that in this study we only focused on the thermodynamic properties of the CO<sub>2</sub> capture reactions, which are essential and critical to determine whether the sorbents can capture CO<sub>2</sub>. Once the capture reaction is thermodynamically favorable, other properties (such as kinetics, mechanical resistance, toxicity, sulfur poisoning resistance, cost, etc.) also play important roles to select proper sorbent candidates for experimental validations. Generally speaking, further simulations can be performed on sorbents to optimize their performance for capturing CO<sub>2</sub>. For example, by calculating the transition states with DFT, the kinetic properties of CO<sub>2</sub> capture reactions can be evaluated; by conducting mechanical and chemical engineering modeling with finite element method, the mechanical and sintering behaviors of sorbents can be obtained; by performing process modeling, the overall energetic and material costs can be estimated, and then some comparisons with amine-based solution capture technology can be drawn. Poisoning gases (such as SO<sub>x</sub>, NO<sub>x</sub>, H<sub>2</sub>S, etc.) have big effects on the sorbent performance for CO<sub>2</sub> capture. Further exploring the mechanisms of poisoning gases interacting with sorbents

will provide useful information for designing new CO<sub>2</sub> capture technologies.

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