

# Theoretical Study of Solid Materials for CO<sub>2</sub> Capture Technology

Yuhua Duan

National Energy Technology Laboratory, United States Department of Energy, Pittsburgh, PA 15236  
Yuhua.duan@netl.doe.gov

## ABSTRACT

Since the current technologies for capturing CO<sub>2</sub> are still too energy intensive, to develop new materials that can capture CO<sub>2</sub> reversibly with acceptable energy costs are needed. 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<sub>2</sub> sorbent candidates from the vast array of possible solid materials have been proposed and validated at the National Energy Technology Laboratory (NETL). The advantage of this method is that it identifies the thermodynamic properties of the CO<sub>2</sub> capture reaction as a function of temperature and pressure without any experimental input beyond crystallographic structural information of the solid phases involved.

**Keywords:** CO<sub>2</sub> capture, solid sorbents, *ab initio* thermodynamics

## 1 INTRODUCTION

Carbon dioxide is one of the major combustion products which once released into the air can contribute to global climate change.[1-6] It is generally accepted that current technologies for capturing CO<sub>2</sub> are still too energy intensive and thus cost prohibitive for implementation on coal based power plants. Hence, there is a critical need for development of new materials that can capture CO<sub>2</sub> reversibly with acceptable energy costs. Accordingly, solid sorbents have been reported in several previous studies to be promising candidates for CO<sub>2</sub> sorbent applications through a reversible chemical transformation due to their high CO<sub>2</sub> absorption capacities at moderate working temperatures.[3, 7, 8] Solid sorbents containing alkali and alkaline earth metals have been reported in several 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.[9-11]

During past few years we 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 first-principles density functional theory (DFT) and lattice phonon dynamics.[9-18] As shown in Fig.1, the primary outcome of our screening scheme is a list of promising CO<sub>2</sub> sorbents with optimal energy usage.

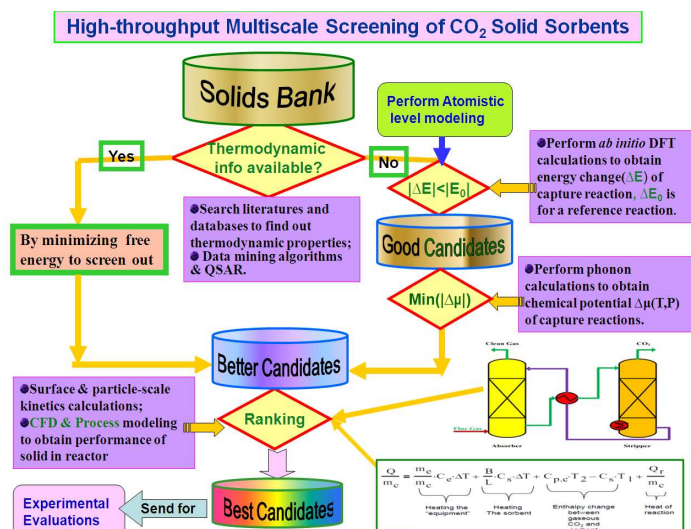
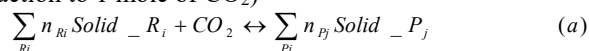


Fig. 1. Schematic of our screening methodology.

## 2 CALCULATION METHODS

The complete description of the computational methodology together with relevant applications can be found in our previous publications.[9-16, 19] 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. 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[6, 9-16, 19]

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

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 the 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.  $\Delta F^{\text{PH}}$

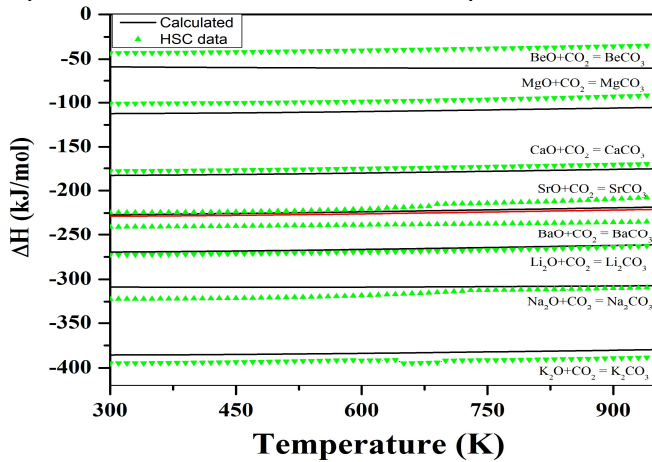
is the phonon free energy change excluding zero-point energy (which is already counted into the  $\Delta E_{ZP}$  term) between the solids of products and reactants.  $P_{CO_2}$  is the partial pressure of  $CO_2$  in the gas phase and  $P_0$  is the standard state reference pressure taken to be 1 bar. The heat of reaction ( $\Delta H^{cal}(T)$ ) can be evaluated through the following equation

$$\Delta H^{cal}(T) = \Delta \mu^0(T) + T[\Delta S_{PH}(T) - S_{CO_2}(T)] \quad (3)$$

where  $\Delta S_{PH}(T)$  is the difference of entropies between product solids and reactant solids. The free energy of  $CO_2$  ( $G^0_{CO_2}$ ) can be obtained from standard statistical mechanics,[10, 11, 16] and its entropy ( $S_{CO_2}$ ) can be found in the empirical thermodynamic databases.[20] Equation (1) provides the relationships of Gibbs free energy change of reaction (a) versus temperature and  $CO_2$  pressure. Obviously, when set  $\Delta G=0$ , the P-T relationship (van't Hoff plot) is obtained to determine the turnover temperature  $T_t$ :

$$T_t = \frac{\Delta \mu^0(T)}{R \ln \frac{P_{CO_2}}{P_0}} \quad (4)$$

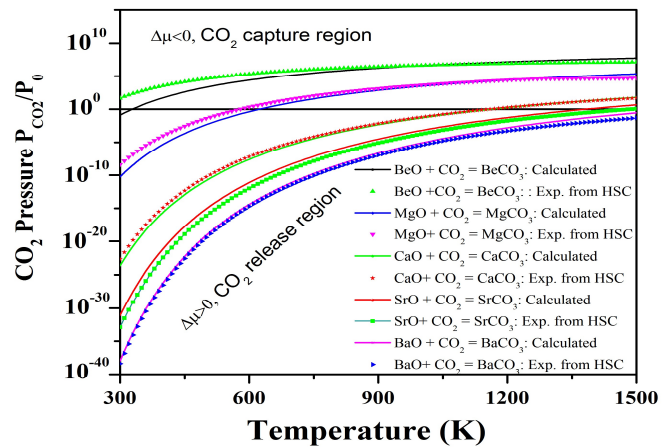
Based on it, at giving  $CO_2$  pressure  $P_{CO_2}$ , the turnover temperature  $T_t$  can be determined for each capture reaction.



### 3 RESULTS AND DISCUSSION

#### 3.1 Method Validation: Applications to alkali and alkaline earth metal oxides and hydroxides

As an example, Figure 2 shows the calculated and experimental measured thermodynamic properties of the reactions for alkali and alkaline earth metal oxides capture of  $CO_2$ . 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 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.



**Fig. 2.** (left) The calculated heats of reaction as a function of temperature for eight metal oxides. The solid lines were computed from DFT including phonon contributions. The dashed lines were computed from the HSC package. The discontinuities in the HSC curves indicate phase transitions; (right) The calculated chemical potentials (Gibbs free energy) versus  $CO_2$  pressures (in logarithm scale) and temperatures for the reactions of oxides capturing  $CO_2$  without water involved.

#### 3.2 Mixing Solid Sorbents to Adjust Operating Temperature

For a given  $CO_2$  capture process, its optimal working conditions ( $CO_2$  pressures of pre- and after-capture, absorption/desorption temperature range ( $\Delta T_0$ ), etc.) were fixed. However, at a given  $CO_2$  pressure, the turnover temperature ( $T_t$ ) of an individual solid capture  $CO_2$  reaction is fixed. Such  $T_t$  may be outside the operating temperature range  $\Delta T_0$  for a particularly capture technology. In order to adjust  $T_t$  to fit the practical working through reversible chemical transformations, the chemical properties of solids must be modified to change the  $\Delta G(T, P)$  in Eq. (1). If we want to increase the  $T_t$  to high temperature range, the  $\Delta G(T,$

$P)$  should be more negative. To achieve it, we can either destabilize the reactants (sorbents) or stabilize the products or do both. On contrary, if we want to decrease  $T_t$  to low temperature range, the  $\Delta G(T, P)$  should be less negative, which can either stabilize the reactant (sorbents) or destabilize the products or do both. In other words, mixing stabilizer/destabilizer in solid could change the thermodynamic properties of their  $CO_2$  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 simple mixture (e.g.  $MgO+Na_2CO_3$ ) to change the chemical properties of reactants and products. Depending on the main captor A and the direction of  $T_t$  shifts, 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, in order to focus

exploring the nature of mixtures; here we restrict ourselves with cases of two and three mixed solids.

**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)	New formed sorbent C	Examples of CO <sub>2</sub> capture reaction	Effect on CO <sub>2</sub> capture capacity & operating T	Refs.
N <sub>2</sub> O, N=Li, Na, K	SiO <sub>2</sub> , TiO <sub>2</sub> , ZrO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , MeO (Me: transition metal)	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>	(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.	[[10, 12, 19, 21-23]]
MO, M=Mg, Ca	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>	<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> 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>0</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.	[[24-26]]
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) T <sub>t</sub> may shift to low- 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> + ( <sup>2-x</sup> / <sub>2</sub> )Li <sub>2</sub> CO <sub>3</sub> + <sup>x</sup> / <sub>2</sub> 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> = ( <sup>2-x</sup> / <sub>2</sub> )Li <sub>2</sub> CO <sub>3</sub> + <sup>x</sup> / <sub>2</sub> N <sub>2</sub> CO <sub>3</sub> + Li <sub>2</sub> SiO <sub>3</sub>	(1) B stabilizes A and portion of B (N <sub>2</sub> O) also involves 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.)	[[17]]

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 important of interests due to their easy 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 turnover temperatures T<sub>t</sub> are very high and only can 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<sub>t</sub> 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 turnover temperature of the newly resulted system (T<sub>C</sub>) is located between those of A and B (T<sub>A</sub>, T<sub>B</sub>) individuals. 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<sub>A</sub>>T<sub>B</sub>. Also, we assumed that the desired operating temperature T<sub>0</sub> is between T<sub>A</sub> and T<sub>B</sub> (T<sub>A</sub>>T<sub>0</sub>>T<sub>B</sub>). Depending on the properties of A and B, as shown in Table 1 we have typically three scenarios to synthesize the mixing sorbent C, as demonstrated in Fig. 3.

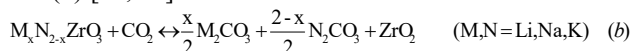
In the case of Li<sub>2</sub>O, it is a very strong CO<sub>2</sub> sorbent which forms Li<sub>2</sub>CO<sub>3</sub>. However, its regeneration from Li<sub>2</sub>CO<sub>3</sub> only can occur at very high temperature (T<sub>A</sub>). In order to move its T<sub>A</sub> to lower temperatures, one can mix some weak CO<sub>2</sub> sorbents (such as SiO<sub>2</sub>, ZrO<sub>2</sub>). With different mixing ratio of Li<sub>2</sub>O/SiO<sub>2</sub>(or ZrO<sub>2</sub>), different stable lithium silicates (zirconates) can be formed. By performing thermodynamic property calculations of these solids capturing CO<sub>2</sub> reactions,[10, 12, 19, 21-23] the relationship of Gibbs free

energy, 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 can be obtained. Fig. 3(a) shows the turnover temperature and the CO<sub>2</sub> capture capacity of Li<sub>2</sub>O/SiO<sub>2</sub> and Li<sub>2</sub>O/ZrO<sub>2</sub> mixtures versus the ratio of Li<sub>2</sub>O/SiO<sub>2</sub> or Li<sub>2</sub>O/ZrO<sub>2</sub>. [9-12, 19, 21, 22] 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, the turnover temperatures of mixed sorbents (T<sub>t</sub>) are shifted more to lower temperature range.

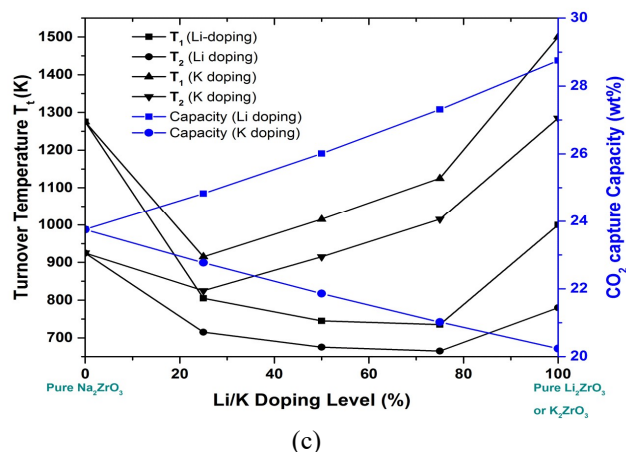
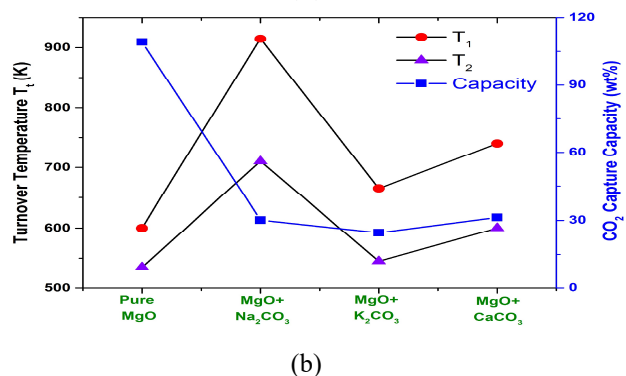
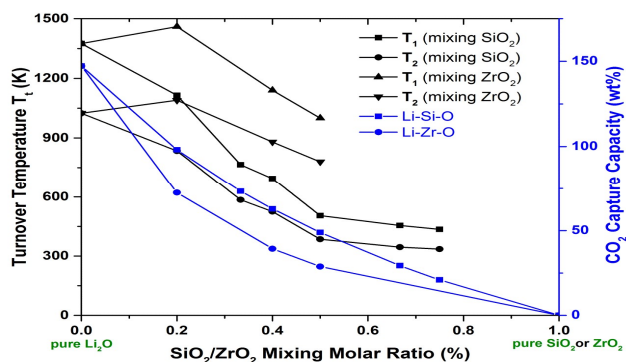
Opposite to previous case, in this case, we want to increase turnover temperature (T<sub>t</sub>). Since T<sub>B</sub> is lower than T<sub>0</sub>, by mixing A into B will increase the turnover temperature T<sub>C</sub> of the C solid to values closer to T<sub>0</sub>. In this way, the function of A is either to destabilize solid A or to stabilize the captured products. For example, pure MgO has a very high theoretical CO<sub>2</sub> capture capacity. However, its turnover temperature (250 °C) is lower than the required temperature range of 300-470 °C used in warm gas clean up technology and its practical CO<sub>2</sub> capacity is very low, and therefore, it cannot be used directly as a CO<sub>2</sub> sorbent in this technology.[25-27] Fig. 3(b) shows an example of mixing Na<sub>2</sub>O (or Na<sub>2</sub>CO<sub>3</sub>) with MgO to shift the T<sub>t</sub> of MgO to higher temperature range.

Another case is that we want both A and B components are active to capture CO<sub>2</sub>, and the CO<sub>2</sub> 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 in order to have faster reaction rates. Such a mixing scenario doesn't show too much

advantage in shifting the capture temperature, but may enhance the kinetics of the capture process and eventually make the mixtures more efficient. Fig. 3(c) shows a case of Li-/K- doped  $\text{Na}_2\text{ZrO}_3$  capture  $\text{CO}_2$  through the following reaction (b):[17, 28]



Compared to pure  $\text{Na}_2\text{ZrO}_3$ , overall, the Li- and K-doped mixtures  $\text{Na}_{2-x}\text{M}_x\text{ZrO}_3$  have lower turnover temperatures ( $T_t$ ). The calculated results show that the shift in  $T_t$  depends not only on the doping element, but also depends on the doping level.



**Fig. 3** The calculated turnover temperatures and  $\text{CO}_2$  capture capacity versus mixed/doped solids.  $T_1$  are the turnover temperatures under pre-combustion conditions with  $\text{CO}_2$  partial pressure at 20 bars, while  $T_2$  are the turnover temperatures under post-combustion conditions with  $\text{CO}_2$  partial pressure at 0.1 bar. (a)  $\text{Li}_2\text{O}/\text{SiO}_2(\text{ZrO}_2)$  mixing systems, (b)  $\text{MgO}/\text{XCO}_3(\text{X}=\text{Na}, \text{K})$

(c) mixing systems, (c)  $\text{Na}_x\text{M}_{2-x}\text{ZrO}_3$  and  $\text{M}_2\text{ZrO}_3(\text{M}=\text{Li}, \text{Na}, \text{K}, x=0, 0.5, 1.0, 1.5, 2.0)$  doping systems

## 4 CONCLUSIONS

The obtained results can be used to provide insights for designing new  $\text{CO}_2$  sorbents. Therefore, although one single material taken in isolation might not be an optimal  $\text{CO}_2$  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  $\text{CO}_2$  sorbent formulations which can fit the industrial needs. Our results also show that computational modeling can play a decisive role for identifying materials with optimal performance.[17, 18, 29-37]

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