

Theoretical Synthesis of Mixed Materials for CO₂ Capture Applications

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ABSTRACT

Since the current technologies for capturing CO₂ are still too energy intensive, to develop new materials that can capture CO₂ reversibly with acceptable energy costs are needed. At a given CO₂ pressure, the turnover temperature (T_t) of an individual solid capture CO₂ reaction is fixed. Such T_t may be outside the operating temperature range (ΔT_o) for a practical capture technology. In order to adjust T_t to fit the practical ΔT_o , in this study, by combining thermodynamic database mining with first principles density functional theory and phonon lattice dynamics calculations, three scenarios of mixing schemes are explored. 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.

Keywords: CO₂ capture, mixed solid sorbents, ab initio thermodynamics

1 INTRODUCTION

Nowadays, the burning of fossil fuels is still the main energy source for the world's economy. One consequence of the use of these fuels is the emission of huge quantities of CO₂ into the atmosphere creating environmental problems such as global climate warming.¹⁻⁵ In order to solve such problems, there is a need to reduce CO₂ emissions into atmosphere by capturing and sequestering CO₂.^{4, 6, 7} One approach to solve such environmental problems is to capture and sequester the CO₂. Current technologies for capturing CO₂ including solvent-based (amines) and CaO-based materials are still too energy intensive. Hence, there is critical need for development of new materials that can capture and release CO₂ reversibly with acceptable energy costs. In particular, solid oxide sorbent materials have been proposed for capturing CO₂ through a reversible chemical transformation leading primarily to formation of carbonate products. Solid sorbents containing alkali and alkaline earth metals have been reported in several previous studies to be promising candidates for CO₂ sorbent applications due to their high CO₂ absorption capacity at moderate working temperatures.⁸⁻¹⁰

During past few years we developed a theoretical methodology to identify promising solid sorbent candidates for CO₂ capture by combining thermodynamic database searching with *ab initio* thermodynamics obtained based on first-principles density functional theory (DFT) and lattice

phonon dynamics.⁸⁻¹⁵ The primary outcome of our screening scheme is a list of promising CO₂ sorbents with optimal energy usage.

For a practical CO₂ capture technology, it has optimal operating conditions, such as the absorption/desorption temperature range (ΔT_o). As a good sorbent, its CO₂ capture/release temperature should fit into such range. However at a given CO₂ pressure, the turnover temperature (T_t) of an individual solid capture CO₂ reaction is fixed. Such T_t may be outside the operating temperature range (ΔT_o) for a particularly capture technology. In order to adjust T_t to fit the practical ΔT_o , in this study, we demonstrate that by mixing different types of solids, it's possible to shift T_t to the range of practical operating conditions.

The complete description of the computational methodology together with relevant applications can be found in our previous publications.⁸⁻¹⁶ From the calculated relationships among the Gibbs free energy, temperature and CO₂ pressure (P_{CO_2}), at given P_{CO_2} for pre- and post-combustion capture technologies, the turnover temperature T_t can be determined for each capture reaction.

2 RESULTS AND DISCUSSION

For a given CO₂ capture process, its optimal working conditions (CO₂ pressures of pre- and after-capture, absorption/desorption temperature range (ΔT_o), *etc.*) were fixed. However, at a given CO₂ pressure, the turnover temperature (T_t) of an individual solid capture CO₂ reaction is fixed. Such T_t may be outside the operating temperature range ΔT_o 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 CO₂ 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+Na₂CO₃) 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_2 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_2 capture

Main captor A	Mixed solids B (one or more)	New formed sorbent C	Examples of CO_2 capture reaction	Effect on CO_2 capture capacity & operating T	Refs.
N_2O , N=Li, Na, K, MO, M=Mg, Ca	SiO_2 , TiO_2 , ZrO_2 , Al_2O_3 , MeO (Me: transition metal) Two solids mixing with different ratios	Lithium silicates, lithium zirconates, calcium aluminum oxides	$\text{Li}_4\text{SiO}_4 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3$ $\text{Li}_2\text{ZrO}_3 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{ZrO}_2$ $^{1/12}\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + \text{CO}_2 = \text{CaCO}_3 + ^{7/12}\text{Al}_2\text{O}_3$	(1) B stabilizes A, but does not capture CO_2 ; (2) Compared to pure N_2O , the T_t shifts to low-T range; (3) The maximum CO_2 capture capacity decreases with increasing solid B.	[^{9, 11, 16, 18-20}]
MO, M=Mg, Ca	N_2O or N_2CO_3 , N= Li, Na, K Two solids mixing with different ratios	MO+N ₂ O MO+N ₂ CO ₃ MgO+CaCO ₃	$\text{MgO} + \text{Na}_2\text{CO}_3 + \text{CO}_2 = \text{Na}_2\text{Mg}(\text{CO}_3)_2$ $\text{MgO} + \text{CaCO}_3 + \text{CO}_2 = \text{MgCa}(\text{CO}_3)_2$	(1) N_2O (or N_2CO_3) stabilizes the product to form double salt and does not capture CO_2 in the ΔT_0 range; (2) Compared to pure MO, the T_t shifts to high-T range; (3) The maximum CO_2 capture capacity decreases with B.	[²¹⁻²³]
N_2O , N= Li, Na, K	$\text{SiO}_2 + \text{MeO}$ Three solids mixing with different ratios	$\text{Li}_2\text{MeSiO}_4$ (Me= Fe, Co, Ni, Mg, Mn, Zn, etc.)	$\text{Li}_2\text{MeSiO}_4 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{MeSiO}_3$	(1) B stabilizes both A and product. The final effect depends on the bonding strength of MeO with A and SiO_2 ; (2) T_t may shift to low- and high-T range; (3) The maximum CO_2 capture capacity decreases with B;	
N_2O , N= Li, Na, K	$\text{N}_2\text{O} + \text{SiO}_2$ $\text{N}_2\text{O} + \text{ZrO}_2$ MO+ SiO_2 Three solids mixing with different ratios	$\text{Li}_{2-x}\text{Na}_x\text{ZrO}_3$ $\text{Li}_{2-x}\text{K}_x\text{ZrO}_3$ $\text{Li}_{4-x}\text{Na}_x\text{SiO}_4$ They also can be treated as doped materials	$\text{Li}_{2-x}\text{N}_x\text{ZrO}_3 + \text{CO}_2 = \text{ZrO}_2 + ^{(2-x)/2}\text{Li}_2\text{CO}_3 + ^x/2\text{N}_2\text{CO}_3$ $\text{Li}_{4-x}\text{N}_x\text{SiO}_4 + \text{CO}_2 = ^{(2-x)/2}\text{Li}_2\text{CO}_3 + ^x/2\text{N}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3$	(1) B stabilizes A and portion of B (N_2O) also involves in CO_2 capture; (2) T_t may shift to low-T range; (3) The maximum CO_2 capture capacity decreases with weaker portion of B (SiO_2 , ZrO_2 , etc.)	[^{24, 25}]

As shown in Table 1, as effective main CO_2 captors through chemical reactions to form carbonates, alkali and alkaline earth metal oxides are important of interests due to their easy reacting with CO_2 and low costs. The problem is that they can strongly react with CO_2 to form carbonates, but their turnover temperatures T_t are very high and only can be regenerated at very high temperatures which are unsuitable for many CO_2 capture technologies. Hence, mixing with other solids to shift their T_t becomes important for their suitability as CO_2 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_C) is located between those of A and B (T_A , T_B) individuals. Here it was assumed that A is a strong CO_2 sorbent while B is a weak CO_2 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 have typically three scenarios to synthesize the mixing sorbent C:

Case I: $T_A \gg T_B$ and the A component is the key part to capture CO_2

In this case, by mixing B into A, a new solid C is formed. Since B does not capture CO_2 , it serves as a

stabilizer to stabilize A to form solid C which reaction possesses lower energy than A and B individuals. Therefore, the energy state of reactant is lower than pure A. therefore, the mixed sorbent shifts T_t to lower temperature range. The amount of shifted temperature depends on the mixing ratio.

An example of this case is represented by Li_2O . Li_2O is a very strong CO_2 sorbent which forms Li_2CO_3 . However, its regeneration from Li_2CO_3 only can occur at very high temperature (T_A). In order to move its T_A to lower temperatures, one can mix some weak CO_2 sorbents (such as SiO_2 , ZrO_2). With different mixing ratio of $\text{Li}_2\text{O}/\text{SiO}_2$ (or ZrO_2), different stable lithium silicates (zirconates) can be formed, such as Li_8SiO_6 , Li_4SiO_4 , $\text{Li}_6\text{Si}_2\text{O}_7$, Li_2SiO_3 , $\text{Li}_2\text{Si}_2\text{O}_5$, $\text{Li}_2\text{Si}_3\text{O}_7$; Li_8ZrO_6 , $\text{Li}_6\text{Zr}_2\text{O}_7$, Li_2ZrO_3 , etc. Fig. 1 shows the turnover temperature and the CO_2 capture capacity of $\text{Li}_2\text{O}/\text{SiO}_2$ and $\text{Li}_2\text{O}/\text{ZrO}_2$ mixtures versus the ratio of $\text{Li}_2\text{O}/\text{SiO}_2$ or $\text{Li}_2\text{O}/\text{ZrO}_2$.^{8-11, 16, 18, 19}

When the $\text{SiO}_2/\text{Li}_2\text{O}$ or $\text{ZrO}_2/\text{Li}_2\text{O}$ ratios are increased by adding more SiO_2 or ZrO_2 into Li_2O , as shown in Fig.1, the turnover temperatures of mixed sorbents (T_t) are shifted more to lower temperature range. Therefore, by controlling the mixing ratio, it's possible to move its CO_2 capture

temperature down to the right range required by certain capture technology.

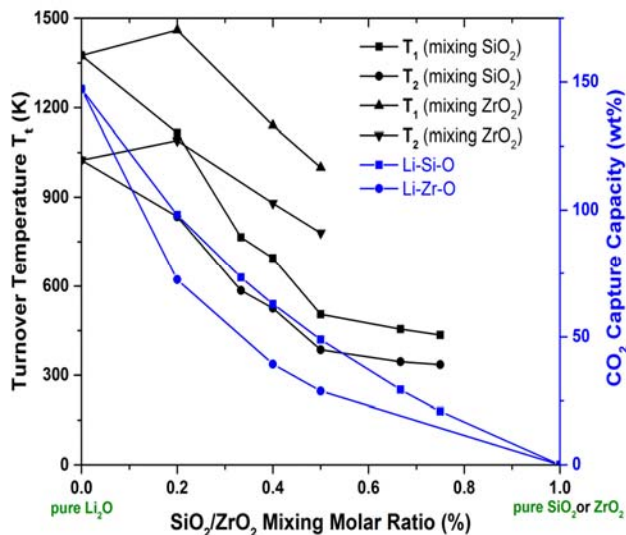


Fig. 1 The calculated turnover temperatures and CO₂ capture capacity versus molar percentage of SiO₂ or ZrO₂ in the lithium silicates or zirconates. T₁ are the turnover temperatures under pre-combustion conditions with CO₂ partial pressure at 20 bars, while T₂ are the turnover temperatures under post-combustion conditions with CO₂ partial pressure at 0.1 bar.

Case II: T_A >> T_B and B component is the key part to capture CO₂

Opposite to previous case, in this case we want to increase turnover temperature (T₁). Since T_B is lower than T_O, by mixing A into B will increase the turnover temperature T_C of the C solid to values closer to T_O. 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 CO₂ 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 CO₂ capacity is very low, and therefore, it cannot be used directly as a CO₂ sorbent in this technology.^{22, 23, 26} Fig. 2 shows an example of mixing Na₂CO₃ (or K₂CO₃, CaCO₃) with MgO to shift the T₁ of MgO to higher temperature range.

Since the mixed carbonates do not react with the reactant MgO directly, but react exothermically with the carbonate MgCO₃ to form double salt (such as Na₂Mg(CO₃)₂) and stabilize the product. Therefore, the turnover temperature of Na₂CO₃-promoted MgO sorbent capturing CO₂ is higher than pure MgO. Generally, as shown in Fig.2, by mixing alkali metal oxides M₂O (M=Na, K, Cs, Ca) or carbonates (M₂CO₃) into MgO, the corresponding newly formed mixing systems have higher turnover temperatures making them useful as CO₂ sorbents through the reaction MgO + CO₂ + M₂CO₃ = M₂Mg(CO₃)₂.^{21, 22}

From Fig. 2, one can see that in the CO₂ capture reactions, the Na₂CO₃-promoted MgO possesses larger T₁ shift to higher temperature range than the K₂CO₃+MgO and

CaCO₃+MgO do. Obviously, since the T₁ of the mixture is lower than the dissociation temperature of promoters (Na₂CO₃, K₂CO₃, CaCO₃), during CO₂ capture sorption process, these promoters act as stabilizers to react with MgCO₃ to form double salt, while during the CO₂ desorption, the double salt dissociates to MgO and the promoter.

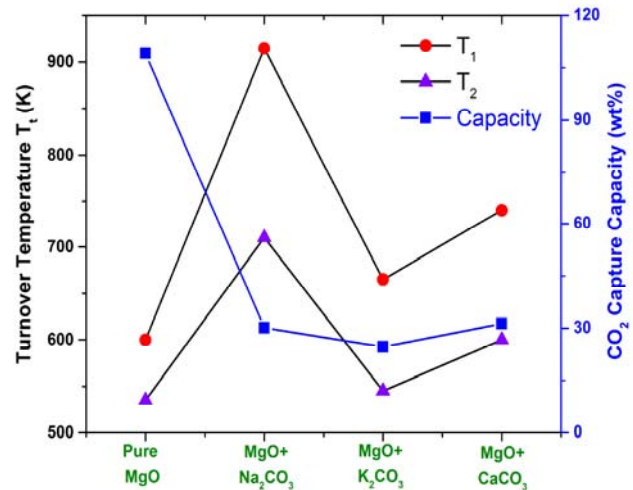
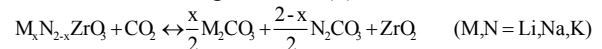


Fig. 2 The calculated turnover temperatures and CO₂ capture capacity of pure MgO and its carbonate-promoted sorbents.

Case III: Both A and B are active for CO₂ capture

In this case, we want both A and B components are active to capture CO₂, and the CO₂ 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. Although up to know there is no such report in literature, we think such an attempt is worthwhile and are working on several doped systems. For example, the Li-/K- doped Na₂ZrO₃ capture CO₂ have the following reaction (b).^{24, 25}



When the Na₂ZrO₃ doped with different molar ratio of Li or K, the thermodynamic properties of the doped systems are quite different from pure Na₂ZrO₃. The turnover temperatures versus the Li-/K- doping levels are shown in Fig.3.

Based on the calculated relationships among the Gibbs free energy change, CO₂ pressure and temperature for CO₂ capture reactions by Na_{2-x}M_xZrO₃ (M= Li, K, x= 0.0, 0.5, 1.0, 1.5, 2.0), compared to pure Na₂ZrO₃, overall, the Li- and K-doped mixtures Na_{2-x}M_xZrO₃ have lower turnover temperatures (T₁) shown in Fig.3. The calculated results show that the shift in T₁ depends not only on the doping element, but also depends on the doping level. The Li-doped systems have larger T₁ decreases than the K-

doped systems. When increasing the Li-doping level x , the T_t of corresponding mixture $\text{Na}_{2-x}\text{Li}_x\text{ZrO}_3$ decreases further to a low temperature range. However in the case of K-doped systems $\text{Na}_{2-x}\text{K}_x\text{ZrO}_3$, although initial doping of K into Na_2ZrO_3 can shift its T_t to lower temperature range, further increasing the K-doping level x results in an increase in T_t . Therefore, compared to K-doping, lithium inclusion into Na_2ZrO_3 structure has a larger influence on the CO_2 capture performance.

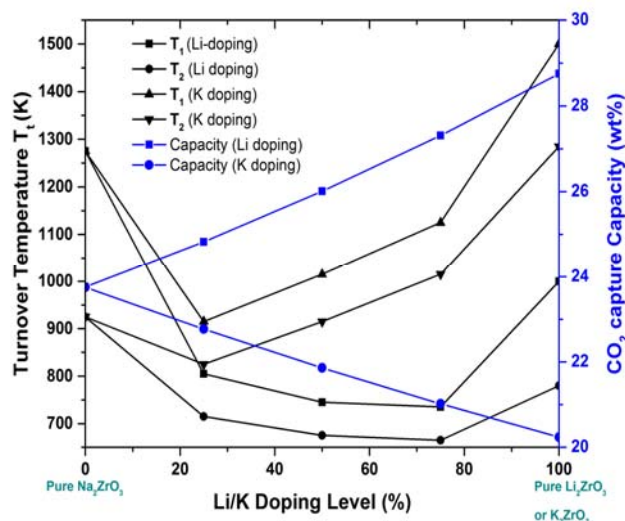


Fig. 3 The dependence of the turnover temperatures and of CO_2 capture capacity on Li/K doping molar percentage in $\text{Na}_x\text{M}_{2-x}\text{ZrO}_3$ ($M=\text{Li}, \text{K}$).

3 CONCLUSIONS

The obtained results showed that by changing the mixing ratio of solid A and solid B to form mixed solid C it's possible to shift the turnover T_t of the newly formed solid C to fit the practical CO_2 capture technologies. In this study, we investigated three scenarios of mixing schemes. The obtained results can be used to provide insights for designing new CO_2 sorbents. Therefore, although one single material taken in isolation might not be an optimal 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 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.

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