Computational Screening of Solid Materials for CO_2 Capture

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Motivation

- Due to the environmental issues that the world faces today, there is significant interest to develop materials capable to capture CO_2 for pre- and post-combustion technologies.
- Solid materials are potential candidates for CO_2 sorbents.
- By combining the database mining with *ab initio* thermodynamic calculation, we implemented a novel theoretical methodology to identify solid materials (such as oxides, hydroxides, salts, complex solids, *etc.*) with improved CO_2 capture capabilities.[1-9]

Theoretical Methods [1-9]

For the CO_2 absorption reaction by a solid ([...] are optional):

$$\text{solid_sorbent} + CO_2 \pm [H_2O] \rightarrow \text{sorbent_}CO_2 + [\text{solid}]$$

The chemical potential ($\Delta\mu$) of the reaction can be calculated as:

$$\Delta\mu(T,P) = \Delta\mu^0(T) - RT(\ln P_{CO_2} \pm \ln P_{H_2O})$$

A. Search for thermodynamic properties of solids from known databases and literatures. If all of them are known, obtain the optimal candidates by minimizing free energies based on operating conditions.

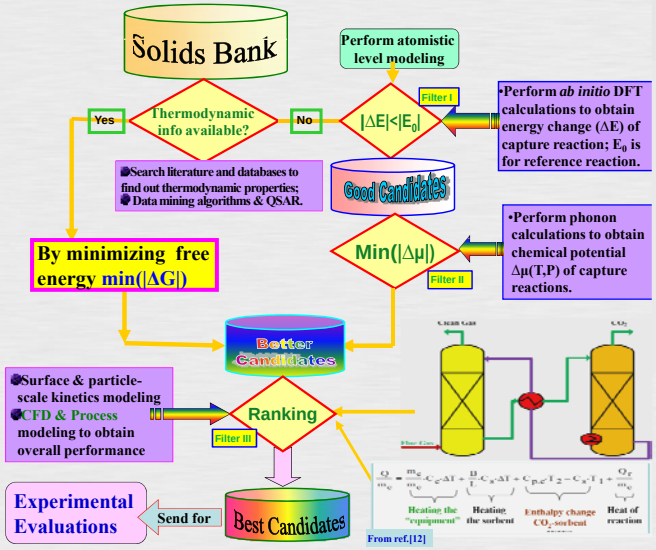
B. If their thermodynamic properties are unknown, calculate by

Chemical Potential: $\Delta\mu^0(T) \approx \Delta E^{DFT} + \Delta E_{ZPE} + \Delta F_{PH}(T) - (G_{CO_2}(T) \pm G_{H_2O}(T))$

Reaction Heat: $\Delta H(T,P) = \Delta\mu(T,P) + T(\Delta S_{PH}(T,P) - S_{CO_2}(T,P) \mp S_{H_2O}(T,P))$

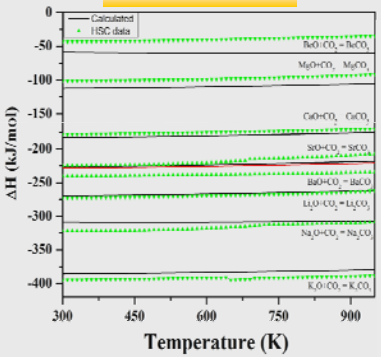
where
- G_{CO_2}, S_{CO2}, and G_{H2O} and S_{H2O} are evaluated from statistical mechanics;
- ΔE^{DFT} is calculated by density functional theory[10];
- ΔE_{ZPE}, $\Delta S_{PH}(T)$ and $\Delta F_{PH}(T)$ are evaluated through phonon dispersions[11].

High-Throughput Screening Methodology[1-9]



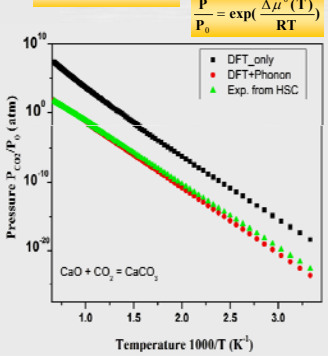
Preliminary Results for Oxides and Hydroxides[1,2,4,7]

Heat of Reaction

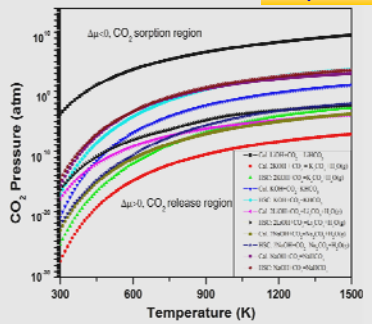


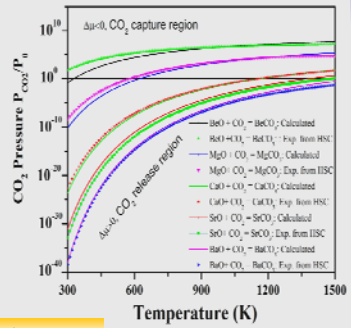
Van't Hoff Plot

$$\frac{P}{P_0} = \exp\left(\frac{\Delta\mu^0(T)}{RT}\right)$$

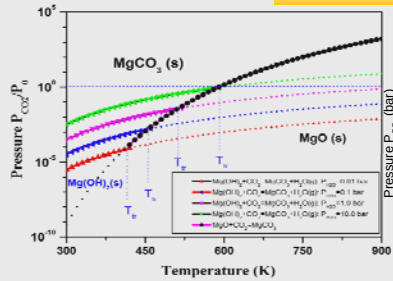


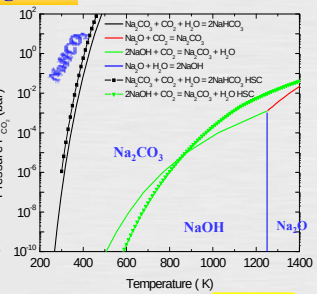
Δμ-T-P Relationships

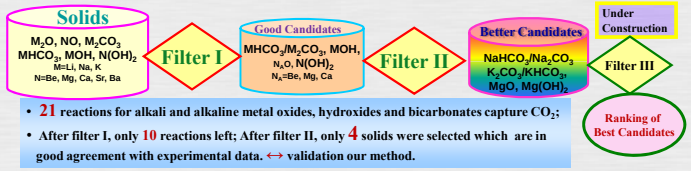




Phase-diagram

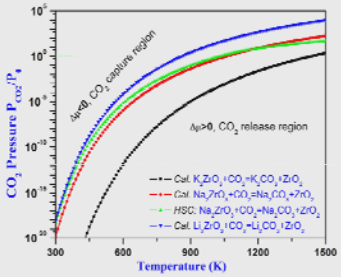






- 21 reactions for alkali and alkaline metal oxides, hydroxides and bicarbonates capture CO_2;
- After filter I, only 10 reactions left; After filter II, only 4 solids were selected which are in good agreement with experimental data. ↔ validation our method.

Preliminary Results for Zirconates and Silicates[3-7]



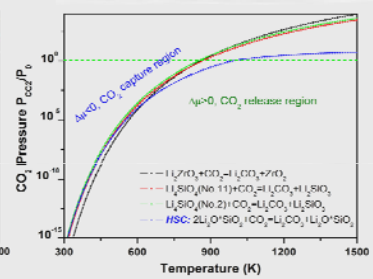


Table I. The weight percentage of CO_2 capture, the calculated energy change ΔE^{DFT}, the zero-point energy changes ΔE_{ZP} and the thermodynamic properties (ΔH, ΔG) of the CO_2 capture reactions by zirconates and silicates. (unit: kJ/mol). The turnover temperatures (T_1 and T_2) of the reactions of CO_2 capture by solids under the conditions of pre-combustion (P_{CO2}=20 bar) and post-combustion (P_{CO2}=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
$K_2ZrO_3+CO_2 \leftrightarrow K_2CO_3+ZrO_2$	20.24	-223.158	5.813	-238.490	-187.884	hT	1285
$Na_2ZrO_3+CO_2 \leftrightarrow Na_2CO_3+ZrO_2$	23.76	-140.862	2.236	-158.327 -151.403[a]	-114.121 -105.252[a]	1275	925
$Li_2ZrO_3+CO_2 \leftrightarrow Li_2CO_3+ZrO_2$	28.75	-146.648	11.311	-158.562 -162.69[a]	-103.845 -113.18[a]	1000	780
$\frac{1}{3}Li_6Zr_2O_7+CO_2 \leftrightarrow Li_2CO_3+\frac{2}{3}ZrO_2$	39.28	-155.942	8.6243	-169.500	-117.564	1140	880
$\frac{1}{2}Li_4Zr_2O_7+CO_2 \leftrightarrow Li_2CO_3+\frac{1}{2}Li_2ZrO_3+\frac{1}{2}ZrO_2$	26.19	-160.583	7.2808	-174.962	-124.417	1220	930
$Li_6Zr_2O_7+CO_2 \leftrightarrow Li_2CO_3+2Li_2ZrO_3$	13.09	-174.525	3.2501	-191.369	-144.997	1500	1110
$Li_4SiO_4+CO_2 \leftrightarrow Li_2CO_3+Li_2SiO_3$	36.72	-148.704	5.9706	-143.548	-93.972	1030	780

[a] from HSC-Chemistry database package

Conclusions

- Our theoretical approach can obtain similar results as experimental measurements and can be used to identify optimal sorbents.
- The strength of our method is to screen complex sorbent materials for which their thermodynamic properties are not available.
- Hundreds of solid materials have been investigated. Currently, we are working on screening multi-component systems, substituted, doped, and mixed materials for CO_2 sorbent applications.
- Perform multi-scale modeling to obtain the overall performance and the associated costs of solid sorbent for pre- and post-combustion technologies (filter III).
- As a long time goal: to build a database of solid sorbents for CO_2 capture which satisfies industrial operational requirements.

References

1. Y. Duan, *Proc. of 7th, 8th, 9th & 10th Ann. Conf. on Carbon Capture & Sequestration*, (Pittsburgh, 2008~ 2011)
2. Y. Duan, D. C. Sorescu, *Phys. Rev.* **B79**, 014301(2009); *J. Chem. Phys.* 133(2010)074508
3. Y. Duan, *J. Renewable & Sustainable Energy* 3(2011)013102; *Phys. Rev.* **B**77, 045332(2008)
4. Y. Duan, B. Zhang, D. C. Sorescu, J. K. Johnson, *J. Solid State Chem.* 184(2011)304-311
5. Y. Duan, K. Parlinski, *Phys. Rev. B* in press (2011)
6. Y. Duan, *J. Renewable & Sustainable Energy*, submitted (2011)
7. Y. Duan, D.C. Sorescu, D. Luebke, *Proc. 28th Ann. Int. Pittsburgh Coal Conf.* (Pittsburgh, 2011)
8. Y. Duan, *et al.*, to be submitted.
9. B. Zhang, Y. Duan, J. K. Johnson, to be submitted.
10. G. Kresse, J. Hafner, *Phys. Rev.* **B47**, 558(1993)
11. K. Parlinski, **Software PHONON** (2010)
12. H. W. Pennline, *et al*, *Proc. Ann. NETL CO_2 Capture Technology R&D Meeting*, (Pittsburgh, 2009)

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