



Density functional theory study of the thermodynamic properties and pathways of SrO, Sr(OH)₂ and Sr(OH)₂.8H₂O capturing CO₂ reactions

Manh Tien Nguyen, Dominic Alfonso, Christopher M. Marin, Douglas Kauffman, Yuhua Duan

National Energy Technology Lab

CO₂ Capture using SrO

Reactive capture uses metal oxides and solid carbon to capture/convert CO₂

Capture: Thermally heating a mixture of CO₂ and metal oxide forms a stable metal carbonate:

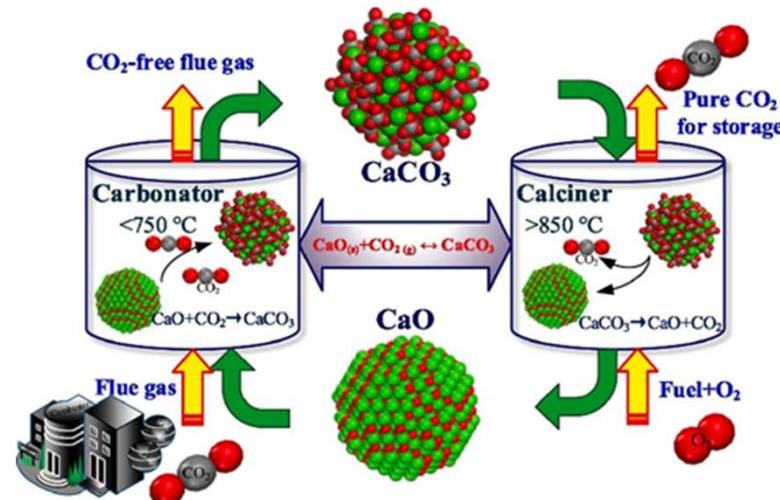


Conversion: Subsequently heating the MCO₃ and solid carbon produces carbon monoxide and regenerates the sorbent

1. MCO₃ + C → 2CO + MO (commercially useful)
2. MCO₃ → CO₂ + MO

CaO has been used due to relatively low-cost and abundance

SrCO₃/SrO showed much better CO selectivity than CaCO₃/CaO



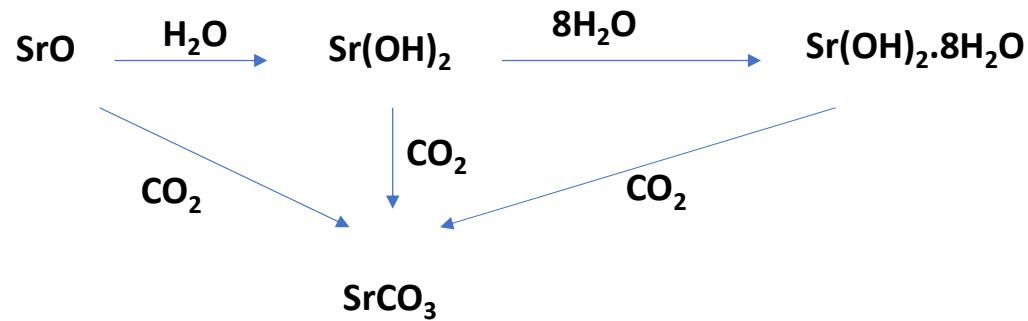
Wang, N., Feng, Y., & Guo, X. (2020). *Applied Surface Science*, 532, 147425.

CO₂ Adsorption and Desorption on Surfaces



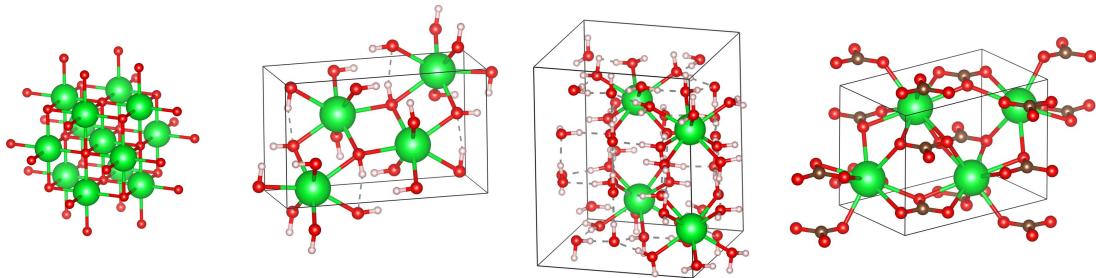
CO₂ adsorption first happens on the surface before CO₂ diffuses into the bulk

SrO can react with H₂O in flue gas to from Sr(OH)₂ and Sr(OH)₂.8H₂O



Surface calculations

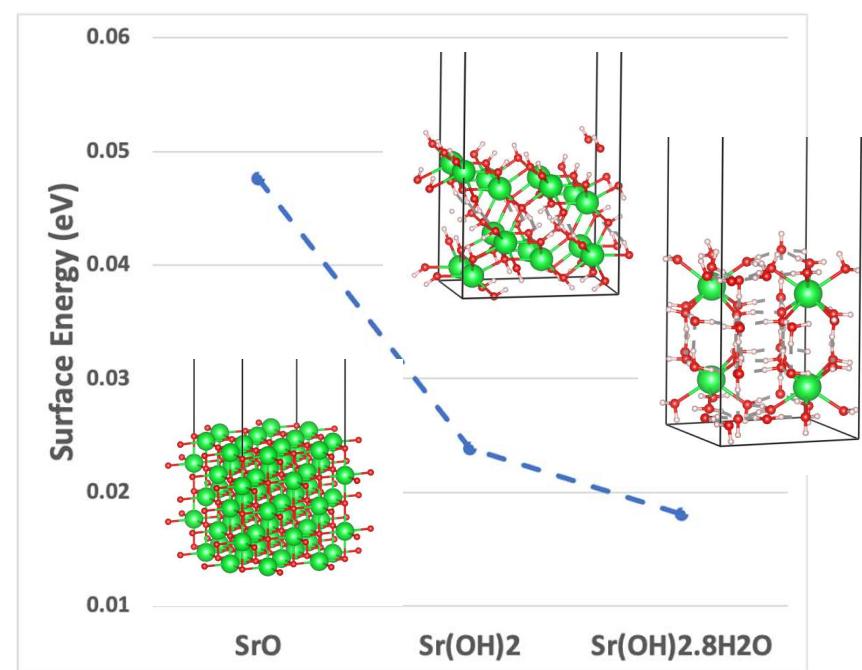
Crystal	Calculated	Experiment
SrO	5.17x5.17x5.17 Å	5.16x5.16x5.16 Å
Sr(OH)2	9.84x3.94x6.03 Å	9.89x3.92x6.12 Å
Sr(OH)2.8H2O	8.94x 8.95x 11.37 Å	9.02x9.02x11.61 Å
SrCO3	5.19x 8.51x 6.05 Å	5.09x8.36x6.00 Å



Most stable surfaces

	Surface
SrO	100
Sr(OH)2	101
Sr(OH)2.8H2O	001
SrCO3	011

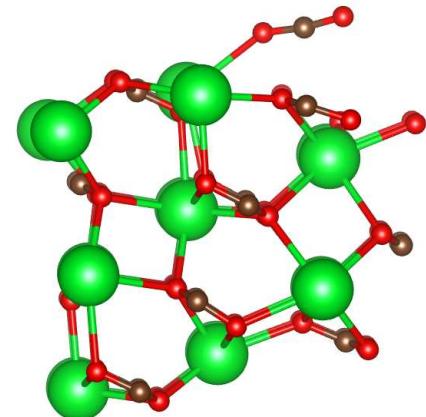
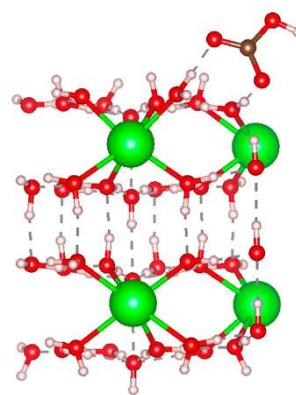
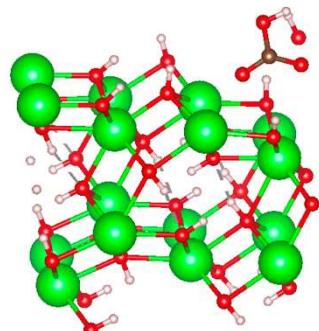
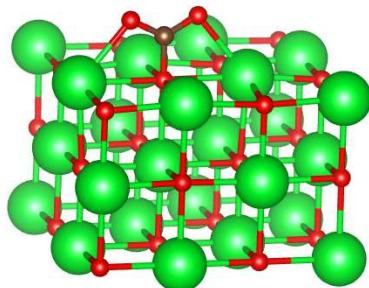
Surface becomes more stable with more H₂O



CO₂ adsorption and desorption energy

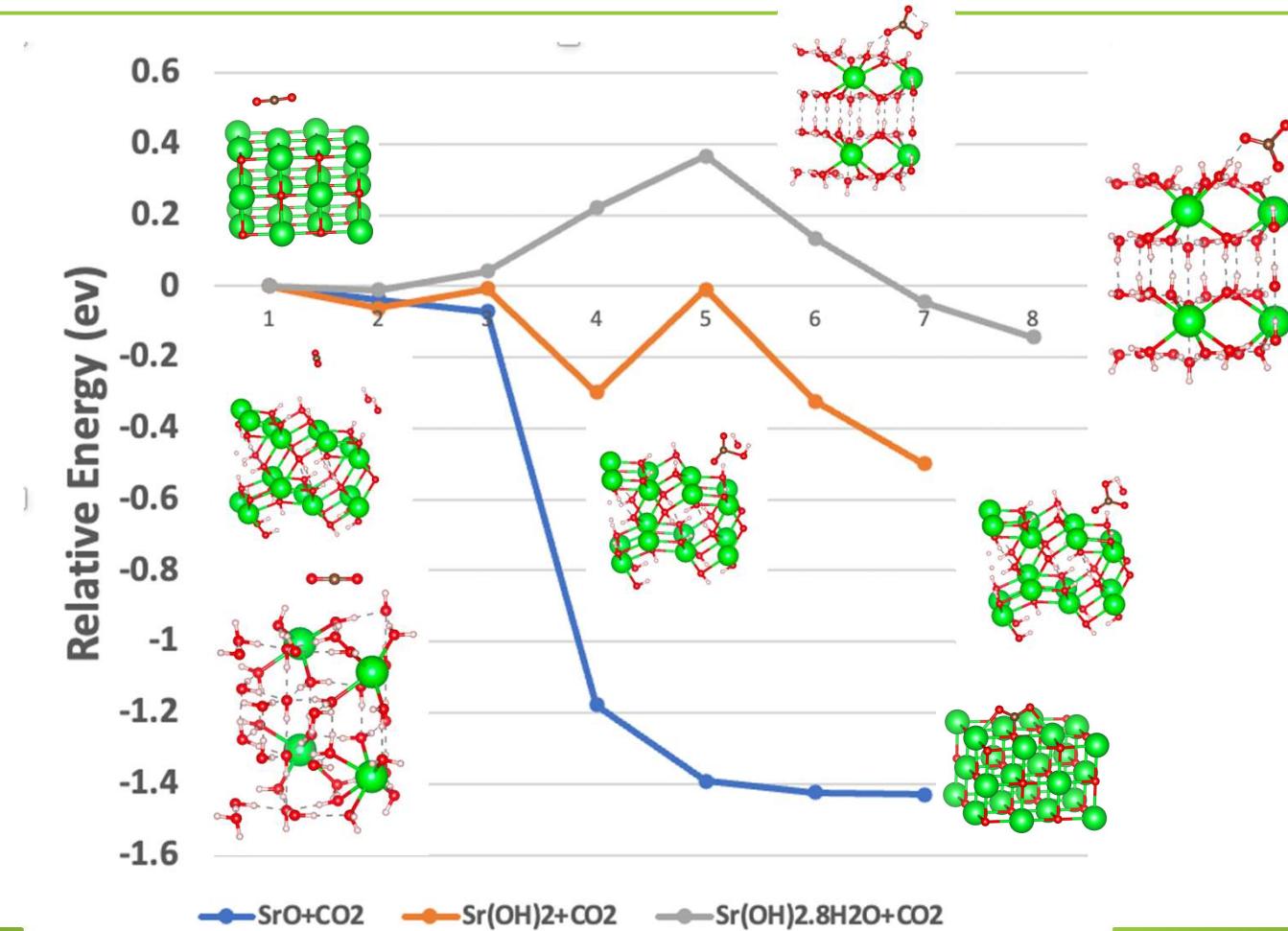


Surface reaction	Energy
SrO + CO ₂	-1.7 eV / -164.069 KJ/mol
Sr(OH) ₂ + CO ₂	-0.52 eV / -49.8 KJ/mol
Sr(OH) _{2.8} H ₂ O + CO ₂	-0.14 eV / -13.14 KJ/mol
SrCO ₃ => SrO + CO ₂	3.16 eV / 304.5 KJ/mol

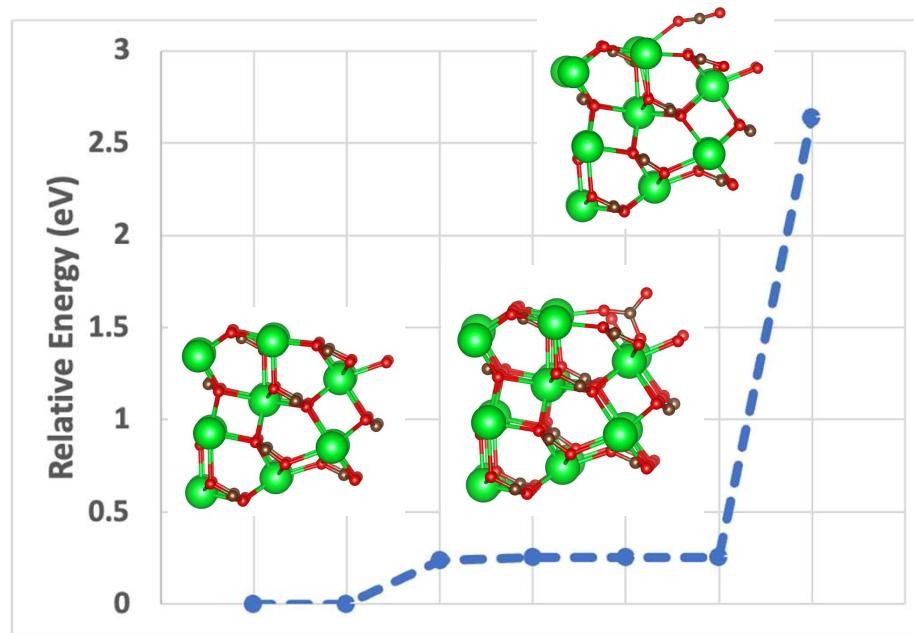


The more stable the surface, the less energetic favorable the CO₂ adsorption is

CO₂ adsorption reaction pathways



CO₂ desorption reaction pathway

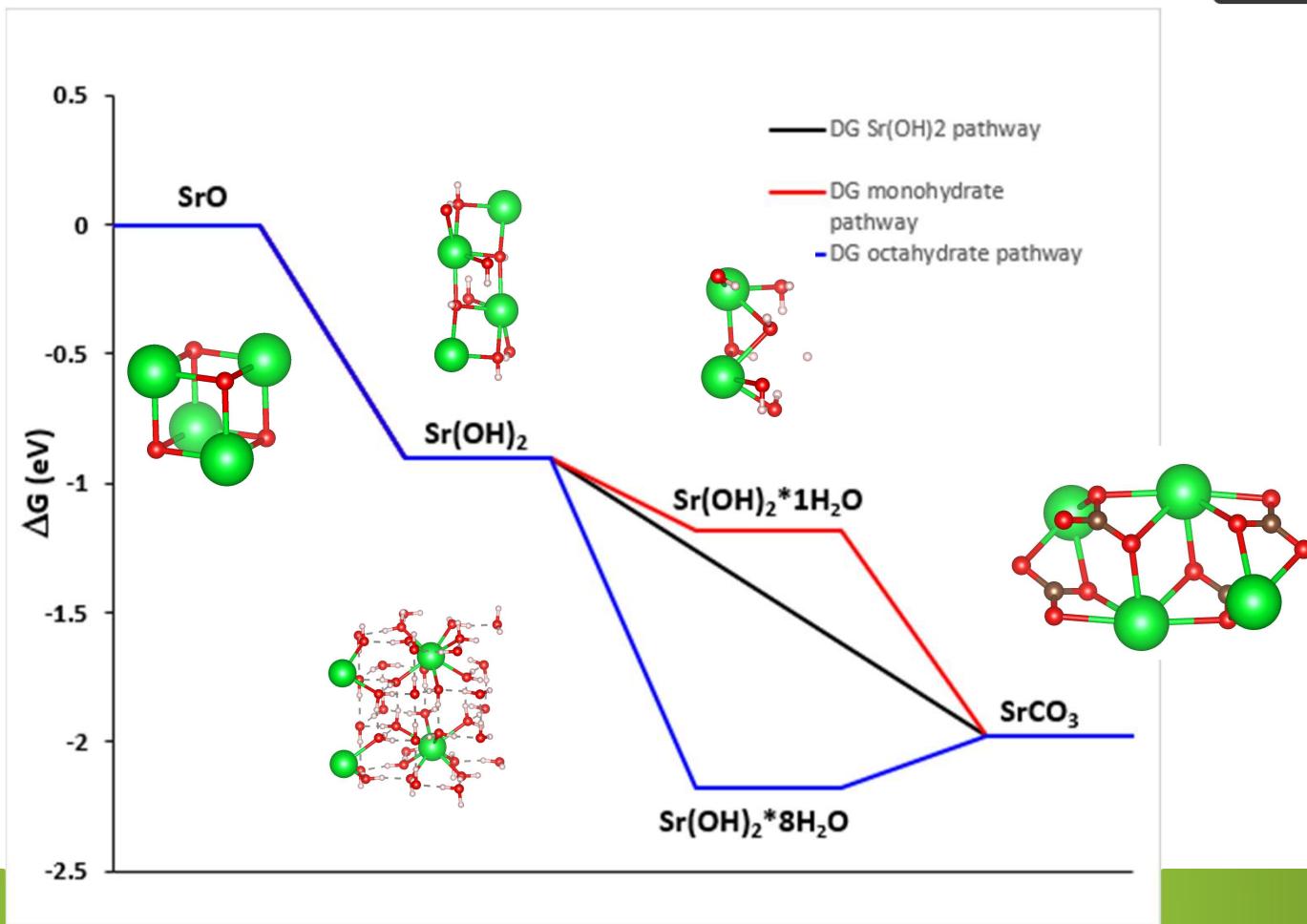


CO₂ reaction thermodynamics



#	Reaction	ΔE_{DFT} (eV)	ΔG 300K (eV)	ΔG .ref* 298K
1	SrO + CO ₂ = SrCO ₃	-2.10	-1.99	-1.96
2	SrO + H ₂ O (liquid) = Sr(OH) ₂	-0.88	-0.90	
3	Sr(OH) ₂ + H ₂ O(liquid) = Sr(OH) _{2.1} H ₂ O	-0.34	-0.28	
4	Sr(OH) ₂ + 8H ₂ O(liquid) = Sr(OH) _{2.8} H ₂ O	-1.41	-1.28	
5	Sr(OH) ₂ + CO ₂ = SrCO ₃ + H ₂ O(liquid)	-1.23	-1.08	-1.10
6	Sr(OH) _{2.1} H ₂ O + CO ₂ = SrCO ₃ + 2H ₂ O(liquid)	-0.89	-0.80	
7	Sr(OH) _{2.8} H ₂ O + CO ₂ = SrCO ₃ + 9H ₂ O(liquid)	0.19	0.20	

CO₂ reaction thermodynamics



Conclusion

- We examined the adsorption reactions of CO_2 on SrO , $\text{Sr}(\text{OH})_2$ and $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ surfaces
- The predicted CO_2 adsorption is $164.04 \text{ kJ mol}^{-1}$ on the SrO surface, 49.8 kJ mol^{-1} on the $\text{Sr}(\text{OH})_2$ surface and
- The carbonation of SrO is barrierless, whereas the CO_2 reaction on the $\text{Sr}(\text{OH})_2$ surface follows a bicarbonate pathway with an activation barrier of 23.8 kJ mol^{-1} .
- The CO_2 reaction on $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ surface also follows a bicarbonate pathway with an activation barrier of 36.4 kJ mol^{-1}
- Furthermore, the regeneration of SrO from SrCO_3 (011) surface is transition-state-free with a reaction energy of $304.5 \text{ kJ mol}^{-1}$.
- The thermodynamics of bulk reaction is also addressed

Acknowledgement



- We thank the computational resource at NETL