

Density functional theory study of the thermodynamic properties and pathways of SrO , Sr(OH)_2 and $\text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O}$ capturing CO_2 reactions

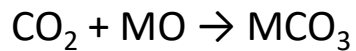
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CO₂ Capture using SrO

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:

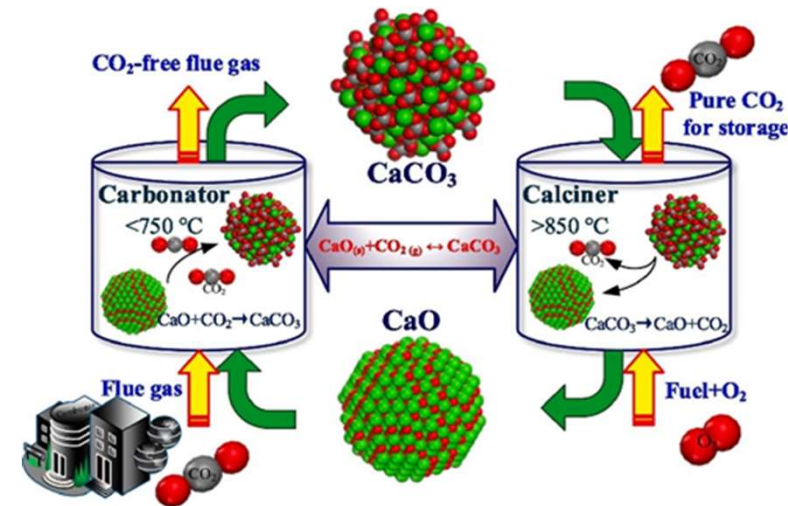


Conversion: Subsequently heating the MCO₃ and solid carbon produces carbon monoxide and regenerates the sorbent

1. $\text{MCO}_3 + \text{C} \rightarrow 2\text{CO} + \text{MO}$ (commercially useful)
2. $\text{MCO}_3 \rightarrow \text{CO}_2 + \text{MO}$

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

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

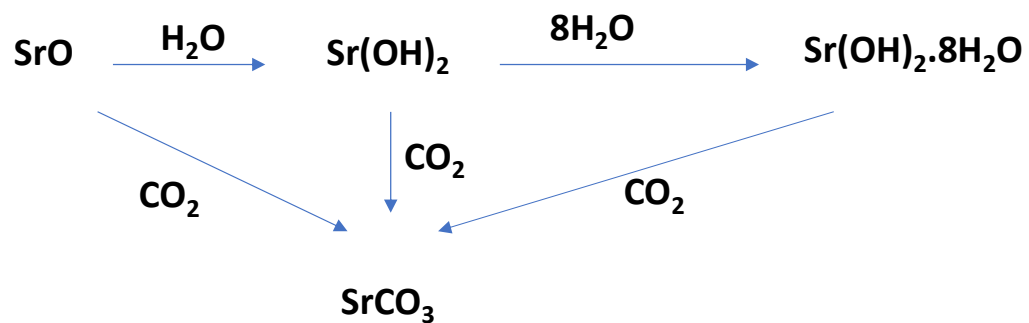


Wang, N., Feng, Y., & Guo, X. (2020). *Applied Surface Science*, 532, 147425.

CO₂ Adsorption and Desorption on Surfaces

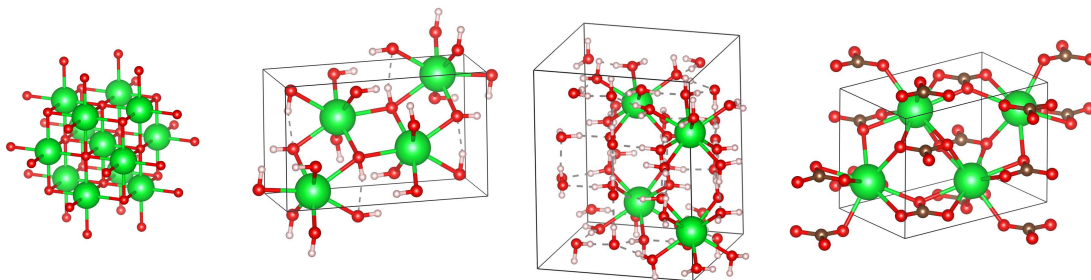
CO₂ adsorption first happens on the surface before CO₂ diffuses into the bulk

SrO can react with H₂O in flue gas to form Sr(OH)₂ and Sr(OH)₂·8H₂O



Surface calculations

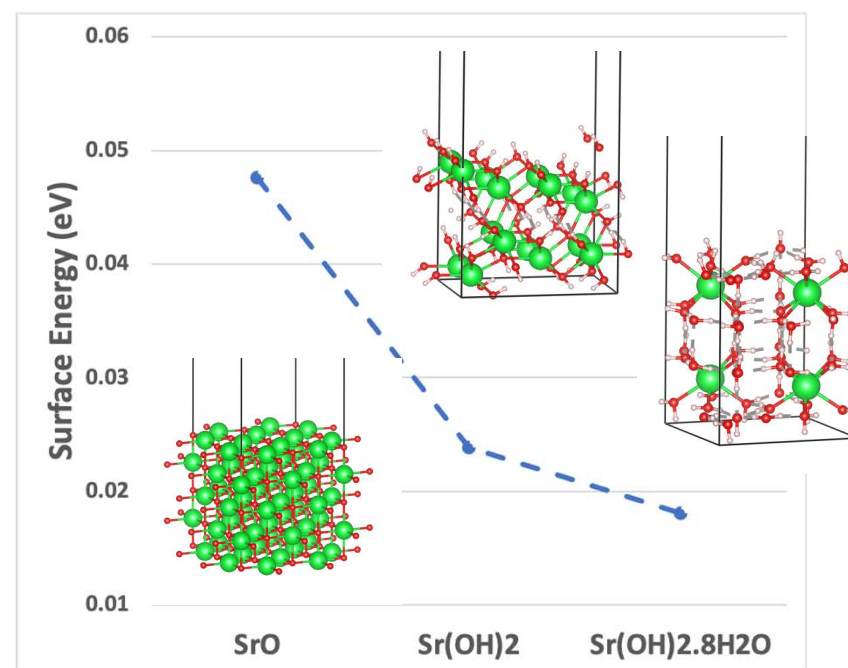
Crystal	Calculated	Experiment
SrO	5.17x5.17x5.17 Å	5.16x5.16x5.16 Å
Sr(OH) ₂	9.84x3.94x6.03 Å	9.89x3.92x6.12 Å
Sr(OH) ₂ ·8H ₂ O	8.94x 8.95x 11.37 Å	9.02x9.02x11.61 Å
SrCO ₃	5.19x 8.51x 6.05 Å	5.09x8.36x6.00 Å



Most stable surfaces

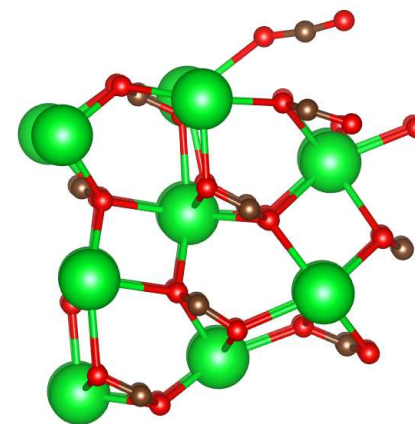
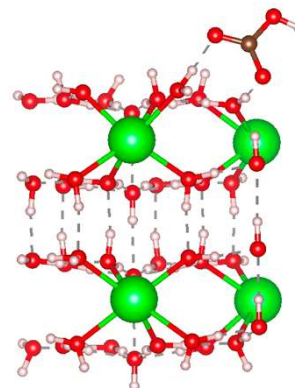
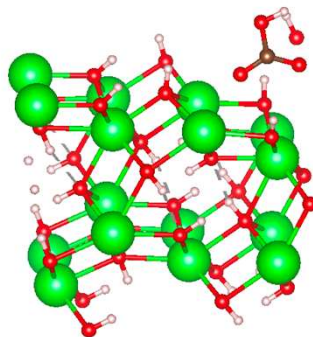
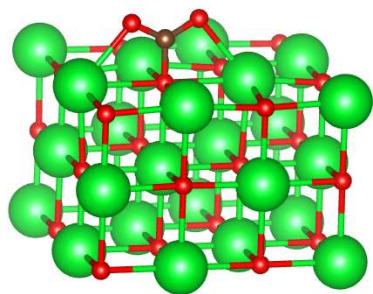
	Surface
SrO	100
Sr(OH) ₂	101
Sr(OH) ₂ ·8H ₂ O	001
SrCO ₃	011

Surface becomes more stable with more H₂O



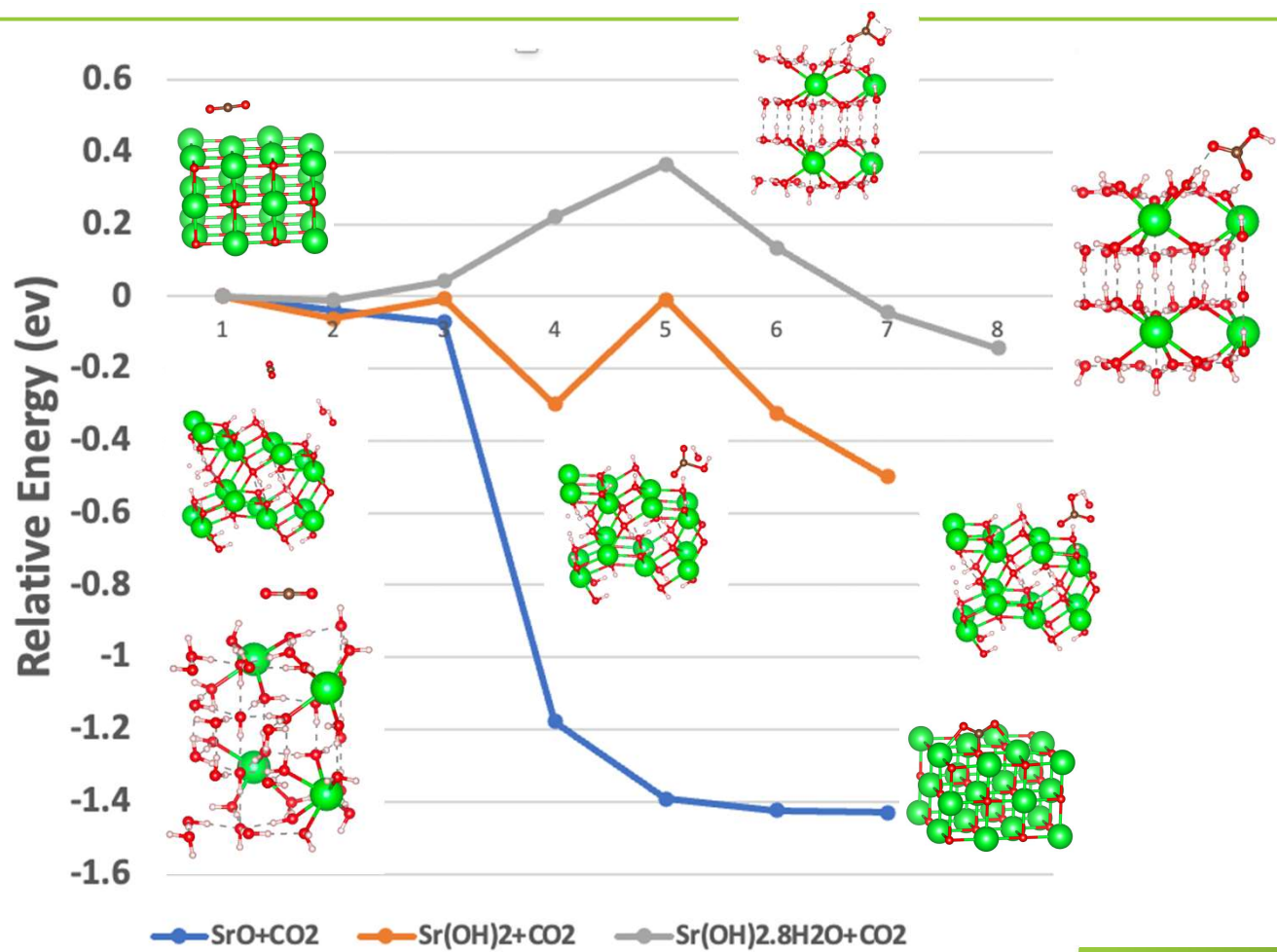
CO₂ adsorption and desorption energy

Surface reaction	Energy
$\text{SrO} + \text{CO}_2$	-1.7 eV / -164.069 KJ/mol
$\text{Sr(OH)}_2 + \text{CO}_2$	-0.52 eV / -49.8 KJ/mol
$\text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O} + \text{CO}_2$	-0.14 eV / -13.14 KJ/mol
$\text{SrCO}_3 \Rightarrow \text{SrO} + \text{CO}_2$	3.16 eV / 304.5 KJ/mol

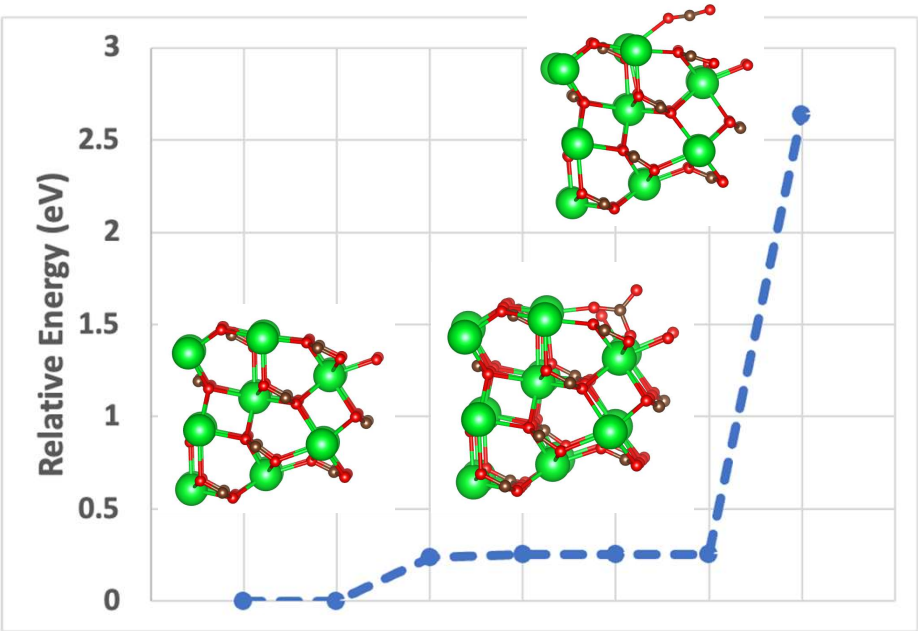


The more stable the surface, the less energetic favorable the CO₂ adsorption is

CO2 adsorption reaction pathways



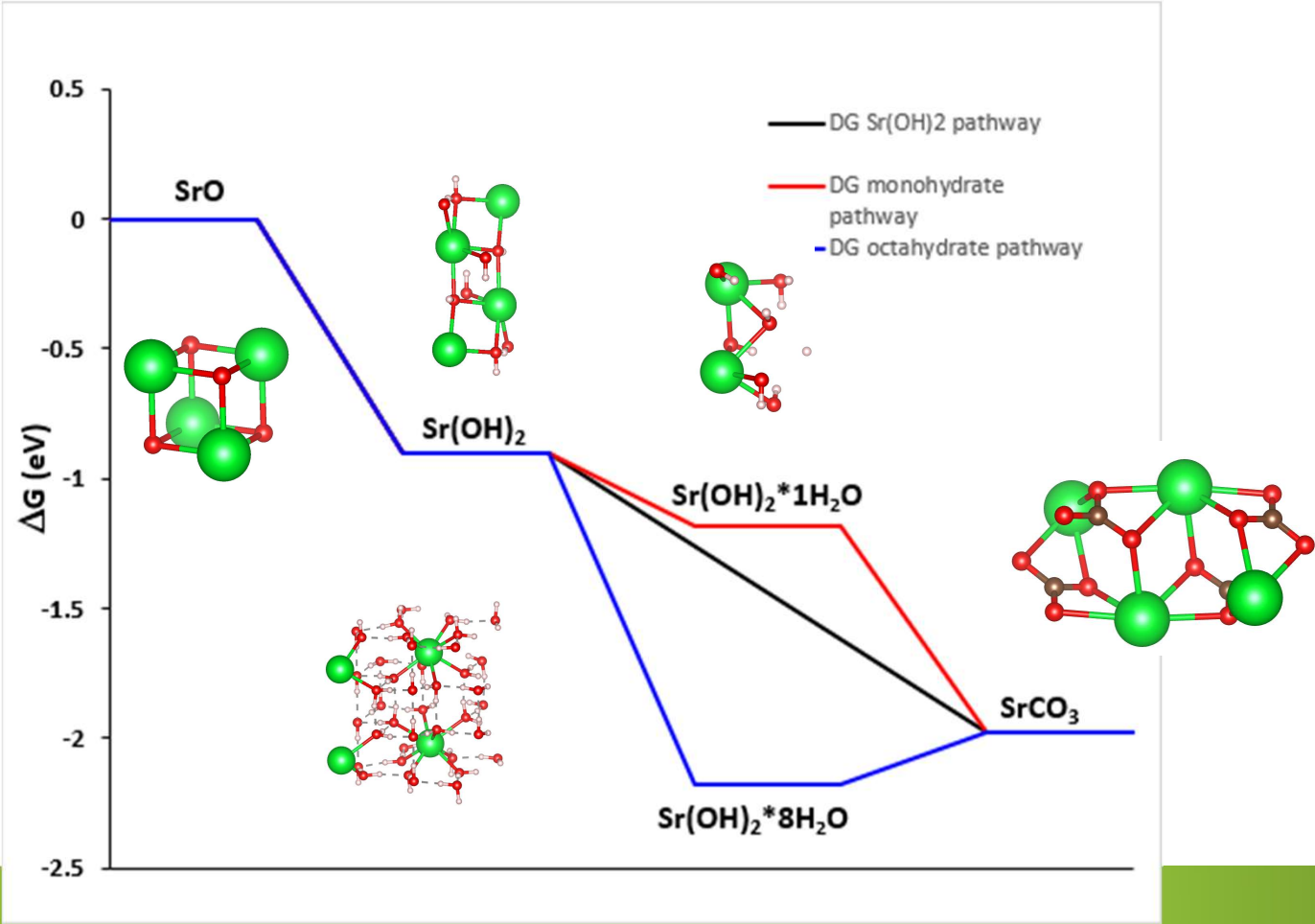
CO2 desorption reaction pathway



CO2 reaction thermodynamics

#	Reaction	ΔE_{DFT} (eV)	ΔG 300K (eV)	$\Delta G.ref^*$ 298K
1	$SrO + CO_2 = SrCO_3$	-2.10	-1.99	-1.96
2	$SrO + H_2O (liquid) = Sr(OH)_2$	-0.88	-0.90	
3	$Sr(OH)_2 + H_2O(liquid) = Sr(OH)_2 \cdot 1H_2O$	-0.34	-0.28	
4	$Sr(OH)_2 + 8H_2O(liquid) = Sr(OH)_2 \cdot 8H_2O$	-1.41	-1.28	
5	$Sr(OH)_2 + CO_2 = SrCO_3 + H_2O(liquid)$	-1.23	-1.08	-1.10
6	$Sr(OH)_2 \cdot 1H_2O + CO_2 = SrCO_3 + 2H_2O(liquid)$	-0.89	-0.80	
7	$Sr(OH)_2 \cdot 8H_2O + CO_2 = SrCO_3 + 9H_2O(liquid)$	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