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Supplementary information

Insights into the capture mechanism of CO_2 by diamine-appended Mg_2(dobpdc): a combined DFT and microkinetic modeling study

*Kuan-Yu Lin, Zhong-Ming Xie, Lu-Sheng Hong, and Jyh-Chiang Jiang**

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

Corresponding Author

*Email: jcjiang@mail.ntust.edu.tw (J.-C. J.)

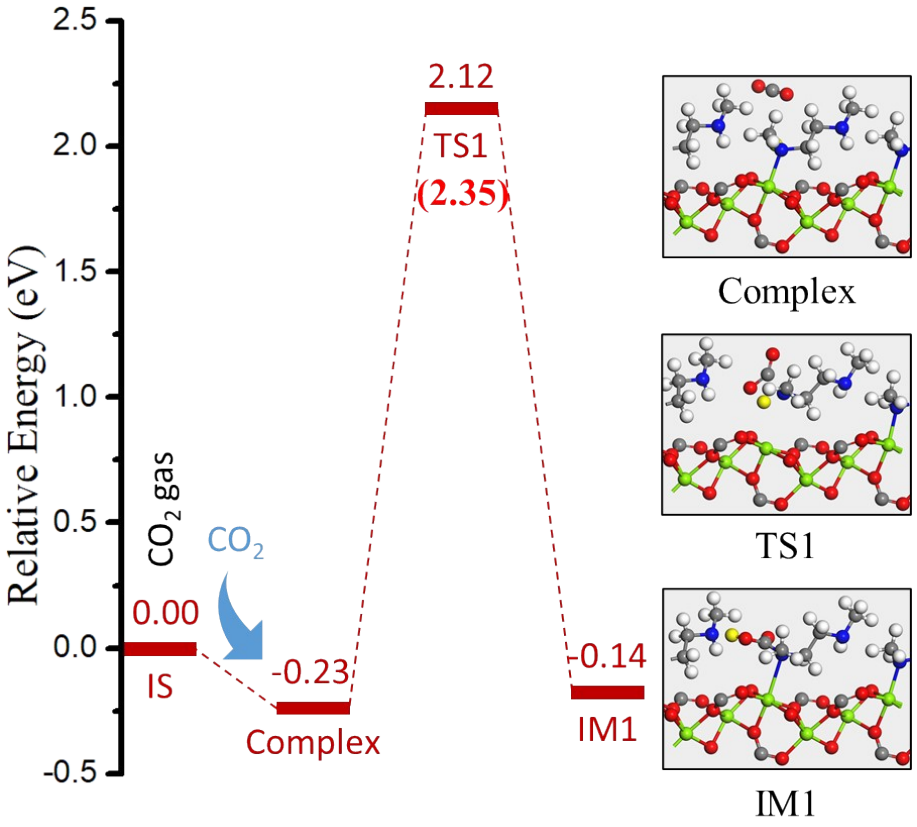

Fig. S1. Potential energy surface of CO_2 adsorption on the inner amine of the mmen molecule in the mmen-Mg_2(dobpdc) structure. Side views of the optimized geometries of CO_2 adsorption along reaction path 2. [Color code: green-magnesium; gray-carbon; blue-nitrogen; red-oxygen; white-hydrogen.]

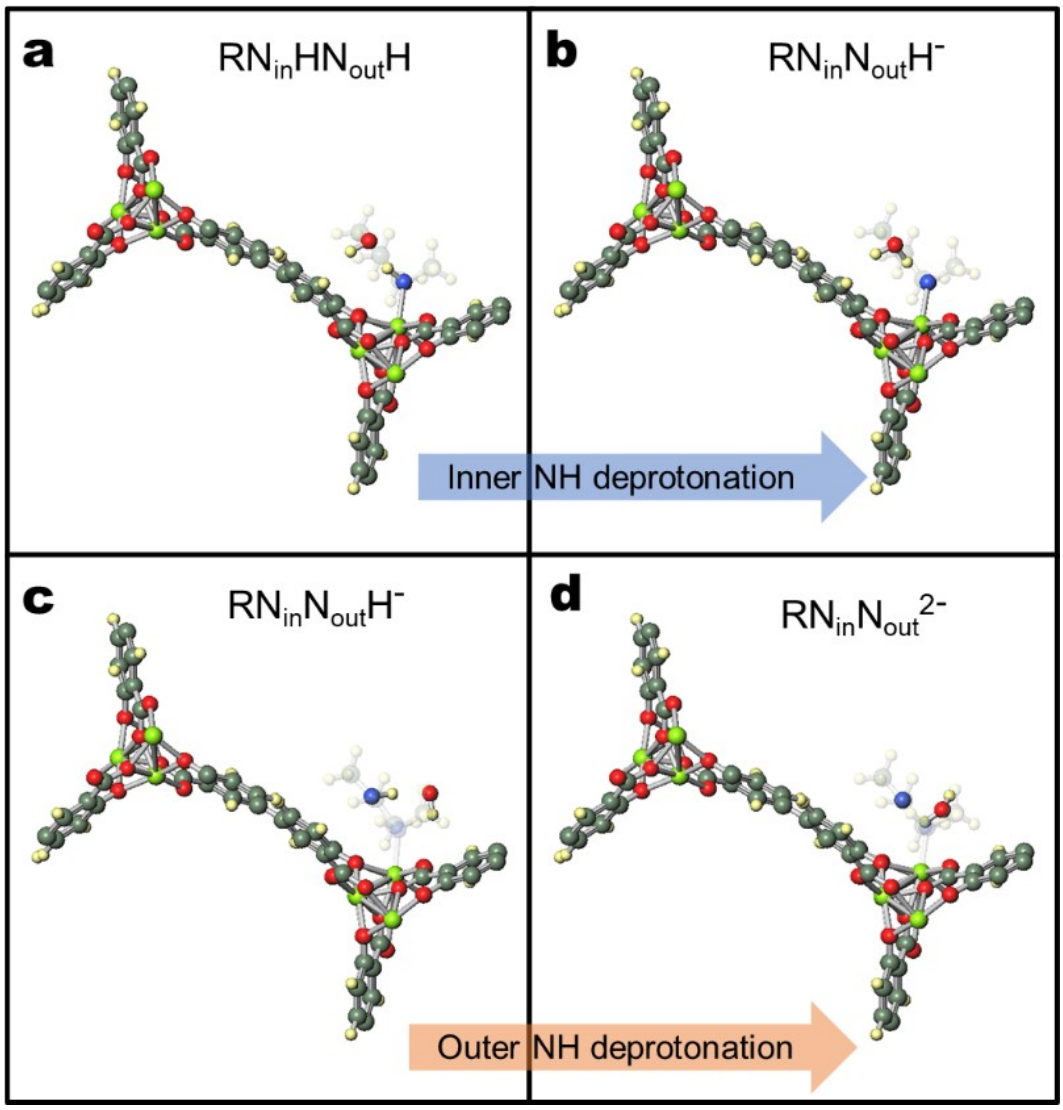

Fig. S2. Optimized structures of the deprotonation reaction of the inner and outer amine in Mg_2(dobpdc) within an alkaline solution (1M KOH). The reaction was investigated using Quantum Espresso with the 3D-RISM solution method.

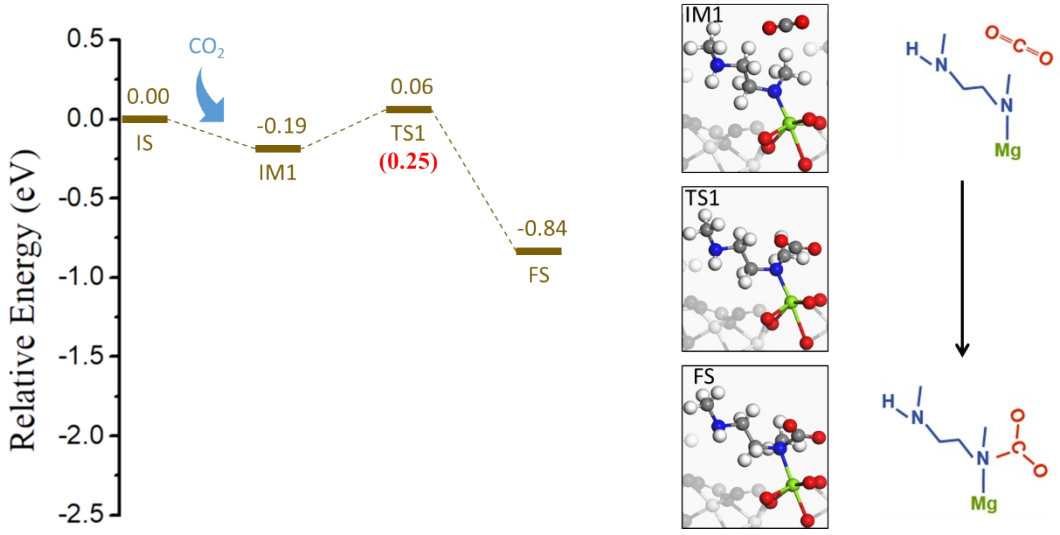

Fig. S3. Potential energy surface of CO_2 adsorption on the inner amine of the mmen molecule in mmen-Mg_2(dobpdc) in an alkaline environment. [Color code: green-magnesium; gray-carbon; blue-nitrogen; red-oxygen; white-hydrogen.]

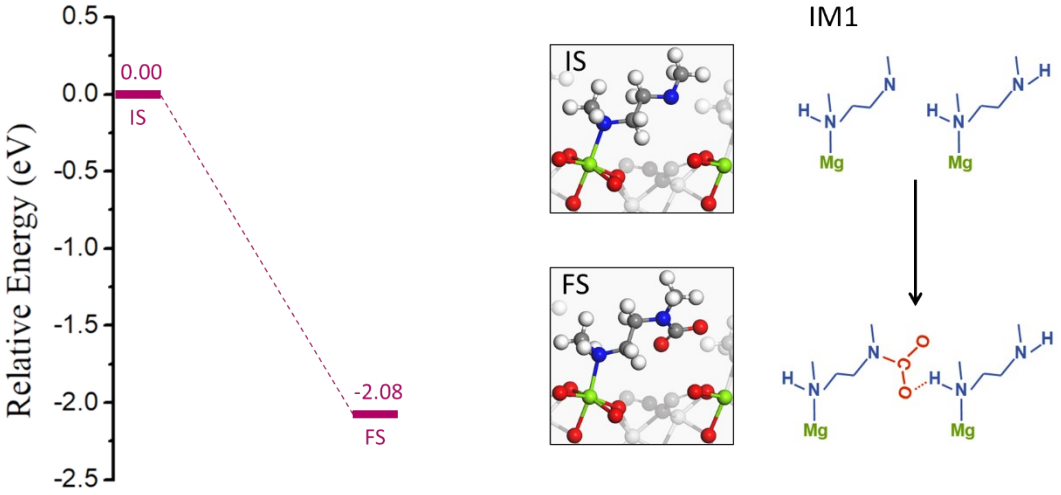

Fig. S4. Potential energy surface of CO_2 adsorption on the outer of the mmen molecule in mmen-Mg_2(dobpdc) in an alkaline environment. [Color code: green-magnesium; gray-carbon; blue-nitrogen; red-oxygen; white-hydrogen.]

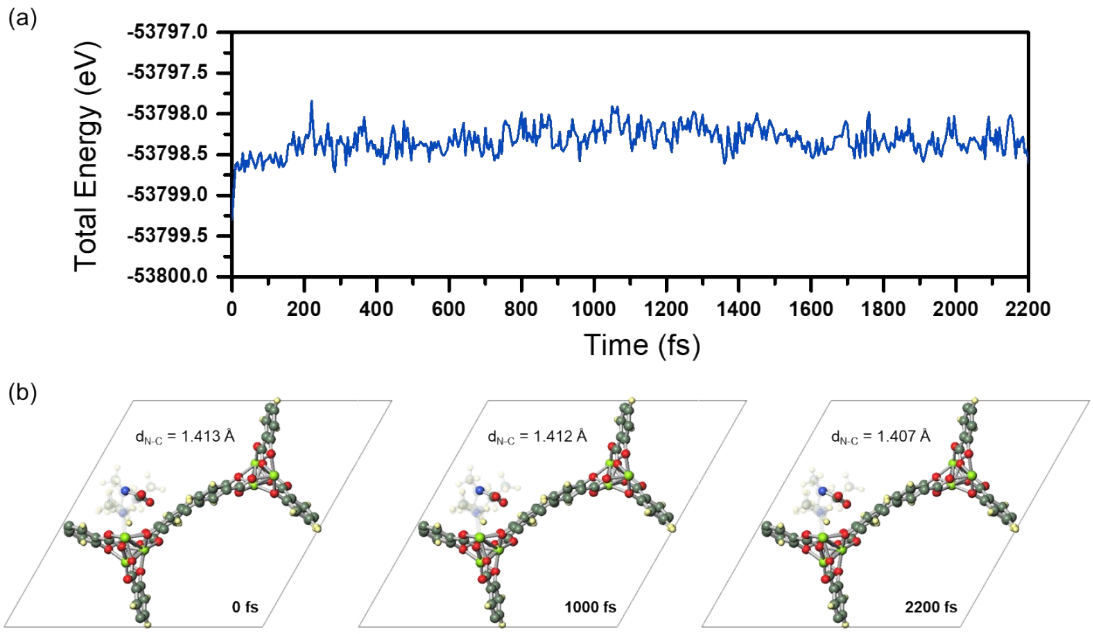

Fig. S5. (a) The calculated total energy (eV) as a function of the simulation time (fs) was computed for CO_2 adsorption on the outer amine site in mmen-Mg_2(dobpdc) under an alkaline environment with pH = 14. (b) Side views of snapshots are presented at simulation times of 0, 1000, and 2200 fs.

Table S1. Selected geometrical parameters (Å) of CO_2 molecule adsorbed on the inner amine site of the mmen molecule in the mmen-Mg_2(dobpdc) structure along reaction path 1.

	N^1-H	N^2-H	O^2-H	C-O^1	C-O^2	C-N^1	Mg-N^1	Mg-O^1
IS	1.03	3.27	-	-	-	-	2.25	-
TS1	1.61	1.19	-	-	-	-	2.13	-
IM1	2.83	1.04	-	-	-	-	2.04	-
IM2	2.86	1.04	5.48	1.18	1.18	6.32	2.04	-
TS2	-	1.04	2.63	1.21	1.21	2.25	2.18	-
IM3	-	1.61	1.05	1.23	1.34	1.41	2.79	3.88
TS3	-	1.66	1.05	1.24	1.34	1.37	3.53	3.25
FS	-	1.60	1.06	1.26	1.33	1.36	-	2.02

Table S2. Selected geometrical parameters (Å) of CO_2 molecule adsorbed on the outer amine site of the mmen molecule in the mmen-Mg_2(dobpdc) structure along reaction path 3.

	N-H	O^2-H	C-O^1	C-O^2	C-N	Mg-N	O^3-H
IS	1.03	-	-	-	-	-	-
IM1	1.03	3.97	1.18	1.17	3.09	2.25	-
TS1	1.22	1.38	1.21	1.29	1.59	2.27	-
IM2	2.44	0.98	1.23	1.38	1.37	2.26	3.13
TS2	-	0.98	1.22	1.35	1.45	2.26	2.40
FS	-	1.01	1.25	1.35	1.37	2.25	1.65

Table S3. Activation energies and backward barrier energies of each reaction pathway used for microkinetic simulations.

Path 1	Total Energy (eV)			Activation Energy (eV)			Backward Barrier (eV)		
	DFT Energy	ZPE	△G	DFT Energy	ZPE	△G	DFT Energy	ZPE	△G
IS	-1425.394	-1415.295	-1416.550						
TS1(H shift)	-1423.707	-1413.774	-1414.989	1.687	1.521	1.561	0.068	-0.065	-0.127
IM1(NH_2)	-1423.775	-1413.710	-1414.861						
IM2(CO_2 ads)	-1423.979	-1413.889	-1414.621	-0.204	-0.179	0.240			
TS2	-1423.557	-1413.436	-1414.139	0.422	0.453	0.482	1.989	1.947	1.949
IM3(HCOON)	-1425.546	-1415.383	-1416.089						
TS3	-1425.512	-1415.384	-1416.158	0.034	-0.001	-0.070	0.699	0.668	0.599
FS(Mg-O)	-1426.211	-1416.052	-1416.757						

Path 2	Total Energy (eV)			Activation Energy (eV)			Backward Barrier (eV)		
	DFT Energy	ZPE	△G	DFT Energy	ZPE	△G	DFT Energy	ZPE	△G
IS	-1425.394	-1415.295	-1416.550						
IM1(CO_2 ads)	-1425.636	-1415.529	-1416.372	-0.242	-0.234	0.178			
TS1	-1423.283	-1413.294	-1414.064	2.352	2.236	2.308	2.263	2.090	2.025
IM2(HCOON)	-1425.546	-1415.383	-1416.089						

Path 3	Total Energy (eV)			Activation Energy (eV)			Backward Barrier (eV)		
	DFT Energy	ZPE	△G	DFT Energy	ZPE	△G	DFT Energy	ZPE	△G
IS	-1425.394	-1415.295	-1416.550						
IM1 (CO_2 ads)	-1425.629	-1415.496	-1416.236	-0.236	-0.200	0.314			
TS1	-1424.345	-1414.292	-1415.037	1.284	1.203	1.198	1.229	1.116	1.148
IM2 (HCOON)	-1425.575	-1415.409	-1416.185						
TS2	-1425.058	-1414.901	-1415.593	0.517	0.508	0.592	0.836	0.810	0.866
FS (H bond)	-1425.894	-1415.711	-1416.460						

We calculated the ratio of deprotonated mmen molecules according to the following equations:

$$A\ (aq) + OH^-(aq) \rightleftharpoons B^-\ (aq) + H_2O(l)$$

$$\Delta G = -RT\ln K$$

$$K = \frac{[B-]}{[A][OH-]}$$

where ΔG, R, and K indicates the free energy change of reaction, the constant of 8.314 J/(mol·K), and the equilibrium constant at room temperature, respectively.

Table S4. The Reaction energy (ΔG in eV), rate constant (K_{eq}) of deprotonation reaction of inner and outer amine, and the ratio of deprotonated mmen molecules (B/A) were determined under an alkaline environment of 1M KOH.

	A	B	ΔG (eV)	K_{eq}	B/A
pH=11	$RN_{in}HN_{out}H$	$RN_{in}N_{out}H^-$	0.105	0.893	8.9E-04
	$RN_{in}N_{out}H^-$	$RN_{in}N_{out}^{2-}$	0.164	0.838	7.5E-07
	A	B	ΔG (eV)	K_{eq}	B/A
pH=14	$RN_{in}HN_{out}H$	$RN_{in}N_{out}H^-$	0.148	0.853	0.853
	$RN_{in}N_{out}H^-$	$RN_{in}N_{out}^{2-}$	0.170	0.833	0.710