Electronic Supplementary Material (ESI) for Industrial Chemistry & Materials.

Supplementary Information

Theoretical Investigation of Carbon Dioxide on MgH_2 with Cobalt Catalyst

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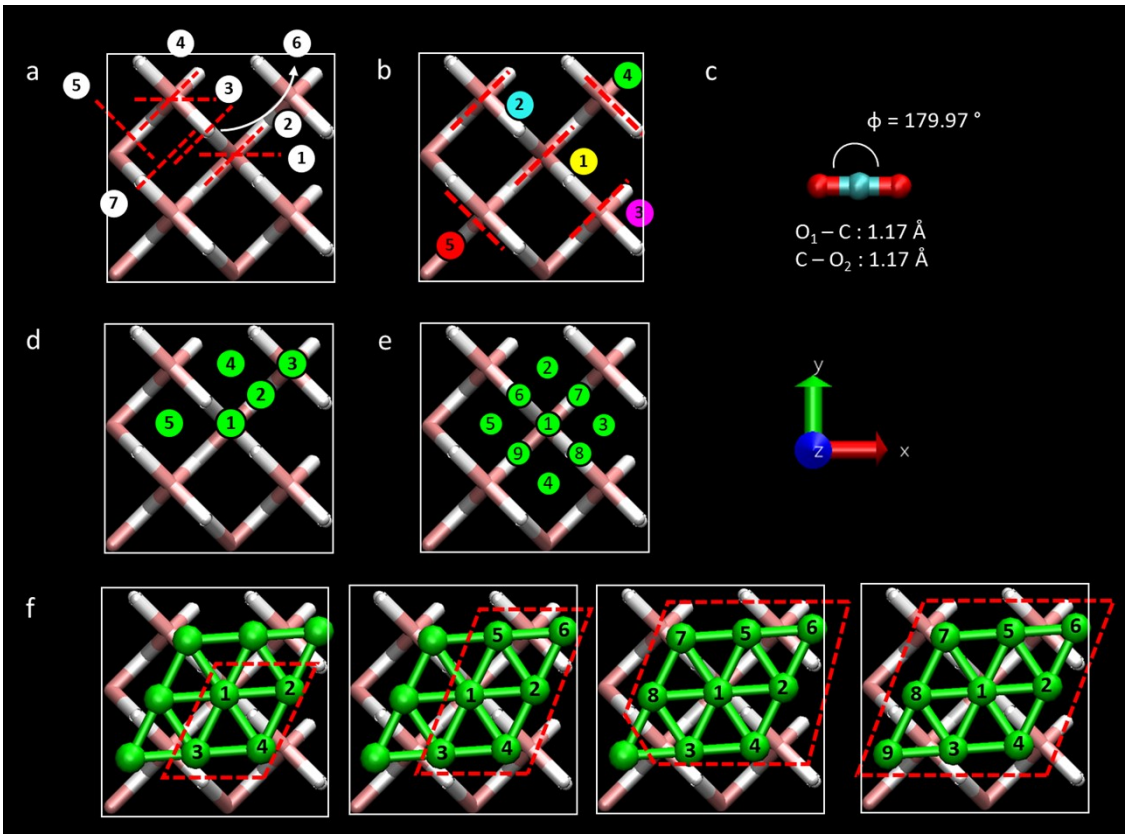


Fig. S1. Initial arrangement of the seven considered sites for the CO_2 molecule adsorption (a); the 1 to 5 CO_2 molecules considered adsorption sites (b); the isolated CO_2 molecule properties after optimization (c); the Co SAC studied sites (d); the Co clusterization atoms sites and order (e); and the Co layer growing disposition (f) on the MgH_2 clean slab. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt.

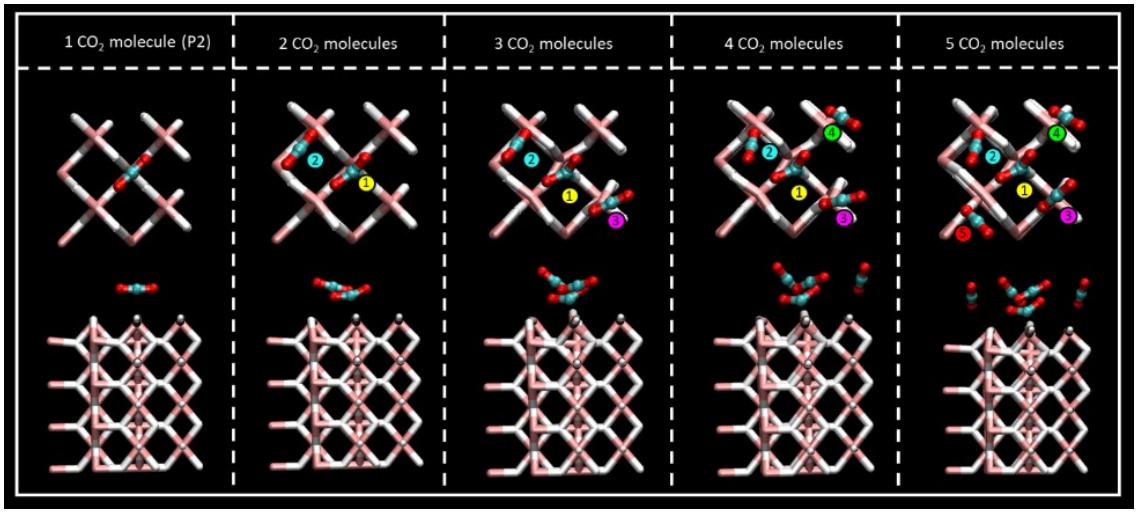
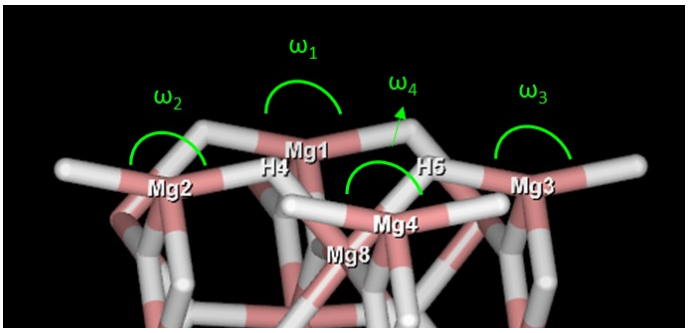


Fig. S2. Top- and side-view of the 1 to 5 CO_2 adsorption structures. Atom color code: (white) hydrogen, (pink) magnesium, (red) oxygen, (blue) carbon.

Table S1. MgH_2 first layer bond distances (Å) and angles (deg.) deformation after geometric optimization for the most stable studied structures.



	ω / degree				r / Å								
System	ω_1	ω_2	ω_3	ω_4	r_{H4-H5}	r_{H4-Mg2}	r_{H5-Mg3}	r_{H4-Mg8}	r_{H5-Mg8}	r_{H4-Mg1}	r_{H5-Mg1}	r_{H4-Mg4}	r_{H5-Mg4}
MgH_2 Slab	157.78				2.70	1.82	1.82	2.02	2.02	3.44	3.44	3.44	3.44
CO_2 P2	159.78	157.06	156.97	159.53	2.67	1.82	1.82	2.03	2.04	3.36	3.39	3.39	3.35
CO_2 P7	156.42	157.09	163.08	156.41	2.62	1.81	1.82	2.02	1.96	3.42	3.49	3.36	3.26
4 CO_2	160.46	149.94	174.35	168.26	2.62	2.31	1.81	2.70	1.82	3.02	3.35	3.35	2.91
Co SAC / C2	157.78	133.91	132.37	159.04	3.10	1.86	1.86	3.15	3.21	3.46	3.56	3.49	3.42
Co SAC / C1	164.15	158.00	160.82	163.94	2.41	1.90	1.84	2.11	2.11	3.21	3.23	3.23	3.22
7 Co	128.04	123.71	147.37	157.59	2.77	2.05	2.51	2.36	2.31	4.38	2.68	2.71	4.04
4/4 Co	108.90	140.01	133.06	122.26	2.13	2.18	2.05	2.22	2.24	3.45	3.62	3.70	3.25
C3 CO_2 ‖	147.95	153.42	151.27	49.84	2.53	1.83	1.93	2.08	2.08	2.24	3.32	5.03	3.99
2 Co CO_2 ‖	162.23	157.13	168.92	149.47	2.49	1.95	2.13	2.28	2.05	3.60	2.95	2.90	3.74
C2 CO_2 + 4 H_2	169.00	156.71	154.22	157.53	2.38	2.71	1.84	2.12	2.44	4.10	3.80	2.38	2.26
2 Co CO_2 + 4 H_2	160.91	160.61	158.65	161.06	2.31	2.09	1.98	2.24	1.94	3.30	3.25	3.03	3.41

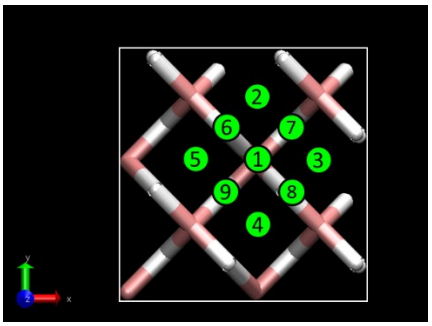
Table S2 Adsorption energy (per atom) for n Co atoms clusterization (1 to 9 atoms) on MgH_2 surface. The value for the configuration with the highest energy (7 Co) is reported in bold.

Cluster Co	E_{ads} (eV)
1 Co	-7.93
2 Co	-8.16
3 Co	-9.70
4 Co	-9.43
5 Co	-3.09
6 Co	-5.24
7 Co	**-10.55**
8 Co	-8.75
9 Co	-8.80

Table S3 Adsorption energy (per atom) for n Co atoms MgH_2 surface coverage (1/4 to 4/4 coverage). The value for the configuration with the highest energy (4/4 Co coverage) is reported in bold.

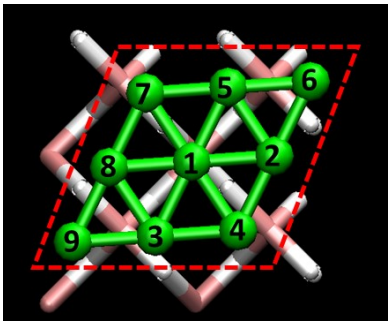
Layer Co	E_{ads} (eV)
1/4	-7.18
2/4	-7.78
3/4	-8.98
4/4	**-9.43**

Table S4. Interatomic distances in Å, between cobalt atoms for the 1 to 9 atoms cluster formation structures. Subscripts indicate Co atom number, as well as the addition order. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt.



	Cluster Co								
	1 Co	**2 Co**	**3 Co**	**4 Co**	**5 Co**	**6 Co**	**7 Co**	**8 Co**	**9 Co**
r_{1-2} / Å	-	2.17	2.25	2.28	2.25	2.46	3.89	3.76	3.60
r_{1-3} / Å	-	-	2.26	2.20	2.25	2.19	2.73	3.40	2.59
r_{1-4} / Å	-	-	-	2.28	2.23	2.29	2.23	2.31	2.55
r_{1-5} / Å	-	-	-	-	2.22	2.30	2.84	2.65	3.65
r_{1-6} / Å	-	-	-	-	-	2.26	2.25	2.26	2.32
r_{1-7} / Å	-	-	-	-	-	-	2.27	2.30	2.28
r_{1-8} / Å	-	-	-	-	-	-	-	2.24	2.23
r_{1-9} / Å	-	-	-	-	-	-	-	-	2.28
r_{2-3} / Å	-	-	2.29	2.38	3.46	2.25	-	-	-
r_{2-6} / Å	-	-	-	-	-	2.21	2.25	2.21	2.40
r_{2-7} / Å	-	-	-	-	-	-	2.70	2.66	2.28
r_{3-4} / Å	-	-	-	2.6	2.77	3.83	4.23	-	-
r_{3-7} / Å	-	-	-	-	-	-	2.22	2.29	2.36
r_{4-5} / Å	-	-	-	-	3.58	2.30	3.38	3.99	-
r_{4-8} / Å	-	-	-	-	-	-	-	2.32	2.26
r_{5-2} / Å	-	-	-	-	2.73	-	-	-	-
r_{5-6} / Å	-	-	-	-	-	2.24	2.39	2.25	2.31
r_{5-9} / Å	-	-	-	-	-	-	-	-	2.57

Table S5. Interatomic distances in Å, between cobalt atoms of the 1/4 to 4/4 coverage layer of Co structures. Numbers indicate Co atom number, as well as the addition order, where 1/4 coverage corresponds to 1-4 atoms, 2/4 coverage to 1-6 atoms, 3/4 coverage to 1-8 atoms and 4/4 coverage to 1-9 atoms. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt.



$r_{Co\text{-}Co}$ / Å	Co cluster			
	$\frac{1}{4}$ Co	$\frac{2}{4}$ Co	$\frac{3}{4}$ Co	$\frac{4}{4}$ Co
r_{1-2}	2.40	2.31	2.41	2.29
r_{1-3}	2.32	2.32	2.83	2.28
r_{1-4}	2.20	2.43	2.21	2.81
r_{1-5}	-	2.32	2.56	2.41
r_{1-7}	-	-	2.25	2.61
r_{1-8}	-	-	2.27	2.27
r_{2-4}	2.27	2.16	2.30	2.45
r_{2-5}	-	2.26	2.30	2.31
r_{2-6}	-	2.19	2.24	4.15
r_{3-4}	2.28	2.20	2.26	2.38
r_{3-8}	-	-	4.03	3.05
r_{3-9}	-	-	-	2.17
r_{5-7}	-	-	2.34	2.64
r_{7-8}	-	-	2.21	2.60
r_{8-9}	-	-	-	2.26

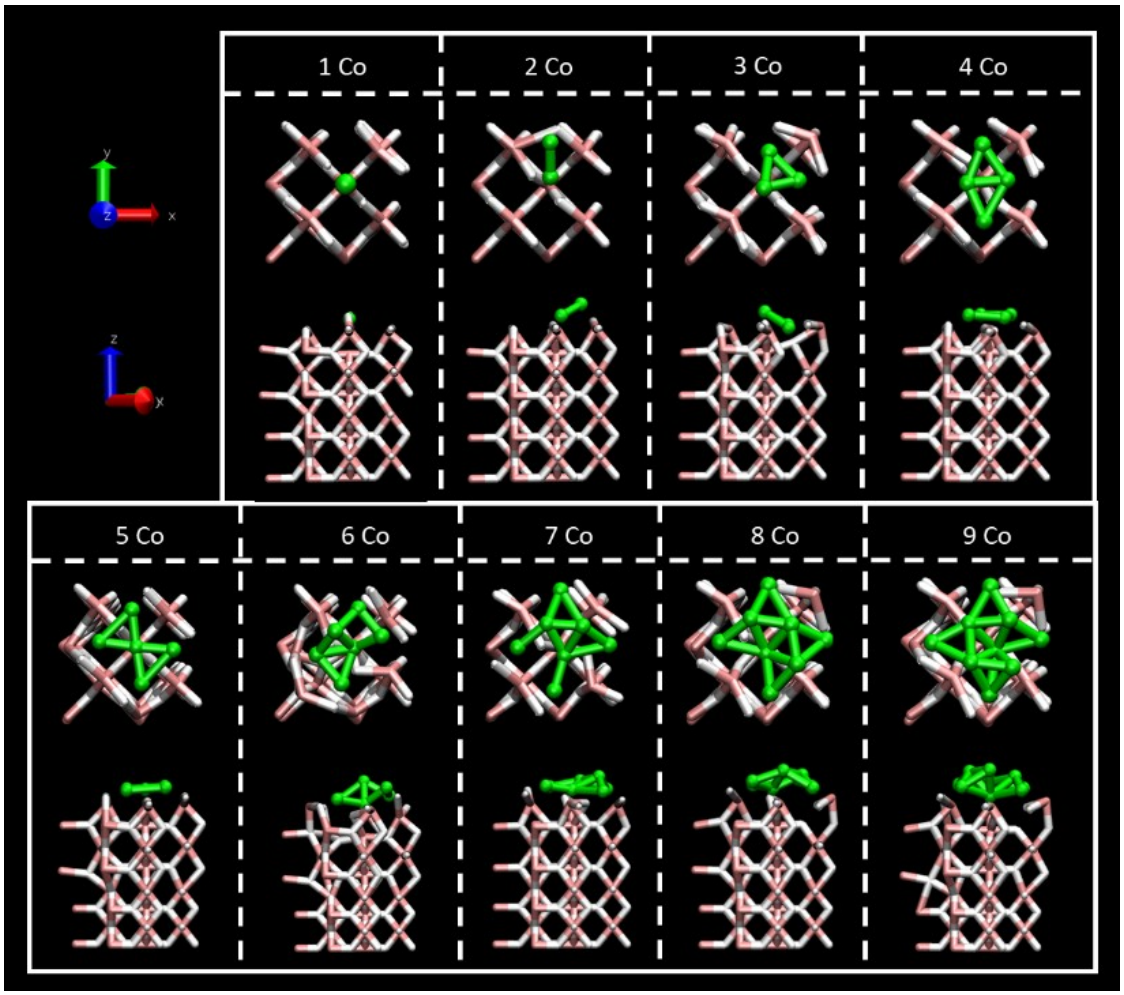


Fig. S3. Top- and side-view of the Co clusterization (1 to 9 atoms) structures. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt.

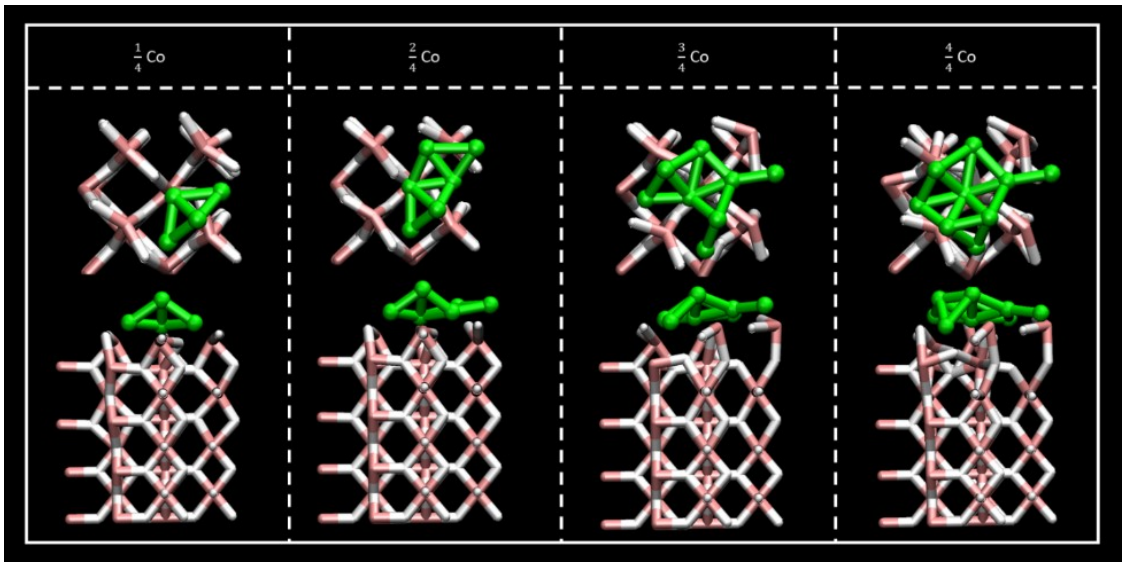


Fig. S4. Top- and side-view of the Co coverage (1/4 to 4/4 slab coverage) structures. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt.

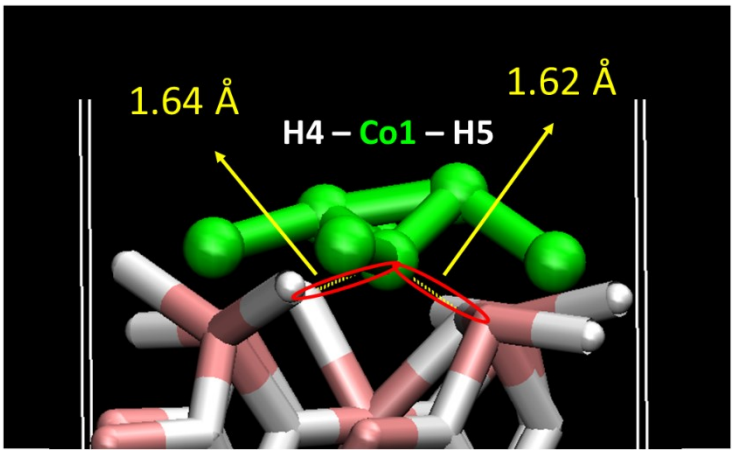


Fig. S5. Detail of the of the geometric parameters related to 7 Co on MgH_2 structure.

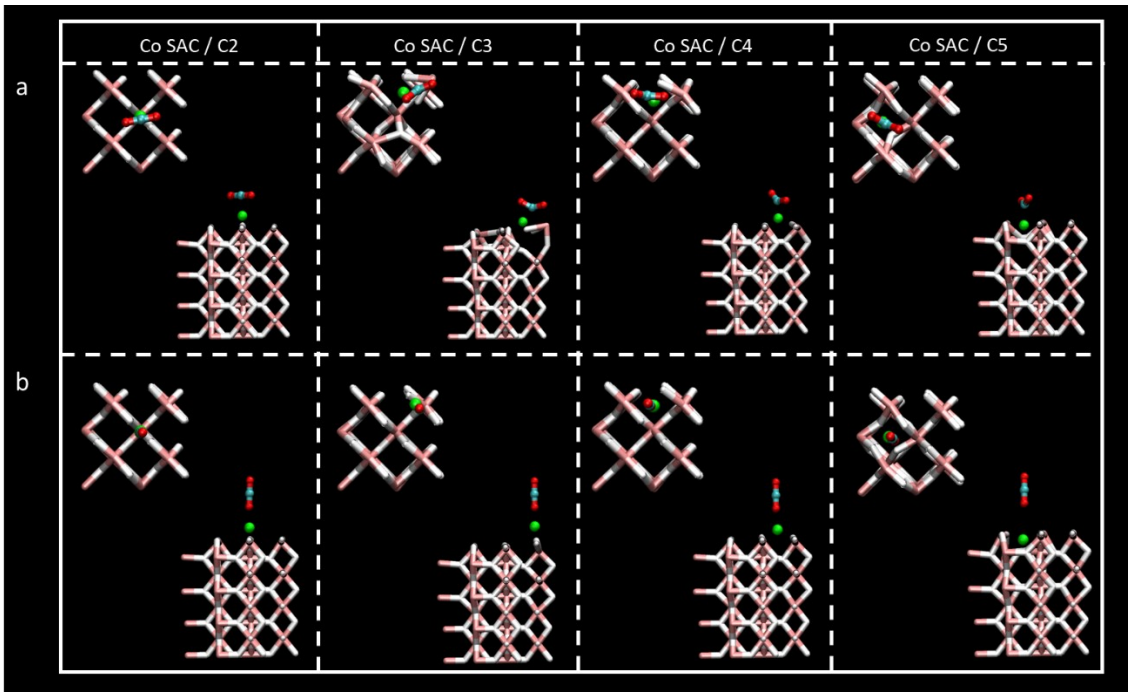


Fig. S6. Top- and side-view of the CO_2 adsorption on Co SAC structures for the C2 – C5 sites and considering parallel (a) and perpendicular (b) CO_2 orientation with respect to slab surface. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt, (red) oxygen, (blue) carbon.

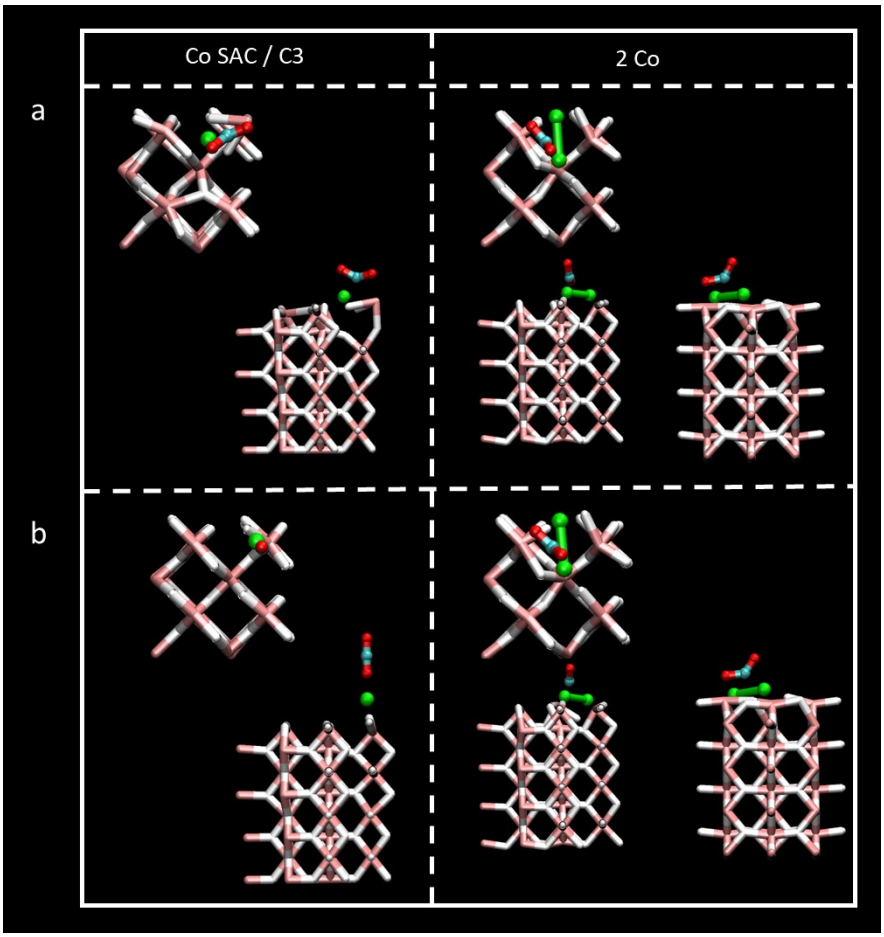


Fig. S7. Top- and -side view of the CO_2 adsorption on C3 Co SAC and 2 Co doped structures considering parallel (a) and perpendicular (b) CO_2 disposition with respect to slab surface. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt, (red) oxygen, (blue) carbon.

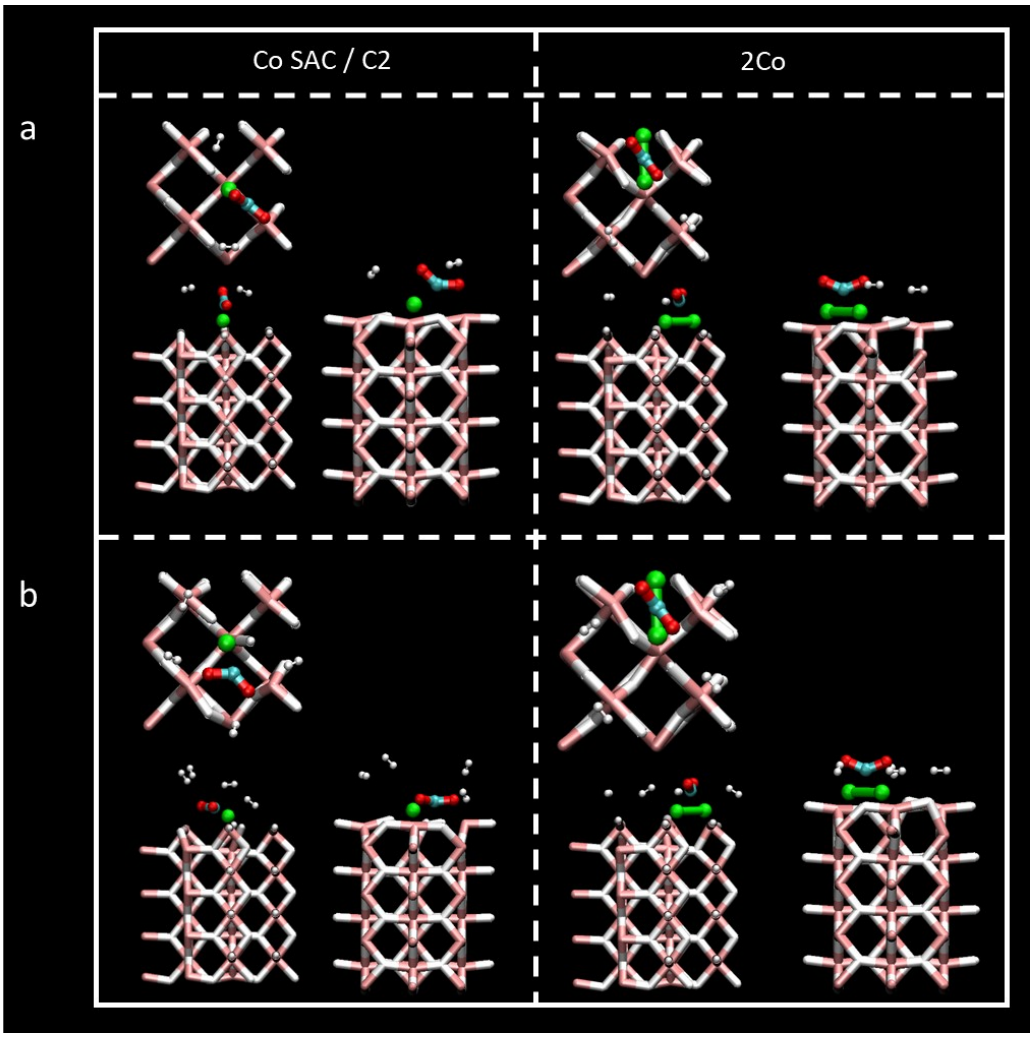
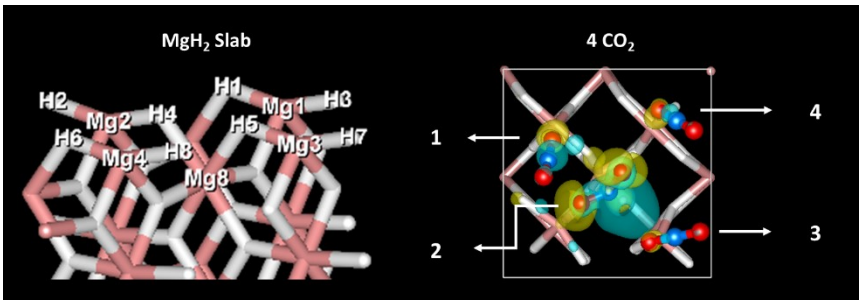


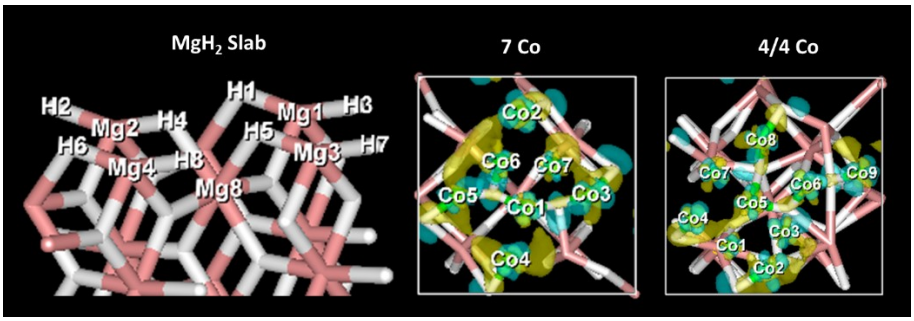
Fig. S8. Top- and -side view of 1 CO_2 + 2 (a) and 4 (b) H_2 adsorption on C2 Co SAC and 2 Co doped structures. Atom color code: (white) hydrogen, (pink) magnesium, (green) cobalt, (red) oxygen, (blue) carbon.

Table S6. Bader ionic charges for CO_2 (C_1, O_1 and O_2) and surface (first and second MgH_2 layer, H_1 – H_8 and Mg_1 – Mg_8) atoms after CO_2 adsorption on MgH_2 for configuration P2, P7 and 4 CO_2.



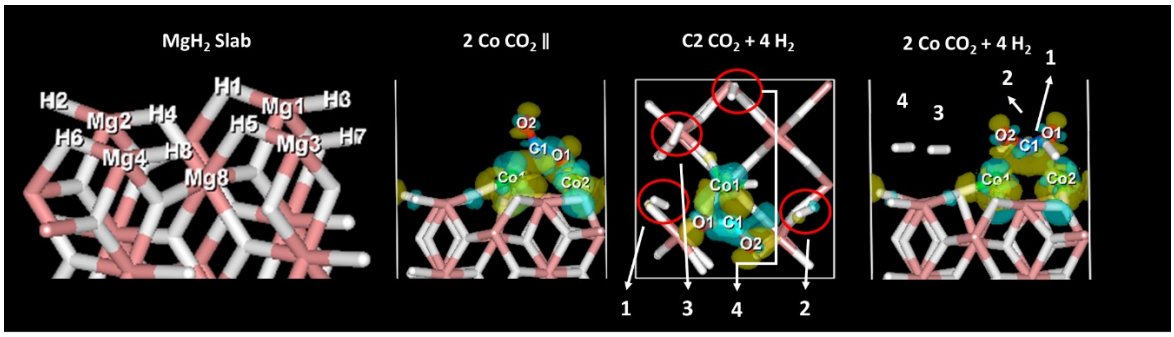
	Atom	MgH_2 Slab	CO_2	1 CO_2 P2	1 CO_2 P7	4 CO_2
		Ionic charges				
First layer (MgH_2)	H_1	-0.76	-	-0.76	-0.76	-0.74
	H_2	-0.75	-	-0.76	-0.76	-0.74
	Mg_1	+1.55	-	+1.56	+1.53	+1.60
	Mg_2	+1.55	-	+1.55	+1.54	+1.57
	H_3	-0.78	-	-0.76	-0.75	-0.76
	H_4	-0.76	-	-0.74	-0.76	-0.16
	H_5	-0.76	-	-0.75	-0.76	-0.74
	H_6	-0.76	-	-0.76	-0.75	-0.74
	Mg_3	+1.55	-	+1.55	+1.57	+1.59
	Mg_4	+1.55	-	+1.56	+1.54	+1.58
	H_7	-0.75	-	-0.76	-0.76	-0.75
	H_8	-0.76	-	-0.76	-0.76	-0.74
Second layer (MgH_2)	Mg_8	+1.56	-	+1.57	+1.57	+1.58
CO_2	$O_1(1)$	-	+0.22	-1.02	-1.07	-1.07
	$O_2(1)$	-	+0.22	-0.99	-1.01	-0.95
	$C_1(1)$	-	-0.44	+1.95	+2.11	+1.98
	$O_1(2)$	-	-	-	-	-1.12
	$O_2(2)$	-	-	-	-	-1.22
	$C_1(2)$	-	-	-	-	+1.56
	$O_1(3)$	-	-	-	-	-1.01
	$O_2(3)$	-	-	-	-	-1.10
	$C_1(3)$	-	-	-	-	+2.07
	$O_1(4)$	-	-	-	-	-1.02
	$O_2(4)$	-	-	-	-	-1.07
	$C_1(4)$	-	-	-	-	+2.05

Table S7. Bader ionic charges for Co (Co_1 - C_9) and surface (first and second MgH_2 layer, H_1 – H_8 and Mg_1 – Mg_8) atoms after Co adsorption in configuration C2, 4/4 Co and 7 Co.



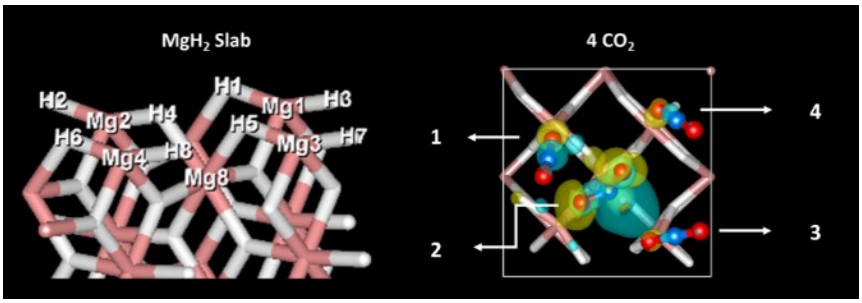
		MgH_2 Slab	Co	1 Co C2	4/4 Co	7 Co
	Atom			**Ionic charge**		
First layer (MgH_2)	H_1	-0.76	-	-0.76	-0.43	-0.50
	H_2	-0.75	-	-0.76	-0.80	-0.77
	Mg_1	+1.55	-	+1.52	+1.52	+1.49
	Mg_2	+1.55	-	+1.56	+1.48	+1.50
	H_3	-0.76	-	-0.76	-0.53	-0.51
	H_4	-0.76	-	-0.56	-0.26	-0.35
	H_5	-0.76	-	-0.56	-0.36	-0.28
	H_6	-0.76	-	-0.75	-0.32	-0.48
	Mg_3	+1.55	-	+1.56	+1.53	+1.50
	Mg_4	+1.55	-	+1.53	+1.50	+1.55
	H_7	-0.75	-	-0.76	-0.48	-0.76
	H_8	-0.76	-	-0.75	-0.53	-0.54
Second layer (MgH_2)	Mg_8	+1.56	-	+1.58	+1.55	+1.55
Co	Co_1	-	-4.60×10^{-5}	-0.32	-0.05	-0.26
	Co_2	-	-	-	-0.30	-0.04
	Co_3	-	-	-	-0.21	-0.03
	Co_4	-	-	-	-0.43	-0.49
	Co_5	-	-	-	-0.37	-0.32
	Co_6	-	-	-	-0.23	-0.31
	Co_7	-	-	-	-0.12	-0.24
	Co_8	-	-	-	-0.20	-
	Co_9	-	-	-	-0.38	-

Table S8. Bader ionic charges for CO_2 (C_1, O_1 and O_2), H_2 (H_1 and H_2), Co (Co_1 – C_9) and surface (first and second MgH_2 layer, H_1 – H_8 and Mg_1 – Mg_8) atoms after CO_2 / H_2 adsorption in configuration C3 CO_2 ‖, 2 Co CO_2 ‖, C2 CO_2 + 4 H_2 and 2 Co CO_2 + 4 H_2.



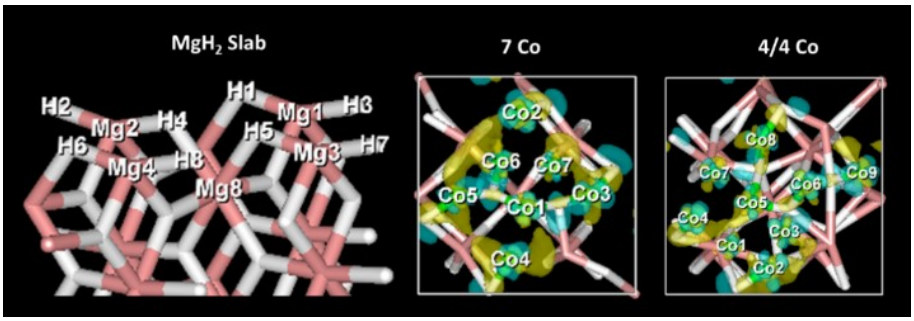
	Atom	MgH_2 Slab	H_2	C3 CO_2 ||	2 Co CO_2 ||	C2 CO_2 + 4 H_2	2 Co CO_2 + 4 H_2
		Ionic charge					
First layer (MgH_2)	H_1	-0.76	-	-0.78	-0.63	-0.75	-0.60
	H_2	-0.75	-	-0.79	-0.75	-0.76	-0.75
	Mg_1	+1.55	-	+1.56	+1.55	+1.59	+1.57
	Mg_2	+1.55	-	+1.55	+1.55	+1.61	+1.58
	H_3	-0.76	-	-0.76	-0.75	-0.75	-0.75
	H_4	-0.76	-	-0.79	-0.64	-0.40	-0.61
	H_5	-0.76	-	-0.65	-0.51	-0.59	-0.55
	H_6	-0.76	-	-0.36	-0.77	-0.75	-0.75
	Mg_3	+1.55	-	+1.51	+1.60	+1.56	+1.55
	Mg_4	+1.55	-	+1.60	+1.53	+1.55	+1.55
	H_7	-0.75	-	-0.79	-0.75	-0.76	-0.75
	H_8	-0.76	-	-0.50	-0.50	-0.75	-0.55
Second layer (MgH_2)	Mg_8	+1.56	-	+1.59	+1.57	+1.57	+1.57
CO_2	O_1	-	-	-0.99	-1.14	-1.14	-1.01
	O_2	-	-	-1.16	-1.03	-1.15	-1.02
	C_1	-	-	+1.22	+1.11	+1.21	+1.06
Co	Co_1	-	-	+0.20	-0.03	+0.43	+0.06
	Co_2	-	-	-	+0.19	-	+0.10
H_2	H_1 (1)	-	+0.97	-	-	+1.00	+0.97
	H_2 (1)	-	+1.03	-	-	+1.01	+1.04
	H_1 (2)	-	-	-	-	+0.95	+0.94
	H_2 (2)	-	-	-	-	+1.06	+1.08
	H_1 (3)	-	-	-	-	+1.06	+1.01
	H_2 (3)	-	-	-	-	+0.97	+1.01
	H_1 (4)	-	-	-	-	+0.99	+1.03
	H_2 (4)	-	-	-	-	+1.02	+1.00

Table S9 Valence Bader charges difference (charge before adsorption – charge after adsorption) for the CO_2 (C_1, O_1 and O_2) and the surface (first and second MgH_2 layer, H_1 – H_8 and Mg_1 – Mg_8) atoms after the CO_2 adsorption in configuration P2, P7 and 4 CO_2.



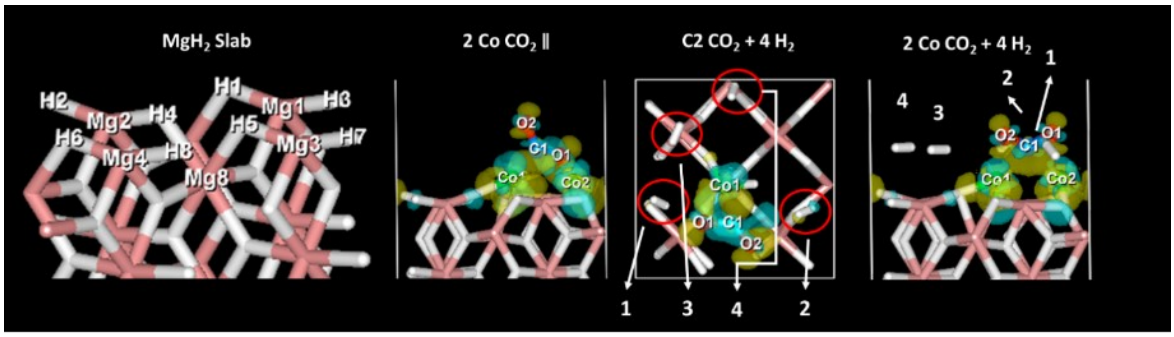
	Atom	1 CO_2 P2	1 CO_2 P7	4 CO_2
		Charge difference		
First layer (MgH_2)	H_1	0.00	0.00	-0.01
	H_2	0.00	0.00	-0.01
	Mg_1	-0.01	+0.01	-0.05
	Mg_2	0.00	0.00	-0.02
	H_3	0.00	-0.01	+0.01
	H_4	-0.01	0.00	-0.60
	H_5	-0.01	0.00	-0.02
	H_6	0.00	0.00	-0.02
	Mg_3	0.00	-0.02	-0.04
	Mg_4	-0.01	+0.01	-0.03
	H_7	0.00	0.00	0.00
	H_8	0.00	+0.01	-0.01
Second layer (MgH_2)	Mg_8	-0.01	-0.01	-0.01
CO_2	$O_1(1)$	+0.80	+0.85	+0.85
	$O_2(1)$	+0.76	+0.79	+0.73
	$C_1(1)$	-1.51	-1.67	-1.54
	$O_1(2)$	-	-	+0.90
	$O_2(2)$	-	-	+1.00
	$C_1(2)$	-	-	-1.12
	$O_1(3)$	-	-	+0.79
	$O_2(3)$	-	-	+0.87
	$C_1(3)$	-	-	-1.63
	$O_1(4)$	-	-	+0.80
	$O_2(4)$	-	-	+0.84
	$C_1(4)$	-	-	-1.61

Table S10 Valence Bader charges difference (charge before adsorption – charge after adsorption) for the Co (Co_1 - C_9) and the surface (first and second MgH_2 layer, H_1 – H_8 and Mg_1 – Mg_8) atoms after the Co adsorption in configuration C2, 4/4 Co and 7 Co.



	Atom	1 Co C2	4/4 Co	7 Co
		Charge difference		
First layer (MgH_2)	H_1	0.00	-0.33	-0.26
	H_2	+0.01	+0.05	+0.01
	Mg_1	+0.02	+0.02	+0.06
	Mg_2	-0.01	+0.07	+0.04
	H_3	0.00	-0.23	-0.25
	H_4	-0.20	-0.50	-0.41
	H_5	-0.20	-0.40	-0.47
	H_6	0.00	-0.43	-0.28
	Mg_3	-0.01	+0.02	+0.05
	Mg_4	+0.02	+0.05	0.00
	H_7	+0.01	-0.28	0.00
	H_8	0.00	-0.22	-0.22
Second layer (MgH_2)	Mg_8	-0.02	+0.02	+0.01
Co	Co_1	+0.32	+0.05	+0.26
	Co_2	-	+0.30	+0.04
	Co_3	-	+0.21	+0.03
	Co_4	-	+0.43	+0.49
	Co_5	-	+0.37	+0.32
	Co_6	-	+0.23	+0.31
	Co_7	-	+0.12	+0.24
	Co_8	-	+0.20	-
	Co_9	-	+0.38	-

Table S11 Valence Bader charges difference (charge before adsorption – charge after adsorption) for the CO_2 (C_1, O_1 and O_2), the H_2 (H_1 and H_2), the Co (Co_1 – C_9) and the surface (first and second MgH_2 layer, H_1 – H_8 and Mg_1 – Mg_8) atoms after the CO_2 / H_2 adsorption in configuration C3 CO_2 ||, 2 Co CO_2 ||, C2 CO_2 + 4 H_2 and 2 Co CO_2 + 4 H_2.



	Atom	C3 CO_2 ‖	2 Co CO_2 ‖	C2 CO_2 + 4 H_2	2 Co CO_2 + 4 H_2
		Charge difference			
First layer (MgH_2)	H_1	+0.02	-0.13	-0.01	-0.16
	H_2	+0.04	-0.01	0.00	-0.01
	Mg_1	-0.01	0.00	-0.04	-0.03
	Mg_2	-0.01	0.00	-0.06	-0.03
	H_3	0.00	0.00	-0.01	0.00
	H_4	+0.04	-0.12	-0.36	-0.15
	H_5	-0.11	-0.25	-0.17	-0.21
	H_6	-0.39	+0.01	0.00	0.00
	Mg_3	+0.04	-0.05	-0.01	0.00
	Mg_4	-0.06	+0.02	0.00	-0.01
	H_7	+0.03	-0.01	0.00	0.00
	H_8	-0.26	-0.25	0.00	-0.20
Second layer (MgH_2)	Mg_8	-0.03	-0.01	-0.01	-0.01
CO_2	O_1	+0.77	+0.93	+0.92	+0.79
	O_2	+0.94	+0.81	+0.93	+0.79
	C_1	-0.78	-0.67	-0.77	-0.62
Co	Co_1	-0.20	+0.03	-0.43	-0.06
	Co_2	-	-0.19	-	-0.10
H_2	H_1 (1)	-	-	+0.03	0.00
	H_2 (1)	-	-	-0.02	+0.02
	H_1 (2)	-	-	-0.02	-0.03
	H_2 (2)	-	-	+0.03	+0.05
	H_1 (3)	-	-	+0.09	+0.03
	H_2 (3)	-	-	-0.06	-0.02
	H_1 (4)	-	-	+0.01	+0.05
	H_2 (4)	-	-	-0.01	-0.03

Table S12: k-points grid convergence set for MgH_2 clean systems. For this test, a 2×2 supercell has been employed.

***k-points* grid**	**E_{sys} (Ry)**

4×4×4	-71.9781
5×5×5	-71.9797
6×6×6	-71.9801
8×8×8	-71.9800
12×12×12	-71.9800
16×16×16	-71.9800
20×20×20	-71.9800
24×24×24	-71.9800
28×28×28	-71.9800

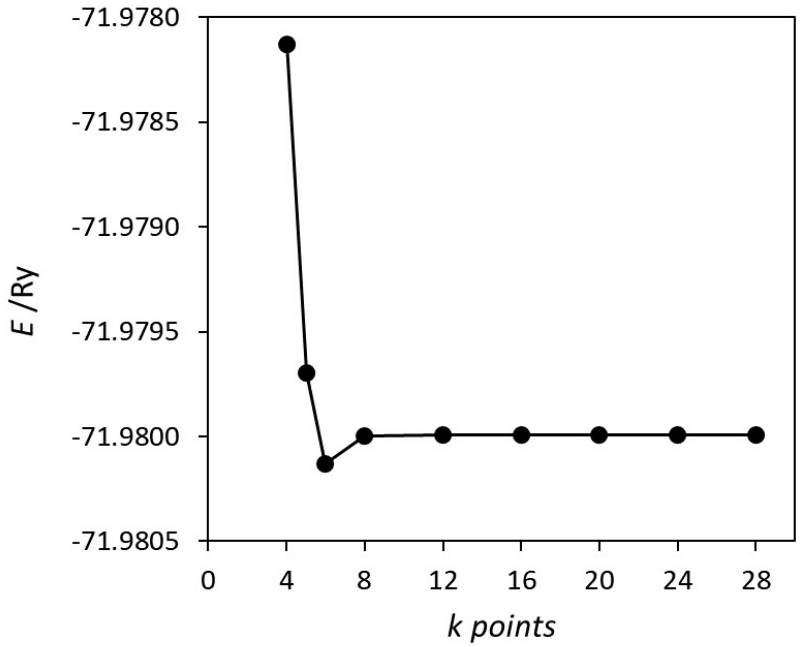


Figure S9. Surface energy for MgH2 clean structure as a function of the k-points grid.