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First principles study of Co-catalyzed MgH_2 for CO_2 capture and conversion

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1. INTRODUCTION

- Greenhouse gases emissions, especially CO_2, have dramatically increased in the last decades. Hence, concern over the reduction of the rising CO_2 atmospheric concentration (above 400 ppm) have led to the development of carbon capture and utilization (CCUs) technologies or carbon capture and storage (CCSs) methods.
- For this purpose, designed materials with high carbon dioxide affinity are needed. Previous experimental works reported by our group[1] have shown reduction and conversion of carbon dioxide pure gas employing magnesium hydride as hydrogen supplier showing great cobalt catalytic activity.
- In this work, Density Functional Theory was applied to comprehend, from an atomistic point of view, the interaction mechanism of carbon dioxide adsorption on magnesium hydride and cobalt catalyzed magnesium hydride systems.

2. COMPUTATIONAL METHODS

- DFT simulations were performed with the PW package in the Quantum Espresso suite (v. 6.3) and Periodic Boundary Conditions. Projected Augmented Wave (PAW) pseudopotentials were used together with the PBE exchange-correlation functional. Dispersion forces were corrected semi-empirically by Grimme, DFT-D3.
- MgH_2 tetragonal ($P4_2$ mnm) system was considered, with (030) surface and lattice parameters a = b = 8.88 Å and c = 30.46 Å. Bulk crystal comprise 3 layers depth, with the bottom layer atoms fixed.

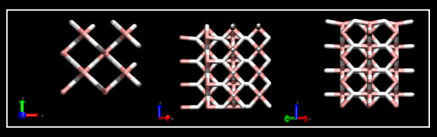


Fig. 1. . Top- and side-views of starting optimized clean MgH_2 slab.

- Optimal k-points were a $12 \times 12 \times 12$ Monkhorst-Pack grid, along with a cut-off of 544.23 eV.
- The following scenarios were considered on MgH_2 interactions: CO_2 molecule, Co single atom catalyst (SAC), 1 to 5 CO_2 molecules, 1 to 9 Co atoms slab coverage and 1 CO_2 molecule on Co SAC.
- The adsorption energy, E_{ads}, was determined as follows:

$$E_{ads} = E_{suf+X} - E_{suf} - E_X \quad X = CO_2, Co$$

and charge transfer was evaluated by Bader code.

3. RESULTS AND DISCUSSION

CO_2 GAS ADSORPTION

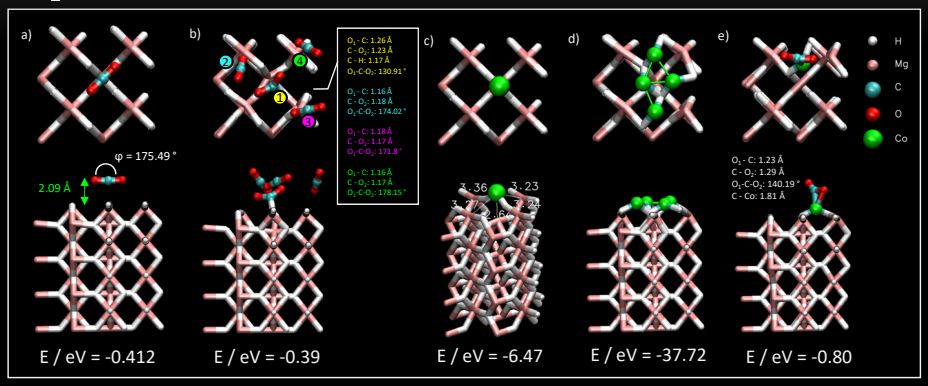


Fig. 2. Top- and side-view, E_{ads}, bond distances and angles of CO_2 molecule adsorption (a), 4 CO_2 molecules adsorption (b), Co SAC (c), 4 Co atoms catalyst (d) and 1 CO_2 molecule adsorption on Co – SAC.

DENSITY OF STATES

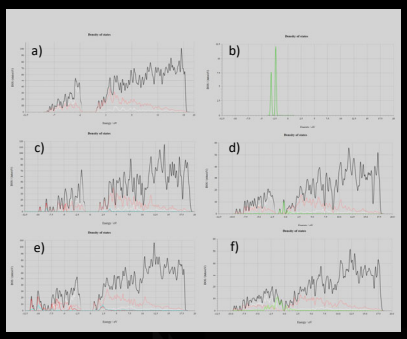


Fig. 3. DOS for MgH_2 clean slab (a), Co atom (b) and CO_2 (c), Co SAC (d), 4 CO_2 molecules (e) and 4 Co atoms (f) adsorbed on MgH_2. PDOS for the slab (Mg – salmon, H – white), as well as CO_2 (C – blue, O – red) and Co (green) are also shown.

ELECTRONIC DENSITY

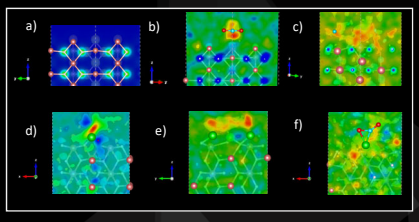
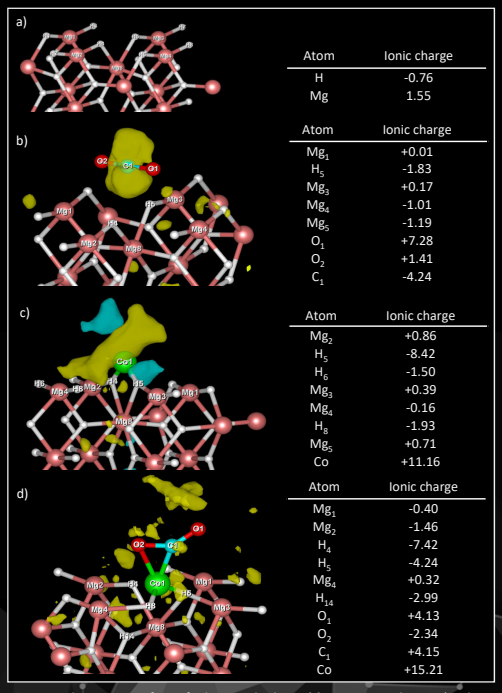


Fig. 4. Charge density difference at distinct lattice plains after the absorption of CO_2 and Co atoms with regard to MgH_2 clean slab. Red and blue colors represent electronic charge accumulation and depletion, respectively.

CHARGE TRANSFER



Atom	Ionic charge
H	-0.76
Mg	1.55

Atom	Ionic charge
Mg_1	+0.01
H_5	-1.83
Mg_3	+0.17
Mg_4	-1.01
Mg_5	-1.19
O_1	+7.28
O_2	+1.41
C_1	-4.24

Atom	Ionic charge
Mg_2	+0.86
H_5	-8.42
H_6	-1.50
Mg_3	+0.39
Mg_4	-0.16
H_8	-1.93
Mg_5	+0.71
Co	+11.16

Atom	Ionic charge
Mg_1	-0.40
Mg_2	-1.46
H_4	-7.42
H_5	-4.24
Mg_4	+0.32
H_{14}	-2.99
O_1	+4.13
O_2	-2.34
C_1	+4.15
Co	+15.21

Fig. 5. Charge transfer of the studied systems (a-d) with regard to MgH_2 clean slab. Yellow and blue colors represent the negative and positive electron density, respectively.

Table 1. Ionic charge (Bader electronic densities) of slab first layer (Mg, H), CO_2 and Co atoms after adsorption.

4. CONCLUSIONS

- Quantum calculations (DFT) show large affinity of carbon dioxide with the hydride material, and so, the feasibility of magnesium hydride to capture CO_2.
- Regarding the adsorption mechanism, charge density and atomic charges before and after gas adsorption allow us to conclude that CO_2 molecules adsorption on non-catalyzed MgH_2 possess a net physisorption character. However, MgH_2 catalyzed systems show important bending of carbon dioxide molecules, greater MgH_2-CO_2 interaction energies and higher charge transfer values, together with the density of states plots analysis, a chemisorption character of the adsorption process is inferred.

5. ACKNOWLEDGEMENT

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[1] G. Amica, S. Rozas, S. Aparicio, F. C. Gennari, Catalysis effect on CO2 methanation using MgH2 as a portable hydrogen medium, Phys. Chem. Chem. Phys., 22 (2020), pp. 14720-14730