Supporting Information

Advancing Next-Generation Nonaqueous Mg-CO$_2$ Batteries:

Insights into Reaction Mechanisms and Catalyst Design

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Calculation methodology

The charge density difference for the intermediate species adsorbed α-Mo$_2$C (001) was calculated based on the expression $\rho_b = \rho_{adsorbed\ state} - (\rho_{adsorbent} + \rho_{cat})$, where $\rho_{adsorbed\ state}$, $\rho_{adsorbent}$, and ρ_{cat} denote the charge density of the catalyst with adsorbed reaction intermediates, isolated intermediate species, and the catalytic surface, respectively.[1]
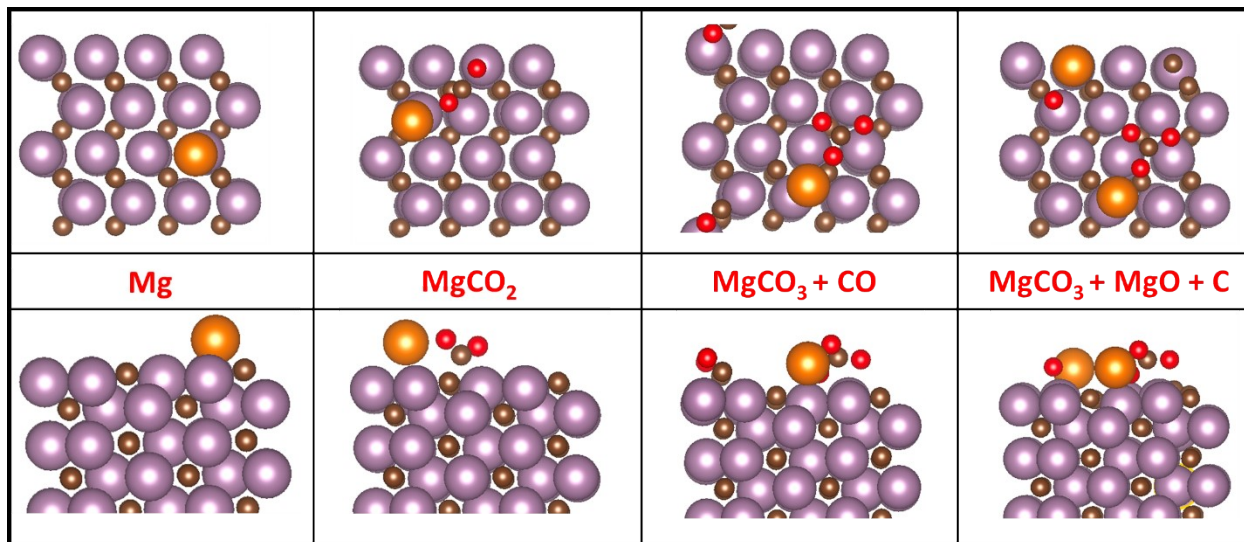

Figure S1. Top and side views of the most stable geometric configuration of MgCO$_3$ nucleation (Path I)
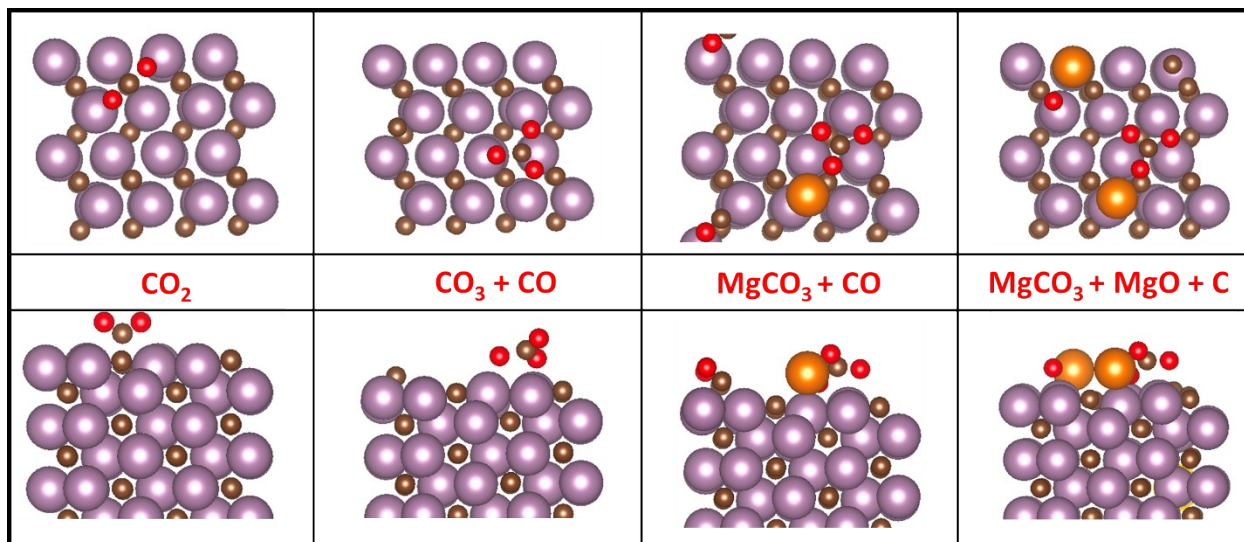

Figure S2. Top and side views of the most stable geometric configuration of MgCO$_3$ nucleation (Path II)

S1. Density of states (DOS) calculations

We calculate the density of states (DOS) to understand the electronic structure of the α-Mo$_2$C (001) catalyst both before and after the adsorption of reaction intermediates. Figure S3 illustrates that the α-Mo$_2$C (001) catalyst is metallic in nature with electron states around the Fermi level, indicating the material's electronically conductive properties. Furthermore, a comparison of the total density of states (TDOS) before and after intermediate adsorption reveals that electronic conductivity is maintained after adsorption. Furthermore, the d-band center analysis for both MgC$_2$O$_4$ and MgCO$_3$ nucleation showed that the value of MgC$_2$O$_4$ (-1.062 eV) is closer to the Fermi level than MgCO$_3$ (-1.076 eV).
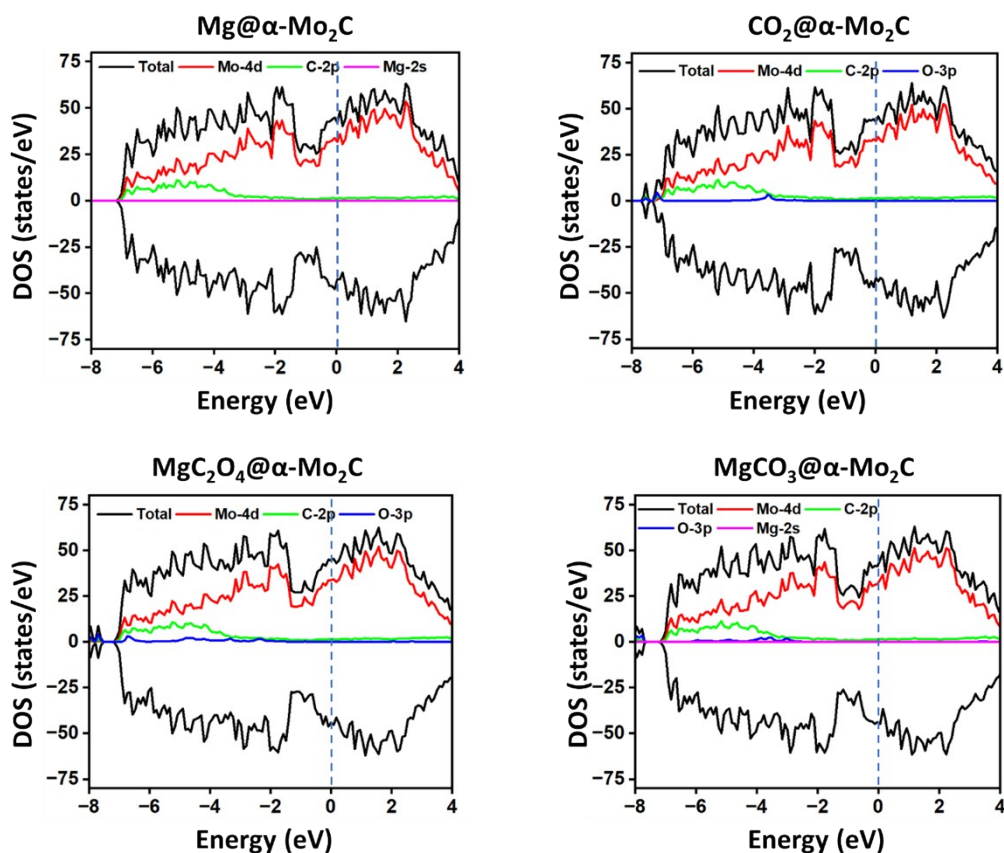

Figure S3. The projected density of states of various reaction intermediate (Mg, CO$_2$, MgC$_2$O$_4$ and MgCO$_3$) adsorbed α-Mo$_2$C (001) surface. The Fermi level is denoted by the dotted line.
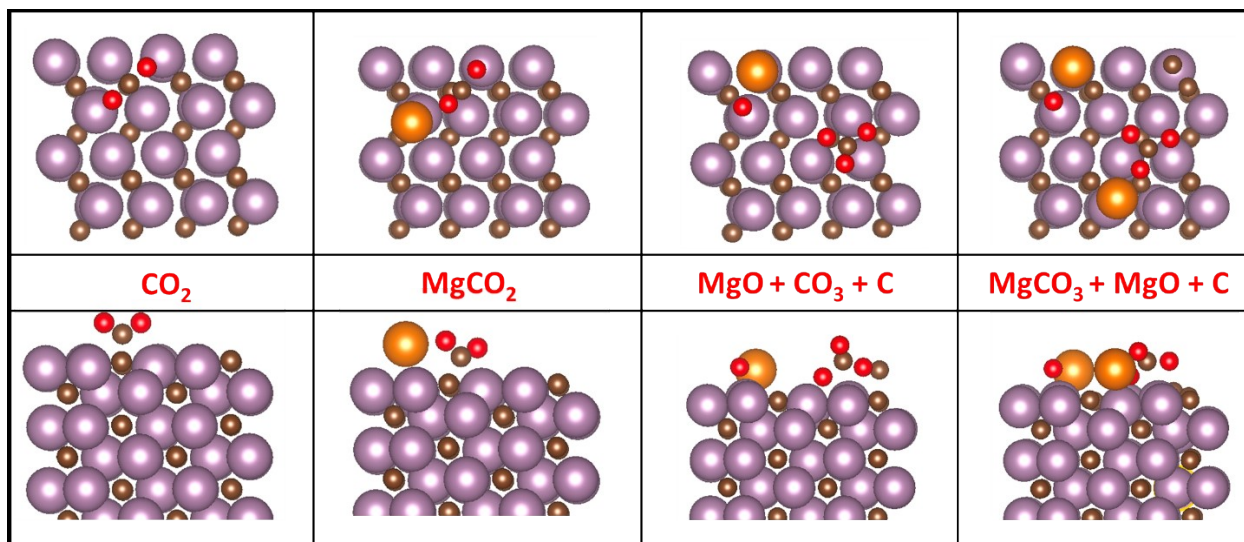
Figure S4. Top and side views of the most stable geometric configuration of MgCO$_3$ nucleation (Path V)
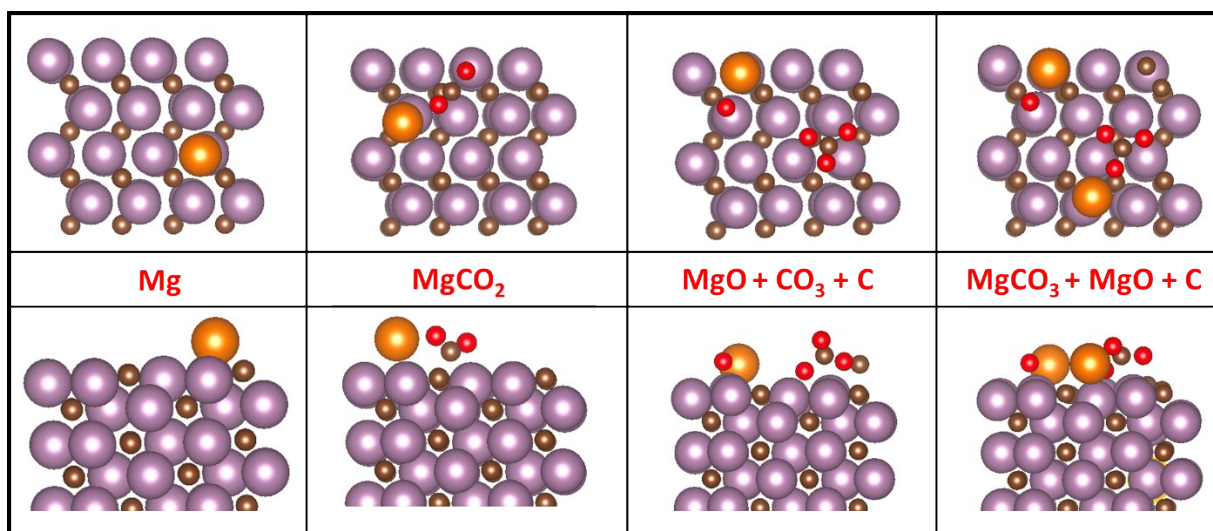

Figure S5. Top and side views of the most stable geometric configuration of MgCO$_3$ nucleation (Path VI)
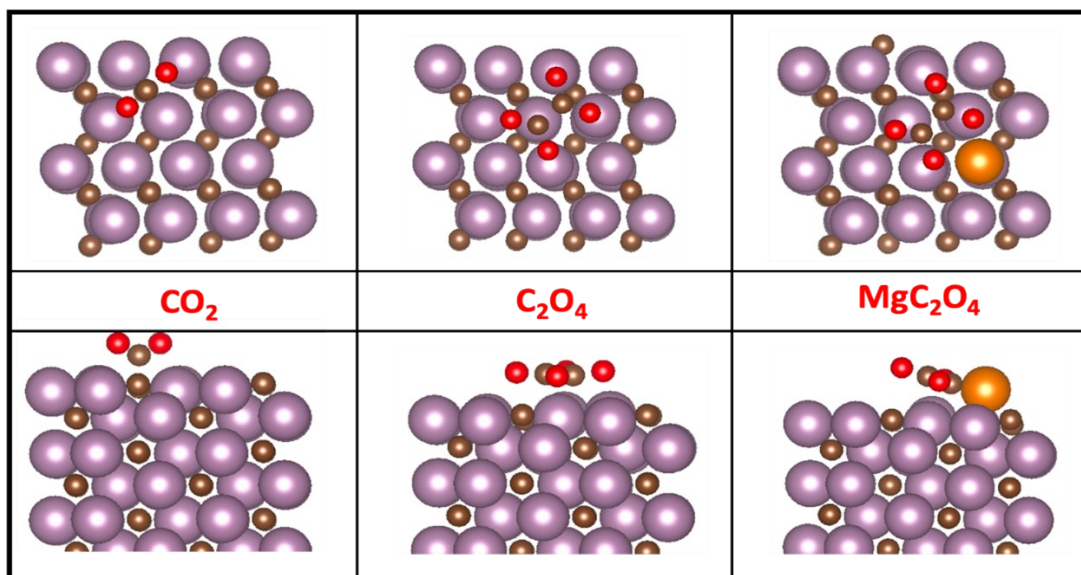
Figure S6. Top and side views of the most stable geometric configuration of MgC$_2$O$_4$ nucleation (Path III)
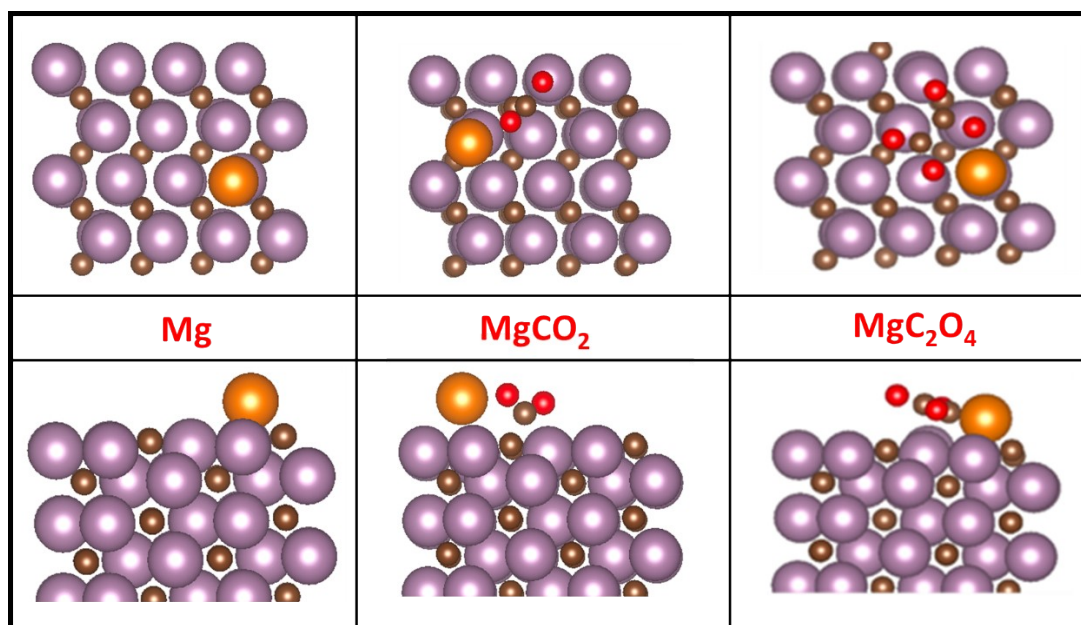

Figure S7. Top and side views of the most stable geometric configuration of MgC$_2$O$_4$ nucleation (Path IV)
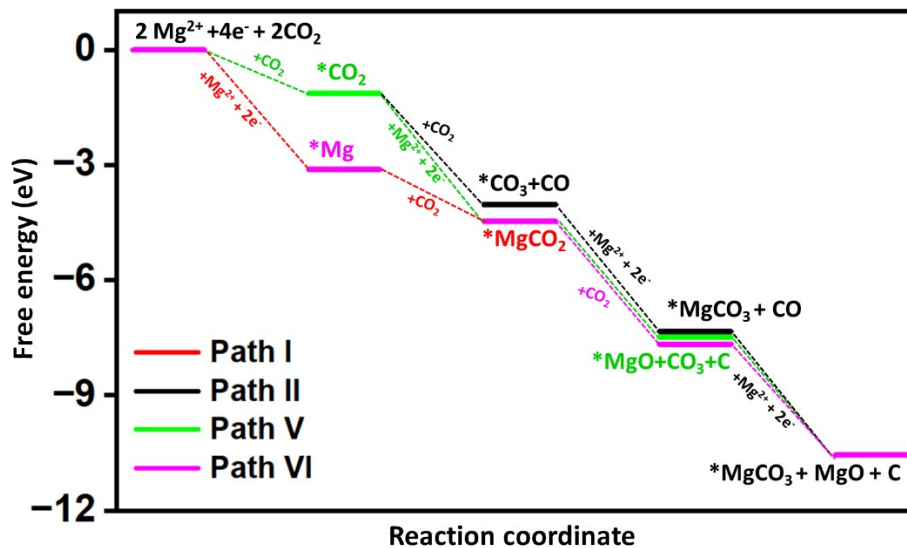
Figure S8. Computed Gibbs free energies of various reaction intermediate pathways for MgCO$_3$ nucleation at U=0V
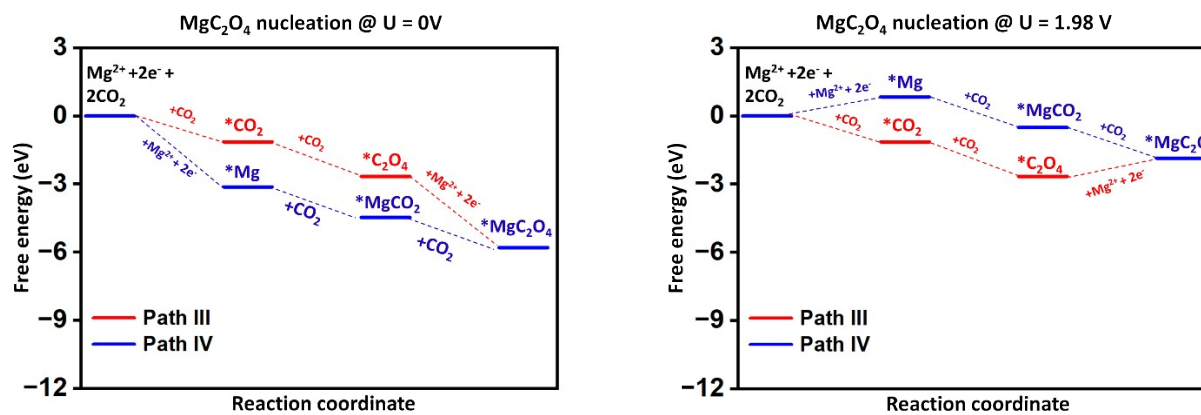

Figure S9. Computed Gibbs free energies of various reaction intermediate pathways for MgC$_2$O$_4$ nucleation at U=0V and 1.98 V
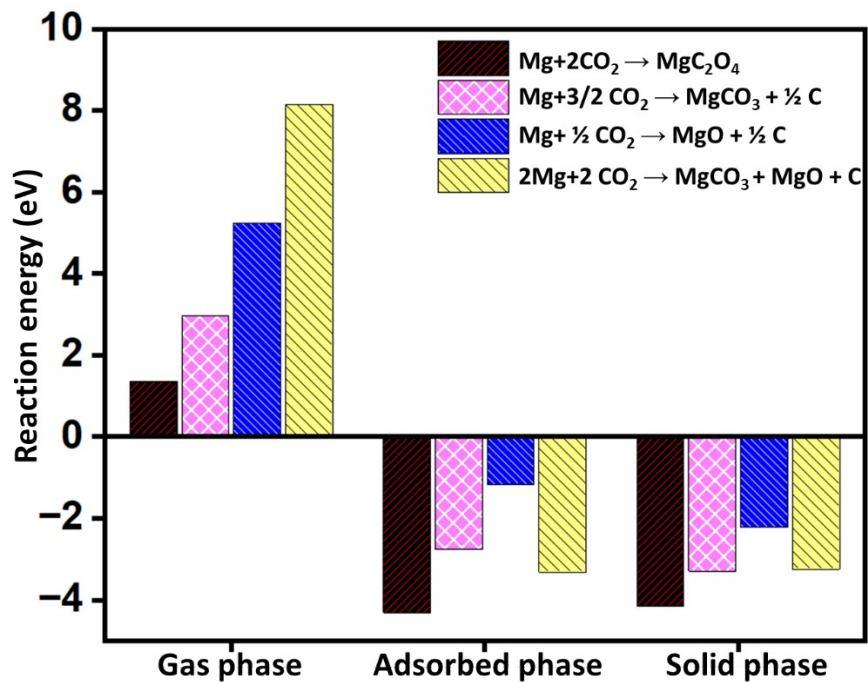
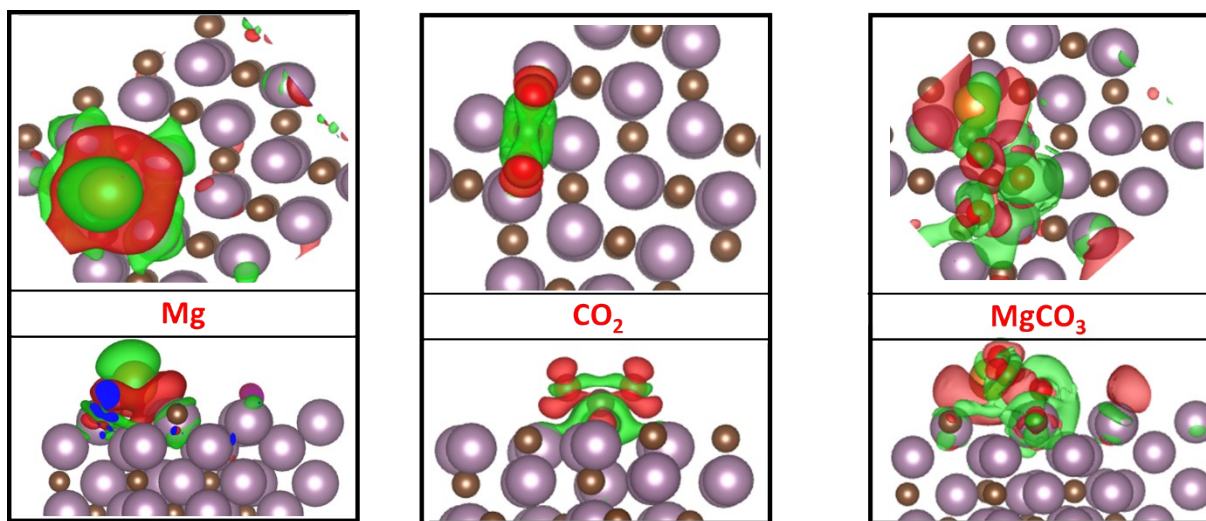**Figure S10. The calculated reaction energies for the formation of various Mg salts in gas, adsorbed, and solid phases**

Figure S11. Snapshot of charge density difference (DCD) for Mg, CO_2 and $MgCO_3$ adsorbed α-Mo_2C (001)

Standard Gibbs Free energies and equilibrium voltage calculations

For $MgCO_3$ and MgC_2O_4 nucleation, the overall chemical reaction can be written as

$$2Mg\ (s) + 2\ CO_2\ (g) \rightarrow MgCO_3\ (s) + MgO\ (s) + C\ (s) \tag{1}$$
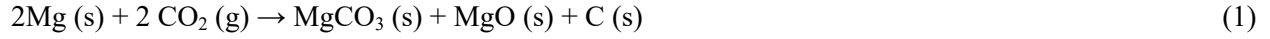
$$Mg\ (s) + 2\ CO_2\ (g) \rightarrow MgC_2O_4\ (s) \tag{2}$$

From the above chemical reactions, the standard Gibbs free energies of both $MgCO_3$ (s) and MgC_2O_4 (s) can be calculated as

$$\Delta G^0_f\ (MgCO_3)_s = \ G^0\ (MgCO_3)_s + \ G^0\ (MgO)_s + G^0\ (C)_s\ - 2\ G^0\ (Mg)_s - 2\ G^0\ (CO_2)_g \tag{3}$$

$$\Delta G^0f\ (MgC_2O_4)_s = G^0\ (MgC_2O_4)_s - G^0\ (Mg)_s - 2\ G^0\ (CO_2)_g \tag{4}$$

Overall, from the standard free energy calculations, the value of $\Delta G^0_f\ (MgCO_3)_s$ and $\Delta G^0f\ (MgC_2O_4)_s$ was calculated to be -8.55eV and -3.98 eV, respectively. From the Nernst equation,

$$\mathbf{U_0\ (M) = -\ \Delta G^0_f/\ ne} \tag{5}$$

where n and e represent the number of transferred electrons and electronic charge and the value of equilibrium potential $U_0\ (MgCO_3)$ and $U_0\ (MgC_2O_4)$ was calculated to be 2.13 V and 1.98 V.

Electrochemical free energy changes during the discharging and charging processes

For the studied catalyst, the electrochemical free energy change for the most favorable pathway during the discharging/charging process is calculated based on the expression:

$$(\Delta G_E\ (Mg\text{-}CO_2)) = E_{total} - \{E_{prev} + n_{Mg}\ (\mu_{Mg}) + n_{CO_2}\ (\mu_{CO_2})\} \tag{6}$$

E_{total} and E_{prev} represents energy of the total system and energy of the previous step. n_{Mg}, n_{CO_2}, μ_{Mg} and μ_{CO2} denotes the number of Mg, CO_2 and chemical potential of Mg and CO_2.

$$\text{Discharge overpotential } (\eta_{dis}) = U_{eq} - U_{dis}, \tag{7}$$

$$\text{Charge overpotential } (\eta_{chg}) = U_{chg} - U_{eq}, \tag{8}$$

$$\text{Total overpotential } (\Delta E_{total}) = \eta_{dis} + \eta_{chg} \tag{9}$$

Table S1

The calculated zero-point energies and entropies for all the studied reaction intermediates for the studied α-Mo$_2$C (001) substrate

Reaction intermediates	ZPE	TS
Mg	0.037	0.146
CO$_2$	0.332	0.178
MgCO$_2$	0.368	0.217
MgCO$_3$ + CO	0.657	0.306
MgCO$_3$ + MgO + C	0.693	0.277
CO$_3$ + CO	0.613	0.266
MgO + CO$_3$ + C	0.647	0.297
C$_2$O$_4$	0.648	0.235
MgC$_2$O$_4$	0.681	0.261

References

1 K. Momma and F. Izumi, *J Appl Cryst*, 2011, **44**, 1272–1276.