Supporting Information

Ag Single-Atom Modification of MgAl-LDH to Enhance the CH_4 Product Selectivity in CO_2 Reduction：A DFT Study

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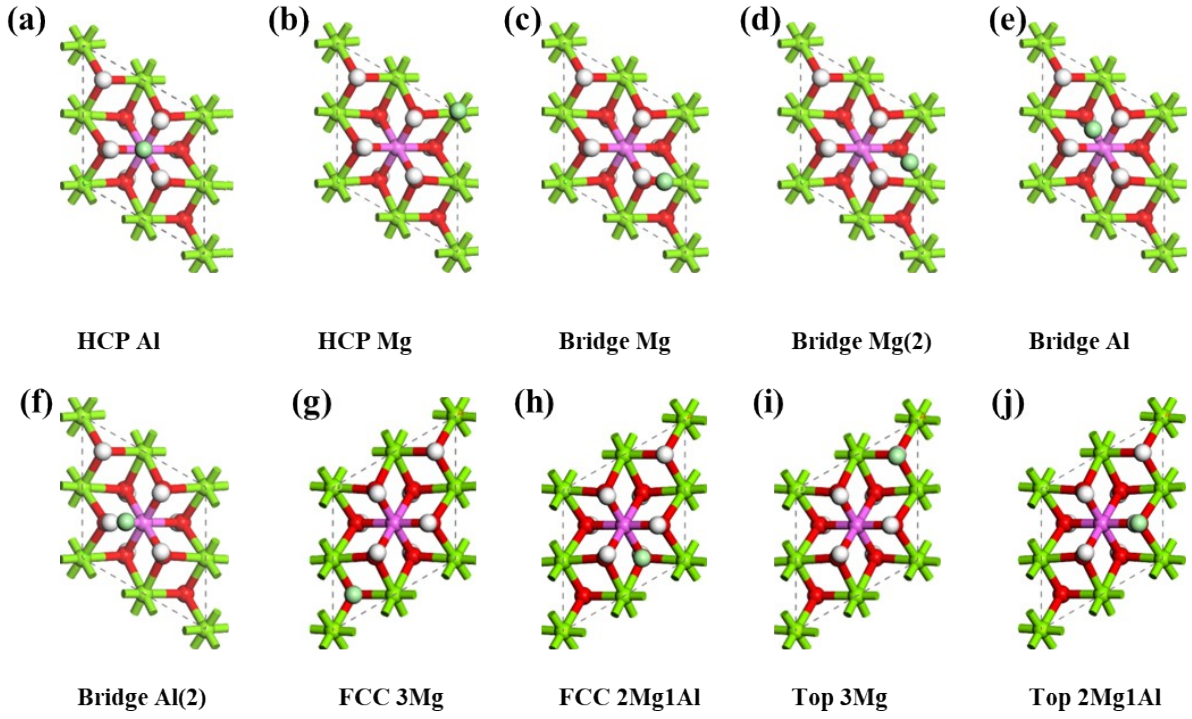

Figure S1. Optimized LDH structures with different Cl^- sites.

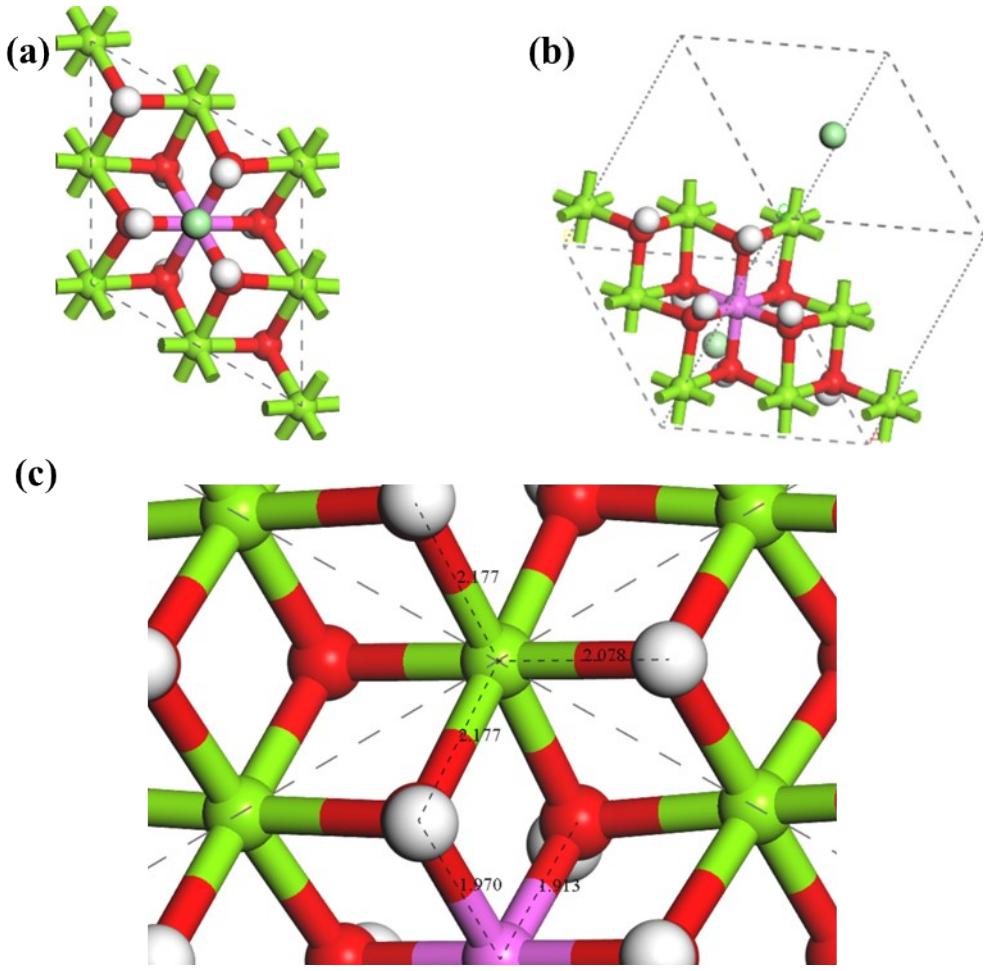

Figure S2. (a) Top view and (b) oblique view of the optimized MgAl-LDH structures with Cl^- sites at HCP Al. (c) Bond length of the Mg-O and Al-O.

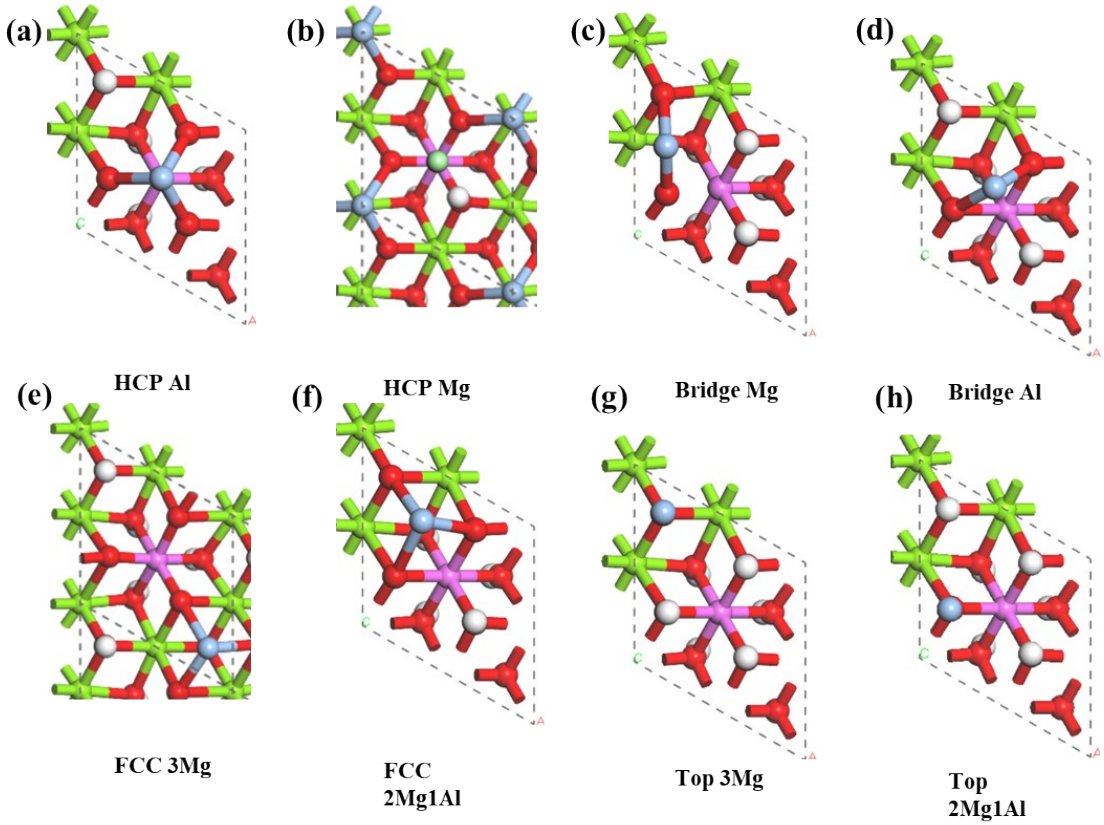

Figure S3. Optimized Ag/MgAl-LDH structures with different Ag sites.

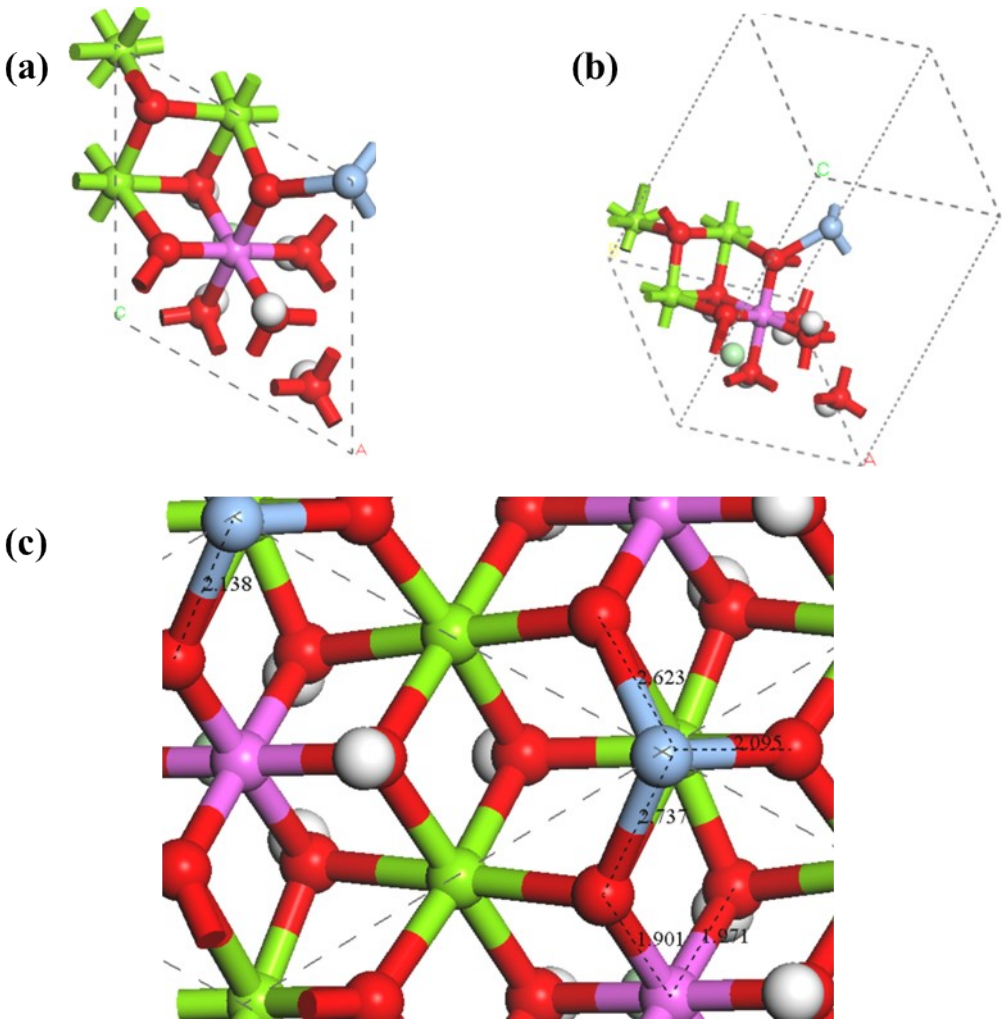

Figure S4. (a) Top view and (b) oblique view of the Optimized Ag/MgAl-LDH structures with Ag-sites at HCP Mg. (c) Bond length of the Mg-O and Al-O.

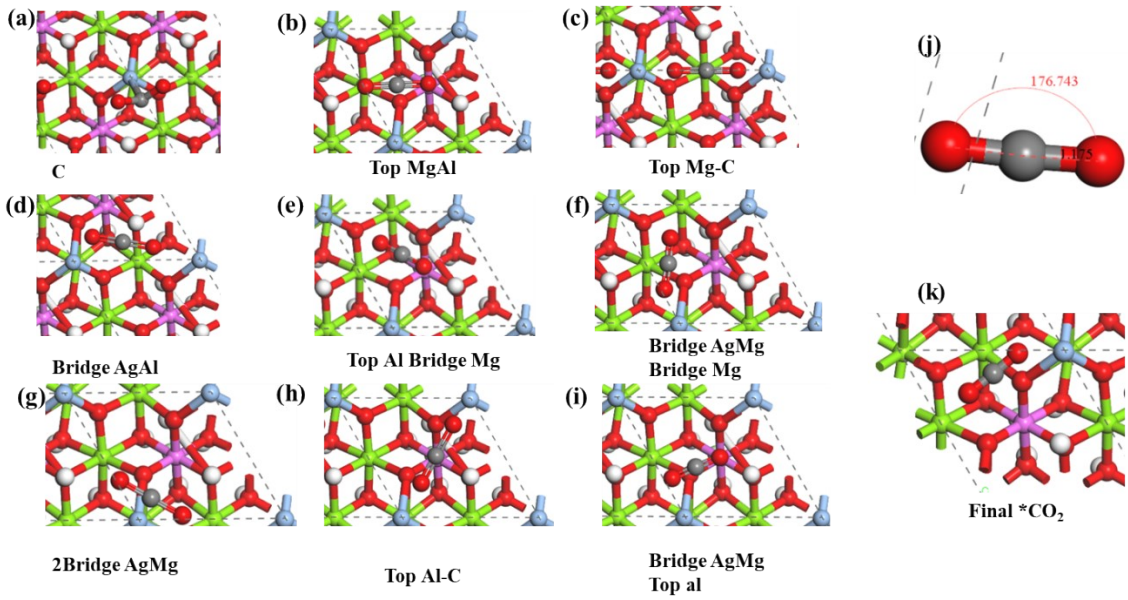

Figure S5. Possible initial adsorption configuration of *CO_2 on Ag/MgAl-LDH.

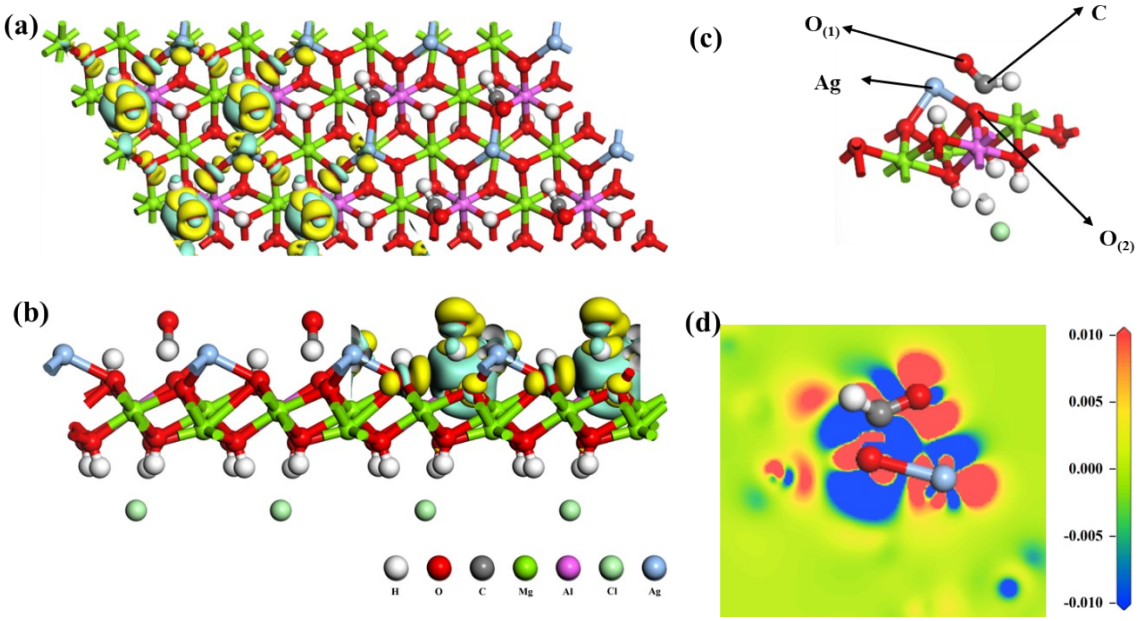

Figure S6. The charge density difference of *COH intermediates on the Ag/MgAl-LDH at (a) top view, (b) front view, (c) oblique view, and (d) the slice plot.

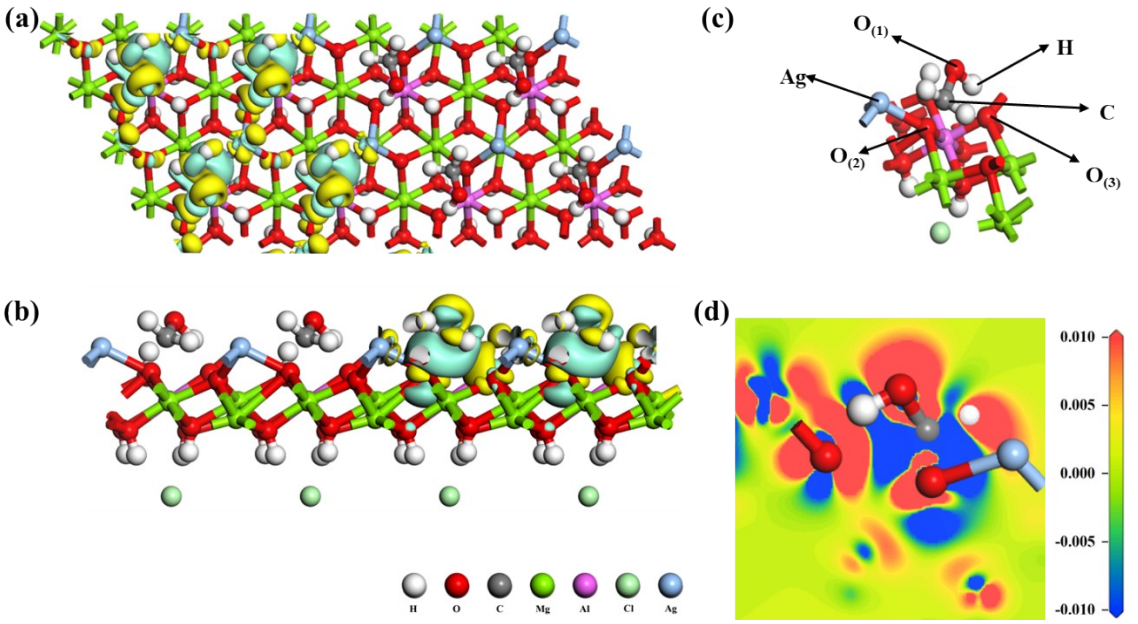

Figure S7. The charge density difference of *CH_2OH intermediates on the Ag/MgAl-LDH at a) the top view, b) front view, c) oblique view, and d) the slice plot.

Table S1. Lattice parameters of the bulk MgAl-LDH.

Lattice parameters(A)		Cell Angles(°)	
a	3.10373	α	89.990705
b	3.10372	β	90.009106
c	7.64898	γ	120.01846

Table S2. Monolayer MgAl-LDH optimization energies with different Cl^- sites.

Structure	Single-point approximation energy (eV)	Structural optimization energy (eV)
HCP Al	-9266.8506	-9269.1885
HCP Mg	-9266.2993	-9269.0818
Bridge Mg	-9266.4028	/
Bridge Mg(2)	-9266.3168	/
Bridge Al	-9266.7623	/
Bridge Al(2)	-9266.7623	/
FCC 3Mg	-9267.2903	-9269.0325
FCC 2Mg1Al	-9267.7403	/
Top 3Mg	-9267.4670	/
Top 2Mg1Al	-9267.7430	/

Table S3. Binding energies of Ag single atom with MgAl-LDH at different Ag sites.

Structure	Structural optimization energy (eV)	Combination energy E_b (eV)
HCP Al	-13219.7881	-4.9365
HCP Mg	-13220.1257	-5.4173
bridge Mg	-13238.4887	-4.5160
bridge Al	-13238.4425	-4.2307
FCC 3Mg	-13219.6144	-4.9975
FCC 2Mg1Al	-13220.0944	-5.3386
Top3Mg	-13256.3828	-3.0166
Top2Mg1Al	-13256.4371	-2.9207

Table S4. The standard theoretical values of Gibbs free energy change for the reactions generating different C1 products (the values are based on the NIST-JANAF database).

Reactions	ΔG(kJ·mol^{-1})	ΔG(eV)
$CO_2+H_2=CO+H_2O$ (l)	20.085	0.2082
$CO_2+4H_2=CH_4+2H_2O$ (l)	-130.661	-1.3542
$CO_2+2H_2=CH_2O+H_2O$ (l)	47.327	0.4905
$CO_2+H_2=HCOOH$ (l)	36.847	0.382
$CO_2+3H_2=CH_3OH$ (l)$+H_2O$ (l)	-9.632	-0.0998
$CO_2+H_2=CO+H_2O$ (l)	20.085	0.2082

Table S5. Population analysis of *COH intermediate.

Element	Mulliken charge	Bond	Bond population
C	0.3	C-$O_{(1)}$	1.04
$O_{(1)}$	-0.51	C-$O_{(2)}$	0.63
$O_{(2)}$	-0.76	C-Ag	-0.32
Ag	0.65	Ag-$O_{(1)}$	0.03

Table S6. Population analysis of *CH_2OH intermediate.

Element	Mulliken charge	Bond	Bond population
H	0.34	H-$O_{(3)}$	0.21
C	-0.05	C-$O_{(1)}$	0.63
$O_{(1)}$	-0.65	C-$O_{(2)}$	0.46
$O_{(2)}$	-0.77	C-Ag	-0.38
$O_{(3)}$	-0.94		
Ag	0.8		

Detailed structure parameters could be retrieved from the CCDC number 2436716 for MgAl-LDH and 2436715 for Ag/MgAl-LDH.