

Supplemental Material for

Theoretical Study on the Topotactic Transformation and Memory Effect of M(II)M(III)-Layered Double Hydroxides

Qing-Ting Meng, Hong Yan,*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China

* Corresponding authors. Tel: +86-10-64448331; Fax: +86-10-64425385.

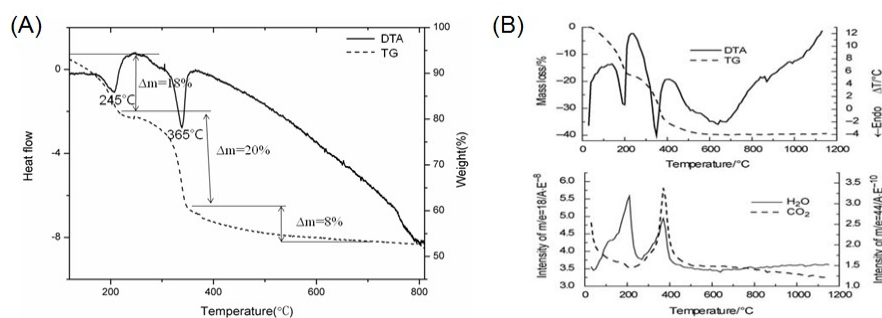


Figure S1. TG-DTA curves of the LDHs sample (A) NiAl-LDHs; [40] (B) MgFe-LDHs and evolved gas analysis (H_2O and CO_2) [42]

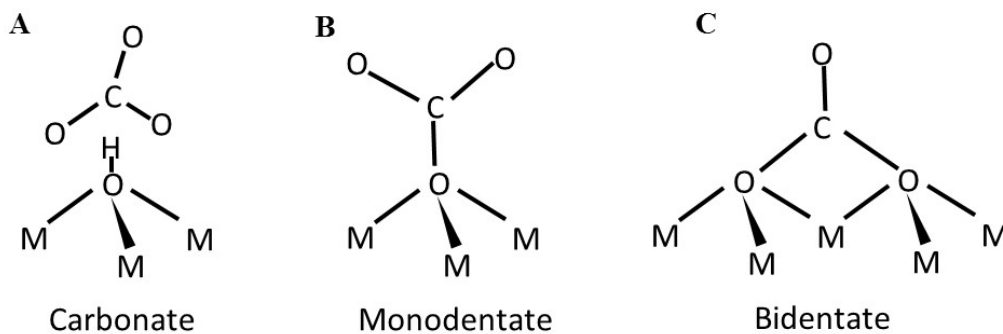


Figure S2. Schematic structures of (A) carbonate-LDH, (B) monodentate-LDH and (C) bidentate-LDH.

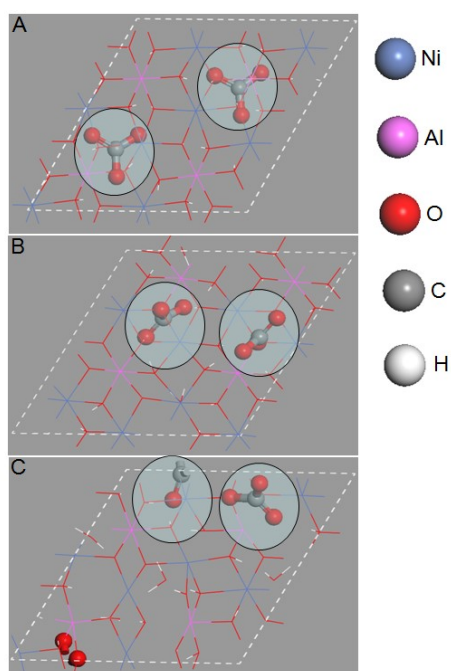


Figure S3. Top views of (A) Ni-carbonate-LDH, (B) Ni-monodentate-LDH and (C) Ni-bidentate-LDH.

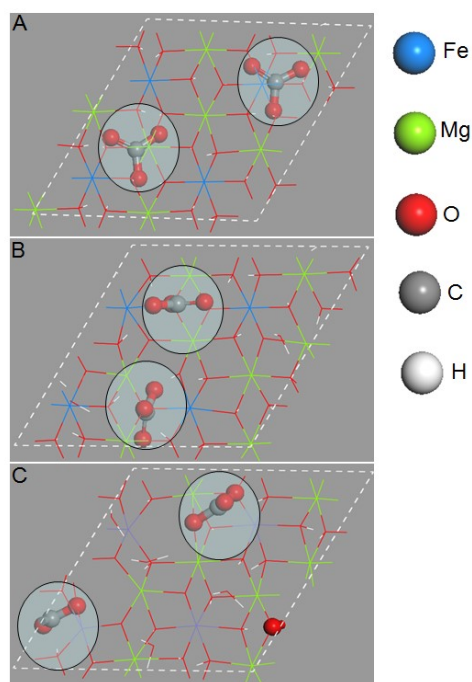


Figure S4. Top views of (A) Mg-carbonate-LDH, (B) Mg-monodentate-LDH and (C) Mg-bidentate-LDH.

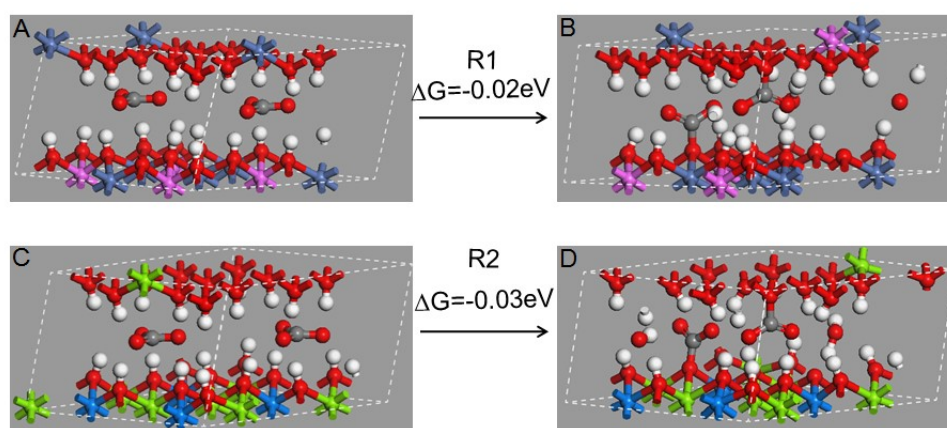


Figure S5. the snapshots at 30 ps of the *NVT* (365, 380 °C respectively) dynamic simulations of (A) Ni-C-LDH, (B) Ni-Mono-LDH, (C) Mg-C-LDH, (D) Mg-Mono-LDH with ΔG .

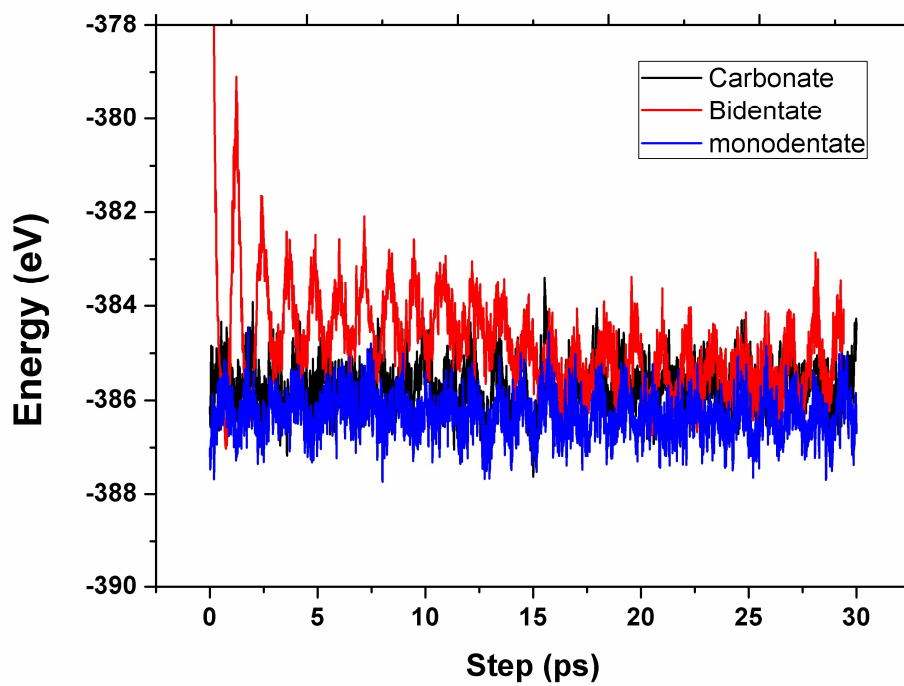
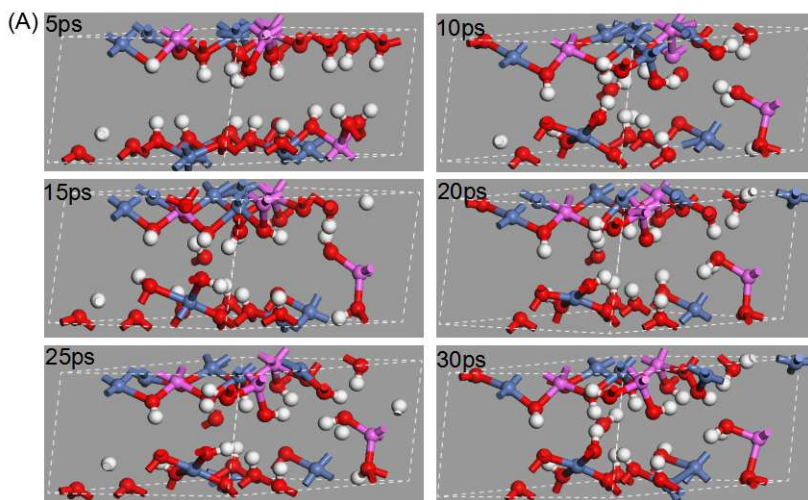


Figure S6. Free energy along MD trajectory of Ni-carbonate-LDH, Ni-monodentate-LDH and Ni-bidentate-LDH, respectively.



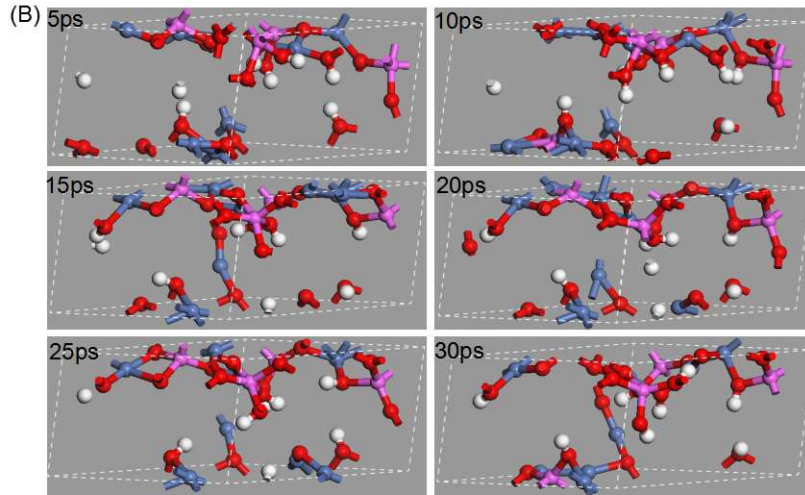


Figure S7. Snapshots at 5, 10, 15, 20, 25, 30ps of the *NVT* (365, 800 °C) dynamic simulations of (A): Ni-CLDH-1 (B): Ni-CLDH-5 to show the migration of cations and the structure variations.

Calculation of Gibbs free energy

The Gibbs free energy (G) of a given structure is calculated according to the definition:

$$G=H-TS \quad (1)$$

where T is temperature of the system; H and S represent the calculated enthalpy and entropy, respectively.

For solid, the influence of the pressure on H and S and the translational and rotation contributions can be neglected, thus H and S are determined by eqs 2 and 3:

$$H(T)=E_{\text{elec}}+E_{\text{ZPE}}+E_{\text{vib}}(T) \quad (2)$$

$$S(T)=S_{\text{conf}}+S_{\text{vib}}(T) \quad (3)$$

where E_{elec} is the total electronic energy of the system at 0 K; E_{ZPE} is the zero-point vibrational energy which is a linear sum of the fundamental harmonic frequencies; $E_{\text{vib}}(T)$ is the vibration contribution; S_{conf} and $S_{\text{vib}}(T)$ are the configurational and vibrational entropy, respectively.

According to statistical mechanics, the vibrational partition function

$$q_{\text{vib}} = \sum_i \frac{1}{1 - \exp(-h\nu_i/kT)} \quad (4)$$

Thus the E_{ZPE} and vibration energy E_{vib} , using the harmonic oscillator approximation, at the temperature T are calculated as:

$$E_{\text{ZPE}} = \frac{R}{k} \frac{1}{2} \sum_i h\nu_i \quad (5)$$

$$E_{\text{vib}} = \frac{R}{k} \sum_i \frac{h\nu_i \exp(-h\nu_i/kT)}{1 - \exp(-h\nu_i/kT)} \quad (6)$$

where k is Boltzmann's constant; R is the ideal gas constant; ν_i is the i -th normal vibration frequency; h is Planck's constant.

S_{conf} and $S_{\text{vib}}(T)$ are defined by eqs 7 and 8, respectively.

$$S_{\text{conf}} = -RN_{\text{T}}(X_{\text{A}} \ln X_{\text{A}} + X_{\text{W}} \ln X_{\text{W}} + X_{\text{V}} \ln X_{\text{V}}) \quad (7)$$

$$S_{\text{vib}}(T) = R \sum_i \frac{h\nu_i/kT \exp(-h\nu_i/kT)}{1 - \exp(-h\nu_i/kT)} - R \sum_i \ln[1 - \exp(-h\nu_i/kT)] \quad (8)$$

where, N_{T} is the total moles of species; X_{A} , X_{W} and X_{V} are the mole fraction of anion, water molecule, and vacancy, respectively.

For the gas molecules, the translational and rotation contributions must also be considered.

Thus the enthalpy in the ideal gas approximation is given by

$$H_{\text{g}}(T) = E_{\text{elec}} + E_{\text{ZPE}} + E_{\text{vib}}(T) + E_{\text{rot}}(T) + E_{\text{trans}}(T) + RT \quad (9)$$

where $E_{\text{trans}}(T)$ is the translational enthalpy; $E_{\text{rot}}(T)$ is the rotational enthalpy. They are equivalent to $3/2RT$, and R is the gas constant. RT is equivalent to the pV term, that is necessary to obtain the enthalpy of a gas.

The entropy of gas in this study is calculated as

$$S_g(T) = S_{\text{trans}}(p, T) + S_{\text{rot}}(T) + S_{\text{vib}}(T) \quad (10)$$

where $S_{\text{trans}}(T)$ is the translational entropy; $S_{\text{rot}}(T)$ is the rotational entropy, respectively.

The translational and rotational partition functions are

$$q_{\text{trans}} = \left(\frac{\sqrt{2\pi M k T}}{h} \right)^3 \quad (11)$$

$$\text{and } q_{\text{rot}} = \left(\frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \right) \left[\frac{8\pi^2 k T}{h^2} \right]^{3/2} \quad (\text{non-linear molecule}) \quad (12)$$

Thus the translational entropy and rotational entropy are determined by

$$S_{\text{trans}}(p, T) = k \left\{ \ln \left[\frac{2\pi M k T}{h^2} \right]^{3/2} \frac{k T}{p} \right\} + 5/2 \quad (13)$$

$$S_{\text{rot}}(T) = k \left\{ \ln \left[\frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left(\frac{8\pi^2 k T}{h^2} \right)^{3/2} \right] + x \right\} \quad (14)$$

where I_A , I_B and I_C are the moments of inertia of the molecule; h is Plank constant; σ is the symmetry number; x equals 3/2 for water and 1 for CO_2 ; p is 0.1 MPa and M is the molecular mass.

References

- [1] Costa DG, Rocha AB, Souza WF, et al. Ab initio simulation of changes in geometry, electronic structure, and gibbs free energy caused by dehydration of hydrotalcites containing Cl^- and CO_3^{2-} counteranions. J Phys Chem B [Internet]. 2011;115:3531-3537. Available from: <http://pubs.acs.org/doi/abs/10.1021/jp110668s>
- [2] Kresse G, Furthmuller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Compu Mater Sci [Internet]. 1996;6:15-50. Available from: <http://journals.aps.org/prb/abstract/10.1103/PhysRevB.54.11169>

