Supporting Information

# First-Principles Molecular Dynamics Study on the Surface Chemistry and Nanotribological Properties of MgAl Layered Double Hydroxides

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## 1. Structure of LDH in sliding contact



**Fig. S1**. Minimum and maximum energy stacking configuration of Mg(OH)2 –LSH (a and b) and MgAl-LDH (c and d). (e) The bond length between metal cation with oxygen in the LDH structure. Orange, Blue, Red, and White represent Mg, Al, O, and H atoms, respectively



**Fig. S2**. The optimized structure of two LDH surfaces at the minimum stacking configuration when the coverage of the hydroxyl group on the surface is reduced.

2. Effects of hydroxide anions on the frictional behaviors of Mg<sub>2</sub>Al<sub>1</sub>-LDH



Fig. S3. The potential energy surface of Mg<sub>2</sub>AL<sub>1</sub>-LDH with an OH anion and different hydroxyl coverages. (a)  $\theta_{hyd} = 100\%$ , (b)  $\theta_{hyd} = 66.6\%$  and (c)  $\theta_{hyd} = 33.3\%$ . The bottom two graphs illustrate the energy profile and lateral force along the chosen sliding paths shown in the PES.

The introduction of OH anions may affect the tribological properties of the LDH system. Hence, the additional simulation was carried out to investigate the potential energy surface of Mg<sub>2</sub>AL<sub>1</sub>-LDH with an OH anion and different hydroxyl coverages, as shown in **Fig. S3**. As compared with the case of without anion in **Fig. 2b** and **Fig. 4**, the introduction of OH anion can increase the friction force at high hydroxyl coverages. However, the phenomenon is opposite at the low hydroxyl coverage. It has been found that the lateral force increase from 1.6 to 25.4 and 86.4 meV/Å per atom when the hydroxyl coverage decreases from 100 % to 66.6 % and 33.3 %, respectively, for the case without anion (**Table 2**), the corresponding values for the case with OH anion are 4.5, 5.9 and 77.1 meV/Å per atom respectively (**Fig. S3**). Nonetheless, both cases show the same tendency, i.e., the friction increases when the hydroxyl coverage is reduced. It is expected that this tendency could change when the type of anions or confined molecule changed. However, considering different anions/confined molecules will require a huge amount of work, and a detailed investigation needs to be carried out in the future.



## 3. Roles of hydroxyl groups in friction reduction of Mg(OH)<sub>2</sub>-LSH

**Fig. S4.** The potential energy surface of Mg(OH)<sub>2</sub>-LSH with different hydroxyl coverages. (a)  $\theta_{hyd} = 66.6\%$  and (b)  $\theta_{hyd} = 33.3\%$ . Bottom two graphs illustrate the energy profile and lateral force along the chosen sliding paths shown in the PES.

In comparison with the case of Mg<sub>2</sub>Al<sub>1</sub>-LDH , the Mg(OH)<sub>2</sub>-LSH model shows similar frictional behavior. As shown in **Table 2**, when the hydroxyl coverage of Mg<sub>2</sub>Al<sub>1</sub>-LDH decreases from  $\theta_{hyd} = 100 \%$  to  $\theta_{hyd} = 66.6\%$  and  $\theta_{hyd} = 33.3\%$ , the lateral force increases from 1.6 into 25.4 and 86.4 meV/Å per atom, respectively. Meanwhile, the calculated lateral force in the case of Mg(OH)<sub>2</sub>-LSH displays a similar increase from 23.8 to 74.5 and 243.5 meV/Å per atom when the coverage decrease from  $\theta_{hyd} = 100 \%$  to 66.6 % and 33.3 %, respectively. It is worth mentioning that the lateral force of Mg(OH)<sub>2</sub>-LSH is much higher than that of Mg<sub>2</sub>Al<sub>1</sub>-LDH.

## 4. Structure of intercalated molecules in sliding contact



**Fig. S5**. Distribution of the water/anion orientation as obtained from AIMD of a system of a single (a) and double (b) water/anion layers. The blue and red lines indicate the location of the lower and upper LDH surfaces, respectively.



**Fig. S6**. Distribution of water molecules as obtained from AIMD of a system with one (a) and two (b) water/anions layers confined between two LDH slabs. The grey dot lines indicate the hydrogen bonds, while the blue circle marks the OH anion.



**Fig. S7**. Distribution of the O-H bond length as obtained from AIMD simulation of a system of only (without LDH surfaces) 20 molecules (16  $H_2O$  + 4 OH anions). The cut-off for the O-H bond is 1.5 Å.



**Fig. S8**. Distribution of a selected OH anion orientation as obtained from AIMD of a system with two water layers confined between two LDH slabs. The cut-off for the O-H bond is 1.5 Å.



Fig. S9. The dissociation of the H atom on the MgAl-LDH during the sliding.



**Fig. S10**. Distribution of the water orientation (a) the intramolecular O-H bond length (b) as obtained from AIMD of a system with a single water layer confined between two LDH slabs in the sliding process. The cut-off for the O-H bond is 1.5 Å.



**Fig. S11**. Distribution of the water orientation (a) the intramolecular O-H bond length (b) as obtained from AIMD of a system with two water layers confined between two LDH slabs in the sliding process. The cut-off for the O-H bond is 1.5 Å.

#### 5. Metadynamics simulation

In metadynamics simulation, a bias potential is applied along a defined set of collective variables (CVs) to encourage efficient sampling of the associated free energy surface. The history-dependent bias takes the form of Gaussian functions to allow the system to escape beyond high energy barriers, thus allowing for faster sampling of the reaction surface. The sum of the deposited bias potentials is used to reconstruct the free energy surface. The detail about the method can be found in the literature.<sup>1</sup>

In this work, the collective variables are a function of coordination number (CN). The analytical expression of the coordination number is:

$$CN_{X-Y} = \sum_{ij} \frac{1 - \left(\frac{d_{X_i Y_j}}{d_{XY}^0}\right)^m}{1 - \left(\frac{d_{X_i Y_j}}{d_{XY}^0}\right)^n}$$

where  $d_{X_iY_j}$  is the interatomic distance between the atoms  $X_i$  and  $Y_j$  out of selected sets of atoms  $\{X_i\}$ and  $\{Y_j\}$  and  $d_{XY}^0$  is a cut-off distance. The constant *m* and *n* control the steepness of the CN function. In this study, we use a cut-off distance of 1.5 Å. The parameters *m* and *n*, which we adapted from the previous work of Jinggang et al.<sup>2</sup>, are 16 and 56, respectively.

#### References

1. Barducci, A.; Bussi, G.; Parrinello, M., Well-Tempered Metadynamics: A Smoothly Converging and Tunable Free-Energy Method. *Phys. Rev. Lett.* **2008**, *100* (2), 020603.

2. Lan, J.; Rybkin, V. V.; Iannuzzi, M., Ionization of Water as an Effect of Quantum Delocalization at Aqueous Electrode Interfaces. *J. Phys. Chem. Lett.* **2020**, *11* (9), 3724-3730.