Supplemental material for the revision of AM8765

Effects of crystal chemistry on adsorption, occurrence and mobility of water in palygorskite tunnelsJinhong

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1. Additional information: detailed RH values and corresponding chemical potentials

Table S1 RH values and corresponding chemical potentials.

RH (%)	0.002	0.010	0.100	2.450	5.690	10.260	14.400	23.850
μ_w (kcal/mol)	-16.780	-15.637	-14.273	-12.500	-12.000	-11.650	-11.450	-11.150

RH (%)	35.600	71.400	83.000	100.000
μ_w (kcal/mol)	-10.900	-10.500	-10.410	-10.300

2. Coordination of Na$^+$ ions in NaMgPlg at RH=0.01%.

While RH increases to 0.01%, the Na$^+$ ion prefers to form a four-coordinate hydration shell: One Na$^+$ ion coordinates with two SurfaceO linked with Al-tetrahedral substitution and two zeolitic WaterO atoms
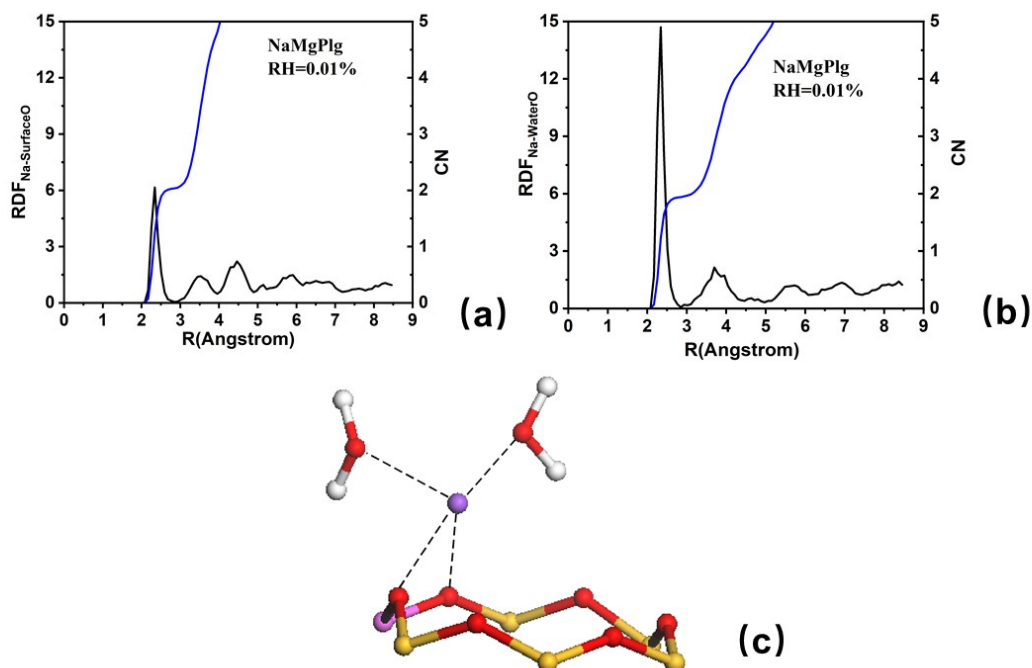
Figure S1 RH=0.01%, RDFs and CNs of (a) Na^+ and tunnel SurfaceO; and (b) Na^+ and WaterO, (c) Na^+ coordinated with oxygen atoms in NaMgPlg.

3. Additional information for the *x, y,* and *z* components of MSD separately.

The MSD of each component is calculated by equation as follow:

$$D = \frac{1}{2}\frac{d\langle r^2\rangle}{dt} \qquad (1)$$

By comparing the MSD of each component with the total MSD (Figure S1), it is clear that the major contribution is from *z* component. Therefore, the diffusion of zeolitic water on *x* and *y* component could be negligible.
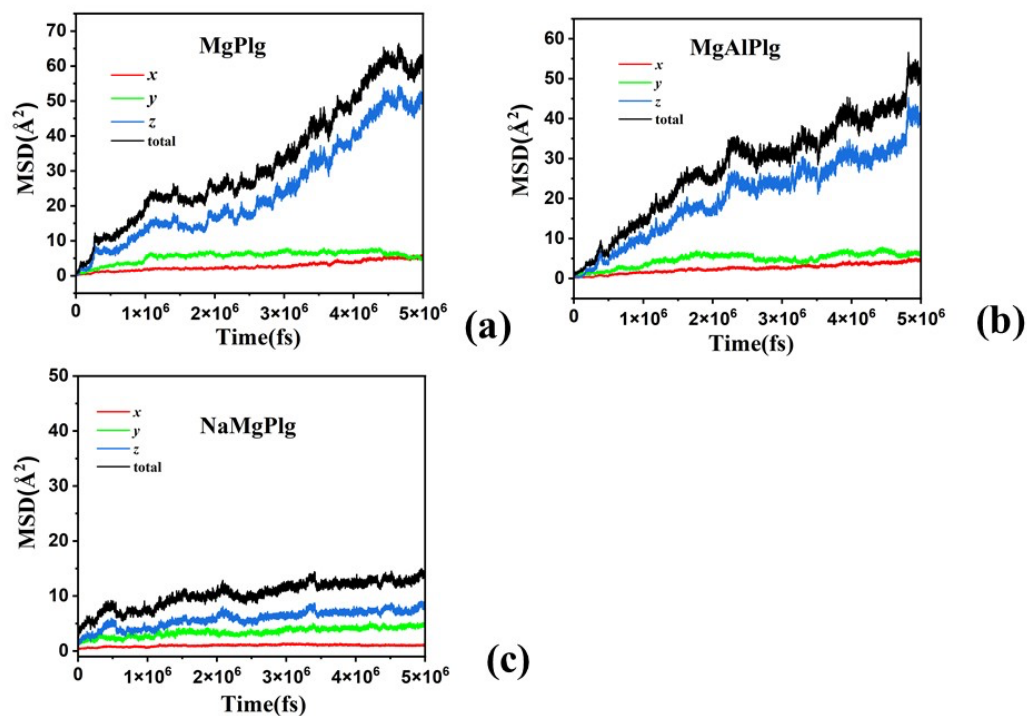
Figure S2 MSD of zeolitic water on each component in (a) MgPlg; (b) MgAlPlg; (c) NaMgPlg.

2. Comparison of different supercell size

By taking MgPlg system ($2 \times 1 \times 4$, $26.572 \times 17.848 \times 20.968$ Å³) as an example, we rerun the simulations with a larger supercell of $2 \times 2 \times 4$ ($26.572 \times 35.696 \times 20.968$ Å³). We chose two RHs (5.69% and 100%) to check the GCMC simulations with larger supercells. The deviation of zeolitic water content is within 5%, which corresponds to 0.1 to 0.2 water molecules per unit cell (Table S2).

Table S2 Results of GCMC calculation:

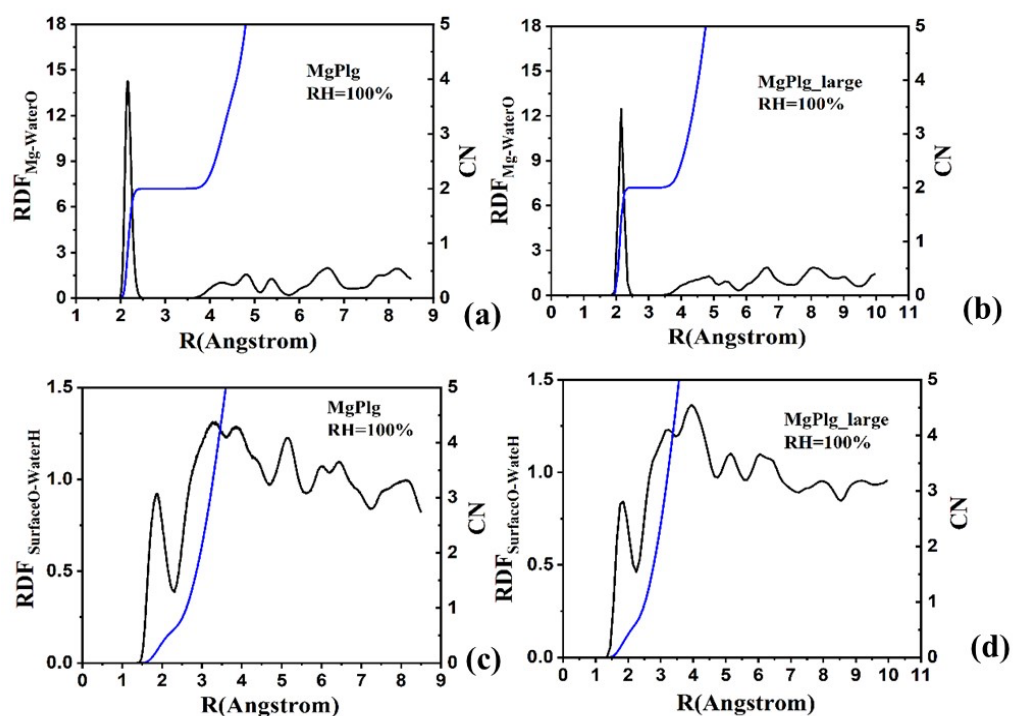| RH (%)	Original model	Large model	Deviation
5.69	9.06 g$_{water}$/100g	8.92 g$_{water}$/100g$_{clay}$	1.5 %~0.1 water molecules per unit cell
100.00	9.64 g$_{water}$/100g	9.35 g$_{water}$/100g$_{clay}$	3.0 %~ 0.2 water molecules per unit cell

Figure S3 RDFs of the edge Mg atoms and WaterO atoms of MgPlg (a) and MgPlg_large (b); RDFs of the SurfaceO atoms and WaterH atoms of MgPlg (c) and MgPlg_large (d).
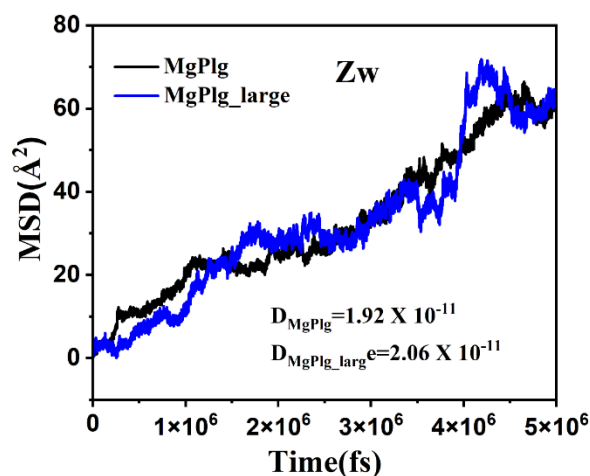
Figure S4 MSDs of zeolitic water in the models of MgPlg and MgPlg_large.

From Figure S3, we can observe that the RDFs of Mg and WaterO are similar. The coordination numbers are both 2. This means the amount of bound water are the same in both systems. The RDFs of the SurfaceO atom and WaterH are also similar. There are first small peaks in both systems denoting to the zeolitic water attracted by OH groups. The MSDs of zeolitic water in both systems are also similar, and the diffusion coefficients are also close (Figure S4). Therefore, the results from GCMC and MD simulations of the larger supercell indicate that original model is already big enough for investigating these properties.