Adsorption/Desorption and Transport of Water in Two-Dimensional Hexagonal Mesoporous Silica

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S1. Comparison of adsorption–desorption isotherms of water on Zr-MPS obtained by gravimetric and volumetric methods.

Figure S1 shows the adsorption–desorption isotherms of water on Zr-MPS obtained by gravimetric and volumetric methods at 298 K.

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S2. Enlarged view of Figure 5 (Curve fitting of relaxation curves)

Figures S2a-I, S2a-II, S2b-I, and S2b-II show the enlarged view around $t = 0$ of Figures 5a-I, 5a-II, 5b-I, and 5b-II, respectively.

Figure S2. Curve fitting of the relaxation curves of (a) water adsorption and (b) water desorption shown in Figure 4. The adsorbed mass, m , was normalized by the equilibrium value, m_{eq} . The

fitting functions are (I) $m/m_{\text{eq}} = \text{sgn}(m/m_{\text{eq}}) \left[1 - \sum_{n=1}^{10} (C_n \sin \zeta_n / \zeta_n) \exp(-\zeta_n^2 k_1 t) \right]$ (eq. 2) and (II)

$$m/m_{\text{eq}} = \text{sgn}(m/m_{\text{eq}}) (k_2 t)^{1/2} - A \quad (\text{eq. 3}).$$

S3. Exact solution of water diffusion in mesoporous silica in continuum dynamics

Consider one-dimensional water diffusion in a parallel plate of thickness $2d$. Non-dimensional water concentration in mesoporous silica, distance from the interface, and time are defined as $c' = (c - c_0)/(c_{eq} - c_0)$, $x' = x/d$, and $t' = (Dt)/d^2$, respectively. Here, c_0 and c_{eq} are the initial and equilibrium water concentrations and D is diffusivity of water in mesoporous silica. The interfaces are at $x' = \pm 1$, and the water concentration distribution at any instant must be symmetrical about the midplane ($x' = 0$). If the adsorbed water is initially at a uniform concentration ($c'(x', 0) = 0$) and comes into contact with air with different humidity at the interface ($c'(\pm 1, t') = 1$), the resulting concentration profiles can be obtained by solving the following equation:

$$\frac{\partial c'}{\partial t'} = \frac{\partial^2 c'}{\partial x'^2}. \quad (S1)$$

An exact solution to this equation is of the form

$$c' = 1 - \sum_{n=1}^{\infty} C_n \exp(-\zeta_n^2 t') \cos(\zeta_n (1 - x')), \quad (S2)$$

where $\zeta_n = (\pi/2)(2n - 1)$ and $C_n = (4 \sin \zeta_n)/(2\zeta_n + \sin(2\zeta_n))$. The amount of adsorbed water as a function of time can be given by

$$m' = \int_0^1 c' dx' = 1 - \sum_{n=1}^{\infty} \frac{C_n \sin \zeta_n}{\zeta_n} \exp(-\zeta_n^2 t') \quad (\text{S3})$$

Here, it was assumed that $m' = 0$ at $t' = 0$ at the initial condition. For long-time approximation ($t' > 0.2$), the infinite series solution of eq. S3 can be approximated by the first term of the series. Specifically,

$$m' = 1 - \frac{C_1 \sin \zeta_1}{\zeta_1} \exp(-\zeta_1^2 t') = 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{4} t'\right), \quad (\text{S4})$$

On the other hand, the short-time approximation ($t' < 0.2$) can be given by

$$m' = \left(\frac{4}{\pi} t'\right)^{1/2}. \quad (\text{S5})$$

Figure S3 shows the $m' - t'$ curves obtained from eqs. S3–S5. Figure S3 shows that eq. S3 is well approximated by eq. S4 at $t' > 0.2$ (or $0.5 < m' < 1$), whereas it is approximated by eq. S5 at $t' < 0.2$ (or $0 < m' < 0.5$). Eqs. S3–S5 can also be given in the dimensional form:

$$\frac{m}{m_{\text{eq}}} = 1 - \sum_{n=1}^{\infty} \frac{C_n \sin \zeta_n}{\zeta_n} \exp\left(-\zeta_n^2 \frac{D}{d^2} t\right), \quad (\text{S6})$$

$$\frac{m}{m_{\text{eq}}} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{4} \frac{D}{d^2} t\right), \quad (\text{S7})$$

$$\frac{m}{m_{\text{eq}}} = \left(\frac{4}{\pi} \frac{D}{d^2} t \right)^{1/2}, \quad (\text{S8})$$

where m_{eq} is the equilibrium adsorbed mass of water. In Figure 5, the time course of m/m_{eq} is

fitted by the following two equations: $m/m_{\text{eq}} = 1 - \sum_{n=1}^{10} (C_n \sin \zeta_n / \zeta_n) \exp(-\zeta_n^2 k_1 t)$ (eq. 2) and

$m/m_{\text{eq}} = (k_2 t)^{1/2} - A$ (eq. 3), where k_1 , k_2 , and A are fitting parameters. If eq. 3 is the short-time approximation of eq. 2, $k_2 = (4/\pi)k_1$ and $A = 0$.

Figure S3. $m' - t'$ curves obtained from eqs. S3–S5.