Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Study of diffusion properties of zeolite mixtures by combined gravimetric analysis, IR spectroscopy and inversion methods (IRIS)

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Equation for surface barrier limitations.[1]

In the analysis of relative uptake and fractional coverage curves, the conventional approach involves fitting a solution of Fick's second law for diffusion limitation (Equation 1 in the manuscript) or an exponential curve for surface barrier limitation to the experimental data (Equation 1 below):

$$\frac{m_t}{m_\infty} = 1 - \exp\left(-\alpha\frac{\Omega}{V}t\right) = 1 - \exp\left(-\tau_{surf}^{-1}t\right) \quad (1)$$

Where D and α represent the intracrystalline diffusivity and surface permeability, respectively. In this analysis, the equivalent radius of a cube is assumed to be r = a/2, ensuring that the surface-to-volume ratios Ω/V for both the cube and the sphere (equal to 3/r) are the same.[1]

Details of the inversion numerical procedure

This part details the procedure used to obtained the distribution functions of diffusion time constant τ^{-1}, by using inversion methodology. In this case, 2D Infrared Inversion Spectroscopy (2D-IRIS) is based on the inversion of the infrared spectra that consist of inverting the diffusion integral equation describing by the following equation (Absorbance vs. time):

$$A(\upsilon,t) - A(\upsilon,0) = \int_0^\infty f(\upsilon,\tau^{-1})K(t,\tau_k^{-1})d\tau^{-1} \quad 2$$

Where $f(\upsilon,\tau^{-1})$ is the distribution function of diffusion time constant, and $K(t,\tau_i^{-1})$ is the functional dependence of the fractional uptake on time t by considering a bimodal distribution of spheres in the system, expressed as:[2]

$$K(t,\tau_k^{-1}) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_e}{9\ L^2}t\right) \qquad 3$$

With $\tau^{-1} = \frac{D_e}{L^2}$

To discretize **equation 2**, the $A(\upsilon,t) - A(\upsilon,0)$, the functional $K(t,\tau_k^{-1})$ and the distribution function $f(\upsilon,\tau^{-1})$ are represented by matrixes which elements are given by:

$A_{ij} = A(\upsilon_i,t_j) - A(\upsilon_i,0) \qquad i = 1,\ldots,m\,;\, j = 1,\ldots,n$

$K_{jk} = K(t_j,\tau_k^{-1}) \qquad k = 1,\ldots,q$

$f_{ki} = f(\upsilon_i,\tau_k^{-1})$

The q τ_k^{-1} values are linearly spaced in the interval [τ_{min}^{-1}, τ_{max}^{-1}]:

$$\tau_k^{-1} = \tau_{min}^{-1} + \frac{k-1}{\Delta\tau^{-1}} \qquad 4$$

With $\Delta\tau^{-1} = \frac{\tau_{max}^{-1} - \tau_{min}^{-1}}{q-1}$

The left-hand member of the **equation 2** is approximated by numerical quadrature, which consists in approximating the integral by the weighted sum of the values of the function under integral:

$$\int_0^{+\infty} q(t_j,\tau_k^{-1})(\upsilon,\tau^{-1})d\tau^{-1} \approx \sum_{k=1}^{q} w_k q_{jk} f_{ki} \qquad 5$$

The weighting coefficients w_k are determined by the following expression:

$$w_k = \begin{cases} \Delta\tau^{-1}, \ 2 \le k \le q-1 \\ \dfrac{\Delta\tau^{-1}}{2}, \ k = 1,q \end{cases} \qquad 6$$

Discretization of **equation 2**, thus the results in the following system of linear algebraic equations:

$$A_{ij} = \sum_{k=1}^{q} w_k q_{jk} f_{ki} \qquad i = 1,..., m \,; j = \ 1,..., n \ and \ k = 1,..., q \qquad 7$$

Denoting:

$$\Theta_{jk} = w_k q_{jk} \qquad 8$$

The following matrix equation is obtained:

$$A = \Theta f \qquad 9$$

Denoting A_i and f_i the vectors of absorbance values A_{ij} and distribution function values f_{ki} at the wavenumber υ_i, this linear system could be solved with respect to f by minimizing the residuals using a least-squares method, i.e. by minimizing:

$$\Phi_{LS}(f) = \sum_i \|\Theta f_i - A_i\|^2 = \sum_i (\Theta f_i - A_i)^T (\Theta f_i - A_i) \qquad 10$$

However, because of the smoothness of the kernel Θ, which varies slowly with τ_k^{-1}, this is a numerically ill-posed problem:[3] the small experimental errors in $A(\upsilon,t)$ can lead to large changes in the optimum solutions f. This problem is solved using a classical procedure known as Tikhonov regularization[4] which consisting of enforcing the smoothness of the solution by adding a weighted constraint λS to the objective function to be minimized, where λ is the regularization parameter and S a measure of the smoothness of the distribution function. However, the solution function $f(\upsilon,\tau^{-1})$ is that which minimize the functional:

$$\Phi_{reg}[f] = \Phi_{LS}[f] + \lambda S[f] \tag{11}$$

Where $\Phi_{LS}[f]$ is the sum of squared residuals and $\lambda S[f]$ is the penalty function where λ is the regularization parameter ($\lambda \geq 0$) which controls the level of smoothing to be applied and $S[f]$ is a measure of the smoothness of f. The $S[f]$ is the norm of the second derivative of f with respect to τ^{-1} was calculated by the numerical quadrature:

$$S[f] = \left\| \frac{\partial^2 f}{\partial \tau^{-12}} \right\|^2 \approx \sum_i \sum_{k=1}^{q} (f_{(k-1)i} - 2f_{(k-1)i} + f_{(k+1)i})^2 \frac{\Delta \tau^{-1}}{(\Delta \tau^{-1})^4} \tag{12}$$

Where $f_{(-1)i} = f_{0i} = f_{qi} = f_{(q+1)i} = 0$. This choice enforces the solution to be smoothed towards zero values at τ_{max}^{-1} *and* τ_{min}^{-1} which is appropriate for a distribution function. However, with this choice, the **equation 12** can be expressed as a matrix equation:

$$S[f] = \sum_i f_i^T S f_i \tag{13}$$

Where S is a symmetric matrix defined by:

$$S = \frac{1}{(\Delta \tau^{-1})^3} \begin{pmatrix} 6 & -4 & 1 & 0 & \dots & 0 & 0 \\ -4 & 6 & -4 & -1 & \dots & 0 & 0 \\ 1 & -4 & 6 & -4 & \dots & 0 & 0 \\ 0 & 1 & -4 & 6 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & 0 & \dots & 6 & -4 \\ 0 & 0 & 0 & 0 & \dots & -4 & 6 \end{pmatrix}$$

By using **equation (10)** and **(13),** the **equation (11)** can be will be written:

$$\Phi_{reg}[f] = \sum_i (\Theta f_i - A_i)^T (\Theta f_i - A_i) + \lambda f_i^T S f_i \tag{14}$$

After the expansion of and dropping the constant term, the problem of minimizing $\Phi_{reg}[f]$ amounts to solve the quadratic programming (QP) problems:

$$\Phi_{reg}[f] = f_i^T(\Theta^T\Theta + \lambda S)f_i - 2A_i^T\Theta f_i \tag{15}$$

With the non-negativity constraint, which can be solved by most of the numerical computational packages under its standard form, i.e. minimize:

$$\Phi_{reg}[f] = \frac{1}{2}f_i^T Q f_i + c^T f_i \tag{16}$$

With $Q = 2\Theta^T\Theta + 2\lambda S$ and $c^T = -2A_i^T\Theta$ subject to the constraint $f_i \geq 0$.

For the present study, the numerical calculations were carried out with Python, especially Spectrochempy library,[5] using the quadprog routine to solve the quadratic programming problem (**Equation 16**).[6]

Complementary of the results of the paper:

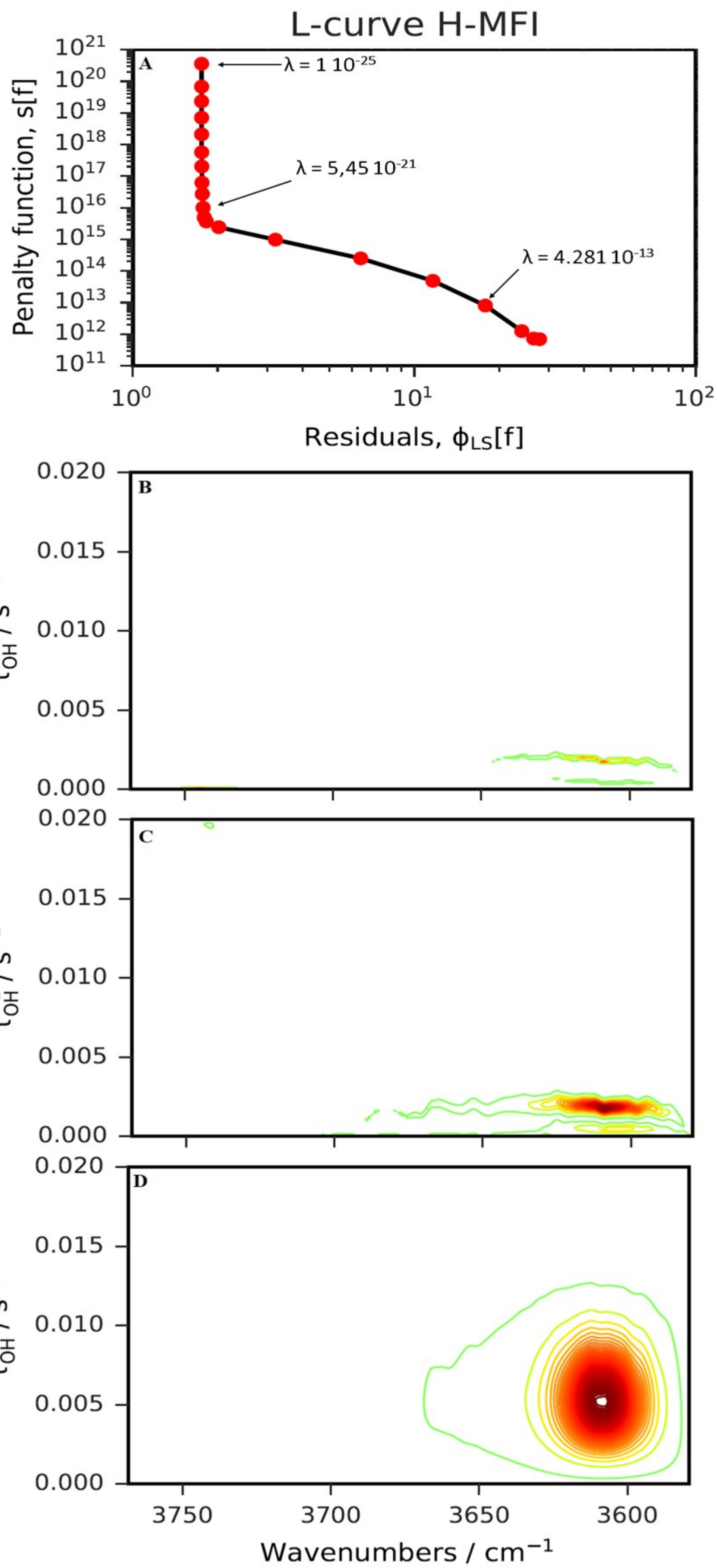

Figure S 1. (A): L-curve plot for determining the optimum choice of regularization parameter λ, (B, C and D): 2D distribution function $f(\upsilon,\tau^{-1})$ obtained by inversion spectroscopy for $\lambda = 1\ 10^{-25}$ (B), $\lambda = 5.45\ 10^{-21}$ (C), and $\lambda = 4.281\ 10^{-13}$ (D).

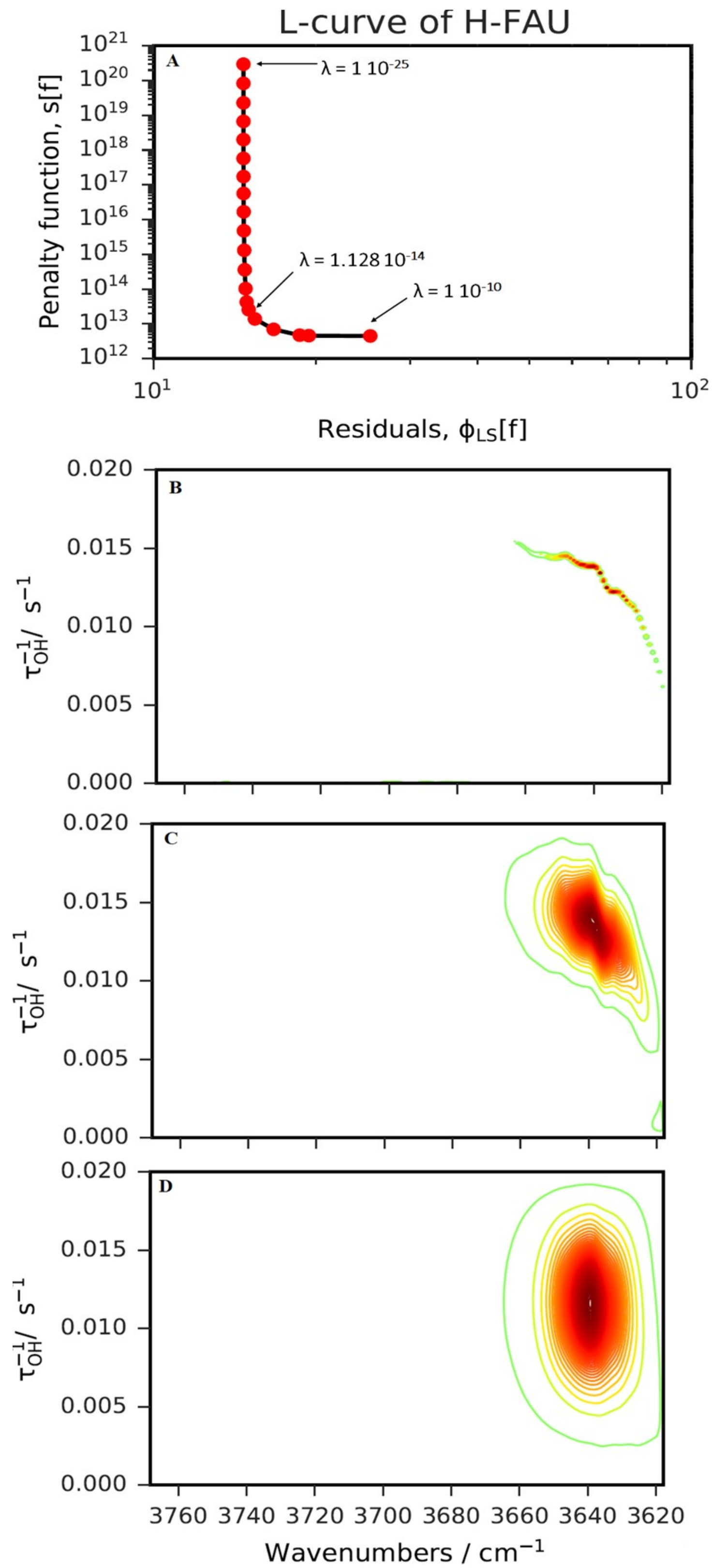

Figure S2. (A): L-curve plot for determining the optimum choice of regularization parameter λ, (B, C and D): 2D distribution function $f(\upsilon,\tau^{-1})$ obtained by inversion spectroscopy for $\lambda = 1\ 10^{-25}$ (B), $\lambda = 1.128\ 10^{-14}$ (C), and $\lambda = 110^{-10}$ (D).

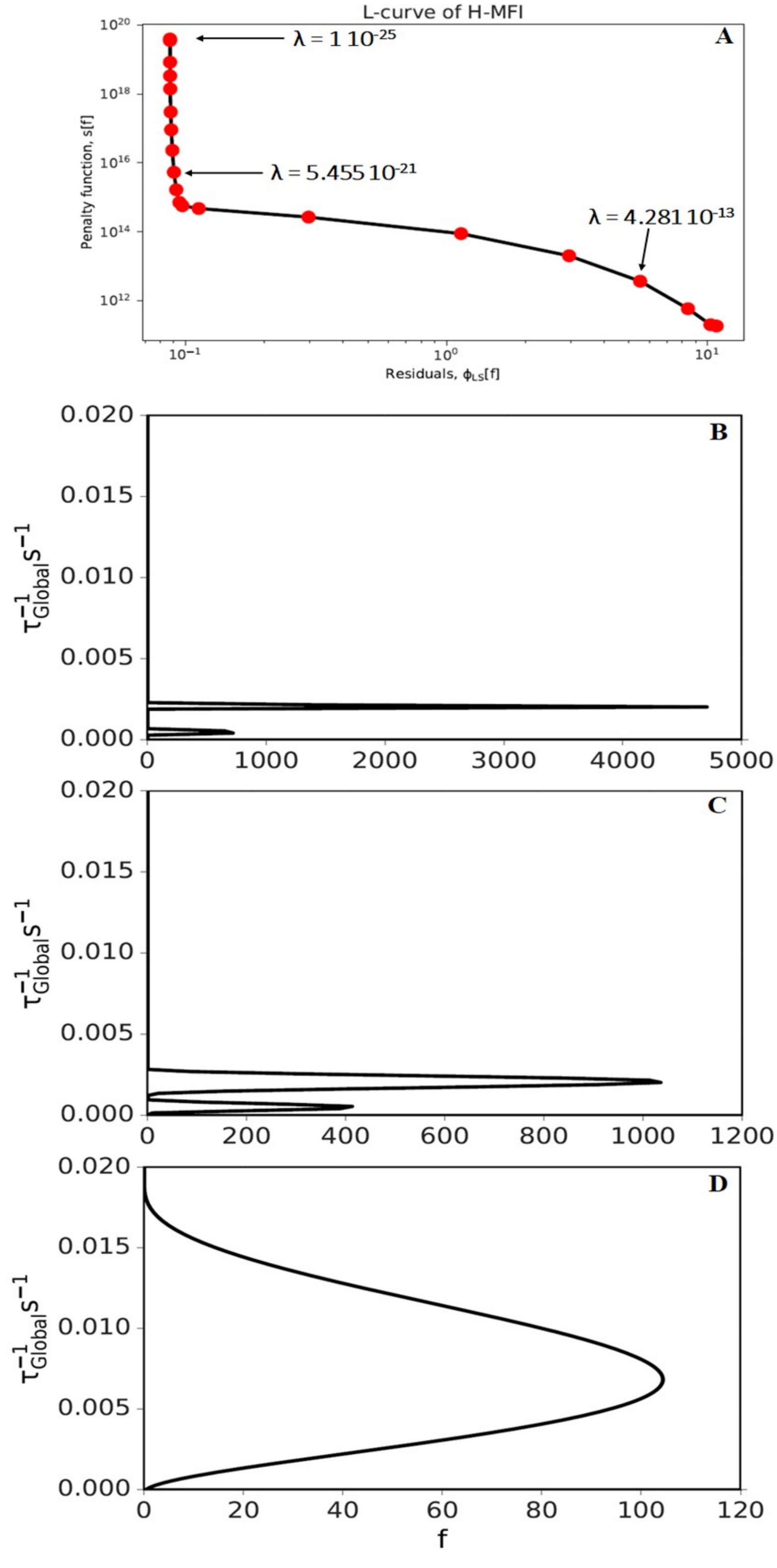

Figure S3. L-curve plot for determining the optimum choice of regularization parameter λ, (B, C and D): 1D distribution function $f(\upsilon)$ obtained by inversion gravimetric uptake for $\lambda = 1\ 10^{-25}$ (B), $\lambda = 5.455\ 10^{-21}$ (C), and $\lambda = 4.281\ 10^{-13}$ (D).

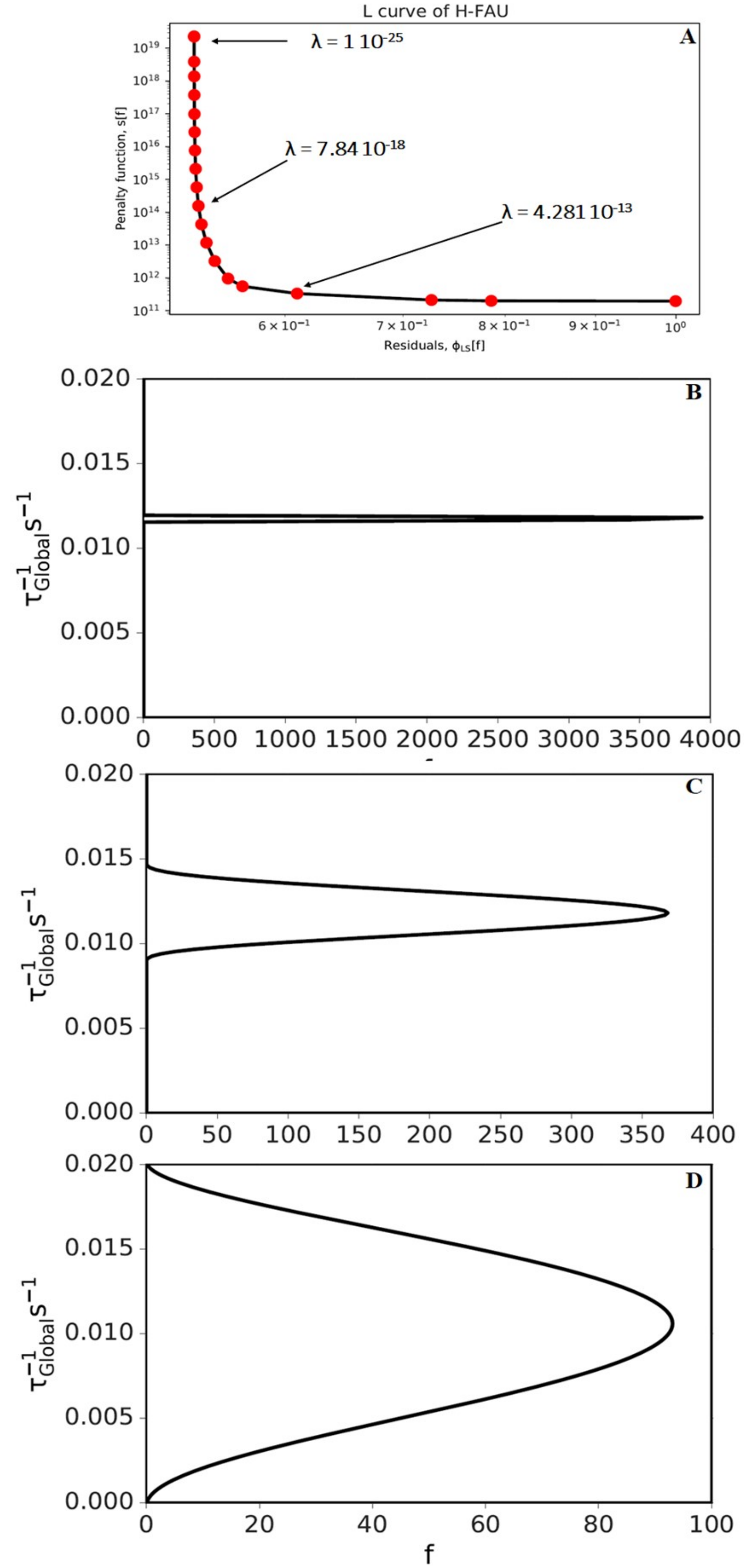

Figure S4. (A): L-curve plot for determining the optimum choice of regularization parameter λ, (B, C and D): 1D distribution function $f(\upsilon)$ obtained by inversion gravimetric uptake for $\lambda = 1\ 10^{-25}$ (B), $\lambda = 7.84\ 10^{-18}$ (C), and $\lambda = 4.281\ 10^{-13}$ (D).

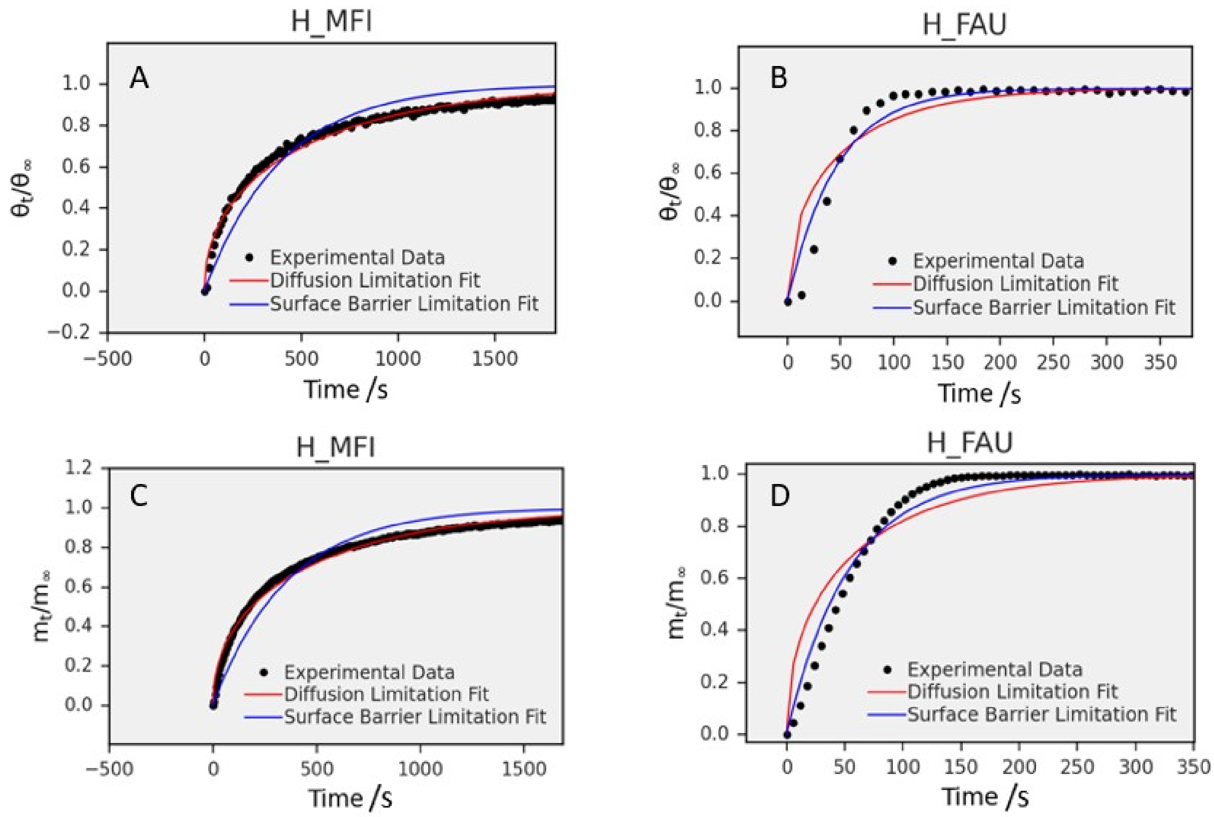

Figure S5. (A and C): Fractional coverage (black points) and relative uptake (black points) of H-MFI obtained by IR and gravimetric measurement, respectively , (B and D): Fractional coverage (black points) and relative uptake (black points) of H-FAU obtained by the same methods. The red and blue cures represent the fits of the diffusion-limited and surface-barrier-limited analytical expressions, respectively.

References:

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