Supplementary Information for

Direct Assessment of Molecular Transport in Mordenite: Dominance of Surface Resistances

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Experimental Section

Materials: Mordenite was synthesized by hydrothermal crystallization. In a typical synthesis, 1.72 g of $NaAlO_2$ (technical grade, Riedel de Häen) and 2.24 g of NaOH (Merck, > 99%) were added to 40 g of colloidal silica solution (Ludox Am30, Sigma-Aldrich). The resultant mixture was mortared for 10 min and aged at room temperature for 50 min. The gel was then transferred to a teflon-lined steel autoclave with a full capacity volume of 75 mL. The autoclave was heated in a preheated oven at 443 K under static condition for 4 d. The autoclave was afterwards quenched with tap water. The precipitated product was washed four times with batches of 200 mL of hot water (348~353 K). The powder product was filtered, dried at 333 K overnight, and calcined in static air at 823 K for 10 h (ramp 2 K/min). The as-synthesized mordenite was treated in 1.2 M NH_4NO_3 solution (1 g of mordenite / 100 g of solution) at 343 K for 7 hours. To avoid the attrition between the crystals, only the upper layer of the solution was gently stirred (100 rpm). The process was repeated 4 times. Thus obtained NH_4-form sample was converted to H-form by calcination at 723 K for 6 h. The H-form mordenite was converted back to Na-form by treating the sample in 1.2 M $NaNO_3$ solution (1 g of mordenite / 100 g of solution) at 343 K for 5 times, 1 hour for the first time, 7 hours for the rest. The sample was finally calcined at 823 K for 10 h (ramp 2 K/min), yielding the Na-form mordenite **NaMOR** used in this study. The sample showed a BET surface area of 325 m^2/g, micropore volume of 0.17 cm^3/g with negligible mesopore volume (nitrogen physisorption).

Diffusion measurements: TEOM measurements were performed using a Rupprecht & Pataschnick TEOM 1500 pulse mass analyzer. A LabView program was used to operate the set-up and record the results. A detailed description of the set-up is provided in Ref. 1. Na-form mordenite (~ 30 mg) was loaded in a 100 µL sample container and held between two layers of quartz wool. The sample was heated in a flow of N_2 (40 mL/min) at 393 K for 2 h and 623 K for 14 h, followed by cooling down to room temperature. *n*-Hexane was introduced by an ISCO 260D syringe pump with a flow rate of 5 µL/min and carried by nitrogen gas (80 mL/min) to flow through the sample bed. The total pressure was maintained at 1.3 bar during the measurement.

Infrared Microscope measurements were performed using a Bruker Hyperion 3000 consisting of a spectrometer Bruker Vertex 80v and a microscope with a Focal Plane Array detector. The FPA detector consists of an array of 128 × 128 single detectors with a size of 40 µm × 40 µm each. By means of a 15x objective, a resolution of 2.7 µm × 2.7 µm was realized in the focal plane. The beam is focused with a maximum beam width of 23.5 °. Each single detector of the FPA records an IR signal. For one scan, 16384 spectra were recorded. The intensity of the IR light as a function of the wavelength, *i.e.*, the transmission spectrum, is determined by means of the spectrometer by using Fourier transformation. The integrals under characteristic absorbance bands of the guest molecules in these spectra were assumed to be proportional to the integrals of the local concentration in the direction of the IR beam. A detailed description can be found in Ref. 2. The mordenite sample was loaded in an optical cell and evacuated at 673 K (ramp 0.5 K/min) for 6 h and cooled down to room temperature. After selecting a crystal, the uptake measurement was initiated by introducing *n*-hexane with a pressure of 0.037 mbar. The measurement of IR spectra and thus the local concentrations at different acquisition times allowed us to plot the overall uptake curve for the chosen crystal. The integrals were calculated as area under the band in the region 3060 – 2850 cm^{-1}, enclosed by a straight baseline from 3130 – 2750 cm^{-1}.

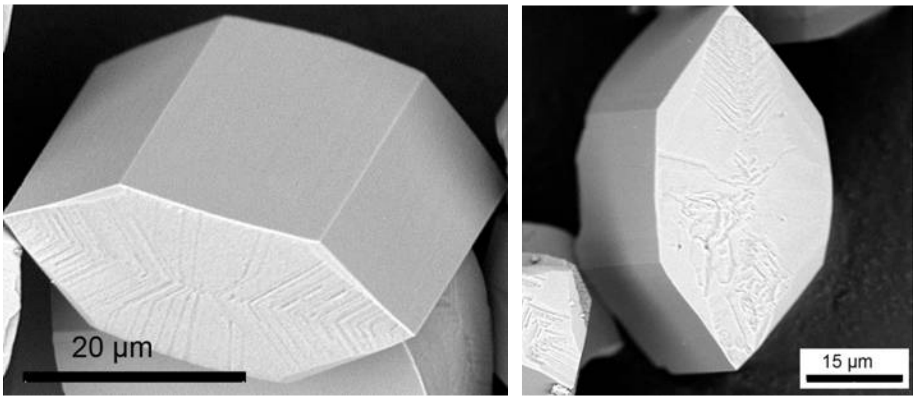

Fig. S1. SEM images of the mordenite crystals.

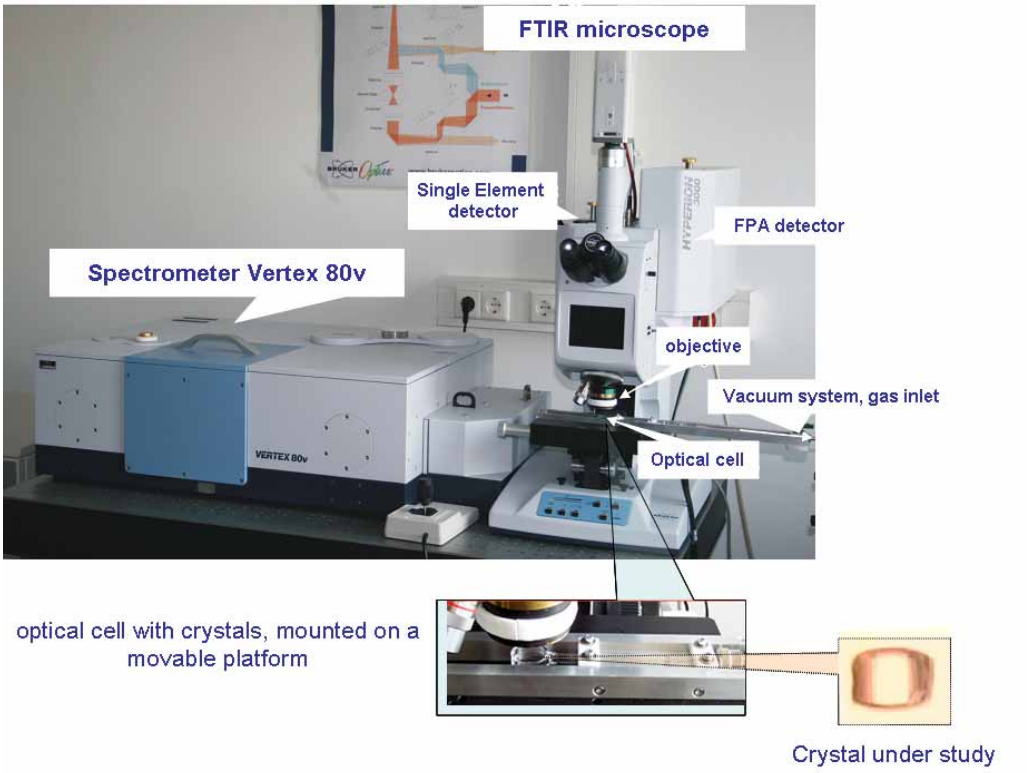

Fig. S2. Photograph of the IR micro-imaging Bruker Hyperion 3000, which consists of a spectrometer Bruker Vertex 80v and a microscope with a Focal Plane Array (FPA) detector.

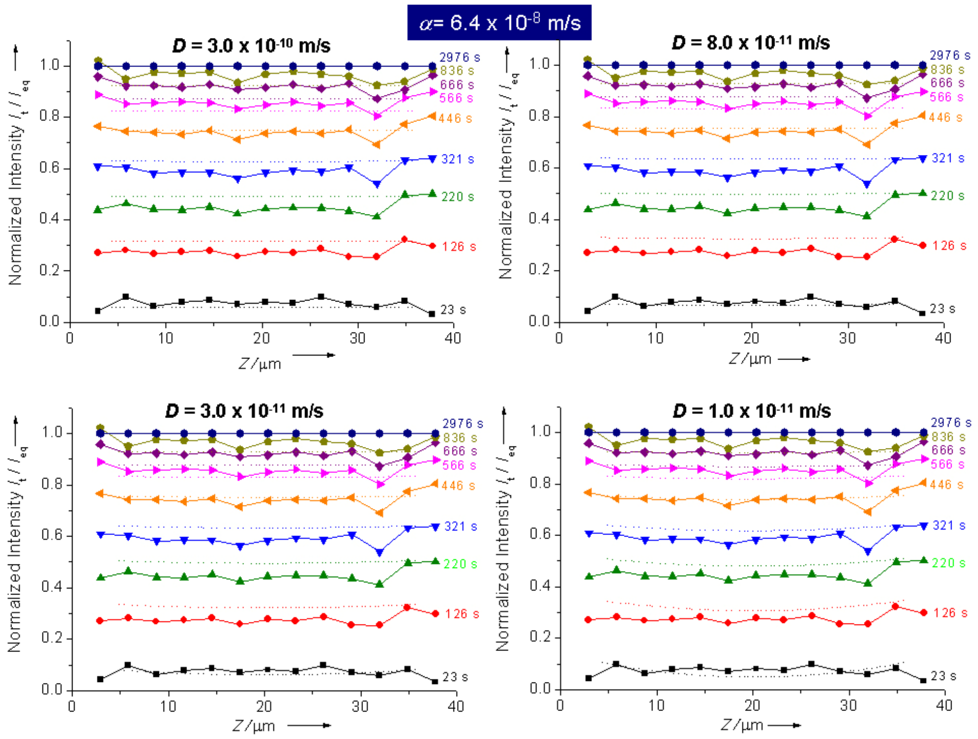

Fig. S3. Experimental concentration profiles and the calculated profiles (dot lines) of *n*-hexane on **NaMOR** assuming a constant surface permeability *α* of 6.4×10^{-8} m/s with different diffusivity *D* values.

Note: Assuming a constant transport diffusivity *D* and a constant surface permeability during the uptake process, the normalized concentration profile within a host particle of length 2*l* is given by the relation [3]

$$c(z,t) = 1 - \sum_{n=1}^{\infty} \frac{2L\cos(\beta_n z/l)\cdot\exp(-\beta_n D t/l^2)}{(\beta_n{}^2 + L^2 + L)\cdot\cos\beta_n}, \qquad (1)$$

wherein the β_ns are the positive roots of

$$L \equiv \frac{l\alpha}{D} = \beta_n \tan\beta_n,$$

c(*z*,*t*) is the concentration of sorbates at time *t* and position *z* along the diffusion pathway, and *l* is the diffusion length, *D* is the intracrystalline diffusivity, *α* is the surface permeability. Since the infrared absorbance intensity is expected to be proportional to the concentration of *n*-hexane adsorbed on the crystal, the normalized intensity to that at equilibrium I_t/I_{eq} is assumed to be equal to the normalized concentration c_t/c_{eq}.

Neglecting the concentration dependencies of the transport parameters allows a rough estimation. Assuming the process is controlled by surface barrier, *α* was estimated to be 6.4×10^{-8} m/s just by fitting the concentration profiles using equation (1) and fixing the *D* to a certain value. Following such a procedure, from the flatness of the calculated profiles the intracrystalline diffusivity can be estimated to be higher than 3.0×10^{-11} m^2/s.

For a more accurate estimation, which takes the influence of the loading dependence into account, the diffusion equation has to be solved numerically. However, one would have to make assumptions about the loading dependence of the diffusivity, since this information can't be obtained from such flat profiles. Therefore, the accuracy of such an advanced analysis wouldn't increase the accuracy of such an estimation substantially.

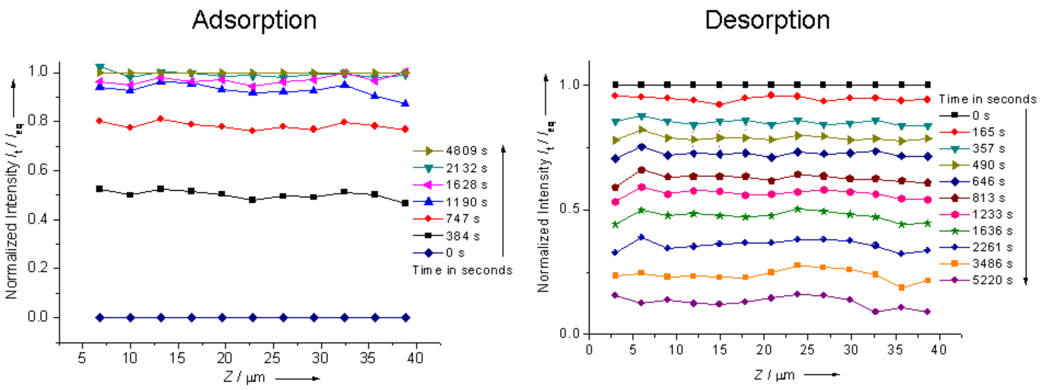

Fig. S4. Concentration profiles of ethane on **NaMOR** during adsorption and desorption.

Note: Before the measurement, the sample was activated at room temperature under vacuum for 1.5 h, and then heated to 673 K with a ramp of 0.2 K/min and kept there for 8 h, then cooled to room temperature in ~1.5 h under vacuum. Pressure step of ethane: 0–116.6 mbar. Desorption was initiated by evacuation of the measurement cell.

Flat profiles were observed for adsorption as well as desorption of ethane on **Na-MOR**, indicating in both cases, passing the surface barrier is the rate-determining step. A simple quantitative analysis is possible based on the time constant of molecular uptake, as represented by the first statistical moment of the uptake curve (see equation 1 of the main paper):

$$\tau = \int_0^\infty \left[1 - m(t)/m_{\mathrm{eq}}\right] \mathrm{d}t \tag{2}$$

The uptake curves can be obtained from the transient uptake profiles by simple integration. The corresponding crystals half-width (half channel length *l*) was 23 µm. Following such a procedure, the time constants were determined to be 750 s for adsorption, and 2000 s for desorption. For similar loading steps, a faster adsorption is usually expected, if the surface permeability increases with increasing loading. This finding is in good agreement with the results for *n*-hexane (see **Fig. S5**).

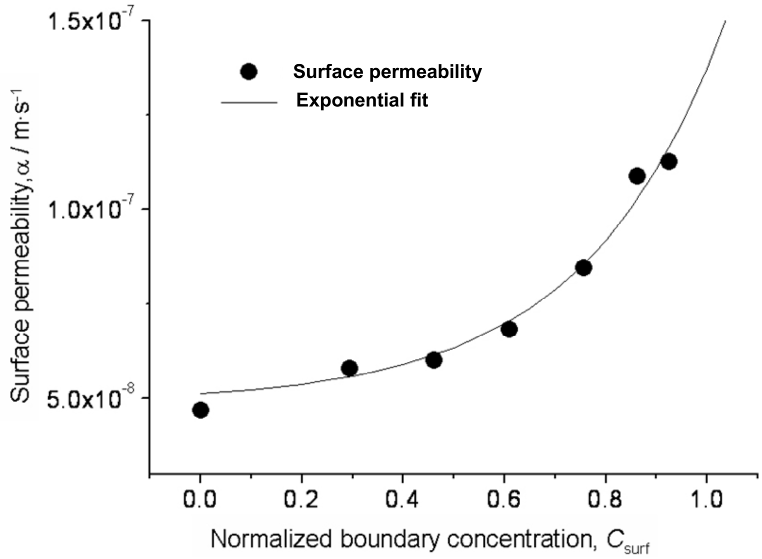

Fig. S5. Loading dependence of the surface permeability determined from IRM data for *n*-hexane uptake with the pressure step 0 – 0.037 mbar. The normalized boundary concentration c_{surf} corresponds to m_t for surface barrier limited uptake processes.

Note: The experimental conditions are identical to that of Fig. 3 in the main paper. Fig. S4 displays the surface permeabilities, calculated, via:

$$j_{\text{surf}} = \alpha \cdot \left(c(z = 0, t) - c_{\infty} \right), \qquad (2)$$

(see equation 2 in the main paper) for each individual time interval $t_{i+1} - t_i$ between the instants t_i of time during which the profiles have been recorded. Here, the fluxes through the surface simply result as (one half of) the area between subsequent profiles divided by the corresponding time interval. The permeabilities are plotted as a function of the relative loading at the end of each individual time interval. The observed dependence (increase with increasing loading) follows the trend of a recent in-depth study of the surface permeability of *n*-alkanes in Zn(tbip) metal-organic framework.[4]

References:

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