Direct quantification of surface barriers in nanoporous materials

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Successful design and application of nanoporous materials are essentially dependent on the molecular diffusion. Two mechanisms, *i.e.* surface barriers and intracrystalline diffusion, may dominate the mass transport. In the previous studies, these two mechanisms are difficult to determine with certainty by dual resistance model [1] (DRM). Here, we derive an expression of uptake rate relying solely on surface permeability, which provides a method to directly quantify the surface barriers. Subsequently, the effects of surface barriers and intracrystalline diffusion could be identified separately.

We derived that for sufficiently small time the relative uptake loading m_t/m_∞ can be described by [2]

$$\frac{m_t}{m_\infty}\Big|^{\sqrt{t}\to 0} \cong \frac{\alpha}{l}\left(\sqrt{t}\right)^2 + O\left(\sqrt{t}^3\right) \qquad (1)$$

where α is the surface permeability, t the uptake time, l the characteristic length of materials.

As shown in Fig. 1a, it is commonly accepted that *S*-shapes of uptake curves were found, and some attributed this to the effect of surface barriers. Eq. (1) can be applied to determine surface permeability α by use of initial uptake data. Then the intracrystalline diffusivity D can be obtained by fitting the whole uptake rate data with DRM. Compared to the method based on DRM with both D and α as free parameters, this approach can significantly reduce the uncertainty of the fitting results.

As can be seen from Fig.1b, the effective diffusivities measured by three macro-methods span over two orders of magnitude. After decoupling the surface barriers from overall mass transfer by Eq. (1), the intracrystalline (transport) diffusivity of methanol in SAPO-34 shows surprising consistence.

The surface barriers and intracrystalline diffusion in SAPO-34 with different crystal size and Si content were quantified, which is shown in Fig. 1c. It is found that the effective diffusivity deviates by two orders of magnitude. After decoupling the surface barriers by Eq. (1), the derived intracrystalline diffusivity is almost invariant with the changes of crystal size. Furthermore, the surface permeability shows a strong acidity-dependence, which is consistent with the observation in [3].

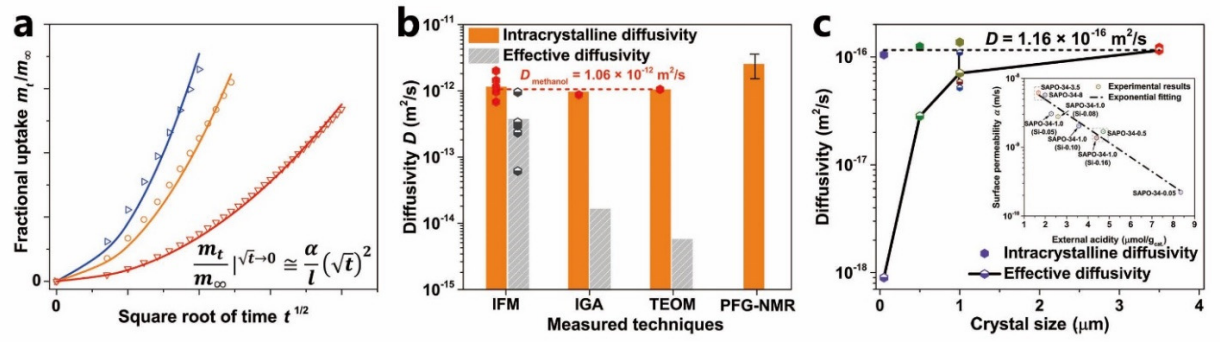

Figure 1: (a) By use of Eq. (1), the surface permeability can be directly quantified from the initial uptake rate data. (b) Diffusion of methanol in SAPO-34 under low molecular loading at 303 K. (c) Uptake of propane over SAPO-34 with different crystal size and Si content at 313 K.

References

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