

INVESTIGATION OF ENHANCED MASS TRANSPORT AND SURFACE BARRIER IN HIERARCHICAL ZEOLITES

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Introduction

Due to its molecular sieving ability, microporous materials have been extensively used in industrial catalysis, separation, adsorption and ion-exchange. Unique micropore structures (pore size ranging from 0.5 to 2 nm) may, however, also present significant difficulties for molecules accessing catalytic active sites located within the micropores due to the slow intracrystalline mass transport in micropore channels. By restricting their effectiveness, activity, selectivity and lifetime, it is well known that diffusion limitations may substantially limit the industrial utilization of these materials in catalysis and adsorption. Introducing secondary mesopores into the intrinsic microporous structures can increase the number of accessible surfaces and reduce the characteristic diffusion length, thereby leading to enhanced catalytic performance.

In the past decade, zeolite catalysts with secondary mesoporous structure, known as hierarchical zeolites, have been synthesized by various methods including soft templating method using organic surfactants, hard templating method using mesoporous carbon and desilication/dealumination method. Hierarchical zeolites with both ordered and disordered mesopores or single nanosheet structures have been tested with a large variety of catalytic reactions. Enhanced catalytic activity, selectivity and catalyst lifetime are often attributed to the reduced diffusion limitation or improved mass transport without providing direct evidence from diffusion measurements. It is worth noting that external surface acid sites and connectivity of mesopores in hierarchical zeolites can also significantly contribute to the catalytic performance of zeolite catalysts. Previous study has also shown that the presence of mesoporosity does not necessarily lead to improved catalytic performance.¹ Therefore, in order to evaluate the benefits derived from mesoporosity, it is necessary to characterize the mass transport behavior by directly measuring molecular diffusivity within hierarchical zeolites and correlate it to the mesopore structures of hierarchical zeolites generated by different synthesis methods.

Despite decades of study on diffusion in zeolites, characterization of diffusion in microporous materials remains a challenging. In general, macroscopic methods that measure the apparent/transport diffusivity (e.g. zero length chromatography, gravimetric, frequency response, interference microscopy) predict diffusivities that are orders of magnitude less than those that measure on a microscopic scale (e.g. quasi elastic neutron scattering, pulsed field gradient-nuclear magnetic resonance), which measure the tracer/self diffusivity. It is proposed that discrepancies in apparent diffusivity result from the variation of length scales between the techniques, with the microscopic methods often measuring over just a few lattice cells.

In this work, firstly the diffusion behavior of cyclohexane in pure silica self pillared pentasil (SPP, sheet thickness ~ 2 nm) and three dimensionally ordered imprinted (3DOM-i) silicalite-1 crystal with a primary particle size of 35 nm were studied and compared to conventional silicalite-1 crystals with varying particle sizes. Diffusional time constants were measured and correlated to characteristic diffusion length providing a simple and direct way to

demonstrate the enhanced molecular transport properties of hierarchical zeolites.² Secondly, we aim to characterize the potential second transport limitation within zeolites by carefully controlling diffusional length scales and measuring the temperature-activated apparent diffusion coefficients.³

Experimental

Material syntheses Pure silica self-pillared pentasil (SPP) zeolite was synthesized according to Zhang et al.⁴ 3DOM-i silicalite-1 was synthesized using a hard template method reported in our previous work.⁵ Conventional silicalite-1 of different particle sizes ranging from 80 nm to 1 μm were synthesized based on published work.⁶ 20 μm silicalite-1 was made according to Gueudré et al.⁷

Diffusion measurements and data analyses Among the available measurement techniques, the zero length column (ZLC) method, developed by Eic and Ruthven, can rapidly measure the intracrystalline diffusivity through microporous materials by monitoring the desorption profile from a previously equilibrated sample.⁸ All gas flow rates were controlled with Brooks 5850E mass flow controllers. Cyclohexane with partial pressure of ~ 2 Torr (>99%, Acros Organics) was maintained by equilibrating a low flow helium stream with a liquid cyclohexane reservoir at 283 K. Transfer lines were maintained at 363 K to eliminate condensation in the tubing. The data were analyzed using linear ZLC analysis of desorption curves developed by Eic and Ruthven using the following equation at long time region in desorption curves

$$\frac{C}{C_0} = \frac{2L}{\beta_1^2 + L(L-1)} \exp\left(-\beta_1^2 \frac{D_{\text{eff}}}{R^2} t\right)$$

where D_{eff} is the effective diffusivity, R is the particle radius, C is the gas phase adsorbate concentration and C_0 is the initial gas phase adsorbate concentration in the effluent. β_1 is the root of

$$\beta_1 \cot \beta_1 + L - 1 = 0$$

and L is

$$L = \frac{1}{3} \frac{FR^2}{KV_s D_{\text{eff}}}$$

where F is the purge flow rate, K is the Henry's law constant, V_s is the adsorbent volume.

Results and Discussion

Figure 1 shows representative SEM image of SPP, 3DOM-i, 200 nm and 20 μm silicalite-1 crystals. As shown in the image, SPP presents mesoporosity created from the "house of card" configuration of the nanosheets. 3DOM-i silicalite-1 reveals highly ordered face center cubic packing of the spherical crystals (diameter ~ 35 nm) with the mesopores formed from the interstices of the spheres. 200

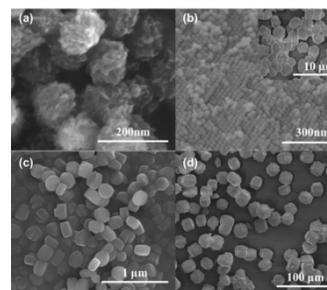


Figure 1. Representative SEM images for (a) SPP, (b) 3DOM-i, (c) 200 nm, and (d) 20 μm silicalite-1 crystals.

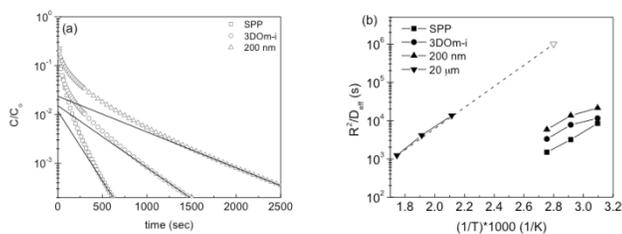


Figure 2. (a) ZLC desorption curves of cyclohexane in SPP, 3DOM-i, and 200 nm silicalite-1 at 363 K. Symbols represent experimental data, and solid lines are the fitted curves. (b) Summary of the effective diffusional time constants (R^2/D_{eff}) obtained from ZLC analysis for silicalite-1 crystals. Data for 20 μm crystal at 363K ($1000/T = 2.75$; open symbol) is determined from the extrapolation of the existing data collected at higher temperatures using an Arrhenius equation for comparison.

nm and 20 μm silicalite-1 crystals synthesized in this study are faceted and monodisperse with typical crystal morphology for large siliceous MFI. In these two samples, no mesoporosity is observed within the particles, which is confirmed by N_2 sorption experiments.

Figure 2 shows the experimental curves and summary of effective diffusional time constants for SPP, 3DOM-i, and 200 nm silicalite-1 at various temperatures. It is apparent that the slope of the long time region is steeper in SPP case, followed by 3DOM-i and 200 nm samples (Figure 2a), which indicates faster cyclohexane desorption from SPP. Compared to large crystals (from the Arrhenius plot in Figure 2b), the effective diffusional time constants are two orders of magnitude smaller for mesoporous/nanocrystalline silicalite-1 at 363 K (via extrapolation). The data clearly indicate that introduction of mesoporosity and formation of nanocrystalline can effectively shorten the diffusional length and improve the molecular transport of cyclohexane in silicalite-1. The data provide quantitative evidence for the enhancement of mass transport of cyclohexane in hierarchical systems.

However, it can be observed that the improvement of the diffusion is not as much as the length scale reduces, i.e., the effective diffusivities are much slower for SPP and 3DOM-i samples, indicating additional mass transport limitations (e.g. surface barriers) should be considered. Thus, for the first time, a complete set of silicalite-1 particles are synthesized with characteristic length scales varying across three orders of magnitude and apparent diffusivity is characterized for each particle, and the data are summarized in Figure

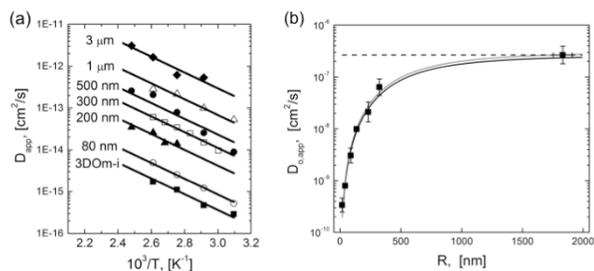


Figure 3. (a) Arrhenius plot for cyclohexane/silicate-1 systems (b) The pre-exponential to the apparent diffusivity (\blacksquare), is observed to decrease over orders of magnitude as particle size becomes smaller. Models for pore narrowing (—) and pore blockage (—) appear to fit the experimental data, while the kinetic surface desorption mechanism (---) does not.

3. It is expected the activation energy for the diffusion process would remain constant due to identical microporous structure in the crystals, and this is consistent with the data reported in Figure 3a. From mesoporous, nanocrystalline to 3 μm silicalite-1, the slopes in the Arrhenius plot are statistically equal, indicating a common transport mechanism through all particle sizes. Notably, the pre-exponential is vastly different and approaches to an asymptotical limit, as shown in Figure 3b, and it shows strong particle size dependency. Three models represent possible mechanisms (pore narrowing, pore blockage, and surface desorption) contributing to the surface barrier were considered and fit with experimental data (Figure 3b). It is found that surface pore narrowing and pore blockage models both agree with the data, while surface desorption does not. Analyses show that the “crust” in the pore narrowing case is estimated around 25 nm, and the additional diffusion length of 740 nm for pore blockage.

Conclusions

Enhancement of mass transport of cyclohexane in silicalite-1 has been demonstrated and quantified by using ZLC technique with SPP, 3DOM-i, 200 nm, and 20 μm silicalite-1 crystals. Diffusional time constant can be improved by two orders of magnitude when mesoporous/nanocrystalline zeolites are employed in contrast to bulk crystals. Discrepancies in effective diffusivity and its strong particle dependence were observed and studied via a set of silicalite-1 with characteristic length spanning three orders of magnitude, from 35 nm to 3 μm . It is concluded that transport control in small particles was likely due to either pore narrowing or additional diffusional path due to pore blockage at the surface of the crystals.

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References

- (1) Kortunov, P.; Vasenkov, S.; Kärger, J.; Valiullin, R.; Gottschalk, P.; Fé Elía, M.; Perez, M.; Stöcker, M.; Drescher, B.; McElhiney, G.; Berger, C.; Gläser, R.; Weitkamp, J., *J. Am. Chem. Soc.* **2005**, *127* (37), 13055-13059.
- (2) Chang, C.-C.; Teixeira, A. R.; Li, C.; Dauenhauer, P. J.; Fan, W., *Langmuir* **2013**, *29* (45), 13943-13950.
- (3) Teixeira, A. R.; Chang, C.-C.; Coogan, T.; Kendall, R.; Fan, W.; Dauenhauer, P. J., *J. Phys. Chem. C* **2013**, *117* (48), 25545-25555.
- (4) Zhang, X.; Liu, D.; Xu, D.; Asahina, S.; Cychosz, K. A.; Agrawal, K. V.; Al, W. Y.; Bhan, A.; Al, H. S.; Terasaki, O.; Thommes, M.; Tsapatsis, M., *Science* **2012**, *336*, 1684-1687.
- (5) Fan, W.; Snyder, M. A.; Kumar, S.; Lee, P. S.; Yoo, W. C.; McCormick, A. V.; Penn, R. L.; Stein, A.; Tsapatsis, M., *Nat. Mater.* **2008**, *7* (12), 984-991.
- (6) Watanabe, R.; Yokoi, T.; Tatsumi, T., *Journal of Colloid and Interface Science* **2011**, *356* (2), 434-441.
- (7) Gueudré, L.; Jolimaite, E.; Bats, N.; Dong, W., *Adsorption* **2010**, *16* (1-2), 17-27.
- (8) (a) Eić, M.; Ruthven, D. M., *Zeolites* **1988**, *8* (1), 40-45; (b) Brandani, S.; Ruthven, D. M., *Adsorption* **1996**, *2* (2), 133-143; (c) Brandani, S.; Ruthven, D. M., *Chem. Eng. Sci.* **1995**, *50* (13), 2055-2059.