COMMENTS

Comment on "Gas Diffusion and Microstructural Properties of Ordered Mesoporous Silica Fibers"

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In a recent paper, Alsyouri and Lin (AL)[1] analyzed the diffusion in ordered mesoporous silica fibers. Their work is highly interesting because it delivers diffusion data for a circularly ordered mesoporous system for the first time and derives conclusions on the nature of the diffusion and on the microstructural properties of the fibers. Especially, they conclude with a helical fiber structure with a high pitch.

However, besides the data on gas uptake, the authors use a widely accepted hypothesis on the properties of this mesoporous material for their conclusions. They assume that only the diffusion along the channels (AC) plays a role for the uptake phenomenon. There are, however, some strong indications for connections between the channels that would allow channel-to-channel (C2C) diffusion: (i) The calcination of the fibers, which can have a length of several millimeters, is going on easily (faster than 1 h) and we have never observed a dependence on the fiber length. This fact is difficult to understand if one assumes that the O_2 and the reaction products are diffusing in counter directions only along the nanochannels that are long and coiled around the axis. (ii) The adsorption and desorption of large dye molecules into these fibers has been observed microscopically in our laboratory and takes only a few minutes. The fibers increase or lose their color homogeneously; no indication of different dynamics at the fiber ends has been seen. (iii) The formation of stable carbon replicas is possible,[2] which is interpreted normally by the existence of connections between the carbon-filled channels.

The C2C connections would change the shape of the uptake curves only slightly, but their quantitative interpretation would lead to very different results. With negligible C2C diffusion, the problem can be described by a plane sheet model as in ref 1, whereas dominating C2C diffusion would lead to a transport problem in cylinder geometry. The mathematical expressions for the solutions are very similar and can be expressed as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{b}{q_n^2} \exp\left(-q_n^2 \frac{D_{\text{eff}}}{a^2} t\right) \quad (1)$$

with

$$b = 2,\ a = L,\ q_n = (n - 1/2)\pi \text{ for plane sheets} \quad (2)$$

$$b = 4,\ a = R,\ J_0(q_n) = 0 \text{ for cylinders} \quad (3)$$

$$b = 6,\ a = R,\ q_n = n\pi \text{ for spheres} \quad (4)$$

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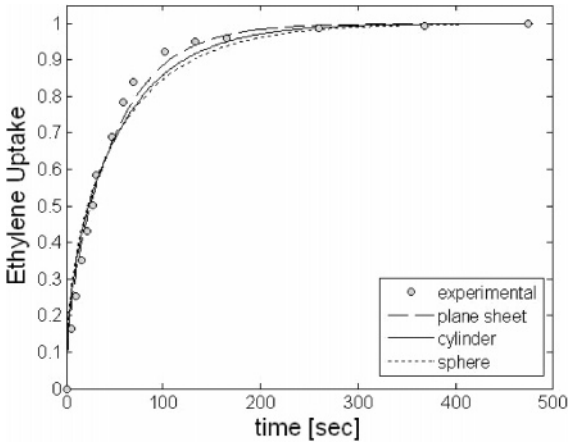

Figure 1. Experimental results of Alsyouri and Lin with three different theoretical interpretations. The curves are least-squares fits of eq 1 with five summands of the series.

TABLE 1: Diffusion Coefficients Deduced for the Two Relevant Models

gas	plane sheets	cylinders
CO_2	2.57×10^{-6} cm^2/s	5.33×10^{-9} cm^2/s
C_2H_2	3.28×10^{-6} cm^2/s	6.17×10^{-9} cm^2/s

Here, J_0 is the Bessel function of order zero, $n = 1, 2, 3, ..., L$ is the length of the fiber, and is R the radius of the fiber or sphere. Because the values of the q_n are rather similar for the three problems, D_{eff}/a^2 is decisive for the kinetics and determines the main diffusion direction of the molecules in the fiber. The solution for spheres is given for comparison and might also be useful to discuss the effects of competing diffusion directions in short fibers. Figure 1 shows the uptake curves measured by AL together with the fitting results of the three models.

All three models fit the experimental data quite well, although the fit of AL is the best one. However, there are also systematic deviations visible for all three fits. In the beginning and toward the end, the uptake is systematically overestimated, whereas an underestimation is visible for intermediate times (between 50 and 150 s). One may ascribe these misfits to the size distribution of the used fibers and to surface diffusion barriers. However, this explanation can be used for every one of the three models. Therefore, the best fitting of the plane sheet model is only a very weak argument in favor of this model.

Although the three models deliver similar uptake curves, the concluded diffusion coefficients differ by several orders of magnitude as shown in Table 1. The decisive reason for these deviations is the relevance of the two different lengths L and R. This results roughly in a factor of $(L/R)^2 = 170$ between the diffusion constants. Because of the arguments given in the beginning, we favor the values deduced from the cylinder model.

Furthermore, important consequences of the diffusion data to the fiber microstructure are given by AL. The authors conclude with a helical run of the channels with a pitch of 1.6 μm. However, this concluded high pitch seems to us not in line with the other information on the fiber structure independent of our above statement on the questionable diffusion coefficient

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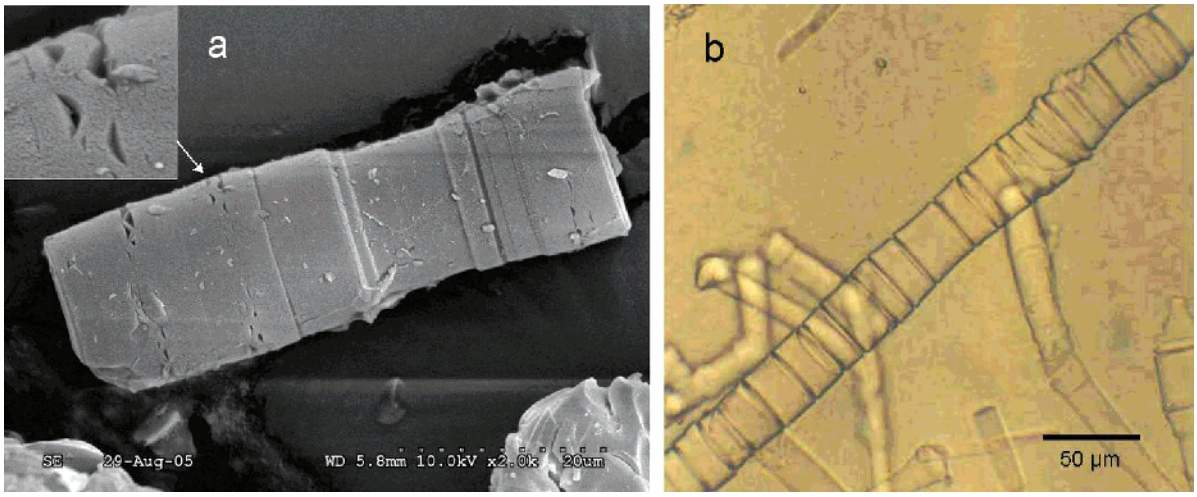

Figure 2. (a) SEM picture of a fiber piece leached 12 min in water. (b) Optical microscopy picture[4] of a calcined fiber.

used. (1) The shape of the fibers is mostly smooth but often also complicated and rotationally symmetric (Figure 2). Screw-like fibers are observed sometimes, however, with an extremely low percentage. (2) After calcination or leaching of the template, thick fibers can show cracks that are either rotationally symmetric or more complicated as shown in Figure 2. For these fibers, a screw-like internal structure (with a high pitch) is very unlikely. (3) In TEM pictures of thin fibers, the channel directions appear parallel at both fiber edges.[3] Our attempts to find fibers with different directions at both edges failed. The channel directions relative to each other can be determined by tilting experiments in TEM investigations with an accuracy of a few degrees.

The arguments (1−3) do not strictly exclude the consequences given in ref 1, but they are strong indications against them and, therefore, against the plane sheet model. However, these arguments support our suggestion of using the cylinder model for uptake data evolution. With this model, further conclusions concerning the explanation of the diffusion coefficient and the internal fiber structure are unfortunately not as nicely possible as in ref 1 because there is not much known about the nature and size of the channel-to-channel connections that allow the diffusion.

Summarizing, we think that one has to include the C2C diffusion in any case in the discussion of uptake measurements to avoid wrong conclusions. Arguments against the model of pure AC diffusion are the calcination behavior and the dye uptake/release; arguments against the structural conclusions of this model are the fiber shape, crack patterns, and TEM investigations. A way to decide finally which diffusion plays the dominating role (C2C or AC) can be a fiber-size-dependent experiment. The detected uptake times must scale with L^{-2} in the case of dominating AC diffusion and with R^{-2} in the case of dominating C2C diffusion. In the case of a dominating role of diffusion barriers at the surface, independence of size (L and R) can be expected.

References and Notes

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