Experimental verification of the crossover between the time-fractional and standard diffusion in a hierarchical porous material

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<u>Summary</u>. A transport process may cross over from the standard to anomalous diffusion. Herein, we experimentally verify the relevant changes of the diffusion regimes via an analysis of the diffusion concentration profiles in a hierarchically porous material. It is shown that at relatively short times the transport process experiences anomalous diffusion, whereas the standard Fickian diffusion is obeyed at relatively long times. The anomalous diffusion is described by the time-fractional diffusion equation with the superdiffusive anomalous diffusion exponent. The observed transitions seem to be associated with the transport in different components of a porous material.

Objectives

The transitions between the diffusion regimes in a porous medium are fairly typical. In a geometrically restricted environment, e. g. microchannels, an increase in the width of a channel governs the change of the diffusion regime from the single-file to the standard Fickian. This phenomenon has been experimentally verified for the transport process in single-wall carbon nanotubes [1]. Moreover, the analytic approaches for evaluation of the transition time have been established [2]. The effect of the pore size may not be the only reason for the diffusion regime transitions. The crossover between different diffusion regimes may also depend on the evolving time. The experimental investigation on the diffusion of silicon atoms in bulk germanium demonstrated the change in the diffusion kinetics from the anomalous superdiffusion to the standard Fickian versus observation time [3]. To this end, investigating the transport peculiarities through a porous material at various time scales is important for better understanding the fundamentals of the anomalous transport.

Linearized solutions of the standard and time-fractional diffusion equations

The experimental configuration is subjected to the following initial and boundary conditions: $C(x, 0) = C_0 = const$, $\partial C(0, t)/\partial x = 0$, $-D \cdot \partial C(L, t)/\partial x = \gamma \cdot C(L, t)$. The relevant linearized solutions of the standard and time-fractional diffusion equations, which are suitable for medium and long times, may be expressed as follows [4]:

$$\ln\left[\ln a - \ln\left[\frac{C(L,t)}{C_0}\right]\right] = \ln\left[\frac{D \cdot \pi^2}{4 \cdot L^2}\right] + \ln t \tag{1}$$

$$\ln\left[\frac{C(L,t)}{C_0}\right] = \ln\left[\frac{4 \cdot L^2 \cdot a}{\pi^2 \cdot K \cdot \Gamma[m-\alpha]}\right] - \alpha \cdot \ln t$$
⁽²⁾

Herein, *L* is the thickness of a solid porous particle, γ is the penetration coefficient, *D* and *K* are the standard and timefractional diffusion coefficients, respectively, *a* is a coefficient defined by the initial and boundary conditions, *a* is a fractional order, *m* is 1 for $0 < \alpha < 1$, and *m* is 2 for $1 < \alpha < 2$, $\Gamma(z)$ is the Euler gamma function. For the standard diffusion, the corresponding solution (eq. (1)) is linearized in the bi-logarithmic coordinates with slope that equals unity. In contrast, the solution of the time-fractional diffusion equation (eq. (2)) admits linearization in the logarithmic coordinates possessing the slope directly proportional to the time-fractional order. To this end, if the slope of the experimental data under the relevant bi-logarithmic transformations deviates from unity, the standard diffusion equation fails to describe the experimental transport kinetics.

Experimental procedure

To identify different transport regimes, a combined porous material with hierarchical porous structure was used. The used porous solid consisted of ZSM-5 zeolite and alumina with zeolite/alumina ratio equal to 1/1 by mass. The porous material was prepared using extrusion technique. The as-prepared porous material was characterized by the low-temperature nitrogen adsorption-desorption isotherm. The textural properties estimated from the isotherm data are as follows: BET surface area is 272 m²/g; pore volume is 0.22 cm³/g; BJH pore diameter is 3.9 nm; external surface area is 21 m²/g; micropore volume is 0.04 cm³/g; mesopores surface area is 177 m²/g. The X-ray diffraction revealed the presence of the crystalline phase relevant to ZSM-5 zeolite and γ -alumina. The latter demonstrated rather low amount of crystalline phase.

Methyl alcohol was utilized as a diffusing agent. The methanol transport through the porous solid material was studied using commercial LHM-72 gas chromatograph with the flame ionization detector equipped by the diffusion cell instead of the chromatograph column. The detailed description of the diffusion cell design, as well as the experimental procedure, may be found in our previous report [5]. The mass transfer was investigated under the following experimental conditions. The purge flow rate (argon) was 30 cm³/min; the temperature inside the diffusion cell was kept 120 °C. The methanol amount injected into the diffusion cell using the syringe for gas chromatography was 0.4 μ l. The thickness of the porous zeolite/alumina particle was 2 mm.

Results

Fig. 1a demonstrates the relative methanol concentration decaying in time obtained in the experiment. At relatively small times, i.e. $C(L, t)/C_0 < 0.30$, the standard diffusion equation fails to describe the experimental data because the experimental slope in the bi-logarithmic coordinates significantly deviate from unity (Fig. 1b). At these times, the time-fractional diffusion equation may be successively utilized (Fig. 1c). The decrease of the relative concentration at the starting point of the calculation from 0.30 to 0.15 results in the change of the diffusion regime from the time-fractional to the standard Fickian (Fig. 1d). Therefore, the transport process studied in the current paper exhibits the anomalous time-fractional diffusion at shorter time crossing over to the standard diffusion at a long time. This phenomenon may be associated with the fact that the standard diffusion equation admits the infinite propagation velocity, which is physically unreliable. To eliminate this issue, the Cattaneo-type diffusion equation has been proposed. The Cattaneo diffusion equation implies finite propagation velocity, which is recovered by introducing a relaxation time τ . The time-fractional Cattaneo diffusion equation is given by:

$$\tau^{\alpha} \cdot \frac{\partial^{\alpha+1}C}{\partial t^{\alpha+1}} + \frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2}$$
(3)

The relaxation time is individual for each diffusing substance and porous material. The higher is the crystallinity of a material, the lower is the relaxation time. The solid porous particle used in the present study consists of the two phases, particularly, the crystal phase of ZSM-5 zeolite and the partially amorphous phase of the alumina. To this end, the relaxation times may be different in different parts of the porous material, e.g. in the micropores of zeolite crystallites and the mesopores of the amorphous alumina matrix. In this respect, the diffusion in zeolite micropores seems to be characterized by smaller relaxation time compared to the diffusion in the alumina mesopores. The pores may be also formed by the cavities between the amorphous alumina globes and zeolite crystallites. In these pores, the relaxation time may be different from the relaxation times in either zeolite micropores or alumina mesopores.



Figure 1: Concentration evolution versus time (a), short time, i.e. $C/C_0 < 0.30$ (b) and (c), and longtime, i.e. $C/C_0 < 0.15$ (d) analysis

Conclusions

Investigation of the mass transfer in a hierarchically porous material consisting of crystalline and amorphous parts provides experimental evidence of the crossover between the anomalous diffusion at relatively short times and the standard diffusion at long times. The time-fractional diffusion equation is successively applied to describe the mass transfer kinetics at relatively short times. Unequal relaxation times in crystalline and amorphous parts of a combined porous material allows obeying either time-fractional or the normal diffusion behavior.

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