

SUPPLEMENTARY INFORMATION

Transport Properties of Hierarchical Micro-Mesoporous Materials

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1 Dynamic Monte Carlo simulations



Fig. 1 Lattice model used for modeling diffusion.

For the purpose of illustrating the computer simulations used in section 4, a cross-sectional cut through a bi-porous model system consisting of mesopores (white channels) and microporous domains (black squares) is presented in the top panel of Fig.1. As shown in the bottom panel, by zooming in, the model is comprised of a simple-cubic lattice. In order to study the transport behavior in the model systems with Dynamic Monte Carlo simulations, probe molecules were inserted. These molecules can only reside on the lattice nodes and are independent of each other, i.e. no specific mutual interactions are considered. Diffusion is simulated by jumps of the molecules between adjacent lattice nodes. The jump rates were determined by local (node-dependent) probabilities. In a three-dimensional random walk manner, molecules randomly choose an adjacent lattice node and attempt a jump, which is accepted with the corresponding local probability. When a jump attempt is rejected, the particle stays in its position. With the help of these local probabilities, the transport behavior in the meso- and microporous domains was modeled. Namely, the transport rate in the microporous space is adjusted by D_{micro} and the rate in the mesopores was determined by D_{meso} . Surface barriers affect inter-domain jumps and are adjusted by the two probabilities $P_{meso \to micro}$ and $P_{micro \to meso}$. The density ratio of the guest molecules between the meso- and microporous space depends on the net flux through the interface and can, thus, be controlled by the latter probabilities as well. A summary of the jump probabilities and densities used in the simulations can be found in Tab.1.

In order to simulate uptake dynamics, the initial model system was prepared in an empty state. Thereafter, molecules were created around the system mimicking a constant high density bulk environment. Due to diffusion simulated by the Dynamic Monte Carlo jumps, molecules entered the geometry until the equilibrium state was attained, i.e. the rate of incoming molecules becomes compensated by the rate of molecules leaving the system. By recording the relative density build-up in the system, the uptake curve and thus, the time constant of uptake and release were calculated (see Eq. (6)).

To carry out the flux simulations, the constant high density bulk environment was applied o one side of the empty geometry, while on the opposite side an empty environment with constant zero-density was considered. Thus, in the dynamics simulations molecules traverse the geometry from the high density to the low density side. After the initial build-up of a density gradient in the system, a steady state distribution of molecules and constant flux through the model was attained. The flux was measured by recording the rate of molecules arriving at the zero-density side using Eq. (14).

In the simulations mimicking catalytic conversion (the results presented in Fig. 23b), the scheme described in the preceding paragraph was used. Here, however, the reactant molecules were considered to be converted into the product ones if they stayed in the microporous space for at least ten consecutive Monte Carlo time steps (modeling, in this way, the reactivity in the micropore space). The effectiveness factor analogue in Fig. 23b shows the fraction of the microporous space containing in the steady state 99% of all reactant molecules. In the remaining space, thus, al-

#	1	2	3	4	5	6
Description	identical fluid densities			higher adsorption in micropores		
	fast D _{micro}	slow D _{micro}	surface barriers	fast D _{micro}	slow D _{micro}	surface barriers
Section	4.2.1	4.2.2	4.2.3	4.3	4.3	4.3
ρ_{micro}/ρ_{meso}	1	1	1	5	5	5
D_{micro}/D_{meso}	0.1	1×10^{-4}	0.1	0.1	1×10^{-4}	0.1
$P_{meso \rightarrow micro}/D_{meso}$	1	1	$1 imes 10^{-4}$	1	1	1×10^{-4}
$P_{micro \rightarrow meso}/D_{meso}$	1	1	1×10^{-4}	0.2	0.2	2×10^{-5}

Table 1 Specification of the parameters used in the simulations.

most no reactions take place (only 1% of the reactant molecules may approach this reagion without being converted).

In order to quantify the microscopic diffusivity D_{msd} , the mean square displacement averageds over an ensemble of molecules diffusing in the system at equilibrium conditions were recorded (see Eq. (8)). Periodic boundary conditions were applied to exclude the finite size effects.

Finally, the exact volume fractions of the mesoporous and the microporous space used in the studied model geometries from **A** to **D** are presented in Tab.2.

2 Fast and slow exchange regimes

As mentioned in section 4.1, the diffusion regimes of the guest molecules in the host material can be characterized by the relations (16) and (17). Tab.3 shows the relative time constants of uptake for the microporous domain τ_{micro}/τ for the simulations performed for geometries **A** to **D** (recall that this is not applicable in the case of the existing surface barriers). For the values lower than 1.0, molecular diffusion is found to be in the fast exchange regime, while for values higher than 1.0 the regime of slow ex-

change is attained.

Geometry	Α	В	С	D
V_{meso}/V_{total}	0.488	0.512	0.48	0.48
V _{micro} /V _{total}	0.512	0.488	0.52	0.52

Table 2 Volume fractions of the mesoporous and microporous domains.

Geometry	Α	В	С	D
$ au_{micro}/ au$				
1	0.12	0.03	0.36	0.18
2	101.41	0.06	322.67	0.22
4	0.06	0.03	0.16	0.22
5	33.82	0.10	105.67	0.32

Table 3 Relative time constants of uptake for the microporous domain. The numbers in the most left column indicate the different parameter sets used in the simulations as shown in the top raw of Tab.1.