

Selective diffusion of small hydrocarbons through acidic zeolites with 8-membered rings

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Acidic zeolites are nanoporous frameworks that serve as efficient catalysts in the methanol-to-olefin (MTO) process [1]. Product selectivity not only depends on the intrinsic rates in the complex reaction network, but also on the mobility of the compounds. The pore size is a key factor for diffusion of MTO intermediates and products through the zeolite channels [2]. During the conversion process, coke formation clutters up the pores of the framework with bulky aromatic compounds that are unable to diffuse, and which may hinder diffusion of ethene. For example in H-SAPO-34, an extensively studied 8-membered ring zeotype catalyst, product selectivity increases with time on stream due to product shape selectivity, which changes with the degree of pore clogging [3].

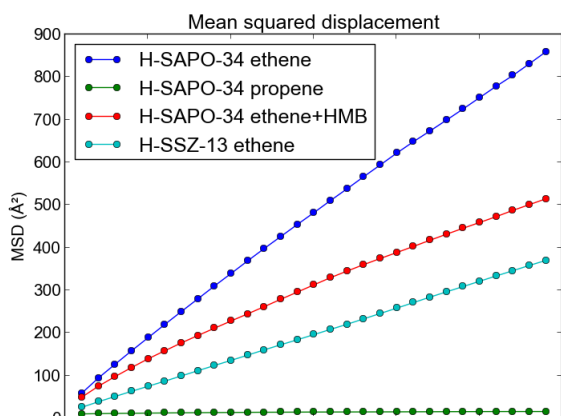


Figure 1 MSD of products at 300K in CHA topology with composition H-SSZ-13 or H-SAPO-34. Hexamethylbenzene (HMB) hampers mobility.

We use molecular dynamics simulations to model ethene and propene diffusion, two major products of the MTO process, in acidic zeolites with the CHA, AFX, and AEI topology. The diameter of the 8-membered rings in the zeolites resembles the size of ethene and propene, such that 'sieving' through these tight-fitting rings is expected to affect selectivity. Diffusion is also modeled in the presence of MTO intermediates inside the cages to investigate the effect of partially blocked channels.

The trajectories show that diffusion of the small guest molecules is essentially a discrete hopping process between the cages through the ring windows. While ethene diffuses freely across the porous networks, the mobility of propene is severely hampered (Figure 1). Not surprisingly,

diffusion is significantly slower in presence of bulky MTO intermediates. Furthermore, diffusion depends strongly on framework topology and chemical composition.

The effect of *temperature* on diffusion is usually seen as an Arrhenius law with a diffusion activation energy. Our structural analysis of all individual rings clearly shows that temperature may also induce framework distortion giving inhomogeneous ring properties. Topologically equivalent rings not necessarily have equal diameters, and individual ring hopping rates vary over two orders of magnitude. Consequently, these zeolites are not simply a set of connected 8-membered rings, and their flexibility gives a strongly anisotropic diffusion tensor at finite temperatures.

References:

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