Molecular Simulation of CO$_2$ and N$_2$ Transport in ZSM-5 Zeolite Membranes with Framework Substitutions

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1. Introduction

Zeolites are crystalline aluminosilicates with an ordered network of micropores. Their uses include membrane separations, catalysis, and sequestration. The zeolite ZSM-5 contains a regular array of straight channels in the $y$-direction, and zigzag channels in the $x$-$z$ plane. The pores have a diameter of $\sim$5.5 Å. The zeolite lattice has a nominal composition of SiO$_2$ but the Si atoms can be replaced by Al atoms, along with extra framework cations, such as Na$^+$, to maintain charge balance.

One possible application of ZSM-5 is the membrane separation of CO$_2$ from flue gases. The molecules CO$_2$ and N$_2$ have different kinetic diameters and a different affinity for the zeolite surface. Therefore, they adsorb into and diffuse through the zeolite pores at different rates, which allow them to be separated in a membrane operation. We considered the cases of 0 and 1 Al substitution of Si in the ZSM-5 unit cell to study the role of heterogeneity. In practice, the concentration of the cation (that accompanies the Al) is a property that can be controlled via ion exchange to tune the adsorptive and diffusive properties of molecules in ZSM-5. Both molecules, but especially CO$_2$, have a strong quadrupolar electrostatic interaction with the Na$^+$ cation.

2. Methodology and Results

We have used molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) simulations of CO$_2$ and N$_2$ diffusing in ZSM-5, with some of the Si atoms substituted by Al$^+$ and Na$^+$ counterions. The MD simulations were run for 20-26 ns at $T = 200$, 300 and 400 K. Diffusivities and residence times around preferred sites were calculated from the simulated trajectories. The diffusivity of CO$_2$ is of the order of $10^{-6}$ - $10^{-5}$ cm$^2$/s, while the diffusivity of N$_2$ is of the order of $10^{-5}$ - $10^{-4}$ cm$^2$/s. The diffusivities of CO$_2$ at $T = 200$ and 300 K are presented in Figure 1. The Na$^+$ causes an increase in the diffusivity at low loading, until crowding effects cause a decrease.

The activation barrier for CO$_2$ strongly increases due to the presence of Na$^+$, with the diffusivity of CO$_2$ showing a maximum. GCMC simulations were used to determine the adsorption isotherms, showing a substantial increase of CO$_2$ loading with Na$^+$ content. Though the N$_2$ molecules are more mobile, they adsorb less strongly than CO$_2$.

To cope with the broad range of time and length scales of membrane transport, we use...
dynamic Monte-Carlo simulations and mean-field theory of diffusion on a site lattice model representing the pore network topology. These coarse-grained simulations make use of the residence times on the sites and the adsorption isotherms calculated using the just described atomistic models. This multi-scale approach allows a calculation of the selectivity of CO₂ over N₂ and the throughput of a membrane.

3. Conclusions

Heterogeneity plays an important role in activated diffusion. The residence times and diffusivities indicate that Na⁺ cations can dramatically affect the behavior of CO₂ and N₂ molecules, allowing for a more rational basis for membrane design and operation.

Figure 1 – The corrected and self diffusivities of CO₂ at T = 200 and 300 K in ZSM-5 with 0 and 1 Al atom per unit cell. The blue (red) curves refer to T = 300 (200) K. The triangles (squares) for each T refer to 0 (1) Al atom per unit cell. The solid (hollow) symbols refer to corrected (self) diffusivities. The hollow circles are the analogous equimolar binary mixture self-diffusivities (at the pure CO₂ loading).