diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Molecular Simulation of CO_2 and N_2 Transport in ZSM-5 Zeolite Membranes with Framework Substitutions

David Newsome, Ton Dammers, Marc-Olivier Coppens

Department of Chemical Engineering, Delft University of Technology, Delft, the Netherlands
Howard P. Isermann Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York, USA
E-mail: D.A.Newsome@tudelft.nl

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 ~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 CO_2 over N_2 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 CO_2 and N_2 molecules, allowing for a more rational basis for membrane design and operation.

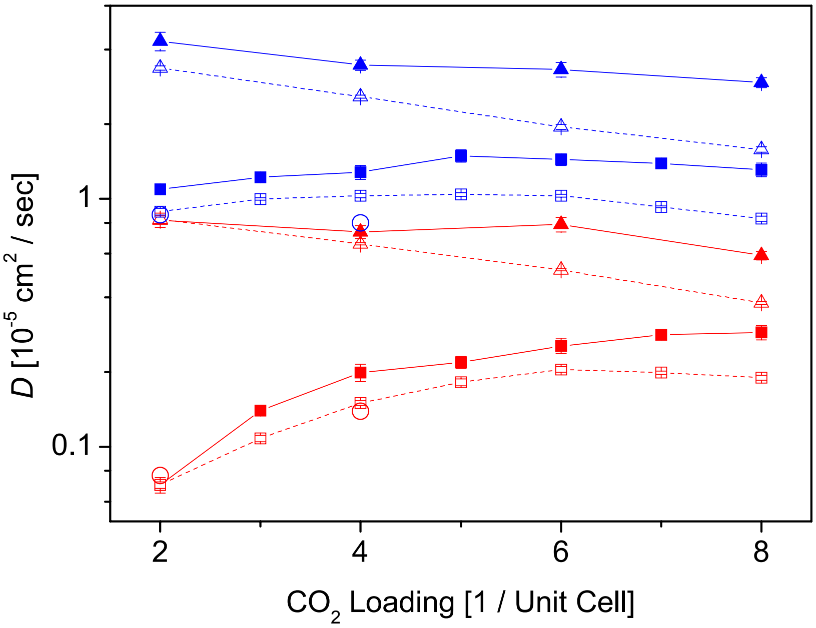

Figure 1 – The corrected and self diffusivities of CO_2 at T = 200 and 300 K in ZSM-5 with 0 and 1 Al atom per unit cell. The blue (red) curves refer to T = 300 (200) K. The triangles (squares) for each T refer to 0 (1) Al atom per unit cell. The solid (hollow) symbols refer to corrected (self) diffusivities. The hollow circles are the analogous equimolar binary mixture self-diffusivities (at the pure CO_2 loading).