Designing nanostructured membranes for selective oxidation: A mass transport modeling approach

Simón E. Albo, Linda J. Broadbelt and Randall Q. Snurr*
Department of Chemical and Biological Engineering and Institute for Catalysis in Energy Processes, Northwestern University, Evanston, IL 60208 USA
*snurr@northwestern.edu

Introduction

The combination of anodic aluminum oxidation (AAO) and atomic layer deposition (ALD) offers a pathway to obtain nanostructured membranes with tailored uniform cylindrical pore geometry and wall composition [1]. Here we focus on developing and applying different modeling tools to study mass transport and selective catalytic oxidation inside these membranes. The main goal is to propose the optimum membrane architecture to maximize a desired product in a reacting system.

Models

The contribution of the possible mass transport mechanisms in pores with diameters between 10 and 150 nm was assessed using a combination of techniques [2]. First, analytical expressions for convection, molecular diffusion and Knudsen diffusion were employed. Then, molecular dynamics (MD) simulations were performed to determine the role of surface diffusion. Lastly, we performed Knudsen dynamics simulations, which are based on the principles of Knudsen diffusion: no interaction among particles and diffusive collisions between particles and the pore wall. This model is less computationally expensive than molecular dynamics and allows simulation of longer pore lengths and timescales than MD while maintaining a level of detail that provides information regarding the residence times of particles in the membranes and the contact between particles and the pore walls. The residence times along with the number and location of hits on the wall can be obtained for cylindrical pores of uniform and variable diameter. These are useful concepts for choosing the best pore dimensions to increase conversion and selectivity while avoiding over-oxidation. The model is being expanded to include oxidation reactions as stochastic events when the particles are in contact with the catalyst on the pore walls.

Results and Discussion

The analytical expressions for convection, molecular and Knudsen diffusion were evaluated at 700 K and atmospheric pressure. A comparison of their contributions to the total mass transport showed that diffusion dominates over convection, with Knudsen diffusion being the dominating mechanism. This trend is accentuated in the smaller pores and at lower pressures. The results from the MD simulations showed that surface diffusion is only present at lower temperatures and is negligible at the conditions of interest here.

The Knudsen dynamics simulations highlighted that the transmission probability (fraction of particles entering the pore at one end and exiting at the opposite end without going back to the initial side) should be considered when designing and operating these membranes for catalysis. The transmission probability is a function of the aspect ratio (pore length/pore diameter) of the pore, and for a typical pore with an aspect ratio of 10^3 this quantity is on the order of 10^{-3}, indicating that a particle must enter the pore many times before it can reach the opposite end. The trajectories that reach the opposite end and those that return to the initial end of the pore yield significant differences in the total number and location of molecule hits with the wall.

Figure 1 shows the distribution of hits along the pore. It can be observed that individual trajectories reaching the opposite end of the pore concentrate the maximum number of hits at the center of the pore, with fewer hits near the ends. On the other hand, trajectories returning to the initial point have the maximum amount of hits near the entrance of the pore and the number of hits drastically decreases with the distance from the entrance. For particles recovered downstream, the distribution of hits has a maximum at the entrance of the pore and decreases linearly with the distance from the entrance. The total number of hits and the residence times for each of these cases can be related through different power laws to the aspect ratio of the pore. These results point out important differences between operating the reactor in a sweep-gas and pass-through mode.

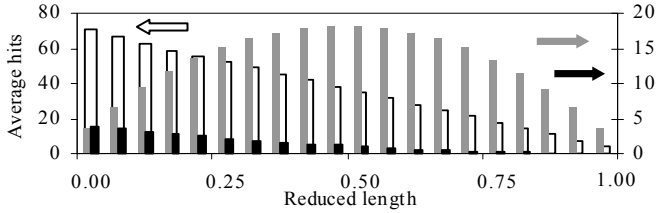

Figure 1: Average number of hits on the wall per section of a L/d=20 pore for individual trajectories that reach the opposite end of the pore (grey), that return to the starting end of the pore (black) and for particles recovered on the downstream end of the membrane (open bars).

For pores with multiple sections of different diameters it was found that the number and location of hits, as well as the transmission probability, could be predicted from the values of the individual sections. The simulations also showed that it is possible to use these pores with variable diameters to concentrate the hits on a particular section of the pore and to tune the total number of hits, which should directly relate to the conversion.

Significance

The combination of AAO and ALD for membrane fabrication offers the possibility to precisely control the geometry of membrane reactors. A multiscale approach, employing analytical equations, molecular dynamics and Knudsen dynamics simulations, determined that Knudsen diffusion is the dominant mass transport mechanism under the conditions for selective oxidation. The number of hits, and therefore the contact of the diffusing particles with the catalyst, can be tuned by controlling the pore dimensions and the operating mode. Introducing a diameter change helps in further controlling the number of hits and their location.

References

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