diffusion-fundamentals

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

CO_2 Transport in Amorphous Silica Membranes: Adsorption, Diffusion, and Mitigation of the Effects of Water

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Silica membranes can be synthesized with nano-porous structures capable of very effective separations of CO_2 and CH_4 in spite of the relatively small difference in kinetic diameters for these molecules (0.34nm versus 0.38 nm). CO_2/CH_4 selectivities of over 100 have been reported. The present work confirms these high selectivities and includes a detailed study of the pressure and temperature dependence of transport, analysis of gas transport through defects, and the short/long term effects of water exposure. Modeling of intrinsic (nano-pore diffusion controlled) single-gas transport is based on the chemical potential gradient driving force and provides a straightforward method for understanding and predicting gas transport behavior as a function of pressure. Single gas permeances are measured for CO_2 and CH_4 over the temperature range 20-350°C and over the differential pressure range 100-2000 kPa. Single gas measurements were also performed for a number of other gases in order to assess extrinsic (defect-related) transport for the same range of conditions. The model provides an excellent description of the pressure dependence of the intrinsic CO_2 permeance over the entire range of temperatures. The Langmuir adsorption parameters derived from that analysis are in excellent agreement with the values derived directly from isotherms measured for amorphous silica. This agreement is obtained without invoking any variation of the intrinsic diffusion coefficient with CO_2 loading, even though the CO_2 loading at the high-pressure side of the membrane is, in some cases, greater than 80% of saturation. This analysis also allows unambiguous allocation of the observed CO_2/CH_4 selectivity into its equilibrium and kinetic components. Though we have shown that silica membranes are quite stable to low- activity exposure to water over considerable periods of time, prolonged exposure to high- activity water (high water loading) leads to irreversible changes in the gas transport properties. These observations are interpreted in terms of a model for silica-water interactions which includes physisorption, chemisorption, and eventual materials migration leading to irreversible changes in the pore structure. Consistent with the proposed model, the effect of water can be alleviated to a large degree by chemical derivitization of the Si-OH moieties at the pore surfaces in the amorphous silica structure. Two methods have been successfully deployed: fluoroform treatment at high temperature (e.g. 400 C) yielding Si - F to replace the Si - OH and CH_3OH treatment at 150 C resulting in Si - CH_3. In both cases, water effects are greatly reduced. The effects of these chemical treatments on transport properties are analyzed as described above. Moderate losses of CO_2 permeance accompany both treatments due in large part to decreases in CO_2 diffusion coefficients.