Expansion of MFI Zeolite Crystals as a Function of Adsorbate Loading and its Effect on Membrane Permeation

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X-ray diffraction measurements showed that silicalite-1 and B-ZSM-5 zeolite crystals expand when n-alkanes, isobutane, ethanol, and SF_6 adsorb at saturation and loadings less than saturation conditions at room temperature. The n-alkane expansion at saturation correlated with the maximum number of carbon atoms in the structure. The higher number of carbon atoms per unit cell, the more the crystals expanded. XRD showed i-butane and low SF_6 loadings contract the MFI crystals. Permporosimetry showed that increases and decreases in helium flow through membranes trended well with the expansion due to adsorbate loading as measured by XRD.

The changes due to adsorbate loading significantly influence the permeation properties of zeolite membranes. When the MFI crystals expand, the size of intercrystalline defects shrink enough to drop the flux of molecules thru the defects by orders of magnitude. Pervaporation was used to measure flux because a liquid feed creates the highest loading in the defects and thus is the most severe test of the zeolite membrane properties. Isooctane was used as a measure of flux thru defects because the kinetic diameter of isooctane is larger than the MFI pore diameter and therefore only transports through membrane defects. When 1% n-alkane was added to liquid isooctane feed of a B-ZSM-5 membrane, the isooctane flux dropped orders of magnitude. The percentage of the original isooctane flux that remained after n-alkane addition correlated well with the XRD volume expansion.