150b Effects of Carboxylic Acids on Liquid-Phase Adsorption of Ethanol and Water by High-Silica Zsm-5

Travis C. Bowen and Leland M. Vane

Adsorption isotherms were measured for each compound adsorbed on commercially available ZSM-5 (Si/Al = 140) powder from binary and ternary liquid mixtures of ethanol, carboxylic acids, and water at room temperature. The amounts adsorbed were measured using a recently developed technique that accurately measures adsorbent/liquid mixture density changes and liquid concentration changes upon adsorption. This technique assumes that the zeolite is a rigid structure that maintains a constant volume as mass is adsorbed into the zeolite channels. Measuring the density change allows the total mass adsorbed from a liquid mixture to be determined, and the adsorbed masses of individual compounds are then determined from the concentration changes.

Carboxylic acids, such as acetic acid and succinic acid are often produced during biomass conversion to ethanol and other biofuels. Methods used to separate ethanol from fermentation broths include adsorption by hydrophobic zeolites and separations using hydrophobic zeolite or zeolite-filled membranes that transport molecules by first adsorbing them. Carboxylic acids present in the broths, however, compete with ethanol for adsorption sites within the zeolite channels because the pore volume is limited. Adsorption isotherms allow this competition to be directly observed.

Amounts adsorbed for pure ethanol and water compared well to values reported in the literature for saturated adsorption on other high-silica ZSM-5 zeolites, including silicalite-1. In addition, the mixture data were fit with dual-site Langmuir adsorption isotherms. Adsorption dependencies on carboxylic acid concentration and liquid pH were investigated. Carboxylic acid dissociation increases as pH increases, and the dissociated ion pairs adsorb less easily than the acidified molecules do. Longer-term adsorption studies (~15 days) were also performed to investigate irreversible effects of carboxylic acids on the zeolite structure.