

## The Role of Cation Identity and Adsorbate Orientation on the Selective Adsorption of p-Xylene in Faujasite Zeolites

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Polyethylene terephthalate (PET) is a thermoplastic polymer that is commonly used in the manufacture of polyester fibers and bottles. Demand in the U.S. for PET was 9.78 billions pounds in 2002. A primary raw material for PET production is p-xylene, which is generated along with m-xylene, o-xylene, and ethylbenzene in processes such as petroleum reforming and pyrolysis. Isolation of p-xylene from the other C8 isomers is a challenge because the xylene isomers and ethylbenzene have similar boiling points, making distillation an ineffective separation option. Faujasite zeolites are often used for this separation in a simulated moving bed (SMB) adsorption process. The selectivity of a particular faujasite for p-xylene depends upon the identity of the non-framework cations. In this study, we modeled the adsorption of p-xylene, m-xylene, o-xylene, and ethylbenzene in Na<sup>+</sup> and K<sup>+</sup> faujasites for a range of Si to Al ratios using grand canonical Monte Carlo simulations. The adsorbate/adsorbate interactions were modeled using previously derived parameters from the literature, and the vapor-liquid coexistence curves for our simulated C8 isomers show good agreement with experimental values. The adsorbate/zeolite interaction parameters were taken from the literature where possible. For the remaining unknown adsorbate/zeolite parameters, the short-range potential parameters were fit to reproduce experimental adsorption isotherms.

Using these parameters, we calculated adsorption from both the liquid phase and the gas phase. The effect of cation mobility on C8 isomer adsorption was examined, and we found that the simulated Henry coefficients in NaX are significantly closer to experimental values when the cations are mobile. This is the result of cation reorganization in site III. However, the effect of cation mobility on the adsorbate Henry coefficients in NaY and KY is minimal, as these zeolites have no site III cations. To determine how the enthalpic and the entropic components of the Gibbs free energy influence selectivity, we examined the distance and orientation of the adsorbate methyl groups with respect to the cations and the faujasite oxygen atoms.