

Progress Report

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Project Title: Use of Organic Monolayers to Tune the Surface Properties of Zeolites for Enhanced Separations

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Distillation of light gases requires significant energy inputs. Sorbents could alleviate this issue, but must be able to separate molecules of similar size and chemical functionality. We sought to enhance separations of gases such as propane and propylene using zeolite 5A modified with phosphonic acids (PAs) of varying alkyl tail length. All PAs slowed diffusion of n-C₄H₁₀, but generally had a smaller effect on the diffusion rate and loading of smaller molecules such as CO₂ and CH₄. However, methylphosphonic acid (C₁PA) decreased by >90% both the diffusion rates and apparent equilibrium uptakes of n-butane and propane. Surprisingly, the achievable loadings of C₃H₆, C₂H₆, CH₄, and CO₂ were affected much less, resulting in a propylene/propane ideal selectivity of 59±14. The unique effects of C₁PA were correlated to a much higher extent of deposition near the zeolite surface, while longer-chain PAs were confined to a monolayer on the external surface.

Work in the most recent grant period focused on more in-depth characterization of the MPA-coated material to better understand the origin of the interesting selectivity effects. We used scanning transmission electron microscopy (STEM) with energy dispersive X-ray spectroscopy (EDS) mapping to analyze the distribution of P in the zeolite crystallites. Analysis of different regions indicated enrichment near the surface of the zeolite, both for C₁₈PA - and C₁PA-modified surfaces (Figure 1). Concentration of P was much higher in the C₁PA-modified samples. Moreover, there was some variation across different C₁PA-modified crystallites, with the P content appearing to be much higher on samples with greater surface roughness. We hypothesize that C₁PA was able to bind in high densities near the external surface of the zeolite to more significantly alter the pore entrance region. Localization of P near the surface was further supported via detailed quantification of different regions of the full zeolite and analysis of cross-sectioned samples of the zeolites; these samples showed lower amounts of P when edges of the particles were excluded, and much lower P content in the center of the cross-sectioned samples.

To complement these techniques, low-energy ion scattering (LEIS) measurements were also carried out to measure the composition of the outermost surface layer. For the C₁₈PA-coated zeolites, only surface C (and no P, Si, or Al) could be detected, consistent with extensive modification of the outer zeolite surface with a dense layer of alkyl ligands. For the C₁PA-coated zeolite, substantial C signal was also detected (not shown), but signals from P, Al, and Si were prominent as well; as discussed below, LEIS experiments conducted following calcination of the samples suggested that P content was significantly higher in C₁PA-coated compared to C₁₈PA-coated samples. The LEIS and STEM measurements were coupled with measurements of bulk elemental composition and crystal structure to demonstrate accumulation of phosphorous in the zeolite 5A near-surface region. Interestingly, high-temperature oxidation treatments caused phosphorous move further into the bulk and altered the measured crystal structure.

We also carried out initial experiments at higher temperatures, finding that operating at temperatures as high as 100 °C appeared to dramatically increase the rate of propylene adsorption while apparently leaving propane adsorption rates unaffected. Finally, we demonstrated the modification of zeolite mordenite with a number of phosphonic acid monolayers, with preliminary surface area measurements suggesting significant incorporation of ligands into the pores. This work is still ongoing.

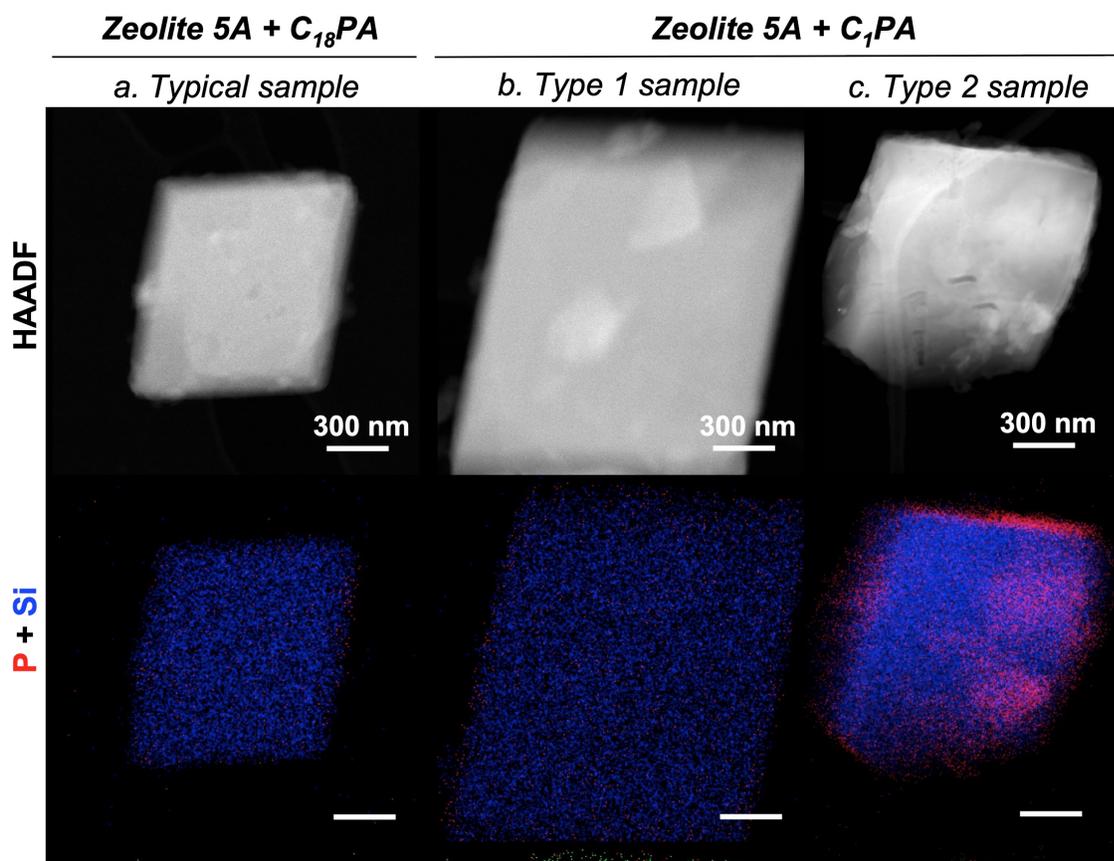


Figure 1. Microscopy and spectroscopy of representative C₁₈PA and C₁PA modified Zeolite 5A particles. High angle annular dark field (HAADF) images and energy dispersive X-ray spectroscopy (EDS) show morphology and elemental overlays (P = red, Si = blue) of a (a.) typical sample, (b.) “smooth” and (c.) “rough” particle.

This research appears to be opening up a new research direction for the career of the PI; his main area of research is in heterogeneous catalysis, and this represent a new direction for applications in separations. Multiple students and postdocs have participated in the research. One student, whose participation was funded by an external fellowship, received his PhD. A manuscript has been submitted and is pending the second round of review. Furthermore, the PIs applied for and recently received a new grant from the National Science Foundation to carry out an in-depth investigation of organic coatings as selectivity modifiers for gas separations in zeolites; the preliminary data for that proposal was obtained by the work on the PRF-ND grant.