

56991-DNI5:

Computational Design of Growth Inhibitors for Tailoring Zeolite Catalysts  
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This ACS PRF grant supported two research thrusts in our lab related to using molecular simulation to understand how small organic molecules can be used to tailor zeolite catalysts. The principal focus of our investigation is on understanding how zeolite growth inhibitors (ZGIs) selectively adsorb to different crystal faces to modulate anisotropic zeolite growth rates during synthesis. Recent experiments show that ZGIs can be used to produce thin zeolite crystals, which exhibit enhanced catalytic lifetimes and performance characteristics. Below, we describe major accomplishments over the past year.

### (1) Solvent structure and dynamics near zeolite surfaces

Over this project year, we have used molecular simulation to investigate the structure and dynamics of solvents near the surfaces of siliceous zeolites. Processes at solid-solvent interfaces are relevant to a variety of applications such as catalysis, corrosion mitigation, electrode design, and pharmaceutical precipitation. Recent experimental investigations, for example, have shown that the size and shape of silicalite-1 crystals can be controlled synthetically using ZGIs, which are small molecules that adsorb and selectively bind to different crystallographic faces to influence anisotropic rates of growth. Fundamental understanding of the key factors governing ZGI adsorption remain limited, however, particularly the influence of solvent structure and dynamics near the surface. We used molecular dynamics (MD) simulations to investigate solvent structuring and dynamics near the (010), (100), and (101) crystallographic faces of silicalite-1, a siliceous analogue of the widely used industrial catalyst ZSM-5. We find that the three surfaces strongly influence solvent properties, altering structure and dynamics within the  $\sim 1$  nm interfacial region (Figure 1). This behavior is found to depend sensitively on the specific chemical features presented on each crystallographic face, suggesting that the anisotropic rates of growth observed in experiment may arise from differences in solvent structure at each surface. We anticipate that the distinct solvent structure on each surface may also strongly influence adsorption of solutes such as ZGIs. To test this hypothesis, we are currently conducting follow-up studies to investigate the adsorption of idealized hydrophilic and hydrophobic solutes to the surfaces of silicalite-1. Analysis of the binding energetics and kinetics of these idealized solutes, and their impact on interfacial solvent structuring, will help to elucidate the role of solvent in governing the adsorption of mechanisms of ZGIs and other solutes.

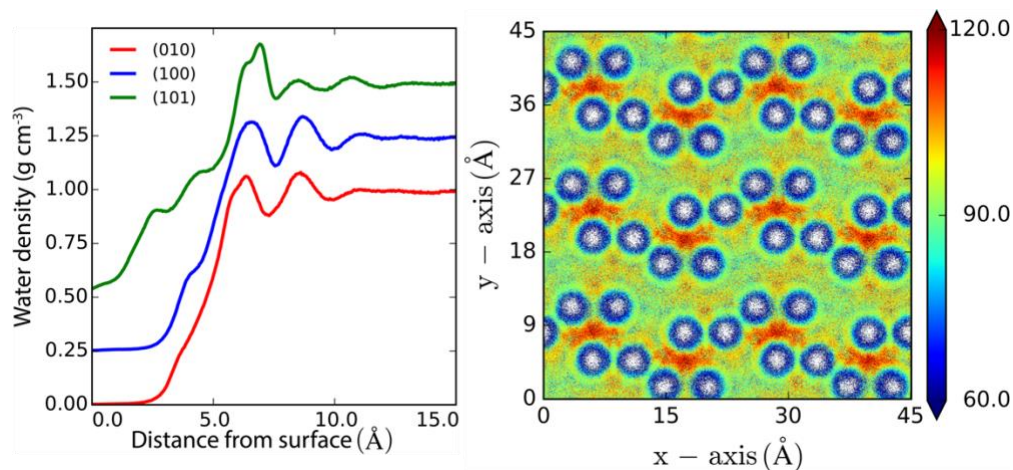


Figure 1. (left) Mass density profiles for water near the (010), (100) and (101) surfaces of silicalite-1. (right) Heat map showing the average dipole moment orientation (angle, in degrees) of water molecules near the 010 surface of silicalite-1.

### (2) Adsorption of ZGIs to the crystallographic surfaces of ZSM-22

We have also performed MD simulations to investigate the adsorption of small-molecule ZGIs to the crystallographic surfaces of zeolite ZSM-22, a commercially relevant catalyst that also shows promise in photonics and drug delivery

applications. ZSM-22 has a TON framework structure, with porous features that consist of one-dimensional straight channels. Synthesis studies have shown that ZSM-22 preferentially forms crystals with needle-like morphologies, where the one-dimensional channels are oriented parallel to the principal axis. Hence, openings to the main channels are exposed on low surface area faces of the crystals, which results in mass transport limitations and diminished catalytic lifetime. Recent experiments show, however, that alcohol compounds can be used as ZGIs to reduce the aspect ratio of ZSM-22 crystals, thereby increasing the relative surface area of crystallographic faces with exposed pore openings. Motivated by these promising results, we performed MD simulations to elucidate the binding mechanisms of alcohol-based ZGIs to the crystallographic surfaces of ZSM-22. Using umbrella sampling MD, we calculated the free energy as a function of the ZGI's center-of-mass-distance from the surfaces of ZSM-22. The small binding free energies from MD simulations ( $< -5$  kJ/mol) reveal that the ZGI-surface interactions are typically relatively weak, consistent with small heats of adsorption measured by complementary calorimetry measurements. Moreover, the simulations also demonstrate that ZGI chemical structure can sensitively influence binding strength and mechanism. In our study, for example, we considered three butane diols  $D4_{1,2}$ ,  $D4_{1,3}$ , and  $D4_{1,4}$ , where the subscripts refer to the location of the alcohol groups along the alkyl backbone. Whereas  $D4_{1,2}$  and  $D4_{1,3}$  have similar binding energies (ca.  $-2$  kJ/mol) on ZSM-22,  $D4_{1,4}$  has slightly stronger interactions (ca.  $-4$  kJ/mol). Binding configurations show that the two alcohol ( $\equiv\text{OH}$ ) groups on each diol form a hydrogen bond with exposed surface silanols ( $\equiv\text{SiOH}/\text{SiO}^-$ ). The proximal spacing of these groups on  $D4_{1,2}$  and  $D4_{1,3}$  promotes binding atop of truncated 6-member ring features (Figure 2). The larger spacing of these groups on  $D4_{1,4}$ , by contrast, leads to a more energetically favorable binding position in which the molecule forms hydrogen bonds with two adjacent 6-MRs and its center sits inside exposed channels formed from truncated 10-MRs (Figure 2). These findings suggest that effective ZGIs have chemical structures that are complementary to features on the exposed zeolite surfaces. We anticipate that this complementarity principle can be exploited to develop computational approaches for rapidly screening ZGIs by employing algorithms that enable molecular structure to be predicted from chemical composition.

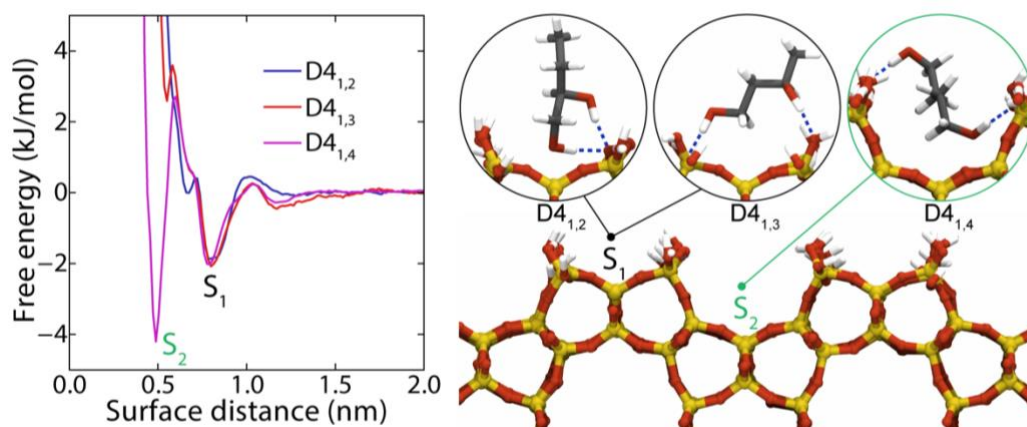


Figure 2. (left) Free energy for three butane diols computed as a function of distance from the (010) surface of siliceous ZSM-22 using umbrella sampling molecular dynamics. The three diols,  $D4_{1,2}$ ,  $D4_{1,3}$ , and  $D4_{1,4}$ , have distinct chemical structures, as indicated by subscripts that denote the location of the alcohol groups along the alkyl backbone. (right) Favorable binding positions for the butane diols near features on the (010) surface formed from truncated 6- and 10-member rings ( $S_1$  and  $S_2$ , respectively). Blue dashed lines show hydrogen bonds formed between the diols and surface silanols.