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Rational control over aluminum sites in zeolite frameworks by a combined theoretical and experimental approach

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1.3 2 nm

The physicochemical properties of zeolites are mainly determined by framework structure, chemical composition, and position of tetrahedral atoms. In this research, more than 40,000 zeolite structures with different topologies, Si/Al ratios Al locations were constructed and evaluated. The results revealed that for a particular framework structure there exist the energetically favorable chemical compositions and atomic positions, which is consistent with the experimental results.

In zeolite syntheses, organic structure-directing agents (OSDAs) have been used. In this work, the design of such OSDAs was focused. As a first step toward designed synthesis of inorganic porous materials by the aids of computations, nanoporous silicas with high surface area and unique pore diameters of 1.3 2 nm were synthesized. The resulting materials possessed the pore diameters identical to the designed values and their surface areas were among the highest values reported for nanoporous silicas.

Zeolites are microporous crystalline silicates, aluminosilicates, and other metallosilicates constructed from corner-sharing, tetrahedrally-coordinated $TO_{4/2}$ primary units (where T is a tetrahedral atom such as Si, Al, Zn, and so on). Specific interactions with ions, molecules, and clusters inside the well-defined pores and channels of molecular dimensions of zeolites can provide ion-exchanging and molecular-discriminating capabilities. They are among the most important key materials in chemical industries, utilized for ion exchange, adsorption, membrane separation, and catalysis.

Isomorphous substitution of Al(III) for Si(IV) in the tetrahedral site (T site) of the zeolite framework generates a negative charge that constitutes a Brönsted acid site when it is counter-balanced by a proton. Besides protons, the counterions located inside the interior cavities can be metal ion species, having various structures and coordination, exhibiting extraordinary redox behaviors. When utilized as catalysts, the location of Al atoms and catalytic sites within zeolite channels strongly influences reactivity and selectivity. For example, Al sitting in the 8-membered ring (8-MR) pockets of mordenite zeolites gave higher reactivity (i.e., faster turnover rate) in the cracking and dehydrogenation of alkanes than those located in the 12-MR channel. This is mainly because the stability of reactants and transition intermediates and thereby the reaction rates can be altered depending on the spatial constraints of reactants and intermediates.

To ensure effective charge-balance of counterion species, the location of the Al atoms at the crystallographic T sites and their distribution in the zeolite framework clearly determine the location, structure, and properties of counterion species, and accordingly the catalytic active sites. So far, attempts to control over the location and distribution of Al atoms have mainly relied upon a trial-and-error approach by alteration of synthesis conditions. For example, the type of organic structure-directing agents (SDAs), the source of Si and Al, and the presence or absence of alkali metal cations were reported to affect the Al distribution in several zeolites. However, the designed synthesis of zeolites with desired Al sites is still an elusive dream in zeolite synthesis mainly because of a lack of understanding in their formation, conventionally occurred through a sophisticated series of "black-box" hydrothermal reactions. If succeed, this would drive the zeolite and catalysis communities toward on-demand applications needing more finely tuned architectures.

In this work, computational chemistry calculations together with experimental works have been carried out to understand the design principles for rational synthesis of zeolites. In particular, organic SDAs that can fit well in the nano-sized cavities of nanoporous silica, as a model material, have been designed by density functional theory (DFT) calculations. In addition, large-scale, systematic computational evaluation of the energetics of aluminosilicate zeolites with all existing framework topologies at different Si/Al ratios using molecular mechanics have been performed to understand the fundamental origins determining the amount and location of substituted Al in zeolite frameworks.

(1) Synthesis of nanoporous silica with controlled pore sizes by using designed organic SDAs

The concept of orthogonal assembly has been employed to enhance the interactions between SDA–SDA and SDA–silica as such enhancement can lead to the formation of nanoporous silica with unique pore diameters. Organic SDAs were designed by DFT calculation at the B3LYP/6-31G(d) level. Nanoporous silicas have been synthesized by using the designed organic SDAs.

(2) Understanding of the energetics of aluminosilicate zeolites with wide ranges of framework topologies, chemical compositions, and aluminum distributions

The systematic computational evaluation of the energetics of aluminosilicate zeolites with 209 existing framework topolo-gies having different Al contents (Si/Al = 1, 3, 7, 15, 31, and   ) and distributions has been performed by a lattice-energy minimization technique using the Sanders–Leslie–Catlow (SLC) interatomic potential assisted by a Monte Carlo sampling. For all topologies, the substituting Al atoms are located randomly or placed at specific crystallographic T sites.

(1) Synthesis of nanoporous silica with controlled pore sizes by using designed organic SDAs

By general definition, zeolite has its pore diameters in the microporous scale (less than 2 nm), while the pore sizes of mesoporous silica are 2–50 nm. However, silica-based nanoporous materials with pore sizes near the boundary of micro- and mesoporous scales are still rare. This micro–meso transition length scale is of great scientific significance because adsorption behavior can change from monolayer to multilayer modes, probably making the classical adsorption theories become inapplicable.

In this work, the synthesis of nanoporous silicas having pore apertures near the micro–meso boundary was achieved by using novel SDAs that can facilitate multiple, orthogonal interactions (see **Figure 1**). To enhance the SDA–SDA interaction, disk-like molecules with rigid, π-conjugated cores have been considered as SDAs because these molecules can interact each other via π–π interactions and thus form one-dimensional stacks. To create the nanopores near the micro–meso boundary, therefore, a benzene core, the smallest moiety that can form columnar assemblies through π–π stacking, was selected.
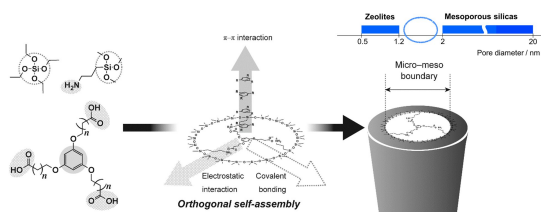

Figure 1. Schematic of the orthogonal self-assembly approach with multi-interactions used for the synthesis of nanoporous silica having pore apertures near the boundary between micro- and mesopores.

The molecular sizes of organic SDAs able to create the pore sizes near the micro–meso boundary, being 1.5–2.5 nm, were computed by DFT optimization at the B3LYP/6-31G(d) level). The resulting nanoporous silicas exhibited some periodicity with high apparent surface areas up to 1,230 m^2 g^{-1}. The pore diameters can be altered across the boundary between micro- and mesopores, (1.5 to 3 nm), depending on the size of SDAs. A possible formation scheme can be explain based on multiple, orthogonal interactions between SDAs, co-SDAs and silica frameworks.

(2) Understanding of the energetics of aluminosilicate zeolites with wide ranges of framework topologies, chemical compositions, and aluminum distributions

43,409 (alumino)silicate zeolite structures were generated with 209 different topologies, Si/Al ratios ranging from 1 to ∞ (Si/Al = 1, 3, 7, 15, 31, and   ), different Al locations (random versus specific), and proton configurations by the aid of the Monte Carlo method. The framework structures were optimized by the lattice-energy minimization technique. The linear relationships between framework energies and framework densities were found to be similar to the previous reports on their siliceous analogues. Comparison of the relative framework energies of each topology with different Al contents indicated that the relative thermodynamic stability of zeolites depends on both the framework topologies and the substituting contents of Al.

In addition, it was found that the framework structures of zeolites at the most energetically favorable Al contents have the T–O–T bond angles close to the typical value for the unstrained Si–O–Si linkages, reflecting the intrinsic influence of structural features of each topologies. For particular framework topologies with the identical Al contents, the aluminosilicate zeolite with Al at a specific location was energetically more stable than those with random distributions. For example, when **BEA**-type zeolite has a Si/Al of 7, all structures with specific Al sites were energetically more stable than that with random distribution, with the lowest energy found at the T6 site (**Figure 2a**). For **BEA** with Si/Al of 15, the relative framework energy of the structure with Al at the T8 site was lower than those with Al at the T9 site and random Al distribution, suggesting that T8 is the most energetic favorable site (**Figure 2b**). Interestingly, the T6 and T8 sites, the most energetically favorable site for **BEA** with Si/Al of 7 and 15, respectively, are a part of the β-ion-exchange-site (see **Figure 2c,d**). The presence of Al in such a β-site has been suggested experimentally for Al-rich **BEA**-type zeolites, suggesting the obtained computational results may somewhat reflect the experimentally observed Al sites in some zeolites.
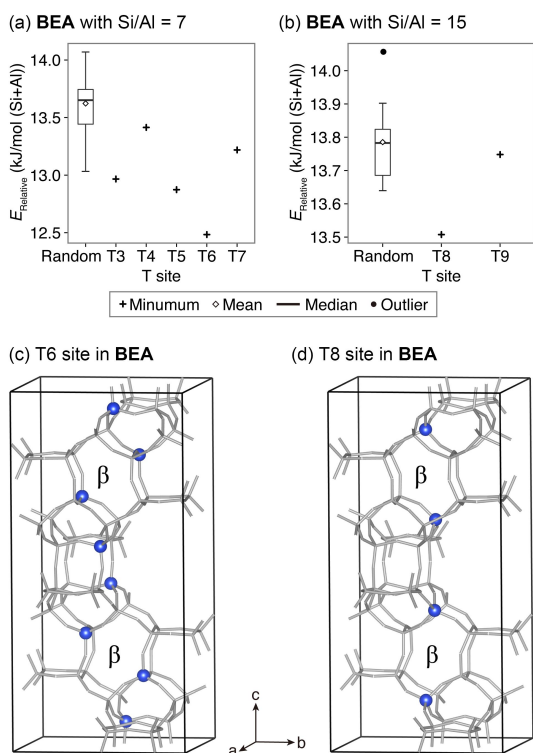
Figure 2. Relative framework energy of the optimized structures with specific Al locations at different T sites, in comparison with random Al distributions of **BEA**-type zeolites with Si/Al of (a) 7 and (b) 15. Crystal structure of **BEA** displaying the β-ion-exchange-site with the highlighted (c) T6 and (d) T8 sites.

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