The Properties of Methylene- and Amine-Substituted Zeolites from First Principles

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Abstract: All-silica zeolite frameworks doped with methylene and amine groups are studied using density functional theory-based electron structure calculations. Strain energies are calculated in a novel way, by comparing zeolite energies with appropriate polymer reference systems. The modified zeolites are found to be mechanically stable structures with surprisingly little strain. Distortions due to impurities result in broadened Si–O–Si angle distributions in the lattice surrounding defects. Our results suggest that zeolites can accommodate both methylene and amine groups at high concentrations with minimal strain. The amine-doped zeolites are strong Lewis bases suggesting novel applications in base catalysis.

1. Introduction

Zeo\textit{}lites are nanoporous crystalline silicates with a wide variety of important properties and applications.\textsuperscript{1} Recent efforts to broaden the scope of zeolite compositions have yielded LTA and MFI frameworks\textsuperscript{2} with bridging oxygen atoms replaced by CH\textsubscript{2} groups.\textsuperscript{3} Such materials may have interesting catalytic, electronic, and structural properties, which remain to be investigated. The work presented here is inspired by these experimental findings; our focus is to provide an atom- and electron-level understanding of the properties and behavior of these materials. Furthermore, we extend the scope from methylene-modified to amine-modified zeolites, to explore whether such structures are energetically feasible and chemically interesting.

CH\textsubscript{2} substitution is likely to produce large framework distortions, and possibly significant strain due to the atom-size mismatch and the coordination differences between carbon and oxygen atoms. It is thus surprising that CH\textsubscript{2}-substituted zeolites can be synthesized. Indeed, the materials produced by Yamamoto et al. contain intrapore Si–CH\textsubscript{3} moieties in addition to bridging Si–CH\textsubscript{2}–Si groups.\textsuperscript{3} This raises the question whether Si–CH\textsubscript{3} groups are required to relieve strain introduced by methylene bridges. Or do methylene-substituted zeolites possess other mechanisms for relieving such strain? Furthermore, the NH substitution is energetically possible. We investigate whether these defects are mechanically stable and provide an atomistic picture of lattice distortions near the impurities. We estimate strain energies due to these substitutions using polymer reference systems and discuss the acid–base properties of these materials. The modified zeolites are found to be mechanically stable structures with surprisingly little strain.

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The remainder of this Article is organized as follows: in section 2 we describe the first-principles computational methods and the model systems, in section 3 we discuss the results, and in section 4 we give concluding remarks.

2. Methods

Structures and stabilities of doped zeolites were analyzed by performing energy minimizations on materials with various doping levels. Energies were calculated using density functional theory (DFT) applied to periodic supercells using the plane-wave pseudopotential method.\textsuperscript{5–7} The Brillouin zone was sampled using Monkhorst–Pack grids, and the calculations were performed within the local density approximation (LDA) of the electron exchange-correlation potential based on Ceperley–Alder data.\textsuperscript{8,9} We found that the 2 \times 2 \times 2 Monkhorst–Pack grid produced high enough \textit{k}-point density for the results to be well converged. Electron ground states were obtained using iterative diagonalization as implemented in the VASP code.\textsuperscript{10–13} Ion
The sodalite cage with a CH₂ impurity substituting a bridging oxygen, relaxed structure.

Figure 1. The sodalite cage with a CH₂ impurity substituting a bridging oxygen, relaxed structure.
to initiate reactions above still provides a good qualitative gauge of acid strength in amine-doped aluminosilicates. Many catalytic applications such as partial oxidation\textsuperscript{26} and halogen elimination\textsuperscript{27} exploit zeolites as Lewis bases, that is, donors of electron density. Here, we might expect an amine-doped zeolite to be more basic than a conventional zeolite. To investigate this, we calculated BF\textsubscript{3} sorption energies in OXY-SOD and NH-SOD as shown below:

\[
\text{Si-O-Si} + \text{BF}_3(g) \leftrightarrow \text{Si-N-Si} + \text{BF}_3(ads)
\]

where \text{Si-X-Si} \rightarrow \text{BF}_3 signifies the formation of a weak X–B bond involving lone-pair electrons on X. For all of the acid–base reactions discussed above, we first performed (i) optimizations of the bare zeolites and isolated guest molecules, using lattice parameters obtained from (f) optimizations of OXY-SOD and NH-SOD. We then performed (i) optimizations of the zeolite–guest complexes. Each of these acid–base reactions was found to be essentially barrierless, so no special coordinate-driving approach was needed to coax the zeolite–guest complexes into geometry optimization.

3. Results and Discussion

Here, we discuss the results of our calculations on chain polymers, on doped-zeolite structures and stabilities, and on acid–base properties of amine-doped sodalites.

To benchmark the reliability of the polymer models, we optimized polyethylene \([PE = (\text{CH}_2\text{CH}_2)_n]\) and \((\text{CH}_3\text{SiH}_2\text{CH}_2\text{SiH}_2)_n\) for comparison with experiment and with the more complex polymers. The results of all our polymer optimizations are summarized in Table 1. The DFT-LDA method predicts a C–C–C angle in PE of 113.9°, in very good agreement with earlier theoretical and experimental results (ref 28 and citations therein). The DFT-LDA method predicts that the four C–Si–C and Si–C–Si angles in \((\text{CH}_3\text{SiH}_2\text{CH}_2\text{SiH}_2)_n\) fall in the range 113.1–113.2°, suggesting that 113–114° is characteristic of carbon and silicon chains without relatively electronegative atoms as oxygen. The two Si–O–Si angles in \((\text{SiO})_2\)–

\[
\begin{array}{ll}
\text{polymer and angle} & \Theta (\text{deg}) \\
\text{CH}_2\text{CH}_2 & 113.9 \\
\text{H–C–H} & 110.2 \\
\text{C–Si–C} & 113.1, 113.2 \\
\text{Si–C–Si} & 113.1, 113.2 \\
\text{H–C–H} & 107.1 \\
\text{H–Si–H} & 107.3 \\
\text{Si–O–Si} & 154.1, 157.6 \\
\text{Si–N–Si} & 129.7 \\
\text{Si–O–Si} & 134.6 \\
\text{Si–C–Si} & 123.7 \\
\text{Si–O–Si} & 130.5 \\
\end{array}
\]

Figure 2. The three relaxed chain polymers used as reference systems. From top to bottom: \((\text{SiO})_2(\text{OH})_4\), \((\text{SiNH})(\text{SiO})(\text{OH})_4\), and \((\text{SiCH}_2)(\text{SiO})_2(\text{OH})_4\). Two repeat lengths of each polymer are shown.

\text{structural data, which find Si–O–Si angles across the range 140–180° depending upon the particular silica polymorph.}\textsuperscript{24} Moreover, attempts to optimize this bond angle in cluster calculations are complicated by termination effects from hydrogen bonding species such as \(-\text{Si(OH)}_3\) groups. This polymer method removes such artifacts and thus may be useful for parametrizing models of silica and other network-forming systems.

To gauge the acid–base properties of amine-doped sodalites, we calculated energies of acid–base reactions for comparison with conventional zeolites. To probe acidity, which is crucial for initiating many petrochemical processes,\textsuperscript{25} we compared the reaction energies for the following processes:

\[
\text{Si–OH–Al} + \text{NH}_3(g) \leftrightarrow \text{Si–O–Al}^{-1} + \text{NH}_4^+(ads)
\]

\[
\text{Si–NH}_2–\text{Al} + \text{NH}_3(g) \leftrightarrow \text{Si–NH–Al}^{-1} + \text{NH}_4^+(ads)
\]

where in both cases the process was modeled in sodalite with a single Brønsted acid site. Also, in both cases, the reactant NH\textsubscript{3} was isolated from the zeolite, while the product NH\textsubscript{4}\textsuperscript{+} was complexed through ion-pair formation with the zeolite conjugate base. As such, these reaction energies reflect heats of ammonia sorption in these materials at 0 K. Although it would be preferable to compare the intrinsic acidities of \text{Si–OH–Al} and \text{Si–NH–Al}, such calculations are extremely}

The strain energy per defect, $E^s$, is shown in Figure 3 for doped sodalites. Strain energies are found to be as small as 0.10 J/mol for $n$-doped CH$_2$ defects per unit cell, the lattice parameter actually increases to 9.02 and 9.40 Å (6.5% increase), respectively, largely because of increasing Si–C bond lengths (more on that below). In ref 3, a lattice parameter expansion of 0.1–0.2% was observed for 1 wt% CH$_3$-doped MFI, as compared to silicalite-1. Thus, the effect of low-to-moderate doping on the lattice parameters is likely to be small.

Strain due to impurity substitutions results in distortions of Si–O–Si angles near defects as shown in Table 2. For example, the Si–O–Si angle of 156.7° in OXY-SOD broadens to 142–172° in CH$_2$-SOD. These distortions are slightly less pronounced for nNH-SOD than for nCH$_2$-SOD. In contrast, Si–O bond lengths in doped sodalites take values nearly unchanged from the 1.59 Å found in OXY-SOD. With 1–3 defects, Si–C and Si–N bond lengths take values of 1.78–1.82 Å, which is consistent with previous results (1.77–1.80 Å) obtained using DFT-LDA with norm-conserving pseudopotentials.

Our results show that distorting Si–O–Si angles is the main stress-relief mechanism in doped sodalite zeolites. In contrast, X–Si–O distortions are found to be relatively small. For example, while O–Si–O angles in OXY-SOD are nearly tetrahedral, C–Si–O angles in CH$_2$-SOD fall in the range 105–118°. Only in the fully doped CH$_2$-SOD system do we find significant distortion of C–Si–C angles, taking values from 97° to 123° in the fully relaxed structure. While our structural data clearly show that distorting Si–O–Si angles provides the lowest-energy route to minimizing strain, the question remains how much residual strain exists in these materials.

The strain energy per defect, $E^s$, is shown in Figure 3 for doped sodalites. Strain energies are found to be as small as 0.10 J/mol.

eV for nCH2-SOD and 0.15 eV for nNH-SOD. The strain energy per CH2 impurity increases at higher doping concentrations as shown in Figure 3. In fully CH2-doped SOD, the strain energy per defect is significantly larger, 1.21 eV, before relaxing the lattice parameter, but it decreases to 0.20 eV after full relaxation. In CH2-doped LTA, the defect strain energy takes values of nearly zero for the (a) site and 0.14 eV for the (b) and (c) sites, indicating that the ability of the lattice to accommodate defects can vary from site to site.

These surprisingly small strain energies arise because of the remarkable ability of silicate materials to adopt a broad range of Si–O–Si angles with little to no energetic cost. This fact, which remains poorly understood at the electronic structure level, underlies the structural versatility of zeolites in particular and silicates in general. Our results show that the Si–CH2 groups found in the materials synthesized by Yamamoto et al.3 may not be required to relieve strain, suggesting that synthesizing analogous materials without Si–CH2 groups should be thermodynamically possible.

Having now described the structure and stability of amine-doped zeolites, we now turn to their properties as adsorbents. Adsorption energies of NH3 at Si–NH2–Al and Si–OH–Al sites in SOD are shown in Table 4. The NH3 adsorption energy at the Si–OH–Al site predicted by DFT-LDA is −1.7 eV, in reasonable agreement with experimental heats of NH3 adsorption which fall in the range 1.1–1.7 eV for low NH3 loading in various high silica zeolites.30 NH3 adsorption at the Si–OH–Al site involves ion-pair formation between NH4+ and Si–O–Al. On the other hand, NH3 adsorption at the Si–NH2–Al site does not involve such ion-pair formation; instead, we find simple physisorption with an adsorption energy of −0.9 eV, large by physisorption standards but smaller than that obtained with the conventional zeolite Brønsted acid site. The N–H and O–H bond lengths of these structures are presented in Table 3. The large distance (1.48 Å) between framework oxygen (O) and H at the Si–OH–Al site after NH3 adsorption further confirms the ion-pair formation.

Adsorption of BF3 was found to be more favorable at the Si–NH–Si site than at the pristine sodalite Si–O–Si site, with adsorption energies of −0.8 and −0.5 eV, respectively, as shown in Table 4. This implies that sodalite becomes a much stronger Lewis base when amine-doped. The N–B distance in Si–NH–Si−BF3 indicates weak bonding involving the donation of N lone-pair electrons into BF3 orbitals, while in OXY-SOD the corresponding distance is somewhat larger (Table 3).

The stabilization of nitrogen lone-pair electrons upon adsorption of BF3 is also reflected in the electronic band structure of the system. The densities of the Kohn–Sham eigenstates of the pristine sodalite and the NH- and CH2-doped sodalites containing one impurity are shown in Figure 4. No significant electronic activity, such as mid-gap states, is present in the pristine or CH2-doped sodalites. However, the NH-doped sodalite exhibits a doubly occupied state 0.7 eV above the valence band edge. Upon BF3 adsorption in the NH-doped sodalite, the energy of this state decreases to a value of 0.1 eV above the valence band edge. While one has to be careful not to confuse Kohn–Sham eigenenergies with physical one-electron energies, these band structure results clearly suggest that the NH impurity is an electron donor.

4. Concluding Remarks

We have computed structural properties of CH2- and NH-doped sodalites, as well as CH2-doped LTA zeolite, using plane-wave pseudopotential DFT-LDA methods. The purpose of this study is to investigate the mechanical stability of doped zeolites, and to examine whether impurities modify the chemical properties of zeolites in useful ways.

We found that Si–C–Si and Si–N–Si angles prefer to have substantially smaller values than the Si–O–Si angle in the pristine structures, while the more floppy Si–O–Si angles in the surrounding crystal take up the strain. Thus, a broad range of Si–O–Si angles is observed. In the CH2-doped sodalites, the strain is also relieved by the contraction of the supercell, while in the NH doped sodalites, the volume change is less significant. At low defect concentrations, the strain contribution to the defect energy is estimated to be small, 0–0.15 eV, and a small increase is observed when the number of impurities increases from 2 to 3 (Figure 3). These strain energies were computed by comparing zeolite energies with energies of polymer reference systems. In the half- and fully doped structures, the defect strain energies have larger values, implying a threshold concentration at which there are not enough Si–
O–Si triplets to relieve the strain. The stability of defects is further supported by the observation that the Kohn–Sham eigenenergy band gap remains close to the pristine sodalite value and no strong electronic activity in the band gap region is detected.

Adsorption energies for various acid–base pairs in NH-doped and undoped sodalites were calculated. These values can be used to estimate the Brønsted acid and Lewis base strengths of the doped system. Sodalite containing Si–OH–Al was found to be a stronger acid than that containing Si–NH2–Al, while Si–NH–Si was found to be a much stronger Lewis base than Si–O–Si. This electron donor property of the NH impurity is further supported by the behavior of the Kohn–Sham eigenstates. The enhanced Lewis base strength of NH doped sodalite suggests that such materials may be useful in base-catalysis applications such as partial oxidation26 or halogen elimination.27

Although we should expect the acidity of amine-doped aluminosilicates to be weaker than that of conventional zeolites because oxygen’s electronegativity exceeds that of nitrogen, the amine-doped systems offer chemical versatility lacking in the oxide acid. In particular, we imagine reactions such as:

\[
\text{[Si–NX–Al]^{-1} + NH_4^+(ads)}
\]

where the moiety X can be varied to tune acid strength to a desired level. For example, setting X = fluorine may increase the acidity; this is explored in a forthcoming publication.

Our results show that doping zeolites can produce minimal strain, even at high dopant concentrations. Furthermore, we have shown that doping can modify the zeolite’s chemical properties in very interesting ways. Further computational studies can help to guide synthetic chemists as they try to design and fabricate new materials with advanced performance. Such computations might include studies of the kinetics of Si–N bond cleavage under synthesis conditions, to explore whether such linkages are likely to persist for long enough time scales.

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