



DFT study of nitrated zeolites: Mechanism of nitrogen substitution in HY and silicalite

Vishal Agarwal^a, George W. Huber^a, W. Curtis Conner Jr.^a, Scott M. Auerbach^{a,b,*}

^a Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA

^b Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA

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ABSTRACT

We have performed embedded-cluster calculations using density functional theory to investigate mechanisms of nitrogen substitution (nitridation) in HY and silicalite zeolites. We consider nitridation as replacing Si–O–Si and Si–OH–Al linkages with Si–NH–Si and Si–NH₂–Al, respectively. We predict that nitridation is much less endothermic in HY (29 kJ/mol) than in silicalite (132 kJ/mol), indicating the possibility of higher nitridation yields in HY. To reveal mechanistic details, we have combined for the first time the nudged elastic band method of finding elusive transition states, with the ONIOM method of treating embedded quantum clusters. We predict that nitridation of silicalite proceeds via a planar intermediate involving a $\equiv\text{Si} < \overset{\text{N}}{\text{O}} > \text{Si} \equiv$ ring with pentavalent Si, whereas nitridation of HY is found to proceed via an intermediate similar to physisorbed ammonia. B3LYP/6-311G(d,p) calculations give an overall barrier for silicalite nitridation of 343 kJ/mol, while that in HY is 359 kJ/mol. Although the overall nitridation barriers are relatively high, requiring high temperatures for substitution, the overall barriers for the reverse processes are also high. As such, we predict that once these catalysts are made, they remain relatively stable.

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1. Introduction

Zeolites are microporous crystalline materials with TO₄ (T = Si, Al) tetrahedra as primary units, joined via bridging oxygens to give cage-like structures [1]. Acidic zeolite catalysts have long been the backbone of the petroleum industry because of their high surface area, large adsorption capacities, and shape-selective properties. All these properties make them promising candidates for biofuel production catalysts. However, biomass is composed of heavily oxygenated compounds that will likely be more effectively activated by basic catalysts. Examples of base-catalyzed reactions important to biofuel processing include condensation reactions that form carbon–carbon bonds, trans-esterification of triglycerides giving bio-diesel, and esterification of organic acids making gasoline additives [2]. Unfortunately, because zeolites form strong acid sites, their base sites tend to be relatively weak. As such, a fundamental need in heterogeneous catalysis is the development of strong, shape-selective solid base catalysts. Effort has recently intensified in making strongly basic zeolites by nitridation, i.e.,

substituting Si–O–Si and Si–OH–Al linkages with Si–NH–Si and Si–NH₂–Al, respectively [3]. Although clear spectroscopic evidence of nitridation is just now emerging [4] after 40 years of research [5], the mechanism of nitridation has yet to be reported. In the present paper, we describe detailed density functional theory calculations revealing nitridation mechanisms in all-silica MFI zeolite (silicalite) and in acidic HY zeolite.

The first report of nitrated zeolites appeared in 1968 by Kerr and Shipman [5], who exposed HY to ammonia at elevated temperatures (>500 °C). Nitrogen was believed to enter the framework as a bridge between Al and Si atoms, though compelling evidence of this was not given. Since then various groups have applied ammono-thermal treatments to zeolites [4,6–14]. Some studies have reported that the resulting materials are active catalysts for reactions typically catalyzed by bases [8–10], such as the Knoevenagel condensation of benzaldehyde with malononitrile, suggesting that new basic sites have been formed by ammono-thermal treatment. However, the nature of the active sites and the resulting framework structure was largely unknown.

Quantum calculations on nitrated zeolites have been performed to investigate amine site stability [15,16], amine site base strength [16], and bifunctional acid–base properties [17–19]. Corma *et al.* performed quantum calculations on small clusters, and found that substituting Si–O–Si with Si–NH–Si is endothermic by ~100 kJ/mol, suggesting that high temperatures are needed for nitridation

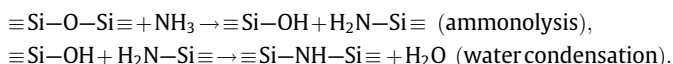
* Corresponding author. Address: Goesmann 222, University of Massachusetts, Amherst, MA 01003-9336, USA. Fax: +1 413 545 4490.

E-mail addresses: vagarwal@ecs.umass.edu (V. Agarwal), huber@ecs.umass.edu (G.W. Huber), wconner@ecs.umass.edu (W.C. Conner Jr.), auerbach@chem.umass.edu (S.M. Auerbach).

[15]. Astala and Auerbach performed periodic DFT calculations on zeolites with small unit cells (SOD and LTA); they found that nitridation in all-silica zeolites introduces minimal strain because of the flexibility of surrounding Si–O–Si angles [16]. Their calculations also predict that the base strength of Si–NH–Si is nearly twice that of Si–O–Si; this was later confirmed by the CO₂ TPD studies of Han et al. [12]. Lesthaeghe et al. performed cluster calculations to investigate the properties of bifunctional acidic/basic zeolites with traditional Brønsted acid sites proximal to nitrated basic sites [17–19]. They found novel catalytic activity in such systems but only when the acid/base moieties are sufficiently removed to avoid auto-neutralization. All these calculations point to the very promising nature of nitrated zeolites, but still leave unclear what actually gets made by ammono-thermal treatment of zeolites, prompting intensified efforts at characterizing these materials.

Han et al. applied IR, Raman and ²⁹Si MAS NMR to zeolites exposed to alkylamines and heat, finding evidence of strong framework-amine interactions [12–14]. Recent ²⁹Si NMR of nitrated zeolites coupled with quantum chemical shift calculations provide unambiguous evidence, for the first time, that ammono-thermal treatment of HY zeolite yields resonances associated with Si–NH₂–Al linkages [4]. This finding underscores the ability of NMR—over other spectroscopies such as IR—to provide “smoking gun” evidence of nitridation in zeolites. This study also featured the use of quantum calculations to extract nitridation yields from the NMR spectra. Despite the promise of this breakthrough, the mechanism of such nitridation is still unclear. Discovering the mechanism(s) may explain observed nitridation rates, provide predictions of base catalyst stability, and shed light on the fundamental aspects of functionalizing zeolites. In the present paper, we investigate nitridation mechanisms using a novel synthesis of computational methods.

In siliceous zeolites, a reasonable nitridation mechanism involves the following two steps:



Our calculations reported below for nitridation in silicalite do actually find this mechanism, but it turns out *not* to be the primary pathway, hence the value of the *ab initio* study. Nitridation in HY is even more complicated involving many more degrees of freedom, defying any initial intuition we may bring.

Modeling nitridation pathways in zeolites such as HY and silicalite is a daunting computational task because of the large unit cells involved, and the many degrees of freedom that likely participate during nitridation. Systems with large unit cells (>250 atoms) make periodic DFT calculations extremely slow [20]; such systems can, however, be treated with embedded-cluster methods such as ONIOM [21]. Although such cluster calculations do not include true long-range interactions present in real materials, the contributions from such interactions cancel when computing reaction barriers in sufficiently large clusters [21]. In the calculations reported below, we have used ONIOM as implemented in Gaussian codes with quantum clusters containing ~30 heavy atoms and total systems with as many as 485 heavy atoms.

The challenge then becomes finding transition states involving cooperative motions of these many degrees of freedom. The nudged elastic band (NEB) approach has emerged as the method of choice for finding elusive transition states [22]. This “chain-of-states” method has been applied to many surface science problems, especially those involving metal surfaces, and has been efficiently implemented in the VASP periodic DFT code [23]. We report below the first combined application of ONIOM and NEB, routinely using 15 system replicas in the NEB chain-of-states. Because this amounts to a total of 485 × 3 × 15 = 21,825° of

freedom, we pay special attention below to the use of optimization algorithms that scale gently for both memory and CPU time.

We find below markedly different mechanisms for nitridation of ≡Si–O–Si≡ and ≡Si–OH–Al≡ sites, including pentavalent Si in the former case. In both cases, however, we find overall barriers on the order of 350 kJ/mol, indicating that high temperatures are generally needed for zeolite nitridation. Because these barriers are well in excess of the reaction endothermicity (~100 kJ/mol), barriers for the reverse process are also quite high, indicating that nitrated zeolites should remain relatively stable up to reasonably high temperatures.

The remainder of this article is organized as follows: in Section 2 we provide computational details of both ONIOM and NEB calculations; in Section 3 we discuss the results of reaction pathway calculations for nitridation in both HY and silicalite zeolites; and in Section 4 we offer concluding remarks.

2. Computational details

2.1. Zeolite models

All calculations in this work were performed using an assumption of a finite cluster. As shown by Fermann et al. [21], calculating energy differences between nearby configurations, such as a reaction barrier, cancels the effect of long-range slowly-varying interactions, leaving reaction energies controlled only by local electronic interactions.

We have studied silicalite and HY zeolites in this work. Silicalite (MFI-type) exhibits orthorhombic symmetry above 340 K and monoclinic symmetry below that temperature [24]. Since the substitution reaction takes place at high temperatures, the clusters have been built assuming orthorhombic symmetry [24,25]. The space group of orthorhombic silicalite is PNMA with 12 crystallographically distinct silicon atoms and 26 distinct oxygens. To investigate how nitrogen substitution reaction energies vary with oxygen location in silicalite, we computed nitridation reaction energies from clusters built around O(8) and O(13). These oxygens are representative in that O(8) has the lowest Si–O–Si angle in silicalite (155°), while O(13) has the highest (176°) [26]. Because the Si–O–Si angle is found to correlate with chemical properties such as Brønsted acid strength and ²⁹Si NMR chemical shift [1], computing nitridation energies at O(8) and O(13) will reveal the extent of variation among oxygen sites in silicalite.

Clusters with the silicalite structure were centered on either O(8) or O(13), containing 143 total silicon (tetrahedral or “T”) atoms and 342 oxygen atoms, hereafter denoted 143 T clusters. Using computational methods described in detail below, we have found that nitridation energies at these sites differ by only 5 kJ/mol, less than 4% of the nitridation energy, indicating that nitridation thermodynamics is fairly insensitive to oxygen location in silicalite. It remains possible that the nitridation mechanism at O(8) may differ from that at O(13). However, because of the computationally intensive nature of these calculations, we have focused on modeling substitution at oxygen O(13) (between silicons Si(2) and Si(8)) [26], which is catalytically relevant because of its direct access to the silicalite channel intersection. Mechanistic calculations were performed on the 143 T cluster centered at O(13). All cluster models (including those of HY) were terminated with oxygen atoms fixed at their crystallographically-determined locations.

HY zeolite (FAU-type) exhibits space group FD $\bar{3}$ M, with a single crystallographically distinct silicon site and four distinct oxygens [27]. Of these oxygens, O(1) and O(4) are the most accessible, being in the 12 T-ring window separating adjacent supercages. To investigate how nitrogen substitution energy var-

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