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Kinetic stability of nitrogen-substituted sites in HY and silicalite from first principles

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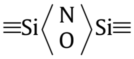
ABSTRACT

We have modeled the formation kinetics of nitrogen-substituted (nitrided) zeolites HY and silicalite; we have also modeled the stability of nitrided sites to heat and humidity. These kinetic calculations are based on mechanisms computed from DFT-computed pathways reported in our previous work. Reactant ammonia and product water concentrations were fixed at various levels to mimic continuous nitridation reactors. We have found that zeolite nitridation — replacing Si–O–Si and Si–OH–Al linkages with Si–NH–Si and Si–NH_2–Al, respectively — proceeds only at high temperatures (>600 °C for silicalite and >650 °C for HY) due to the presence of large overall barriers. These threshold temperatures are in good agreement with experiments. Nitridation yields were found to be sensitive to water concentration, especially for silicalite where nitridation is more strongly endothermic. As a result, overall nitridation yields in silicalite are predicted to be much lower than those in HY. The stability of nitrided sites was investigated by modeling the kinetics of nitridation in reverse, going back to untreated zeolite plus ammonia. Using 10 h as a benchmark catalyst lifetime, nitrided silicalite and HY half-lives exceeded 10 h for temperatures below 275 and 500 °C, respectively, even at saturation water loadings. As such, our calculations suggest that nitrided silicalite and HY zeolites require high temperatures to form, but once formed, they remain relatively stable, auguring well for their use as shape-selective base catalysts.

1. Introduction

Acidic zeolites have proven to be effective and stable catalysts for a variety of petrochemical and fine-chemical processes [1]. Nitrided zeolites — i.e., those with Si–O–Si and Si–OH–Al groups substituted by Si–NH–Si and Si–NH_2–Al — show promise as shape-selective basic catalysts [2–5]. Such materials may find use in carbon–carbon bond-forming reactions for biofuel production [6], as well as in the fine-chemical, pharmaceutical and food industries [7–10]. However, for nitrided zeolites to be useful catalysts, their stabilities to heat and humidity must be investigated and understood. For example, Ernst et al. found that the presence of water can influence the activity of nitrided zeolites [2]. To shed light on this, we have applied molecular modeling to understand the formation and decomposition kinetics of nitrided zeolites HY and silicalite. In our previous work [11], we used DFT to compute pathways and energetics of nitridation in these zeolites. In the present paper, we apply these mechanisms to develop rate equations describing nitridation rates and yields. We also study the reverse processes to investigate the stability of these nitrided materials to heat and humidity.

Our DFT calculations reveal two-step processes for nitridation of HY and silicalite, but with very different intermediates [11]. The intermediate in silicalite involves a 4-ring  $\equiv Si\left\langle \begin{smallmatrix} N \\ O \end{smallmatrix} \right\rangle Si\equiv$ with pentavalent Si, while nitridation in HY involves physisorbed ammonia activated by release from the bidentate ammonium–zeolite ion-pair complex. The overall barriers for nitridation were found to be quite similar in HY and silicalite, around 340–360 kJ/mol, indicating the need for high temperatures during nitridation. However, the reaction energies from gas-phase ammonia to gas-phase water are quite different: 29 kJ/mol for HY and 132 kJ/mol in silicalite, indicating the possibility of higher nitridation yields in HY. Now we turn to making these qualitative statements quantitative by developing kinetic equations that give overall rates and yields.

Our kinetic model is inspired by experimental nitridation, which is typically carried out under high flow rates of dried ammonia at high temperatures (>500 °C) [5,12–14]. We have found in our most recent experimental work that high ammonia flow rates are crucial for generating high-quality nitrided zeolites, with significant nitrogen substitution, good crystallinity and microporosity [14]. The effect of high ammonia flow rates is to keep the concentration of ammonia in zeolite pores high and the concentration of

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water low, hence pulling the endothermic equilibrium to nitrided products by LeChatelier's principle.

The combination of high pressure and temperature means that pores are filled with *very* weakly adsorbed ammonia, which we model as a kind of gas-phase or "free" ammonia at fixed concentration in zeolite pores. This "free" intrapore ammonia can evolve to a more bound species of ammonia, ready to engage in nitridation chemistry as described in our previous work [11], involving intermediates, transition states, and eventually products, consisting of the nitrided zeolite plus bound intrapore water. At the temperatures and ammonia flow rates used in nitridation, this bound species of intrapore water will itself evolve to a more "free" form of intrapore water, whose concentration we will model in our kinetic equations as being fixed to various low values. Because the concentrations of these "free" ammonia and water species inside zeolite pores are not known during nitridation, we will investigate below how varying these concentrations influences rates and yields of nitridation. We will also determine how varying the concentration of "free" water impacts stabilities of nitrided zeolites.

By modeling nitridation at fixed concentrations of free ammonia and water, we consider the process at steady state with respect to these weakly adsorbed species. To implement such a model, we require rate constants describing the bimolecular process of binding free ammonia at zeolite Brønsted sites, and free water at zeolite-nitrided sites. Such rate constants can be estimated using gas-phase collision theory, but such a simple approach ignores the nature of intrapore dynamics and diffusion. Molecular dynamics simulations can in principle account for these effects, but such a treatment is beyond the scope of the present work.

Below we find that nitridation yields are sensitive to free water concentration, especially for silicalite where nitridation is more strongly endothermic. Our calculations also suggest that nitrided silicalite and HY zeolites require high temperatures to form, but once formed, they remain relatively stable, auguring well for their use as shape-selective base catalysts.

The remainder of this article is organized as follows: in Section 2 we set up the kinetic equations and give computational details regarding their parameterization and solution; in Section 3 we give results and discussion of both nitridation kinetics and product stability; in Section 4 we offer concluding remarks; and in A we detail the set of kinetic equations solved in our study.

2. Calculation details

Here, we describe the kinetic equations used to model zeolite nitridation and stability. Then, we discuss the computation of temperature-dependent parameters for these kinetic equations.

2.1. Kinetic equations

As discussed above, zeolite nitridation is best carried out by passing dried ammonia at high pressures in a fixed bed of zeolite at high temperatures [14]. The ammonia flow rate is kept high to maintain high concentrations of ammonia and to remove water formed during nitridation. As such, the reactor can be modeled as a semi-batch-reactive separator, analogous to a batch reactive-distillation system [15], acting as a multifunctional reactor where one of the products (water) is selectively removed.

For nitridation of both HY and silicalite, we posit the presence of both "free" and "bound" species of reactant ammonia and product water, as discussed in the Introduction. Also, for both HY and silicalite, nitridation was found to proceed via two-step mechanisms, starting from bound ammonia and leading to bound water [11]. As such, the full process beginning with free ammonia and ending with free water is given by the following *four-step* mechanism:

$$\begin{aligned}\mathrm{Zeo} + \mathrm{NH_3} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Zeo}\ldots\mathrm{NH_3}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Int} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{NH}-\mathrm{Zeo}\ldots\mathrm{H_2O}] \\ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{NH}-\mathrm{Zeo} + \mathrm{H_2O}. \qquad (1)\end{aligned}$$

In mechanism (1), "Zeo" represents a possible nitridation site. As discussed in our previous work [11], we have investigated kinetics at the following possible nitridation sites: $\equiv\mathrm{Si{-}O{-}Si}\equiv$ at oxygen O(13) in silicalite, and $\equiv\mathrm{Si{-}OH{-}Al}\equiv$ at O(1) in HY. The designation "NH-Zeo" in mechanism (1) indicates the corresponding nitrided sites, i.e., $\equiv\mathrm{Si{-}NH{-}Si}\equiv$ in silicalite and $\equiv\mathrm{Si{-}NH_2{-}Al}\equiv$ in HY. $\mathrm{NH_3}$ signifies *extremely* weakly adsorbed ammonia in silicalite and HY pores, while $\mathrm{Zeo}\ldots\mathrm{NH_3}$ indicates ammonia bound to sites in silicalite and HY that we have considered for nitridation in previous work [11]. Likewise, $\mathrm{H_2O}$ signifies *extremely* weakly adsorbed water in nitrided silicalite and HY pores, while $\mathrm{NH\text{-}Zeo}\ldots\mathrm{H_2O}$ indicates water bound to nitrided sites in silicalite and HY. Finally, Int labels the nitridation intermediates discussed in our previous work [11]; these are activated molecular ammonia in HY, and a 4-ring $\equiv\mathrm{Si} < \genfrac{}{}{0pt}{}{\mathrm{N}}{\mathrm{O}} > \mathrm{Si}\equiv$ with pentavalent Si in silicalite.

The corresponding set of coupled differential equations is given in Appendix A. In these rate equations, we use concentration units of numbers of molecules or sites per unit cell volume. We note that rate equations for free ammonia and water are not present in Appendix A because we hold these concentrations fixed, hence making a steady-state approximation for these species. We also note that the sum of rate equations in Appendix A vanishes, enforcing conservation of mass of the zeolite during nitridation. We solve these rate equations with two different initial conditions to model two distinct experiments. In the first case, we model the nitridation process (denoted "formation") by starting with a certain concentration of Zeo, a fixed high concentration of free ammonia, and various fixed concentrations of free water. In the second case, we model the stability of nitrided catalyst (denoted "stability") by starting with a certain concentration of NH-Zeo, various fixed concentrations of free water, and no free ammonia. This second case investigates the use of nitrided zeolites as catalysts in the presence of various amounts of water.

For *formation* calculations, we report saturated free ammonia concentrations in mmol per gram zeolite, the typical units of experimental adsorption measurements. For all calculations, we report free water concentrations in molecules per unit cell to indicate whether the system is near water saturation or is relatively dilute. For silicalite nitridation at O(13), we assume an initial Zeo concentration of 7.4 sites per unit cell, obtained by dividing the 192 oxygens per MFI unit cell into the 26 crystallographically distinct oxygen locations [16]. The free ammonia concentration in silicalite was fixed at its saturation value of 1.5 mmol/g silicalite (16 molecules per unit cell) [17]. As a point of reference, we note that ammonia becomes saturated at a pressure of 9.8 atm at 25 °C. Free water concentrations for nitridation of silicalite were fixed at values in the range 10^{-6}–10^{-4} molecule per unit cell. As a reference point, these loadings correspond at 800 °C to equilibrium water partial pressures of 4×10^{-7} and 4×10^{-5} atm, respectively. These values were obtained by calculating Henry's law coefficient at 300 °C in the Henry's law regime [18], and extrapolating to 800 °C using the van't Hoff equation. Although drying zeolites so thoroughly is generally difficult, the conditions studied herein of very high temperatures coupled with high flow rates of ammonia make these water concentrations relevant. Nitridation of silicalite was studied at temperatures in the range 700–1000 °C. For both silicalite and HY, calculated nitridation yields are reported as % substitution = $([\mathrm{NH\text{-}Zeo}]_t/[\mathrm{Zeo}]_0) \times 100\%$, for consistency with our recent experimental studies [5,14].

For HY nitridation at O(1), we assume an initial Zeo concentration of 13.5 sites per unit cell, derived as follows. Our recent nitrid-