

## Efficient Use of Bifunctional Acid–Base Properties for Alkylammonium Formation in Amine-Substituted Zeolites

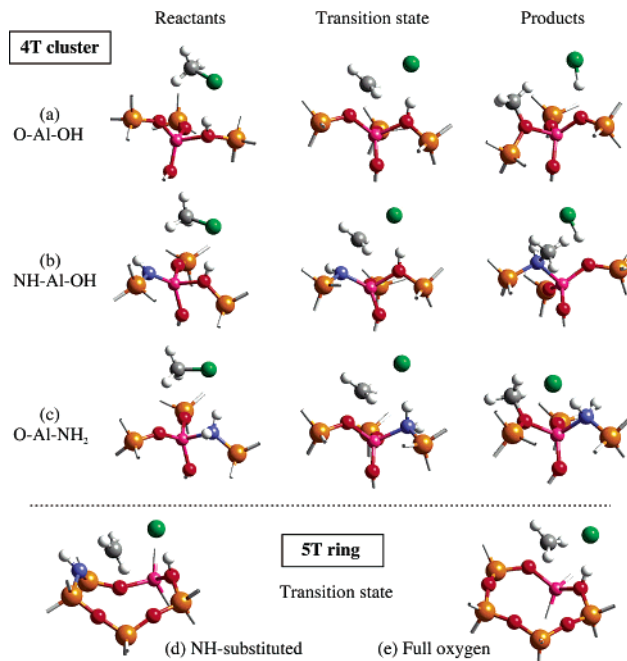
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Zeolites are microporous crystalline aluminosilicates with a wide variety of properties and applications, due mainly to their shape selectivity and Brønsted acid sites. The range of their applications can be extended by a well-chosen organic functionalization,<sup>1</sup> altering the surface properties that control interaction with various guest species. Yamamoto et al. succeeded in synthesizing LTA and MFI frameworks with bridging oxygen atoms replaced by methylene groups.<sup>2</sup> Inspired by these results, Astala and Auerbach provided evidence at the atom and electron levels that zeolites can accommodate methylene and amine groups at high concentrations with minimal strain.<sup>3</sup> Theoretically determined adsorption energies of typical guest molecules such as NH<sub>3</sub> and BF<sub>3</sub> also indicate that Si–NH–Si groups are significantly stronger Lewis bases than the usual Si–O–Si bridges.<sup>3</sup> While only acid or base properties were monitored separately, the chemical behavior of neighboring Brønsted acid–Lewis base sites should be explored thoroughly before actual synthesis of these novel materials.

Many important zeolite-catalyzed reactions in the petrochemical industry include the protonation of olefins and alcohols. In situ spectroscopic studies of the interaction of Brønsted acid sites with adsorbed molecules have demonstrated that carbenium ions are not stable within zeolite cavities<sup>4</sup> but that protonation of adsorbed olefins and alcohols results in the formation of covalent alkoxide species. This was also confirmed by quantum mechanical cluster calculations.<sup>5</sup> It is believed that chemisorption proceeds in a concerted manner, controlled by a bifunctional (acid–base) mechanism, in which both the Brønsted acid site and Lewis base properties of an oxygen atom neighboring the acid site must be carefully balanced. While earlier research focused mainly on the zeolitic acid properties, the basicity of the Lewis base site could be drastically improved by appropriate isoelectronic substitution. Amine substitution in particular might promote alkylammonium formation, subsequently lowering corresponding reaction barriers. Up to now, neither theoretical nor experimental findings have confirmed this hypothesis. This communication provides strong evidence that reaction barriers of important catalytic processes can be significantly lowered by appropriate substitution.

Methanol to hydrocarbon (MTH) and methanol to olefin (MTO) conversions are well-known processes in the production of higher hydrocarbons and other value-added products. In light of sustainable energy production, early patents also report the possibility of converting halomethanes,<sup>6</sup> circumventing the costly formation of synthesis gas and reducing the number of byproducts. As a prototypical reaction step, we studied the first step of the dissociative mechanism in the conversion of chloromethane to hydrocarbons over acidic zeolite catalysts such as H-ZSM-5.<sup>7</sup> Using traditional zeolites, containing only O bridges, this first step leads to the formation of a surface methoxide species and hydrochloric acid, as shown in Figure 1a. Introducing NH bridges into the silicon/aluminum framework leads to the formation of a methylammonium species. The chemical properties and catalytic behavior of these



**Figure 1.** Stationary points for methoxide or methylammonium formation from various initial configurations.

novel materials are explored from a microscopic point of view, simulating the zeolite catalyst by four tetrahedral atoms. Even though these clusters do not fully represent the zeolitic environment, they have been shown to provide an adequate qualitative picture of chemical rearrangements that occur locally on the active site.<sup>8</sup> Full geometry optimizations and frequency calculations were performed within the Gaussian03 software package<sup>9</sup> using DFT, employing Becke's three-parameter B3LYP functional.<sup>10</sup> Activated complexes were validated to be true transition states and to exhibit only one imaginary frequency. Reaction barriers for full-oxygen clusters were calculated for reference purposes (Figure 1a). We stress the fact that we do not aim to perform a detailed study of this particular reaction mechanism; this reaction merely serves to illustrate the effect of amine substitutions on the reaction barrier.

Figure 1b shows a 4T cluster containing a single aluminum substitution with the NH group bridging silicon and aluminum, while a neighboring oxygen site is protonated. The energetic results of the adsorbed species and activated complexes are summarized in Table 1. The adsorption energy increases slightly due to the NH substitution (8.6 kJ/mol), but the main difference can be seen in the activation energy, which is substantially lowered (28.5 kJ/mol). As the process is concerted and the acidity of the OH group is not expected to be significantly altered, the decrease in activation energy must be ascribed to the stronger basic character of the NH group, hereby confirming the preliminary results of Astala and Auerbach.<sup>3</sup> The previous starting configuration is, however, not the energetically

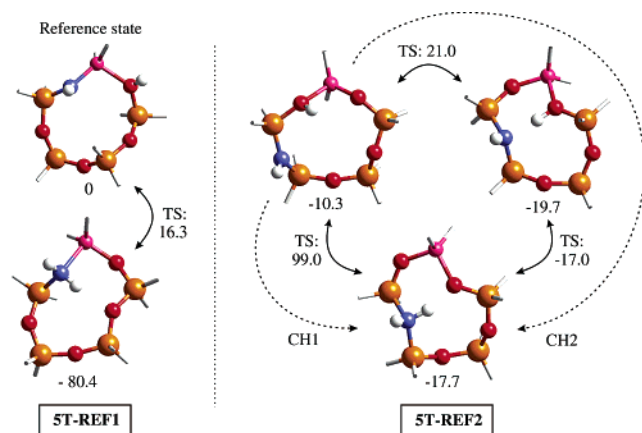
**Table 1.** Energies of Adsorbed Species and Transition States for Methoxide or Methylammonium Formation<sup>a</sup>

B3LYP/6-31G(d)	4T cluster		
	(a) O–Al–OH	(b) NH–Al–OH	(c) O–Al–NH <sub>2</sub>
adsorbed reactants	–15.9	–24.5	–15.3
transition state	145.5	108.4	164.9
adsorbed products	–7.9	–105.1	60.3
energy barrier	161.4	132.9	180.2

	5T ring	
	(d) NH-substituted	(e) full oxygen
adsorbed reactants	–24.5	–16.6
transition state	93.0	153.4
adsorbed products	0.3	2.5
energy barrier	117.5	170.0

<sup>a</sup> All values are relative to the gas-phase reactants and are in kJ/mol.



**Figure 2.** Energy diagram of proton mobility in amine-substituted 5T rings. All energies are in kJ/mol and relative to the reference state (including transition-state energies).

most probable one. Due to the strong basic character of the nitrogen atom, the acidic proton will migrate and create a mildly acidic NH<sub>2</sub> group (Figure 1c). The latter configuration is no longer characterized by optimal acid–base properties and gives rise to an increased energy barrier with respect to the reference material containing only O bridges. This dramatic change finds its origin in the natural neutralization of a zeolite with both strong acid and base sites to a zeolite with weak acid–base properties. Thus, in view of optimizing catalytic performance for typical acid–base reactions, there is no use in synthesizing this type of zeolite in which nitrogen and aluminum substitutions occur on the same T site.

In exploring efficient relative positions for the NH bridge and Al site, proton mobility must be addressed in these new materials. As shown in Figure 2, two 5T rings are considered: a first one with both OH and NH groups located at the same T atom (5T-REF1) and a second cluster with the nitrogen substitution occurring at a neighboring tetrahedral site (5T-REF2). In the 5T-REF1 cluster, amine protonation has a low activation energy and results in a thermodynamically favored configuration, characterized by non-preferable acid–base properties of the zeolite. By ensuring that the nitrogen substitution occurs in a neighboring tetrahedral site, the possibility of amine protonation decreases (5T-REF2). Proton jumps (through a channel indicated by CH1 in Figure 2) between OH- and NH-substituted sites located in the first coordination sphere of a Si atom are now highly activated (109.3 kJ/mol). The only efficient channel (CH2 in Figure 2) for proton mobility leading to a NH<sub>2</sub> substitution is achieved by a two-step process beginning with a common on-site jump between two oxygen atoms followed

by a proton jump between an oxygen and nitrogen atom located at the opposite positions of the 5T ring.

From a different perspective, the 5T-REF2 cluster opens the possibility to new reaction pathways, involving two separate T sites. This could lead to more efficient use of the catalyst: larger molecules will not be restricted to a single tetrahedral site, but they will be able to detach the acid proton from the aluminum site while forming alkylammonium groups at nearby silicon sites. The transition state configuration of a possible reaction involving two T atoms is shown in Figure 1d. Due to the strong basic character of the nitrogen atom, the barrier for alkylammonium formation using two T sites is still substantially lower (52.5 kJ/mol) than for alkoxide formation on the Al site in the full-oxygen ring on one T site (Figure 1e). While the preliminary results on small clusters demonstrate the promising nature of these materials, more advanced calculations using larger 16T clusters yield a qualitatively similar effect (a difference in energy barriers of approximately 37 kJ/mol) and will be discussed in detail in a forthcoming publication.

In conclusion, microscopic calculations present strong evidence that amine-modified zeolites can successfully lower energy barriers for reactions in which both a Brønsted acid and a Lewis base site are involved. If the presence of nitrogen–aluminum bridges can be minimized during synthesis, a proton will only sporadically contaminate the nitrogen sites. Combining fully oxygen-surrounded aluminum sites and nearby Si–NH–Si bridges opens the door to acid–base-catalyzed reactions that are not solely centralized around the aluminum defect but in which two T sites are involved. This unique way of providing more basic sites will improve the chances of an adsorbed molecule undergoing successful reaction, allowing more efficient use of the zeolitic acid site and the surrounding environment.

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