Probing the Mechanism of NO_x Reduction over BaNaY Zeolites: A DFT Study

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Introduction

New catalysts are needed to reduce nitrogen oxide emissions from highly fuel-efficient diesel and "lean burn" engines. Experimental investigations in the literature have revealed the ability of BaNaY catalysts to reduce NO_x using acetaldehyde as the reductant at interesting temperatures for this application. Recently, Yeom et al. proposed a detailed mechanism for NO_x reduction over BaNaY, involving two competing pathways [1]. In our work, quantum chemical calculations have been performed to develop a better understanding of this complex chemistry as a complement to experiment. Several important intermediates in the mechanism of Yeom et al. could not be observed experimentally, so modeling may be able to verify the reasonableness of these proposed species and to provide additional molecular-level details.

Computational Methodology

A single six ring around site II was extracted from the crystal structure of Y zeolite and terminated with hydrogen atoms. We refer to this as the 6T model, where T denotes a tetrahedral framework atom (Si or Al). Ba^{2+} ions substitute for Na^+ ions almost completely at site II [2] in BaY zeolite, and site II was therefore considered as the active site. The atoms of the six ring and the adsorbates were treated quantum mechanically (QM). In some cases, these atoms were embedded in larger clusters of 36T and 96T atoms, and the surrounding atoms were treated using molecular mechanics (MM) to account for van der Waals interactions and steric effects from the surrounding zeolite framework. The SDD basis set [3] and B3LYP DFT method were used for the QM part, with the UFF force field for the MM part. For gas phase reactions, geometries of intermediates and transition state structures were calculated using the 6-311++G** basis set with the B3LYP method. All calculations were performed with the Gaussian 03 software package.

Results and Discussion

Barium is not widely studied using DFT, so the choice of basis set and functional is not obvious. To validate our choice, geometries were determined for gas-phase barium dihalides and compared to experiment. Heats of reaction for gas-phase reactions involving barium were also used for benchmarking. These studies show that the choice of basis set for barium is important and that SDD with B3LYP is a suitable combination of basis set and DFT functional. In addition, adsorption energies, geometries, and frequencies were calculated for adsorbed acetaldehyde, acetic acid, nitromethane, and water and compared to experiment where available.

To study the effect of the zeolite framework on the adsorption properties, the size of the zeolite cluster was increased from 6T to 36T and 96T using the embedded ONIOM method. Inclusion of van der Waals interactions by increasing the size of the MM part only changed the heat of adsorption by a small amount for all of the adsorbates studied. For example, the heat of adsorption of water increased by 1.7 kcal/mol when the size of the cluster increased from 6T to 96T. The calculated heat of adsorption for water on the 96T cluster (-24.3 kcal/mol) is in reasonable agreement the experimental value (-28.7 kcal/mol).

As a prelude to examining the proposed, detailed reaction mechanisms on the zeolite surface, we constructed the free energy landscapes for the corresponding set of reactions in the gas phase. Yeom et al [1] proposed two pathways, both heavily involving ionic species. Figure 1 shows the free energy landscapes for the corresponding gas-phase reactions (pathways 1' and 2'). Transition-state structures between the stable intermediates were also found but are not shown in the figure. In the gas phase, reactions involving neutral molecules are more likely, so we examined the analogous neutral pathways, too (pathways 1 and 2 in Figure 1). These calculations provide some insight into the mechanism, and they will be used as initial structures for future calculations on the BaNaY surface.

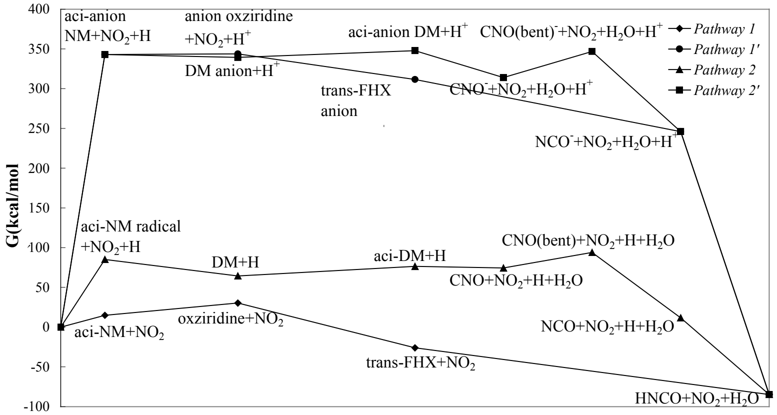

Figure 1. Free energy of gas phase reactions: pathways 1' and 2' are two competing ionic pathways [1]; pathways 1 and 2 are the analogous neutral pathways. NM = nitromethane, DM = dinitromethane, FHX = formohydroxamic acid

Significance

Density functional theory calculations were conducted to determine an appropriate level of theory for further studies of proposed intermediates in selective catalytic reduction of NO_x species over BaNaY zeolites.

References

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