



Impact of long-range electrostatic and dispersive interactions on theoretical predictions of adsorption and catalysis in zeolites

Erum Mansoor^a, Jeroen Van der Mynsbrugge^a, Martin Head-Gordon^{b,c}, Alexis T. Bell^{a,*}

^a Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720-1462, United States

^b Department of Chemistry, University of California, Berkeley, CA 94720-1462, United States

^c Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

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ABSTRACT

In this paper, we review the importance of long-range zeolite framework interactions in theoretical predictions for a variety of zeolite-catalyzed processes, and we show why such interactions must be determined accurately in order to reproduce experimentally measured adsorption and activation energies. We begin with an overview of the different strategies that have been used to account for long-range coulombic and dispersive interactions of zeolite framework atoms with species adsorbed at an active site. These methods include full periodic-DFT calculations and multi-layer hybrid techniques. Electrostatic interactions are observed to have a more significant impact than dispersive interactions on the geometries of ion-pair transition states and adsorbed species. Stabilization of the TS relative to reactant complexes is also dictated by electrostatic interactions. Dispersion effects are found to significantly stabilize both transition and reactant states for adsorbed species, especially those which have dimensions that provide good fits within the zeolite pore or cavity. We also show that the relevance of particular active site configurations can be missed, if the effects of long-range interactions are neglected. As a case in point, we demonstrate that a site previously considered inactive for ethane dehydrogenation, $[\text{GaH}_2]^+$ may in fact be more active than previously thought, when the impact of long-range interactions on the predicted activation energy is taken into account. Finally, the use of hybrid quantum mechanics/molecular mechanics approaches on extended, finite zeolite clusters has emerged as an accurate, highly cost-effective, and versatile alternative towards overcoming some of the present-day limitations of periodic calculations.

1. Introduction

Zeolites are crystalline, microporous aluminosilicates that are widely used as adsorbents and catalysts for numerous industrial processes and for the abatement of automotive pollutants [1]. The framework of zeolites comprises corner-shared TO_4 ($T = \text{Si}$ or Al) tetrahedra, which can form complex 3-dimensional networks of channels and cages of molecular dimensions (0.2–1.2 nm) [2]. Substitution of a trivalent Al atom for a tetravalent Si atom in the zeolite framework introduces a net negative charge, which must be compensated by a proton or an extra-framework cation, resulting in Brønsted or Lewis acid sites, respectively [3]. Given the very large number of zeolite structures that can be formed (over 230 framework types are recognized by the Structure Commission of the International Zeolite Association) [4], the performance of these materials as adsorbents and catalysts is dependent on their composition and structure.

In recent years, theoretical predictions based on electronic structure

calculations have emerged as a powerful tool for understanding the relationships between structure and performance of zeolites at the molecular level. Experience with the use of such methods has revealed that accurate prediction of adsorption and activation energies requires a model for the zeolite framework and a suitable electronic structure method to describe the interactions of adsorbed species at the active sites, as well as the influence of long-range coulombic and dispersive interactions associated with lattice atoms far removed from the catalytically active site.

An accurate description of the long-range electronic effects of the extended lattice atoms surrounding the active site in a computationally efficient manner has been a long-standing challenge in the area of molecular modeling of zeolites [5]. Two approaches have emerged over the past two decades to account for the long-range effects of the zeolite framework; these are referred to as finite cluster and periodic-boundary techniques (See Fig. 1). It is worth noting that both of these methods often focus on a single isolated active site in a perfect crystal, while in

* Corresponding author.

E-mail address: alexbell@berkeley.edu (A.T. Bell).

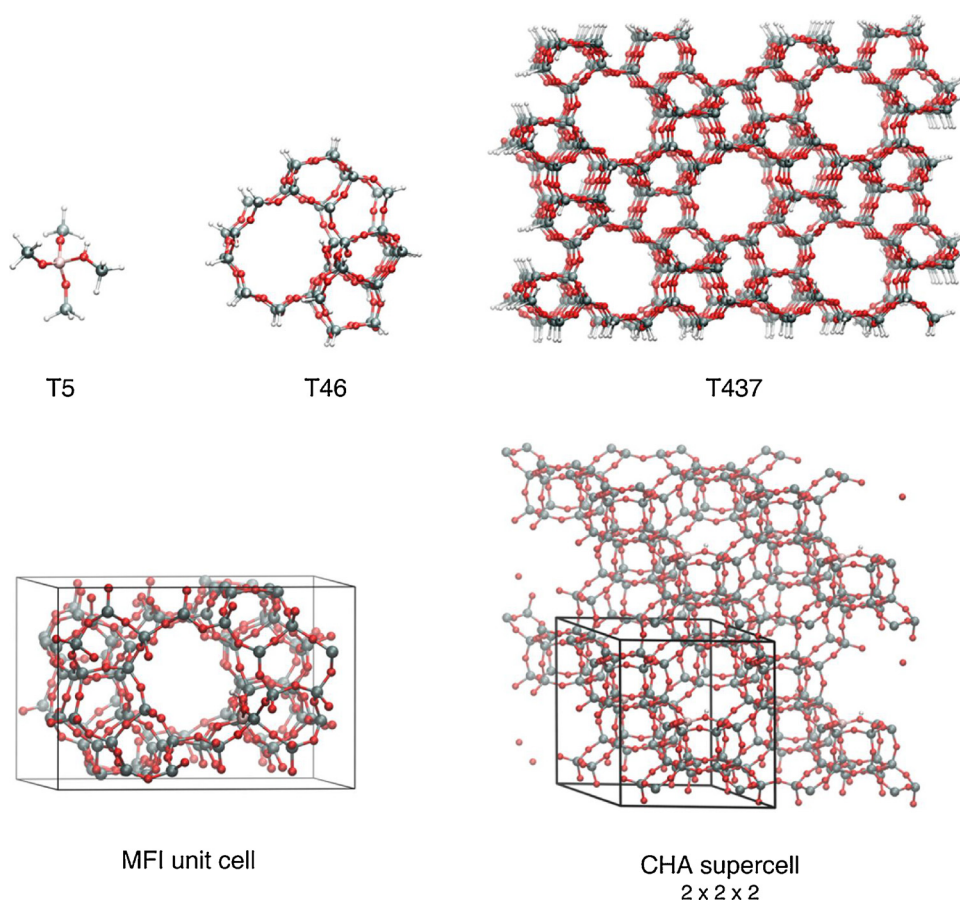


Fig. 1. Examples of finite cluster (T5, T46, T437 H-MFI fragments saturated with terminating hydrogen atoms) and periodic models (MFI unit cell and CHA $2 \times 2 \times 2$ super cell). T refers to number of tetrahedrally coordinated zeolite lattice atoms included in the model. Small cluster models are highly computationally efficient, but cannot capture shape-selective effects, nor the role of long-range electrostatics and dispersion associated with the extended zeolite lattice.

reality, the zeolite catalyst can be heterogeneous at different length and time scales [6,7]. Experimental measurements typically represent averages over local variations, defects (e.g. mesopores and terminal silanol groups) in the framework, extra-framework species and other system-specific complexities in the zeolite lattice. However, gaps between our understanding of idealized and real zeolite systems can be further minimized by judicious selection of an appropriate physical model of the active site, surrounding lattice, and associated long-range interactions for a given system [8].

In the cluster approach, the active center for adsorption or reaction and a portion of the surrounding framework are modeled by a finite zeolite fragment. To construct such a cluster model, several Si–O bonds are cleaved, which subsequently need to be saturated with terminating atoms (typically hydrogens) in order to create a chemically stable complex. Initial theoretical studies employed small clusters consisting of just three to five T-atoms representing only the active site itself. While the limited number of atoms in such a model greatly reduces the computational expense, and therefore enables the use of highly accurate electronic structure methods, the influence of the specific zeolite structure on adsorption thermodynamics and reaction kinetics owing to long-range electrostatic and dispersive interactions between the adsorbates and the framework atoms is neglected. To properly capture these effects, and to achieve agreement between calculated and experimentally measured enthalpies of molecular adsorption, a very large part of the zeolite surrounding the active site must be included. As expected, this strategy results in a rapid rise in computational cost. To offset the issue of computational expense, small clusters are often embedded in an extended hybrid model, which accounts for the long-range electrostatic and dispersive interactions of the zeolite lattice using computationally inexpensive force fields based on classical molecular mechanics or via less expensive quantum mechanical methods. Such multi-layer schemes are discussed in more detail in Section 2.2.

By contrast, in the periodic approach, one or more zeolite unit cells are simulated and infinitely repeated in all three directions by applying periodic boundary conditions. In principle, these simulations provide the most natural representation of the crystal structure and the shape and size of its pore system; however, as illustrated in Fig. 1, some industrially important zeolites exhibit large primitive unit cells (e.g., the MFI unit cell contains 288 atoms [4]), while others (e.g., CHA) require the use of super cells to properly isolate the active sites and avoid unphysical interactions between periodic images of sorbates or charged defects [9,10].

In Section 2, we briefly review commonly used theoretical tools for modeling zeolite adsorption and catalysis, with an emphasis on current implementations that account for long-range electrostatic and dispersive interactions of the zeolite framework. We discuss electronic structure methods (focusing on DFT), and their applications to zeolites in the form of full periodic DFT calculations or multi-layer hybrid schemes. Then in Sections 3–5, we illustrate the impact of long-range interactions on predictions of adsorption energies and activation barriers, as well as on conclusions reached about which sites may be active for promoting zeolite-catalyzed systems. Finally, in Section 6, we propose that the use of cost-effective hybrid quantum mechanics/molecular mechanics approaches on extended zeolite clusters is an attractive alternative to overcoming the shortcomings of periodic calculations, without compromising accuracy.

2. Brief overview of theoretical tools

2.1. Electronic structure methods

In both cluster and periodic studies, Kohn-Sham density functional theory (DFT) [11,12] is used for electronic structure calculations because of its favorable balance between accuracy and computational

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