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Modelling the adsorption of short alkanes in protonated chabazite: The impact of dispersion forces and temperature

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ABSTRACT

The adsorption of alkanes in a protonated zeolite has been investigated at different levels of theory. At the lowest level we use density-functional theory (DFT) based on semi-local (gradient-corrected) functionals which account only for the interaction of the molecule with the acid site. To describe the van der Waals (vdW) interactions between the saturated molecule and the inner wall of the zeolite we use (i) semi-empirical pair interactions, (ii) calculations using a non-local correlation functional designed to include vdW interactions, and (iii) an approach based on calculations of the dynamical response function within the random-phase approximation (RPA). The effect of finite temperature on the adsorption properties has been studied by performing molecular dynamics (MD) simulations based on forces derived from DFT plus semi-empirical vdW corrections. The simulations demonstrate that even at room temperature the binding of the molecule to the acid site is frequently broken such that only the vdW interaction between the alkane and the zeolite remains. The finite temperature adsorption energy is calculated as the ensemble average over a sufficiently long molecular dynamics run, it is significantly reduced compared to the $T = 0$ K limit. At a higher level of theory where MD simulations would be prohibitively expensive we propose a simple scheme based on the averaging over the adsorption energies in the acid and in the purely siliceous zeolite to account for temperature effects. With these corrections we find an excellent agreement between the RPA predictions and experiment.

1. Introduction

Acid zeolites are widely used in industry as catalysts for hydrocarbon conversion reactions. Zeolites are not only very efficient catalysts, the interactions between the hydrocarbon molecules and the inner walls of their cavities also permit to design catalysts with a very good selectivity. The diameter and shape of the pore structure of the zeolites and the interactions of molecules with the zeolite framework is also of decisive importance for their use as molecular sieves.

The simplest way to test the interaction between molecular reactants and the zeolite is to investigate their adsorption properties. For alkanes (saturated hydrocarbon molecules) experiment has demonstrated that the zero-coverage adsorption energy increases roughly linearly with the length of the molecular chain. In an acid zeolite one of the terminal CH_3 groups forms a weak chemical bond to the acid site while the remaining part of the molecule interacts with the zeolite framework through dispersion forces (van der Waals interactions). With increasing length of the alkane chain the adsorption energy increases by a constant increment for each additional CH_2 group. The contribution of the van der Waals (vdW) interactions to the adsorption energy depends on the specific channel and pore geometries of the material. This picture has been confirmed by almost constant differences between the adsorption energies of alkanes in purely siliceous, protonated and Na-exchanged zeolite, independent of the chain length. Eder and Lercher [1] were able to relate the experimentally observed increase in the adsorption energy with increased alkane chain length to the framework density, but an understanding at molecular level cannot be obtained from experiments.

Many theoretical investigations of the adsorption and diffusion of alkanes in zeolites (calculation of adsorption isotherms, diffusion coefficients, . . .) use molecular dynamics simulations based on empirical force fields describing the interactions between the molecules and between the molecules and the zeolite [2]. These techniques even permit predictions about the size- and shape-selectivity of special zeolite structures [3].

Investigations of processes where chemical bonds may be broken and re-formed require, however, a higher level of theory. Stronger chemical bonds between reactants are described with good accuracy by density functional theory (DFT). DFT is based

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on the Hohenberg–Kohn–Sham theorem which states that the ground-state energy of a many-electron system may be expressed as a function of the one-electron density. However, DFT cannot describe the weak dynamical electron–electron correlations which cause the vdW interactions. DFT calculations of the adsorption of alkanes in a zeolite based on semi-local exchange–correlation functionals describe the interaction of the molecules with the acid site with reasonable accuracy, but not the increase of the adsorption energy with increasing chain length [4].

Post-DFT corrections designed to account for dispersion forces have been proposed by Grimme [5]. The corrections are expressed as semi-empirical pair interactions, the force-field parameters are determined by comparison with high-level quantum-chemical calculations for a large molecular training set. The easy implementation and low computational costs made it the method of choice in many studies. At a higher level of theory, the semi-local correlation functional of DFT has been replaced by a non-local functional designed to produce the vdW forces arising from long-range non-local electronic correlations [6]. The non-local part of the functional was constructed using a simplifying approximation to the dielectric function of the system in the Random Phase Approximation (RPA). The approach has been extended to the calculation of the Hellmann–Feynman forces acting on the atoms, permitting fully selfconsistent calculations of the atomistic geometry including the influence of the vdW forces. Recently full many-body calculations of the total energy in the RPA in connection with the Adiabatic-Connection Fluctuation–Dissipation Theorem (RPA-ACFDT) [7,8] have been performed. These calculations include the vdW energy seamlessly and accurately, but can be performed only at a fixed atomic geometry.

Very recently we have investigated the adsorption of small alkanes in Na-exchanged chabazite using fully periodic calculations at all three levels of theory [9]: (i) The force-field approach of Grimme correcting DFT calculations with the gradient-corrected exchange–correlation functional of Perdew, Burke and Ernzerhof [10] – PBE-d. (ii) The non-local “vdW-functional” of Dion et al. [6], and (iii) the RPA-ACFDT. The results of this study have demonstrated that a comparison with experiment is meaningful only if the influence of finite temperature is taken into account. Bučko et al. [11] performed MD simulations of the adsorption of propane in protonated chabazite using the PBE-d method and demonstrated that at elevated temperatures the weak bond between the alkane and the acid cite is frequently broken. On average at 300 K the alkane remains only about two thirds of the time close to the active site. During the remaining time the molecule moves rather freely through the cavity and interacts with the inner wall of the zeolite through dispersion forces. We have used this result to approximate the adsorption energy of all alkanes in Na-exchanged chabazite at $T = 300$ K by the average of the $T = 0$ K adsorption energies in Na-chabazite and in purely siliceous chabazite in the proportion of 2 to 1. This simple and admittedly rather rough approach suggests that the RPA-ACDFT (i.e. the highest level of theory) describes alkane adsorption rather well [9]. Here we extend these studies to the adsorption of methane, ethane, and propane in protonated chabazite and we perform a thorough investigation of temperature effects by performing MD simulations for all three alkanes.

Our paper is organized as follows. After the introduction we provide a very brief summary of the underlying theory and computational methods. It is followed by a section on 0 K-energy minimization calculations, where we describe calculations of adsorption energies at different levels of theory. In the section on MD simulations we investigate the finite temperature effects on adsorption energies and propose an extrapolation mechanism to correct 0 K adsorption energies for those finite temperature effects. In the discussion we try to compare our results to experiment. At the end of the paper we give our conclusions.

2. Theoretical and computational setup

2.1. Theoretical description of the bonding between the alkane and protonated chabazite

The bonding between an alkane and an acid zeolite consists of two contributions. The first contribution stems from the interaction with the acid site and the second contribution originates from the vdW-interactions between the alkane and the zeolite wall. Both interactions present different challenges for the methodology applied.

To create an active site one Si atom in the zeolite structure is substituted by an Al atom. Since Al has one valence electron less than Si a local charge deficit is created. To compensate this charge deficit a H atom binds to one of the activated O atoms and donates its electron to the framework. This leaves a positively charged Brønstedt acid site which can now form a weak bond with the alkane. The character of the bond with the acid site is best illustrated by the difference electron density (= electron density distribution within the alkane-zeolite complex minus the electron densities of the clean zeolite and the isolated alkane molecule, recalculated at their geometries in the adsorption complex) shown in Fig. 1. The alkane molecule is polarized in the electrostatic field of the acid site and a bonding charge is accumulated between the terminal methyl group of the molecule and the acid proton. This charge redistribution is well described within density functional theory. In this work, we will use the generalized gradient approximation

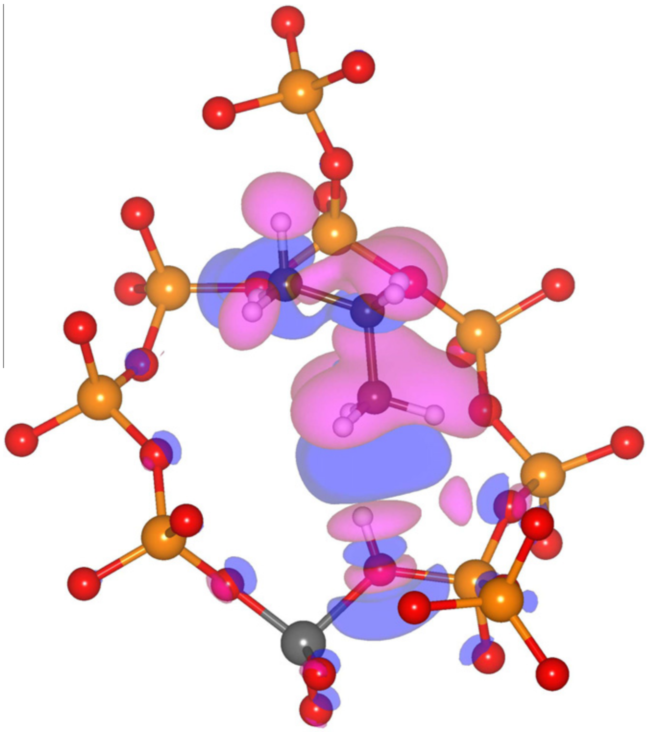

Fig. 1. Contour plot of the electron density redistribution (difference electron density) induced by the binding of a propane molecule at an acid site in chabazite. Si atoms of the framework are shown in yellow, O atoms in red, the Al atom in dark grey. The H atoms of the acid site and of the alkane are shown in white, carbon atoms in light grey. Red constant-density surfaces surround electron depleted regions and blue surfaces surround regions of increased electron density. Isodensity surfaces are drawn at $\pm 2 \times 10^{-3}$ electrons/Å^3. The accumulation of charge in the region between the terminal CH_3 group of the molecule and the acid proton reflects the formation of a weak chemical bond. Note that while both the alkane molecule and the O–H group of the acid site are quite strongly polarized, no charge redistribution is found on the chabazite framework. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)