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Short Communication

Periodic, vdW-corrected density functional theory investigation of the effect of Al siting in H-ZSM-5 on chemisorption properties and site-specific acidity

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Twelve crystallographically distinct Al substitution sites of H-ZSM-5 are modeled by periodic density functional theory using the vdW-DF functional. While the stability of Al substitution and Brønsted acid O–H bond length at different active site positions are similar, the O–H stretch frequency, Si–O–Al bond angle, and adsorption energies of various probe molecules differ notably without observable correlations between these properties. Comparison of adsorption energy values with and without van der Waals corrections demonstrates the significance of the inclusion of dispersion interactions. Our data indicate that theoretical investigations of H-ZSM-5 require a careful selection of the location of the active site.

1. Introduction

Zeolites are versatile materials with the broadest range of applications among heterogeneous catalysts [1]. The activity of these aluminosilicates in catalytic processes is attributed to their acidity, which derives from the replacement of a silicon atom at a tetrahedral site (T site) in the zeolite framework with an aluminum atom. The properties of these acid sites and their respective influence on catalytic activity are of great interest and have been investigated both experimentally and theoretically. To further improve zeolite catalyst performance and enable the design of zeolites with specific properties, a fundamental understanding of the active sites and reliable theoretical methods for the prediction of zeolite functionality are needed.

Theoretical simulations of zeolites have been carried out for more than two decades through force-field approaches and quantum mechanical methods. Among the latter, density functional theory (DFT) has gained significant attention, especially due to its applicability to chemical reactions (contrary to force-field approaches) and its lower computational cost compared to other higher order *ab-initio* methods, such as MP2 (second-order Møller–Plesset perturbation theory) [2]. However, the typically complex structure of zeolite crystals, which are comprised of unit cells containing as many as hundreds of atoms in a 3-dimensional (3D) configuration, imposes many challenges for modeling. The unit cell of MFI (termed H-ZSM-5 in its acidic aluminosilicate form) is composed of 96 T atoms (Si or Al) and 192 oxygen atoms, with a 3D pore network exhibiting two types of interconnected channels: Straight channels oriented along the *b* direction and sinusoidal channels oriented along the *a* direction (see Fig. 1). When creating an acid site in an MFI orthorhombic unit cell model, there are 12 geometrically distinguishable T site locations that can be occupied by Al.

Early modeling efforts used cluster models containing as little as 3 to 5 T sites to represent the active catalytic site [2–5]. The dangling bonds resulting from isolation of the cluster from the remaining zeolite are saturated with hydrogen atoms. It is evident that this approach is not capable of mimicking the complex environment (*i.e.* confinement) of active sites and long-range interactions, *e.g.* the exclusion of van der Waals forces. With embedded cluster methods, such as ONIOM or QM/MM, more sophisticated zeolite framework models can be realized at significantly lower computational cost compared to full *ab-initio* techniques [6–10]. However, embedded cluster models suffer from the strong sensitivity of adsorbate binding energies to the selected force-field and the difficult assignment of the QM/MM boundary [11]. The availability of powerful computational resources, optimized DFT codes, and increasingly accurate exchange-correlation functionals permits fully periodic DFT simulations to be performed, even on large zeolite unit cells, which eliminates many of the shortcomings mentioned above. Nevertheless, in their careful review of periodic DFT simulations applied to catalytic reactions in zeolites, Hafner et al. emphasize the importance of dispersion forces and the challenge associated with selecting a proper exchange-correlation functional [12].

In addition to the judicious selection of the simulation method, the location of the modeled acid site within a given zeolite structure must be carefully considered. As shown in Fig. 1, a Brønsted acid (BA) site in

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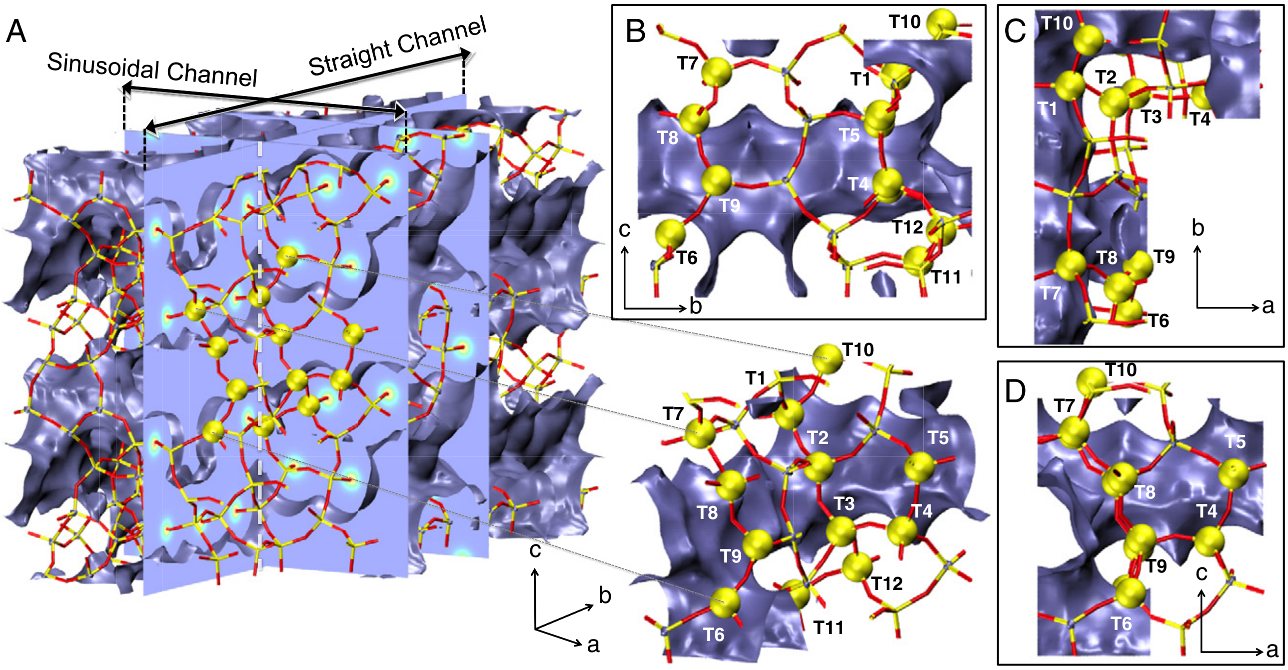

Fig. 1. (A) 3-dimensional (3D) overview of the siliceous MFI framework (Si — yellow, O — red). The sinusoidal channel along the *a* direction and the straight channel along the *b* direction are approximated by an isosurface (purple) of the calculated charge density at 0.004 e/Å^3. The two parallel planes normal to the *b* direction cut through the center of two adjacent sinusoidal channels. The plane normal to the *a* direction cuts through the center of a straight channel. All 12 crystallographically distinct T sites are marked in the enlarged version of the 3D representation and in the corresponding 2D projections in all three directions (panels B–D).

H-ZSM-5 can be located at 12 distinguishable T sites. Prior studies that attempted to experimentally characterize Al siting in the MFI framework report disparate results [13–15], and generally conclude that Al siting is highly sensitive to synthesis protocols [14]. This is consistent with calculated Al site stabilities reporting small variations of *ca.* 0.2 eV, which is approximately equal to the error of DFT simulations [16]. In efforts to avoid computational expense, theoretical investigations of H-ZSM-5 have often focused on specific T site locations, notably T7 and T12, as the most representative active site model(s) [3,7,17–19]. This selection is typically based on the relative stability of the site (*i.e.* T7) and/or its accessibility to reactants/adsorbates (*i.e.* T12), although other T sites have been modeled as well [9]. The heterogeneity of acid sites in zeolite frameworks, however, is an area of active debate [12]. Brändle and Sauer [17] used an embedded cluster approach to study the influence of crystal structure on BA site properties, and reported that the acidity assessed by the deprotonation energy can vary as much as 30 kJ/mol among four different zeolite framework types, including MFI. In contrast, an experimental study by Liu et al. [20] concluded that BA sites in zeolites with MFI and MWW structures exhibit similar behavior. Mihaleva et al. [21] reported significant variations in adsorption and acidity properties of two chabazite (CHA) clusters of different shapes. Yang et al. [22], Gounder and Iglesia [23], and Chu et al. [24] have shown that location dependent confinement effects can alter the catalytic properties of acid sites. Evidently, a comprehensive investigation of the sensitivity of the catalytic properties of BA sites to their location within the zeolite crystal is needed. In the present study, we report structural, vibrational, and energetic properties of all 12 crystallographically distinguishable Al-substituted T sites of zeolite H-ZSM-5 using thorough periodic DFT simulations and a dispersion-corrected functional (vdW-DF) [25,26]. Particular attention is given to properties that have been suggested as a measure of acid strength, including NH_3 and pyridine adsorption energy, O – H stretch frequency, O – H bond length, and the Si – O – Al bond angle. Moreover, we also examined the adsorption of CO, CH_4, and CH_3OH given their relevance to many zeolite catalyzed reactions. An improved understanding of the influence of Al siting combined with novel characterization and synthesis methods that allow for controlled placement of Al atoms in a zeolite framework has the potential to impact the design of tailored zeolites with improved catalytic properties.

2. Computational methods

All DFT calculations were performed using the Atomic Simulation Environment (ASE) [27], the Vienna *ab-initio* simulation package (VASP) [28,29], and the projector-augmented wave (PAW) method. For benchmarking purposes, the PBE, RPBE, PW91, DFT-D2 [30], and the vdW-DF [25,26] exchange-correlation functionals were employed. Conclusions regarding the properties of individual T sites are based on results obtained from the vdW-DF functional, which was identified as the most accurate functional that self-consistently accounts for van der Waals (vdW) interactions, in contrast to the semi-empirical DFT-D type functionals by Grimme [30,31]. Periodic boundary conditions in all three directions of the MFI unit cell were employed with the plane-wave kinetic energy cutoff set at 540 eV. Brillouin-zone sampling was restricted to the Γ-point and Gaussian smearing with $k_bT = 0.1$ eV was used. All atoms in the unit cell were relaxed and the convergence criterion for the net force on each atom was 0.02 eV/Å. The optimized lattice constants of the siliceous MFI unit cell are $a = 20.293$ Å, $b = 19.938$ Å, and $c = 13.275$ Å, which are *ca.* 1% larger than experimental reference values [32]. The same lattice parameters were used for calculations with one Al substitution per unit cell (Si/Al = 95). Binding energies are reported as negative values for exothermic adsorption. VdW contributions were directly extracted from the VASP vdW-DF output, which tends to overestimate the relative contribution of the vdW forces. Vibrational frequencies were obtained in the harmonic oscillator approximation with a displacement of 0.01 Å. Additional information