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The effect of framework organic moieties on the acidity of zeolites: A DFT study

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Abstract

Acidic properties of H-CHA, H-ZOL-C, and H-ZOL-N have been investigated using periodic density functional calculations to understand the effect of organic moiety incorporation on their acidities. Results from NH_3 adsorption energy, deprotonation energy, and relative nucleophilicity calculations are consistent and show that the relative Brønsted acid site strength decreases in the order H-CHA > H-ZOL-C > H-ZOL-N. The geometrical parameters of the optimized structures indicate the easier incorporation of NH rather than CH_2 in the chabazite framework. Moreover, the basicity of the lattice O, N, and C atoms increases in the order C < O < N.

Keywords: Microporous molecular sieves; Hybrid organic–inorganic materials; ZOL; Acidity; DFT

1. Introduction

Hybrid microporous and mesoporous materials are attracting much attention due to their various applications as optoelectronic devices, sensors, sieves, and catalysts [1–4]. Recently, Yamamoto et al. [5,6] have prepared successfully a new family of microporous molecular sieves (MMS) called ZOL. ZOL refers to zeolites with organic groups bridged lattices and are defined as a true hybrid organic–inorganic material, where true means that the organic moieties, i.e., methylene groups (CH_2) are incorporated in the framework of the zeolites. Subsequently, a computational study on sodalite structure by Astala and Auerbach indicated the possible incorporation of organic moieties, viz., CH_2 and NH in high concentrations into the framework with minimal strain [7]. Other computational studies on cluster models by Waroquier and co-workers [8,9] showed the possible application of zeolites with nitrogen in the framework as bifunctional acid–base catalysts due to the presence of basic NH and Brønsted acid site in the same structure. However, the effect of introducing an organic moiety as CH_2 or amine species as NH on the zeolitic Brønsted acid site strength has not been investigated yet. Furthermore, the acidic properties of these materials, and other MMS in general, are of primary significance regarding their applications as solid acid catalysts. Hence, density functional theory (DFT) calculations on chabazite (CHA) topology have been carried out in this study to tackle this goal. In addition to the short comes of using cluster models such as neglecting the long range electrostatic interactions, it is well known that small clusters are not reliable in mimicking zeolite crystals especially when the dangling bonds are close to adsorbates or any reacting molecule [10–12]. Therefore, periodic models of CHA are considered in this study. Choosing CHA topology has three folds. First, its UC is relatively small with 36 atoms. Second, CHA has an analogous structure, i.e., SAPO-34. Third, CHA and SAPO-34 have pronounced catalytic activities in the methanol-to-olefin (MTO) industrial process [13,14].

The energy of ammonia adsorption, deprotonation energy (DPE), and the relative electrophilicity (s_x^+/s_x^-) (i.e., the proton reactivity toward a nucleophilic attack) have been used to measure the changes of the Brønsted acid site strength upon the organic moiety incorporation. It should be mentioned here that the adsorption energy of NH_3 and DPE have been used carefully to measure and to predict the acidic properties of doped AlPO-34 [15], H-MOR [16], and doped AlPO-5 [17]. The choice of these molecular sieves was made on the basis of their potential applications to several industrial processes [13,18,19].

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2. Models and computational details

2.1. Models

To understand the effect of replacing oxygen in the framework by CH_2 or NH group, we started by considering the following molecular species, $H_3SiOSiH_3$, $H_3SiCH_2SiH_3$, and $H_3SiNHSiH_3$ as shown in Fig. 1a–c, respectively. The choice of these molecules was made on the basis of the available experimental geometries for $H_3SiOSiH_3$. This allows making a direct comparison between the calculated and the experimental parameters.

Chabazite (CHA) structure has three-dimensional small pores controlled by 8-membered ring (8-MR) channels [20]. The unit cell (UC) of the acidic structure has the formula ($HAlSi_{11}O_{24}$) and contains equivalent silicon atoms in the tetrahedral (T) positions. Creation of Brønsted acid site was achieved by replacing Si with Al. To keep charge neutrality, a proton was attached to the bridging oxygen O_2 in the 8-MR. The SiOSi in chabazite framework (Fig. 2a) was modified to $SiCH_2Si$ in H-ZOL-C and to SiNHSi in H-ZOL-N as shown in Fig. 2b and c, respectively.

2.2. Computational details

Geometry optimizations and energy calculations were carried out by periodic density functional theory (PDFT) employing the $Dmol^3$ program in the MS Modelling 4.0 package [21–23], at the generalized gradient approximation (GGA) level with the Hamprecht, Cohen, Tozer, and Handy (HCTH) exchange and correlation functional [24–26]. It has been shown that HCTH functional has a greater universality than the previous GGA functionals and performs well with systems of weak interactions [24–26]. Furthermore, HCTH was selected among many other functionals to describe the week interaction between metal organic framework and hydrogen [27]. Double numerical basis set with polarization functions (DNP) has been used in all calculations carried out in this study. This basis set is comparable to 6-31G** set: however, the numerical basis set is much better than the Gaussian basis set of the same size [22,23]. The convergence thresh-

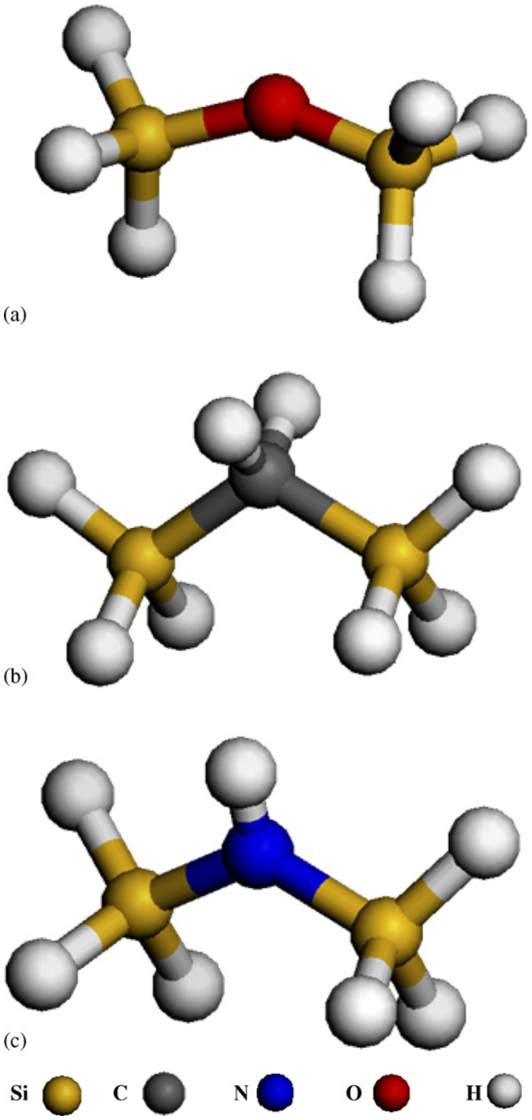

Fig. 1. Three-dimensional optimized structures of the $H_3SiOSiH_3$ (a), $H_3SiCH_2SiH_3$ (b), and $H_3SiNHSiH_3$ (c) molecules.

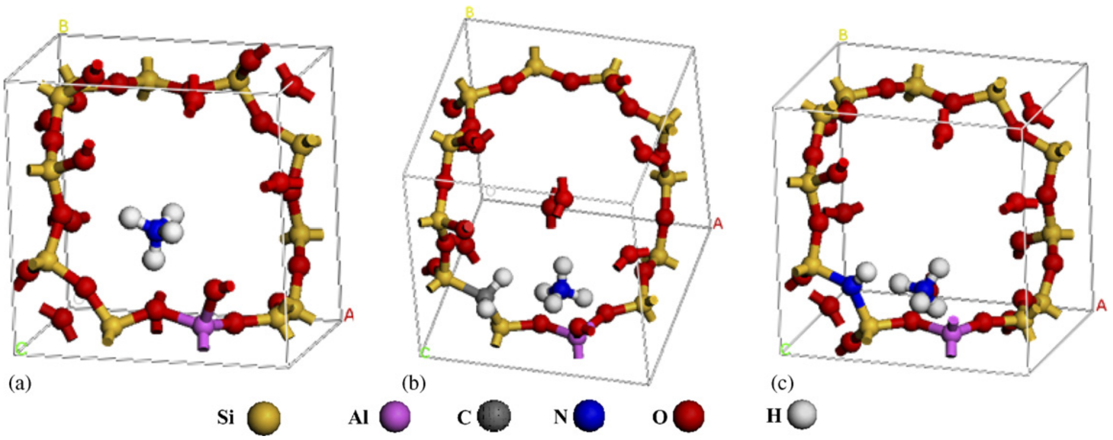

Fig. 2. Three-dimensional optimized periodic models of NH_4-CHA (a), NH_4-ZOL-C (b), and NH_4-ZOL-N (c).