

H-MOR: Density functional investigation for the relative strength of Brønsted acid sites and dynamics simulation of NH₃ protonation–deprotonation

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Received 20 June 2005; received in revised form 2 August 2005; accepted 2 August 2005

Available online 5 October 2005

Abstract

The adsorption energies of NH₃ at different positions in acidic mordenite, viz., main channel, side pocket, and double four-membered rings, are investigated using periodic density functional theory method. Furthermore, for the first time, the dynamic behavior of NH₃ interacting with Brønsted acid site in the main channel has been monitored. The results reveal that the adsorption energies of ammonia on Brønsted acid sites in the main channel (T₄, T₂, and T₁) are higher than that in the side pocket (T₃). Consequently, the strength of Brønsted acid sites follows the same order. Ammonia dynamics results show that the protons are in continuous transfer, where NH₃ acts as a bridge for transferring protons in between ammonium ion and framework oxygen ions.

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Keywords: Mordenite; Brønsted acid sites; Ammonia adsorption; DFT; Molecular dynamics

1. Introduction

In the field of heterogeneous catalysis by molecular sieves, ammonia is extensively used as a basic probe molecule for acidity characterization owing to its accessibility for all acid sites locating in pores, channels, or windows ≥ 4 Å. Some of the encountered problems on using NH₃, in experimental studies, are: (i) strong basicity, which levels out the clear distinction of different acid sites, (ii) the inherent complexity of the vibrational spectra of NH₄⁺ and coordinated NH₃, and (iii) its dissociation on some oxide surfaces. These observations led to the use of other probes viz., CO, pyridine,

alkyl amines, and alkylnitriles [1–4]. However, many valuable quantitative analyses were carried out by fostering the above-mentioned problems on using NH₃ as a probe [5–8]. Recently, we have shown that the adsorption energy of NH₃ can be effectively used to determine the relative strength of Brønsted acid sites, in isomorphously substituted chabazite, and aluminophosphate-34 [9], and Lewis acid sites in microporous molecular sieves [10]. Lamberov et al. [11] showed that NH₃ is more appropriate than CO as a probe for different Lewis acid sites in molecular sieves. Hence, ammonia adsorption is important to scale the strength of different acid sites in microporous molecular sieves. It is well accepted that the interaction between NH₃ and Brønsted acid sites, in zeolites, is strong enough to form NH₄⁺ [12]. Earlier studies indicated the possible interaction of ammonia with the lattice oxygen ions around aluminum site via two, three, or four hydrogen bonds [13–15].

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The important zeolite structure, mordenite (MOR), is known by its pronounced acidity among many other zeolite structures [6,7]. This has led to the use of mordenite for several applications e.g., cracking, isomerization of hydrocarbons, dewaxing of heavy petroleum fractions [16,17]. Therefore, detailed characterization of various acid sites in mordenite is a significant issue for manipulating and understanding its catalytic applications. Moreover, investigating the dynamic behavior of an adsorbate interacting with its host framework will enrich our understanding on how adsorption and desorption processes are taking place at a specific acid site. The two most popular types of computer simulations are Monte Carlo (MC) and molecular dynamics (MD) techniques. MD is more expensive than MC. However, MD simulation is usually more revealing because it provides information on how molecules move. Thus, with MD one can study time dependent phenomena, fluid flow, and other transport phenomena, which cannot be done with MC [18]. Dynamics of several adsorbates as, H₂O [19,20] and CH₃OH [21,22] in zeolites have been studied. Furthermore, the spontaneous proton transfer in between framework oxygen ions of mordenite has been observed recently [23]. Temperature-programmed desorption (TPD) and microcalorimetry techniques (MC) are commonly used for acidity characterization. However, the assignment of its responses to specific acid sites is still unclear. Further, the results depend directly on the experimental conditions [24]. To the best of our knowledge measuring the strength order of Brønsted sites in mordenite could not be tackled in the previous experimental or theoretical studies [4,15, and 25]. This may be due to the complexity of the spectra of probe molecules inside zeolite lattices. Therefore, the aim of this study is to find out the relative strength of Brønsted acid sites in mordenite using NH₃ as a basic probe and to monitor the interaction of NH₃ with Brønsted acid site in the main channel using a novel quantum chemical molecular dynamics (QCMD) code [26].

2. Theory

2.1. Models

Mordenite has an orthorhombic unit cell. In order to create a Brønsted acid site, in silicalite structure, one silicon is replaced by aluminum and proton (H Al Si₄₇ O₉₆). The proton is attached to the bridging oxygen by covalent bond. The main channel (6.7 Å × 7.0 Å) in [0 0 1] direction consists of 12-membered ring (MR) connected with 8-MR side pocket in the [0 1 0] direction as shown in Fig. 1a and b [27]. For labeling the atoms, we followed Alberti et al. notation [28]. It should be mentioned that there are four distinct tetrahedral (T) sites per unit cell: three lies in the main channel T₄, T₂, T₁ and one in the side pocket T₃ (Fig. 1b). Replacement of Si by (Al, H) has been done to produce Brønsted sites. The protons were attached to O₁₀, O₂, O₇, which are accessible to the interaction with adsorbates in main channel

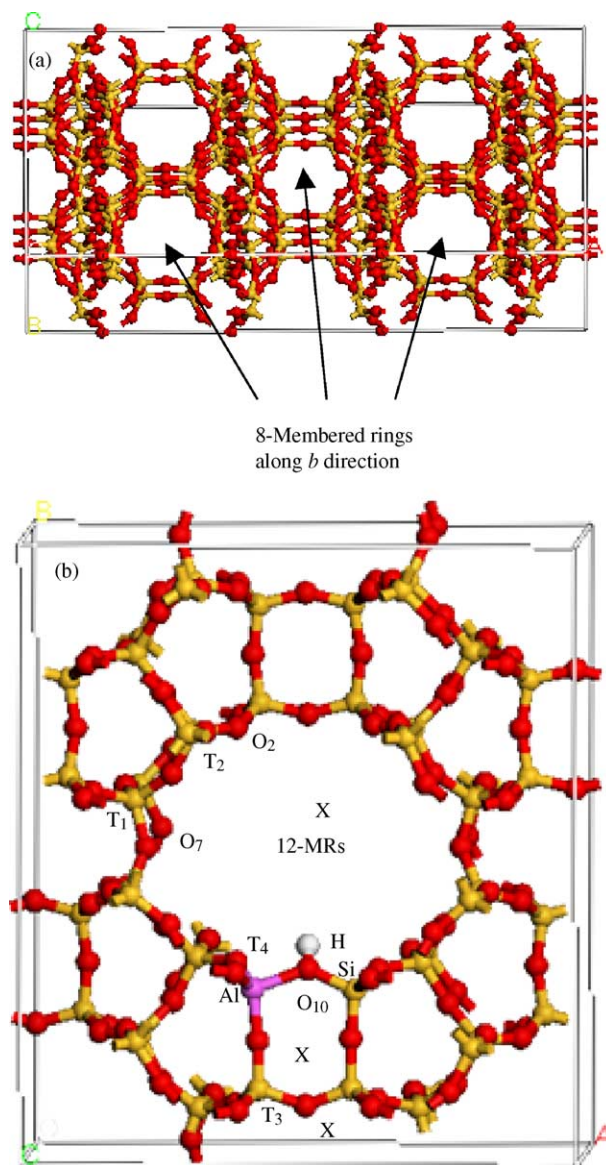


Fig. 1. The optimized structure of acidic mordenite (H-MOR) showing the eight-membered rings along *b* direction (a), and the investigated adsorption sites marked by *x* (b).

and O₉ in side pocket. There are 14 possibilities for placing the proton in the unit cell. Brändle and Sauer [29] and Demuth et al. [30] have found that T₄ is the most preferable location for sitting Al. Hence, we have chosen this site for investigating the dynamics of NH₃ where the proton (H₁) is attached to O₁₀. Here we are interested in high Si/Al ratio, which permits studying the isolated Brønsted acid sites in MOR and could be extended to mesostructures or amorphous materials.

2.2. Computational details

The initial structures of NH₃, H-MOR, and NH₃-H-MOR were optimized by density functional (DF) method at constant pressure employing Dmol³ program package [31–33],

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