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An ONIOM study of amines adsorption in H-[Ga]MOR

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Abstract

The two-layered ONIOM method (B3LYP/6-31G(d,p):HF/3-21G) is used to study the interaction of amines (NH_3, $MeNH_2$, Me_2NH and Me_3N) with H-[Ga]MOR. The optimization of the local structure of H-[Ga]MOR cluster leads to two stable bridging hydroxyl sites ($O_{10}H$ and O_2H) in the zeolite framework, being different from that of H-[Al]MOR. In the adsorption complexes, all amines are protonated by the acidic proton of H-[Ga]MOR, and the protonated amines (HNR_3^+) are stabilized by hydrogen bonds between the negatively charged zeolite oxygen atoms and the hydrogen atoms of the N—H and C—H bonds in the adsorbates. This interaction is confirmed by the structure of the adsorption complexes as well as the calculated IR stretching frequencies. The calculated adsorption energies of amines agree reasonably with the available experimental data. It is found that NH_3 prefers to adsorb at the O_2H Brønsted site, while Me_2NH and Me_3N prefer to adsorb at the $O_{10}H$ site, and $MeNH_2$ can be in equilibrium between O_2H and $O_{10}H$. The relative order of the basicity of amines on the basis of the computed adsorption energies agrees well with the experiments, but differs from those in the gas phase (proton affinity) and in solvents (pK_a).

Keywords: Amines; Adsorption; H-[Ga]MOR; ONIOM; IR frequency

1. Introduction

Zeolites are extensively used as catalysts for chemical industries due to their Brønsted acidity and shape-selectivity. For zeolites to have desired catalytic activity, selectivity and stability, it is necessary to modify the pore structure and the acidity by incorporation of other elements, such as B, Ga, Fe, etc. into the framework. For example, Ga modified HZSM-5 is very efficient for alkylation of benzene with propene [1], TS-1 zeolites are known for their increased catalytic activity in selective oxidation [2], and MFI type zeolite containing Fe element in its framework shows good performance in benzene oxidation [3].

The acidity of zeolites is experimentally estimated by studying the adsorption of probe molecules such as ammonia [4,5] and pyridine [6,7] on their bridging hydroxyl groups using IR and NMR spectroscopic methods. This interaction within zeolite is a critical step in the catalytic process, and strongly affects the catalytic activity and selectivity of reaction and separation efficiency. Thus a better understanding of adsorption behavior of probe molecules in zeolites is of considerable importance for adsorptive and catalytic properties of zeolites. As a result, the investigations of base molecules adsorbed in the acid center have been the topic of many studies, i.e. chemisorption of base molecules studied by temperature-programmed desorption to obtain information of the acid sites.

NH_3 is one of the most frequently used probe molecule for the acidity of zeolite. It becomes NH_4^+ in H-type zeolites and there formed several N—H···O hydrogen bonds in the $[ZeO^- \cdots NH_4^+]$ ion-pair. The successive replacement of hydrogen atoms in NH_3 by methyl groups can produce three amines ($MeNH_2$, Me_2NH and Me_3N) with enhanced basicity and bulky structures, which are expected to have different types and strength of interactions with the zeolite framework.

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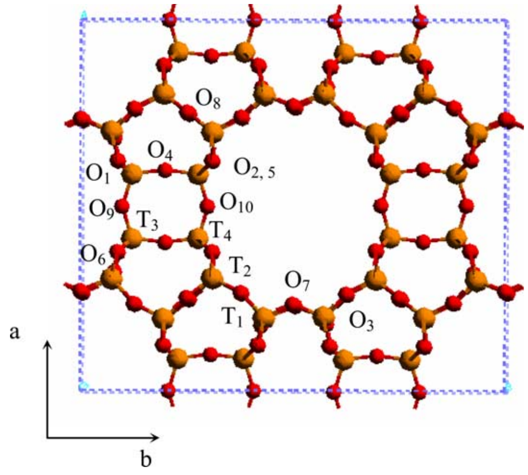

Fig. 1. The structure of mordenite unit-cell viewed down the *c*-axis (T_1–T_4 and O_1–O_{10} are designated. Note that O_2 and O_5 sites are superposed in a projection along the *c*-axis).

This is clearly shown by the study of Su and coworkers [8,9] on the interaction of $MeNH_2$ with several alkali cation exchanged large pore zeolites.

A number of theoretical methods have been proposed to study the interaction of base molecules with zeolite. In order to model the features of real systems, a large enough system and highly accurate ab initio method should be used. However, application of accurate ab initio methods to large system is time-exhausting and sometimes impossible. An effective method to this problem is the hybrid method, such as embedding method [10,11] or the combined quantum mechanical and molecule mechanical method (QM/MM) [12,13]. Sauer et al. have successfully used PM-Pot scheme on ZSM-5 [14,15], as well as the more general ONIOM method by Morokuma and coworkers [16–18] has brought accurate results to large systems. For example, Kasuriya et al. have successively applied ONIOM method to the interaction of aromatic hydrocarbons with H-FAU [19]. It is also applied to the study of chemical reactions [20–22].

In this work, we focus on mordenite (MOR), which is a particularly useful catalyst for several applications including cracking and isomerization of *n*-alkanes [23,24]. It has been shown that the elements such as B, Ga, and Zn, can be introduced into the MOR framework [25,26]. As shown in Fig. 1, MOR has a multiple pore-system with main channels of 12-membered rings that are connected by 8-membered rings. In the unit cell, there are 10 different oxygen sites (O_1–O_{10}) and four crystallographic different tetrahedral sites (T sites, T_1–T_4) at which Al or Ga can be substituted. Earlier theoretical study showed that Ga prefers T_4 site when replacing Si in the MOR framework [27]. Here we use the two-layered ONIOM (ONIOM2) method to study the structure of H-[Ga]MOR, and its interaction with different amines (NH_3, $MeNH_2$, Me_2NH and Me_3N). The adsorption energies and the IR frequencies are satisfactorily compared with the experimental data. The goal of this work is to correlate the type and strength of interaction of H-[Ga]MOR with different amines. This provides the opportunity to develop new probe molecules for acidity and basicity of zeolites.

2. Models and methods

2.1. Models

The coordination of the atoms in this work is taken from the structure of Na-MOR [28]. A 20T model is employed to represent the acid sites and pore structure of MOR, as shown in Fig. 2a, which contains 20 SiO_4 tetrahedron centers (20T) and includes a complete two-layered 12-membered ring. In this cluster a Ga atom replaces the Si atom at one of the T_4 site. To maintain the charge neutrality of the cluster, a charge-balancing proton is produced. The proton was initially put in a position where it is at almost the same distance from the three oxygen atoms around the Ga center. The optimization of this initial structure leads to two stable clusters A and B (see Fig. 2b and c), in which the charge-compensating proton is attached to O_{10} and O_2, respectively. Terminal hydrogen atoms are used to saturate the peripheral oxygen atoms in the cluster. The O–H distances are 1.0 Å, and the orientation of O–H bonds is along the pre-existing O–Si bonds. The clusters simulating the amine adsorption in H-[Ga]MOR are constructed by the partially optimized 20T clusters of H-[Ga]MOR and the free optimized amines. The amine molecules are put pointing to the 12-membered ring with the nitrogen atom closing to the acidic proton (Hz).

2.2. Methods

All calculations in this work are performed by using Gaussian 03 program [29] and the ONIOM2 method. In this ONIOM model, the whole system is divided into two different layers, which are described by two different methods. In the bare cluster of H-[Ga]MOR, the 6T model (shown as ball and stick in Figs. 2–4) forming the high-layer is described at B3LYP/6-31G(d,p) level, and the rest of the clusters forming the low-layer is treated at HF/3-21G level. In the adsorbed complexes, the probe molecules are also included in the high-layer, and this ONIOM2 model can ensure that all the interactions between the adsorbates and zeolite frameworks are included in the high-layer. In order to avoid chemical unreality, three linking H atoms are introduced to replace Si atoms between two layers.

The 20T cluster for the structures of H-[Ga]MOR is partially optimized with the acid sites and their neighboring Si and Ga as well as the oxygen atoms surrounding Ga relaxed, while the rest atoms are fixed to their crystal positions, respectively. To optimize the adsorbed complexes, the parameters of the adsorbate molecule and the atoms described above in the bare H-[Ga]MOR clusters are relaxed with the rest of the clusters fixed.