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Interactions of amino acids with H-ZSM-5 zeolite: An embedded ONIOM study

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Abstract

The adsorption of glycine and L-alanine on the H-ZSM-5 zeolite has been studied at an embedded ONIOM (MP2/6-31G(d,p):UFF) level of theory. The most stable adsorption structure involves ion-pair interactions between the protonated amino acid and the anionic zeolite framework. The adsorption energy is computed to be −31.3 and −34.8 kcal/mol for glycine and L-alanine, respectively. Two hydrogen bonded complexes are identified: one is the cyclic double hydrogen bonded complex via the interactions of the carboxyl group and the zeolite acid site having adsorption energies of −25.4 and −30.0 kcal/mol for glycine and L-alanine, respectively. The second is the hydrogen bonded complex via the interactions of the hydroxyl group and the zeolite acid site having weak interaction energies, −20.7 and −23.9 kcal/mol for glycine and L-alanine, respectively. The zwitterion form is not found in the acidic H-ZSM-5 due to the acid–base reaction, but the glycine zwitterion is found to be stably adsorbed on the Na-ZSM-5 with the adsorption energy of −24.8 kcal/mol. In addition to the interactions with the Brønsted acid site of the zeolite, the interactions with the nearby oxygen framework and van der Waals interactions with the zeolite walls are also found to be important for stabilizing the adsorbed amino acids and zwitterion, suggesting the role of the zeolite framework as a "solid solvent molecule".

Keywords: Adsorption of amino acid; Confinement effect; QM/MM; Zeolites

1. Introduction

The interactions of amino acids with silica alumina compounds and zeolites have aroused the interest of researchers for some considerable time since these materials show the potential to play an important role in prebiotic chemical evolution [1–4] as catalysts for the synthesis of polypeptides and polynucleotides. Smith [5] and Parson et al. [6] have suggested that during the prebiotic period of the earth silica and silica-rich zeolites, due to the presence of surface silanol (≡SiOH) and surface hydroxyls (≡Si—OH—Al≡) embedded inside the nanopores, might be suitable for the catalytic peptide bond synthesis from amino acids to generate biomolecules. Recently, zeolites have found potential applications in amino acid separation [7–11], immobilized enzymatic peptide synthesis [12], and biomedical sensors [13,14]. There have been many experimental [15–20] and theoretical studies [21–23], which have investigated the interactions of biologically active molecules such as amino acids, peptides, and proteins, with the surfaces of inorganic materials such as metals, oxides, clays, and zeolites. Understanding this fundamental phenomenon may be the stepping stone to applications in nanotechnology, biomaterials, and biotechnology processes [19,20].

Zeolites are crystalline aluminosilicate microporous materials with high surface areas. Primarily, because of their shape-selectivity and Brønsted acidity, zeolites have found important applications in catalysis, adsorption, and chemical separations. Molecular modeling and simulations are considered important tools for the study of the

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interactions of probe molecules inside zeolites, providing a detailed understanding of the molecular behavior and interactions within the nanocavity of the zeolite pore network. Some types of zeolites consist of a hundred or more atoms per unit cell. In these cases, the high computational time demand necessary to obtain accurate results in the required "periodic" calculation makes it impractical because of the high cost. However, hybrid methods, such as the embedded cluster or combined quantum mechanics/molecular mechanics (QM/MM) methods, as well as the more general our-Own-N-layered Integrated molecular Orbital + molecular Mechanics (ONIOM) method [24,25], have now made it possible to treat reasonably large systems with reasonable computational times and costs. The ONIOM method takes advantage of combining the density functional theory (to accurately treat the interactions of adsorbed molecules with the Brønsted acid of zeolite) with the universal force field (UFF), (to represent the confinement effect from the extended zeolite structure). This has been demonstrated to yield adsorption energies close to those of experimental ones [26–32].

In this study, structures and interactions of amino acids (glycine and L-alanine) adsorbed on the zeolite Brønsted acid site have been investigated. Glycine (NH_2CH_2COOH) is the simplest and smallest among the twenty most common amino acids found in proteins. Glycine is used as a basic adsorption model and is important for understanding interactions, structures and the reactivity of amino acids and peptides. To the best of our knowledge, the interaction of zeolites with adsorbed amino acids adsorption has not previously been considered from a theoretical point of view. Although many experimental studies on amino acid adsorption in zeolites have been reported and applications in amino acid separation have been proposed [7–11], the fundamentals controlling the interactions of amino acids with zeolites are still unknown.

2. Methods

The 128T cluster model of the nanocavity of the ZSM-5 zeolite, which covers the intersection of the straight and zigzag pore channels, was taken from the X-ray structure [33]. The model cluster was subdivided into two subregions according to the ONIOM method. A 12T cluster, covering the 10-membered-ring window of the zigzag channel of the zeolite, was treated quantum mechanically at the 6-31G(d,p) level of theory. The rest of the 128T extended cluster was treated with the universal force field (UFF) to represent the confinement effect [34–36] of the nanocavity, which mainly originates from dispersive van der Waals interactions. This force field has been previously reported to provide a good description of the short-range van der Waals interactions between sorbate molecules and the zeolitic wall [26–32]. In order to obtain a full description of the interactions of amino acids in the nanopores of a zeolite, it is necessary to take into account the long-range interactions of the infinite zeolitic lattice. The Madelung potential from the zeolite lattice beyond the 12T quantum cluster was introduced by using the "embedded ONIOM2" approach, which has previously been successfully employed [28]. A set of optimized point charges was generated from the infinite zeolite lattice to represent the Madelung potential beyond the 12T quantum cluster.

All structure optimizations were performed at the ONIOM(B3LYP/6-31G(d,p):UFF) level of theory. The Brønsted acid 5T cluster and the interacting probe molecule were allowed to relax while the rest was fixed at the crystallographic coordinate. In order to achieve more reliable adsorption energies, single point energy calculations were carried out at the MP2/6-31G(d,p):UFF//B3LYP/6-31G(d,p):UFF level with counterpoise corrections for the basis set superposition errors (BSSE). All computations were performed with the Gaussian 03 code [37].

3. Results and discussion

3.1. Structures of glycine adsorption complexes

Since amino acids contain both basic amino and acidic carboxyl groups, the net charge of the molecule is pH dependent. At low pH, the amino group is protonated and the molecule carries a positive charge. At high pH, the carboxylic group is dissociated and the molecule has a negative charge. At pH equal to the isoelectric point, the amino acid has a zwitterionic form, where the molecule contains a protonated amino cation and a carboxylate anion and the net charge is zero. Glycine has an isoelectric point at 5.97. In a near-neutral pH solution, glycine is predominantly present as a zwitterion. Therefore, in this study, we consider the adsorption of glycine in its neutral form and zwitterionic form in the ZSM-5 zeolite.

Fig. 1 illustrates the optimized structures of glycine adsorbed via: (a and b) the amino group, (c) the carboxylic group and (d) the hydroxyl of carboxylic group on H-ZSM-5. Selected geometry parameters are presented in Table 1. The interaction energies and the adsorption energies are calculated relative to the gaseous amino acid and the bare zeolite cluster with single point energy calculations at the ONIOM(MP2/6-31G(d,p):UFF) level and counterpoise BSSE corrections (Table 2). In its most stable conformation, glycine is adsorbed via the interactions of its amino group with the zeolite Brønsted acid (Fig. 1a and b). Upon adsorption, the amino group is protonated, as indicated by the break of the acidic O1—Hz bond and the formation of the N—Hz bond (1.05 Å). The N—H_z bond and the other two N—H bonds have virtually equal distances, which indicate a complete proton transfer of the Brønsted acid of the zeolite to the adsorbed glycine. The adsorption complex is in the form of an ion-pair adduct. Fig. 1a and b illustrate that both the amino and the carboxylic groups of glycine are interacting with the zeolite. Two hetero-hydrogen bonds (N—H···O) between the amino group and the zeolite framework and one homo-hydrogen bond (O—H···O) between the carboxylic group and the zeolite framework