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Microporous and Mesoporous Materials 94 (2006) 358–363

MICROPOROUS AND MESOPOROUS MATERIALS

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Simulation of benzene adsorption in zeolite HY using supercage-based docking

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Received 12 January 2006; received in revised form 6 April 2006; accepted 25 April 2006
Available online 16 June 2006

Abstract

The adsorption of benzene in zeolite HY was investigated by a newly developed molecular docking simulation utilizing the Monte Carlo minimization algorithm and the COMPASS force field model. Instead of unit cell-based sampling typically used, the simulation was based on the sampling inside a faujasite supercage. This improved the determination of preferential adsorption sites in the zeolite HY structure. The more effective exploration of the configurational space of benzene in the zeolite HY cavity is illustrated by the higher number of adsorption sites identified per supercage. The simulation predicted a new stable adsorption site, where benzene is located over unprotonated four-membered ring, in addition to confirming the multiple benzene adsorption sites at proton and window sites in the zeolite HY supercage.

Keywords: Molecular docking; Zeolite HY; Benzene adsorption; Supercage; Monte Carlo minimization

1. Introduction

Zeolite HY is an important acid catalyst in petroleum cracking [1]. Identification of the preferential configurations of adsorbate molecules in the zeolite framework is needed for the development and the verification of reaction mechanisms in order to better engineer the catalytic reactions at a molecular level. At a loading of one benzene molecule per supercage, two distinct types of benzene adsorption sites were experimentally identified in zeolite HY (Si/Al = 2.43) by Vitale et al. [2]. For one type, the benzene molecule is facially coordinated to the H(2) proton and located above the six-membered ring in the supercage; in the other type the benzene molecule is framed by the 12-membered ring window. Jousse et al. [3] simulated the adsorption of benzene in zeolite HY (Si/Al = 2.43) in a state of infinite dilution. Four main adsorption types (H1, 2H1, H2, and W, Table 1) were reported [3]. The H2 and W types correspond to the benzene adsorption types deduced by Vitale et al. [2] from their neutron powder diffraction data. However, there are no direct experimental results verifying the existence of the H1 and 2H1 adsorption types, even though the H1 type was calculated to be the most stable benzene adsorption configuration [3].

In their simulation, Jousse et al. [3] used unit cell-based sampling typically employed to simulate the adsorption of hydrocarbons in the faujasite-type zeolites [4–6]. At the loading of one benzene molecule per unit cell, the benzene molecule could be randomly “adsorbed” in any of the eight supercages that form a faujasite unit cell [7]. Because the eight supercages will, in general, have different distributions of aluminum and protons, they are likely to differ significantly in the number and type of adsorption sites present. Therefore, unit cell-based docking may not constitute a representative sampling of the possible benzene adsorption sites in each zeolite HY supercage. In the previous simulation of benzene adsorbed in zeolite HY [3], the

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doi:10.1016/j.micromeso.2006.04.011

Table 1
Benzene adsorption types in zeolite HY

Adsorption type[a]	Description
H1	Benzene facially coordinated to a H(1) proton
2H1	Benzene facially coordinated to two H(1) protons
H2	Benzene facially coordinated to a H(2) proton
W	Benzene framed by a 12-membered ring window
U6	Benzene located over unprotonated six-membered ring
U4	Benzene located over unprotonated four-membered ring

[a] Adsorption type is defined as a group of all equivalent adsorption sites.

300 initial configurations examined in the unit cell correspond to an average of ~38 configurations explored for each different supercage. This number is likely too small to ensure adequate exploration of the entire configurational space (i.e., the combination of three degrees of freedom of location, orientation, and conformation of benzene) in each supercage. This consideration motivated the current effort to try to address this possible limitation.

Reported here is a new approach that was developed to simulate the adsorption of benzene in zeolite HY. Instead of unit cell-based sampling [3–6], this approach is based on faujasite supercage sampling that has a loading level of one benzene molecule per supercage. The objective of the supercage-based docking is to improve the determination of preferential sites of adsorbates in the faujasite-type zeolites by exploring the configurational space of benzene in each zeolite HY supercage to a much greater extent. All initial configurations are in one supercage. To take advantage of the sphere-like geometry of the faujasite supercage, a radius-based approach was developed and embedded in supercage-based sampling. Using this approach the benzene molecule, in a given supercage, is moved randomly relative to the center of this supercage. Compared to the standard Monte Carlo (MC) docking method [5,8,9], radius-based docking provides a higher acceptance ratio for the randomly generated configurations since it results in a lower number of configurations having incorrect steric placement within the zeolite structure (i.e., the steric overlap between the adsorbate and the zeolite). This leads to a more rapid sampling of the configurational space for benzene in the zeolite HY supercage.

In addition to supercage-based sampling introduced here, the Monte Carlo minimization (MCM) algorithm [10] coupled with the COMPASS force field model [11] were utilized. This is the first use of the MCM algorithm to simulate adsorption in a zeolitic system. The MCM algorithm was originally developed to locate the global energy minimum for pentapeptide [Met^5]enkephalin [10], and later successfully applied to docking ligands in proteins [12–14]. Unlike the general MC docking algorithm used before for adsorption in zeolites [3,5,8,9], the MCM docking algorithm utilizes the Metropolis criterion on each energy-minimum configuration found, thus leading the benzene–zeolite configuration towards the global energy minimum [10]. This should provide a more complete set of adsorption sites, and increase the probability of finding the most stable site. The supercage-based docking simulation, using the MCM algorithm coupled with the COMPASS force field model, provides further insight into the adsorption of benzene in zeolite HY by improving the understanding of the preferential benzene adsorption sites. This supercage-based docking methodology can be applied to simulate the adsorption of other organics in faujasites to aid in understanding and improving reactions at specific adsorption sites.

2. Computational methodology

2.1. Force-field method

The force-field method is suitable to model the benzene–zeolite HY system because: (1) benzene is considered to be physically adsorbed in zeolite HY [3,15]; and (2) the nonbonded interactions in this condensed-phase system are difficult to describe accurately using quantum mechanics method [11]. In this investigation, the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field was utilized since it has been parametrized from a variety of molecular classes, including zeolites [11]. The COMPASS force field model has been successfully applied to many zeolitic systems including faujasites [16–18]. The empirical functions used in the COMPASS force field model are identical to those utilized in the CFF-type force fields, where the Lennard-Jones 9–6 potential and the Coulombic potential are applied for the van der Waals and electrostatic interactions, respectively [11]. Since periodic boundary conditions were applied in the present simulation, a nonbonded cutoff of 12.0 Å (i.e., half of the cubic zeolite HY unit cell) was selected for the van der Waals interactions to avoid adsorbate–adsorbate interactions. The Coulombic interactions were calculated using the Ewald summation with the accuracy of ~0.04 kJ mol^{-1} [19].

2.2. Modeling of the zeolite HY structure

The four supercages examined in this investigation were selected from the three different zeolite HY unit cells constructed. The unit cells of zeolite HY were built based on the neutron powder diffraction data of Czjzek et al. [20] for zeolite HY with Si/Al = 2.43, and were characterized by space group $Fd\bar{3}m$, lattice parameter $a = 24.77$ Å, and chemical composition $Si_{136}Al_{56}O_{384}H_{56}$ [3,20]. After constructing unit cells composed of only silicon and oxygen atoms, 56 of the total 192 silicon atoms were substituted by aluminum atoms to obtain a Si/Al ratio of 2.43. To achieve a random aluminum distribution in zeolite Y [21], these substitutions were chosen randomly following Loewenstein's rule [22] that two tetrahedrally coordinated aluminum atoms cannot share an oxygen atom. The initial positions of 56 protons in the unit cells were obtained from randomly selected oxygen sites by using the three rules