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The role of sorbate in the determination of preferential adsorption sites in zeolite HY: A theoretical study

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Abstract

Zeolite HY is a crucial acid catalyst in petroleum refining. The effect of molecular properties of a sorbate on its preferential adsorption site in zeolite HY characterized by non-uniform zeolitic charge distribution was investigated using the recently developed and validated faujasite supercage-based docking method. In the adsorption of benzene, the charge distribution in the zeolite HY structure affects the sorption site. This resulted in either the proton H(1) site or the unprotonated 4-membered ring site as the most stable site. However, only the 12-membered ring window site having the sorption energy of $120.7 \pm 2.5\ \mathrm{kJ\ mol^{-1}}$ was found to be the most stable site for the adsorption of hydrobenzoin, regardless of the charge distribution in the supercages examined. The molecular properties (e.g., size, shape, number of hydrogen bond donors) of hydrobenzoin are thus likely to be the dominating factor that determines the preferential sorbate location. Therefore, the preferred adsorption site of a sorbate in the faujasite supercage may depend either on the charge distribution in the zeolite HY structure or on the molecular properties of the adsorbate itself, depending upon the nature of the adsorbate.

Keywords: Adsorption; Faujasite supercage; Molecular docking; Simulation; Zeolite HY

1. Introduction

Protonated faujasite-type zeolite Y (zeolite HY) is an acid catalyst that is widely used in petroleum refining [1]. The market of zeolite HY is more than US $2 billion per year in sales [2]. Identification of adsorption sites in the faujasite supercages of zeolite HY is required in order to better engineer the catalytic reactions at a molecular level. For zeolite HY, charge distribution depends on both the aluminum and the proton distributions. This charge distribution is an important factor in determining the adsorption sites in zeolite HY [3]. Su et al. [4] have shown that modification of the charge distribution in zeolite HY via the coadsorption of ammonia resulted in the creation of a new adsorption site for benzene. An essential factor that affects the configuration of adsorbates in zeolites having cage-based structures is the molecular size and shape of these sorbates. Using molecular modeling, Burton et al. [5] have demonstrated the importance of this for various structure-directing agent molecules in several zeolites having uniform framework charge distribution (i.e., all-silica framework models). However, it is unclear how significant the sorbate molecular properties are in determining the adsorption sites in zeolite HY, which has non-uniform charge distribution due to the presence of aluminum and protons in its structure.

Recently Jirapongphan et al. [3] illustrated the effect of the charge distribution in zeolite HY on the location of preferential adsorption sites for benzene in the faujasite supercages. This has been investigated using the validated supercage-based docking simulation. Depending on the charge distribution in the zeolite structure, either the proton H(1) site (Fig. 1a) or the unprotonated 4-membered ring site (Fig. 1b) was predicted as the most stable adsorption site in the zeolite HY supercages examined [3]. In the

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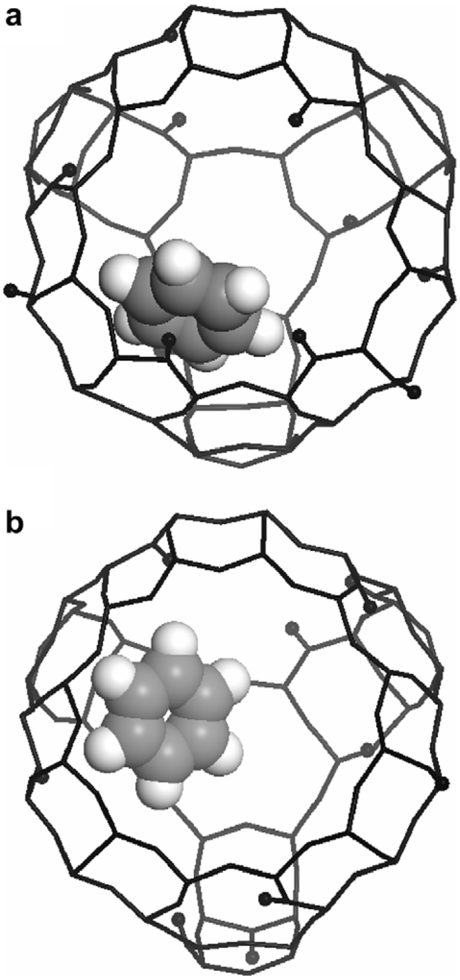

Fig. 1. Examples of preferential adsorption sites for benzene in zeolite HY: (a) the proton H(1) site from supercage Al-2;H-3, and (b) the unprotonated 4-membered ring site from supercage Al-1;H-1 [3]. The supercage diameter is ~12.6 Å. Solid balls attached to the zeolite structure represent protons. The space-filling model represents benzene. For the description of the supercages, see Table 1.

present investigation, this approach is extended to examine the role of sorbate molecule in determining the adsorption sites in zeolite HY. The adsorption of hydrobenzoin (a compound that contains two benzene rings and two hydroxyl groups) in zeolite HY was simulated using the supercage-based docking method and a set of four distinct (i.e., different charge distributions) faujasite supercages. This set of supercages is identical to that employed previously in the modeling of benzene adsorption [3]. The adsorption of hydrobenzoin in zeolite HY illustrates the case where the impact of the charge distribution on the most stable sorption site is less significant compared to that of the molecular properties of the adsorbate.

2. Computational methodology

The adsorption of hydrobenzoin in zeolite HY was simulated by the recently developed and validated docking method [3]. This method utilizes the Monte Carlo minimization algorithm coupled with faujasite supercage-based sampling, and the Compass force field. The Compass force field employs the Lennard–Jones 9–6 potential and the Coulombic potential for van der Waals and electrostatic interactions, respectively [6]. Periodic boundary conditions with a nonbonded cutoff of 12.0 Å (i.e., half of the cubic zeolite HY unit cell) were applied for the van der Waals interactions, while the Ewald summation [7] with an accuracy of ~0.04 kJ mol^{-1} was applied for the Coulombic interactions. A single hydrobenzoin molecule was docked in a zeolite HY supercage. Although the zeolite model is based on a faujasite supercage, the seven remaining supercages in the unit cell, from which the supercage was selected, were still present during simulation to account for their long-range interactions with the hydrobenzoin molecule. The docking simulation was conducted to identify the global energy minimum (i.e., the most stable or preferential adsorption site) for hydrobenzoin in the zeolite HY supercage examined. All calculations were performed using the Discover module in the Materials Studio software package [8].

Models of zeolite HY (Si/Al = 2.43) were constructed based on neutron powder diffraction data [9]. Four supercages having different charge distributions were selected from the three unit cells built. These supercages are termed supercage Al-1;H-1, supercage Al-1;H-2(a), supercage Al-1;H-2(b), and supercage Al-2;H-3 [3]. Supercages Al-1;H-1 and Al-1;H-2(a) have the same aluminum distribution, but different proton distributions. Supercages Al-1;H-1 and Al-2;H-3 have different aluminum distributions, thus also different proton distributions. Supercages Al-1;H-2(a) and Al-1;H-2(b) are two adjacent supercages from the same unit cell with different aluminum and proton distributions. The four supercages as well as the adsorption temperature of 333 K and the loading level of one molecule per supercage are identical to those utilized in the simulation of the adsorption of benzene in zeolite HY [3]. This was done to unambiguously compare the role of sorbate molecules in the adsorption. The representative models for (*R*,*R*)-hydrobenzoin ($C_{14}H_{14}O_2$) were obtained from the conformational analysis using both systematic and random search methods [10]. In the simulation, the adsorbate molecule was flexible, whereas the zeolite structure was held fixed. The flexible zeolite model yielded identical results to those of the rigid framework in terms of the location of preferential adsorption site (vide infra).

3. Results and discussion

Three degrees of freedom for the supercage-based docking simulation include the initial conformation of the adsorbate, the initial orientation of the adsorbate, and the number of iterations in the simulation. For the adsorption of hydrobenzoin in zeolite HY, the simulation depends on only one degree of freedom (i.e., the initial sorbate conformation) when setting the model with appropriate inputs (i.e., 100 iterations and an arbitrary initial sorbate