Computational comparison of the efficiency of nanoporous zeolite frameworks for separation of phenol from water

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ABSTRACT

The adsorption through zeolite is an efficient way of phenol removal from water. The adsorption performance of all-silica zeolites including BEA (Beta), FAU (Faujasite), MFI (silicalite-1), and MOR (Mordenite) to adsorb phenol from phenol/water vapor mixture was predicted and compared through Grand Canonical Monte Carlo (GCMC) simulation. The results show that the adsorption of phenol on zeolites is a function of diameter of largest included sphere and largest free sphere dimensions at high loading (FAU > BEA > MFI > MOR). At low pressure, the phenol adsorption is a function of Framework Density, FD_{Si}, as: MFI > MOR $\sim$ BEA > FAU due to dominant adsorbate–wall attractions compared to other interactions. The preferential siting of zeolite is suggested by both GCMC simulation and quantum mechanics approaches. Hydrogen bonding and dispersion can improve the formation of clusters of organic compounds in the intersection and middle channel of zeolite. In distribution function versus energy curve, FAU shows a clear peak at about -20 kcal mol^{-1} since it possesses supercages with one tetrahedral center. Our results show that both the difference between structures of the zeolites and the interactions can be taken into account to determine the adsorption capacity.

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1. Introduction

Phenol is considered as one of the most serious organic pollutants regarding its damages to human health and aquatic life due to high toxicity even at low concentration [1,2]. The effective removal of organic contaminants from waste effluents is considered as a challenge of increasing interest. Among removal methods, adsorption is an effective process to treat the wastewaters containing organic compounds due to effectiveness, simplicity, and relatively low cost [3–5]. The most widely used adsorbent for water treatment is activated carbon, carbon nanotubes, and alumino-silicates such as zeolites [6,7]. Amongst all mentioned adsorbent materials, zeolites have been considered as efficient adsorbents because of inherent advantages such as uniform and nano-porous nature, extended surface area, low cost, and availability [8]. Their framework consists tetrahedral TO_4 (T = Si and Al). The isomorphic replacement of silicon by aluminum induces surplus negative charge on the lattice compensated by monovalent or divalent cations. TO_4 units are linked by shared oxygen atoms to form nanometer-sized cages interconnected by channels into a three-dimensional framework [9,10].

The adsorbent capacity to adsorb and separate phenol and/or other species depends on several factors such as physical nature of the adsorbent, temperature, and pressure. Main physical specificities of zeolites include pore dimensions with respect to the molecular size, specific surface area, and hydrophilic/hydrophobic property which depends on the type of zeolite and the number of Al atoms substituted in the zeolite framework [6,8,11,12]. Special attention has been paid to know which factor is the main contributor to gain a high separation performance of zeolites for removal phenol from water [13]. Narita et al. [14] have compared the adsorption isotherms of phenol, cresol, and benzyl alcohol from aqueous solution on silicalite and ZSM-5 substrates indicating that the adsorption of aromatic component is facilitated based on the amount of the electric charge. Yonli et al. [15] have studied the isotherm of phenol, ortho-nitrophenol and para-nitrophenol adsorption on HY and BEA zeolites indicating that the removal performance of the zeolites depends on their hydrophobicity and dipole moment of adsorbates which were in agreement with experimental reports of Khalid et al. [16]. Chao et al. [13] have compared the adsorption capacities of benzene, toluene, ethylbenzene, propylbenzene, trichloromethane, *n*-pentanol, *m*-cresol, and phenol indicating that adsorption capacities depend on the water solubility, molecular size, and chemical structure of the tested organic compounds. Cheng et al. [4] have compared the

adsorption performances of 13X, the activated carbon (AC) and X/AC composite for the removal of phenol. Mohammed Ali and Ahmed [17] have examined NaY zeolite as an efficient adsorbent for treatment of antibiotic pollutants in wastewaters.

Although many works [14–16,18] have examined the adsorption efficiency of zeolites to remove phenol from aqueous solution, the computational study of this system has received less attention. Most computational studies have been devoted to nonpolar gases and aliphatic alcohols such as methanol and ethanol. The computational study to consider the adsorption of pure phenol and benzene on the silicalite and H- and Na-forms of ZSM-5 has been reported by Kelmm et al. [19].

Deep understanding of adsorption isotherms and interactions is of a great deal of importance to consider the performance of zeolites. The comparative adsorption of pure and mixture of phenol/water over hydrophobic zeolites including Beta, FAU, MFI, and MOR by Monte Carlo (MC) and Quantum Mechanics (QM) techniques is mainly investigated in the present work. To our knowledge, no comparative computational investigations have been reported on adsorption of phenol/water mixture over all-silica zeolites. The adsorbate–adsorbent interaction through deconvolution of adsorption energy distribution functions into separate Gaussian peaks is presented for the first time in this work. The adsorbate–adsorbent interactions mainly hydrogen bonding considered through quantum mechanical approaches [20,21]. Also, main thermodynamics parameters of phenol adsorption at gas phase and aqueous form were calculated such as enthalpy and entropy of adsorption.

The adsorption capacity of four mentioned zeolites is attributed to both structural properties and host-guest interactions through MC and QM approaches which are consistent based on obtained findings. It continues along the lines of main related works in our former works focusing on the adsorption behavior in the guest/zeolite complex systems [21–23].

2. Computational methods and models

2.1. Models

Four studied zeolites were 3 large-pore types including a Beta type (BEA), a Faujasite type (FAU), and Mordenite type (MOR) with 12-membered oxygen ring apertures and a medium-pore zeolite named MFI, ZSM-5 or silicalite-1, consisting a 10-membered ring aperture. These zeolites were selected since they should be experimentally considered as adsorbent for organic molecules in aqueous medium at literature [14–16,18]. Generally, it has been found that hydrophobic zeolites, with a high content of silica, are appropriate adsorbent to adsorb both aliphatic and aromatic alcohols [14,16,18]. All-silica and defect-free framework of these zeolites are mainly focused in this work. The coordinate of the zeolite framework was taken from X-Ray Diffraction, XRD, patterns based on International Zeolite Association, IZA, database [24,25].

2.1.1. Monte Carlo simulation

Simulation boxes of BEA, FAU, and MFI zeolites are represented by large enough supercells consisting 8 unit cells, $2 \times 2 \times 2$. Also, MOR supercell contains 16 unit cells, $2 \times 2 \times 4$. Zeolite structures were assumed rigid to enhance the computational efficiency during the simulations [26].

2.1.2. Quantum mechanics calculation

The clusters contain eight tetrahedral centers (8T) in which all T sites are silica. In another model, Si sites were substituted by Al atoms. A silicon atom was substituted with an aluminum atom at T_5, T_1, T_{12}, T_4 sites in BEA, FAU, MFI, and MOR, respectively, which was positioned in the intersection channel with maximal available space [27]. The boundary Si atoms were saturated with hydrogen to obtain a neutral cluster. All atoms were relaxed during geometry optimization except edge Si and H atoms which kept fixed. Al substituted models are addressed H-BEA, H-FAU, H-MFI, and H-MOR.

2.2. Methods

2.2.1. Monte Carlo simulation

All adsorption simulations were carried out by Accelrys_Materials Studio 4.3 software package [28]. The adsorption isotherm of phenol, water, and their mixture on purely siliceous zeolites was calculated by performing Grand Canonical Monte Carlo (GCMC) simulations. In GCMC simulations, the random movements of adsorbates generate new configurations which may be accepted or rejected according to Metropolis algorithm [29] based on the configurational energy change till the number of adsorbate molecules in the simulation cell reaches equilibrium.

Each run includes 1×10^7 Monte Carlo steps to achieve equilibrium followed by 1×10^7 steps for production, sampling, and data acquisition. The COMPASS force field was applied to describe the adsorption isotherm in this study which has been confirmed appropriate to describe the adsorption behavior of water/alcohol in zeolite systems [30–32]. The Ewald summation technique was applied to handle the electrostatic interactions. Also, atom based technique was applied for van der Waals interactions. All pairwise interactions were truncated at a spherical cut-off radius slightly smaller than half of shortest length of the simulation cell. The periodic boundary condition (PBC) was imposed in three dimensions during movements in all GCMC simulations.

2.2.2. Quantum mechanics calculation

Quantum mechanical calculations were carried out by GAMESS program package [33]. M06-2X functionals were applied in conjugation with 6-311++G** basis set. The M06 family has been applied as parameterized functionals for host/guest complexes containing dominant dispersive forces to describe the noncovalent and π-stacking interactions. Specifically, M06-2X has been employed to explore the zeolite-catalyzed reactions in which the conventional DFT functionals are not capable to describe the interactions accurately [21,34–36]. In our previous work [21], we showed the promising performance of M06-2X for noncovalent interactions. This method can reproduce the thermodynamic properties appropriately [21,34].

3. Results and discussion

The adsorption behavior of pure and binary mixture of phenol/water is studied and compared over BEA, FAU, MFI, and MOR zeolites. BEA zeolite contains two mutually perpendicular straight channels each with a cross section of 6.6×6.7 Å, as well as a sinusoidal channel of 5.6×5.6 Å generating 3-dimensional intersecting cavities whose sizes are on the order of 12–13 Å. FAU is characterized by pores arranged perpendicularly with a free aperture of diameter 7.4 Å creating a large cavity called "supercage" of diameter of 13 Å. MFI (ZSM-5 or silicalite-1) network consists of 3-dimensional cavities arranged perpendicularly including straight channel of 5.3×5.6 Å and circular sinusoidal channel of 5.1×5.5 Å in diameter. The resulting channel intersections are elongated spherical cavities close to 8.5–9.0 Å in diameter. MOR framework possesses two types of channels including a 12-membered ring channel with an elliptical section of 6.5×7.0 Å interconnected in one direction by 8-membered ring channel of 2.6×5.7 Å in diameters [9,10]. The schemes of the channels are shown in Fig. S1.

The channels diameter indicates the insertion possibility of adsrobate species with van der Waals diameter of about 5.8 Å or lower [37]. The diameter of phenol was determined 5.09 Å which