The GCMC simulations of adsorption of ethanol and water in zeolitic imidazolate frameworks

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Abstract. The adsorption mechanism of ethanol and water in five zeolitic imidazolate frameworks (ZIFs) has been investigated using grand canonical Monte Carlo (GCMC) method. The single adsorption isotherm and the selectivity of mixture adsorption of ethanol and water in ZIFs have been obtained. The results show that, at lower pressures (<10kPa), the adsorption amounts decrease in the order of ZIF-2>10>6≈8≈4. However, when the pressure is higher than 10kPa, the uptakes order is ZIF-10>2>6>8>4. And the water uptake decrease with the order of ZIF-10>2>4>6>8. However, the water uptakes for all the ZIFs is very small. The mixture adsorption of ethanol and water shows that, at a given lower pressure, the selectivity decreases as ZIF-2>8>10>6>4. However, at a given higher pressure, the selectivity is in the order of ZIF-10≈2≈6≈8≈4. It can be concluded that ZIF-2 and -10 are suitable for the adsorption and separation of biofuel of ethanol. The total interaction energy distribution of ZIFs with ethanol/water has also been analyzed to interpret the adsorption mechanism of ethanol and water in ZIFs.

1. Introduction
Biofuel is a renewable resource and an alternative to the conventional petroleum based fossil fuels [1]. The most common biofuel is ethanol and there has been considerable interest to produce water-free fuel-grade ethanol, as water adversely affects the performance [2]. In the past decade, metal-organic frameworks (MOFs) have emerged as a new class of hybrid nanoporous materials [3]. Composed of metal oxide clusters and organic linkers, MOFs have extremely large surface area and high porosity. Most experimental and theoretical studies of MOFs have mainly focused on gas storage and separation [4-6]. Only a few studies were reported to examine the separation of liquid mixtures in MOFs [7,8]. This is because, for the practical application in aqueous media or organic solvents, chemically stable MOFs are desired. However, many common MOFs especially Zn- or Cu-based can not meet this requirement. The design of highly stable MOFs resistant to water and organic solvents is an active research.

Recently, several azolated-based MOFs have been synthesized with good thermal and chemical stability, which is attributed to the strong interaction between metals and azolate linkers relative to carboxylic linkers [9]. For examples, zeolitic-like MOFs (ZMOFs) and zeolitic-imidazolate frameworks (ZIFs) demonstrate exceptional stability and receive considerable interest [10]. Therefore, we have performed molecular simulations attempting to understand the adsorption mechanism of ethanol and water in some ZIFs (ZIF-2, -4, -6, -8, and -10) with different channel types and pore volume. The adsorption properties of pure ethanol and water in these five ZIFs have been simulated using Grand Canonical Monte Carlo (GCMC) method. The adsorption selectivity of ethanol over water were also investigated according to mixture adsorption of ethanol and water. Moreover, the reasons having the
different adsorption and separation behaviors are analyzed according to the total interaction energy distribution of ZIFs and ethanol/water. These results can reveal the mechanism of adsorption and separation of ethanol/water in ZIFs, which may provide some guideline for synthesizing new materials in experiment.

2. Models and computational methods
The experimentally determined crystal structures for ZIF-2, -4, -6, -8, and -10 were taken from the Cambridge Structural Database (CSD) [11]. Each structure was optimized using plane wave density functional theory (DFT) calculation. The adsorption of pure ethanol and water as well as their mixtures were simulated using the GCMC method. During the simulation, adsorbate-adsorbent interaction terms were defined using a Lennard-Jones potential with a cutoff of 13Å and parameters given by the Lorenz-Berthelot combining rules. The universal force field (UFF) was used to mimic the LJ potentials of MOFs [12]. The TraPPE united atom force field was used to model ethanol [13]. This force field accurately represents the bulk phase behaviour of these molecules. Ethanol was represented by a united-atom model with each CH$_3$ as a single interaction site. The water was mimicked by the three-point transferable interaction potential model (TIP3P), which gives reasonably good interaction energy compared to experiment [14].

The chemical potentials of an adsorbate in adsorbed and bulk phases are identical at thermodynamic equilibrium, and the GCMC method allows one directly to simulate adsorption [15]. The simulation boxes are $3 \times 1 \times 1$ supercells for ZIF-2, $2 \times 2 \times 2$ for ZIF-4, -6, -8, and $1 \times 1 \times 2$ supercells for ZIF-10, respectively. The frameworks were assumed to be rigid, and the unit cell was divided into fine grids with the potential energies pre-tabulated and subsequently used by interpolation during simulation. A spherical cutoff equal to half the box length was used to evaluate the LJ interactions and the long-range corrections were added beyond the cutoff. The Ewald summation was used for the Coulombic interactions. The number of trial moves in a typical simulation was $2 \times 10^7$, in which the first $10^7$ moves were used for equilibration and the subsequent $10^7$ moves for ensemble averages. Six different types of trial moves were randomly attempted in the GCMC simulations, namely, displacement, rotation, and partial regrowth at a neighboring position, complete regrowth at a new position, swap between reservoir including creation and deletion with equal probability, and the exchange of molecular identity.

3. Results and discussion
Firstly, the adsorption properties of pure ethanol in the five ZIFs (ZIF-2, -4, -6, -8, and -10) are presented. Their storage capacity is quantitatively assessed according to the adsorption isotherms at 323K with the pressure of 0-100kPa. Then, the adsorption of pure water is discussed, from which the hydrophobicity/hydrophilicity of these five ZIFs is classified. Finally, the separation of ethanol-water mixtures is examined and the highest selectivity is identified.

3.1. pure ethanol
Using the GCMC method, the adsorption isotherms of the ZIFs (ZIF-2, -4, -6, -8 and -10) in a broad range of pressure (0-100kPa) at 323K is obtained, which are shown in Figure 1. Their physisorption amounts under different pressures are obtained, which may compare their ethanol storage capacity. As can be seen in Figure 1, the adsorption amounts increase and saturate with increasing pressure. At lower pressures (<10kPa), the adsorption amounts decrease in the order of ZIF-2>-10>-6>-8>-4. However, when the pressure is higher than 10kPa, the uptakes order is ZIF-10>-2>-6>-8>-4. Therefore, ZIF-2 and -10 have superior ethanol adsorption properties at all pressures, respectively, which are more suitable for ethanol adsorption at room temperature.
3.2 pure water
The adsorption properties of water in ZIF-2, -4, -6, -8 and -10 are also investigated, whose adsorption isotherm with the pressure of 0-100kPa at the temperature of 323K is shown in Figure 2. It can be seen that, the water uptake decrease with the order of ZIF-10>-2>-4>-6>-8. However, the water uptakes for all the ZIFs is very small, which is only 0.2357, 0.1891, 0.1734, 0.1434, 0.1063 mmol/g for ZIF-10, -2, -4, -6, -8, respectively. At the same time, the ethanol uptakes for these ZIFs can reach 6.7401, 3.2848, 1.3028, 2.0639, 1.7008 mmol/g, respectively. Therefore, compared with other ZIFs, although ZIF-2 and -10 have the higher water uptakes, which may be still considered as hydrophobic, and suitable for ethanol adsorption.

3.3 ethanol and water Mixture

Figure 1. The adsorption isotherms of ethanol in ZIF-2, -4, -6, -8 and -10.

Figure 2. The adsorption isotherms of water in ZIF-2, -4, -6, -8 and -10.
Figure 3. Adsorption selectivity of ethanol-water equimolar mixture in ZIF-2, -4, -6, -8 and -10. The mixture adsorption of ethanol and water in the ZIF-2, -4, -6, -8 and -10 with the pressure range of 0-100kPa at the temperature of 323K is also investigated. The separation performance is quantified by selectivity [9]

\[ S_{ad(i,j)} = \left( \frac{Y_i}{Y_j} \right) / \left( \frac{X_i}{X_j} \right) \]

Where \( Y_i \) and \( X_i \) are the compositions of component \( i \) in adsorbed and bulk phase, respectively.

Figure 3 plots the selectivity of ethanol over water in the ZIF-2, -4, -6, -8 and -10 at 323K. It can be seen that, the selectivity of these four ZIFs has the same trend, that is, with increasing the pressure, the selectivity in each ZIF drops. At a given lower pressure, the selectivity decreases as ZIF-2 > ZIF-8 > ZIF-10 > ZIF-6 > ZIF-4. However, at a given higher pressure, the selectivity is in the order of ZIF-10 ≈ ZIF-8 > ZIF-6 > ZIF-2. Therefore, ZIF-2 and -10 have overall better separation performance than other ZIFs.

Figure 4. The total interaction energies of ZIFs and ethanol/water molecules.

In order to analyzing the reasons why ZIFs have different adsorption and separation behaviour, we computed the total interaction energies of ZIFs and ethanol/water molecules, as shown in Figure 4. It can be seen from Figure 4(a), the order of most probable energy of ZIFs and ethanol is ZIF-10 > ZIF-2 > ZIF-6 > ZIF-4 > ZIF-8. The order of most probable energy of ZIFs and water is ZIF-10 > ZIF-2 > ZIF-6 > ZIF-8 > ZIF-4 as shown in Figure
4(b). This illustrates that the adsorption capacity of ZIFs is proportional to the total interaction energy of adsorbate and adsorbents at a whole.

4. Conclusions
By employing the GCMC method, we investigated the adsorption properties of ethanol/water in ZIF-2, -4, -6, -8 and -10. The adsorption isotherms of pure ethanol, pure water and ethanol/water mixture in these five ZIFs with the pressure of 0-100kPa at the temperature of 323K were obtained. The investigated results show that, compared with ZIF-4, -6, and -8, ZIF-2 and -10 have better adsorption selectivity of ethanol over water due to their stronger interaction energy of adsorbate and adsorbents.

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