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Molecular simulation of hydrogen storage in ion-exchanged Mazzite and Levyne zeolites

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ABSTRACT

The ion-exchanged zeolites Mazzite and Levyne with alkali metal cation (Na^+), acid proton (H^+) and alkaline earth metal cation (Ca^{2+}), have been used to analyze the effect of framework structures, micropore volume, pore sizes and exchangeable cations on hydrogen storage at different temperatures and pressures using the grand canonical Monte Carlo (GCMC) method. The simulation data clearly show that a larger micropore volume and a suitable pore size near to the kinetic diameter of a hydrogen molecule are the main factors affecting the hydrogen storage capacity. In addition, choosing an appropriate exchangeable cation could also produce a strong electric field and encapsulate hydrogen in the small cages, which would be beneficial for hydrogen storage.

1. Introduction

Owing to the growing need for energy sources and the demand for environmentally friendly alternative fuels, hydrogen, as a possible future energy resource, has attracted a great deal of attention. The utilization of hydrogen as a possible substitute for fossil fuels requires the solution of a number of problems related to hydrogen production, transportation, storage, and fuel cell technology [1]. Among these, hydrogen storage is the greatest obstacle, detracting from the commercial use of hydrogen. Hydrogen storage by adsorption represents one potential strategy for effective and relatively safe hydrogen storage. Consequently, many studies have been devoted to designing new materials for this purpose. The most important studies include: (i) storage in metals and alloys; (ii) storage in complex hydrides (alanates, borides); and (iii) storage in microporous materials (carbons, metal–organic frameworks, polymers, zeolitic materials) [2]. Among these materials, zeolites are considered as potential sorbents for hydrogen storage, although the high density of the aluminosilicate framework makes zeolites unlikely candidate for hydrogen storage in vehicles [3], their high thermal stability, low cost, adjustable composition and the availability of a variety of porous structures could render zeolites competitive (as compared to other potential hydrogen storage materials) for less demanding stationary applications [4,5].

Zeolites are a large class of highly crystalline aluminosilicate materials, defined by a network of linked channels and cages [6,7]. A general chemical formula for zeolites can be represented as $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$, where M is an exchangeable cation with valency n and w is the number of water molecules. Generally, alkali and alkaline earth cations are presented in the zeolite to balance the framework charges. Many studies have shown that zeolites have the capacity for hydrogen storage [8–16].

Recently, molecular simulation of adsorption in zeolites has emerged as a rapid and effective method for the evaluation of potential adsorbents. As most of the adsorption occurs inside the material, it is very difficult to carry out experiments that can provide enough information at the molecular level. For a detailed understanding of the adsorption mechanisms, experimental information is, however, not always sufficient and accompanying theoretical calculations can be helpful to clarify some questions. Computational chemistry methodologies have been used as a powerful tool to study the adsorption mechanisms and to design new materials [17,18]. The grand canonical Monte Carlo simulation technique is particularly adapted to calculate equilibrium adsorption isotherms. For example, Mahmoud et al. [19] investigated the adsorption of hydrogen molecules on purely siliceous zeolites such as ACO, MEP, ASV, ANA, RWY, and RHO. They found that the number of adsorbed hydrogen molecules at high pressure only depends on the pore diameter. Song and No [20] employed the grand canonical Monte Carlo simulations to investigate the effect of pore size and pore volume on the hydrogen uptake for several model AlPOs. According to the simulation results, the key factors affecting hydrogen adsorption can be discovered. However, little attention

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has been devoted to research into the adsorption mechanism of hydrogen molecules in the zeolites Mazzite and Levyne.

In this study, ion-exchanged zeolites Mazzite and Levyne are used as media for hydrogen storage. The main factors affecting the hydrogen storage are investigated using the grand canonical Monte Carlo (GCMC) calculation, which includes the effect of the framework structures, micropore volume, pore size, exchangeable cations, temperature and pressure, on the hydrogen sorption performance. Moreover, based on the calculated results, the relationships between the hydrogen storage capacities, the hydrogen adsorption sites and adsorption heats are also discussed.

2. Calculation models and methods

Zeolite Mazzite is a natural porous mineral material. Its crystal chemical composition is $\left[(Na_2^+, K_2^+, Ca^{2+}, Mg^{2+})_5Al_{10}Si_{26}O_{72}\right]$. It crystallizes with the hexagonal P6$_3$/mmc space group, with $a = b = 1.8215$ nm, $c = 0.7634$ nm, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 120.00°$ and has 12-ring (0.74 nm × 0.74 nm) and 8-ring (0.31 nm × 0.31 nm) channels [21]. Its aluminosilicate framework consists of columns of gmelinite cages bridged by oxygen atoms to give a 12-ring cylindrical main channel system along the crystallographic *c* axis [22].

Natural Levyne-type zeolites have the general composition $[(Na_2^+, Ca^{2+})_9Al_{18}Si_{36}O_{108}]$. The unit cell has trigonal symmetry, R-3 m, $a = b = 1.3338$ nm, $c = 2.3014$ nm, $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 120.00°$ and all 54 T atoms (Si or Al) are in tetrahedral sites [23]. They are characterized by a bidimensional lattice made of a sequence of single 6-membered rings, and by rather small pores (0.48 nm × 0.36 nm) [24]. Fig. 1 is a schematic drawing of the zeolite pore structure. The simulation boxes used correspond to the Mazzite and Levyne unit cells.

For hydrogen adsorption on the zeolites Mazzite and Levyne, the Lennard-Jones potential energy parameters from Buchart and Universal force field were used [25,26]. The Burchart force field treats the Si and Al atoms of the framework whilst the Universal force field treats the O atoms of the framework and the intramolecular and intermolecular interactions. The parameters for the framework–molecule interactions are derived from parameters from both force fields, combined by the geometric combination rule. Because the zeolite host has been treated as a rigid structure, with fixed atom positions obtained from the minimized structure, only the non-bond interaction energy is calculated for hydrogen adsorption, during all simulations. The total host–guest interaction energy consists of the sum of a long-range coulombic term and a short-range van der Waals (*vdW*) term:

$$E_{total} = E_{el} + E_{vdW} \tag{1}$$

$$E_{el} = \sum_i \sum_{j>i} \frac{q_i q_j}{r_{ij}} \tag{2}$$

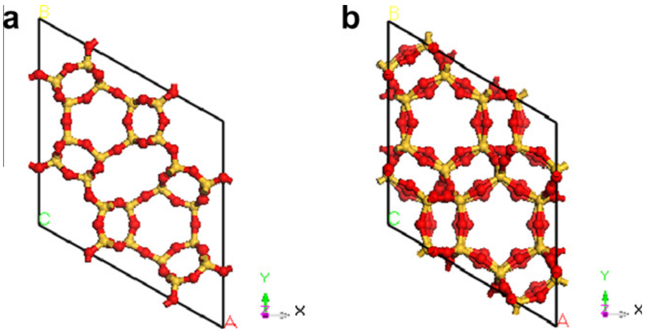

Fig. 1. Framework structures of zeolites (a) Mazzite and (b) Levyne.

where q_i and q_j are the net atomic charges of the *i*th and *j*th atoms, respectively, and r_{ij} is the distance between the the *i*th and *j*th atoms. Since the electrostatic interaction is a long-range interaction and the model systems are periodic, Ewald sums are used for E_{el}. The Lennard-Jones (LJ) type potential energy function has been used to describe the *vdW* interactions as:

$$E_{vdW} = \sum_i \sum_{j>i} D_{ij} \left\{ -2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 + \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} \right\} \tag{3}$$

where D_{ij} and σ_{ij} are the LJ potential parameters and r_{ij} is the interatomic distance between the *i*th and *j*th atoms. The geometric combination rule is applied for the *vdW* interaction parameters, D_{ij} and σ_{ij}. The LJ potential energy parameters used in our calculations are summarized in Table 1.

Hydrogen was modeled as a two-site LJ fluid. The Darkrim and Levesque (DL) hydrogen potential was used [27], which treats hydrogen as a rigid diatomic molecular with H–H distance fixed at 0.074 nm. The simulation box representing both zeolites, Mazzite and Levyne, contain 16 (2 × 2 × 4) and 4 (2 × 2 × 1) unit cells, respectively. The simulations with larger boxes showed that no finite-size effects were present. Considering the real zeolite structures, there has to be enough extra-framework cations to balance the charge of the Al ions, so we use the Locate task in the Sorption module to assign the locations of the cations. The following set of charges [28] was adopted for Mazzite and Levyne: Al (+1.4), Si (+2.4), O (−1.2), Na (+1.0), H (+1.0) and Ca (+2.0). Both of the studied zeolites were treated as rigid frameworks, with atoms frozen at their crystallographic positions during the simulations. The cutoff radii of 1.5 nm and 1.1 nm were applied to the LJ interactions, and the long-range electrostatic interactions were handled by using the Ewald summation technique [29]. Periodic boundary conditions were applied in all three dimensions. For each state point, the GCMC simulation consisted of 2.0×10^6 steps to guarantee the equilibration, followed by 2.0×10^6 steps to sample the desired thermodynamics properties. The simulations were performed using the GCMC implementation available in the Accelrys Materials Studio 4.1 software package [30].

3. Results and discussion

3.1. Evaluation of the calculation accuracy

Fig. 2 shows the calculated adsorption isotherms of hydrogen at 77 K and 0–1.6 MPa obtained from the GCMC simulations. It can be seen that the calculated hydrogen isotherm is very close to the experimental results of Dong et al. [10], but there still some discrepancy between experiment and simulation (Na-MAZ, 12.8%; Na-LEV, 3.8%). The basic reason is that zeolites used in the experiment may contain some amorphous solids which cannot be eliminated and which affects the total hydrogen storage capacity of the

Table 1
Lennard-Jones potential energy parameters used for hydrogen storage on zeolite Mazzite and Levyne.

Atom type	D_0 (kcal/mol)	σ_0 (Å)
Si-z[a]	0.0469	4.2000
Al-z[a]	0.0292	4.2400
O-z[b]	0.0600	3.5000
H[b]	0.0440	2.8860
Na[b]	0.0300	2.9830
Ca[b]	0.2380	3.3990

[a] Lennard-Jones potential energy parameters are come from Burchart force field.
[b] Lennard-Jones potential energy parameters are come from Universal force field.