High-Pressure Hydrogen Adsorption in the Zeolites: A Grand Canonical Monte Carlo Study

Xiuying Liu, Jie He, and Rui Li

College of Science, Henan University of Technology, Henan, Zhengzhou 450001, China

Correspondence should be addressed to Xiuying Liu, liuxiuyingzx@126.com

Received 22 April 2012; Accepted 15 June 2012

Academic Editors: F. E. Little and R. P. Saini

The adsorption of hydrogen molecules on different zeolites at near room temperature and extremely high pressures has been simulated employing Grand Canonical Monte Carlo (GCMC) method. Some important physical amounts under different temperatures and pressures, such as adsorption isotherms, adsorption amounts, and isosteric heats were studied. We predict the storage capacity of hydrogen in ZON and CHA zeolites at different conditions. The results show that the hydrogen storage capacity of CHA is superior to that of ZON. The different hydrogen adsorption behavior between them is explained by the isosteric heats of adsorption at different temperatures. These results may help us to understand different hydrogen adsorption properties of these two zeolites, thus facilitate exploring new hydrogen storage candidates experimentally.

1. Introduction

Hydrogen storage is a key enabling technology for the extensive use of hydrogen as an energy carrier. The aim is to develop economically and environmentally attractive solutions for storage options. Therefore, a number of novel storage techniques are being investigated to complement the currently available methods. These methods mainly include high pressure gas, liquid hydrogen, adsorption on porous materials, complex hydrides, and hydrogen intercalation in metals [1–5]. However, none of these methods completely satisfy all the criteria for the amount of hydrogen that can be supplied from a given weight or volume of tank for transport purposes. Therefore, alternative possibilities for hydrogen storage have to be considered. Recently, physisorption has attracted more attention because the adsorption is reversible, and thus the adsorbent can be recycled. Moreover, physisorption offers the possibility of high hydrogen storage capacity and quick hydrogen desorption. As a result, many investigations have focused on encapsulating hydrogen molecules in microporous materials [6–8].

Zeolites are aluminosilicate crystals extensively used in industrial applications involving separation, adsorption, or preferential adsorption of gases [9]. These applications have motivated theoretical and experimental works devoted to the measurement and computation of the adsorption of simple gases or complex molecular fluids on these materials. Numerical simulations have been realized using a sound model of the interactions between the zeolite crystal and gas molecules, with the aim of evaluating the possibility of computing the amount of gas adsorbed at a given pressure and temperature with acceptable precision.

The objective of the present work is concerned with the adsorption of H₂ on the different zeolites. Here, we have investigated three zeolites with different channel diameters and pore volumes. The physisorption properties of hydrogen molecules on RHO, ZON, and CHA zeolites have been simulated employing GCMC method. Figure 1 shows a schematic drawing of the zeolite pore structure investigated [10].

2. Simulation Details

Investigation on the adsorption isotherms of H₂ molecules in zeolites were based on the GCMC method. For the grand canonical statistical ensemble, the chemical potential, volume, and system temperature were all fixed. The average number of adsorbate molecules at the imposed chemical potential (or fugacity) was obtained from the simulation. To describe the interactions between adsorbates and adsorbents,
COMPASS force field was used. The COMPASS force field employs the Lennard-Jones (LJ) potential to describe the van der Waals interactions and the Coulomb potentials to describe the electrostatic interactions. Most parameters of the COMPASS force field were derived based on ab initio data, and the COMPASS force field had been parameterized to predict various properties for covalent molecules including most common organics, small inorganic molecules, and polymers in isolation and in condensed phases.

During the simulation, the zeolites structure was assumed to be rigid structure during the adsorption process. Eight unit cells of zeolites are used to construct the simulation box ($2 \times 2 \times 2$ cells), and periodic boundary conditions are applied in three dimensions in order to simulate an infinite system.

3. Results and Discussion

At room temperature, experimental data of hydrogen adsorption on zeolites is rare, and larger storage capacities are possible when the pressure is high. The adsorption isotherms are given in the form of uptake plots, that is, the uptake as a weight percentage is given as a function of gas pressure. Figure 2 shows that the calculated adsorption isotherms of hydrogen at 80 K obtained from the GCMC simulations are compared with the experimental results of Kumer et al. [10]. It can be seen that our computed adsorption isotherms are in good agreement with experimental results. Therefore, the model and COMPASS force field used in this work are correct and reliable.

Then, we predict the hydrogen storage capacity of ZON and CHA zeolites at near room temperature and extremely high pressures. Figure 3 shows the adsorption isotherms of the ZON and CHA zeolites in a broad range of temperature (273 K, 298 K, and 350 K) and pressure (0–2000 MPa). Their physisorption amounts under different temperatures and pressures were obtained, which may compare their hydrogen storage capacity. It can be seen from Figure 3 that the adsorption amounts increase and saturate with increasing pressure, which are in agreement with experiments on porous carbons [11]. And the adsorption amounts correspondingly increase with decreasing temperature. This is because zeolite has a characteristic high internal surface area, approximately of a similar order of magnitude to the surface area of activated carbon, a material which can exhibit appreciable hydrogen uptake values at cryogenic temperatures. Differently, the adsorbed amounts of CHA are larger than those of ZON at the same conditions. This is because the hydrogen adsorption capacity of zeolite mainly depends on the framework, channel size, pore volume and the interaction of molecular hydrogen with the internal surfaces of the micropores.

In order to explain the reason causing such differences of hydrogen storage in ZON and CHA zeolites, isosteric heats of adsorption of the later were calculated by applying the Clausius-Clapeyron equation at different temperatures. Isosteric heat is a physical quantity which may estimate the energetic interaction between zeolites and hydrogen molecule. The isosteric heat of adsorption versus the adsorbed amounts is shown at 298 K, as shown in Figure 4. We may see that the isosteric heat decreases with increasing the adsorbed amounts. This is due to the existence of different adsorption sites in these porous materials where the strongest binding sites are occupied at lower adsorbed amounts, while those possessing a lower adsorption enthalpy are occupied only at higher hydrogen concentrations. On the other hand, repulsive interaction between the adsorbed hydrogen molecules might appear at higher loading which then decreases at the heat of adsorption. The mean value of isosteric heat of adsorption $Q_h$ of each zeolite may reflect the interaction of zeolite with hydrogen molecule. We can see that the value $Q_h$ of in CHA is larger than that in ZON. This is why the storage capacity of CHA is superior to that of ZON.

4. Conclusions

Using GCMC method, we have studied the physisorption properties of ZON and CHA zeolites at the different conditions. Firstly, in order to validate correctness and accuracy of the model and compass parameters, the computed adsorption isotherms of RHO at 80 K and pressures (0–100 mbar) were compared with corresponding experimental results.
Then, we predicted the hydrogen storage of CHA and ZON zeolites using the GCMC method. Some important physical amounts under different temperatures and pressures, such as adsorption isotherms and adsorption amounts, were obtained. The results show that the physisorption properties of CHA zeolite are superior to those of ZON zeolite at all conditions. The reasonable theoretical explanations are given by calculating the isosteric heats of adsorption at the different temperatures.

**Acknowledgments**

This work was supported by the Natural Science Foundation of Education Bureau of Henan Province, China (Grant no. 2011B140005) and Henan University of Technology Foundation (Grant no. 2009BS025).

**References**


