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Molecular simulation of methane adsorption in aluminophosphate molecular sieve $AlPO_4$-11

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Abstract

Grand canonical Monte Carlo (GCMC) technique is employed to simulate the adsorption of methane in aluminophosphate $AlPO_4$-11 molecular sieve. Adsorption isotherms over the temperature range of 296–673 K are simulated and compared with the experimental data. Two steps occur in these isotherms, which represent different adsorbed phases. The minimum average total potential is existed in the whole adsorption process, which corresponds to the most stable state of the adsorption system and to the adsorbed phase with four methane molecules per unit cell. Methane molecules predominantly occupy the 10-member ring channels of $AlPO_4$-11. The initial heat of adsorption for methane estimated by Henry constants is −20.5 kJ/mol, which is in agreement with experimental data.

Keywords: $AlPO_4$-11; AEL; Zeolites; Adsorption; Grand canonical Monte Carlo; Simulation; Methane; Potential

1. Introduction

The aluminophosphate molecular sieves ($AlPO_4$-*n*) were first reported by Flanigen et al. [1,2], which exhibit properties similar to those of zeolites and have been investigated for applications as adsorbents, catalysts and catalyst supports [3,4]. Moreover, substituted networks (MeAPO, SAPO, and MeAPSO) are potentially interesting as heterogeneous catalysts for acidic or oxidation reactions [5,6]. Microporous crystalline $AlPO_4$-11 (AEL framework topology) is a member of the aluminophosphate molecular sieves family, which has a unique three-dimensional structure with orthorhombic symmetry [7]. $AlPO_4$-11 and its corresponding substituted materials have been investigated as catalysts in the methanol-to-olefin conversion [8], the hydroisomerisation of *n*-paraffins [9].

Understanding the adsorption of hydrocarbons in zeolites is a prerequisite for optimizing catalytic processes using these materials [10]. Computer simulations appear to be an attractive alternative to experimentation for investigating the adsorption behaviors at conditions of interest. In previous works, simulations on the adsorption process of hydrocarbon molecules in various type zeolites have been performed using molecular dynamics or Monte Carlo techniques. In the family of aluminophosphate molecular sieves, $AlPO_4$-5 has received much attention in recent years [11–18], moreover, studies on $AlPO_4$-11 have also been performed, for example, Maesen et al. [12] have calculated the Henry coefficients and the adsorption enthalpies at zero coverage for several linear and branched paraffins in $AlPO_4$-11 using configurational-bias Monte Carlo technique, and investigated the shape selectivity of paraffins hydroconversion in these molecular sieves and found that normal and monomethylparaffins can fully enter the pores, Domokos et al. [19] have carried a study on the interaction and transport of several hydrocarbon molecules in $AlPO_4$-11 using molecular dynamics calculations.

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In this paper, the simulations of methane in $AlPO_4$-11 molecular sieve is performed using the grand canonical Monte Carlo (GCMC) method. The isotherms and initial heat of adsorption are obtained and compared with the experimental data from the literature. In addition, Henry constants, the adsorbed phase structures, probability distribution and the average potential are investigated.

2. Simulation details

2.1. The $AlPO_4$-11 structure

Microporous $AlPO_4$-11 is composed of strictly alternating AlO_4 and PO_4 tetrahedra which make its framework electrically neutral. This material is characterized by a unidimensional system of channels parallel to c axis with elliptical 10-member ring and pore dimensions of 3.9×6.3 Å, space group of Ibm2 and cell constants of $a = 13.5336$ Å, $b = 18.4821$ Å, $c = 8.3703$ Å.

2.2. Simulations

The simulations are performed in the grand canonical ensemble, meaning that the chemical potential, temperature, and volume are fixed during the simulations.

The simulation box consists of 45 (3 in the a-direction, 3 in the b-direction and 5 in the c-direction) unit cells of the $AlPO_4$-11 molecular sieve, and the periodic boundary is applied in three-dimension to simulate an infinite system. Methane molecules are considered as single interaction centers. Intermolecular interactions are described by the 12-6 Lennard-Jones potential. In this work, the cutoff radius of potential for all interactions is 13.8 Å, and the usual tail corrections are applied. The zeolite framework is assumed to be rigid [20], indicating that the molecular sieve structure is not altered by loading of guest molecules, and zeolite–alkane interactions are assumed to be dominated by dispersive forces involving mainly oxygen atoms [20,21]. These interactions are also modeled with 12-6 Lennard-Jones potential.

For the grand canonical simulations of methane, three types of Monte Carlo moves are included: insertion move, deletion move and displacement move, and the distribution of these moves is as follows: 40% insertions, 40% deletions, and 20% displacements. Total cycles at least 2×10^5 are performed and half of the cycles (i.e., 1×10^5) are performed for equilibration, which are used to sample. The number of trial moves in a MC cycle is equal to the number of adsorbed molecules.

Table 1
Lennard-Jones parameters used in this work

	CH_4–CH_4	CH_4–O
σ (Å)	3.72	3.60
ε/k_B (K)	158.5	98.2***a***

a, the value of ε_{CH4-O}/k_B in Ref. [22] is 96.5 K.

The size and energy parameters of Lennard-Jones potential for methane derived by Ref. [17] and the size parameter of Lennard-Jones potential for zeolite–methane from Vlugt [22] are used in calculation and given in Table 1. However, the value of energy parameter for zeolite–methane of 98.2 K used in this work is about 1.8% larger than that used in Ref. [22] for CH_4 group in silicalite. Although the size and the polarizability of Al, P, and Si atoms in zeolites are much smaller than those of O atoms, the contribution of Al, P, and Si atoms to the total potential is different. By using the modified energy parameter for zeolite–methane, the simulated isotherms agree well with the experimental ones. These parameters are fit to reproduce the Henry constants and the initial heat of adsorption for methane in $AlPO_4$-11 in this work. In Section 3.4, the details on these calculations are given.

3. Simulation results and discussion

3.1. Adsorption isotherms for methane in $AlPO_4$-11

Adsorption isotherms for methane in $AlPO_4$-11 at 296 and 313 K simulated using Lennard-Jones parameters listed in Table 1 are shown in Fig. 1, which agree well with the experimental data of Ref. [23]. However, small errors are still existed, which can be explained by the fact that zeolites are considered pure crystal in simulations, while structural defects and/or impurities consist in synthesized crystal, and sometimes sorption capacities are different for the same zeolite used different preparation methods under the same conditions [24]. For this, it is possible for the experiments to permit the adsorption amount of departure from the calculated results, so these parameters are suitable for $AlPO_4$-11, and the model and programs used in this work are verified reliable.

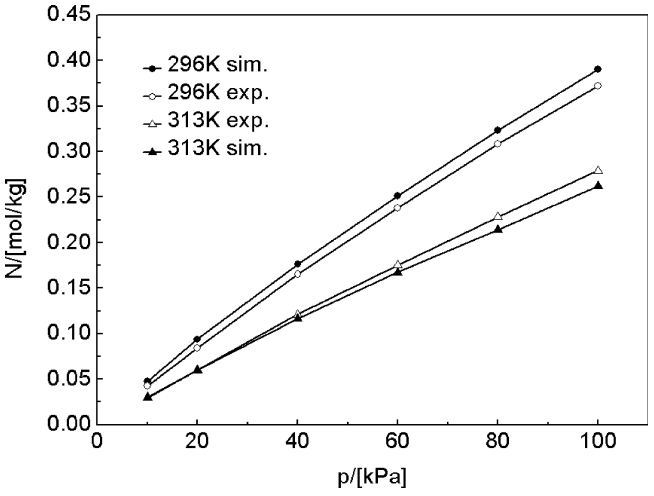

Fig. 1. Comparison of simulated adsorption isotherms with experimental data for methane in $AlPO_4$-11 at 296 K (circle symbols) and 313 K (triangle symbols). The closed and the open symbols represent the simulated and experimental data, respectively.