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Molecular simulations of methane, ethane and propane adsorption on TON*

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Abstract: The aim of this study was to understand and characterize the adsorption of small alkanes, namely methane, ethane and propane, in zeolite TON through detailed Monte Carlo simulations. The isotherms of pure components were calculated and showed good agreement with experimental data. The adsorption positions, adsorption energy of pure components and isotherms of mixtures were also simulated and the results are discussed.

Key words: Monte Carlo simulations, Zeolite, Adsorption
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INTRODUCTION

Zeolites have attracted considerable attention in recent decades owing to their potential application as adsorbents, catalysts, ion exchangers, sensors, etc. (Karasawa and Goddard, 1989; Eder, 1997; Hozalski *et al.*, 1999; Amine and Zoubir, 2004; Greathouse and Cygan, 2006; Walton *et al.*, 2006; Berge-Lefranc *et al.*, 2008). Understanding the adsorption of hydrocarbons in zeolites is essential for optimizing the processes involved in these applications. This adsorption behavior is usually quantified by means of the adsorption isotherm, which represents the amount of hydrocarbon adsorbed in a pressure range at a given temperature. The experimental determination of adsorption isotherms can be quite time-consuming because of the slow diffusion of long-chain hydrocarbons in the pores of a zeolite. Although experimental data are available on adsorption of pure components in various zeolites, experimental data on mixture sorption are very scarce; this scarcity of experimental data results from difficulties in experimentation with mixtures (Talu, 1998). To interpret the adsorption process of zeolite, we need insights into the energetics and sitting of adsorbed molecules during the process. Such information is difficult to obtain from experiments (Smit and Krishna, 2003). Molecular simulation can provide a cost-effective way to obtain this information (Smit and Krishna, 2003; Nascimento, 1999; Zhang *et al.*, 2007), especially under conditions not readily amenable to experiments (high pressures and temperatures).

TON zeolite contains a medium-pore and 1D-channel system, which makes it an ideal “pore mouth” and “key-lock” catalysis, and it plays an important role in shape-selective conversion (Webb *et al.*, 1999; Pieterse *et al.*, 2000). Some investigations have been made into the adsorption process in the pores of TON including experiments (Eder, 1997; Savitz *et al.*, 1998) and computer studies (Ndjaka *et al.*, 2004), but a systematic study of adsorption energy over a wide range of temperatures, the siting of

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adsorbed molecules and the isotherms of mixtures is still lacking.

This paper describes a molecular simulation of the adsorption of small alkanes in TON performed using the grand-canonical Monte Carlo (GCMC) method. The simulation results are compared with experimentally obtained adsorption isotherms of alkanes from the literature (Savitz *et al.*, 1998). In addition, the siting of molecules adsorbed in TON, the adsorption energy at different temperatures under certain pressures, and isotherms of mixtures are investigated.

COMPUTATIONAL METHOD

TON structure

A TON silicalite crystal structure was used in the simulations. This is represented by the CMCM space group, with lattice parameters a=1.3859 nm, b=1.7420 nm, c=0.5038 nm, $\alpha=\beta=\gamma$=90°. The silicalite unit cell contains 24 silicon and 48 oxygen atoms (Fig.1). The crystal block is composed of 5-, 6- and 10-oxygen rings (Fig.2), but the 5- and 6-oxygen rings are too small for molecules to penetrate, so the only useful column channel is circumscribed by 10-oxygen rings (the ten-membered ring, 10MR) extending along one dimension (Yu and Song, 2005). The size of the 10MR is 0.46 nm×0.57 nm (Fig.1). The zeolite crystal structure was taken from the material studio (MS) package, which contains 3D atomistic documents of zeolite framework structures.

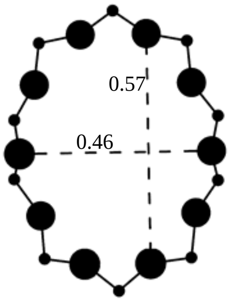


Fig.1 10-oxygen ring structure (unit: nm)

Force field

The COMPASS force field was used for alkane adsorption on zeolite TON. COMPASS is an *ab initio* force field, most parameters of which were derived from *ab initio* data. It has broad coverage in covalent molecules including most common organics, small inorganic molecules and polymers. For these molecular systems, the COMPASS force field has been parameterized to predict various properties for molecules in isolation and in condensed phases. The properties include molecular structures, vibrational frequencies, conformation energies, dipole moments, liquid structures, crystal structures, equations of state and cohesive energy densities. The COMPASS force field is suitable for the calculation of the adsorption of small alkanes on zeolite TON. Although a force field calibrated by the experimental data is more accurate than an *ab initio* one, it is extremely time-consuming. The accuracy offered by a force field fitted by *ab initio* data is sufficient for research and engineering (Nascimento, 1999; Smit and Krishna, 2003; Zhang *et al.*, 2007).

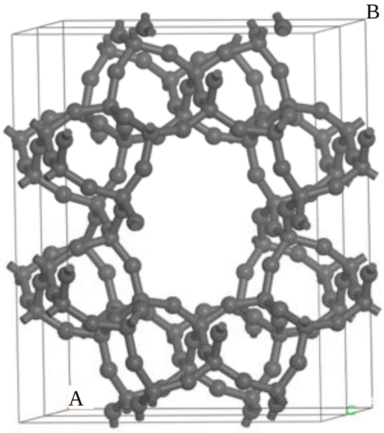


Fig.2 Structure of TON cell unit

Monte Carlo method

A Monte Carlo simulation traditionally samples from the constant ensemble, but the technique can also be used to sample from different ensembles. In the GCMC simulation, the chemical potential, volume and temperature of the ensemble are constant, while the number of particles may change during the simulation. There are three step types for a canonical ensemble: conformer, rotation and translation. A step type is selected at random, using the weight as specified at the start of the calculation run. The selected step type is applied to a random sorbate of a random component, including conformer, rotation, translation and regrowth. At least 1.5×10^5 total cycles are performed including 0.5×10^5 for equilibration. In the simulation, the periodic boundary conditions were imposed in three dimensions. The atom based model was employed to describe the van der Waals forces, and the cut-off distance was 1 nm; the long-range electrostatic interactions were calculated using the Ewald summation technique (Karasawa and Goddard, 1989).

RESULTS AND DISCUSSION

Isotherms and adsorption positions of pure component on TON

A series of adsorption isotherms of ethane, methane and propane on zeolite TON were calculated at 273, 298 and 323 K, and the comparisons of simulation data and experimental data showed the same trends (Fig.3). The deviations can be explained by the fact that zeolites are considered pure crystal in simulation while structural defects and/or impurities exist in synthesized crystal. Also, sometimes sorption capacities are different for the same zeolite when different preparation methods are used under the same conditions (Martin *et al.*, 1998). The agreement of trends between experimental and simulated isotherms of these small alkanes indicates that the simulation properly describes the adsorption behavior of these small alkanes on TON zeolite.

The maximum number of alkane molecules on a single crystal cell were calculated according to the simulated isotherms. Based on the maximum number of adsorbed alkane molecules, the locations of alkane molecules adsorbed in zeolite were simulated (Fig.4). The alkane molecules were adsorbed only in the 10-oxygen rings. This can be attributed to the fact that the sizes of 5- and 6-oxygen rings are too small to fit between alkane molecules (Yu and Song, 2005).

Two steps occur in all investigated adsorption isotherms, which correspond to different adsorbed phases (Fig.3). Starting from low pressure, as the pressure increases quickly, the loadings of the three kinds of alkanes increase until the inflection point is reached. When the isotherms pass the inflection point, the influence of pressure on loadings reduces and they stabilize, which means the adsorption has become saturated. The inflection point pressures of methane, ethane and propane were 1×10^6, 100 and 100 kPa, respectively, and the corresponding saturated loadings were 2.65, 1.35 and 1.30 mmol/g.

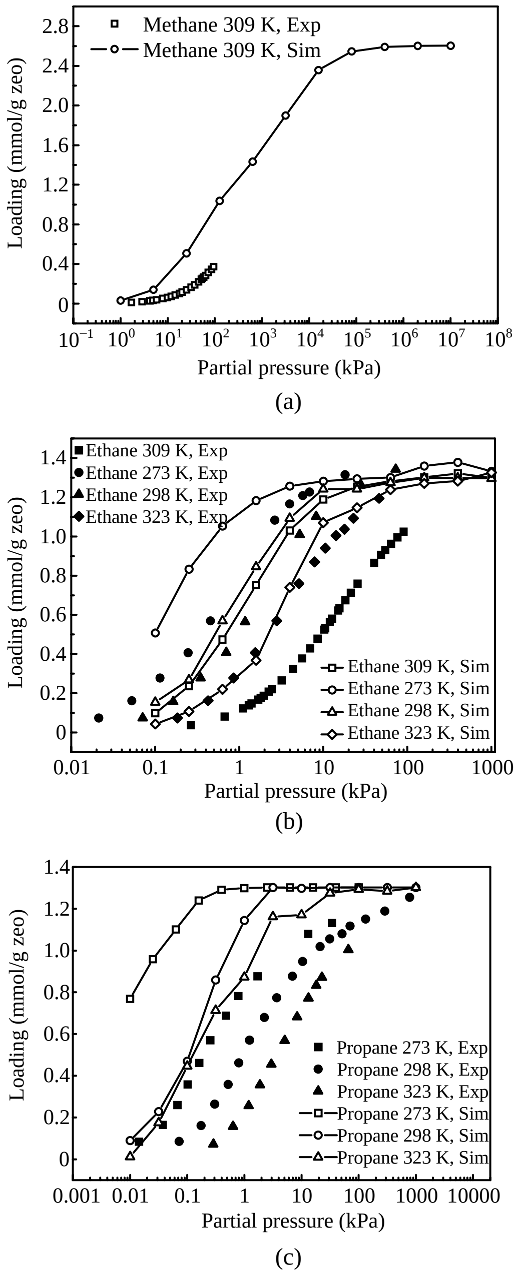


Fig.3 Comparison of simulated results of adsorption isotherm of (a) methane, (b) ethane and (c) propane on TON with experimental results

Exp: experiment; Sim: simulation; zeo: zeolite

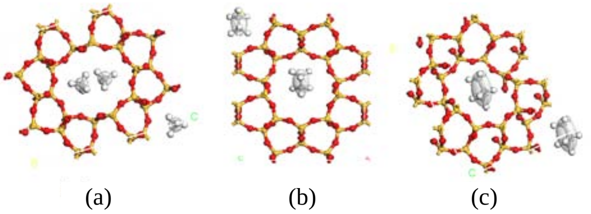


Fig.4 Adsorption position of (a) methane, (b) ethane and (c) propane on TON

Instead of a smooth intermediate zone between the first and second steps, an obvious inflection point exists between the two steps of each isotherm (Fig.3). Some zeolites have complicated channels, cross sections and various pore sizes, which can all affect molecular adsorption on zeolites, giving a smooth intermediate zone between the first and second steps (Lin *et al.*, 2007). As the only adsorbed position of small alkanes on TON zeolite is in the 10-oxygen rings and the channels formed by 10-oxygen rings are a 1D-mecropore zeolite, there are no cross sections or variations in pore sizes. So once the 1D and stable pore size channels are filled with molecules, the adsorption reaches saturation and the transition between the two steps is abrupt. This phenomenon is most obvious in the isotherms of propane adsorption.

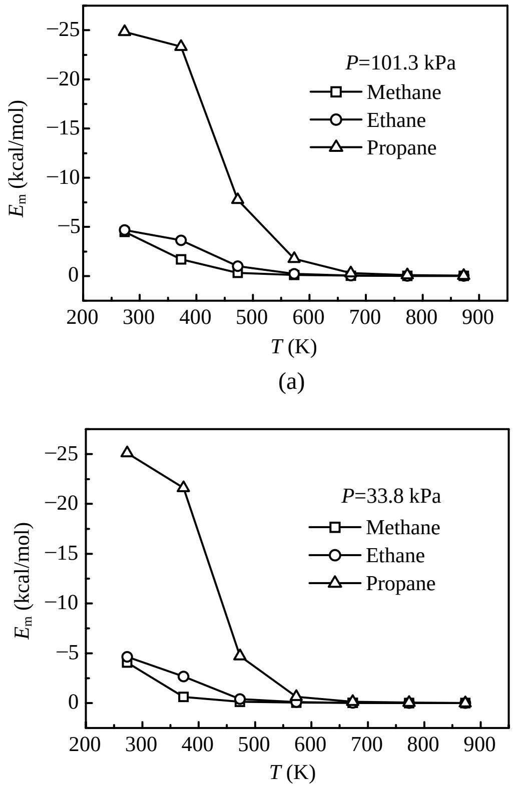
Adsorption energy of pure alkane on TON

A further criterion for investigating adsorption is given by the analysis of the total energy of the system. The total adsorption energy E_{m} of the simulation is given as

$$E_{\mathrm{m}} = E_{\mathrm{m}}^{\mathrm{SS}} + E_{\mathrm{m}}^{\mathrm{SF}} + U_{\mathrm{m}}^{\mathrm{S}}, \qquad (1)$$

where $E_{\mathrm{m}}^{\mathrm{SS}}$ is the intermolecular energy between the sorbate molecules, $E_{\mathrm{m}}^{\mathrm{SF}}$ is the interaction energy between the sorbate molecules and the zeolites, and $U_{\mathrm{m}}^{\mathrm{S}}$ is the total intramolecular energy of the sorbate molecules, as a sum of intramolecular energies of all sorbates. The intramolecular energy of the framework is not included as the framework is fixed throughout the simulation. The reduction of $E_{\mathrm{m}}^{\mathrm{SS}}$ and $E_{\mathrm{m}}^{\mathrm{SF}}$ can both lower the total energy of the system configuration.

The effects of temperature on adsorption energy of methane, ethane and propane on TON with pressures of 101.3 and 33.8 kPa are shown in Fig.5. At 273 K, the ranking of the three alkanes from high to low in order of their absolute adsorption energy is propane, ethane and methane, with propane being much higher than the others. With an increase in temperature, the absolute adsorption energy of these small alkanes decreases rapidly. When the temperature reaches 573 K the absolute adsorption energies of methane and ethane are almost the same and when it reaches 773 K, all three are the same. When the temperature goes beyond 773 K, the effect of temperature on adsorption energy reduces.



(a)

(b)

Fig.5 Adsorption energy (E_{m}) of methane, ethane and propane on TON vs temperature (T). (a) P=101.3 kPa; (b) P=33.8 kPa

Because the polarities of these three kinds of small alkanes are so weak that their intramolecular energies are negligible, their adsorption energies on TON are composed mainly of the intermolecular energies and the van der Vaals forces between adsorbed alkanes and the zeolite framework. With an increase in temperature, the intermolecular forces of sorbates and van der Vaals forces between sorbates and the zeolite framework decrease, which means that the absolute system adsorption energy declines. The total energy E_{m} is relative to the adsorbed molecules in the system, so a decline in total absolute energy means a decrease in adsorbed molecules and the enhancement of desorption capability.

Almost all the adsorption energies within the experimental temperature range are below 100 kJ/mol, which means all the adsorptions are physical adsorptions (Zhao, 2005) and desorption process could be carried out.

The change in absolute adsorption energy with variation in temperature is of great significance to the practical desorption operation of zeolite TON.

Isotherm of mixture

In practical engineering, the mixture isotherm is of significant practical importance but the experimental mixture isotherm calculation is complicated and expensive (Talu, 1998). In this study, the molecular simulation of mixture sorption was carried out with methane, ethane and propane in a constant volume proportion of 1:1:1 at 300 K. The isotherm of the mixture is shown in Fig.6.

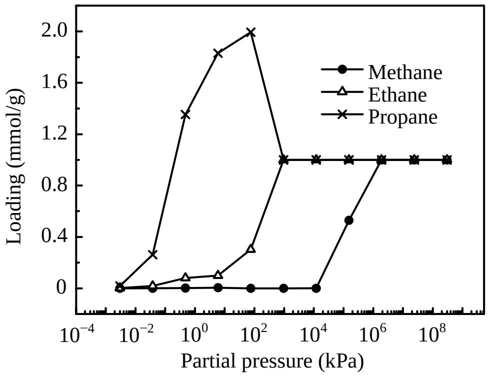


Fig.6 Adsorption isotherm of mixture of methane, ethane, and propane with the constant volume proportion of 1:1:1 on TON, 300 K

Under low pressure, the propane is adsorbed first and then the ethane is adsorbed slightly, but the methane shows little adsorption (Fig.6). With an increase in pressure, the propane adsorption first increases and then decreases to a certain quantity and stabilises, while the ethane and methane adsorptions increase in order and become constant after having reached a certain quantity. Finally, when the pressure reaches 1×10^7 kPa, the adsorption capacities of these three alkanes become the same. The propane capacity reaches a maximum at a pressure of 100 kPa, the ethane at 1×10^3 kPa and the methane at 0.5×10^6 kPa.

In the isotherm of the mixture, under low pressure the adsorption of the three alkanes is independent (Fig.6). With an increase in temperature, the longest alkane will reach a maximum and then decrease to a certain quantity; then the second longest alkane adsorption will increase and then stabilise at a certain number, and then the shortest one. The shorter the alkane chain, the higher the pressure of saturation. This phenomenon is in accord with the results of Lu (2005). It means that at low pressure the longest propane will be adsorbed with first priority. Its adsorption capacity will first increase and then decrease after the climax of adsorption and stabilize at a certain number. The short alkane will not be adsorbed until at high pressure and its adsorption will increase with the increase in temperature until it reaches saturation.

The alkane with long chains has more isothermic heat of adsorption, so it will be adsorbed first at low pressure. Once the pressure has increased gradually to a high level, the sieve will be almost full, so entropy will be the main influencing factor. A sieve filled with short alkane will have higher entropy than one filled with long alkane, and so under high pressure the number of adsorbed molecules of short alkane will increase gradually and that of long alkane will decrease. This agrees with the results of Talbot (1997). The difference in adsorption among the different gas components in a mixture at different pressures will be of great importance for the adsorption/separation process of mixture gases in environmental engineering.

CONCLUSION

The adsorption characteristics of methane, ethane and propane on zeolite TON were simulated using the GCMC method. The following conclusions could be drawn:

(1) The behavior of pure component adsorption of methane, ethane and propane on zeolite TON was almost the same: with an increase in pressure the adsorption capacity of each alkane will increase until it reaches a saturation quantity.

(2) With pure components, at low pressure (below 101.3 kPa) and low temperature (below 273 K) the ranking in adsorption energy order is inversely proportional to the length of the chain in each alkane. The adsorption energy of the alkanes will decrease with an increase in temperature and will become almost the same when the temperature reaches 773 K. All the adsorptions are physical adsorption and desorption process could be carried out. The variance of adsorption energy over the temperature range will be

significant for practical operation.

(3) The only adsorption position of alkane on TON is in the 1D 10-oxygen ring channel which means that the transition between the two steps of the adsorption isotherm is an abrupt inflection point rather than a smooth intermediate zone.

(4) The results of a simulated mixture isotherm showed that: under low pressure, the long chain alkane will be adsorbed with priority and its adsorption will first increase and then decrease to a certain number as the pressure increases; under low pressure, there will be little adsorption of short chain alkane but it will increase with increasing pressure; at high pressure, the adsorption of the three kinds of alkane is almost the same. The variance of adsorption of each alkane in a mixture will be of significant interest in gas separation.

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