



Adsorption of Thiophene in MCM-22 Zeolite by Grand Canonical Monte Carlo Simulation

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The grand canonical ensemble Monte Carlo simulation was employed for investigating adsorption behaviour of thiophene in MCM-22 zeolite, the practice from which we gain some information of adsorption isotherm, heat of adsorption and distribution of thiophene. Result shows that the adsorption and distribution of thiophene are greatly affected by temperature and pressure and heat of adsorption is hardly affected by temperature and pressure. Thiophene distribute widely in 10-MR pore and 12-MR supercage of MCM-22 zeolite and their preferential adsorption positions are at upper and lower part of supercage and in independent 10-MR pore. Through the investigation on the calculation of potential energy surface produced by thiophene crossing 10-MR window, we gain the information that thiophene can migrate freely within 12-MR supercage and that when thiophene migrates from one supercage to its adjacent supercage, high potential energy employed by its crossing 10-MR window needed to be overcome, potential energy is 100 kJ/mol.

Key Words: Thiophene, MCM-22, Grand canonical Monte Carlo simulation, Adsorption, Migration.

INTRODUCTION

In the chemical and petroleum industry, the physico-chemical property of sulfocompound arouses wide concern. The method that is employed to remove sulfocompound in chemical production has become hotspot of scientists' research all over the world, the fact which is employed by constantly improving standard of exhaust emission from automobiles and laboratories. Thiophene is one of the most common sulfocompounds in chemical production and automobiles' exhaust emission, so the method mentioned above bears significantly on many issues. The investigation showed that it is easy to separate thiophene or remove by means of adsorption and catalytic process of microporous molecular sieve^{1,2} *i.e.*, method that is employed to separate thiophene from petrol can be through the way of using preferential adsorption of synthetic molecular sieve^{3,4}. Adsorption desulfurization technique fits for deep desulfurization because of its simple operation, secure investment as well as its mild reaction condition. This technique can be employed to remove sulfocompound from petroleum benzene without lowering its olefinic content, is a great promising method of desulfurization. Nevertheless, it is very difficult to gain information of thiophene molecular's adsorption behaviour on molecular sieve surface through experiment, so it is still in the fuzzy understanding of thiophene molecular's adsorption mechanism at molecular level.

Microporous molecular sieve is widely employed as catalyst, ion exchange and adsorbent due to its ordered

structure and large specific surface area. In recent years, investigation shows that thiophene preferentially absorbed well by Y-sieve^{5,6} and ZSM-5 zeolite⁷. In Y-sieve, faujasite zeolites interpenetrate through 12-MR along the direction of three crystal axis, forming a crystal cell. 12-MR is the main window of faujasite, whose aperture is 0.74 nm. ZSM-5 zeolite consist of straight elliptic channel and Z-form channels perpendicular to the former, the opening of the Z-form channels are approximately 10 member rings. We suppose preferential adsorption of thiophene is affected by microporous⁸ structure of 12-MR pore and 10-MR pore. MCM-22 zeolite is synthesized by Mobil Company, U.S.A., which consists of two types of independent pores. One of its pores is sine wave form build by 10-MR pore, the other is 12-MR supercage pore connected by 10-MR windows. MCM-22 zeolite has both structure characteristics of Y-sieve and ZSM-5 zeolite. It has been widely investigation because of its unique structure⁹⁻¹⁰. So, it is presumed that the thiophene would be preferentially absorbed well by MCM-22 zeolite. Nevertheless, there is less research on how to remove thiophene by MCM-22 zeolite and little information about the adsorption and adsorption mechanism of thiophene in MCM-22 zeolite.

Molecular simulation bears significantly on the investigation of adsorption position and separation effect in molecular sieve, because molecular simulation builds up organic relation between micro-mechanism and macro phenomenon. Grand canonical Monte Carlo simulation is involved in molecular

simulation which is widely employed in the study on adsorption of molecular sieve and plays an important role to gain information about adsorption mechanism of adsorbate in Monte Carlo simulation^{10,11}. The studies on the adsorption position, heat of adsorption and adsorption isotherm of thiophene in Monte Carlo simulation plays an important role to gain information about its adsorption and catalytic reactor. The grand canonical ensemble Monte Carlo simulation and molecular force method were employed to discuss adsorption mechanism, distribution and migration characteristics of thiophene in MCM-22 zeolite, after which we gain information about how temperature, pressure and other factors effect the distribution and adsorption position and about thiophene's migration characteristics, when it migrates from one 12-MR supercage to another through 10-MR window.

COMPUTATIONAL METHODS

MCM-22 zeolite has high Si-Al molar and distribution of Al atom in molecular sieve is uncertain, therefore, computer simulates the real Si-Al MCM-22 zeolite by its model which is provided by Nascimento¹². Periodic boundary condition is employed in this simulation and its basic unit $2 \times 2 \times 2$ unit cell, including totally 1728 skeleton atoms. Space group P6/mmm, unit cell parameters $a = 1.41145$ nm. Thiophene consists of C, H, S elements, its structural optimization through DFT (B3LYP/6-311++G (d, p)).

The simulation mentioned above employed all atoms forcefield model, which choose CVFF force field. The CVFF forcefield can help gain adequate acquaintance of interaction between covalent bond and non-bond in this system. All custom parameters employ default value.

In the process of Monte Carlo simulation, the temperature is 298, 363 and 393 K, pressure is 0.01-10 kPa, 6×10^6 configurations are tested, configurations in which the former 3×10^6 are tested for balance and the latter 3×10^6 are employed as OSCA in order to get the result.

In Monte Carlo simulation, conformation of molecular sieve is allowed to change, but the distance between C-C and C-S in adsorbate is forced. Nascimento¹² molecular simulation software package is employed to calculate on the origin server.

RESULTS AND DISCUSSION

Adsorption of thiophene in MCM-22 zeolite: Above all, different forcefields (Burchart-Dreiding, CVFF and COMPASS), we investigated the adsorption isotherm of thiophene in 363 K and between 0.01-10 kPa (Fig. 1). Fig. 1 shows that, computational result from CVFF forcefield is close to that of COMPASS forcefield, which are both reaching basic adsorption balance at 0.1 kPa and also adsorption capacity are close to each other at the same pressure. Nevertheless, adsorption capacity of adsorption isotherm getting from Burchart-Dreiding forcefield is sharply less than that from CVFF and COMPASS forcefield. According to the work of Hou¹³, in which he employed CVFF and Burchart-Dreiding force field to compare adsorption of benzene in MCM-22 zeolite with the experimental value, showed that it's more close to the experimental value under the condition of CVFF force field. Thiophene and benzene have similar structure and property,

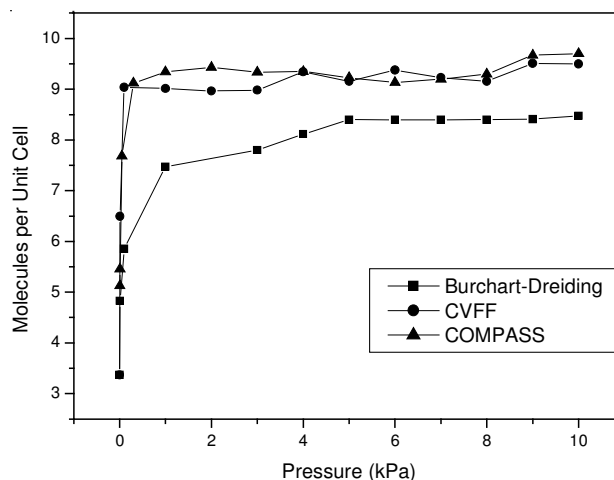


Fig. 1. Adsorption isotherm for thiophene in MCM-22 zeolite with different forcefield (Burchart-Dreiding, CVFF and COMPASS) at 363 K

so it's reasonable to use CVFF or COMPASS force field to simulate. CVFF force field is employed in this work.

Fig. 2 shows that the adsorption isotherm of thiophene at 298, 363 and 393 K, under the pressure between 0.01-10 kPa from this figure comes to the result that adsorbance of thiophene is 0 at 0 kPa and increases fast as the pressure is lower than 0.1 kPa. And adsorbance changed slowly as the pressure increases after the pressure is higher than 0.1 kPa. There is strong interaction between thiophene and MCM-22 zeolite, which causes the high adsorbance of thiophene at low pressure. Meanwhile, under the condition of the same pressure and different temperature, adsorbance of thiophene reduces a little as the temperature increases, which can employed by the endothermic adsorption process. Besides, kinetic energy of adsorbate is increased by higher temperature; leading to its diffusion motion overcoming the adsorption energy of molecular, increasing temperature slows down the speed of adsorption. Monte Carlo simulation^{14,15} and experiment⁵⁻⁷ have been employed to investigate the adsorption of thiophene in H-ZSM zeolite and Y-sieve. Nevertheless, there is little investigation on adsorption of thiophene in MCM-22 zeolite, causing relevant data deficiency. The type of adsorption isotherm in MCM-22 zeolite is close to that in MOR and MFI.

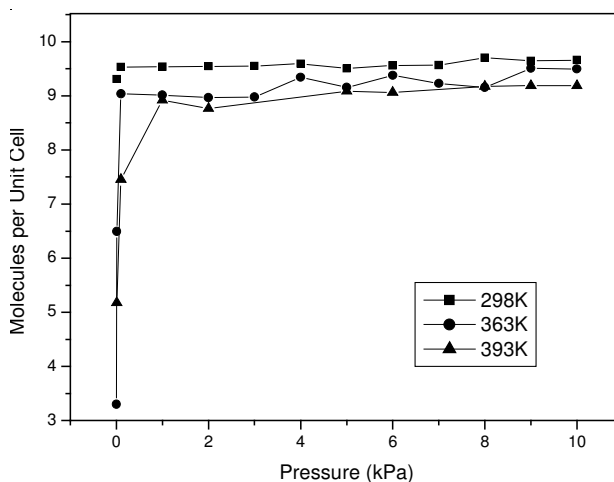


Fig. 2. Adsorption isotherm of thiophene in MCM-22 zeolite at different temperature (298K, 363K and 393K)

Heat of adsorption is an indispensable parameter to describe adsorption process and how strong the interaction energy is between adsorbates and adsorbent, the concept which provides important data of removing adsorbate after its preferential adsorption process in adsorbent. The heat of adsorption is represented by isosteric heat of adsorption, H_{st} ,

whose definition is $H_{st} = R \left(\frac{\partial \ln P}{\partial \frac{1}{T}} \right)_N$, in which, R is a

constant, P is the adsorption pressure, T is the adsorption temperature and N represents the adsorption molecular number. Definition shows that H_{st} changes little at different temperature, result is around 75-81 kJ/mol. Experimental value of thiophene heat of adsorption in MCM-22 zeolite is deficiency, so we can not get the result of heat of adsorption of thiophene at different temperature. There were some reports² on H_{st} thiophene in Na-ZSM-5 zeolite and Na-Y-sieve, experimental value are respectively 76.63-79.10 kJ/mol and 79.84-81.93 kJ/mol. Pore of MCM-22 zeolite is similar to that of ZSM-5 zeolite, besides, diameters of two pores are almost same, therefore, H_{st} of thiophene in MCM-22 zeolite is suppose to be close to 80 kJ/mol.

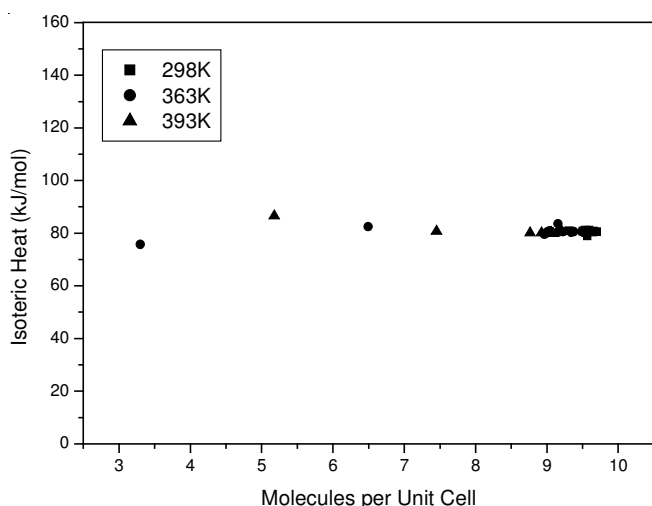


Fig. 3. Isosteric heat of adsorption of thiophene in MCM-22 zeolite at different temperature

In order to discover the effect of different temperature and pressure to the distribution of thiophene in MCM-22 zeolite, we compared the different distributions of thiophene in MCM-22 zeolite on the condition of the same temperature and different pressure as well as on the condition of the same pressure and different temperature. Fig. 4 shows the computational result. The results of Fig. 4a and 4b show that at the same temperature and low pressure, adsorption capacity of thiophene is little, thiophene distributes mainly in independent 10-MR pore system and at upper and lower part of the supercage, on the contrary, adsorption capacity of thiophene is little at the center of supercage and at the window of 10-MR, when adsorption pressure is higher, adsorption capacity of thiophene increases obviously. The adsorption behaviour can be found in both independent pores. We can suppose that preferential adsorption position of thiophene is in independent 10-MR pore and at upper and lower part of supercage.

Meanwhile, thiophene at the center of supercage is difficult to be absorbed but easy to diffuse, the fact which is employed by narrow and crooked pore of independent 10-MR, there is strong interaction energy between atoms on the wall of molecular and thiophene, by the huge space at the center of supercage, where there is weak interaction energy between atoms in the supercage and thiophene. Fig. 4a and 4b show that thiophene is easy to be absorbed at the same pressure at low temperature. The fact which is employed by adsorption proves an exothermic process and kinetic energy is increased by a higher temperature. The results correspond to that of adsorption isotherm.

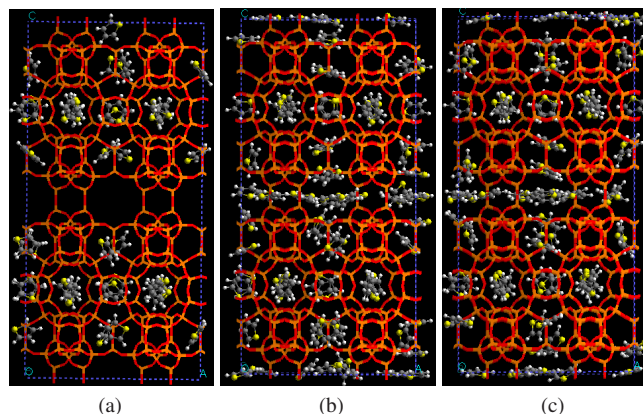


Fig. 4. (a) Distribution of thiophene in MCM-22 zeolite at 0.01 kPa and 393K; (b) Distribution of thiophene in MCM-22 zeolite at 10 kPa and 393K; (c) Distribution of thiophene in MCM-22 zeolite at 0.01 kPa and 298 K

Migration of thiophene in MCM-22 zeolite: According to the distribution figure of thiophene in MCM-22 zeolite, we find that migration of thiophene is mainly within the supercage system, the fact which is employed by that is difficult to migrate in narrow and crooked pore of 10-MR. There is no high potential barrier when thiophene migrates within supercage system because of its huge space of inner part in supercage system. Nevertheless, high potential barrier must be overcome when thiophene migrates from one 12-MR to its adjacent 12-MR through 10-MR window because these two 12-MRs are connected by one 10-MR window.

In order to estimate the energy needed for the migrating of thiophene from one supercage to its adjacent supercage. Molecular mechanics is employed to investigate interaction energy between molecular and thiophene when thiophene migrates from one supercage to its adjacent supercage, by means of which, Hou¹⁶ predicted energy needed for benzene's migration in MCM-22 zeolite supercage. We use the molecular mechanics to simulate this process. Conformation of thiophene is allowed to change during computational process; MCM-22 zeolite skeleton is fixed on crystallographic coordinate. Optimize selection of periodic boundary condition. Starting point of motion path is set near to 10-MR window of supercage, where thiophene is located. Motion of thiophene keeps vertical to surface of 10-MR window. Step size of thiophene is set at 0.02 nm low-lying minima is found on the motion path and the non-bound interaction energy between thiophene and molecular is calculated at ever spot on motion path.

Fig. 5 shows the relationship of the distance between sulfur atom and 10-MR window when thiophene migrates and non-bond interaction energy. From Fig. 5, we find that four summits appear during the overall motion process of thiophene: A and D is potential barrier that needed by thiophene to overcome when it go through 10-MR window. These two potential barriers are key factors for the migration of thiophene between two supercages. After calculation, we find that the energy needed by thiophene to migrate from one supercage to another is approximately 100 kJ/mol. The result is closed to that of Hou¹⁶ simulation, excitation energy needed by benzenz to migrate between two supercages in MCM-22 zeolite. There are also two lower potential barriers existing when thiophene migrates within supercage, providing approximately 30 kJ/mol, which has little impact on migration of thionphene. Compared to "interaction energy needed by benzene to migrate within supercage" curve, which comes from Hou's simulation, we find that potential energy produced by the diffusion of thiophene within supercage is not symmetry. Benzene is highly symmetrical, so the interaction energy is the same when benzene leaves or comes towards to 10-MR window on the two sides symmetrical position of supercage center. Nevertheless, thiophene is lowly symmetrical, so the interaction energy is different when thiophene leaves or comes gradually towards 10-MR window during its migration on the two sides of supercage.

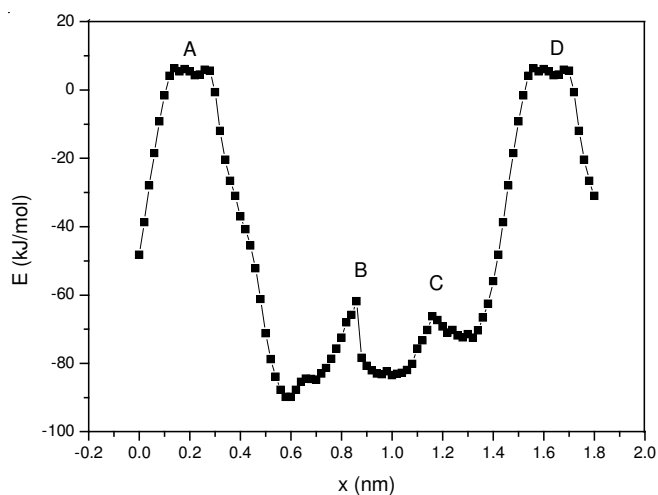


Fig. 5. Relation of the distance of the sulfur atom in thiophene to the window of 10-MR channel with the energy of non-bonding interaction

Conclusion

Monte Carlo calculation shows that adsorption temperature and adsorption pressure can effect adsorption capacity and position of thiophene in MCM-22 zeolite but affect little to the heat of adsorption. Thiophene can be absorbed both in 10-MR and 12-MR supercage system of MCM-22 zeolite and can be preferential absorbed on the upper and lower part of 10-MR pore system and supercage. Simulation, by means of molecular mechanics, shows that thiophene can not only migrate freely within supercage, but also migrate from one supercage to its adjacent supercage, the latter process which needs approximately 100 kJ/mol.

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