The Grand Canonical Monte Carlo Simulations of Benzene and Propylene in ITQ-1 Zeolite

Li Li ZHU, Ting Jun HOU, Xiao Jie XU*

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871

Abstract: Grand Canonical Monte Carlo (GCMC) simulations have been performed to study the localization and adsorption behavior of benzene and propylene, in purely siliceous MWW zeolite (ITQ-1). By analyzing the locations of benzene and propylene in ITQ-1, it can be deduced that the alkylation of benzene and propylene will mainly happen in 12-MR supercages at the external surface or close to the external surface. The adsorption isotherms of benzene and propylene at 315K and 0~3.5kPa are predicted, and the results for benzene generally coincide with the trend from the experiments of a series of aromatic compounds.

Keywords: Grand Canonical Monte Carlo (GCMC), ITQ-1, adsorption, diffusion.

The alkylation of benzene with propylene to produce cumene, a starting material for the production of acetone and phenol, is very important in hydrocarbon process. Compared with some mineral acids including $AlCl_3$ and others, zeolites seem to be more clean catalysts, moreover, they can effectively reduce the amount of less desired products such as diisopropylbenzenes.

Several zeolites including H-ZSM-5, USY, β and MCM-22 have been tested for the reaction of the alkylation of benzene with propylene, and it has been found that β, USY and MCM-22 are very reactive[1]. Zeolite MCM-22 (IZA code MWW) is a novel zeolite discovered recently by scientists at Mobil[2]. Compared with other usual types of zeolites, MCM-22 possesses an interesting and unusual framework structure: two independent pore systems formed by interconnected sinusoidal 10-MR pores with a 4-5.5Å diameter and an independent 12-MR supercage with 18.2-7.1Å linked by 10-MR windows. The unusual framework topology, high thermal stability, large surface area and good sorption capacity render this kind of zeolite very interesting for catalysis. To our knowledge, no work has been undertaken until now to investigate the adsorption properties of benzene and propylene in MWW type zeolites by means of grand canonical Monte Carlo (GCMC) technique. In the present work, GCMC simulations are used to predict the migration characteristics of benzene and propylene in ITQ-1 zeolite.

Methodology

Considering the difficulty in experimentally determining Al distributions in disordered zeolites and the high Si/Al ratio of MCM-22, meanwhile, in order to simplify the

simulation process, the pure silica analogue of MCM-22, ITQ-1, is adopted. In the simulations, the silicon and oxygen atoms of the zeolite framework are fixed at their crystallographic positions. The zeolite and the sorbates are assumed to interact *via* a pairwise-additive potential between atoms of the adsorbed molecules and those of zeolite. The site-site interactions are modeled with a Lennard - Jones plus Coulombic potential, and the Burchart-Dreiding forcefield is employed[3, 4]. The partial charges for the atoms in benzene and propylene are computed from the fit of electrostatic potential by using AM1 method, available in MOPAC 7.0.

The grand canonical Monte Carlo (GCMC) techniques simulate the equilibria of a collection of adsorbates in a micropore at constant chemical potential, volume, and temperature or pressure. The bulk pressure can be determined from the chemical potential using a Lennard-Jones equation. So the GCMC simulations enable one to study many important characteristics of the full-loaded zeolites under certain pressure and temperature.

Eight unit cells of zeolite are used to construct the simulation box and periodic boundary conditions are applied. First, GCMC simulations have been carried out in the condition with constant temperature (300K) and constant pressure (1atm), then, a series of simulations are performed to predict the adsorption isotherms for benzene and propylene. All calculations are accomplished in the Cerius[2] molecular simulation package[5] on SGI R10000 workstation.

Results and Discussion

Adsorption and migration behaviors of benzene and propylene in ITQ-1. **Figure 1**(a) depicts the distribution of interaction energy of a benzene molecule with other sorbates and the zeolite. The distribution curve is roughly single-peaked, with a maximum around -19.9 kcal.mol^{-1}, and a shoulder from $-17.5 \sim -15.0$ kcal.mol^{-1}. From the mass clouds in **Figure 2**(a), it can be noted that the spatial distribution of benzene molecules can be partitioned into four regions: one in 10-MR channels and three others in 12-MR supercages, which have been named as S1, S2, S3 and S4. S1 resides at the center of the 10-MR channel intersections. S2 is located near the 10-MR facing to 6-MR in supercages, while S3 and S4 all near the center of 12-MR supercages.

The benzene molecules near S1 site possess relatively lower interaction energy, but they seem to distribute within a very restricted area around the 10-MR intersections. The benzene molecules at S2 site also possess relatively lower interaction energies, although a little higher than those at S1 site, which distribute generally localized. Other two interesting sites are located near the center of the supercages (the S3 and S4 sites). Obviously, the benzene molecules at the S3 and S4 sites show different adsorption behavior compared with those at the S1 and S2 sites, which are considerably delocalized in the vicinity of its preferred sites of adsorption. It seems that the migrations of benzene molecules mainly happen in the same supercage, and the intercage motions should be temperature-activated. Nevertheless, the migration of benzene along 12-MR cavities is much easier than that along 10-MR channel systems.

Figure 1 (a) benzene/zeolite potential energy distribution. (b) propylene/benzene potential energy distribution.
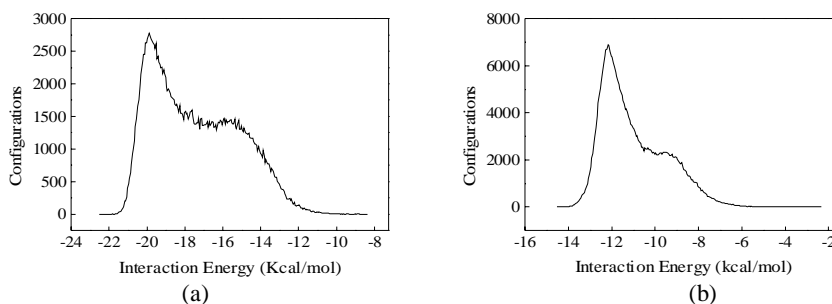

(a) (b)

Figure 2 (a) Mass cloud for benzene in ITQ-1. (b) Mass cloud for propylene in ITQ-1
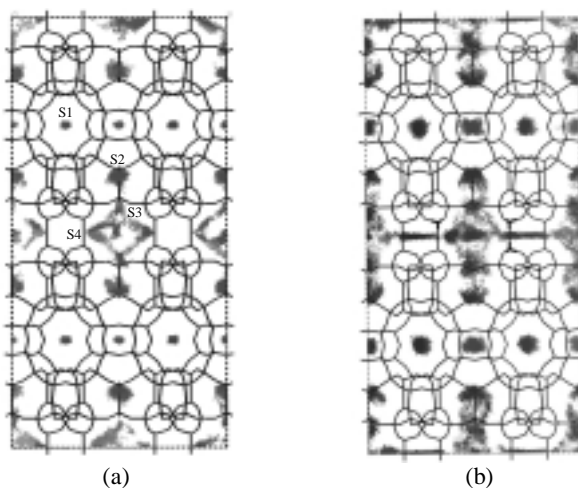

(a) (b)

Figure 1(b) depicts the distribution of interaction energy of propylene with other sorbate molecules and the zeolite. **Figure 2**(b) shows that the propylene molecules located in 10-MR system channel are also generally localized, but a much wider area is covered. Moreover, the propylene molecules almost fill all the possible positions in one supercage. It can be seen that the propylene molecules can be steadily located in the short 10-MR conducts around 3Å long, very differently with the mass cloud of benzene molecules.

Predictions of adsorption isotherms for benzene and propylene. In order to investigate the adsorption behaviors of benzene and propylene more deeply, a series of simulations have been performed to get the adsorption isotherms at a temperature of 315K, and some pressure ranging from 0.0kPa to 3.0kPa. The calculated adsorption isotherms of pure propylene and benzene in ITQ-1 at 315K are shown in **Figure 3**, and the experimental isotherm of toluene is used as a comparison.

Figure 3 Simulated adsorption isotherms of benznene and propylene at 315K and experimental values for toluene
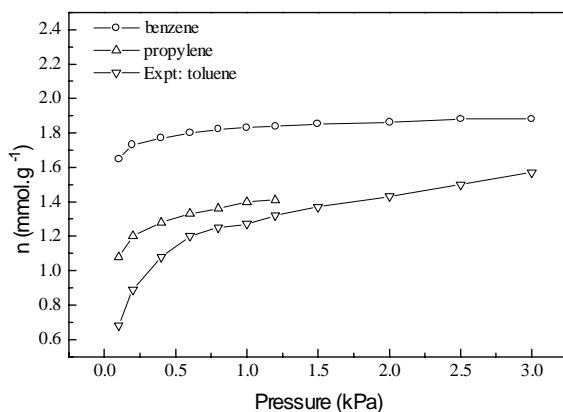
Only from the viewpoint of volume, the benzene molecules are relatively small, so their adsorption loading should be remarkably higher than that of toluene, which can be well indicated from our simulations. Previous experiments combined adsorption-microcalorimetric study have been applied to the adsorption-diffusion behaviors of toluene, meta- and ortho-xylene, and 1,2,4-trimethylbenzene with different kinetic diameters in MCM-22[6], and the adsorption isotherms have validated that the zeolite update significantly relies on the size of adsorbate molecules. The simulations have validated that the interaction energy for propylene is much higher than that of benzene, which means propylene may be more unfavorable in zeolite than benzene. So in some conditions especially under low pressure, the unfavorable interaction energy will make the uptake of propylene lower than that of benzene.

Acknowledgment

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