Measurement and Molecular Simulation on Adsorption Equilibrium and Adsorption Kinetics of the Chlorinated Hydrocarbons into High Silica Zeolite

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Introduction

Molecular simulation has now become powerful tool for the study of adsorbed molecules in zeolites, and the Grand Canonical Monte Carlo (GCMC) method is especially useful for predicting adsorption equilibria. However, information on forcefield parameters and charges are often inadequate, even in systems where the structure is well known. From the environmental point of view, the adsorption of chlorinated hydrocarbons by the use of zeolites may have some potential utilities in ground water or soil remediation and other areas. Mellot et al. recently reported new force field parameters and charges for chlorinated hydrocarbons in the faujasite zeolite: NaX, NaY and siliceous Y [1].   These yield heats of adsorption that are in good agreement with calorimetric data [2].

In this study, their force field parameters were used to simulate adsorption isotherms and isosteric heats of adsorption for chloroform and tetrachloroethylene in USY6.18 zeolite and in ZSM-5 type zeolite: Pentasile-2 zeolite, respectively. The results were compared with gravimetric and chromatographic experiments.

Experimental

Gravimetric Method

Figure 1 shows experimental apparatus for gravimetric analysis. The zeolite sample (about 0.7g) was placed in a quartz basket (K). Then the adsorbate in flask (B) was fed to adsorption tube (N). The whole apparatus was in a constant temperature air bath. The temperature range was 303-323 K. The amount adsorbed was measured corresponding to the pressure of the vapor in the tube. The pressure was measured by pressure sensor (P) at higher pressure range (> 0.013 atm) and baratron (O) at lower pressure range (<0.013 atm). In this way, adsorption isotherms were obtained (Figure 5-8).

Chromatographic Method [4]

In order to study the isotherm at lower pressure range, we used a pulse response method with a gas chromatograph.The gas chromatograph (GC 9-A; Shimadzu Co., Ltd.) was used with helium carrier. Siliceous zeolite was pelletized, crashed and screened to obtain particle size between 4.95×10^{-4} to 8.33×10^{-4} m (an average particle diameter of 6.64×10^{-4} m) and packed to the column (length, 30cm, diameter, 3mm). Pulse responses of vaporized chlorinated hydrocarbon with helium were detected by TCD. Response data were stored and processed by a personal computer. From retention time of pulse response, adsorption equilibrium constant at zero coverage was obtained and plotted as van't Hoff plot to get heat of adsorption and adsorption equilibrium constant extrapolated to 303 K on all the adsorbates. This extrapolated value was revealed as initial slope.
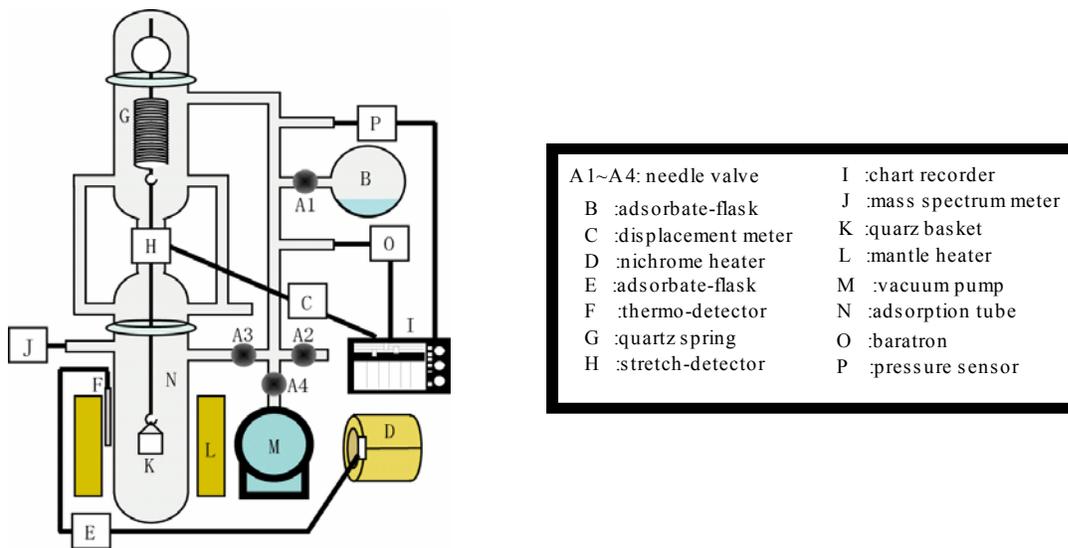
Figure1. Experimental apparatus to measure adsorption equilibrium

A1~A4: needle valve		I :chart recorder
B :adsorbate-flask		J :mass spectrum meter
C :displacement meter		K :quarz basket
D :nichrome heater		L :mantle heater
E :adsorbate-flask		M :vacuum pump
F :thermo-detector		N :adsorption tube
G :quartz spring		O :baratron
H :stretch-detector		P :pressure sensor

Simulation

Cerius2 (Accelrys Inc.) was used throughout the simulations. Force field parameters obtained by Mellot et al. are listed in Table 1 [2]. The Grand Canonical Monte Carlo method (under constant chemical potential ( ), volume (V), temperature (T)) was used to get the equilibrium amount adsorbed and the heat of adsorption.

Also, molecular dynamic calculation (MD) was tried target micropore diffusivity.

Table 1. Van der Waals parameter

	Epsilon/K [deg]	R_Min[Å]
Si – Si	0.000	0.000
O – O	0.000	0.000
O – Cl	87.058	3.253
O – C	162.000	3.430
O – H	90.535	2.698
C – C	25.860	3.753
C – Cl	55.650	3.787
C – H	26.730	3.358
Cl – Cl	119.800	3.822
Cl – H	57.530	3.392
H – H	27.630	2.963
X – X	0.000	0.000
X – H	0.010	6.000
X – Cl	0.010	6.000
X – C	0.010	6.000

Zeolite Models

2 models were considered here for USY6.18. Pure siliceous faujasite (Y-type) (Figure 2) was in the database of Cerius2. Dummy atoms were put in sodalite cages to avoid impossible occupation of adsorbates. USY6.18 has the silica-alumina ratio of SiO_2/Al_2O_3=6.18. Then we put acid sites as in Figure 3.

ZSM-5 type zeolite (Figure 4) was in the database of Cerius2. Pentasile-2 has the silica-alumina ratio of SiO_2/Al_2O_3= 30. Then we put 1 acid site.
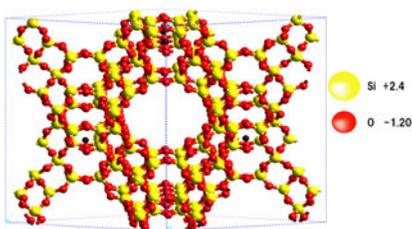
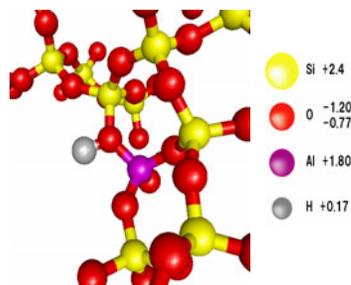**Figure 2**. Pure Siliceous Type model
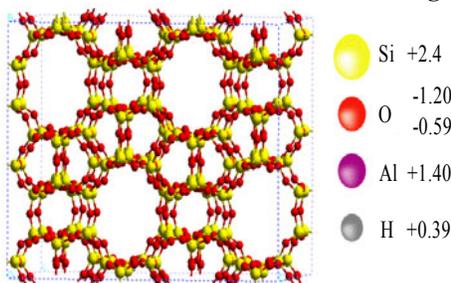

Figure 3. Acid Site model

Figure 4. ZSM-5 Type model

RESULTS AND DISCUSSION

Adsorption Equilibrium for the System of USY6.18

In Figure 5 and 6, experimental adsorption isotherms for chloroform and tetrachloroethylene in USY6.18 at 303 K are shown, respectively. Initial slopes for 303 K are also shown. This whole range of adsorption isotherm at 303 K could be compared with simulation. At higher pressure (>0.01 atm), all the simulations were coincident and almost correspond to gravimetric data. At lower pressure, the simulation by the acid site model was found to be good agreement with the experiment, but not the pure siliceous model for chloroform. In case of tetrachloroethylene both model could almost simulate the experimental data.

In Table 2 and 3, experimental heats of adsorption obtained by chromatography at zero coverage were compared with simulated heats of adsorption for 2 models. Here, simulations for the acid site model were closer to the experimental values than the pure siliceous model for chloroform. However, the data and the simulated by both models were the same as for tetrachloroethylene. These differences were attributed to the polarity.
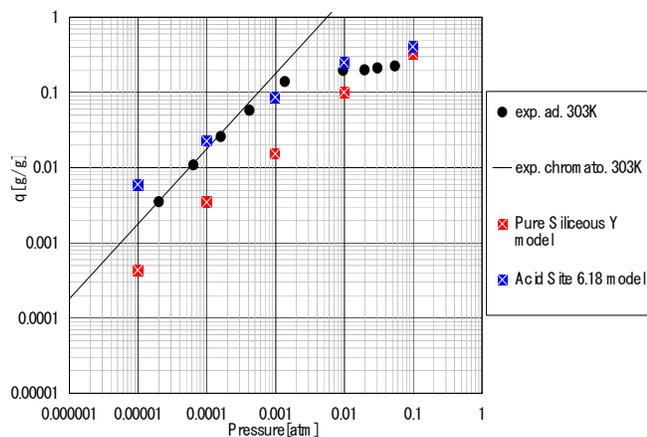
Figure 5. Comparison between exp. and simulation for adsorption
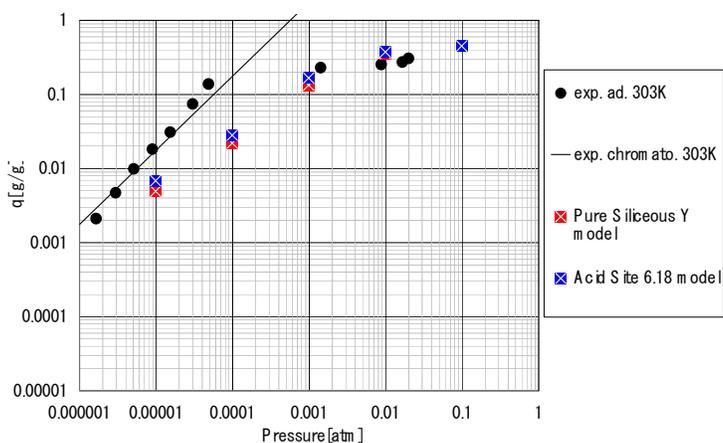isotherms of USY6.18-chloroform system

Figure 6. Comparison between exp. and simulation for adsorption isotherms of
USY6.18-tetrachloroethylene system

Molecular Simulation was found to be reasonable in these cases, from two standpoints, i.e., amount adsorbed and heat of adsorption, which were the key factor in adsorption equilibrium.

Table 2. Heat of Adsorption [kJ/mol] (USY6.18-chloroform)	
EXP. Chromato.	45.2
Pure Siliceous Y	34.1
Acid site 6.18	50.3

Table 3. Heat of Adsorption [kJ/mol] (USY6.18-tetrachloroethylene)	
EXP. Chromato.	47.5
Pure Siliceous Y	41.2
Acid site 6.18	43.4

Adsorption Equilibrium for the System of Pentasile-2

In Figure 7 and 8, experimental adsorption isotherms for chloroform and tetrachloroethylene in Pentasile-2 at 303 K are shown, respectively. Initial slopes for 303 K are also shown. This whole range of adsorption isotherm at 303 K could be compared with simulation.At higher pressure (>0.01 atm), the simulations of chloroform were coincident and almost correspond to gravimetric data. However, At lower pressure, both the simulation were not in agreement with chromatographic data and baratron data.

Experimental heats of adsorption obtained by chromatography at zero coverage were compared with simulated heats of adsorption in Table4 and 5, respectively. Here, also, both the simulations were larger value compared with the experiment.

Force field parameters obtained by Mellot seems not to be adequate for this system. As, performing simulation in ZSM-5 type, it is necessary to calculate using a different electric charge and force field parameters from faujasite (Y-type).
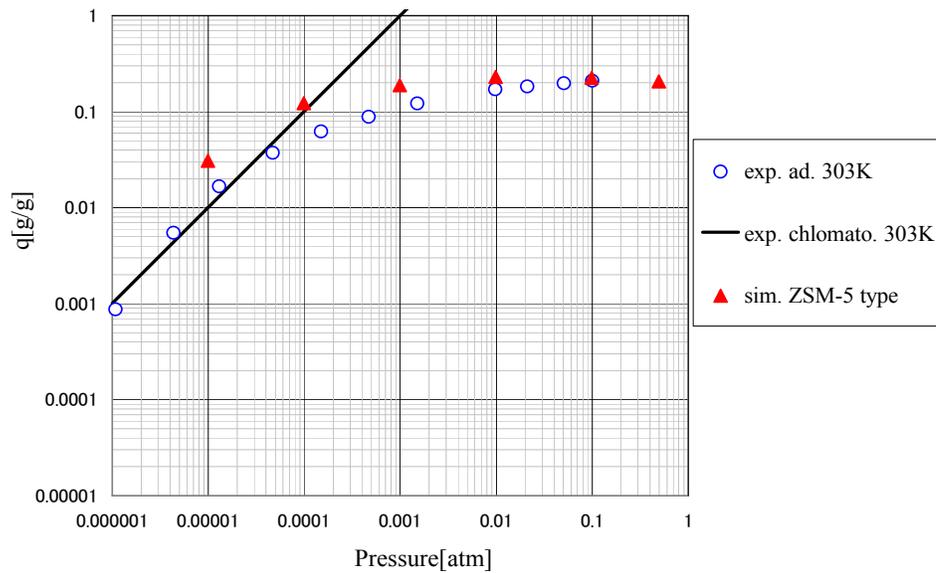

Fig 7. Comparison between exp. and simulation for adsorption isotherms of
Pentasile-1-chloroform system

Table 4 .   Heat of Adsorption [kJ/mol]
(Pentasile-2- chloroform)

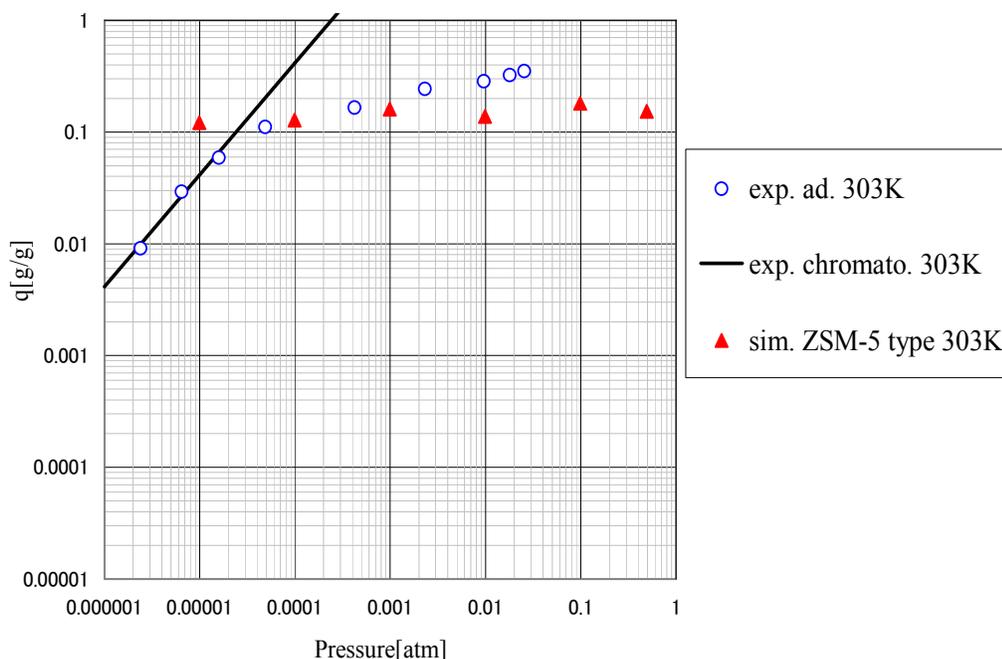|	
EXP. Chromato.	34.4
ZSM-5 Type	62.6

Fig 8. Comparison between exp. and simulation for adsorption isotherms of
Pentasile-1-tetrachloroethylene system

Table5. Heat of Adsorption [kJ/mol]
(Pentasile-2- tetrachloroethylene)

EXP. Chromato.	61.5
ZSM-5 Type	70.9

Micropore Diffusion in USY6.18

In Fig.9, the behaviour of chloroform, moving from cage to cage, which means diffusion in Y-type zeolite, could be confirmed by MD calculation. As a result, the diffusivities in micropore of Y-type zeolite by the MD method were obtained through MSD plot.

The diffusion coefficients of chloroform thus obtained within the zeolite lattice were compared with the experimental value by the chromatographic method to be not so good coincident up to now (Table6). The diffusion coefficients by chromatograph method were very small value compared with MD results. In order to obtain exact diffusion coefficients by MD method, it was thought that bigger system and time step might be necessary.
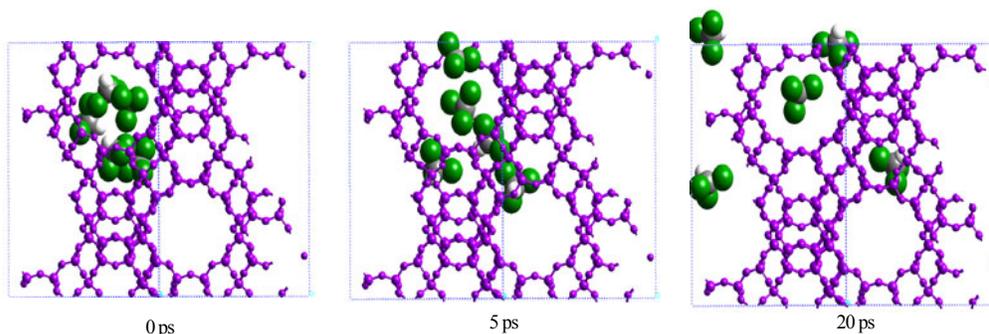
0 ps   5 ps   20 ps

Fig9. Snapshots of MD calculation

(Ensemble: NVT, Temperature: 393.15K, Time step: 1fs,
Number of steps: 100000steps, Temperature control method: Nose)

Table 6 Diffusion coefficients of chloroform into microscope

Temperature [K]	Chromatograph Method [cm^2/sec]	MD Method [cm^2/sec]
393.15	4.40×10-10	1.34×10-4
453.15	2.60×10-9	1.65×10-4

CONCLUSIONS

Adsorption equilibria and isosteric heats of adsorption for the system of chloroform and tetrachloroethylene- USY6.18 and ZSM-5 were studied.

The adsorption equilibria were measured using a gravimetric method and were expressed as isotherms. A chromatographic method was used to get the initial slope of the isotherms. In the simulation, GCMC method was used to calculate amounts adsorbed for faujasite (Y-type) and ZSM-5. To get better coincidence between experimental data and simulation, we tried simulation of acid site model, which was the modification from pure siliceous Y zeolite. Then, it was found to be necessary to account for aluminium. As a conclusion, FF parameters were confidently applied. And modified structure models were effective for simulation of faujasite (Y-type).

In ZSM-5 Type, it is necessary to improve an electric charge and some models.

The behaviour of chloroform, moving from cage to cage, which means diffusion in Y-type zeolite, could be confirmed by MD calculation. As a result of comparing the diffusion coefficients by the MD method with those by chromatograph method, it was suggested that behaviour of adsorbates in micropore of zeolite might be estimated by the MD calculation.

Reference
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