# Diffusion of Chlorinated Hydrocarbons in High Silica Zeolite - Comparison Between Chromatographic Data and Molecular Dynamic Simulation

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## 1. Introduction

In this study, we investigated diffusion of chlorinated hydrocarbons in high silica zeolite by chromatographic method and molecular dynamics simulation.

Adsorption measurement of various chlorinated hydrocarbons on FAU-type and MFI-type zeolites were performed using the chromatographic method to examine the adsorption phenomena. Dichloromethane (DCM), chloroform (TCM), trichloroethylene (TCE), and tetrachloroethylene (PCE), were used as adsorbate, and HSZ-390HUD, PQ-USY, USY-6.18, Na-Y, Pentasile-2 and Pentacile-1 were used as adsorbent. By introducing the concentration pulse of adsorbate to the carrier gas stream at the inlet of the adsorbent column, the concentration elution curve at the outlet of the column was measured. Chromatographic peaks were analyzed by moment analysis equation. Van't Hoff plot and Arrhenius' plot were drawn with the use of adsorption equilibrium constant $K^*$ and micropore diffusivity $D$.
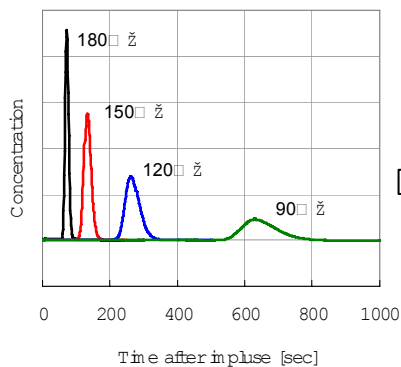


Fig.1 Typical chromatographic peaks
Adsorbate:chloroform[TCM]
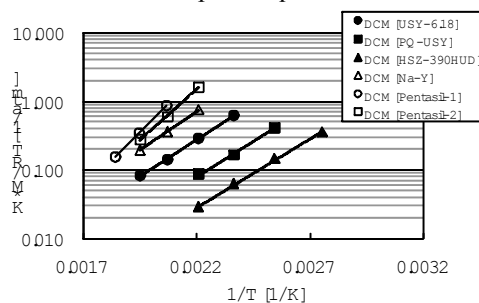Adsorbent:Y-type zeolite[HSZ-390HUD]



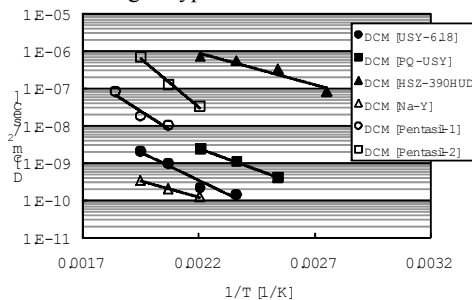Fig.2 Typical Van't Hoff Plot



Fig.3 Typical Arrhenius' Plot

## 2. Result and Discussion

Isoteric heat of adsorption $q_{st}$ and activation energy in micropore diffusion $E$ were determined by the slope. The amount adsorbed and isosteric heats of adsorption became low, when $SiO_2/Al_2O_3$ ratio of zeolite became high. The isosteric heats of adsorption were roughly 1.4 to 2.0 of the heats of vaporization. The activation energies of diffusion in the micropore of zeolite were found to be almost 130 % to 150 % of the isosteric heats of adsorption. Figs. 4 and 5 show "Correlation of Isosteric Heat of Adsorption with Heat of Vaporization" and "Correlation of activation energy of the micropore diffusion with isosteric heat of adsorption".
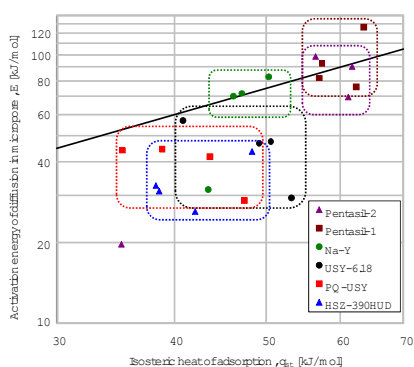


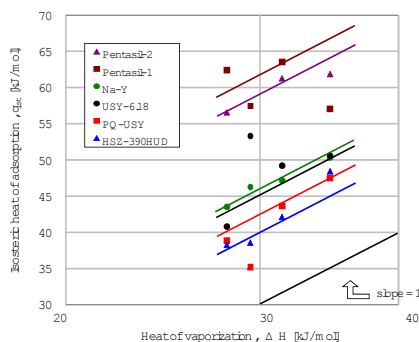Fig. 4 Correlation of isosteric heat of adsorption with heat of vaporization



Fig. 5 Correlation of activation energy of micropore diffusion with isosteric heat of adsorption

## 3. Conclusion

In addition Molecular Dynamics (MD) simulations for diffusion of the chlorinated hydrocarbons in the zeolites were performed using the Accelrys® MATERIALS STUDIO 4.3 simulation package. Self-diffusion coefficients were calculated from Mean Square Displacement (MSD) using the Einstein equations. The computed results were also compared with the experimental data.
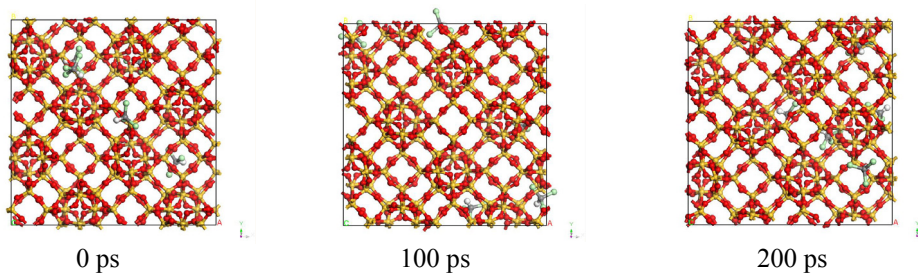


0 ps          100 ps          200 ps

Fig. 6 Dynamic behavior of TCM in FAU-type zeolite at 423 K