

THEORETICAL STUDY ON SPE METHOD USING HIGH RESOLUTION α_s -PLOT FOR EVALUATION OF MICROPORE STRUCTURES OF ACTIVATED CARBONS

N. Setoyama, T. Suzuki and K. Kaneko

Physical Chemistry, Material Science, Graduate School of Science and Technology, Chiba university, 1-33 Yayoi, Inage, Chiba 263, Japan.

Introduction

Although the routine BET analysis has been commonly used to determine the specific surface area (SSA) of solid surfaces, it has a serious problem in the SSA determination of microporous carbons. We proposed subtracting pore effect method (SPE method) to determine total SSA for microporous activated carbons [1]. The SPE method is based on the concept of α_s analysis proposed by Sing et al [2]. Some typical α_s -plot from nitrogen adsorption at 77K is shown in Fig.1. The slope of dotted line is proportional to SSA. The areas deviated from the dotted line are termed as filling swing (FS) and cooperative swing (CS) in this work. The FS and CS are associated with the excess adsorption due to micropores. Molecular simulation studies have been helpful to understand adsorption in micropores [3]. We constructed the theoretical α_s -plot using GCMC simulation and examined the basis of the SPE method in order to determine the accurate micropore structure of activated carbon [4].

Construction of Theoretical α_s -Plot

We assume a slit-shaped pore as a model for the micropore structure of activated carbon. The slit pore consists of a pair of semi-infinite graphite slabs. The inter-graphite surface distance H was converted to the effective pore size (w). We approximated w by $w = H - 0.34$ in nm. We used the one-center Lennard-Jones (LJ) potential:

$\sigma_{ff} = 3.75\text{\AA}$ and $\varepsilon_{ff}/k_B = 95.2\text{K}$ in this study. The interaction of graphitic surface and a molecule was approximated by Steele's 10-4-3 potential function. Adsorption simulation was carried out by GCMC simulation with applying Metropolis sampling to justify a configurations of fluid particles inside the unit cell. The trial steps performed 3×10^6 times to obtain an equilibrium condition.

Results and Discussion

We simulated the adsorption isotherms of nitrogen for various pore widths. The simulated adsorption isotherm had the two-stage adsorption process. The low pressure uptake

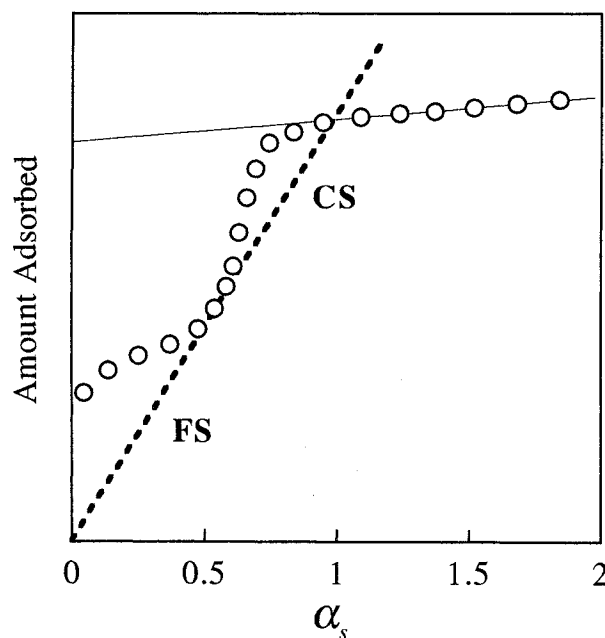


Figure 1. The representative α_s -plot.

of the simulated isotherm below $P/P_0 = 10^{-3}$, which corresponds to the completion of the monolayer on both pore walls. The higher pressure adsorption uptake observed at $P/P_0 > 10^{-3}$ is ascribed to the volume filling into a residual spaces on the monolayer-coated pore, called as cooperative adsorption. The relative pressures corresponding to these both uptakes changed sensitively with the variation of the pore width.

Standard adsorption isotherm is necessary for the construction of α_s -plot. As no enhancement in the molecule-surface interaction was observed for the pore size of $w = 3.5\text{nm}$, the simulated adsorption isotherm on the pore of $w = 3.5\text{nm}$ below $P/P_0 = 0.6$ was used as the standard isotherm. We used the α_s value ranged between 0 to 1.2, which comes from the limitation of the standard adsorption isotherm below $P/P_0 = 0.6$.

The α_s -plots for pores of $w = 0.4\text{--}2.5\text{ nm}$ are shown in Figs. 2(a) and (b). The α_s -plot for the standard adsorption isotherm becomes linear in the whole α_s range, which is shown by the bold solid line. The upward deviations from the linear plot suggest to the presence of the excess adsorption caused by the enhanced surface-molecule interaction and/or the intermolecular interaction. At the range of $0 < \alpha_s < 0.5$, a marked FS is observed for pores of $w < 0.9\text{nm}$. CS is observed for pores of $w > 1.0\text{nm}$ and departs from the standard line at $\alpha_s > 0.5$. CS corresponds to the high pressure adsorption uptake ($P/P_0 > 10^{-3}$). The boundary of α_s value between CS and FS should be situated at $\alpha_s = 0.5$. Almost all α_s -plots gather at $\alpha_s = 0.5$ except for α_s -plot for $w < 0.6\text{nm}$. Then the slope of the α_s -plot which passes the gathering point at $\alpha_s = 0.5$ gives the correct SSA. The simulated α_s -plots for pores of $w = 1.2\text{--}2.5\text{ nm}$ had a good linear region below $\alpha_s = 0.5$, and thereby SSA can be correctly determined by the SPE method. Therefore the SPE method has a clear evidence for its effectiveness. However, the SPE method is available for the pores of $w > 0.6\text{ nm}$.

References

1. K. Kaneko, C. Ishii, M. Ruike, and H. Kuwabara, *Carbon* 1992, **30**, 1075.
2. P.J.M. Carrott, R.A. Roberts, and K.S.W. Sing, *Carbon* 1987, **25**, 769.
3. C. Lastoskie, K.E. Gubbins, and N. Quirke, *J. Phys. Chem.* 1993, **97**, 4786.
4. N. Setoyama, T. Suzuki, and K. Kaneko, *Carbon*, in press.

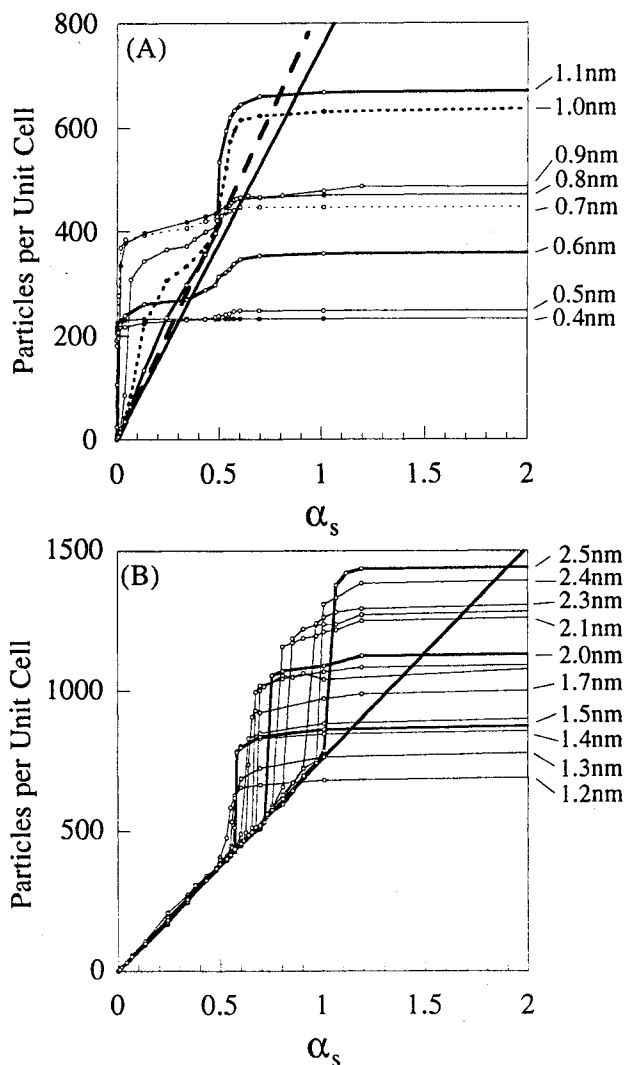


Figure 2. The simulated α_s -plots.