STRUCTURAL ANALYSIS OF A CARBON MOLECULAR SIEVE BY HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY AND GAS ADSORPTION

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Introduction

Measurement method of pore structure of activated carbons was studied by high resolution transmission electron microscopy (HRTEM) and image analysis. Pore size distribution obtained by the method was compared to results of gas adsorption. Ultramicropores of activated carbons, of witch pore size are under 0.7nm, are generally difficult to be detected by gas adsorption. The ultramicropores can be observed by HRTEM. The image depends on phase contrast transfer function of objective lens of the HRTEM (hereinafter referred to as the transfer function) in high-resolution observation. More specifically, the transfer function must be comprehended for exact observation of amorphous structured materials such as activated carbons.

In this study, we observed amorphous carbon film with HRTEM on different defocus values (Δf's) in order to determine the transfer function of the HRTEM as well as simulation of the transfer function. Power spectra of the HRTEM images of the amorphous carbon film obtained by 2 dimensional (2D) fast Fourier transform (FFT) were compared to the simulation data. The analysis method was applied to a carbon molecular sieve and compared to gas adsorption.

Experimental

We used 200kV acceleration voltage HRTEM (JEOL 2010FEF, field emission type). The transfer function $\cos(\chi)$ of HRTEM is obtained by the following equation [1].

$$\cos(\chi) = \cos\left[\frac{\pi}{2} - \frac{2\pi}{\lambda} C_S \frac{(2\theta)^4}{4} + \frac{2\pi}{\lambda} \Delta f \frac{(2\theta)^2}{2}\right] \qquad (1)$$

θ is Bragg angle, C_s is the spherical aberration constant of the lens, Δf is the underfocus value, and λ is de Broglie wavelength of the electrons. C_s of JEOL 2010FEF is 1.6mm, and λ is 0.002508nm when acceleration voltage is 200kV. Resolution of HRTEM is

limited by the special coherence of the electron beam and by chromatic effects. An effective transfer function can be obtained by multiplying a damping curve of these effects on the transfer function. The optimum Δf 'Scherzer focus' of the HRTEM is 60nm obtained by the equation of $1.2(C_s\lambda)^{1/2}$nm.

Amorphous carbon film of supporting lamella of TEM grid is observed by the HRTEM under some different Δf's in order to determine the transfer function of the HRTEM. A CCD camera, which is equipped in the HRTEM, is used for observation in order to obtain a linear brightness image in the intensity of electron beam. Power spectra of the HRTEM images of amorphous carbon film are obtained by 2D-FFT [2,3]. The power spectra are represented by graphs by integration of rotative direction around the center points of them. The power spectra are compared to the effective transfer functions of the HRTEM.

A carbon molecular sieve (sample KUA1B8), which contain ultramicropore, prepared in A. Linares-Solano's laboratory by blocking the microporosity of a previously prepared activated carbon [4] are observed by the HRTM with 200kV acceleration voltage and under focus value of Scherzer focus (Δf =-60nm). The property of adsorption of the carbon molecular sieve is measured by Micromeritics (ASAP 2010, USA) with pure N_2 or Ar at 77.35K and87.29K.

Results and Discussion

A HRTEM image of amorphous carbon film of TEM grid is shown in figure 1(a). The defocus value Δf of the image is selected to be -255nm because peaks of power spectrum obtained by 2D-FFT are well indicated with the large declination from the just focus. The power spectrum of figure 1(a) shown in figure 1(b) was obtained by 2D-FFT.

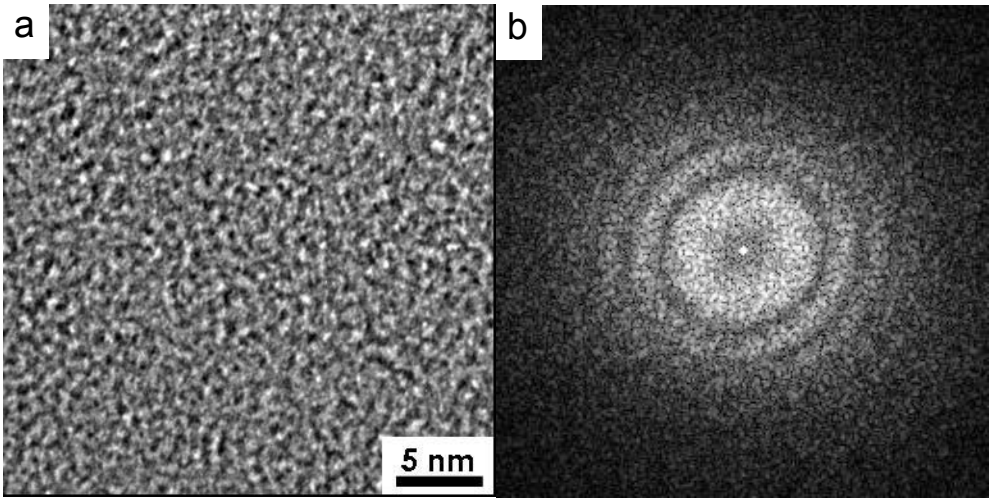

Figure 1. (a) HRTEM image of amorphous carbon film, and (b) power spectrum of (a) obtained by 2D-FFT. The defocus value Δf is -255nm.

In order to remove the effect of discontinuity of the edges of image, the window treatment is performed to the HRTEM image (figure 1(a)) before 2D-FFT operation [5]. The components of the spectrum are distributed concentrically. The symmetric property of the center point of the power spectrum indicates the isotropic structure of the amorphous carbon film.

The power spectrum (figure 1(b)) was transformed into a graph shown in figure 2(a) by integration of rotative direction around the center points of it. 180° is enough as the integration angle since the power spectrum is symmetric with respect to the center point. The integration data was divided by the distance from the center point in order to make a one-dimensional graph. The virtual axis of figure 2(a) shows the intensity of the integrated spectrum and the spectrum is shown in logarithmic scale. The space frequency is transferred to the space wave length on the horizontal axis. The transfer function at Δf =-255nm is shown in figure 2(b). The red curve L_1 is the transfer function without damping calculated by equation (1). The orange curves L_2 show the damping envelope function. The blue curve L_3 is an effective transfer function which was obtained by imposing the envelope function L_2 on the transfer function L_1. The positions of peaks of the power spectrum on the horizontal axis (figure 2(a)) approximately equal to the positions of under peaks of the transfer function (figure 2(b)). It is shown that the transfer function is calculated correctly. Same HRTEM observation and calculation of the transfer function carried out at different defocus values from -60 to -510nm, and verified.

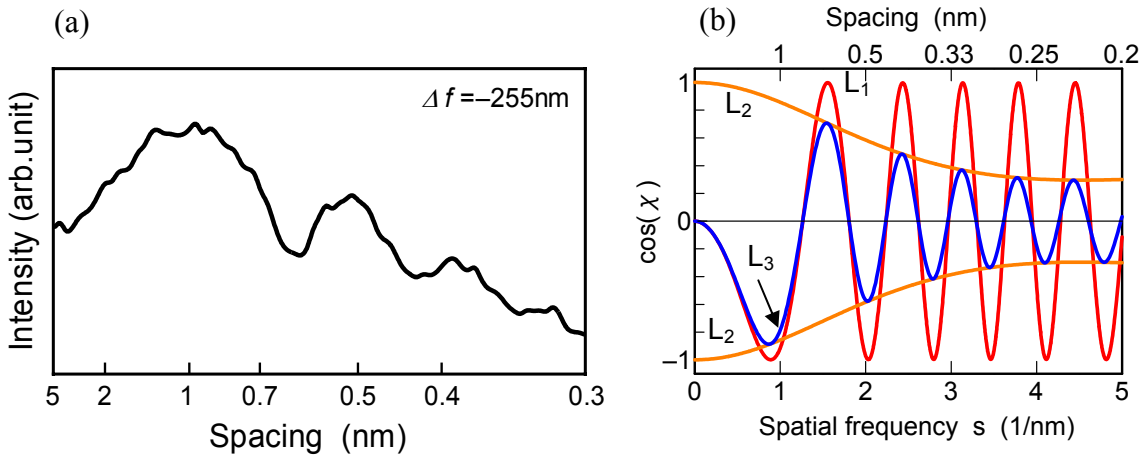

Figure 2. (a) Power spectrum of HRTEM image of amorphous carbon film obtained by 2D-FFT. (b) Phase transfer function of objective lens of the HRTEM. The defocus value Δf is -255nm. (L_1: the transfer function without attenuation obtained by equation (1), L_2: the damping envelope curves, L_3: the effective transfer function modified by the damping envelope function)

The HRTEM image of the carbon molecular sieve (sample KUA1B8), which contains ultramicropore, is shown in figure 3(a). The defocus value Δf is -60nm. The power spectrum shown in figure 3(b) was obtained from the HRTEM image (figure 3(a)) by the

same operation applied to figure 1(a). Figure 4(b) was represented by a graph shown in figure 4(a) by integration around the center point of it. The graph is displayed linearly in the perpendicular axis in order to detect sensitively the brightness transition of the HRTEM image of the carbon molecular sieve. The transfer function shown in figure 4(b) was calculated like that of figure 2(b).

The HRTEM image has a good contrast when the absolute value of the transfer function is larger than 0.5. Thus the transfer function figure 4(b) shows that a good contrast of the HRTEM image is obtained in the range from 0.24 to 0.92nm, which is indicated by dashed lines. The range for good contrast is shown in figure 4(a) except hatched area. The ultramicropores must appear in figure 3(a) as well as aromatic carbon layers considering the observation range of good contrast. In fact, the aromatic carbon layers can be observed in figure 3(a) and spaces between the layers are thought to be micro pores.

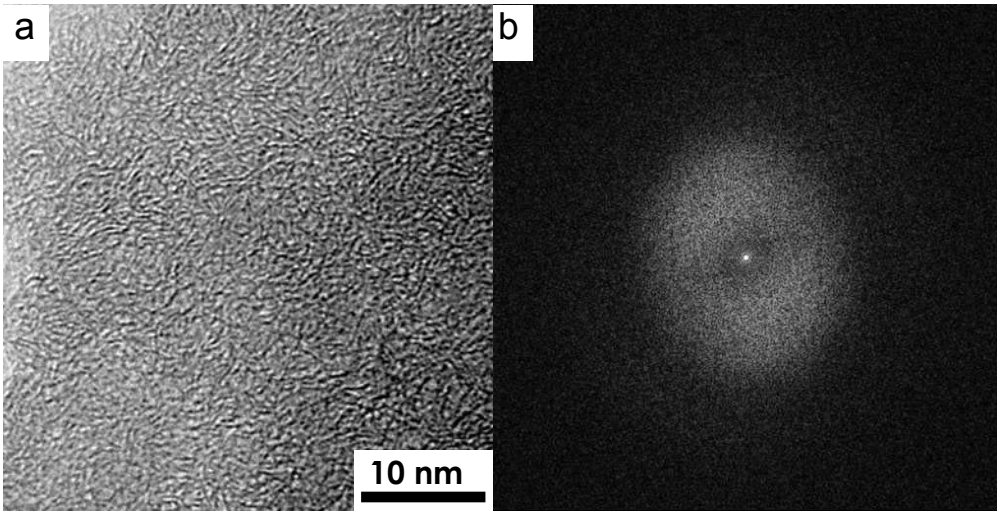

Figure 3. (a) HRTEM image of the carbon molecular sieve (sample KUA1B8), and (b) power spectrum of (a). Defocus value Δf is -60nm, Scherzer focus.

The distribution of space frequency of HRTEM image (figure 3(a)) of the carbon molecular sieve is shown in figure 4(a). The peaks of power spectrum correspond to the cycles of the brightness that appear in the HRTEM image (figure 3(a)), and they involve pore size distribution of the carbon molecular sieve. This method can detect the pores under 0.92nm in size including ultramicropores. The carbon molecular sieve which contains ultramicropore could not adsorb N_2 or Ar. A. Linares-Solano's group deduced micorpore size distribution of activated carbons which contains ultramicropore by high-pressure CO_2 and CH_4 adsorption [4]. HRTEM and image analysis thought to be another useful method for measurement of ultramicropore size distribution.

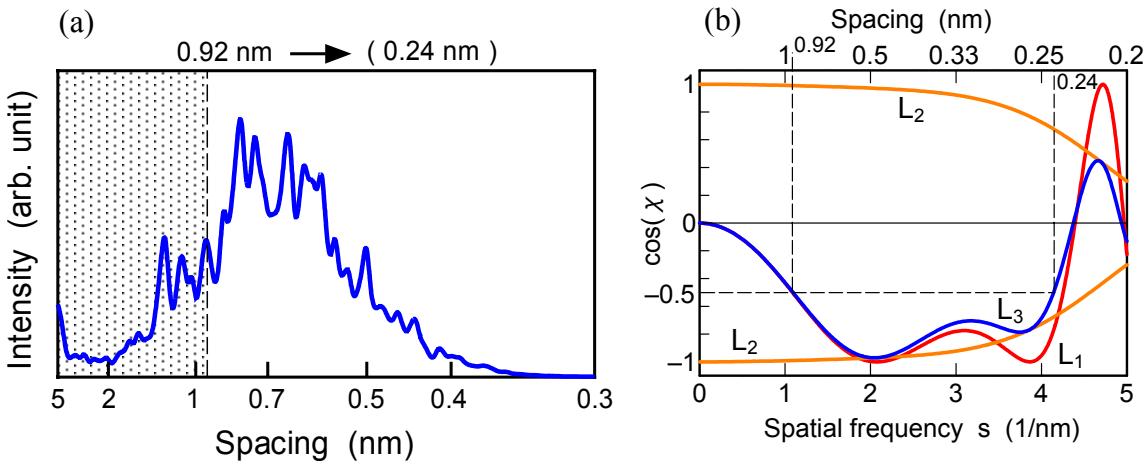

Figure 4. (a) Power spectrum of HRTEM image of the the carbon molecular sieve (sample KUA1B8) obtained by 2D-FFT and (b). Phase transfer function of objective lens of the HRTEM. The defocus value Δf is -60nm. (L_1: the transfer function without attenuation obtained by equation (1), L_2: the damping envelope curves, L_3: the effective transfer function modified by the damping envelope function)

Conclusions

The transfer function of the HRTEM was verified by comparing the power spectrum of the HRTEM image with the effective transfer function calculated logically. In the view of this result, the measurement method by HRTEM and image analysis was applied to the carbon molecular sieve and the ultramicropores can be observed precisely. The HRTEM combined with image analysis was shown to be useful for structural analysis of ultramicropore and was expected to be an independent technique for confirmation of gas adsorption usefulness.

Acknowledgements

The supports of the Japan Society for the Promotion of Science [work for ‘Japan-France Research Cooperative Programs’] and of Ministry of Education, Sports, Culture, Science and Technology of Japan [the work partly supported by a grant-in-aid for ‘Scientific Research (No.14550311)’] are gratefully acknowledged. Part of the research was supported by the Research Foundation for Electrotechnology of Chubu.

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