Pore-Size Control of Carbon Nanospace with Ultrasonic Irradiation

T. Ohkubo[*], R. Hori[**], K. Tsuchiya[**], H. Sakai[*, **] and M. Abe[*, **]

[*] Institute of Colloid and Interface Science, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

[**] Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

E-mail: tkohkubo@rs.noda.tus.ac.jp

ABSTRACT

In this study, we examined the micropore-size control on activated carbons by ultrasonic irradiation with various conditions. Pitch-based activated carbon fiber (ACF) was used for the sample having relatively uniform micropores whose micropore size was determined as 1.15 nm from the measurement of nitrogen adsorption isotherm at 77 K and high-resolution α_S-plot analysis. Also, the ultrasonic irradiations to ACF were carried out in the water bath with various irradiation times and at three irradiation frequencies (40 kHz, 200 kHz, and 1 MHz). The results indicate that we can decrease the pore volume and average pore widths of ACFs with longer irradiation time. Also, we examined the dependence of ultrasonic frequencies on micropore-size control. The average pore width of ACF irradiated by 40 kHz was decreased over 10 % from the original one. This result suggests that the nanospaces of ACF are collapsed as a result of sonication. Besides, larger pores are more easily collapsed selectively.

Keywords: activated carbon fiber, ultrasonic irradiation, micropore, nitrogen adsorption isotherm

1 INTRODUCTION

Remarkable progress in nanoporous materials, after publications about carbon nanotubes [1, 2] and MCMs [3, 4], has attracted a great deal of research on both the fundamental and practical aspects of these materials. Here, MCMs generally have ordered pore structures and a uniform pore shape. From the aspects of fundamental science, the advantage of the material having a uniform pore shape is that the characterization of the material can be carried out by using not only experimental techniques but also theoretical calculations, because these materials are easier to build a ideal model and we need not to include the non-ideal effect such as pore size distribution (PSD). However, surfaces of pore walls for MCMs are electrically "disordered" compared with those of general carbon materials; a large number of surface functional groups of MCMs can work for the specific adsorption sites and the equilibrium structure of confined molecules is more or less different from that adsorbed in nanospaces without any specific sites. Therefore, if we can produce a nanoporous carbon material having uniform and regular pores, it will be widely used in various fields not only in the fundamental science but also in the applications.

Here, the impurity of pitch-based activated carbon fibers (ACFs) is less than 10 % [5] and the PSD of these carbons is relatively lower. Therefore, we can use ACFs for quasi-ideal adsorbents having relatively regular pores. Recently, the pore-size control of ACFs has been carried out by the treatment with high temperature conditions [5] or microwave irradiations [6]. However, these techniques can change the surface chemistry of ACFs and, as a result, we can obtain no carbon materials having chemically ideal pore structure.

In this study, we examined the micropore-size control on ACFs by ultrasonic irradiation with various conditions and compare the properties of ACFs before and after the irradiation.

2 EXPERIMENTAL SECTION

2.1 Ultrasonic Irradiation to ACF

The pitch-based ACF (P20; AD'ALL Co. Ltd.) was used, which was produced by a steam activation process. Also, the ultrasonic irradiations to ACF were carried out in a water bath with various irradiation times and at three irradiation frequencies (40 kHz; Alex Co. Ltd., 200 kHz; Kaijo Co. Ltd., and 1 MHz; Honda Electronics Co. Ltd.).

2.2 Nitrogen Adsorption Isotherms

The samples were pre-evacuated at 1 mPa and 423 K for 2 h. The high-resolution nitrogen adsorption isotherms were measured at 77 K using a automated volumetric system (AUTOSORB-1-MP; Quantachrome Co. Ltd.). The pore parameters were obtained from high-resolution α_S-plot analysis of the nitrogen adsorption isotherm [7, 8] using subtracting pore effect (SPE) method [9, 10]. In addition, the PSDs were obtained from the nitrogen adsorption isotherms by non local density functional theory (NLDFT).

3 RESULTS AND DISCUSSION

First, we obtained the dependence of irradiation time to ACF. Figures 1(a) and (b) show the nitrogen adsorption

isotherms on ultrasonic-irradiated ACF at 77 K. Figure 1(a) shows that the total adsorbed amounts of nitrogen for irradiated samples are decreased compared to that of non-irradiated one. However, from Figure 1(b), the adsorbed amount at $P/P_0 < 10^{-4}$ region is similar to each other, indicating the total volume of micropores on ACF is not effectively decreased by the ultrasonic irradiation. Also, adsorbed amount irradiated for 30 and 40 minutes below $P/P_0 = 10^{-1}$ is not so different to each other, although the amount irradiated for 40 minutes over this relative pressure is smaller than that of any other samples. These results indicate that we can control the pore structure to reduce the total adsorbed amount with no decrease of narrower micropores.

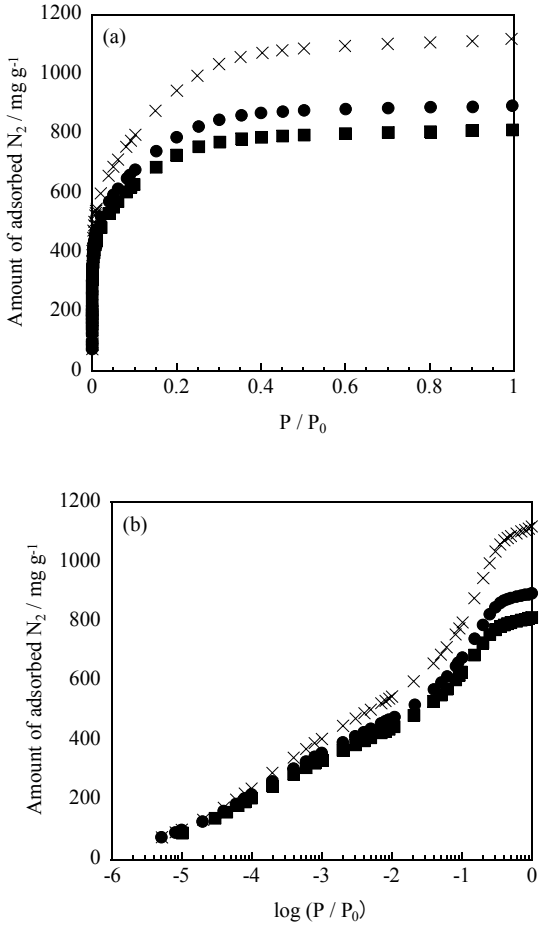

Figure 1: N_2 adsorption isotherms on ACFs irradiated by 40 kHz of ultrasound for various times. Here, the abscissa of Figure 1(b) is represented by logarithm scale. (●: irradiated for 30 min., ■: irradiated for 40 min., and ×: original ACF)

Table 1 summarizes the pore parameters such as total surface area a_{tot}, external surface area a_{ext}, and micropore volume W_0 obtained from the α_s-plot analysis. Also, the average pore width w of slit-shaped micropores can be evaluated from both the surface area and pore volume using the simple geometrical relation as shown in equation (1).

$$w = \frac{2W_0}{a_{tot} - a_{ext}} \quad (1)$$

These results indicate that we can decrease the micropore volume and average pore width of ACF with longer irradiation time. Also, the external surface areas after ultrasonic-irradiated samples are smaller than that without any irradiation, indicating that the larger pores are selectively vanished by the ultrasonic irradiation.

We also examined the dependence of ultrasonic frequencies on micropore-size control by irradiating for 40 min. Figures 2(a) and (b) show nitrogen adsorption isotherms on original ACF and ACFs irradiated by ultrasound at various frequencies for 40 min. Figure 2(a) show that the total adsorbed amount of nitrogen on ACF is smaller when we reduce the frequency of ultrasounds. However, even if the total amount of adsorbed nitrogen was reduced after ultrasonic irradiation, the adsorbed amount below $P/P_0 = 10^{-4}$ is similar to that of original ACF. This result also indicates that the narrower micropores are still remained even after the ultrasonic irradiation. Thus, the total adsorbed amount can also be controlled by the frequencies.

In order to determine the pore parameter, we applied the SPE method for the high-resolution α_s-plot. Figure 3 shows α_s-plot of ACF irradiated by 40 kHz ultrasound and original ACF. The slope of the solid line gives the total surface area and the upward deviations indicate the presence of micropores, respectively. Here, the line between the point at α_s=0.5 and the origin provides an approximate value of the surface area of 10 % error according to the grand canonical Monte Carlo simulation study [10]. The slope of ACF irradiated by ultrasound is lower than that of original one, indicating the reduction of total surface area after the ultrasonic irradiation. Although the upper deviation from the solid line for ultrasonic-irradiated ACF whose α_s range is between 0.6 and 0.8 is smaller than that of original one, the deviation under α_s=0.5 is similar to each other. This result also suggests that the micropores whose pore widths are smaller than 1 nm cannot be vanished even after the ultrasonic irradiation. Hence, we can control the micropore size to decrease wider nanospaces and to keep the narrower micropores.

Table 1: Pore parameters obtained by α_s-plot analysis irradiated by 40 kHz.

Irradiation time / min.	a_{tot} / m^2 g^{-1}	a_{ext} / m^2 g^{-1}	W_0 / ml g^{-1}	w / nm
0	2350	37	1.33	1.15
30	2040	17	1.08	1.07
40	1900	21	0.98	1.04

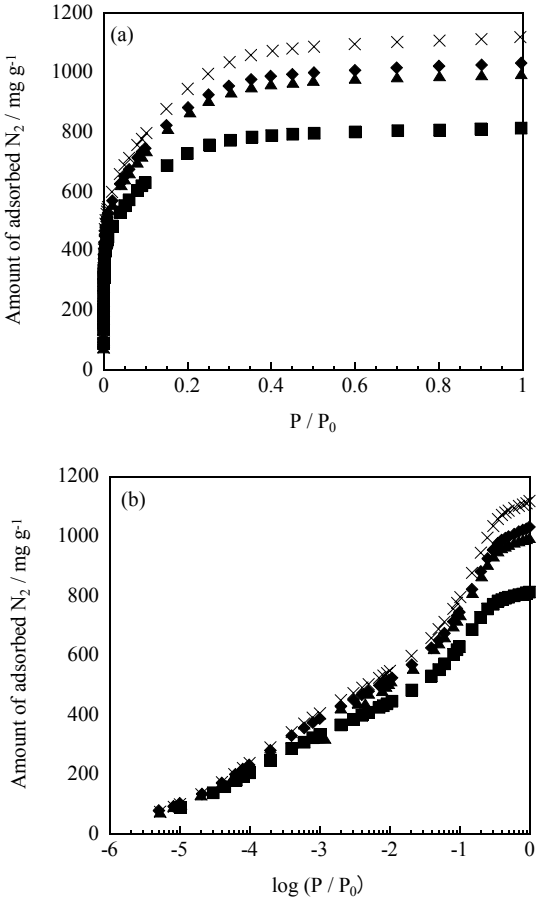

Figure 2: N_2 adsorption isotherms on ACFs irradiated for 40 minutes of ultrasound with various frequencies. Here, the abscissa of Figure 1(b) is represented by logarithm scale. (■: 40 kHz, ▲: 200 kHz, ♦: 1 MHz, and ×: without irradiation)

Table 2 summarizes the pore parameters obtained by the α_s-plot analysis. All parameters of ultrasonic-irradiated ACFs are smaller than that of original one. The effect of ultrasonic irradiation is stronger when we use the ultrasound with low frequencies. For instance, the average micropore width of ACF treated by ultrasound of 40 kHz is 1.04 nm, which are smaller than that of original one over 10 %. Here, as we denoted at previous paragraph, the narrower nanospaces are not vanished, we can obtain ACF samples having smaller PSD. Figure 4 supports this tendency because this figure shows that the amount of nanospaces of ultrasonic irradiated ACF over 1 nm effectively decreases compared with that of original one. Hence, we can arrange the pore sizes of ACF by ultrasonic irradiation and prepare the carbon sample having narrower micropores.

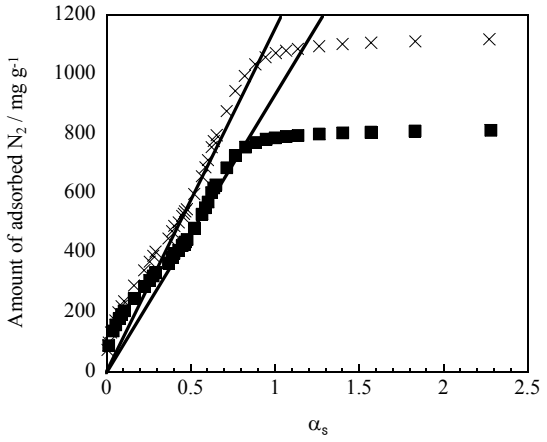

Figure 3: α_s-plots for adsorption isotherms of nitrogen on ACF irradiated by 40 kHz for 40 minutes (■) and no irradiated ACF (×).

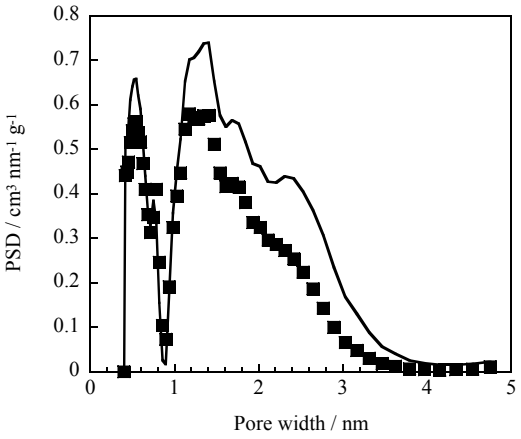

Figure 4: Pore size distributions of ACF irradiated by 40 kHz for 40 minutes (■) and no irradiated ACF (solid line).

Table 2: Pore parameters obtained by α_s-plot analysis irradiated for 40 min.

Frequency	a_{tot} / m^2 g^{-1}	a_{ext} / m^2 g^{-1}	W_0 / ml g^{-1}	w / nm
40 kHz	1900	21	0.98	1.04
200 kHz	2190	23	1.20	1.11
1 MHz	2240	34	1.23	1.12
Original	2350	37	1.33	1.15

4 CONCLUDING REMARKS

We present the possibility of the micropore-size control on activated carbons by ultrasonic irradiation with various conditions. The results indicate that we can decrease the pore volume and average pore widths of ACFs with longer irradiation time and lower frequency of ultrasound. The average pore width of ACF irradiated by 40 kHz was decreased by 0.11 nm from the original one. However, the narrower micropores are still remained even after the ultrasonic irradiation. This result suggests that the nanospaces of ACF are collapsed as a result of sonication, besides, larger pores are more easily collapsed selectively.

5 ACKNOWLEDGEMENT

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