Effect of Carbonization Temperature on Adsorption Isotherms of Wood Charcoals

Shuji Yoshizawa¹, Takayuki Utsugi¹, Kazunori Shibano^{1, 2}, Sumio Goto³ and Hirofumi Yajima⁴

 ¹Asian Center for Environmental Research, Meisei University, 2-1-1, Hodokubo, Hino, Tokyo 191-8506, Fax: 81-42-591-7346, e-mail: <u>yoshizaw@chem.meisei-u.ac.jp</u>
²Tokyu Construction Co., Ltd., 1-16-14, Shibuya, Shibuya, Tokyo 150-0834, Japan
³National Institute for Environmental Studies, 16-2, Onogawa, Tsukuba, Ibaraki 305-8506, Japan

⁴Tokyo University of Science, 1-3, Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

Carbonization condition of wood affects the adsorption property of chemical compounds. Wood specimen was chipped and meshed into 1 - 9.5 mm size. The carbonization temperature from 400°C to 1,100°C was adopted in nitrogen gas flow which contains oxygen of 0.3%. Adsorption-disorption isotherms by charcoals were measured. Nitrogen, carbon dioxide and water were selected as an adsorbate gas. The isotherms of N₂ showed that as the carbonization temperature increased micropores formed in the charcoal. In the distribution of micropore radius, micropores having the size under ca. 0.7 nm increased in the charcoal carbonized at 600°C and above. In adsorption-disorption isotherms of water, V-typed isotherms were observed in the charcoal prepared at 600°C and above. This result also shows existence of mesopores and macropored in the charcoal carbonized at 600°C was 400 m²/g by N₂ adsorption at 77 K and CO₂ adsorption at 195 K, respectively. As the carbonization temperature increased, the specific surface area by both N₂ and CO₂ adsorption drastically increased and 800 m²/g was obtained in the charcoals heat-treated at 1,000°C. Key words: carbonization, wood, adsorption, isotherms

1. INTRODUCTION

Since charcoal carbonized from wood and bamboo has porous microstructure, chemical compounds and water can be adsorbed into the pore surface. Charcoal board as a building interior material has been newly developed by adhering charcoal powder with binder.[1]-[4] The charcoal board is used for adsorbing volatile organic compounds (VOCs) such as formaldehyde, toluene and ammonia in indoor air.

The specific surface area, the pore radius distribution and the chemical structure of the pore surface depend upon the carbonization temperature of wood.[5]-[10] Consequently the adsorption capability of VOCs and water is influenced by the carbonization temperature. [6][7][11]

In this report, we studied the effect of carbonization temperature of wood on the absorption property of the charcoal. Formation of the micropore is discussed from the results of the pore radius distribution and the specific surface area estimated by using different adsorbates.

2. EXPERIMENTAL

2.1 Carbonization

Chips of sap wood of Hinoki (Chamaecyparis obutusa) several mm in size were used as a raw material. Apparatus for carbonization of wood is shown in Fig. 1. Wood chips of about 10 g were placed in the center of a quartz tube of 113 mm in inner diameter and 600 mm in length. The quarts tube was heated in a cylindrical electric furnace. Nitrogen gas was introduced into the quartz tube at the rate of 200 cm³/min during the

carbonization process. Oxygen concentration was measured at the outlet of the quarts tube, which was 0.3 % during the carbonization. The sample was heated to the carbonization temperature from 400°C to 1,100°C with a heating rate of 20°C/min and held at the carbonization temperature for 120 min. After the carbonization, the sample was cooled to room temperature with furnace cooling for about several hours.

2.1 Adsorption-disorption isotherms

The adsorption-disorption isotherms for the charcoals were measured with an adsorption apparatus (BELSORP 18). In order to eliminate gas component and H_2O from



Fig. 1. Apparatus for carbonization.

the surface of the charcoal pore, the charcoal sample of 0.2 g in the sample tube was pre-heated at $305^{\circ}C$ for 5 hour in vacuo.

 N_2 , CO_2 and H_2O were used as adsorbate gases which were absorbed into the charcoal and then disorbed from the charcoal at 77 K, 195 K and 298 K, respectively. The specific surface area and the pore radius distribution of the charcoal were estimated with BET equation and HK-plots, respectively, applied for the adsorption isotherms.

3. RESULTS AND DISCUSSION

I-typed adsorption-disorption isotherms of N_2 at 77 K for the charcoal carbonized at temperature from 400°C to 1,100°C are shown in Fig. 2. In the vicinity of *P/P*°-0 the absorption amount increases drastically, and gradual increase is observed above *P/P*°-0.1. With increasing the carbonized temperature the adsorption amount increases. In the charcoal prepared at 1,100°C, the absorption amount decreases. These results suggest that as the carbonization temperature increases micropores forms in the charcoal, but at 1,100°C micropores are reduced.

Distribution of micropore diameter of the charcoals carbonized at temperatures from 400°C to 1,100°C, which are estimated in the N_2 adsorption isotherms, is shown in Fig. 3. In the charcoal carbonized at 400°C, no pores of diameter under 1.5 nm were observed. Micropores having the size under ca. 0.7 nm increase in the charcoals prepared at 600°C and above. In the charcoals carbonized at 800°C and above, the peaks at 0.8 nm and 1.1 nm appear. In the charcoal prepared at 1,100°C size of micropores of the size under 0.7 nm is reduced.

In Fig. 4, effect of carbonization temperature on pore volume of the charcoal estimated by N_2 adsorption isotherms. The pore volume of micropore and mesopore was estimated by MP-plots and DH-plots, respectively. The both pore volumes increase with increase of the carbonization temperature and those decrease in the charcoal prepared at 1,100°C.



Fig. 2. Adsorption-desorption isotherms of N_2 for the charcoal carbonized at 400, 600, 800, 1000, 1100 °C.

In Fig. 5, adsorption-disorption isotherms of water at 298 K (25°C) are shown on the four charcoal samples carbonized at 400°C to 1,000°C. V-typed isotherms are appeared in the charcoal carbonized at 600°C showing existence of mesopores and macropores in the charcoal. In the carbon prepared 800°C and 1,000°C, definite hysteresis in isotherms is observed, which means that capillary condensation of water vapor takes place in mesopores. It is evident from the isotherms shown in Figs. 2 and 5 that the hysteresis loop of the water isotherms is notably different from those of the nitrogen isotherms. The area of the hysteresis loop in the water isotherms is large compared with those in the nitrogen isotherms. The experimental findings for charcoal at 800°C and 1,000°C, suggests that the capillary condensation of water vapor takes place in the mesopores.[12]



Fig. 3. Distribution of maicropores diameter of the charcoal estimated by N_2 adsorption isotherms at 77 K.



Fig. 4. Effect of carbonization temperature on pore volume of the charcoal estimated by N_2 adsorption isotherms.

The adsorption isotherms of N_2 , CO_2 and H_2O for the charcoal carbonized at 1000°C are shown in Fig. 6. In the N_2 adsorption at 77 K and in the CO_2 adsorption at 195 K, the I-typed adsorption isotherm is observed where abrupt increase in the low pressure region, which suggests the existence of micro pores in the charcoal. In the H_2O adsorption at 298 K (25°C), the V-typed adsorption isotherm is observed showing the existence of mesopores and macropores in the charcoal.

Distribution of maicropores diameter of the charcoal estimated CO_2 adsorptin isotherms is shown in Fig. 7. In the charcoal carbonized at 400°C, formation of micropores is observed, though no pores of diameter under 1.5 nm in the distribution estimated N₂ adsorption isotherms were observed as shown in Fig. 3. Micropores



Fig. 5. Adsorption-desorption isotherms of H_2O for the charcoal carbonized at 400, 600, 800, 1000 °C.



Fig. 6. Adsorption-desorption isotherms of N_2 , CO_2 and H_2O for the charcoal carbonized at 1000 °C.

increases with increase of carbonization temperature. In the charcoal prepared at $1,100^{\circ}$ C micropores is reduced, which is the same as the results of N₂ adsorption.

Figure 8 shows change of the specific surface area of the charcoals vs. the carbonization temperature from 400°C to 1,100°C. In N₂ adsorption experiment the specific surface area increases with increasing the carbonization temperature, which corresponds to the results of the pore radius distribution in Figure 3. In the charcoal carbonized at 400°C, the specific surface area is small value, 10 m²/g. However, the specific surface volume estimated by CO₂ adsorption for the charcoal carbonized ad 400°C is 380 m²/g, and the volume increases gradually with the increase of the temperature. These results suggest that in the lower carbonization



Fig. 7. Distribution of maicropores diameter of the charcoal estimated by CO_2 adsorption isotherms at 195 K.



Fig. 8. Effect of carbonization temperature on specific surface area of the charcoal estimated by N_2 and CO_2 adsorption isotherms.

temperature the number of sub-nm pores increases. As the size of CO_2 molecule is 0.4 nm, which is a little larger than that of N₂ (0.32 nm). CO_2 can disperse easily into micropores because adsorption taken place at 195 K. [13]

4. CONCLUSIONS

It was found that carbonization temperature affects the adsorption of adsorbate gases; N2, CO2 and H2O. The isotherms of N₂ showed that as the carbonization temperature increased micropores formed in the charcoal. In the distribution of micropore radius, micropores having the size under ca. 0.7 nm increased in the charcoal carbonized at 600°C and above. In adsorption-disorption isotherms of water, V-typed isotherms were observed in the charcoal prepared at 600°C and above. Those results shows existence of mesopores and macropored besides micropores in the charcoal. The specific surface area of the charcoals estimated with the BET equation of the charcoal carbonized at 600°C was 400 m²/g by N₂ and CO₂ adsorption, respectively. As the carbonization temperature increased, the specific surface area by both N₂ and CO₂ adsorption drastically increased and 800 m²/g was obtained in the charcoals heat-treated at 1,000°C.

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[1] K. Shibano, S. Yoshizawa and Y. Ogawa, Proc. 2nd Inter. Sympo. on Environmentally Conscious Design and Inverse Manufacturing (EcoDesign 2001), IEEE Computer Society, (2001) pp. 1110-1113.

[2] K. Shibano, S. Yoshizawa, S. Goto and Y. Ogawa, Proc. 9th Inter. Conf. on Indoor Air Quality and Climate (Indoor Air 2002), (2002) pp. 694-699.

[3] K. Shibano, S. Yoshizawa and Y. Ogawa, *TANSO*, **204**, 166-170 (2002).

[4] T. Asada, A. Yamada, S. Ishihara, T. Komatsu, R. Nishimaki, T. Taira and K. Oikawa, *TANSO*, **211**, 10-11 (2002).

[5] K. Nishimiya, T. Hata, Y. Imamura and S. Ishihara. J. Wood Sci., 44, 56-61 (1998).

[6] I. Abe, S. Iwasaki, Y. Iwata, H. Kominami and Y. Kera, *TANSO*, **185**, 277-284 (1998).

[7] M. Mori, Y. Saito, S. Shida and T. Arima, *Mokuzai Gakkaishi*, **46**, 355-362 (2000).

[8] T. Kai, S. Yamamoto and S. Ishihara, *Shigen Shori Gijutsu*, **47**, 132-139 (2000).

[9] T. Kitamura and H. Katayama, *Mokuzai Gakkaishi*, 47, 164-170 (2001).

[10] S. Yoshizawa, T. Utsugi, K. Shibano, S. Goto and H. Yajima, Extended Abstracts of Carbon 2004, Providence, RI, July (2004) J036 (pp. 1-4).

[11] T. Asada, S. Ishihara, T. Yamane, A. Toba, A.

Yamada, K. Oikawa, J. Health Sci., 48, 473-479 (2002). [12] H. Naono and M. Hakuman, J. Colloid Interface

Sci., 158, 19-26 (1993).

[13] Technical Report No. 008, Bel Japan, Inc., 2002.

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