COMPARATIVE CHARACTERIZATION STUDY OF MICROPOROUS CARBONS BY HRTEM IMAGE ANALYSIS AND GAS ADSORPTION

M. Endo*, Y. J. Kim*, T. Hayashi*, K. Oshida[†], T. Miyazaki[†]
D. Lozano-Castello [§], D. Cazorla-Amoros [§], A. Linares-Solano [§],
* Faculty of Engineering, Shinshu Univ., 4-17-1 Wakasato, Nagano 380-8553, Japan
[†] Nagano National College of Technology, 716 Tokuma, Nagano-shi, 381-8550, Japan
[§]Departamento de Quimica Inorganica, Univ. de Alicante, E-03080, Alicante, Spain

Introduction

Activated carbon materials (activated carbons (AC) and activated carbon fibres (ACF)) are being used in many different application fields such as anti-pollution system (i.e., water purification, VOC abatement, selective remove of SO_x/NO_x, etc.) and energy devices (electric double-layer capacitors for electronics and electric vehicles) because of their high specific surface area (SSA) and the pore structure. From this high potential in various applications, numerous scientists have been devoted to clarify the pore structure of these materials with diverse methods. Characterization in terms of pore size distribution (PSD) is indispensable for the utilization and tailoring of improved carbon materials in those and many other applications. In general, pore analysis techniques based on gas adsorption methods have been well developed and quite successfully applied to characterize activated carbons, allowing to obtain quite reasonable micropore size distributions (MPSDs).

Among gas adsorption techniques, nitrogen adsorption is the most-widely used technique owing to the considerable sensitivity in both the micropore and mesopore regimes. However, when it is used for the characterization of microporous solids, diffusional problems of the molecules inside the narrow porosity range (size < 0.7 nm) occur. To overcome this problem the use of other adsorptives is necessary, such as CO_2 adsorption at 273K [1-3] or CH_4 at 298 K [4,5]. In a previous work [6], the micropore size distributions (MPSDs) of two activated carbons and a carbon molecular sieve were assessed by high-pressure methane and carbon dioxide adsorption isotherms. Although the results showed a quite good consistency between both gases, despite the different gas characteristics (CH_4 and CO_2), and adsorption conditions (298 K, supercritical conditions, and 273 K, subcritical conditions, respectively), independent techniques are needed to confirm gas adsorption usefulness.

In a very recent works [7,8] PSD of activated carbons were obtained using image analysis of micrographs obtained from TEM. The results obtained suggested that the method could be a powerful and useful tool to characterize especially the microporous materials. Thus, the objective of the present work is to obtain MPSD by TEM technique and compare these MPSD with those obtained with more established techniques, such as gas adsorption. Thus, the same two activated carbons and the carbon molecular

sieve, which were characterized by high-pressure CO_2 and CH_4 adsorption [6] have been selected for further investigation by HRTEM image analysis.

Experimental

The series of activated carbons includes: (i) a carbon molecular sieve (sample KUA1B8) prepared in our laboratory by blocking the microporosity of a previously prepared activated carbon; and (ii) two activated carbons prepared by chemical activation with KOH of a Spanish anthracite (KUA1GC and KUA1L26).

Porous texture analysis of all the samples was carried out by subatmospheric N_2 and CO_2 adsorption at 77 K and 273 K, respectively, in a Micromeritics (ASAP 2010, Micromeritics, USA) instrument. CO_2 and CH_4 adsorption isotherms at 273K and 298K, respectively, and at high pressures (up to 4 Mpa) were obtained in a Sartorius high-pressure microbalance.

MPSD measurements of samples were tried by means of image analysis of TEM micrographs. Samples were inserted in a glass tube filled with ethanol and they were dispersed by supersonic wave. Samples dispersed in methanol were mounted on the microgrid for TEM observation by surface tension several times. The microgrid was dried for about 3 hours. Observation was performed from low magnification to high magnification by HRTEM (JEM2010FEF, JEOL Co, Ltd., acceleration voltage of 200kV). TEM image obtained at ×200,000 magnification (Δf = -60 nm) was converted to a 512×512 pixel, 8 bits grayscale image in order to perform the 2-dimensional fast Fourier transform (2D-FFT). The resultant 2D power spectrum did confirm the isotropy of the specimen. The strength of the 2D-power spectrum around the concentric circles that were centered at the center of the image was integrated to get the 1D-integrated spectrums. The 1D-integrated spectrum had pore diameters preferentially aligned along the x-axis, and the intensity of each value is evaluated along the y-axis, to obtain the PSD.

Results and discussion

Figure 1(a) presents the N_2 adsorption-desorption isotherms at 77 K corresponding to the activated carbons. The adsorption for the carbon molecular sieve (sample KUA1B8) was negligible because this sample presents a very narrow microporosity, not accessible to N_2 at 77K [1,2]. The kinectics of N_2 adsorption is extremely slow at 77K, and extremely long times are necessary to reach the equilibrium at each point of the isotherm. Nitrogen adsorption isotherms obtained for the others are Type I, indicating the presence of only micropores.

Considering the curvature radius of the knee of the isotherm before reaching the saturation plateau, each sample can be clearly distinguished: KUA1GC shows very sharp knee compared to those of the others; KUA1L26 has the largest adsorption capacity. These detailed adsorption behaviors in the low relative pressure are presented in logarithm scale in Fig. 1(b). It is worth while to note that the amount of nitrogen adsorbed by KUA1GC at very low pressure is higher than the other samples, even though it shows lower adsorption capacity at the high relative pressure range. Considering that in the low-pressure region, adsorption capacity of porous materials with narrow micropores is high due to the enhanced molecule-surface interaction, the high adsorption at low relative pressure of the sample KUA1GC implies that the porosity of this sample has an important contribution from narrow micropores. From these adsorption isotherms, no information about pore texture of sample KUA1B8 (a carbon molecular sieve) can be obtained due to the too narrow pore size of this sample.
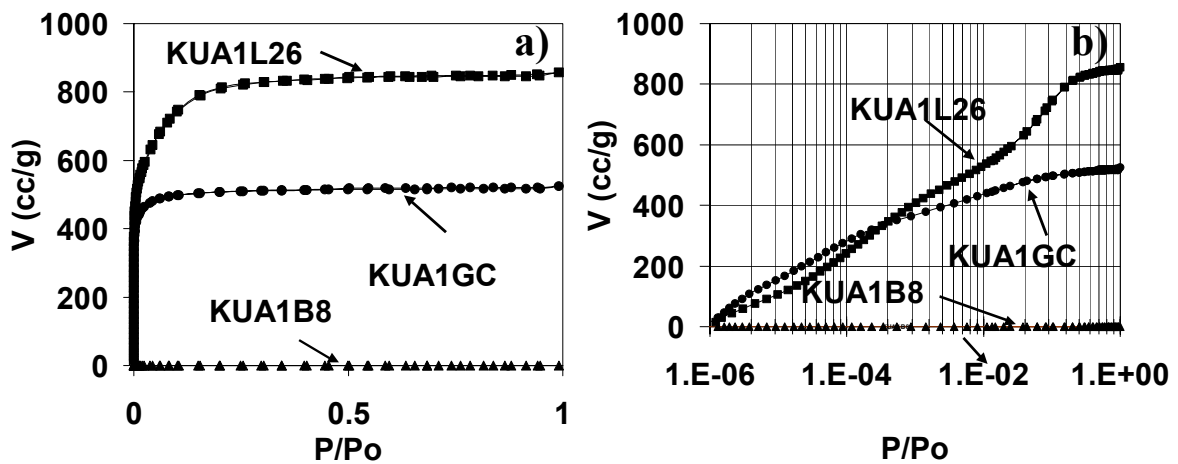

Figure 1. Nitrogen adsorption-desorption isotherms at 77 K . Linear scale on abscissa (a), and logarithmic scale on abscissa (b).

Figure 2 contains the MPSD obtained from CO_2 adsorption data (sub-atmospheric and high-pressure adsorption data). It can be seen that the narrowest MPSDs corresponds to the carbon molecular sieve (sample KUA1B8), and that the mean pore size shifts to a higher value for sample KUA1GC followed by sample KUA1L26.
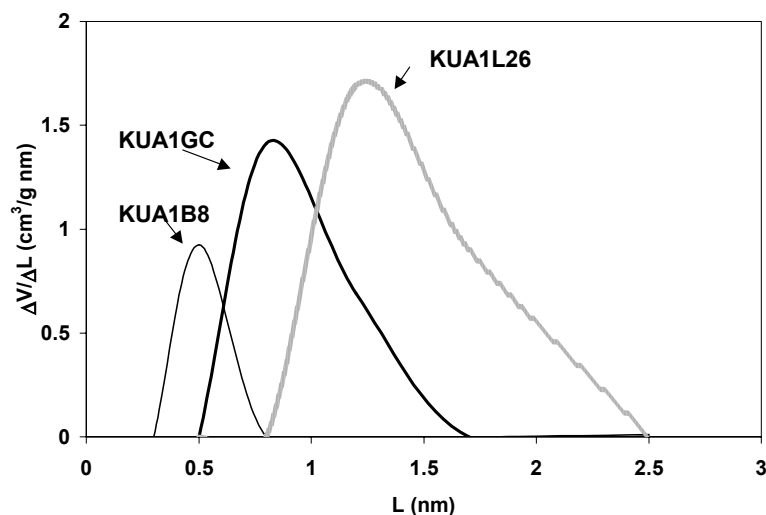
Figure 2. MPSDs obtained from the CO_2 adsorption data (sub-atmospheric and high-pressure adsorption data) for the three samples used in the present study

Figure 3 shows high-resolution TEM images taken at the magnification of × 200k and the power spectrums obtained by carrying out a 2D-FFT of original images. In the TEM images, the bright sections are considered as pores, which was confirmed by TEM image simulation [9]. We have confirmed that there is no abrupt structural change, which can affect to the results of pore size distribution by image analysis with varying the observation place from part to part. Furthermore, overall structures of samples were also observed. All samples show very complex pore configurations, having various dimension and irregular shape. In Figure 4, micropore size distributions (MPSDs) obtained by integration around the center point of the power spectrum are presented. The abscissa, denoted as spacing, corresponds to the "effective" pore size (without including the carbon atom forming the pore) and the ordinate implies the intensity with arbitrary units. The MPSDs in Fig. 4 were obtained normalizing each curve to the maximum of each profile. Therefore, intensity in this MPSD can hardly be used as an absolute value such as adsorption amount in gas adsorption methods. In these results, only peak location and relative intensity is considered.
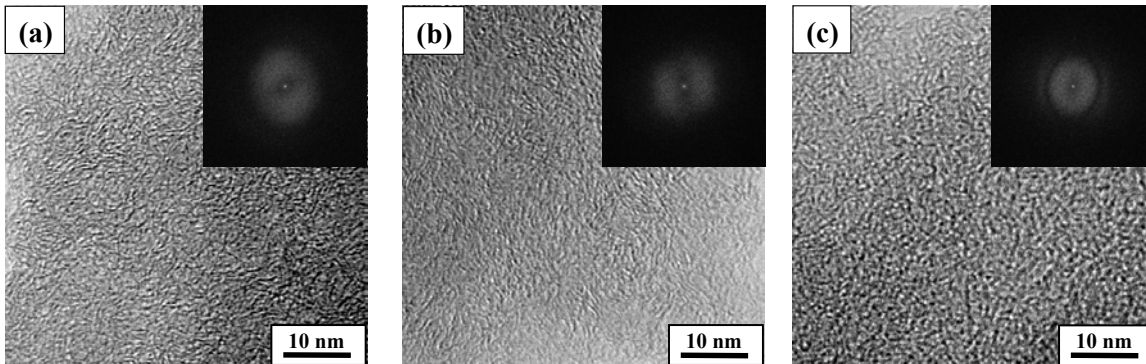
Figure 3. High resolution TEM photographs and the power spectrum obtained from fast Fourier transform. Each sample designate as follows; (a) KUA1B8, (b) KUA1GC, (c) KUA1L26. Shown in the insets are the power spectrums.

Figure 4(a) presents the PSD for sample KUA1B8 obtained by image analysis. It can be observed that, according to this result most of the porosity of this sample is narrow microporosity (pore size below 0.8 nm approximately), which agrees with the molecular sieve properties of this sample. It must be remarked that, the narrow porosity existing in this sample, which could not be characterized by N_2 adsorption at 77 K, has been analyzed by image analysis. In addition, the MPSD obtained with this technique is very concordant to that obtained with high-pressure CO_2 adsorption (see Figure 2). This result obtained with a technique, which is completely different to gas adsorption verify that high-pressure CO_2 adsorption is a suitable technique to characterize narrow microporosity and confirm the goodness of the method developed to obtain MPSD. The MPSD obtained for sample KUA1GC (Figure 4(b)) reveals the existence of narrow microporosity also in this sample. In addition, it can be observed that the MPSD of this sample shifts to wider pore sizes, which agrees with that obtained with CO_2 adsorption (Figure 2). Finally, in Figure 4(c) it can be seen that, in the case of the sample KUA1L26, there is a decrease in the amount of narrow micropores and the MPSD presents a shift to wider micropores, compared to the previous samples, which also agrees with the conclusions obtained from CO_2 MPSD (Figure 2).
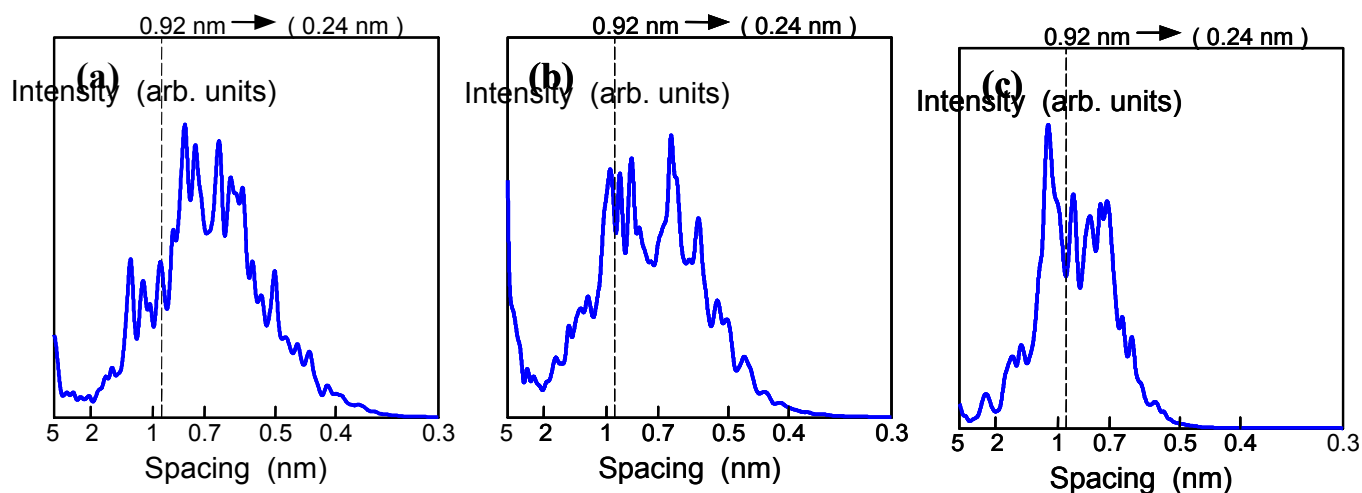
Figure 4. Pore size distributions (PSDs) obtained by image analysis using TEM photographs corresponding to samples (a) KUA1B8, (b) KUA1GC, (c) KUA1L26

Conclusions

The present work presents for the first time an useful comparison of MPSDs obtained from gas adsorption and image analysis of HRTEM micrographs The use of HRTEM has allowed to obtain MPSD of a carbon molecular sieve (sample KUA1B8), which could not be characterized by N_2 adsorption at 77 K due to diffusional problems. It has been shown that the MPSD obtained for this sample is very concordant to those obtained from high-pressure CO_2 and CH_4 adsorption in a previous work. This concordance obtained between two very different techniques verifies, once more, the usefulness of CO_2 to characterize narrow microporosity and the suitability of the method developed to obtain MPSD. The MPSDs obtained by image analysis show that sample KUA1B8 has the largest fraction of micropore with less than 0.5 nm size. The amount of very narrow pores (less than 0.5 nm) decreases from this sample (KUA1B8) followed by KUA1GC to KUA1L26. In addition, the mean pore size of the MPSDs shifts to higher values following also this sequence. These results show a very good agreement with those obtained in a previous work by high-pressure CO_2 and CH_4 adsorption isotherms.

Acknowledgements

References

[1] Cazorla-Amorós D, Alcañiz-Monge J, Linares-Solano A. Characterization of activated carbon fibres by CO_2 adsorption. Langmuir 1996; 12(11), 2820-2824.

[2] Cazorla-Amorós D, Alcañiz-Monge J, De la Casa-Lillo MA, Linares-Solano A. CO_2 as an adsorptive to characterize carbon molecular sieves and activated carbons. Langmuir 1998; 14(16): 4589-4596.

[3] Linares-Solano A, Salinas-Martínez de Lecea C, Alcañiz-Monge J, Cazorla-Amorós D. Further advances in the characterization of microporous carbons by physical adsorption of gases. Tanso 1998; 185: 316-325.

[4] Sosin KA, Quinn DF. Journal of Porous Materials 1995; 1: 111.

[5] Sosin KA, Quinn DF,MacDonald JAF. Changes in PSD of progressively activated carbons obtained from their supercritical methane isotherms. Carbon 1996; 34(11): 1335-1341.

[6] Lozano-Castello D, Cazorla-Amoros D, Linares-Solano A, Quinn D. Micropore size distribution of activated carbons and carbon molecular sieves assessed by high-pressure methane and carbon dioxide adsorption isotherms. Journal Physical Chemistry B, 2002; 106:9372-9379.

[7] Endo M, Kim YJ, Ishii K, Inou T, Nomura N, Mihashita N, Dresselhaus MS. Heat-treatment retention time dependence of polyvinylidene chloride-based carbons on their application to electric double-layer capacitors. Journal of Material Research 2003; 18(3): 693-701,.

[8] Endo, M; Kim, Y.J.; Hayashi, T.; Oshida, K.; Miyazaki, T. The pore structure of activated carbons as studied by TEM and applications for pore size control. "New frontiers in carbon materials". Carbon 2003 Precongress Short Course. Alicante (Spain). pp. 33-38.

[9] El-Merraoui, M.;Tamai. H.; Yasuda, H.; Kanata, J.; Mondori, K.; Nadal, K.; Kaneko, K. "Pore structure of activated carbon fibers from organometallics/pitch composites by nitrogen adsorption"Carbon, 36 (12), 1769-1776, 1998.