The characterization of carbon nanofibres based on N_2 adsorption isotherms at 77K

Chao Zhang   Xuesheng Lu   Anzhong Gu

Institute of Refrigeration and Cryogenics, Shanghai JiaoTong University, shanghai, China, 200030

The BJH method is applied to determine the pore size distribution of several carbon nanofibres based on N_2 adsorption isotherms at 77K. The study results show that the carbon nanofibres used in the present study include abundant mespores of 20nm. The adsorption data between 0.01 and 0.99 of relative pressure show features of gas adsorption in mespores adsorbents, and only the mesopores size distribution could be determined with the BJH method. The adsorption data at lower relative pressure (<0.01) must be collected if the micropores size distribution is determined.

INTRODUCTION

The determination of the structural proprieties of porous adsorbents is important in the field of gas and liquid adsorption. Indeed, the pore shape, the pore dimensions and the chemical structure of the walls are the main characteristics to be considered when studying the potentiality of a given adsorbent to fit a given application. The problem of relating such basic structural properties to the thermodynamic and kinetic behavior of a system involving the considered adsorbent and a complex liquid or gas of industrial interest is far from being solved. Carbon nanofibres are porous adsorbents specially developed for hydrogen adsorption storage [1]. The microstructure characterization of carbon nanofibres is critical for its application in hydrogen storage and understanding of supercritical hydrogen adsorption mechanism. In this paper gas adsorption method [2-6] is used to the determination of pore size distribution of carbon nanofibres.

EXPERIMENTS

The materials used in the present study are carbon nanofibres made from acetylene with flowing catalytic method [7]. The FESEM images are shown in Figure 1. The sample was respectively purified with nitric acid and sulfuric acid oxidation method (qb5), kali permanganate, water and sulfuric acid oxidation method (qb7), carbon dioxide oxidation method (qb2), water vapor oxidation for 4 hours (qb8) and water vapor oxidation for 5 hours (qb9). The N_2 adsorption isotherms at 77K have been measured with Micromeritics ASAP2000 auto-analytic instrument. The adsorption isotherms are typical type-II isotherms, as showed in Figure 2.
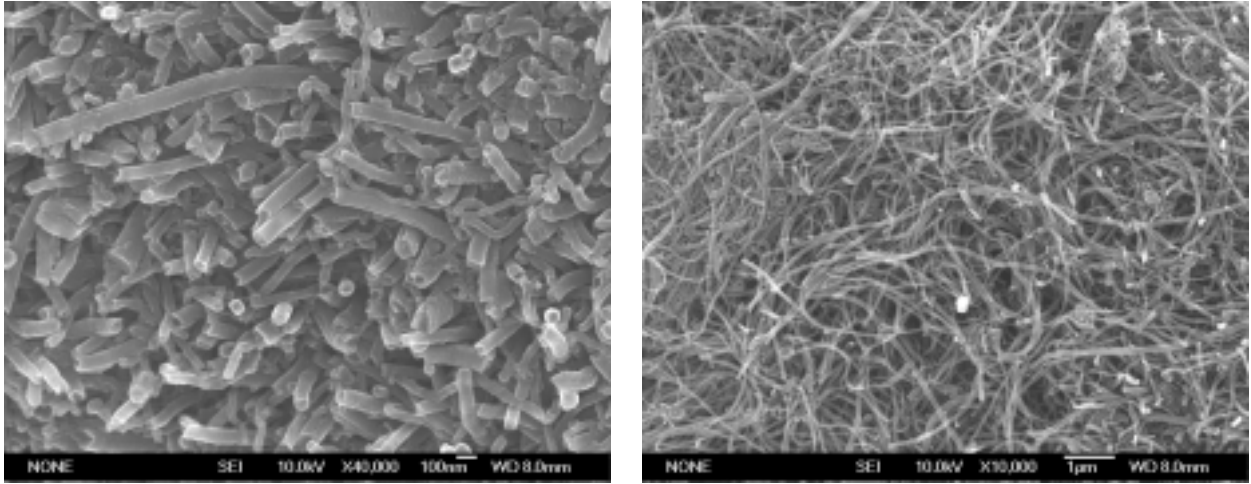
Figure1. The FESEM images of the carbon nanofibres made from acetylene

DETERMINATION OF MESOPORE SIZE DISTRIBUTION

The BJH method is used to determine the mesopore size distribution of carbon nanofibres. The BJH method is based on Kelvin equation and Halsey equation, and it has been proved that the BJH method could acculately determine the mesopores size distribution [3]. The detailed calculation equation is shown in reference [8]. The calculated results are shown in Figure 3. As shown in Figure 3, all the carbon nanofibres include abundant mesopores of 20nm, and the difference is just the volume of 20nm mesopores. The calculated results are consistent with the FESEM images of samples, and prove that different purification methods could not change the basic structure of carbon nanofibres, and only get rid off impurifies in different degrees. The volume of 20nm mesopores of carbon nanofibres purified with water vapor oxidation for 5 hours is maximal, then it indirectly justify the validity of water vapor oxidation.
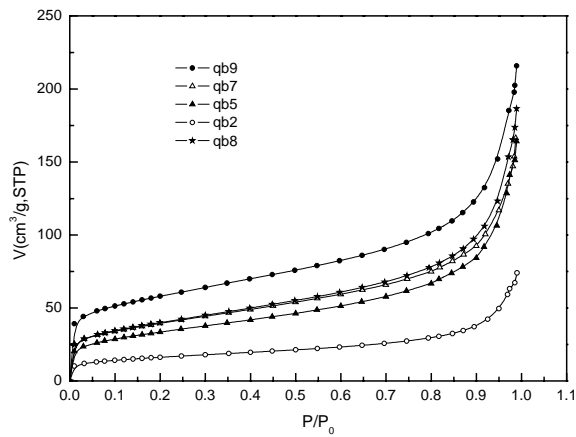

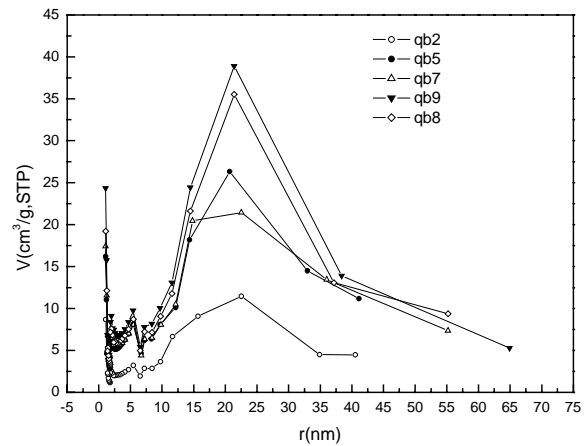Figure2. The N_2 adsorption isotherms at 77K

Figure3. The pore size distribution of carbon nanofibres

DETERMINATION OF MICROPORE SIZE DISTRIBUTION

For porous adsorbents including micropores and mesopores, at lower adsorption pressure, gas adsorption may occur both in micropores and mesopores at the same time. So the adsorption isotherms in micropores must be determined before characterization of micropores size distribution. At some adsorption pressure, the adsorption amount can be described as,

$$V = V_{mic}{}^0 \theta_{mic} + \frac{V_{mes}{}^0 V_s(0.4)}{V_s{}^0} \frac{V_s}{V_s(0.4)} \qquad (1)$$

Which $V_{mic}{}^0$ is the max adsorption in micropores, θ_{mic} are defined as micropore filling degree, and $V_{mes}{}^0$ is the adsorption of single molecular layer in mesopores. $V_s{}^0$ and V_s is respectively the saturation adsorption of single layer and the adsorption in nonporous adsorbents, and $V_s(0.4)$ is the adsorption in nonporous adsorbents when relative pressure is 0.4. The data of N_2 adsorption in nonporous adsorbents is shown in references [9-11]. When the relative pressure is enough, the micropores are filled and the adsorption V and the $V_s/V_s(0.4)$ is in line relationship. Then the relative pressure while the micropores are filled, the $V_{mes}{}^0 V_s(0.4)/V_s{}^0$ and the micropores volume $V_{mic}{}^0$ could be determined with the line slope and intercept. So the adsorption isotherms may be corrected according to equation (1). The relationship between the adsorption V and the $V_s/V_s(0.4)$ of the N_2 adsorption in carbon nanofibres is shown in Figure4.
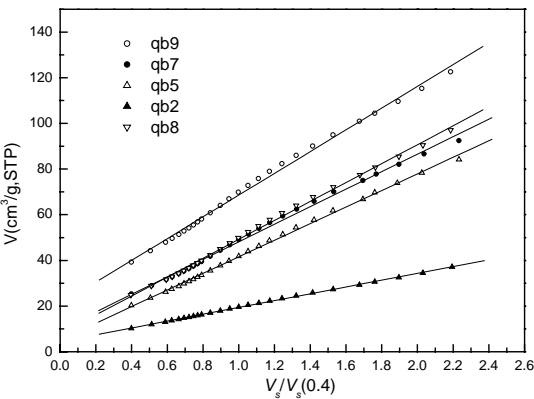

Figure4. The relation curves of the V and the $V_s/V_s(0.4)$ of N_2 adsorption in carbon nanofibres

As shown in Figure 4, the adsorption data are all on a line among measured pressure, which is the feature of gas adsorption in mesopores. But the lines do not go through the origin of coordinate, which proves that the adsorption of N_2 in micropores occurs. But at the point of the initial measure pressure the micropores are already filled. So the pressure when the micropores are filled could not be determined. But we can get the micropores volume according to the intercept, as shown in Table1. The maximal micropores volume is only 20.94cm^3/g (STP, Standard Temperature and Pressure). Because the adsorption data at the relative pressure less than 0.01 could not be obtained with equipments, so the micropores size distribution can't be determined. But it is unnecessary to determine the micropores size distribution because of little micropores volume.

Table1 The micropore volume of carbon nanofibres

Materials	Micropores Volume cm^3/g, STP	Materials	Micropores Volume cm^3/g, STP
Qb9	20.94	Qb7	9.77
Qb5	5.22	Qb2	4.47
Qb8	7.81		

CONCLUSION

The mesopores size distributions are determined with BJH method based on N_2 adsorption isotherms at 77K. The results show that the carbon nanofibres includes abundant mesopores of 20nm, which is consistent to the FESEM images of samples. By correcting the original adsorption isotherms, it is found that among relative pressure of 0.01~0.99, the adsorption data show features of gas adsorption in mesopores. And the micropores volume are determined with the intercept of the line between V and $V_s/V_s(0.4)$. The micropores volume of carbon nanofibres purified by water vapor oxidation for 5 hours is maximal, about 20.94cm^3/g. And in order to determine the micropore size distribution, the adsorption data at relative pressure less than 0.01 must be gotten. But it seems unnecessary to determine the micropores size distribution because of little micropores volume.

ACKNOWLEDGEMENT

REFERENCES

1. Kaylene A, Siegmar R, Michael H, etc., Carbon nanostructures: An efficient hydrogen storage medium for fuel cells? Fuel Cells Bulletin (2001) 4(38) 9-12

2. Carrott P.J.M., Ribeiro Carrott M.M.L., Evaluation of the Stoeckli method for the estimation of micropore size distributions of activated charcoal cloths, Carbon (1999) 37 647-656

3. Valladares D.L., Rodriguez Reinoso F. and Grablich G.Z., Characterization of active carbons: The influence of the method in the determination of the pore size distribution, Carbon (1998) 36(10) 1491~1499

4. Stoeckli F., Guillot A., Hugi-Cleary D., Slasli A.M., Pore size distributions of active carbons assessed by different techniques, Letters to the editor/Carbon (2000) 38 929~941

5. Bereznitski Y., Gangoda M., Jaroniec M., and Gilpin R.K., Adsorption Characterization of Active Carbons Modified by Deposition of Silica, Langmuir (1998) 14: 2485~2489

6. Carrot P.J.M., Ribeiro Carrott M.M.L., Mays T.J., Comparison of methods for estimating micropore sizes in active carbons from adsorption isotherms, Fundamentals of adsorption (1998) 6 677-682

7. Huiming Chen. Carbon nanotubes-synthesis, Microstructure, Properties and Applications, Chemistry industry Press. Beijing, China (2002)

8. Jiming Yan, Qiyuan Yan. Adsorption and condensation- surface and porous of solid, Science publisher, Beijing, China (1979)

9. Carrott P.J.M., Roberts R.A. and Sing K.S.W., Standard nitrogen adsorption data for nonporous carbons, Carbon (1987) 25(6) 769~77

10. Mietek Jaroniec, Michal Kruk, Standard Nitrogen Adsorption Data for Characterization of Nanoporous Silicas, Langmuir (1999) 15 5410~5413

11. Carrott P.J.M., Roberts R.A. and Sing K.S.W., Adsorption of nitrogen by porous and non-porous carbons, Carbon (1987) 25(1) 59~68