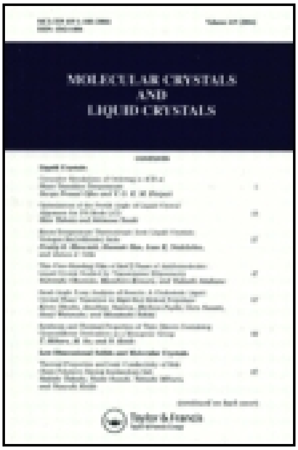

Molecular Crystals and Liquid Crystals

Nano-structure control in carbon spheres by air oxidation - derivation of master curves -

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NANO-STRUCTURE CONTROL IN CARBON SPHERES BY AIR OXIDATION
– DERIVATION OF MASTER CURVES –

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Pore structure in nanometric scale in carbon spheres prepared from resol-type phenol resin was controlled by air oxidation. The yield values of oxidation at different temperatures were able to be superimposed by shifting along the axis of logarithmic residence time and to get a master curve at a reference temperature 400°C, a linear dependence of shift factors on the reciprocal absolute temperature of oxidation giving apparent activation energy of 200 kJ/mole. Based on the conversion between oxidation temperature and time, all experimental data of the pore parameters could be converted to the values at 400°C. Total pore volume increased with increasing in residence time at 400°C up to 40 h, but tended to reduce by further oxidation gradually.

Keywords: nano-structure; carbon spheres; air oxidation; master curve; pore structure

INTRODUCTION

Recent energy and environmental problems demand exact control of pore structure in carbon materials [1,2]. For examples, the development of capacitors depends strongly on carbon electrodes with well-controlled pore structure and macroporous carbons were used to collect gasoline vapor in the tank during parking of car to reuse (car canister). Some of recent applications of these carbon materials required macropores, even spaces between entangled fibrous particles [3], and so these carbon materials were proposed to classify as porous carbons [4], including conventional activated carbons. Some of applications asked not only well-controlled pore structure but also high density to these porous carbons. In this respect, carbon spheres are believed to have a high possibility if their pore structure could be well controlled. One of authors [M.I.] has studied on pore structure

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in carbon spheres derived from phenolic resin by carbonization in a controlled atmosphere by gas adsorption and direct observation under STM [5–10] and their application for the adsorption of trihalomethanes from its aqueous solution [11,12]. Similar studies have been carried out by different authors [13–15].

In order to control the pore structure in carbon materials, different processes have been used, which have been called activation; heating with $Zn(OH)_2$ and KOH, heating in water vapor, etc. One of the authors (M.I.) started to try to control the pore structure of carbon materials in nanometric scale by air oxidation, which is the simplest in the equipments, the mildest in thermal conditions, and also energy- and resources-saving in materials economy.

In the present work, pore structure in nanometric scale was controlled by the oxidation in a flow of air and the process of pore structure development was tried to understand by deriving the mater curves at a reference temperature.

EXPERIMENTAL

The commercially available resol-type phenol resin spheres with average diameter of 50 μm, which were produced through emulsion process, were carbonized in Ar atmosphere. The heating rate was 400℃/h and the sample spheres were kept for 1 h at 1000℃. After the carbonization the sample was kept spherical shape, on their surface no pores were detected by high magnification scanning electron microscope and their structure was amorphous in X-ray diffraction, so-called glass-like carbon.

Air oxidation of these carbon spheres was performed at different temperatures between 350 and 450℃ for various periods in a flow of air passing through distilled water at 40℃. Flow rate of air was kept a constant at 50 ml/min during oxidation. The yield after oxidation was determined. Nano-structure developed by air oxidation was characterized by the adsorption measurements of nitrogen at 77 K. Their surface area was calculated by BET method, and pore size distribution and pore volume, total pore volume, micropore and mesopore volumes, and ratio of mesopore volume, were determined by following the BJH method.

RESULTS AND DISCUSSION

Master Curve for Air Oxidation Yield

In Figure 1a, the yield after the oxidation at different temperatures was plotted against residence time at each temperature in logarithmic scale.

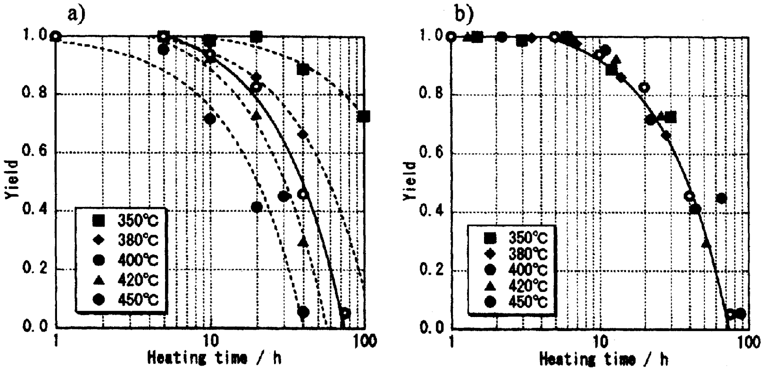

FIGURE 1 Oxidation yield vs. logarithm of residence time at different oxidation temperature a) experimntal curves and b) the master curve obtained by shifting experimental points.

Curves observed at different oxidation temperatures are similar with each other. In order to analyze the oxidation process, the procedure, which has been employed in the study of relaxation phenomena in the field of rheology and also in the analyses of graphitization of different graphitizing carbons[16–18], was applied. Each experimental points on oxidation yield plotted against logarithm of residence time at different temperatures are superimposed on the curve for a reference temperature 400°C by the translation along the log t axis. This superimposition of all experimental points gave a smooth curve, being called the master curve, as shown in Figure 1b. From the translated values plotted against the reciprocal absolute temperature of oxidation, apparent activation energy ΔE was calculated to be about 200 kJ/mol.

To have a master curve revealed that the oxidation of the carbon spheres can be considered as a single process, of which temperature and residence time can be converted with each other, though the conversion has to be limited in the range of experimental conditions, carbon spheres carbonized up to 1000°C, oxidation in a flow of air passed through 40°C water, oxidation temperature between 350 and 450°C. It has to be mentioned that the observed activation energy value 200 kJ/mol is in between those for CO and CO_2 formation reactions (111 and 394 kJ/mol, respectively).

Nano-structure of Carbon Spheres Air-oxidized

For the carbon spheres oxidized at 400°C for 5, 10, 20 and 40 h, cumulative pore volume and pore size distribution are plotted in Figures 2a to d, respectively. The SEM micrographs of a single sphere are shown on the

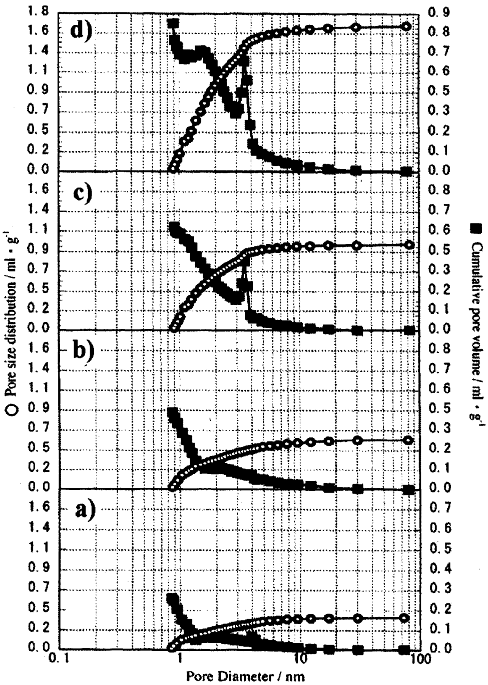

FIGURE 2 Cumulative pore volume and pore size distribution on carbon spheres oxidized at 400℃. a) Oxidized for 5 h, b) for 10 h, c) for 20 h, and d) for 40 h.

starting spheres and the ones oxidized at 400℃ for 5 and 20 h in Figures 3a to c, respectively.

After oxidation of carbon spheres at 400℃ for 5 h, micropores were formed, only a small amount of mesopores being detected, of which BET surface area was calculated to be 470 m^2/g. Under SEM, many craters were

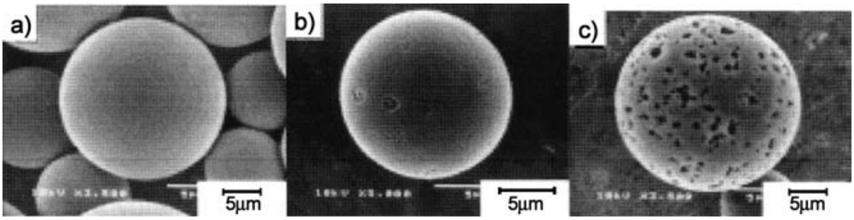

FIGURE 3 SEM micrographs of carbon spheres. a) starting carbon sphere, b) oxidized at 400°C for 5 h and c) for 20 h.

observed on the surface of spheres. From these observations, the micropore formation in the beginning of oxidation was supposed to be due to the opening of micropores hidden inside of the spheres through gasification of carbon walls by oxidation, upon this oxidation a small amount of mesopores being formed.

By extending oxidation time, total pore volume increases, the increase in the amount of micropore being more pronounced than that of mesopores, and BET surface area also increases to be 910 m^2/g after 20 h oxidation. On SEM, the concentration of craters becomes very high, as shown in Figure 3c. Further oxidation, for more than 20 h at 400℃, increases preferentially micropore volume, as shown in Figure 2d on 40 h oxidation, and BET surface area close to 1000 m^2/g. However, both total pore volume and BET surface area tend to decrease with increasing residence time more than 40 h at 400℃.

Since the conversion factors between oxidation temperature and time were obtained from apparent activation energy, pore structure parameters, total pore volume, BET surface area, micropore and mesopore volumes,

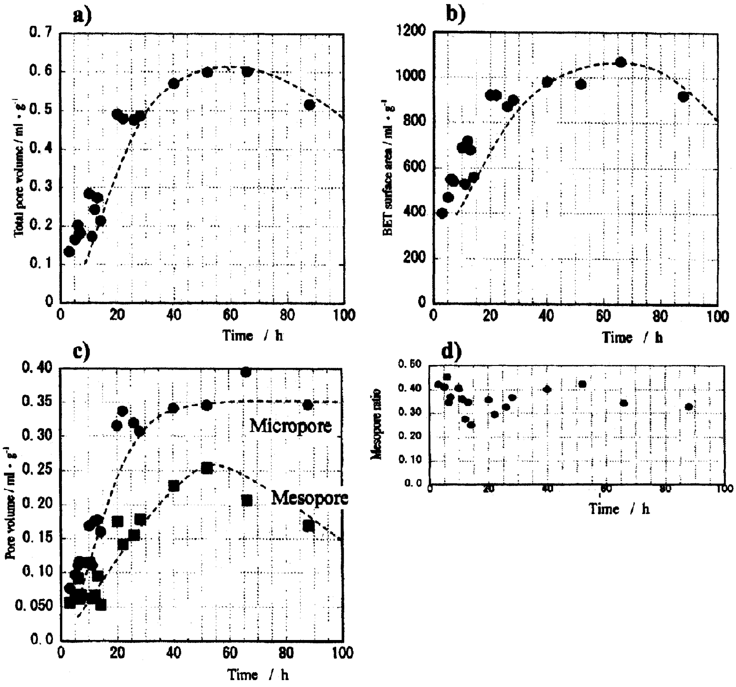

FIGURE 4 Pore parameters plotted against converted residence time at 400℃. a) Total pore volume, b) BET surface area c) micropore and mesopore volumes, and d) ratio of mesopores.

and ratio of mesopores, were plotted against converted residence time at 400°C in Figures 4a to d, respectively. Micropore and mesopore volumes were determined by dividing the cumulative curve pore volume at the pore diameter of 2 nm, and the mesopore ratio was calculated by dividing the mesopore volume thus determined by total pore volume.

Total pore volume (Fig. 4a) and BET surface area (Fig. 4b) increase rapidly with increasing residence time at 400℃ and reaches maxima around 40 h oxidation, which are about 0.6 ml/g and 1000 m^2/g, respectively. Passing through maxima, both parameters tend to decrease gradually with further increase in residence time at 400°C. Both micropore and mesopore volumes increase rapidly up to about 40 h oxidation, but show a little different behavior above 40 h, micropore volume keeps almost constant but mesopore volume decreases (Fig. 4c). Mesopore ratios on all samples (Fig. 4d) seem almost constant at around 0.35. Therefore, the decrease in total pore volume by the oxidation for more than 40 h seems to be due to the decrease in mesopore volume, which may be caused by widening mesopores to macropores.

CONCLUSIONS

The present results revealed on carbon spheres prepared from phenol resin that pore structure in nanometric scale in carbon materials can be controlled by air oxidation. The process of oxidation of carbon spheres by using wet air was able to be expressed as master curves on oxidation yield at a reference temperature 400°C. By using conversion factors calculated from apparent activation energy, master curves on various pore structure parameters, total pore volume, micropore and mesopore volumes and BET surface area, could also be derived.

The master curves of oxidation yield and pore structure parameters obtained on carbon spheres in the present work are valuable for limited conditions; oxidation of carbon spheres, which were prepared from resol-type phenol resin and have amorphous structure, by wet air at a range of temperatures from 350 to 450°C. For different conditions, such as oxidation by dry air, therefore, we have to expect a little different master curves. However, the present results reveals that the control of nano-structure in carbon materials is possible by air oxidation.

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