

# Preparation of Porous Carbon Particles using a Spray-Drying Method with Colloidal Template

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**Abstract**—A spherical porous carbon particles with controllable porosity with a mean size of 2.5 $\mu$ m have been prepared using a spray drying method with organic particle colloidal template. As a precursor, a mixing solution of carbon nanopowder and polystyrene (PS) particles as a template was used. The result showed that the particles with a good porous structure could be obtained. The pore size and shape (spherical) were identical to the initial template, giving a potential way for further developments. The control of particle porosity was also possible and reported in this paper, in which this control could be achieved by means of PS concentration.

**Keywords**—Porous structure particle; Carbon nanoparticles; Catalyst; Spray-drying method.

## I. INTRODUCTION

RECENTLY, attention to the fabrication of highly ordered porous particles has been tremendously increased. Potential application in wide range of fields (e.g. optics, electronics, devices, sensors, and catalysts) makes them to be intensively studied. There have been many attempts to fabricate this material, especially when it correlates with a high surface area and low density. Carbon has been well-known materials, which can be used as a catalyst support.[1]

Many preparation methods have been developed for the fabrication of porous materials have been known, involving template-assisted techniques.[2] However, current techniques to produce porous structure (i.e. SBA-, MCM-, and HMM-series[3]) have been found a problems, especially related to the non-spherical pores and limitation of pore sizes (typically in the mesoporous range) have been found. In addition, pore size less than 5 nm causes difficulties in the mass transfer, the diffusivity, and the penetration of molecules into and out the pore system, creating problems for several applications[3].

To address the above disabilities, the template replication using an organic particle template technique has been suggested as a promising method[4]. The good porous structure and the ability in controlling porosity, pore shape, and pore size can be achieved and potential for many applications[5]. However, to the best of our knowledge, not so many papers reported the preparation of porous carbon particles using this technique.

In previous studies, porous inorganic material with a controllable pore size was successfully prepared in both film[2, 6] and particle[4, 5, 7-9] form using a colloidal template. Besides, we also succeeded in preparing carbon nanotubes with controllable tube number and diameter[10, 11]. Herein, as a continuation of our study[12], we report a simple organic template-driven self-assembly procedure for the preparation of porous carbon particles. Since we have experiences in the use of a spray-drying method, we used this technique to achieve the preparation of porous carbon particles in this study. Experimental results showed that the produced particles were spherical and had a good pore structure. The concept in how the porous could be formed was also verified by a confirmation of electron microscope analysis for each processing step. Investigation of optimum condition for preparing particles with controllable porosity was also reported, based on PS/carbon ratio, which would be important for further studies.

## II. EXPERIMENTAL METHOD

Porous carbon particles were prepared from a precursor that was contained carbon nanopowder (40 nm, Mikuni Color Co., Ltd, Japan) and PS particles (Japan Synthetic Rubber, Tokyo, Japan; a mean diameter of 300 nm). To produce particles with a good structure (spherical shape), the precursor was initially dispersed in an aqueous solution with a concentration of 0.224 wt% and sonicated (Ultrasonic bath, NE-U17, Omron Co. Ltd.) for several minutes to ensure that all components were dispersed homogeneously. The mass ratio of PS to carbon in the suspension was ranging from 1.00 to 2.00. In addition, to increase mechanical strength of the prepared particles, we also added sucrose (Kanto Chemical Co., Inc., Japan) as the additive, which were added in the initial precursor with mass ratio of sucrose to carbon of 0.3. The precursor suspension was then sprayed using a two-fluid nozzle spray dryer (Mini Spray Dryer B-290, Nihon BUCHI K., Tokyo, Japan). A schematic diagram of the experimental apparatus is shown in Figure 1. Compressed air (ranging in pressure from 500 to 800 kPa), which previously heated, was included into the two-fluid nozzle system. Then, when the compressed air introduced together with the PS/Carbon suspension (at a flow rate ranging from 3 to 30 mL/min), the precursor was atomized. In this study, the precursor solution was continuously fed through a nozzle with an inner diameter of 0.7 mm at a feed rate of 3 mL/min. The flow rate of compressed air is 470 L/h. The generated droplets were then introduced into a drying cylinder with an inner diameter of 60 cm and a length of 110 cm. The water in the precursor droplets was evaporated by the heat of the hot

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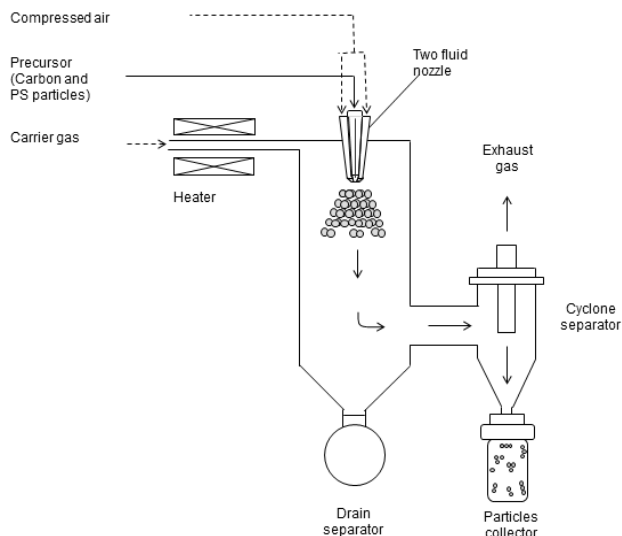


Fig. 1 Illustration of the spray-drying apparatus. Adapted from reference [7]

compressed air and carrier gas. The inlet and outlet temperatures of the carrier gas were maintained at 200 °C and 100 °C, respectively, and the flow rate of carrier gas (aspiration) was maintained at 20 m<sup>3</sup>/h. Solid particles consisted a continuous structure of the carbon with approximately uniform distribution of PS particles and it formed as a result of the spray drying procedure. The solid particles were collected from the carrier gas using a cyclone separator, while the carrier gas (exhaust) was expelled from the system. The percentage of the collected powder with the solution (solid part) to be spray dried is around 50% in weight/mass (including the residual moisture content). To obtain porous particles, the collected composite particles were re-heated at a temperature of 600 °C for several minutes to remove PS. The morphology of the prepared particles was examined using a scanning electron micrograph (SEM, Hitachi S-5000 operated at 20 kV). In addition, to determine the optimum temperature for removing PS, thermogravimetric-differential thermal analysis (TG-DTA, TG-DTA 6200, Seiko Instrument Inc., Tokyo, Japan).

### III. RESULTS AND DISCUSSIONS

When using the spray-drying method to produce porous particles, several factors should be determined to make a good arrangement of pores: type of material, precursor properties (i.e. concentration, viscosity, density, and particle size (if the precursor is a nanoparticle sol or suspension)), and spray-drying condition (i.e. flow, temperature, and humidity). [5] However, in this paper, we focused only on the development of porous carbon under the effect of template concentration to control the pore number/porosity in the particle, while other parameters would be reported in our future work.

The TG-DTA patterns of heat-treated carbon and spray-dried PS/carbon under different annealing conditions are shown in Figure 2. High temperatures under different heat conditions (i.e. carrier gas) can lead the stability of carbon material. Therefore,

the optimum condition of heat treatment should be investigated to produce particles without changing the quality of the product. Different trends between carbon and PS/carbon particles under different heat treatment conditions (i.e. under air (Figure 2a) and nitrogen (Figure 2b) atmospheres) were obtained.

In the case of carbon slurry (with concentration of 30 wt% in ethanol solution) under air condition (Figure 2a, dashed line), decrease of mass was obtained at less than 100 °C, while after 100 °C mass was relatively constant. This verified that all solvents (ethanol) were evaporated at this range of temperature. Then, at temperature of more than 500 °C, further loss of mass was found. The effect of heat treatment under air condition on the change of mass of PS/carbon particles is shown in Figure 2a, solid line. Because as-prepared PS/carbon particles did not consist any solvents, the constant masses at 100 °C were obtained. However, in the range of temperature of 270 °C, decrease of mass was obtained, confirming that PS evaporation started [7]. The loss of mass was continued until the temperature of 450-500 °C. Similar to carbon nanoparticles, further decrease of mass was also found at temperature of more than 500 °C.

Figure 2b shows heat treatment of carbon and PS/carbon particles under N<sub>2</sub> atmosphere. Dashed line illustrates heat treatment of carbon particles, while solid line is PS/carbon particles. For the case of carbon nanoparticles, similar trend to Figure 2a was obtained in the decrease of mass at temperature of below 100 °C, confirming the evaporation of solvent. The mass was then constant until the temperature of 500 °C. However, after 500 °C, there was no change in the mass. This confirmed that during this temperature range, carbon nanoparticles were possibly oxidized (by O<sub>2</sub>) and transformed into carbon oxide (either CO or CO<sub>2</sub>). However, when using N<sub>2</sub>, because there was no oxidizing agent, carbon nanoparticles were typically stable, confirmed by the stable mass plot. This style was also observed for the case of PS/carbon particles. The mass was changed from 270 °C, but it stopped after 500 °C. The mass was maintained at about 10%, confirming no oxidation or no loss of mass when using N<sub>2</sub> atmosphere. From these results, we confirmed that the heat treatment at 600 °C under N<sub>2</sub> atmosphere was the best and an effective tool to remove the PS.

Figure 3 shows the morphology of the spray-dried particles before and after template removal. Carbon nanoparticles and PS particles were arranged in the droplet, which formed as a result of spraying the solution, due to buoyancy and surface forces. After travelling in the spray-drying, droplet turned on solid particles with raspberry-like arrangements, as shown in Figure 3a. Particles with dense arrangement with no any holes were produced. Then, the primary prepared particles were re-heated in the higher temperature under N<sub>2</sub> atmosphere to remove the PS. The effects of removal process of the templating agent via heat treatment are shown in Figure 3b. PS particles were completely removed and leaving holes in the carbon particles, confirming our above hypothesis in Figure 2. As shown in this figure, the external dimensions of the final porous particles remained unchanged and the sizes of the hole

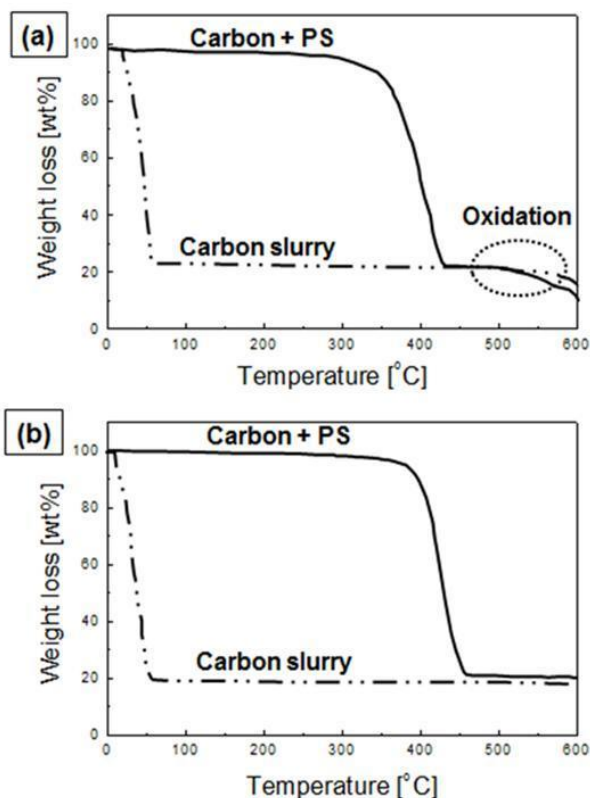


Fig. 2. TG-DTA analysis of carbon and PS/carbon particles under different heat treatment carrier gases: (a) air and (b)  $N_2$

were identical to the size of initial PS. This confirmed that our process was reliable to the quality of the product and driving the possibility in the control of pore size.

Consistent with our previous study, porous morphologies were defined by the concentration of the PS in the initial solution (Figure 4). Using similar condition as investigating in Figure 3, we used different PS/carbon ratios: 1.00; 1.30; and 1.80, corresponding to Figure 4a, b, and c, respectively. The result showed that the porosity of the prepared particles could be controlled by changing PS concentration in the solution. When ratio of 1.00 was used, porous particles could be prepared (Figure 4a). Increase of PS number into the initial precursor resulted in the increase of number of holes in the particles (Figure 4b). From these results, we could conclude that the PS occupied inside the droplet. Then, after PS particles were released by heat treatment, they left hole. When PS with larger number/concentration was used, more hole number could be produced. However, further increase of PS concentration caused to produce brittle and broken particles (Figure 4c).

To be relevant for industrial applications, porous particles should be mechanically stable. This reason drives to the importance of enhancing mechanical performance of the prepared particles.

Figure 5 shows the effect of additional mechanical strength additive to the porous particles. In this study, we used sucrose as the additive because drying this additive at  $600^\circ$  would have produced additional carbon, in which this additional carbon

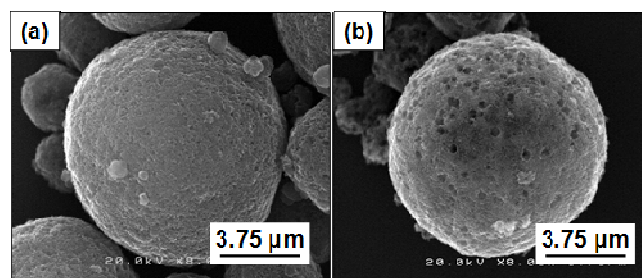


Fig. 3 SEM images of spray-dried particles: (a) as-sprayed particles (PS/carbon) and (b) after additional heat treatment (porous carbon)

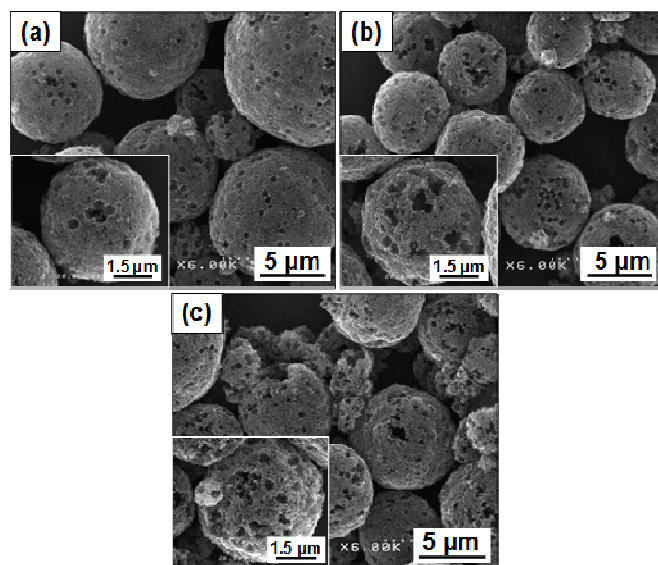


Fig. 4 SEM images of particles prepared by different PS/carbon ratios: (a) 1.00; (b) 1.50; (c) 1.80

would have coated, positioned, and placed in the free space between arrangement of carbon nanoparticles in the particle. Figure 5a and b show particles with and without additive, respectively. Particles with and without any additional additive were identical (Figure 5a,1 and b,1), informing that there is no effect of additive on the macropore structure. However, when mechanical stress analysis was added to the both types of samples, different results were obtained. Particles with no additional additive were broken (Figure 5a,2), while particles with additional additive were still in their structure (Figure 5b,2). These results confirmed that additional additive was effective to prepare stable porous monolayer. In addition, in this study, we used ultrasonication process (more than 10 minutes) to confirm this mechanical strength of the particle. Therefore, further mechanical strength analysis would be required and performed in our future work.

Although this demonstration of the preparation of highly ordered porous carbon particles had been succeeded, several inadequate data and disadvantages/exceptions from our method were still found and needing further studies (i.e. particle porosity, surface area, particle order (e.g. low angle X-ray Diffraction), catalytic ability, etc). Material performances (e.g. XRD analysis and material composition and pattern-related characterization) were not reported in this paper because we

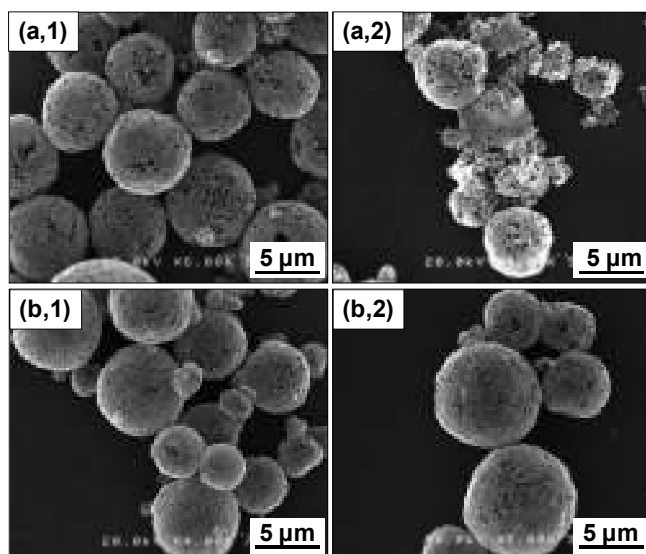


Fig. 5 Mechanical strength analysis of the particles prepared with no additional additive (a) and with additional sucrose (b). a1 and b1 are the SEM analysis of as-prepared particles (before mechanical strength analysis), while a2 and b2 are the SEM analysis of after mechanical strength analysis

used commercial carbon nanoparticles, and the heat treatment with a low-heating rate (5 °C/min) and short-holding time (600 °C; 5 minutes) would not change the material phase and pattern. However, we believe that further insights gained from research such as the present study should make other fabrication innovations possible due to its very relatively fast-fabrication, facile production, and possibility in the scaling-up production.

#### IV. CONCLUSION

In summation, macroporous carbon particles were successfully prepared using a spray-drying method. Experimental results showed that the prepared particles had a good porous arrangement and the porosity could be controlled by means of PS amount. The pore size and shape (spherical form) was identical to the initial PS, giving a potential way to control pore size.

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