Studies on Solid Carbons. I. The Formation of Solid Carbons*

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The physical and chemical properties of solid carbons are markedly affected by differences in manufacturing methods and starting material.

Many works[1-15] have reported findings by a number of researchers on the reaction kinetics of carbon formation by the pyrolysis of hydrocarbons and on the properties of the

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carbons produced, but much remains unexplored.

In this report, we are presenting the physical properties of carbons produced by the pyrolysis of hydrocarbons, which have been studied by means of electron microscopy, X-ray diffraction the B. E. T. method and the Kelvin method.

Experimental

Materials.—The applied hydrocarbons, benzene, toluene naphthalene and *n*-hexane were " extra pure grade " reagents supplied by the Wako Junyaku Co., Ltd. Ethylene was prepared by dehydrating ethyl alcohol with concentrated sulfuric acid; it was then purified by vacuum distillation. Methane was provided by the Nihon Kei Kinzoku Co., Ltd. and was passed through a concentrated potassium hydroxide aqueous solution and a calcium chloride tube. Further, this was distilled in vacuo for purification.

Apparatus and Procedure.—The apparatus used for the reaction, constructed of soda-glass except for the reaction tube, is shown in Fig. 1. In this figure, A_1 is a graduated sample vessel which was used for benzene, toluene or *n*-hexane. A_2 is a gas reservoir for methane or ethylene, and A_3 is a side tube of the reservoir. **B** is a reaction tube made of transparent quartz 2.5 cm. in diameter and 100 cm. long. In the reaction tube, porcelain insulators 0.5 cm. in diameter and 2.5 cm. long are packed to facilitate the pyrolysis of hydrocarbons.

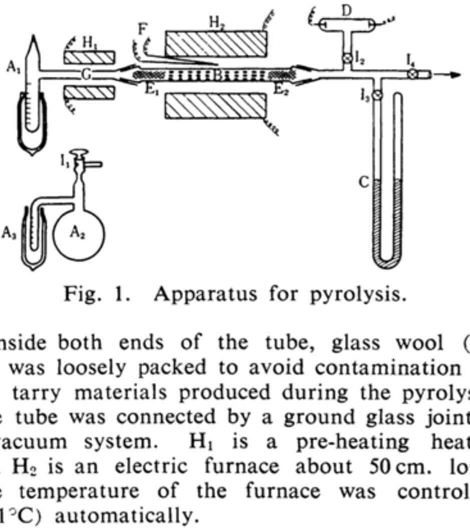


Fig. 1. Apparatus for pyrolysis.

Inside both ends of the tube, glass wool (E_1, E_2) was loosely packed to avoid contamination by the tarry materials produced during the pyrolysis. The tube was connected by a ground glass joint to a vacuum system. H_1 is a pre-heating heater, and H_2 is an electric furnace about 50 cm. long. The temperature of the furnace was controlled (±1°C) automatically.

In the case of liquid materials, a certain amount (5 cc.) of each material in A_1, kept at the temperature of liquid oxygen (−183°C), was evacuated. The liquid oxygen bath was then removed to melt the frozen material and to draw off any gas involved in it. In order to remove the gas completely, such treatments were repeated three times.

In the cases of methane and ethylene, A_2 was used instead of A_1. The materials (10 cc. of liquid state) were introduced to A_3 by cooling with a liquid oxygen bath (for methane) or with a conical aluminum powder bath, the top of which was immersed in liquid oxygen to maintain the temperature of the bath at −135°C (for ethylene).

In the case of naphthalene, 10 g. of it was loosely packed in an inlet, G.

The pyrolysis was carried out at two temperatures, 800 and 1100°C, and the flow rate of the materials was kept constant at 2.5 cc. per hour, by controlling the opening of tap I_4 and also the temperature of the sample vessel, A_1, A_3 or G. For benzene, toluene and *n*-hexane, the temperatures of the sample vessel were 23, 47 and 12°C respectively, while for methane and ethylene, they were −183 and −135°C respectively. That of naphthalene was 140°C. At these temperatures, the same vapor pressure (83 mmHg) held for all materials. The rates of the consumption of materials were measured with the graduations of the sample vessel. During the pyrolysis, part G was always heated at 200°C (except in the case of naphthalene) to prevent condensation of the materials. After a certain amount of the liquid material had been consumed, A_1 was cooled with a liquid oxygen bath to stop the reaction. In the cases of ethylene and methane, tap I_1 was closed to the stop position. Then tap I_4 was opened completely, and the reaction system was evacuated to remove the tarry substances formed during the reaction; the reaction tube was cooled, it was cut off, and the insulators which had been covered with the carbon produced were taken out. The impurities contained in all the carbon were removed by treating them with aceton and carbone tetrachloride.

The surface areas and the micro-pore size distributions of the carbons were obtained from the adsorption and the desorption of methane gas at the temperature of liquid oxygen (−183°C). The B. E. T. method was applied on the results of the adsorption isotherms to determine the surface areas of the carbons by assuming 18.1 Å^2 as the cross-sectional area of methane; Kelvin's equation was applied to the desorption isotherms to determine the micro-pore size distributions.

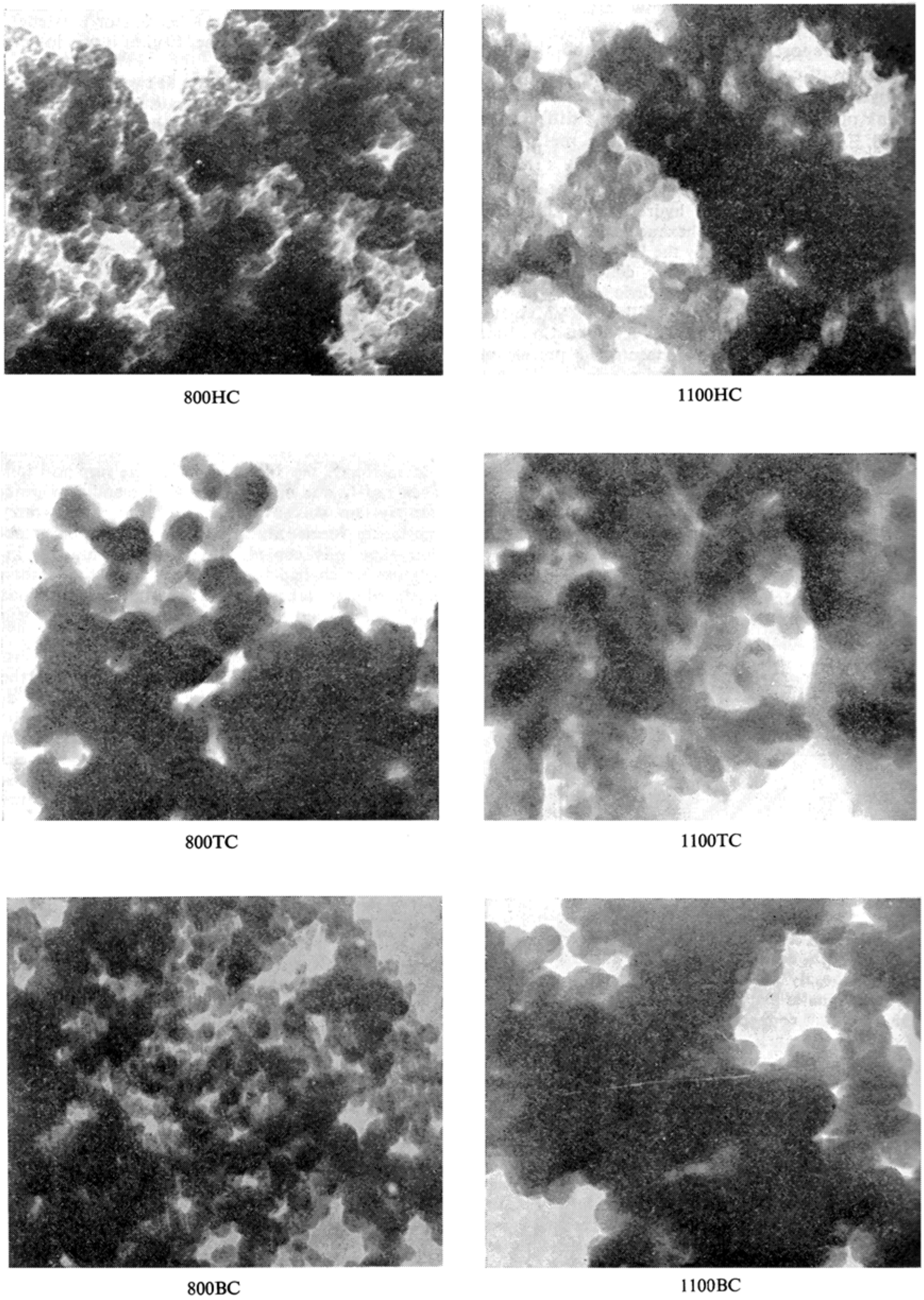
The particle shapes of the carbons were observed with an electron microscope (Type JEM-5G) made by the Japanese Electron Optics Laboratory Co., Ltd. The specimens were prepared by dispersing the carbons in alcohol by an ultrasonic waves apparatus and by scooping them on collodion film supported on a copper mesh.

The degrees of crystallization by X-ray diffraction were measured with a " Geigerflex " made by the Rigaku Denki Co., using Cu(Ni)K_α radiation after the carbons had been pulverized with a mortar.

Results and Discussion

The electron micrographs of the carbons are shown in Figs. 2 and 3. The nomenclatures 800BC, 800TC, 800HC, 800EC and 800MC denote the carbons obtained by the pyrolysis of benzene, toluene, *n*-hexane, ethylene and methane respectively at 800°C. Similarly, 1100BC, 1100TC, 1100NC, 1100EC and 1100MC denote those obtained at 1100°C.

800HC is composed of aggregates of very small particles, the shape of which can not be



800HC

1100HC

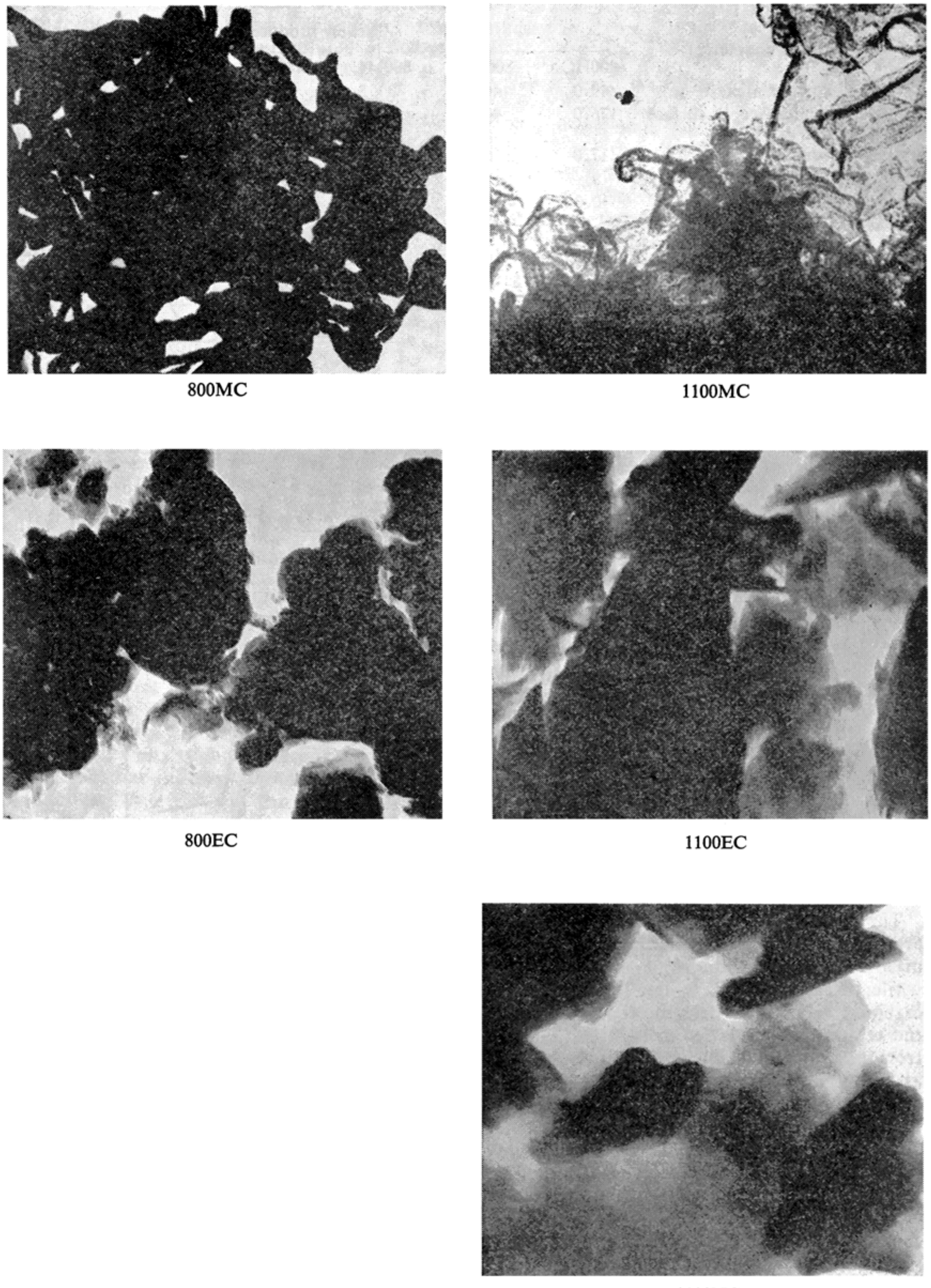
800TC

1100TC

800BC

1100BC

Fig. 2. Electron micrographs of the carbons ($\times 54000$).



800MC

1100MC

800EC

1100EC

1100NC

Fig. 3. Electron micrographs of the carbons (×54000 .

TABLE I. SURFACE CHARACTERISTICS OF THE CARBONS

Surface character	Carbon produced					
	800HC	800TC	800MC	1100HC	1100TC	1100MC
B.E.T. surface area, m²/g.	49.0	44.0	11.5	4.7	2.9	1.9
Electron microscopic surface area, m²/g.	176.0	40.0	—	—	—	—
Particle diameter, mμ	17.0	75.0	—	—	—	—
Peak micro-pore radius, Å	9	12	18	9	12	18
Micro-pore volume, cc./g.	0.06	0.07	0.03	0.01	0.01	0.01

determined exactly. From the photograph, however, we can estimate their diameters to be about 17 mμ. The samples, 800BC and 800TC, are composed of an aggregation of spherical particles with average diameters of 40 and 75 mμ respectively. The particle sizes of 800TC are almost equal, but those of 800BC are not equal to one another. 800EC is composed of irregular and thin particles. 800MC has a fiber-like shape; the intensity of its photograph is greater than that of the others, since their state is apparently more compact in the aggregation of the crystallites. The rate of the pyrolysis of naphthalene was very slow at 800°C, and no detectable amounts of carbon could be obtained. When the temperature was raised to 1100°C, the rate increased markedly. This fact accords with the findings of Kinney and DelBel³⁾.

In the cases of 1100BC, 1100TC and 1100HC, most of the boundaries of the particles become obscure or disappear, causing the formation of uniform plates. However, the diameters of the spherical particles which are found therein do not differ so from those of 800°C. On the other hand, the shape of 1100NC, 1100EC and 1100MC is plate-like, and its uniformity is greater than that of the others. Among them, that of 1100NC is the greatest*.

The results of the surface area measurement are shown in Table I. In the table, the area of 800HC is nearly the same as that of 800TC, while that of 800MC is one-fourth of these carbons; all of them decrease remarkably when the temperature is raised to 1100°C. The electron microscopic area of 800TC calculated by assuming 2.0 as their density (40 m²/g.) coincides with the B.E.T. area (44 m²/g.); however, a great difference was found in 800HC, i. e., 49 m²/g. for the B.E.T. method and 176 m²/g. for the electron microscopic method.

X-Ray diffraction patterns of produced carbons are shown in Fig. 4. The results show that the degree of crystallization depends greatly upon the reaction temperature, but not upon the starting materials, and that the crystallization advances markedly when the temperature is raised from 800 to 1100°C.

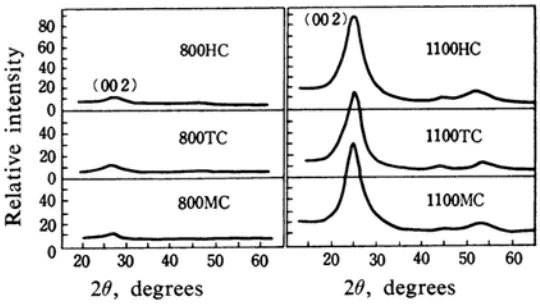


Fig. 4. X-Ray diffraction patterns of the carbons.
Cu(Ni)K_α, 30 kV., 10 mA, 32-0.8-4 sec., $2\,{}^1/_2{}^\circ-2\,{}^1/_2{}^\circ$-0.2 mm., 1°−1 cm./min.

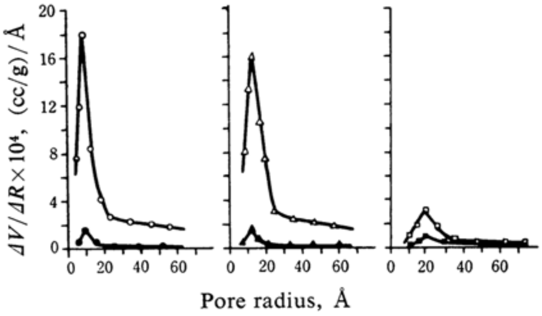


Fig. 5. Micro-pore size distribution curves for the carbons.
○ : 800HC, △ : 800TC, □ : 800MC, ● : 1100HC, ▲ : 1100TC, ■ : 1100MC.

The micro-pore size distribution is shown in Fig. 5, and the peak radii and the micro-pore volumes, which were calculated from the figures, are shown in Table I. It should be noted that each carbon kept its inherent peak radii according to the kind of starting material and that their radii did not vary with the change in the reaction temperature. This interesting result is similar to that of the study by Kipling and Wilson¹⁶⁾, who found that the

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* To know whether the particle shapes of the carbons produced are affected by the flow rate, an experiment was carried out by changing the flow rate in the range of 0.3 cc./hr. and 10 cc./hr. No obvious change was found in the shape as long as the reaction temperatures were the same.

16) J. J. Kipling and R. B. Wilson, *Trans. Faraday Soc.*, **56**, 557 (1960).

pore structure of polymer carbon was controlled by the starting material. However, further studies are required to interpret this phenomena. The micro-pore volume of 800HC was almost the same as that of 800TC, but greater than that of 800MC, and when the reaction temperature was raised to 1100°C, the volume decreased remarkably in every sample and came to be the same as the others.

The significant feature of the electron microscopic observation is as follows: in the cases of benzene, toluene and *n*-hexane, the carbons produced are composed of spherically shape particles, but not, in the cases of ethylene, methane and naphthalene. Those are composed of irregular plate-like or fiber-like shape particles. From this fact, it can be said that the shape of carbons depends upon the starting material; i. e., when the material is liquid (benzene, toluene and *n*-hexane), the shape of the carbons produced is spherical, when it is gas (ethylene and methane) or solid (naphthalene), the sharp is irregular. It can thus be assumed that the liquid material will be pyrolyzed not in the state of gas but in the state of droplets, while the solid material will be pyrolyzed in the state of gas formed by the sublimation.

A great difference in the surface area of 800HC was found between the B.E.T. area and the electron microscopic area. The occurrence of this difference would seem to be due to something about the aggregation of the minute particles; i. e., observation with the electron microscope showed that the aggregation is recognizably very tight. Therefore, it can be considered that the gas used in the observation of the B.E.T. area was not permitted to penetrate the interstices of the minute particles. A very small peak radius was found in the micro-pore size distribution curve of 800HC (see Table I). This result might be ascribed to the fact that this carbon is composed of minute particles aggregated very tightly. Such a supposition agrees well with the observation made about the discrepancy found in both areas. When the reaction temperature was raised to 1100°C, remarkable decreases in the B.E.T. area and in the micro-pore volume of the carbons and a change in the carbon particle shape were observed. This result would be due to the development of the crystallization.

Quantative interpretation of the mechanism of carbon formation will be made in further studies.

Summary

The pyrolysis of six different pure organic compounds (benzene, toluene, naphthalene, ethylene, *n*-hexane and methane) has been studied to discover the relation between the starting materials and the carbon produced. The B.E.T. area, micro-pore size distribution, particle shape, and degree of crystallization have been measured in the carbon produced. The carbonization has been carried out by pyrolyzing the material by means of the flow method at the two temperatures of 800 and 1100°C, keeping the flow rate constant at 2.5 cc./hr. and the vapor pressure at 83 mmHg.

The order of the B.E.T. areas, A, of the carbons produced by pyrolysis is as follows: at 800°C, A(hexane), 49.0 $>$ A(toluene), 44.0 $>$ A(methane), 11.5, and at 1100°C, A(hexane), 4.7 $>$ A(toluene), 2.9 $>$ A (methane), 1.9 respectively.

The peak radii, $\boldsymbol{R}$, of the micro-pore size distribution curves are not changed by the raising of the reaction temperature (800, 1100°C); the order of the radii is R(methane), 18 $>$ R(toluene), 12 $>$ R(hexane), 9. Notwithstanding the fact that the peak radii are not changed by the reaction temperature, the micro-pore volumes diminish remarkably.

Electron microscope observation has shown that the shape of the particle is affected by the physical state of the starting material during pyrolysis. If the material is gaseous, plate-like carbon is obtained. If the material is liquid, spherical carbon is obtained.

X-Ray diffraction has shown that the degree of crystallization is not affected by the kind of material. When the temperature of pyrolysis is raised from 800 to 1100°C, the crystallization advances markedly.

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