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Surface Treatment of *meso*-Carbon Microbeads by Oxygen Plasma

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A surface treatment of *meso*-carbon microbeads was carried out using an oxygen plasma to improve the wettability in aqueous solution. The surface acidity of *meso*-carbon microbeads increased with treating time and the pH of the aqueous dispersion shifted to lower values. The zeta potential varied with treating time from a positive to a negative value. Further, the turbidity behavior of aqueous dispersion with treating time was similar to that of surface acidity. From these results, it was found that the surfaces of *meso*-carbon microbeads were oxidized by oxygen plasma, resulting in an enhancement of wettability of *meso*-carbon microbeads in an aqueous solution.

It is well known[1] that a mesophase transformation takes place in graphitizable organic materials (such as pitches) during pyrolysis at temperatures between 350 and 500 °C. During the heat treatment of pitches, mesophase spherule is formed due to an accumulation of oriented polycondensed aromatic hydrocarbons. The mesophase spherules that separated as quinoline insolubles from the mesophase pitches are called *meso*-carbon microbeads.

These do not melt or fuse upon a heat treatment and do not dissolve at room temperature in organic solvents such as quinoline, pyridine and benzene. From the chemical reactivity,[2] the pore structure,[3] the adsorption-desorption isotherms, and the heat-of-immersion,[4] of the *meso*-carbon microbeads, it has been recognized that the constituent unit of *meso*-carbon microbeads is a micelle composed of the molecules and that the micelles lie perpendicular to a pole of the sphere, as in the Taylor model.[5] The exteriors of *meso*-carbon microbeads melt in a medium of polynuclear aromatic hydrocarbons or pitch materials during a heat treatment. The *meso*-carbon microbeads in liquids similar to pitch under heat treatment behave in a similar manner as mesophase spherules produced in pitch during a heating.

In polycyclic aromatics, the reactivity of the edge carbon atoms at the periphery is very high, as is well known. Therefore, the surfaces of *meso*-carbon microbeads are interesting from the view point of the surface chemistry of solids. Hagiwara *et al.*[6] examined the possibility of using *meso*-carbon microbeads as a chromatographic filler. They confirmed that benzene derivatives could be separated using *meso*-carbon microbeads treated with a Friedel-Crafts reaction. When *meso*-carbon microbeads are used in an aqueous solution, there is a wetting problem since *meso*-carbon microbeads exhibit hydrophobic properties.

Recently, as one method for surface treatment, a plasma treatment[7] has become attractive, probably due to it being a dry process at low temperatures with a relatively low-pressure gas.

In this work, changes in the surface properties of *meso*-carbon microbeads upon a treatment of oxygen plasma were examined by measuring the surface acidity, surface charge, turbidity, and pH of *meso*-carbon microbeads in an aqueous solution.

Experimental

Materials. *Meso*-carbon microbeads were obtained through a separation from heat-treated quinoline soluble coal-tar pitch. The physical properties of the obtained *meso*-carbon microbeads were as follows: quinoline insoluble, 92.3%; benzene insoluble, 97.0%; volatile matter, 17.3%; ash, 0.3%; C/H=2.314; diameter, 2-15 μm.

Procedure. About 3 grams of *meso*-carbon microbeads were charged into a reactant vessel, followed by degassing down to 1.5 Torr. Then, oxygen gas was flowed at a rate of 100 ml/min into the vessel while evacuated *meso*-carbon microbeads were being treated with an oxygen plasma under various high-frequency powers and treating times. The pressure during the treatment was kept at about 3 Torr†. The high-frequency power used in this study was 25, 50, and 100 W, and the treating times were 1, 2, 3, and 4 h, respectively.

Measurements. About 0.1 grams of *meso*-carbon microbeads were put into 50 ml of deionized water, boiled for 15 min, then allowed to stand for 2 d. The, thus obtained, suspension's pH was measured with a pH meter (Denki Kagaku Keiki Co. Ltd.).

The zeta potential of the suspension used for the pH measurement was determined by an electrophoresis apparatus (Laser-Zee Model 500, Pen Kem.).

About 0.1 grams of *meso*-carbon microbeads were put into a sedimentation tube and 30 ml of deionized water was added. Then the solution was dispersed by supersonic waves for half an hour and the turbidity of the dispersion was measured after 1 d of standing.

The acidity of surface functional groups of *meso*-carbon microbeads was determined by a titration method which was the same as that Boehm[8] used. About 1 gram of *meso*-carbon microbeads and a 50-ml aqueous solution of 50 ml ($NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$) of 0.05

† 1 Torr=133.322 Pa.

to 0.1 M†† were placed in an Erlenmeyer flask. After shaking for 1 d at 25 °C, it was allowed to stand for 4 d; then, after centrifuging, 20 ml of the supernatant solution was titrated with 0.1 M HCl. At the same time, a blank test was carried out. From the difference in the titrations, the acidity of *meso*-carbon microbeads was evaluated.

Results and Discussion

The *meso*-carbon microbeads were treated with the oxygen plasma under conditions such as high-frequency power (25, 50, and 100 W) and an oxygen-flow rate of 100 ml min^{-1}. The plasma-treated samples were used for measuring the turbidity in an aqueous solution. The result is given in Fig. 1. The turbidity of the samples increased with an increased treating time. A maximum value appeared at 3 h; then, it decreased slightly for three different high-frequency powers. Further, the turbidity of the treated *meso*-carbon microbeads decreased upon increasing the high-frequency power. Thus, from the turbidity results, it is apparent that the *meso*-carbon microbeads become wettable in an aqueous solution upon treatment with an oxygen plasma.

To elucidate the surface charge of *meso*-carbon microbeads treated with the oxygen plasma, the zeta potential of treated samples in an aqueous solution was measured. At the same time, the pH of the dispersion was also measured. As shown in Fig. 2, the zeta potential of the untreated sample was positive. After the plasma treatment, the zeta potential became negative and reached a constant value after 1 h. It should be noted that the magnitude of zeta potential of the sample treated with the oxygen plasma increased upon decreasing the high-frequency power. From the facts that the pH of the aqueous dispersion of the plasma-treated samples was at around 5—4.5 and their zeta potential values were negative, the surface functional groups formed by the oxygen plasma treatment were acidic groups. Indeed, Ihara *et al.*[9] examined the surface functional groups of carbon black treated with oxygen plasma and they found that these groups were carboxyl, phenolic, and carbonyl groups and the concentrations of these groups varied with the

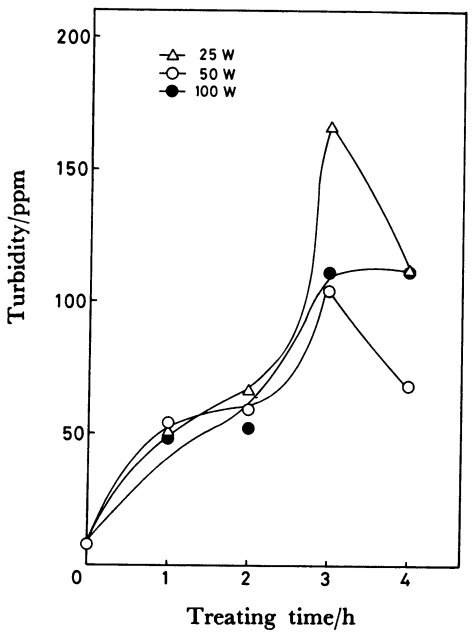

Fig. 1. The turbidity of aqueous dispersion of *meso*-carbon microbeads treated with oxygen plasma under various conditions.

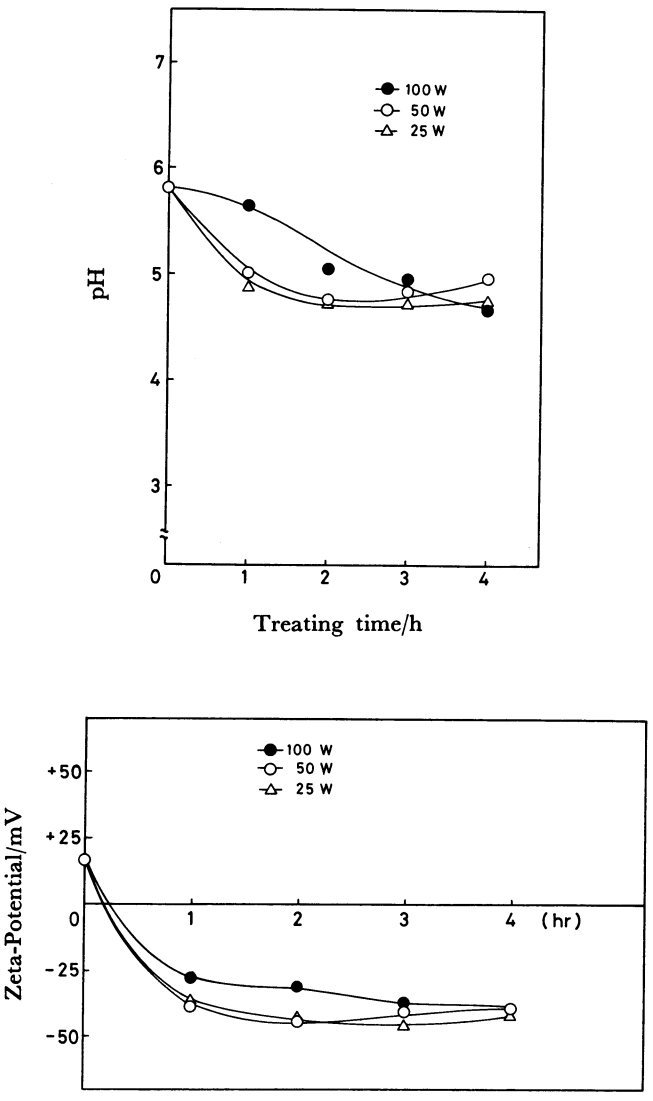

Fig. 2. The zeta potential and pH of aqueous dispersion of *meso*-carbon microbeads treated with oxygen plasma under various conditions.

1 M=1 mol dm^{-3}.

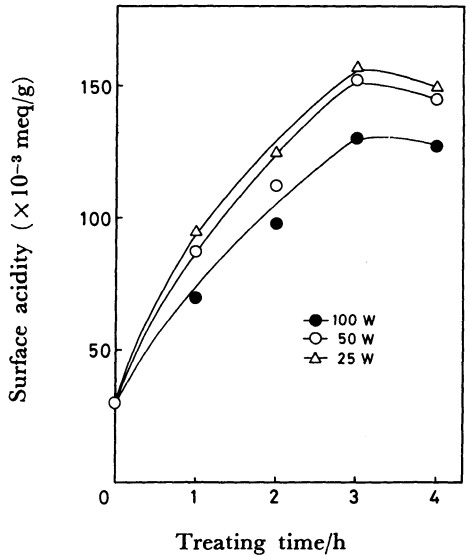

Fig. 3. The change in concentrations of surface functional groups as a function of treating time under various high-frequency powers.

Table 1. Concentrations of surface functional grours by oxygen plasma

Frequency power (W)	Treating time (h)	$\times 10^{-3}$ meg/g			
		Carboxyl	Phenolic	Carbonyl	Total
Untreated		5	12.5	12.5	30
25	1	60	15	20	95
	2	65	57.5	0	125
	3	70	70	17.5	157.5
	4	95	55	0	150
50	1	42.5	20	25	87
	2	82.5	15	15	112.5
	3	87.5	37.5	27.5	152.5
	4	65	0	67.2	132.2
100	1	30	40	0	70
	2	50	45	0	95
	3	100	30	0	130
	4	62.5	30	35	127.5

high-frequency power and treating time. In this work, the concentrations of surface functional groups were also determined by titration. The results are shown in Table 1 and Fig. 3. These functional groups(-COOH, -OH, C=O) were formed by the oxidation of *meso*-carbon microbeads as the oxygen plasma and the concentrations of these groups increased with the treating time, reached a maximum and then decreased. At each treating time, the order in the total concentrations of these groups was as follows: 25 W>50 W>100 W. This decrement in the total concentration of functional groups with longer treating times is probably due to a burn-off of the functional groups by a further oxygen plasma. Accordingly, in order to attain a maximum concentration of functional groups, a proper condition should be selected. It is noteworthy that even after the oxygen-plasma treatment, the surface area of the *meso*-carbon microbeads determined by nitrogen gas adsorption changed only a little compared with that for an untreated sample.

Compared with carbon black,[9] the *meso*-carbon microbeads were less oxidized due to the oxygen plasma. A maximum concentration of functional groups for *meso*-carbon microbeads was obtained at a treating time of 3 h. However, the concentrations of functional groups for carbon black[9] increased linearly with the treating time.

From the above results, it is concluded that the surfaces of *meso*-carbon microbeads become oxidized through the oxygen plasma, resulting in the formation of surface functional groups such as -COOH, -OH. Also, the wettability of *meso*-carbon microbeads treated with oxygen plasma in an aqueous solution is improved. Therefore, it is anticipated that the adsorption capacity for water-soluble materials would be enhanced upon using the *meso*-carbon microbeads treated with an oxygen plasma as the adsorbent.

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