Fixation of Ultra-fine Platinum Particles On Meso-carbon microbeads

Hitoshi Nozaki, Masaya Kodama, Kunio Esumi, Kenjiro Meguro, and
Hidemasa Honda

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Department of Applied Chemistry and Institute of Colloid and
Interface Science, Science University of Tokyo, 1-3 Kagurazaka,
Shinjuku-ku, Tokyo 162

Fixation of ultra-fine platinum particles on meso-carbon microbeads was carried out. The fixation of the platinum particles with negatively charges was enhanced when the microbeads were treated with ammonia plasma due to electrical attraction forces between negatively charged platinum and positively charged microbeads in aqueous solution. Further, the magnitude of the fixation was dependent on the preparation method and heat-treatment temperature of microbeads.

KEYWORDS: *Meso-carbon microbeads, Fixation, Ultra-fine platinum particles, Plasma treatment.*

Introduction

It is widely known^{1),2)} that mesophase transformation takes place in graphitizable organic materials, such as pitches, during pyrolysis at temperatures between 350 and 500°C. In the primary stage of mesophase formation, the carbonaceous mesophase appears as optically anisotropic small spherules suspended in the optically isotropic matrix. Since these mesophase spherules are usually insoluble in a number of organic solvents, they can be separated from the pitch matrix by solvent fractionation, and named "meso-carbon microbeads"³⁾. Recently, meso-carbon microbeads have been prepared by spheroidization of fusible bulk mesophase pitch in liquid medium⁷⁾.

Although several works¹⁾⁻⁶⁾ relating to the meso-carbon microbeads have been reported, most of the works have been limited to formation mechanism and structure analysis. Since meso-carbon microbeads have a relatively large electroconductivity⁸⁾, it is expected that meso-carbon microbeads can be used as catalyst support for an electrode. In this work as a first step for preparing catalyst using meso-carbon microbeads as a support, the fixation of colloidal platinum particles to meso-carbon microbeads

was studied by measuring the zeta-potential of meso-carbon microbeads and the adsorbed amount of platinum particles on meso-carbon microbeads.

Materials

Meso-carbon microbeads separated by heat treatment of coal-tar pitch are classified into two groups; one has free carbon (quinoline insoluble fraction) around the surface of beads which is called MCB-1 (Type-M) and another one without free carbon is called MCB-2 (Type-C). Meso-carbon microbeads spheroidized⁷⁾ in liquid medium from fusible bulk mesophase pitch at a high temperature are called MCB-3. The analytical values for these MCB are given in Table 1.

Table 1 Analytical data for meso-carbon microbeads.

Sample	Quinoline insoluble (wt%)	Volatile matter (wt%)	Ash (wt%)	Density (g/cm ³)	Diameter (μm)
MCB-1	92.0	13.2	0.20	1.4	24.0
MCB-2	97.3	7.7	0.14	1.4	14.3
MCB-3	38.9	—	<0.10	1.4	22.2

Experimental

Preparation of platinum sol

Platinum sol was prepared by reduction of chloroplatinic acid with sodium citrate⁹). The details of the preparation procedure were as follows: 960 cm³ of water was heated in a round-bottomed flask to the required reaction temperature (100°C) and then 30 cm³ of aqueous chloroplatinic acid solution was added. After the temperature was reestablished, 120 cm³ of 1 wt% aqueous sodium citrate was then added and the mixture was vigorously stirred at 100°C for 2 hours. Then, the mixture was cooled rapidly to room temperature. Excess sodium citrate and some unreduced chloroplatinic acid were removed from the colloidal platinum with a mixed-bed ion exchange (Amberlite MB1) until the conductivity was $<10^{-1} \Omega^{-1} \text{cm}^{-1}$. Particle size obtained by this method was about 20 Å, which was determined by means of a transmission electron microscopy.

Plasma treatment

About 5 g of MCB was charged into a rotary reactor, followed by evacuating to 3 Torr. Each gas was then passed at a rate of 100 ml min⁻¹ into the reactor while MCB were treated using glow discharge generated by a rate frequency of 13.57 MHz under high-frequency. The high-frequency power used in this study was 50 W, and the treatment times were 30 minutes (NH₃), and 1 hour (N₂).

Measurements

About 0.02 g of plasma-treated MCB were dispersed in water, and then the platinum sol was added into it, where the total volume was made 50 ml by addition of some water. Then, platinum particles were adsorbed on the MCB for 10 minutes under ultrasonic treatment. After centrifuging the suspension to separate MCB, the absorbance of the supernatant solution at 400 nm, which is assigned to platinum sol, was measured. The adsorbed amount of platinum particles was determined from the differences of the absorbance before and after the addition of platinum sol. Here, it should be noted that the platinum particles were not sedimented under the centrifugation condition.

The zeta-potentials of MCB and platinum

particles were determined by an electrophoretic method.

The rinsing of platinum adsorbed MCB to study interaction force between platinum particle and MCB was carried out as follows: The suspension (platinum sol + MCB) prepared above was centrifuged and the supernatant was discarded. Then, 50 ml of deionized water was added into the platinum adsorbed MCB and the suspension was dispersed by ultrasonic waves for 10 min. The zeta-potential of the platinum adsorbed MCB was measured. This rinsing process was continued to five times.

The ESCA spectra of MCB treated by the plasma were recorded on a ESCALAB MkII (VG Scientific).

Dip coating method

About 1 g of MCB was put into 50 ml of chloroplatinic acid solution (Pt 0.2 mg ml⁻¹), and impregnated for 100 hours at room temperature¹⁰). After drying, the samples were reduced at 500°C in a nitrogen atmosphere.

The amount of platinum adsorbed on MCB by the dip coating was determined from the difference of the absorbance before and after the samples impregnated. The fixation state of platinum on the MCB was observed by a transmission electron microscopy.

Results and discussion

The changes in the zeta-potentials of the platinum particles, non-plasma-treated MCB, and the ammonia plasma-treated MCB in various pH of aqueous solution are given in Fig. 1. It is seen that the ammonia plasma treatment renders the zeta-potentials of MCB much more positive, and the isoelectric point shifts to higher values. It is noteworthy that the ammonia plasma treatment renders MCB wettable in aqueous solution. From the ESCA spectrum, a new band for the ammonia plasma-treated MCB-1 was observed at 401 eV which was assigned to the amino group. Esumi *et al.*¹¹) also reported that the amino group formation on MCB is confirmed by FTIR spectra. Thus, it is suggested that the increment in the zeta-potential of ammonia plasma-treated MCB-1 is due to the formation of amino group, resulting in basic surface property. However, non-treated

MCB were hardly wetttable in aqueous solution. In particular, in this study, fixation of platinum particles on MCB is notably affected by dispersibility of MCB in aqueous solution. On the other hand, the zeta-potentials of the platinum particles were constant against pH (Fig. 1).

Fig. 1 Zeta potentials of Pt particles, non-plasma treated MCB, and ammonia plasma treated MCB vs. pH in aqueous solution:

- , MCB-1 (as-prep.),
- △, MCB-1 (ammonia plasma),
- , MCB-2 (as-prep.),
- ▲, MCB-2 (ammonia plasma),
- ◐, MCB-3 (as-prep.),
- ◑, MCB-3 (ammonia plasma),
- , Pt particles.

Thus, it is found that the plasma-treated MCB have positive charge, while the platinum particles have negative charge in acidic region. Accordingly, the fixation of platinum particles on MCB was performed in acidic region (pH4), because their zeta-potentials were opposite and the difference in the magnitude of the zeta-potential was significant.

The changes in the zeta-potential of non-plasma-treated and the ammonia plasma-treated MCB-1 upon addition of various amounts of platinum sol and of the adsorbed amount of platinum particles on each MCB are given in Fig. 2(a). As the platinum sol was added to the aqueous dispersion of the plasma-treated MCB, the zeta-potentials of MCB decreased and became negative, finally reached constant values. Cor-

Fig. 2. Changes in zeta potentials and adsorbed amount of Pt for MCB with additive amount of Pt sol.

- (a) MCB-1; closed symbols, non-plasma treated MCB
- ; open symbols, ammonia plasma treated MCB.

Fig. 2 (b) MCB-2; ammonia plasma treated.

Fig. 2 (c) MCB-3; ammonia plasma treated.

responding to the change in the zeta-potentials, the adsorbed amount of platinum particles increased and became constant. This result indicates that since the platinum particles having negative charge are adsorbed on the surface of MCB, the zeta-potentials of MCB decrease and become constant when the adsorption is saturated. On the other hand, the adsorbed amount of platinum particles on non-plasma-treated sample was considerable small as compared with that on the ammonia plasma-treated MCB, because non-plasma-treated MCB was hardly wettable and its aqueous dispersion was unstable. A similar behavior was observed for MCB-2 and MCB-3 (Figs. 2(b) and 2(c)). However, the adsorbed amount of platinum particles on MCB-3 was considerably small compared with those of MCB-1 and MCB-2, indicating that the ammonia plasma treatment is less effective for MCB-3 than for the others. These differences may be derived from differences in chemical components and orientation of molecules consisting the mesophase structure among three kinds of MCB. The interaction force between MCB and platinum particles was examined indirectly using the rinsing process. The change in the zeta-potentials of MCB adsorbing platinum particles by the number of rinsing is given in Fig. 3. The zeta-potentials of each sample hardly changed with the number of rinsing, indicating that most of the platinum particles are still

Fig. 3 Changes in zeta potentials of MCB adsorbing Pt particles with number of rinsing:
○, MCB-1; △, MCB-2; □, MCB-3.

adsorbed on MCB, probably due to electric attraction forces.

Further, the fixation of platinum particles on the heat-treated and plasma-treated MCB was examined. The MCB (MCB-1) were heat treated over a range from 500 to 1000°C for 1 hr in a nitrogen atmosphere. It has already been reported¹²⁾ that the isoelectric point of heat-treated MCB-1 shifts to a higher values by the ammonia plasma treatment, but the effect of the plasma treatment becomes weak with an increase of the heat treatment temperature. This result has been interpreted as follows: MCB are carbonized with increasing the heat treatment temperature, resulting in increase of the ratio of C/H of MCB. Therefore, the chemical reactivity of MCB becomes lower with increasing heat treatment temperature. The zeta-potential and adsorbed amount of platinum particles on the heat-treated and plasma-treated MCB-1 are shown in Fig. 4. The adsorbed amount of platinum particles on as-prepared sample was largest and it decreased as follows; 700°C > 500°C > 1000°C. At 700°C, the orientation of lamellae structure in MCB is most distorted by pyrolysis and polycondensation reactions¹³⁾. As a result, many slit-like micropores which are attributed to the inter-lamellae spacings are formed, so that the adsorbed amount would increase.

Fig. 4 Zeta potential and adsorbed amount of Pt particles on heat treated and nitrogen plasma treated MCB-1:
○, △, non-heat treated; ●, ▲, 500°C;
⦿, ⬤, 700°C; ⦿, ⬤, 1000°C.

Fig. 5 Transmission electron micrographs of MCB-1.

- (a) as-prep. MCB-1. (b) nitrogen plasma treated MCB-1.
(c) colloidal Pt on nitrogen plasma treated MCB-1.

The adsorption state of platinum particles on MCB was observed by a transmission electron microscopy (Fig. 5). From the micrography images, it is observed that the platinum particles are adsorbed to some extent as coagulate.

The fixation of colloidal platinum particles was compared with the impregnation method whose results are given in Table 2. The impregnated amount on the ammonia plasma-treated MCB was also larger than that of non-plasma-treated sample, probably due to lower wettability of non-plasma-treated sample in aqueous solution. The chloroplatinic acid ion is a complex anion, and it can be adsorbed on the positively charged sites on MCB which were formed by the ammonia plasma treatment.

Table 2 Impregnated amount of Pt on meso-carbon microbeads treated with plasma

Sample	Plasma treatment	Impregnated amount (mg-Pt/g)
MCB-1	as-prep.	3.6
	N ₂	5.6
	NH ₃	5.2
MCB-2	as-prep.	1.6
	NH ₃	6.2
MCB-3	as-prep.	2.7
	NH ₃	3.6

Accordingly, the ammonia plasma-treated MCB showed a large impregnated amount. Compared with the colloidal method, the fixed amount of

platinum particles on MCB by the dip coating method is smaller. However, it seems likely from the microscopy images that the platinum particle size by the dip coating method is smaller than that by the colloidal method.

This study shows that fixation of ultra fine platinum particles on MCB is greatly enhanced by the ammonia plasma treatment of MCB due to electric attraction forces. The magnitude of the fixation depends on the preparation method of MCB; MCB-1 and MCB-2 (Type-M and Type-C) show a large fixation capacity compared with that by spheroidization of fusible bulk mesophase pitch in a liquid medium. Further, it is found that the fixation amount of platinum particles by the colloidal method is larger than that by the dip coating method.

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