JOURNAL OF MATERIALS SCIENCE 26 (1991) 1363–1367

Synthesis and properties of platinum-dispersed carbon by pressure pyrolysis of organoplatinum copolymer

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Platinum-dispersed carbon was synthesized by pressure pyrolysis of divinylbenzene-*bis*(2-allylphenyl)platinum (APPt) and phenylacetylene-APPt at 550 °C and 125 MPa. The crystallinity of platinum dispersed in the carbon matrix synthesized from phenylacetylene(PA)-APPt was higher than that from divinylbenzene(DVB)-APPt. Platinum particles less than 60 nm were dispersed in the carbon matrix synthesized from DVB-APPt at 550 °C and 125 MPa. The carbon matrix formed from PA-APPt contained platinum particles of about 120 nm. The specific area of platinum-dispersed carbon synthesized at 550 °C and 125 MPa increased on subsequent heat treatments in argon, and reached 90 $m^2 g^{-1}$ after heat treatment at 800 °C for 1 h. The activity of platinum-dispersed carbon for the hydrogenation of cyclohexene increased with increasing specific area. Platinum-dispersed carbon formed from DVB-APPt was more active for hydrogenation reaction than that from PA-APPt. The highly active platinum-dispersed carbon could be synthesized from DVB-APPt at 520 °C. The surface area reached 154 $m^2 g^{-1}$ after heat treatment at 800 °C.

1. Introduction

Metal-dispersed carbon of controlled morphology is used in many kinds of applications such as magnetic materials and catalysts. Organometallic polymers are versatile starting materials for the synthesis of carbons dispersed finely with metal particles by the pyrolysis method. Pressure pyrolysis of organometallic polymer for the synthesis of carbon has the great advantages of a high yield of carbon as well as control of the carbon morphology [1–11]. Several ferromagnetic and alloy particles, such as Fe [3, 9], Co [4], Ni [5], Fe compounds [3, 7], and Fe–Co alloy [6], can be dispersed uniformly in the carbon matrix by pressure pyrolysis of organometallic polymers.

The magnetic properties of metal-dispersed carbon reflect the crystallinity and the particle size of metals, which have been found to depend strongly upon the properties of both the carbon–metal bond of organometallic compounds and the carbon–carbon bond of the polymer matrix [4, 7, 8]. Three-dimensional cross-linkage of starting divinylbenzene polymer is favoured over polystyrene in terms of the dispersion state of fine metal particles in the resulting carbon [7]. A thermally stable cobalt–carbon bond is suitable for the synthesis of carbons with finely dispersed cobalt particles [4]. The morphology of as-prepared carbon is affected by the concentrations of metals and water in the starting polymer, as well as pyrolysis conditions [3, 10]. Spherulitic carbons dispersed with magnetite particles could be synthesized by pressure pyrolysis of divinylbenzene-vinylferrocene and water mixture [10].

The present paper describes the synthesis and properties of platinum-dispersed carbon by pressure pyrolysis of organoplatinum copolymers. Two kinds of organic compounds, divinylbenzene (DVB) and phenylacetylene (PA), were used as parent polymer matrices. The properties of platinum-dispersed carbon were investigated in order to elucidate the chemical characteristics of two kinds of starting polymers. DVB was found to be superior to PA for the synthesis of platinum-dispersed carbon with high catalytic activity.

2. Experimental procedure

2.1. Starting materials

Bis(2-allylphenyl)platinum (APPt) was prepared according to Aresta and Nyholm [12]. Commercially available divinylbenzene (a mixture of 55% *m*-and *p*-divinylbenzene and 45% ethylbenzene) and phenylacetylene were employed for the synthesis of starting polymer matrix.

2.2. Synthesis of platinum-dispersed carbon

Pressure pyrolyses were carried out in a hydrothermal apparatus of the cold-seal type [2]. A mixed solution of *bis*(2-allylphenyl)platinum (APPt) and divinylbenzene (DVB) or phenylacetylene (PA) was sealed

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into a thin-walled gold capsule of 3.0 or 5.0 mm diameter and 50 mm length.

Various solutions of DVB or PA containing APPt were polymerized at 300 °C and 100 MPa for 2 h and then pyrolysed at temperatures from 520 to 550 °C and 125 MPa for 3 h. The heating rate was 10 °C min^{-1} at 125 MPa. The pressure was kept constant by releasing water as the pressure-transporting medium during heating. The pressure was measured with a calibrated Heise gauge and the temperature was measured with a calibrated sheathed thermocouple set inside the pressure vessel. The sample was quenched after each experimental run.

2.3. Characterization of organoplatinum copolymer and platinum-dispersed carbon

Infrared spectra were measured using a liquid-film method using a KBr plate and by a KBr disc method.

The yield of carbon was as high as about 80% of the starting copolymer in weight. The carbonized product was analysed by X-ray diffraction (XRD) analysis with CuK_α radiation. Synthesized platinum-dispersed carbons were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction analysis.

As-prepared platinum-dispersed carbon set in a graphite crucible was heat-treated at temperatures from 400 to 800 °C in a flow of argon. Then, the specific surface area was measured by a BET analyser utilizing the continuous flow method.

2.4. Hydrogenation of cyclohexene with platinum-dispersed carbon

The hydrogenation reaction of cyclohexene was carried out as follows. Cyclohexene (141.2 mg, 1.68 mmol) and platinum-dispersed carbon (30 mg containing 2.0 wt % Pt) were mixed in 5 ml *n*-hexane as a solvent in a reaction flask. The flask was purged with hydrogen gas and then the reaction mixture was stirred in hydrogen at room temperature. The reaction mixture was analysed by gas chromatography (GC) after 24, 48 and 72 h.

3. Results and discussion

3.1. Synthesis of platinum-dispersed carbon

3.1.1. Synthesis of starting organoplatinum copolymers

Divinylbenzene (DVB) and phenylacetylene (PA) have two double bonds and a triple bond, respectively, for copolymerization with *bis*(2-allylphenyl)platinum (APPt). After heat treatment of both starting mixtures at 300 °C and 100 MPa for 2 h, the absorption bands at 1530 and 1260 cm^{-1} ascribed to the double bond of APPt [12] disappeared in their infrared spectra.

3.1.2. Pyrolysis of DVB-APPt and PA-APPt

DVB-2.5 mol % *bis*(2-allylphenyl)platinum (APPt) (2.0 wt % Pt) and PA-1.1 mol % APPt (2.0 wt % Pt) were copolymerized at 300 °C and 100 MPa for 2 h and then pyrolysed at 550 °C and 125 MPa for 3 h.

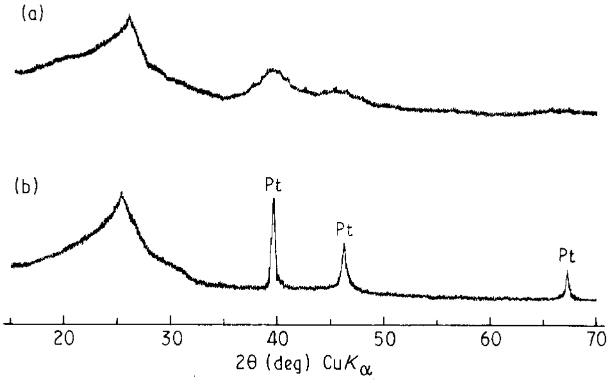

Figure 1 X-ray diffraction profiles of platinum-dispersed carbon synthesized from organoplatinum copolymer at 550 °C and 125 MPa. (a) Platinum-dispersed carbon synthesized from DVB-2.5 mol % APPt (2.0 wt % Pt). (b) Platinum-dispersed carbon formed from PA-1.1 mol % APPt (2.0 wt % Pt).

XRD profiles of the products from DVB-APPt and PA-APPt are shown in Fig. 1a and b, respectively. The broad diffraction peak centred at $2\theta = 25.5°$ of both the products is attributed to the turbostratic carbon structure. The sharp reflections at $2\theta = 39.8°$, 46.2° and 67.5° in Fig. 1b are based upon the 1 1 1, 2 0 0 and 2 2 0 reflections of platinum. The broad diffractions from $2\theta = 35°$ to 50° in Fig. 1a are ascribed to those of platinum with low crystallinity.

The crystallinity of platinum dispersed in the carbon matrix formed from the PA-APPt copolymer is higher than that from the DVB-APPt copolymer. The crystallinity of platinum dispersed in the resultant carbon matrix was strongly dependent on the nature of the bond of the starting copolymers. DVB is known to form a three-dimensional structure via the benzene ring after pressure polymerization [2, 13], whereas no such three-dimensional structure is formed in the pressure-polymerized PA. The three-dimensional matrix of DVB polymer prevents the aggregation of metal particles more effectively than polystyrene [7]. Similarly, the aggregation and crystallization of platinum particles are more favourable in PA copolymer than in DVB copolymer.

3.2. Particle size of platinum in the resultant carbon

Microstructures of pyrolysis products from DVB-2.5 mol % APPt (2.0 wt % Pt) and PA-1.1 mol % APPt (2.0 wt % Pt) at 550 °C and 125 MPa are shown in Fig. 2a and b, respectively. The black particles dispersed in the carbon matrix were confirmed to be platinum by electron diffraction.

The size of the platinum particles synthesized from DVB-APPt was less than 60 nm, while particles up to 120 nm were dispersed in the carbon matrix formed from PA-APPt. The difference in the size of the platinum particles reflects the different three-dimensional structures of the starting polymers. The platinum particles in the carbon matrix formed from PA-APPt both have higher crystallinity and a larger particle size than those from DVB-APPt.

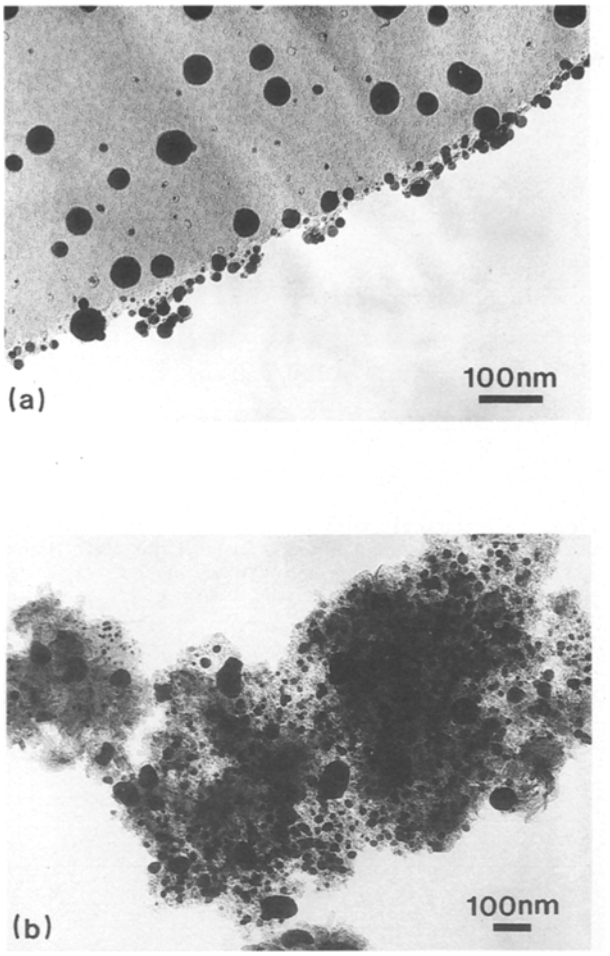

Figure 2 Microstructure of carbon dispersed with platinum particles. (a) Carbon formed from DVB-2.5 mol % APPt at 550 °C and 125 MPa. (b) Carbon formed from PA-1.1 mol % APPt at 550 °C and 125 MPa.

3.3. Effect of heat treatment on properties of platinum-dispersed carbon

3.3.1. Changes of specific area by heat treatment

Platinum-dispersed carbon was synthesized from DVB-2.5 mol % APPt (2.0 wt % Pt) at 550 °C and 125 MPa for 3 h. The surface area of the as-prepared platinum-dispersed carbon was several $m^2 g^{-1}$.

The variation of specific area with heat-treatment temperature is shown in Fig. 3. The specific area increased with increasing heat-treatment temperature from 400 to 800 °C. The specific area of platinum-dispersed carbon increased to above $50 m^2 g^{-1}$ on heat treatment above 600 °C (Fig. 3).

Fig. 3 also shows the specific area of platinum-dispersed carbon formed from PA-APPt. The surface area increased similarly to the case of DVB-APPt on subsequent heat treatment. However, the specific area after heat treatment at 800 °C was only $23 m^2 g^{-1}$, which was less than one-third that from DVB-APPt.

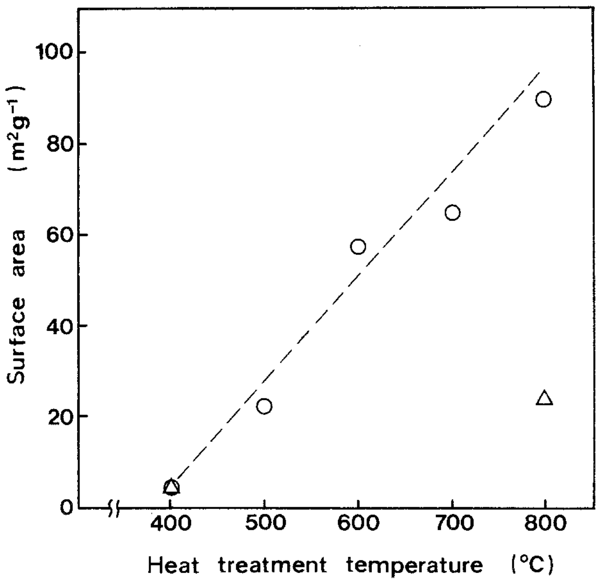

Figure 3 Changes of specific area of platinum-dispersed carbon synthesized from organoplatinum copolymers at 550 °C and 125 MPa with subsequent heat treatment from 400 to 800 °C in flow of argon. (○) Platinum-dispersed carbon from DVB-APPt, (△) platinum-dispersed carbon from PA-APPt.

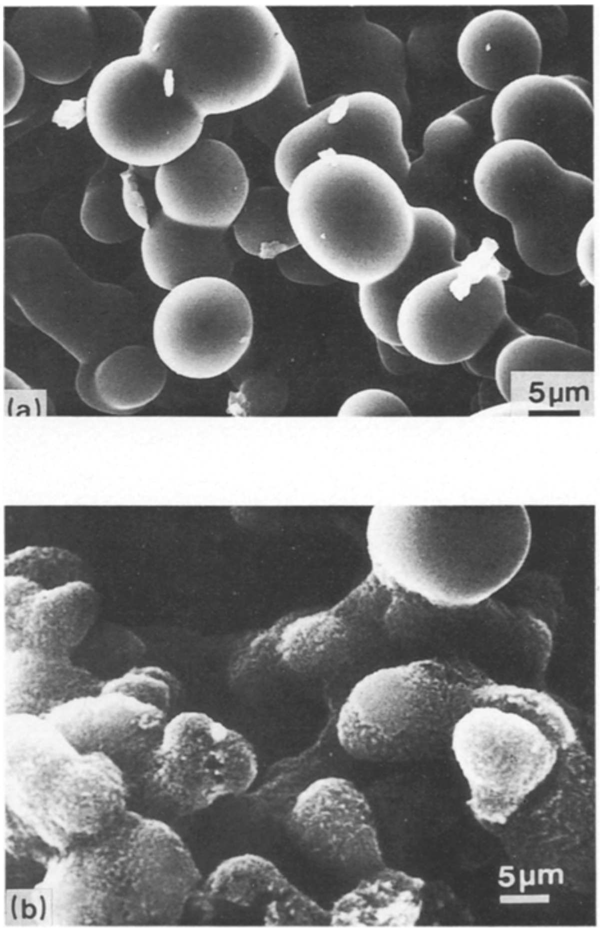

Figure 4 Morphology of platinum-dispersed carbon formed from DVB-2.5 mol % APPt. (a) As-prepared platinum-dispersed carbon at 550 °C and 125 MPa. (b) After heat treatment of (a) at 800 °C for 1 h in a flow of argon.

3.3.2. Morphological change of the carbon matrix on heat treatment

Fig. 4a and b show morphologies of platinum-dispersed carbon before and after heat treatment at 800 °C for 1 h, respectively. Coalescing spherulites of uniform diameter from 5 to 10 μm were obtained by pyrolysis of DVB-APPt copolymer (2.0 wt % Pt) at 550 °C and 125 MPa (Fig. 4a). After heat treatment, the smooth surface of the original carbon spherulites became rough, with many pores of less than 0.3 μm as shown in Fig. 4b. It turns out from this observation that the increase in surface area is attributable to the formation of micropores and channels in the carbon matrix by subsequent heat treatment.

3.4. Hydrogenation of cyclohexene with platinum-dispersed carbon

The catalytic property of platinum-dispersed carbon thus prepared was investigated using the hydrogenation of cyclohexene as shown in Equation 1

$$C_6H_{10} + H_2 \rightarrow C_6H_{12} \qquad (1)$$

Platinum-dispersed carbons were synthesized from DVB-APPt and PA-APPt copolymers (Pt 2.0 wt %) at 550 °C and 125 MPa for 3 h. The as-prepared platinum-dispersed carbon was heat-treated at temperatures between 400 and 800 °C prior to its use as the catalyst in the hydrogenation reaction.

3.4.1. *Hydrogenation of cyclohexene with platinum-dispersed carbon from PA-APPt*

The conversion yield of cyclohexane and the reaction time are correlated to the heat-treatment temperature of as-prepared platinum-dispersed carbon synthesized from PA-APPt (Fig. 5). The conversion yield of cyclohexane increased with increasing reaction time, and reached 100% after 48 h, when the specimen heat-treated at 800 °C was employed as a catalyst. The conversion yield also increased, as the heat treatment temperature of as-prepared platinum-dispersed carbon increased from 400 to 800 °C at the same reaction time.

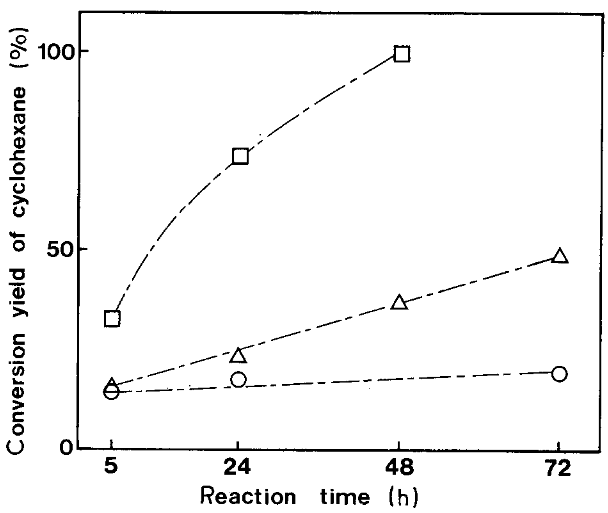

Figure 5 Variations of conversion yield of cyclohexane with reaction time using platinum-dispersed carbons (PA-APPt, 550 °C, 125 MPa) heat-treated from 400 to 800 °C: (○) as-pyrolysed; (△) 400 °C for 1 h; (□) 800 °C for 1 h.

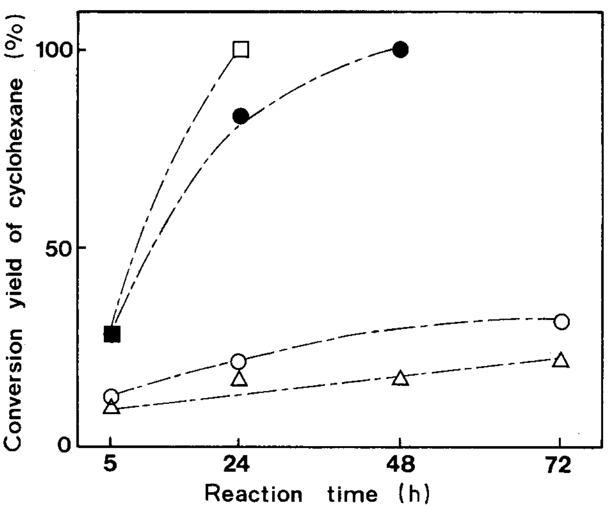

Figure 6 Changes of conversion yield of cyclohexane with reaction time using platinum-dispersed carbons (DVB-APPt, 550 °C, 125 MPa) heat-treated at temperatures between 400 and 800 °C: (○) as-pyrolysed; (△) 400 °C for 1 h; (●) 600 °C for 1 h; (□) 800 °C for 1 h.

3.4.2. *Hydrogenation of cyclohexene using platinum-dispersed carbon from DVB-APPt*

Cyclohexene was hydrogenated in the presence of platinum-dispersed carbon formed from DVB-APPt, and the results are summarized in Fig. 6. The as-pyrolysed platinum-dispersed carbon had a comparable activity with that treated at 400 °C. The heat treatment above 600 °C was effective in enhancing the catalytic activity of platinum-dispersed carbon. The conversion yield of cyclohexane was 100% for the reaction time of 24 h. The yield was higher than that shown in Fig. 5, when the same heat-treatment temperature of 800 °C was compared.

The increase in the yield of cyclohexane corresponds to the increase of surface area of the catalyst as shown in Fig. 3. The enhanced activity of platinum-dispersed carbon by heat treatment above 600 °C (Fig. 6) indicated that the specific area larger than 50 $m^2 g^{-1}$ is required for the improvement of activity of as-pyrolysed catalyst. The smaller particle size of platinum in the carbon matrix from DVB-APPt than that from PA-APPt is also considered to be responsible for the higher activity of platinum-dispersed carbon from DVB-APPt than that from PA-APPt.

DVB-2.5 mol % APPt copolymer was pyrolysed at 520 °C and 125 MPa, and then heat-treated at 800 °C in argon. The platinum-dispersed carbon had a specific area of 154 $m^2 g^{-1}$, and hydrogenated cyclohexene completely to cyclohexane within 5 h. The lower pyrolysis temperature of parent copolymer leaves more uncarbonized, volatile components, as reported previously [7]. The increased activity of platinum-dispersed carbon results from the increased surface area obtained by the carbonization of organic components remaining in the as-prepared carbon.

Not only the size of the platinum particles but also the surface area of the carbon matrix play important roles in the catalytic activity of platinum-dispersed carbon.

4. Conclusions

Divinylbenzene (DVB)-*bis*(2-allylphenyl)platinum (APPt) and phenylacetylene (PA)-APPt were pyrolysed under pressure to synthesize carbons with finely dispersed platinum particles. The properties of platinum-dispersed carbon formed from DVB-APPt copolymer were compared with those synthesized from PA-APPt copolymer. The results may be summarized as follows.

1. Phenylacetylene-APPt gave carbons dispersed with platinum particles of larger size with higher crystallinity than those formed from DVB-APPt.
2. The specific area of platinum-dispersed carbon increased with increasing heat-treatment temperature of as-prepared carbon.
3. Platinum-dispersed carbons synthesized from DVB-APPt had a higher specific area and contained platinum particles of smaller size than those from PA-APPt, which resulted in a better catalytic activity than that from PA-APPt.
4. Platinum-dispersed carbon synthesized at 520 °C had a specific area of 154 $m^2 g^{-1}$, and showed much higher catalytic activity than that formed at 550 °C.

DVB was found to be a better starting material than PA for the synthesis of platinum-dispersed carbons with higher catalytic activity.

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Received 2 October 1989
and accepted 9 April 1990