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Platinum Nanosheets Intercalated Natural and Artificial Graphite Powders

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This manuscript dedicates Prof. Andy Hor for his 65th birthday.

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Abstract: Insertion of sheet-type platinum particles (platinum nanosheets) between graphite layers was achieved by a thermal treatment of a mixture of platinum chloride (IV) and graphite powder (natural graphite or artificial graphite) under 0.3 MPa of chlorine at 723 K, followed by the treatment under 40 kPa of hydrogen pressure. Similar platinum nanosheets, which were 1-3 nm in thickness and 100 - 500 nm in width and had a number of hexagonal holes and edges with 120° angle, were formed between the layers of both natural graphite or artificial graphite; however, their location in the graphite layers depended on the type of graphite used. A number of platinum nanosheets were observed in the edge region of natural graphite particles which have flat surface. On the other hand, a number of platinum nanosheets were found inside and away from the edge of the artificial graphite particles especially in the vicinity of the cracks. Both the platinum nanosheet-containing artificial and natural graphite samples showed high selectivity to cinnamyl alcohol in cinnamaldehyde hydrogenation under supercritical carbon dioxide conditions, while spherical platinum particles, which were located on the surface of natural and artificial graphite, showed lower selectivity.

Introduction

Nanomaterials having ultrathin structure show good properties than three-dimensional structure.^[1] Platinum loaded carbon materials are used in several fields of chemical processes, such as heterogeneous catalysts and electrodes, and the morphology of platinum metal particles are critical for their properties.^[2] Twodimensional platinum nano particles are expected to exhibit peculiar properties. Graphite has a layered structure and each layer (graphene) consists of carbon atoms which are twodimensionally connected through sp² hybrid orbitals. Because graphite layer can donate and accept electrons and bound to each other with a weak van der Waals force, various compounds can be introduced between graphite layers to produce graphiteintercalated-compounds (GIC)^[3]. Several metal chloride species can be inserted between graphite layers by mixing solid metal chloride with graphite powder and following thermal treatment under a vacuum or a chlorine atmosphere^[3]. It is expected that metal particles with nano size order can be formed by the reduction of the corresponding metal chloride intercalated between two-dimensional graphite layers because of the steric hindrance of the upper and lower graphite layers. We have succeeded to produce sheet-shaped platinum particles with 1-3 nm thickness and 100-300 nm width (platinum nanosheets)^[4], disk-shaped iridium particles with 1-3 nm thickness and 1-14 nm diameter (iridium nanodisks)^[5], and spherical palladium particles with 3 nm size (palladium nano particles)^[6] between the layers of artificial graphite by the insertion of the corresponding noble metal chloride between layers and following the hydrogen reduction. However, the location of platinum nanosheets in the graphite particles is not yet well understand. We also have reported that the noble metal particles between graphite layers showed high selectivity and activity than those on graphite layers for cinnamaldehyde (CAL) hydrogenation. Platinum nanosheets were highly selective to cinnamyl alcohol (COL) in supercritical carbon dioxide^[7], and palladium nano particles were highly active in organic solvent than particles on graphite surfaces^[6]. One probable explanation for the different selective catalysis of metal particles intercalated between graphite layers from those on graphite support is the adsorption characteristics of the reactant on active sites.

There are two types of graphite, natural and artificial varieties. Both have the same layered structure; however, several local structure such as, surface roughness and crystalline nature vary due to the difference in their preparation and generation processes, hence it is expected to that platinum particles would get intercalated with different insertion structures in natural and artificial graphite samples. In this work, we studied the formation of platinum nanosheets between the layers of natural and artificial graphite samples, which have similar particles size of 5 μ m. The location of platinum nanosheets in graphite particles and their behaviors in cinnamaldehyde hydrogenation are also discussed.

Results and Discussion

Natural and artificial graphite samples

In this study, we used two types of graphite samples, artificial graphite (average particle size 5 μ m, BET surface area 16.2 m²g⁻¹) (hereinafter we refer to as SGP5) and natural graphite (average particle size 5 μ m, BET surface area 9.6 m² g⁻¹, which were provided by SEC CARBON, Ltd. (hereinafter we referred to as SNO5). Diffraction peaks of (002) and (004) from the stacking of graphene layers were observed at 20 = 26.5° and 54.6° in the X-ray diffraction peaks attributed to (100), (101), and (102) of hexagonal structure were also observed at 20 = 42.3°, 44.5°, and 54.6° for both samples, respectively. Besides, diffraction peaks attributed to (101), (012), and (104) of

rhombohedral structure were observed at 2θ = 43.2°, 46.1°, and 56.6°, respectively, in natural graphite SNO5 ^[8].

A crack was observed in the artificial graphite particle, on the other hand, the surface of the natural graphite particle was flat as observed in the SEM images of SGP5 and SNO5 samples (Supporting information). Natural graphite is obtained by crushing and flotation of mineral ore, while artificial graphite is manufactured by the treatment of the mixture of pitch and additives such as iron oxide at 1273 K and graphitization at 3273 K. Cracks are formed and rhombohedral structure is partially broken during graphitization for the artificial graphite sample, indicating that the in-plane crystallinity of the graphite layer of the artificial graphite sample is lower than that of the natural graphite sample.

Insertion of platinum chloride (IV) between graphite layers

The mixture of both graphite samples and platinum chloride was treated at 723 K under 0.3 MP of chlorine atmosphere for 1 week to produce platinum chloride intercalated compounds (PtCl₄-SGP5-GIC and PtCl₄-SNO5-GIC). Their XRD patterns are shown in Figure 1. In addition to the graphite peaks, new peaks were observed at $2\theta = 9.8^{\circ}$, 14.6°, and 20.3° in both samples, respectively, which were also seen in the platinum chloride intercalated artificial graphite KS6 (Timrex)^[4]. The positions of three peaks are in good agreement with the calculated values for (002), (003) and (004) reflections from the repeat distance along with the c axis (c=1.76 nm). From the size of platinum chloride ^[9] and graphite layer (0.3354 nm), we propose that both PtCl₄-SGP5-GIC and PtCl4-SNO₅-GIC samples have third stage structure, in which a periodicity of one platinum chloride and three graphene layers^[4].





Platinum nanosheets between layers of artificial and natural graphite

Figure 2 shows TEM images of a sample obtained by the reduction of the PtCl₄-SGP5-GIC sample at 573 K under 40 KPa of hydrogen for 1 hour (we refer Pt-SGP5-GIC). XMA analysis confirmed that black images are of platinum. Figure 2(a) shows a sheet-like platinum particle with a number of hexagonal holes. The sizes of the hexagonal holes were not uniform; however, the directions of the sides of the hexagonal holes (AB, BA, and CA) were parallel to each other and angles between two sides (ABC, BCA, and CAB) of holes and edges were 120° (Figure 2(a) and 2(c)). Figure 2(b) is another image of Pt-SGP5-GIC sample, in which several rod-like platinum images are seen in parallel with graphite layers. Void spaces are also observed in the edges of the platinum sheets. Figure 2(a) is a top view and 2(b) is a side view of platinum nanosheets intercalated between graphite layers. We have reported that similar platinum nanosheets (1-3 nm thickness and 100-300 nm width) were observed for platinum intercalated artificial graphite KS6^[4]. Figure 2 shows that similar platinum nanosheets were formed in different artificial graphite sample SGP5. When platinum chloride was reduced and agglomerated to metal particles between graphite layers, sheetlike structure is formed because it aggregates between a twodimensional space sandwiched by two graphene layers. The interaction between platinum chloride and carbon atoms in two graphene layers, which are hexagonal, would affect the orientation of sides of holes and edges [4].



Figure 2. TEM images of Pt-SGP5-GIC. (a) top view, (b) side view, (c) enlarged of (b) and (d) Schematic of platinum nanosheets within graphite layers.

A Pt-SGP5-GIC image at low magnification in Figure 3(a) shows the insertion position of platinum nanosheets in the artificial particles. Since the thickness of the platinum nanosheets is of few nanometers, the contrast of platinum to carbon is low. Figure 3(b) is a magnified image of Figure 3(a). It can be seen that platinum nanosheets are located inside from the edge of an artificial graphite particle and platinum nanosheet in Pt-SGP5-GIC has hexagonal holes and edges at an angle of 120°.

Another image of Pt-SGP5-GIC at low magnification in Figure 4(a) shows the overlayer of graphite and cracks in the artificial particles. The magnified image (Figure 4(c)) shows that platinum nanosheets are located in the vicinity of cracks and at the edges



of graphene overlayers. Figures 3 and 4 show that platinum nanosheets located at cracks and edges of overlayers in an artificial graphite sample.



Figure 3. TEM images of Pt-SGP5-GIC. (a) top view, (b) side view, (c) enlarged of (b), and (d) schematic of platinum nanosheets within graphite layers.



Figure 4. TEM images of Pt-SGP5-GIC. (a) top view and (b) enlarged of (a).

Figure 5 shows a TEM image of a sample obtained by the reduction of $PtCl_4$ -SNO5-GIC at 573 K for 1 hour under hydrogen atmosphere of 40 KPa (We refer Pt-SNO5-GIC). The platinum sheets having a number of hexagonal holes and edges with 120° angle were densely packed at the outside of the graphite particle (Figure 5(a). Another image shows that rod-like platinum particle with 3 nm thickness are located parallel to graphite layers (Figure 5(b)). This figure shows that similar platinum nanosheets with 1-

3 nm thickness and hexagonal holes were formed between natural graphite layers.

Figure 6(a) shows a Pt-SNO5-GIC image at low magnification. The position of the platinum nanosheets is marked in Figure 6(b). It is shown that platinum nanosheets are present around the outer edge of a GNO5 graphite particle. The enlarged image Figure 6(b) shows that platinum nanosheets having hexagonal holes and edges with 120° angle are densely packed at the outer portion of natural graphite particles.



Figure 5. TEM images of Pt-SNO5-GIC. (a) top view and (b) enlarged of (a).



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Figure 6. TEM images of Pt-SNO5-GIC. (a) tip view, (b) side view, and (c) enlarged of (b).

Platinum nanosheets with hexagonal hole and edges with 120° angle were intercalated between both artificial and natural

graphite samples by the thermal treatment of the mixture of platinum chloride and graphite powder samples under chlorine atmosphere followed by the reduction with hydrogen gas. However, the locations of platinum nanosheets in graphite particles were different in artificial and natural graphite samples. The platinum nanosheets were located on inner portion of artificial graphite particles while, they were located densely at the outer portion of natural graphite particles. The different locations of Pt nanosheets would be due to the difference in surface structure of two graphite samples. Artificial graphite sample has a lot of cracks in the surface and platinum chloride would intercalate from the cracks. Platinum nanosheets were formed by the reduction of platinum chloride intercalated near the cracks. On the other hand ,the surface of natural graphite sample is smooth and flat. Only the edge of layers is the location where platinum chloride can enter into the layers and platinum nanosheets are formed by the reduction of metal chloride located near the edge of graphite layers.

Platinum metal particles on artificial and natural graphite surface

Figures 7 shows the TEM images of Pt-SGP5-Gmix and Pt-SNO5-Gmix in which 5wt% of platinum metal particles were supported on SGP5 or SNO5 by the impregnation of platinum precursor followed by hydrogen reduction. Spherical platinum metal particles less than 20 nm were loaded on the artificial (a and b) and natural (c and d) graphite surfaces. The size of platinum metal particle on SGP5 were a little smaller than that of SNO5. On SGP5 surface, a number of platinum particles of less than 10 nm diameter were observed, on the other hand, several larger particles of more than 10 nm were seen on SNO5 (Figures 7(c) and (d)). The artificial graphite sample SGP5 has cracks and the surface area value is 16.2 m²g⁻¹. The natural graphite SNO5 sample has plain surface and the area value (9.6 m²g⁻¹) was smaller than that of SGP5. The larger platinum metal particles were formed on SNO5 surface because of the larger surface area and much smooth surface than SGP5 surface.



Figure 7. TEM images of Pt/SGP5-Gmix (a, b) and Pt/SNO5-Gmix (c, d).

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Hydrogenation of cinnamaldehyde over Pt-GIC and Pt/Gmix

Cinnamaldehyde (CAL) is an unsaturated compound and has three types of unsaturated bonds: aromatic ring, carbon-carbon double bond (C=C), and aldehyde group (C=O). The CAL hydrogenation is a structure sensitive reaction. The selectivity to cinnamyl alcohol (COL), which is produced by the hydrogenation of C=O bond in CAL molecules, and to 3-phenyl propionaldehyde (HAL), which is a product by the hydrogenation of C=C bonds, depends on metal species and the structure of metal particles. Supported platinum catalysts are active for the CAL hydrogenation and form hydrogenation products as cinnamyl alcohol, 3-phenyl propionaldehyde, and 3-phenyl-1-propanol (HCOL), which is produced by both C=C and C=O bonds^[10]. The catalytic behavior of supported platinum catalysts for the CAL hydrogenation, especially the difference of selectivity to COL is closely related to the structure of platinum sites. The CAL hydrogenation over platinum nanosheets between graphite layers and particles on graphite surface in a supercritical carbon dioxide solvent was studied with an expectation that different selectivities would be observed for platinum nanosheets intercalated between graphite layers and spherical platinum particles located on graphite surface. Conversion and selectivity were determined as follows, conversion (%) = (total amount of products) / ((total amount of products) + (amount of unreacted cinnamaldehyde)) x 100, selectivity (%) = (quantity of each product) / (total quantity of each product) x 100.

Figures 8 and 9 show the conversions and product yields of the CAL hydrogenation in supercritical carbon dioxide with graphite supported platinum catalyst with the same platinum metal loading of 5wt%. All the catalysts were active for the hydrogenation and COL, HAL, and HCOL were formed. However, COL selectivity depended on the catalyst. The platinum nanosheets intercalated between graphite catalysts (Pt-SGP5-GIC and Pt-SNO5-GIC) showed high COL selectivity of 70% or more (Figure 8) regardless the reaction time and conversion. On the other hand, the COL selectivity for the platinum supported on graphite surface (Pt/SGP5-Gmix and Pt/SNO-Gmix) was not so high and was about 55% and dehydroxylation products such as β-methyl styrene and propyl benzene) were formed (Figure 9) regardless reaction time and conversion. The higher UOL selectivity over platinum intercalated (Pt-GIC) samples than that over Pt/Gmix samples would be explained by the preference adsorption of C=O bond in CAL molecules on platinum nanosheets compared with spherical platinum particles. For the system with Pt-GICs (platinum nanosheets between graphite layers), supercritical carbon dioxide solvent would transport CAL molecules between the graphite layers. CAL molecules interact with the upper and lower graphene layers, and the benzene ring exists parallel to the layers, resulting in the adsorption of end functional aldehyde group of CAL molecules at the edge of platinum nanosheets. On the other hand, in the Pt/Gmix (platinum particles on graphite surface), platinum particles existed on the graphite surface, and the CAL molecules dissolved in supercritical carbon dioxide are adsorbed on the platinum particles without any spatial preference, which led to generate both HAL and COL leading to low COL selectivity

The initial conversion over Pt-SGP5-GIC (50% for 30 min) was higher than that over Pt-SNO5-GIC (43%). Similar platinum nanosheets were formed in SGP5 and SNO5 layers; however, the number of active platinum sites, on which CAL molecules could adsorb, would be larger in Pt-SGP5-GIC than in Pt-SNO5-GIC

(Figures 3 and 6) because the artificial SGP5 graphite sample had a lot of cracks and platinum nanosheets were located near these cracks. Further study to determine the number of active sites are needed.



Figure 8. Cinnamaldehyde hydrogenation (a) Pt-SGP5-GIC and (b) Pt-SNO5-GIC (products: cinnamyl alcohol (COL), 3-phenyl propionaldehyde (HAL), and 3-phenyl-1-propanol (HCOL)).



Figure 9. Cinnamaldehyde hydrogenation (a) Pt/SNO5-Gmix and (b) Pt/SNO5-Gmix. (products: cinnamyl alcohol (COL), 3-phenyl propionaldehyde (HAL), 3-phenyl-1-propanol (HCOL), β -methyl styrene and propyl benzene).

Conclusion

By the treatment of a mixture of graphite powder (natural graphite and artificial graphite) and platinum chloride under 0.3 MPa of chlorine at 723 K, followed by the reduction with 40 kPa of hydrogen, intercalation of platinum nanosheets between the graphite layers was achieved. In both natural and artificial graphite samples, platinum nanosheets were of 1-3 nm thickness and 100-500 wide and had a number of hexagonal holes and edges at an angle of 120°. The natural graphite particles had a flat surface and platinum nanosheets were located on the edges of the graphite particles. The artificial graphite particles had cracks and platinum nanosheets were located in the vicinal area of the cracks and the edge of graphene overlayers on surface. The platinum nanosheets intercalated in natural and artificial graphite (Pt-SGP-GIC and Pt-SNO5-GIC) samples were active for CAL hydrogenation and more selective to COL than platinum particles located on the surface of natural and artificial graphite (Pt/SGP5-Gmix and Pt/SNO5-Gmix) samples. Pt-SGP5 was more active than Pt-SNO5 and both samples showed high cinnamyl alcohol selectivity.

Experimental Section

Two types of graphite powder samples (natural graphite powder (SNO5, SEC CARBON, Ltd.) and artificial graphite powder (SGP5, SEC CARBON, Ltd.) were used in this study. Solid platinum chloride (PtCl₄ (IV), Aldrich) and graphite powder (SGP5 or SNO5) was mixed in a round flask and the mixture was treated at 723 K for 1 week under 0.3 MPa chlorine to give platinum chloride intercalated compounds (PtCl₄-SGP5-GIC or PtCl₄-SNO5-GIC). The platinum chloride insertion compounds were reduced at 573 K for 1 hour under 40 kPa of hydrogen to produce a platinum metal intercalation compound (Pt-SGP5-GIC or Pt-SNO5-GIC) in a batch system. The platinum metal loadings in Pt-SGP5-GIC and Pt-SNO5-GIC were 5wt%, respectively.

Platinum metal supported on graphite samples were prepared by an impregnation method. The slurry of aqueous solution of chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Wako Chemicals) are mixed in a round flask, and the mixture is treated at 573 K for 1 hour under 40 kPa of hydrogen to obtain platinum metal particles supported on graphite surface (Pt/SGP5-Gmix or Pt/SNO5-Gmix). The platinum metal loadings in Pt/SGP5-Gmix and Pt/SNO5-G-mix were 5wt%, respectively.

Hydrogenation of cinnamaldehyde was carried out in a SUS batch reactor (inner volume space 50 mL). 20 mg of catalyst, 1.98 mmol of *trans*cinnamaldehyde (Wako Chemical) are placed in the reactor, 0.5 MPa of argon is repeatedly introduced, and it is released three times. It was purged by and then heated to 373K. Next, hydrogen was introduced up to 5 MPa. After a predetermined reaction time, the reactor was submerged in an ice bath and rapidly cooled to room temperature. The mixture of liquid products and catalysts were recovered with acetone and filtered to remove the catalyst. Products dissolved in acetone were analysed by gas chromatography on Agilent Technologies, model HP-6890N, using a DB-WAX capillary column equipped with a flame ionization detector (GC-FID).

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Keywords: Graphite intercalated compounds • Platinum nanosheet • Cinnamaldehyde hydrogenation • Graphite • Supercritical carbon dioxide

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Platinum nanosheets having 1-3 nm in thickness and 100 - 500 nm in width and a number of hexagonal holes and edges with 120° angle were prepared between layers of graphite (natural and artificial). Platinum nanosheets were located in the edge region of natural graphite particles which have flat surface. On the other hand, they were found inside the artificial graphite particles especially in the vicinity of the cracks.