

Formation of platinum nanosheets between graphite layers

Masayuki Shirai,* Koichi Igeta and Masahiko Arai

Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba, Sendai, 980-8577, Japan.
E-mail: mshirai@icrs.tohoku.ac.jp

Received (in Cambridge, UK) 13th August 1999, Accepted 3rd March 2000

Platinum nanosheets with thickness 2–3 nm containing hexagonal holes were formed between graphite layers by hydrogen reduction of platinum chloride–graphite intercalation compounds.

The size and shape of metal particles formed in a matrix are determined by its structural features. Platinum nanowires are formed in the mesotubes of FSM-16^{1,2} and nanorods and nanoparticles are produced in the channels of carbon nanotubes.^{3–6} Graphite has a layered structure, and each layer is a regular hexagonal net of carbon atoms. The interlayer spacing is equal to 0.335 nm with the layers interacting *via* van der Waals forces. Because the interaction between graphite layers is fairly weak, a variety of chemical substances can be inserted into the interlayer space to produce graphite intercalated compounds (GICs). Transition metal particles intercalated in graphite layers (M–GICs) are formed *via* the insertion of transition metal chlorides into graphite and subsequent reduction.^{7–9} Commercially available M–GICs (Graphimet)¹⁰ have numerous applications for catalytic reactions.^{11–16} Graphimets are obtained by treating the graphite–metal chloride with lithium biphenyl at 223 K under a helium atmosphere and small metal particles (1–10 nm) were observed by HRTEM observations.¹⁷ In the present work using different preparation procedures, we report the formation of platinum metal nanosheets containing hexagonal holes, intercalated within graphite layers.

Platinum(IV) chloride and graphite (KS6, Lonza) were mixed in a thick walled Pyrex reactor under nitrogen atmosphere and dried *in vacuo* at 423 K for 2 h. The intercalation reaction was performed in the reactor at 723 K for 2 weeks under 0.3 MPa of chlorine (Takachiho, 99.999%), to obtain the platinum chloride intercalated compounds (PtCl₄–GIC). The PtCl₄–GIC samples were reduced at 573 K for 1 h under 40 kPa hydrogen to produce the platinum metal intercalated compounds (Pt–GIC).

The XRD pattern of 5 wt% PtCl₄–GIC (platinum loading: 5 wt%) shows new peaks at $2\theta = 10.0, 14.6$ and 20.3° .† The peaks ascribed to platinum chloride disappeared and the (002) diffraction peak of graphite at $2\theta = 26.57^\circ$ was weakened after the reaction under chlorine atmosphere. The three new peaks remained unaltered after 12 days exposure to air, indicating that PtCl₄–GIC is stable in air. Peaks ascribed to platinum chloride and graphite were observed on XRD patterns of a reference mixture of platinum chloride and graphite [PtCl₄/G (mix)]. The platinum chloride peaks of PtCl₄/G(mix) changed after a few days exposure to air because of the hygroscopicity of platinum chloride. The diffraction peak positions calculated for (002), (003) and (004) reflections for PtCl₄–GIC of the repeat distance along the *c* axis (*c* = 1.76 nm) were 10.0, 15.1 and 20.2° , respectively, in good agreement with the experimental peaks. The distance of 1.76 nm corresponds to the sum of three graphite layers and one intercalated layer (0.75 nm). This result shows that platinum chloride is intercalated in every three graphite layers (stage three structure) in the 5 wt% PtCl₄–GIC sample. With an increasing amount of platinum chloride inserted from 1 to 15 wt% Pt loadings, the three peaks increased and the diffraction for (002) of graphite decreased. No other peaks except for the three peaks and graphite peaks were observed. The XRD results indicate that platinum chloride is intercalated in graphite layers with the stage three structure for

1–15 wt% Pt loading. The maximum amount of platinum chloride that can be intercalated is *ca.* 38 wt%, and thus platinum chloride intercalated compounds with the stage three structure are mixed with the graphite matrix at low platinum chloride loadings under our experimental conditions. EXAFS analysis showed the existence of Pt–Cl–Pt bonds in the 5 wt% PtCl₄–GIC sample, indicating that some platinum chloride molecules aggregate with each other within graphite layers at low platinum loadings.

Fig. 1(a) shows TEM image of 5 wt% Pt–GIC reduced at 573 K. This image reveals large sheets with a number of hexagonal holes with the edge angles of the large sheets being 120° . X-Ray microanalysis (XMA) results confirmed the dark images to be

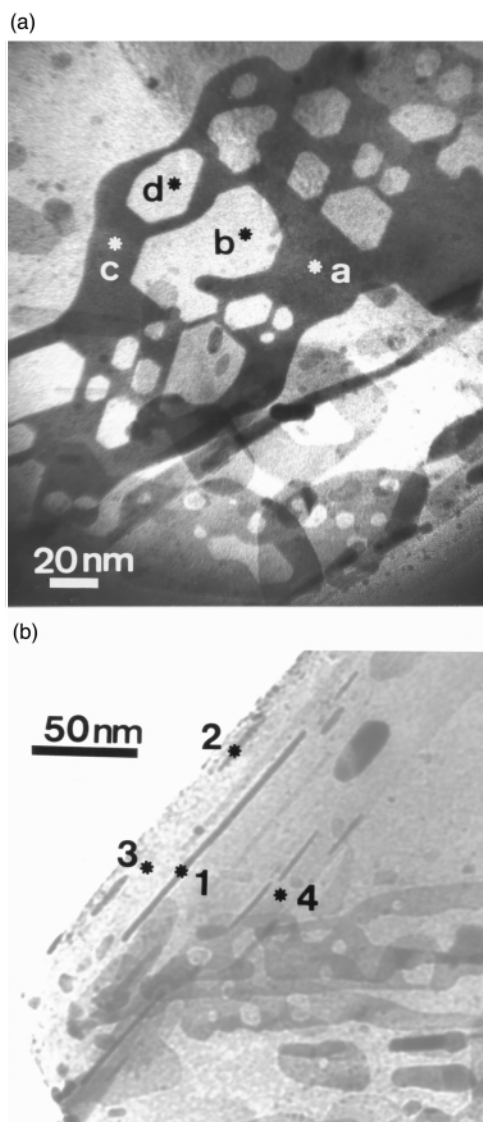


Fig. 1 TEM images of 5 wt% Pt–GIC showing Pt nanosheets; (a) top view and (b) side view.

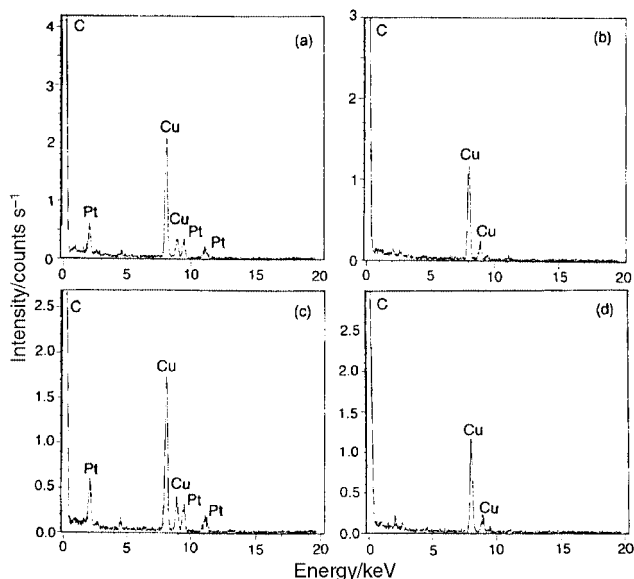


Fig. 2 XMA results of 5 wt% Pt-GIC at points a, b, c and d as indicated in Fig. 1(a).

platinum metal (Fig. 2).[‡] Fig. 1(b) shows the presence of dark images in a parallel rod-like arrangement. XMA scans obtained from regions 1 and 2 showed that the dark material corresponded to platinum metal while XMA scans obtained from regions 3 and 4 indicated the absence of platinum metal, indicating that the dark features correspond to platinum layers. The TEM images show the structure of the platinum nanosheets, which are 2–3 nm thick and 5–300 nm wide. The observation of a number of sheets in parallel presumably indicates that platinum sheets exist between graphite layers. Platinum chloride can aggregate only two dimensionally between graphite layers during reduction because of the steric hindrance of graphite layers, so that the resulting platinum metal particles of Pt-GIC have two-dimensional structures. Platinum chloride molecules are reduced in a small area to produce small particles (1–10 nm) and do not move between graphite layers upon low temperature reduction at 223 K.^{14,15,17} On the other hand, platinum atoms and/or platinum chloride molecules can migrate along a regular hexagonal net of carbon atoms during hydrogen reduction at 573 K. Movement during the reduction will determine the morphology of the resulting platinum nanosheets which have hexagonal holes. A number of nanosheets with hexagonal holes were also observed in TEM images of the 5 wt% Pt-GIC sample reduced at 773 K for 1 h after reduction at 573 K for 1 h. Large spherical particles still were not observed because the platinum nanosheets are still prevented from moving freely between graphite layers. For comparison, the mixture 5 wt% PtCl₄/G(mix) upon reduction at 573 K [Pt/G(mix)] led to spherical platinum particles according to TEM (Fig. 3).[§] For PtCl₄/G(mix) samples platinum chloride molecules on the graphite surface can aggregate in a three dimensional manner and there is no interfering factor for the growth of metal particles, and so large platinum particles are formed.

In conclusion, platinum nanosheets can be prepared between graphite layers for Pt-GIC sample and such complex materials may show interesting properties owing to their structural features and metal-graphite interactions.

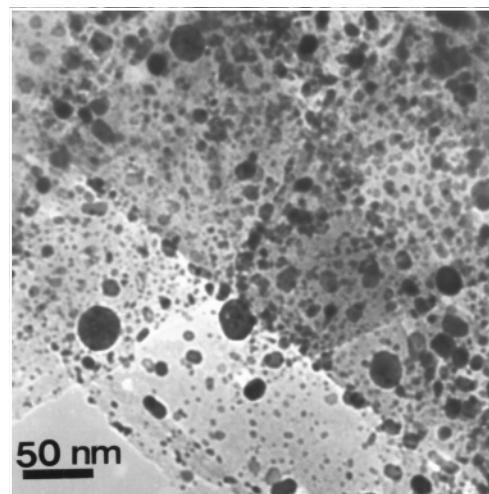


Fig. 3 TEM image of 5 wt% Pt/G(mix).

We thank Dr E. Aoyagi and Dr Y. Hayasaka (High Voltage Electron Microscope Laboratory of Tohoku University) for the TEM and XMA analysis.

Notes and references

[†] X-Ray diffraction measurements were performed on a Shimadzu XD-D1 instrument (30 kV, 20 mA) using a copper K α source.

[‡] TEM and XMA measurements were performed on a JEOL JEM-3010 instrument (300 keV) using copper grids.

[§] TEM measurements were performed on a JEOL JEM-2000ExII instrument (200 keV) using copper grids.

- 1 M. Sasaki, N. Higashimoto, A. Fukuoka and M. Ichikawa, *Microporous Mesoporous Mater.*, 1998, **21**, 597.
- 2 M. Sasaki, M. Osada, N. Higashimoto, T. Yamamoto, A. Fukuoka and M. Ichikawa, *J. Mol. Catal. A*, 1999, **141**, 223.
- 3 T. Kyotani, L. Tsai and A. Tomita, *Chem. Commun.*, 1997, 701.
- 4 B. K. Pradhan, T. Toba, T. Kyotani and A. Tomita, *Chem. Mater.*, 1998, **10**, 2510.
- 5 Y. Li, J. Chen, Y. Ma, J. Zhao, Y. Qin and L. Chang, *Chem. Commun.*, 1999, 1141.
- 6 P. Chen, X. Wu, J. Lin and K. L. Tan, *J. Phys. Chem. B*, 1999, **22**, 4559.
- 7 M. E. Volpin, Y. N. Novikov, N. D. Lapkina, V. I. Kasatochkin, Y. T. Struchkov, M. E. Kazakov, R. A. Stukan, V. A. Povitskij, Y. S. Karimov and A. V. Zvarikina, *J. Am. Chem. Soc.*, 1975, **97**, 3366.
- 8 J. Tilquin, R. Cote, G. Veilleux, D. Guay, J. P. Dodelet and G. Denes, *Carbon*, 1995, **33**, 1265.
- 9 J. Walter and H. Shioyama, *Phys. Lett. A*, 1999, **254**, 65.
- 10 J. M. Lalancette, *US Pat.* 3847963 (November 12, 1974).
- 11 S. I. Chii, A. L. DeVera and M. C. Hawley, *Fuel*, 1986, **65**, 1432.
- 12 A. Frusta, F. Hofer and H. Weidmann, *J. Catal.*, 1989, **118**, 502.
- 13 G. Sirokman, A. Mastalir, A. Molnar, M. Bartok, Z. Schay and L. Gucci, *J. Catal.*, 1989, **117**, 558.
- 14 G. Sirokman, A. Mastalir, A. Molnar, M. Bartok, Z. Schay and L. Gucci, *Carbon*, 1990, **28**, 35.
- 15 F. Notheisz, A. Mastalir and M. Bartok, *J. Catal.*, 1992, **134**, 608.
- 16 A. Mastalir, F. Notheisz, M. Bartok, T. Haraszti, Z. Kiraly and I. Dekany, *Appl. Catal. A*, 1996, **144**, 237.
- 17 D. J. Smith, R. M. Fisher and L. A. Freeman, *J. Catal.*, 1981, **72**, 51.

Communication a906596b