Catalytic Linear Grooving of Graphite Surface Layers by Pt, Ru, and PtRu Nanoparticles

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Platinum, Ru, and $Pt_{0.5}Ru_{0.5}$ nanoparticles prepared from respective metal complexes have been found to form grooves, i.e., nanochannels, on cleavage planes of HOPG at 900 °C under a gas mixture stream of hydrogen and nitrogen. The mutual orientation of these grooves observed by HRSEM and AFM was 30 or 60 degrees.

Chemical interactions of catalyst metal nanoparticles with carbon materials are of significant interest for the preparation of carbon-supported metal catalysts as well as the synthesis of carbon nanotubes.[1] One of the important issues for the development of polymer electrolyte fuel cells is the design of CO-tolerant anode catalysts, such as carbon-supported alloy catalyst; Pt–Ru/C.[2] During the impregnation process, which is a typical process for the preparation of carbon-supported alloy catalysts, metal complexes loaded on carbon black are thermally decomposed in a gas mixture stream of hydrogen and an inert gas. Although such catalysts are usually prepared at moderate temperatures, between 150 to 300 °C, some of them are prepared above 500 °C in order to promote alloying of the metal elements or to improve the stability of the catalyst metal particles on the carbon support.[3]

Here we report the instabilities in the carbon supports for the metal nanoparticles using a model catalyst method[4] at high temperatures under a hydrogen atmosphere.[5] With HOPG (Highly Oriented Pyrolytic Graphite) disks as the carbon support, three different model catalysts, Pt/HOPG, Ru/HOPG, and $Pt_{0.5}Ru_{0.5}$/HOPG were prepared on their cleavage planes, because such model catalyst method is useful for the clarification of the etching phenomena of carbon supports by metal particles at an atomic or quasi-atomic scale.[5,6]

Prior to the visual investigation of the metal–carbon interaction by the model catalyst method, a TG (Thermal Gravimetry) was conducted for FC-HOPG (finely crushed HOPG) supported metal precursors;[7] $Pt(NH_3)_2(NO_2)_2$, $Ru(NO_3)_3$, and $Pt(NH_3)_2(NO_2)_2 + Ru(NO_3)_3$. Figure 1 shows the decomposition process of the precursors of the respective catalyst metals and the consumption of the carbon support as a function of temperature in a gas mixture stream of high-purity H_2(10%) + N_2(90%). The thermal decomposition of the precursors was accomplished at less than ca. 220 °C; however, a further decrease in the mass of each catalyst was observed above ca. 750 °C for Ru/C and ca. 800 °C for Pt/C and $Pt_{0.5}Ru_{0.5}$/FC-HOPG catalysts. These mass changes suggest the partial consumption of the carbon black support in a hydrogen atmosphere at high temperatures.

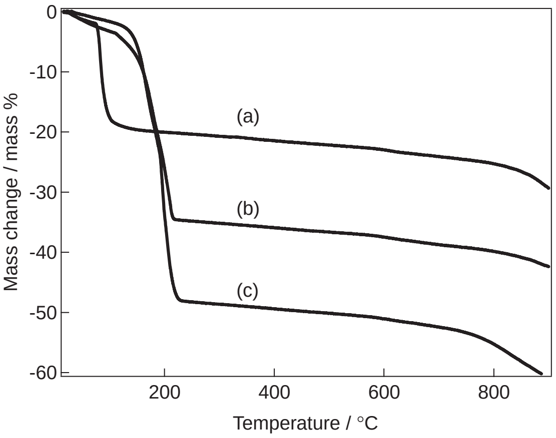

Figure 1. TG curves for the FC-HOPG (finely crushed HOPG) supported metal precursors. (a) $Pt(NH_3)_2(NO_2)_2$/FC-HOPG, (b) $Pt(NH_3)_2(NO_2)_2 + Ru(NO_3)_3$/FC-HOPG, and (c) $Ru(NO_3)_3$/FC-HOPG.

For the model catalysts using HOPG supports, a clear change in the surface morphology was observed at rather higher temperatures. Figure 2 shows typical HRSEM (High-Resolution Scanning Electron Microscopy) images of Pt/HOPG, Ru/HOPG, and $Pt_{0.5}Ru_{0.5}$/HOPG model catalyst surfaces prepared at 900 °C for 2 h.[8] These secondary electron images revealed grooves, i.e., nanochannels, formed on the surface layer of the cleavage plane of HOPG by the metal nanoparticles in each case. The first noteworthy finding is that the nanoparticles grooved the HOPG only from the edges of the HOPG surfaces. The nanoparticles on the terrace planes did not appear to groove the graphite surface. The second interesting finding is that the linear grooves were mutually oriented in specific directions—30° or 60°—on HOPG, though a few exceptions were found.[5] The third notable finding is the difference in the extent of the "grooving" by the three kinds of metal nanoparticles. Although a number of linear grooves were observed on Ru/HOPG, significantly fewer grooves were seen on Pt/HOPG. This is likely due to the high activity and mobility of Ru nanoparticles for the grooving of the HOPG surface layers at 900 °C. At the ends of the grooves on the specimens, metal nanoparticles were mostly observed. In the case of $Pt_{0.5}Ru_{0.5}$/HOPG, the extent of grooving was between that for the Ru and Pt nanoparticles. When the model catalysts were prepared at 800 °C, this order of reactivity was more evident. Namely, few or no grooves were observed on Pt/HOPG though many linear grooves were observed on Ru/HOPG surface. AFM (Atomic Force Microscopy) of the $Pt_{0.5}Ru_{0.5}$/HOPG model catalyst prepared at 900 °C clarified that the depths of the grooves, i.e., the nanochannels, were ca. 0.7–8 nm, which corresponds to 2–20 layers of the graphene layers normal to the *c* axis; however, the depth of most of the grooves was only a few graphite layers. Gas chromatography detected methane during the grooving of the HOPG by Ru nanoparticles at 900 °C. Similar grooving phenomena of HOPG by various metal particles under hydrogen atmosphere,[5] as well as by oxides or metal particles under oxygen atmosphere,[6] have

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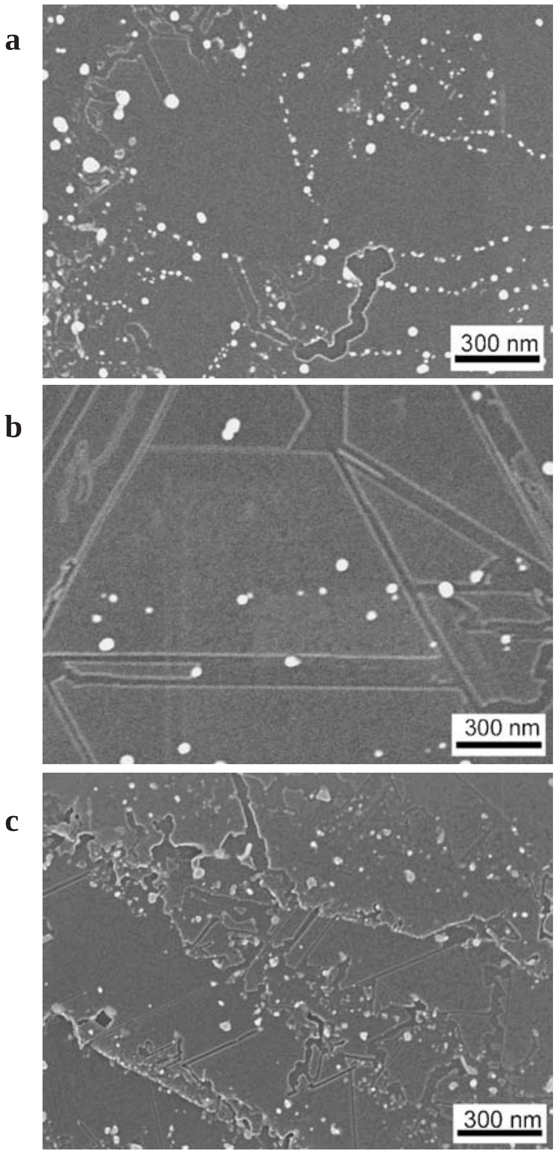

Figure 2. Typical HRSEM images (top view) of the (a) Pt/HOPG, (b) Ru/HOPG, and (c) $Pt_{0.5}Ru_{0.5}$/HOPG model catalysts.

so far been reported; however, those by PtRu alloys have not yet been clarified. A STEM-EDX analysis (Scanning Transmission Electron Microscopy-Energy Dispersive X-ray Micro Analysis) of the $Pt_{0.5}Ru_{0.5}$ particles on the HOPG revealed that the platinum content of individual particles with different particle size (d) was 0.41 (at $d = 2.5$ nm), 0.49 (at $d = 5$ nm), 0.45 (at $d = 10$ nm), 0.52 (at $d = 15$ nm), and 0.48 (at $d = 20$ nm).

Although the reason for the "grooving" of HOPG by the metal nanoparticles and the consequent grooving of a few surface layers remains unclear, a possibility is that formation of a "carbide-like surface layer"[5] at the interface of the metal nanoparticles with the edge-site carbons of HOPG prior to the formation of methane. Successive formation of a "carbide-like surface layer" could have assisted the moving of the metal nanoparticles, resulting in the grooving of the surface layer of the HOPG. The precise mechanism of the linear grooving of the metal nanoparticles along the specified directions of the hexagonal carbon atom network,[5] especially 30 degrees, by the metal nanoparticles and the effect of the particle size on the channeling phenomena are currently under investigation.

In conclusion, the grooving phenomena of HOPG by Pt, Ru, and $Pt_{0.5}Ru_{0.5}$ nanoparticles have been clarified by TG, HRSEM, AFM, and STEM-EDX. The information on the catalytic grooving provides visual information on the catalytic hydrogenolysis[5] and the preparation conditions of carbon-supported catalysts as well as the possible creation of nanotextures on the surface of carbon materials.

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7 The specimens used for thermal gravimetry were prepared by introducing appropriate amounts of finely crushed HOPG (FC-HOPG) into aqueous solutions of $Pt(NH_3)_2(NO_2)_2$ and $Ru(NO_3)_3$, or a 1:1 molar ratio of $Pt(NH_3)_2(NO_2)_2$ and $Ru(NO_3)_3$. After thorough mixing, the precursor solution was allowed to dry at 60 °C to a powder. The specimens were heated at 5 °C/min in a flowing gas mixture of $H_2(10\%) + N_2(90\%)$.
8 For the preparation of the model catalysts, 0.12 mM (M: mol dm^{-3}) aqueous solutions of $Pt(NH_3)_2(NO_2)_2$ and $Ru(NO_3)_3$ complexes were used as the source for Pt and Ru, respectively. After small amounts of the precursor solutions, 0.01 cm^3, were dropped onto the cleavage plane of HOPG (ca. 0.2 cm^2), the specimens were placed on a Pt boat, placed in a fused silica furnace tube, dried at 60 °C under flowing N_2, and then heated at 900 °C for 2 h in a flowing gas mixture of $H_2(10\%) + N_2(90\%)$.

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