In-situ gas study and 3D quantitation of titania photocatalysts by advanced electron microscopy

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Abstract. Titanium dioxide (TiO$_2$) with metal nanoparticles exhibits a high photocatalytic activity by a charge separation. Recently the size of the nanoparticles has been reduced to less than 1 nm. In contrast, the size of TiO$_2$ support particles has been kept at sub-micron sizes to ensure stability for practical use at high temperatures. For visualizing and analyzing the metal nanoparticles which are supported on different positions of those complex substrates, a high voltage transmission electron microscope (HVEM) shows a strong performance because of its high transmission capability to view whole areas of the catalysts. Electron tomography is also important to quantify the three-dimensional morphology such as size, density, surface area and nearest particle distance. Here we report the data obtained by using He-cooled 3D TEM/STEM, a newly developed 1MV high voltage environmental TEM/STEM and a 200kV aberration corrected TEM/STEM. Nanostructures of catalytic samples are characterized using these EMs as well as measurement of their chemical activity.

1. Introduction

Oxides supporting precious metals act as oxidation catalysts. Platinum supported on titania (Pt/TiO$_2$) is an especially active oxidation photocatalyst. Examples of photocatalysis such as aqueous photo-degradation, antibacterial activity and environmental cleanup are already seen in many products familiar to the public. Since the early 19th century, many researchers have tried to develop methods to achieve high photocatalytic activity by controlling nano-structures of platinum on titania, e.g., producing fine particles or porous configurations with large surface areas and controlled sizes of Pt clusters on the TiO$_2$ surface as the effective reaction sites [1]. Although Pt dots on TiO$_2$ particles of several hundred nm’s diameter can be analyzed by spectroscopic methods including X-ray diffraction, it is rather difficult to obtain useful data on the dots of less than a few nm.

Transmission electron microscopy (TEM) is one of the most effective methods to analyze such supported nanodot structures, although information obtained from the images is limited to two-dimensions (2D). In 1992, “electron tomography” was proposed in order to obtain three-dimensional (3D) structure information from 2D TEM images [2]. In electron tomography, 3D structures of samples are reconstructed from many TEM images taken in various orientations, in the same manner as X-ray computed tomography (CT). In recent years, electron tomography using high angle annular...
dark field scanning TEM (HAADF-STEM) images has been expected to be a more powerful method to observe 3D structures of crystalline materials than using TEM images [3,4]. In the present study, cryogenic high-angle annular dark field scanning transmission electron microscopy (Cryo-HAADF STEM) tomography has been used to obtain 3D structural information about metallic nanodots on TiO$_2$ particle surfaces as well as high-resolution SEM.

2. Experimental procedure

The platinum (Pt) nanoparticles were prepared on titanium dioxide by photo-electrocrystallization in water and 5 wt% tetrachloroauroic acid. Titanium oxide powder (Ishihara Sangyou Co.) and tetrachloroauroic acid were aged after adding in water. Then UV light (10W × 2, $\lambda = 310$ ~ 400nm) was used to irradiate the mixture stirring at 300K for 5 minutes. The mixture was filtered off and the recovered solid was thoroughly washed with ethanol and acetone and oven-dried with UV irradiation for 12 hours.

The morphology was evaluated by high-resolution scanning electron microscope (Hitachi, SU8000) at 800V. Then electron tomography was performed for analysis of Pt nanoparticles. Scanning transmission electron microscopy (STEM) images were recorded with tilt angles ranging from -76 to +74 degrees in 1 degree increments using 300kV He-cooled TEM/STEM (FEI, Tecnai Polara G2). A high-angle annular dark field(HAADF) detector (100 mrad inner collection angle) was used for obtaining Z-contrast images. Due to Howie’s detector[5], one can use incoherent thermal diffuse scattering (TDS) electrons and obtain Z-contrast STEM tilt images. The IMOD suite of programs [6,7] was used for 3D re-construction of the tilt series. After adjusting experimental data such as image sizes, orientation and image drift, 3D reconstruction was performed. By calculating the three-dimensional coordinates and intensities of the images, the pore size, volume fraction of pores and specific surface areas of the porous structures could be analyzed using IMOD and in-house programs. The atomic structure of Pt clusters on the TiO$_2$ surface and the interface structure were investigated by using double aberration corrected(AC) TEM/STEM (JEOL, JEM-2100CS). In-situ observations in gas atmospheres were also performed with a 1MV high voltage environmental TEM/STEM (JEM-1000K RS) in Nagoya University.

3. Results and discussion

Figure 1 is a SEM image of the present Pt/TiO$_2$ catalyst. The arrowed particles are typical octahedra consisting of anatase TiO$_2 \{101\}$ planes. Average particle size of the octahedron

![Figure 1. SEM image of the Pt/TiO$_2$ catalyst on the edge of a microgrid.](image-url)
nanoparticles was estimated as 174±18nm. On such three-dimensional substrates, the spatial resolution and image contrast of deposited Pt nanoparticles are strongly affected by the location and orientation of the TiO$_2$. Pt particles were not visible using the present SEM with a high-resolution thermal field emission gun system.

Figure 2 is a spherical aberration corrected STEM image of the Pt/TiO$_2$. The crystal structure of the Pt nanoparticles and atomic interfaces with the TiO$_2$ substrate were characterized by aberration corrected high-resolution STEM. The HAADF-STEM observations have clarified the single crystalline nature of Pt nanoparticles (atomic number; Z = 78), which show stronger contrast than the anatase substrate (atomic number in “gray atom approximation”; Z = 12.7). Furthermore, localized growth was also visualized by the HAADF-STEM analysis. On the corner site of the octahedron particle (white-arrowed in Fig. 2) Pt nanoparticles were hardly detected.

![Figure 2. Aberration-corrected(AC) HAADF-STEM image of the Pt/TiO$_2$ interface.](image)

The growth site of the Pt nanoparticles was quantitatively studied by electron tomography. Figure 3 shows a tilt series and reconstructed tomogram of a Pt/TiO$_2$ prepared in water solution. Fig. 3(a)-(g) are HAADF-STEM images with tilt angles of -60, -40, -20, 0, 20, 40 and 60 degrees. Fig. 3(h) shows the reconstructed 3D structure of the Pt/TiO$_2$ particle. We can clearly observe fine Pt nanoparticles about 1-3 nm diameter located on the TiO$_2$ surface without the artifacts which result from a missing wedge or digital quantum noise. After 3D reconstruction based on the back-projection method, we have analyzed quantitatively the size, volume and number of Pt nanoparticles for each unit area on the titania surface by using the IMOD and in-house measurement programs [8].

In Table 1, the morphology of the Pt/TiO$_2$ is summarised. The present study is the first application of electron tomography to analysis of the 3D shape and distribution of Pt nanoparticles (2.86 nm in diameter) on the TiO$_2$ particle surface. Pt volume, surface area and nearest neighbour particle distance were accurately measured in real space.

Figure 4(a) is a histogram of the intensity distribution of the reconstructed tomogram. This histogram shows that there are three types of area. We set two threshold values of 864 and 892 between vacuum, TiO$_2$ and Pt. All voxels corresponding to Pt intensity were categorized by distance from edge of the octahedron (d$_n$) as shown in Figure 4(b). Localized growth of Pt nanoparticles is described by Pt volume fraction and density at each distance from the edge of the particle as shown in Figs. 5 and 6.
These results indicate that in the present photo-electrocystallization process larger Pt particles are present with higher density on the TiO$_2$ surface away from the corners or edges of octahedron. Although we need further experiments to discuss the influence of the TiO$_2$ support morphology on the growth process, especially in complex liquid phase reaction, electron tomography is undoubtedly the best method for clarifying the process.

Table 1. Quantitative morphology of the Pt nanoparticles on a TiO$_2$ support.

<table>
<thead>
<tr>
<th>Number of particle</th>
<th>Average volume [nm$^3$]</th>
<th>Average surface area [nm$^2$]</th>
<th>Nearest neighbour distance [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>664</td>
<td>9.8</td>
<td>26</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Figure 3. Tilt-series(a-g) and reconstructed tomogram(h) of the Pt/TiO$_2$.

Figure 4. (a) Intensity histogram of the tomogram in Fig 3(h), and (b) diagram of a TiO$_2$ particle with Pt nanoparticles (small dots), where $d_n$ is the distance from the edge. These results indicate that in the present photo-electrocystallization process larger Pt particles are present with higher density on the TiO$_2$ surface away from the corners or edges of octahedron. Although we need further experiments to discuss the influence of the TiO$_2$ support morphology on the growth process, especially in complex liquid phase reaction, electron tomography is undoubtedly the best method for clarifying the process.
Figure 5. Local density (a) and volume (b) of Pt nanoparticles in a Pt/TiO$_2$ catalyst. The polygonal graphs show variation of the standard deviation.

Figure 6. Spatial distribution of Pt nanoparticles on TiO$_2$ surfaces measured from the tomography.

Figure 7. TEM images of the Pt/TiO$_2$ with non-aberration corrected(n-AC) 200kV(a), AC 200kV(b) and n-AC 1MV TEMs(c). The arrowed areas in (c) are overlapped areas, even where small Pt clusters are observed clearly due to the use of HVEM.
Finally, we will discuss future prospects for transmission electron microscopy (TEM) in heterogeneous nanocatalysis. As you can see in Figure 7(a), Pt nanoparticles (2-5nm in diameter) are very difficult to visualise with conventional TEM when supported on sintered oxide substrates such as TiO$_2$, CeO$_2$, and Al$_2$O$_3$. Recently spherical aberration correction has enabled improvement of spatial resolution and image contrast around zero focus. Figure 7(b) is an AC-TEM image obtained with 200kV accelerating voltage. In suitably thin areas, this image contains enough information to measure the Pt distribution. In the present study we also used ultra high voltage TEM for visualizing complex nanostructures of a beam sensitive photocatalyst. Figure 7(c) is a TEM image obtained with 1MeV electrons[9]. The result clarified that improved transmittance makes it much easier to observe Pt nanoparticles, which aggregated on grain boundaries of sintered TiO$_2$ (arrowed in Fig. 7(c)). Careful consideration about irradiation damage is important when performing ultra high voltage TEM (and for STEM even at 200kV), and the relatively low exposure time is required (less than 0.5 seconds) particularly in gas atmosphere of O$_2$ and N$_2$[9]. Aberration correction in such ultra high voltage transmission electron microscopes would contribute drastically to in-situ study of nanostructured and heterogeneous catalysts, as clearly seen by our in-situ observation also in 300kV[10].

4. Conclusion

In the present study, we have performed three-dimensional electron tomography of catalytic nanoparticles by using the HAADF-STEM and 1MV TEM newly installed in Nagoya University. One of the recent key topics in catalysis is metal particles on TiO$_2$ and CeO$_2$ and their interfaces, which drastically enhance the catalytic activity. For visualizing and analyzing the metal nanoparticles which are supported on different positions of those complex substrates, high voltage transmission electron microscopy is well performed because of its ability to image thick samples. Electron tomography was successfully used to quantify the three-dimensional morphology of Pt nanoparticles on TiO$_2$, including the size, density, surface area and nearest particle distance. We are also performing in-situ gas observation by using a newly developed 1MV high voltage environmental TEM/STEM and 300kV environmental TEM. Nanostructures of samples are characterized in gas atmospheres, and the catalytic activity for a CO oxidation reaction and a methylene blue (MB) degradation reaction are evaluated for understanding of the relationship between their 3D structures and catalytic performance.

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References