Comparison of High-Resolution Scanning Electron Microscopy with Transmission Electron Microscopy for the Characterization of Ultrafine Palladium Particles Embedded on Active Carbon

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Synopsis. Ultrafine palladium particles supported on powdery active carbon have been characterized by high-resolution scanning electron (secondary and reflection electron images) and transmission electron microscopies. The former was advantageous for the simultaneous observation of metal catalyst particles (smaller than 1.5 nm in diam.) as well as the surface morphology of their support.

Observations of metal particles dispersed on supporting materials have usually been made by transmission electron microscopy (TEM); however, the morphology of the outer and inner surfaces of porous catalyst supports cannot be well characterized by this method, since it can give only transmitted images.[1] The authors previously demonstrated that high-resolution scanning electron microscopy (HR-SEM) can be applied for the observation of the ultrafine metal particles of supported metal catalysts when the catalyst is electroconductive.[2,3]

This report presents high-resolution scanning electron micrographs in both the secondary and the reflection (back scattered) electron modes of the microstructure of an active-carbon support (AC), as well as the palladium particles supported on it. Transmission electron microscopy was also performed for the characterization of the catalyst for a comparison.

Experimental

A powdery active carbon-supported palladium catalyst (5%-Pd/AC) was prepared by a usual impregnation method using active carbon made from wood and an aqueous solution of palladium chloride. A high-resolution scanning electron microscope (Hitachi model S-5000) was employed to observe the supported palladium catalyst. The microscope has a field-emission electron gun and an in-lens detector. The system can be evacuated up to the 10^{-8} Pa range with turbo-molecular and ion pumps. For SEM observations a powdery catalyst sample was placed on a sample holder on which a small amount of carbon paste was painted. Before placing the sample holder into the SEM chamber, a soft strike was given to the holder in order to remove any excess powdery sample. No heat treatments were effected on the specimen so as to avoid any deleterious effects. To prepare specimens for TEM observations, the powdery catalyst was finely crushed with an agate mortar, followed by dispersing it into methanol. Some of it was then dipped up with a sheet mesh onto which a collodion film was placed.

Results and Discussion

Fig. 1 shows scanning electron micrographs of typical (a) flat and (b) rough planes of the sample (magnification: ×200000). Over both planes, dispersed

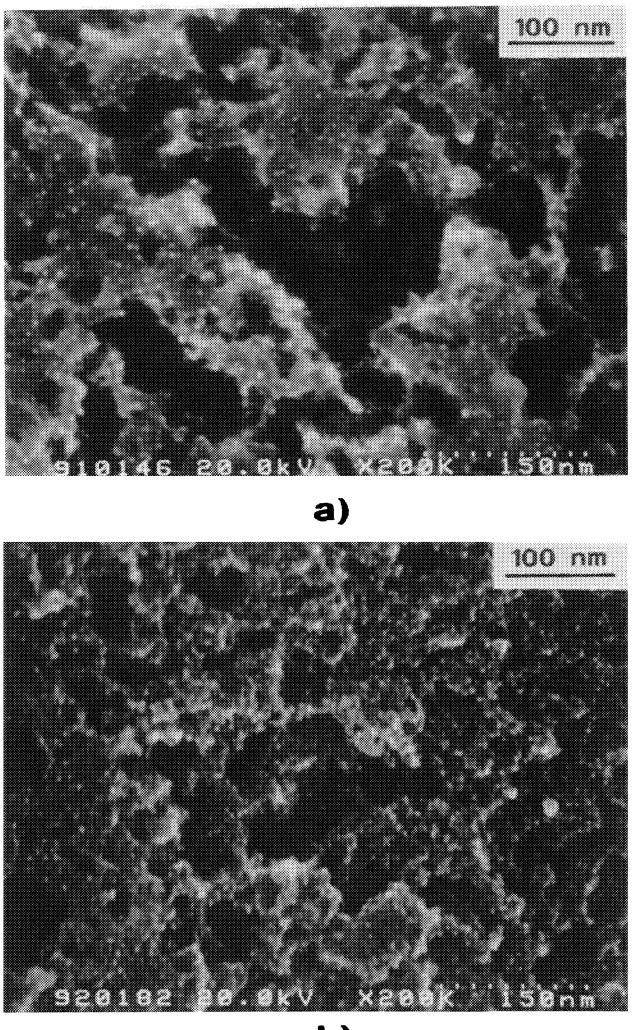
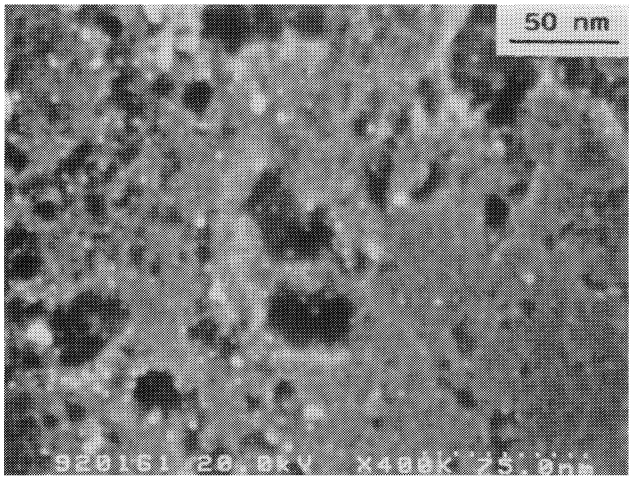


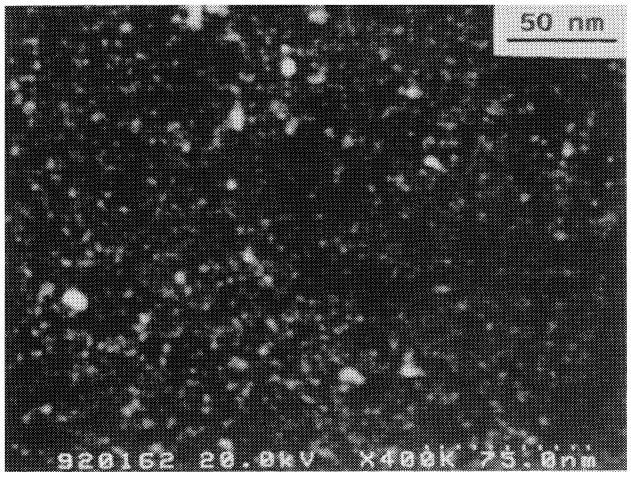
Fig. 1. Scanning electron micrographs of the 5%-Pd/AC catalyst. Mode: a secondary electron image, Part: a) a flat part; b) a rough part, Magnification: ×200000.

palladium particles and the sites of the support where the particles are embedded can be clearly observed. The reason for the clear contrast between the palladium particles and their active carbon support is that the emission probability of secondary electrons from the former is higher than that from the latter. In Fig. 2 the secondary (a) and reflection (b) electron images of the same part are presented (magnification: ×400000). From these two types of HR-SEM images, one can recognize the dispersion states of the ultrafine palladium particles, not only on the uppermost part, but also beneath the surface of the active-carbon support.

Figure 3 (magnification; ×400000) and Fig. 4 (magnification: ×3000000) show transmission electron micrographs of this supported palladium catalyst. From the lattice images clearly visualized in Fig. 4, it is revealed that the palladium particles comprise various kinds of twin crystallites. Although the resolution of this transmission microscope is much higher than that of the HR-SEM, the former cannot provide the surface morphology of the catalyst support, or the dispersion state of the supported palladium particles.



a)



b)

Fig. 2. Scanning electron micrographs of the flat part of the 5%-Pd/AC catalyst. Mode: a) a secondary electron image, b) a reflection electron image, Magnification: ×400000.

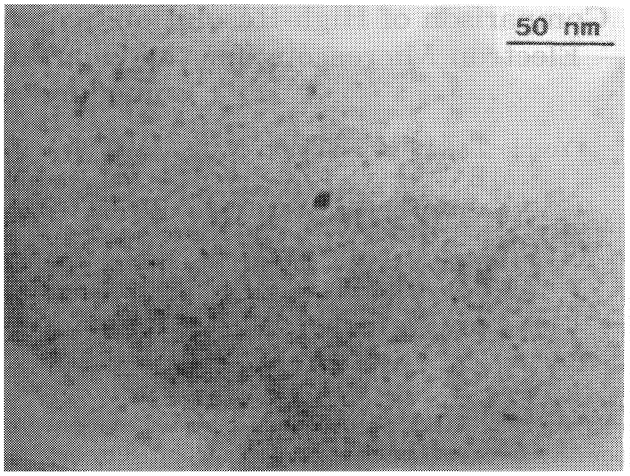


Fig. 3. Transmission electron micrograph of the 5%-Pd/AC catalyst. Magnification: ×400000.

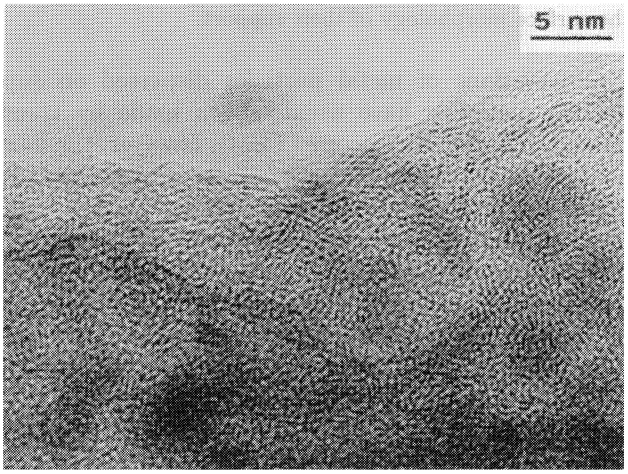


Fig. 4. Transmission electron micrograph of the 5%-Pd/AC catalyst. Magnification: ×3000000.

In conclusion, it has been demonstrated that high-resolution scanning electron microscopy (HR-SEM) is adoptable for the characterization of active carbon-supported metal catalysts. This microscopy can simultaneously give direct information concerning the dispersion state of ultrafine metal particles, and the surface morphology of their catalyst supports. The reflection electron image of it can add helpful information concerning the dispersion state of the small metal particles on and just beneath the porous catalyst support. Although transmission electron microscopy (TEM) cannot provide decisive information concerning the surface morphology of a catalyst support, it can visualize even the lattice image of the ultrafine metal particles, due to its much higher resolution than that of the HR-SEM. This suggests that a conbination of these two electron microscopies may be preferable for the characterization

of supported metal catalysts.

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