Support of Ultrafine Palladium Particles upon a Glassy Carbon Substrate by a Chemical Method

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Synopsis. Isolated ultrafine palladium particles prepared by a gas-evaporation method have been chemically supported on a flat glassy carbon substrate using a silane coupling agent. The modification of the ultrafine palladium particles with the silane coupling agent was confirmed by FT-IR spectroscopy and transmission electron microscopy (TEM). The supported palladium particles did electrochemical sorption–desorption of hydrogen in an acidic solution.

Ultrafine metal particles have been used as catalysts in petrochemistry, catalysts in gas-diffusion electrodes, elements in the inclined materials, and modification species of optical materials. There have been proposed many methods for the supporting of the ultrafine metal particles such as ion exchange, impregnation, and vacuum evaporation.[1] In these methods, it is not easy to prepare small metal particles of uniform size. On the other hand, the preparation of ultrafine metal particles has already been established in the field of colloid chemistry[2] and of vacuum technology, e.g. the gas-evaporation method,[3] where ultrafine metal particles are prepared by sublimation of metal under ~kPa of an inert gas. Since the sizing of the fine metal powders is not difficult, it may be possible to prepare the uniform size of supported metal particles if one succeeded in the surface modification of fine metal particles followed by supporting them on substrates. It is interesting, in this regard, that Kakuta used a silane coupling agent for the surface modification of iron particles in order to inbed them into an organic polymer.[4]

In this investigation, we have attempted for the first time to support ultrafine palladium particles, prepared by a gas-evaporation method, on a glassy carbon substrates after modification of the surface of palladium particles with a silane coupling agent. The reasons for the use of glassy carbon support are as follows: (1) it enables us easy to observe the supported metal particles by electron microscopy, and (2) it can serve as the support of an electrode for the evaluation of the electrochemical property of the supported ultrafine palladium particles.

Experimental

The ultrafine palladium particles (Vacuum Metallurgical Co., Ltd., about 50 nm in diameter) prepared by a gas-evaporation method were modified with a silane coupling agent of 3-aminopropyltriethoxysilane (Shinetsu Chemical Co., Ltd., LS-3150) as follows. The palladium particles (0.05 g) and a dispersing agent of α-phenyl-ω-hydroxydeca(oxyethylene)(0.5 ml) were added into 100 ml of distilled water. After it was dispersed ultrasonically for 30 min, 0.1 ml of the silane coupling agent was added, and then the suspension was dispersed ultrasonically for 2 h. After the procedure the sample was centrifuged and thoroughly washed with distilled water. A glassy carbon substrate (Tokai Carbon Ltd., GS-20S 10×10×1 mm), on the other hand, was polished with a fine alumina suspension (about 60 nm in diameter) using a cloth followed by washing it ultrasonically with acetone and distilled water, successively. Next, the glassy carbon was exposed to refluxing in nitric acid (61%) for 4 h followed by reacting with thionyl chloride (Wako Pure Chemical) for 2 h in order to introduce surface functional groups.

Both the palladium particles modified with the silane coupling agent and the dispersing agent of α-phenyl-ω-hydroxydeca(oxyethylene)(0.5 ml) were added to 100 ml of distilled water, and dispersed ultrasonically for 15 min. Into this suspension the surface-treated glassy carbon was dropped. After stirring of the suspension for 30 min, the glassy carbon was pulled up, and then it was washed with distilled water followed by drying at 110 °C for 30 min.

A diffuse reflectance Fourier transform infrared spectroscometer (Bio-Rad FTS-40), a transmission electron microscope (JEOL Ltd., JEX-1200II) and a scanning electron microscope (Akashi Seisakusho Ltd., Alpha-30) were used for the characterization of the ultrafine palladium particles modified with the silane coupling agent and the supported palladium particles on a glassy carbon.

Electrochemical measurements were done with a beaker-type electrolysis cell containing about 0.2 dm^3 electrolytic solution of 0.005 M $HClO_4$ (1 M=1 mol dm^{-3}). The counter and the reference electrodes were a platinum plate and a silver–silver chloride electrodes, respectively. Before measurement, electrodes were pre-treated by continuous potential cycling between 0 and 1.4 V (vs. RHE) at 500 mV s^{-1} for 10 min.[1]

Results and Discussion

Figure 1 shows FT-IR spectra of the silane coupling agent (a) and the ultrafine palladium particles chemically modified with the coupling agent (b). The characteristic absorption bands of the silane coupling agent are observed at 1100 cm^{-1}(Si–O–Si) and 2900 cm^{-1} (CH_2, CH_3).[5—7] The transmission electron micrograph, in Fig. 2, of the chemically modified ultrafine palladium particles with the silane coupling agent shows a dark uniform film (about 3 nm in width) around the surface of ultrafine palladium particles. This film can be assigned to the layer of the silane coupling agent. Since the surface of ultrafine palladium particles is liable to be oxidized to form PdO in air,[8] the silane coupling

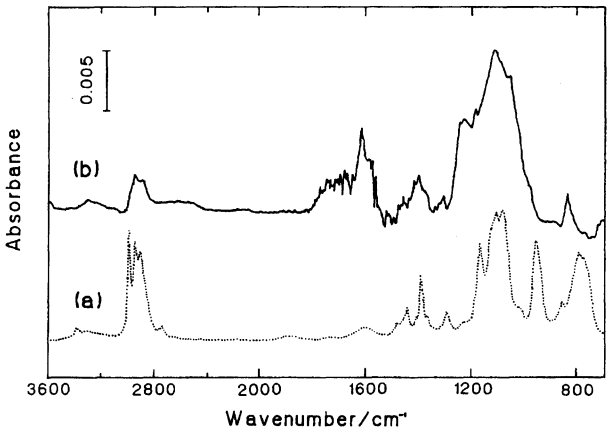

Fig. 1. FT-IR spectrum of silane coupling agent 3-aminopropyltriethoxysilane (a) and that of ultrafine palladium particles modified with the silane coupling agent (b).

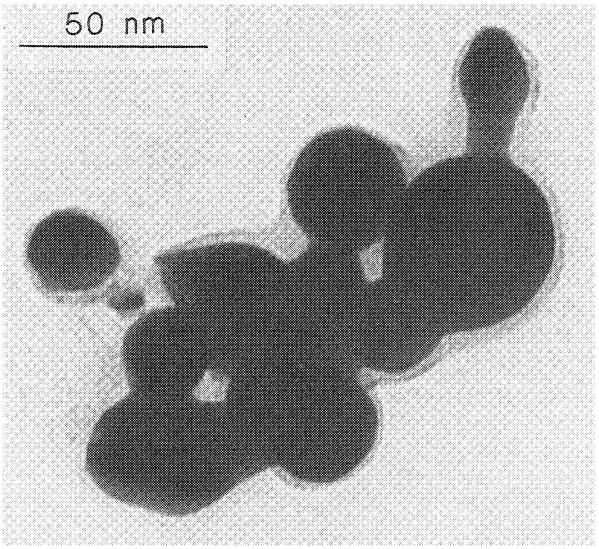

Fig. 2. TEM micrograph of the ultrafine palladium particles modified with the silane coupling agent.

agent might have reacted with some surface hydroxy groups probably existing on the palladium particles. It must be noted that the palladium particles aggregated with each other, forming second order particles. The formation of the second order particles was not avoided even when the experimental conditions, such as concentration of silane coupling agent, reaction time for silane coupling treatment, and kind of solvent, were varied. It is unclear at present in which process the second order palladium particles formed, i.e. (1) in the preparation of the palladium particles by the gas-evaporation process, (2) in the silane coupling process of the palladium particles, or (3) in the supporting process of the silane-coupled palladium particles with the surface-treated glassy carbon.

Figure 3 presents scanning electron micrographs of the ultrafine palladium particles (small white spots) which are chemically supported on the glassy carbon substrate with the silane coupling agent. Macroscopically, the ultrafine palladium particles are supported almost homogeneously on the glassy carbon substrate. When the ultrafine palladium particles were not modified with the silane coupling agent, they could not be supported upon the glassy carbon substrate.

Figure 4 shows the cyclic voltammograms for the non-treated glassy carbon (a), the surface treated glassy carbon (b) and ultrafine palladium particles-supported glassy carbon (c). The third electrode, (c), indicates characteristic features of palladium, i.e. it gave cathodic and anodic peaks due to hydrogen adsorption, absorption and desorption around 0—0.25 V (vs. RHE), and a cathodic current peak due to the reduction of the surface Pd oxide layers around 0.7 V.[9] Such a result suggests that charge transfer occurred across the film of silane coupling agent between the glassy carbon substrate and the ultrafine palladium particles. This means that the palladium particles prepared by this method serve

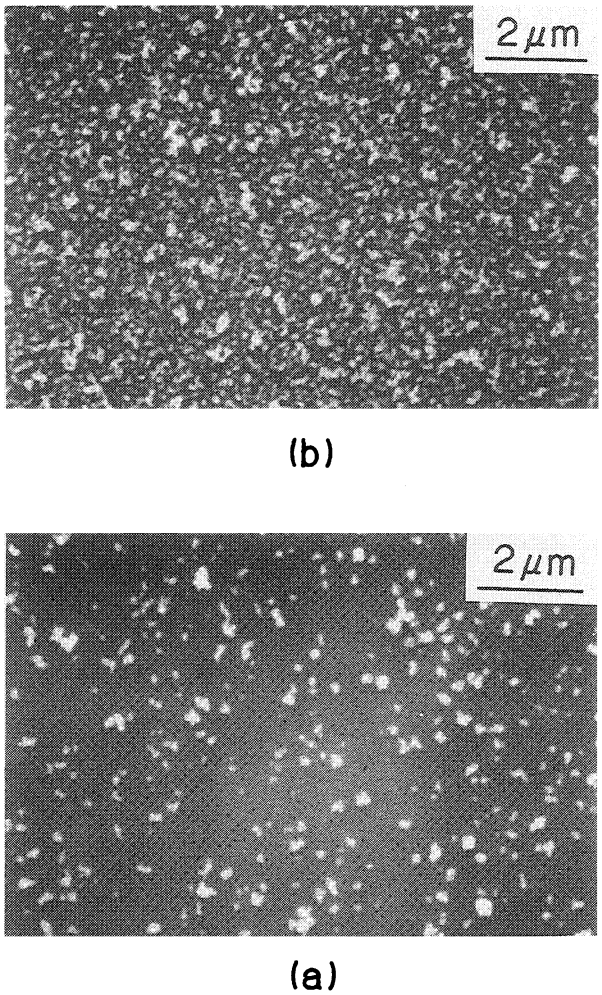

Fig. 3. SEM micrographs of the ultrafine palladium particles supported on a glassy carbon substrate. The reaction time of the palladium particles with the silane coupling agent: (a) 30 min, (b) 2 h.

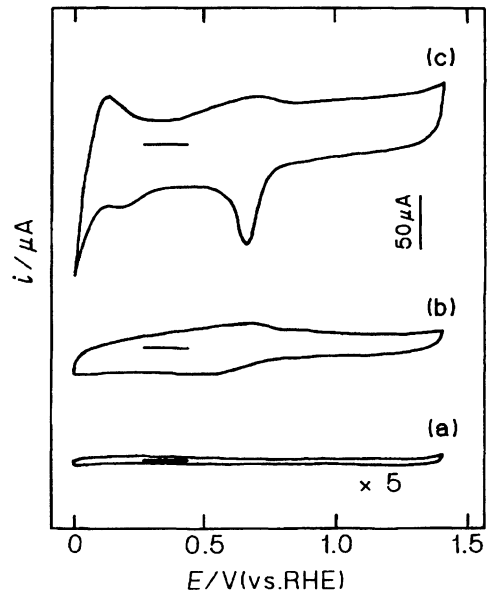

Fig. 4. Steady state cyclic voltammograms for a non-treated glassy carbon (a), the surface treated glassy carbon (b) and the glassy carbon-supported ultrafine palladium particles (c). Sweep rate: 50 $mV\,s^{-1}$, Electrolyte: 0.005 M $HClO_4$, 25 °C.

as an electrode. Scanning electron microscopy showed little change in the electrode before and after the electrochemical measurement, so long as the observation with magnification of ×10000.

Concludingly, the surface of the ultrafine palladium particles (about 50 nm in diameter) prepared by a gas-evaporation method have been almost homogeneously coated with a silane coupling agent, and the modified particles have been successfully supported onto a flat plane of a glassy carbon substrate. The use of silane coupling agent must be the first attempt for the supporting of ultrafine metal particles onto inorganic substrates. The glassy carbon supported palladium particles prepared by this method have done electrochemical sorption–desorption of hydrogen in an aqueous solution of $HClO_4$.

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