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AN APPLICATION OF A MODEL CATALYST METHOD TO A STUDY ON A SUPPORTED CATALYST ELECTRODE. EFFECTS OF PARTICLE SIZE ON THE ELECTROCHEMICAL DESORPTION BEHAVIOR OF HYDROGEN FROM SMALL PLATINUM PARTICLES

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A model catalyst-electrode has been applied for the first time to a cyclic voltammetry study with respect to the adsorption-desorption behavior of hydrogen in an aqueous solution of H_2SO_4. The peak potentials for the desorption of hydrogen were found to depend greatly on the platinum particle size.

Effects of metal particle size on the catalytic properties of supported metal catalyst-electrodes have not yet been revealed clearly.$^{1-4)}$ The difficulty in such study must be caused mainly by the complexity of the structure of "practical" supported metal catalyst-electrodes. The size effects may be examined more precisely by using a model catalyst electrode, consisting of metal particles embedded on a flat and electric conducting substrate by vacuum evaporation. This method enables us to observe the shape of the particles by transmission electron microscopy (TEM), and the particle size can easily be controlled.$^{5)}$ Moreover, any effect of pore structure of the substrate on the desorptive properties can be neglected because of the flatness of the substrate of the model catalyst. The valence band structure of the supported small metal particles of the model catalyst can also clearly be observed by ultraviolet photoelectron spectroscopy.$^{6)}$ We have now investigated the effect of particle size for a Pt/GC (glassy carbon) catalyst-electrode on the desorption of hydrogen in an aqueous solution of H_2SO_4.

The support for the electrode was a glassy carbon rod (Tokai Carbon, GC-10, 5.3 mm in diam.). The base of the rod was polished with a cloth and alumina powder (ca. 0.3 μm). The amount of platinum evaporated onto the base of the glassy carbon support rod was determined with a quartz thickness monitor (Anelva, EVM-32B), i.e. the amount of incident platinum was determined as the mass. Electrochemical measurements were carried out by using a glass beaker cell which was filled with 0.2 dm^3 of 1.0 or 0.05 mol dm^{-3} H_2SO_4 solution at 25 °C. The counter and the reference electrodes were a platinum plate (3 x 3 cm^2) and a SCE, respectively.

Figure 1 shows a typical electron micrograph of the Pt/GC model catalyst, which was prepared by evaporation of platinum by 3.8×10^{15} atoms cm^{-2}, after an electrochemical aging, i.e. the electrode was treated by sweeping the potential repeatedly between -0.190 V (-0.240 V in case of 0.05 mol dm^{-3} H_2SO_4) and +0.920 V (vs. SCE) at a sweep rate of 300 mV s^{-1} for 10 min. The platinum particles are seen as spots on the micrograph. The numerical mean diameter $\bar{d}$ of the catalyst is

2.5 nm, while that of as evaporated was 2.2 nm. Before the electrochemical aging, the mean diameter of the specimens, determined by the TEM, evaporated by an amount of 0.8 x 10^{15}, 1.5 x 10^{15}, and 2.3 x 10^{15} Pt atoms cm^{-2} were 1.5, 1.7, and 1.9 nm, respectively.

In Figs. 2-a and 2-b, typical cyclic voltammograms for some Pt/GC model catalyst-electrodes under a steady state are shown along with those of a glassy carbon and a platinum wire. Prior to the recording of these voltammograms, the electrodes were treated by the aging

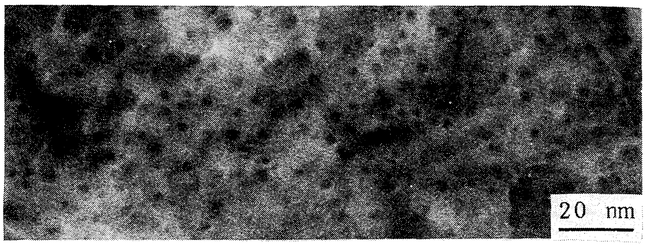

Fig. 1. Electron micrograph of a Pt/GC model catalyst-electrode after the electrochemical aging.
The amount of the incident platinum atoms measured by the quartz thickness monitor : 3.8 x 10^{15} Pt atoms cm^{-2}; Mean diameter of the platinum particles $\bar{d}$: 2.5 nm; Electrolyte : 1.0 mol dm^{-3} H_2SO_4, 25 °C.

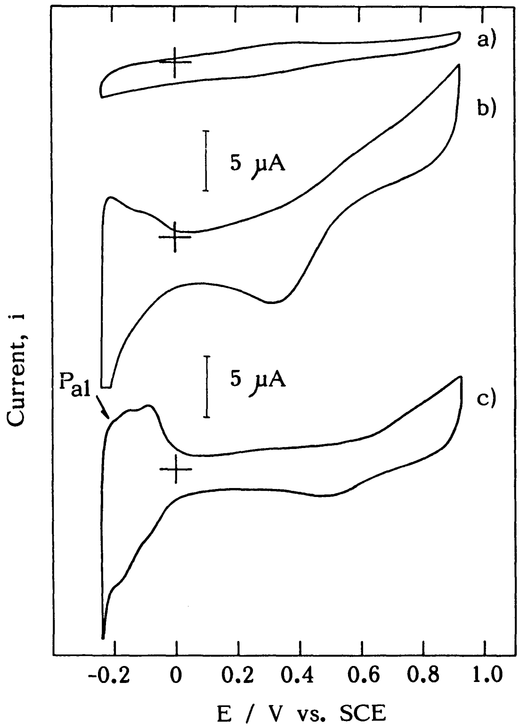

Fig. 2-a. Steady state cyclic voltammograms for a glassy carbon and two Pt/GC electrodes.
Electrolyte : 0.05 mol dm^{-3} H_2SO_4, 25 °C; Sweep rate : 100 mV s^{-1}; Working electrode : a) glassy carbon, b) Pt/GC (the amount of the incident platinum atoms : 3.8 x 10^{14} Pt atoms cm^{-2}), c) Pt/GC (7.6 x 10^{14} Pt atoms cm^{-2}).

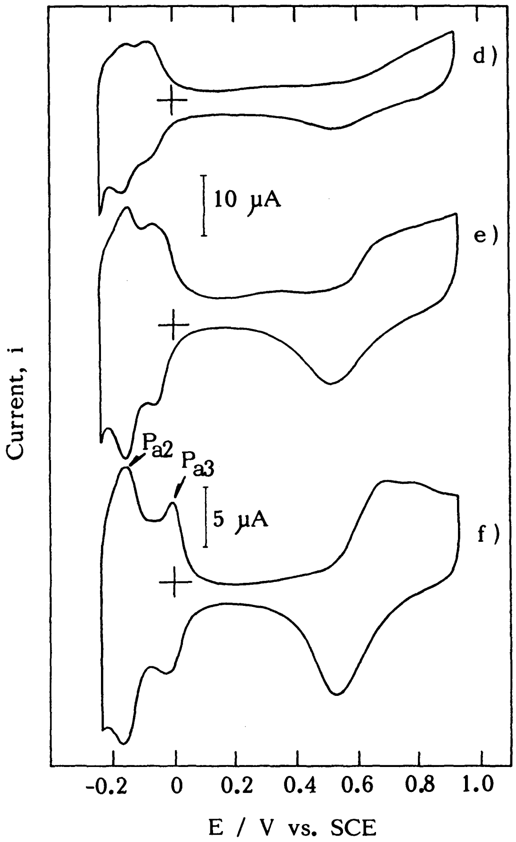

Fig. 2-b. Steady state cyclic voltammograms for two Pt/GC and a platinum wire electrodes.
Electrolyte and Sweep rate : see Fig. 2-a; Working electrode : d) Pt/GC (1.5 x 10^{15} Pt atoms cm^{-2}), e) Pt/GC (3.8 x 10^{15} Pt atoms cm^{-2}), f) platinum wire.

described above. Three anodic peaks, P_{a1}, P_{a2}, and P_{a3}, which originated from the adsorbed hydrogen, appeared with different peak height ratios. It should be noted that the peak potential $E_{P_{a3}}$ greatly shifted to the negative potential with decreasing the amount of platinum evaporated. The tendency can be seen clearly in Fig. 3. Since we have obtained now few TEM data on the size of platinum particles, the each peak potential in Fig. 3 was plotted against the surface area of platinum particles estimated by the total amount of electricity used for the anodic desorption of the adsorbed hydrogen.[7,8] The mean particle size increased with increasing the surface area and the amount of platinum evaporated in this region studied. The peak potential $E_{P_{a2}}$ on the other hand, shifted a little to the positive potential with decreasing the size of platinum particle. It is not easy to distinguish the anodic peak P_{a1}, especially on the voltammograms for the platinum wire electrode and for the Pt/GC electrodes consisted of larger platinum particles, however, the peak grew evidently with decreasing the amount of platinum evaporated. If P_{a1} was caused by an anodic desorption of hydrogen chemisorbed on a certain crystal plane of platinum particles, it should be said that the ratio of the plane to the other crystal planes increased with decreasing the platinum particle size. It might also be probable, however, that the peak partly reflected the anodic oxidation of molecular hydrogen which was formed during the cathodic sweep. The anodic peaks, P_{a2} and P_{a3} appeared on the voltammogram f), can be identified as the hydrogen from Pt(110) and Pt(100) planes, respectively.[9-11] The shifts of the peak potentials mean that each corresponding crystal plane over the small platinum particles have somewhat different adsorption energies from those planes of single crystals. Such effect was remarkable for P_{a3}, suggesting that the Pt(100) plane, or any other plane similar to the crystal plane, which adsorbs hydrogen most strongly, is great-

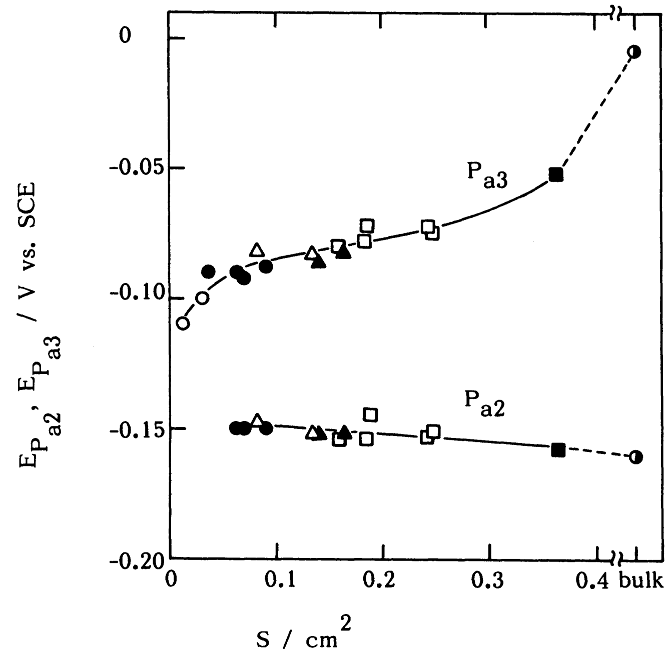

Fig. 3. Relations between the peak potentials of anodic desorption of hydrogen and the surface area of platinum particles, on a unit geometrical area of the Pt/GC electrodes, estimated by the total amount of electricity used for the anodic desorption of the adsorbed hydrogen.[7,8]
The experimental condition : see in Figs. 2-a and 2-b; Amount of platinum evaporated : ○(3.8×10^{14} Pt atoms cm^{-2}), ●(7.6×10^{14} Pt atoms cm^{-2}), △(1.5×10^{15} Pt atoms cm^{-2}), ▲(2.3×10^{15} Pt atoms cm^{-2}), □(3.8×10^{15} Pt atoms cm^{-2}), ■(11.4×10^{15} Pt atoms cm^{-2}), ◑ (Pt wire).

ly affected by the size of platinum particles. That is, the adsorption strength of hydrogen on the surface grew weaker with decreasing the particle size. This corresponds to the fact that the activation energy for the desorption of hydrogen from Pt/SiO_2 catalysts decreased with decreasing the platinum particle size.12)

For the consequence of the particle size effects on the adsorptive properties of supported small metal particles, various explanations can be proposed : (a) characteristic configuration of the surface atoms of small metal particles; i.e. the ratio of low coordinated surface atoms increases with decreasing the particle size,13) (b) characteristic electronic state of small metal particles,6,14) or (c) the extent of the interaction between the metal particles and the support. The authors have observed that the largest state density in the valence band of small palladium particles supported on a graphite plate shifted to the higher binding energy with decreasing the particle size.6) Although such electronic state may relate to the adsorptive property of small metal particles, both of the electronic state and the geometry of surface palladium atoms change with the decrease in particle size of crystallites. Therefore, more precise examination, especially on the morphorogy of small metal particles, must be performed by the model catalyst method in order to clarify the main factor governing the chemical properties of small metal particles.

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