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Size Effects of Small Platinum Particles on the Electrocatalytic Oxidation of Methanol

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Synopsis. A cyclic voltammetry study of a platinum-glassy carbon model catalyst-electrode (Pt/GC) in an aqueous solution of H_2SO_4 revealed that the peak potentials for the anodic oxidation of methanol shifted a little to the negative potential and that the current densities decreased greatly with the decrease in the size of the platinum particles.

A model catalyst, consisting of metal particles embedded on a flat and electric conducting substrate by means of vacuum evaporation, enables us to examine precisely the effects of metal-particle size on the catalytic properties of supported metal catalyst-electrodes.[1] Since the substrate is flat, not only is the observation of the shape of the particles by transmission electron microscopy (TEM) easy, but also any effect of the pore structure of the substrate on the catalytic properties can be neglected. This study will discuss the effect of the particle size of Pt/GC catalyst-electrode on the electrocatalytic oxidation of methanol in an aqueous solution of H_2SO_4.

Experimental

The support for the electrode was a glassy carbon rod (Tokai Carbon, GC-10, 0.53 cm in diam.). The base of the rod was polished with a cloth and alumina powder (ca. 0.3μm in diam.). The amount of platinum evaporated onto the base of the glassy carbon rod was determined with a quartz thickness monitor (Anelva, EVM-32B); i.e.,the amount of incident platinum was determined as the mass. The platinum particles were observed by means of a TEM (JEOL, JEM-200 CX). The electrochemical measurements were carried out by using a glass beaker cell filled with 0.2 dm^3 of a 1.0 $mol\,dm^{-3}$ H_2SO_4 solution at 25 °C containing 1.0 $mol\,dm^{-3}$ CH_3OH. The counter and reference electrodes were a platinum plate (3×3 cm^2) and a saturated calomel electrode (SCE) respectively.

Results and Discussion

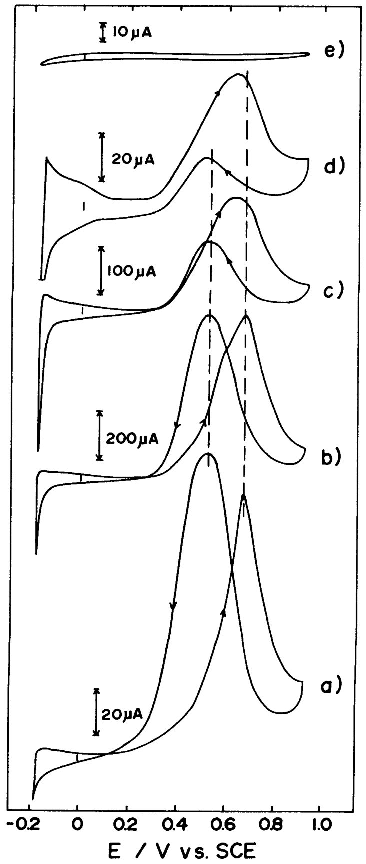


Fig. 1. Steady-state cyclic voltammograms for platinum wire, glassy carbon, and Pt/GC model catalyst electrodes in an aqueous solution of H_2SO_4 containing CH_3OH. Electrolyte: 1.0 $mol\,dm^{-3}$ H_2SO_4, 1.0 $mol\,dm^{-3}$ CH_3OH, 25°C. Sweep rate: 100 $mV\,s^{-1}$. Working electrode: a) platinum wire (geometric surface area; S_g=0.019 cm^2, real surface area determined by a cyclic voltammetry in 1.0 $mol\,dm^{-3}$ H_2SO_4; S_r=0.093 cm^2), b) Pt/GC (S_r= 0.393 cm^2, the amount of the incident platinum atoms on the substrate; M=7.6×10^{15} Pt atoms cm^{-2}, mean diameter of platinum particles determined by TEM; $\bar{d}$=2.3 nm), c) Pt/GC (S_r=0.190 cm^2, M=2.3×10^{15} Pt atoms cm^{-2}, $\bar{d}$=1.9 nm), d) Pt/GC (S_r=0.067 cm^2, M=7.6×10^{14} Pt atoms cm^{-2}, $\bar{d}$= 1.5 nm), e) glassy carbon (S_g=0.22 cm^2).

Figure 1 shows same typical cyclic voltammograms for a platinum-wire, a galssy-carbon, and three Pt/GC model catalyst-electrodes under a steady state. Prior to the measurements of these voltammograms, the electrodes were treated by means of electrochemical aging; i.e., the electrode potential was swept repeatedly between −0.190 V and +0.920 V (vs. SCE) at a sweep rate of 300 $mV\,s^{-1}$ for 10 min. By this treatment, the numerical mean diameter of the platinum particles, $\bar{d}$, increased a little; e.g., the $\bar{d}$ of a specimen evaporated with 3.8×10^{15} Pt atoms cm^{-2} increased 20% after the treatment. The anodic peak which appeared around 0.65 V (vs. SCE) during the anodic sweep and that around 0.5 V during the cathodic sweep are termed P_{a1}, and P_{a2} respectively. The first noticeable feature in Fig. 1 is that the anodic peak potential, $E_{P_{a1}}$, for the platinum-wire electrode (0.665 V) was higher than that for the Pt/GC electrodes which consisted of smaller platinum particles (0.622 V). A shoulder peak was found for the Pt/GC electrode with larger platinum particles (voltammogram b)), as had also been observed by Sobokowsky and his co-workers.[2] Similar shifts of the peak potential can also be observed for $E_{P_{a2}}$, although the potential shift is only about 0.02 V. The second noticeable feature is that the ratio of the

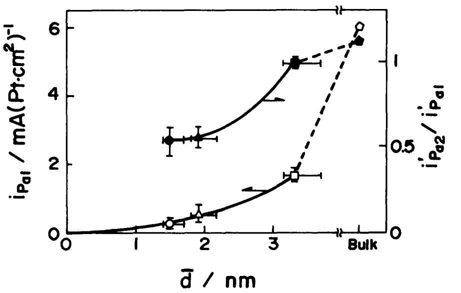
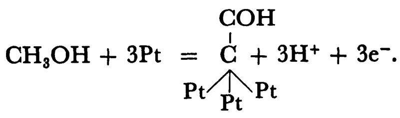


Fig. 2. The ratio of the peak current for P_{a1} and P_{a2} and the peak current density of P_{a1} for the oxidation of CH_3OH, as a function of mean diameter of platimum particles. The experimental conditions: see in Fig. 1. Amount of platinum evaporated. ○, ●: (M=7.6×10^{14} Pt atoms cm^{-2}), △, ▲: (M=2.3×10^{15} Pt atoms cm^{-2}), □, ■: (M=7.6×10^{15} Pt atoms cm^{-2}), ◇, ◆: (Platinum wire).

peak currents for P_{a1} and P_{a2}, $i'_{P_{a2}}/i'_{P_{a1}}$, decreased with a decrease in the platinum particle size, $\bar{d}$, as is illustrated in Fig. 2. In order to determine the current density per surface area of the platinum particles, the real surface area of the platinum particles, S_r, was estimated from the total amount of electricity used for the anodic desorption of adsorbed hydrogen on the platinum particles in a 1.0 mol dm^{-3} H_2SO_4 solution after the electrochemical aging of the electrodes.[3,4] The current density for P_{a1} is shown in Fig. 2. It is worth noting that the peak current density, $i_{P_{a1}}$, abruptly decreased with a decrease in the size of the platinum particles.

As regards the size effects on the catalytic properties of supported platinum particles, the following aspects must be considered: a) the geometry of surface atoms,[5] b) the electronic state of the surface,[6] and c) the interaction with the substrate. The anodic oxidation of methanol on platinum is a typical structure-sensitive reaction;[7–9] i.e., Clavilier et al. found that the (110) plane of a single crystal was the most active in the initial stage, but that it became less active during continuous cycling, while the Pt(100) plane was the most electroactive plane under steady state conditions.[7] Contrary to their results, we observed that the ratio of the peak current due to the desorption of hydrogen from Pt(110) to that from Pt(100), $i'_{Pt(110)}/i'_{Pt(100)}$, decreased with a decrease in the size of the platinum particles [Ref. 1 Fig. 2, 2-a, b)].[1] However, the peak potential for the Pt(100) plane decreased with a decrease in the particle size, while that for the Pt(110) increased a little.[1] In order to explain the size effects, therefore, we must consider the contribution of each of the crystal planes of the small metal particles, which have rather different properties from those of the single crystals, to the electrocatalytic properties. Moreover, it has been suggested that methanol requires three adjacent sites for the adsorption, viz;[9,10]



$$CH_3OH + 3Pt = \underset{Pt\ \ Pt\ \ Pt}{\overset{COH}{C}} + 3H^+ + 3e^-.$$

It may not be easy for small platinum particles to provide such suitable sites with respect to the adsorption of methanol. The shifts of the anodic-peak potentials [Fig. 1] and the change in the peak-current ratio [Fig. 2], $i'_{P_{a2}}/i'_{P_{a1}}$, with the particle size must be caused by the ease of the formation of either the oxide layer of platinum or the oxidized adsorbed species of methanol, which interfere with the methanol oxidation, on the smaller rather than on the larger platinum particles. This speculation can be supported by the fact that the peak potentials for the reduction of the surface-oxide layer of platinum particles, as measured by a cyclic voltammetry in an aqueous solution of H_2SO_4, shifted to the negative potential with a decrease in the platinum-particle size.[1,11]

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