

Size effects of ultrafine Pt–Ru particles on the electrocatalytic oxidation of methanol

Yoshio Takasu,* Hiroyuki Itaya, Tomoya Iwazaki, Ryo Miyoshi, Takefumi Ohnuma, Wataru Sugimoto and Yasushi Murakami

Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386-8567, Japan. E-mail: ytakasu@giptc.shinshu-u.ac.jp

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The specific activity, $i_{sp}/A\ m^{-2}$ (current density per real surface area), of Cl-free well-homogenized Pt–Ru particles at 25 and 60 °C in aqueous acidic solutions has been found to decrease with a decrease in the size of the Pt–Ru alloy particles, and the mass activity, $i_{mass}/A\ g^{-1}$ (current density per mass of catalyst metal loaded), showed the same dependency when the size of the alloy particles was < ca. 3 nm in diameter.

For the development of methanol fuel cells,¹ many investigations have been made on the catalytic activity of Pt–Ru alloy electrocatalysts which perform as active anodes for methanol and carbon monoxide-containing hydrogen.² Among the various factors possibly affecting the catalytic activity of the Pt–Ru alloy catalysts for methanol oxidation, the dependence of the Pt–Ru particle size on the catalytic oxidation of methanol, e.g. the 'size effect', is an important factor for recognizing the fundamental catalytic properties of ultrafine alloy particles. The size effect of platinum particles of Pt/C catalysts for the oxidation of methanol has been examined by some research groups;³ however, that for well-homogenized Pt–Ru alloy particles has not yet been reported. Ultrafine catalyst metal particles are often more active compared to larger ones probably due to their higher concentration of low-coordinated surface metal atoms.

The present investigation has been carried out to clarify the 'size effect' for the electrocatalytic oxidation of methanol on well-homogenized ultrafine Pt–Ru particles supported on a carbon. The alloy composition used was Pt₅₀–Ru₅₀, (Pt:Ru = 1:1 mol/mol), since this composition was the most active in the binary alloy catalyst system.⁴ The Pt₅₀–Ru₅₀/C catalyst powders were prepared by an impregnation method with carbon black powder (Vulcan XC72R; 254 m² g⁻¹) and ethanolic solutions of Pt(NO₂)₂(NH₃)₂ and RuNO(NO₃)_x. The combination of these metal complexes can give well-homogenized alloy particles.⁴ The decomposition of the metal complexes supported on the carbon black powder was made in a stream of H₂ + N₂ at 450 °C to attain almost complete alloying, while the catalytic activity for the oxidation of methanol decreased with the preparation temperature from 200 to 450 °C.⁴

Fig. 1 shows high-resolution scanning electron micrographs of Pt₅₀–Ru₅₀/C catalysts with different loading amounts of the alloy. The mean size of Pt₅₀–Ru₅₀, d , determined from these electron micrographs increases with the amount of catalyst loading. As shown in Fig. 2, the X-ray diffraction patterns of these Pt₅₀–Ru₅₀/C catalysts show that the lattice constant of the fcc Pt₅₀–Ru₅₀ alloys is almost the same value as measured by Gasteiger *et al.* using a bulk Pt₄₈–Ru₅₂ alloy, 0.38624 nm.⁵

Fig. 3 shows the relationships between the catalytic activities,⁶ specific activity (i_{sp}) and the mass activity (i_{mass}), for the oxidation of methanol in 0.5 mol dm⁻³ H₂SO₄ at 60 °C and the loading amount of the alloys. Some of the mean particle sizes of the Pt₅₀–Ru₅₀ particles are marked on the figure. It should be noted that i_{sp} decreases with a decrease in the particle size of Pt₅₀–Ru₅₀ at all potentials studied, while i_{mass} gives a maximum value at 40 mass% of alloy loading at all polarization potentials,

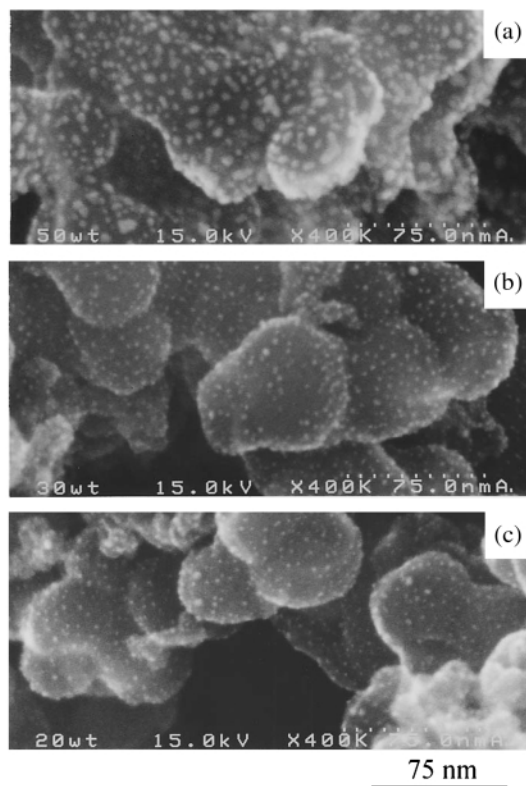


Fig. 1 High-resolution scanning electron micrographs (Hitachi, S-5000) of Pt₅₀–Ru₅₀/C catalysts with different loadings. Loading amount: (a) 20 mass%, (b) 30 mass%, (c) 50 mass%.

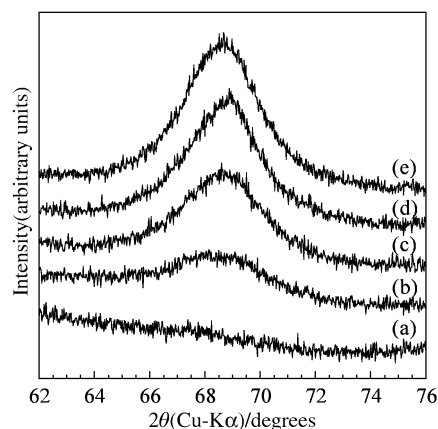


Fig. 2 XRD patterns of Pt₅₀–Ru₅₀/C catalysts with different loadings. Loading amount of Pt–Ru and the mean particle size, d , determined from the high-resolution SEM: (a) 10 mass% ($d = 1.9\ \text{\AA} \pm 0.7\ \text{nm}$), (b) 20 mass% ($d = 2.1\ \text{\AA} \pm 0.7\ \text{nm}$), (c) 30 mass% ($d = 2.7\ \text{\AA} \pm 0.6\ \text{nm}$), (d) 40 mass% ($d = 3.0\ \text{\AA} \pm 0.8\ \text{nm}$), (e) 50 mass% ($d = 3.5\ \text{\AA} \pm 1.0\ \text{nm}$).

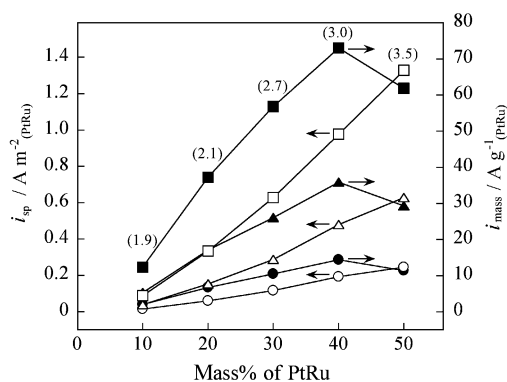


Fig. 3 Dependence of the specific activity (i_{sp}) and mass activity (i_{mass}) for the oxidation of methanol on the size of alloy particles of Pt₅₀-Ru₅₀/C electrodes in 0.5 mol dm⁻³ H₂SO₄ containing 1 mol dm⁻³ MeOH at 60 °C. The values of i_{sp} and i_{mass} correspond to mean quasi-steady state current densities at 30 min after polarization at each electrode potentials per real surface area of alloy particles and per mass of alloy particles, respectively. Open symbols (○, △, □): i_{sp} . Solid symbols (●, ▲, ■): i_{mass} . Polarization potential of the test electrode (vs. RHE): ○ and ●, 400 mV; △ and ▲, 450 mV; □ and ■, 500 mV.

where d is *ca.* 3 nm. The fact that the specific activities of the larger Pt₅₀-Ru₅₀ particles are higher than the smaller ones suggests a larger surface area of alloy particles is more effective for the oxidation. A similar size effect was observed in the experiments at 25 °C. The possible effect of adsorption of the anion, SO₄²⁻, on the oxidation of methanol can be neglected because similar size effects were also observed in the reaction in 0.020 mol dm⁻³ HClO₄. Since no obvious difference in the average distance between Pt₅₀-Ru₅₀ particles in Fig. 1 (a)–(c) is found, the ‘size effect’ observed in the catalytic activity is not caused by the diffusion interference between the spherical diffusion areas around the alloy particles.³ The findings of this investigation suggest, at least, that low-coordinated surface atoms should not be the limiting factor for the electrocatalytic oxidation of methanol.

In order to clarify the origin of the ‘size effect’ found in this investigation, the electronic structure and surface alloy composition⁶ of the Pt-Ru particles as well as the surface species⁷ of OH_{ad}, CO_{ad} and CHO_{ad} should be characterized. Such information; however, concerns the overall properties of the alloy catalysts. Furthermore, characterization of the exposed crystal planes⁸ and the precise shapes of the alloy particles and elucidation of the optimum ensemble of the surface Pt and Ru atoms⁹ for the oxidation of methanol are needed as a function of particle size.

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