

Effect of Sn in Pt–Ru–Sn Ternary Catalysts for CO/H₂ and Methanol Electrooxidation

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The activity for methanol oxidation of Pt₃Ru₂Sn/C was significantly higher than that of Pt/C or PtRu/C catalyst by improving CO tolerance. The higher CO tolerance property of Pt₃Ru₂Sn/C was caused by the synergic effects of Ru as a water activator and Sn as an electronic modifier of Pt. In ternary alloy catalyst including the efficient water activator, the Pt–CO bond strength could become important factor.

The electrooxidation of methanol has attracted considerable attention as an interesting subject because of its significance in the field of direct methanol fuel cell (DMFC). It is well known that methanol oxidation involves the successive sequence of methanol adsorption, its dehydrogenation, and the CO oxidation. Although Pt has been currently accepted as the most effective electrode catalyst in fuel cell, the employment for the anode material in DMFC has limited due to its deactivation by CO poisoning. The dissociation of water on Pt for the oxidation of the adsorbed CO occurs at high potential (ca. 0.7 V vs RHE),¹ which is less appropriate property for Pt as an anode catalyst. In order to improve the catalytic activity for methanol oxidation, second promoter is needed to oxidize sufficiently the adsorbed CO on Pt at much lower potentials. The Pt–Ru and Pt–Sn systems have been reported to improve CO tolerance of the catalyst.^{2,3} It is noted that their promotion mechanisms for the CO oxidation are different each other, and furthermore contradictory results have been reported on the promotion effects of binary Pt–Sn and ternary Pt–Ru–Sn catalysts for methanol oxidation.⁴

In our previous work, Pt–Ru–Sn ternary catalysts showed the significantly higher activity for methanol oxidation than Pt and Pt–Ru catalysts.⁵ However, to date, the synergistic promotion mechanism of the ternary catalyst was unclear and there are few reports of systematic studies about it. The present paper describes the roles of Ru and Sn in ternary catalyst, and the synergistic effects of Pt–Ru–Sn catalyst for methanol electro-oxidation by electrochemical experiments using non-alloy (Pt–M/C) and alloy catalysts (PtM/C).

Carbon-supported alloy catalysts were prepared by reverse microemulsion method. Reverse microemulsions were consisted of isooctane as an oil phase, Igepal CA-630 (Octylphenoxy polyethoxyethanol with 9 units of ethylene oxide per mole, Sigma) as a surfactant, 2-propanol as a cosurfactant and aqueous precursor solution. The metal precursor solution was obtained by dissolving H₂PtCl₆·6H₂O, H₂RuCl₆ solution, and SnCl₄ to highly pure water (18.2 MΩ cm) and the concentration of total metal precursor was 0.04 M. The reverse microemulsions of metal precursors and NaBH₄ were prepared by injecting the aqueous solutions to the previous isooctane solution containing surfactants and stirring sufficiently at room temperature until the solutions change to be clear and stable. The water volume fraction (ϕ_w) was 0.108. The amount of NaBH₄ was 20 times that of total mole of the metal precursors for complete reduction of metal ions into the elementary state. To synthesize the alloy nanoparticles, the reverse microemulsion con-

taining NaBH₄ was added dropwise to that of metal precursors at same volume and stirred constantly at room temperature. Then the appropriate amount of carbon powder (Ketjenblack, specific surface area of 1000 m² g⁻¹) was added into the prepared particle solution. After sufficient mixing, water was added to separate the phase. Carbon-supported mixed catalysts were prepared by impregnation and chemical reduction. Appropriate amount of commercially available Pt/C (Tanaka Kikinzoku Kogyo Co., Ltd., 20 wt % of Pt) was added into the aqueous metal precursor solution. After sufficient mixing, NaBH₄ solution was added to reduced into metal. The resulting powders were washed sufficiently by ethanol and water. The absence of sodium ion was checked by XPS. Both powders were dried at 60 °C for 12 hours. The bulk and surface compositions of catalysts (both of non-alloy and alloy catalyst) were measured by EPMA and XPS, respectively. The various compositions of the resulting catalysts were in agreement with the composition of the initial precursor solution. The crystal structure of metal particle was examined from by X-ray diffraction measurements using Cu K α radiation ($\lambda = 0.1542$ nm). From the broadening of (111) diffraction peak in XRD patterns, the average crystal size and lattice constant were calculated. Electrochemical characterization of catalysts was performed in an electrochemical cell with three electrodes using a rotating disk electrode at room temperature. A Pt disk and Ag/AgCl (in saturated KCl) were used as the counter and reference electrodes, respectively. The fabrication of working electrode and the electrochemical measurements of both CO/H₂ and methanol oxidations were performed as described in the reference 6.

The XRD patterns of carbon-supported non-alloy and alloy catalysts are shown in Figure 1. The alloy states of catalysts were examined by the shift of Pt diffraction peaks. The Pt peaks of all non-alloy catalysts coincided with those of Pt/C. The non-alloy catalysts containing Sn showed the SnO₂ peaks, and the Ru peaks

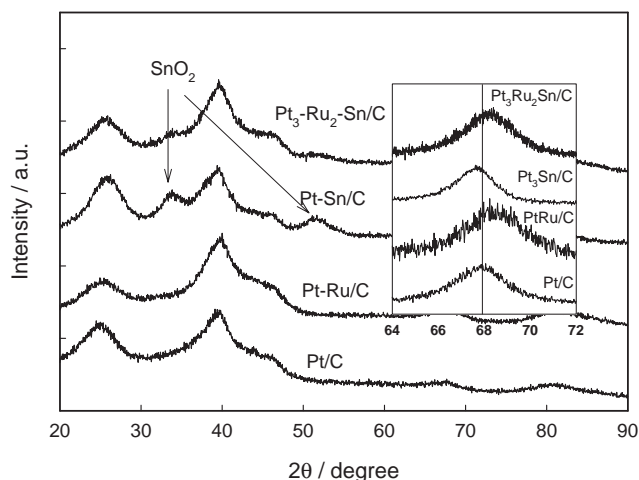


Figure 1. XRD patterns of carbon-supported non-alloy and alloy catalysts. The inset shows (220) peaks of alloy catalysts.

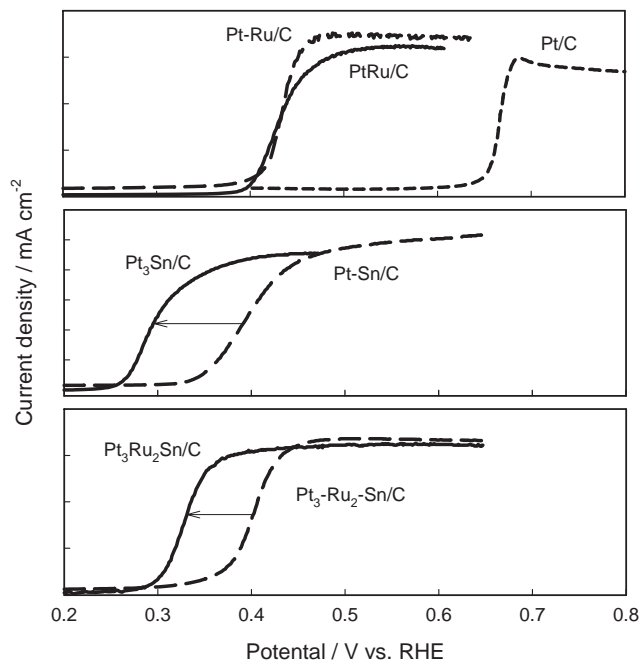


Figure 2. The potentiodynamic oxidation of 0.5% CO/H₂ on the carbon-supported catalysts at room temperature (potential sweep rate: 1 mV s⁻¹, electrolyte: 0.1 M H₂SO₄, rotating speed: 2500 rpm, loading weight of catalyst: based on constant 18 μg_{Pt}/cm² for alloy catalyst and 30 μg_{Pt}/cm² for non-alloy catalyst).

were not found for catalysts containing Ru. The peaks of PtRu/C were shifted to higher 2θ values as compared to Pt/C. By contrast, those of Pt₃Sn/C were shifted to lower values. Such shifts represent that the PtRu and PtSn alloy phases are formed in the prepared alloy catalysts. The ternary alloy, Pt₃Ru₂Sn/C has an intermediate value between PtRu/C and Pt₃Sn/C, then it is expected that both Ru and Sn were partially alloyed to Pt. Also, from the XPS measurements, the binding energy of Pt 4f_{7/2} of the alloy catalysts was shifted into the lower value compared to that of Pt/C. On the other hand, the binding energy of Pt 4f_{7/2} of the non-alloy catalysts was akin with that of Pt/C. These negative shifts of the alloy catalysts mean that the electron transfer from Ru and/or Sn to Pt occurs by alloying between Pt and Ru and/or Sn.

Figure 2 shows the results of the potentiodynamic oxidation of 0.5% CO/H₂. It is certified that all catalysts were homogeneous state and well dispersed on carbon support by showing the pure characteristic of the binary or ternary catalysts without other peaks such as that of Pt in the potentiodynamic and CO stripping measurements. For Pt/C, H₂ oxidation was completely suppressed until ca. 0.66 V by CO poisoning. The onset potentials of CO/H₂ oxidation were ca. 0.42, 0.36, and 0.38 V for Pt-Ru/C, Pt-Sn/C, and Pt₃-Ru₂-Sn/C, respectively. Both Ru and Sn were seen as a promoter to improve the CO-oxidation. It is reported that the water is dissociated on Ru and Sn at low potentials and the CO oxidation activity is enhanced by the adsorbed oxygen species on Ru and Sn (bifunctional mechanism). For alloy catalysts, the CO oxidation activity of PtRu/C was similar to that of Pt-Ru/C, whereas the activity of PtSn/C was significantly improved as compared with that of Pt-Sn/C (negative shift of ca. 0.10 V). The electron donation from Sn to Pt in PtSn alloy was reported from XANE and XPS analysis,^{5,7} which is main cause for the high CO-oxidation activity by the weaker binding of CO on catalyst (ligand effect). On the other hand, the ligand effect of PtRu alloy catalyst is known to

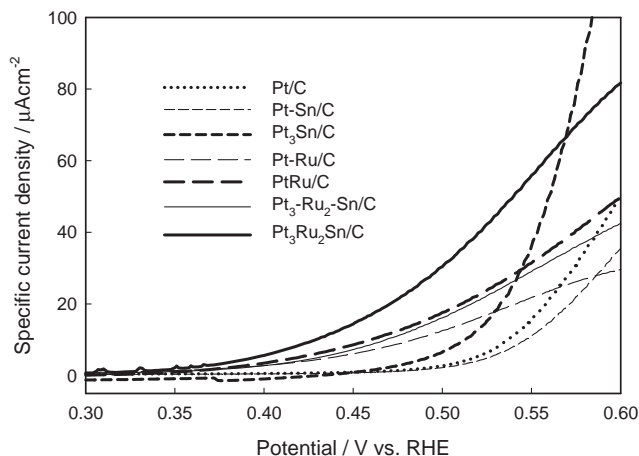


Figure 3. The potentiodynamic oxidation of methanol on the carbon-supported catalysts at room temperature (potential sweep rate: 1 mV s⁻¹, electrolyte: 0.1 M H₂SO₄, 0.5 M methanol, loading weight of catalyst: based on constant 18 μg_{Pt}/cm² for alloy catalyst and 30 μg_{Pt}/cm² for alloy catalyst).

be significantly less prominent. In the case of the ternary catalyst, the onset potential of CO/H₂ oxidation of Pt₃Ru₂Sn/C was shifted to more negative potential ca. 0.08 V as compared to Pt₃-Ru₂-Sn/C. This result suggests that the CO oxidation activity of ternary alloy catalyst was improved by the electronic modification of Pt by Sn comparing with PtRu/C.

To examine the methanol oxidation activity of the ternary alloy catalysts, the potentiodynamic oxidation of methanol was performed at room temperature. The Pt-Sn/C and PtSn/C were slightly higher active and Pt-Ru/C and PtRu/C had a significant higher activity than Pt/C as shown in Figure 3. From our results of methanol oxidation, it is considered that Ru is much higher active than Sn (in the form of adatom not alloy component) as a promoter for methanol oxidation. And the alloying effect for promoting methanol-oxidation activity in binary catalysts was relatively a little. It is reported that the alloying effects was significantly less prominent in the PtRu binary catalyst and the activity of PtSn catalyst was retarded or slightly increased by alloying.^{4,8} However, it is noted that the alloying effect in ternary catalyst was significant. The Pt₃-Ru₂-Sn/C was less active than PtRu/C (slightly more active than Pt-Ru/C by the optimization of surface composition), whereas the activity of Pt₃Ru₂Sn/C was prominently enhanced and higher than PtRu/C. From the results, the high activity of Pt₃Ru₂Sn/C for methanol oxidation was caused by the synergic effect of Ru as a water activator and Sn as an electronic modifier of Pt. In ternary alloy catalyst including the efficient water activator, the Pt-CO bond strength could become important factor.

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