

The Roles of Rh and Pt in Electrochemical Toluene Hydrogenation on Rh-Modified Pt Nanoparticle-Loaded Carbon Catalysts

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A couple of toluene (TL)/ methylcyclohexane (MCH) is a promising candidate of hydrogen carriers for large-scale hydrogen storage/transportation. Electrochemical TL hydrogenation (ETH) can achieve energy saving compared to hydrogenation using molecular hydrogen on appropriate catalysts.¹ We found that the Pt₃Ru alloy catalyst had the highest activity among Pt_xRu/C (x = 1, 3, 4) catalysts.² Moreover, in our preliminary experiments, it has been found that Rh was the best partner for Pt among Pt₃M (M = Rh, Au, Pd, Ir) alloy catalysts. Recently, we have found that Rh-modified Pt nanoparticle-loaded carbon (Rh_x/Pt/C) catalysts showed higher ETH activity than commercial Pt/C catalyst. However, electrochemical surface areas (ECSAs) of Rh and Pt for Pt-Rh binary catalysts could not be individually determined by hydrogen adsorption/desorption peaks because these peaks of Rh and Pt overlapped each other. In this study, we found how to individually evaluate the ECSAs of Rh and Pt and the Rh coverage (θ_{Rh}) by CO-stripping technique, and discussed the effect of the θ_{Rh} on the ETH activity per ECSA of Pt or Rh to clarify the roles of both components.³

HAADF-STEM images and EDX line scanning profiles showed that the distribution of Pt and Rh overlapped each other, and pure Rh particles were not observed, suggesting that Rh was modified only on the Pt nanoparticles. The θ_{Rh} initially increased with the Rh/Pt mole ratio of Rh_x/Pt/C, but plateaued at about 0.20, whereas the ECSA of Rh continued increasing. Thus, the accumulation of Rh on the modified Rh surfaces occurred prior to the epitaxial growth of Rh on the Pt surface after θ_{Rh} reached about 0.20. Based on LSVs and Tafel plots, the Rh_x/Pt/C electrodes had higher ETH activity than the Pt/C electrode, and addition of adsorbed atomic hydrogen (H_{ads}) to TL was rate-determining for each electrode. The dependence of geometric reduction current density at 0 V vs. RHE ($j_{\text{geo},0}$) on the Rh/Pt mole ratio was similar to that of θ_{Rh} . Platinum showed higher activity in ETH and lower activity in the hydrogen evolution reaction than rhodium.¹ TL is adsorbed on the Rh surface more strongly than on the Pt surface.⁴ Therefore, it is concluded that Rh and Pt sites in ETH work for H_{ads} generation and TL adsorption, respectively, and the enhanced catalytic activity is attributed to the increased coupling of H_{ads} generated on the Rh surface and TL adsorbed on the Pt surface at the interface between Pt and Rh.

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