Methanol Oxidation on Pt(111)/Ru in Alkaline Media

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Spontaneous deposition of Ru on Pt(111) produces nanoscale Ru islands on Pt(111) terraces. These islands are stable during potential cycling and during oxidative treatment at high potentials in alkaline media (Fig. 1). The stability of Pt/Ru surfaces in alkaline media suggests that Pt/Ru catalysts could be a good choice for application as anode electrocatalysts in alkaline DMFCs [1].

The deposition of Ru on Pt(111) significantly enhances the surface catalytic properties with respect to methanol oxidation (Fig. 2). Although Ru acts as a bifunctional promoter by supplying adsorbed OH at low potential, the bifunctional effect is much weaker in alkaline media than in acidic media, since Pt defect sites are also capable of supplying adsorbed OH at low potential when they are not blocked by Ru.

In contrast, perturbations in Pt electronic structure caused by deposition of Ru result in a significant methanol oxidation activity enhancement. These Ru ligand effects are manifested in at least three distinct enhancements:

1. Ru increases the activity of nearby Pt sites for methanol dehydrogenation to CO.
2. Ru causes the resulting CO to diffuse away from the Pt/Ru edge, making Pt/Ru less sensitive to CO poisoning than pure Pt.
3. Ru promotes CO oxidation by weakening CO adsorption on nearby Pt sites, making the CO more reactive for oxidation by OH adsorbed on Ru (E < 0.7 V) or by OH adsorbed on Pt (E > 0.7 V).

Although each of these effects is significant in promoting methanol oxidation on Pt(111)/Ru in alkaline media, the catalytic activity is still limited by the low intrinsic activity of Pt(111) for methanol oxidation [2]. This low activity is evident in a comparison with Pt(10 10 9). The (110) oriented steps on Pt(10 10 9), accounting for only 5% of the surface sites, nonetheless cause the methanol dehydrogenation activity to increase by a factor of 6 with respect to well-ordered Pt(111) (Fig. 2). In contrast, deposition of 0.18 ML of Ru on Pt(111) only causes the methanol dehydrogenation activity to double. Therefore, there is reason to expect that Ru-modified Pt surfaces with geometry more favorable for methanol dehydrogenation, including Pt(110), Pt(100), and stepped Pt surfaces, may be even more active than Pt(111)/Ru for methanol oxidation in alkaline media.

References


Fig. 1. STM images of Pt(111)/Ru in 0.1 M NaOH. Each image shows the same 27 × 27 nm area of the surface, with θ_{Ru} = 0.18 ML. (A) After Ru deposition; (B) after 6 potential cycles between 0.05 and 0.85 V; (C) after 60 potential cycles between 0.05 and 0.85 V; (D) after 100 min. at 0.95 V. E_{surface} = 0.10 V, E_{tip} = 1.0 V (RHE).

Fig. 2. Oxidation of 0.1 M methanol at 0.45 V (RHE) in 0.1 M NaOH. Space between lines represents 95% confidence intervals. Black: Pt(111); Red: Pt(111)/Ru; Blue: Pt(10 10 9).