Surface Structure Manipulation of Ruthenium Islands on Pt(hkl) Surfaces via Electrochemical Control

A. Crown, C. Johnston and A. Wieckowski

Department of Chemistry
University of Illinois at Urbana-Champaign
600 S. Mathews Ave.
Urbana, IL 61801-3792

In the quest for highly catalytic surfaces that withstand carbon monoxide poisoning during methanol oxidation, multiple Pt/Me bimetallic surfaces have been probed as possible anode catalysts.[1-3] Ruthenium has been known for a few decades to enhance the performance of platinum towards methanol, and more specifically, carbon monoxide oxidation.[2] We have recently deposited controlled amounts of ruthenium onto platinum nanoparticles via the so called "spontaneous deposition" procedure and found that the Pt/Ru nanoparticles prepared in this way were twice as active as commercially available Pt/Ru alloy catalysts.[4] In order to investigate the mechanism of enhancement of these specially prepared catalysts, we performed the same deposition on a Pt(111) electrode (Pt(111) has been shown previously to be the most active surface of the low-index planes towards methanol electrooxidation[5,6]) and explored the island characteristics utilizing both ex situ and in situ STM.

We have used Scanning Tunneling Microscopy (STM) to examine spontaneously deposited ruthenium and osmium adlayers on the well-defined Pt(111), Pt(100) and Pt(110) electrodes.[5,7] We have also utilized the spontaneous deposition procedure to obtain higher coverage values by sequentially repeating the deposition experiment up to four times and found that on the (111) face, the islands grow in multi-layer form readily.[8] We confirmed this utilizing in-situ STM imaging and found that various potential steps to the surface can control the size and distribution of the islands, as depicted in Figure 1. Figure 1A shows the Pt(111) surface (35 x 35 nm) held at 0.43 V after two multiple depositions. The island size ranges from 2-5 nm and the island height distribution is large. That is, only 50% of the islands are a monolayer high, while 30% are two monolayers high and 20% are three monolayers or higher. However, when the surface potential is scanned to a higher potential (0.93 V) and then negative to the original potential (0.43 V) the islands are much smaller (figure 1B), from 0.5 nm to 2 nm diameter, and now the 97% of the islands are a monolayer high. The images at the higher potential, 0.93 V (not shown), indicate that the island size increases by 2 to 3 nm. We suggest, then, that the islands are being oxidized at 0.93 V and upon reduced electric potential, the islands break up into smaller, monolayer size islands that have a high dispersion across the Pt(111) surface.These findings are correlated to surface activity via electrochemical measurements in methanol-containing solutions.

We will attempt to address the surface mobility of the ruthenium and osmium islands at various admetal coverage values. Examination, in situ, of the growth process will further elucidate the formation process, e.g., whether the islands tend to merge when the surface is exposed to a supporting electrolyte (sulfuric or perchloric acids).

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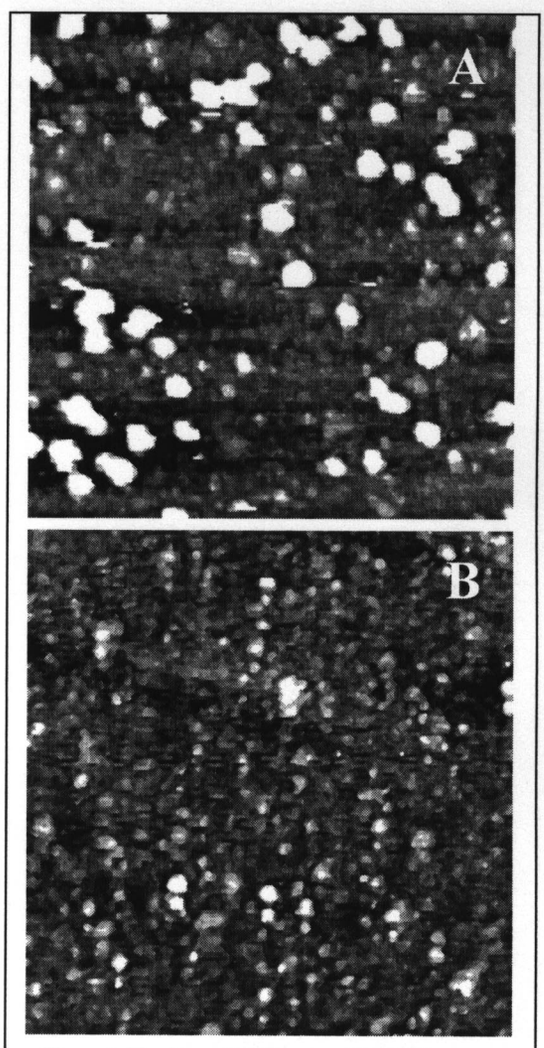

Figure 1. 35 x 35 nm STM images of Pt(111)/Ru prepared via two repetitive spontaneous depositions. A) Immediately after second deposition at 0.43 V vs RHE. B) Same area at 0.43 V after holding at 0.93 V