

CH₃OH Oxidation Activity for a Range of PtRu Catalysts

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INTRODUCTION

The direct methanol fuel cell (DMFC) is emerging as potential commercial power source for portable devices and transportation purposes. Among other obstacles, the performance of the anode catalysts towards the oxidation of methanol to CO₂ needs to be improved. Pt/Ru catalysts show a superior performance as compared to pure Pt for the CH₃OH oxidation reaction [1]. It is known that the ratio and distribution of Pt and Ru catalyst sites influence the CH₃OH oxidation kinetics [2-4]. The chemical state of the Ru ad-metal is also believed to influence the CH₃OH oxidation kinetics [5]. In more recent work it has been reported that bimetallic PtRu alloy catalyst show a significantly poorer activity for the CH₃OH oxidation reaction (ca. 250 times lower extrapolated exchange current density values per gram catalyst) than bulk mixtures of Pt metal, Pt hydrous oxides and hydrous and dehydrated RuO₂ [5]. Based on these results, it was recommended that the use of bimetallic PtRu alloy catalysts in DMFC's is to be avoided [5].

In this work, the CH₃OH oxidation activities of a range of Pt/Ru catalysts are compared. The catalysts were prepared using different methods and treatments to obtain different chemical states of the Ru ad-metal.

RESULTS AND DISCUSSIONS

The CH₃OH oxidation activities were obtained for Pt/Ru powders and Pt/Ru films. The latter were prepared by chemical vapor deposition (CVD). Both the powders and the films were prepared and/or treated under different conditions to obtain different chemical states of the Ru ad-metal, namely, Ru metal as well as hydrous and anhydrous Ru-oxides. An attempt was made to maintain the atomic ratio of Pt and Ru constant, either 70:30 or 50:50 atomic % and the catalysts were characterized using a range of techniques (XRD, XPS, Auger, etc.). CH₃OH oxidation activities were obtained in 0.5 M CH₃OH and 0.5 M H₂SO₄ solutions at 20 and 60°C from current density-time transients (J_{ox}-t) recorded at constant potential and slow sweep cyclic voltammograms (CV's). The CH₃OH oxidation activities obtained from the J_{ox}-t and CV experiments showed the same dependence on the type of catalyst over a broad range of tested potentials (0.3 to 0.55 V vs. reversible hydrogen electrode (RHE)).

In this work, the CH₃OH oxidation activities of the different catalysts were generally compared in current per real Pt area, i.e., J_{ox}. This comparison appeared to be justified, as surface area measurements (particle size, BET and anodic stripping CO voltammetry) consistently indicated differences in catalyst surface areas of at least 10 times.

For all catalysts studied, it was found that the PtRu alloys show a better CH₃OH oxidation activity (J_{ox}) than the Pt/(rutile)RuO₂ catalyst independent of the temperature, i.e., at 20 and at 60 °C. The PtRu alloys were also "oxidized" in a stream of O₂/saturated H₂O at 100 °C (converting a fraction of the Ru(0) sites to hydrous Ru-oxide [5]) or treated in a H₂ atmosphere at elevated temperatures. Essentially the same J_{ox} values were found for all three Pt/Ru catalysts, i.e., the attempted oxidative or reductive treatment of the PtRu alloy did not significantly influence the CH₃OH activity. However, major changes in the catalyst surface area were observed, thus explaining observed

difference, of close to one order of magnitude, in the CH₃OH oxidation activity reported in current per grams of catalyst (i_{ox}/g_{cat}). In this work, the CH₃OH oxidation activities expressed in i_{ox}/g_{cat} were conclusively found to be poorer for all H₂ treated Pt/Ru catalyst. This dependence of the i_{ox}/g_{cat} value on the catalyst treatment is consistent with results reported in previous work [5], however, for the particular catalysts studied in this work the difference is assigned to be due to a change in catalyst surface area rather than state of the Ru ad-metal.

XPS studies for the PtRu alloys indicated the presence of a mixture of Ru metal and partially oxidized Ru sites, while only the PtRu alloy peak was observed in the XRD spectra. This likely indicates that a fraction of surface Ru is oxidized and possibly forms a hydrous and amorphous form of Ru-oxide on the surface of these catalysts. This is further supported by the fact that background CV studies for all PtRu alloys (used as prepared as well as oxidatively and reductively treated catalysts) in 0.5 M H₂SO₄ showed Ru oxidation characteristics at low potentials (ca. 0.3V vs. RHE), i.e., nearly 0.1 V lower than observed for Pt/(rutile) RuO₂ catalysts. Based on these results it is believed that the chemical state of the Ru ad-metal influences the catalytic CH₃OH oxidation reaction. For the catalysts studied in this work, the best CH₃OH oxidation performance per real Pt area was found for catalysts that appear to contain hydrous Ru-oxide on the surface. This oxide can be formed during the catalyst preparation or in aqueous electrolyte solution under potential control. Furthermore, such a hydrous Ru-oxide phase is believed to be formed on Pt-Ru alloys in air and/or in aqueous electrolyte solutions.

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