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Effect of heat treatment on the electrocatalytic properties of nano-structured Ru cores with Pt shells

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Ru@Pt core–shell particles are relevant for application as electrocatalysts in fuel cells. The Ru core is expected to influence the activity of the Pt in the shell through a compression of bond lengths and electronic interaction with the core. In this work Ru@Pt core–shell (Ru core and Pt shell) and pure Ru nanoparticles of diameter below less than 5 nm were synthesized and supported on carbon black (Vulcan XC-72). The supported catalysts were heat-treated at temperatures up to 500 °C. Analysis of the catalysts by TEM, EXAFS, XRD, and CO-stripping indicates a strongly segregated architecture with Ru in the core of the particles. Upon heat-treatment we observed moderate particle growth, increased extent of alloying, and a decrease of the Pt–Pt bond lengths. The Pt–Pt bond lengths decreased uniformly with heat-treatment temperature in the entire range. The extent of alloying and particle growth were significant (i.e. beyond measurement uncertainties) only at a heat-treatment temperature of 500 °C. The electrocatalytic activity for oxidation of adsorbed CO (CO-stripping) increased in the entire temperature interval. The activity for methanol oxidation only increased when catalysts were heated to 500 °C. The results indicate that the surface concentration of ruthenium in the pristine Ru@Pt catalysts is small.

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1. Introduction

Efficient and stable catalysts for oxidation of CO and small organic molecules such as methanol are important for low- to medium temperature fuel cells fueled by CO-containing hydrogen or organic fuels directly. Bimetallic Pt–Ru catalysts often have a superior activity for these reactions as compared to Pt and Ru mono-metallic catalysts. This is frequently explained by a conceptual splitting of the effects of alloying into a bifunctional mechanism [1,2] and a ligand effect [3,4]. The bifunctional mechanism assumes that both metals are available at the surface, forming adsorption sites. The ligand effect only depends on one of the metals being close enough to the surface to influence the other electronically.

Often bi-metallic PtRu electrocatalysts containing equal amounts of Pt and Ru are prepared in the form of alloys. The optimum fraction of Ru surface sites has, however, been asserted to be well below 50% [5–7] and is temperature-dependent [5]. Particle size [8,9], agglomeration and surface structure [10–13], the type of carbon support [14–18], and the oxidation state of Ru [19–37] are additional factors that all appear to influence the activity as well.

Catalyst architectures other than alloys, such as core–shell structures [38–46], can change the catalytic activity and stability of electrocatalysts significantly. Recent results indicate that encapsulating Ru inside a shell of the more stable Pt may retain a significant fraction of the electrocatalytic activity for oxidation of pre-adsorbed CO (CO-stripping) whilst inhibiting dissolution of Ru [43]. However, the performance of a direct-methanol fuel cell employing the Ru@Pt catalyst was little different from one employing Pt at the anode [47]. Additionally, the peak potential observed in voltammograms in methanol-containing solutions at the Ru@Pt catalyst is little different from Pt [47].

The structure of Pt–Ru systems depend on the preparation conditions. Thus, the surface of PtRu catalysts has been reported both to be enriched in either Ru [48–51,38,52,53] or Pt [23,37,34]. The pristine

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catalysts are typically partially oxidized [48,52,53], but the oxidation state can change during operation [48,51]. Heat-treatment of the catalysts in hydrogen or vacuum at low or moderate temperatures promote alloying [52,53,51]. In some cases indications of Pt segregation to the surface have been reported [38,54,34]. Heating in air or CO at similar temperatures leads to de-alloying.

For these reasons it becomes important to investigate the influence of heat treatment on the Ru@Pt core–shell catalysts. Ru@Pt catalysts were demonstrated in Ref. [43] to be substantially more stable under potential cycling than alloys; Heat treatment may serve as an alternative way for investigating the stability of the core–shell structure, particularly for their possible application in intermediate-temperature methanol fuel cells [47]. Associated with possible structural changes in the catalyst upon heat-treatment one may also expect concomitant changes in electrochemical performance.

Below we report the results of such heat-treatment of Ru@Pt core–shell electrocatalysts. We first report the structural and electrochemical characteristics of the ruthenium cores, and then the structural and electrochemical characteristics of the Pt-covered Ru-cores, all supported on Vulcan XC-72. We provide further indications of the completeness of the Pt-shells and their ability to retain the Ru inside the catalyst. The structural changes appearing during the heat treatment are then correlated with the electrocatalytic properties of the catalyst.

2. Experimental

2.1. Materials and chemicals

$PtCl_2$ and $Ru(acac)_3$ (acac = acetylacetonate) were provided by Johnson Matthey. Ethylene glycol (EG) and polyvinylpyrrolidone (PVP, MW = 55000) came from Sigma Aldrich and Vulcan XC-72 from Cabot.

2.2. Synthesis of nanoparticles

The Ru@Pt 1:1 core–shell nanoparticles were synthesized by using a sequential polyol process [41]. $Ru(acac)_3$ was initially reduced in refluxing ethylene glycol (EG) in the presence of polyvinylpyrrolidone (PVP) stabilizer. The resulting Ru cores were thoroughly washed in order to remove traces of chlorine and stabilizer (PVP). The Ru particles were then deposited on the carbon support by stirring at room temperature, followed by washing with acetone and centrifuging. For the core–shell particles an aliquot Ru/PVP (solution) was added to a $PtCl_2$/EG mixture and heated to 200 °C. The resulting Ru@Pt particles were deposited on carbon by stirring at room temperature, then washed with acetone and centrifuging. The uncoated Ru cores (also carbon supported) were used as a metallic Ru reference.

All nanoparticles were deposited with 9–16% nominal loadings on the carbon support (Vulcan XC-72) and dried at 100 °C. Catalysts receiving no further treatment are referred to below as as-prepared, pristine, or labelled as 100 °C.

2.3. Catalyst characterization

A small amount of the catalyst powder was dispersed in ethanol, pippeted on a copper grid, and transmission electron microscopy (TEM) images of these were obtained at a Jeol JEM-2100. The loading was determined with a thermogravimetric analyzer (TGA Q500, TA instruments). The sample was placed in an alumina crucible and heated to 800 °C at a rate of 20 °C/min under a flow of synthetic air ($80\ \mathrm{ml\ min}^{1}$ of nitrogen and $20\ \mathrm{ml\ min}^{1}$ of oxygen). The data were corrected for formation of RuO_2. The catalyst weight was found as the difference in sample weight before and after carbon decomposition, from which the nominal loading was calculated. We note that the calculated loading may be affected by the presence of any remaining PVP in the catalyst. However, the actual loading does not affect the conclusions to be drawn below and this is therefore of no consequence here. The ratio between platinum and ruthenium was ascertained by EDS/SEM using an Oxford instruments Aztec EDS system attached to a Hitachi S-3400N SEM.

High-resolution X-ray data were collected at the BM01B beamline (ESRF, France) combined XRD and XAS setup. A small amount of the catalyst (10–20 mg) was immobilized between quartz wool in a 2 mm glass capillary. A flow of argon was maintained through the compacted catalyst for oxygen removal. The catalyst surface was first exposed to argon at room temperature, then rapidly brought to temperature, and kept there for 30 min. The samples were then quenched to room temperature before the XAS spectrum and XRD diffractogram (wavelength 0.500798 ± 0.000006 Å) were recorded. After a short rest period the sample was brought quickly to the next temperature and so on. The XRD-data were recorded in a range of 2θ from 7° through 45° with step size 0.003. The XRD results were analyzed with help of Topas software (Bruker). A Pawley-type full-pattern fitting approach was used [55].

Extended X-ray absorption fine structure (EXAFS) data were collected at the Ru K edge (22.117 keV) and the Pt L3 (11.564 keV) in the transmission mode (monochromatic radiation, Si(3 1 1) double crystal) also at the Swiss-Norwegian beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF Grenoble, France). All XAS data were processed using Athena. The extracted EXAFS spectra were fitted to the theoretical IFEFFIT [56] standards using the Artemis program. These spectra were multiplied by k^3-weighting factors and fitted simultaneously in R-space. Standard deviations calculated by the software are reported below. (Note however that the standard deviations calculated by the software are only estimates of precision (reflecting statistical errors in the fitting). This may overestimate the accuracy somewhat, particularly in the case of a high degree of correlation between parameters. Estimated standard deviations for the first-shell distances are 0.01–0.02 Å and 10% for the coordination numbers [57–59,53].) Particle diameters were calculated from the EXAFS data according to procedures in papers by Frenkel et al. [60] and Karim et al. [61].

2.4. Electrochemical characterization

The electrochemical measurements were conducted in a standard electrochemical glass cell using an Autolab potentiostat, type PGSTAT302N. The working electrode was prepared by applying the same (small) amount of the catalyst to a glassy carbon disk and coating with a thin film of Nafion® according to procedures elaborated by Schmidt et al. [62]. For all results presented here a Pt plate of 1.5 cm^2 was used as a counter electrode. Experiments were performed at room temperature in 0.5 $\mathrm{mol\ d\ m}^{-3}$ $HClO_4$. Potentials were determined using a reversible hydrogen electrode (RHE).

CO gas was bubbled through the electrolyte for 140 s at 50 mV to ensure full coverage of the electrode surface by adsorbed CO. The solution was purged then with argon for 30 min again to remove dissolved CO. All currents for the electrodes tested for methanol oxidation are normalized by the active area of the electrode. The active area was determined from the charge of the CO oxidation peak in the first CO stripping voltammogram.

3. Results and discussion

3.1. Characterization of uncoated Ru particles on carbon

Fig. 1 shows TEM images of the untreated Ru/C and the sample heated at 500 °C under argon flow. Most of the particles appear to

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