



A comparative in situ XPS study of PtRuCo catalyst for CH₃OH and CO oxidation using water.

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Introduction

Fuel cells using methanol as a fuel are promising future energy technology. Methanol is electro-oxidized in the presence of water at the anode generating CO₂, hydrogen ions and the electrons that travel through the external circuit as the electric output of the fuel cell. The excellent catalytic activity of Pt for methanol oxidation makes this metal electrocatalysts ideal for use as an anode in Direct Methanol fuel cells (DMFCs). However, Pt metal surface is easily poisoned at low temperatures by trace amounts of CO, which exists as a byproduct of methanol electrooxidation. Theoretical and experimental studies have shown that ternary PtRuCo catalyst significantly promotes the methanol oxidation reaction [1]. In this study we investigate the PtRuCo surface for the CH₃OH and CO oxidation in the presence of H₂O.

Experimental

The Pt_{37.5}Ru_{37.5}Co₂₅ catalyst was prepared by combustion synthesis and pre-treated in-situ under oxidation (0.5 mbar O₂ at 400°) and reduction (0.5 mbar H₂ at 300°) cycles. XP spectra were recorded at 300° under steady state conditions using depth profiling by variation of the incident photon energy. The overall pressure was 0.5 mbar and the CH₃OH:H₂O and CO:H₂O mixing ratios were 1:2 and 1:10 respectively. Spectra under CO, H₂O, O₂ and H₂ atmospheres were also recorded as a reference. Synchrotron radiation delivered by the undulator U49/2 was used. Changes in the gas phase composition were monitored by on-line mass spectrometry simultaneously to the spectroscopic characterization of the catalyst surface.

Results

On line Mass Spectrometry data for CH₃OH and CO oxidation are given in fig. 1a and b respectively. The activity of the catalyst is demonstrated by the detection of the reaction products (H₂ and CO₂) in the gas phase and the consumption of CH₃OH when the catalyst was heated in the reaction mixture. Blank experiments were performed in order to support the above picture.

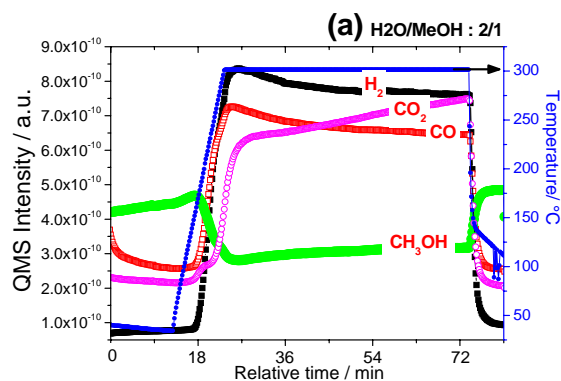


Figure 1: On line Mass Spectrometry data a) Methanol oxidation

Surface segregation, i.e. the enrichment of one element at the surface relative to the bulk, is a ubiquitous phenomenon in metal alloys [2]. In situ XPS gives a unique opportunity to determine the surface composition under various gas atmospheres. In figure 2 the calculated C, Ru, Pt, Co and O atomic concentration at the first 4 atomic layers (electron KE = 180 eV) are presented under various atmospheres. From the results is concluded that Pt segregates on the surface during methanol oxidation, while for CO oxidation the picture changes and cobalt enrichment occurs accompanied by higher O amounts and the de-

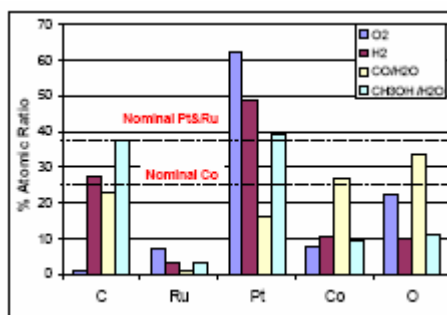


Figure 2: The surface atomic concentration calculated from XPS intensities recorded under various gas atmospheres

crease of Pt. The chemical state of surface elements is very much depended on the type of the reaction. In figure 3 characteristic C1s&Ru3d_{5/2}, Pt 4f, Co 2p_{3/2} and O 1s spectra are presented. In Fig 3a graphitic carbon at 284.4eV dominates C1s region, while a surface located component at 288.1 eV corresponds most probable to adsorbed CO. Ru 3d_{5/2} peak is found at 279.8 eV, very close to the binding energy of metallic Ru. A comparison of Pt 4f peaks for methanol and CO oxidation (fig. 3b) reveals that in the later case a new Pt doublet at 72.5 eV is needed in order to fit the overall spectrum. This peak is primarily surface located and can be attributed to hydroxyl-Pt complexes [3] as supported also from O1s spectra (see below). In fig. 3c, Co 2p_{3/2} spectra under reaction as well as under H₂ and O₂ atmospheres are presented. For methanol oxidation cobalt found completely reduced (778.1 eV), contrary to CO oxidation where it is partially oxidized. O 1s spectra in fig. 3d showed a complex structure, also due to gas phase peaks appear above 534 eV.

Assignment of the O 1s peak is speculative and should be done taking into account characteristics of the Pt and Co peaks. During CO oxidation non-gas phase peaks are centered at 529.5 and 531.1 eV. Depth analysis showed that the peak at 531.1 eV is mainly surface located testifying for the presence of hydroxyl species on the surface. The bulk component at 529.5 eV is probably related to the oxidized cobalt as showed in fig. 3c. In case of methanol oxidation two broad O1s compounds were found at 530.4 and 532.2 eV. Although definitely assignment of these compo

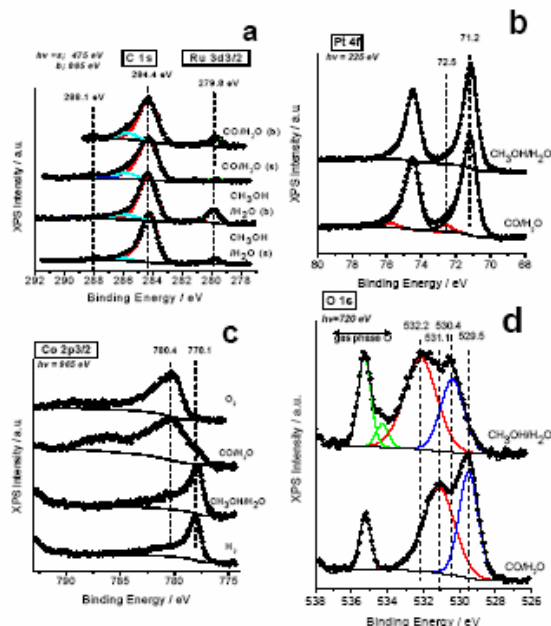


Figure 3: XPS spectra recorded at 300°

nents is unfeasible, it comes out that different oxygen species are involved in each reaction.

In summary, it was showed that the composition and the chemical state of PtRuCo surface depend on the performed reaction, indicating the dynamic character of the catalyst. It was found that the oxidation state of Co varies, probably acting as a carrier or reservoir of oxidation agents participating in the reaction. This nicely correlates with observations on realistic fuel cells, where PtRuCo found to facilitate CO oxidation at lower potentials compared to Pt and PtRu [1]. The excess of oxidized species on the surface, related with the presence of cobalt, promotes CO oxidation most probable providing OH species on Pt where CO oxidation actually takes place.

References

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