STABILITY OF CATALYSTS IN SOLID OXIDE FUEL CELLS

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INTRODUCTION

Due to the increasing need for sustainable and environmentally friendly energy transport and conversion, carbon rich fuel gases in combination with Solid Oxide Fuel Cells (SOFCs) is a promising alternative.

To increase reaction rates and selectivity as well as decreasing operating temperatures in SOFCs, catalysts are used. The first part presents the dynamic of Carbon on Nickel in-situ by X-ray Photoelectron Spectroscopy (XPS) and Surface X-ray Diffraction (SXRD).

The second part presents the stability of a Copper-Zinc catalyst during CO-Oxidation by ex-situ XPS and Atomic Force Microscopy (AFM).
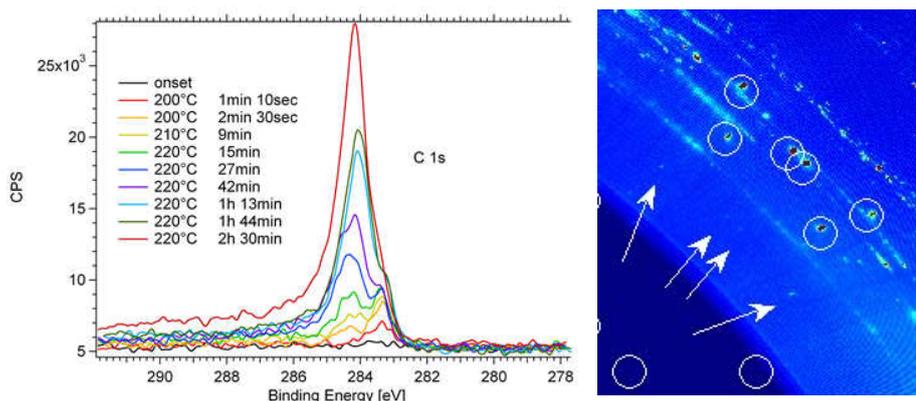
EXPERIMENTS AND RESULTS

When SOFCs are directly exposed to e.g. Methane ($CH_4 + 2\,O_2 \rightarrow 2\,H_2O + CO_2$) the pyrolysis of Methane leads to carbon deposition, segregation and the formation of graphene/graphite as well as nanotubes on the catalyst. This can lead to deactivation (by covering active sites for the reaction) up to the mechanical destruction of the catalyst (by stress induced from nanotubes to the catalyst).

The first part of this work investigates carbon adsorption, segregation, formation and possible ways to suppress carbon formation on Nickel. In particular, the role of the clock-reconstructed on Ni(111) surface carbide regarding further C-growth and dissolution is tested and experimental data are compared to the structural models proposed in the literature[1].

One main goal in understanding, improving or designing new catalysts is to pinpoint where the reaction takes place on a microscopic scale. This place is called the "active site". Here, a clear understanding of all physical and chemical conditions coming together during the

Picture 1: In-situ XPS spectra of carbide and graphene/ite growth on Ni-foam(left) and SXRD of carbide on Ni(111) (right)

reaction is desired. This depends critically on used materials and preparation conditions as well as possible transformations during the reaction. As a first characterization, the amount of active sites on a catalytic surface is estimated by test reactions. This is used to determine the Turn Over Frequency (TOF) which quantify the reactions per site and per second. A commonly used and structural insensitive test reaction is CO- Oxidation ($2\,CO + O_2 \rightarrow 2\,CO_2$). The second part of this

work is CO- Oxidation on Zincoxide (ZnOx) supported by Copper (Cu). A comparison of the Langmuir- Hinshelwood
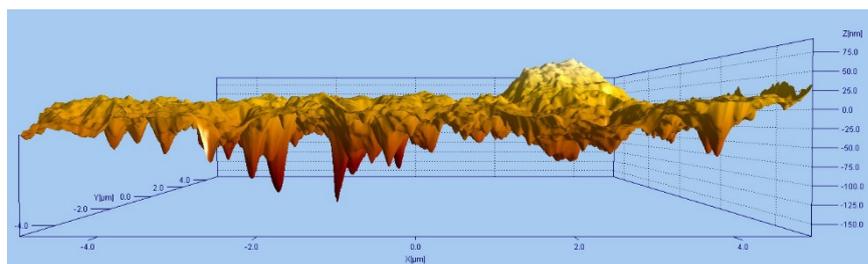

Figure 2: AFM measurements on a CuZn catalyst after CO-Oxidation. Shown is a 10x10μm area where top to bottom is 250nm. The "blob" on the right side is suspected to be a ZnOx-cluster.

Experiments were performed at the following beamlines and Ultra High Vacuum (UHV)-systems:

I.   In-situ XPS at the beamline ISISS-PGM of BESSY II, Berlin

II.   SXRD at the ID03 beamline of ESRF

III.   Additional ex-situ experiments in UHV system, Innsbruck [2]

CONCLUSION

As shown in Fig 1, sequential formation of carbide and graphene/ite could be observed both on Ni foam and Ni (111). In addition, the coexistence of surface carbide and graphene/ite in a certain temperature region was observed as well as the preferential dissolution of the surface carbide at >= 670 K. After thermal dissolution of the carbidic clock-reconstructed $(39)^{1/2}R16.1°x(39)^{1/2}R16.1°$phase at 700 K, as indicated by the loss of the related diffraction intensities, the presence of epitaxial and unrotated graphene domains is indicated by the absence of rotated graphene reflections, together with a strong alteration of the specular reflectivity of the surface. These results complement recent structural investigations by Scanning Tunnelling Microscopy (STM) [3, 4]. Structure modelling of SXRD data to confirm the most plausible configurations of unrotated graphene on Ni(111) will be presented.

As shown in Fig 2, the CuZn catalyst did partake in the reaction and is structurally altered. In addition, after the first reaction cycle the catalyst did deactivate due to the strong oxidizing conditions. This shows a limitation of a classic Langmuir-Hinshelwood mechanism, where the catalyst is not changed by the reaction.

REFERENCES

[1] F.Mittendorfer, er al., Phys. Rev. B (2011) 201401

[2] L. Mayr, er al, Review of Scientific Instruments 85.5 (2014) 055104

[3] L. Patera, C. Africh, R. Weatherup, R. Blume, S. Bhardwaj, C. Castellarin-Cudia, A. Knop-Gericke, R. Schloegl, G. Comelli, S. Hofman, C. Cepek, ACS Nano, (2013) 7(9) pp7901-7912

[4] P. Jacobson et al., ACS Nano (2013) 6(4), pp3564-357