

NANOPARTICLE EXOLUTION: ENHANCING CATALYST REACTIVITY UNDER REACTION CONDITIONS

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INTRODUCTION

In heterogeneous catalysis surfaces decorated with uniformly dispersed, catalytically highly active (nano)particles are a key requirement for excellent performance. Besides the standard catalyst preparation routines, e.g. impregnation or precipitation, with limitations in terms of controlling exactly the desired catalyst structure (i.e. particle size distribution or dispersion of nanoparticles), we present here an innovative, time efficient route to exactly tailor the catalyst surface directly under reaction conditions.

Perovskite-type oxides are a large class of materials with many interesting properties. Their general chemical formula is ABO_3 , the possibility of choosing different elements for the cations and of doping either of the sites allows to adjust these properties and makes them highly versatile.

An emerging concept in catalyst design, and the scope of our ERC project, is to selectively and reversibly tune and modify the surface chemistry/structure of Perovskite-type catalysts by electrochemical polarisation in operando^[1]. The catalysts can incorporate catalytically highly active elements, either as a main component or as dopants. Upon electrochemical polarisation (applying voltage to the system), these elements emerge from the oxide lattice to form catalytically active clusters or nanoparticles on the surface (by exsolution), figure 1. In consequence, this leads to a strong modification or enhancement of catalytic selectivity and activity.

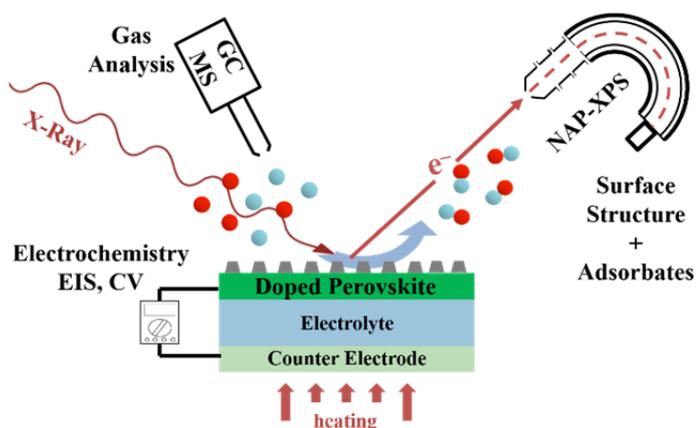


Figure 1: Setup for operando measurements

EXPERIMENTAL

Different perovskite materials were prepared via a modified Pecchini method^[2]. Structural characterization was done by (in situ) XRD, XPS and SEM. Catalytic testing was performed in a custom made tubular flow reactor with gas analysis by micro GC and MS. We investigated the water-gas shift reaction (WGS) and the reverse WGS (rWGS). For experiments with electrochemical polarization, electrochemical cells (figure 1) were prepared by depositing electrodes on (100)-oriented 9.5 mol % yttria-stabilized zirconia (YSZ) single crystals using pulsed laser deposition. With these cells, we performed in-situ NAP-XPS experiments for direct correlation (simultaneous experiments) of surface chemistry with catalytic activity, selectivity and the applied polarization, using our lab based in-situ NAP-XPS system.

RESULTS

For the newly synthesized perovskite materials, we could show by in-situ XRD and SEM the formation of nanoparticles on the surface (by exsolution) under reducing conditions, figure 2. The different perovskites were compared with respect to their reduction behaviour. We found that a doping with Co facilitates the exsolution process.

On the other hand, we compared the catalytic performance of the various perovskites for WGS and rWGS. The catalyst doped with Co had a significantly higher catalytic activity for rWGS than all the other materials. This is due to the fact, that it is the only catalyst where exsolution is possible under the chosen reaction conditions. The exsolved nanoparticles consist of catalytically active elements and have a large surface area, thus greatly enhancing the performance of the catalyst. We confirmed nanoparticle formation from the Co doped catalyst during rWGS by operando XRD experiments and SEM.

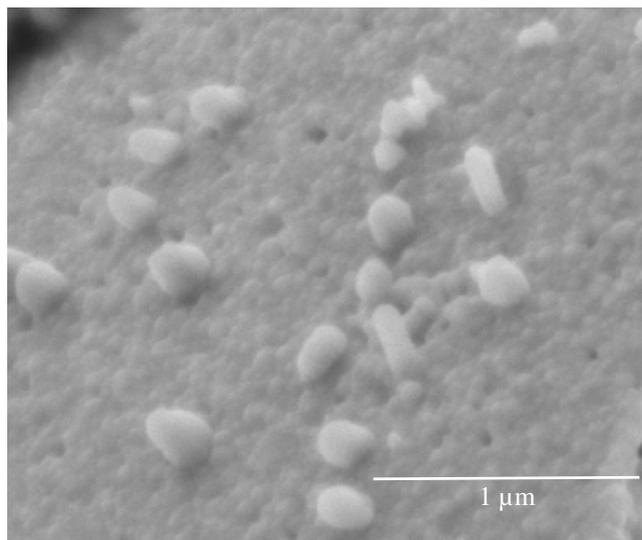


Figure 2: SEM after Fe nanoparticle exsolution from $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$

CONCLUSION

The structural changes when exsolution occurs have a great impact on catalytic reactivity. Therefore, our goal is a deeper understanding of the process and the ability to control it accurately. This enables the precise tuning of the catalyst surface and thereby the regulation of the catalytic behaviour. A thorough investigation of the exsolution process is possible with our in-situ NAP-XPS system.

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REFERENCES

- [1] Mao, X. W.; Tian, W. D.; Wu, J.; Rutledge, G. C.; Hatton, T. A., *Journal of the American Chemical Society* 2015, 137 (3), 1348-1355.
- [2] Pechini, M. P., Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor, U.S. Patent 3.330.697, July 11th, 1967