Characterisation of Novel Doped Perovskite Catalysts by XRD, XPS and SEM – Tailored Exsolution of Metal Nanoparticles

L. Lindenthal[1], J. Popovic[1], J. Raschhofer[1], R. Rameshan[1], A. Nenning[2], A.K. Opitz[2], C. Rameshan[1]

1 Technische Universität Wien, Institute of Materials Chemistry, Vienna, Austria

2 Technische Universität Wien, Institute of Chemical Technologies and Analytics, Vienna, Austria

Perovskite-type oxides are a large class of materials with many interesting properties, including piezo- and pyroelectricity, mixed ionic-electronic conductivity and high catalytic activity. Thus, there is a wide range of applications, for example the use as sensors or as electrode materials in solid oxide fuel cells. Their general chemical formula is ABO_3, with two different cations A (bigger) and B (smaller). The ideal structure is cubic, but it is often distorted as can be seen for $La_{0.9}Ca_{0.1}FeO_3$ (figure 1). The high versatility of the material class is due to the possibility of adjusting the properties by choosing different elements for the cations. Doping either one or both of the cation sites opens up an even larger matrix for materials design.

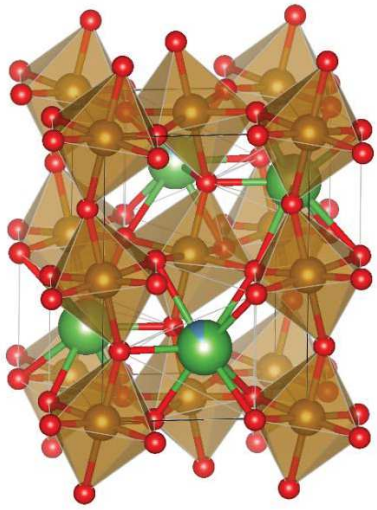

Figure 1: Distorted perovskite structure of $La_{0.9}Ca_{0.1}FeO_3$, data from XRD measurement (La/Ca-green/blue, Fe-brown, O-red).

In terms of catalysis, another recently shown outstanding property of perovskites is the exsolution of metal nanoparticles under reducing conditions. This surface modification (by migration of cations to the surface) can change the catalytic activity

and selectivity of the perovskite surface completely and is the core topic of our ERC project.

Several perovskite-type oxides (e.g. $La_xCa_{1-x}FeO_3$ or $Nd_xCa_{1-x}FeO_3$), that are promising catalyst materials, have been synthesised and subsequently characterised. These perovskites are promising catalyst materials for several energy related reactions, such as the (reverse) water gas shift reaction. Using different reducing conditions, the stability and reducibility of the synthesized perovskites were investigated. X-ray diffraction (XRD) allowed structural determination, while X-ray photoelectron spectroscopy (XPS) gave additional chemical information on the surface state. These characterisations have been complement by additional analytical methods (e.g. SEM). It was possible to show the reversible exsolution of metal nanoparticles in an ideal metastable window (figure 2).

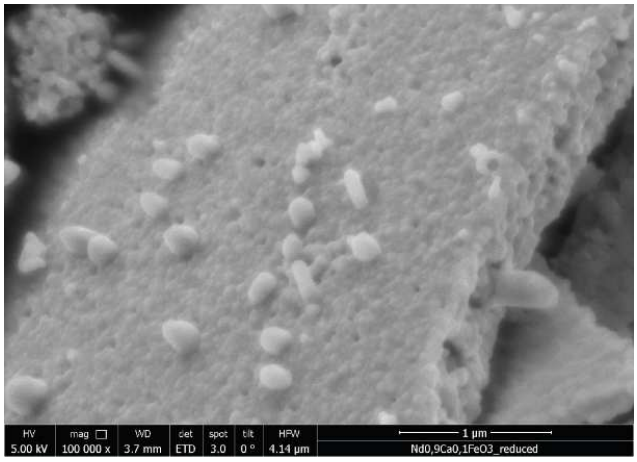

Figure 2: SEM picture of exsoluted nanoparticles on $Nd_{0.9}Ca_{0.1}FeO_3$.

Following the basic characterisation, further experiments were conducted with a new lab-based Near-Ambient-Preassure XPS system (NAP-XPS). This was designed and set up in cooperation with SPECS, specifically for the investigation of electrode materials (e.g. for the use in solid oxide fuel cells). With this setup, it is possible to combine catalytic experiments, NAP-XPS and electrochemical measurements at the same time, thereby correlating catalytic activity of the material with its surface state and its electrochemistry. Thus, it directly gives access to information as to how exsolution changes the catalytic properties of a perovskite material.

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