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Measurement of EELS standards and application on oxidation state determination of a MeOH catalyst

Dr. Daniela Ramermann[1], Dr. Elisabeth H. Wolf[1], Dr. Michael Poschmann[1], Dr. Christoph Göbel[1], Dr. Lukas Pielsticker[1], Dr. Holger Ruland[1], Dr. Walid Hetaba[1]

[1]Max Planck Institute for Chemical Energy Conversion, Department of Heterogeneous Reactions, Mülheim an der Ruhr, Germany

Background & aims

Electron energy loss spectroscopy (EELS) is a powerful technique, foremost allowing determination of the elemental composition, but furthermore investigation of electronic properties like chemical bonding and oxidation states. This information can be collected with high spatial resolution on today´s scanning transmission electron microscopes. Most common for the analysis of EELS data is the use of cross-section models. These are often sufficient for determination of the elemental composition, but to extract information like oxidation states, a different analysis approach is necessary: Spectra of well-known reference materials (standards) improve the quantification results and allow fitting of the edge shapes to investigate and map oxidation states. These reference spectra can either be obtained by measuring well-defined materials or by using EELS reference databases [1-3]. Since their content is mostly not exhaustive to provide a set of reference spectra for each element and oxidation state for a given material, the process of obtaining commercially available materials, evaluating them for their ability to be usable as standards and using the obtained set of standards to map the oxidation states of a Cu-based MeOH catalyst [4] post-catalysis is presented.

Methods

The investigated catalyst [4] consists of Cu, ZnO and Al_2O_3. The standard materials needed to cover possible oxidation states are Cu, Cu_2O, CuO, Zn, ZnO and Al_2O_3. Of each material a commercially available sample has been obtained and investigated for its purity and oxidation state via XRD and in the TEM using EDX and EELS. Storage and sample transfer under inert conditions are considered mandatory for all samples that could oxidise further. Sample parts suitable for the measurement of standard spectra are identified, measured and spectra extracted and then imported into Gatan GMS3 as references. An EELS map of the MeOH catalyst [4] after catalytic reaction, that has been transferred under inert conditions into the microscope to preserve the oxidation states, has been acquired. This map is evaluated for materials and oxidation states based on the measured standard spectra.

Results

First it was tested via XRD if the bought materials are as described, with a focus on additional phases that can result from trace metals or different oxidation states than expected. Two materials show a deviation, Cu showed ~5% oxidation and ZnO exhibited an additional unknown phase. EDX maps of each material led to the following results: We found ~3-5% O in Cu, non-homogeneous oxidation and a slightly less O content in Cu_2O, while CuO was homogeneous as described. Some oxidation of ~5-7% was found in the Zn sample and additional O in the ZnO. The oxidation layer on the Zn appears to be amorphous, otherwise it would have been detected in the XRD. Trace elements in all cases are Al, Si and Zn for the Cu-based materials, and Al, Si and Cu for the Zn-based materials, with each amount less than 0,2 at.%. They do not explain the additional phase in the ZnO, so additional bulk EDX has been measured in SEM at low magnification, again revealing no additional elements present. Due to the O excess likely resulting from the production process, there is a high probability that this phase determined by XRD consists of zinc hydroxides.

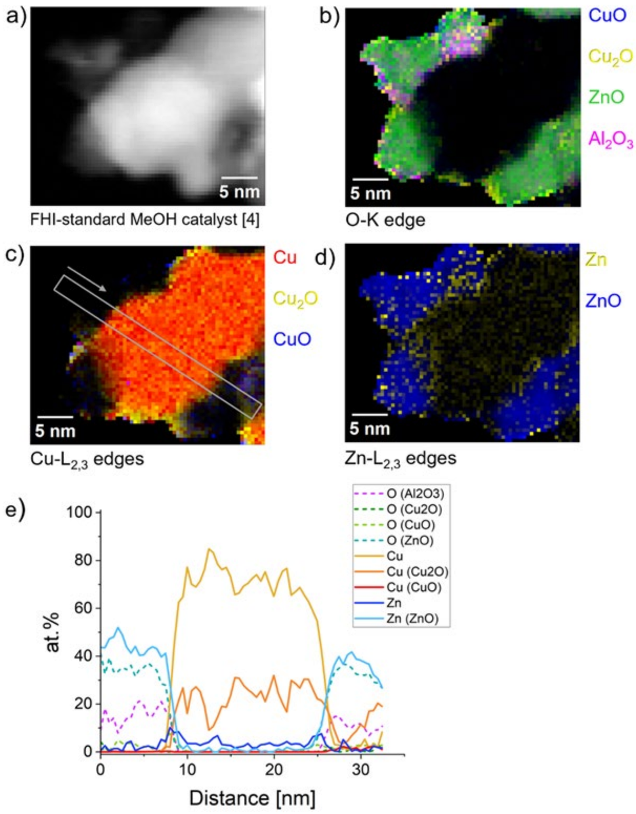
In all EDX maps a region on the sample can be found, where the desired material in the specific state is likely to be present. Therefore, EELS spectrum images have been acquired and evaluated as elemental mappings, allowing to identify a region of this spectrum image where the material has the desired composition and oxidation state. Of this region the standard spectra for each element and oxidation state have been obtained, integrating over several single spectra. The concurrent standards fit using these spectra on the spectrum image of the MeOH catalyst is able to differentiate between elements and oxidation state, resulting in a detailed, spatially resolved map for each (figure 1).

Conclusions

By careful combination of analysis techniques, it is possible to obtain self-measured EELS standards from commercially available standard materials. These allow to evaluate EELS data also for oxidation states with high quality, allowing deeper insight in the properties of catalysts.

Figure 1: a) HAADF image of the MeOH catalyst, from the EELS spectrum image. b) Fit result for the O K edge using self-measured standards for CuO, Cu_2O, ZnO and Al_2O_3. Mostly ZnO is present, some Al_2O_3 and very few Cu oxides. c) Fit result for the Cu $L_{2,3}$ edges using self-measured standards for Cu, CuO and Cu_2O. It shows mostly pure Cu, slightly oxidised. The region from which the line profile in e) is obtained is highlighted in this image. d) Fit result for the Zn $L_{2,3}$ edges using self-measured standards for Zn and ZnO. e) Line profile across the calculated maps, quantifying the fit result.

Graphic:



Keywords:

EELS, Oxidation state, Standards, catalysis

Reference:

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