Karlsruhe Institute of Technology

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Announcement of student theses

At the Institute for Chemical technology and Polymer Chemistry at the Karlsruhe Institute of Technology

Master thesis

With the Topic

Application of advanced analysis methods in the in situ/operando characterization of multi-metallic catalysts using synchrotron-based X-ray techniques

is open

Description:

The interest in the development of multimetallic catalyst is growing fast due to the important role played by these catalysts in the field of energy, environment and industry. These multimetallic nanoparticle catalysts are promising because the synergy between two or more metals can offer new opportunities in catalyst design. The modification of monometallic supported nanoparticle catalysts with secondary metals is a common strategy to enhance catalyst activity, selectivity, and stability. Assessing the structure-activity relationship of these complex catalyst system is a major challenge. Central to these investigations is the understanding of the active site in the catalyst. However, these catalysts are often heterogeneous (e.g., different particle sizes and shapes in one sample), have low metal concentrations.

With the increased sensitivity of modern synchrotrons and improved analysis methods, X-ray based methods have become a standard technique for the structural characterization of catalytic nanoparticles. Using high-energy X-rays, it is possible to conduct experiments under realistic reaction conditions, i.e., high temperature, pressure, and flow of reactants. To perform such in situ/operando time resolved experiments, portable cells and set-ups are designed based on various applications. Other than developing the in situ/operando reactor set-up to perform advance characterization of the multimetallic systems, the development of new theoretical as well as analysis methods is also required to understand the large amount of data recorded during experiments. Application of experimental techniques combined with these newly developed analysis method methods can provide information about the active sites of the catalyst which would not be possible to gather with conventional characterization techniques/methods.

In the present master thesis, one of these emerging methods modulation excitation spectroscopy (MES) will be combined with synchrotron based X-ray spectroscopy (XAS). MES makes it possible to probe changes on catalyst surfaces as a function of different reaction conditions and the kinetics of reaction occurring at the time scale of the MES measurements. In an MES experiment, the catalytic system is modulated by periodically alternating between two externally applied conditions (e.g. concentration, reactants, temperature, pressure, pH) while the data are acquired continuously. MES is thus becoming more and more applied in conjunction with a number of time-resolved spectroscopic

techniques such as XAS, X-ray diffraction (XRD), Raman, and IR. Recently, it has been shown that MES coupled with suitable time-resolved spectroscopic measurements can not only resolve the changes taking place on catalyst surfaces but can also evaluate the comparative degree of changes due to the variation in reaction conditions.[1]
Another method to be studied under this project is Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) which can isolate the species and obtain their concentrations in the mixture automatically and without prior knowledge of standards. However, the spectra obtained from MCR-ALS analysis needs to be related to meaningful references reported in the literature or at least ascertained by complementary information for further identification. Also, the combination of MCR-ALS with MES coupled spectroscopy can be very useful to obtained important information about the different intermediate phases and their variation during transient experiments.
The results of this thesis will showcase applications for these new and powerful methods. Also, discussing the advantages and limitation will be a central point when applied to complex catalytic systems under in situ/operando conditions.

[1] Gaur et al. ACS Catal. 2022, 12, 633−647, [2] Gaur et al. ACS Catal. 2019, 9, 2568−2579

Tasks:

- Understanding the theory of Modulation excitation spectroscopy and its application in combination with X-Ray absorption spectroscopy
- Performing MES analysis on the existing XAS data measured under transient conditions using the available Matlab scripts and work on the further development of scripts
- Developing method to perform EXAFS fitting of phase resolved data obtained from MES analysis for extracting the structural parameters
- Additionally employing Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) on the time resolved data measured to extract the number of components

Requirement:

- Interest in the field of catalyst characterization employing synchrotron-based techniques
- Programming experience (e.g. preferably in Matlab, Python)
- Familiarity with X-ray absorption spectroscopy is an advantage
- Independent, structured and interdisciplinary work
- Good knowledge of English (spoken and written)

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