Helmholtz - OCPC - Programme 2017-2021
for the Involvement of Postdocs in Bilateral Collaboration Projects with China

PART A

Title of the project: **In-situ investigation of clusters and single atom catalysts by pair distribution function analysis and 4D-scanning transmission electron microscopy**

Helmholtz Centre and institute:
Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology (INT)
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Project leader:
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Description of the project (max. 1 page)**:**

Supported metal catalysts are among the most important ones in heterogeneous catalysis due to their outstanding catalytic behavior widely used in industries. Previous studies revealed that the active sites of the catalyst responsible for the specific chemistry are often low-coordinated atoms. Synthesis of supported metal nanocatalysts with extremely small particle sizes or even single atoms is an effective way to promote their performance[1, 2]. However, catalytical mechanism of these novel catalysis is still under debates due to a lack of correlation between the dynamic evolution of their structure and the catalytic behavior under realistic chemical environment. Aberration-corrected (scanning) transmission electron microscopy ((S)TEM) has been used as an important tool to characterize nanocatalysts. However, strongly distorted crystalline structure of the nanoclusters and obscure contrast of the single atoms on the support material limit the application of conventional imaging techniques. The ideal conditions such as ultrathin specimen with ultraclean surface required by the atomic resolved imaging do not represent the realistic chemical environment. The need for in-situ or even operando conditions further complicates the situation.

Atomic pair distribution function (PDF) obtained from diffraction[3], measuring the

interatomic distance and coordination, directly probes the atomic configuration, particularly, of strongly distorted or disordered materials, which is commonly the case in cluster or single-atom catalysts. In contrast to the X-ray and neutron diffraction, the electron diffraction in TEM provides highly flexible spatial resolution from micro- to tens of nanometer[4]. The recently developed 4D STEM-PDF[5] at KIT-INT even offers the PDF with sub-nanometer spatial resolution and, at the same time, samples a statistically meaningful area representing the samples global properties. The power to answer structural questions of complex materials has been demonstrated, e.g. analyzing the bond changes during cycling of batteries[6,7] or the structure of metallic nanoglasses[8].

In this project, we will apply the TEM based PDF analysis to investigate structural evolution of metal nanocatalysts *in-situ* under reaction conditions for understanding their structure-activity relationship (SAR). As a starting point, dynamics of the reconstruction of Pt catalyst on carbon support for selective oxidation and degradation of Au catalyst for low-temperature water-gas-shifting[9] will be investigated in terms of the atomic distance, coordination number and bonding between the catalysts and their support. In addition, 4DSTEM based imaging techniques, such as differential phase contrast (DPC), with sensitivity in single atom imaging, will also be used as complementary methods to the PDF and conventional (S)TEM. Afterwards, the study will be extended to other novel nanocatalysts. The in-situ (S)TEM will be implemented using a Protochips gas environment holder in a double aberration corrected (S)TEM equipped with versatile advanced detectors for chemical structure analysis, located at KIT-INT. The TEM results will be correlated with other in-situ techniques, such as extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy located at SJTU, to obtain a comprehensive understanding of the catalytic SAR question. The knowledge gained from the project will help to predict the optimized cluster sizes and dispersion rates in the design of high-efficient and environmental-benign catalysts.

[1] E. C. Tyo et al, Nat. Nanotechnol. 10, 577–588 (2015). [2] A. Wang et al, Nature Rev. Chem. 2, 65 (2018) [3] T. Egami et al., Underneath Bragg Peaks Struct. Anal. Complex Mater. 16, 55 (2012). [4] X. Mu et al, J. Appl. Crystallogr. 46, 1105 (2013). [5] X. Mu et al, Ultramicroscopy 168, 1 (2016). [6] Z. Li et al, Nat. Commun. 9, 5115 (2018). [7] C. Zhu et al, Nano Lett. 14, 5342 (2014). [8] Y. Ivanisenko et al, Adv. Eng. Mat, 1800404, 1 (2018). [9] J. H. Carter et al, Angew. Chemie Int. Ed. 56, 16037 (2017).

Description of existing or sought Chinese collaboration partner institute (max. half page)**:**

KIT-INT has intensively worked on electron microscopic characterization of the structure of catalysts. Intensive discussion with Prof. Dr. Liu Xi and his colleagues in the chemistry department at SJTU for developing novel microscopic techniques for heterogeneous catalysis research have started in 2018. Both of us are interested to explore how to identify structural transformations of metal clusters related to their catalytic performance, which will clarify the structure-activity relationship of catalysts and help catalyst design and modification. The electron diffraction-based PDF method developed at KIT-INT will be the key experimental technique in the proposed work in Karlsruhe. The PDF method is expected to be established also in the probe corrected environmental STEM (ESTEM) located in SJTU, to complement the strategy of using the in-situ gas holder. The electron microscopic results will be evaluated and correlated with the versatile in-situ techniques (ESTEM, XPS, EXAFS)

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located at SJTU. In addition to the direct catalytic insights, the proposed work will also help evaluate/establish the proposed novel electron microscopy methods in extension of solving broader chemistry questions at both KIT and SJTU in the future. The coordinator of the Chinese partner will be Prof. Dr. Liu Xi, Prof. Dr. Liwei Chen, School of Chemistry and Chemical Engineering, Shanghai Jiaotong University.

Required qualification of the post-doc:

- PhD in chemistry, physical chemistry, material science or related area.
- Experience with catalytical chemistry, transmission electron microscopy.
- Comprehensive understanding of diffraction and scattering will be a significant plus.

PART B

Documents to be provided by the post-doc, necessary for an application to OCPC via a postdoc-station in China, which is affiliated to a research institution like a university:

- Detailed description of the interest in joining the project (motivation letter)
- Curriculum vitae, copies of degrees
- List of publications
- 2 letters of recommendation
- Proof of command of English language

PART C

Additional requirements to be fulfilled by the post-doc:

- Max. age of 35 years
- PhD degree not older than 5 years
- Very good command of the English language
- Strong ability to work independently and in a team

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