

Abstract:**In-situ Investigations on the Geometric and Electronic Properties of Paramagnetic Sites in Heterogeneous Catalysts under relevant Conditions****Co-supervisor 1: Thomas Risse, FU-Berlin, IMPRS, EC²****Co-supervisor 2: Elias Frei, FHI, SFB 1349**

This project aims at the development and installation of an *in-situ* EPR spectroscopy setup with online product analysis. "*In-situ*" focuses within this context on two main approaches, EPR spectroscopy during catalysis and the formation of defects in the EPR spectrometer by gaseous reactants. The methodology allows to gain atomic scale insight into the electronic and geometric properties of catalytic systems studied in UniSysCat. In particular, metal complexes immobilized in porous solid frameworks will be investigated an important class of catalysts studied in research area A2 of UniSysCat. Furthermore, ZnO is chosen as an exploratory reference system, which offers manifold possibilities: i) A pronounced defect chemistry, ii) anionic doping (nitride or fluoride) and iii) in combination with Cu an important catalytic system. As catalytic reaction the hydrogenation of CO₂ is selected. Investigations on the fluoride doping connect directly to the SFB 1349, which combines fundamentals and application from the fluorine perspective.

Extended version of the project:

Title of Project: In-situ Investigations on the Geometric and Electronic Properties of Paramagnetic Sites in Heterogeneous Catalysts under relevant Conditions

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1. Overall goal of the project

Within this project an *in-situ* EPR spectroscopy experiment will be setup, which combines X-band EPR measurements of heterogeneous powder catalysts under catalytically relevant conditions and the characterization of their catalytic properties by monitoring online the gas phase composition using gas chromatography. The experiments aim at correlating the electronic and geometric properties of paramagnetic species in the catalytic systems with their catalytic performance to reveal atomic level insight into the paramagnetic species present under catalytic turn over conditions. This information is of great importance for systems investigated both in UniSysCat as well as the SFB 1349 "Fluorine specific interactions: basics and applications". In particular, it will be applied to reveal the geometric and electronic properties heterogenized paramagnetic metal complexes being a central class of materials studies in area A2 of UniSysCat as well as the impact of paramagnetic defects in fluoride and nitride doped Cu/ZnO on the catalytic properties of these system. In addition, the doping of ZnO and the accompanied creation of defects will be investigated *in-situ* from a fundamental perspective.

2. State of the art

In-situ EPR spectroscopy of heterogeneous powder catalysts has been established at the gas/solid as well as at the liquid/solid interface. The methodology has been successfully applied to a variety of heterogeneous catalysts including paramagnetic species in bulk oxides such as vanadium-phosphorous oxides, chromia or nickel catalysts. Apart from paramagnetic centers in bulk solids the technique was shown to work on isolated transition metal centers such as transition metal ion loaded zeolithes. These investigations concur with a large body of *in-situ* studies using other methods, which clearly show, that geometric and electronic properties of catalytic systems will oftentimes differ substantially if comparing *in-situ* conditions with typical experimental *ex-situ* conditions. The Cu/ZnO system, which is an important industrial catalyst is one of the examples for which this has been established in the past using a variety of techniques. While it may sometimes be possible to quench the catalytically active system and investigate the properties of catalytically important species in these quenched systems, preliminary experiments on the Cu/ZnO-system already showed that such an approach will fail as the samples show significant changes over time even if observed under defined *ex-situ* conditions. This effect is related to the activation process of the CuO/ZnO system before applied as Cu/ZnO catalyst. The gained high energy structure of the active catalysts is a sensitive state, impossible to stabilize *ex-situ*. These observations are not restricted to heterogeneous catalysts, but is similarly found for homogeneous transition metal catalysts e.g. used to catalyze water splitting, which on the one hand illustrates that particular care has to be taken to gain information on catalytically relevant species but on the other hand provide clear evidence that *in-situ* EPR spectroscopy can provide interesting new insight into the systems.

3. Specific aims and how they may be reached:

To meet the objectives laid out above, the project is subdivided into three main work packages. The first work package is about the setup of an *in-situ* EPR experiment at X-band (10 GHz) to study paramagnetic species under catalytic turn over conditions at the gas-solid interface. The other two refer to the application of the methodology to samples interesting for the scientific questions in UniSysCat and the SFB 1349, respectively. Besides the correlation of the EPR spectroscopy results to the catalytic performance by *in-situ* studies, also the development of the EPR signals by *in-situ* creating defective structures will be part of the project. With respect to *in-situ* EPR experiment, a catalytic reactor will be fitted into a high temperature X-band cavity, which will build on the experience of the FHI group with *in-situ* conductivity measurements using microwave cavities. The isothermal catalytic CO₂ hydrogenation performance via e.g. the reverse water-gas-shift reaction (r-WGSR) under defined gas and flow conditions is monitored online by a gas chromatograph equipped with a TCD and FID detector. The *in-situ* setup will be used for two main classes of samples belonging to the activity within project area A2 of UniSysCat and the SFB 1349. Within the former immobilized paramagnetic transition metal complexes (e.g. Cu, Fe or Co based systems) will be elucidated. Within this project an iterative procedure will be pursued. First, systems exhibiting interesting catalytic properties will be identified. These samples will be subject to a detailed EPR characterization of the as prepared and spent catalysts. To this end, cw- as well as pulsed EPR spectroscopic measurements possible at different microwave frequencies will be performed to characterize geometric (arrangement of ligands, interactions with support etc.) and electronic (spin state, zero-field splitting etc.) properties whose interpretation will benefit from theoretical efforts in the group of M. Kaupp. These systems will be mainly prepared by the group of Arne Thomas and will incorporate transition metal complexes from other synthetic groups within Unisyscat (e.g. M. Schwalbe, K. Ray, C. Limberg). Finally, the samples will be studied under catalytic turn over conditions using the *in-situ* EPR setup and the results will be correlated to the catalytic performance of the systems. From the analysis of the results obtained from the as prepared catalysts, the used samples, the *in-situ* results new insights into the paramagnetic species as well as their modifications during catalytic turn over are expected. These results should usually in comparison with complementary techniques done in other groups allow to draw conclusions on the structural and electronic properties of the catalytically active state. It may also allow to gain insight into unwanted side effects such as deactivation, phase separation tendencies or changes of selectivity in the course of the reaction. The second set of experiments will focus on the doped Cu/ZnO catalysts. At first the ZnO material is synthesized following a co-precipitation approach. The doping is carried out subsequently with gaseous reactants. Gaseous reactants are of advantage, since *in-situ* monitoring the defect manipulation offers valuable fundamental knowledge on defects induced by anionic dopants. A change of the defect situation in ZnO (oxygen defects/vacancies, shallow donor states, Zn(I) interstitials, etc.) is expected to influence the EPR signals as well. The formation of new or vanishing defects, respectively, allows a proper signal identification. The *in-situ* EPR spectroscopy experiments will be performed on Cu/ZnO samples for which Cu is added via incipient-wetness-impregnation. A selection of suitable samples is carried out based on standard characterization results (XRD, BET, XPS, surface titration etc.) and *ex-situ* catalytic tests. The fluoride doping is conducted by dosing diluted HF and/or F₂ mixtures, which has already been verified within the SFB 1349. The nitride incorporation is realized by e.g. mixtures of NH₃ and derivatives.

Finally, the *in-situ* gained information on the defect situation in combination with the online product analysis enables a correlation of the measured activity and a certain defect concentration or occurrence. These results on anionic doped Cu/ZnO reference systems serve as benchmark for establishing this analytic tool and blueprint for other systems.