



# Understanding ICON & friends!

CRC 1487 Symposium 03.-05.09.2024 Darmstadt, Germany

# Dear participants of the CRC 1487 symposium,

We welcome you in Darmstadt and are happy to have you here. On the following pages, you will find further information, the program, the abstracts for oral presentations and posters and a list of participants.

Whenever you have questions, please contact the CRC 1487 coordination team!

We are looking forward for three days full of exciting science on "Understanding Iron & friends".



# Further information

# **Further information**



### Venue

Stadtmitte S1|03, Hochschulstraße 1, 66289 Darmstadt

All scientific talks will take place in the Wilhelm-Köhler-Saal (room 283) and coffee breaks and lunchs in the Foyer (room 284). The poster session will be in room 204. Venues of the social events see below. An overview of the rooms you can find on the last page.

# Poster

The poster session is scheduled for Sept 3rd. Please ensure that you fix your poster latest during the afternoon coffee break on the 3rd, in room 204 to the respective wall. There will be a list in the room telling you where you can put up your poster.

# Talks

Please make sure, that on the day of your presentation, you upload your presentation ideally as .pptx to the presenting computer prior to the beginning of the respective session.

# Wifi

For Wifi, you can use Eduroam. If you do not yet have an account, you can obtain access data at the reception desk.

# **Social Events**



### Wednesday, 04.09.2024 - 16:30

city tour for registered persons (Meeting point: in front of the main entrance of conference venue)



#### Wednesday, 04.09.2024 - 20:00

conference dinner for registered persons (https://dasroeders.de/ | Rheinstraße 99 | 64295 Darmstadt)



# Program

# Tuesday, 03.09.2024



## ARRIVAL (9:00 - 10:00)

10:00 - 12:10		CHAIR: Prof. Christian Hess
10:00 - 10:15	Prof. Ulrike Kramm, Technische Universität Darmstadt	Welcome
10:15 - 11:00	Prof. Robert Schlögl, Alexander von Humboldt- Stiftung/Fritz-Haber-Institut der Max-Planck-Gesellschaft	Catalysis with Iron Surfaces: What is Special in Relation to Noble Metals
11:00 - 11:20	Hannah Lamers, Technische Universität Darmstadt	Iron-based catalysts for the selective Acetylene Hydrogenation
11:20 - 11:50	Dr. Bruno Chaudret, LPCNO INSA-CNRS Toulouse	Iron Based Nanoparticles for Magnetically Induced Catalysis
	LU	INCH
14:00 - 15:45		CHAIR: Prof. Vera Krewald
14:00 - 14:45	Prof. Frank Neese, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr	Exploring High Valent Iron chemistry with a Combination of Quantum Chemistry and Spectroscopy
14:45 - 15:05	Carlos M. Jimenez-Muñoz, Technische Universität Darmstadt	Electronic structure of mononuclear iron phthalocyanine complexes in matrix isolation spectroscopy: experiment challenges theory
15:05 - 15:25	Mathias L. Skavenborg, University of Southern Denmark	Iron Complexes as Charge Carriers in All Iron Redox Flow Batteries
15:25 - 15:45	Dr. Young-Joon Song, Goethe-Universität Frankfurt Niklas von Rhein, Technische Universität Darmstadt	Computational Models for FeNC catalysts - A detailed view on electronic structures from molecular to periodic models

### **COFFEE BREAK**

16:15 - 17:05		CHAIR: Prof. Christina Thiele
16:15 - 16:45	Dr. ing. Daniël L. J. Broere, Utrecht University	A Tale of Two Irons: Synthesis and Reactivity of Well- defined Diiron Expanded Pincer Complexes
16:45 - 17:05	Dr. Stephan Müssig, Friedrich-Alexander-Universität Erlangen-Nürnberg	Control of magnetic dipole-dipole interactions in iron oxide-based supraparticles

GROUP PICTURE (17:05 – 17:15) POSTER SESSION, Room 204 (17:15 – 19:15)

# Wednesday, 04.09.2024



08:30 - 10.20		CHAIR: Prof. Jan Philipp Hofmann
08:30 - 09:00	Prof. Matthias Bauer, Universität Paderborn	Photoactive Iron complexes and time-resolved X-ray spectroscopy - New friends
09:00 - 09:20	Dr. Dimitrios Bessas, European Synchrotron Radiation Facility	Nuclear Resonance Scattering of synchrotron radiation for iron and its friends
09:20 - 09:40	Dr. Juliusz A. Wolny, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau	Insight into the Dynamics of Spin Crossover Transitions and Cooperativity with Nuclear Inelastic Scattering and Density Functional Theory
09:40 - 10:00	Sun Myung Kim, Technische Universität Darmstadt	Electronic Structure and Redox Properties of Iron in Different Environments Studied by Valence and Core Level Spectroscopies
10:00 - 10:20	Nicole Segura-Salas, Technische Universität Darmstadt	Manipulating FeNC model catalysts with metal nanoparticles: Effect on activity and selectivity for CO <sub>2</sub> RR

#### **COFFEE BREAK**

10:50 - 12.20		CHAIR: Prof. Herbert Plenio
10:50 - 11:20	Prof. Christine McKenzie, University of Southern Denmark	Local Environment Influence on High Valent Non- heme Iron
11:20 - 11:40	Dr. Lukas Kaltschnee, Technische Universität Darmstadt	Transient intermediates of the [Fe]-hydrogenase catalysis characterized by sensitivity-enhanced NMR
11:40 - 12:00	JunProf. Alicia Casitas, Philipps-Universität Marburg	High-Valent Organometallic Iron Complexes
12:00 - 12:20	Justin Krampe, Technische Universität Darmstadt	Analysis of spin interactions in µ-oxo bridged copper, nickel and iron di-nuclear complexes

#### LUNCH

14:00 - 16.00		CHAIR: Prof. Angela Möller
14:00 - 14:30	Prof. Martin Muhler, Ruhr Universität Bochum	Selective Catalytic Oxidation of Alcohols and Olefins over Cobalt-based Spinel and Perovskite Nanoparticles
14:30 - 14:50	Prof. Oliver Clemens, Universität Stuttgart	Fe-containing perovskites – Topochemistry and a Playground of Functional Properties
14:50 - 15:10	Hannah Wilhelm, Technische Universität Darmstadt Jan Welzenbach, Technische Universität Darmstadt	Mechanistic insight into iron molybdate catalysts during oxidative dehydrogenation using coupled operando spectroscopy and diffraction
15:10 - 15:30	Dr. Michael Lammer, Graz University of Technology	Iron-based oxygen carrier development for hydrogen production and purification
15:30 - 16:00	Prof. Jan-Dierk Grunwaldt, Karlsruher Institut für Technologie	Looking at iron and friends at work: Fascinating elements for catalysis and X-rays

COFFEE BREAK (16:00 – 16:30) CITY TOUR (16:30 –18:30) CONFERENCE DINNER (from 20:00)

# Thursday, 05.09.2024



	CHAIR: Prof. Ulrike Kramm
Dr. Deborah J. Myers, Argonne National Laboratory	Iron-based catalysts for proton-exchange membrane fuel cells and anion-exchange membrane water electrolyzers
Prof. Jörg Schneider, Technische Universität Darmstadt	Isolating single iron-nitrogen centers in carbon nanostructures
Mohsin Muhyuddin, University of Milano-Bicocca	Evolution of Active Sites in Iron Phthalocyanine Functionalized Carbon during Pyrolysis: Transforming into Active Fe-N <sub>x</sub> -C Electrocatalysts for Oxygen Reduction Reaction
Julia Buschermöhle, Deutsches Zentrum für Luft- und Raumfahrt e. V.	High-performance MOF-based Fe-Sn-N-C catalysts for the ORR in HT-PEM fuel cells
Dr. Kaltum Abdiaziz, Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr Dr. Lingmei Ni, Technische Universität Darmstadt	Spectroelectrochemical EPR and Mössbauer for Identifying Active Sites in FeNC Catalysts.
	Dr. Deborah J. Myers, Argonne National LaboratoryProf. Jörg Schneider, Technische Universität DarmstadtMohsin Muhyuddin, University of Milano-BicoccaJulia Buschermöhle, Deutsches Zentrum für Luft- und Raumfahrt e. V.Dr. Kaltum Abdiaziz, Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr Dr. Lingmei Ni, Technische Universität Darmstadt

### COFFEE BREAK

11:05 - 12:45		CHAIR: Prof. Rolf Schäfer
11:05 - 11:35	Prof. Jasnamol Palakkal, Georg-August-Universität Göttingen	Growth Optimization of Fe-based Epitaxial Tellurides Using Hybrid PLD
11:35 - 11:55	Dr. Imants Dirba, Technische Universität Darmstadt	Upgrading magnetism of iron by interstitial nitrogen
11:55 - 12.15	Giovanni d'Andrea, Technische Universität Darmstadt	Materials Science of Nitrogen Ion Implantation in $\alpha$ - Fe
12.15 - 12.45		Concluding Remarks

LUNCH



# Abstracts

# Tuesday, 03.09.2024 | 10:15 - 11:00



#### Catalysis with Iron Surfaces: What is Special in Relation to Noble Metals

Robert Schlögl<sup>1,2</sup> <sup>1</sup> Fritz-Haber-Institut der MPG, Dep ISC, Germany <sup>2</sup> Alexander von Humboldt Foundation, Germany

Iron in elemental form is a prominent catalyst material. Hydrogenation of CO and di-nitrogen are key applications. In oxidic form iron is a co-catalyst for de-hydrogenation and selective oxidation. When looking at the broad reactivity activated by iron the question arises in as much iron could replace noble metals. This was studied extensively with molecular catalysts from which we can learn some conceptual insights.

One would argue that the local electronic structure of iron and noble metals is substantially different giving the general reason why the simple insights gained from the periodic table is not sufficient. Manipulating the band structure of metals by alloying is a prominent research field and should enable us to perform the desirable chemical mimicking. A successful example of an Fe-Al alloy will be shown.

Highly relevant is the insight gained from the concept of self-generated active catalysts occurring during operation from dissolution-segregation steady states of the synthesized pre-catalyst. The reactivity of hydrogen and nitrogen to hydrides and nitrides will be discussed from which we may deduce why it is merely the reaction conditions and not a fundamental impossibility why it is still a great challenge to replace noble metals by iron in catalysis.

# Tuesday, 03.09.2024 | 11:00 - 11:20



#### Iron-based catalysts for the selective Acetylene Hydrogenation

Hannah Lamers,<sup>1</sup> Martin Lucas,<sup>1</sup> Marcus Rose<sup>1</sup> <sup>1</sup> Technical University of Darmstadt, Technical Chemistry 2, Darmstadt, Germany \*hannah.lamers@tu-darmstadt

#### Introduction:

Ethylene is one of the most important monomers for polymer production and is required in high purity to ensure reproducible product quality in olefin-based polymers. Since polyunsaturated impurities such as acetylene from petroleum-based ethylene sources lead to catalyst poisoning in polymerization reactions, the generation of ethylene-rich streams with acetylene concentrations below 1 ppm is essential.<sup>[1,2]</sup> State-of-the-art catalysts for selective acetylene hydrogenation are alumina supported palladium-silver alloyed nanoparticles.<sup>[3,4]</sup> Due to high palladium prices and low availability, innovative, sustainable and highly active catalyst systems are needed. Iron-based catalysts are promising substitutes due to their high natural abundance, non-toxicity and known hydrogenation activity.<sup>[2]</sup> In preliminary studies, we demonstrated the suitability of zero-valent iron catalysts using unsupported  $\alpha$ -Fe nanoparticles, which showed very high activity and selectivity in the semi-hydrogenation of acetylene. To further improve the catalytic activity by modification of particle size, surface area and dispersion, we are currently investigating alumina supported iron nanoparticles with different iron loadings.

#### Materials and Methods:

Supported iron nanoparticles are synthesized by incipient wet impregnation on alpha-alumina with different metal loadings. All catalyst precursors are calcined and subsequently reduced to the zero-valent iron species prior to use. The supported iron catalysts are analyzed by X-ray diffraction (XRD), N2-physisorption and X-ray fluorescence spectroscopy (XRF), and temperature programmed reduction (TPR). The catalytic testing of the supported iron nanoparticles is performed in a continuously operated reactor with a modeled feed composition of industrial acetylene removal units under front-end conditions.<sup>[4,5]</sup> In a typical reaction sequence, 200 mg of catalyst is used while varying the temperature between 30 °C and 90 °C at 22.5 bar and a flow of 12.5 L h-1.<sup>[5]</sup>

#### **Results and Discussion:**

Alpha-alumina supported catalysts with 1 wt%, 5 wt% and 10 wt% iron loading, respectively, were successfully synthesized and the iron content was monitored by XRF. The reduction profiles of the supported iron catalysts were determined by TPR and indicate complete reduction to Fe0 at 900 °C. The diffraction patterns of the unreduced catalyst show typical reflections of different iron oxides, while the reduced catalyst shows the reflections of  $\alpha$ -Fe. The catalysts have been used in the semi-hydrogenation of acetylene under industrial front-end conditions and show excellent activity at 90 °C.<sup>[6]</sup> The reaction rate increases significantly with decreasing iron loading. The ethane production is low at all temperature intervals. This indicates no significant acetylene over hydrogenation or ethylene hydrogenation. These results underline the great suitability of iron catalysts as promising sustainable alternatives to conventional palladium-based materials.

#### **References:**

- 1. S. Sahebdelfar, Samane Komeili, *Rev. Chem. Eng.*, **2018**, 215-237.
- 2. S. Hock, C. V. Reichel, A.-M. Zieschang, B. Albert, M. Rose, *ACS Sustain. Chem. Eng.* **2021**, 9, 16570-16576.
- 3. A. Pachulski, R. Schödel, P. Claus, Appl. Catal. A 2012, 445-446, 107.
- 4. S. Hock, L. Iser, M. Lucas, M. Rose, *Chem. Ing. Tech.* **2022**, 94, 1704.
- 5. J. Gislason, W. Xia, H. Sellers, J. Phys. Chem. A **2002**, 106, 767.
- 6. H. Lamers, M. Lucas, M. Rose, manuscript in preparation.

## Tuesday, 03.09.2024 | 11:20 - 11:50

#### Iron Based Nanoparticles for Magnetically Induced Catalysis

#### Bruno Chaudret

Laboratoire de Physique et Chimie des Nano-Objets UMR 5215, INSA, UPS, CNR - Université de Toulouse, 135 avenue de Rangueil 31077 Toulouse (France) ; chaudret@insa-toulouse.fr

Magnetic nanoparticles (MNPs) display both interesting core physical properties and interesting surface chemical properties. The composition of the particles allows to modulate their magnetic properties in terms of saturation magnetization, magnetic anisotropy and Curie temperature and hence heating power. Thus, magnetic nanoparticles heat when submitted to an alternating magnetic field. Magnetic heating is instantaneous and in principle the best way to transform electrical energy into heat.

We have developed in Toulouse a new generation of ironbased nanoparticles (NPs) of unprecedented heating power. We have prepared iron carbide particles by carbidization of preformed monodisperse Fe(0) nanoparticles under a CO/H<sub>2</sub> atmosphere at 150°C. They consist essentially of



crystalline Fe<sub>2.2</sub>C, display a SAR (heating power) of up to 3.3 kW/g and are able to hydrogenate CO<sub>2</sub> into methane in a flow reactor after addition of a catalytic Ru or Ni layer and excitation by an alternating magnetic field.<sup>1</sup> Iron Cobalt NPs have been prepared from  $\{Fe[N(TMS)_2]_2\}_2$  and the relative {Co[N(TMS)<sub>2</sub>]<sub>2</sub>}. These soft magnetic bimetallic FeCo NPs<sup>2</sup> with a high Curie Temperature allow performing high temperature catalytic reactions such as propane dehydrogenation or methane and propane dry reforming. Iron nickel nanoparticles have been synthesized from iron amide and nickel amidinate precursors and found very active for CO<sub>2</sub> hydrogenation.<sup>3</sup> In addition, submitting nanoparticles of iron carbide or iron nickel to magnetic heating in solution leads to high local overheating and to perform in apparent mild conditions and under a low H<sub>2</sub> pressure difficult reactions typically performed at high temperature and pressure such as such as hydrodeoxygenation of biomass derived platform molecules, C-O bond cleavage in complex molecules or alcohol amination.<sup>4-6</sup> In solution, it is possible to measure a temperature at the surface of the MNPs much higher than the mean temperature of the solvent (for example, 236°C in toluene for a mean temperature of 110°C). The lecture will briefly present the synthesis and properties of "organometallic" nanoparticles particles, their magnetic properties, their surface modification to deposit a catalytic layer and their catalytic properties both in solid state and in solution. Further developments of the technique using alternative iron-based heating materials<sup>8</sup> and high pressure (up to 50 bars) for various applications of magneto-induced catalysis including water electrolysis will also be described.<sup>8</sup>

#### References:

- 1. A. Bordet et al. Angew.Chem.Int. Ed. 2016, 55,15894 –15898
- 2. C. Garnero et al. Nano Letters 2019, 19, 1379-1386 ; J. Marbaix et al. ACS Appl NanoMat 2020, 3767-3778, 3
- 3. D. De Masi et al. . Angew. Chem. Int. Ed. 2020, 59, 6187-6191
- 4. J.M. Asensio et al. Angew. Chem. Int. Ed. 2019, 58, 11306-11310
- 5. I. Mustieles Marin et al. Green Chem 2021, 23, 2025 ;
- 6. V. Varela-Izquierdo et al. Angew. Chem. Int. Ed. 2024, e202412340
- 7. Z.J. Diaz Puerto et al. Nanoscale 2021, 13, 12438-12442
- 8. S. Gosh et al. Chem Mat 2023, 35, 7542
- 9. C. Niether et al. Nature Energy 2018, 3, 476-483
- 10. For a review : M. Estrader et al. Angew.Chem.Int. Ed. 2022, 61, e202207301



#### Exploring High Valent Iron chemistry with a Combination of Quantum Chemistry and Spectroscopy

Prof. Dr. Frank Neese<sup>1,\*</sup>

<sup>1</sup> Department of Molecular Theory and Spectroscopy, Max-Planck Institut für Kohlenforschung, Mülheim an der Ruhr/Germany \*frank.neese@kofo.mpg.de

High-valent iron centers have fascinated inorganic chemists for a long time. Ever since the Fe(IV)=O motif has been identified in a number of enzymes such as Cytochrome P450, the mechanisms by which these centers activate C-H bonds has been under intense debate by theoreticians as well as experimentalists. Important contributions were made by Schwarz, Shaik, Schröder and co-workers when they introduced the concept of two-state reactivity [1]. In this concept, a reaction proceeds on two different potential energy surfaces with distinct spin multiplicity. Such a mechanism has been proposed for Fe(IV)=O centers with a spin triplet ground state [2]. However, the crucial spin quintet state has never been experimentally observed and thus far all information on it has been derived exclusively from calculations. Since spin state energetics are notoriously difficult to calculate with any quantitative accuracy, an experimental determination of the triplet-quintet gap would provide an important benchmark for theory and would provide direct insight into the nature of two-state reactivity. In this study we report such an analysis that uses a combination of different advanced spectroscopic techniques such as MCD and RIXS coupled to high-level multireference ab initio electronic structure calculations. The lecture will also highlight the challenges in treating such electronic structure problems with contemporary quantum chemistry.

#### References

[1] Schröder, D., Shaik, S., Schwarz, H. *Acc. Chem. Res.*, **2000**, <u>33</u>, 139

- [2] Hirao, H,M Kumar, D.; Que Jr, L.; Shaik, S. J. Am. Chem. Soc., **2006**, <u>128</u>, 8590
- [3] Rice, D.B.; Wong, D.; Weyhermüller, T.; Neese, F.; DeBeer, S. 2024, in press



#### Electronic structure of mononuclear iron phthalocyanine complexes in matrix isolation spectroscopy: experiment challenges theory

<u>Carlos M. Jimenez-Muñoz<sup>1\*</sup></u>, Stefan Germmer<sup>2</sup>, Hans-Jörg Himmel<sup>2</sup>, Markus Enders<sup>2</sup>, Vera Krewald<sup>1</sup> <sup>1</sup> Theoretische Chemie, Technische Universität Darmstadt, Darmstadt, Germany <sup>2</sup> Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany \*carlos.jimenez@tu-darmstadt.de

Hemoproteins possess a characteristic iron center with a square-planar coordination sphere that has been recognized as a crucial chemical environment in nature. For this reason, FeN<sub>4</sub> motifs have been used to inspire man-made catalysts as an alternative to platinum-based catalysts for oxygen reduction reactions [1]. Iron phthalocyanine (FePc) complexes possess a similar coordination environment, however, suffer from low solubility limiting their study in solution or even their use in homogeneous catalysis [2,3]. Bulky substituents on FePc have been shown to prevent the formation of aggregates and improve its solubility [2].

Matrix isolation experiments have been carried out to characterize such FePc units, a well-known technique that minimizes extrinsic effects such as solvation or aggregation and allows the characterization of the electronic structure via spectroscopic methods (IR, NIR, and UV/Vis) [3]. Consequently, the spectra obtained possess distinctive narrow bands, a perfect basis for benchmarking theoretical protocols.

Herein, we present a comparison of DFT and CASSCF/NEVPT2 calculations with matrix isolation spectra. In both approaches, spin-orbit coupling (SOC) effect can be included to determine its influence on the electronic structure. Initial results suggest the possibility of a strongly correlated ground state where SOC plays a fundamental role. At the DFT level of theory, there are disagreements between the predicted spectra and the matrix isolation results. At the SOC-CASSCF/NEVPT2 level of theory, the features missing in the DFT spectra are found. The analysis reveals detailed insights into the electronic structure which is represented by the iron 3d-orbitals and the Gouterman orbitals.



Figure. Active space for iron phthalocyanine unit

#### References

 C. Gallenkamp, U. I. Kramm, V. Krewald, FeN4 Environments upon Reduction: A Computational Analysis of Spin States, Spectroscopic Properties, and Active Species. 2024. JACS Au, 4(3):940–950/
 C. Iwanov, M. P. Hopp, D. Lorenz, J. Ballmann, M. Enders, Dioxygen Activation and Reduction by a Soluble Iron Phthalocyanine. 2023. Chemistry A European J, 29(70):e202302761.

[3] H. Jiang, P. Hu, J. Ye, R. Ganguly, Y. Li, Y. Long, D. Fichou, W. Hu, C. Kloc, Hole Mobility Modulation in Single-Crystal Metal Phthalocyanines by Changing the Metal- $\pi/\pi$ - $\pi$  Interactions. 2018. Angew. Chem. Int. Ed., 57(32):10112–10117.

# Tuesday, 03.09.2024 | 15:05 - 15:25



#### Iron Complexes as Charge Carriers in All Iron Redox Flow Batteries

<u>Mathias L. Skavenborg</u>,<sup>a\*</sup> Mads Radmer Almind,<sup>b</sup> Johan Hjelm,<sup>b</sup> Christine J. McKenzie<sup>a</sup> <sup>a</sup>Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, 5230 Odense M, Denmark. <sup>b</sup>Technical University of Denmark, Department of Energy Conversion and Storage, 2800 Kgs Lyngby,

> *Denmark* \*Skavenborg@sdu.dk

Redox flow batteries (RFBs) are large scale batteries that store electrical energy in a liquid form using dissolved redox active charge carriers. Electrolytes and charge carriers are stored in tanks which are connected to a stack where electrochemical conversion occurs. We have recently discovered a charge carrier for a symmetric all-cobalt organic RFB with a remarkable span of 1.75 V between reversible Co<sup>III/II</sup> and Co<sup>II/I</sup> couple.<sup>[1]</sup> Low solubility and ligand instability at cathodic potentials however restricts applicability. In addition, sustainability concerns with respect to mining and using cobalt will also limit real-world potential. A robust, aqueous, all-iron RFB (IRFB) as a low cost, and eco-friendly energy storage system is highly desired. The redox chemistry of the current IRFB technology is based on FeCl<sub>2</sub> cycling between the 0/2+ and 2+/3+ oxidation states (Figure 1a). However, this system faces serious challenges: Rust formation on the anodic side and competing hydrogen evolution reaction (HER) at the cathodic side. A fully decoupled system where high solubility and a fast reversible electrochemical response (Fe<sup>3+</sup>/Fe<sup>2+</sup>) within the stability window of water are desired.

In the search for suitable iron complexes for aqueous IRFBs we have screened the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couples in water for a library of complexes (Figure 1b). This has provided some inspiration for the design of new ligands and our progress towards finding the perfect candidate will be described in this contribution.



**Figure 1.** (a) Schematic representation of a commercialized IRFB. (b) Evaluation of aqueous  $Fe^{3+}/Fe^{2+}$  redox couples.

#### References

[1] Skavenborg, M. L.; McPherson, J. N.; Pasadakis-Kavounis, A.; Hjelm, J.; Waite, T. D.; McKenzie, C. J. Leveraging coordination chemistry in the design of bipolar energy storage materials for redox flow batteries. *Sustainable Energy & Fuels* **2022**, *6* (9), 2179-2190, 10.1039/D1SE01966J. DOI: 10.1039/D1SE01966J.





# Computational Models for FeNC catalysts: A detailed view on electronic structures from molecular to periodic models

<u>Niklas von Rhein<sup>1,\*</sup>, Young-Joon Song<sup>2,\*\*</sup></u>, Charlotte Gallenkamp<sup>1</sup>, Martin Diefenbach<sup>1</sup>, Genís Lleopart<sup>3</sup>, Vera Krewald<sup>1</sup> and Roser Valenti<sup>2</sup>

<sup>1</sup> Department of Chemistry, Quantum Chemistry, Technische Universität Darmstadt, 64287 Darmstadt. Germanv

<sup>2</sup> Institut für Theoretische Physik, Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Germany <sup>3</sup> Departament de Ciéncia de Materials i Química Física and Institut de Química Teóretica I Computacional (IQTC), Universitat de Barcelona, 08028 Barcelona, Spain \*niklas.von rhein@tu-darmstadt.de

\*\*ysong@itp.uni-frankfurt.de

The promising catalytic properties of single-atom-based systems make them of great interest as an alternative to platinum-based catalysts. Especially promising are so-called FeNC catalysts with FeN<sub>4</sub> centers embedded in graphene-like structures. Despite a multitude of theoretical and experimental studies dedicated to uncovering the structural and ground state electronic properties of the catalytic centers, those remain unclear.[1,2]

A key method for investigating FeNC catalysts is Mössbauer spectroscopy, which, however, necessitates the use of mostly theoretical models[3]. Hereby, different ways for modeling the active sites exist: In molecular models, the graphene-like structure is handled as a finite molecule, while in periodic models an infinitively large graphene plane is created by periodic boundary conditions. In both approaches, a sufficiently large size of either the molecule or the unit cell needs to be chosen to simulate surface conditions while maintaining a feasible computational time frame.

In our cooperation, we investigate various system sizes for different FeNC models, both molecular and periodic, via density functional theory calculations to determine a sensible system size. We further examine their electronic structure in greater detail, identifying possible electronic states, discussing the influence of the model size and shape on the electronic ground state, and comparing the molecular and the periodic approach.

#### References

[1] C. Gallenkamp, U. I. Kramm, J. Proppe, V. Krewald, Calibration of computational Mössbauer spectroscopy to unravel active sites in FeNC catalysts for the oxygen reduction reaction, Int. J. of Quantum Chemistry 121 (2021) e26394

[2] L. Ni, C. Gallenkamp, S. Wagner, E. Bill, V. Krewald, U. I. Kramm, Identification of the Catalytically Dominant Iron Environment in Iron- and Nitrogen-Doped Carbon Catalysts for the Oxygen Reduction Reaction, J. Am. Chem. Soc. 144 (2022) 16827

[3] P. Gütlich, E. Bill, A. X. Trautwein, Mössbauer Spectroscopy and Transition Metal Chemistry, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011.



# A Tale of Two Irons: Synthesis and Reactivity of Welldefined Diiron Expanded Pincer complexes

Daniël L. J. Broere

Organic Chemistry and Catalysis, Institute for Sustainable and Circular Chemistry, Faculty of Science, Utrecht University, Utrecht, 3584 CG, The Netherlands

Various metalloenzyme active sites feature complex architectures that enable multiple metals and ligands to work together to facilitate bond activation processes that are essential to enzyme function. Inspired by this, our group is exploring ligand systems that can both host multiple transition metals in close proximity and also contain design elements that enable metal-ligand cooperativity. This presentation will detail the journey of using our 'expanded pincer' ligands towards diiron making well-defined diiron complexes in various spin states. Some protons, H atoms and iron atoms will be lost on the way, and we will even bind some  $N_2$ , but we hope to arrive at a point where you ask us to send over some ligand or complexes.



### Tuesday, 03.09.2024 | 16:45 - 17:05

#### Control of magnetic dipole-dipole interactions in iron oxide-based supraparticles

Stephan Müssig<sup>1,\*</sup>, A. Wolf<sup>1,2</sup>, K. Mandel<sup>1,2</sup>

<sup>1</sup> Friedrich-Alexander-Universität Erlangen-Nürnberg, Professorship for Inorganic Chemistry, 91058 Erlangen, Germany

<sup>2</sup> Fraunhofer-Institute for Silicate Research ISC, 97082 Würzburg, Germany

\*stephan.muessig@fau.de

shape and composition of superparamagnetic (SPIONs) or The size. ferrimagnetic magnetite/maghemite nanoparticles determines their magnetic and colloidal properties. Their defined assembly into micron-scaled powders (so called supraparticles) by spray-drying facilitates their defined arrangement and their combination with various other materials (polymers, silica, ....). Due to the close proximity of the nanoparticles within supraparticles, interaction phenomena arise and novel functionalities can be obtained [1].

It has recently been shown that magnetic particle spectroscopy (MPS) [2] is very sensitive towards dipole-dipole interaction changes of iron oxide nanoparticles within such supraparticles.

In this contribution, it is shown how different supraparticle architectures are synthesized in order to exploit the interaction (changes) within iron oxide-based supraparticles for novel applications such as magnetic recording of elapsed temperature events. Specific examples for control of the interactions are show. For instance, how a silica shell with various thicknesses around iron oxide nanoparticles affects the temperature-dependent oxidation and thus represents a tool to control the high-temperature (up to 1000 °C) behavior of magnetic supraparticles (Figure 1) [3].

The presentation will introduce the concepts of magnetic supraparticles, the readout technique magnetic particle spectroscopy and give several examples of material combinations and their functionalities in hierarchically structured supraparticles from a material chemistry perspective.



Figure 1. Schematic working principle of high-temperature event recording magnetic supraparticles (SPs). a) Magnetic nanoparticle toolbox containing SPIONs with silica (SiO2) shells that protect SPIONs from oxidation at higher temperatures (400–1000°C).b) Structurally emerging functionality of SPs to record elapsed temperature events based on the purposeful oxidation of non-shelled and thin-shelled SPIONs to decrease dipole-dipole interactions. The resulting structure-property relation can be resolved in MPS. Reprinted from [3].

#### References

- [1] S. Wintzheimer, L. Luthardt, K. A. Le Cao, I. Imaz, D. Maspoch, T. Ogi, A. Bück, D. P. Debecker, M. Faustini, K. Mandel, Adv. Mater. 2023, 35, e2306648.
- [2] S. Biederer, T. Knopp, T. F. Sattel, K. Lüdtke-Buzug, B. Gleich, J. Weizenecker, J. Borgert, T. M. Buzug, J. Phys. D: Appl. Phys. 2009, 42, 205007.
- [3] A. Wolf, J. Sauer, K. Hurle, S. Müssig, K. Mandel, Adv. Funct. Mater, 2024, 2316212.

# Wednesday, 04.09.2024 | 08:30 - 09:00



#### Photoactive Iron complexes and time-resolved X-ray spectroscopy - New friends

Matthias Bauer

Paderborn University, Faculty of Science, Chemistry Department, Paderborn (Germany) matthias.bauer@upb.de

Photoactive metal complexes, especially those based on iron, are of great interest in research due to their potential applications in photocatalysis and solar energy conversion. Iron is a particularly attractive metal because of its availability and environmental friendliness, although the complexity of its electronic structures and the resulting rapid dynamics pose a challenge. These dynamics, often occurring on the femtosecond to picosecond timescale, significantly influence the efficiency and functionality of photoactive iron complexes.<sup>[1]</sup>

With this contribution, new approaches to extend the excited state lifetimes in Fe<sup>II</sup> and Fe<sup>III</sup> complexes based on rational ligand design will be presented. These initiatives include N-heterocyclic carbene<sup>[2]</sup> and cyclometalated<sup>[3]</sup> ligands as well as bichromophoric compounds combining an iron complex with an organic chromophore.

While lab based spectroscopic techniques are important to asses ground and excited state properties, X-ray spectroscopy on different time scales offers unique insights into the reaction mechanism of iron catalyzed photoreactions and the excited state landscape of iron-based photoactive systems. Especially ultrafast X-ray spectroscopy at X-ray free electron lasers allows the tracking of electronic and structural changes in real-time, providing a detailed understanding of short-lived intermediate states. This will be demonstrated on a Fe-Co dyad active in photoactalytic proton reduction, which is shown in Figure 1. In this dyad, an ultrafast charge transfer from the iron(II)-tetra-NHC photosensitizer to a cobaloxime catalyst could be detected by transient X-ray emission spectroscopy in a two-colour experiment, which will be explained in detail in the contribution.<sup>[4]</sup>



Figure 1. Early ultrafast dynamics of a Fe-Co dyad studied by transient X-ray emission spectroscopy.

#### References

[1] P. Dierks, Y. Vukadinovic, M. Bauer, Inorganic Chemistry Frontiers, 9 (2022) 206-220.
[2] P. Zimmer, L. Burkhardt, A. Friedrich, J. Steube, A. Neuba, R. Schepper, P. Müller, U. Flörke, M. Huber, S. Lochbrunner, M. Bauer, Inorg. Chem., 57 (2018) 360-373.

[3] J. Steube, L. Burkhardt, A. Päpcke, J. Moll, P. Zimmer, R. Schoch, C. Wölper, K. Heinze, S. Lochbrunner, M. Bauer, Chemistry – A European Journal, 25 (2019) 11826-11830.

[4] M. Nowakowski, M. Huber-Gedert, H. Elgabarty, J. Kubicki, A. Kertem, N. Lindner, D. Khakhulin, F.A. Lima, T.-K. Choi, M. Biednov, N. Piergies, P. Zalden, K. Kubicek, A. Rodriguez-Fernandez, M.A. Salem, T.D. Kuhne, W. Gawelda, M. Bauer, Adv. Sci., DOI: 10.1002/advs.202404348





#### Nuclear Resonance Scattering of synchrotron radiation for iron and its friends

<u>D. Bessas<sup>1,\*</sup></u>, I. Kupenko<sup>1</sup>, R. Rüffer<sup>1</sup>, A. I. Chumakov<sup>1</sup> <sup>1</sup> *European Synchrotron Radiation Facility, Grenoble, France* \*bessas@esrf.fr

Iron resides in the second half of the *3d* transition metal series of the periodic table. The physicochemical properties of the elements down the 8<sup>th</sup> group of the periodic table complement with the ones along the 4<sup>th</sup> period of the periodic table. Such elements usually substitute each other isoelectronically or isovalently in compounds/complexes. A better understanding of the physicochemical properties of such elements in compounds/complexes may shed light on numerous applications spanning from magnetism and superconductivity all the way to catalysis and medicine.

Nuclear Resonance Scattering of synchrotron radiation is a well-established technique for obtaining information relevant to physicochemical properties of compounds/complexes containing iron and/or its friends. The valence state (isomer shift), the local electronic environment (quadrupole splitting), the magnetic state, and the lattice dynamics may be revealed ex-situ/in-situ, and operando using Nuclear Resonance Scattering of synchrotron radiation.

Nuclear Resonance Scattering comprises mainly of synchrotron Mössbauer spectroscopy [1,2], Nuclear Forward Scattering [3,4], Nuclear Inelastic Scattering [5,6], as well as complementary methods such as Synchrotron Radiation Perturbed Angular Correlation spectroscopy [7,8] and Time Domain Interferometry [9,10]. These methods are in particularly useful when:

(i) conventional Mössbauer spectroscopy is impractical, *e.g.*, a relevant radioactive source does not exist or its lifetime is short,

(ii) the experimental setup requires a collimated or a small-size beam, *e.g.*, thin flims or samples under high pressure,

(iii) element-specific lattice dynamical characterization is required.

In this talk examples of nuclear resonance scattering of synchrotron radiation by <sup>57</sup>Fe [11], <sup>61</sup>Ni [12], <sup>99</sup>Ru [13] and <sup>187</sup>Os [14] first nuclear excited states will be presented.

The added value, in terms of photon flux (up to an order of magnitude for <sup>61</sup>Ni and <sup>99</sup>Ru), energy resolution (down to 100 µeV for phonon spectroscopy by <sup>57</sup>Fe), and beamsize (down to 200 nm for X-ray *nanoscopy* by <sup>57</sup>Fe) of the brand-new nuclear resonance beamline ID14 at the European Synchrotron Radiation Facility will be shown. Room for potential development and collaborations will be given.

#### References

[1] G.V. Smirnov, U. van Bürck, A. I. Chumakov, A. Q. R. Baron, R. Rüffer, Phys. Rev. B 55 (1997) 5811.

[2] V. Potapkin, A. I. Chumakov, G. V. Smirnov, J.-P. Celse, R. Rüffer, C. McCammon, L. Dubrovinsky, J. Synchrotron Rad. 19 (2012) 559.

[3] J. B. Hastings, D. P. Siddons, U. van Bürck, R. Hollatz, U.Bergmann, Phys. Rev. Lett. 66 (1991) 770.

[4] U. van Bürck, D. P. Siddons, J. B. Hastings, U. Bergmann, and R. Hollatz, Phys. Rev. B 46 (1992) 6207.

[5] M. Seto, Y. Yoda, S. Kikuta, X. W. Zhang, and M. Ando, Phys. Rev. Lett. 74 (1995) 3828.

[6] W. Sturhahn, T. S. Toellner, E. E. Alp, X. Zhang, M. Ando, Y. Yoda, S. Kikuta, M. Seto, C. W. Kimball, B. Dabrowski, Phys. Rev. Lett. 74 (1995) 3832.

[7] A. Q. R. Baron, A. I. Chumakov, R. Rüffer, H. Grünsteudel, H. F. Grünsteudel, O. Leupold, Europhys. Lett. 34 (1996) 331.

[8] I. Sergueev, U. van Bürck, A. I. Chumakov, T. Asthalter, G. V. Smirnov, H. Franz, R. Rüffer, and W. Petry, Phys. Rev. B 73 (2006) 024203.

[9] A. Q. R. Baron, H. Franz, A. Meyer, R. Rüffer, A. I. Chumakov, E. Burkel, W. Petry, Phys. Rev. Lett. 79 (1997) 2823.

[10] G. V. Smirnov, U. van Bürck, H. Franz, T. Asthalter, O. Leupold, E. Schreier, W. Petry, Phys. Rev. B 73 (2006) 184126.

[11] I. Kupenko, G. Aprilis, D. M. Vasiukov, C. McCammon, S. Chariton, V. Cerantola, I. Kantor, A. I. Chumakov, R. Rüffer, L. Dubrovinsky, C. Sanchez-Valle, Nature 570 (2019) 102.

[12] I. Sergueev, A.I. Chumakov, T.H. Deschaux Beaume-Dang, R. Rüffer, C. Strohm, U. van Bürck, *Phys. Rev. Lett*, 99 (2007) 097601.

[13] D. Bessas, D. G. Merkel, A. I. Chumakov, R. Rüffer, R. P. Hermann, I. Sergueev, A. Mahmoud, B. Klobes, M. A. McGuire, M. T. Sougrati, and L. Stievano, Phys. Rev. Lett. 113 (2014) 147601.

[14] D. Bessas, I. Sergueev, D. G. Merkel, A. I. Chumakov, R. Rüffer, A. Jafari, S. Kishimoto, J. A. Wolny, V. Schünemann, R. J. Needham, P. J. Sadler, and R. P. Hermann, Phys. Rev. B 91 (2015) 224102.

# Wednesday, 04.09.2024 | 09:20 - 09:40



#### Insight into the Dynamics of Spin Crossover Transitions and Cooperativity with Nuclear Inelastic Scattering and Density Functional Theory

Juliusz A. Wolny<sup>1,\*</sup>, Volker Schünemann<sup>1</sup> <sup>1</sup> Department of Physics, University of Kaiserslautern-Landau, Germany \*wolny@rptu.de

In this contribution, we show how density functional theory (DFT) modeling enables the understanding of the cooperativity of the spin transition in 1D chains of polynuclear Fe(II) complexes with rigid bridging ligands. It is shown that a defect with low or high spin in a matrix with different spin causes a stretching of the metal-ligand bonds. The high-spin defect undergoes compression in the low-spin matrix, while the low-spin defect shows bond stretching in the high-spin matrix [1,2]. These effects are confirmed by synchrotron based inelastic nuclear scattering (NIS) experiments. Recently, we have performed time-resolved laser-pumped NIS probe experiments [3] now with a time resolution of up to 200 ps. The obtained time structure of the partial phonon density of states (pDOS) was modeled by DFT. It is shown that the relaxation after photoexcitation involves a switch between different spin isomers with different distribution of spin centers within the 1D chains. The possibility of the DFT modelling for the molecular crystals is proposed.

#### References

[1] S. Rackwitz, W. Klopper, V. Schünemann, J.A.Wolny, Phys. Chem. Chem. Phys., 15, (2013) 15450. [2] K. Jenni, L. Scherthan, I. Faus, J. Marx, C. Strohm, M. Herlitschke , H.-C. Wille, V. Schünemann, J. A. Wolny, Phys. Chem. Chem. Phys., 19, (2017) 18880.

[3] S. Sadashivaiah, J. A. Wolny, L. Scherthan, K. Jenni, A. Omlor, C. S. Müller, I. Sergueev, M. Herlitschke, O. Leupold, H.-C. Wille, R. Röhlsberger, V. Schüneman, J. Phys. Chem. Lett. 12, (2021) 3240

# Wednesday, 04.09.2024 | 09:40 - 10:00



Sun Myung Kim<sup>1,\*</sup>, David Büchner<sup>2</sup>, Young-Joon Song<sup>3</sup>, Vera Krewald<sup>4</sup>, Rolf Schäfer<sup>2</sup>, Roser Valentí<sup>3</sup> Jan Philipp Hofmann<sup>1</sup> <sup>1</sup> Surface Science Laboratory, Department of Earth and Materials Sciences, TU Darmstadt, Darmstadt, Germany <sup>2</sup>Eduard-Zintl-Institute, TU Darmstadt, Darmstadt, Germany <sup>3</sup> Institut für Theoretische Physik, Goethe-Universität Frankfurt, Frankfurt, Germany <sup>4</sup> Theoretische Chemie, TU Darmstadt, Darmstadt, Germany \*skim@surface.tu-darmstadt.de

Redox properties determine the corrosion process of iron as a construction material, as well as its use for heterogeneous catalysts. For modern applications iron has been targeted for solar fuels production and electrocatalysts for the oxygen evolution reaction. In our work we revisit the electronic structure of iron in context with the redox properties. The absolute potential equals the vacuum level on the physical scale  $E_{abs}$  (-4.44 V) = - $E_{vac}$  (0 eV) establishing the connection between the redox properties and the electronic structure according to Trasatti [1]. The work function in turn is determined as the difference between the vacuum level and the Fermi level.

We present the electronic structures of iron as single crystals (100), (110) and (111). Additionally, our work shows a method how to reduce iron oxide effectively in a matter of a few hours, eventually exhibiting a (1x1) structure. During this process, the single crystals exhibited a contaminated sulfur overlayer structure on the Fe single crystals which is evaluated with LEED. At the same time the reaction of Fe single crystals to H<sub>2</sub>O is observed by XPS, the effects on the valence band by UPS and a structural characterization is given by LEED. TPD on the single crystals rounds off the investigation of iron's response to water. We complement the experimental results with theoretical calculations of the electronic structure.

On Fe(100) it is shown that water adsorption barely has any effect and is nowhere to be found in XPS or LEED against expectations stating the formation of c(2x2)O surface structure after water adsorption [2]. TPD shows three water desorption peaks [3]. For polycrystalline water with small traces of oxygen, water is successfully adsorbed as seen in the growth of the O1s peak at 530 eV and OH at 532 eV in synchrotron based XPS.

These results are summarised in a Born-Haber cycle that connects the ionisation potential to the free energies of hydration. So far, attempts on measurements of the hydration free energies have only been of theoretical nature. We will discuss both experimental and theoretical methods that provide insight into the quantification of the hydration free energy [4].



Figure 1. Clean Fe(100) with (1x1) structure (left) and Fe2p spectrum.

#### References

[1] S. Trasatti, Pure & Appl. Chem. Vol. 58, No. 7 (1986) 955
[2] W.-H. Hung, Surf. Sci. 294 (1993) 21
[3] W.-H. Hung, Surf. Sci. 248 (1991) 332
[4] K. P. Kepp, J. Phys. Chem. A, 123 (2019) 653

Fe

Iron, upgraded!



# Manipulating FeNC model catalysts with metal nanoparticles: Effect on activity and selectivity for CO<sub>2</sub>RR.

<u>Nicole Segura-Salas<sup>1,2</sup></u>, Nils Heppe<sup>1</sup>, Rifael Z. Snitkoff<sup>2</sup>, Pascal Theis<sup>1</sup>, Kathrin Hoffmann<sup>1</sup>, Lior Elbaz<sup>2</sup>, Ulrike I. Kramm<sup>1</sup>

<sup>1</sup>Technische Universität Darmstadt Catalysts and Electrocatalysts group, Department of Chemistry, Otto-Berndt-Str. 3, 64287 Darmstadt/Germany

<sup>2</sup>Bar-Ilan Center for Nanotechnology and Advanced Materials and the Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

The CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) into value-added products or as a mean for chemical energy storage is a very promising strategy to tackle the carbon neutrality challenge. Amongst all potential catalysts, materials like metal-nitrogen-doped carbons (MNC) offer a wide variety of activities and selectivities by the selection of the metal due to their differences in binding energy to the CO intermediate.<sup>1</sup> Particularly in the FeNC case, high kinetic activity is observed for CO production at low overpotentials; however, at more significant current densities and larger cathodic potentials, the hydrogen evolution reaction (HER) becomes dominant. In our previous work we were able to show that a change from initial CuN<sub>4</sub> moieties to Cu<sup>0</sup> coincided with a change in selectivity.<sup>2</sup> This raises the question of whether FeN<sub>4</sub>, from where Fe can leach into Fe<sup>0</sup> will be relevant for CO or H<sub>2</sub> selectivities. Moreover, it is known that nanoparticle modification of FeNCs can influence the selectivity for ORR,<sup>3</sup> and that it might affect also the electronic properties.<sup>4</sup>

Having this in mind, we wanted to explore and understand the effect of such a manipulation of an FeNC catalyst with nanoparticles (Au, Ag). The effect of doping is understood by the correlation between the work function and the chemical shifts obtained via UPS and XPS and the product analysis is done through online gas chromatography analysis and mass spectrometry. Moreover, we are able to bridge the theoretical concept between the Fermi level and the redox potential by using Fourier-transformed alternating current voltammetry (FTacV)<sup>5</sup> to reveal the underlying electron transfers during the reaction. By comparing the activity of the modified catalysts to their reference material, in combination with their structural analysis, we can identify the origin of the effect of the modification on the activity of the FeNC.

#### **References**:

1. Li, J.; Pršlja, P.; Shinagawa, T.; Martín Fernández, A. J.; Krumeich, F.; Artyushkova, K.; Atanassov, P.; Zitolo, A.; Zhou, Y.; García-Muelas, R.; López, N.; Pérez-Ramírez, J.; Jaouen, F. ACS Catal. 2019, 9 (11), 10426–10439.

2. S. Paul, Y. L. Kao, L. Ni, R. Ehnert, I. Herrmann-Geppert, R. van de Krol, R. W. Stark, W. Jaegermann, U. I. Kramm and P. Bogdanoff, *ACS Catal.*, **2021**, 11, 5850–5864.

3. V. Gridin, M. Kübler, T. Hanstein, N. Heppe, N. Segura-Salas, P. Theis, K. Hofmann and U. I. Kramm, J. Power Sources, **2023**, 561, 232713.

4. Prössl, C.; Kübler, M.; Paul, S.; Ni, L.; Kinkelin, S. J.; Heppe, N.; Eberhardt, K.; Geppert, C.; Jaegermann, W.; Stark, R. W.; Bron, M.; Kramm, U. I. *J. Mater. Chem. A.* **2021**, 10 (11), 6038–6053.

5. R. Z. Snitkoff-Sol, A. Friedman, H. C. Honig, Y. Yurko, A. Kozhushner, M. J. Zachman, P. Zelenay, A. M. Bond and L. Elbaz, *Nat. Catal.*, **2022**, 5, 163–170.

#### Acknowledgement

A scholarship for N.S.S by the Bar-Ilan University through the Sandwich Scholarship program is appreciated. This work is financially supported by the DFG funded project CRC 1487, *Iron, upgraded!* (443703006)

# Wednesday, 04.09.2024 | 10:50 - 11:20



#### Local Environment Influence on High Valent Non-heme Iron

<u>Christine J. McKenzie</u><sup>\*</sup>, Mathias L. Skavenborg, James N. McPherson, Christina Wegeberg, Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, DK-5230 Odense M. Denmark.

\*<u>mckenzie@sdu.dk</u>.

The generation and reactivity of high-valent non-heme iron-based oxidants, and their precursors, obviously depends on supporting ligand choice, however the significant perturbation by local environment (first/second coordination sphere, supramolecular interactions, solvent and pH) are difficult to predict. By utilizing gas phase techniques we have exposed a latent *S*=2 Fe(IV)oxo system, otherwise inaccessible in the solution phase, and performed limited spectroscopic and reactivity studies (Figure 1a).<sup>1</sup> Enzyme pocket-like supramolecular and electronic roles for the *cis* carboxylate donor and second coordination sphere base in a bifunctional ligand are proposed to be important for C-H substrate association and oxidation (Figure 1b).<sup>2</sup> Supramolecular halogen bonding interactions with a precursor Fe(III) complex are essential for mobilizing and activating insoluble hypervalent iodosylbenzene (PhIO).<sup>3</sup> This produces an Fe-OIPh system that catalyzes oxygen transfer reactions faster and more selectively than homogenous catalytic mixtures using soluble oxygen transfer agents (Figure 1c). Similarly circumventing radical Fenton-like chemistry, spectroscopy and kinetic studies suggest an unexpected supramolecular co-activation of hypochlorite and water in a diiron(III) system (Figure 1d). This host-guest complex is a precursor for the generation of two equivalents of an oxidizing Fe(IV)oxo complex in an atom-economic reaction.<sup>4</sup>



**Figure (a)** A gas phase S=2 Fe(IV)oxo complex. **(b)** Halogen bonding stabilization of hypervalent PhIO. **(c)** Cis-carboxylate and second coordination sphere base participation in C-H substrate binding and oxidation. **(d)** { $(CIOH) \subset [(L)Fe^{III}(\mu-O)Fe^{III}(HL)]$ }<sup>3+</sup>.

#### References

[1] W. A. Donald, C. J. McKenzie, R. A. J. O'Hair, Angew. Chem., Int. Ed., 2011, 50, 8379; M. Swart,

- [3] D. P. de Sousa, C. Wegeberg, M. S. Vad, S. Mørup, C. Frandsen, W. A. Donald, and C. J. McKenzie, *Chemistry, Eur. J.* **2016**, *22*, 3521
- [4] J. N. McPherson, C. J. Miller, C. Wegeberg, Y. Chang, E. D. Hedegård, E. Bill, T. D. Waite, C. J. McKenzie, *J. Am. Chem. Soc.*, **2021**, 143, 15400.

W. A. Donald, C. J. McKenzie, unpublished.

<sup>[2]</sup> C. Wegeberg, M. L. Skavenborg, A. Liberato, J. N. McPherson, W. R. Browne, E. D. Hedegård and C. J. McKenzie, *Inorg. Chem.*, **2021**, *60*, 1975.

# Wednesday, 04.09.2024 | 11:20 - 11:40



#### Transient intermediates of the [Fe]-hydrogenase catalysis characterized by sensitivity-enhanced NMR

L. Kaltschnee<sup>1,\*</sup>, A. N. Pravdivtsev<sup>2</sup>, M. Gehl<sup>3</sup>, G. Huang<sup>3</sup>, G. L. Stoychev<sup>4</sup>, C. Riplinger<sup>4</sup>, M. Keitel<sup>5</sup>, F. Neese<sup>6</sup>, J.-B. Hövener<sup>2</sup>, A. A. Auer<sup>6</sup>, C. Griesinger<sup>5</sup>, S. Shima<sup>3</sup>, S. Glöggler<sup>5</sup>

<sup>1</sup> Technical University Darmstadt, Darmstadt, Germany
 <sup>2</sup> Molecular Imaging North Competence Center (MOIN CC), Kiel University, Kiel, Germany.
 <sup>3</sup> Max-Planck-Institute for Terrestrial Microbiology, Marburg, Germany.
 <sup>4</sup> FAccTs GmbH, Köln, Germany.
 <sup>5</sup> Max-Planck-Institute for Multidisciplinary Sciences, Göttingen, Germany.
 <sup>6</sup> Max-Planck-Institut für Kohlenforschung, Mühlheim an der Ruhr, Germany.
 \* Lukas.kaltschnee1@tu-darmstadt.de

Hydrogenases are enzymes that achieve hydrogen activation or production under mild and biocompatible conditions. The understanding of their catalytic mechanisms helps using these enzymes in biotechnological applications such as light-driven<sup>[1]</sup> hydrogen production and it guides the design of artificial hydrogen conversion catalysts<sup>[2,3]</sup>.

A central challenge when studying hydrogenase catalysis is to experimentally characterize the activesite bound hydrogen species. While for paramagnetic intermediates, EPR enables detailed studies of hydrogens near the paramagnetic center<sup>[4,5]</sup>, for diamagnetic intermediates challenging this was only possible in exceptional cases, using super-high resolution X-ray diffraction (XRD)<sup>[6]</sup> or nuclear resonance vibrational spectroscopy (NRVS)<sup>[7]</sup>.

In this work we first demonstrate that parahydrogen-enhanced NMR<sup>[8,9]</sup> enables studying the activesite bound hydrogen atoms in a hydrogenase during catalytic turnover. For the [Fe]-hydrogenase<sup>[10]</sup>, we first characterize two catalytic intermediates created upon hydrogen activation, and we obtain a kinetic model describing their interconversion under turnover<sup>[11]</sup>.



**Figure 1.** Center: [Fe]-Hydrogenase catalytic cycle with sensitivity-enhanced species highlighted. Right: Singlescan NMR spectrum showing hydrogen signals obtained for  $H_2$  and HD after release from the enzyme (1  $\mu$ M [Fe]-hydrogenase concentration). Left: Overlay of measured and simulated parahydrogen enhanced chemical shift saturation transfer (PHIP-CEST) data directly probing the hydrogen atoms in an enzyme bound state.

#### References

- [1] J. Appel, V. Hueren, M. Boehm, K. Gutekunst, Nature Energy, 5 (2020), 458.
- [2] S. Ogo *et al.*, Science, 339 (2913), 682.
- [3] D. Schilter, *et al.*, Chem. Rev., 116 (2016), 8693.
- [4] J. P. Whitehead et al., J. Am. Chem. Soc., 115 (1993), 5692.
- [5] S. Foerster et al., J. Am. Chem. Soc., 125 (2003), 83.
- [6] H. Ogata, K. Nishikawa, W. Lubitz, Nature., 520 (2015), 571.
- [7] H. Ogata et al., Nat. Commun., 6 (2015), 7890.
- [8] C. R. Bowers, D. P. Weitekamp, J. Am. Chem. Soc., 109 (1987), 5541.
- [9] S. Duckett, N. J. Wood, Coord. Chem. Rev., 252 (2008), 2278.
- [10] G. Huang *et al.*, Nat. Catal., 2 (2019), 537-543.
- [11] preprint available on bioRxiv doi: <u>10.1101/2023.05.10.540199</u>

## Wednesday, 04.09.2024 | 11:40 - 12:00



#### **High-Valent Organometallic Iron Complexes**

Jun.-Prof. Dr. Alicia Casitas

Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str. 4, 35032 Marburg

High-valent iron compounds (where the metal is found in oxidation states +4 or +5) are invoked as key reaction intermediates in a myriad of relevant biological processes catalyzed by metalloenzymes.<sup>[1]</sup> A large number of synthetic high-valent iron complexes stabilized by strong  $\pi$ donor ligands such as oxido (O<sup>2-</sup>), imido (RN<sup>2-</sup>) or nitrido (N<sup>3-</sup>) are known.<sup>[2]</sup> On the other hand, organometallic iron complexes in formal high oxidation state that contain either metal–carbon  $\sigma$ bonds or metal–carbon multiple bonds (alkylidenes and carbynes) are scarce and, consequently, the comprehension of their reactivity is narrow.<sup>[3]</sup>

Herein, I will discuss our efforts towards the synthesis, characterization and exploration of the reactivity of organometallic iron(IV) complexes. First, I will present novel synthetic strategies to prepare Fe(III) and Fe(IV) cyanide complexes using cyclic cyano  $\lambda^3$ -iodane reagents, along with in-depth mechanistic investigations.<sup>[4, 5]</sup> Then, the synthesis of highly reactive organometallic Fe(III) and Fe(IV) complexes and their involvement in carbon-carbon bond-forming reactions will be disclosed.<sup>[6]</sup> Overall this work provides fundamental insights into the reactivity of organoiron species in high oxidation state that may ultimately find application in catalysis towards organic synthesis.



**Figure 1.** Reactivity of iron(II) with cyano  $\lambda^3$ -iodane to form iron(IV) cyanide complex upon group transfer and two consecutive single electron transfer processes.

#### References

[1] The biology and chemistry of high-valent iron-oxo and iron-nitrido complexes. J. Hohenberger, K. Ray, K. Meyer, *Nat. Commun.* **2012**, *3*, 720.

[2] Biomimetic High-Valent Mononuclear Nonheme Iron-Oxo Chemistry. J. E. M. N. Klein, L. Que Jr. **2016**, pp 1-22. In *Encyclopedia of Inorganic and Bioinorganic Chemistry*. Ed: R.A. Scott, John Wiley, Chichester.

[3] Selected examples: a) Transition Metal Bicyclo[2.2.I]hept-I-yls. B. K. Bower, H. G. Tennent, *J. Am. Chem. Soc.* **1972**, *94*, 2512-2513; b) Isolation and structural and electronic characterization of salts of the decamethylferrocene dication. M. Malischewski, M. Adelhardt, J. Sutter, K. Meyer, K. Seppelt, *Science* **2016**, *353*, 678-682; c) Two Exceptional Homoleptic Iron(IV) Tetraalkyl Complexes. A. Casitas, J. Rees, R. Goddard, E. Bill, S. DeBeer, A. Fürstner, *Angew. Chem. Int. Ed.* **2017**, *56*, 10108-10113.

[4] Synthesis of Fe(IV) cyanide complexes using hypervalent iodine(III) reagents as cyanotransfer one-electron oxidants. C. Souilah, S. A. V. Jannuzi, D. Demirbas, M. Swart, S. Ivlev, S. DeBeer, A. Casitas, *Angew. Chem. Int. Ed.* **2022**, *61*, e202201699.

[5] Iron-catalyzed group-transfer reactions with iodine(III) reagents. A. Casitas, P. Andreetta. Book chapter in ACAT 74: Earth-Abundant Transition Metal Catalyzed Reactions. Ed: M. Diéguez, T. Ollevier. *accepted* **2024.** 

[6] Synthesis of Fe(IV) Alkynylide Complexes and Their Reactivity to Form 1,3-diynes. C. Souilah,<sup>#</sup> S. A. V. Jannuzzi,<sup>#</sup> D. Demirbas, S. Ivlev, X. Xie; S. Peredkov; S. DeBeer, A. Casitas. *under review (# equal contribution)* 

# Wednesday, 04.09.2024 | 12:00 - 12:20



#### Analysis of spin interactions in µ-oxo bridged copper, nickel and iron di-nuclear complexes

<u>Justin Krampe</u>, Prof. Dr. Vera Krewald, Technische Universität Darmstadt, Quantenchemie, Peter-Grünberg-Str. 4, 64287 Darmstadt

On a quantum mechanical level, magnetism in small metal dimers results from the interaction of electron spins, which are mostly located along the chemical bridge between the metal centers. These interactions give rise to a energy splitting of the different spin state energies, which can be interpreted using models like the effective Heisenberg-Dirac-van-Vleck-Hamiltonian.<sup>[1]</sup> Therefore, coupling stength constants are be defined which are positive for ferromagnetic (J>0) and negative for anti-ferromagnetic cases (J<0). Chemically these interaction pathways can be interpreted using magnetic orbitals which are based on the empirical concepts of Goodenough, Kanamori and Anderson.<sup>[2]</sup>

Comparing the experimental results with calculated J couplings given by different theories like complete active space (CAS) methods or density functional theory (DFT). The obtained theoretical results often differ by up to one magnitude, due to their differences handling the two electron interaction terms. Especially for iron dimers this can be a problem, where higher excitations like double-shell effects or relativistic effects like spin-orbit-coupling can dominate the strength of the magnetic coupling.<sup>[3]</sup>

Using an Hartree-Fock formalism based on the studies of Hofman and Malrieu, we are able to identify quantitative contributions of the magnetic orbitals in µoxo bridged dinuclear complexes given by CAS-SCF and broken symmetry DFT calculations.<sup>[4,5]</sup> The presented approach will be used to characterize the strength of magnetic interaction pathways in homovalent copper, nickel and iron complexes in different sized active spaces.

Literature:

[1] J. Coey, Cambridge university press, 2010.

[2] a) J. Kanamori, *Journal of Phys. and Chem. of Solids*, **1959**, 10, 87-98. b) J.
B. Goodenough, **1963**. c) P. W. Anderson, *Solid state phys*. **1963**, 14, 99-214.
[3] A. Mihail, N. Spiller, F. Neese, *Physical Chemistr*, **2022**, 24, 20760-20775.
[4] H. P. Jeffrey, J. C. Thibeault, and R. Hoffmann, *Journal of the American Chemical Society* **1975**, 97, 4884-4899.

[5] C. J. Calzado, J. Cabrero, J. P. Malrieu, R. Caballol, *The Journal of chemical physics* **2002**, 116, 2728-2747.

# Wednesday, 04.09.2024 | 14:00 - 14:30



# Selective Catalytic Oxidation of Alcohols and Olefins over Cobaltbased Spinel and Perovskite Nanoparticles

Prof. Dr. Martin Muhler, Laboratory of Industrial Catalysis, Ruhr University Bochum

The selective oxidation of organic molecules to value-added products is one of the major challenges in chemical industry. At high temperatures in the gas phase the Mars-van Krevelen mechanism dominates in the few established large-scale processes based on vanadia and molybdena catalysts such as the synthesis of acrolein and acrylic acid, maleic anhydride or phthalic anhydride. In contrast, selective oxidation in the liquid phase occurs at much lower temperatures over metals and oxides without involving changes of the bulk structure.

In my talk I will first present the selective oxidation of 2-propanol over  $Co_3O_4$  nanoparticles in the gas phase and in the liquid phase covering the involved mechanism and the active sites, structure sensitivity, and the role of iron substitution leading to the size of the catalytically active ensemble. All results originate from the fruitful collaboration within the TRR/CRC 247 comprising the research areas synthesis, analysis and catalysis.

Then, I will address the selective oxidation of more complex molecules such as cyclohexene over substituted  $LaCoO_3$  pointing out the role of radicals and cinnamyl alcohol using *tert*-butyl hydroperoxide as oxidant. Non-catalytic processes have to be taken into account properly, and the used solvent may participate in the catalytic cycle.

# Wednesday, 04.09.2024 | 14:30 - 14:50



#### Fe-containing perovskites – Topochemistry and a Playground of Functional Properties

Oliver Clemens<sup>1,\*</sup>

<sup>1</sup> University of Stuttgart, Institute for Materials Science, Materials Synthesis Group, Heisenbergstraße 3, 70569 Stuttgart \*oliver.clemens@imw.uni-stuttgart.de

Fe-containing perovskites  $AFeX_{3-d}$  (X = O, OH, F; A = alkaline earth or lanthanide) show a broad structural flexibility within the different perovskite-derived structures. These include so-called hexagonal perovskites (i. e., perovskite materials with partial h-type stacking of  $AX_{3-d}$  layers) and various distortion and vacancy ordering variants derived from the high symmetry cubic perovskite.

The flexibility of such ferrates is not only limited to structural aspects, but also to functional properties which arise depending on the detailed composition and corresponding structural details. These properties comprise catalytic activity for the oxygen reduction reaction, magnetic properties ranging from (canted) antiferromagnetism to ferromagnetism, proton conductivity.

In this talk, I will summarize the findings made by my group (and others) over the last decade, highlighting resulting questions to answer in order to discover new functional materials.



*Figure.* Crystal structures and vacancy ordering patterns of BaFeO<sub>2.67</sub> and BaFeO<sub>2.33</sub>F<sub>0.33</sub> (left) in comparison to BaFeO<sub>2.5</sub> (right).

#### References

[1] O. Clemens, M. Kuhn, R. Haberkorn, J. Solid State Chem., 184 (2011) 2870-2876.

[2] O. Clemens, F.J. Berry, A.J. Wright, K.S. Knight, J.M. Perez-Mato, J.M. Igartua, P.R. Slater, J. Solid State Chem., 206 (2013) 158-169.

[3] O. Clemens, A.J. Wright, F.J. Berry, R.I. Smith, P.R. Slater, J. Solid State Chem., 198 (2013) 262-269.

[4] O. Clemens, M. Groeting, R. Witte, J. Manuel Perez-Mato, C. Loho, F.J. Berry, R. Kruk, K.S. Knight, A.J. Wright, H. Hahn, P.R. Slater, Inorg. Chem., 53 (2014) 5911-5921.

[5] O. Clemens, J. Solid State Chem., 225 (2015) 261-270.

[6] P.L. Knoechel, P.J. Keenan, C. Loho, C. Reitz, R. Witte, K.S. Knight, A.J. Wright, H. Hahn, P.R. Slater, O. Clemens, J. Mater. Chem. A, 4 (2016) 3415-3430.

[7] A. Benes, A. Molinari, R. Witte, R. Kruk, J. Broetz, R. Chellali, H. Hahn, O. Clemens, Materials, 11 (2018) 52.

[8] A.I. Waidha, L. Ni, J. Ali, M. Lepple, S. Dasgupta, S. Wollstadt, L. Alff, U.I. Kramm, O. Clemens, J. Mater. Chem. A, 8 (2020) 616-625.

[9] S. Wollstadt, Y. Ikeda, A. Sarkar, S. Vasala, C. Fasel, L. Alff, R. Kruk, B. Grabowski, O. Clemens, Inorg. Chem., 60 (2021) 10923-10933.

## Wednesday, 04.09.2024 | 14:50 - 15:10



#### Mechanistic insight into iron molybdate catalysts during oxidative dehydrogenation using coupled *operando* spectroscopy and diffraction

Jan Welzenbach<sup>\*</sup>, Hannah Wilhelm<sup>\*</sup>, Kathrin Hofmann, Barbara Albert, Christian Hess Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt <sup>\*</sup>jan.welzenbach@tu-darmstadt.de, hannah.wilhelm@tu-darmstadt.de

Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> has been used commercially as a catalyst for oxidative dehydrogenation (ODH) of methanol to formaldehyde.<sup>1</sup> Recent studies have shown its potential for the ODH of ethanol (EtOH).<sup>2</sup> Gaur et al. used XAS/XRD and Raman spectra for phase analysis to investigate the loss of molybdenum oxide in iron molybdate catalyst with a Mo/Fe ratio of 2.<sup>3</sup> Recently, new mechanistic insight into iron molybdate catalysts during propane ODH was obtained using *operando* Raman, UV-Vis, impedance and transient IR spectroscopy.<sup>4</sup> Within this work we present a detailed structural analysis of a stoichiometric iron molybdate (Mo/Fe=1.5) during EtOH ODH using a coupled *operando* Raman-XRD set-up to address both (sub-)surface and bulk dynamics, as well as *operando* UV-Vis and impedance spectroscopy.

The Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> catalysts were prepared using co-precipitation as described elsewhere.<sup>2</sup> Coupled *operando* Raman/XRD experiments where performed in a custom-built reaction cell using a Bragg-Brentano geometry, 532 nm Raman excitation and quantitative IR gas-phase analysis. After heating the catalysts to elevated temperature (10 %  $O_2/N_2$ ), the feed composition was modulated between oxidative (10 %  $O_2/N_2$ ) and reactive (5 % EtOH/10 %  $O_2/N_2$ ) conditions (Fig. 1a). Lattice parameters were refined using the Rietveld method. Raman/XRD results for the same conditions were averaged.

Under EtOH ODH conditions, the volume of the elemental cell increases (Fig. 1b), indicating the formation of bulk oxygen defects and the reduction of metal atoms. Coupled Raman spectra show a small but reproducible red-shift of the 780 cm<sup>-1</sup> antisymmetric stretch of MoO<sub>4</sub> (Fig. 1d),<sup>4</sup> suggesting sub-surface oxygen defect formation. Both effects are visible at high acetaldehyde selectivity (280 °C, X: 5 %, S: 98 %), demonstrating their relevance for EtOH ODH, and increase with increasing EtOH conversion (Fig. 1c). These results are fully consistent with *operando* impedance spectra (not shown), revealing a correlation of conductivity with EtOH conversion.

Using a combination of *operando* methods (Raman/XRD, impedance) the participation of the bulk and (sub-)surface of iron molybdate in the ODH of ethanol is demonstrated, providing a new approach to elucidate the mode of operation of bulk oxidation catalysts.



**Fig. 1:** Scheme of the measurement (a). Development of the refined cell volume (b) and Raman shift (d) with temperature under oxidative (gray) and reactive (blue) conditions, as well as the corresponding conversion (purple) and selectivity (orange) (c).

#### References

- 1. C. Hess, R. Schlögl (Eds.), Nanostructured Catalysts: Selective Oxidation, RSC Publishing, Cambridge, 2011.
- 2. N. Oefner, F. Heck, M. Dürl, L. Schumacher, H. Siddiqui, U. Kramm, C. Hess, A. Möller, B. Albert, B. Etzold. *ChemCatChem* **2022**, 14, e2021012.
- 3. A. Gaur, M. Schumann, K. V. Raun, M. Stehle, P. Beato, A. D. Jensen, J.-D. Grunwaldt, M. Høj. *ChemCatChem.* **2019**, 11, 4871-4883.
- 4. L. Schumacher, M. Radtke, J. Welzenbach, C. Hess. Commun. Chem. 2023, 6, 230.
- 5. A. P. V. Soares, M. F. Portela, A. Kiennemann. Catal. Rev., 2005, 47, 125-174.

## Wednesday, 04.09.2024 | 15:10 - 15:30



V. Hacker<sup>1</sup>, F. Blaschke<sup>1</sup>, M. Pauritsch<sup>1</sup>, C. Pröll<sup>1</sup>, <u>M. Lammer<sup>1,\*</sup></u> <sup>1</sup>Institute of Chemical Engineering and Environmental Technology, TU Graz, Austria \*Michael.Lammer@tugraz.at

The transport and provision of energy in the form of high-purity green hydrogen on an industrial scale requires new energy sources that are economically available in large quantities and are ideally non-toxic, non-flammable and non-gaseous. The Institute of Chemical and Environmental Engineering at Graz University of Technology has developed a special chemical looping process based on the reformer steam iron cycle (RESC) for storing and transporting energy. The RESC is suitable for the decentralised production of green hydrogen and enables the use of a wide range of biofuels as feedstock. The iron-based oxides are used for redox cycles with reducing gases and steam as an oxidant for fixed-bed chemical cycles with very stable oxygen carriers (OC). The results of this innovative material research are the key to the development of this future energy carrier and to a significant reduction in the cost of producing and transporting hydrogen.

To maintain the functionality of the oxygen carrier over more than 100 cycles, new materials based on structured ceramic carriers with mixed ionic and electronic conductivity (MIEC materials) have been developed. The results of this innovative materials research are key to developing this future energy source and significantly reducing the cost of producing and transporting green hydrogen. The advantages and challenges of using iron and other metals for energy transport are presented and discussed [1,2,3,4].



*Figure.* Fixed bed reactor setup for gravimetric determination of the oxygen exchange capacity of pelletized oxygen carrier samples (a). Sequence of a cycle of the lifetime tests in the fixed bed system (b) [1].

#### References

[1] F. Blaschke, M. Bele, Š. Polak, B. Bitschnau, V. Hacker, Core-shell iron-based oxygen carrier material for highly efficient green hydrogen production by chemical looping, **Materials Today**, 2024, <u>https://doi.org/10.1016/j.mattod.2024.03.016</u>.

[2] S. Bock, B. Stoppacher, K. Malli, M. Lammer, V. Hacker, Techno-economic analysis of fixed-bed chemical looping for decentralized, fuel-cell-grade hydrogen production coupled with a 3 MWth biogas digester. **Energy Convers Manag**, 2021, <u>https://doi.org/10.1016/j.enconman.2021.114801</u>.

[3] B. Stoppacher, S. Bock, K. Malli, M. Lammer, V. Hacker, The influence of hydrogen sulfide contaminations on hydrogen production in chemical looping processes, **Fuel**, 2022, <u>https://doi.org/10.1016/j.fuel.2021.121677</u>.

[4] F. Blaschke, M. Bele, B. Bitschnau, V. Hacker, The effect of microscopic phenomena on the performance of ironbased oxygen carriers of chemical looping hydrogen production. **Appl Catal B Environ**, 2023, <u>https://doi.org/10.1016/j.apcatb.2023.122434</u>.

Fe

Iron, upgraded!

GRC 1487

# Wednesday, 04.09.2024 | 15:30 - 16:00



# Looking at iron and friends at work: Fascinating elements for catalysis and X-rays

<u>J.-D. Grunwaldt<sup>1,2,\*</sup></u>, M. Casapu<sup>1</sup>, D.E. Doronkin<sup>1,2</sup>, A. Gaur, F. Maurer<sup>1</sup> <sup>1</sup> Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology

(KIT). Karlsruhe. Germany

<sup>2</sup> Institute of Catalysis Research and Technology, KIT, Eggenstein-Leopoldshafen, Germany

\*grunwaldt@kit.edu

Iron and the neighboring elements are widely used in catalysis. Furthermore, metallic iron is discussed as metal fuel. Examples from our research are Fe-zeolite catalysts for NO<sub>x</sub>-reduction by ammonia [1], oxidation reactions of fine chemicals [2], iron as a component of the famous bismuth-molybdate catalyst for propylene and butadiene oxidation to acroleine and methacroleine as well as methanol oxidation to formaldehyde [3], ammonia synthesis and decomposition catalysts [4], as well as in Fischer-Tropsch synthesis over Co and Fe-based catalysts [5], methanation of CO<sub>2</sub> in NiFe-catalysts and methanol synthesis in NiFeGa-catalysts [6]. In addition, they are attractive for oxidation of pollutants despite they are by far less active than noble metal based catalysts [7] and are prone to deactivation. Lastly, we have studied the oxidation/reduction of bulk iron for application as metal fuel [8].

The structure of iron species is as manifold as their application and can consist of iron single sites, clusters and particles in oxidation states. Fe(0), Fe(II), Fe(III) and even Fe(IV) are discussed in some applications. But what is the structure of active species? How does it change under reaction conditions? Apart from Mößbauer spectroscopy, X-ray based techniques have been very valuable to identify their structure, especially under operating conditions, so-called operando measurements. The most straightforward technique is X-ray diffraction (XRD), but also bulk-averaging and spatially resolved techniques as well as X-ray diffraction tomography have been applied. However, in most cases the structure of iron species is disordered giving rise to high surface area and many defects that act as active centers - hence, e.g. XRD is not sensitive enough. In those cases, X-ray absorption spectroscopy (XAS) in terms of X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) is the more straightforward tool - particularly when it is applied operando, including demanding reaction conditions like high temperature, high pressure, or even in iron flame. Selected examples will show various insights on iron and friends during their catalysis and thus give important inspiration for improving them. Notably, newer spectroscopic approaches like High Energy Resolution Fluorescence Detected XAS (HERFD-XAS), X-ray Emission Spectroscopy (XES), Resonant Inelastic X-ray Scattering (RIXS) and valence to core XES (vtc-XES) give further possibilities to identify the electronic structure of iron. This concerns the possibility to differentiate d<sup>4</sup>, and d<sup>5</sup>/d<sup>6</sup>-systems as well as high-spin/low spin iron for d<sup>5</sup> and d<sup>6</sup> systems.

The talk aims at giving an overview and inspiration for further use of these unique tools in the concert with other complementary spectroscopic, microscopic and scattering techniques (Mößbauer, X-ray photoelectron and UV-vis spectroscopy, electron microscopy, small angle X-ray scattering).

#### References

[1] A. Boubnov, H.W.P. Carvalho, D.E. Doronkin, T. Günter, E. Gallo, A.J. Atkins, C.R. Jacob, J.-D. Grunwaldt, J. Am. Chem. Soc. 136 (2014) 13006; D. Zengel, S. Barth, M. Casapu, J.-D. Grunwaldt, Catalysts, 11 (2021) 336.

[2] P. Treu, D. Gonçalves, A.R. Lakshmi Nilayam, J.-D. Grunwaldt, E. Saraçi, ChemCatChem, (2024) e202400626; P. Treu, B.B. Sarma, J.-D. Grunwaldt, E. Saraçi, ChemCatChem, 14 (2022), e202200993.

[3] L. Klag, S. Weber, R. Horn, T.L. Sheppard, J.-D. Grunwaldt, Catal. Sci. Technol. 14 (2024), 863;

L. Klag, A. Gaur, M. Stehle, S. Weber, S.; T.L. Sheppard, J.-D. Grunwaldt, ACS Catalysis, 13 (2023) 14241; A. Gaur, M. Stehle, K.V. Raun, J. Thrane, A.D. Jensen, J.-D. Grunwaldt, M. Høj, Phys. Chem. Chem. Phys. 22 (2020) 11713.

[4] S. Chen, J. Jelic, et al., Nature Commun., 15 (2024) 871.

[5] M. R. Nielsen, A.B. Moss, A.S. Bjørnlund, et al., J. Energy Chem. 51 (2020) 48.

[6] M.-A. Serrer, A. Gaur, J. Jelic, S. Weber, C. Fritsch, A.H. Clark, E. Saraçi, F. Studt, J.-D. Grunwaldt,

Catal. Sci. Technol. 10 (2020), 7542; T. Smitshuysen, M.R. Nielsen, et al. ChemCatChem, 12 (2020), 3265. [7] M. Tepluchin, D.K. Pham, M. Casapu, L. Mädler, S. Kureti, J.-D. Grunwaldt, Catal. Sci. Technol. 5 (2015) 455; M. Tepluchin, M. Casapu, A. Boubnov, H. Lichtenberg, D. Wang, S. Kureti, J.-D. Grunwaldt, ChemCatChem 6 (2014) 1763.

[8] L. Braun, J. Spielmann, D.E. Doronkin, C. Kuhn, A. Maliugin, D.I. Sharapa, I. Huck, J. Bao, T. Tischer, F. Studt, O. Deutschmann, U.I. Kramm, J.-D. Grunwaldt, ChemSusChem (2024) e202401045.

# Thursday, 05.09.2024 | 08:30 - 09:15



The sluggish kinetics of oxygen electrocatalysis and the resulting high overpotentials necessary to achieve useful current densities limit the development of promising technologies, such as fuel cells, water, and carbon dioxide electrolyzers, and metal-oxygen batteries.<sup>1</sup> The best catalysts for both the oxygen reduction and oxygen evolution reactions (ORR and OER, respectively) are based on precious, platinum group metals (PGMs), such as platinum and iridium, leading to limitations in the cost-effective implementation of these technologies.<sup>2-4</sup> The development of alternative catalysts, with comparable or higher activity and durability to the PGM catalysts and derived from earth-abundant materials has thus been an active research area for decades.

Incredible progress has been made over the past decade in increasing both the ORR activity and durability of PGM-free proton-exchange membrane fuel cell (PEMFC) catalysts.<sup>5</sup> The class of catalysts demonstrating the highest ORR activities are those typically denoted as "Fe-N-C" and synthesized by heat treating iron salts and zinc-based zeolitic imidazolate frameworks (ZIFs) and/or phenanthroline, as carbon and nitrogen sources, or by heat treating iron-substituted ZIFs. In addition to their high intrinsic activity, under certain preparation conditions these catalysts are free of crystalline iron species, with iron atomically dispersed in a nitrogen-doped carbon matrix, as determined using high-resolution electron microscopy, X-ray absorption spectroscopy, and Mössbauer spectroscopy. This presentation will discuss the application of multiple characterization techniques to understand the nature of the active site in Fe-N-C catalysts, including nuclear resonance vibrational spectroscopy, temperature-programmed desorption, and in situ Mössbauer and X-ray absorption spectroscopies as a function of potential in aqueous acidic electrolyte.

Incredible progress has also been made in improving the activity of PGM-free electrocatalysts for the OER in alkaline environments, with nickel-iron oxyhydroxides showing activities comparable to PGMbased catalysts. Recent improvements in the performance of these OER catalysts in anion-exchange membrane water electrolyzers have been achieved by increasing the specific surface area and thus active site density using novel synthesis techniques.<sup>6</sup> This presentation will discuss the application of characterization techniques to understand the nature of the active site and the role of iron in enhancing the OER activity of nickel in this class of catalysts, including in situ X-ray absorption spectroscopy.

#### References

- [1] H. Yang, Adv. Func. Mater., 31 (2021) 2007602.
- [2] B. Pivovar, Nature Catalysis, 2 (2019) 562.
- [3] S. Thompson and D. Papageorgopoulos, Nature Catalysis, 2 (2019) 558.
- [4] X.X. Wang, et al., Nature Catalysis, 2 (2019) 578.
- [5] L. Osmieri, et al., Current Opinion in Electrochemistry, 25 (2021) 100627.
- [6] L. Osmieri, et al. Applied Catalysis B: Environment and Energy, 348 (2024) 123843.

#### Acknowledgements

Support was provided by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Technologies Office, ElectroCat 2.0. This research used the resources of the Advanced Photon Source (APS), a DOE Office of Science User Facility operated by Argonne National Laboratory (ANL) under Contract No. DE-AC02-06CH11357. ANL is managed for DOE by the University of Chicago Argonne, LLC, also under contract DE-AC-02-06CH11357.

Fe

Iron, upgraded!

CRC 1487

# Thursday, 05.09.2024 | 09:15 - 09:35

#### Isolating single iron-nitrogen centers in carbon nanostructures

Jörg J. Schneider <sup>1\*</sup>, Chandrajeet Mohapatra <sup>1</sup>

<sup>1</sup> Technische Universität Darmstadt, Department of Chemistry, Eduard-Zintl-Institute for Inorganic and Physical Chemistry, Darmstadt, Germany \*joerg.schneider@tu-darmstadt.de

Carbon nanostructures like graphene (G), carbon nanotubes (CNTs) are accessible by straightforward synthetic approaches and are meanwhile versatile materials in the nanoscience community. Often, they display various defect sites in their graphitic like framework. Those defects are anchor points for a chemical functionalization with different heteroatoms. In the context of this work, we were interested in introducing nitrogen atoms via gas phase routes to obtain N donor sites embedded in the extended carbon framework of CNTs. In such N-doped CNTs, nitrogen functionalization of the carbon framework is part of a pyridinic or pyrolic ring system. Both are often in close vicinity to each other, allowing metal coordination in a multidentate fashion.

Fe<sub>x</sub>N<sub>y</sub> centers in an unordered and therefore less defined carbon surrounding are typically obtained by pyrolysis reactions of molecular precursors and are well known for their reactivity to promote the fourelectron pathway in the oxidation reduction reaction ORR <sup>[1,2]</sup> or in CO<sub>2</sub> reduction <sup>[3]</sup> However, unambiguous characterization and therefore exact determination of the exact iron nuclearity of these catalytic sites is important but elusive<sup>[4]</sup> and proves to be cumbersome being still subject of intense research activities.

Herein we focus on (i) wet chemical and (ii) gas phase approaches to introduce isolated iron atoms into N-doped CNTs. Although the obtained hybrid materials contain an iron content of only about 1% or even less these materials show significant activity in ORR. Nevertheless, an unequivocal experimental and theoretical understanding which pinpoints the active catalyst sites remains elusive.<sup>[5]</sup>



**Fig. 1** a,b: HRTEM image (80 eV) and Fe-EELS spectra of a single N-doped CNT (aperture locates the region where EELS data have been collected) indicating the presence of isolated single iron centers (green arrows). Measurements are obtained with chromatic and spherical aberration correction (in collaboration with U. Kaiser and K. Cao at SALVE microscopy center, Ulm).

#### References

[1]A Zitolo, V. Goellner, V. Armel, M-T. Sougrati, T. Mineva, L. Stievano, E. Fonda F. Jaouen, Nature Mater. 14, (2015), 937

[2] X.-F.Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, Acc. Chem. Res. 46, (2013), 1740

[3] Y. Cheng et al. S. Zhao, B. Johannessen, J.-P. Veder, M. Saunders, M. R. Rowles, M. Cheng, C. Liu, M. F. Chisholm, R. De Marco, H-M. Cheng, S.-Z. Yang, . P. Jiang, Adv. Mater. 30 (2018), 1706287

[4] T. Zhang, Nano Lett., 21, (2021), 9835

[5] M. Chen, Y. He, J. S. Spendelow, G. Wu, ACS Energy Lett. 4, (2019), 1619

# Thursday, 05.09.2024 | 09:35 - 09:55

Mohsin Muhyuddin<sup>1\*</sup>, Enrico Berretti<sup>2</sup>, Seyed Ariana Mirshokraee<sup>1</sup>, Jacopo Orsilli<sup>1</sup>, Roberto Lorenzi<sup>1</sup>, Laura Capozzoli<sup>2</sup>, Francesco D'Acapito<sup>3</sup>, Eamonn Murphy<sup>4</sup>, Shengyuan Guo<sup>4</sup>, Plamen Atanassov<sup>4</sup>, Alessandro Lavacchi<sup>2</sup>, Carlo Santoro<sup>1</sup>,

- <sup>1</sup> Department of Materials Science, University of Milano-Bicocca, U5, Via Cozzi 55, 20125, Milano, Italy
- <sup>2</sup> Istituto di Chimica Dei Composti OrganoMetallici (ICCOM), Consiglio Nazionale Delle Ricerche (CNR), Via Madonna Del Piano 10, 50019 Sesto Fiorentino, Firenze, Italy
- <sup>3</sup> CNR-IOM-OGG, c/o ESRF LISA CRG, Avenue des Martyrs 71, 38000 Grenole, France
- <sup>4</sup> Department of Chemical and Biomolecular Engineering, University of California, Irvine, CA, 92697, United States

#### \*m.muhyuddin@campus.unimib.it

Fe-Nx-C electrocatalysts for the oxygen reduction reaction (ORR) are primarily produced via atmosphere-controlled pyrolysis at high temperatures. Despite being the main methodology for the formation of an active site structure in the electrocatalyst, it remains a poorly understood phenomenon. At its core, in materials science, the processing conditions of a material determines its structure, which in turn influences its performance. Therefore, a systematic study was undertaken to analyze the influence of the pyrolysis conditions i.e. temperature and atmosphere on the nucleation, evolution and transformation of active sites in the development of Fe-Nx-C during the pyrolysis of an iron phthalocyanine (FePc)-functionalized carbon black. State-of-the-art in situ and ex situ characterizations confirmed that the atomic level dispersion of Fe-Nx type moieties remains up to 600 °C, from which iron oxide nanoparticles start forming and continue to grow over the course of the pyrolysis. Remarkably, different fingerprints acquired during in-situ and ex-situ X-ray absorption spectroscopy probed the attachment of oxygen as a fifth ligand on the Fe-based sites upon exposure to the open room environment. Using the rotating ring disc electrode (RRDE) technique, the ORR activity was elucidated in acidic and alkaline conditions, with the best activity observed when Fe-N<sub>x</sub>-C was pyrolyzed at 600 °C. However, as the pyrolysis temperature is increased passed the threshold of 600 °C, the ORR activity decays drastically with a categorical alteration in the reduction route, shifting from a tetra-electronic to bi-electronic fashion. To evaluate this discrepancy, surface-to-reactivity analysis was performed ascertaining the relationship between the surface chemistry/morphology and electrocatalytic parameters.

#### References

M. Muhyuddin, E. Berretti, S. A. Mirshokraee, J. Orsilli, R. Lorenzi, L. Capozzoli, F. D'Acapito, E. Murphy, S. Guo, P. Atanassov, A. Lavacchi, C. Santoro, Applied Catalysis B: Environmental, 343 (2024) 123515.

Fe

Iron, upgraded!

CRC 1487

### Thursday, 05.09.2024 | 09:55 - 10:15



#### High-performance MOF-based Fe-Sn-N-C catalysts for the ORR in HT-PEM fuel cells

<u>J. Buschermöhle<sup>1,2,\*</sup>, J. Müller-Hülstede<sup>1</sup>, H. Schmies<sup>1</sup>, D. Schonvogel<sup>1</sup>, P. Wagner<sup>1</sup>, M. Wark<sup>2</sup></u> <sup>1</sup> Institute of Engineering Thermodynamics, German Aerospace Center (DLR), Carl-von-Ossietzky-Str. 15, 26129 Oldenburg, Germany <sup>2</sup> Institute of Chemistry, Carl von Ossietzky University of Oldenburg, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany \*julia.buschermoehle@dlr.de

Metal-nitrogen-carbon (M-N-C) compounds are promising catalysts for the oxygen reduction reaction (ORR) at the cathode of high-temperature proton exchange membrane fuel cells (HT-PEMFC) due to their promising activity and their tolerance to poisoning by phosphoric acid electrolyte.<sup>[1]</sup> However, low volumetric activities compared to commonly used Pt nanoparticles on carbon blacks (Pt/C) and insufficient stabilities have been observed so far.<sup>[2]</sup> Therefore, the activity and stability of M-N-Cs and M-M-N-Cs with Fe and Sn based on metal-organic frameworks (MOFs) are investigated in this study. The MOF precursor ZIF-8 provides a unique platform to control metal and nitrogen doping of the carbon. Iron and tin are used in different ratios to assess the influence of metal ratio on catalytic activity and stability towards ORR. Stable and highly active catalysts were obtained and therefore the presentation will highlight the beneficial aspects of introducing the second metal tin for the ORR. The catalysts are physically and electrochemically characterized using the rotating ring disk electrode (RRDE) technique. Fe-Sn-N-C catalysts show excellent mass activities (MA) of 8.2 A g<sup>-1</sup> (Fe-Sn-N-C 1:1) and 19.3 A g<sup>-1</sup> (Fe-Sn-N-C 1:0.3), exceeding those of the commercial Fe-N-C catalyst (PMF-D14401, Pajarito Powder) and even surpassing the MA of a commercial Pt/C catalyst (Tanaka) (Figure 1a) and current Fe-Sn-N-C catalysts reported in literature (4.8 A g<sup>-1</sup>, 0.1 mol L<sup>-1</sup> HClO<sub>4</sub>, Luo et al.).<sup>[3]</sup> In contrast, the MA of the Sn-N-C without incorporated iron is significantly lower at 0.5 A g<sup>-1</sup>, which implies that sufficient activity of only Sn-containing catalysts is not given. Furthermore, an accelerated stress test (AST) is applied to evaluate the stability of the catalysts and reveals promising results for the Fe-Sn-N-C with a Fe:Sn ratio of 1:1 (Figure 1b). The decreased stability of the Fe-Sn-N-C (1:0.3) shows the stability enhancing effects of Sn due to the lower amount of Sn. Future studies will examine the Fe-Sn bonding situation to discuss the synergistic effects of the metals and also testing under HT-PEMFC conditions.



**Figure.** a) ORR curves of different catalysts in O<sub>2</sub>-saturated 0.5 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> at 1600 rpm with a catalyst loading of 400  $\mu$ g cm<sup>-2</sup> and a scan rate of 5 mV s<sup>-1</sup> and b) mass activities of different catalysts before and after the AST with the activity decrease in percent.

#### References

- [1] Y. Hu, J. O. Jensen, C. Pan, L. N. Cleemann, I. Shypunov, Q. Li, Appl. Catal. B: Environ., 234 (2018), 357.
- [2] J. Müller-Hülstede, H. Schmies, D. Schonvogel, Q. Meyer, Y. Nie, C. Zhao, P. Wagner, M. Wark, Int. J. Hydrogen Energy, 50 (2023), 921.
- [3] F. Luo, A. Roy, M. T. Sougrati, A. Khan, D. A. Cullen, X. Wang, M. Primbs, A. Zitolo, F. Jaouen, P. Strasser, J. Am. Chem. Soc., 145 (2023), 14737.
### Thursday, 05.09.2024 | 10:15 - 10:35



<u>Kaltum Abdiaziz</u><sup>1</sup>, Lingmei Ni<sup>2</sup>, Sonia Chabbra<sup>1</sup>, Hendrik Haak<sup>2</sup>, Pascal Theis<sup>2</sup>,Derya Demirbas<sup>1</sup>, Ulrike I. Kramm<sup>2</sup>, Alexander Schnegg<sup>1</sup> <sup>1</sup> Max-Planck-Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany <sup>2</sup> Technische Universität Darmstadt, Darmstadt, Germany \*kaltum.abdiaziz@cec.mpg.de

FeNC, featuring FeN4 active sites, are regarded as top candidates for replacing noble metals like platinum (Pt) for the oxygen reduction reactions (ORR) in fuel cells. However, FeNC catalysts suffer from pyrolysis-induced inhomogeneity, containing various iron/ iron oxide species. These species can be identified through <sup>57</sup>Fe Mössbauer spectroscopy and some are accessible to electron paramagnetic resonance (EPR) spectroscopy. [1] Separately, in-situ Mössbauer (MS) and in-situ (quasi) EPR spectroscopy can be very powerful in identifying iron species and determining their oxidation and spin states, especially those crucial to the catalytical mechanism, however not without ambiguity. Therefore, we present a combinational in-situ Mössbauer and EPR spectroscopy study of FeNC catalysts in order to shed much-needed light on the ambiguity surrounding the assignment of Fe sites in FeNC materials. Correlation of in situ Mössbauer and in situ EPR spectroscopy identifies the generally observed and catalytically relevant MS doublet D1 as responsible for the EPR signal observed in FeNC materials. EPR spectroscopy indicates this Fe site is comprised of a distribution of high-spin Fe<sup>III</sup> ions (S = 5/2) with slightly different zero-field splitting and rhombicities (g=4.3 and g=2), as well as inorganic clustered iron (g=2). Dehydration of the FeNC catalyst gives rise to a g=6 signal traditionally observed for square planar FeN<sub>4</sub> in phathaolocyanaines and heme group. However, the assignment of high-spin Fe<sup>III</sup> ions environment is ambiguous, as similar EPR signals can be found in oxygen-coordinated glass [2] and iron zeolites ZSM-5 [3] Molecular structures of [LFe(n2-NO<sub>3</sub>)] [4] or Fe-N<sub>3</sub>-O<sub>3</sub> [5]



**Figure 1.** (A) In-situ EPR and in-situ Mössbauer cell, (B) Quasi in situ X-band CW EPR (T = 10K) spectra of FeNC catalyst in O<sub>2</sub> at different potentials, 0.9 V (orange), 0.75 V (green), 0.6 V (purple) and 0.2 V (yellow) (C) In situ Mössbauer (298 K) spectroscopy of FeNC catalysts (D) Bar graph of EPR intensity of signal at g = 4.3 and g = 2.6 to 1 signal as a function of potential (left) and of MS absorption areas of different fitted Fe species in FeNC catalysts.

#### References

[1] L. Ni, Gallenkamp. C..., et al. Advanced Energy and Sustainability Research 2.2 (2021), 2000064
[2] Ceglia, A. et al. Journal of Analytical Atomic Spectrometry 30.7 (2015),1552
[3] K. G. Padmalekha,...& V. Schünemann. Hyperfine Interactions 238 (2017), 1
[4] J. B. Strautmann,..& T. Glaser. Inorganic chemistry 47.15 (2008), 6804
[5] X. J. Sup, O. O. Huang, & L. J. Zhang, Acc. Omega 2.9 (2017), 5850

Fe

Iron, upgraded!

CRC 1487

### Thursday, 05.09.2024 | 11:05 - 11:35



#### Growth Optimization of Fe-based Epitaxial Tellurides Using Hybrid PLD

<u>Jasnamol Palakkal</u><sup>\*</sup>, Anna Tschesche, Pia Henning, Anika Jonelagadda Institute of Materials Physics, Georg-August-University of Göttingen, Göttingen 37077, Germany \*jpalakkal@uni-goettingen.de

2D materials and high-entropy materials are currently hot topics of materials science research. 2D materials offer flexible device fabrication, and high-entropy materials offer multifunctionality, including magnetic memory devices and catalysis applications.

Epitaxial 2D materials can offer high stability compared to conventional mechanically exfoliated flakes. To fabricate 2D high-entropy epitaxial materials, we developed a hybrid pulsed laser deposition (PLD) system by attaching molecular beam sources, as shown in Figure 1. Transition metal dichalcogenides like MoS<sub>2</sub> were reported to be grown using a similar hybrid technique. <sup>1</sup> As a first step, we prepared chromium telluride ( $Cr_{(1+\delta)}Te_2$ ) thin films of various  $\delta$  for tuning their ferromagnetic properties according to the Cr: Te ratio. <sup>2</sup> The Cr was supplied from the PLD target, and Te was provided from the chalcogen molecular beam source. Stabilization of different phases of the telluride viz. CrTe, Cr<sub>2</sub>Te<sub>3</sub>, and CrTe<sub>2</sub> were achieved by increasing the flux rate of Te-source. These stoichiometry-controlled films show different magnetic transition temperature (T<sub>c</sub>), anisotropic magnetoresistance (AMR), and a metal-to-insulator transition (MIT) near the T<sub>c</sub>, with the highest T<sub>c</sub> of 324 K exhibited by Cr<sub>2</sub>Te<sub>3</sub>.

After the successful growth of  $(Cr_{(1+\delta)}Te_2)$  using the hybrid PLD, we changed the Cr PLD target to a medium-entropy target, FeCrNi, and fabricated its telluride. FeCrNi thin films were non-magnetic but upon adding Te, the (FeCrNi)Te shows ferromagnetic behavior with strong perpendicular magnetic anisotropy.

In this talk, we will discuss various growth parameters used for fabricating these tellurides using the hybrid PLD set up and their structural and magnetic properties. We also measured the oxygen evolution activity of the tellurides; however, after a few cycles the epitaxial tellurides were completely exfoliated out of the substrate and could not finish the experiment. We believe that our fabrication system has the potential to develop further high entropy 2D materials and are in trial to find experimental solutions to measure their catalytic properties.



Figure 1. Schematic of the hybrid PLD (left) and the inside view of the UHV chamber during deposition (right).

#### References

 Bertoldo, F.; Unocic, R. R.; Lin, Y.-C.; Sang, X.; Puretzky, A. A.; Yu, Y.; Miakota, D.; Rouleau, C. M.; Schou, J.; Thygesen, K. S.et al. ACS Nano, 15 (2021), 2858.
 Yang, J.; Zhu, C.; Deng, Y.; Tang, B.; Liu, Z. iScience, 26 (2023), 106567.

### Thursday, 05.09.2024 | 11:35 - 11:55



#### Upgrading magnetism of iron by interstitial nitrogen

I. Dirba<sup>1,\*</sup>, Y. Ablets<sup>1</sup>, S. Das<sup>1</sup>, D. Bravard<sup>1</sup>, H. Zhang<sup>3</sup>, L. Alff<sup>2</sup>, O. Gutfleisch<sup>1</sup> <sup>1</sup> Functional Materials, Institute of Materials Science, Technical University of Darmstadt, 64287

Darmstadt, Germany

<sup>2</sup> Advanced Thin Film Technology Division, Institute of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany

<sup>3</sup> Theory of Magnetic Materials, Institute of Materials Science, Technical University of Darmstadt,

64287 Darmstadt, Germany

\*imants.dirba@tu-darmstadt.de

The fascinating phase diagram of iron-nitrogen provides a variety of interesting materials with their magnetic properties tunable in a broad range depending on the nitrogen content. As expected, magnetism correlates with the iron amount, starting from nonmagnetic FeN to ferromagnetic Fe<sub>4</sub>N with high magnetization and spin polarization and even further to Fe<sub>8</sub>N. The remarkable impact of interstitial nitrogen is first manifested in Fe4N where N atoms isotropically expand the unit cell of nonmagnetic  $\gamma$ -Fe turning it into a ferromagnet with high magnetization and Curie temperature [1]. Perhaps the most attention is attracted by the disordered  $\alpha'$ -Fe<sub>8</sub>N [2] and the ordered tetragonal superstructure  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> [3] due to its unique combination of high saturation magnetization with enhanced magnetocrystalline anisotropy [4]. In addition, in this talk we will discuss how nitrogen can be used to induce tetragonality by reversible absorption-extraction reactions in chemically ordered Fe-Ni alloys and by Ge doping in Fe<sub>3</sub>GeN<sub>x</sub>.



**Figure 1.** Positions of the octahedral interstitial sites in bcc and fcc lattices with the corresponding iron octahedra occupied by N atom in  $\alpha$ '-Fe<sub>8</sub>N<sub>x</sub> (left) and  $\gamma$ '-Fe<sub>4</sub>N (right).

#### References

[1] I. Dirba, M. Baghaie Yazdi, A. Radetinac, P. Komissinskiy, S. Flege, O. Gutfleisch, L. Alff, J. Magn. Magn. Mater. 379, 151-155 (2015).

[2] I. Dirba, P. Komissinskiy, O. Gutfleisch and L. Alff, J. Appl. Phys. 117, 173911 (2015).

[3] I. Dirba, C. A. Schwöbel, L. V. B. Diop, M. Duerrschnabel, L. Molina-Luna, K. Hofmann, P. Komissinskiy, H.-J. Kleebe, O. Gutfleisch, Acta Mater. 123, 214-222 (2017).

[4] H. Zhang, I. Dirba, T. Helbig, L. Alff, and O. Gutfleisch, APL Mater. 4, 116104 (2016).

### Thursday, 05.09.2024 | 11:55 - 12:15



#### Materials Science of Nitrogen Ion Implantation in *α*-Fe

<u>Giovanni d'Andrea<sup>1,\*</sup>, S. Zhou², G. Gkouzia¹, P. Rani¹, M. Major¹ and L. Alff¹</u>

<sup>1</sup> Technische Universität Darmstadt, Institute of Materials Science, Peter-Grünberg-Straße 2, 64287

<sup>2</sup> Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research,

Bautzner Landstrasse 400, 01328 Dresden, Germany

\*giovanni.dandrea@tu-darmstadt.de

Nitrogen interstitials are a candidate to achieve structural tetragonalization in  $\alpha$ -Fe which is predicted to lead to extremely high magnetocrystalline anisotropy. Here, we have studied the effects of high-dose nitrogen ion implantation on the structural and magnetic properties of  $\alpha$ -Fe. We have achieved by this method a nitrogen interstitial concentration of  $\alpha'$ -Fe<sub>8</sub>N<sub>x</sub> (x>1) with a stabilized elongation of the *c*-lattice constant beyond the maximum value reported so far in literature of 3.146 Å [1]. This represents a significant advance that sheds light on whether this material could serve as a competitive candidate for gap magnets [2]. This material is of particular interest due to the average magnetic moment per iron atom and magnetocrystalline anisotropy, both of which increase with the tetragonality of the material's lattice, driven by the homogeneous distribution of interstitial nitrogen within the film [3, 4].

In order to increase the nitrogen atomic percentage, we employed ion-implantation, a widely used nonequilibrium method that prevents the formation of thermodynamically stable compounds with varying stoichiometries [5]. Our study used 30 nm thin iron thin films grown on MgO (100) substrates that underwent ion-implantation at 13 keV with doses ranging between  $4 \times 10^{16}$  cm<sup>-2</sup> and  $10 \times 10^{16}$  cm<sup>-2</sup>. At even higher doses, film amorphization was observed, which in turn weakens the magnetic anisotropy.

Despite slow annealing attempts at both low and high temperatures, crystallization of the metastable phase beyond the initial volume fractions found after implantation was unsuccessful, or it resulted in the decomposition of the film, due to the unmatched energy threshold required for the crystallization of the amorphous film and the low decomposition temperature of the material [6, 7].

In order to induce re-crystallization while maintaining a homogeneous nitrogen distribution, a rapid laser annealing approach (few minutes) in ultra-high vacuum (10<sup>-9</sup> mbar) above decomposition temperatures (above 300°C) is investigated. This method leads to an ultrafast crystallization of iron in the thin films. We demonstrate the effect of annealing temperature and time on the necessary short-range diffusion for crystallization while at the same time undesired iron nitride formation or out-diffusion is avoided.

#### References

[1] K. Toda, M. Honda, Y. Orihara, et al., Key Eng. Mater. 181 (2000) 213.

- [2] J. Cui, M. Kramer, L. Zhou et al., Acta Mater. 158 (2018) 118.
- [3] I. Dirba, P. Komissinskiy, O. Gutfleisch et al., J. Appl. Phys. 117 (2015) 173911.
- [4] H. Zhang, I. Dirba, T. Helbig et al., APL Mater. 4 (2016) 116104.
- [5] P. Gupta, H. Fielder, S. Rubanov et al., J. Magn. Magn. Mat. 517 (2021) 167388.
- [6] S. Yamamoto, R. Gallage, Y. Ogata et al., Chem. Commun. 49 (2013) 7708.
- [7] M. Widenmeyer, T.C. Hansen, and R. Niewa, Z. Anorg. Allg. Chem 639.15 (2013) 2851.



# Poster

## **Overview Poster I**



No.	Name, Institution	Title
1	Danny Stark, Technische Universität Darmstadt	Highly efficient Synthesis of C2-Building Blocks via Oxydehydrogenation of Bioethanol Mo-doped Iron Catalysts
2	Jan Welzenbach, Technische Universität Darmstadt	Elucidating surface and bulk dynamics of iron molybdate catalysts during oxidative dehydrogenation using operando spectroscopies
3	Hannah Wilhelm, Technische Universität Darmstadt Jan Welzenbach, Technische Universität Darmstadt	Coupled Operando Raman Spectroscopy and X-Ray Diffraction of $Fe_2(MoO_4)_3$ Catalysts during Ethanol Selective Oxidation
4	Hannah Wilhelm, Technische Universität Darmstadt	Lattice Parameters of Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> -type Catalysts during Ethanol Selective Oxidation
5	Dr. Kathrin Hofmann, Technische Universität Darmstadt	Insight into the role of iron in ferric molybdate using isostructural compounds Fe <sub>2-x</sub> M <sub>x</sub> (MoO <sub>4</sub> ) <sub>3</sub> (M = Al, Cr, In)
6	Anna Katharina Weber, Johannes Gutenberg-Universität Mainz	Easy-Axis and Easy-Plane Iron(II)-Sites: Competing Interactions and Magnetic Structure
7	Konrad Koschnick, Technische Universität Darmstadt	Gas-Phase Raman Spectroscopy in the Oxidative Dehydrogenation of Ethanol
8	Dr. Young-Joon Song, Goethe-Universität Frankfurt	First-principles microscopic modeling of spin states of iron-based systems
9	Niklas von Rhein, Technische Universität Darmstadt	Understanding vibrational temperature effects on Mössbauer parameters using a sampling approach
10	Johannes Pfeiffer, Technische Universität Darmstadt	New mechanistic insight into the oxidative dehydrogenation of ethanol over iron vanadate catalysts
11	Lanjie Jiang, Technische Universität Darmstadt	Influence of gas atmosphere on iron signatures in $Fe_2(MoO_4)_3$ as catalysts for the selective oxidation of ethanol
12	Tim Diederich, Universität Heidelberg	Magnetism and Reactivity of Square Planar Iron
13	Nicole Segura-Salas, Technische Universität Darmstadt	Revealing underlying electronic transfer of FeN <sub>4</sub> - derived catalyst during CO <sub>2</sub> RR using Fourier- transformed alternating current voltammetry
14	Dr. Chandrajeet Mohapatra, Technische Universität Darmstadt	Precisely Embedded Iron/Nitrogen Centers in N- doped Carbon Nanotubes for Electrocatalysis
15	Timon Zankel, Technische Universität Darmstadt	Spectroscopic and magnetic properties of iron phthalocyanines

## **Overview Poster II**



No.	Name, Institution	Title
16	Dr. Anna Ostroverkh, Technische Universität Darmstadt	The instability of FeNC catalysts in PEMFC and its dependence on carbon corrosion
17	Ansuree Ghosh, Technische Universität Darmstadt	Synthesis and Properties of Novel Macrocyclic FeN <sub>4</sub> - Complexes
18	Zihan Zhang, Friedrich-Alexander-Universität Erlangen-Nürnberg	Molecular and Electronic Structures of High-valent Iron Nitrido Complexes
19	Kilian Heckenberger, Technische Universität Darmstadt	Operando NMR spectroscopic investigation of a Kumada-type iron-catalysed cross-coupling reaction
20	Pascal Theis, Technische Universität Darmstadt	New insights into the longterm storage degradation of FeNC catalysts
21	Hendrik Haak, Technische Universität Darmstadt	Post-mortem Mössbauer spectroscopy on PEM fuel cell degradation of an FeNC catalyst
22	Dr. Kaltum Abdiaziz, Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr Dr. Lingmei Ni, Technische Universität Darmstadt	Spectroelectrochemical EPR and Mössbauer for Identifying Active Sites in FeNC Catalysts
23	Dr. Lingmei Ni, Technische Universität Darmstadt	Effects of Au nanoparticles on the oxygen reduction reaction activity of $\text{FeN}_4$ centers
24	Eva Körber, Friedrich-Alexander-Universität Erlangen-Nürnberg	Low Valent Iron Complexes Utilizing Variations of the TIMMN Ligand Framework
25	Sumin Lim, Technische Universität München	Developing a channel flow cell for tracking the dissolution during operando measurements
26	Jannik Mehmel, Technische Universität Darmstadt	Magnetism of transition-metal doped tetrel nanoclusters: Multi-reference character and spin- orbit effects in Sn <sub>12</sub> TM (TM = Cr, Mn, Fe)
27	Bingyu Zhang, Technische Universität Darmstadt	In situ Monitoring of Hydrogenation and Isotope Scrambling Reactions by High-Field NMR
28	Bo Zhao, Technische Universität Darmstadt	Machine learning modelling of Mössbauer spectroscopy for Fe-based intermetallic compounds
29	Magdalena Pauritsch, Graz University of Technology	Iron Oxides for Innovative, Safe and Sustainable Energy Storage

#### Highly efficient Synthesis of C2-Building Blocks via Oxydehydrogenation of Bioethanol on Mo-doped Iron Catalysts

Danny Stark<sup>1\*</sup>, Alfons Drochner<sup>1</sup>, Bastian Etzold<sup>2</sup>

 <sup>1</sup> Technische Universität Darmstadt, Ernst-Berl-Institute for Technical Chemistry and Macromolecular Science, Darmstadt, Germany
 <sup>2</sup> Friedrich-Alexander-Universität Erlangen-Nürnberg, Power-To-X Technologies, Fürth, Germany

\*danny.stark@tu-darmstadt.de

#### Introduction

Modern chemical industry is increasingly emphasizing highly efficient and sustainable processes. Rather than relying on crude oil, coal and natural gas as primary feedstocks, a rapidly growing number of waste reduction, reutilization, and circular strategies is being engineered. One important approach is the utilization of bio based raw materials to develop drop-in technologies for the substitution of existing processes. A very promising substrate for this approach is bioethanol. Nowadays already over 100 billion litres of bioethanol are produced annually by the fermentation of starch- and sugar-based feedstocks alone.<sup>1</sup> One possible route for the utilization of ethanol is its conversion to acetaldehyde via oxidative dehydrogenation (ODH), a route analogous to the well-established *Formox* process used in industry for the large-scale production of formaldehyde from methanol. While this process utilizes iron molybdenum mixed oxide catalysts, the applicability of this system for the conversion of ethanol to acetaldehyde was hardly investigated.<sup>2</sup> Therefore, this study evaluates this mixed oxide system as a prospective catalyst for the ODH of ethanol to acetaldehyde.

#### **Materials and Methods**

Iron molybdenum mixed oxide catalysts of varying composition were prepared by coprecipitation of their respective metal salts. Performance and stability of these catalysts were investigated in a continuous flow fixed bed tubular reactor. Steady state as well as transient response methods were applied for kinetic investigations. Off-gas was analyzed by a quadrupole mass spectrometer and an online gas chromatograph. Structural characterization of catalysts was done by N<sub>2</sub>-Physisorption, NH<sub>3</sub>-TPD, ICP-OES, Raman spectroscopy, XRD, SEM and XPS.

#### **Results and Discussion**

The evaluation of catalysts with varying compositions highlights an interesting finding: while pure iron oxide promotes the combustion reaction of ethanol, even the introduction of small molybdenum quantities provides catalysts with excellent acetaldehyde selectivity, allowing for single pass yields exceeding 90 %. Furthermore, these iron rich catalysts demonstrate superior activity compared to the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> benchmark and enable almost full ethanol conversion at low temperatures while maintaining high selectivity. Alongside achieving equivalent yields at lower reaction temperatures, the use of iron-enriched catalysts has the additional benefit of extending the catalysts lifetime. Our research demonstrates that the deactivation of molybdenum oxide-based catalysts in the ODH of ethanol proceeds via the depletion of active material by volatilization, analogous to the deactivation when employing methanol as the substrate.<sup>3</sup> However, the deactivation is kinetically hindered at lower temperatures allowing the highly active iron rich catalysts to retain their activity, while the benchmark shows decreasing ethanol conversion and acetaldehyde selectivity over time. We will delve into the immense changes in both performance and stability among catalysts with different compositions, considering disparities in their structural and surface composition, as corroborated by a range of characterization techniques, i.e. we were able to correlate differences in product selectivities with differences in specific surface acidity, as evidenced by NH<sub>3</sub>-TPD experiments.

- 1. J. R. Melendez, B. Mátyás, S. Hena, D. A. Lowy, A. El Salous, Renewable and Sustainable Energy Rev, 160 (2022), 112260.
- 2. N. Oefner, F. Heck, M. Dürl, L. Schuhmacher, H. K. Siddiqui, U. I. Kramm, C. Hess, A. Möller, B. Albert, B. J. M. Etzold, ChemCatChem, 14 (2022).
- 3. K. V. Raun, L. F. Lundegaard, J. Chevallier, P. Beato, C. C. Appel, K. Nielsen, M. Thorhauge, A. D. Jensen, M. Høj, Catalysis Science and Technology, 8 (2018), 4626.



## Elucidating surface and bulk dynamics of iron molybdate catalysts during oxidative dehydrogenation using *operando* spectroscopies

Jan Welzenbach<sup>1\*</sup>, Leon Schumacher<sup>1</sup>, Mariusz Radtke<sup>1</sup>, Christian Hess<sup>1</sup> <sup>1</sup>Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technical University of Darmstadt, 64287 Darmstadt, Germany <sup>\*</sup>jan.welzenbach@tu-darmstadt.de

#### Introduction

 $Fe_2(MoO_4)_3$  has been used commercially as a catalyst for oxidative dehydrogenation (ODH) of methanol to formaldehyde,<sup>1,2</sup> Anyway its mode of operation is still poorly understood, particularly regarding the role of iron. To gain a detailed mechanistic understanding of  $Fe_2(MoO_4)_3$  catalysts during propane<sup>5</sup> and ethanol (EtOH) ODH<sup>3</sup> reactions we applied in situ (transient) and operando methods, addressing both (sub)surface and bulk processes.

#### **Materials and Methods**

The Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> catalysts were prepared using co-precipitation by adding an Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution to an (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O solution and stirring for 3 h at 100 °C, followed by calcination at 500 °C for 10 h.3 The reaction feed contained 5% EtOH/ 10% O<sub>2</sub>/ N<sub>2</sub> or 12.5% propane/ 12.5% O<sub>2</sub>/ He. *Operando* Raman, UV/vis and impedance spectroscopy<sup>4,5</sup>, were performed in a commercial reaction cell.

#### **Results and Discussion**

The reactivity behavior shows a dependency on the substrate (propane, EtOH), however, the observed structural dynamics are largely comparable. *Operando* Raman spectra during propane ODH at 385 nm excitation, shown in the left panel of Fig. 1, reveal a dynamic of the signals at 320 and 780 cm<sup>-1</sup>, originating from antisymmetric MoO<sub>4</sub> stretching, when switching between oxidative and propane ODH conditions at 500 °C.<sup>5</sup> This behavior indicates the reduction of the catalyst and diffusion of oxygen from the subsurface region to the surface.

To enhance the understanding of transport properties, we applied *operando* powder impedance spectroscopy. When the gas phase is switched from oxidative to reactive conditions, an increase in the conductivity is observed, as shown in the right panel of Fig. 1 for propane ODH at 500°C caused by increased lattice oxygen movement between lattice defects.



Fig.1: (a) Operando Raman spectroscopy at 500 °C. (b) Operando impedance spectroscopy at 500 °C

#### Significance

For a better mechanistic understanding of ODH reactions over  $Fe_2(MoO_4)_3$  catalysts a combination of different operando and transient spectroscopies was applied, providing direct insight on the (sub)surface and bulk dynamics, including oxygen transport to the surface and active-site identification.

- 1. C. Hess, R. Schlögl. Nanostructured Catalysts: Selective Oxidation. RSC Publishing 2011.
- 2. C. Brookes, M. Bowker, P. Wells. Catalysts 2016, 6, 92.
- 3. N. Oefner, F. Heck, M. Dürl, L. Schumacher, H. Siddiqui, U. Kramm, C. Hess, A. Möller, B. Albert, B. Etzold. ChemCatChem **2022**, 14, e2021012.
- 4. M. Ziemba, M. Radtke, L. Schumacher, C. Hess. Angew. Chem. Int. Ed. 2022, 61, e202209388.
- 5. L. Schumacher, M. Radtke, J. Welzenbach, C. Hess. Commun. Chem **2023**, DOI: 10.1038/s42004-023-01028-8.

## Coupled *Operando* Raman Spectroscopy and X-Ray Diffraction of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> Catalysts during Ethanol Selective Oxidation

Hannah Wilhelm<sup>1\*</sup>, Jan Welzenbach<sup>1\*</sup>, Kathrin Hofmann<sup>1</sup>, Christian Hess<sup>1</sup>, Barbara Albert<sup>1</sup> <sup>1</sup> Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Germany hannah.wilhelm@tu-darmstadt.de, jan.welzenbach@tu-darmstadt.de

Iron molybdate Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> is a catalyst used commercially to produce formaldehyde via oxidative dehydrogenation (ODH) of methanol.<sup>1</sup> Recent studies have shown its additional potential for the ODH of ethanol (EtOH) as a more energy-efficient and sustainable alternative towards acetaldehyde compared to the currently used Wacker-Hoechst process.<sup>2</sup> Within this work we present the development of a lab-based setup for coupled *operando* X-ray diffraction and Raman spectroscopy and its application to iron molybdate catalysts during EtOH ODH. This combined approach has the potential to address both bulk and (sub-) surface dynamics during the reaction.

Time-resolved studies, varying the gas atmosphere and temperature, were carried out for Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, prepared by co-precipitation<sup>2</sup>. After switching from reactive to reductive conditions (5 % EtOH/N<sub>2</sub> at 210 °C) for 18 h significant changes were observed (Figure 1). The most intense Raman signal at 782 cm<sup>-1</sup> ( $v_{as}$ (MoO<sub>4</sub>)) decreased after the first minutes of the reductive treatment. In the XRD patterns the most intense reflection of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> (22.77 °/2 $\theta$ ) decreased with time, whereas a reflection at 32.88 °/2 $\theta$  (Fe<sub>2</sub>O<sub>3</sub>) appeared and increased in intensity with time. This reflection may indicate the loss of molybdenum during catalysis. The changes in the Raman spectra are visible on shorter time scales. They indicated the (sub-) surface to react more quickly to changes in the gas atmosphere, whereas changes in the XRD patterns confirmed the bulk material to follow and participate in the process. Coupling both analysis methods thus enable the simultaneous observation and interpretation of depth-dependent processes in the catalyst that occur at different time scales. Summarizing, we developed a new operando-XRD-Raman setup and demonstrated for iron molybdate catalysts.



**Figure 1:** Time-resolved changes of the characteristic Raman signal (black) and XRD reflections of  $Fe_2(MoO_4)_3$  (red) and  $Fe_2O_3$  (green) after switching from reactive to reducing conditions **(a)**, EtOH conversion (orange) and acetaldehyde (AcH) selectivity (blue) **(b)**, scheme of the depth-dependent reduction process **(c)**.

#### References

[1] C.Hess, R. Schlögl. Nanostructured Catalysts: Selective Oxidation. RSC Publishing **2011**.
[2] N. Oefner, F. Heck, M. Dürl, L. Schumacher, H. Siddiqui, U. Kramm, C. Hess, A. Möller, B. Albert, B. Etzold. *ChemCatChem* **2022**, 14, e2021012.



#### Lattice Parameters of Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>-type Catalysts during Ethanol Selective Oxidation

Hannah Wilhelm<sup>1\*</sup>, Jan Welzenbach<sup>1</sup>, Kathrin Hofmann<sup>1</sup>, Anna Wenzel<sup>1</sup>, Christian Hess<sup>1</sup>, Barbara

Albert<sup>1</sup>

<sup>1</sup> Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität

Darmstadt, Germany

hannah.wilhelm@tu-darmstadt.de

Iron molybdate  $Fe_2(MoO_4)_3$  is a catalyst used commercially to produce formaldehyde via oxidative dehydrogenation (ODH) of methanol.<sup>1</sup> Recent studies have shown its additional potential for the ODH of ethanol (EtOH) as a more energy-efficient and sustainable alternative towards acetaldehyde compared to the currently used Wacker-Hoechst process.<sup>2</sup> We developed a custom-built *operando* XRD-Raman setup with is based on a *in situ* XRD/Raman cell newly designed together with Anton Paar GmbH for the investigations of  $Fe_2(MoO_4)_3$  as a catalyst for EtOH ODH.

In this work the lattice parameters of  $Fe_2(MoO_4)_3$  under reactive conditions were investigated. Firstly,  $Fe_2(MoO_4)_3$  was treated under oxidative conditions (10 % O\_2/N\_2 in 100 mL/min, 350 °C, 1 h), then under reactive conditions (5 % EtOH/10 % O\_2/N\_2 in 100 mL/min, 350 °C, 2 h) and finally under oxidative conditions for one hour to check the reversibility of the changes. The ethanol conversion under reactive conditions is 76.0 % and the selectivity towards acetaldehyde is 34.9 %. Lattice parameters were refined using the Rietveld method based on *in situ* XRD patterns (Figure 1). An increase in the lattice parameters *a*, *b*, *c* and *V* could be observed during the transition from oxidative to reactive conditions. Thus, the change to reactive conditions had a reversible influence of the lattice parameters, proving the bulk material followed and participated in the catalytic process.



**Figure 1**: a) Rietveld refinement after 1 h under reactive conditions at 350 °C. b) Development of the refined lattice parameters of  $Fe_2(MoO_4)_3$  under oxidative and reactive conditions at 350 °C.

For a better understanding of the role of iron atoms in  $Fe_2(MoO_4)_3$ , it was substituted in parts with chromium and indium atoms. For example, isostructural compounds  $Fe_{1.5}Cr_{0.5}(MoO_4)_3$  and  $Fe_{1.5}In_{0.5}(MoO_4)_3$  were also tested as catalysts for the EtOH ODH and the effects of the reactive conditions on the lattice parameters were investigated.

#### References

[1] C. Hess, R. Schlögl in *Nanostructured Catalysts: Selective Oxidation*, RSC Publishing, **2011**.
[2] N. Oefner, F. Heck, M. Dürl, L. Schumacher, H. Siddiqui, U. Kramm, C. Hess, A. Möller, B. Albert, B. Etzold. *ChemCatChem* **2022**, 14, e2021012.

## Insight into the role of iron in ferric molybdate using isostructural compounds Fe<sub>2-x</sub>M<sub>x</sub>(MoO<sub>4</sub>)<sub>3</sub> (M = AI, Cr, In)

Kathrin Hofmann<sup>1\*</sup>, Hannah Wilhelm,<sup>1</sup>, Anna Wenzel<sup>1</sup>, Lanjie Jiang<sup>1</sup>, Jan Welzenbach<sup>1</sup>, Felix Reinauer<sup>1</sup>, Christian Hess<sup>1</sup>, Ulrike Kramm<sup>1</sup>, Barbara Albert<sup>1</sup>

<sup>1</sup> Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt,

Germany

\*kathrin.hofmann@tu-darmstadt.de

Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> is an important catalyst for the oxidative dehydrogenation (ODH) of alcohols. In order to understand the mechanism of the catalyzed ODH of ethanol in general and the role of iron in the catalyst in detail, isostructural compounds in which iron is substituted by aluminum-, chromium-, or indium atoms are interesting in comparison to pure  $Fe_2(MoO_4)_3$ . The solid solutions  $Fe_2 \times M_x(MoO_4)_3$  (M = Al, Cr, In) were synthesized by an adapted co-precipitation method<sup>1</sup> and were thoroughly characterized. The composition of phase ratios within the three solid solutions were determined by Rietveld fits of the Xray powder patterns and by energy-dispersive spectroscopy in a scanning electron microscope (SEM-EDS). Mössbauer spectra of samples on the aluminum-rich side of the solid solution  $Fe_{2-x}Al_x(MoO_4)_3$  (x = 1.8 - 1) show an increase in the s-electron density at the Fe nuclei with increasing AI content. More interestingly, compared to the typical Fe(III) high-spin (HS) state in Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, a new shoulder can be observed on the left hand side of the spectra. This feature has the strongest effect in the sample Fe2- $_xAI_x(MoO_4)_3$  with x = 1 and is not yet fully understood, but could be caused by changes in the ironcoordination. It can be shown that the aluminum-substituted samples are also active for ethanol ODH, but compared to pure Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, the conversion of ethanol and the selectivity to acetaldehyde are shifted to higher reaction temperatures. For example, comparative studies of pure  $Fe_2(MoO_4)_3$  and Fe<sub>0.5</sub>Al<sub>1.5</sub>(MoO<sub>4</sub>)<sub>3</sub> show that the yield for the Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>-catatyzed reaction is significantly higher at temperatures below 300 °C.



**Figure.** Mössbauer spectra for  $Fe_{2-x}AI_x(MoO_4)_3$  with x = 1.8, 1.6, 1.4, 1.2, 1 (left) and comparison of yields in ethanol ODH for  $Fe_2(MoO_4)_3$  and  $Fe_{0.5}AI_{1.5}(MoO_4)_4$  (right).

As part of the optimization of the syntheses of  $Fe_{2-x}In_x(MoO_4)_3$  ( $2 \ge x \ge 0.6$ ) the crystal structure of a formerly unknown intermediate product,  $In(MoO_4)OH$ , was determined and refined from X-ray powder diffraction data. It crystallizes similar to  $Fe(SO_4)OH^2$  and  $Fe(MoO_4)OH^3$  in space group *C*2/*c*. In this structure,  $MoO_4$ -tetrahedra are connected to chains of corner-shared  $InO_6$ -octahedra. The H-atom is bound to the corner-sharing oxygen atom. With the above-mentioned co-precipitation method,  $In_{1-x}Fe_x(MoO_4)OH$  with  $2 \ge x \ge 0.6$  can be observed. At iron-contents of > 80 %  $Fe_{2-x}In_x(MoO_4)_3$  ( $0.4 \ge x \ge 0.6$ ) is formed directly and can already be observed as intermediate products during synthesis.

#### References

[1] N. Oefner, F. Heck, M. Dürl, L. Schumacher, H. Siddiqui, U. Kramm, C. Hess, A. Möller, B. Albert, B. Etzold. *ChemCatChem* **2022**, 14, e2021012.

[2] M. Avdeev, S. Singh, P. Barpanda, C. D. Ling. Inorg. Chem. 2021, 60, 15128.

[3] M. Foroughian, T. M. Smith Pellizzeri, C. D. McMillen, K. Ivey, J. W. Kolis, *Solid State Sci.*, **2024**, 107403.



#### Easy-Axis and Easy-Plane Iron(II)-Sites: Competing Interactions and Magnetic Structure

<u>Anna Katherina Weber<sup>1,\*</sup></u>,Lenka Kubíčková <sup>1</sup>, Martin Panthöfer<sup>1</sup>, Stuart Calder<sup>2</sup>, Angela Möller<sup>1</sup> <sup>1</sup> Department of Chemistry, Johannes Gutenberg University Mainz, Germany <sup>2</sup> Neutron Scattering Devision, Oak Ridge National Laboratory, United States \*wannakat@uni-mainz.de

The trillium lattice is composed of equilateral triangles of magnetic ions in 3D and belongs to the class of strongly frustrated magnets. In the acentric compound Cs<sub>2</sub>Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> two disparate trillium lattices are interlinked and decorated with Fe(II) of the easy-axis and easy-plane single-ion anisotropy, respectively. Here, we present electronic structure calculations on the basis of the Angular-Overlap Model and elaborate on the two ground states that govern the magnetic responses. Details on the thermodynamic properties and <sup>57</sup>Fe-Mössbauer spectroscopic results will be given. Beyond the crystallographic (nuclear) structure, we discuss the non-collinear magnetic structure with respect to the two individual Fe-sites and their magnetic moments respectively. Neutron diffraction data support short-range magnetic order (diffuse scattering) below 20 K and development of long-range magnetic order below 1.0 K. These results support the presence of strong competing interactions and allow an estimate of the frustration parameter,  $f \approx |\Theta_{CW}|/T_N \approx 20$ .

Acknowledgement. This work has received support from the DFG (443703006–CRC 1487 and 442589410), EU (MCS 101066568), and DOE (ORNL, IPTS-31426.1).

#### References

[1] L. Kubíčková, A. K. Weber, M. Panthöfer, S. Calder, A. Möller, Chem. Mater. 2024 under review.

## Gas-Phase Raman Spectroscopy in the Oxidative Dehydrogenation of Ethanol

<u>K.Koschnick<sup>1,2,\*</sup></u>, A. M. Ferris<sup>1,3</sup>, M. Stark<sup>1,2,4</sup>, D. Stark<sup>5</sup>, A. Weinmann<sup>4</sup>, A. Drochner<sup>5</sup>, B. Etzold<sup>5</sup>, D. Geyer<sup>2</sup>, A. Dreizler<sup>1</sup>

<sup>1</sup> Reactive Flows and Diagnostics, Department of Mechanical Engineering, Technical University of Darmstadt, Otto-Berndt-Straße 3, 64287 Darmstadt, Germany

<sup>2</sup> Optical Diagnostics and Renewable Energies, Department of Mechanical and Plastics Engineering, University of Applied Sciences Darmstadt, Schöfferstraße 3, 64295 Darmstadt, Germany

<sup>3</sup> Ferris Research Group, Department of Mechanical and Aerospace Engineering, Princeton University, New Jersey 08544, USA

<sup>4</sup> Department of Mathematics and Natural Sciences, University of Applied Sciences Darmstadt, Schöfferstraße 3, 64295 Darmstadt, Germany

<sup>5</sup> Ernst Berl Institute for Macromolecular and Technical Chemistry, Technical University of Darmstadt, Alarich-Weiß-Straße 8, 64287 Darmstadt, Germany

\*koschnick@rsm.tu-darmstadt.de

The importance of sustainable and more energy-efficient synthesis methods of feedstock chemicals motivates recent developments in heterogeneous catalytic processes, e.g. the oxidative dehydrogenation (ODH) of ethanol to acetaldehyde using an iron-molybdate catalyst. To develop and validate the performance of catalysts with sufficient selectivity and high process stability, experimental measurements acquired within the reaction process (operando) are required. Gas-phase Raman spectroscopy is a powerful tool that can probe the full thermochemical state of a gas, providing both temporally and spatially resolved information that can help to unravel molecular transport and potential gas-phase reactions.

A novel optically accessible catalytic channel (OACC) is employed, featuring a flow homogenization system, as well as multiple heating elements and thermocouples to regulate temperature and flow across the catalytic surface. A catalyst pellet, composed of iron-molybdate with a 20:1 iron to molybdenum ratio, is integrated flush into the reactor chamber floor, allowing optical access from five sides. A newly designed dual-track Raman spectrometer (DTRS) includes two optical paths ("tracks") used for dual-resolution measurements. The first track uses a holographic transmission grating for broad spectral range concentration measurements, while the second track employs a 'grism' (grating and two prisms) for a highly resolved nitrogen spectrum, crucial for Raman thermography. Raman scattering is excited by a 100 W continuous wave laser at 532 nm.

A 2D image of the thermochemical state in the ethanol ODH was captured through scanning measurements conducted with the OACC positioned on a computer-controlled 3-axis traverse. A novel spectral fitting routine was utilized to measure the concentrations of major species and temperature within this field. The results are depicted in maps, such as Fig. 1, which illustrates the relative acetaldehyde concentration. This map distinctly reveals the production of acetaldehyde in the vicinity of the pellet (from -5 to 5 mm in the flow direction). An asymmetrical conversion pattern around the pellet, influenced by the flow dynamics, is evident. Downstream of the pellet, the acetaldehyde concentration diminishes due to diffusive mixing with unreacted gases.

Overall, the integration of gas-phase Raman spectroscopy with an optically accessible catalytic channel offers unprecedented insights into the oxidative dehydrogenation of ethanol, that arecrucial for understanding transport phenomena and optimizing catalyst performance in practical applications.



*Figure 1.* Map of the acetaldehyde relative concentration for an average gas phase temperature of approximately 190 °C and a bulk flow velocity of 50 mm/s.



## First-principles microscopic modeling of spin states of iron-based systems

Young-Joon Song<sup>1,\*</sup>, Niklas von Rhein<sup>2</sup>, Charlotte Gallenkamp<sup>2</sup>, Genís Lleopart<sup>3</sup>, Vera Krewald<sup>2</sup>, and Roser Valentí<sup>1</sup>

 <sup>1</sup> Institut für Theoretische Physik, Goethe-Universität, 60438 Frankfurt am Main, Germany
 <sup>2</sup> Fachbereich Chemie, Theoretische Chemie, Technische Universität Darmstadt, 64287 Darmstadt, Germany
 <sup>3</sup> Departament de Ciéncia de Materials i Química Física and Institut de Química Teórica i Computacional (IQTC), Universitat de Barcelona, c/ Martí i Franqués 1-11, 08028 Barcelona, Spain \*ysong@itp.uni-frankfurt

The promising catalytic properties of single iron-based systems have attracted a lot of interest as an alternative to Pt-based catalysts. Despite a multitude of theoretical and experimental studies that have been dedicated to uncovering the ground state electronic and magnetic structure of iron, they still remain unclear. Here we address the microscopic investigation of the spin state of iron in various single iron-based systems via density functional theory-based calculations with the periodic boundary condition. Focusing on iron porphyrin-type molecules and FeN<sub>4</sub> center-embedded graphene systems, we examine how different environments influence the ground state of iron's spin. Our analysis, including a choice of optimal exchange-correlation functionals to properly deal with the 3*d* iron orbitals, suggests that differences in nitrogen environments result in different ground spin states of iron, which can influence an absorption process. Details will be discussed in the presentation.

This research was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for funding through CRC 1487.

#### Understanding vibrational temperature effects on Mössbauer parameters using a sampling approach

Niklas von Rhein<sup>1,\*</sup>, Vera Krewald<sup>1</sup>

<sup>1</sup> Department of Chemistry, Quantum Chemistry, Technische Universität Darmstadt, 64287 Darmstadt, Germany

\*Niklas.von\_rhein@tu-darmstadt.de

<sup>57</sup>Fe-Mössbauer spectroscopy is a powerful tool for investigating iron-containing species[1]. As an isotope specific method, it is especially useful for amorphous iron systems, such as FeNC catalysts[2,3]. While it yields information on spin state, oxidation state, and the iron atoms' coordination geometry, it lacks the ability to elucidate their exact chemical surroundings on its own. This can be overcome by using reference data from model complexes, which are often investigated theoretically using quantum chemistry methods[2].

In comparing experiment and theory, however, a problem arises: while experimental Mössbauer spectroscopy is temperature dependent[1], quantum chemical calculations assume resting nuclei at absolute zero. This necessitates the use of low temperature Mössbauer experiments, usually below 77 K, to enable comparison with quantum chemical calculations[2,3]. Such low-temperature measurements can be experimentally highly demanding and cannot probe reactive conditions, thus limiting the use of theoretical model complexes to non-reactive Mössbauer experiments.

We are aiming to develop a theoretical method that can account for the temperature dependence of the quadrupole splitting. To this end, the influence of structural deformation due to vibrations, which has a pronounced effect on the coordination symmetry, is probed via an ensemble of structures. Computationally investigating a large ensemble of chemically similar structures also promises a deeper understanding of the other Mössbauer parameters and their dependence on electronic and structural properties.



**Figure 1.** Schematic representation of the used theoretical approach for an exemplary FeN4 center: First, an ensemble at a given temperature is created from an initial structure. Then, the Mössbauer parameters of each structure are calculated.

#### References

[1] P. Gütlich, E. Bill, A. X. Trautwein, Mössbauer Spectroscopy and Transition Metal Chemistry, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011.

[2] C. Gallenkamp, U. I. Kramm, J. Proppe, V. Krewald, Calibration of computational Mössbauer spectroscopy to unravel active sites in FeNC catalysts for the oxygen reduction reaction, Int. J. of Quantum Chemistry 121 (2021) e26394

[3] L. Ni, C. Gallenkamp, S. Wagner, E. Bill, V. Krewald, U. I. Kramm, Identification of the Catalytically Dominant Iron Environment in Iron- and Nitrogen-Doped Carbon Catalysts for the Oxygen Reduction Reaction, J. Am. Chem. Soc. 144 (2022) 16827

#### New mechanistic insight into the oxidative dehydrogenation of ethanol over iron vanadate catalysts

Johannes Pfeiffer<sup>1,\*</sup>, Jan Welzenbach<sup>1</sup>, Christian Hess<sup>1</sup> <sup>1</sup> Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technical University of Darmstadt, 64287 Darmstadt, Germany \*johannes.pfeiffer@tu-darmstadt.de

Bulk mixed metal oxide catalysts, such as metal vanadates, show promising properties in the heterogeneous catalysis of various oxidative dehydrogenation (ODH) reactions. A major challenge associated with bulk oxides has been to unravel their mode of operation including the nature of active sites.<sup>1,2</sup> A surface enrichment of vanadium has been observed for iron vanadate FeVO<sub>4</sub> leading to the formation of amorphous VO<sub>x</sub> structures,<sup>2</sup> which have been shown to be active for ODH reactions.<sup>3</sup> In this study, *in situ* (transient) and *operando* methods are used to gain mechanistic insight into the ODH of ethanol over FeVO<sub>4</sub>, including surface and subsurface processes.

The FeVO<sub>4</sub> catalyst was synthesized by a co-precipitation method.<sup>4</sup> A solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O was added to a solution of NH<sub>3</sub>VO<sub>3</sub> (Fe:V = 1:0.9) and stirred for 1h at 100°C. The product was calcinated at 600°C for 10h. XPS was carried out for determination of element concentration on the surface. *Operando* Raman (514 nm), UV/vis and DRIFT spectroscopy were performed using a reaction feed of 5% EtOH/10% O<sub>2</sub>/N<sub>2</sub>. Transient modulation excitation (ME)-DRIFTS was performed by switching between 5% EtOH/10% O<sub>2</sub>/N<sub>2</sub> and 10% O<sub>2</sub>/N<sub>2</sub> and analyzed using phase-sensitive detection (PSD).<sup>5</sup>

Results of the activity study for ethanol ODH over FeVO<sub>4</sub> are shown in the left panel of Fig.1, FeVO<sub>4</sub> shows a high selectivity for acetaldehyde (>90%) for conversions up to ~55%. XPS analysis reveals a Fe:V surface ratio of 1:2.6, confirming vanadium enrichment at the FeVO<sub>4</sub> surface. *Operando* UV/vis spectroscopy during ethanol ODH at 170°C indicates a reduction of surface vanadium species, while *operando* DRIFT spectra at 170°C, shown in the right panel of Fig.1, display a decrease of the vanadyl peak (1000 to 1060 cm<sup>-1</sup>) corresponding to amorphous VO<sub>x</sub> structures.<sup>2,6</sup> The results of transient ME-DRIFTS confirm that amorphous surface VO<sub>x</sub> serves as active site within the catalytic mechanism of ethanol ODH over FeVO<sub>4</sub>. The application of *operando* DRIFT and transient ME-DRIFT spectroscopy provides a detailed insight into the adsorbate dynamics, as illustrated by the feature in the difference spectrum (2800 to 3000 cm<sup>-1</sup>) corresponding to dissociatively adsorbed ethoxy species.



Fig.1: (a) Activity study for ethanol ODH over FeVO<sub>4</sub>. (b) Operando DRIFT spectroscopy at 170°C.

In order to achieve a detailed mechanistic understanding of ethanol ODH over bulk FeVO<sub>4</sub> catalysts, (sub)surface processes are investigated using different *operando* and transient spectroscopic methods. In particular transient DRIFT spectroscopy is shown to be a powerful method for the surface investigation of bulk mixed metal oxides.

#### References

[1] C. Hess, R. Schlögl, eds., Nanostructured catalysts: selective oxidations. RCS, (2011).

- [2] K. Routray, W. Zhou, C.J. Kiely, I.E. Wachs, ACS Catal., 1 (2010) 54.
- [3] L. Schumacher, J. Pfeiffer, J. Shen, T. Gutmann, H. Breitzke, G. Buntkowsky, K. Hofmann, C. Hess, ACS Catal., 13 (2023), 8139.
- [4] J. Deng, J. Jiang, Y. Zhang, X. Lin, C. Du, Y. Xiong, Appl. Catal., B, 84 (2008) 468.
- [5] L. Schumacher, M. Radtke, J. Welzenbach, C. Hess, Commun. Chem., 6 (2023) 230.
- [6] D. Nitsche, C. Hess, J. Phys. Chem. C, 120 (2016) 1025.



## Influence of gas atmosphere on iron signatures in Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> as catalysts for the selective oxidation of ethanol

Lanjie Jiang<sup>1\*</sup>, Jan Welzenbach<sup>1</sup>, Hannah Wilhelm<sup>1</sup>, Anna Wenzel<sup>1</sup>, Kathrin Hofmann<sup>1</sup>, Christian Hess<sup>1</sup>, Barbara Albert<sup>1</sup>, Ulrike I. Kramm<sup>1</sup>

<sup>1</sup> Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt,

Germany

\*Lanjie.jiang@tu-darmstadt.de

Since several decades, iron molybdate (Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, noted as FMO) has been the industrial catalyst in oxidative dehydrogenation (ODH) of methanol (MeOH) to produce formaldehyde.[1] In the industrial catalyst, iron molybdate is typically prepared with an excess of molybdenum to enable good stability. The same kind of materials can be employed for ODH of ethanol (EtOH) with high selectivity and conversion to acetaldehyde, but rarely studied yet.[2] On the one hand, it is of crucial interest as FMO catalysts represent a non-toxic and cheap substitutional catalyst for acetaldehyde production in comparison to the Pd catalysts used in the Wacker-Höchst process. On the other hand, the exact role of Fe in the redox chemistry of the related reactions is not clear. To get further insights on the role of iron, by using Synchrotron <sup>57</sup>Fe Mössbauer spectroscopy couped to an *in situ* oven reactor, we like to follow structural changes at reductive and oxidative conditions of the catalyst.

In this work we will present lab-based in situ Mössbauer spectroscopic results to discuss the influence of gas atmosphere and temperature on the Mössbauer parameters as well as to deduce changes in absorption probability caused by gas atmosphere and temperature.

These results are important for the concrete design of experiment at the synchrotron.

- C. Brookes, M. Bowker, P. Wells, Catalysts for the Selective Oxidation of Methanol, Catalysts 6 (2016) 92. https://doi.org/10.3390/catal6070092.
- [2] N. Oefner, F. Heck, M. Dürl, L. Schumacher, H. Khatoon Siddiqui, U.I. Kramm, C. Hess, A. Möller, B. Albert, B.J.M. Etzold, Activity, Selectivity and Initial Degradation of Iron Molybdate in the Oxidative Dehydrogenation of Ethanol, ChemCatChem 14 (2022). https://doi.org/10.1002/cctc.202101219.



#### Magnetism and Reactivity of Square Planar Iron

<u>Tim Diederich<sup>1,\*</sup></u>, Maximilian Schrodt<sup>1</sup>, Markus Enders<sup>1</sup> <sup>1</sup> Karls-Ruprecht-Universität Heidelberg, Anorganisch-Chemisches Institut, Heidelberg, Germany \*t.diederich@stud.uni-heidelberg.de

Iron in a square-planar coordination is known to easily bind molecules in the vacant axial positions and transform them in catalytic or stoichiometric reactions. Most notably is the role of square-planar iron porphyrins systems used by nature for the transport and catalytic conversion of oxygen for example in proteins like cytochrome P450 and hemoglobin. Hence these systems have been studied extensively, yet there are many unresolved questions about the interactions of the iron center and its environment in these proteins. Even though model systems like porphyrins or phthalocyanines can be synthesised easily, they have a major drawback: Aggregation in the absence of axial ligands leading to low solubility. Therefore, we synthesised a scope of novel and known soluble non-aggregating four-coordinate iron phthalocyanine derivatives by incorporation of bulky substituents.<sup>[11]</sup> The resulting paramagnetic compounds show a high solubility even in non-coordinating solvents, giving the opportunity of a more in depth study of such systems by paramagnetic NMR spectroscopy. The selection of the bulky substituents allows for a change of the electronic structure leading to an additional insight in the paramagnetic nature of iron. NMR spectroscopy in combination with the high solubility further allowed to investigate and monitor the reactivity of such systems with a wide array of reagents in particular the stoichiometric and catalytic reaction with oxygen.<sup>[1]</sup>



Figure: Investigated bulky iron(II) phthalocyanines.

#### References

[1] Christian Iwanov, Moritz Hopp, Domenik Lorenz, Joachim Ballmann, Markus Enders, Dioxygen Activation and Reduction by a Soluble Iron Phthalocyanine, *Chem. Eur. J.*, 70 (2023) e202302761

#### Revealing underlying electronic transfer of FeN4-derived catalyst during CO<sub>2</sub>RR using Fouriertransformed alternating current voltammetry

Nicole Segura-Salas,<sup>1</sup> Rifael Z. Snitkoff-Sol,<sup>2</sup> Lior Elbaz,<sup>2</sup> Ulrike I. Kramm<sup>1</sup>

#### <sup>1</sup>Technische Universität Darmstadt

Catalysts and Electrocatalysts group, Department of Chemistry, Otto-Berndt-Str. 3, 64287 Darmstadt/Germany

## <sup>2</sup>Bar-Ilan Center for Nanotechnology and Advanced Materials and the Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

The electrochemical reduction of CO<sub>2</sub> (eCO<sub>2</sub>RR) has stood out as a promising method for converting CO<sub>2</sub> into value-added products. Significant progress has been made in recent years, particularly in terms of understanding the catalytic process through the dynamic changes of the active sites, <sup>1</sup> relying mostly on an *operando* spectroscopy approach.<sup>2–4</sup> However, the limited availability of these techniques can slow down the road to catalyst optimization. Other most common techniques, such as the dc I-V response at relevant potentials, do not offer the possibility of detailed analysis due to the high catalytic currents that dominate. As an alternative, Fourier-transformed alternating voltammetry (FTacV) presents a superior alternative to dc voltammetry, offering enhanced faradaic-to-non-faradaic current ratios. FTacV employs a large-amplitude sinusoidal perturbation as the alternating potential, allowing linear contributions, such as capacitance, to be isolated from the non-linear (Faradaic contributions). <sup>5</sup>

In this study, we explore iron phthalocyanine (FePc) adsorbed in high-surface carbon as a catalyst for the CO2RR. The bulk electrolysis characterization reveals a higher activity of the FePc/BP to  $CO_2RR$  as the production of CO is maintained even at high overpotentials. Under simple dc voltammetry, we were able to isolate the redox transitions before the reaction step, as well as during CO<sub>2</sub>RR. With FTacV, a process observed exclusively under CO<sub>2</sub> saturated electrolyte. was revealed. We show how, with this technique, it is possible to discover the overlaying redox processes during reaction-relevant conditions. This information can be used as a fast diagnostic tool for electrochemists, which can speed up the optimization strategies for molecular catalysts.

#### References

- 1 I. E. I. Stephens, K. Chan, A. Bagger and et al, *J Phys Energy*, 2022, **4**, 042003.
- 2 W. Zhu, S. Liu, K. Zhao, G. Ye, K. Huang and Z. He, *Small*, 2024, **20**, 1–9.
- 3 R. Khakpour, K. Farshadfar, S. T. Dong, B. Lassalle-Kaiser, K. Laasonen and M. Busch, *Journal of Physical Chemistry C*, 2024, **128**, 5867–5877.
- 4 Y. Zeng, J. Zhao, S. Wang, X. Ren, Y. Tan, Y. R. Lu, S. Xi, J. Wang, F. Jaouen, X. Li, Y. Huang, T. Zhang and B. Liu, *J Am Chem Soc*, 2023, **145**, 15600–15610.
- 5 M. J. Honeychurch and A. M. Bond, *Journal of Electroanalytical Chemistry*, 2002, **529**, 3–11.

#### Acknowledgments

A scholarship for N.S.S by the Bar-Ilan University through the Sandwich Scholarship program is appreciated. This work is financially supported by the DFG funded project CRC 1487, *Iron, upgraded!* (443703006)

#### Precisely Embedded Iron/Nitrogen Centers in N-doped Carbon Nanotubes for Electrocatalysis

Chandrajeet Mohapatra<sup>\*</sup>, Jörg J. Schneider <sup>1</sup> Technische Universität Darmstadt, Department of Chemistry, Eduard-Zintl-Institute for Inorganic and Physical Chemistry, Darmstadt, Germany \*chandrajeet.mohapatra@tu-darmstadt.de

FeN<sub>x</sub> doped carbon materials are very interesting for their electrocatalytic applications in the Oxygen Reduction Reaction (ORR).<sup>1</sup> The most documented routes for synthesis of these materials are pyrolysis of a combination of precursors which usually form larger metal clusters or nanoparticles along with the desired materials and other less well defined and characterized centers.<sup>2</sup> We are focusing on the development of a metal cluster impurity free method for synthesis of FeN<sub>x</sub> doped vertically aligned carbon nanotubes (Fe@VA-NCNTs) by implementing a kinetically controlled <u>solvated metal atom</u> dispersion, SMAD method for introducing single atom iron centers.<sup>3</sup> The successfully isolated material has also been characterized by SEM, TEM and EADX. The material also shows the desired electrocatalytic activity.



Fe@VA-NCNTs

Figure. SEM image and the ORR activity.

- [1] A. Zitolo, V. Goellner, et al., Nat. Mater., 14 (2015), 937.
- [2] R. Jiang, L. Li, et al., J. Am. Chem. Soc. 140 (2018), 11594.
- [3] K. Huang, L. Zhang, et al., Nat. Commun., 10 (2019), 606.



#### Spectroscopic and magnetic properties of iron phthalocyanines

<u>T. Zankel<sup>1,\*</sup></u>, J. Krampe<sup>2</sup>, R. Kornievskii<sup>2</sup>, K. Heckenberger<sup>1</sup>, V. Krewald<sup>2</sup>, C. M. Thiele<sup>1</sup> <sup>1</sup> Technische Universität Darmstadt, Clemens-Schöpf-Institut für Organische Chemie und Biochemie, Darmstadt, Germany <sup>2</sup> Technische Universität Darmstadt, Theoretische Chemie, Darmstadt, Germany

\*tzankel@thielelab.de

In iron phthalocyanines the central iron atom is coordinated by the phthalocyanine ring in square-planar geometry. Analogous to porphyrin systems in nature, these complexes exhibit catalytic activity due to the presence of unoccupied coordination sites in axial position<sup>[1,2]</sup>. Phthalocyanines are generally easily accessible, regarding cost and straightforward preparation, and their properties can be controlled by substitution of the ring system.<sup>[3]</sup> Electron-withdrawing substituents for example increase the stability and catalytic activity of phthalocyanines in oxidation reactions.<sup>[4,5]</sup> One of such complexes is perfluorinated iron phthalocyanine FePcF<sub>16</sub>.<sup>[6]</sup> Although iron phthalocyanines are often used as catalysts, there is a lack in knowledge of the mechanisms for these reactions.<sup>[1]</sup> In order to explain the chemistry of these complexes, their properties must first be understood.

Herein we present a study on FePcF<sub>16</sub> and its corresponding oxidized version [FePcF<sub>16</sub>]<sub>2</sub>O, as both of these species seem to be relevant for catalytic processes. We investigate their spectroscopic and magnetic properties with both experimental measurements and density functional theory analysis. We use UV/Vis spectroscopy together with TD-DFT calculations to gain information on the electronic structures of the complexes. Furthermore, we use (paramagnetic) NMR spectroscopy, including the Evans method,<sup>[7]</sup> to gain information on the magnetic properties of the complexes, including their spin state. We also aim to use NMR spectroscopy as a tool for structure elucidation of the complexes. However, if one attempts to measure the NMR spectra of the complex and its oxidation product, signal quantification does not give the expected results. The reason for this observation needs to be clarified. Understanding these complexes will help to fill the gaps of mechanisms in phthalocyanine chemistry.



Figure 1. Structures of hexadecafluoro iron phthalocyanine FePcF<sub>16</sub> and the µ-oxo-complex [FePc<sub>16</sub>]<sub>2</sub>O.

- [1] A. B. Sorokin, Chem. Rev., 10 (2013) 8152-8191. https://doi.org/10.1021/ic035263j
- [2] C. Iwanov, M. Hopp, D. Lorenz, J. Ballmann, M. Enders, *Chem. Eur. J.*, 70 (2023). https://doi.org/10.1002/chem.202302761
- [3] G. Löbbert, Phthalocyanines, in: Ullmann's Encyclopedia of Industrial Chemistry, (Ed.), 2012.
   Wiley-VCH Verlag GmbH & Co. KGaA
- [4] M.-S. Liao, T. Kar, S. M. Gorun, S. Schreiner, *Inorg. Chem.*, 22 (2004) 7151-7161. https://doi.org/10.1002/chem.202302761
- [5] F. Puls, F. Seewald, V. Grinenko, H.-H. Klauß, H.-J. Knölker, Chem. Eur. J., 67 (2021) 16776-16787. https://doi.org/10.1021/ic035263j
- [6] J. G. Jones, M. V. Twigg, *Inorg. Chem.*, 9 (1969) 2018-2019. https://doi.org/10.1021/ic50079a045
- [7] D. F. Evans, J. Chem. Soc., (1959) 2003-2005. https://doi.org/10.1039/jr9590002003



## The instability of FeNC catalysts in PEMFC and its dependence on carbon corrosion

<u>A.S. Ostroverkh\*</u>, V. Gridin, S. Yadav, P. Theis, H. Siddiqui, N. Segura-Salas, J. J. Schneider, U.I. Kramm

Technical University of Darmstadt, Department of Chemistry, Catalysts and Electrocatalysts Group, Otto-Berndt-Straße 3, 64287 Darmstadt, Germany \*anna.ostroverkh@tu-darmstadt.de

Clean energy issues are paramount in the transition to hydrogen energy and in achieving zero carbon dioxide emissions by 2050. At present, the cost and scarcity of platinum group materials is a major limitation to the widespread use of hydrogen-based energy sources. However, when used in electrochemical energy sources such as fuel cells, these materials are exemplary in activity and stability. FeNC catalysts are considered as possible alternative to platinum, but suffer during long-term operation.

The complexity of the synthesis of FeNC material consists in the creation of active catalytic centres, when the active iron atom is located between nitrogen atoms of pyrrole type [1], without the formation of inorganic iron components, such as iron nitride, iron carbide, iron oxide, etc. [2].

In principle several different degradation mechanisms are discussed. [3] In this work, we will explore the influence of carbon corrosion on the degradation of FeNC catalysts in PEMFC application. The concept is illustrated in Fig. 1. We are focusing on the *in situ* investigation of real fuel cell exhaust coupled with quadrupole mass spectrometry for the detection of CO<sub>2</sub> and applied this approach to a set of FeNC catalysts prepared at different pyrolysis temperatures and durations. [4].

We will discuss to what extent carbon oxidation contributes to the degradation and how the preparation conditions affect the degradation in the kinetic vs. mass transport regime.



*Figure.* Experimental set-up for accelerated stress testing: fuel cell system coupled with a quadrupole mass spectrometer.

#### References

[1] L. Ni, C. Gallenkamp, S. Wagner, E. Bill, V. Krewald, U. I. Kramm, J. Am. Chem. Soc. 144 (2022) 16827.

[2] U. I. Kramm, L. Ni, S. Wagner, Adv.Mater., 31 (2019) 1805623.

[3] V. Gridin, N. Segura-Salas, V. A. Saveleva, P. Theis, S. Haller, C. C. Ribeiro, K. Hofmann, R. Stark, U.I. Kramm, ACS Catal. 14 (2024) 10951.

[4] J. Scharf, M. Kubler, V. Gridin, W. D. Z. Wallace, L. Ni, S, D, Paul, U. I. Kramm, SusMat, 2 (2022) 630.



With a view to the importance of FeN<sub>4</sub> complexes in the oxygen reduction reaction (ORR), we have synthesized two series of novel Fe(II)N<sub>4</sub> complexes: In the 1<sup>st</sup> series the electronic nature of ligands (EDG, EWG) was systematically varied; in the 2<sup>nd</sup> series the  $\pi$  system of the ligands was enlarged to approximate the graphene backbone typical for FeN<sub>4</sub> materials. The respective Fe(II) complexes were synthesized using Fe(OAc)<sub>2</sub> in *n*-butanol at 180 °C. Fe(II) was oxidized to Fe(III) with CCl<sub>4</sub>. The redox chemistry of iron complexes exhibits up to four redox events involving iron and the ligand.



#### **References**

- [1] T. Marshall-Roth, N. J. Libretto, A. T. Wrobel, K. J. Anderton, M. L. Pegis, N. D. Ricke, T. V.
- Voorhis, J. T. Miller, Y. Surendranath, Nat. Commun., 11 (2020) 5283.
- [2] B. Weber, I. Käpplinger, H. Görls, E.G.J. Jäger, Eur. J. Inorg. Chem., 4 (2005) 465.

Fe

Iron, upgraded!

#### Molecular and Electronic Structures of High-valent Iron Nitrido Complexes

Zihan Zhang<sup>1\*</sup>, Weiqing Mao<sup>1</sup>, Frank W. Heinemann<sup>1</sup>, and Karsten Meyer<sup>1</sup>

<sup>1</sup> Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Department of Chemistry and Pharmacy, Inorganic Chemistry, Egerlandstraße 1, 91058 Erlangen, Germany \*zihan.zhang@fau.de

Employing the N-anchored tripodal N-Heterocyclic Carbene (NHC) ligand, TIMMN<sup>Mes</sup> (*tris*-[2-(3-mesitylimidazol-2-ylidene)methyl]amine), has facilitated the synthesis of iron complexes characterized by unique bonding patterns[1,2] and the unprecedented Fe(VII) oxidation state.[3] To further stabilize super-oxidized iron complexes, novel supporting ligands were developed, namely the saturated (<sup>sat</sup>TIMMN<sup>Mes</sup>) and its methylated derivative (<sup>Me2</sup>TIMMN<sup>Mes</sup>). These ligands were employed to stabilize new Fe(IV), Fe(V), and Fe(VI) nitrido complexes. Comprehensive structural, spectroscopic, and electrochemical analyses reveal the intricate molecular and electronic structures of this unique series of high-valent iron species.

#### References

[1] M. Keilwerth, L. Grunwald, W. Mao, F. W. Heinemann, J. Sutter, E. Bill, K. Meyer, *J. Am. Chem. Soc.* **2021**, *143*, 1458-1465.

[2] M. Keilwerth, W. Mao, S. A. V. Jannuzzi, L. Grunwald, F. W. Heinemann, A. Scheurer, J. Sutter, S. DeBeer, D. Munz, K. Meyer, *J. Am. Chem. Soc.* **2023**, *145*, 873–887

[3] M. Keilwerth, W. Mao, M. Malischewski, S. A. V. Jannuzzi, K. Breitwieser, F. W. Heinemann, A. Scheurer, S. DeBeer, D. Munz, E. Bill, K. Meyer, *Nat. Chem.* **2024**, *16*, 514-520.

### Operando NMR spectroscopic investigation of a Kumada-type ironcatalysed cross-coupling reaction

<u>Kilian Heckenberger<sup>1,\*</sup></u>, Christina M. Thiele<sup>1</sup> <sup>1</sup> Technical University of Darmstadt, Clemens Schöpf Institute for Organic Chemistry and Biochemistry, Darmstadt, Germany. \*kheckenberger@thielelab.de

Iron-catalysed cross-coupling reactions have gained increasing popularity in organic synthesis in the last two decades, therefore sparking interest in their mechanistic investigation as well.<sup>[1]</sup>

The majority of investigations have been conducted on the Kumada-type cross-coupling reaction, which uses magnesium as the transmetalating reagent. Among the Kumada-type reactions, different variants have been established. One of these is the CAHIEZ protocol, which uses *N*-methyl pyrrolidone (NMP) as a cosolvent. <sup>[2]</sup> The role of NMP in these reactions has been extensively studied (in particular by the NEIDIG group), using mainly Mössbauer, MCD and EPR spectroscopic techniques. <sup>[3]</sup>

NMR spectroscopy, being a highly multi-faceted tool in mechanistic analysis,<sup>[4]</sup> has been used before to characterise ferrate species in iron-catalysed cross-coupling reactions.<sup>[5,6]</sup> These studies highlight the difficulties of investigating iron-catalysed reactions in NMR, mostly originating in iron's paramagnetic nature. The effects are, for example, the paramagnetic shift of the signals, making chemical shifts hard to interpret, as well as fast spin relaxation which makes many 2D methods challenging to apply. Likely for that reason, a detailed *operando* NMR spectroscopic study has not yet been reported for these reactions.

Here, we use *operando* NMR spectroscopy to investigate the reaction of isobutyl magnesium bromide and methyl 4-chlorobenzoate with  $Fe(acac)_3$  as the precatalyst and THF-d<sub>8</sub> and NMP as solvent and cosolvent. Using the *operando* approach, we aim to correlate the behaviour of different reaction participants (ferrate species, reagents/products, solvent), therefore gaining a better picture of the reaction process as a whole.

- [1] A. Fürstner, Bull. Chem. Soc. Jpn., 2 (2021) 666-677.
- [2] G. Cahiez, H. Avedissian, Synthesis, 8 (1998) 1199-1205.
- [3] N. Bakas, M.L. Neidig, ACS Catal., 14 (2021) 8493-8503.
- [4] Y. Ben-Tal, P.J. Boaler, H.J.A Dale, R.E. Dooley, N.A. Fohn, Y. Gao, A. García-Domínguez, K.M. Grant, A.M.R. Hall, H.L.D. Hayes, M.M. Kucharski, R. Wei, G.C. Lloyd-Jones, *Prog. Nucl. Magn. Reson. Spectrosc*, (2022) 28-106.
- [5] R.B. Bedford, P.B. Brenner, E. Carter, P.M. Cogswell, M.F. Haddow, J.N. Harvey, D.M. Murphy, J. Nunn, C.H. Woodall, *Angew. Chem. Int. Ed.*, 7 (2014) 1804-1808.
- [6] V.J. Geiger, G. Lefèvre, I. Fleischer, Chem. Eur. J., 62 (2022) e202202212.



#### New insights into the longterm storage degradation of FeNC catalysts

Pascal Theis <sup>1</sup>, Xiaohua Yang <sup>2</sup>, Kathrin Hofmann<sup>1</sup>, Henrik Hoyer <sup>1</sup>, Miriam Seebach <sup>1</sup>, Lingmei Ni <sup>1</sup>, Ulrike I. Kramm<sup>1</sup>

<sup>1</sup>Technische Universität Darmstadt, Darmstadt, Germany <sup>2</sup>Institut national de la recherche scientifique, Québec, Canada \* Pascal.Theis@TU-Darmstadt.de

In case you include an image, please ensure that the copywrite is given and it can be reproduced in the frame of the meeting (book of abstract, homepage) FeNC materials are widely regarded as an enviromentally friendly and cost efficient alternative to precious group metal catalysts for the oxygen reduction reaction (ORR) in low temperature fuel cells (FC) [1]. While FC activity, operational stability as well as structural changes during operation are thoroughly investigated for these materials [2-3], very little is reported in a systematic way on the degradation of FeNC catalysts during storage [4].

In this work, we investigate the storage behavior of polypyrrole-based FeNC catalysts with different compositions introduced by different pyrolysis temperatures [5]. The catalysts were stored at different temperatures and gas atmospheres and the catalyst structure, composition and performance was measured at certain intervals (initially, 8 and 32 weeks). The aim was to understand if the degradation mechanism is independent from these parameters (i.e. always the same) or changes depending on the exact conditions.



*Figure 1:* FeNC catalyst degradation and impact on catalyst composition derived from the deconvoluted 5.5 K Mössbauer spectra of the initial catalyst (violet), and for different storage conditions (black, blue, red).

As shown in Figure 1 the investigated FeNC catalysts changes in its structural composition in all cases. Here the decomposition rate of the FeN<sub>4</sub> sites present in the catalyst increases with temperature as well with the gas atmosphere (compared to inert storage under argon). Further we can correlate the iron distribution inside the catalyst with it's performance which confirms our findings and further helps to understand the role of different iron species inside the catalyst.

- [1] M. Kübler, S. Wagner, T. Jurzinsky, S. Paul, N. Weidler, E. D. Gomez Villa, C. Cremers, U. I. Kramm, Energy Technol. 8 (2020), 202000433.
- [2] V. Gridin, M. Kübler, T. Hanstein, N. Heppe, N. Segura Salas, P. Theis, K. Hofmann, U. I. Kramm, J. Power Sources, 561 (2023), 232713.
- [3] L. Ni, C. Gallenkamp, S. Wagner, E. Bill, V. Krewald, U. I. Kramm, J. Am. Chem. Soc., 144 (2022), 16827.
- [4] J. Liu, X. Wan, S. Liu, X. Liu, L. Zheng, R. Yu, J. Shui, Adv. Mater., 33 (2021), 2103600.
- [5] J. Scharf, M. Kübler, V. Gridin, W. D. Z. Wallace, L. Ni, S. D. Paul, U. I. Kramm, SusMat, 2 (2022), 630.



## Post-mortem Mössbauer spectroscopy on PEM fuel cell degradation of an FeNC catalyst

Hendrik Haak<sup>1,\*</sup>, R. Snitkoff-Sol<sup>2</sup>, L. Elbaz<sup>2</sup>, U. I. Kramm<sup>1</sup> <sup>1</sup> Technical University of Darmstadt, Department of Chemistry, Catalysts and Electrocatalysts Group, Otto-Berndt-Straße 3, 64287 Darmstadt, Germany <sup>2</sup> Bar-Ilan University, Bar-Ilan Center for Nanotechnology and Advanced Matericals and the Department of Chemistry, 5290002 Ramat-Gan, Israel \*Hendrik.Haak@tu-darmstadt.de

The utilisation of hydrogen as an energy carrier in fuel cells represents a zero-emission solution for converting chemical energy into electric energy and heat. However, the kinetics of the oxygen reduction reaction (ORR) is sluggish making large amounts of catalysts necessary. Usually, platinum-based catalysts are used, but they are expensive and considered as critical raw materials by the EU. FeNC catalysts prepared from inexpensive precursors (C, N and Fe sources) can be used to substitute Pt/C. However, their stability needs to be improved. There are different degradation mechanisms reported for FeNC: demetallation [1], protonation [2], carbon oxidation [3], or micropore flooding [4]. The dominating mechanism might change depending on the reaction conditions and the type of FeNC catalyst.

In this work, we performed potential hold experiments to follow stepwise the degradation of an FeNC catalyst by *in situ* Fourier Transformed alternating current Voltammetry (FTacV) and *post mortem* Mössbauer spectroscopy. FTacV enables to track changes in side densities associated with redox active species, while *post mortem* <sup>57</sup>Fe Mössbauer spectroscopy, [5-6] gives an integral of iron-related changes induced by the different times of potentiostatic holds in a H<sub>2</sub>/Air fuel cell. By applying room temperature and low temperature Mössbauer spectroscopy we can discriminate FeN<sub>4</sub> moieties from iron oxide clusters [7]. Surprisingly, the amount of redox active iron is increasing while the overall performance and amount of FeN<sub>4</sub> sites goes down. We will discuss which iron environments were identified, how their composition changed over time and what conclusions may be drawn about the degradation mechanisms in the fuel cell on the basis of these results.

#### References

[1] M. Ferrandon, X. Wang, A. Kropf, D. Myers, G. Wu, C. Johnston, P. Zelenay, Electrochimica Acta, 110 (2023), 282.

[2] J. Herranz, F. Jaouen, M. Lefèvre, U. I. Kramm, E. Proietti, J. Dodelet, P. Bogdanoff, S. Fiechter, I. Abs-Wurmbach, P. Bertrand, T. Arruda, S. Mukerjee, The Journal of Physical Chemistry C, 115, 32 (2011), 16087.

[3] X. Wang, M. Swihart, G. Wu, Nature Catalysis, 2 (2019), 578.

[4] J. Choi, L. Yang, T. Kishimoto, X. Fu, S. Ye, Z. Chen, D. Banham, Energy & Environmental Science, 10, 1 (2017), 296.

[5] U. I. Kramm, M. Lefèvre, P. Bogdanoff, D. Schmeißer, J. Dodelet, The Journal of Physical Chemistry Letters, 5, 21 (2014), 3750.

[6] R. Snitkoff-Sol, A. Friedman, H. Honig, Y. Yurko, A. Kozhushner, M. Zachman, P. Zelenay, A. Bond, L. Elbaz, 5, 2 (2022), 163.

[7] L. Ni, C. Gallenkamp, S. Paul, M. Kübler, P. Theis, S. Chabbra, K. Hofmann, E. Bill, A. Schnegg, B. Albert, V. Krewald, U. I. Kramm, Advanced Energy & Sustainability Research, 2, 2 (2021), 2000064.



#### Spectroelectrochemical EPR and Mössbauer for Identifying Active Sites in FeNC Catalysts

<u>Kaltum Abdiaziz</u><sup>1</sup>, Lingmei Ni<sup>2</sup>, Sonia Chabbra<sup>1</sup>, Hendrik Haak<sup>2</sup>, Pascal Theis<sup>2</sup>,Derya Demirbas<sup>1</sup>, Ulrike I. Kramm<sup>2</sup>, Alexander Schnegg<sup>1</sup> <sup>1</sup> Max-Planck-Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany <sup>2</sup> Technische Universität Darmstadt, Darmstadt, Germany \*kaltum.abdiaziz@cec.mpg.de

FeNC, featuring FeN4 active sites, are regarded as top candidates for replacing noble metals like platinum (Pt) for the oxygen reduction reactions (ORR) in fuel cells. However, FeNC catalysts suffer from pyrolysis-induced inhomogeneity, containing various iron/ iron oxide species. These species can be identified through <sup>57</sup>Fe Mössbauer spectroscopy and some are accessible to electron paramagnetic resonance (EPR) spectroscopy. [1] Separately, in-situ Mössbauer (MS) and in-situ (quasi) EPR spectroscopy can be very powerful in identifying iron species and determining their oxidation and spin states, especially those crucial to the catalytical mechanism, however not without ambiguity. Therefore, we present a combinational in-situ Mössbauer and EPR spectroscopy study of FeNC catalysts in order to shed much-needed light on the ambiguity surrounding the assignment of Fe sites in FeNC materials. Correlation of in situ Mössbauer and in situ EPR spectroscopy identifies the generally observed and catalytically relevant MS doublet D1 as responsible for the EPR signal observed in FeNC materials. EPR spectroscopy indicates this Fe site is comprised of a distribution of high-spin Fe<sup>III</sup> ions (S = 5/2) with slightly different zero-field splitting and rhombicities (g=4.3 and g=2), as well as inorganic clustered iron (g=2). Dehydration of the FeNC catalyst gives rise to a g=6 signal traditionally observed for square planar FeN<sub>4</sub> in phathaolocyanaines and heme group. However, the assignment of high-spin Fe<sup>III</sup> ions environment is ambiguous, as similar EPR signals can be found in oxygen-coordinated glass [2] and iron zeolites ZSM-5 [3] Molecular structures of [LFe(n2-NO<sub>3</sub>)] [4] or Fe-N<sub>3</sub>-O<sub>3</sub> [5]



**Figure 1.** (A) In-situ EPR and in-situ Mössbauer cell, (B) Quasi in situ X-band CW EPR (T = 10K) spectra of FeNC catalyst in O<sub>2</sub> at different potentials, 0.9 V (orange), 0.75 V (green), 0.6 V (purple) and 0.2 V (yellow) (C) In situ Mössbauer (298 K) spectroscopy of FeNC catalysts (D) Bar graph of EPR intensity of signal at g = 4.3 and g = 2.6 to 1 signal as a function of potential (left) and of MS absorption areas of different fitted Fe species in FeNC catalyst.

#### References

[1] L. Ni, Gallenkamp. C..., et al. Advanced Energy and Sustainability Research 2.2 (2021), 2000064
[2] Ceglia, A. et al. Journal of Analytical Atomic Spectrometry 30.7 (2015),1552
[3] K. G. Padmalekha,...& V. Schünemann. Hyperfine Interactions 238 (2017), 1
[4] J. B. Strautmann,...& T. Glaser. Inorganic chemistry 47.15 (2008), 6804

[5] Y. J. Sun, Q. Q. Huang, & J. J. Zhang, *Acs Omega* 2.9 (2017),5850



## Effects of Au nanoparticles on the oxygen reduction reaction activity of FeN<sub>4</sub> centers

Lingmei Ni<sup>1</sup>, Kosovare Zullufi <sup>2</sup>, Nicole, Segura Salas<sup>1</sup>, Ashim KP, Muhammed <sup>1</sup> Ulrike I. Kramm<sup>1</sup> <sup>1</sup>Technische Universität Darmstadt, Darmstadt, Germany \*lingmei.ni@tu-darmstadt.de

Proton exchange fuel cells (PEFCs) are a clean technology for efficient conversion of chemical into electrical energy and are specifically promising for the decarbonization of heavy-duty vehicles. [1] To reduce the overall system cost, Iron-nitrogen-carbon (FeNCs) electrocatalysts hold great promise for replacing Pt-based catalysts for the oxygen reduction reaction (ORR). FeNCs are usually prepared by a high temperature pyrolysis (600-1000°C). While higher pyrolysis temperatures are beneficial for carbon conductivity and corrosion resistance, [2] as higher the temperature gets as larger is the probability that FeNC catalysts contain iron, iron oxide or iron carbide species beside the ORR active FeN<sub>4</sub> moieties. [2-4] In our recent work we showed that the removal of side phases leads to better activity and stability in FC. [5]

The addition of small quantities of precious group metal nanoparticles to FeNC was reported to change the ORR performance. [6-9] Depending on the selection of metal either a lowering of H<sub>2</sub>O<sub>2</sub>, acting as a radical scavenger or varying the electron density on iron centers were discussed as possible origins of changing performance. The discrepancy in interpretation might (partially) originate from the heterogeneity of the catalysts. This impedes to fully understand their impact on the FeN4 moieties. Based on this, herein we focus on Fe-phthalocyanine supported on carbon (FePc/C) as a model system containing the FeN4 motif. FePc/C was modified with different quantities of Au nanoparticles and the impact on ORR activity and selectivity was explored in 0.1 M KOH. We will discuss to what extent the performance data change depending on the amount of added nanoparticles, as exemplarily shown in **Figure 1**. Together with other physical characterization, such as <sup>57</sup>Fe Mössbauer spectroscopy, or Transmission electron microscopy, some insights about the mechanisms will be provided.



**Figure1.** (a) Comparison of kinetic current density and (b)  $H_2O_2$  yield for FePC/C and a gold modified FePc/C. Measurements performed in 0.1 M KOH with a catalyst loading of 0.51 mg cm<sup>-2</sup>.

#### References

[1] M. K. Debe, Nature. 486, 2012, 43

[2] J. Scharf, M. Kübler, V. Gridin, W. D. Z. Wallace, L. Ni, S. D. Paul, & U. I. Kramm. SusMat, 2022, 2(5), 630

[3] U.I. Kramm, I. Abs-Wurmbach, I. Herrmann-Geppert, J. Radnik, S. Fiechter, & P. Bogdanoff. Journal of the Electrochemical Society, 2010, 158(1), B69.

[4] U.I. Kramm, J. Herranz, et al. Phys. Chem.Chem.Phys. 14, 2012,11673

[5] V. Gridin, N. Segura-Salas, A. Saveleva, V. P. Theis, S. Haller, ... & U. I. Kramm. ACS Catalysis, 2024,14, 10951

[6] J-Y.Park, et al. Journal of Catalysis 359, 2018, 46-54.

[7] AK. Mechler, et al. Journal of The Electrochemical Society 165.13, 2018, F1084.

[8] V. Gridin, et al. Journal of Power Sources 561,2023, 232713.

[9] C. Prössl, M. Kübler, S. Paul, L. Ni, S. J. Kinkelin, N. Heppe, ... & U. I. Kramm. Journal of Materials Chemistry A, 2022, 10 (11), 6038

#### Low Valent Iron Complexes Utilizing Variations of the TIMMN Ligand Framework

<u>E. Körber<sup>1,\*</sup></u>, L. Gravogl<sup>1</sup>, F. W. Heinemann<sup>1</sup>, K. Meyer<sup>1</sup> <sup>1</sup> Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Department of Chemistry and Pharmacy, Inorganic Chemistry, Egerlandstraße 1, 91058 Erlangen, Germany \*eva.koerber@fau.de

The established TIMMN<sup>Mes</sup> ligand *tris-[(3-mesitylimidazol-2-ylidene)methyl]amine* and the new adamantyl derivative were utilized to synthesize the corresponding iron complexes [(TIMMN<sup>R</sup>)Fe<sup>II</sup>(CI)]<sup>+</sup> (1), [Fe<sup>I</sup>(TIMMN<sup>Ad</sup>)]<sup>+</sup> (2) and [(TIMMN<sup>Mes</sup>)Fe(L)]<sup>+</sup> (L = free site  $\eta^{1}$ -N<sub>2</sub>, CO, py) (3) complexes. Complexes 1 – 3 demonstrate the notable steric and electronic flexibility of the TIMMN<sup>R</sup> framework by variation of the Fe–N anchor and Fe–carbene distances, as well as the variable size of the axial cavity. This is illustrated by the oxidation of 3<sup>Mes</sup>-N<sub>2</sub> and 2 in a reaction with benzophenone to yield the corresponding, charge-separated Fe(II) radical complex [(TIMMN<sup>R</sup>)Fe(OCPh<sub>2</sub>)]<sup>+</sup> (4). Further reduction of 3<sup>Mes</sup>-N<sub>2</sub> leads to the Fe(0) complex [(TIMMN<sup>R</sup>Fe(CO)<sub>3</sub>] (5). In conclusion, the tris(carbene) chelate is not only capable of stabilizing the super-oxidized Fe(VI) and Fe(VII) nitrides but equally supports the iron ion in very low oxidation states, namely 0 and +1.

#### References

[1] M.Keilwerth, W.Mao, M.Malischewski, S.A.V.Jannuzzi, K.Breitwieser, F.W.Heinemann, A.Scheurer, S.DeBeer, D.Munz, E.Bill, K.Meyer, *Nat. Chem.*, 16 (2024) 514.
[2] L.Gravogl, M.Keilwerth, E.Körber, F.W:Heinemann, K.Meyer, submitted.

## Developing a channel flow cell for tracking the dissolution during operando measurements

Sumin Lim<sup>1</sup>, Pallabi Bhuyan<sup>1</sup>, Marc Ledendecker<sup>1,\*</sup>

#### <sup>1</sup> Sustainable Energy Materials, Technical University of Munich, Straubing

#### \*marc.ledendecker@tum.de

The stability of iron (Fe) is a major concern for the oxygen reduction reaction (ORR) since it is prone to dissolution in aqueous media.<sup>[1,2]</sup> Coupling of a channel flow cell (CFC) with an inductively coupled plasma mass spectrometry (ICP-MS) is imperative for tracking the dissolution of the ORR catalysts and this objective mandate the development of an appropriate CFC<sup>[3]</sup>. In this study, a new leakage-free CFC has been designed, and the performance of this setup has been investigated by comparing the corresponding measurements with those of a typical rotating disk electrode (RDE) setup. A schematic illustration of the CFC setup at room temperature is presented in Figure 1(a). We have employed a circular glassy carbon electrode as a working electrode in our cell design to obtain a homogenous catalyst layer. A close look at Figure 1(a) reveals that both, the working and the reference electrodes can be easily installed and uninstalled, making the cell geometrically flexible for batch measurements. In addition, the measurements were also carried out at higher temperatures to study the degradation behavior under operating condition of PEMFC. The CFC set-up can be effectively coupled to ICP-MS (Figure 1(b)) for tracking dissolution during operando measurements. As a proof of concept, the performance of the CFC set-up has been assessed on Fe-based and Pt-based catalysts for the ORR.



Figure 1: Schematic showing the coupling of the CFC (a) with the ICP-MS (b) to track the dissolution during operando measurements.

- [1] M. Ledendecker, S. Krick Calderón, et al. Angew. Chem. Int. Ed. 2015, 54, 12361.
- [2] M. Ledendecker, J. S. Mondschein, et al. Angew. Chem. Int. Ed. 2017, 56, 9767.
- [3] ] E. Kolle-Görgen, Master thesis, 2021

#### Magnetism of transition-metal doped tetrel nanoclusters: Multi-reference character and spin-orbit effects in $Sn_{12}TM$ (TM = Cr, Mn, Fe)

Jannik Mehmel<sup>1\*</sup>, Carlos M. Jimenez-Muñoz<sup>1</sup>, Filip Rivic<sup>1</sup>, Alexander Macion<sup>1</sup>, Vera Krewald<sup>1</sup>, Rolf Schäfer<sup>1</sup>\_ <sup>1</sup> Technical University of Darmstadt, Eduard-Zintl-Institute, Peter-Grünberg-Straße 8, 64287 Darmstadt

\*jannik.mehmel@wihi.tu-darmstadt.de

The magnetic behavior of endohedrally transition-metal doped tetrel clusters Sn<sub>12</sub>TM (TM = Cr, Mn, Fe) was investigated by a combined experimental and theoretical approach. Based on an improved experimental setup, the magnetic deflection was measured over a wide temperature range of  $T_{nozzle}$  = 16 - 240 K. From a Curie analysis of the experimentally observed single-sided shift at high nozzle temperatures, the spin multiplicities and g-factors were determined. It was observed that all three nanoclusters analyzed are paramagnetic, with  $Sn_{12}Mn$  being a sextet with  $q = 2.1 \pm 0.1$ , while  $Sn_{12}Cr$ is a quintet with the same q-factor and  $Sn_{12}Fe$  is also a quintet but with a higher q-factor of 2.4 ± 0.1. In order to better understand the interplay of geometric and electronic structure and their influence on the magnetism, a global geometry optimization followed by a guantum-chemical analysis of the electronic structure using density functional theory (DFT) and wavefunction methods was carried out. The multi-reference calculations proved particularly important for Sn<sub>12</sub>Fe because DFT fails to predict the value of the g-factor correctly. To describe the electronic ground state of Sn<sub>12</sub>Fe, two reference configurations must be taken into account. A charge transfer from the Sn ligands to Fe manifests in very low-lying electronic excitations. These charge transfer excitations lead to a significant increase in the g-factor compared to the value of the free electron due to the large spin-orbit coupling constant of Sn. As a result, in contrast to  $Sn_{12}$ Mn and  $Sn_{12}$ Cr, the spin density of  $Sn_{12}$ Fe is strongly delocalized over the entire cluster framework.



*Figure 1:* Magnetic beam deflection shows an enhanced g-factor for  $Sn_{12}Fe$ . CASSCF calculations reveal the multi-reference character of  $Sn_{12}Fe$  and a charge transfer from Sn 5p to Fe 3d orbitals. Spin-orbit contributions of the Sn atoms enhance the g-factor.

#### In situ Monitoring of Hydrogenation and Isotope Scrambling Reactions by High-Field NMR

Bingyu Zhang<sup>1,\*</sup>, J. Kergaßner <sup>1</sup>, F. Theiß<sup>1</sup>, J. Lins<sup>1</sup>, T. Gutmann<sup>1</sup>, G. Buntkowsky<sup>1</sup> <sup>1</sup> Eduard-Zintl-Institute for Inorg. and Phys. Chemistry, Darmstadt, Germany \*bingyu.zhang@tu-darmstadt.de

An overview on the progress made in subproject C04 is given, focusing on the development and application of an experimental setup for NMR investigation of the heterogeneously iron-catalyzed hydrogenation of alkynes and alkenes. The aim of this subproject is to enhance the understanding of the hydrogenation process on iron containing catalysts through HD-scrambling experiments and to explore the potential of parahydrogen induced hyperpolarization (PHIP).

A versatile experimental setup has been constructed capable of performing hydrogenation reactions with normal or parahydrogen both *in-situ*, within an NMR spectrometer, and *ex-situ*, in a specially designed reaction chamber. The optimized setup allows for mixing of hydrogen/parahydrogen and alkenes/alkynes in gas phase, and in solution by bubbling relevant gases through the reaction mixture. To evaluate the new experimental setup, a range of model catalysts, including platinum and palladium on different support materials, have been tested. It has been found that all tested catalysts are effective for both *in-situ* and *ex-situ* hydrogenation within the designed setup. However, so far, the PHIP effect has only been obtained for *in-situ* gas phase experiments using parahydrogen and Pt, Pd catalysts. Additionally, PHIP has been achieved for dissolved propene in the presence of a rhodium catalyst with an iron-containing ligand system <sup>1</sup> (Figure 1), marking a significant milestone for the subproject C04.



**Figure 1.** <sup>1</sup>H spectrum of propene, dissolved in MeOD containing an Rh-catalyst and an iron containing ligand. The experiment was performed by bubbling para-enriched hydrogen through the solution in-situ. The spectrum shows the typical PHIP signal pattern for the product propane.

**Figure 2.** Experimental curves of the four catalysts applied in HD isotope scrambling reaction obtained with the automated setup.

Next to this, a novel technical testing framework for in-situ and ex-situ hydrogenation experiments has been established on a 500 MHz spectrometer. The test approach involves background measurement, activation measurement, gas leakage measurements, and HD exchange experiments and was evaluated at four different catalysts. The results obtained with the automated setup show that the Pt catalyst has a unique impact on HD exchange reactions (Figure 2) while the other catalysts show almost the same behavior. To understand this, currently research is being conducted on surface hydrogen using variable temperature <sup>2</sup>H solid-state NMR. Furthermore, gas phase Raman analysis is planned in collaboration with the subproject A03 to clearly distinguish between HD gas and H<sub>2</sub> gas produced during experiments.

#### References

[1] S. Nasemann, R. Franz, D. Kargin, C. Bruhn, Z. Kelemen, T. Gutmann, R.\* Pietschnig, At the Limits of Bisphosphonio-substituted Stannylenes. Chem. Asian J.,19 (2024) e02300950.

#### Machine learning modelling of Mössbauer spectroscopy for Febased intermetallic compounds

Bo Zhao\*, K. Hu2, H. Zhang1

<sup>1</sup> Institute of Materials Science, Technische Universität Darmstadt, Darmstadt, Germany <sup>2</sup> School of Materials Science and Engineering, Central South University, Changsha, PR China \*bo.zhao@tmm.tu-darmstadt.de

Mössbauer spectroscopy plays a crucial role in materials characterization by providing detailed information about the local environment and electronic structures of specific atomic species, including their oxidation state, coordination geometry, and spin configuration. However, extracting meaningful insights from Mössbauer spectra often requires sophisticated analysis techniques and a deep understanding of the underlying crystal structures, which can be challenging to determine experimentally, especially for complex materials systems. In this work, we demonstrate a quantitative mapping between the local crystalline environments and Mössbauer spectra based on accurate density functional theory (DFT) calculations and machine learning techniques. The scarcity of high-quality data is remedied by establishing and performing high-throughput DFT workflows to evaluate the Mössbauer spectra of 28, 408 Fe-based binary intermetallic compounds, including the chemical shift, the quadruple splitting and the hyperfine fields. Based on the datasets, we further employ machine learning techniques to model the mapping between the local crystalline environments and the Mössbauer spectra. It is observed that the machine learning accuracy for the hyperfine fields can be as high as 94%. This paves the way for automatized analysis of the experimental observations and mapping of the local crystalline environments and spectra.



#### Iron Oxides for Innovative, Safe and Sustainable Energy Storage

<u>Magdalena Pauritsch1</u>\*, M. Lammer<sup>1</sup>, C.Pröll<sup>1</sup>, C. F. Blaschke<sup>1</sup>, V. Hacker<sup>1</sup> <sup>1</sup> Institute of Chemical Engineering and Environmental Technology, Graz University of Technology, Austria \*magdalena.pauritsch@tugraz.at

Chemical looping as a novel approach to energy conversion holds immense promise for sustainable hydrogen storage. Among the various materials used in chemical looping processes, iron stands out as a particularly effective and versatile candidate. Utilizing the unique properties of iron, chemical looping opens doors to efficient hydrogen storage, carbon capture, and beyond, offering a pathway to a cleaner and more sustainable energy landscape [1].

At the heart of chemical looping with iron lies the principle of redox reactions, where iron-based materials undergo cyclic oxidation and reduction reactions. This facilitates the conversion of energy carriers such as hydrogen or carbonaceous fuels [2]. Furthermore, iron-based chemical looping offers a versatile platform for integrated energy systems, enabling synergies between hydrogen production, carbon capture, and renewable energy sources. By coupling chemical looping with renewable energy sources such as solar or wind, excess energy can be stored as energy potential in the material during periods of low demand and subsequently released when needed, enhancing grid stability and reliability. In the context of an energy storage system, iron serves as an oxygen carrier for the chemical looping hydrogen (CLH) process HyLoop. The research group at CEET has investigated the CLH process regarding the material for the oxygen carrier and used this in hydrogen production as a process step for purifying the produced hydrogen. Numerous publications in recent years show the enormous potential of the technology as well as its competitiveness with other materials and currently available storage technologies [3], [4], [5]. A recent study then showed the potential to also utilize natural iron ores directly for cheap and environmentally friendly energy storage [6].



Figure 1. Schematic depiction of an iron-based storage system for seasonal energy storage called HyLoop

#### References

[1] B. Stoppacher, T. Sterniczky, S. Bock, and V. Hacker, **Energy Convers. Manag**., vol. 268, 2022. doi.org/10.1016/j.enconman.2022.115971

[2] M. Lammer and V. Hacker, Current Trends and Future Developments on (Bio-) Membranes: New Perspectives on Hydrogen Production, Separation, and Utilization, **Elsevier** Inc., 2020, pp. 225–240.

[3] T. Block and M. Schmücker, "Metal oxides for thermochemical energy storage: A comparison of several metal oxide systems," **Solar Energy**, vol. 126, pp. 195–207, 2016, <u>doi: 10.1016/j.solener.2015.12.032</u>.

[4] S. P. Heiniger, Z. Fan, U. B. Lustenberger, and W. J. Stark, "Safe seasonal energy and hydrogen storage in a 1 : 10 single-household-sized pilot reactor based on the steam-iron process," **Sustain Energy Fuels**, vol. 8, no. 1, pp. 125–132, Nov. 2023, <u>doi: 10.1039/d3se01228j.</u>

[5] L. Brinkman, B. Bulfin, and A. Steinfeld, "Thermochemical Hydrogen Storage via the Reversible Reduction and Oxidation of Metal Oxides," vol. 35, pp. 18756–18767, 2021, <u>doi:</u>

10.1021/acs.energyfuels.1c02615.

[6] S. Bock, M. Pauritsch, S. Lux, and V. Hacker, "Natural iron ores for large-scale thermochemical hydrogen and energy storage," **Energy Convers Manag**, vol. 267, p. 115834, Sep. 2022, <u>doi:</u> 10.1016/j.enconman.2022.115834.


# List of participants

## List of Participants

Name	Institution	Country
Dr. Kaltum Abdiaziz	Max Planck Institute for Chemical Energy Conversion, Mülheim a. d. Ruhr	Germany
Prof. Dr. Barbara Albert	Technical University of Darmstadt	Germany
Prof. Dr. Lambert Alff	Technical University of Darmstadt	Germany
Prof. Dr. Marc Armbrüster	Chemnitz University of Technology	Germany
Prof. Dr. Matthias Bauer	Paderborn University	Germany
Dr. Dimitrios Bessas	European Synchrotron Radiation Facility, Grenoble	France
DrIng. Daniël L J Broere	Utrecht University	Netherlands
Prof. Dr. Gerd Buntkowsky	Technical University of Darmstadt	Germany
Julia Buschermöhle	Deutsches Zentrum für Luft- und Raumfahrt e. V. (DLR), Oldenburg	Germany
JunProf. Alicia Casitas	Philipps-Universität Marburg	Germany
Dr. Bruno Chaudret	LPCN0 INSA-CNRS Toulouse	France
Prof. Dr. Oliver Clemens	University of Stuttgart	Germany
Giovanni d'Andrea	Technical University of Darmstadt	Germany
Tim Diederich	Heidelberg University	Germany
Dr. Imants Dirba	Technical University of Darmstadt	Germany
Prof. DrIng. Alfons Drochner	Technical University of Darmstadt	Germany
Prof. Dr. Markus Enders	Heidelberg University	Germany
Prof. Dr. Tanja Franken	FAU Erlangen-Nürnberg	Germany
Prof. DrIng. Dirk Geyer	Darmstadt University of Applied Sciences	Germany
Ansuree Ghosh	Technical University of Darmstadt	Germany
Prof. Dr. Jan-Dierck Grunwaldt	Karlsruher Institut für Technologie	Germany
apl Prof. Dr. Torsten Gutmann	Technical University of Darmstadt	Germany
Hendrik Haak	Technical University of Darmstadt	Germany
Kilian Heckenberger	Technical University of Darmstadt	Germany
Prof. Dr. Christian Hess	Technical University of Darmstadt	Germany
Prof. Dr. Jan Philipp Hofmann	Technical University of Darmstadt	Germany
Dr. Kathrin Hofmann	Technical University of Darmstadt	Germany
Lanjie Jiang	Technical University of Darmstadt	Germany

Iron, upgraded! CRC 1487

## List of Participants

Name	Institution	Country
Carlos M. Jimenez-Muñoz	Technical University of Darmstadt	Germany
Dr. Lukas Kaltschnee	Technical University of Darmstadt	Germany
Sun Myung Kim	Technical University of Darmstadt	Germany
Eva Körber	FAU Erlangen-Nürnberg	Germany
Konrad Koschnick	Technical University of Darmstadt	Germany
Prof. Dr. Ulrike Kramm	Technical University of Darmstadt	Germany
Justin Krampe	Technical University of Darmstadt	Germany
Prof. Dr. Vera Krewald	Technical University of Darmstadt	Germany
Dr. Lenka Kubickova	Johannes Gutenberg University Mainz	Germany
Hannah Lamers	Technical University of Darmstadt	Germany
Dr. Michael Lammer	Graz University of Technology	Austria
Sumin Lim	Technical University of Munich	Germany
Prof. Dr. em. Hans-Heinrich Limbach	Freie Universität Berlin	Germany
Prof. Dr. Christine McKenzie	University of Southern Denmark	Denmark
Jannik Mehmel	Technical University of Darmstadt	Germany
Dr. Chandrajeet Mohapatra	Technical University of Darmstadt	Germany
Prof. Dr. Angela Möller	Johannes Gutenberg University Mainz	Germany
Mohsin Muhyuddin	University of Milano Bicocca	Italy
Dr. Stephan Müssig	FAU Erlangen-Nürnberg	Germany
Prof. Dr. Martin Muhler	Ruhr University Bochum	Germany
Dr. Deborah J. Myers	Argonne National Laboratory	USA
Prof. Dr. Frank Neese	Max-Planck-Institut für Kohlenforschung	Germany
Dr. Lingmei Ni	Technical University of Darmstadt	Germany
Dr. Anna Ostroverkh	Technical University of Darmstadt	Germany
DiplIng. Magdalena Pauritsch	Graz University of Technology	Austria
Prof. Dr. Jasnamol Pezhumkattil Palakkal	Georg-August-University of Göttingen	Germany
Johannes Pfeiffer	Technical University of Darmstadt	Germany

Iron, upgraded! CRC 1487

## List of Participants

Name	Institution	Country
Prof. Dr. Herbert Plenio	Technical University of Darmstadt	Germany
Prof. Dr. Marcus Rose	Technical University of Darmstadt	Germany
Dr. Christian Rurainsky	LANXESS Deutschland GmbH	Germany
Prof. Dr. Rolf Schäfer	Technical University of Darmstadt	Germany
Prof. Dr. Dr. h.c. Robert Schlögl	Alexander von Humboldt Foundation /Fritz Haber Institute of the MPG	Germany
Dr. Alexander Schnegg	MPI for Chemical Energy Conversion	Germany
Prof. Dr. Jörg Schneider	Technical University of Darmstadt	Germany
Nicole Segura Salas	Technical University of Darmstadt	Germany
Mathias L. Skavenborg	University of Southern Denmark	Denmark
Young-Joon Song	Goethe University Frankfurt	Germany
Danny Stark	Technical University of Darmstadt	Germany
Pascal Theis	Technical University of Darmstadt	Germany
Prof. Dr. Christina Marie Thiele	Technical University of Darmstadt	Germany
Niklas von Rhein	Technical University of Darmstadt	Germany
Anna Katharina Weber	Johannes Gutenberg University Mainz	Germany
Jan Welzenbach	Technical University of Darmstadt	Germany
Hannah Wilhelm	Technical University of Darmstadt	Germany
Dr. Juliusz Wolny	RPTU Kaiserslautern-Landau	Germany
Timon Zankel	Technical University of Darmstadt	Germany
Bingyu Zhang	Technical University of Darmstadt	Germany
Zihan Zhang	FAU Erlangen-Nürnberg	Germany
Bo Zhao	Technical University of Darmstadt	Germany

### **Overview rooms**



