Research Project #25

Operando investigation of materials for ammonia cracking (INW-1 & INW-4)

Green ammonia (NH_3) holds significant potential for renewable energy storage and transportation. Due to its high hydrogen capacity, favorable liquefaction properties, and well-established global infrastructure for distribution and handling, it is considered as one of the most promising hydrogen carriers [1-4]. Hydrogen regeneration from ammonia involves an endothermic cracking reaction

$$2NH_3 \rightleftharpoons N_2 + 3H_2 \quad \Delta H = 91.2 \text{ kJ/mol}$$

This reaction is typically carried out at high temperatures (> 400 °C) and relatively high pressures (up to tens of bar) [2,3]. It is accelerated using a heterogeneous catalyst (e.g., Ru, Ni, Fe, Co, Fe–Co) [2-4]. An associated challenge is the potential for materials degradation due to nitridation. The harsh cracking environment causes atomic nitrogen to react with the steel surface of the reactor and/or the active components of the catalyst. This may result in restructuring of the material and the formation of undesired nitride layers. Under true reaction conditions, the respective phenomena are challenging to investigate mechanistically. For example, hardly any data for rapid nitridation of steel above 600°C exists [5]. To ensure high performance and longevity of reactors and catalysts, it is essential to gain a comprehensive understanding of these degradation processes.

Towards this end, **this PhD project aims to investigate the atomic scale and microstructural degradation of materials during ammonia cracking through advanced *in situ* and *operando* X-ray characterization techniques**. By employing both surface- and bulk-sensitive X-ray-methods — such as diffraction, reflectometry, spectroscopy, and imaging [6] — we seek to gain detailed **mechanistic insights into material behaviour under true reaction conditions**. Understanding changes in (bulk) structure, surface properties, and oxidation states across scales is essential for optimizing catalysts and reactor materials for the cracking process.

A central focus of the project is to examine the nitridation of reactor walls under reaction conditions, a phenomenon that can accelerate reactor degradation [7]. Various types of steel, including austenitic and high-strength alloys, will be tested. Additionally, the project will explore the effects of the bulk nitridation on the active components of catalysts, investigating both reversible and irreversible structural and surface changes that occur during the cracking process [8]. Catalysts based on Ru, Ni, Co, and Fe will be characterized across different modifications and supports. The *operando* studies of catalyst behaviour under reaction conditions will provide essential information to support the development and testing of promising new catalyst candidates, where nitridation can be suppressed. We expect that we will unravel the time-scales of nitridation and long-term evolution and stability of nitride layers. The insights we gain can guide the proposal and selection of enhanced reactor and catalyst materials for ammonia cracking.

To accomplish these goals, we will use a combination of various complementary X-ray methods to reveal structure, morphology, and chemistry of nitride layers. We will employ sample systems of various complexity, from thin films and steel sheets in gas environment to realistic reactors during operation. A specialized experimental setup will be designed to enable measurements under realistic process conditions, including controlled gas flow and high temperatures and pressures. This setup will be carefully adapted to meet the unique requirements of each characterization technique and will be initially tested using state-of-the art laboratory X-ray machines on model materials such as thin iron films and bulk catalyst crystals. Upon optimization, the setup will be used to conduct experiments on actual reactors and respective realistic components and catalysts. These investigations will also be carried out using international large-scale research facilities, such as synchrotron X-ray sources. These are located for example in Grenoble/France, Hamburg/Germany, Chicago/US, or Stanford/US. This will enable high time resolution and high-throughput investigations under systematically varied conditions to generate large combinatorial data sets, which are analysed using advanced big data analytics and

machine learning approaches. The X-ray experiments will be complemented with comparable experiments using neutrons or electrons.

In summary, the PhD project will involve the following key tasks:

- Development of experimental setup for *in situ* X-ray-based characterization during ammonia cracking
- Investigation of reactor steel wall nitridation during reaction conditions (at synchrotron sources)
- Investigation of catalyst nitridation during reaction conditions (at synchrotron sources)
- Analysis and interpretation of experimental data, including big data analytics
- Presentation of research findings at conferences and publication in peer-reviewed scientific journals

Location of the HITEC Fellow	Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy - Catalytic Interfaces for Chemical Hydrogen Storage (INW-1), Director: Prof. Dr. Hans-Georg Steinrück https://www.fz-juelich.de/de/inw/unsere-bereiche/inw-1
Partners of the HITEC Project	Forschungszentrum Jülich, Institute for a Sustainable Hydrogen Economy - Process and Plant Engineering for Chemical Hydrogen Storage (INW-4), Director: Prof. Dr. Andreas Peschel https://www.fz-juelich.de/de/inw/unsere-bereiche/inw-4
Specific **requirements**	M.Sc. in Physics, Materials Science, or Chemistry. Experience with structural characterization methods — such as scattering, spectroscopy, or imaging using neutrons, X-rays, or electrons — is highly desirable. Proficiency in data analysis, particularly with Python, is also an advantage.
For **project specific** questions please **contact**	Prof. Dr. Hans-Georg Steinrück, INW-1, h.steinrueck@fz-juelich.de Prof. Dr. Andreas Peschel, INW-4, a.peschel@fz-juelich.de

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[2] S. Sun *et. al.*: Ammonia as hydrogen carrier: Advances in ammonia decomposition catalysts for promising hydrogen production. (2022) *Renew. SustEnerg. Rev.* 169, p. 112918.
[3] M. Asif *et. al*: Recent advances in green hydrogen production, storage and commercial-scale use via catalytic ammonia cracking. (2023) *Chem. Eng. J.* 473, p. 145381.
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[5] N. Laws *et al.*: Design and Performance Assessment of an Experimental Rig to Conduct Material Nitridation Studies at Extreme Ammonia Conditions (2023) *Turbo Expo: Power for Land, Sea, and Air*. Vol. 86946. American Society of Mechanical Engineers.
[6] J. Baruchel *et al.* (1994). *Neutron and synchrotron radiation for condensed matter studies. Volume 1: theory, instruments and methods.* 1st edition, Springer Berlin, Heidelberg.
[7] F. Yanagimoto *et al.*: Stress corrosion cracking of steels in liquid ammonia: A comprehensive literature review (2025) *Int. J. Hydrogen Energy* 120, p.89.
[8] S. Pperego *et al.*: No Time for Nitrides: How Cobalt Alloying Promotes Iron Catalysts for Ammonia Decomposition (2025) *ACS Catal.* 15, p. 16690.