

STXM study of Fe-based NH₃ synthesis and decomposition catalyst

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The conversion of dinitrogen to ammonia is a process of fundamental biological and industrial importance. Although the industrial Haber-Bosch process is known for over 100 years now, the exact mechanism by which the heterogeneous Fe-based catalysts cleave the triple bond of dinitrogen remains unknown. Much of our current understanding is based on pioneering studies by Ertl, Somoraji and many others, who investigated idealized iron surfaces and suggested that dinitrogen was absorbed as surface nitrides. However, despite decades of research, the surface nitrides have never been observed in the industrial catalyst and there are still many open questions regarding their nature and the oxidation state of the “active” iron.

For the purpose of *in operando* studies of Fe-based ammonia synthesis and decomposition catalyst STXM (Scanning Transmission X-ray Microscopy) was used. The samples were loaded into nanoreactors which allow for achieving pressures up to several bars and at the same time provide enough transmission for soft X-rays. The very high spatial resolution of ~25 nm which the STXM method offers is essential for the unique identification of the surface and bulk nitrides which are formed during the catalytic process. XAS spectra were measured at N K-, O K- and Fe L-edges.

The obtained *in situ* spectra allowed for the evolution of the catalyst at different stages of the reaction to be observed. Comparison to the *ex situ* reference samples of the calcined and reduced catalyst confirmed the successful calcination, and consequent full reduction of the catalyst. Also, preliminary *in situ* spectra of the catalyst under pressure of N₂ were collected. We believe that the use of *in situ* STXM nanoreactors will provide fundamental insights into the mechanism by which iron-based catalysts can effectively enable dinitrogen reduction. Hence, these results form a basis for future knowledge-inspired catalytic design.

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