The Haber-Bosch process revisited: On the real structure and stability of "ammonia iron" under working conditions

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Dedicated to the Ammonia Laboratory of BASF SE in Ludwigshafen on Occasion of the 100th Anniversary of the Haber-Bosch Process

Ammonia synthesis is the largest process in chemical industries. It was first operated at BASF one hundred years ago based on the fundamental work of Fritz Haber[1] and process engineering by Carl Bosch. Haber combined feed gas recycling with application of high pressure and an effective catalyst, e.g. Osmium, to achieve sufficiently high conversions of nitrogen according to $N_2 + 3 H_2 \rightarrow 2 NH_3$. This success enabled the large scale production of artificial fertilizers and today, approximately 80% of the worldwide ammonia output of 136 Mtons[2] (2011) is used for this purpose.

Only little has changed in the actual ammonia synthesis step.[3] It is operated at typical temperatures of 500 °C and pressures around 200 bar, resulting in ammonia concentrations in the exhaust gas of up to 18 vol.%. A key development for the modern Haber-Bosch process has been the unique catalyst synthesis developed at BASF by Alwin Mittasch in the early 20th century.[4] To achieve a highly active iron catalyst, magnetite (Fe_3O_4) was promoted by fusing it together with irreducible oxides (K_2O, Al_2O_3, later also CaO) in an oxide melt. The fused magnetite is mechanically granulated and carefully reduced in the syngas feed to finally give the α-Fe catalyst.[5] This special synthesis leads to certain crucial properties of the resulting α-Fe phase, which is commonly termed "ammonia iron" and still in industrial practice today.

Ammonia synthesis has always been a test case for the maturity of catalysis science opposed to an already mature technology. Today, due to the enormous efforts in surface science, physical and theoretical chemistry, and chemical engineering a consistent picture of the reaction mechanism and of the role of the Fe catalyst and its promoters has emerged. Key contributions to the modern understanding of the ammonia synthesis reactions were elaborated by the teams of Gerhard Ertl[6], Michel Boudart[7], Gabor Somorjai[8], Haldor Topsøe[9] and Jens K. Nørskov[10], just to mention a few. However, even after 100 years of application and research there still is scientific interest in the Haber-Bosch process as there still is a gap between the model studies that were conducted with well-defined simplified materials with clean surfaces at low pressures to elaborate the current knowledge of ammonia synthesis. These so-called pressure and materials gaps prevent straightforward extrapolation of the results to the industrial process. Thus, the question of a dynamical change of the catalyst under true reaction conditions remains to be studied by *in situ* experimentation.

It is well known from steel hardening[11] and catalytic ammonia decomposition[12] that iron can be easily nitrided by ammonia. The dissociative chemisorption of di-nitrogen on the iron surface is the rate limiting step in ammonia synthesis[6a] and opens possibilities for sub-surface diffusion of the atomic nitrogen.[13] Ertl et al. proposed the surface dissolution of nitrogen into iron forming a surface nitride of the approximate composition Fe_2N and the presence of *in situ* formed metastable γ-Fe_4N,[6a] while Herzog et al. proposed formation of subnitrides of the type $Fe_{10-20}N$ based on a diffraction study on an industrial material, but at ambient pressure.[14] The partial pressures of ammonia and hydrogen determine the thermodynamical nitriding ability of the gas stream and the formed phases.[11a] In the Haber-Bosch process, p_{NH3} is high due to the high total pressure and the relatively high product concentration. According to the Lehrer-Diagram[11a] the existence of metastable γ'- (fcc Fe sublattice, ca. 20 at.% N) or ε-FeN (hcp, 15 – 33 at.% N) is thermodynamically expected at the partial pressures of the Haber-Bosch process (see supporting information, SI). The discrimination of these bulk iron nitrides from α-Fe (bcc, < 0.4 at.% N) by diffraction is straightforward, as they have different crystal structures.[11e] However, the (reversible) formation of these Fe-N phases in ammonia synthesis was so far not directly observed, which might be related to the lack of experimental methods that are suitable for these demanding conditions. Thus, the (*in situ*)-nitriding of the ammonia synthesis catalysts has been debated in the literature.[14-15]

Herein, we report *in situ* neutron diffraction of an industrial catalyst under conditions close to the Haber-Bosch process to answer the question if dynamical bulk nitridation occurs. This method and the experimental setup used have been recently shown to enable direct *in situ* observation of the bulk structural properties of working catalysts.[16] Ammonia synthesis was conducted on an industrial catalysts provided by BASF in a tubular fixed bed reactor made of a Nickel alloy at conditions of 425 °C and 75 bar given by the safety limits of the setup. Syngas ($N_2:D_2$ = 1:3) was fed through the catalyst bed at a low space velocity to approach thermodynamic equilibrium of the ammonia synthesis reaction corresponding to a product concentration of 14.7 vol-% NH_3 (measured: 12.6 vol.% ND_3). The experiment was performed at the SPODI beamline[17] of FRM-II. The reactor walls and the catalyst bed were penetrated by

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the neutron beam during the experiment and high resolution neutron diffraction data was recorded. According to the phase diagram, the conditions are sufficient for formation of iron nitrides. At 425 °C and 75 bar the transition from the α-phase to γ′ happens at 0.9 vol.% NH$_3$ for pure iron, while the ε-phase is expected at 7.6 vol.% NH$_3$. Milder conditions were applied before and after the reaction to check for reversible changes.
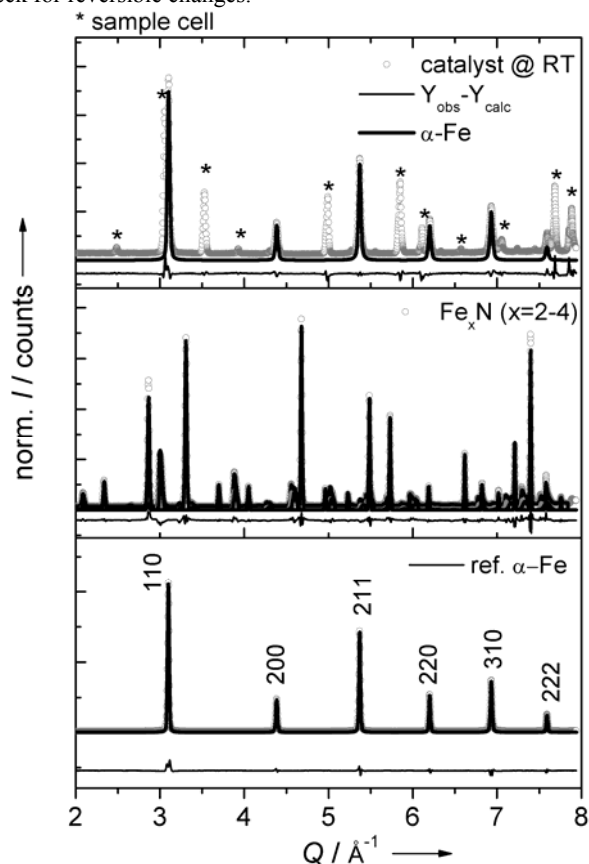

Figure 1. Neutron diffraction patterns and Rietveld refinements of commercial iron powder (bottom) and iron nitride (middle, Fe$_{2-4}$N) and the post-reaction industrial ammonia synthesis catalyst at room temperature (top). Rietveld refinement revealed the presence of α-Fe (black profile) and peaks due to the reactor cell walls (marked).

In Figure 1, the neutron diffraction pattern of the post-reaction industrial catalyst is compared to two reference materials, commercial iron (α-Fe) and iron nitride (Fe$_{2-4}$N). The commercial iron nitride has been prepared from iron by nitridation with ammonia and quenching. In the pattern of this reference sample, the γ′-Fe$_4$N$_{1-y}$ (63 wt.%), ε-Fe$_3$N$_{1.245}$ (24 wt.%) and ε-Fe$_3$N$_1$ (13 wt.%) phases of iron nitride can be identified. As seen from the comparison and confirmed by Rietveld refinement, all peaks of the Fe phase in the post reaction catalyst can be explained by the presence of α-Fe, and a phase transformation induced by nitridation leading to a stable bulk iron nitride can be excluded.

To check for the possibility of a reversible formation of a metastable Fe-N phase during operation, as expected from the phase diagram, the patterns of the activated catalyst in the pre-reaction state, of the fresh catalyst at 425 °C and 75 bar at time-on-stream (TOS) = 0 h, and of the *in situ* pattern recorded at a self-generated NH$_3$ (viz. ND$_3$) concentration of 12.6 vol.% at 88 h TOS, as well as of the post reaction state are compared in Figure 2. In addition to the peaks of the metallic iron, a faint contribution of an additional magnetite phase (Fe$_3$O$_4$, see SI) phase was observed in the pre-

reaction catalyst. The presence of magnetite is a consequence of the kinetic difficulty to fully reduce the catalyst and single-crystalline magnetite particles are proposed to act as spacers to prevent the metallic Fe-platelets from sintering.[18] However, the crystalline magnetite disappeared at TOS = 26 h due to the high reducing potential of the syngas at working conditions and the catalyst is found to be in a strongly reduced state.[19] The lattice parameter of α-Fe is constant at 288.43 pm during ammonia synthesis at 425 °C. After cooling, it is again similar that of the reference α-Fe at room temperature (286.79 pm *vs.* 286.78 pm).

It is evident from Figure 2 that no *in situ* transformation into metastable bulk nitrides has taken place due to inclusion of nitrogen atoms from the generated ammonia despite the high p$_{NH3}$ (viz. p$_{ND3}$). Like the post-reaction state (Figure 1), the catalyst in working condition can be described to a first approximation by a single α-Fe phase. We can safely conclude that the virtual pressure of nitrogen during the experiment was not sufficient for nitriding of the bulk, because no peaks of the Fe$_{2-4}$N reference pattern (Fig. 1) were observed at any time. Such phases were recently described[11f] and are commonly observed in Fe-based catalysts for ammonia decomposition.

In comparison with the α-Fe reference, the peak profiles of the catalyst are significantly broadened as seen in Figure 3 indicating a difference in the microstructure of both materials. Also the intensity ratio of the α-Fe peaks differs for the reference anisotropic peak broadening of the 200 and 310 profiles was observed, which might be related to the presence of endotactic chemical impurities in the lattice of the α-Fe host lattice (see SI).[9, 19-20] These observations clearly indicate a microstructural and textural effect of the preparation and activation process and/or additives on the catalyst. Earlier studies revealed that the activated ammonia catalyst shows a strongly hierarchical microstructure[21] with Fe platelets in the surface near region.[19] Therefore, the deviation of the catalyst's peak intensities and breadths from the α-Fe powder reference[22] can be interpreted as "structural anisotropy" of the ammonia-iron caused by defects, size and strain effects.[23] It seems likely that the unexpected stability of the α-Fe phase in the catalyst is related to these microstructural effects.

While the difference between catalyst and reference was obvious, it was surprising to see hardly any changes in the peak shapes of the catalyst upon changing the conditions (Fig. 2, 3). This observation strikingly confirms the stability not only of the iron bulk against nitridation, but also of the catalyst's peculiar microstructure. After the activation procedure, neither thermal annealing of defects, nor any major reversible or irreversible change of the catalyst's structural features could be clearly observed. The only faint variation of the peak breadths corresponds to a slight growth of the α-Fe apparent domain size with TOS from 26 nm ±5 nm (TOS = 0 h), which is in good agreement with earlier reports[20b, 24] to 32 nm ±7 nm (TOS = 88 h). The structural stability of the α-Fe phase in the catalyst and of its lattice imperfections suggest that the crucial properties of "ammonia iron" have been developed already during the catalysts activation in the feed gas and not during the actual ammonia synthesis experiment at higher p$_{NH3}$ (viz. p$_{ND3}$).

We emphasize that the interpretation of the above results is largely consistent with and a confirmation of the common literature view on the active catalyst. The non-nitrided α-Fe clearly is the major phase of the catalyst, limiting possible nitrogen dissolution to a small fraction of the catalyst located at the surface of the large aggregates (d ∼ 100 nm[22]). This results in a situation that can be described as a Fe-N surface phase (0.8-0.96 monolayers[6d, 25]), which is not detectable by diffraction, and supported on a core of

unaffected α-Fe, which dominates the diffraction pattern. This picture is in agreement with the model that the bulk α-Fe provides the skeleton for a surface Fe-species, which is supposed to play the crucial role in the catalytic process.[14, 18-19, 26] A representative high resolution TEM image of the near surface region of the post-reaction catalyst is shown in Figure 4b. An anisotropic, platelet-like morphology of crystalline α-Fe domains of a size of a few nanometers is observed at the edge of the large aggregates.
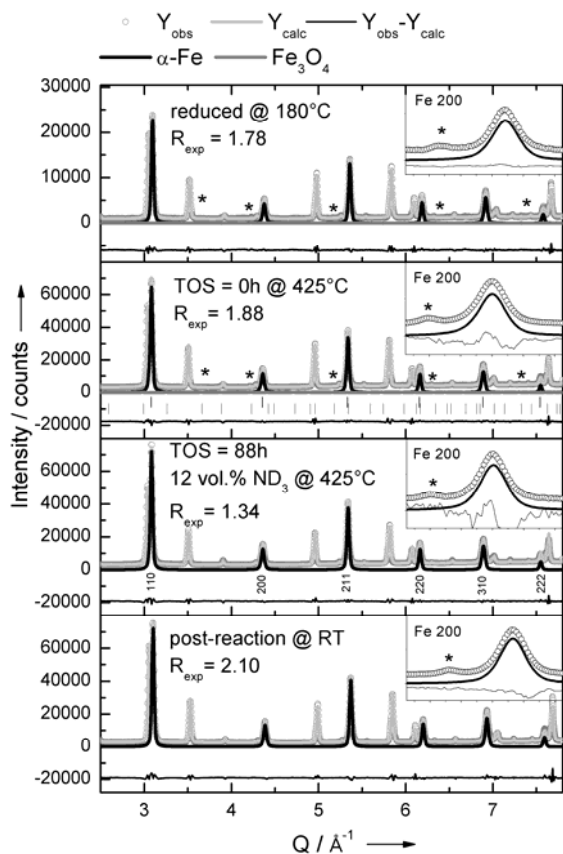

Figure 2. Neutron diffraction patterns of the ammonia synthesis catalysts at different conditions. The black line indicates the fitted contribution α-Fe phase to the patterns. a) reduced, initial catalyst in 4.4 bar D_2 at 180 °C (the dark grey line is the profile of magnetite, peaks additionally marked by asterisks); b) pre-reaction catalyst at 425 °C under 75 bar syngas at TOS=0h; c) *in situ* reaction state at 425 °C under 75 bar syngas, which is converted to yield 12 vol.% ND_3 at TOS=88 h d) post-reaction catalyst in 75 bar Ar at room temperature. The insets show the magnification of the 200 peak of α-Fe, wherein the black asterisks marks the contribution from the Ni-reactor tube.

In conclusion, this work has provided experimental evidence that validates the understanding obtained on iron model catalysts from surface science in low-pressure experimentation and theoretical model approaches for the industrial high pressure ammonia synthesis reaction. No major dynamic phase changes due to nitridation have been observed on an industrial ammonia synthesis catalyst when subjected to a self-generated NH_3 (viz. ND_3) concentration of 12.6 % at 75 bar and 425 °C, i.e. close to the conditions in the Haber-Bosch process. The stability of the α-Fe phase in the catalyst could not be expected based on the thermodynamics of pure iron at such ammonia partial pressures. In comparison to reference Fe, the industrial catalyst shows a complex and defective microstructure that was inherited from the preparation and activation processes. Also this unique microstructure was stable

and hardly any structural healing was observed during 88 h of operation. The absence of nitridation is thus not due to the general absence of a gap between low and high pressure, but can be rather explained by the cancellation of the expected pressure effect by the materials effect. While the former thermodynamically favors bulk nitridation, the latter kinetically stabilizes the defective α-Fe phase – likely a result of the presence of additives and of the preparation history of Mittasch's synthesis. The complex real structure of this catalyst after activation and its stability appears to be a prerequisite for high performance and should be target of any alternative synthesis approaches for ammonia synthesis catalysts aiming at a simpler and more elegant preparation.
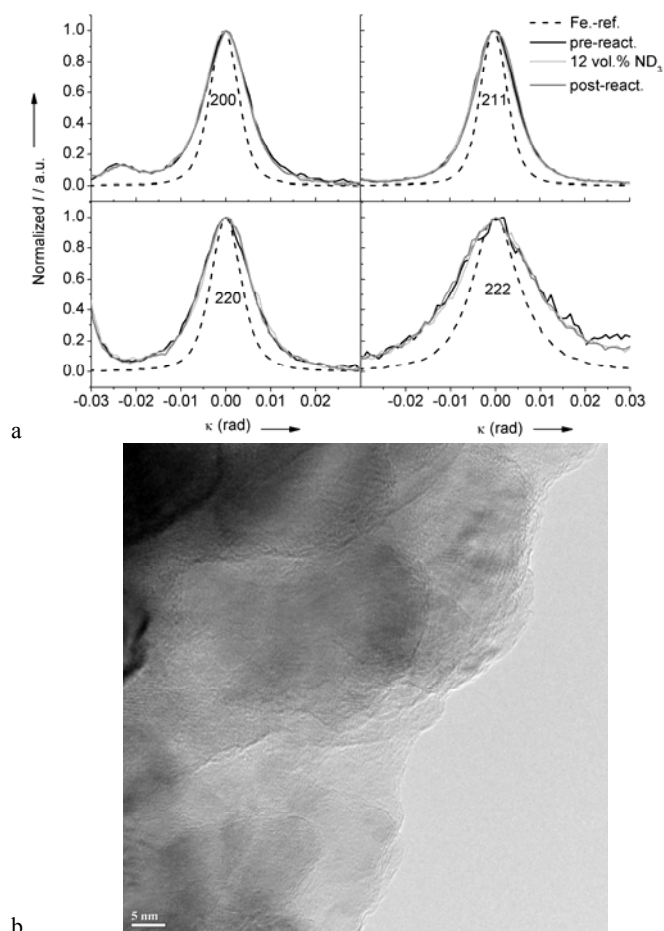

Figure 3. a) Normalized peaks profiles of the 200 (top left), 211 (top right), 220 (bottom left) and 222 (bottom right) of the catalyst's α-Fe reflections. The thermal shift (reference-iron, dashed, and post-reaction state, dark grey: 28 °C; pre-reaction state, black: 180 °C; *in situ* ammonia synthesis, light grey: 425 °C) was compensated by normalizing to the peak maxima on the x-axis. b) Representative HRTEM micrograph of the post-reaction ammonia catalyst.

Experimental Section

A BASF S6-10 catalyst was carefully reduced, dried, transferred via an Ar-glovebox into the flow cell for the neutron experiment and sealed air-tight. The experiment was carried out on the high-resolution thermal neutron diffractometer SPODI[17] at the research reactor Heinz Maier-Leibnitz (FRM II) of the Technical University Munich in Garching, Germany. For the *in situ* studies a modified version of a continuous flow-cell was used, which was already described elsewhere.[16a] At the beamline, the pre-reduced catalyst was activated by heating up slowly from RT to 180 °C with a heating rate of 1 Kpm in a D_2 stream of 9.6 l/h at 4.4 bar. Further heating to

reaction state was done under 75 bar $D_2/N_2/Ar$-Syngas (72:23:6) with a rate of 0.5 Kpm to 425 °C. The reaction slowly approached a steady state concentration of ND_3 of 12.6 vol.% after 88 h TOS, which is close to equilibrium. For each reaction state, pre-reaction, *in situ* (TOS = 0 and 88 h) and post-reaction, 3 diffraction pattern (each 30 min) were acquired and the ND_3 yield was determined by bubbling the exhaust stream through water and subsequent titration. Analysis of the patterns was carried out by Rietveld-refinement and pattern decomposition. Further details of the experiment and the evaluation can be found as SI.

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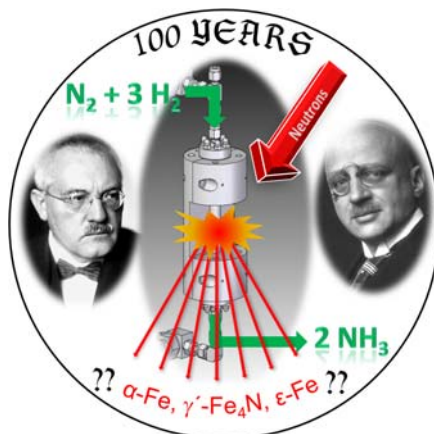
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Layout 1:

In-situ neutron diffraction was used to study the structural properties of an industrial ammonia synthesis catalyst under working conditions close to those of the Haber-Bosch process. Despite favourable thermodynamics, no indications of a reversible bulk nitridation of the iron catalyst was observed in a self-generated ammonia concentration of 12 vol.% at 425 °C and 75 bar after 88 hours on stream.