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# Heterogeneous Catalysis under pressure - *In-situ* neutron diffraction under industrial conditions

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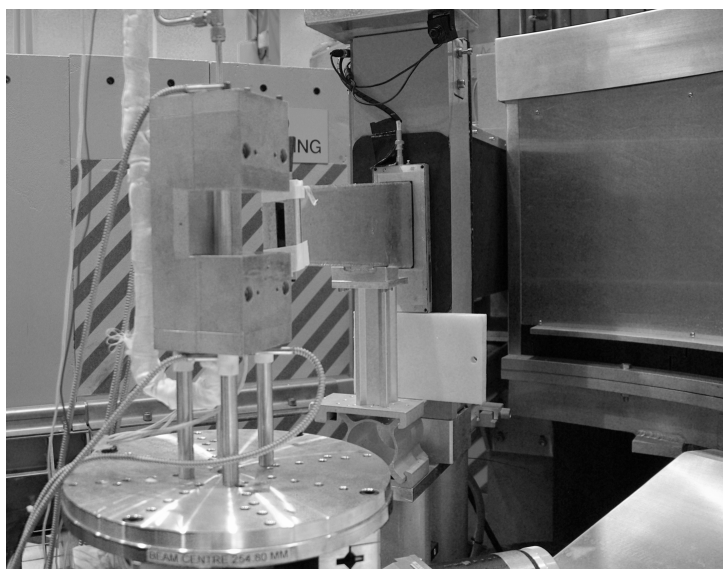
**Abstract.** The present work describes the application of a tubular reactor that allows *in-situ* neutron diffraction on working catalysts at high pressures. The designed reactor enables the application to a sample of industrially-relevant reaction conditions, *i.e.*, in a temperature range up to  $330^\circ\text{C}$  and  $60\text{ bar}$  pressure, coupled with online gas-analysis. Application of the cell is demonstrated by ammonia synthesis over a commercial catalyst with diffraction data obtained from the high-resolution powder diffractometer, Echidna, at the Australian Nuclear Science and Technology Organisation, ANSTO.

## 1. Introduction

Neutron diffraction is a unique tool to gain information on crystalline phases, the crystal structure, structural disorder, crystalline domain size and shape, lattice strain and defect structure, of materials including catalysts [1]. Nowadays, catalyst are considered as dynamic materials whose active centres are formed or transformed under reaction conditions. *In-situ* characterization methods are needed to obtain information about such structural dynamics, which are typically applied in the pressure range from ultra-high vacuum to ambient. The structural properties of the catalyst may change with the partial pressure of the reactants or products, and investigations of catalysts at high pressures and near industrially-relevant working conditions using *in-situ* neutron diffraction can provide valuable information on the nature of the catalytically active sites. Due to the high penetration depth of neutrons, they can scatter from samples deep within conventional metallic reactors without the use of specialized neutron-beam transparent windows, enabling the application of demanding sample environments that are not easily used with conventional X-ray diffraction. Additionally, the relatively large  $Q$  ( $=2\pi/d$ ) coverage and non-decreasing scattering factors at high  $Q$  make neutron diffraction a suitable tool for *in-situ* studies of working catalysts, enabling crystallographic information at reasonable counting times to be obtained. This contribution presents the application of a custom-made high-pressure cell to the ammonia-synthesis reaction.

## 2. Experimental

For the purpose of *in-situ* neutron diffraction a high-pressure continuous flow reactor was designed. The flow cell, made out of an AlMg<sub>3</sub> alloy, is suitable for reaction temperatures from ambient to 330°C and a maximum pressure of 60 bar.[2]. Mass spectrometry was used during

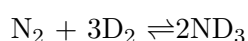


**Figure 1.** Flow reactor mounted on the Echidna instrument. The incident neutron-beam window is shown in the background.

the *in-situ* neutron diffraction experiment for online gas analysis. Previous experiments in the laboratory have demonstrated the reactor functionality for the pretreatment of the catalysts, and continuously-running, stable catalytic conversions have been achieved. Relatively fast changes of the gas atmosphere are possible to introduce various probe gases (*e.g.*, N<sub>2</sub>O reactive-frontal chromatography for copper-based catalysis [3]). The example described here was carried out on the high-resolution powder diffractometer, Echidna, at the OPAL reactor facility using a Ge 335 monochromator to provide a beam at a wavelength of  $\lambda=1.622\text{\AA}$ . A large array of 128 position sensitive <sup>3</sup>He detectors enabled an angular range of 4°-164° in 2 $\Theta$  to be covered, corresponding to a Q-range of 0.28 $\text{\AA}^{-1}$  to 7.7 $\text{\AA}^{-1}$  [4, 5].

## 3. Application example: Ammonia synthesis

Ammonia synthesis is not only one of the largest-volume synthetic chemical-processes applied in chemical industries, but also serves as a prototype reaction for heterogeneous catalysis research. Significant efforts to investigate the surface chemistry of model catalysts have been made in the last few decades using this reaction, as well as practical tests of high-performance catalysts [6]. Ammonia synthesis from nitrogen and hydrogen/deuterium (*see [7] for detailed mechanism*) is a structure-sensitive reaction, which does not occur on every form of metallic iron:



Commercial catalysts are so called "bulk-catalyst" with varying amounts of promoter species. The catalytically-inactive precursor material typically consists of fused iron oxides, *e.g.*, approximately 80 vol.% magnetite, Fe<sub>3</sub>O<sub>4</sub>, and 20 vol.% wuestite, FeO. The specific BET-surface

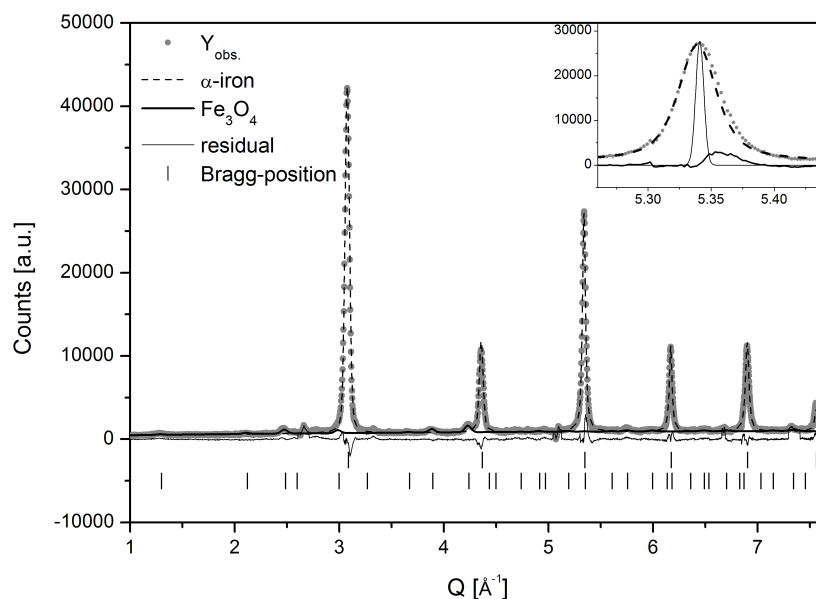
area of the catalyst is around  $10 \text{ m}^2\text{g}^{-1}$ , while the mean particle size of the wuestite/magnetite-precursor is roughly  $10 \text{ }\mu\text{m}$ . The catalytically-active form is called "ammonia iron" [8], which is produced from the fused iron-oxides by a complex thermal treatment in a reducing reactant gas-feed. Studies have shown [9] that the precursor material exhibits a disk-like internal microstructure, leading to long-term stable aggregates of  $\alpha$ -iron-platelets separated by oxide spacers, which are favorable for the conversion of di-nitrogen. There is evidence that the active surface undergoes reversible reconstruction [10] under working conditions leading, for instance, to the formation of nitrides. In addition to pure iron [11], a metastable non-iron para-crystalline metal structure [12], a skin of  $\text{Fe}_4\text{N}$  or its under-stoichiometric variants [13] are discussed as catalytically-active phases.

The pre-activated  $\alpha$ -iron catalyst was transferred under inert gas into the flow cell. After inserting the cell into the reactor the catalyst bed was carefully heated at  $1 \text{ K min}^{-1}$  under the reaction feed-gas to the reaction temperature of  $330^\circ\text{C}$ , a guard-reactor with the same catalyst was operated at  $250^\circ\text{C}$ . After reaching the reaction temperature, the cell was pressurized to 60 bar. When the detected ammonia concentration at the exhaust was stable, diffraction patterns with an exposure time of 2 h were acquired. For a stoichiometric gas feed of  $100 \text{ Nml min}^{-1}$ , a conversion of 3.63% was achieved while the productivity was  $7.59 \text{ mg}_{\text{ammonia}} \text{ g}_{\text{catalyst}}^{-1}\text{h}^{-1}$ . For accurate determination of the instrumental peak profile a  $\text{LaB}_6$ -standard was measured. Line broadening analysis using a pseudo-voigt-type peak-function with an axial-divergence term allowed to deconvolute angular dependencies on the integral breaths of the Lorentzian and Gaussian components.

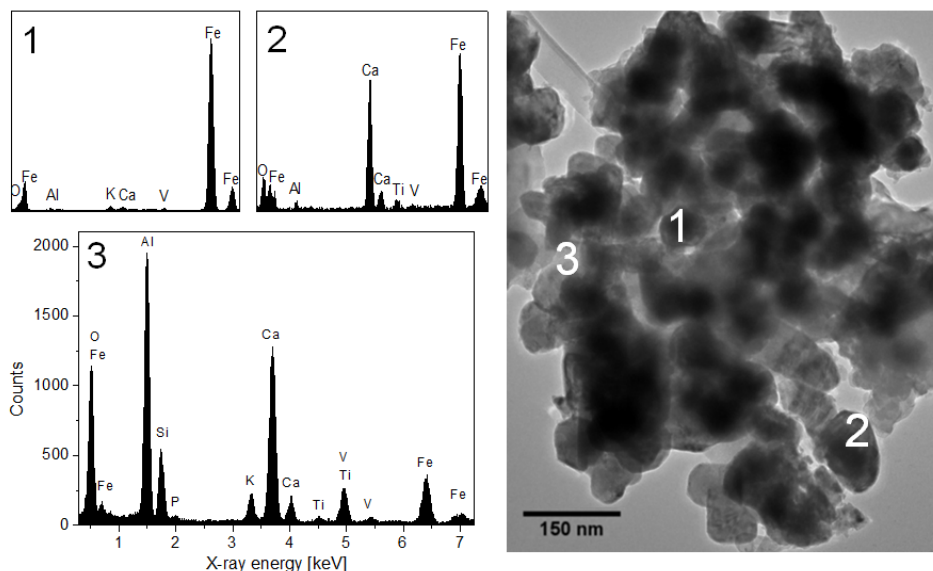
#### 4. Results

Fig. 2 shows the diffraction pattern of a commercial iron-catalyst in operation at  $330^\circ\text{C}$  and 60 bar, wherein diffraction peaks arising from the cell were removed. Strong diffraction peaks of  $\alpha$ -Fe (- - -) can be clearly distinguished and indexed. After deconvolution of the instrumental broadening from the diffracted intensities, the complex microstructure of the catalytically active  $\alpha$ -Fe phase of the catalyst is indicated by the asymmetric peak broadening of the reflections as exemplified for the 211 profile shown in Fig. 2 (inset). In addition to metallic iron ( $a = 2.87840 (\pm 0.00013) \text{ \AA}$ ), there is also a noticeable contribution of a spinel phase ( $a = 8.38415 (\pm 0.00022) \text{ \AA}$ ), which can be refined using magnetite ( $\text{Fe}_3\text{O}_4$ ) as a structural model (—). The refined lattice parameter is significantly shorter than expected for pure magnetite at  $330^\circ\text{C}$  ( $8.4179$  and  $8.4245 \text{ \AA}$  at  $300^\circ\text{C}$  and  $350^\circ\text{C}$ , respectively [14]). On the other hand, it is much larger than expected for  $\text{FeAl}_2\text{O}_4$  (Hercynite,  $8.1695 \text{ \AA}$  at  $400^\circ\text{C}$  [15]), which has been reported to form in ammonia-synthesis catalyst from FeO and the  $\gamma$ - $\text{Al}_2\text{O}_3$  promoter during reduction [16]. Our results suggest the presence of a non-stoichiometric and defective  $(\text{FeO})_x \cdot (\text{Al}_2\text{O}_4)_\gamma$  spinel-phase, in which the iron-cations are not reduced under *in-situ* conditions probably due to the interaction with Al in the spinel lattice. Transmission electron microscopy (TEM) studies (Fig. 3) revealed a complex composite microstructure of the catalyst with metallic iron particles and an embedding oxide matrix, wherein the promoter species (Ca, Al, K, Si, Ti, V) are enriched. This suggests that additional faint reflections arising in the level of background noise are attributable to small calcium ferrite crystallites. A careful correction for background artefacts will be mandatory for further evaluation.

*In-situ* neutron diffraction experiments as shown here are useful as a starting point for the further investigation of the structural changes occurring to a working catalyst during variation of the reaction conditions. Importantly, this information can be correlated to changes to catalytic performance. More detailed results of the ammonia-synthesis catalysts will be published elsewhere.



**Figure 2.** Neutron powder diffraction pattern of a working commercial ammonia catalyst at 330 °C and under 60 bar of syngas. A Rietveld-refinement based phase deconvolution was applied to the data. Bragg-positions of  $\alpha$ -iron (top) and a spinel phase (structural model:  $\text{Fe}_3\text{O}_4$ , bottom) are marked, the difference between the model and the data is shown by the solid line above. The inset compares the asymmetric peak broadening of the 211 reflex of the  $\alpha$ -iron-phase to the instrumental resolution function (narrow peak).



**Figure 3.** TEM micrograph and energy dispersive X-ray (EDX) spectra of the sample used during in-situ neutron diffraction. The point analysis spectra reveal that in addition to the  $\alpha$ -iron particles (1) areas which are enriched in oxygen and in the promoter species are also present (2,3). These areas are found near the edges of the iron particles (2) and as an embedding matrix consisting of partially crystalline calcium ferrite/iron aluminum spinel (3).

## 5. Conclusions

The constructed high-pressure continuous-flow reactor was successfully used in *in-situ* neutron diffraction on an ammonia-synthesis catalyst, working at 330°C under a pressure of 60 bar. The preliminary data analysis confirms that all microstructural deviations of "ammonia-iron" that were derived at ambient pressure qualitatively also prevail at the technical harsh operation conditions. In particular, the absence of a stoichiometric iron nitride phase and the non-equilibrium structure of working metallic iron were confirmed to be no artefacts of low-pressure experimentation.

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