# Oxygen Poisoning in Laboratory Testing of Iron-Based Ammonia Synthesis Catalysts and its Potential Sources

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The influence of oxygen poisoning on a state-of-the-art multipromoted iron-based industrial catalyst for ammonia synthesis as well as the effectivity of different gas purification methods to prevent oxygen poisoning for experiments on laboratory scale were studied in detail. Additionally, the observed results were compared to a common oxygen poisoning test from literature, which on the one hand confirmed its usability in a wide range of conditions, but on the other hand also demonstrated the limitations of this test.

**Keywords:** Ammonia synthesis, Carbon2Chem®, Gas purification, Iron catalyst, Oxygen poisoning

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## 1 Introduction

Nowadays, alternative feedstocks are discussed for utilization in synthesis gas processes [1, 2]. Especially, the use of industrial exhaust gases together with hydrogen based on renewable resources provides the opportunity to combine reducing industrial $CO_2$ emissions with storing renewable energies in a chemical compound. As these gases differ in composition and impurity level from the usually applied sources, additional studies are needed to enable their utilization. Therefore, within the cross-industry approach of Carbon2Chem®, where exhaust gases from steel mills should be supplied as a possible feedstock for processes, such as methanol or ammonia synthesis, a detailed investigation of possible impurities as well as the required gas cleaning will be one key for achieving industrial application [3]. One part in this joint project is to focus on providing a synthesis gas of highest reasonable quality for chemical production. Therefore, the validation of the envisaged processes like, e.g., ammonia synthesis (Eq. (1), [4]) based on steel mill exhaust gases within poisoning limits has to be investigated in detail. To validate the significance of various gas cleaning methods, the removal of possible poisoning compounds from the supplied feed gas is mandatory and has to be considered precisely in every laboratory-scaled test reaction to enable the determination of the impact of the impurities.

$$1.5\,H_2 + 0.5\,N_2 \rightleftharpoons NH_3 \quad \Delta H_r^0 = -46.22\ \text{kJ mol}^{-1} \qquad (1)$$

It is well known that the iron-based catalyst for industrial ammonia synthesis is highly sensitive to poisoning by various components that can be present in the synthesis gas for this reaction [4–7]. These components poison the catalyst mostly by reacting with the active iron surface and blocking its active sites except for halogens like Cl, which react with the potassium promoter of the catalyst [5, 6]. Depending on the components the poisoning can be reversible or irreversible. While gaseous species containing elements like S, P, As, or Cl lead to a permanent poisoning [4, 5] it is possible to fully regenerate an ammonia synthesis iron catalyst after poisoning by oxygen and oxygen-containing species ($H_2O$, CO, $CO_2$) as long as the iron nanostructure has not been damaged by the temporal oxidation [8, 9]. Already ppm and sub-ppm levels of these poisons in the feed gas can have a significant influence on the catalytic activity in ammonia synthesis [4]. Therefore, the purification of the feed gas for ammonia synthesis needs to be handled with tremendous care to ensure a high activity of the catalyst. In industrial use this is achieved by an extensive amount of purification steps, where next to the classical synthesis gas purification methods like hydrodesulfurization, $CO_2$ scrubbing, and methanation additional high-purity steps like molecular sieve dehydration, liquid nitrogen washing, or liquid ammonia washing are added [4]. Additional care needs to be taken for ammonia synthesis experiments on laboratory

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scale to obtain reliable kinetic data and to conduct meaningful poisoning studies to determine the impact of the impurities on the catalytic performance. This can be achieved by purification methods like a guard reactor filled with reduced iron catalyst. For measurements in ammonia synthesis on laboratory scale usually the only poisons that have to be considered are oxygen species as they are the predominant impurities in a normal laboratory gas supply using gases with high purity.

The presence of oxygen-containing impurities in the feed gas can be tested by a method introduced by Fastrup and Nygård Nielsen [10]. This method is based on the fact that oxygen poisoning is reversible. While oxygen chemisorbs strongly on the iron surface leading to its oxidation/poisoning (Eq. (2), [11]), the iron surface is reduced/regenerated by converting the adsorbed oxygen in a reversible reaction with hydrogen to water (Eq. (3), [12]).

$$0.5\,O_2 + * \rightarrow O_{ads} \qquad \Delta H_r^0 = -210\ \text{kJ mol}^{-1} \tag{2}$$

$$O_{ads} + H_2 \rightleftharpoons H_2O + * \qquad \Delta H_r^0 = 117\ \text{kJ mol}^{-1} \tag{3}$$

(* = free adsorption site at the iron surface).

Under steady-state conditions the poisoning leads to an equilibrium between oxygen on the iron surface and oxygen-containing species in the gas phase. The equilibrium depends on parameters like oxygen partial pressure, total pressure and temperature and responds quite slowly to changes of the conditions. If one of the parameters is changed fast, oxygen poisoning becomes visible as the time to achieve a new steady state is prolonged. For this method it is required that the measured activity of the catalyst is far below the thermodynamic equilibrium of the ammonia synthesis reaction, but also high enough to detect a reliable amount of ammonia production. For highly active industrial catalysts this can be achieved at temperatures between 300–400 °C. Also, the systems for the parameter changes should have a fast response, e.g., a good temperature control. Furthermore, Fastrup and Nygård Nielsen [10] recommend measurements at atmospheric pressure to keep the gas amount in the reactor low and, therefore, reduce the response delays. However, this test is also feasible at higher pressures.

In this work, we report a study on the oxygen poisoning of an industrial catalyst on laboratory scale by using different purification methods with a varying effectiveness as well as study the classical test method for oxygen poisoning.

## 2 Experimental

### 2.1 Catalyst

All catalytic tests were performed with a state-of-the-art iron-based multipromoted industrial catalyst. The working catalyst was obtained by reduction of a precursor consisting mainly of iron oxide and small amounts of several different promoters.

### 2.2 Setup

The ammonia synthesis tests were conducted in a modified commercial ammonia synthesis catalyst test rig purchased from ILS (Integrated Lab Solutions GmbH) equipped with a guard reactor and a synthesis reactor. For quantitative product gas analysis an online infrared (IR) detector for $NH_3$ and $H_2O$ (Emerson X-Stream Enhanced IR Gas Analyzer) was used. This setup allows the testing of catalyst materials for ammonia synthesis in a continuous operation mode with sample masses of a few gram at high temperatures and pressures up to 500 °C and 90 bar. The molar flow of the feed gas can be adjusted in a broad range allowing a broad variability of the space velocity. A schematic flow scheme of the major components of the setup is given in Fig. 1.

All components of the setup are connected with all-stainless-steel tubing. The feed gas mixture of the setup can be individually regulated by mass flow controllers (MFCs) at the inlets. Besides the reactants (hydrogen and nitrogen), it is also possible to add argon to the feed gas mixture as an inert compound. All gases are introduced in high purity (99.999 %) and are further purified from oxygen species and water in the sub-ppm range with OXISORB® oxygen scrubber cartridges for each gas line. According to the datasheet, the concentrations of oxygen-containing compounds in the filtered gases are reduced below the following values: <0.1 ppm $O_2$, <0.5 ppm $H_2O$ [13]. The high pressure that is necessary for the catalytic measurements is built up by a reciprocating compressor with buffer volume elements before and behind the compressor to absorb the pressure pulses caused by its unsteady operation mode and to guarantee a constant gas flow for the following reactors. Behind the compressor and volume elements an additional MFC adjusts the total feed gas flow rate to the reactors. As this MFC has to adjust different possible gas compositions a mini CORI FLOW™ MFC (Bronkhorst GmbH) is applied, which allows setting a mass flow independent from the composition of the feed gas.

Before the feed gas enters the synthesis reactor, usually residual oxygenates and other catalyst poisons in the feed gas are removed by means of a guard reactor filled with ca. 150 g of a reduced magnetite-based industrial Fe catalyst. Its temperature is kept at 40 °C during measurement to ensure no ammonia formation is taking place. The guard reactor is regenerated by re-reducing the industrial catalyst before every catalytic measurement by heating it in a constant gas flow of 75 % $H_2$ and 25 % $N_2$ with 1 °C min$^{-1}$ to 450 °C and keeping the temperature until the water signal at the reactor outlet is constant to ensure that no oxygenate species break through the guard reactor during the measurement.

Additionally, for varying poisoning experiments and for comparison measurements the setup was modified by installing a high-performance gas purifier for the ppt range (MicroTorr® MC1-904 gas purifier) at two different positions of the setup: one time directly before the guard reactor and behind the compressor and one time before the compressor

  

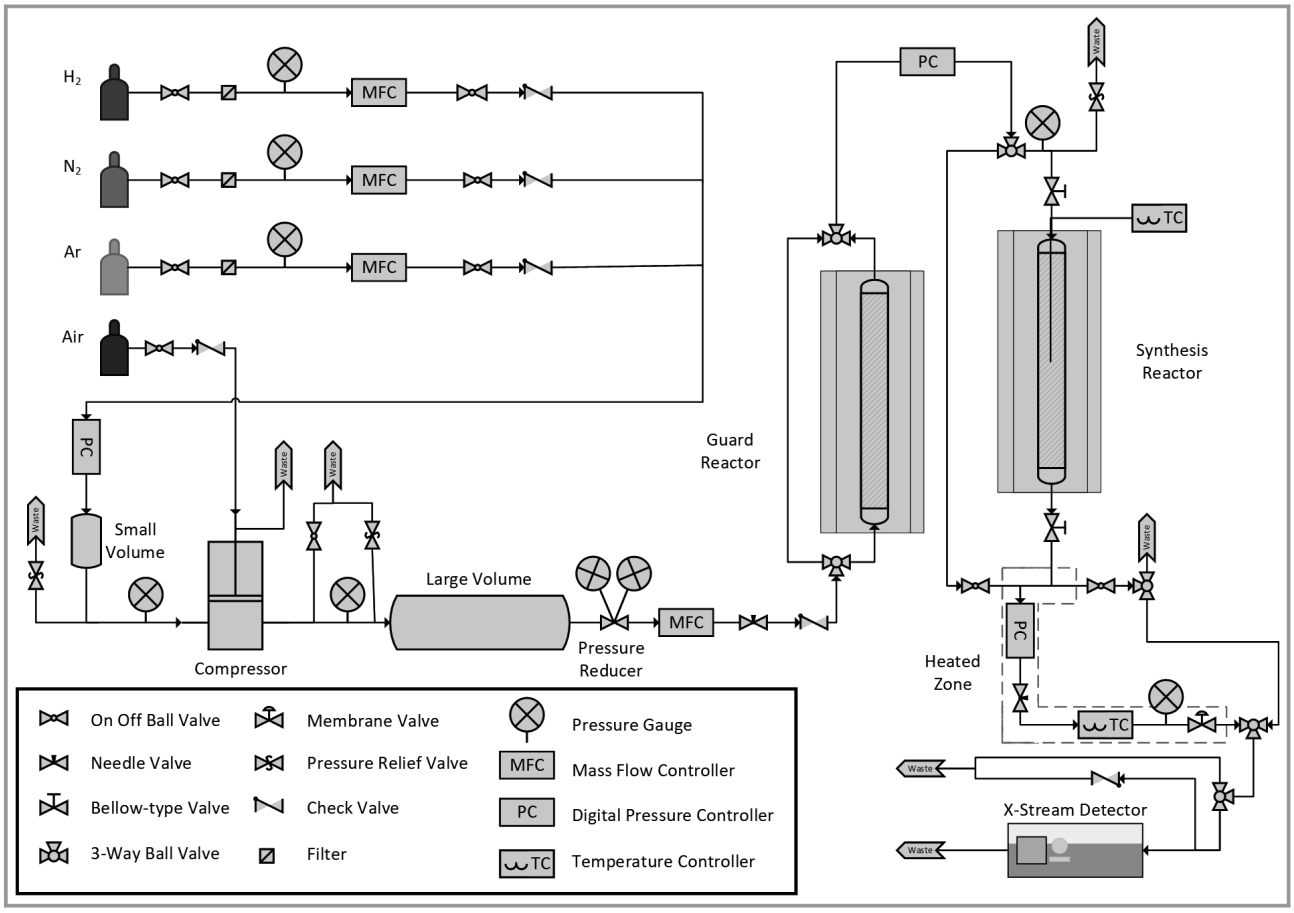


**Figure 1.** Schematic flow scheme of the ammonia synthesis catalyst test setup.

and behind the three MFCs. According to the datasheet the concentrations of oxygen-containing compounds in the filtered gas are reduced below the following values: <100 ppt $O_2$, <100 ppt $H_2O$, <100 ppt CO, <100 ppt $CO_2$ [14].

The IR detector for product gas analysis allows the detection and quantification of ammonia and water in the effluent gas flow up to a detection limit in the ppm range. It is equipped with three different channels: one for detection of low ammonia concentrations (0–3 vol %), one for detection of high ammonia concentrations (3–100 vol %) and one for detection of low water concentrations (0–1 vol %).

### 2.3 Catalytic Testing

For a measurement 3 g of iron oxide precursor (particle fraction 250–425 µm) were diluted with 3.9 g SiC (average particle size 154 µm). The catalyst bed was placed in the synthesis reactor between pure SiC and held in position by glass wool plugs at the entrance and exhaust of the tube reactor (catalyst bed length $L$ = 48 mm, inner reactor diameter $d_r$ = 10 mm, outer diameter of thermocouple hull inside the reactor $d_T$ = 3.175 mm). For reduction the sample was heated up with a temperature program to 500 °C in synthesis gas (75 % $H_2$, 25 % $N_2$) applying a flow of 286 NmL $g_{cat}^{-1}min^{-1}$ (volumetric flow at standard conditions, 0 °C, 1.013 bar) at an elevated pressure of 30 bar. The precursor was reduced in three temperature steps with different heating rates: from room temperature to 250 °C with 1.2 °C $min^{-1}$, 250–400 °C with 0.3 °C $min^{-1}$ and 400–500 °C with 0.2 °C $min^{-1}$. Afterwards, the conditions were kept constant for ca. 4.5 h. In total, the reduction procedure took 24 h.

For catalytic testing, the temperature was kept at 500 °C while the pressure was increased to 60 bar with a pressure ramp of 1 bar $min^{-1}$. Different poisoning experiments were performed in a temperature range of 300–425 °C and at different total flow rates of 119–600 NmL $g_{cat}^{-1}min^{-1}$. Additionally, further experiments as well as similar temperature and flow rate variations were conducted at atmospheric pressure.

## 3 Results and Discussion

All measurements were performed with a multipromoted industrial catalyst. It was assumed that a full purification of the synthesis gas and the maximal possible activity of the catalyst can be achieved by further gas cleaning with the guard reactor, as 150 g of a reduced industrial iron-based

  

catalyst should be sufficient to filter any potential poison for a long time on stream at the applied flow rates. Therefore, the activity of the catalyst with purification by the guard reactor was set to 100 % for each of the applied standard measurement conditions that are used in this work.

In this work, the oxygen poisoning test originally developed by Fastrup and Nygård Nielsen [10] was performed with fast changes of the temperature and of the total flow rate (Fig. 2). The change of the parameters of the applied setup is slightly slower compared to the one used by Fastrup and Nygård Nielsen [10]. This can be related to its larger scale leading to a higher overall residence time as well as its high-pressure capability. Especially, due to the larger scale, the temperature control is not as fast leading to a slight overheating or overcooling at the end of a temperature change. Nevertheless, it is possible to observe a very good response of the ammonia signal for the parameter changes when the guard reactor is online (Fig. 2a). The change of the flow rate leads to a clear leap of the ammonia signal and for the change of the temperature also the overheating and overcooling can be observed in the ammonia signal. According to the test classification there is no sign for oxygen poisoning of the catalyst. However, without a further purification step a clear response delay in the ammonia signal can be observed, even when high-purity gases with a purity of 99.999 % and additional purification of the supplied gases by oxygen scrubber cartridges are used for the measurements (Fig. 2b).

Additional tests were performed with a high-performance gas filter to investigate its effectiveness in comparison to the guard reactor. As the filter can be applied also at elevated pressures of up to 69 bar it was installed within the setup directly before the guard reactor. Here, the first tests were performed at a pressure of 60 bar. After achieving steady-state conditions the guard reactor was set to bypass (Fig. 3).

As it can be seen in Fig. 3a, there is absolutely no change in the catalytic activity after the synthesis gas is only purified by the high-performance filter. The sharp peak in the activity accompanying the switching of the guard reactor to bypass is caused by a short drop of the gas flow rate as the bypass line of the guard reactor was at atmospheric pressure and its switching leads to a pressure drop in the setup. The constant activity after the switching for more than 92 h without any loss of activity proves that the high-performance filter operates with a high level of purification similar to the guard reactor, which is far beyond the critical

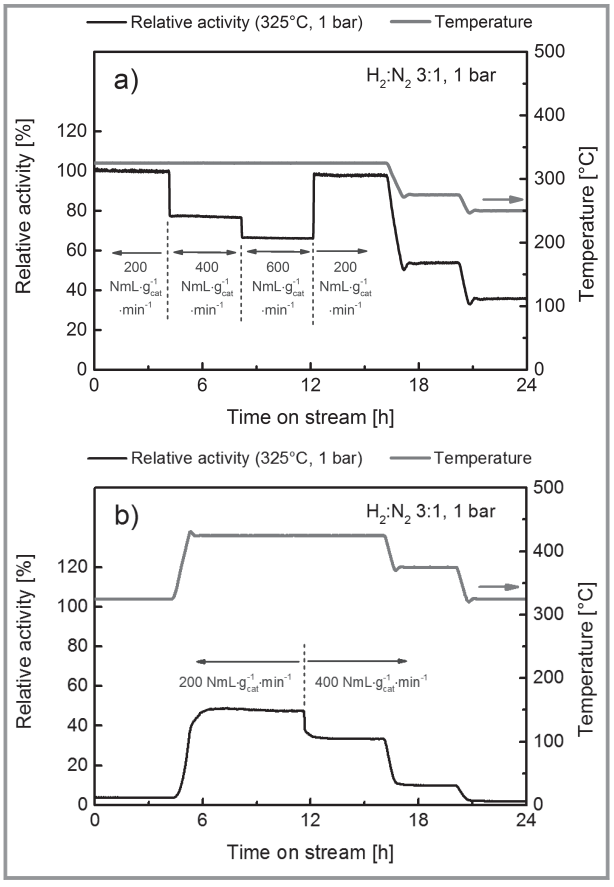


**Figure 2.** Oxygen poisoning test at atmospheric pressure a) with synthesis gas purified by the guard reactor and b) without purification by the guard reactor.

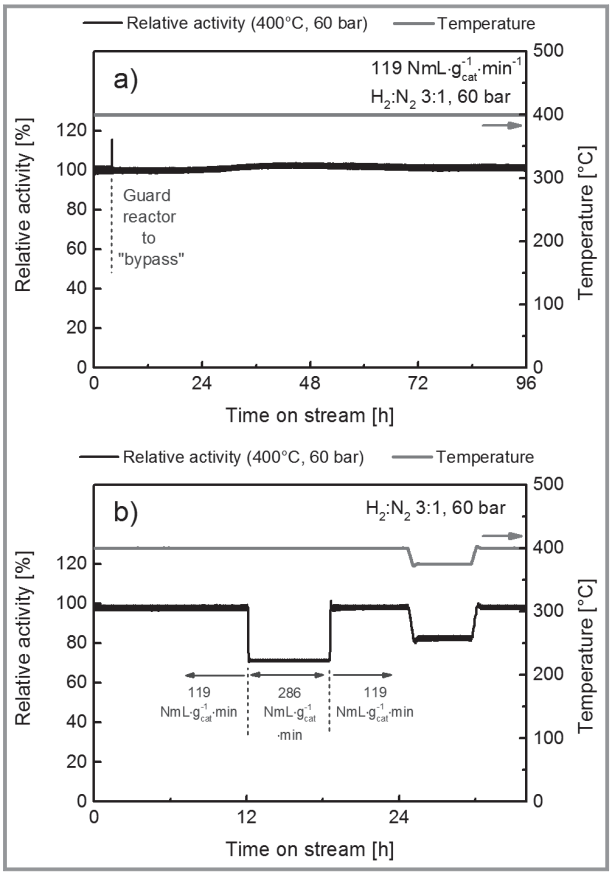


**Figure 3.** a) Relative ammonia synthesis activity with synthesis gas purified by the guard reactor and/or the high-performance filter installed directly before the guard reactor. b) Oxygen poisoning test at 60 bar with synthesis gas purified by the high-performance filter.

  

amount of impurities that lead to a poisoning of the catalyst. Furthermore, the oxygen poisoning test shows a direct response to the changed reaction conditions indicating the absence of any poisoning of the catalyst (Fig. 3b). Accordingly, a purification down to the ppt range given by the high-performance filter seems to be suitable to protect an ammonia synthesis catalyst from poisoning and the purification on the macroscopic scale is comparable to the purification by a conventionally applied guard reactor.

Subsequent to the described oxygen poisoning test the high-performance filter was set to bypass and almost immediately an activity loss could be observed (Fig. 4). The direct response of the ammonia concentration to the introduction of oxygen to the synthesis gas indicates that the whole catalyst bed contributes to the measured catalytic activity and it is possible to observe how the poisoning slowly proceeds throughout the catalyst bed. It took around 37 h for a full poisoning of 3 g catalyst under the applied reaction conditions until a new steady-state is established. During this time the catalyst lost around 75 % of its original activity.

The progress of the poisoning effect can be separated into two different processes: a relatively fast poisoning effect at beginning of the test and after a turning point at around 27 h time on stream a much slower loss of the activity. This can most likely be explained by an initial kinetically driven covering of the catalyst with oxygen, while afterwards a slow alignment of the final equilibrium between oxygen on the surface and in the gas phase takes place. After the new steady-state was achieved, an additional oxygen poisoning test was performed. Here, fast changes of the total flow rate led to a long equilibration of the ammonia signal indicating clearly the expected oxygen poisoning, as Fastrup and Nygård Nielsen [10] showed already a visible poisoning with 1.6 ppm oxygen.

Actually, the oxygen amount for this test seems to be far higher than expected as the gas supply of the setup is purified by standard oxygen scrubber cartridges, which should purify poisons in the synthesis gas to levels of <0.1 ppm $O_2$ and <0.5 ppm $H_2O$. By an additional experiment, where the high-performance filter was installed before the compressor of the setup, it could be verified that the compressor was the main cause for this higher amount of oxygen impurities. With the high-performance filter installed before the compressor and the guard reactor behind the compressor, a similar catalyst poisoning as observed before (see Fig. 4) occurs when the guard reactor is removed (Fig. 5). As the high-performance filter has been proven to be sufficient for a full removal of catalyst poisons from the synthesis gas, the oxygen must be introduced by the compressor. With its movable parts sealed by plastic O-rings and, therefore, unavoidable leak rate the compressor seems to be responsible for a major part of the presence of the oxygen impurities. It could be also possible that the lubricant or other polymer parts of the compressor release further poisons like S-, P- or F-containing compounds. However, as can be seen in Fig. 4 it was possible to restore the initial activity by enabling a full gas purification again indicating that the observed effect is only caused by a reversible oxygen poisoning.

Furthermore, to investigate the effect of the gas supply purified by standard oxygen scrubber cartridges a measure-

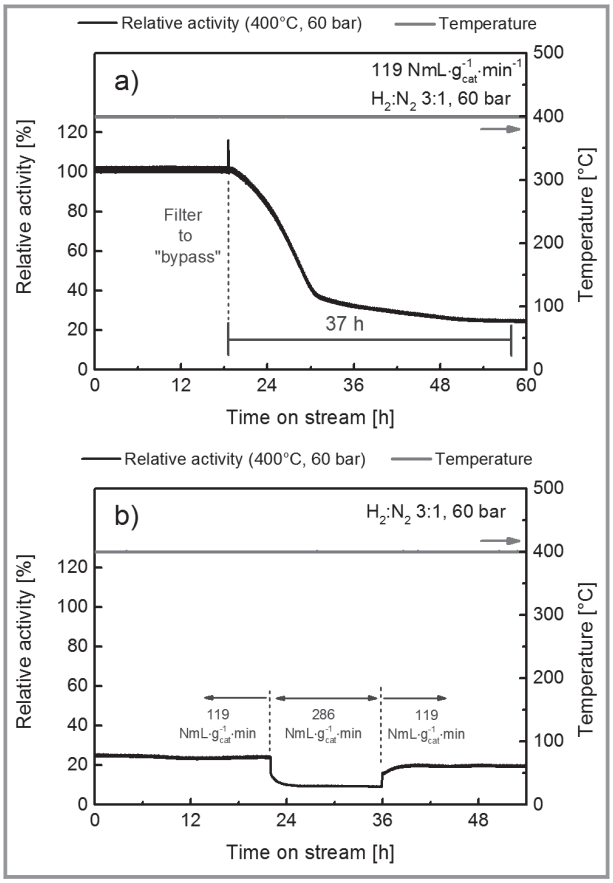


**Figure 4.** a) Poisoning of the catalyst after switching the high-performance filter to bypass. b) Oxygen poisoning test at 60 bar without any further purification.

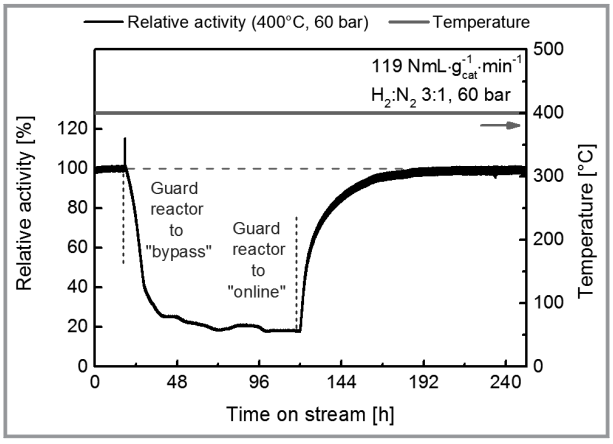


**Figure 5.** Catalyst poisoning without guard reactor and high-performance filter installed before the compressor as well as subsequent regeneration of the catalyst.

  

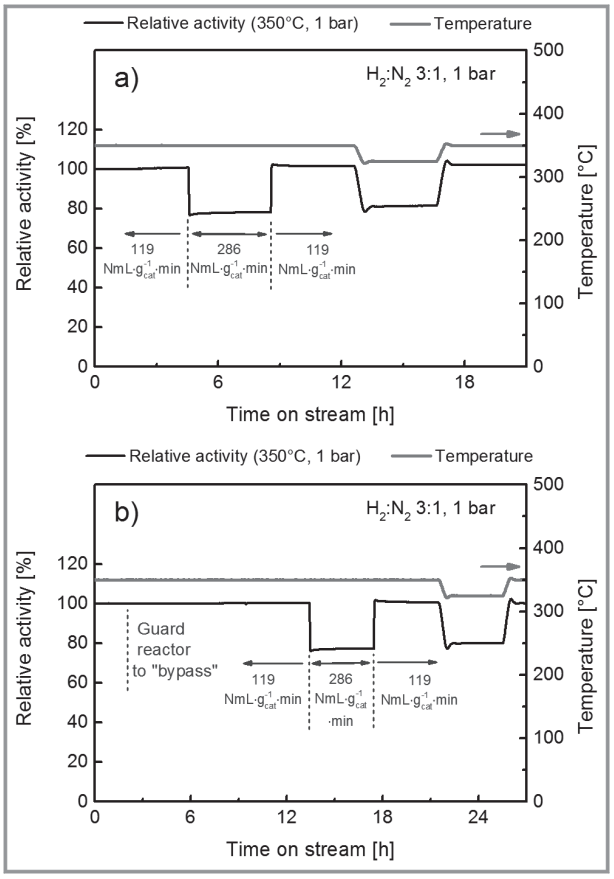


**Figure 6.** Oxygen poisoning test with synthesis gas purified by a) guard reactor and high-performance filter and b) high-performance filter at atmospheric pressure.

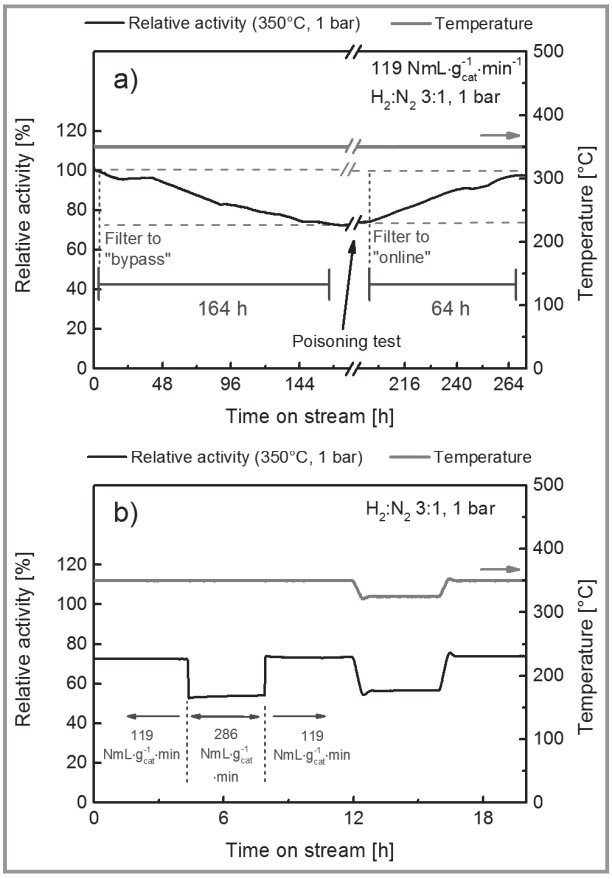


**Figure 7.** a) Catalyst poisoning at atmospheric pressure with synthesis gas purified by standard oxygen scrubber cartridges and without further purification as well as subsequent regeneration of the catalyst. b) Oxygen poisoning test with synthesis gas purified by standard oxygen scrubber cartridges at atmospheric pressure.

ment was conducted where the compressor was bypassed. As the compressor is needed within the setup to build up elevated pressures this measurement could only be performed at atmospheric pressure. For comparability the oxygen poisoning test was repeated at atmospheric pressure with synthesis gas purified by the guard reactor (Fig. 6a) and synthesis gas purified only by the high-performance filter (Fig. 6b). These measurements were performed at a lower standard temperature of 350 °C to ensure that the produced ammonia concentration is still far below the thermodynamic equilibrium as the equilibrium value decreases with decreasing pressure. The results of these oxygen poisoning tests are similar to the measurements at 60 bar. For both measurements no oxygen poisoning could be observed and, furthermore, no difference between the purification by the guard reactor and by the high-performance filter can be determined.

In a final measurement the effectiveness of a purification only by standard oxygen scrubber cartridges was investigated. These cartridges lower the amount of oxygen to <0.1 ppm and water to <0.5 ppm in the feed gas. After switching the additional purification devices to bypass a very slow poisoning of the catalyst was observed (Fig. 7a), which took around 167 h until a new steady-state was achieved. During this equilibration time the catalyst lost around 25 % of its initial activity under the applied conditions.

Here, the poisoning takes far longer and the activity loss is far lower compared to the oxygen poisoning induced by the compressor, but an activity loss of 25 % is still significant. Therefore, even oxygen impurities below 1 ppm can have a strong negative effect on the catalytic activity of iron-based ammonia synthesis catalysts. However, although a clear poisoning of the catalyst could be observed, it was not possible to identify any signs for poisoning with a subsequent test for oxygen poisoning (Fig. 7b). Accordingly, the oxygen poisoning test developed by Fastrup and Nygård Nielsen [10] has its limitations. While a poisoning with 1.6 ppm oxygen is still detectable applying this method, concentrations below 1 ppm are apparently too low to have a visible impact on the equilibration time of the ammonia synthesis activity, despite the fact that they still have a major influence on the catalytic activity. Additionally, in the end the initial activity could be restored also under these conditions by enabling a full gas purification again proving that

  

the observed effect is only caused by a reversible oxygen poisoning.

## 4 Conclusions

In total it could be demonstrated how highly sensitive an iron-based ammonia synthesis catalyst is toward oxygen poisoning and that a standard laboratory gas supply as well as some standard laboratory purification methods might be insufficient to prevent this poisoning. Even impurities below 1 ppm of oxygen lead to a significant loss in activity. The oxygen poisoning test for iron-based catalysts in ammonia synthesis introduced by Fastrup and Nygård Nielsen [10] does work, but also has its limitations. At oxygen amounts of less than 1 ppm it is not possible to identify an oxygen poisoning by this method, although this concentration leads already to a clear reversible deactivation of the catalyst in long-term. Therefore, the most sensitive detector for oxygen-containing impurities in the feed gas is the catalyst itself.

Poisoning in this range can originate from many potential sources and the components of a setup for activity and kinetic measurements need to be evaluated carefully in this regard. As it could be seen by the example of the applied compressor, already one component can prevent the ability to measure the full catalytic activity. However, a sufficient protection of the catalyst can be achieved by purification of the synthesis gas from any oxygen species down to the ppt range by a guard reactor or a high-performance filter. Such devices have to be considered while designing a test setup for kinetic and poisoning tests. Not only for iron catalysts in ammonia synthesis this may be crucial, also for poisoning studies in other reactions like Cu-based catalyst in methanol synthesis it can be essential to ensure a clean feed gas to obtain reliable information on the poisoning effect of the investigated compounds.

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## Abbreviations

| | | |
|---|---|---|
| $\Delta H_r^0$ | [kJ mol$^{-1}$] | standard enthalpy of reaction |

## References

[1] M. Oles, W. Lüke, R. Kleinschmidt, K. Büker, H.-J. Weddige, P. Schmöle, R. Achatz, *Chem. Ing. Tech.* **2018**, *90 (1–2)*, 169–178. DOI: https://doi.org/10.1002/cite.201700112
[2] G. Deerberg, M. Oles, R. Schlögl, *Chem. Ing. Tech.* **2018**, *90 (10)*, 1365–1368. DOI: https://doi.org/10.1002/cite.201800060
[3] J. Schittkowski, H. Ruland, D. Laudenschleger, K. Girod, K. Kähler, S. Kaluza, M. Muhler, R. Schlögl, *Chem. Ing. Tech.* **2018**, *90 (10)*, 1419–1429. DOI: https://doi.org/10.1002/cite.201800017
[4] M. Appl, Ammonia, 2. Production, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim **2011**.
[5] *Ammonia Catalysis and Manufacture* (Ed: A. Nielson), Springer, Heidelberg **1995**.
[6] A. Nielsen, *An Investigation on Promoted Catalysts for the Synthesis of Ammonia*, Jul. Gjellerups Forlag, Copenhagen **1968**.
[7] *Catalytic Ammonia Synthesis: Fundamental and Practice* (Ed: J. R. Jennings), Springer, Boston, MA **1991**.
[8] K. C. Waugh, *Catal. Lett.* **1994**, *24 (1–2)*, 197–210. DOI: https://doi.org/10.1007/BF00807390
[9] J. A. Almquist, C. A. Black, *J. Am. Chem. Soc.* **1926**, *48 (11)*, 2814–2820. DOI: https://doi.org/10.1021/JA01690A008
[10] B. Fastrup, H. Nygård Nielsen, *Catal. Lett.* **1992**, *14 (2)*, 233–239. DOI: https://doi.org/10.1007/BF00765236
[11] V. I. Tsarev, E. L. Aptekar, A. V. Krylova and N. S. Torocheshnikov, *React. Kinet. Catal. Lett.* **1980**, *14 (3)*, 279–282. DOI: https://doi.org/10.1007/BF02073491
[12] P. Stoltze, *Phys. Scr.* **1987**, *36*, 824–864. DOI: https://doi.org/10.1088/0031-8949/36/5/010
[13] www.linde-gase.de/produkte/armat/Reinigungspatronen.pdf (accessed April 24, 2020)
[14] www.saespuregas.com/Library/specifications-brochures/MicroTorr_Brochure.pdf (accessed April 24, 2020)

  