Handbook

Generation of a Reference Data Set

for the

AmmoRef

project

part of the

Leitprojekt
TransHyDE

GEFÖRDERT VOM

Bundesministerium
für Bildung
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1. Introduction

The advantages of ammonia as a chemical hydrogen storage medium are primarily that it is a carbon-free carrier whose production is highly optimized and which can be liquefied and transported comparatively easily.[1,2] However, the use of ammonia as a storage molecule requires that the re-release of hydrogen can be carried out efficiently on a large scale. The splitting of ammonia into its elements is an endothermic equilibrium reaction, so high reaction temperatures (> 450°C) are required to achieve a technically interesting conversion (see Figure 1). Post-purification is inevitable if traces of ammonia and of by-products in the released hydrogen have to be avoided. The cleavage of the ammonia molecule has often been used as a model reaction to study ammonia synthesis catalysts. However, with the goal of producing hydrogen under relevant reaction conditions (high ammonia concentration), the reaction has only recently been increasingly studied,[2-7] but a technical process has not yet been established for this purpose.

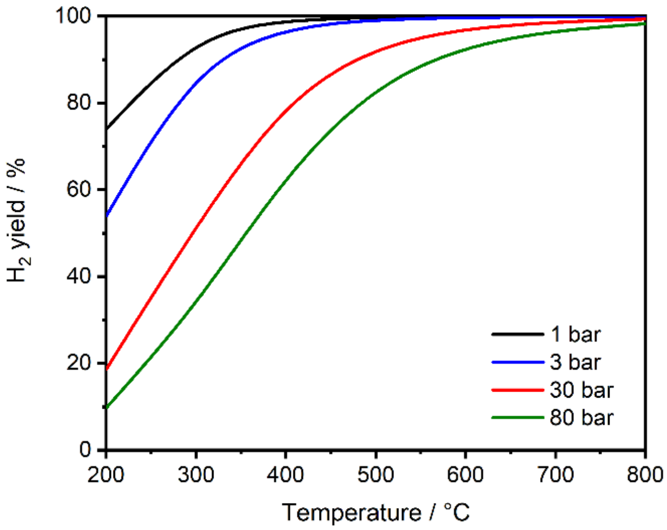

Figure.1: Temperature dependence of the equilibrium yield of hydrogen in ammonia decomposition at 1, 3, 30 and 80 bar.

Big data analysis and methods of data mining and machine learning are currently undergoing renewed interest in heterogeneous catalysis with the aim to discover catalysts with improved performance in reactions that are influenced by a multitude of parameters.[8,9]

Data science requires extensive datasets that contain reliable experimental data. It is known that ammonia decomposition catalysts are subject to strong changes under reaction conditions.[10] Not only for the application of artificial intelligence methods, but also for the direct comparison of catalysts synthesized and investigated in different laboratories, **it is therefore extremely important that the experiments are carried out in such a way that they allow comparability**. This enables a faster narrowing down of promising highly active and, in particular, stable catalyst systems within the activities of the entire consortium in the AmmoRef project.

This book gives the **Minimum Requirements** for catalytic tests in ammonia decomposition and basic characterization methods, complemented by advanced characterization techniques (not available in every laboratory), to ensure a constant quality level of all relevant data and enough intercept points with theory.

The presented requirements are mandatory.

Each scientist should feel free about adding additional experiments (e.g., additional methods in catalyst characterization or other test reactions). The quality of spectroscopic measurements can be improved (e.g. to achieve higher resolution, etc.). But the specified workflow of the **catalytic testing** must be **strictly** followed in order to obtain reliable results on the possible restructuring of the catalyst under reaction conditions that allow conclusions on long-term stability.

2. General Information

The heterogeneous catalyst (generally an amorphous or crystalline inorganic or organic solid or a composite material) must be synthesized in large batch size (15-20 g) to guarantee that catalytic testing and comprehensive catalyst characterization is performed using the same batch.

After synthesis, the “green” catalyst precursor needs to be thermally treated in synthetic air, inert gas or another gas atmosphere (gas composition, flow rate, heating rate, holding time, *etc.* depending on the chemistry of the catalyst) before the catalytic test and before the characterization of the **fresh catalyst** obtained by thermal treatment. Characterization of green catalyst precursors is desirable, but not mandatory for this project.

⚠**The reaction temperature in the catalytic test must not exceed the temperature of thermal activation. In other words, it is essential to thermally treat the catalyst at temperatures higher than the highest reaction temperature prior to the catalyst test in order to avoid unforeseen purely thermally induced conversions or decompositions in the reactor.**

The thermally treated catalyst is pressed (the pressure has to be adopted to the chemistry of the catalyst), crushed, and sieved to a particle size of **200–300 µm (split)**. The catalyst obtained in this way is called **fresh catalyst**. To avoid contamination, dedicated sieves have to be used for every catalyst type. The described procedure is different from the workflow of catalyst preparation in industry, but more suitable for catalyst investigations in laboratory scale.

The required catalyst mass is 15-20 g of a thermally pre-treated sieve fraction (200–300 µm) (fresh catalyst).

Generally, heterogeneous catalysts exhibit a dynamic behavior in contact with the reacting gas or liquid. The chemistry of the solid catalyst responses to the chemical potential of the surrounding atmosphere, which changes by varying feed composition, reaction temperature, and contact time. The dynamic changes might be reversible and affect just a thin surface layer, but irreversible structural changes of the catalyst bulk are also frequently observed. Processes, such as sintering of primary catalyst particles or active components, changes in the formal oxidation state of the constituent elements, phase transformation, phase segregation, deposition of intermediates, side and consecutive products, or loss of volatile components may lead to phenomena like **formation periods** (increasing activity and/or changing selectivity at the beginning of a catalytic test) or catalyst **deactivation** (loss in activity and selectivity with increasing time on stream).

Rapid tests for the purpose of catalyst screening shall be carried out in all laboratories according to the same defined program. Here, only temperature variation is used to screen whether the catalysts are active and whether they change significantly under reaction conditions. Comprehensive kinetic data are collected without exception in “**steady-state**” operation of the catalyst, *i.e.*, no macroscopic changes in activity (substrate conversion) and product selectivity are observed with time on stream (TOS) under the applied reaction conditions. It is necessary to wait for steady-state after any kind of change in reaction conditions (T, p, feed composition, contact time).

Since changes in catalyst composition and structure during the catalytic test have to be expected, it is necessary to characterize the catalyst **before** inserting the catalyst into the reactor (**fresh catalyst**) and

after removing the catalyst from the reactor (**used catalyst**). If possible, the used catalyst should be removed from the reactor and handled for storage and further characterization under inert conditions like for example in a glovebox with < 0.1 ppm O_2 and < 0.1 ppm H_2O. At the same time the used catalyst samples should also be transferred and characterized under inert conditions, if the used characterization method allows it. For transport and sending of the samples used catalyst samples airtight transport vessels are recommended. A simple transport vessel for inert conditions can be obtained by using steel parts with Kleinflansche (KF)/Quick Flanges (QF) as connections. Steel parts with KF connections are standard parts in ultra-high vacuum technology and therefore available in a very broad range of sizes and shapes. A KF connection has a very low leaking rate ($< 10^{-9}$ mbar L/s) and the steel body makes it very robust for transportation. A small transport vessel can be bought for example from VACOM Vakuum Komponeten & Messtechnik GmbH with following parts:

- 1x KF Straight connector, DN40, stainless steel 316L, length 130mm (Order Nr. 302503)
- 2x KF Blank flange, DN40, stainless steel 316L (Order Nr. 302007)
- 2x KF Centering ring, DN40, stainless steel 316L / FKM (Order Nr. 302076)
- 2x KF Clamp chain, DN40, aluminum (Order Nr. 303289)

There are also commercial caskets for inert sample transport available, but to our experience they are more expensive, less size adaptable and have the same or a worse leaking rate than a KF connected vessel.

Generally, the catalyst volume and therefore the sample mass, which is inserted into the test reactor, is limited. Therefore, the characterization of the used catalyst has to be performed frequently with lower precision compared to the characterization of the fresh catalyst. The differences in precision have to be taken into account in the interpretation of the results.

The following **basic** characterization techniques are **mandatory** (Table 1). Advanced characterization techniques will be performed when available in the corresponding laboratory and only after a rapid activation of the catalyst in the corresponding reaction feed.

The selection of the samples to be used for the advanced methods will be discussed in regular “selection meetings”. Active as well as non-active catalysts should be selected.

Table 1. Basic and advanced catalyst characterization

Information	Fresh catalyst	Reduced catalyst	Used catalyst	Technique	Section
Basic methods					***5***
Chemical composition	X	X	X	XRF, ICP-OES, EDX (EDX only in case of used catalyst when too little catalyst mass is available), CHNS analyzer for carbon-based catalysts	5.5
Near surface chemical composition		X	X	Laboratory XPS	5.7
Formal oxidation states of elements near the surface		X	X	Laboratory XPS	5.7
Phase composition and structural parameters	X	X	X	XRD	5.1
Surface area and pore size distribution	X	X		Nitrogen sorption	5.2

Oxidation / reduction equivalents	X	X	X	Temperature-programmed oxidation-reduction (TPO-TPR) cycles	5.3,5.4
Reactions with ammonia		X	-	NH3 TPD	
Morphology (size, shape, structure, particles)	X	X	X	SEM	5.8
Vibrational spectroscopy	X	X	X	IR, Raman	5.9
Metal dispersion		X	-	H2 or CO adsorption	

Advanced methods					***6***
Surface work function	X		X	Kelvin probe measurement	6.1
Wetting ability	X		X	Contact angle measurement	6.2

Information summarized in a table, e.g.:

	Catalyst preparation				Characterization					Catalysis				
	Synthesis		Activation		XRD				…	*Ammonia decomposition*				…
Catalyst ID	Synthesis technique	…	T_{max} [°C]	…	ICSD	*a* [Å]	…	…		Feed	*r* (300°C) [mmol g^{-1} h^{-1}]	*r* (300°C) [mmol m^{-2} h^{-1}]	E_a [kJ mol^{-1}]	
1	HT		650							Standard				
2	P									Standard				
…														

Reference points (conversion at a reference temperature and stability factor at reference temperature) need to be determined after the first test. The determination and discussion will take place during a “selection meeting”.

3. Catalyst Testing for low-pressure ammonia decomposition

Before catalytic testing in a laboratory reactor, every sample has to be tested in a TPR experiment under the conditions described in section 5.3 and 5.4 to evaluate the reducibility of the sample. Due to the broad range of different catalyst classes in this project the reduction behavior of the samples will differ strongly and might require different activation procedures, which have to be adjusted to the kind and reducibility of the material.

The laboratory reactor must be capable of continuous, steady-state operation under isobaric, isothermal, and ideal flow conditions and concentration gradients must be avoided.[11] In the ammonia decomposition, plug flow reactors are preferred for catalyst testing. Ideal flow pattern in such a micro-reactor require a maximum **sieve fraction** size of 1/10 of reactor inner diameter.

Specifically, the catalytic experiments have to be carried out in such a way that the common criteria for a plug flow model are fulfilled or at least approached, *i.e.*:

$$\frac{L}{d_p} > 50 , \frac{d_r}{d_p} > 10 , \frac{L}{d_r} > 5$$

Equations (1-3)

with L being the length of the catalytic bed [mm], d_r the diameter of the reactor [mm] and d_p the diameter of the catalyst particles [mm]. If it should not be possible to meet the criteria in an existing setup, the conditions will be approached.

For catalytic testing the sample fraction of **200 µm – 300 µm** should be diluted in a mass ratio of 1:2 with silica carbide (SiC) in the sieve fraction of 300 µm – 400 µm as inert filling material. This should allow a better heat conduction in the reactor and ensure isothermal conditions over the whole catalyst bed as ammonia decomposition is a strongly endothermic reaction and could lead to temperature gradients over a concentrated catalyst bed. The particle size of SiC needs to be above the particle size of the catalyst fraction to allow a separation via sieving after catalytic testing and to keep the pressure drop in the reactor minimal. By shaking in a sieve the catalyst can be removed from the SiC. The rest of the reactor can be filled with SiC or other inert filling materials (e.g. quartz sand or quartz wool). The filling level should always be constant.

For all laboratory reactors there must be a blank measurement where the sample fraction is replaced with SiC and measured under all reaction conditions of catalytic testing to verify the effect of non-catalyzed thermal ammonia decomposition. Especially at higher temperatures (>600 °C) non-catalyzed thermal ammonia decomposition could lead to significant conversions and need to be taken into account for the evaluation of the performance of a catalyst sample.

- Devices applied to supply constant feed need to be calibrated
- Volume flow rates are always stated at norm conditions [NmL min^{-1}] (T = 273.15 K, p = 1.013x10^5 Pa)
- Weight/flow (Katalysatorbelastung) is always given in volume flow rate normalized to catalyst mass [NmL min^{-1} g^{1}]
- Catalyst stress can additionally be given as gas hourly space velocity (GHSV) [h^{-1}] if there is a possibility to measure the bulk volume of the catalyst bed V_{cat}.

$$GHSV = \frac{\dot{V}_{gas}}{V_{cat}} \qquad \text{Equation (4)}$$

- Purity for standard gases (NH_3, N_2, O_2, He, Ar, H_2, synthetic air, Kr, Ne, etc.) has to be at least 5.0, but it is recommended to ensure further purification with for example in-line gas cleaning traps (e. g. Entegris GateKeeper supplied by Rainer Lammertz pure gas products, suitable type of trap depends on the used gas and flow rate range, purification to < 100 ppt O_2, < 100 ppt H_2O, < 100 ppt CO, < 100 ppt CO_2)

- For basic comparison of all measurements under identical conditions the effluent ammonia mole fraction x_{NH3} [%] needs to be provided.

Furthermore, the conversion of ammonia X_{NH3} [%] and the conversion rate of ammonia r_{NH3} [$kg_{NH3}\ kg_{cat}^{-1}\ h^{-1}$] are required key parameters. Both can be calculated from the molar flow rate of ammonia at the reactor inlet ($\dot{n}_{NH3,in}$) and reactor outlet ($\dot{n}_{NH3,out}$) and the catalyst mass (m_{cat}).

$$X_{NH3} = \frac{\dot{n}_{NH3,in} - \dot{n}_{NH3,out}}{\dot{n}_{NH3,in}} \qquad \text{Equation (5)}$$

$$r_{NH3} = \frac{\dot{n}_{NH3,out} - \dot{n}_{NH3,in}}{m_{cat}} \qquad \text{Equation (6)}$$

And with additional parameters also from the volume flow rate ($\dot{V}_{NH3}$) and mass flow rate ($\dot{m}_{NH3}$) of ammonia (as volume flow rates are always stated at norm conditions: T = 273.15 K and p = 1.013x10^5 Pa).

$$\dot{n}_{NH3} = \frac{p * \dot{V}_{NH3}}{R * T} \qquad \text{Equation (7)}$$

$$\dot{n}_{NH3} = \frac{\dot{m}_{NH3}}{M_{NH3}} \qquad \text{Equation (8)}$$

The ammonia flow rate at the reactor inlet is known for all measurements. Depending on the detection capabilities of the set-up, it could not be possible to directly measure the ammonia flow rate at the reactor outlet. If this is the case it is possible to calculate the key parameters from the effluent ammonia mole fraction x_{NH3}, but it should be noted that the volume expansion of the ammonia decomposition reaction needs to be taken into account for the calculation of X_{NH3} and r_{NH3} from x_{NH3}. Depending on the set-up this can be done by internal standard correction or under the theoretical assumption of 100% selectivity and that the not-ammonia part of the outlet gas mixture consists only of hydrogen and nitrogen in a ratio of 3:1.

Other parameters can be provided additionally depending on the detection capabilities of the used reactor set-up and work group.

Selectivity S [%] and yield Y [%] can be provided if the used set-up has the capability to detect side products. Literature reports the possibility of hydrazine as side product of ammonia decomposition under certain reaction parameters. Some set-ups will have the capability to investigate the existence of side products under the planned measurement conditions.

The apparent activation energy [kJ mol^{-1}] of ammonia decomposition including standard deviation is determined based on the rates determined at minimum five different reaction temperatures and has to be taken in a range of conversion, which is far from any limitation by the thermodynamic equilibrium of ammonia decomposition.

Absence of external and internal transport limitations should be verified by calculating the dimensionless Mears and Weisz-Prater criteria[12].

All catalysis apparatus must be verified by regular (at the beginning of the project more often, experience value) measurements of a benchmark. **The following samples were selected as benchmarks:**

- **AmoMax NH_3 synthesis catalyst (Wüstit) provided by Clariant**
- **ReforMax100 Ni-based catalyst provided by Clariant**
- **Ru@C , 5wt% loading, water content ≤1.0 %,** PubChem Substance ID: 24852384, provided by Sigma Aldrich. Specifications from supplier: Surface area by N_2 adsorption and BET analysis 900 m^2/g, particle size 19 µm

The reference catalysts have to be stored in a cabinet. Before characterization the catalysts have to be dried at 80 °C for 4h.

⚠ **Before catalytic testing, every sample has to be tested in a TPR experiment under the conditions described in section 5.3 and 5.4.**

3.1 Fast screening

The fast screening measurement should give a first impression about the general ammonia decomposition activity of a sample and should serve as an indicator to identify promising samples for further much more time-consuming detailed kinetic measurements and analysis. Therefore, the entirety of the fast screening measurement from the insertion of one sample to the possible insertion of a next sample has to take around 24 h to allow a testing rate of one measurement per workday.

All fast screening measurements need to follow a 3-step measurement protocol (activation/reduction, activity measurement, cooling/purging) and can be chosen **with a variable reduction temperature** depending on the tested catalyst type. Some sample types will require a high temperature for a full reduction of the sample (e.g Fe/Co oxide catalysts), while other sample types could not withstand or do not need a high temperature reduction (e.g Ni/Ru catalysts).

For a fast screening measurement the reactor should be filled with 200-500 mg of the sample fraction (200-300 µm), which is diluted with SiC in a mass ratio sample : SiC of 1 : 2.

Fast screening measurement for samples with **variable Reduction / Pretreatment**

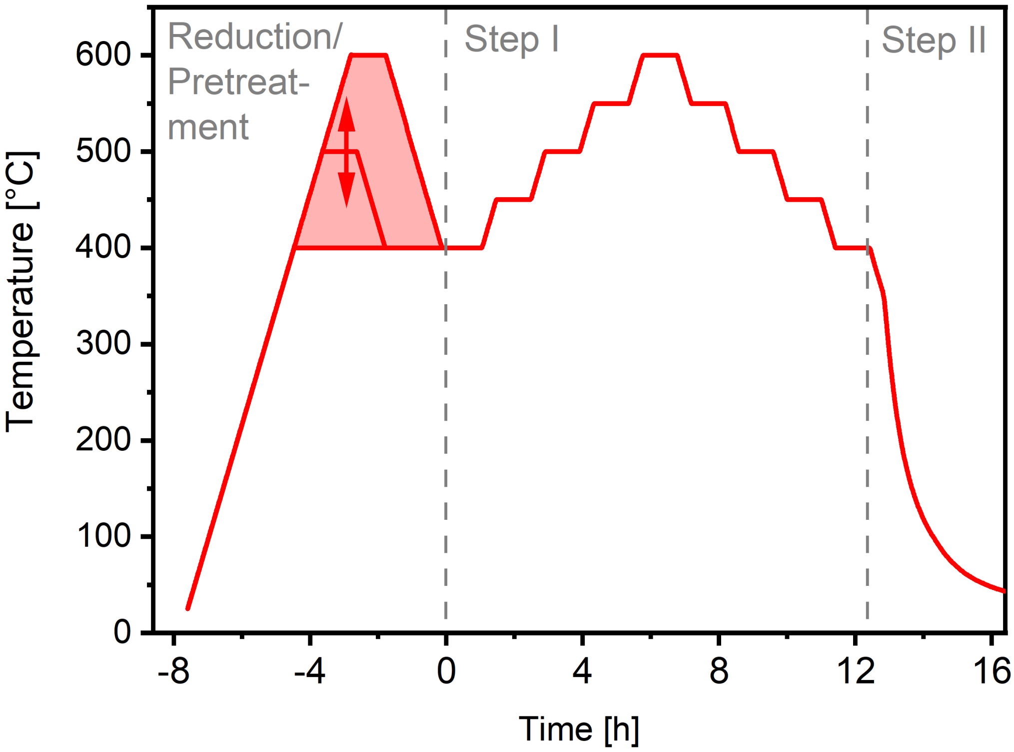

Figure.1: Temperature profile of the fast screening with variable Reduction/Pretreatment (example with 400, 500 and 600 °C reduction)

Reduction/Pretreatment

The activation step brings all samples in a reduced metallic state. Requirements for this step may differ for each sample type. **Therefore, reduction parameters like H_2-content, temperature and total duration can be varied over a broad range, depending on the requirements of the samples, but it should be tried to keep the reduction of at least similar sample classes as identical as possible.** The possible ranges for the samples are defined as:

- Gas composition of 10-75 % H_2 and 90-25 % N_2
- Volume flow of 1000 NmL min^{-1} g^{-1} (e.g. 100 NmL min^{-1} for 100 mg)
- Temperature ramp from room temperature to **400-600 °C** (depends on catalyst sample) with a heating rate of 2 °C min^{-1}, constant holding of **400-600 °C** (depends on catalyst sample) for 1 h, cooling with 2 °C min^{-1} to 400 °C and constant holding of 400 °C for at least 10 min (total duration 7 h 37 min)
- Atmospheric pressure

⚠ A difference from the produced catalyst samples of the project are the benchmark catalysts that are used as references for comparability. **The benchmark catalysts need to be activated at all measurements under identical conditions. A specific reduction procedure is defined for each benchmark catalyst:**

AmoMax NH_3 synthesis catalyst (Wüstit):

- Gas composition of 100 % H_2
- Volume flow of 1000 NmL min^{-1} g^{-1} (e.g. 100 NmL min^{-1} for 100 mg)
- Temperature ramp from room temperature to 400 °C with a heating rate of 0.8333 °C min^{-1}, from 400 to 600 °C with 0.3333 °C min^{-1} and constant holding of 600 °C for 6 h (total duration 24 h)
- cooling with 2 °C min^{-1} to 400 °C and constant holding of 400 °C for at least 10 min
- Atmospheric pressure

ReforMax100 Ni-based catalyst:

- Volume flow of 1000 NmL min^{-1} g^{-1} (e.g. 100 NmL min^{-1} for 100 mg)
- Heat up in N_2 from room temperature to 100 °C with 0.5 °C min^{-1}
- Heat up in N_2 from 100 °C to 120 °C with 0.0833 °C min^{-1}
- Heat up in 20 % H_2 / 80 % N_2 from 120 °C to 500 °C with 0.8333 °C min^{-1}
- Hold at 500 °C for 10 h (total duration 24 h)
- cooling with 2 °C min^{-1} to 400 °C and constant holding of 400 °C for at least 10 min
- Atmospheric pressure

Ru@C, 5wt% loading, water content ≤1.0 %:

- Gas composition of 10 % H_2 and 90 % N_2
- Volume flow of 1000 NmL min^{-1} g^{-1} (e.g. 100 NmL min^{-1} for 100 mg)
- Temperature ramp from room temperature to 400 °C (depends on catalyst sample) with a heating rate of 2 °C min^{-1}, constant holding of 400 °C (depends on catalyst sample) for 1 h, (total duration)
- Atmospheric pressure

Step I: Activity Measurement

The activity measurement allows a comparison of the catalytic ammonia decomposition of a sample at a for an industrial process relevant temperature range and gas composition with following conditions:

- Gas composition of 100 % NH_3
- Volume flow of 600 NmL min^{-1} g^{-1} (e.g. 60 NmL min^{-1} for 100 mg)
- Temperature program with eight steps from 400 °C to 600 °C and back to 400 °C (400, 450, 500, 550, 600, 550, 500, 450 and 400 °C). All temperature steps are kept constant for 1 h and each temperature step (except the first 600 °C step, *T* already kept from activation/reduction) is reached with a heating ramp of 2 °C min^{-1}
- Atmospheric pressure

Step II: Cooling and Purging

While the reactor is cooled to room temperature the reactor is purged with inert gas to allow a safe removal of the used catalyst for characterization:

- Gas composition of 100 % N_2 (or another inert gas)
- Volume flow of 600 NmL min^{-1} g^{-1} (e.g. 60 NmL min^{-1} for 100 mg)
- Cooling from 600 °C as fast as possible for the used set-up
- Atmospheric pressure

3.2 Kinetic measurement and stability

Detailed kinetic measurements should only be done for samples who showed a promising catalytic performance in the fast screening measurements. No sample that has in the fast screening an activity below the activity of the reference catalyst (see definition section 3) is rated as a promising sample!

The kinetic measurements should give for a promising sample at minimum a more detailed insight in the temperature-activity relationship than the fast screening including an apparent activation energy, a test of the influence of catalyst stress variation on the sample and information on the long-term stability of the sample. This requires at least seven steps for the kinetic measurements, which have to be measured for all promising samples. Further steps can be added depending on the requirements of each project partner and catalysts and are subject to change through the ongoing of the project in consultation with all partners. The following list gives the current minimal required steps for a kinetic measurement of a promising sample.

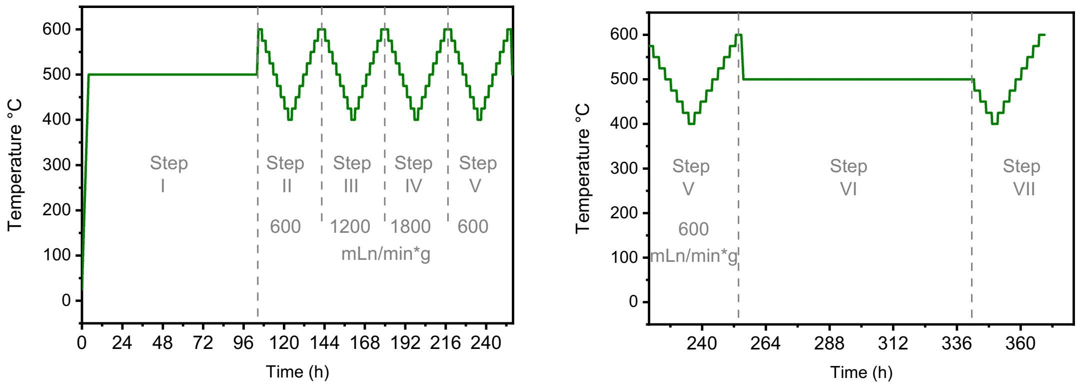

Figure.3: Temperature profile of a kinetic (a) and stability measurement (b) with the minimal required steps.

Step I: Activation/Reduction

The activation/reduction can follow the same reduction conditions as the fast screening measurement (section 3.1), but depending on the sample type it might be possible to do before the kinetic measurement an optimization of the reduction parameters for a specific promising sample. Especially a variation of gas composition, heating rate and maximum temperature could lead for some samples to a higher catalytic performance. Only the reduction of the benchmark catalysts needs to always follow the same reduction protocols as described in chapter 3.1. **In all cases the reduction should be followed by a stabilization phase at 500 °C for at least 96 h to ensure that the catalyst is fully activated and operates in a steady state.**

Step II: Activity Measurement with more detailed temperature steps

The activity measurement should at least follow the same temperature range as the activity measurement for fast screening, but with more temperature steps and prolonged temperature steps to get a more detailed temperature-activity relationship. If it is experimentally useful for the sample, the temperature range could also be enlarged to lower temperatures.

- Gas composition of 100 % NH_3
- Volume flow of 600 NmL min^{-1} g^{-1} (e.g. 60 NmL min^{-1} for 100 mg)
- Temperature program with 25 °C steps from 600 °C to 400 °C and back to 600 °C. All temperature steps are kept constant for 2 h and each temperature step (except the first 600 °C step, T already kept from activation/reduction) is reached with a heating ramp of 2 °C min^{-1}
- Atmospheric pressure

Step III-V: Flow rate variation

Flow rate variation for especially active catalyst samples. Useful flow rate range might depend on the overall activity of the project catalyst samples. Each flow rate test should also include a temperature variation.

- Gas composition of 100 % NH_3
- volume flow variation to 1200 NmL min^{-1} g^{-1}, 1800 NmL min^{-1} g^{-1} and a final step back to reference value of 600 NmL min^{-1} g^{-1}
- Identical temperature program to Step II
- Atmospheric pressure

Step VI: Stability test

Long-term stability should be tested for the most promising samples as long as possible, but at least for 72 h. Flow rate and temperature for long-term stability test might change during the ongoing project depending on the overall performance of the investigated catalyst samples.

- Gas composition of 100 % NH_3
- Volume flow of 600 NmL min^{-1} g^{-1} (e.g. 60 NmL min^{-1} for 100 mg)
- Constant temperature of 500 °C for at least 72 h
- Atmospheric pressure

Step II: Temperature variation after stability test

Gives a better impression of the effect of possible deactivation during the stability test on the performance of the catalyst sample. Flow rate and temperature might change during the ongoing project depending on changes on the long-term stability test.

- Gas composition of 100 % NH_3
- Volume flow of 600 NmL min^{-1} g^{-1} (e.g. 60 NmL min^{-1} for 100 mg)
- Temperature program with 25 °C steps from 500 °C to 400 °C and back to 600 °C. All temperature steps are kept constant for 2 h and each temperature step (except the first 600 °C step, *T* already kept from activation/reduction) is reached with a heating ramp of 2 °C min^{-1}
- Atmospheric pressure

4. Catalyst Testing for high-pressure ammonia decomposition

Input: BASF, BasCat

5. Basic Catalyst Characterization

5.1 Powder XRD – Minimum Requirements

XDR characterization is to be performed for:

- Fresh catalysts (before catalytic testing)
- Used catalysts (after catalytic testing)
- Corresponding “reference samples”, if applicable
  (example: for a series of supported catalysts with varying loading, the “reference” would be the “zero-loading” sample, i.e. the bare support, but treated in the same way (like washing, drying, calcining etc.) as if it was loaded)
- Suitable instrument standards (certified NIST standard reference materials)

Powder diffractometers vary from lab to lab, thus:

- All measurements belonging to the same series (fresh/used/”reference” as defined above) must be performed on the same diffractometer with the same measurement conditions
- An in-house (MPI CEC) measurement procedure is defined (see section 5.1.3)
- Guidelines for optimizing portability/comparability of conditions between labs are given (see section 5.1.4)

5.1.1 Samples to be Provided

- Fresh catalysts (including “reference samples” as defined above) must be in the same state as if they were to be loaded into the catalytic test rector (same pre-loading treatment like e.g. calcination)
- The samples may be ground before measurement for better sample preparation
- A minimum sample volume of **0.3 ml, typically ≥100 mg in reflection geometry (≥1 mg in transmission geometry),** must be provided (XRD is a destruction-free method, i.e. the sample can be distributed to other analysis methods after XRD)

5.1.2 Instrument Standards:

- A measurement of a NIST standard reference material (SRM) with certified lattice parameters (e.g. sintered corundum plate SRM1976a-c, Si powder SRM640a-f, LaB_6 powder SRM660a-c) which is suitable for the respective instrument geometry should be performed[13]
- Same measurement conditions (range, sample geometry, slits, filters, sollers etc.) as for catalyst samples
- Instrument standard and sample measurement should be performed in temporal proximity (at least within one month), without changes of diffractometer hardware or calibration between the two measurements
  → instrument standard measurement must be repeated whenever necessary
- As a result, there should be (at least) one valid instrument standard measurement available for every sample measurement (several sample measurements may share a common instrument standard measurement)

5.1.3 MPI CEC In-House Procedure

- Measurements in Bragg-Brentano (reflection) geometry on Bruker Phaser D2 2nd Generation (*i.e.*, CuKα_{1+2} radiation, Ni filter, energy dispersive position sensitive LynxEye detector)
- Si low background sample holder with cavity
- Fixed divergence slit 0.6mm ≈ 0.36°
- Angular range 10 to at least 120° 2θ
- "Step size" 0.01-0.04° (actual value can be adjusted to have sufficient data quality per sample type)
- Counting time ~1 second/step (adjust to have >10000 counts on intense reflections above background)
- Instrument standard: sintered corundum plate

5.1.4 Guideline for Diffractometers in other Labs

- Cu radiation
- Bragg-Brentano geometry with powder-bed sample holder, if available, is preferred
- Details of geometry, including monochromatization, need to be stated by operator (example: Bragg-Brentano or Debye-Scherrer geometry; primary or secondary monochromator, mirror, energy dispersive detector, Ni filter)
  → information should be sufficient to deduce the fine structure of the radiation used, e.g. pure Cu Kα_1 (primary or secondary monochromator), Cu Kα (Ni-filter used), Cu Kα + possible Kβ and other satellites (unfiltered) for standardized data evaluation
- IF Bragg-Brentano (or similar) geometry is used, the measurement must be performed with fixed divergence slit, not with variable divergence slit
- Minimum angular range 10-100° 2θ
- Measurements with point detectors (0D detector, e.g. scintillation counter) and position sensitive (1D) solid state detectors (preferable): >7 points above FWHM for good data quality and possibility of Rietveld refinements , high enough time per step to reach at least 10.000 counts above background with intense reflections
- For Samples with high Iron or Cobalt content, use fluorescence suppression with Cu Kα if available or different irradiation source.
- Measurements with older (counting wire) position sensitive (1D) detectors should be avoided (data quality depends too much on detector performance)
- Instrument standard (NIST, with certified lattice parameters) should be suitable for respective measurement geometry

XRD results:

ICSD	*a* [Å]	*b* [Å]	c [Å]	*α* [°]	*β* [°]	*γ* [°]	*Unit cell volume*	*Phase composition when multiphase*	*Crystallite sizes (ideally from Rietveld analysis and Strain consideration)*

5.2 Surface Area Determination

5.2.1 Sample Amount and Pretreatment

- The sample amount depends on the sensitivity of the instrument and the surface area
- As rule-of-thumb the absolute surface area must be **0.5-1 m^2** and higher

➔ With 10-100 m^2/g only 10 mg is needed, with <10 m^2/g about 100 mg.

- Samples in sieve fraction of 200 µm – 300 µm
- Pretreatment in vacuum for 16 h at 120 °C
- Final pressure ~ 10^{-4} mbar

5.2.2 Measurement Conditions

- DIN ISO 9277
- Nitrogen adsorption at 77 K
- Measurement of full adsorption-desorption isotherms> 40 steps adsorption, 40 steps desorption

5.2.3 Data analysis

- Determination of the specific surface area S_{BET} according to the multipoint Brunauer-Emmett-Teller method (BET) in the **linear** p/p_0 = 0.05-0.3 pressure range
- N_2 cross sectional area **A_{N2} = 0.162 nm**
- C (BET parameter) > 0
- Determination of specific pore volume at p/p_0 = 0.99
- Perform BJH calculations for the desorption branch of the isotherm; The Halsey thickness curve should be used for the BJH calculations. Determine the modal pore diameter $D_{BJH,des}$ from the desorption branch of the isotherm
- Perform DFT analysis for Carbon based materials using QSDFT-Method or similar
- Validation: N_2 adsorption on alpha-Al_2O_3 (BAM-PM-102) for small surface areas and TiO_2 (BAM-P106) for mesoporous materials

Nitrogen sorption results:

S_{BET} [m^2/g]	$V_{0.99}$ [cm^2/g]	d_{BJH} [nm]

5.3 Temperature Programmed Reduction – TG-MS

TG-MS characterization aims to quantify adsorbed surface species of the fresh catalysts. TG-MS characterization has to be performed in a flow of 5 %H_2 in Ar with 6 Kpm from 40 °C to 1000 °C. **Important: Should the sample have melting, decomposition or sublimation point within the temperature range, the maximum temperature should not exceed this point.** The thermochemical property has to be proofed in advance before the measurement. The dataset has to meet following criteria:

5.3.1 TG Requirements and Settings

- Instrumental Resolution 0.1 µg, Temperature precision 0.1 K
- Data Acquisition Rate: 100 points/min
- Correction for the buoyancy force: blank run with empty crucible
- Baseline drift 30-1000 °C: ±200 µg
- Crucible material: Al_2O_3, 85 µl
- Total minimum mass change: 50 µg
- Noise: ±2 µg

- Gases: Ar 5.0, O_2 5.0 additionally dried.
- Total flow: 80 ml/min
- Gas Flow stability: ±0.1 ml/min
- Precision of sample mass: 0.01 mg

5.3.2 MS Requirements and Settings

- Ionization Energy: 50-70 eV
- Monitored mass to charge ratio m/z: 12, 14, 15, 16, 17, 18, 28, 30, 32, 35, 36, 37, 44, 48, 64 (minimum, more masses are allowed)
- dwell time 0.2 sec/amu
- Background stability

TG-MS results:

Information about purity of the fresh catalyst, determination of the temperature range of desorption of water, carbonate and residues from catalyst synthesis.

5.4 Temperature-Programmed Reduction

TPR characterization aims to investigate the reduction behavior of the catalyst samples.

The thermochemical property has to be proofed in advance before the measurement. The dataset has to meet following criteria:

- 20 mg sample (if possible particle fraction 200-300 µm)
- Gas composition of 5 % H_2 and 95 % Ar with a total gas flow 80 mln/min
- Temperature program from room temperature to 1000 °C with a heating ramp of 6 $°C\ min^{-1}$

Important: Should the sample have melting, decomposition or sublimation point within the temperature range, the maximum temperature should not exceed this point.

These TPR conditions might not fit to all available TPR set-ups and sample types. If different TPR set-ups require different sample masses adjust flow rate to new sample mass. In case a sample type does not give any useful results under these conditions, the parameters can be adjusted in a way that the Monti-Baker criterion[14] (55 s < K_{MB} < 140 s) and the Malet-Caballero criterion[15] (p_{MC} < 20 K) are met.

TPR results:

Reduction profile vs. temperature	*Number of reduction peaks → Number of different reduction reactions*	*Position of peak maximum of reduction peaks [°C]*	*Temperature range of reduction under TPR conditions [°C]*	*Integrated H_2 consumption of reduction [mmol] (If possible separately integrated for each reduction peak) → Amount of reducible species in sample [mmol]*

5.5 Elemental Analysis: XRF and ICP-OES

XRF allows fast and accurate analysis of selected elements and an elemental screening over the periodic table. This method should be applied as standard characterization method for the precise determination of sample composition of known elements with a relative error below 1 % for the major components and about 5 % for the minor components and also for the fast check for unknown components. This includes the purity check within the limits of detection that is about 0.1 %.

All elements starting with atomic number 11 (Sodium) are accessible, excluding Rh due to the fact, that the XRF instrument in operation has an Rh-anode source and therefore a very high Rh-background.

Systems not accessible to the XRF can be analyzed by ICP – with the drawback of the necessity to dissolve the sample prior to analysis.

5.5.1 Requirements for Analysis

- Elements from z = 11 excluding Rh
- Concentration in the sample not below 0.1 % (by mass);
- Unknown elements: **XRF** → 100 mg of sample (to be consumed)
- Elements accessible by ICP OES and not by XRF, essentially Li and Rh;
- Sample amount available below 20 mg;
- Concentration of the target element below 0.1 %:
  ICP OES →At least 10 mg of sample (to be consumed)

5.5.2 XRF Sample Pretreatment / Conditioning

Best results are obtained with perfect homogeneous specimen measured in vacuum; this is realized with solid solution in glass matrix.

Samples should be dissolved in a Li-B-glass by fusing them with a Li-borate. Most versatile for this purpose is di-Lithiumtetroborate (LTB); for preparation of 40 mm diameter glass discs 100 mg of sample are molten with 8.90 g of LTB.

The LTB should be of spectral grade. The platinum crockery, especially the coquilles, should have smooth surfaces and are best cleaned in concentrated aquatic solutions of citric acid assisted by ultra-sound.

Excluded from this procedure are samples with either highly volatile compounds ore compositions affecting the platinum; among the last are strong oxidizers and noble metals dissolving in the platinum. An alternative preparation is the pressing of pellets. Most versatile as pelleting agent is boric acid.

For a 34 mm pellet at least 100 mg of sample are mixed with 3.5 g of boric acid. Mixing is crucial and the pellet should be as homogeneous as possible. Best results are archived by wet grinding in a mortar adding i-propanol. The quantification of light elements (as Na or Al) with very low information depth in the µ or even sub-µ range is only possible with ideal homogeneous samples – the analysis of these elements from pressed pellets mostly fails.

By regular check of blank samples contamination of the chemicals or the material has to be checked!

5.5.3 XRF Calibration and Evaluation

The evaluation is best done if based on appropriate standards with a matrix close ore ideally identic to the analyte. A calibration is only valid for a given set of parameters, as sample conditioning, measuring mode (vacuum, He) and spectrometer mode (excitation tube parameters, analyzer parameters as collimator, diffraction crystal-plane, type of counter and counter mode). If the quantification is based on a calibration not specific to the sample, at least all components should be included to give the iterative *Lachance-Traill* formalism a chance. A simple and effective criterion is the mass balance: The quantified components should ideally sum up to 100 % of the sample mass analyzed (for this purpose the mass of sample has to be weighed with accuracy); a deviation of more than 10 % is indicative for significant uncertainties in the result.

As threshold or detection limit (LLD) the 3 σ above baseline criterion holds. In general, this limit ranges from 0.1 % to about 100 ppm for elements analyzed by high energetic lines in a light matrix.

5.5.4 ICP-OES – The Method

The method depends on dissolved samples in liquid phase. The analysis of organic solvents is possible but associated with pronounced perturbance. The standard procedure is based on aquatic solutions. The (linear) detection range of the method spans over 5 order of magnitude or even more; the lower detection limit is roughly in the mid ppb-range, depending on the target element and the matrix. Nonetheless the method is known to be insensitive to matrix impact, severe distortions may occur in concentrated analyte solutions with high electrolyte load. If analyte and matrix components are all in the lower ppm rang, the distortions are normally insignificant. The pH of the solution is an issue, as the excitation and line distribution (excitation of different oxidation states and or complexes) is affected. The preparation of acidic analyte solution is the most common procedure. The calibration with (certified) standard should be run with solutions close to the analyte composition; that is same pH-range and same matrix.

5.5.5 ICP-OES Dissolution – Preparation of Analyte Solution

The crucial part in the analytic chain is the dissolution of solid samples. The operation of microwave autoclave is a standard procedure in ICP analysis. Depending on target elements and concentrations pa-grade or ultra-pure reagents are used: Generally, the analysis of trace elements demands for the use of highest purity reagents. The water used is of high purity grade, 0.05 µScm^{-1}. To generate acidic analyte solutions, the dissolution should be run in acidic medium as well. The recipes are manifold. The majority of samples can be dissolved in concentrated to half concentrated nitric acid or in hydrofluoric acid or in a mixture of both.

The relative error of the method is in the lower percentage range and the entire procedure aligned accordingly. To keep the error in this range, the sample mass for dilution weighed with an analytical balance should be at least 10 mg. If possible, more than one analyte solutions of one sample should be prepared to control the reliability of the process.

5.5.6 ICP-OES Calibration and Evaluation

For every analytical session a calibration has to be run. Certified standard solutions for the ICP OES are commercially available from several suppliers. Often the use of multi-element standards is advantageous compared to single element standards as spectral interferences become apparent and with some ICP OES instruments the reprocessing of data allows the determination of elements not included initially.

The calibration is described by linear function and forced through the origin. In regard to the formalism, one measured point is sufficient to describe the calibration; anyhow, the application of at least two concentrations for calibration is recommended for quality check. This is best done by constructing the calibration with standards of different origin.

The spectral blank solution is normally water; the signal is subtracted. The reagent-blank is a solution mirroring the entire process, including autoclave dissolution and so on without sample; the resulting concentration in a given element is subtracted from the net-concentration found for the sample. As threshold or detection limit the 3 σ above underground criterion is valid.

Results: Composition in wt% and at%

5.6 Elemental Analysis: CHNS

5.6.1 Requirements for analysis

CHNS analyzer from MPI CEC analytic service group

- - classical combustion analysis in oxygen gas
- - sample mass ~5 mg
- - typical determination errors of 0.02 %

Results: Composition in wt% and at%

5.7 Near Surface Analysis by Laboratory XPS

4.7.1 Sample mounting

Depending on the orientation of the sample holder, either use the sample as is (that is, in powder form) or press the powder into pellets. If press is used, make sure that the surface of the pellet shall not be contaminated. We at FHI will use pellets.

4.7.1 Measurement conditions

X-ray source: use Al Kα or Mg Kα radiation, such that overlap of important core levels and Auger lines are minimized. If possible, Mg Kα is preferred.

Spectrometer: use constant and reasonably chosen pass energy suitable to achieve a good compromise between resolution and signal-to-noise ratio. The binding energy scale should be regularly calibrated (e.g. by the Cu2p and Au4f levels of Cu and Au foils).

Survey spectrum should be collected to identify the contributing elements. Thereafter, narrower detailed scans of selected peaks should be used to evaluate chemical composition and oxidation state of the samples in the near-surface region.

Check for beam damage, in which the most important (e.g. the most redox relevant) core level is measured first and the measurement is repeated at the end. Mention it in the data analysis if differences are observed.

4.7.2 Data analysis

On insulating samples, a high-resolution spectrum of C1s should be collected and the binding energy scale may be referenced to adventitious hydrocarbon on the surface. If charging is corrected in such a way, mention the magnitude of charging correction.

For quantitative analysis, provide details, i.e. source of cross sections, sensitivity factors, etc. We at FHI will use cross sections from J. J Yeh, I. Lindau, At. Data Nucl. Data Tables 32, 1985, 1-155; and correct for the different inelastic mean free path of photoelectrons by computing IMFP based on S. Tanuma, C. J. Powell, D. R. Penn: Surf. Interf. Anal., Vol. 21, 1993, 165.

Results: Composition in wt% and at%, oxidation states, VB spectrum

5.8 Scanning electron microscopy (SEM) and Energy dispersive X-Rays (EDX)

5.8.1 Sample mounting for SEM

Sample is placed as powder or as pellet on electrical conducting tape. Make sure that the sample forms a flat surface normal to the incident electron beam to prevent shadowing effects. For bad conducting samples the sample sickness should be as small as possible to lower charging effects.

5.8.2 Measurements with SEM and EDX

To gain insights on the sample's morphology multiple photographs at different magnifications should be taken that show the typical morphology. For a good comparison of different samples, photographs should always be taken at identical magnifications.

Samples homogeneity should be proven by 4-5 EDX spectra at different positions recorded on small scale areas (Diameter ~20 µm). With multiphase samples, the phase distribution should be proven by high quality EDX mappings at selected but not atypical regions.

5.9 Infrared and Raman spectroscopy

5.9.1 Sample mounting for Raman spectroscopy

Small portion of powder or pelletized sample is placed onto a flat surface and focused with the attached microscope.

5.9.2 Sample mounting Infrared spectroscopy

Small portion of powdered sample is placed on ATR crystal and stamp is pressed onto powder. Ensure powder forms a dense layer between ATR crystal and stamp.

5.9.3 Measurement conditions Raman spectroscopy

Photographs of the sample are taken before each measurement to check later for beam damage. Measurements are done with low laser power of <4 mW and short irradiation times ~1 second to prevent sample heating and beam damage. Repetitive measurements result in mean spectrum with low noise. If no change in repetitive spectra occurs and after measurement the sample looks like before measurement started (taken photograph), beam damage can be excluded. Repeat measurement with same conditions at 10 points in total to allow judgement on homogeneity.

5.9.4 Measurement conditions Infrared spectroscopy

Spectra should be recorded repetitively to gain good signal to noise ratio similarly to Raman spectroscopy. Spectra should be measured on multiple preparations to allow judgement on homogeneity.

5.9.5 Data analysis

Excitation laser wavelength should be mentioned because some Raman signals are energy dispersive. Compare spectra with spectra of comparable samples measured with same laser wavelength and assign visible absorption bands. Fitting and deconvolution of absorption bands allow the extraction of samples characteristics compared to reference samples.

6. Advanced Catalyst Characterization

Advanced characterisation should only take place on well-defined catalysts that have been characterised with standard methods and comprehensively kinetically tested.

6.1 Kelvin probe measurement

6.1.1 Sample mounting

Sample is placed as powder or as pellet on electrical conducting tape. For bad conducting samples the sample sickness should be as small as possible to lower unwanted charging effects.

6.1.2 Measurement principle

A probe tip is positioned near the samples surface. Due to the different work functions of the electrical connected materials a charge potential and electric field is built up.

6.2 Contact angle measurement

Pelletized sample with flat clean surface is placed horizontally in the apparatus. From a small distance a drop of a designed liquid is dripped onto the surface. The drop should have circular shape. A digital microscope is adjusted onto the surface height and parallel to the surface. The spots of visible surface, drop and air-interface need to be focused. Photographs are taken and the angle between drop surface and pellet surface are measured on each side of the drop. The mean values determined from 5-10 drops gives the contact angle. For placing a new drop keep sure the surface is dry and no residuals of the previous one is present. The contact angle is anti-proportional to the interaction strength between the sample and the used liquid.

7. Data collection and analysis

The data analysis will be performed in collaboration with the involved AmmoRef partner. Data will be collected in an online Labjournal provided by the MPI CEC.

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