Retrofittable plug-flow reactor for in situ high-temperature vibrating sample magnetometry with well-controlled gas atmospheres

Almind, Mads R.; Engbæk, Jakob S.; Hansen, Mikkel F.; Vendelbo, Søren B.; Mortensen, Peter M.; Damsgaard, Christian D.; Veile, Thomas; Chorkendorff, Ib; Frandsen, Cathrine

Published in:
Review of Scientific Instruments

Link to article, DOI:
10.1063/5.0113493

Publication date:
2023

Document Version
Peer reviewed version

Retrofittable plug-flow reactor for in situ high-temperature vibrating sample magnetometry with well-controlled gas atmospheres

Mads R. Almind,[†] Jakob S. Engbæk,[‡] Mikkel F. Hansen,[¶] Søren B. Vendelbo,[‡] Peter M. Mortensen,[§] Christian D. Damsgaard,[†,‖] Thomas Veile,[†] Ib Chorkendorff,[†] and Cathrine Frandsen[*,†]

†*Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

‡*Danish Technological Institute, DK-2630 Taastrup, Denmark*

¶*Department of Health Technology, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

§*Haldor Topsøe A/S, DK-2800 Kgs. Lyngby, Denmark*

‖*DTU Nanolab, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

E-mail: *fraca@fysik.dtu.dk

Abstract

We have developed an in situ sample-holder - akin to a quartz-based plug-flow reactor - for vibrating sample magnetometry (VSM) in gas-controlled environments at ambient pressure and temperatures up to approximately 1000 °C. The holder matches onto a specific type of vibrating sample magnetometer (Lake Shore model 7404-S), but the principles are applicable to other types of VSM. The holder has been tested

on powder samples of Co particles on $MgAl_2O_4$ support in both reducing and oxidizing atmospheres. The results show control of gas composition and sample reduction/oxidation. In comparison to conventional sample cups, the in situ holder shows similar measurement sensitivity, but better repeatability due to the well-controlled gas atmosphere. Moreover, the in situ holder uses a closed gas tubing system such that the active gas only passes by the sample and it is not in contact with the VSM and oven parts. At the outlet, the gas can be collected for analysis and safe handling.

I. Introduction

Vibrating sample magnetometry (VSM) is one of the most commonly used techniques to measure hysteresis properties and Curie temperatures of magnetic samples. The wide use of VSM relies on its accuracy, ease of operation, and large flexibility in terms of samples that can be measured. In practice, VSMs typically have a measurement sensitivity of 10^{-8} Am^2,[1 2] corresponding to that a sample of 6 μg Co with a saturation magnetization of 162.5 $\frac{Am^2}{kg}$[3] can be measured to 1 % repeatability.[2] VSM also allows for doing magnetometry at elevated temperatures (>75 °C). Commercial instruments allow for measurements of up to 1000 °C.[4 5] However, at elevated temperatures the sample may change. For instance, powder samples may, depending on conditions of the sample environment, oxidize, anneal, and/or sinter during measurements. In recent years, there has been a rising interest in heating chemical reactions electrically by induction heating[6–12] using magnetic materials at high temperatures. This puts further emphasis on the importance of being able to measure and characterize magnetic samples at relevant high-temperature conditions.

However, implementing the capability of doing in situ measurements with well-controlled gas atmosphere in a conventional VSM at high temperatures comes with several challenges: the sample holder needs to be non-magnetic or otherwise not interfere with the measurements, be able to handle the vibration of the VSM while keeping the sample fixed in the holder, as well as take into account the maximal mass load of the vibration head and the spatial constraints of the particular oven option.

Only a few in situ high-temperature magnetometers with a gas-controlled sample environment exist: Claeys et al. invented a combined chemical reactor and vibrating sample magnetometer[13] in order to be able to study catalytic particles in situ by magnetometry during reactions like the Fischer-Tropsch process.[14–16] This VSM is a state-of-the-art custom-built instrument with a stainless steel reactor tube for magnetometry at chemical conditions in controlled gas atmospheres, up to 600+ °C, 50+ bar, and 2 T.[16] The steel tube accommodates the sample under plug-flow conditions and is sufficiently long to leave its ends outside

the sensitive region for the signal during measurements.[13] Chernavskii et al.[17] presented a similar reactor idea for the gas flow but using a quartz tube for studies at ambient pressure. For many research groups, acquiring or implementing these sort of in situ solutions can be costly or impractical, especially in cases where the group already has a conventional VSM for high-temperature measurement. In most cases, the VSM oven is closed below the sample and therefore cannot acommodate a long tube with gas outlet below the sample.

Here, we show the proof-of-concept of a new in situ VSM holder based on quartz tubes, which can expose a powder sample to a chosen gas-mixture at high temperatures up to ca. 1000 °C), at atmospheric pressure, for extended periods of time, while being inexpensive and easily retrofittable onto commercially available VSMs due to its gas inlet and outlet above the sample oven.

II. Experimental details

A. Conventional state-of-the-art sample holders

We used a VSM of type Lake Shore 7400, which in its original format (despite its high-temperature option) is not intended for in situ studies with well-controlled gas atmospheres. For high-temperature measurements (up to 1000 °C), Lake Shore offers commercial boron nitride (BN) sample cups (type 730937) to be used together with their 7400 series VSM and a Lake Shore 74034 oven option. The holder and oven principle are shown in Fig. 1a. Here the sample material (typically 10-50 mg) is loaded into a BN cup, which is screwed onto a quartz sample tail and connected via a screw to the head drive of the VSM. The gas environment around the BN sample holder is typically Ar, which is recommended by Lake Shore mainly to prevent oxidation of the oven and the sample at elevated temperatures. We have commonly used Ar with 2.4 vol.% H_2 to support a reducing atmosphere near the BN samples, but this is not the recommended procedure by LakeShore. The threading in the BN cups does not create a leak-tight seal, and gas might diffuse in and out of the sample holder,

as illustrated in Fig. 1. This can exploited to adjust the sample environment. However, as the gas flow in and out of the sample is not forced, the actual gas environment of the sample is subject to large uncertainty during measurement. For instance, a concern is that water desorption from the particle surfaces can remain in the holder and enhance particle oxidation and sintering with increasing temperature for unspecified time and temperature ranges. With the BN cup solution, it is not possible to use reactive gasses such as O_2 or H_2 as this would be detrimental to the oven. Also, the system is open and its free outlet of gasses to the nearby work environment can be harmful.

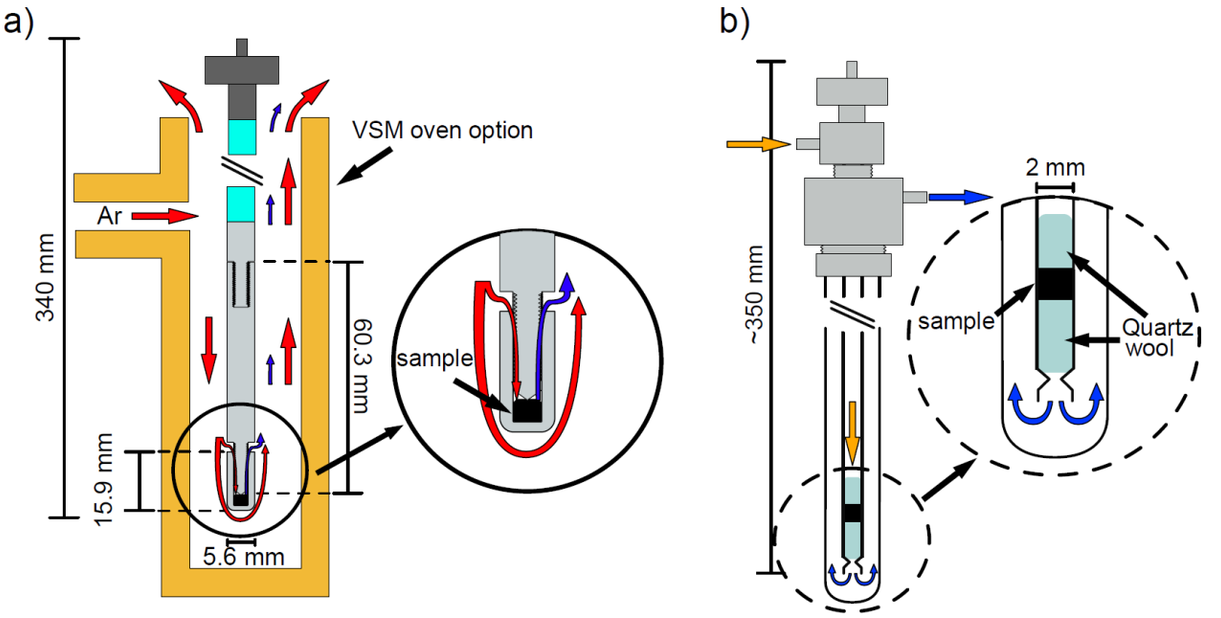


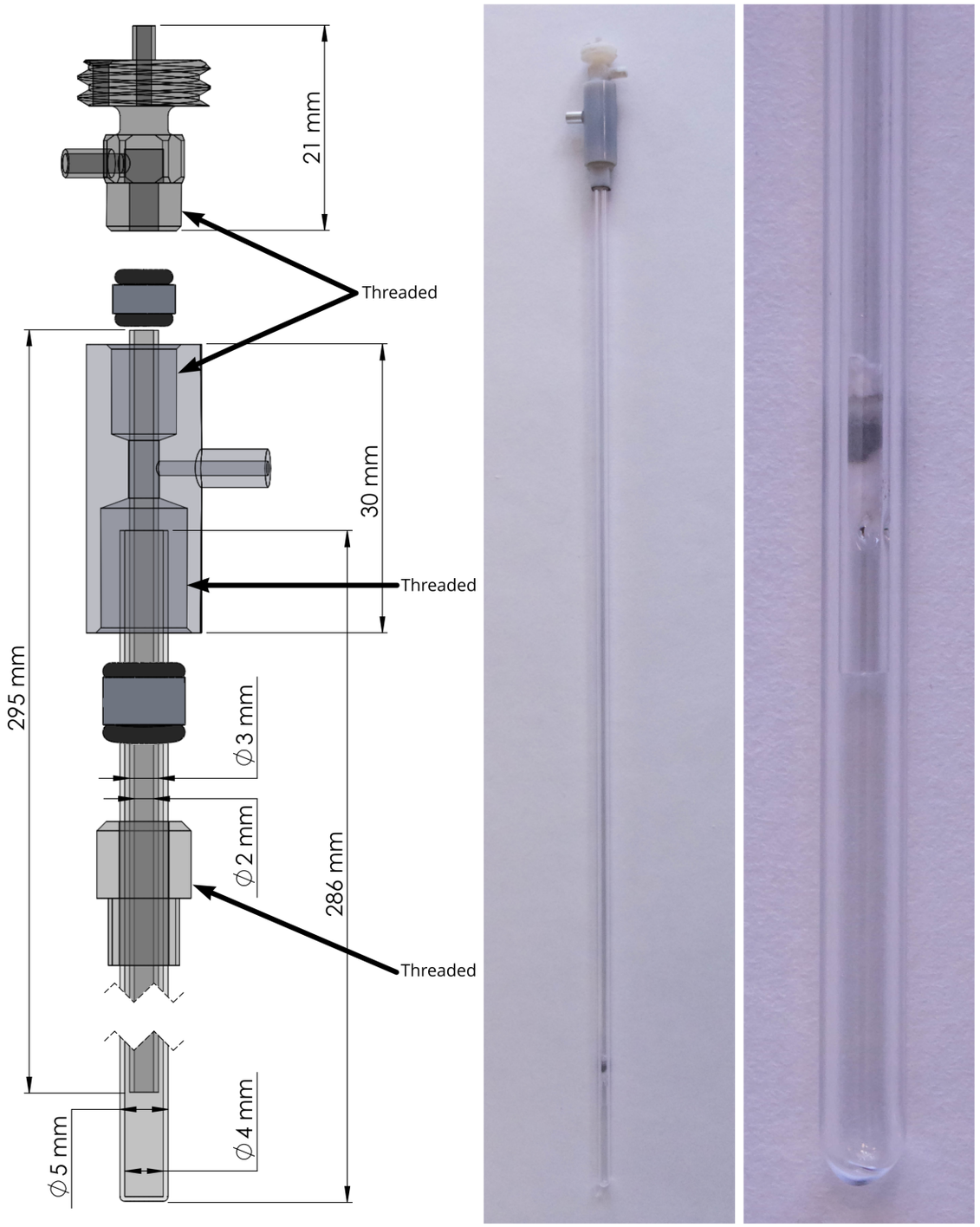
Figure 1: a) Sketch of the conventional boron-nitride (light grey) sample cup from Lake Shore in the oven geometry (yellow) with Ar gas (red arrows), with close-up of the less than optimal degree of gas-diffusion, gas in (red), gas out (blue). The heating elements of the oven are placed in the region around the sample. b) Sketch of the new in situ holder that can be used with the oven in a. The sample is loaded into the inner quartz tube. There is a forced gas-flow though the sample, gas in (yellow), gas out (blue). The outer quartz tube ensures that the sample gas is separated from the surrounding oven and the inert Ar gas that protects the oven.

B. The new in situ sample holder

In order to have a controlled gas environment of samples during high-temperature VSM measurements, we developed an in situ sample holder akin to a plug-flow reactor, which is retrofittable to a standard VSM with an oven that is closed below the sample such as it is the case for LakeShore 7400-series VSM (cf. Fig. 1a).

The entire holder is made to match a maximum load of 23 g on the head drive, and to be able to fit into the 7 mm opening of the Lake Shore 74034 oven option. The in situ holder consists of an inner and an outer quartz tube together with an assembly that connects the quartz tubes to the gas system and the VSM head drive. The holder vibrates with the head drive. The gas is led into the holder from the top, through the sample, and out again at the top without the gas being in contact with the VSM oven or other VSM parts. At the same time the oven is kept in Ar gas as recommended by Lake Shore. The principle of the forced gas flow through the sample in the in situ holder is shown in Fig. 1b.

Further schematics of the holder can be seen in Fig. 2. In detail, the assembly consists of: a top screw, a body, a bottom screw, two plastic spacers, all 3D printed in plastic, and four o-rings. The top screw connects to the VSM head drive via a screw made to fit into the Lake Shore head drive. The whole assembly sits just below the head drive (see Fig. 3b), far from the heating zone of the oven. The lower part of the top screw is hollow, and is equipped with a spout for letting in gas and can be screwed into the body. Two NBR 90 o-rings (inner diameter 3 mm, outer diameter 6 mm) and a plastic spacer fit over the inner quartz tube. These o-rings clamp down on the tube when the top screw is screwed into the body. This is what holds on to the inner quartz tube when the holder vibrates, and also prevents gas from flowing from the head screw and out of the body without flowing through the inner tube. The body is equipped with a spout which functions as gas outlet. The outer quartz tube is held by two NBR 70 o-rings (5 mm inner diameter, 8.5 mm outer diameter) in the same way as the inner quartz tube, when the bottom screw is screwed into the body.



(a) (b) (c)

Figure 2: The in situ holder. (a) Technical drawing of the in situ holder consisting of an inner and outer quartz tube and an assembly for connection to gas system and the head drive. The threading on the top and bottom screws is M8x1. (b) Picture of the fabricated in situ holder. (c) Close-up picture of the concentric quartz tubes with sample (black powder) loaded in the inner quartz tube.

When gas is let in through the spout in the top part, it travels down through the inner quartz tube, where the sample is situated, then up through the outer quartz tube, and out through the spout in the body part. The sample is situated in the inner quartz tube, in a plug-flow reactor style, sandwiched between two layers of Insulfrax quartz wool,[18] cf. Fig. 2. The inner tube is approximately 300 mm long, with an outer diameter of 3 mm, and an inner diameter of 2 mm. Two indents were made approx. 10 mm from the bottom of the inner tube. These are used to anchor the bottom layer of quartz wool that the sample rests on. The inner tube is considered disposable and is loaded with approximately 10 mm^3 (5-10 mg) sample material. The outer tube is approx. 300 mm long with an inner diameter of 4 mm and an outer diameter of 5 mm. The outer tube is closed at the bottom end.

Plug flow conditions will ensure that the material in the inner quartz tube will be uniformly exposed to the gas flowing through the quartz tube. In this case the gas will only have to diffuse through the porous support particles to achieve uniform exposure to the gas, while in the conventional BN cup the gas has to diffuse through the threading of the BN cup, and then through the porous support, in order to uniformly expose the sample.

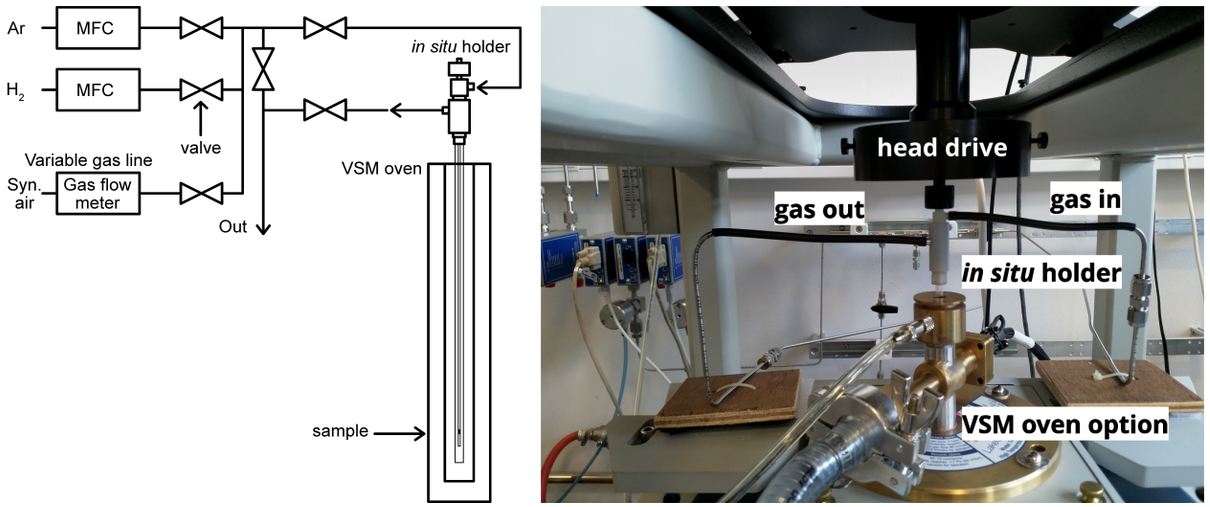
As a rule of thumb, to achieve plug flow conditions the particle size of the sample support powder must be at least 10 times smaller than the reactor diameter, and at least 50 times smaller than the height of the sample bed.[19] The $MgAl_2O_4$-support used in this study (PURALOX MG 28[20]) has a particle size of 30 μm, which is approx. 65 times smaller than the width of the inner quartz tube (2 mm, see Fig. 2), and 100 times smaller than the bed height (approx. 3 mm). This fulfills the rules of thumb for establishing plug flow conditions.

C. Gas system

Figure 3a shows a diagram of the gas-system that we set up to handle the inlet and outlet gas to the in situ holder. The gas tubing outside the VSM is 1/8" stainless steel, and mass flow controllers of type MKS GM50A supply gasses (i.e., hydrogen and argon, in this study). Synthetic air (20 vol.% O_2 in N_2) was supplied at the variable gas line via a gas flow meter.

Pneumatic valves open for the flow of gas, that can either be led through the in situ holder, or through the bypass.

Figure 3b shows a picture of the gas inlet and outlet to in situ holder mounted in the VSM. It is important that the tubes from the gas system to the sprouts on the sample holder are sufficiently flexible to not affect the vibration of the holder. For this we chose tubes of ISO-VERSINIC (a fluoroelastomer) seen as black tubes in Fig. 3b. The ISO-VERSINIC is connected to the 1/8" steel tubing and the spouts of the in situ holder by simply sliding the tubes over the steel tubing and the plastic sprouts. The system might be optimized by more leak-tight solutions. However, no leakage was detected from these tubes, or anywhere else in the system, when searching for leaks with a Testo 316-EX leak detector. Even after several days of running experiments, and multiple exposures of the tip of the sample holder (where the sample is situated, see Fig. 2c) to 950°C, no leaks were detected.



(a) (b)

Figure 3: The gas system. (a) Diagram of the system supplying gas to the in situ holder. (b) Picture of the gas supply to the in situ holder mounted underneath the VSM head drive together with the VSM oven.

D. Test samples

Preparation of sample material

In order to test the functionality of the in situ holder, we prepared ex situ a sample material of partially oxidized Co nanoparticles (/partially reduced cobalt oxide particles) on porous $MgAl_2O_4$ spinel support. Metallic Co is ferromagnetic up to 1121 °C, whereas a fully oxidized cobalt sample (CoO/Co_3O_4) possesses a close-to-zero magnetic moment. The moment of Co enables magnetic centering of the sample for VSM measurements. Moreover, this material allowed us to follow the oxidation and reduction in the in situ holder via change of the magnetic moment.

For the preparation, a batch of 2 g of $MgAl_2O_4$ with 10 wt.% cobalt was made by incipient wetness impregnation of cobalt-nitride salt ($Co(NO_3)_2$) on PURALOX MG 28 ($MgAl_2O_4$) support from Sasol.[20] The impregnated sample was dried at 80°C on a hot plate overnight followed by calcination of the cobalt-nitride salt to cobalt oxide (CoO/Co_3O_4) nanoparticles at 450 °C in air for 1 hour. Afterwards, the cobolt oxide particles were partially reduced by heating the sample in an atmosphere of 2.4% H_2 in Ar, first to 110 °C for 2 h to remove any moisture in the sample, and then to 850 °C where it was left for 45 min. Afterwards the sample was cooled to room temperature. Transmission electron micrographs showed $Co/CoO/Co_3O_4$ particles with sizes of 21±4 nm on porous $MgAl_2O_4$ support.

Types of samples

Eight samples were taken from the batch of $Co/CoO/Co_3O_4$ particles on $MgAl_2O_4$ spinel support. Four of the samples (BN1-4) were measured on a Lake Shore 7407 model VSM in commercial boron-nitride (BN) cups. The other four samples (INSITU1-4) were measured in the in situ holder on a 7404-S model Lake Shore VSM.[21] All samples were measured vs. temperature in a reducing atmosphere of 2.4 vol.% H_2 in Ar. One of the in situ samples (INSITU4) was subsequently oxidized (to INSITU4-oxi) and then re-reduced in the VSM. The two VSMs are very similar and differences in the measurements presented below are considered a consequence of variations in samples and sample holders and not in the VSMs.

Sample loading into in situ holder

Sample material was loaded into the inner quartz tube of the in situ holder by the following procedure. First, a 1.5 mm thick steel rod was used to gently guide the quartz wool down to the indents from the top of the tube. Then, a pipette tip was put into the opening at the top of the tube to act as a funnel for the sample powder. Powder was then deposited into the pipette tip, and the quartz tube gently tapped on the table surface in order for any powder stuck to the side of the quartz tube to trickle down and settle on top of the quartz wool. Afterwards, another layer of quartz wool was put on top of the sample, and the layered structure (wool - sample - wool) was gently, but firmly, pressed together, in order for the layered structure not to move by the vibration of the VSM.

Sample mass determination

Quantitative VSM measurements of sample magnetizations rely on sample mass determination. For the BN holders, the empty cups were first measured five times. Then, each cup was filled with 10-40 mg of sample powder, closed, and also weighed five times. The mass for each sample (listed in Table 1) was determined from the differences of the averages. Weighing was performed on an Ohaus PA224C balance with 0.1 mg precision.

The average mass-specific saturation magnetization σ_S for the samples in the BN holders at RT at 1.5 T was determined from their magnetic moment measured by VSM divided by their sample mass (cf. Table 1) to 12.3 ± 0.4 $\frac{\mathrm{Am}^2}{\mathrm{kg}}$. For pure Co, a σ_S of 162.5 $\frac{\mathrm{Am}^2}{\mathrm{kg}}$ is expected, hence for 10 wt% Co a magnetization of 12.3 $\frac{\mathrm{Am}^2}{\mathrm{kg}}$ shows that the sample as prepared is partly reduced Co (approx. 76 % of the cobalt is reduced to metallic Co).

For the in situ holders, the sample mass was determined in a different way than for the BN samples, as our balance could not accommodate the 300 mm quartz tubes. Specifically, we determined the sample mass in the in situ holders from their magnetic moment at 1.5 T at RT (listed in Table 1) divided by the average mass-specific magnetization of the BN samples at 1.5 T at RT (12.3 $\frac{\mathrm{Am}^2}{\mathrm{kg}}$). The derived sample masses are given in Table 1 (denoted by *). This method is relies on the assumptions that all the samples have the same mass

specific magnetization at RT at 1.5 T and that the masses of the samples in the BN cups are well determined. The uncertainty on the sample mass in the in situ holders is estimated to approx. 3 %.

As presented in Table 1, the masses of the INSITU samples varied between 6-10 mg. With the loading of 10 % cobalt, this meant that the samples contained about 0.6-1 mg of Co.

Table 1: Sample masses for the as-prepared samples together with their sample magnetic moments $m_{RT,1.5\mathrm{T}}$ at RT and 1.5 T, and the mass-specific magnetizations $\sigma_{RT,1.5\mathrm{T}}$ for the samples in BN holders at RT and 1.5 T. The masses for the samples in the in situ holder (marked with *) have been calculated as $m_{RT,1.5\mathrm{T}}$ divided by the average $\sigma_{RT,1.5\mathrm{T}}$ obtained for the samples in BN cups (12.3 $\mathrm{Am^2/kg}$, † in the table).

Sample holder	sample mass [mg]	$m_{RT,1.5\mathrm{T}}$ [$\mu\mathrm{Am^2}$]	$\sigma_{RT,1.5\mathrm{T}}$ [$\frac{\mathrm{Am^2}}{\mathrm{kg}}$]
BN1	22.3	288	12.9
BN2	32.1	393	12.2
BN3	14.1	173	12.3
BN4	16.3	192	11.8
INSITU1	8.8*	109	12.3†
INSITU2	6.0*	74	
INSITU3	10.2*	125	
INSITU4	6.4*	78	

Temperature evaluation

The Curie temperature of Co is above the maximum operation temperature of the VSM oven. Hence, in order to estimate the accuracy of the sample temperature in the in situ holder, e.g. that the samples were not cooled by the gas flow, the Curie temperature of Ni and Fe samples were measured. The Fe sample consist of a 25 μm thick foil of α-Fe cut into small pieces of 1-2 mm. For the nickel sample, NiO powder was mixed 50/50 wt% with $MgAl_2O_4$ and reduced to Ni at 850 °C in 5 % H_2/Ar for 4 hours. Sample masses of 10.3 mg and 7.1 mg Fe foil, and 8.3 mg and 10 mg Ni powder were loaded into in situ and BN sample

holders, respectively. For these experiments, the outer quartz tube had an outer diameter of 6 mm (i.e. not 5 mm as typically applied). The magnetization was measured during cool down at 1 °C/min in an applied field of 10 mT after the temperature had been increased to 100 °C above the expected Curie temperature (355+100 °C for Ni and 770+100 °C for α-Fe). For the in situ holder, a flow of 10 ml/min of 5 % H_2/Ar was set through the sample. For both the BN and the situ holders, a flow of 80 ml/min of 2.4 % H_2/Ar was set around the holders. The Curie temperature was determined by the two-tangent-method.[22]

III. Results and discussion

We measured the magnetization of the $Co/CoO/Co_3O_4$ particles on $MgAl_2O_4$ support under reducing conditions with increasing temperature and time (Figs. 4, 5) and under oxidizing conditions (Fig. 6).

Figure 4 shows the magnetization of five samples (BN3, BN4, INSITU3, INSITU4, INSITU4-oxi) in an applied field of 1 T while heated in a reducing gas of 2.4 vol.% H_2 in Ar to 850 °C in the VSM (after heating in the VSM to 200 °C at the same gas conditions and remaining there for 2 hours to facilitate evaporation of water moisture in the samples). For all five samples, it is seen from the increase in magnetization that the reduction starts at around 300 °C. The oxidised sample (INSITU4-oxi) starts from a close to zero magnetization (around 0.3 $\frac{\mathrm{Am}^2}{\mathrm{kg}}$, blue curve). The other samples start at higher magnetization, as these were already partially reduced (76 %) when introduced to the VSM. Upon increasing temperature, the magnetization in all five cases rises to a peak, after which the magnetization decays. The decay is caused by the drop in magnetization as temperature approaches the Curie temperature of the samples. It is noticable that the behavior is almost identical for the similar samples in the in situ holder (INSITU3 and INSITU4), but less consistently reproduced for similar samples in the BN cups (BN3, BN4) probably due to the less optimal gas flow.

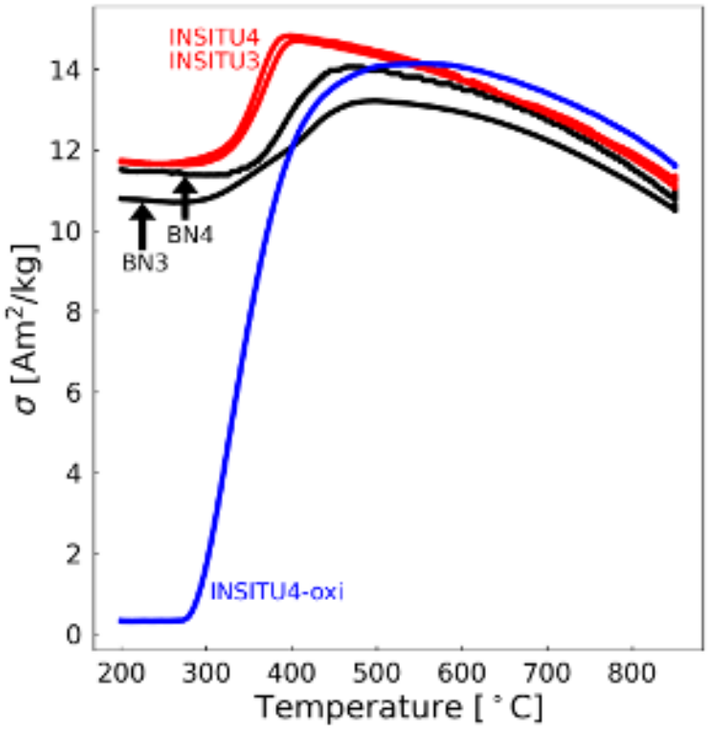


Figure 4: Mass-specific magnetization σ as function of temperature while heating samples of $Co/CoO/Co_3O_4$ nanoparticles on a porous $MgAl_2O_4$ support to 850 °C, in an atmosphere of 2.4 vol.% H_2 in Ar. The measurements were performed in an applied field of 1 Tesla. Samples measured in the in situ quartz holder are coloured red. Samples measured in a BN cup are coloured black. The blue curve is from the sample that had also been oxidized in the in situ holder prior to this measurement (Fig. 6).

After heating all samples in an applied field of 1 T under the gas conditions described in the above paragraph, the samples were then continuously measured in the VSM at 850 °C for up to 20 hours under the same gas and field conditions (Fig. 5). As evident from Fig. 5, there is significant variation in the measured curves. In principle, the variation between the curves is not very large on an absolute scale, only roughly 5 % at the end of the 20 hours (note the scale of the y-axis). Some of the variation could originate from uncertainty in sample mass, positioning of the sample, and calibration of the VSM. However, this does not explain the variation in curve shapes between the in situ samples and the BN samples.

The four curves seen in Fig. 5 for the BN1-4 samples show very different behavior. Two curves increase in a linear fashion, and then suddenly transition to another linear part with a

much lower slope. One curve is almost flat (except for a noisy part), and one does not follow the same trend as the others at all. The different behaviors might be caused by different rates of diffusion in different sample cups, perhaps by how tightly they are screwed together. For instance, the increase in magnetization, seen for sample BN4 after ca. 8 hours at 850 °C in Fig. 5, might be due to a delayed reduction in part of the sample e.g. due to trapped gasses in the holder. This matches with the less effective reduction seen for sample BN4 vs. sample BN3 in Fig. 4 during the temperature ramp to 850 °C. In case of the BN samples, the magnetization never reached a saturation value, not even after 20 hours.

In contrast, the magnetic behaviour for the INSITU1-4 samples during heating (Fig. 5) are consistently similar. They are represented by a fast initial increase in magnetization that asymptotically flattens out to a plateau as the sample approaches full reduction. This reproducible behavior points to a much more controlled gas environment in the in situ holders. There are only minor deviations to be noted. For instance, the magnetization of the INSITU samples were originally set to equal the same value (12.3 Am2/kg) at RT at 1.5 T, but the magnetization evolves slightly different between 200 and 850 °C (cf. samples INSITU3 and INSITU4 in Fig. 4), and this leads to different magnetization for the INSITU samples at 850 °C (± 0.2 Am2/kg (or ± 2%), cf. time=0 in Fig. 5). We do not have sufficient information to conclude what can be the cause for these minor changes in the magnetization. It may be inherent to the samples (e.g. inhomogeneities from grain size variations) or to the setup (e.g. instability). Addition of a mass spectrometer to analyse the exit gas, which is possible at the outlet of the in situ holder, could enable further enlightening of subtle changes in samples over the course of an experiment.

The blue curve in Fig. 5 is for the sample (INSITU4-oxi) that was oxidized and then re-reduced using the same experimental profile as the others. The extra treatment could have induced changes in the sample, such as sintering, morphological changes caused by differences in diffusion rates (Kirkendall effect), etc., so it is not surprising that it does not follow the trend of the other in situ samples.

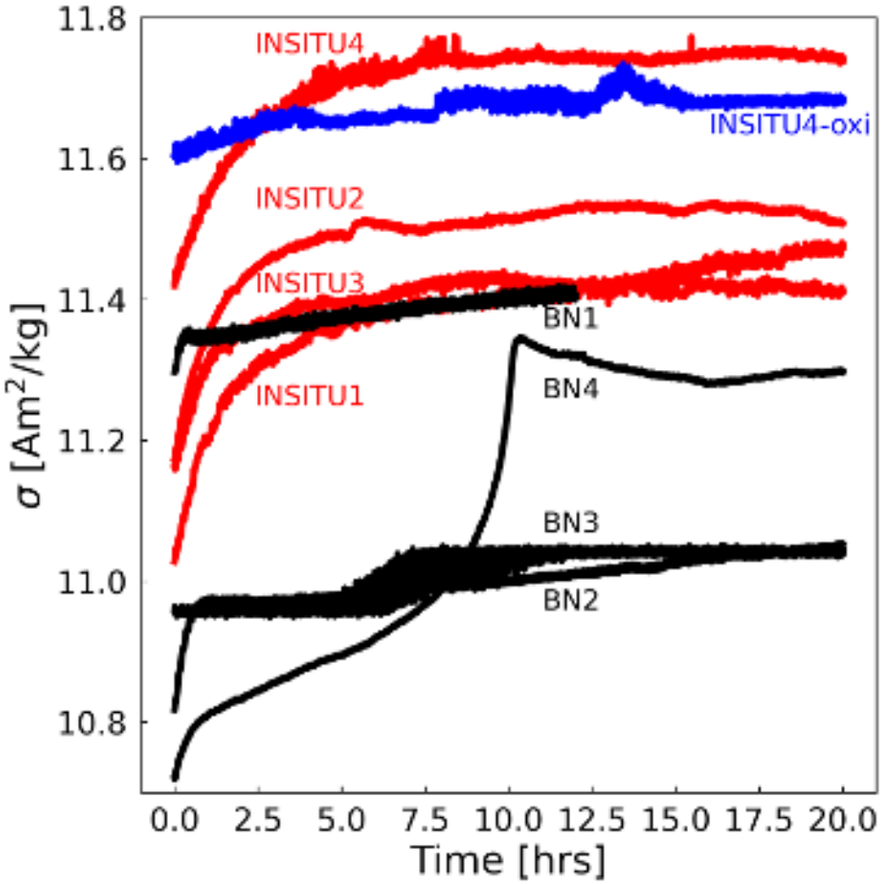


Figure 5: Magnetization curves showing the reduction of samples of $Co/CoO/Co_3O_4$ particles on porous $MgAl_2O_4$ as a function of time. The measurements are taken at 850°C in an applied magnetic field of 1 T. INSITU samples are coloured red, with the oxidised INSITU sample coloured blue. BN samples are coloured black.

The gas flow of 10 $\frac{\text{mL}}{\text{min}}$, and the estimated sample volume of 10 mm^3, makes for an exchange of sample volume in gas approximately 17 times per second. If pure H_2 gas had been chosen instead of H_2 in Ar, it is likely that the samples in the in situ holders would reduce even faster than what is shown in this paper. The use of pure H_2 is a possibility only in the in situ holder, as pure hydrogen would not go to the bottom of the oven (too light) and pure hydrogen would also be a safety hazard in the open air system used for the BN sample cups.

For the measurements of the INSITU samples (Fig. 5) we note some fluctuations in the magnetisation. For instance, after 10 hours at 850 °C, the samples INSITU1 and INSITU2

deviate somewhat (increase and decrease, respectively) from their approach to saturation. Such variations could originate from small mechanical instabilities of the holder, e.g. from the inner quarts tube moving or flexing slightly inside wall of the outer quartz tube. However, the data obtained after 10 hrs of measurements (Fig. 5) shows a maximal variation of approx. 0.04 $\frac{\mathrm{Am}^2}{\mathrm{kg}}$, which is equivalent to less than 3 per mille variation in the measurement. This uncertainty is 10 times less than that from weighing the sample. Moreover, these fluctuations correspond to variations in measured magnetic moment of less than approx. 3×10^{-7} Am^2, which can then be viewed as the current sensitivity when using the in situ holder with the oven option and a measurement time of 0.3 s per datapoint. This is close to the instrument sensitivity given by the manufacturer (i.e., ca. 10^{-8} Am^2, when using the oven option and similar data acquisition times[21]).

We also performed measurements at 950 °C (not shown). The in situ system showed stability also at this high temperature. Measurements at 950 °C took approx. 2 hrs and were done twice or more per sample. No changes of the sample holder were observed, neither to the assembly, nor to the inner disposable quartz tubes and the re-used outer quartz tube.

This shows that the in situ holder performs very well, i.e. that we have succeeded in constructing a stable and durable holder for in situ high-temperature VSM studies. It is possible that the any minor mechanical instabilities in the holder can be fully remediated by e.g. having fixating quartz wool between the inner and outer quartz tubes or by making the holder assembly in a more rigid material than plastic, e.g. aluminium, but it is not necessarily needed.

In order to demonstrate the application of in situ holder also for oxidation studies, we heated the sample INSITU4 in air. The oxidation of INSITU4 can be seen in Fig. 6. Here, the gas fed to the in situ holder was switched from 2.4 vol.% H_2 in Ar, to synthetic air (20 vol.% O_2 in N_2), at room temperature, in an applied magnetic field of 1 T, whereafter the temperature was increased in steps up to 400 °C. From the figure, it is clearly seen, that as the temperature in the VSM oven option is raised, magnetization drops, as a result of the

oxidation of the sample. Full oxidation is reached at 300 °C. Hereafter, only a magnetization of around 0.3 $\frac{\mathrm{Am}^2}{\mathrm{kg}}$ remained. This kind of investigation is not possible in conventional high-temperature VSM using a BN sample cup, as the oven cannot handle exposure to oxidizing atmospheres at elevated temperatures.

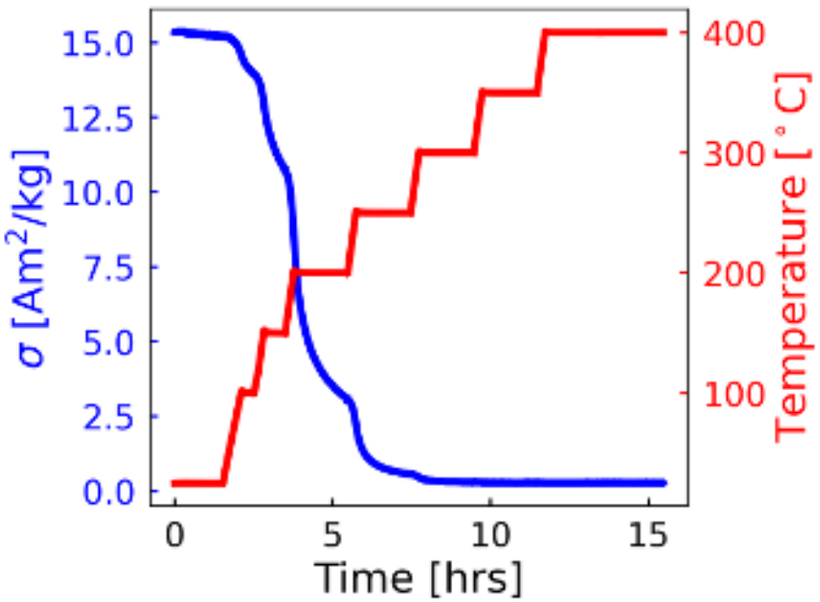


Figure 6: Magnetization σ and temperature as a function of time for a Co nanoparticle sample on porous $MgAl_2O_4$ support during oxidation in the in situ VSM holder. In this experiment the sample was exposed to a flow of synthetic air and an applied field of 1 Tesla.

The data presented above showed, that the in situ holder can measure just as well as the BN system in experiments where a sample is reduced, and the magnetic properties investigated in a weakly reducing atmosphere. Additionally, the in situ holder works for studies in an oxidizing atmosphere of synthetic air.

In order to also evaluate the accuracy of the sample temperature in the new in-situ holder, samples of Ni powder and Fe foil were measured during cooling, cf. Fig. 7. The Curie temperatures were found to be 342 °C and 748 °C, when using the in situ holder, and 354 °C and 757 °C when using BN cups. Hence, the in-situ holder reports a lower Curie temperature than that from the BN cup, but with a consistent shift (ca. 10 °C), which makes it possible to calibrate the temperature measurements. The lower Curie temperature implies that the

sample temperature is higher than the measured temperature. Most likely, the temperature lag is due to the significantly (> 100 times) lower thermal conductivity of quartz compared to that of BN. The heat capacity of the two sample holders are similar and not expected to explain the difference. In this connection, it is noticeable that the change in magnetization near the Curie temperature (Fig. 7) occurs over a significantly smaller temperature sweep for the in situ holder. This is possibly due to smaller temperature gradients in the quartz holder caused by low thermal conductivity.

The measurements suggest that the sample temperature is not affected by the gas flow in the in-situ holder. Calculations of the heat capacity of the gas flow support that the cooling effect from the gas is insignificant. This is further supported by Curie temperature measurements in gas flows of 5 and 20 ml/min which show no discernible difference (less than 0.2 °C). The lower thermal conductivity of the in-situ holder made in quartz is to be kept in mind when changing temperatures, and sufficient time for thermal equilibration should be included. In cases, where fast temperature sweeps are desirable, improvements to the in situ holder could include using a material with larger heat conductivity than quartz.

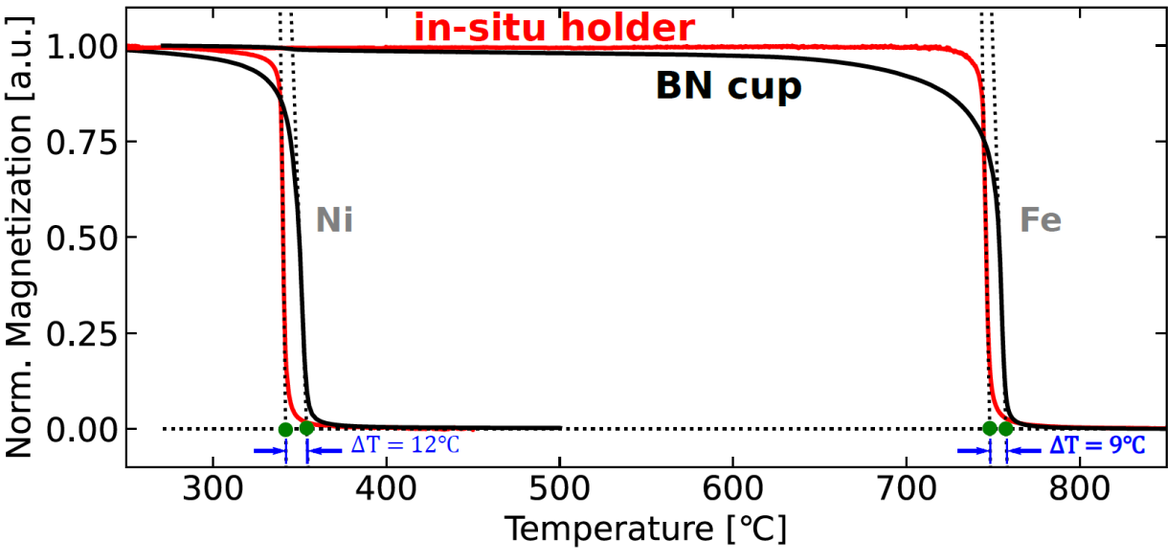


Figure 7: Normalised magnetisation of nickel powder and iron foil in an applied field of 10 mT measured using the in-situ holder and the BN cup.

The advantage of the system presented in this paper lies in the freedom to expose the sample to various gas-mixtures, which is not possible in the conventional VSM where the gas will interact with the oven. Here, we limited the investigations to a hydrogen-argon mix and synthetic air, but these investigations can be expanded to many different gas mixtures. Other advantages of the in situ system include the possibility to analyze the exit gas, and that this system is made of relatively inexpensive materials, that can be easily manufactured. Further improvement could include better estimation of the sample mass in the quartz tube, a more heat conducting material than quartz, and a holder design allowing for higher-risk gasses to be sent through the system, such as CO.

IV. Conclusions

In this study, we presented proof-of-concept for an in situ VSM sample holder to operate at high-temperatures with a well-controlled gas-atmosphere at the sample. The holder can withstand the vibration of the VSM, temperatures of 950°C for prolonged periods of time, at atmospheric pressure, and expose the sample to a gas mixture defined by the user (hydrogen, argon and synthetic air in this study). The results presented here indicate a more controlled reduction of cobalt in the in situ holder than in conventional boron-nitride cups. This is most likely related to a better controlled exposure of the sample to gas. Moreover, with the in situ holder it is possible to do VSM studies in an oxidizing atmosphere at high-temperature, an option not allowed by the conventional VSM setup with BN cups. More measurements are needed to firmly establish the advantages of the in situ holder, and to optimize it, but the results as of now indicate that this system can perform the same measurements as a conventional system, but has the added features of the user being able to change and control the atmosphere that the sample is exposed to. Future versions of this holder could include a larger sample volume as well as a gas-tight holder capable of working with poisonous gasses, adding several more gas-lines, adding an option for introducing water vapour, and a

quadrupole mass-spectrometer to analyse the exit gas.

Acknowledgement

We thank Miriam I. Varon for preparing the samples. This work has been funded by the Innovation Fund Denmark, Grant number: 5160-00004B, and the Villum Center for the Science of Sustainable Fuels and Chemicals (V-SUSTAIN grant 9455).

Author declaration

Conflict of interest

The autors MRA, JAE, IC, and CF have Patent WO2022189504 pending.

References

(1) Dodrill, B. C. *The Performance of the Model 7400 VSM: Sensitivity*; https://www.lakeshore.com/docs/default-source/product-downloads/application-notes/the-performance-of-the-model-7400-vsm-sensitivity.pdf?sfvrsn=425ec765{_}1, accessed 18/10-2020.

(2) Graham, C. D. High-sensitivity magnetization measurements. *Journal of Materials Science and Technology* **2000**, *16*, 97–101.

(3) Myers, H.; Sucksmith, W. The Spontaneous Magnetization of Cobalt. *Proceedings of the Royal Society of London Series A-mathematical and Physical Sciences* **1951**, *207*, 427–446.

(4) Cryogenic Limited - High Temperature VSM probe. http://www.cryogenic.co.uk/products/high-temperature-vsm-probe.

(5) *Lake Shore 7400-S Series VSM*; https://www.lakeshore.com/docs/default-source/product-downloads/catalog/vsmcatalog7400-s.pdf?sfvrsn=252b6d1a{_}1, accessed 18/10-2020.

(6) Ceylan, S.; Friese, C.; Lammel, C.; Mazac, K.; Kirschning, A. Inductive Heating for Organic Synthesis by Using Functionalized Magnetic Nanoparticles Inside Microreactors. *Angewandte Chemie International Edition* **2008**, *47*, 8950–8953.

(7) Bordet, A.; Lacroix, L.-M.; Fazzini, P.-F.; Carrey, J.; Soulantica, K.; Chaudret, B. Magnetically Induced Continuous CO 2 Hydrogenation Using Composite Iron Carbide Nanoparticles of Exceptionally High Heating Power. *Angewandte Chemie International Edition* **2016**, *55*, 15894–15898.

(8) Mortensen, P. M.; Engbæk, J. S.; Vendelbo, S. B.; Hansen, M. F.; Østberg, M. Direct Hysteresis Heating of Catalytically Active Ni–Co Nanoparticles as Steam Reforming Catalyst. *Industrial & Engineering Chemistry Research* **2017**, *56*, 14006–14013.

(9) Vinum, M. G.; Almind, M. R.; Engbæk, J. S.; Vendelbo, S. B.; Hansen, M. F.; Frandsen, C.; Bendix, J.; Mortensen, P. M. Dual-Function Cobalt–Nickel Nanoparticles Tailored for High-Temperature Induction-Heated Steam Methane Reforming. *Angewandte Chemie* **2018**, *130*, 10729–10733.

(10) Almind, M. R.; Vendelbo, S. B.; Hansen, M. F.; Vinum, M. G.; Frandsen, C.; Mortensen, P. M.; Engbæk, J. S. Improving performance of induction-heated steam methane reforming. *Catalysis Today* **2020**, *342*, 13–20.

(11) Varsano, F.; Bellusci, M.; La Barbera, A.; Petrecca, M.; Albino, M.; Sangregorio, C. Dry reforming of methane powered by magnetic induction. *International Journal of Hydrogen Energy* **2019**, *44*, 21037–21044.

(12) Marbaix, J.; Mille, N.; Lacroix, L.-M.; Asensio, J. M.; Fazzini, P.-F.; Soulantica, K.; Carrey, J.; Chaudret, B. Tuning the Composition of FeCo Nanoparticle Heating Agents for Magnetically Induced Catalysis. *ACS Applied Nano Materials* **2020**, *3*, 3767–3778.

(13) Claeys, M.; van Steen, E.; Visagie, J.; van de Loosdrecht, J. Magnetometer. 2014; Patent no.: US20110204884A1.

(14) Claeys, M.; Dry, M.; van Steen, E.; du Plessis, E.; van Berge, P.; Saib, A.; Moodley, D. In situ magnetometer study on the formation and stability of cobalt carbide in Fischer–Tropsch synthesis. *Journal of Catalysis* **2014**, *318*, 193–202.

(15) Fischer, N.; Clapham, B.; Feltes, T.; van Steen, E.; Claeys, M. Size-Dependent Phase Transformation of Catalytically Active Nanoparticles Captured In Situ. *Angewandte Chemie International Edition* **2014**, *53*, 1342–1345.

(16) Claeys, M.; Dry, M. E.; van Steen, E.; van Berge, P. J.; Booyens, S.; Crous, R.; van Helden, P.; Labuschagne, J.; Moodley, D. J.; Saib, A. M. Impact of Process Conditions on the Sintering Behavior of an Alumina-Supported Cobalt Fischer–Tropsch Catalyst Studied with an in Situ Magnetometer. *ACS Catalysis* **2015**, *5*, 841–852.

(17) Chernavskii, P. A.; Lunin, B. S.; Zakharyan, R. A.; Pankina, G. V.; Perov, N. S. Experimental setup for investigating topochemical transformations of ferromagnetic nanoparticles. *Instruments and Experimental Techniques* **2014**, *57*, 78–81.

(18) Home — Unifrax - A Global Specialty Fibers Company. https://www.unifrax.com/.

(19) Chorkendorff, I.; Niemantsverdriet, J. *Concepts of modern catalysis and kinetics*, : 2., revised and enlarged edition ed.; Wiley-VCH Verlag: Germany, 2007.

(20) PURAL MG and PURALOX MG. https://products.sasol.com/pic/products/home/grades/ZA/5pural-mg-and-puralox-mg/index.html.

(21) 7400-S Series VSM. https://www.lakeshore.com/products/categories/specification/discontinued-products/discontinued-products/7400-s-series-vsm.

(22) Grommé, C. S.; Wright, T. L.; Peck, D. L. Magnetic Properties and Oxidation of Iron-Titanium Oxide Minerals in Alae and Makaopuhi Lava Lakes, Hawaii. *Journal of Geophysical Research (1896-1977)* **1969**, *74*, 5277–5293.