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In Situ Ptychography of Heterogeneous Catalysts using Hard X-Rays: High Resolution Imaging at Ambient Pressure and Elevated Temperature

Sina Baier,¹ Christian D. Damsgaard,^{2,3} Maria Scholz,⁴ Federico Benzi,¹ Amélie Rochet,¹ Robert Hoppe,⁵ Torsten Scherer,^{6,7} Junjie Shi,⁸ Arne Wittstock,⁸ Britta Weinhausen,⁹ Jakob B. Wagner,² Christian G. Schroer,^{4,10} and Jan-Dierk Grunwaldt^{1,11,*}

¹Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

²Center for Electron Nanoscopy, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

³Center for Individual Nanoparticle Functionality, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

⁴Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

⁵Institute of Structural Physics, Technische Universität Dresden, 01062 Dresden, Germany

⁶Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

⁷Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

⁸Angewandte und Physikalische Chemie, University of Bremen, 28359 Bremen, Germany

⁹European Synchrotron Radiation Facility, 38043 Grenoble, France

¹⁰Department Physik, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

¹¹Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

Abstract: A new closed cell is presented for *in situ* X-ray ptychography which allows studies under gas flow and at elevated temperature. In order to gain complementary information by transmission and scanning electron microscopy, the cell makes use of a Protochips E-chipTM which contains a small, thin electron transparent window and allows heating. Two gold-based systems, 50 nm gold particles and nanoporous gold as a relevant catalyst sample, were used for studying the feasibility of the cell. Measurements showing a resolution around 40 nm have been achieved under a flow of synthetic air and during heating up to temperatures of 933 K. An elevated temperature exhibited little influence on image quality and resolution. With this study, the potential of *in situ* hard X-ray ptychography for investigating annealing processes of real catalyst samples is demonstrated. Furthermore, the possibility to use the same sample holder for *ex situ* electron microscopy before and after the *in situ* study underlines the unique possibilities available with this combination of electron microscopy and X-ray microscopy on the same sample.

Key words: ptychography, X-ray microscopy, *in situ*, heterogeneous catalysis, synchrotron radiation, annealing, nanoporous gold

INTRODUCTION

To understand the function of heterogeneous catalysts and to improve catalytic properties, structure-activity relationships are required. As catalysts may change their structure with respect to the environment, it is invaluable to study the catalysts under reaction conditions (Grunwaldt & Clausen, 2002; Weckhuysen, 2002; Topsøe, 2003; Grunwaldt et al., 2004; Bañares, 2005). However, such *in situ* or *operando* studies require dedicated techniques. For catalyst characterization X-ray-based techniques are largely used (Clausen et al., 1991; Iwasawa, 1996; Weckhuysen, 2004; Andreasen et al., 2006; Grunwaldt & Frenkel, 2009; Beale et al., 2010; Frenkel & van Bokhoven, 2014) and information has to be gained on different length scales (Weckhuysen, 2009; Beale et al., 2010; Grunwaldt et al., 2013; Thomas et al., 2013; Merkle et al., 2014). For atomic scale imaging, transmission

electron microscopy (TEM) is applied. However, there are also limitations of environmental TEM (ETEM), e.g. restriction to low pressure with the exception of specially designed cells (Creemer et al., 2008), interactions with the electron beam, restrictions in probing different angles for three-dimensional (3D) measurements, or the need for complementary techniques for spectroscopic information (Egerton et al., 2004; Simonsen et al., 2008; Benavidez et al., 2012; Wagner et al., 2012; Hansen et al., 2013). In contrast, spatially resolved information on the meso scale (50 nm–1 μ m) and below (<50 nm) can be gained by X-ray microscopy, which enables *in situ* studies at both ambient and elevated pressure (Thomas & Hernandez-Garrido, 2009; Grunwaldt & Schroer, 2010; Buurmans & Weckhuysen, 2012; Gonzalez-Jimenez et al., 2012; Cats et al., 2013). Furthermore, due to the much higher penetration depth of X-rays compared to electrons, studies can be performed on realistic samples and conditions (e.g., corrosive gases or liquids). For these purposes, special *in situ* cells with X-ray transparent windows have been designed. For high resolution

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*Corresponding author. grunwaldt@kit.edu

images, scanning transmission X-ray microscopy (STXM) has usually been used in the soft X-ray regime (Drake et al., 2004; de Smit et al., 2008; de Groot et al., 2010; Falcone et al., 2011). The area of interest of the sample is scanned under a focused beam and the desired signal is detected for each point of the scan. For this technique, the resolution is dependent on the size of the beam spot on the sample. To achieve a focused X-ray beam focusing optics are used. These include Fresnel zone plates (Oltman, 1953; Camus et al., 1967), Kirkpatrick–Baez mirrors (Suzuki & Uchida, 1991; Ruhlandt et al., 2012), waveguides (Krüger et al., 2012), and refractive X-ray lenses (Suehiro et al., 1991; Snigirev et al., 1996; Lengeler et al., 1999). Compared to full-field techniques, where the whole image is acquired in one shot, which is especially suitable for dynamic processes, the advantage of scanning techniques lies in the combination of different spectroscopic contrasts (e.g., X-ray fluorescence (XRF), X-ray absorption (XAS) and X-ray diffraction (XRD)) (de Groot et al., 2010; Grunwaldt et al., 2013). Additionally, projection images with spatial resolution on the micrometer scale can be gained without the use of X-ray optics avoiding aberrations. In the hard X-ray range, full-field microscopes based on magnified imaging with an objective lens typically reach spatial resolutions of several tens of nanometers (Chu et al., 2008), and for soft X-rays (200–2,000 eV) resolutions down to 15 nm have been reached by STXM (de Smit et al., 2008). However, the shorter penetration depth of soft X-rays compared to hard X-rays can cause problems with respect to *in situ* cell design and the possibility of measurements at ambient pressure (Drake et al., 2004; Grunwaldt & Schroer, 2010). Therefore, hard X-rays are more favorable for the purpose of *in situ* measurements and nowadays, focusing optics used for hard X-rays are able to realize beam spot sizes of about 50–80 nm (Schroer et al., 2010). In order to achieve higher resolution, scanning coherent X-ray diffraction imaging, which is also called X-ray ptychography, can be used (Rodenburg & Faulkner, 2004; Thibault et al., 2008). In this technique, the desired sample area is scanned with a coherent X-ray beam and the far-field diffraction patterns are recorded with a partial overlap between the adjacent points in real space. Real space images are calculated by iteratively working phase retrieval algorithms, which are used to consistently reconstruct both the object and the illumination in the object plane. Hence, ptychography is self focusing, and the exact sample positioning along the optical axis is not critical as long as the sample stays within the depth of focus during the ptychographic scan. Currently, in soft X-ray ptychography, a resolution of 5 nm can be achieved (Shapiro et al., 2014), whereas in hard X-ray ptychography a resolution below 10 nm for strongly scattering objects is possible (Vila-Comamala et al., 2011; Schropp et al., 2012). Nevertheless, those measurements were performed on ideal samples under *ex situ* conditions. For *in situ* conditions, Høydalsvik et al. (2014) achieved a resolution of roughly 200 nm on lithium zirconate particles, but the measurement was not performed in a closed environment as holes for the X-ray beam were kept open. Another *in situ* study was performed by Kiss et al. (2015) studying resonantly the

oxidation of nickel powder by full-field X-ray microscopy achieving a resolution of 55 nm. Coherent diffraction imaging in Bragg geometry has also recently been applied in *in situ* and *operando* studies (Ulvestad et al., 2014; Clark et al., 2015), even for studying ultrafast processes using X-ray free electron lasers (Clark et al., 2013). Ptychography, as a scanning technique, can also be combined with chemical imaging (Beckers et al., 2011; Hoppe et al., 2013; Shapiro et al., 2014) and is therefore a very promising technique for nanoscale imaging of catalysts (Hoppe et al., 2013) and energy materials (Hitchcock & Toney, 2014), material sciences (Schropp et al., 2011; Esmaili et al., 2013; Dam et al., 2015), and life sciences (Luu et al., 2014).

In catalysis, interesting examples for studying catalysts at the medium scale are porous structures containing different pore volumes (Vantomme et al., 2007), their influence on sintering studies (Dumee et al., 2014), and core-shell particles (Ding et al., 2015; Güttel, 2015). These are also of interest for modeling (Matera & Reuter, 2012). Here, as examples, we study the annealing of 50 nm gold particles and nanoporous gold structures in synthetic air. Starting from the 1980s, gold became an interesting element for heterogeneous catalysis. Most popular is CO oxidation over gold nanoparticles (Haruta et al., 1993). Besides supported catalysts, unsupported skeletal gold has received strong interest within the last few years (Wittstock & Bäumer, 2014). Hence, a further investigated sample is nanoporous gold (np-Au), which can be obtained by dealloying of AgAu using nitric acid, and is composed of a sponge-like 3D network (Zielasek et al., 2006). The pores and ligaments forming the macroscopic material show sizes in the range of tens of nanometers and have several kinks and steps, which support the catalytic activity (Fujita et al., 2012). Np-Au has been modified by creating “inverse catalysts”, where a metal oxide is supported on a pure metal, which show promising catalytic activity (Rodriguez et al., 2007; Wichmann et al., 2013a; Bagge-Hansen et al., 2014; Shi et al., 2014). In particular, such inverted np-Au catalysts are suitable for different reactions such as CO oxidation (Iizuka et al., 2004; Zielasek et al., 2006), oxidation of alcohols (Wittstock et al., 2010) or water gas shift reaction (Shi et al., 2014). Np-Au surprisingly showed high activity for oxidation reactions at low temperatures (Wittstock et al., 2009), but at higher temperatures (around 773 K), coarsening of both the ligaments and the pores occurred (Chen-Wiegar et al., 2012; Wang et al., 2012). The coarsening of the nanostructures impedes the application and durability of the material at higher temperatures. Suitable modification with metal-oxides (CeO₂, TiO₂) resulted in a stabilization of the nanostructure at temperatures above 773 K (Wichmann et al., 2013b).

Here, we report on the annealing of 50 nm gold particles and np-Au-based catalysts in order to follow the coarsening at different temperatures. The *in situ* ptychography study was performed in a specially designed closed cell, which enabled gas flow and heating. A beneficial aspect is that the same cell can be used as the “sample support” (TEM heating chip) for ptychography measurement and electron microscopy. In this way, multiple methods can be used for the same sample to acquire complementary information, e.g., high-resolution

images obtained by *ex situ* TEM, and *in situ* observation during the desired process on the meso scale by X-ray microscopy.

MATERIALS AND METHODS

Design of the *In Situ* Cell

In principle, the *in situ* cell is based on a TEM sample heating chip, a Protochips E-ChipTM, which is designed for TEM studies (Allard et al., 2009a; Simonsen et al., 2015). Heating is provided through resistive heating of a conductive ceramic membrane (Allard et al., 2009b) of ~120 nm containing Si and C. For electron transparent areas, holes in this membrane are covered with an ~50 nm thick silicon nitride thin film. Using this chip we were able to use it either *ex situ* in a TEM or scanning electron microscope (SEM), or inside the developed *in situ* cell for hard X-ray microscopy/spectroscopy, which enables complementary information on the same sample. The cell is composed of a stainless steel body with X-ray transparent windows where the E-chipTM was placed. To provide a controlled reaction environment, the cell has a gas inlet and outlet. Gas flow through the cell was adjusted by mass flow controllers (Bronkhorst) and controlled by a script written in NI LabVIEW 2013. Heating was realized by resistive heating within the E-ChipTM, which is connected to a Keithley 6220 DC current source. The temperature is related to the heating power, but it is to a certain extent different from chip to chip up to 50 K at ambient conditions. Temperature estimation was realized by comparing the heating powers used in this experiment to similar heating powers with other E-chipsTM, where the temperature was determined with an infrared thermography camera. With the E-ChipTM, the user benefits from the thin silicon nitride electron transparent window within the chip. This is crucial for TEM measurements on the area of interest. This window is incorporated into the cell and is used as an X-ray transparent window in the *in situ* cell. To close the cell body, another window made by Kapton[®] foil is used. Figure 1 shows a schematic representation of the design of the *in situ* cell. The E-ChipTM is placed on the bottom part, so that the sample faces the inside of the cell. Following this, an O-ring enables tight connection to the middle part with the gas inlet and outlet. The cell is closed by adding the top part with another O-ring and the Kapton[®] window. For electrical connection, another piece is fixed to the cell, connecting the electrodes of the E-ChipTM to a power supply. Figure 2 shows two photographs of the cell visualizing the same parts as in the schematic representation in Figure 1.

Preparation and Characterization

Sample Preparation

Three gold samples were prepared on the Protochips E-ChipsTM: (1) A commercial solution of citrate stabilized 50 nm colloidal gold nanoparticles (Sigma Aldrich) was deposited on a E-Chip with a SiN membrane by dropcasting. (2) About 100 nm thick np-Au films were prepared by dealloying of AgAu alloy leaves (American White Gold,

Figure 1. Schematic representation of the *in situ* cell designed for combination of X-ray microscopy and electron microscopy. The sample is placed on a commercial TEM chip, can be heated by using the resistive heating possibility by the chip, and can be kept under a desired gas flow. X-ray transparent windows are realized by the TEM chip itself and by a Kapton[®] window placed on top of the cell.

Figure 2. Photographs of the *in situ* cell. The bottom view (left) and side view (right) are shown.

12 Karat, Noris Blattgold) using concentrated nitric acid (Sigma Aldrich, puriss p.a. ≥65%). The sample was carefully washed (floating on deionized water) and transferred onto a copper TEM grid (100 mesh) and further processed by focused ion beam (FIB) milling (see below). (3) The CeO₂/np-Au was prepared by impregnation of the np-Au on the copper TEM grid with 10 μL of an ethanolic solution of cerium nitrate (Ce(NO₃)₃, 1 mol/L). After drying in air for at least 30 min, the sample was calcined at 523 K for 2 h yielding the oxide.

The as prepared samples from (2) and (3) were then transferred to a FIB microscope. Independently, aluminum frames of approximately L × W × H = 60 × 60 × 13 μm were prepared by FIB milling, which were used to stabilize the sample. The frame was fixed on the np-Au based samples by deposition of platinum on the outside of the frame. Afterwards, the stabilized sample was milled out and fixed on the E-ChipTM by platinum deposition. In this way, one pure np-Au and one CeO₂/np-Au sample were deposited on separate E-ChipsTM. To evaluate the effect of temperature on the X-ray image, non-changing structures could be added as a future reference. FIB milling was performed using a Zeiss Auriga 60 or a FEI Strata dual beam FIB system at the Karlsruhe Nano Micro Facility (KNMF), located at the Institute for Nanotechnology (INT) at KIT.

Ex Situ Characterization

SEM imaging was performed *ex situ* using the FIB-SEMs Zeiss Auriga 60 and FEI Strata as described above. A secondary electron (SE) in-lens detector was used for imaging.

Synchrotron Experiment

The experiment was carried out at the nanofocus endstation of the beamline ID13 at the European Synchrotron Radiation Facility (ESRF) during 7/8 + 1 mode operation (868 bunches, scheduled ring current 200 mA). The *in situ* cell was mounted on a kinematic mount and was scanned through the nanofocused beam. The beam was focused onto the sample by nanofocusing lenses to provide an illumination with a full width half maximum spot size of around 150 nm. In the present case, the depth of focus is about 100 μm and stability of the setup on this scale is guaranteed. The acquisition was performed at 14.9 keV photon energy (Si (111) channel cut monochromator). Far-field diffraction patterns were recorded with a Maxipix detector (pixel size: 55 μm) with a sample–detector distance of 1 m for np-Au based samples, covering a q range up to 0.53 nm^{-1} , and 2 m for the 50 nm Au sample (q range up to 0.27 nm^{-1}). An area of $2 \times 2 \mu\text{m}$ was scanned with a step width of 50 nm and the X-ray beam first passed the “bottom” of the cell (see Fig. 1), where the window is presented by the silicon nitride membrane of the E-ChipTM. At each position of the scan, a diffraction pattern was recorded for 0.03 s, leading to a signal in the range of 10^4 photons per pixel in the most intensive parts of the diffraction pattern. About 10–15 min were required to record one complete ptychogram per temperature step and for image reconstruction, respectively. The algorithm used for reconstruction is based on the (e)PIE algorithm presented by Maiden and Rodenburg (Maiden & Rodenburg, 2009). Further technical details and details on the algorithm are given in the Online Supplementary Information (OSI).

Supplementary Material

Supplementary Material can be found online. Please visit journals.cambridge.org/jid_MAM.

In situ experiments were carried out by using the as prepared E-chipsTM inside the cell using the heating and gas dosing possibilities. Synthetic air (20% O_2/N_2) was used for the annealing treatment to create a controlled atmosphere.

RESULTS AND DISCUSSION

As a model sample, 50 nm Au particles were studied to investigate the applicability and the feasibility of *in situ* ptychography with a resolution below 100 nm. The results obtained for the 50 nm particles are shown in Figure 3. By *ex situ* SEM before the annealing treatment, an agglomeration of such particles was identified. The same part of the sample was studied inside the cell by ptychography using hard X-rays. As shown in Figure 3b, the same structure could be observed in the phase contrast images without gas flow as well as with a flow of 1 mL/min of synthetic air (Fig. 3c). Even though single particles were not imaged in detail, the

general shape of the agglomeration can be extracted. This measurement indicates the feasibility of *in situ* measurements and shows that a gas flow at ambient pressure does not influence the image quality. For testing the heating capability, the Au nanoparticle model sample was annealed at different temperatures, thereby the heating power, which was directly measured, is given together with an estimated temperature gained by comparison to IR thermography data on other chips. After annealing for 45 min at 180 mW (around 720 K), a coarsening of the structure could be observed (Fig. 3d), which increased after a second annealing treatment of 25 min at 260 mW (around 870 K), and is presented in Figure 3e. These measurements underline the feasibility of *in situ* studies in the developed cell. This demonstrates the possibility to image samples before and after temperature treatment within the same gas atmosphere with a resolution better than 100 nm.

To test the possibility of *in situ* measurements during heating and gas flow, the np-Au based samples were used and the experimental design and sample-detector distance were optimized to get a higher resolution. Pure np-Au was used for testing heating at high temperatures and its influence on imaging possibilities. Then $\text{CeO}_2/\text{np-Au}$ was used for annealing in smaller temperature steps.

For pure np-Au, a crack (artifact from FIB-milling) was studied at different temperature steps with a flow of 3 mL/min of synthetic air. At 130 mW a temperature of roughly 520 K was reached and at 190 mW the temperature was around 770 K. After further heating the sample with a power of 315 mW, the melting point of the aluminum frame (around 933 K) was reached. As shown in Figure 4b, the structure acquired by ptychographic reconstruction at room temperature during gas flow is in agreement with the SEM image. This is even more obvious in the overlay of the colorized and inverted SEM image on the phase contrast image gained by ptychography (Fig. 4h). Structures of 35 nm, i.e., the width of the crack marked in Figure 4c, could be resolved, using the high-resolution setup (covering a q range up to 0.53 nm^{-1}). The overall resolution achieved in ptychography is estimated to be about 40 nm as detailed in the OSI. While heating at 59 mW at around 330 K (Fig. 4c), either the first changes, marked by an arrow, already occurred at this low temperature or the resolution became slightly worse, which could have happened due to thermal vibrations. However, the 35 nm structure is still visible. At higher temperature during heating at 130 mW, around 520 K (Fig. 4d), clear changes appeared in the structure, which are marked as well. The changes became more obvious during further annealing treatment (Fig. 4e and 4f), resulting in less dense areas and an increased density in other parts of the sample. This is in agreement with a coarsening of the three dimensional network structure (Chen-Wiegart et al., 2012; Wang et al., 2012). Destruction of the framework depicted in Figure 4g can be explained by melting of the aluminum frame during heating at 315 mW (around 933 K), which was later confirmed by *ex situ* SEM. It can be concluded from these measurements that coarsening of the unmodified

Figure 3. 50 nm Au particles deposited on the SiN membrane. (a) Scanning electron microscope (SEM) image in SE contrast, (b) phase contrast image of the same area in the ptychographic measurement without gas flow, (c) phase contrast image with a flow of 1 mL/min synthetic air, (d) phase contrast image at room temperature after the first annealing treatment at 180 mW (around 720 K) without gas flow showing the beginning coarsening of the agglomerate structure, (e) phase contrast image at room temperature after the second annealing treatment at 260 mW (around 870 K) without gas flow showing a complete degradation of the original structure.

np-Au set in at a temperature of around 520 K, which is in agreement with previous studies under ambient conditions (Biener et al., 2010). While the first changes at this

temperature occurred only at small length scales around 10 nm, increasing the temperature to around 770 K led to an obvious structural change with increased coarsening.

Figure 4. Np-Au on a SiN membrane studied by scanning electron microscope (SEM) (SE contrast) and ptychography at different annealing steps with a flow of 3 mL/min synthetic air. (a) *Ex situ* SEM image in SE contrast before any thermal treatment, (b) phase contrast image of the same area in the ptychographic measurement at room temperature, (c) phase contrast image at a power of 59 mW (around 330 K) (d) phase contrast image at a power of 130 mW (around 520 K), (e) phase contrast image at a power of 194 mW (around 770 K), (f) phase contrast image at a power of 270 mW (>870 K), (g) phase contrast image at a power of 315 mW (around 930 K), (h) colorized and inverted SEM image (red) overlaid on (b).

Figure 5. $\text{CeO}_2/\text{np-Au}$ on a SiN membrane studied by scanning electron microscope (SEM) (SE contrast) and ptychography at different annealing steps with a flow of 3 mL/min synthetic air. (a) *Ex situ* SEM image in SE contrast before any thermal treatment, (b) phase contrast image of the same area in the ptychographic measurement at room temperature, (c) phase contrast image at a power of 24 mW (around 300 K), (d) phase contrast image at a power of 65 mW (around 330 K), (e) phase contrast image at a power of 107 mW (<520 K) showing the field of view marked by a rectangle, (f) *ex situ* SEM image in SE contrast after the thermal treatment.

For comparison, the inverse catalyst $\text{CeO}_2/\text{np-Au}$ was tested by *in situ* ptychography and the results are depicted in Figure 5. The measurements were performed on a natural crack on the border of the sample. In contrast to the pure np-Au sample, fewer changes were observed, which was expected and in agreement with annealing in smaller temperature steps and at lower temperature. For correlation, the highest temperature used in this experiment was slightly lower than the one that resulted in clearly visible changes in Figure 4d. However, also at these relatively low temperatures, a structural change caused by the annealing treatment could be observed. Mainly the top part of the studied structure, which is marked with an arrow, was already flattened at a low heating power of 65 mW around 330 K (Fig. 5d). At a heating power of 107 mW below 520 K (Fig. 5e), coarsening first became visible by contrast changes, which might result from density changes in the sample. The coarsening was confirmed by *ex situ* SEM imaging after the annealing treatment, as shown in Fig. 5f. Figure 5d and 5e show artifacts, as the field of view was at a slightly different position compared to the previous measurements.

When evaluating the data on the np-Au-based samples, it has to be taken into account that a three dimensional sample is studied in transmission geometry, resulting in a projected two dimensional image. The studied changes are therefore changes in sample density all over the probed direction. In general, and for thick samples, the local structure inside the sample can only be reliably evaluated in tomography studies. Here, the samples were relatively thin (~ 100 nm compared to about 40 nm spatial resolution) and single projection images along the thin direction give good insight into the structure. In a next step, the imaging scheme can be extended to tomography. The resolution around 40 nm gained in this experiment is comparable to that in the work by Kiss et al. (2015). Besides the possibility of measuring resonantly around an absorption edge, which is possible with both methods, ptychography offers the advantage of combining spatially resolved fluorescence measurements in parallel as the sample is scanned in the beam. Furthermore, the resolution in ptychography is not restricted by aberrations in an objective lens. For real samples, which usually scatter less than reference objects, the resolution gained in the presented study is still less than the maximum resolution reported for strongly scattering objects (Vila-Comamala et al., 2011; Schropp et al., 2012; Shapiro et al., 2014). However, the resolution gained with this presented cell is by a factor of 4 better than in previously reported *in situ* ptychography studies (Høydalsvik et al., 2014). Apart from the possibilities of safer measurements (due to the closed cell) for dangerous gases, the cell is beneficial during experimental use: the heated area is smaller than 1 mm^2 and does not require cooling to prevent the surrounding equipment from being heated. Furthermore, due to its small size and light weight, positioning of the whole cell on a high precision piezo stage is possible, which is required for accurate sample movement during scanning probe techniques. Finally, the main advantage of the presented cell

compared to state-of-the-art sample surroundings for *in situ* experiments is the possibility for complementary electron microscopy measurements on the same sample before and after *in situ* treatment. The E-ChipTM can be easily mounted on a TEM holder or can be used for SEM. This enables the user to combine high resolution knowledge gained by TEM together with insight from *in situ* studies at lower resolution on the same sample area.

CONCLUSIONS

In situ hard X-ray ptychography was performed in a closed cell with a resolution of 40 nm at elevated temperature and during gas flow. The design and application of the *in situ* cell for ptychography was demonstrated on a model sample of 50 nm Au particles and for real catalyst samples based on np-Au. By using the model sample, the applicability of the cell for heating tests was proven and *in situ* ptychography measurements during gas flow are presented. As *in situ* measurements were performed up to temperatures of around 990 K, it indicates that with the presented setup, there is hardly any influence on image quality, neither by gas flow nor heating treatment during image acquisition.

By this study, it is further shown that coarsening of pure np-Au and the inverse catalyst material $\text{CeO}_2/\text{np-Au}$ already starts at a relatively low temperature below 520 K. At this low temperature and with the resolution gained in the experiments, no significant differences were observed between the pure and the inverse catalyst. However, further studies are required to investigate the annealing behavior and the influence of ambient pressure *in situ* at higher resolution.

The advantages of the presented *in situ* cell, namely the possibility of using the same E-ChipTM for both X-ray ptychography and electron microscopy, were demonstrated by performing *ex situ* SEM on the same sample before and after the thermal treatment. This possibility for complementary techniques allows for additional high resolution information on the studied system if the E-ChipTM is used for TEM. However, real *in situ* information in a controlled atmosphere at ambient pressure, during a realistic gas flow and at elevated temperature, can only be gained by X-ray techniques such as ptychography. By further improving the resolution in X-ray microscopy investigations and by exploiting this electron microscopy/X-ray microscopy approach, better insights into hierarchically structured materials can be gained.

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REFERENCES

- ALLARD, L.F., BORISEVICH, A., DENG, W., SI, R., FLYTZANI-STEPHANOPOULOS, M. & OVERBURY, S.H. (2009a). Evolution of gold structure during thermal treatment of Au/FeOx catalysts revealed by aberration-corrected electron microscopy. *J Electron Microsc* **58**, 199–212.
- ALLARD, L.F., FLYTZANI-STEPHANOPOULOS, M. & OVERBURY, S.H. (2009b). A novel heating technology for ultra-high resolution imaging in electron microscopes. *Microscopy Today* **17**, 50–55.
- ANDREASEN, J.W., RASMUSSEN, F.B., HELVEG, S., MOLENBROEK, A., STAHL, K., NIELSEN, M.M. & FEIDENHANS, R. (2006). Activation of a Cu/ZnO catalyst for methanol synthesis. *J Appl Crystallogr* **39**, 209–221.
- BAGGE-HANSEN, M., WICHMANN, A., WITTSTOCK, A., LEE, J.R.I., YE, J., WILLEY, T.M., KUNTZ, J.D., VAN BUUREN, T., BIENER, J., BAUMER, M. & BIENER, M.M. (2014). Quantitative phase composition of TiO₂-coated nanoporous Au monoliths by X-ray absorption spectroscopy and correlations to catalytic behavior. *J Phys Chem C* **118**, 4078–4084.
- BANARES, M.A. (2005). Operando methodology: combination of *in situ* spectroscopy and simultaneous activity measurements under catalytic reaction conditions. *Catal Today* **100**, 71–77.
- BEALE, A.M., JACQUES, S.D.M. & WECKHUYSEN, B.M. (2010). Chemical imaging of catalytic solids with synchrotron radiation. *Chem Soc Rev* **39**, 4656–4672.
- BECKERS, M., SENKBEIL, T., GORNIK, T., REESE, M., GIEWEKEMEYER, K., GLEBER, S.-C., SALDITT, T. & ROSENHAHN, A. (2011). Chemical contrast in soft X-ray ptychography. *Phys Rev Lett* **107**, 208101/1–4.
- BENAVIDEZ, A.D., KOVARIK, L., GENG, A., AGRAWAL, N., LARSSON, E.M., HANSEN, T.W., KARIM, A.M. & DATYE, A.K. (2012). Environmental transmission electron microscopy study of the origins of anomalous particle size distributions in supported metal catalysts. *ACS Catal* **2**, 2349–2356.
- BIENER, J., WITTSTOCK, A., BIENER, M.M., NOWITZKI, T., HAMZA, A.V. & BAUMER, M. (2010). Effect of surface chemistry on the stability of gold nanostructures. *Langmuir* **26**, 13736–13740.
- BUURMANS, I.L.C. & WECKHUYSEN, B.M. (2012). Heterogeneities of individual catalyst particles in space and time as monitored by spectroscopy. *Nat Chem* **4**, 873–886.
- CAMUS, J., GIRARD, F. & CLARK, R. (1967). Fresnel zone plate generation. *Appl Opt* **6**, 1433.
- CATS, K.H., GONZALEZ-JIMENEZ, I.D., LIU, Y., NELSON, J., VAN CAMPEN, D., MEIRER, F., VAN DER EERDEN, A.M.J., DE GROOT, F.M.F., ANDREWS, J.C. & WECKHUYSEN, B.M. (2013). X-ray nanoscopy of cobalt Fischer-Tropsch catalysts at work. *Chem Commun* **49**, 4622–4624.
- CHEN-WIEGART, Y.-C.K., WANG, S., CHU, Y.S., LIU, W., McNULTY, I., VOORHEES, P.W. & DUNAND, D.C. (2012). Structural evolution of nanoporous gold during thermal coarsening. *Acta Mater* **60**, 4972–4981.
- CHU, Y.S., YI, J.M., DE CARLO, F., SHEN, Q., LEE, W.-K., WU, H.J., WANG, C.L., WANG, J.Y., LIU, C.J., WANG, C.H., WU, S.R., CHIEN, C.C., HWU, Y., TKACHUK, A., YUN, W., FESER, M., LIANG, K.S., YANG, C.S., JE, J.H. & MARGARITONDO, G. (2008). Hard-X-ray microscopy with Fresnel zone plates reaches 40 nm Rayleigh resolution. *Appl Phys Lett* **92**, 103119/1–3.
- CLARK, J.N., BETTRA, L., XIONG, G., HIGGINBOTHAM, A., FRITZ, D.M., LEMKE, H.T., ZHU, D., CHOLLET, M., WILLIAMS, G.J., MESSERSCHMIDT, M., ABBEY, B., HARDER, R.J., KORSUNSKY, A.M., WARK, J.S. & ROBINSON, I.K. (2013). Ultrafast three-dimensional imaging of lattice dynamics in individual gold nanocrystals. *Science* **341**, 56–59.
- CLARK, J.N., IHLI, J., SCHENK, A.S., KIM, Y.-Y., KULAK, A.N., CAMPBELL, J.M., NISBET, G., MELDRUM, F.C. & ROBINSON, I.K. (2015). Three-dimensional imaging of dislocation propagation during crystal growth and dissolution. *Nat Mater* **14**, 780–784.
- CLAUSEN, B.S., STEFFENSEN, G., FABIUS, B., VILLADSEN, J., FEIDENHANS, R. & TOPSOE, H. (1991). In situ cell for combined XRD and online catalysis tests - studies of Cu-based water gas shift and methanol synthesis. *J Catal* **132**, 524–535.
- CREEMER, J.F., HELVEG, S., HOVELING, G.H., ULLMANN, S., MOLENBROEK, A.M., SARRO, P.M. & ZANDBERGEN, H.W. (2008). Atomic-scale electron microscopy at ambient pressure. *Ultramicroscopy* **108**, 993–998.
- DAM, H.F., ANDERSEN, T.R., PEDERSEN, E.B.L., THYDEN, K.T.S., HELGESEN, M., CARLE, J.E., JORGENSEN, P.S., REINHARDT, J., SONDERGAARD, R.R., JORGENSEN, M., BUNDGAARD, E., KREBS, F.C. & ANDREASEN, J.W. (2015). Enabling flexible polymer tandem solar cells 3D ptychographic imaging. *Adv Energy Mater* **5**, 1400736/1–6.
- DE GROOT, F.M.F., DE SMIT, E., VAN SCHOONEVELD, M.M., ARAMBURO, L.R. & WECKHUYSEN, B.M. (2010). *In-situ* scanning transmission X-ray microscopy of catalytic solids and related nanomaterials. *ChemPhysChem* **11**, 951–962.
- DE SMIT, E., SWART, I., CREEMER, J.F., HOVELING, G.H., GILLES, M.K., TYLISZCZAK, T., KOOYMAN, P.J., ZANDBERGEN, H.W., MORIN, C., WECKHUYSEN, B.M. & DE GROOT, F.M.F. (2008). Nanoscale chemical imaging of a working catalyst by scanning transmission X-ray microscopy. *Nature* **456**, 222–239.
- DING, W., KLUMPP, M., LEE, S., REUF, S., AL-THABAITI, S.A., PFEIFER, P., SCHWIEGER, W. & DITTMAYER, R. (2015). Simulation of one-stage dimethyl ether synthesis over a core-shell catalyst. *Chem Ing Tech* **87**, 702–712.
- DRAKE, I.J., LIU, T.C.N., GILLES, M., TYLISZCZAK, T., KILCOYNE, A.L.D., SHUH, D.K., MATHIES, R.A. & BELL, A.T. (2004). An *in situ* cell for characterization of solids by soft X-ray absorption. *Rev Sci Instrum* **75**, 3242–3247.
- DUMEE, L.F., SHE, F., DUKE, M., GRAY, S., HODGSON, P. & KONG, L. (2014). Fabrication of meso-porous sintered metal thin films by selective etching of silica based sacrificial template. *Nanomaterials* **4**, 686–699.
- EGERTON, R.F., LI, P. & MALAC, M. (2004). Radiation damage in the TEM and SEM. *Micron* **35**, 399–409.
- ESMAEILI, M., FLOYSTAD, J.B., DIAZ, A., HØYDALSVIK, K., GUIZAR-SICAIRIS, M., ANDREASEN, J.W. & BREIBY, D.W. (2013). Ptychographic X-ray tomography of silk fiber hydration. *Macromolecules* **46**, 434–439.

- FALCONE, R., JACOBSEN, C., KIRZ, J., MARCHESINI, S., SHAPIRO, D. & SPENCE, J. (2011). New directions in X-ray microscopy. *Contemp Phys* **52**, 293–318.
- FRENKEL, A.I. & VAN BOKHOVEN, J.A. (2014). X-ray spectroscopy for chemical and energy sciences: the case of heterogeneous catalysis. *J Synchrotron Radiat* **21**, 1084–1089.
- FUJITA, T., GUAN, P., MCKENNA, K., LANG, X., HIRATA, A., ZHANG, L., TOKUNAGA, T., ARAI, S., YAMAMOTO, Y., TANAKA, N., ISHIKAWA, Y., ASAO, N., YAMAMOTO, Y., ERLEBACHER, J. & CHEN, M. (2012). Atomic origins of the high catalytic activity of nanoporous gold. *Nat Mater* **11**, 775–780.
- GONZALEZ-JIMENEZ, I.D., CATS, K., DAVIDIAN, T., RUITENBEEK, M., MEIRER, F., LIU, Y., NELSON, J., ANDREWS, J.C., PIANETTA, P., DE GROOT, F.M.F. & WECKHUYSEN, B.M. (2012). Hard X-ray nanotomography of catalytic solids at work. *Angew Chem, Int Ed* **51**, 11986–11990.
- GRUNWALDT, J.-D. & FRENKEL, A.I. (2009). Synchrotron studies of catalysts: from XAFS to QEXAFS and beyond. *Synchrotron Radiat News* **22**, 2–4.
- GRUNWALDT, J.-D. & SCHROER, C.G. (2010). Hard and soft X-ray microscopy and tomography in catalysis: bridging the different time and length scales. *Chem Soc Rev* **39**, 4741–4753.
- GRUNWALDT, J.-D., WAGNER, J.B. & DUNIN-BORKOWSKI, R.E. (2013). Imaging catalysts at work. A hierarchical approach from the macro- to the meso- and nano-scale. *ChemCatChem* **5**, 62–80.
- GRUNWALDT, J.D., CARAVATI, M., HANNEMANN, S. & BAIKER, A. (2004). X-ray absorption spectroscopy under reaction conditions: suitability of different reaction cells for combined catalyst characterization and time-resolved studies. *Phys Chem Chem Phys* **6**, 3037–3047.
- GRUNWALDT, J.D. & CLAUSEN, B.S. (2002). Combining XRD and EXAFS with on-line catalytic studies for *in situ* characterization of catalysts. *Top Catal* **18**, 37–43.
- GÜTTEL, R. (2015). Structuring of reactors and catalysts on multiple scales: potential and limitations for Fischer-Tropsch synthesis. *Chem Ing Tech* **87**, 694–701.
- HANSEN, T.W., DELARIVA, A.T., CHALLA, S.R. & DATYE, A.K. (2013). Sintering of catalytic nanoparticles: particle migration or Ostwald ripening? *Acc Chem Res* **46**, 1720–1730.
- HARUTA, M., TSUBOTA, S., KOBAYASHI, T., KAGEYAMA, H., GENET, M.J. & DELMON, B. (1993). Low-temperature oxidation of CO over gold supported on TiO₂, α -Fe₂O₃, and Co₃O₄. *J Catal* **144**, 175–192.
- HITCHCOCK, A.P. & TONEY, M.F. (2014). Spectromicroscopy and coherent diffraction imaging: focus on energy materials applications. *J Synchrotron Radiat* **21**, 1019–1030.
- HOPPE, R., REINHARDT, J., HOFMANN, G., PATOMMEL, J., GRUNWALDT, J.D., DAMSGAARD, C.D., WELLENREUTHER, G., FALKENBERG, G. & SCHROER, C.G. (2013). High-resolution chemical imaging of gold nanoparticles using hard X-ray ptychography. *Appl Phys Lett* **102**, 203104–203104.
- HØYDALSVIK, K., FLOYSTAD, J.B., ZHAO, T., ESMAEILI, M., DIAZ, A., ANDREASEN, J.W., MATHIESEN, R.H., RONNING, M. & BREIBY, D.W. (2014). *In situ* X-ray ptychography imaging of high-temperature CO₂ acceptor particle agglomerates. *Appl Phys Lett* **104**, 241909/1–5.
- IZUKA, Y., KAWAMOTO, A., AKITA, K., DATÉ, M., TSUBOTA, S., OKUMURA, M. & HARUTA, M. (2004). Effect of impurity and pretreatment conditions on the catalytic activity of Au powder for CO oxidation. *Catal Rev - Sci Eng* **97**, 203–208.
- IWASAWA, Y. (1996). *X-ray absorption fine structure for catalysts and surfaces*. Singapore: World Scientific.
- KISS, A.M., HARRIS, W.M., NAKAJO, A., WANG, S., VILA-COMAMALA, J., DERIY, A. & CHIU, W.K.S. (2015). *In situ* heater design for nanoscale synchrotron-based full-field transmission X-ray microscopy. *Microsc Microanal* **21**, 290–297.
- KRÜGER, S.P., NEUBAUER, H., BARTELS, M., KALBFLEISCH, S., GIEWEKEMEYER, K., WILBRANDT, P.J., SPRUNG, M. & SALDITT, T. (2012). Sub-10 nm beam confinement by X-ray waveguides: design, fabrication and characterization of optical properties. *J Synchrotron Radiat* **19**, 227–236.
- LENGELER, B., SCHROER, C.G., RICHWIN, M., TUMMLER, J., DRAKOPOULOS, M., SNIGIREV, A. & SNIGIREVA, I. (1999). A microscope for hard X-rays based on parabolic compound refractive lenses. *Appl Phys Lett* **74**, 3924–3926.
- LUU, M.B., VAN RIESSEN, G.A., ABBEY, B., JONES, M.W.M., PHILLIPS, N.W., ELGASS, K., JUNKER, M.D., VINE, D.J., MCNULTY, I., CADENAZZI, G., MILLET, C., TILLEY, L., NUGENT, K.A. & PEELE, A.G. (2014). Fresnel coherent diffractive imaging tomography of whole cells in capillaries. *New J Phys* **16**, 093012/1–15.
- MAIDEN, A.M. & RODENBURG, J.M. (2009). An improved ptychographical phase retrieval algorithm for diffractive imaging. *Ultramicroscopy* **109**, 1256–1262.
- MATERA, S. & REUTER, K. (2012). When atomic-scale resolution is not enough: spatial effects on *in situ* model catalyst studies. *J Catal* **295**, 261–268.
- MERKLE, A.P., GELB, J., ORCHOWSKI, A. & FUCHS, J. (2014). X-ray microscopy: the cornerstone for correlative characterization methods in materials research and life science. *Microsc Microanal* **20**, 986–987.
- OLTMAN, H.G. (1953). The focusing of short electromagnetic waves by means of the Fresnel half-period zone plate. *Phys Rev* **92**, 1093–1093.
- RODENBURG, J.M. & FAULKNER, H.M.L. (2004). A phase retrieval algorithm for shifting illumination. *Appl Phys Lett* **85**, 4795–4797.
- RODRIGUEZ, J.A., MA, S., LIU, P., HRBEK, J., EVANS, J. & PEREZ, M. (2007). Activity of CeO_x and TiO_x nanoparticles grown on Au(111) in the water-gas shift reaction. *Science* **318**, 1757–1760.
- RUHLANDT, A., LIESE, T., RADISCH, V., KRUEGER, S.P., OSTERHOFF, M., GIEWEKEMEYER, K., KREBS, H.U. & SALDITT, T. (2012). A combined Kirkpatrick-Baez mirror and multilayer lens for sub-10 nm x-ray focusing. *AIP Adv* **2**, 012175.
- SCHROER, C.G., BOYE, P., FELDKAMP, J.M., PATOMMEL, J., SCHROPP, A., SAMBERG, D., STEPHAN, S., BURGHAMMER, M., SCHODER, S., RIEKEL, C., LENGELER, B., FALKENBERG, G., WELLENREUTHER, G., KUHLMANN, M., FRAHM, R., LUTZENKIRCHEN-HECHT, D. & SCHROEDER, W.H. (2010). Hard X-ray microscopy with elemental, chemical, and structural contrast. *Acta Phys Pol, A* **117**, 357–368.
- SCHROPP, A., BOYE, P., GOLDSCHMIDT, A., HOENIG, S., HOPPE, R., PATOMMEL, J., RAKETE, C., SAMBERG, D., STEPHAN, S., SCHROEDER, S., BURGHAMMER, M. & SCHROER, C.G. (2011). Non-destructive and quantitative imaging of a nano-structured microchip by ptychographic hard X-ray scanning microscopy. *J Microsc* **241**, 9–12.
- SCHROPP, A., HOPPE, R., PATOMMEL, J., SAMBERG, D., SEIBOTH, F., STEPHAN, S., WELLENREUTHER, G., FALKENBERG, G. & SCHROER, C.G. (2012). Hard X-ray scanning microscopy with coherent radiation: beyond the resolution of conventional X-ray microscopes. *Appl Phys Lett* **100**, 253112/1–4.
- SHAPIRO, D.A., YU, Y.-S., TYLISZCZAK, T., CABANA, J., CELESTRE, R., CHAO, W., KAZNATCHEEV, K., KILCOYNE, A.L.D., MAIA, F., MARCHESINI, S., MENG, Y.S., WARWICK, T., YANG, L.L. & PADMORE, H.A. (2014). Chemical composition mapping with nanometre resolution by soft X-ray microscopy. *Nat Photonics* **8**, 765–769.

- SHI, J., SCHAEFER, A., WICHMANN, A., MURSHED, M.M., GESING, T.M., WITTSTOCK, A. & BÄUMER, M. (2014). Nanoporous gold-supported ceria for the water-gas shift reaction: UHV inspired design for applied catalysis. *J Phys Chem C* **118**, 29270–29277.
- SIMONSEN, S.B., AGERSTED, K., HANSEN, K.V., JACOBSEN, T., WAGNER, J.B., HANSEN, T.W. & KUHN, L.T. (2015). Environmental TEM study of the dynamic nanoscaled morphology of NiO/YSZ during reduction. *Appl Catal, A* **489**, 147–154.
- SIMONSEN, S.B., DAHL, S., JOHNSON, E. & HELVEG, S. (2008). Ceria-catalyzed soot oxidation studied by environmental transmission electron microscopy. *J Catal* **255**, 1–5.
- SNIGIREV, A., KOHN, V., SNIGIREVA, I. & LENGELER, B. (1996). A compound refractive lens for focusing high-energy X-rays. *Nature* **384**, 49–51.
- SUEHIRO, S., MIYAJI, H. & HAYASHI, H. (1991). Refractive lens for X-ray focus. *Nature* **352**, 385–386.
- SUZUKI, Y. & UCHIDA, F. (1991). X-ray focusing with elliptic Kirkpatrick-Baez mirror system. *Jpn J Appl Phys, Part 1* **30**, 1127–1130.
- THIBAUT, P., DIEROLF, M., MENZEL, A., BUNK, O., DAVID, C. & PFEIFFER, F. (2008). High-resolution scanning X-ray diffraction microscopy. *Science* **321**, 379–382.
- THOMAS, J.M., DUCATI, C., LEARY, R. & MIDGLEY, P.A. (2013). Some turning points in the chemical electron microscopic study of heterogeneous catalysts. *ChemCatChem* **5**, 2560–2579.
- THOMAS, J.M. & HERNANDEZ-GARRIDO, J.-C. (2009). Probing solid catalysts under operating conditions: electrons or X-rays? *Angew Chem, Int Ed* **48**, 3904–3907.
- TOPSOE, H. (2003). Developments in operando studies and *in situ* characterization of heterogeneous catalysts. *J Catal* **216**, 155–164.
- ULVESTAD, A., SINGER, A., CHO, H.-M., CLARK, J.N., HARDER, R., MASER, J., MENG, Y.S. & SHPYRKO, O.G. (2014). Single particle nanomechanics in operando batteries via lensless strain mapping. *Nano Lett* **14**, 5123–5127.
- VANTOMME, A., LEONARD, A., YUAN, Z.-Y. & SU, B.-L. (2007). Self-formation of hierarchical micro-meso-macroporous structures: generation of the new concept “Hierarchical Catalysis”. *Colloids Surf, A* **300**, 70–78.
- VILA-COMAMALA, J., DIAZ, A., GUIZAR-SICAÍROS, M., MANTION, A., KEWISH, C.M., MENZEL, A., BUNK, O. & DAVID, C. (2011). Characterization of high-resolution diffractive X-ray optics by ptychographic coherent diffractive imaging. *Opt Express* **19**, 21333–21344.
- WAGNER, J.B., CAVALCA, F., DAMSGAARD, C.D., DUCHSTEIN, L.D.L. & HANSEN, T.W. (2012). Exploring the environmental transmission electron microscope. *Micron* **43**, 1169–1175.
- WANG, J., XIA, R., ZHU, J., DING, Y., ZHANG, X. & CHEN, Y. (2012). Effect of thermal coarsening on the thermal conductivity of nanoporous gold. *J Mater Sci* **47**, 5013–5018.
- WECKHUYSEN, B.M. (2002). Snapshots of a working catalyst: possibilities and limitations of *in situ* spectroscopy in the field of heterogeneous catalysis. *Chem Commun* **2**, 97–110.
- WECKHUYSEN, B.M. (2004). *In-situ spectroscopy of catalysts*. Los Angeles: Amer Scientific Pub.
- WECKHUYSEN, B.M. (2009). Chemical imaging of spatial heterogeneities in catalytic solids at different length and time scales. *Angew Chem, Int Ed* **48**, 4910–4943.
- WICHMANN, A., WITTSTOCK, A., FRANK, K., BIENER, M.M., NEUMANN, B., MADLER, L., BIENER, J., ROSENAUER, A. & BÄUMER, M. (2013a). Maximizing activity and stability by turning gold catalysis upside down: oxide particles on nanoporous gold. *ChemCatChem* **5**, 2037–2043.
- WICHMANN, A., WITTSTOCK, A., FRANK, K., BIENER, M.M., NEUMANN, B., MAEDLER, L., BIENER, J., ROSENAUER, A. & BÄUMER, M. (2013b). Maximizing activity and stability by turning gold catalysis upside down: oxide particles on nanoporous gold. *ChemCatChem* **5**, 2037–2043.
- WITTSTOCK, A. & BÄUMER, M. (2014). Catalysis by unsupported skeletal gold catalysts. *Acc Chem Res* **47**, 731–739.
- WITTSTOCK, A., NEUMANN, B., SCHAEFER, A., DUMBUYA, K., KUEBEL, C., BIENER, M.M., ZIELASEK, V., STEINRUECK, H.-P., GOTTFRIED, J.M., BIENER, J., HAMZA, A. & BÄUMER, M. (2009). Nanoporous Au: an unsupported pure gold catalyst? *J Phys Chem C* **113**, 5593–5600.
- WITTSTOCK, A., ZIELASEK, V., BIENER, J., FRIEND, C.M. & BÄUMER, M. (2010). Nanoporous gold catalysts for selective gas-phase oxidative coupling of methanol at low temperature. *Science* **327**, 319–322.
- ZIELASEK, V., JUERGENSEN, B., SCHULZ, C., BIENER, J., BIENER, M.M., HAMZA, A.V. & BÄUMER, M. (2006). Gold catalysts: nanoporous gold foams. *Angew Chem, Int Ed* **45**, 8241–8244.