In situ X-ray ptychography imaging of high-temperature CO₂ acceptor particle agglomerates

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Imaging nanoparticles under relevant reaction conditions of high temperature and gas pressure is difficult because conventional imaging techniques, like transmission electron microscopy, cannot be used. Here we demonstrate that the coherent diffractive imaging technique of X-ray ptychography can be used for *in situ* phase contrast imaging in structure studies at atmospheric pressure and elevated temperatures. Lithium zirconate, a candidate CO₂ capture material, was studied at a pressure of one atmosphere in air and in CO₂, at temperatures exceeding 600 °C. Images with a spatial resolution better than 200 nm were retrieved, and possibilities for improving the experiment are described. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4884598>]

High-resolution imaging of functional nanoparticles *in situ* is important for a better understanding of their structure and function, crucial for improving their design and performance.^{1–7} Nanoparticles are extensively used as catalysts, and a long standing desire in the research community is to be able to image the nanoparticles at industrially relevant processing conditions involving harsh environments with high gas pressures and temperatures. Due to the high heterogeneity and polydispersity associated with many catalytic systems, results from small-angle scattering and X-ray powder diffraction line-shape analysis are difficult to interpret, while operating conditions of high temperature and pressure preclude the use of electron microscopies. Being able to directly monitor morphology changes of individual particles, and also the spatial distribution and dynamics of particle ensembles, would be of considerable interest.

CO₂ capture and storage have drawn much attention in recent years.^{8–14} For the capture and transport of CO₂, a material that reacts reversibly with CO₂ is needed. Originally suggested by Nakagawa and Ohashi,⁸ a candidate material is lithium zirconate, Li₂ZrO₃, which is considered one of the most promising materials for CO₂ separation from flue gas at high temperature.¹⁵ Lithium zirconate reacts reversibly with CO₂ to form lithium carbonate and zirconia according to the reaction⁸

where the forward reaction takes place at high partial pressure of CO₂ within the range 400 < *T* < 700 [°C],¹⁵ whilst the reverse reaction proceeds mainly at temperatures above 600 °C (Ref. 8) when the CO₂ partial pressure is low. High-resolution imaging of CO₂ storage materials would be useful for providing insight into the CO₂ sorption and desorption

processes, important for improving the design, and thus cost-effectiveness, of CO₂ removal technologies. However, imaging these materials under relevant processing conditions is challenging since, for the reactions to take place, a certain gas pressure and temperature are required.

A standard technique for nano- and atomic-scale imaging is transmission electron microscopy (TEM), and for *ex situ* studies in vacuum, TEM works excellently.¹⁶ By using environmental TEM (ETEM), where differential pumping makes it possible to have a gas pressure of a few millibars in the sample stage, several *in situ* studies on functional nanoparticles have been performed.^{17–19} The limitation of ETEM is the interaction between the gas molecules and the electrons in the probing beam.²⁰ In scanning transmission X-ray microscopy (STXM), a focused X-ray beam is scanned laterally across the sample and transmission scattering patterns are measured at each raster point. This method allows maps to be synthesized showing the specimen transmission, or phase contrast obtained by integration of differential phase contrast in both detector dimensions. Also dark-field contrast can be obtained by integrating intensity outside the focused beam. The resolution is limited by the beam spot size on the specimen, and consequently dependent on the focusing optics.²¹ Using soft X-rays (200–2000 eV), STXM yields a spatial resolution down to 15 nm,¹ and the main experimental challenge to overcome when applying the technique *in situ* is the strong attenuation of soft X-rays by matter. On the contrary, X-ray radiation of energy above a few keV penetrates gas and bulky sample environments, thus opening for high-resolution *in situ* imaging of functional materials. A disadvantage is that the hard X-ray beam is not easily focused and the resolution deteriorates. Another X-ray microscopy variant is full-field TXM, which, for example, has yielded high-resolution (≥30 nm) images of 20 μm iron oxide particles.⁵ For small particles (~100 nm) consisting of light elements such that the sample object transmission is

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close to unity, the information related to phase shift of the incoming X-ray wave field becomes increasingly important.

Here, we demonstrate the use of the upcoming coherent X-ray diffraction imaging technique of ptychography for imaging catalytically active particles *in situ* under highly demanding conditions. X-ray ptychography has recently emerged as an elegant technique for imaging objects down to length scales of a few tens of nm.^{22–28} Resonant spectroscopic ptychography has, for example, been used to image the local chemical state of gold nanoparticles with high spatial resolution (20–30 nm), but *ex situ* under ambient conditions.²⁹ The technique produces real-space images from far-field diffraction patterns by numerically retrieving the phase of the X-ray wave field. This retrieval is facilitated by measuring and combining partially overlapping exposures on the sample, and the images are obtained by retrieving the phases of the diffraction patterns by an iterative procedure.^{22,23} Advantages of ptychography include that the reconstruction algorithm is robust, that the field of view in principle can be made arbitrarily large, and that both absorption and phase images are simultaneously obtained.

Lithium acetate and zirconyl nitrate (molar ratio 2:1) were dissolved in water, followed by evaporation at 100 °C overnight to obtain a mixed solid. The resulting solid was calcined at 600 °C (5 °C/min) for 5 h. The obtained lithium zirconate powder was leached in water for 12 h and then centrifuged in ethanol. A small amount was transferred into ethanol followed by ultrasonic treatment for 2 min. A drop of this solution was deposited on a Si₃N₄ membrane and left to dry at room temperature for ~30 min.

The experiment was performed at the cSAXS beamline at the Swiss Light Source (Paul Scherrer Institut, Villigen, Switzerland),³⁰ and the experimental setup is illustrated schematically in Fig. 1. A 21 cm long plexiglass sample enclosure on the optical table served as a chamber for controlling the atmosphere. A custom-made furnace enabled heating the samples to $T \geq 600$ °C. To avoid disturbing the wavefront when passing through the sample stage, the furnace and the plexiglass box had small entrance and exit openings (~mm) for the beam. A double Si(111) monochromator defined the X-ray wavelength to $\lambda = 2.00$ Å, and a Fresnel zone plate (FZP) with 200 μ m diameter and focal length 100 mm was mounted upstream of the sample membrane. An order-sorting aperture (OSA) of diameter 30 μ m was mounted 10 mm in front of the sample membrane. The distance between the sample membrane and the Pilatus 2M detector³¹ was 7.265 m, and for most of this distance the beam passed through a helium-filled flight tube in order to reduce absorption and air scattering.

STXM was used for obtaining lower resolution overview images where interesting areas on the sample membrane could be identified. STXM was performed by placing the sample in the focus plane of the FZP and scanning the sample in a continuous fashion while acquiring frames with the Pilatus 2M detector as described in Ref. 32. For these measurements, we used a step-size 0.5 μ m and a counting time of 0.05 s at each scanning position.

The ptychography measurements were performed by positioning the sample membrane approximately 1 mm after the focal point, where the beam had a radius of 1 μ m. The sample was scanned laterally across the beam using a piezoelectric

FIG. 1. The experimental setup shown schematically (not to scale). (a) The coherent X-ray beam comes in from the synchrotron and beamline optics at the left is focused by a Fresnel zone plate, and passes the order-sorting aperture. The distances between the components are indicated. The plexiglass sample enclosure, enabling control of the atmosphere surrounding the sample, had small holes allowing the beam to enter and exit. The purple arrows indicate the lateral scan directions. The particles were dispersed on an X-ray transparent membrane placed in a custom-designed furnace. (b) Magnified view emphasizing the sample enclosure with the small furnace.

stage in a pattern of concentric circles with a radial step size of 0.5 μ m, as described elsewhere,²⁴ and counting time 0.1 s per point. A diffraction pattern was recorded with the 2D-detector at each of the 176 measurement positions. Each scan took about 1 min to measure and covered a field of view of $\approx 10 \times 10 \mu\text{m}^2$. From the collected data both the scattering object and the illuminating wave field were reconstructed using algorithms and methods described elsewhere.^{23,24} For the reconstructions, 192×192 detector pixels of $0.172 \times 0.172 \text{ mm}^2$ were used, giving a pixel size of 44 nm in the reconstructed image.

Scanning electron microscopy (SEM) measurements were performed *ex situ* to samples prepared following the described procedure, including calcination at 600 °C for 5 h. Fig. 2 shows a micrograph for an area of relatively large

FIG. 2. Scanning electron micrograph of Li₂ZrO₃-clusters after calcination at 600 °C for 5 h, measured *ex situ*.

clusters. Fresh samples were prepared at the synchrotron following the same recipe, and Fig. 3 shows results from STXM and ptychography measurements. The rather coarse STXM overview images had insufficient sensitivity to detect the individual particles, resolving only a few distinct particle agglomerates within the measured field-of-view of $30 \times 30 \mu\text{m}^2$. Using ptychography we observe the weaker scattering objects; reconstructed amplitude and phase images obtained at 620°C for the sample in air and in CO_2 are shown in Figs. 3(c)–3(f), in both cases showing particles or small agglomerates. With the resolution we achieved in this ptychography experiment of $\sim 200\text{ nm}$, the particles appear similar when measured in air and in CO_2 . The ripples surrounding the particles, including pixels with phase shift >0 and transmission

FIG. 3. (a) and (b) Overview STXM images, measured in air at 620°C , (a) integrated phase and (b) dark-field. (c) and (d) The results from the ptychography scan measured in air at 620°C shortly after the STXM measurement. (c) Reconstructed phase and (d) amplitude images of the $5 \times 5 \mu\text{m}^2$ area marked by the red square in (a) and (b). Due to thermal drifts, the imaged area may have moved slightly, and the distinct particles observed by STXM cannot be seen in this ptychography scan. The red line indicates the position of the line-plot shown just below. (e) and (f) The results from a ptychography scan measured after the sample cell was filled with CO_2 . (e) Reconstructed phase and (f) amplitude images. The STXM integrated phase (a) and the amplitude images (d) and (f) have been corrected such that the average phase shift and transmission for the empty areas are 0 and 1, respectively. The average phase shift of the empty areas of the phase images (c) and (e) was already close to 0, and no offset corrections were necessary in these images.

>1 , are artifacts arising from insufficient counting statistics and/or mechanical instabilities. Post-exposure re-focusing, as sometimes done in ptychography,³³ did not improve the image quality notably, and separate simulations (not shown) supported that propagation effects were not the cause of the artifacts. In the reconstructed images, the particles appear to have a diameter in the range of 200–350 nm, suggesting that they are in fact smaller than 200 nm after deconvoluting the experimental resolution. The phase shift was found to be $|\Delta\phi| \lesssim 0.06$ radians for these thin and weakly scattering particle agglomerates and is consistent with the phase shift expected from a 90 nm layer of Li_2ZrO_3 .

The experiment shown here demonstrates that small aggregates of CO_2 storing particles can be directly imaged using ptychography under challenging experimental conditions involving high gas pressure and temperature. We have additionally seen evidence for particles irregularly moving around on the supporting membrane (not shown), but owing to the problems with disentangling these movements from the thermal drift and related instabilities of the relative focus point of the probe, we have not been able to quantify this observation.

For future experiments, attention should be given to improving the mechanical stability,³⁴ in particular, the thermal drift associated with the furnace, and also gas convection flows caused by the sample heating. By using an optical feedback mechanism the relative position of the sample and the beamline optics can be actively stabilized, which compensates for low-frequency vibrations of the system as well as thermal drifts.²⁶ For this to work, the gas environment should be limited to a small enclosure around the sample, in such a way that the sample enclosure is scanned together with the sample using the piezo stages. We note that the resolution is somewhat inferior in the case measured with CO_2 , which we ascribe to reduced counting statistics caused by increased absorption of the X-ray beam in the long sample enclosure, where the transmission in CO_2 is $\sim 75\%$ compared to air, and a smaller gas enclosure would improve the transmission. Adding fiducial markers on the sample-carrying membrane would be helpful for both maintaining the same field of view and choosing the optimal defocusing of the X-ray probe. We do not expect further complications when using other sample environment gases at pressure of around one atmosphere. However, for significantly increased pressures windows will be needed, which may affect reconstructions negatively due to wavefront distortion effects. Considering that solid sorbent particle agglomerates have been clearly observed under atmospheric pressure of air and CO_2 at elevated temperatures in this proof-of-principle experiment, and that the improvements listed would be straightforward to implement, we consider it fair to claim that the lensless X-ray imaging technique of ptychography holds great promise for future studies of particle morphology and dynamics under realistic processing conditions.

In conclusion, we have demonstrated that X-ray ptychography allows direct imaging of small particles at operating conditions relevant to catalysis and other industrial processes involving high temperature and comparably high gas pressures. We have studied the particular system of Li_2ZrO_3 particles relevant for CO_2 capture, and we have

succeeded in imaging these weakly scattering small particle agglomerates at $T = 620^\circ\text{C}$ first in air and then in CO_2 .

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