Reactor for nano-focused x-ray diffraction and imaging under catalytic in situ conditions

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Reactor for nano-focused x-ray diffraction and imaging under catalytic *in situ* conditions

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A reactor cell for *in situ* studies of individual catalyst nanoparticles or surfaces by nano-focused (coherent) x-ray diffraction has been developed. Catalytic reactions can be studied in flow mode in a pressure range of 10^{-2} – 10^3 mbar and temperatures up to 900 °C. This instrument bridges the pressure and materials gap at the same time within one experimental setup. It allows us to probe *in situ* the structure (e.g., shape, size, strain, faceting, composition, and defects) of individual nanoparticles using a nano-focused x-ray beam. Here, the setup was used to observe strain and facet evolution of individual model Pt catalysts during *in situ* experiments. It can be used for heating other (non-catalytically active) nanoparticles (e.g., nanowires) in inert or reactive gas atmospheres or vacuum as well. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.5000015>]

I. INTRODUCTION

Catalysis has become the heart of our modern chemical industry. Catalysts are the key enablers in 90% of chemical manufacturing processes. Catalysis plays an increasingly important role in fields ranging from energy, environment, and agriculture. It is of particular interest for the petrochemical industry,¹ fuel cell technology, and automobile exhaust gas purification.² To avoid using trial-and-error approaches to design catalysts, a complete understanding of all the phenomena taking place in a real catalyst is necessary on many different lengths and time scales. It is also needed to bridge the “pressure gap,” i.e., to study catalysts under practical operating conditions, as they may behave differently at high pressures and high temperatures compared to ultra high vacuum (UHV) and low-temperature conditions used in the traditional surface science approach.³ Furthermore, studying an extended single crystal under model conditions is still far from studying a real catalyst under operating conditions. On extended surfaces, one excludes the effects of the particle size and shape and the interaction of the particles with the support. This gap between single-crystal model catalysts and real catalysts is called the “materials gap.” Recent progress in the fabrication techniques has enabled the synthesis of metal nanoparticles with precisely controlled size, shape, and composition. The pioneering work of Sun *et al.* has resulted in the controlled synthesis of regularly shaped Pt particles⁴ as well as alloys of platinum group metals (PGMs) with high-index facets (HIF).⁵ In contrast to close-packed low-index faceted single crystals, nanoparticles with atomically open (high-index) surfaces are often more active—and even more active than conventional nanoparticles enclosed by low-index facets.⁶ Atomic steps, edges, and kinks usually serve as active sites for breaking

chemical bonds. Studying single particles will allow probing the reactivity of these high-index facets.

Recently, a growing number of surface-science techniques are being adapted to operate under “realistic” reaction conditions.⁷ Examples are the development of reactors for high-pressure transmission electron microscopy,⁸ for high-pressure surface x-ray diffraction,^{9,10} or for *in situ* x-ray ptychography.¹¹ The weak interaction of x-rays with matter, which results in a negligible attenuation during the transmission through gases at atmospheric or higher pressures, makes x-ray based techniques suitable for studying catalysts at realistic conditions.

Recent developments in focusing x-rays to the nanometer-scale and in investigating coherent x-ray diffraction from nanoscale objects promise new insights into structure-property or structure-performance relationships.^{12,13} Understanding a reaction at a single catalyst particle level is a prerequisite for understanding the behavior of ensembles of particles because of unavoidable dispersion of non-homogeneous samples. This individual nanoparticle model catalysis approach will permit us to understand why nanoparticles are active or passive during heterogeneous catalysis. It should allow setting-up for individual nanoparticles structure-activity, structure-selectivity, and structure-stability relationships in heterogeneous catalytic systems. While with nano-focused coherent x-ray beams it is possible to measure one particle at a time, reactivity data are collected from the whole ensemble. Nano-focused x-ray beams can provide structural information about individual nanocrystals and guide the design of new nanomaterials. A fundamental understanding of the interplay between shape, size, strain, faceting, composition, and defects at the nanoscale is needed for a knowledge-based catalyst design. Up to now, only a few sample environments compatible with nano-focused

x-ray beams (i.e., small working distance of focusing optics, low loading weight of the nano-positioners (few hundreds of grams), and mechanical stability to keep the particle aligned with the nano x-ray beam) have been reported: compact ultra-high vacuum chambers,¹⁴ a gas flow cell,¹⁵ and a liquid environmental x-ray cell.¹⁶ The next step for x-ray nanobeam technologies will be to perform a full range of experiments while the sample is maintained under catalytically relevant conditions of high temperatures and controlled gas environments. This is a highly challenging task as it requires a high control over the mechanical stability and reproducibility of the setup taking into account limitations in terms of accessible space for sample movement and sample environment. Sample environments have to be compatible with nanopositioning stages, low loading weight of the piezostages, and the small working distance of focusing optics (from a few mm to a few cm). High temperature results in thermal drifts in the sample position, and hence, alignment time and alignment stability are affected. Electrical or gas connections usually mean position-dependent forces and torques onto the sample stage or goniometer and consequently reduce the mechanical stability of the setup.

In this paper, we introduce a lightweight reactor setup compatible with a nano-focused x-ray beam and gaseous environment including temperature control in the range from room temperature to 900 °C. This instrument allows for both bridging the pressure and materials gaps while keeping the option of studying extended single crystals. It enables us to study the structure (e.g., shape, size, strain, faceting, composition, and defects) of individual nanoparticles under defined reaction conditions. We have studied one example of reactions, CO oxidation on Pt nanoparticles, as a showcase to demonstrate the capability of the reactor. First, we describe the design of the nano-beam reactor before demonstrating the performance of the instrument.

II. X-RAY NANO-BEAM *IN SITU* REACTOR DESIGN

A reactor compatible with nano-focused x-ray diffraction and gaseous environment has been developed at the upgraded ID01 beamline of the European Synchrotron Radiation Facility (ESRF) (see Fig. 1). The reactor fulfills the constraints of weight (mass smaller than 300 g) and size of the three-axis piezoelectric positioning stage (Physik Instrumente GmbH & Co. KG) as well as the constraints of stability and movement precision issues. The piezoelectric stage translates the reactor with an accuracy of 20 nm over lateral distances of 200 μm and a vertical range of 200 μm . The fixture connecting the reactor to the piezoelectric stage is rigid in order to allow this precision to be maintained; as the reactor and stage are rotated by a (3 + 2 circles) goniometer (sample and detector, respectively), the sample and detector support are mechanically decoupled to prevent sample vibrations due to the detector arm movements. The base of the reactor consists of an octagonal aluminum plate (no stainless steel to avoid reactions with gases in the chamber) with eight mounting openings to be fixed to the piezoelectric stage. The constraint of limited space between the sample and the focusing optics (which are separated by ~2 cm at the ID01 beamline, see Sec. III) has been taken into

FIG. 1. Schematic overview of the reactor compatible with nano-focused x-ray beam and gaseous environment.

account. The hexagonal bottom part of the reactor is made of aluminum. Its sides are used for gas inlet, gas outlet, and electrical connectors for heating and temperature sensing. The connections to the reactor consist of Teflon® gas lines, which are in principle flexible enough to prevent vibrations at atmospheric pressure. A gas rig with mass flow controllers can be connected.

The *in situ* reactor consists of a compact cell (pressure of 10^{-3} mbar using a primary and a turbomolecular vacuum pumps), in which the sample is mounted on a small resistive button heater (HeatWave Labs, Inc.) compatible with air and gases such as H_2 , CO, or O_2 . The heater has a diameter of 8 mm for which the electrical current is provided by a feedthrough in the base of the instrument. The heater can host samples as large as $10 \times 10 \text{ mm}^2$. The sample fixation is chosen on a per-experiment basis: using either ceramic (boron nitride) glue or custom-designed sample holders.

The temperature at the heater is measured with a thermocouple type S. Such a thermocouple does not contain nickel, which reacts and forms volatile carbonyls when CO is used. The temperature is controlled either manually or automatically thanks to a well-tuned PID (proportional-integral-derivative) controller (Eurotherm 2408), which is interfaced with the diffractometer control software SPEC. At 800 °C, the measured temperature fluctuation is 0.023° (standard deviation). The sample can be heated up to 900 °C using our own-design Be dome. Other domes made of different materials (PolyEtherEtherKetone: PEEK®, polycarbonate, and polystyrene) can be used. When used, the working temperature should not exceed the melting point of these materials (PolyEtherEtherKetone: 334 °C, polycarbonate: 230 °C, and polystyrene: 240 °C). The polycarbonate dome has the advantage to be transparent and allows observing the sample with a microscope. The domes have a thickness of 300 μm and a diameter of 25 mm. These domes provide the maximum possible range of scattering geometries, guaranteeing access to the full 2π hemisphere of incoming and diffracted photons. The choice of the dome depends on different parameters: x-ray absorption, transparency, and working temperature. Transmission tests have been performed at the ID01-ESRF beamline demonstrating that the domes made of polystyrene, polycarbonate, PEEK, and Be transmit

70%, 53%, 53%, and 63% of the incoming x-ray beam at 8 keV, respectively. Samples can be exchanged by unscrewing the dome.

The partial pressures of the reactant gases are fully controllable by a set of mass flow controllers in a range of flows between 1 and 100 ml/min standard temperature and pressure (STP). Mass flows are reported for standard temperature and pressure (STP) conditions. A pressure controller can be used to regulate the total pressure in the reactor. The reactor can thus work in flow mode to allow mapping out the precise behavior of individual nanocatalysts as a function of gas composition and temperature or as a function of time under constant gas and temperature conditions.

III. *IN SITU* NANO-DIFFRACTION IMAGING OF CATALYSTS

The setup has been successfully tested in a number of experiments already. The results of these experiments will be published elsewhere. Here, we provide a showcase

FIG. 2. Photograph (a) and technical drawing (b) of the reactor installed onto the piezo-positioner stage. Note that the order sorting aperture (OSA) from the focussing optics is close to the dome. The hexapod allows x , y , and z -translations of the sample within a range of 5 mm and an accuracy of 100 nm.

FIG. 3. Scanning electron microscopic images of an assembly of THH Pt particles.

example: nano-beam *in situ* Bragg coherent diffraction imaging on individual high-index faceted Pt particles.

The operation of the sample environment was tested during *in situ* x-ray studies of *single* nano-catalysts at ID01. The x-rays with photon energy of 8 keV were focused to a spot size of 170 (vertically) $\times$ 465 (horizontally) nm² by a Fresnel zone plate (FZP) in order to illuminate a *single* particle. The zone plate had a diameter of 300 μ m and an outermost zone width of 70 nm, giving a focal length of 13.6 cm at 8 keV. Unfocused radiation transmitted by the FZP is eliminated using

FIG. 4. Three dimensional x-ray reciprocal space maps around the 002 Pt reflection for an individual 330-nm diameter THH Pt nanoparticle at 200 °C and upon exposure of different gas (recorded in 6 min): (a) 20 ml/min He and 5 ml/min CO and (b) 25 ml/min He.

a combination of a 50 μm central stop placed just before the FZP and an order sorting aperture (OSA) with a 50 μm diameter positioned at 2.3 cm in front of the sample. A coherent portion of the monochromatic x-ray beam was selected with high precision slits by matching their horizontal and vertical gaps with the transverse coherence lengths of the beamline [60 μm (horizontally) and 250 μm (vertically) before the FZP]. The scattered x-rays were detected using a two-dimensional (2D) Maxipix pixel detector¹⁷ (516 $\times$ 516 pixels with 55 μm pixel size). Figure 2 displays a photograph of the reactor installed onto the piezoelectric stage.

Here, we focus on the role of Pt nanoparticles in the catalytic oxidation of carbon monoxide. This reaction is considered as a prototype reaction for understanding fundamental concepts in heterogeneous catalysis.¹⁸ It is relevant for exhaust gas purification.¹⁹

The experiment was realized under flow conditions: a constant flow of He (25 ml/min—standard conditions for temperature and pressure) was maintained during the whole experiment unless otherwise specified. The sample consists of high-index tetrahedral (THH) Pt nanocrystals randomly oriented as shown in Fig. 3. The Pt THH particles have been synthesized on glassy carbon (GC) electrodes by a square-wave-potential method with a saturated calomel reference electrode (SCE) and a Pt foil counter electrode in 2 mM H_2PtCl_6 and 0.1M H_2SO_4 electrolyte following the procedure

described in Ref. 4. The GC electrode is first subjected to a potential of +1.20 V for 2 s to clean the surface and then -0.35 V for 60 ms to create Pt nuclei. The Pt nuclei grew to THH particles by applying a square-wave potential between +0.04 V and +1.09 V at 100 Hz for 10 min. The THH shape can be described as a cube whose faces are capped by square-based pyramids, leading to 24 high-index planes of $hk0$ type ($h \neq k \neq 0$).²⁰ The particles have been electrochemically synthesized at the electrochemical laboratory of ESRF. The diameter of the Pt NCs varies from 50 to 600 nm.

Here, we report on structural modifications induced on Pt nanoparticles by CO at elevated temperature (200 $^\circ\text{C}$). The three-dimensional (3D) 002 Pt Bragg peak (theoretical Bragg angle equals to 23.269 $^\circ$) of a *single* Pt nanoparticle (diameter of 330 nm) was tracked using a nano-focused beam at a temperature of about 200 $^\circ\text{C}$ and upon exposure to different gas. Figure 4 displays 3D reciprocal space maps of an individual Pt particle under (a) 5 ml/min CO + 20 ml/min He and (b) 25 ml/min He as a function of reciprocal space coordinates (Q_x , Q_y , and Q_z) of the scattering vector $\vec{Q}$. Each measurement lasted 10 min. To look into more details at the possible gas-induced changes, two-dimensional reciprocal space maps are displayed in Fig. 5. The black contour lines and the colored patterns correspond to the diffraction patterns of the particle under exposure to 5 ml/min CO or pure He, respectively. The red boxes indicate changes between the diffraction patterns with (black contour lines) and without (colored patterns) CO, such as the disappearance of some streaks, implying a change of faceting of the particle.

FIG. 5. (a) Q_x - Q_y (summed up along Q_z) and (b) Q_y - Q_z (summed up along Q_x) two dimensional x-ray reciprocal space maps around the 002 Pt reflection for an individual 330-nm diameter THH Pt nanoparticle at 200 $^\circ\text{C}$. The black contour lines and the colored patterns correspond to the diffraction patterns of the particle under exposure to 5 ml/min CO or pure He, respectively. The red boxes indicate changes between the diffraction patterns with (black contour lines) and without CO (colored patterns).

FIG. 6. X-ray reciprocal space maps around the 002 Pt reflection for an individual 200-nm diameter THH Pt-Ni nanoparticle at 200 $^\circ\text{C}$ and upon exposure of different gas: (a) 20 ml/min He and 5 ml/min H_2 and (b) 20 ml/min He and 5 ml/min CO.

The diffraction pattern of an *individual* sub-surface Ni alloyed Pt particle was also tracked. Figure 6 displays Q_y - Q_z reciprocal space maps of the individual particle. At 200 °C and under $H_2 + He$ gas atmosphere (20 ml/min He and 5 ml/min H_2), each streak around the 002 Pt Bragg reflection corresponds to a facet of the nanoparticle. In Fig. 6(a), the interference fringes are due to the finite size of the nanocrystal, interference between streaks from two parallel facets, revealing a particle size of 190 nm. Then, we observe the scattered signals to change upon CO [see Fig. 6(b)], revealing structural changes of the single Pt-Ni nanoparticle under catalytic conditions. The diffraction pattern displayed in Fig. 6(b) does not reveal anymore facet streaks and well-defined thickness fringes. This is the signature of an inhomogeneous strain field inside the particle with possible defects leading to destructive interference effects.²¹ This implies that strain evolution inside the particle occurred during exposure to CO gas at elevated temperature.

IV. CONCLUSION

The described lightweight reactor allows nano-focused x-ray diffraction studies in various gas environments and under a range of temperatures of interest for the study of *in situ* processes in materials with relevance for heterogeneous catalysis. The possibility of using a polycarbonate dome allows for optical access by a microscope, while the Be dome allows it to go higher in temperature. All the domes can be used and easily exchanged during the experiment. The specific showcases described here demonstrate that nano-focused coherent x-ray diffraction imaging can be applied using a small reactor designed for high-stability and nano-positioning precision. The setup is easily transportable and can be used on other beamlines. It has already been used at the ID01 beamline of ESRF and the P10 beamline of PETRA III and is available to users. The reactor cell can easily be extended for *operando* catalytic experiments by adding a mass spectrometer at the outlet of the cell. Although current mass spectrometers may not be sensitive enough to follow the product of a single particle of catalysts, there may be other ways to detect the product/activity of a single particle such as electrochemistry and super-resolution fluorescence/surface plasmon resonance microscopes.²² It opens new ways to study nanoscale materials using a nano-focused x-ray beam combined with *in situ* heating in a controlled gas environment. The next several years will see an increasingly fast development of worldwide x-ray light sources with orders-of-magnitude improvements in brightness provided by multi-bend achromat electron storage rings. The flux increase will allow better time resolution

and sample stability (shorter measurements). The possibility of sample damage should also be taken into account. These facilities will vastly extend the application of x-ray nano-beams. The design of environments with even lower mass and greater stability will have an important role to face challenges at the nanoscale.

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