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Report

on the PhD thesis of

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Title of the thesis

Propriétés catalytiques à l'échelle nanométrique sondées par diffraction des rayons X de surface et imagerie de diffraction cohérente

This thesis has been submitted by David SIMONNE for the degree of Docteur de l'Université Paris-Saclay in Physics. It reports on the study of the catalytic properties at the nanoscale employing surface X-ray diffraction, Bragg coherent X-ray diffraction imaging, and X-ray photoelectron spectroscopy at 3rd generation synchrotron sources combined with mass spectrometry. The submitted manuscript of 204 pages is well written in English and divided into 5 chapters plus two appendices, which are discussed in more detail below, addressing the main achievements and any deficiencies.

The first chapter introduces the interest of catalytic processes, in particular, with respect to air pollution by NO_x and greenhouse effects of NO. Both gases are by-products of the oxidation of ammonia NH_3 to produce nitric acid which is an important actor in multiple industrial processes. The oxidation of ammonia is well described including a very brief historical background of the discoveries made in the beginning of the 20th century. It is followed by a short state-of-the-art of heterogeneous catalysis with a focus on Pt catalysts highlighting the importance of atomic steps on the catalyst's surface on the catalytic activity as well as the dependence of the catalytic activity on the type of facets. As underlined by D. Simonne, most of the experiments so far were performed under high vacuum conditions which is far from actual industrial processes taking place at several bars and temperatures of up to 900 °C. The few studies under industrial relevant conditions existing in literature were mostly performed *ex-situ*. Therefore, a pressure and a material gap exist limiting the understanding of the catalyst operation which is the main motivation of this thesis. A short state-of-the-art on *operando* surface X-ray diffraction (SXRD) during catalysis and a very brief summary of *in situ* Bragg coherent X-ray diffraction imaging (BCDI) are given towards the end of the first chapter which are actually the techniques of choice in this thesis to investigate catalytic processes. It would have been desirable to have a dedicated and more extensive (sub-)chapter on the state-of-the-art of *in situ* and *operando* BCDI and SXRD, in particular, during catalysis.

The second chapter is dedicated to the theory of catalysis and the experimental methods employed throughout this thesis. Here, heterogeneous catalysis is described in detail presenting three different catalytic mechanisms and highlighting the active sites during the processes. It is followed by a clear discussion of the basic principles of the interaction of X-rays with matter. Next, the theory of X-ray diffraction is well explained deducing Bragg's law as well as the structure factor and lattice factor. The basic concepts of coherence are then introduced which is at the basis of BCDI, one of the techniques employed in this thesis to image individual Pt nanoparticles and the strain therein in 3D.
After the introduction of the theoretical background, D. Simonne details the experimental techniques, namely surface X-ray diffraction (SXRD), Bragg coherent X-ray diffraction imaging (BCDI), and X-ray photoelectron spectroscopy (XPS), which are compatible with near-ambient pressure conditions. Each technique is firstly presented followed by the description of the respective experimental procedure. In the case of BCDI, D. Simonne further explains the retrieval of the phase that is lost during an X-ray diffraction experiment using dedicated algorithms that were developed over the past twenty years. A very important aspect of BCDI, namely its spatial resolution is also shortly addressed.
All experiments within this thesis were actually performed at the 3^{rd} generation synchrotron sources SOLEIL and DIAMOND in France and in the UK, respectively. The working principle of a synchrotron is very briefly illustrated followed by the presentation of the beamline SixS at SOLEIL synchrotron where most of the work was conducted. For *operando* catalysis experiments dedicated reactors were used which are described in detail. In the case of BCDI, which bases on the retrieval of the lost phase, D. Simonne has written the open source software *Gwaihir* using *python 3.9*. The capabilities of this tool are well presented. It offers a graphical user interface and allows to perform the data pre-processing and phase retrieval up to the data post-processing. It reduces the analysis time significantly and thus helps for more solution-driven BCDI experiments. The package with a graphical user interface is precious for the coherence community and will also facilitate the use of BCDI for newcomers in the field. It will further support the efforts on the reproducibility of data obtained from different beamlines at various synchrotron sources which is of utmost importance.

The third chapter focuses on complementary *operando* SXRD and *operando* BCDI studies of Pt nanoparticles during catalytic processes. The samples used for these studies, which were obtained by the dewetting of a platinum layer on a sapphire substrate and which were provided by the Technion in Haifa (Israel), are presented. While SXRD was performed on a sample containing homogeneously distributed Pt nanoparticles, thus giving access to their collective behavior, BCDI was carried out on patterned samples allowing for the investigation of individual Pt nanoparticles.
Studying the collective behavior of the Pt nanoparticles by SXRD, a progressive increase of the diffracted intensity for specific facets was evidenced while the intensity for other facets progressively decreased when introducing oxygen into the reactor at temperatures of 600 °C. These findings were related to a reshaping of the nanoparticles as a function of the O_2/NH_3 ratio. In addition, the strain within the nanoparticles was found to vary depending on the oxygen partial pressure. At the same

time, D. Simonne followed the catalytic activity of the nanoparticles by mass spectrometry showing the production of N_2, NO, and N_2O.

Complementary studies on three individual Pt nanoparticles having different sizes and shapes were performed by *operando* BCDI. Changes in faceting of the single nanoparticles as a function of temperature were imaged in 3D. In addition, the variation of the out-of-plane strain was imaged in 3D during ammonia oxidation cycles. However, only one Bragg peak was measured limiting the strain information along one direction. The nanoparticles could not all be fully reconstructed either due to strain or to defects present. Very careful analysis of the interplanar spacings and the full width at half maximum of the diffraction peaks were conducted to overcome limitations in the 3D reconstructions of the nanoparticles and to extract a maximum of information from the data. D. Simonne could show that each nanoparticle actually behaved differently depending on its initial shape and the potential presence of defects. While the few selected nanoparticles may not be a statistical representation of the complete sample, these studies clearly demonstrate the strength of *operando* BCDI to study the effect of catalytic processes on both the shape and the strain state at the nanoscale in 3D. These *operando* experiments demonstrate a mastering of the employed SXRD and BCDI techniques. The experimental findings are discussed with respect to different reaction mechanisms taking place at the surface.

The fourth chapter concentrates on the *operando* SXRD and near-ambient pressure (NAP-) XPS of bulk Pt(111) and Pt(100) single crystals to study the structural and chemical evolution at the two surfaces during catalysis and to link the surface structure with surface moieties and reaction products. D. Simonne was able to evidence different surface reconstructions. On the one hand, a Pt(111)-p(6x6)-R±8.8° surface reconstruction was found evolving towards a Pt(111)-p(8x8)-R0° surface reconstruction after longer exposure to oxygen. On the other hand, a Pt(100)-p(2x2)-R0° surface reconstruction was revealed that evolved to a Pt(100)-p(10x10)-R0° reconstruction during reaction conditions. In addition, two different kinds of platinum oxides, namely α-PtO_2 and Pt_3O_4 were identified on the Pt(111) and the Pt(100) surface, respectively. X-ray reflectivity further allowed to reveal more important surface roughness changes on the Pt(100) surface than on the Pt(111) surface during the oxidation cycle. D. Simonne was able to demonstrate by NAP-XPS that the Pt(100) surface is actually more easily oxidised than the Pt(111) surface, which also explains the larger surface roughness. Moreover, the reacting conditions were found to be linked with the surface reconstructions on Pt(100), in contrast to Pt(111).

The final chapter provides a summary of the major findings of this thesis and presents interesting perspectives for future research works. As future directions, D. Simonne proposes to further close the pressure gap in the study of catalytic reactions with respect to industrial processes by designing new reactors resistant to highly oxidising atmospheres and compatible with the ammonia/nitrogen gas family. Amongst others, higher oxygen pressures may reveal a role of platinum oxides during ammonia oxidation invisible at lower pressures. In addition, BCDI at extremely brilliant 4^{th} generation synchrotron sources are suggested, which may allow to study the facet strain in much more detail than in the present work. The measurement of three independent Bragg reflections providing access to the full strain tensor will further give invaluable information of the actual processes. Moreover, D. Simonne proposes the development of efficient simulation workflows to better understand and decorrelate the effects of interfacial strain from adsorbant strain. Last but not least, further work on the data reduction automatization is suggested which may reduce the necessary time and facilitate the analysis of multiple particles at various conditions.

A good supplementary section is provided containing details on residual gas analyser data during Pt nanoparticles study and single crystal investigations as well as 3D reconstructions of the three individual Pt nanoparticles during *operando* catalysis.

In summary, D. Simonne shows the mastering of three synchrotron X-ray techniques, namely surface X-ray diffraction and near-ambient pressure X-ray photoelectron spectroscopy as well as Bragg coherent X-ray diffraction imaging, which he applied on complex catalytic processes. He performed very complicated *operando* experiments employing the three abovementioned methods. He was able to demonstrate that the structural evolution of Pt nanoparticles depends on the size, shape, facet coverage and initial strain state. These experimental findings on the Pt nanoparticles as well as the different surface reconstructions of Pt(111) and Pt(100) surfaces are proof of very careful and precise measurements. D. Simonne further demonstrated a very deep and accurate analysis helping to paint a complete picture of the catalytic processes happening at the crystal surfaces and at the nanoscale by combining the results inferred by the different experiments.
Besides, D. Simonne developed the open source software *Gwaihir* which brings together the functionalities of the *PyNX* package for phase retrieval and *bcdi* package for the pre- and post-processing of the data in a graphical user interface built for the *Jupyter* framework. This open source tool, which is available on GitHub, is extremely valuable for the BCDI community.
So far, D. Simonne published only one article as first author in the Journal of Applied Crystallography focusing on the abovementioned software. The work has been presented at a number of national and international conferences and meetings. The results on the complementary *operando* BCDI and *operando* SXRD experiments on Pt nanoparticles during catalysis clearly merit to be published in an international scientific peer-reviewed journal. The same holds true for the combined *operando* SXRD and NAP-XPS studies on the Pt single crystals.
The research is of a standard commensurate with the PhD qualification, and as such I recommend the public examination and defense of the thesis for the degree of Docteur de l'Université Paris-Saclay.

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