APS General User Proposal

Proposal Id: 58888

Printed date: 07/10/2018

Proposal Title: In situ Pair Distribution Function (PDF) analysis to reveal and control the early stages of platinum nanoparticle synthesis

Principal Investigator: Kirsten Marie Jensen

Total shifts requested for the life of the proposal: 6

1st Choice Beamline(1st BTR): 11-ID-B

Requested Shifts(1st BTR): 6

Proposal Abstract

Understanding the formation of nanomaterials is key to develop synthesis methods for nanoparticles with controlled properties (size, shape, composition, etc.) so that their performances (activity, stability, selectivity, etc.) can be optimized for specific applications (catalysis, energy, medicine, etc.). We have developed a new, industrially relevant synthesis method of precious metal nanoparticles (e.g. platinum) in alkaline mono-alcohols from platinum chloride salts. Compared to previously applied synthesis methods, enhanced catalytic properties are obtained, and the production method shows promising features for industrial applications.[1] Size is controlled in the range 1-6 nm in a simple, scalable and resource efficient way via a nucleation-and-growth process.[2] The nature of the solvent, the base and the precursor used for synthesis are simple yet important parameters. From previous studies using SAXS and EXAFS, we have established that they control the kinetics of the formation, as well as the growth phase of the nanoparticles.[3] However, the characterization techniques used so far are best suited to study early or late stages of the formation: before and after the nucleation. To understand and control further the growth mechanism, we need insight into the atomic structures of the pre-nucleation clusters and into the structural transformation that takes place from ionic clusters to solid particles. Our hypothesis is that the nature of the precursor/pre-nucleation species during the steps just prior to the nucleation are key. In situ pair distribution function (PDF) analysis is an ideal and unique technique to investigate this hypothesis. Our synthesis is performed at low temperature (< 80 °C) which makes it ideal for in-situ PDF measurements with second to minute scale time resolution without requiring extensive cell design. This will allow us to deduce the structural changes that take place, as platinum chloride complexes rearrange and form platinum nanoparticles.

General Information

Proposal Status: Active

Requested Project Status: No

Submitted Date: 02-MAR-18

Review Panel: Structural Sciences

Spoken to a beamline staff? No
Research Subject: Chemistry, Materials science
Attached File (s): APS_Pt_Figure.pdf
Macromolecular Crystallography: N
Proprietary Proposal: N
Classified: N
Mail-in Status: N
Human Subject/Materials: N
Live Animals: N
Known Safety Hazard: N
Funding: Foreign

Beam Time Request(s)

Scheduling Period: 2018-2

1st Choice Beamline: 11-ID-B
2nd Choice Beamline: not selected
3rd Choice Beamline: not selected
Requested Shifts: 6
Requested Min Shifts: 3
Instrument Request: 11-ID-B 2D detector PDF
Scheduling Requirements:
Equipment Requirements: We will use the goniometer and cryostream available at the beamline.
Prefer Date: From: 01-AUG-18 To: 20-AUG-18
Unacceptable Date: From: 30-MAY-18 To: 08-JUL-18
Proposal Progress:
Publications:

Experimenters' Information

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Purpose and Importance of the Research

We have developed a new synthesis method bearing potential for industrial applications.[1] Platinum is synthesized from platinum chloride in very dilute solution in alcohols (2.5-10mM), and the product characteristics can be precisely controlled by precursor concentration, solvent, temperature, time and additives. Our synthesis method is sensitive to several parameters. [2] For instance the solvent, i.e. the type of monoalcohol, influences the growth mechanism as observed through X-ray absorption spectroscopy (XAS), in-situ small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and Fourier Transform Infra-Red (FTIR) spectroscopy.

However, important knowledge on the nucleation stage is still missing. In situ PDF analysis is a missing piece to give a complete picture of what we hypothesize to be the key step to control the growth of the nanoparticles: the step just prior and after the nucleation (defined as the point when several Pt-Pt bonds start forming). We have previously performed preliminary PDF measurements on Pt synthsis solution mixtures ex-situ: before the synthesis is induced. An effect of the solvent could be observed on the precursor cluster structure, where signals from different Pt-Cl complexes could be identified. This is encouraging to expect that more information could be obtained by 'in-situ' measurements performed as the synthesis actually occurs. Preliminary data are shown in Figure 1, also illustrating how the large majority of the scattering signal arises from the solvent, which must be subtracted before Fourier transformation. In situ studies of dilute reactions are highly challenging, and call for synchrotron measurements with the high photon flux available.

The in situ PDF studies will complement existing EXAFS and SAXS data and establish if prior to the nucleation, the solvent influences the nature of the precursor and intermediate species formed as we will be able to deduce atomic structure of pre-nucleation species. This knowledge should help to rationalize the mechanism at stake before or in the early stage of the nucleation. This will lead to strategies to control the kinetics and size achieved during nanoparticle production. For example the results will help to select/design further optimized precursor-solvent combination for reliable nanoparticle production.

Time resolved in situ measurements will furthermore allow us to directly follow the nucleation mechanisms. The influence of the solvent and the related kinetics of formation of key intermediate species will be identified. Further knowledge will be gained on the general growth mechanism of the precious metal crystals.

Reason for APS

Synchrotron radiation is needed for in situ PDF studies of dilute reactions. The APS offer the high photon flux and energy needed for this kind of experiments.

Reason for Beamline Choice

11-ID-B is one of only few beamlines in the world dedicated to Pair Distribution Function analysis. For dilute in situ experiments, we need very high flux of X-rays for data acquisition at an appropriate rate: Here, the Pt concentration in the reaction solution is on the mM scale (10-20 mM), and the vast majority of the signal will arise from scattering from the solvent. 11-ID-B offers the flux and background minimization needed, and is the

most suited beamline for these experiments. We have previously done succesful in situ studies of iron oxide formation mechanisms (GUP 53675, manuscript in preparation) at a comparable dilution level with excellent results at 11-ID-B.

Previous Experience with Synchrotron radiation and Results

The Jensen groups are experienced synchrotron users, and the research in the Jensen group focuses on nanostructure studies with PDF analysis. We have extensive expertise in performing in situ PDF experiments to gain insight into the structural changes that take place as solid nanoparticles form from ionic clusters in solution. The group has performed multiple successful in situ experiments at 11-ID-B (Refs 4-5), as well as other facilities. Jonathan Quinson has experience in SAXS and EXAFS and is an expert in nanoparticle synthesis.

Description of Experiment(s)

We will perform in situ studies and complementary ex situ studies to get insight into nucleation mechanisms. High quality ex situ data from two different precursors (platinum salts in alkaline solutions) in different solvents/with different additives will be measured. This should take ca. 2 hours (including tests, background measurements, and buffer time).
The in situ studies will reveal the Pt formation mechanisms from pre-nucleation clusters. The effect of the solvent, the nature of the alkaline additive, the nature of the precursor and its concentration (2 values for each parameter) can be studied in 8 in-situ experiments. Based on previous SAXS in-situ measurements, the nucleation happens in ca. 4-6 hours, depending on the synthesis conditions. These experiments should then take ca.: 2h + 6x4h + 2x8 h + background measurements, setting up, tests and buffer time = 48 hours.

The reaction mixtures will be made of H2PtCl6 at 2.5-10 mM in alkaline methanol or ethanol with a base/Pt ratio of 0 or 20 in a similar way to our previous studies.[1-4] The reaction proceeds at low temperatures (50-70C), and SAXS studied have shown that the reaction can be done in closed capillaries heated up with a hot airblower. We will use kapton capillaries, which can be heated using a cryostream.

Estimated Amount of Beam Time, Number of Visits, Number of Shifts (approximately)

We apply for 48 hours of beamtime, i.e. 6 shift scheduled as one visit during the proposal period.

Modification Summary

Not a continuation

Publications resulting from work done at the APS

Publications originating in work done at 11-ID-B

Suzannah R Wood, Keenan N Woods, Paul N Plassmeyer, David A Marsh, Darren W Johnson, Catherine J Page, Kirsten MO Jensen, David C Johnson
Same Precursor, Two Different Products: Comparing the Structural Evolution of In-Ga-O 'Gel-Derived' Powders and So-lution-Cast Films using Pair Distribution Function Analysis
Journal of the American Chemical Society, 2017, 139 (15), 5607-5613

Kirsten M. Ø. Jensen, Pavol Juhas, Marcus Tofanelli, Christine L. Heincke, Gavin Vaughan, Christopher Ackerson, Simon J. L. Billinge: Polymorphism in magic sized Au144(SR)60 clusters
Nature Communications, 7, 11859, 2016

Kirsten M. Ø. Jensen, Christoffer Tyrsted, Martin Bremholm, Bo B. Iversen: In situ studies of solvothermal synthesis of energy materials
ChemSusChem, 7, 1594-1611, 2014

Kirsten M. Ø. Jensen, Mogens Christensen, Haraldur P. Gunnlaugsson, Nina Lock, Espen D. Bøjensen, Thomas Proffen, Bo B. Iversen: Defects in hydrothermally synthesized LiFePO4 and LiFe1 xMnxPO4 cathode materials
Chemistry of Materials, 25, 2282-2290, 2013

Kirsten M. Ø. Jensen, Mogens Christensen, Pavol Juhas, Christoffer Tyrsted, Espen D. Bøjesen, Nina Lock, Simon J. L. Billinge, and Bo B. Iversen: Revealing the Mechanisms behind SnO2 Nanoparticle formation and Growth during Hydrothermal synthesis: An In Situ Total Scattering Study,
Journal of the American Chemical Society, 134, 6785-6792, 2012

Christoffer Tyrsted, Kirsten M. Ø. Jensen, Espen Drath Bøjesen, Nina Lock, Mogens Christensen, Simon J. L. Billinge, and Bo B. Iversen: Understanding the Formation and evolution of Ceria Nanoparticles under Hydrothermal Conditions,
Angewandte Chemie, International Edition. 51, 9030-9033, 2012

Another 4 papers based on work from 11-ID-B are in preparation.

References

[1] J. Quinson, S. Kunz, M. Arenz, Patent application pending, 2017.
[2] J. Quinson, et al. In preparation.
[3] J. Quinson, et al. In preparation.
[4] Jensen, K. M. Ø.; Tyrsted, C.; Bremholm, M.; Iversen, B. B. ChemSusChem 2014, 7, 1594-1611.
[5] Jensen, K. M. O.; Christensen, M.; Juhas, P.; Tyrsted, C.; Bojesen, E. D.; Lock, N.; Billinge, S. J. L.; Iversen,

B. B. J. Am. Chem. Soc. 2012, 134, 6785-6792.