



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:  
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

#### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

### Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

#### Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

#### Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Understanding the fate of Palladium-Gallium catalysts employed in CO <sub>2</sub> hydrogenation	<b>Experiment number:</b> CH-5889
<b>Beamline:</b> ID-31	<b>Date of experiment:</b> from: 07/07/21 to: 11/07/21	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Marta Mirolo	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Scott Docherty* <sup>1</sup> , Xiaoyu Zhou* <sup>1</sup> , Paula Abdala* <sup>2</sup> , Gina Noh <sup>1</sup> , Christoph Müller <sup>2</sup> , Christophe Copéret <sup>1</sup> <sup>1</sup> Laboratorium für Anorganische Chemie, Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland; <sup>2</sup> Laboratory Energy Technology Laboratory of Energy Science and Engineering Leonhardstrasse 21, LEE P201 CH - 8092 ZUERICH		

## Report:

### Overview:

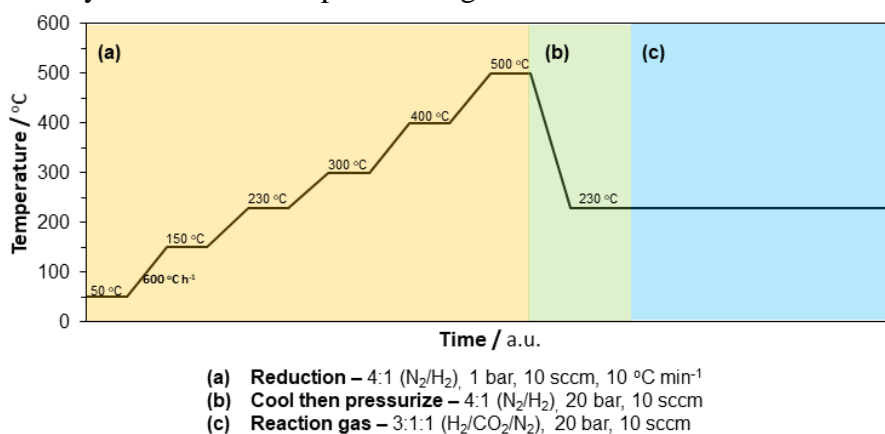
Palladium-gallium based catalysts are highly active for the hydrogenation of CO<sub>2</sub> to methanol. In spite of this, the origin of this reactivity remains poorly understood. To delineate the origin of this reactivity, we have used surface organometallic chemistry (SOMC) to develop a model PdGa catalyst, supported on silica containing surface-isolated Ga sites (PdGa@SiO<sub>2</sub>). While this system is both highly active and selective in the hydrogenation of CO<sub>2</sub> to methanol, the small size (<2 nm) of the nanoparticles obtained by this approach, in combination with the low metal loadings (<4 wt%) preclude structural analysis by lab-based diffraction methods, due to both intrinsic disorder and high signal dispersion. However, using *in situ* X-ray absorption spectroscopy (XAS), we have previously been able to show that alloying and de-alloying occur under reaction conditions, and may play a key role in the catalytic performance of these materials.

Thus, to gain detailed atomic scale insights into the working catalysts we turned to synchrotron-based pair-distribution function (PDF) analysis. Experiments were designed to enable analysis of the as-synthesized material, the dynamics of the alloy formation, and the how the material evolves under reaction conditions – using differential pair distribution function (dPDF) analysis to specifically investigate changes to the introduced metals (Ga, Pd) on the atomic scale and beyond. The goals of this study were to (i) gain insight into the catalyst structure and changes thereof under reaction conditions; and (ii) explore how the alloy is formed during synthesis.

### Data Obtained and experimental parameters:

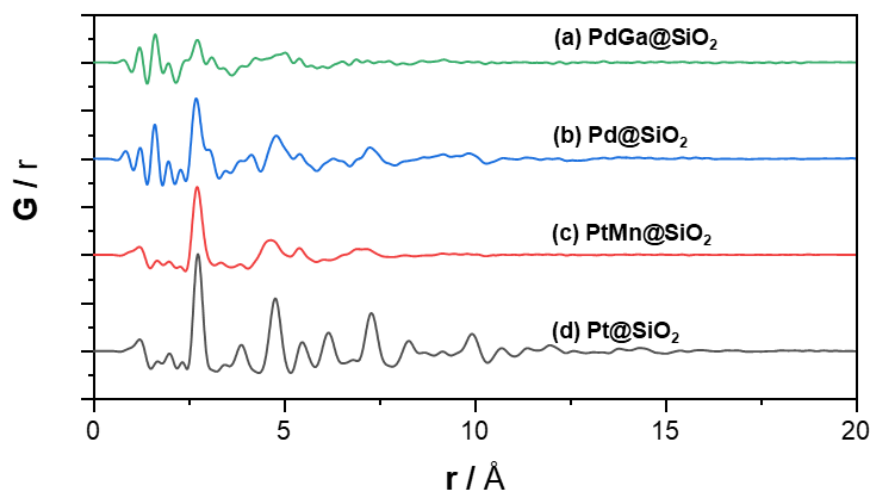
*In situ* X-ray total scattering data were collected on powdered samples of SiO<sub>2</sub>, Ga@SiO<sub>2</sub>, Pd@SiO<sub>2</sub> and PdGa@SiO<sub>2</sub> using a quartz capillary cell (o.d. 1 mm, i.d. 0.9 mm). All samples were supported on Degussa AEROSIL-200 (204 m<sup>2</sup> g<sup>-1</sup>), to enable efficient subtraction of background signal for dPDF. Additional TPR data for other systems were also recorded (Pt@SiO<sub>2</sub>, PtMn@SiO<sub>2</sub>). Data were collected at a detector-to-sample-distance of 30 cm for all experiments, the beam energy was 66 keV. Flow rates (CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>) were controlled

via mass-flow controllers (Bronkhorst), and pressure was retained using a back pressure regulator (Bronkhorst, EL-PRESS). Temperatures (50-500 °C) were maintained using a gas blower, temperature calibration was performed using a K-type thermocouple mounted inside a sample cell and the obtained values were used thereafter. A CeO<sub>2</sub> NIST standard was utilized to determine dampening and broadening of PDF peaks due to experimental resolution. Outlet gas composition was monitored using a mass spectrometer (MS, Pfeiffer vacuum) mounted directly behind the back-pressure regulator.



**Figure 1.** Schematic representation of temperature profile and gas composition/pressure for a typical experiment.

In a typical experiment, data was acquired at a series of points (50 °C, 150 °C, 230 °C, 300 °C, 400 °C, 500 °C) during temperature-programmed reduction (TPR, Figure 1A) to track changes during hydrogen treatment. The capillary reactor was then cooled to reaction temperature and pressurized (Figure 1B), before reaction gas introduced (Figure 1C). Data was recorded until steady state was obtained (confirmed by MS). A series of comparable dPDF plots for data acquired under identical conditions during TPR (230 °C) are shown in Figure 2. The attenuation of signal reflects particle size, and illustrates the increased disorder associated with bimetallic materials, when compared to their monometallic counterparts.



**Figure 2.** Representative dPDF plots for (a) PdGa@SiO<sub>2</sub>, (b) Pd@SiO<sub>2</sub>, (c) PtMn@SiO<sub>2</sub>, (d) Pt@SiO<sub>2</sub>. Conditions: 230 °C, 1 bar(g), 10 sccm, 4:1 (N<sub>2</sub>/H<sub>2</sub>). dPDF obtained through subtraction of Aerosil-200 measured under equivalent conditions. Data processing performed in PDFxGet3.

#### Further work and anticipated output:

Currently the data is being further processed, and the structures simulated with models obtained from expected crystal structures, in addition to insights from XAS and high-resolution transmission electron microscopy (HR-TEM). A manuscript is expected to be published containing the results of the study of PdGa and Pd, in combination with complementary data from further studies using XAS and DFT calculations, in the coming months. In addition, TPR experiments on the discussed Pt and PtMn systems will be included in a manuscript that is to be submitted in the coming months.