

## 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>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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 cause of synergy in supported bimetallic catalysts for selective CO oxidation under reaction conditions	<b>Experiment number:</b> CH-3639
<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: 14/9/2013 to: 19/9/2013	<b>Date of report:</b> 14/8/2013
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Suresh Gattla	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Andrew M. Beale (Inorganic Chemistry and Catalysis, Utrecht University)* Ines Lezcano-Gonzalez (Inorganic Chemistry and Catalysis, Utrecht University)* M. Sankar (Inorganic Chemistry and Catalysis, Utrecht University)*		

### Report:

Supported bimetallic nanoalloys, containing two metallic species, exhibit substantially different, often enhanced, properties compared to their monometallic analogues, which makes them very attractive for technical applications, especially as catalysts. Precise control over structural parameters such as (a) size dependent compositional variation, (b) morphology and (c) mono-dispersity of particle size are crucial to fully harness the catalytic power of these bimetallic nanoalloys. Conventionally, supported nanoalloys are prepared by wet-impregnation ( $C_{Im}$ ) methods using an aqueous solution containing two metal precursors. Catalysts prepared by this route can contain metallic entities ranging from sub-nm clusters to particles a few microns in size. To overcome this broad size distribution problem, size-controlled nanoalloys, have been prepared in aqueous solutions in the presence of stabilizer ligands, such as polyvinyl alcohol (PVA) or poly(vinylpyrrolidone) (PVP). Then these particles are immobilized onto a solid oxide support to form catalysts with almost all the metal particles within the 2-10 nm range (*i.e.* sol-immobilization ( $S_{Im}$ ) method). However, supported nanoalloys prepared by the  $S_{Im}$  method still tend to exhibit a size dependent compositional variation. Recently, Sankar *et al.* reported an excess anion modification of the  $C_{Im}$  method, (modified impregnation ( $M_{Im}$ ) method) for the synthesis of supported gold-palladium nanoalloys, which afforded a more precise control over the size, composition and morphology of these nanoalloys. In this beamtime we performed EXAFS measurements at the Au  $L_3$  and Pd K-edges in order to unravel the structure of AuPd catalysts prepared by this  $M_{Im}$  method. These data were subsequently compared with Scanning Transmission Electron Microscopy (STEM) data on the same samples.

The resultant bimetallic coordination numbers from an analysis of the EXAFS data are given below. For the 1% AuPd/TiO<sub>2</sub> (M<sub>Im</sub>) sample, confirmation of the presence of bimetallic species can be seen immediately from the Fourier Transform (FT) data at both edges (Fig 1). Two intense peaks in the FTs are observed as a consequence of a ‘ $\pi$  phase flip’ in the backscattering amplitude from 6 Å<sup>-1</sup> for Au (or indeed for all elements where  $Z > 78$ ) resulting in a splitting of the major contribution in the FT into a high and low  $r$  component. This occurs when two elements are present in equivalent amounts; often the splitting and intensity of the low  $R$  contribution becomes more intense with an increasing number of bimetallic bonds. A mismatch in the total coordination number from an analysis of the Au L<sub>3</sub>- edge (7.3) and Pd (3.0) K-edge data is testament to a large number of Au-Au contributions due to the presence of large (~ $\mu\text{m}$  sized) clusters in the sample in addition to bimetallic species. From a Pd K-edge perspective the smaller overall coordination number suggests that much of the Pd is associated with Au although the higher Au contribution (consistent with STEM data) suggests these larger species to be Au-rich. These observations clearly indicate that EXAFS is a complimentary technique to electron microscopy for characterizing these supported bimetallic nanoalloys. From the above characterization data, it is evident that the bimetallic catalysts have a homogeneous random alloy structure. The substantial enhancement in the catalytic activity of these catalysts, often termed as synergistic effect, could be the result of the intimate mixing of two metals in the bimetallic crystals. This observed synergistic effect has been hypothesized to occur as a result of either the formation of unique metal (A) – metal (B) bonds, often termed as an ensemble (geometric) effect, or a change in the electronic state by the formation of metal (A) – metal (B) bonds in the surface or a combination of both. With the currently available evidence, it is not possible for us to prove/disprove either of the two hypotheses, however efforts are underway to understand the reason for this remarkable measured synergistic effect.

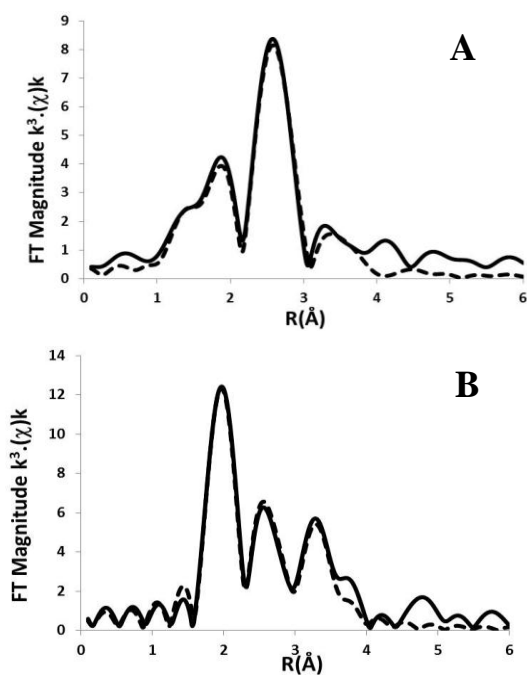


Figure 1. Fourier-Transforms of the EXAFS data and 2-shell fits for 1% AuPd/TiO<sub>2</sub> (M<sub>Im</sub>) catalysts. [A & B]. A: Au L<sub>3</sub> edge; B : Pd K-edge. Solid line : raw data ; dashed line : fit.