

## Report on beam time: MA617, ID15b, Sept 2008

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### Time resolved, high energy diffraction study of *in situ* dynamic structural reactive change in supported noble metal nanoparticles .

This proposal was exceptionally successful. Within the 18 shifts allocated we were to mount, test and demonstrate a new experimental methodology, fusing time resolved hard X-ray diffraction, infrared spectroscopy, and mass spectrometry for the *in situ* time-resolved study of powder materials such as catalysts. Moreover, the results obtained went far beyond the original expectations of the proposers and lead directly to a number of new and potentially important lines of research in this field.

Figure 1 shows some representative data obtained for three of the cases investigated and pertaining to the structural dynamic behaviour of support Pd nanoparticles during redox cycling.

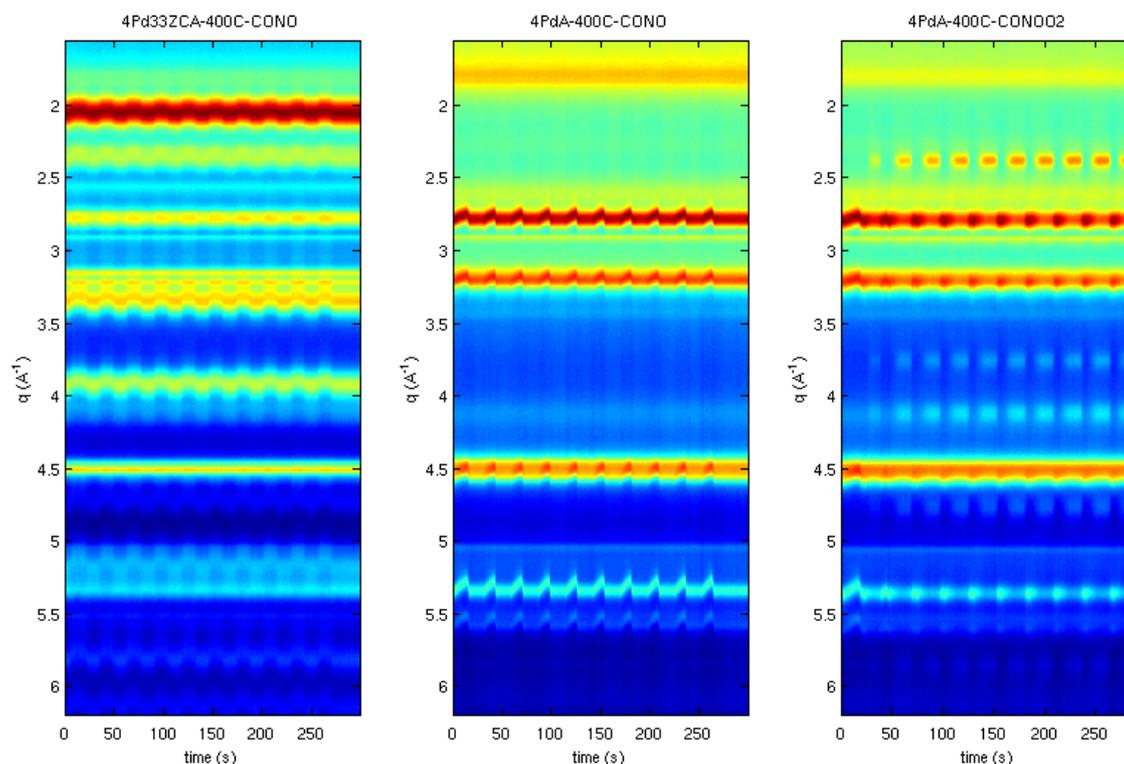


Figure 1. Colour maps showing the diffraction pattern behaviour of three catalysts systems during redox cycling (as indicated) at 673K. Diffraction images were collected using 90 keV X-rays and at a repetition rate of 2.5Hz. In the titles  $A = \gamma\text{-Al}_2\text{O}_3$ , 33ZCA = 33wt%  $\text{CeZrO}_4/\text{Al}_2\text{O}_3$

We believe that these diffraction data are the first of their type and, as they are collected synchronously acquired (at 3Hz) diffuse reflectance infrared spectroscopy (DRIFTS) and mass spectrometry they comprise a completely unique and very powerful experiment.

Within the range of Q space shown in figure 1 (which is not the maximum that can be achieved with the current setup) a variety of aspects of the structural reactive behaviour of these systems are very clearly divined, enhancing greatly the knowledge that we have already obtained from the equivalent time resolved

EXAFS studies made on ID24 [1,2]. Moreover, at least 2 novel aspects of the catalyst behaviour, that are either invisible to the Pd K edge EXAFS experiment, or, to a first approximation, extremely difficult to quantify using XAFS, can be clearly observed in diffraction.

The first is the zero order increase in Pd-Pd lattice parameter occurring during the CO cycle of the redox modulation over the 4Pd/Al<sub>2</sub>O<sub>3</sub> sample. This appears to be indicative of an unexpected (from a traditional surface science point of view) surface chemistry: that of CO dissociation by Pd. Moreover this new chemistry can be directly correlated with aspects of the development of the CO infrared spectrum during the CO cycle, and, with hindsight, subtle changes in the XANES region of the Pd K edge dispersive EXAFS experiment.

The second regards the 4Pd/33ZCA sample during the same redox cycling. Here we can verify the assertion of EXAFS that the average Pd nanoparticle is much smaller than its cousins supported to the same loading on Al<sub>2</sub>O<sub>3</sub>. However, we also observe that: (a) there is now no evidence for the formation of an expanded Pd phase during the CO cycle -indeed the Pd nanoparticles themselves appear to show no obvious structural modifications; and (b) in this case, we see that the CeZrO<sub>4</sub> support becomes the dynamic structural entity, changing lattice constant over a wide range and reversibly during the cycling.

For the first time, we believe, we have directly observed, from a long-range structural and time resolved point of view, the oxygen storage and release functions of the CeZrO<sub>4</sub> phase. It is these functions that lie at the very heart of their commercial utility as a components in auto-exhaust and other types of catalyst.

The extensive data obtained from this experiment is currently undergoing analysis and we believe that this highly successful demonstration of a new experiment will lead to several highly quality publications in 2009/10. Rietveld analysis of diffraction patterns will work out details of the above mentioned phenomena. Moreover, this data points to a plethora of areas, such as nanoparticle shape/size/lattice dynamic changes where an experiment of this type, and derivations of it, could make highly novel and significant contributions by giving specific information concerning each one of the structural phenomena involved in catalytic systems operating at "real conditions".

Lastly, we would like to thank Dr M. Di Michiel for the extensive support he has given this experiment. Without his support and know-how it could not have been the success that it has turned out to be.

From an overall perspective we note that the only significant (beamline) limitation to the furtherment of this experiment currently lies in the computing hardware and software available to run the Pixium 2D detector. We were restricted to collecting data at 2.5 Hz because of these issues. It is clear, however, that the full potential (an order of magnitude faster) of the pixium is not currently able to be exploited because of these issues and we would urge that these are resolved on ID15 as soon as is possible.

## References

1. M. A. Newton, C. Belver, A. Martínez-Arias, M. Fernández-García. *Nature Materials*, **2007**, *6*, 528-532.
2. M. A. Newton, C. Belver-Coldeira, A. Martínez-Arias, M. Fernández-García., *Angew. Chem. Intl Ed.*, **2007**, *46*, 8629.