

## Electron Microscopy Informed Catalyst Design

Christopher J. Kiely<sup>1,2\*</sup>, Li Lu<sup>1</sup>, Sultan Althahban<sup>1</sup>, Qian He<sup>2</sup> and Graham J. Hutchings<sup>2</sup>

<sup>1</sup> Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA

<sup>2</sup> Cardiff Catalysis Institute, Department of Chemistry, Cardiff University, UK

\* Corresponding author: chk5@lehigh.edu

Aberration corrected scanning transmission electron microscopy (AC-STEM) studies of supported metal catalysts can now in principle allow us to perform meaningful *microscopy informed catalyst design*. The key underlying concept of this approach is that if the most active species in a complex multi-species heterogeneous catalyst system can be positively identified by electron microscopy, then appropriate modifications to the catalyst preparation route can be devised in order to increase the number density of these desirable species, and hence improve the overall activity of the catalyst.

Supported Au catalysts have been extensively studied for many important reactions, including low temperature CO oxidation [1], acetylene hydrochlorination [2] and the water-gas shift reaction [3] to name but a few. It is now known that a wide range of supported Au species (*i.e.*, dispersed atoms, dimers, trimers, sub-nm clusters, rafts, nanoparticles of various sizes) can *co-exist* in such materials which often creates debate over the identity of the active species for a particular reaction. Recent work on the Au/FeO<sub>x</sub> catalyst for CO oxidation has brought new insight to this problem and provided new direction towards settling the ongoing debate over the identity of the active Au species [4]. An experimental protocol has been developed, based on HAADF imaging in the AC-STEM, for measuring the population densities of *all* the supported species present in such a catalyst system in a statistically relevant manner. By correlating the populations of the various Au species present with catalysis results are able to demonstrate that a size-dependent activity hierarchy exists in the Au/FeO<sub>x</sub> low temperature CO oxidation catalyst, (with an activity trend of sub-nm clusters > 1-3 nm nanoparticles >> 3-7 nm particles >> dispersed atoms). We propose that the activity of this well studied system, and most likely many other supported metal catalyst systems, are the result of a complex population versus activity hierarchy relationship where the measured overall catalytic activity needs to be thought of as a weighted sum of the activity of each of the different species present combined with their relative population densities (*i.e.*, total activity  $A = \sum_i \rho_i \varepsilon_i$ , where  $\rho_i$  and  $\varepsilon_i$  represent the population fraction and intrinsic activity for the  $i^{\text{th}}$  active species). Once the optimal morphology of the supported metal has been identified, then the catalyst synthesis route can be modified in a deliberate manner to maximize the population of the most active (desirable) species, thus making more efficient use of the supported precious metal.

We have now also shown using a combination of HAADF-STEM imaging and synchrotron based XAFS studies that atomically dispersed cationic Au species are the most crucial for the acetylene hydrochlorination reaction [5]. This has led to the development of a simple and industrially scalable preparation method that can reproducibly generate this specific nanostructure. This latter reaction is important for the production of vinyl chloride monomer which can subsequently be polymerized to form PVC. In fact, an optimized Au/C catalyst (called Pricat MFC) is now being tested by Johnson Matthey on a large scale for VCM production in China as a replacement for the environmentally unfriendly and highly problematic HgCl<sub>2</sub> catalyst. Furthermore, another catalyst has recently been developed,

comprised primarily of atomic-layered raft-like clusters of Au on an  $\alpha$ -MoC support, which is superbly effective for the low-temperature water-gas shift reaction [6].

The spectrum of chemical reactions for which supported Au can be used as a catalyst can be significantly broadened by (i) alloying it with another metal such as Pd and (ii) choosing an optimized support material for the specific reaction of interest. XEDS analysis and HAADF imaging in the AC-STEM have both played key roles in characterizing the compositional homogeneity from particle-to-particle and elemental distribution within individual particles in these supported bimetallic systems. They have also led to a much greater understanding of the how the bimetallic particle interacts with the support. Using our microscopy informed catalysts design strategy, it has been possible to determine that small Au-rich core/Pd-rich shell morphology particles on TiO<sub>2</sub> are the most desirable catalysts for the direct production of H<sub>2</sub>O<sub>2</sub> from molecular H<sub>2</sub> and O<sub>2</sub>, whereas larger random alloy AuPd particles supported on TiO<sub>2</sub> are better for the selective oxidation of benzyl alcohol [7]. In both instances, simple new preparation routes have been developed to generate the desired optimized catalyst morphology.

From such studies, it is now known, but not widely appreciated, that most commonly used synthesis methods for generating supported bimetallic particles will give rise to a distribution of particle sizes in which the composition varies systematically with particle diameter, the details of which are highly dependent on the nucleation and growth kinetics inherent to the preparation method. Hence, we are now exploring new synthesis strategies, such as the continuous production and immobilization of colloidal AuPd nanoparticles in millifluidic reactors, in order to suppress such undesirable effects [8]. We have also recently shown that in some specific instances, it is highly desirable to remove the support material altogether from the catalyst formulation as it can prove be detrimental to the reaction. This is the case for colloidal AuPd nanoparticles which are found to be much more effective for the partial oxidation of methane to methanol when simply suspended in an aqueous medium as opposed to being dispersed on a TiO<sub>2</sub> support [9].

#### References:

- [1] M. Haruta, *CatTech*, **6**, (2002), 102.
- [2] G.J. Hutchings, *Journal of Catalysis*, **96**, (1985), 292.
- [3] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science*, **301**, (2003), 935.
- [4] Q. He, S.J. Freakley, J.K. Edwards, A.F. Carley, A. Borisevitch, Y. Mineo, M. Haruta, G.J. Hutchings and C.J. Kiely, *Nature Communications*, **7**, (2016), 12905.
- [5] G. Malta, S.A. Kondrat, S.J. Freakley, C.J. Davies, L. Lu, S. Dawson, A. Thetford, E.K. Gibson, D.J. Morgan, W. Jones, P.P. Wells, P. Johnston, C.R.A. Catlow, C.J. Kiely and G.J. Hutchings, *Science*, **355**, (2017), 1399.
- [6] S. Yao, X. Zhang, W. Zhou, R. Gao, W. Xu, Y. Ye, L. Lin, X. Wen, P. Liu, E. Crumlin, J. Guo, Z. Zuo, W. Li, J. Xie, L. Lu, C.J. Kiely, L. Gu, C. Shi, J.A. Rodriguez and D. Ma, *Science*, **357**, (2017), 389.
- [7] R.C. Tiruvalam, J. Pritchard, N. Dimitratos, J.A. Lopez-Sanchez, J.K. Edwards, A.F. Carley, G.J. Hutchings and C.J. Kiely, *Faraday Discussions*, **152**, (2011), 63.
- [8] S. Cattaneo, S. Althahban, S.J. Freakley, M. Sankar, T.E. Davies, Q. He, N. Dimitratos, C.J. Kiely and G.J. Hutchings, *Nanoscale*, (2019), *in press*.
- [9] N. Agarwal, S.J. Freakley, R. McVicker, S. Althahban, N. Dimitratos, Q. He, D.J. Morgan, R.L. Jenkins, D.J. Willock, S.H. Taylor, C.J. Kiely and G.J. Hutchings, *Science*, **358**, (2017), 223.