Electron Microscopy Investigations of Precious Metal Catalysts: Towards Controlled Synthesis of Ultra-Small Nanoparticles

Qian He,^{1, 2,} Thomas Davies,^{1, 2} Chloe Dixon,² Sultan Althahban,³ Li Lu,³ Simon Freakley,^{1, 2} Laura Abis,^{1, 2} Nishtha Agarwal,^{1, 2} Margherita MacIno,^{1, 2} Stefano Cattaneo,^{1, 2} Sankar Meenakshisundaram,^{1, 2} Nikolaos Dimitratos,^{1, 2} Graham Hutchings^{1, 2} and Christopher Kiely ^{1, 2, 3}

Precious metal nanoparticles have important applications in catalysis. In order to maximize the atomic efficiency and therefore reduce the usage of valuable resources, the particle size, morphology and their interaction with the support need to be carefully controlled and optimized. In the case of monometallic Au and Pt catalysts prepared via wet chemical routes, advanced electron microscopy has allowed us to obtain an unprecedented and more complete view of the complex dispersion of metal entities present, including nanoparticles, sub-nm clusters, and atomically dispersed species. With this new information, a better understanding of the catalytically active sites/species can be established. [1] By correlating catalytic performance data with the nanostructures generated by various catalyst preparation methods the most active species can be identified and specifically targeted for synthesis, thus significantly improving the atomic efficiency.

Making nanoalloys is another way of improving atomic efficiency for precious metal catalysts. In some cases, an earth abundant metal is combined with the precious metal, in an effort to maximize the exposure of the latter on the particle surface. Quite often, a synergistic effect can be observed, meaning that the nanoalloy performs better than either of its individual components working in isolation. Fabricating nanoalloy catalysts is however, considerably more difficult than it sounds because the dispersion of two metals needs to be controlled simultaneously. Using Pd-based bimetallic systems [2] as an example, we will demonstrate how advanced electron microscopy, which provides atomic level structural and chemical analysis, can help us to achieve such a goal. With the help of electron microscopy, metal-support interactions can be identified and in some cases manipulated to improve the performance complex bimetallic catalyst systems. [3]

Finally, we will highlight our recent attempts to investigate the structure of nanoalloy colloids at early stages of their formation, in an effort to understand how different synthesis conditions (e.g. different reducing agents, different stabilizing ligands) can affect the size and composition distribution of the resultant particles. A combination of in-situ spectroscopies and electron microscopy has been used to monitor the nucleation and growth of such colloidal metal nanoparticles. We will share our findings on the quenching the embryonic colloidal solutions using plunge freezing techniques. We will also use high surface area support materials (e.g. carbon black) to immobilize the particles at later stages of the growth and study the composition distribution of the two metals. These will bring insights into the particle formation mechanisms and lead us to a better control of size, morphology and composition of the bimetallic nanoparticles [4].

^{1.} Cardiff Catalysis Institute, Cardiff University, Cardiff, United Kingdom.

² School of Chemistry, Cardiff University, Cardiff, United Kingdom.

^{3.} Department of Materials Science and Engineering, Bethlehem, Pennsylvania, United States.

References:

- [1] Q He, S Freakley, JK Edwards et al, Nature Communication 7 (2016), p.12905.
- [2] M Sankar, Q He and M Morad, ACS Nano 6 (2012) p. 6600.
- [3] S Freakley, Q He, J Harrhy et al, Science 351 (2016) p. 965.
- [4] The authors gratefully acknowledge funding from the EPSRC & NSF. Q.H., S.M., N. D. thank Cardiff University for the University Research Fellowships.