PROGRESS REPORT FOR AINGRA09119

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<th>PROJECT TITLE</th>
<th>TEM characterisation of novel supported silver and gold nanoparticle catalysts</th>
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<td>INVESTIGATOR(S)</td>
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<td>Specialist Committee</td>
<td>Materials Properties and Engineering</td>
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SCIENTIFIC OBJECTIVES

This project is an extension of TEM work conducted on a previous AINSE funded project AINGRA08066, and aims to use the TEM, STEM/HAADF, EDS and plasmon imaging facilities at ANSTO to structurally characterize novel supported silver nanoparticle catalysts for ozone abatement, and supported gold catalysts for low temperature CO oxidation. The catalysts, fabricated at the University of Auckland, comprise Ag or Au nanoparticles of diameter 1-5 nm deposited on 3-dimensionally ordered macroporous (3DOM) inverse opal silica, titania, alumina and zirconia supports (Ag or Au loadings 1-5 wt. %). From the work, we expect to determine Au particle sizes and size distributions, as well as SiO2, TiO2, Al2O3 and ZrO2 crystallite sizes in the 3DOM supports.

PROGRESS REPORT and RESEARCH OUTCOMES

Colloidal crystal templating is a novel and versatile approach for the fabrication of 3-dimensionally ordered macroporous (3DOM) oxide materials. The Waterhouse research group at Auckland University has used this approach to fabricate a wide range of 3DOM oxide supports (including SiO2, TiO2, Al2O3, ZrO2 and combinations thereof). The diagram below schematically outlines the colloidal crystal template method. In the first step, monodisperse spheres of PMMA (diameter around 300 nm) are prepared then induced to self-assemble (crystallize) on a fcc lattice. In the second step, the colloidal crystal template "synthetic opal" is infiltrated with a metal oxide precursor using sol-gel chemistry. In the final step, the infiltrated colloidal crystal template is carefully calcined at 450-550 °C to remove the PMMA template, yielding a metal oxide "inverse opal".

Due to their 3DOM structure, high surface area and macroporosity, metal oxides with inverse opal structures are particularly desirable as catalyst supports, an advantage the Auckland group is presently exploiting in a wide range of heterogeneously catalysed reactions.
AINGRA09119 aimed to use the excellent TEM facilities at ANSTO to characterize a number of different catalysts prepared using 3DOM oxide supports. The catalysts comprised Ag and Au nanoparticles dispersed on 3DOM SiO$_2$ and 3DOM TiO$_2$ supports. The Ag/3DOM SiO$_2$ system is extremely efficient at catalysing the decomposition of O$_3$ (a cause of respiratory illness at tropospheric level), while the Au/3DOM SiO$_2$ system is very efficient at catalysing the oxidation of CO to CO$_2$. The use of supported silver and gold nanoparticles as catalysts requires careful catalyst preparation, centred on achieving a very small metal particle size and narrow size distribution. Figures 1-11 summarise TEM data collected at ANSTO on this grant. A brief description of each figure is given below.

Figure 1 shows SEM (taken at Auckland Uni) and TEM (ANSTO) micrographs of a 3DOM SiO$_2$ support. The 3DOM structure of the inverse opal SiO$_2$ support is clearly evident in the micrographs.

Figure 2 shows TEM micrographs for Ag nanoparticles dispersed on the 3DOM SiO$_2$ support (fresh catalyst). Ag particles were easy to distinguish from the SiO$_2$ in bright field TEM images, and importantly Ag particle diameters were small (~5 nm) even at Ag loadings of 5 wt. %. This catalyst is very active for ozone decomposition, which results from the high surface area of the 3DOM support, and more importantly the small size and narrow size distribution of the Ag particles on the surface of the oxide support. The TEM work at ANSTO has thus proved invaluable in rationalizing the excellent function of this catalyst.

Figure 3 shows TEM micrographs of Ag nanoparticles (5 wt. %) dispersed on the 3DOM SiO$_2$ support following exposure to ozone. The figure clearly show that the small Ag particles have been oxidized following reaction with O$_3$ – this is consistent with complimentary XPS and XRD data we have for this reaction.

Figures 4 shows TEM micrographs of Ag nanoparticles dispersed on 3DSOM SiO$_2$ support at a Ag loading of 10 wt. % (fresh catalyst). Again, very small Ag particles were observed and easily distinguish fromed the oxide support in bright field TEM images. SADP showed no bright spots, providing further evidence that the Ag particle size was indeed small (the 3DOM support is amorphous and thus gives only a broad diffuse halo in the SADP images). This catalysts exhibits excellent activity for ozone decomposition and also potent anti-fungal and anti-bacterial properties.

Figure 5 shows TEM images of Au nanoparticles dispersed on a 3DOM SiO$_2$ support. Au particles were easy to identify in the bright field images and using point mode EDS.

Figure 6 shows TEM micrographs for gold nanoparticles dispersed on Boehmite and Rutile nanofibre supports.

Figure 7 shows TEM and SADP images of 3DOM ZrO$_2$ support. The SADP analysis revealed the nanocrystalline nature of tetragonal zirconia grains in the walls of the inverse opal, a result consistent with our previous powder XRD measurements.

Figures 8 and 9 shows TEM micrographs for platinum nanoparticles embedded in mesoporous carbon supports. The Auckland group, in conjunction with collaborators at Tokushima University (Japan), are attempting to fabrication novel carbon-based electrodes for fuel cells and sensing applications by carburisation of agar gel precursors containing K$_2$PtCl$_4$. Figure 8 and 9 show the effect of carburisation temperature on platinum grain size. SADP images perfectly compliment the bright field images. We are now attempting to fabrication 3DOM carbon by the colloidal crystal template method described above.

Figures 10 and 11 show TEM images of C/CoFe$_2$O$_4$, C/Fe$_3$O$_4$, PANI nanotubes and nanofibres. Excellent images were obtained for each sample.

In summary, excellent TEM data collected has been collected at ANSTO for these catalysts, and the knowledge obtained from this work is being successfully exploited in the fabrication of improved supported Ag and Au nanoparticle catalysts. The value of the ANSTO work to our ongoing research efforts is immeasurable, and the work of Mark Blackford and AINSE in collecting the images and supporting our research, respectively, is greatly appreciated.

DATA (Please summarise the data collected within this Award. You may use tables, graphs or diagrams)
Figure 1 – SEM (left) and TEM (right) images of a SiO$_2$ inverse opal.

Figure 2 - Ag nanoparticles dispersed on an inverse opal SiO$_2$ support (Ag loading = 5 wt.%)

Figure 3 – Ag/ inverse opal SiO$_2$ catalyst (Ag loading = 5 wt.%) after exposure to ozone, showing oxidized Ag particles (Ag$_2$O surrounding a Ag core).
Figure 4 – Ag nanoparticles dispersed on an inverse opal SiO₂ support (Ag loading = 10 wt.%). SADP shows few bright spots indicating that the Ag particles size remains small even at high Ag loadings.

Figure 5 – Au nanoparticles dispersed on an inverse opal SiO₂ support (Au loading = 5 wt.%). SADP shows few bright spots indicating that the Ag particles size remains small even at high Ag loadings.
Figure 6 – Au decorated Boehmite nanofibres (left) and Au decorated Rutile nanofibres (right).

Figure 7 – Inverse opal ZrO₂ support (Ag loading = 10 wt.%). SADP shows few bright spots indicating that the nanocrystalline ZrO₂ particles.

Figure 8 – Pt/Carbon 1 wt.%). 400°C. SADP shows few bright spots indicating that the nanocrystalline Pt particles.
Figure 9 – Pt/Carbon 1 wt.%. 800°C. SADP shows few bright spots indicating that the nanocrystalline Pt particles.

Figure 10 - C/CoFe$_2$O$_4$ (left) and C/Fe$_3$O$_4$ (right)

Figure 11 – TEM micrographs of PANI nanotubes (left) and nanofibres (right)
**PUBLICATIONS / REPORTS arising as a result of your work.**

Four journal articles relating to AINGRA08066 and AINGRA09119 are presently being prepared (the TEM work for AINGRA09119 was only recently completed). It is expected that these 4 articles will all be submitted for publication prior to March 31, 2010. AINSE support will be acknowledged.

A book chapter “Photoreactions over model TiO₂ Single Crystal Surfaces” for “On Solar Hydrogen and Nanotechnology”, Wiley, 2009, containing a TEM image taken on AINGRA08066 has been submitted for publication. AINSE support was acknowledged.

**PhD STUDENTS**

Not Applicable