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Development of nanoparticle catalysts and total internal reflection (TIR) Raman spectroscopy for improved understanding of heterogeneous catalysis

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Overall conclusions

Model heterogeneous catalyst systems have been prepared using deposited near-monodisperse nanoparticles with the ultimate goal of studying surface catalysed processes *in situ* using total internal reflection (TIR) Raman spectroscopy. To this end monodisperse nanoparticles have been synthesised (with a range of metal and capping agent combinations, such as silver, platinum, polyvinylpyrrolidone, oleylamine, and oleic acid, which displayed controlled particle size and shape). Such systems also included the use of copper, and silver/copper bimetallic nanoparticles synthesised for use in furfural hydrogenation and with the long term goal of being suitable for improving understanding of ethylene epoxidation. Langmuir Blodgett (LB) trough deposition allowed for the subsequent formation of uniform and tightly packed nanoparticle films, for which bulk and TIR Raman studies took place. These studies allowed for the monitoring of various nanoparticles with increased spectral sensitivity seen with the use of TIR Raman spectroscopy. The identification of bands assigned to the capping agent species confirmed the ability of TIR Raman spectroscopy to detect small amounts of organic moieties at a nanoparticle catalyst surface. Further validation of the assignment of spectral bands for the organic capping agent came from the use of plasma cleaning in conjunction with TIR Raman spectroscopy. Plasma cleaning provided an efficient method of cleaning the surface, in advance of *in situ* monitoring of nanoparticle catalysts. For the copper system variation in a number of experimental parameters was undertaken in order to increase understanding, and allowed for the targeted synthesis of small and monodisperse copper nanoparticles. A number of variables were seen to be crucial, and their impact upon the particle nucleation and growth, and the corresponding particle properties achieved was ascertained allowing for the optimisation of synthesis conditions. The variation of reaction parameters suggested that the optimum reaction conditions utilised a 1 h ripening time, at a temperature of 200 °C, with an oleylamine capping agent, in the presence of a strong reducing agent such as morpholine borane complex. For bimetallic nanoparticles adaptation of the monometallic copper preparation was required in order to give particles with low size dispersity, and sufficiently large enough to be characterised by transmission electron microscopy (TEM) imaging. The continuation of TIR Raman spectroscopic studies was attempted, with expansion of the system for the *in situ* monitoring of ethylene hydrogenation over a monolayer deposited nanoparticles platinum nanoparticle catalysts. Initial *in situ* studies of ethylene hydrogenation (using the same Raman system as that used in Chapter 3), over a monolayer deposited nanoparticle catalyst, did not resolve any spectral

features. The use of an optimised TIR Raman system and spectrometer indicated the successful sensing of the capping agents on the nanoparticle surfaces, with advancements seen in reproducibly sensing monolayer concentration of nanoparticles deposited at the substrate surface. Plasma cleaning again allowed for the removal of capping agents, providing a clean surface for spectroscopy and catalysis. Despite the increased suitability demonstrated for use of the optimised TIR Raman system, *in situ* studies of monolayer deposited nanoparticles (platinum/oleylamine), attempted for ethylene hydrogenation, revealed that the sensitivity of the present instrument arrangement was not sufficient to allow for resolution of any peaks attributed to the presence of adsorbates at the catalyst surface. Further modification of the system would therefore be required in order to allow for detection of such (predominantly gas phase) species under these *in situ* conditions. Finally examples showing the use and applicability of nanoparticles prepared in Chapters 3 and 4 towards use for a variety of heterogeneous catalytic applications was explored. For the catalytic application of nanoparticle systems silver catalysed amide bond formation was studied. The sensitivity of the catalyst, and the product conversion rates seen (with regards to oxidation/reduction of the silver) were very dramatic, and results allowed for the dismissal of a previous hypothesis regarding support effects related to the requirement of both basic and acid sites on the support material. Further modification of the copper nanoparticles developed in Chapter 4 allowed for use a galvanic displacement method, carried out for the first time on the nanoparticles rather than the supported catalyst, which enabled the demonstration of the Single Atom Alloy (SAA) effect for the hydrogenation of furfural. Finally palladium nanoparticles were prepared with the specific attributes needed to develop a hierarchical catalyst, in which different metals were preferentially inserted in the small (meso-) and large (macro-) pores of the material. This system was used to control the order of a cascade reaction and demonstrated the sequential oxidation of cinnamyl alcohol to cinnamaldehyde and then cinnamic acid with high selectivity.

Key findings are summarised below:

- Near monodisperse nanoparticles with a number of different capping agents were prepared and characterised by TEM. In particular a new, robust synthesis was developed for the formation of small metallic copper nanoparticles (down to 4 nm) using an amine-borane complex as a reducing agent.
- For the first time, TIR Raman spectroscopy was applied to the study of species absorbed on the surface of nanoparticles (in the first instance those species inherently present as capping agents from the synthesis). Sensitive detection of

small (monolayer) concentrations of organic moieties at the surface of a substrate was achieved, in comparison with Bulk Raman spectroscopy where only higher concentrations were detected.

- An optimised TIR Raman system and spectrometer was developed and allowed for reproducibly sensing monolayer concentration of nanoparticles deposited at the substrate surface, however attempts to detect absorbed gas species during *in situ* ethylene hydrogenation remained beyond the sensitively of the instrument.

- Nanoparticles prepared/developed for the TIR Raman study were also demonstrated as useful catalysts in a range of transformations and catalytic problems, such as furfural hydrogenation, where copper nanoparticles provided a new route to galvanostatic displace surface atoms with palladium to form surface atom alloys, or in cascade oxidation reactions where size control of the palladium nanoparticles enabled selective deposition in only the larger pores of the oxide support.