Durham E-Theses

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

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Future work

A variety of suggestions for future work, for each of the major topics focused upon within this thesis, are given below.

In extension to the systematic study of key variables towards the synthesis of small monodisperse copper nanoparticles a variety of additional recommendations could be made to increase fundamental understanding in a variety of areas. Firstly in Chapter 4, Section 4.1.1.1.1 it was found that for a 1 h ripening time temperature variation lead to particles with a more highly facetted shape, which we believed to be due to either restructuring of the particles formed at lower temperatures, or a differing process taking place for the higher preparation temperatures. In order to further explore which of these two routes is in operation prolonged ripening could be explored at the lower temperatures (such as 200 °C) in order to investigate if the re-structuring pathway takes place. If no such effects are seen the temperature could be gradually increased to see if such effects are induced, and results compared to a system which is immediately ramped up to this higher temperature. A further recommendation could be made in response to the use of additional capping agent explored in Section 4.1.1.2.2. It was postulated that the addition of oleic acid after ripening with oleylamine, (a commonly used procedure in the literature) leads to low product yields (as determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis), as the acid facilitated the oxidation of the easily oxidised copper nanoparticles. To test this hypothesis a less easily oxidised metal (such as silver) could be used in the preparation under otherwise identical conditions. Another approach that could be trialled would be the addition of oleic acid after synthesis of copper nanoparticles under conditions in which we expect the copper nanoparticles to be less easily oxidised (such as the use of strong reducing agent morpholine borane complex, or a very strongly bound capping agent such as a thiol moiety). An increase in the product yield (determined by ICP-OES analysis) using either of these approaches would further indicate that the ease of oxidation of the copper nanoparticle was responsible for the low yields currently reported.

Although beyond the scope of what was required within this work further optimisation of the bimetallic silver/copper nanoparticle preparation (Chapter 4) could be undertaken. A variety of experimental parameters (particularly those which had a key influence upon the monometallic copper nanoparticle preparation, such as preparation temperature or the use of a reducing agent) could have been further explored for their impact upon the bimetallic. This could also have included the use of sequential addition of the two metal salts. This would

give staggered silver and copper nanoparticle nucleation, and could have a significant impact upon the properties of the particles obtained.

For the *in situ* Raman studies shown in Chapter 5 the following suggestions can be made for future work. Firstly despite the selection of the 660 nm laser for this system, a reduction in the laser wavelength (for example to a 532 nm laser) would be expected to result in higher signal intensities (signal intensity is proportional to the fourth power of the laser frequency).[1] The initial laser selection was made in order to reduce fluorescence from samples, but limited evidence of fluorescence was seen for the platinum/oleylamine nanoparticle (platinum/OAm np) system studied within this section (it is believed that significant fluorescence was seen exclusively for the polyvinylpyrrolidone capped nanoparticles explored in preliminary studies in Chapter 3 Section 3.5, and Chapter 5 Section 5.1.2). Therefore, a reduced laser wavelength would be suggested, given that the low signal intensity has been a major factor in not being able to sense species at the hemisphere surface, for the studies within this section. Secondly, despite the motivations for studying ethylene hydrogenation, ethylene has a fairly low Raman scattering interaction. Choosing an absorbing species with a higher magnitude of Raman scattering interaction (such as carbon monoxide for which the value is orders of magnitude higher) would also be likely to increase the probability of sensing interactions with such a species.[2] A further suggestion for future work would be the use of polarisers used in combination with Fresnel equations to exploit 1) signal, and 2) geometric effects at the surface. Firstly to optimise signal we can focus upon optimising the incident light, and then if the surface is flat enough geometric effects can be explored. However, for the exploration of geometric effects it is necessary to take into account the orientation of the nanoparticle itself as well as the absorbed gas molecules. For example such effects have been taken into account in the work of Albrecht *et al.,*[3] near edge X-ray absorption fine structure (NEXAFS) spectroscopy was used to explore bond orientation of carbon monoxide as well as the geometry and orientation of CO absorbed on nanoparticles. A further extension of the *in situ* use of TIR Raman spectroscopy for heterogeneous catalysis could be made by looking at supported catalysts, such as those created by washcoating and spincoating. Similar work has been undertaken using attenuated total reflectance infrared (ATR-IR) spectroscopy by Hardacre *et al.*.[4]

For the amide bond formation work undertaken in Chapter 6 a number of recommendations for future work could be made. The first focus would be upon gaining reproducible results following Satsuma's method of catalyst synthesis (*i.e.* that explored in Chapter 6 Section 6.1.1 in the absence of nanoparticles). This would be undertaken in order to see if

reproducible results could be received and if the high activity of Satsuma's catalyst could be repeated. The work within Section 6.1.1 would indicate that two key areas to explore are the catalyst reduction time, and support effects. For reduction time exploration of a variety of intermediate reduction times (between the 10 min and 3 h times trialled) might be instructive as results appeared to indicate that a very specific extent of oxidation (effect of reduction time) and acid/base sites (effect of support) was required at the catalyst surface in order to provide high catalytic yields. Further to this such effects could be explored for example the catalyst could be fully reduced and greater control of the oxidation state could then be gained by using a liquid oxidant. Support effects were not explored within Section 6.1.1, and given that support effects studied in Section 6.1.2 were seen to be not only important but also to give differing results from those reported by Satsuma *et al.*.[5] Therefore it would be instructive to try a variety of support materials such as ceria, or silica. Since it is also possible that the batch of alumina used could impact upon catalytic properties, a variety of calcination times and temperatures could be explored for the synthesis of γ-alumina. From this improved understanding of the Satsuma type catalyst further studies upon the nanoparticle type catalyst could take place. A variety of particle sizes could be explored in combination with variation of supports with varying pore diameters. Use of 10 min reduced nanoparticle catalysts (rather than the 30 min used) could be trialled for the silica and cerium dioxide supports in order to see if the unexpectedly high catalytic conversions seen were replicated. As these supports contain only acidic or basic sites it is possible that the unusually high conversion seen was related to a more metallic surface, a shorter reduction time may give a mixture of silver and silver oxide, these conditions may be more favourable for the alumina support which contains both acidic and basic sites. *In situ* spectroscopic techniques could be used to allow for further deduction of the reaction mechanism, including whether the reaction goes *via* the intermediate pathway (benzylaldehyde and piperidine, or benzylaldehyde and benzylamine depending upon the amine used) or not, or deduction of the nature of the reaction surface after differing catalyst oxidation times. Such techniques could include the use of TIR Raman in a complimentary fashion with other spectroscopic techniques such as sum frequency generation (SFG), attenuated total reflectance infrared (ATR-IR), or diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS). TIR Raman spectroscopy could be of potential use in sensing silver-oxygen bonding, allowing for possible deduction of the acidic or basic sites at the reaction surface believed to be a crucial factor in providing the uniquely high product yields seen by Satsuma *et al.*.[5] The surface sensitivity, and good spectral resolution of SFG spectroscopy make it suitable for looking at surface

intermediates (such as the aldehyde intermediates suspected within this reaction), and could therefore be of use in determining if intermediate formation occurs and so in establishing which reaction pathway is taken. DRIFTS, or ATR-IR spectroscopies can provide information on both the structure and environment of molecules. This could allow for further deduction of reaction intermediates, as well as allowing us to see if reactants present at the reaction surface are in acidic or basic environments. This could allow for correlation of product yield and the localised acidity or basicity of the reactants. For example one experimental approach might be to try varying key parameters such as: differing bases (such as caesium carbonate, or sodium methoxide), or trying differing reduction conditions (such as no reduction, short 10 min reduction, long 3 h reduction) and using these *in situ* techniques to collect additional data about the nature of the surface as a function of product yield under these varying conditions.

Further characterisation of the platinum$_1$copper$_{83}$ Single Atom Alloys (SAAs) studied in Chapter 6 could be undertaken in order to allow for detection of the palladium atoms. Techniques suitable for allowing such detection include aberration corrected (AC)-TEM suitable due to the ultra-high resolution achievable. This would allow the identification of the platinum atoms in the copper matrix directly. The use of Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy might also be recommended. As was discussed in Chapter 1 EXAFS spectroscopy is based upon the backscattering interactions from neighbouring atoms, and so can provide information about the atoms local environment. The number, type and distance from coordinating atoms can be distinguished.[6] Hence, the technique would be expected to be suitable for allowing detection of single platinum atoms within the SAA material by determination of the average platinum-platinum co-ordination number.

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