

Durham E-Theses

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

LAURA MARIA BINGHAM

How to cite:

BINGHAM, LAURA MARIA (2017) Development of nanoparticle catalysts and total internal reflection (TIR) Raman spectroscopy for improved understanding of heterogeneous catalysis. Doctoral thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a <https://etheses.durham.ac.uk/id/eprint/12445/> is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.

Table of Contents

Chapter 1. Introduction.....	1
1.1. An introduction to heterogeneous catalysis, and the need for surface sensitive characterisation, and model catalysts.....	1
1.1.1. Why study heterogeneous catalysts <i>in situ</i> ?	4
1.2. <i>In situ</i> techniques for studying heterogeneous catalysts	5
1.2.1. Sum frequency generation (SFG).....	5
Case study	6
1.2.1.1. Challenges to the analysis of nanoparticle catalysis via SFG	8
1.2.2. Attenuated total reflectance infrared (ATR-IR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)	8
1.2.3. Extended X-ray absorption fine structure (EXAFS)/X-Ray absorption near edge structure (XANES) spectroscopy.....	9
Case study	10
1.2.4. Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS).....	12
Case study	12
1.2.5. Summary of the use of <i>in situ</i> techniques for studying heterogeneous catalysis	14
1.3. Raman Spectroscopy with <i>in situ</i> heterogeneous catalysis	14
1.3.1. Why use Raman spectroscopy?	14
1.3.2. Literature use of Raman spectroscopy to study heterogeneous catalysts <i>in situ</i>	17
1.3.2.1. Operando Raman spectroscopy	17
1.3.2.2. Quantitative Raman spectroscopy	18
1.4. TIR Raman, and its applicability to <i>in situ</i> studies of heterogeneous catalysis	18
1.5. Nanoparticles as a model catalysts	19
1.5.1. Methods of synthesising nanoparticles	20
1.5.1.1. Top-up and bottom-down synthesis	20
1.5.1.2. Metal salt reduction	21

1.5.1.3. Capping agents	21
1.5.1.3.1. Capping agents and catalysis	24
1.5.2. Nanoparticle growth and nucleation	24
1.5.2.1. Classical nucleation theory	25
1.5.2.2. Classification of growth mechanisms	26
1.5.2.3. Ostwald ripening	26
1.5.2.4. Digestive ripening.....	27
1.5.3. Introduction to the synthesis of small, stable, and size controlled copper nanoparticles.....	28
1.5.3.1. Methods for the creation of small, stable, and size controlled copper nanoparticles.....	29
1.5.3.2. Variation of synthetic parameters for furthering understanding of small copper nanoparticle synthesis	30
1.5.3.2.1. The effect of variation of the reaction temperature upon copper nanoparticle synthesis.....	30
1.5.3.2.2. The effect of variation of the capping agent upon copper nanoparticle synthesis.....	32
1.5.3.2.3. Redox effects: The effect of variation of the reducing agent upon copper nanoparticle synthesis, focusing upon the reduction of copper metal and the stability of synthesised nanoparticles to oxidation	35
1.5.3.2.4. The effect of variation of the reaction time upon copper nanoparticle synthesis.....	38
1.5.3.2.5. Mechanistic studies	38
1.5.3.2.5.1. Reduction mechanisms.....	38
1.5.3.2.5.2. Mechanistic interpretation of temperature effects on particle size and shape	39
1.5.3.2.6. Microwave synthesis and other alternatives	40
1.5.3.3. Summary of the overview of the state of the art	41
1.6. Catalytic systems and metals of interest to this study	41
1.6.1. Ethylene epoxidation, catalysts and mechanisms	42

1.6.1.1. Ethylene epoxidation mechanisms.....	43
1.6.1.1.1. Summary of mechanisms for ethylene epoxidation	46
1.6.1.2. Ethylene epoxidation catalysts: traditional and alloy type catalysts, for ethylene epoxidation	46
1.6.1.3. Further exploration of alloy type catalysts, for ethylene epoxidation	48
1.6.1.3.1. Probing of reaction mechanism and Rate Determining Step (RDS)	49
1.6.1.3.1.1. Variation of copper content, and reaction feedstock for the monometallic and alloy catalysts	49
1.6.1.3.2. Determination of reaction order, from variation of reaction feedstock and temperature	50
1.6.1.4. Mechanistic insights into copper as an epoxidation catalyst: DFT modelling, and in situ XPS studies of the nature of the copper-silver alloy catalyst surface.....	51
1.6.2. Furfural hydrogenation	52
1.6.3. Platinum catalysis and nanoparticles	53
1.6.4. Silver catalysts and nanoparticles	54
1.6.5. Palladium catalysis and nanoparticles	54
1.7. Aims of the thesis.....	55
1.8. Bibliography	56
Chapter 2. Methodology and experimental	79
2.1. Methodology.....	79
2.1.1. Transmission electron microscopy (TEM).....	79
2.1.2. Scanning electron microscopy (SEM)	80
2.1.3. X-ray photoelectron spectroscopy (XPS)	80
2.1.3.1. Quantification.....	81
2.1.3.2. Background fitting.....	82
2.1.4. Ultraviolet-visible (UV-vis) spectroscopy.....	82
2.1.4.1. UV-visible (UV-vis) spectroscopy for the elucidation of surface plasmon absorbance bands in metal nanoparticles.....	83

2.1.5. Raman spectroscopy underlying theory and practical considerations	83
2.1.5.1. Theory	83
2.1.5.2. Selection rules: gross and specific for vibrational Raman with comparison to infrared (IR) spectroscopy	85
2.1.5.2.1. Diatomics and polyatomics.....	86
2.1.5.3. Practical considerations: potential advantages and disadvantages of Raman spectroscopy in comparison to other in situ techniques.....	87
2.1.5.4. Total internal reflection (TIR) Raman spectroscopy	87
2.1.5.5. Fresnel coefficients and polarisation.....	89
2.1.5.6. CCD, edge filter, and diffraction gratings: design and considerations for Raman spectroscopy	90
2.1.5.6.1. Edge filters.....	90
2.1.5.6.2. Diffraction gratings.....	91
2.1.5.6.3. CCD.....	92
2.1.6. Langmuir Blodgett (LB) deposition techniques.....	92
2.1.6.1. Studying surface pressure with the LB trough.....	94
2.1.7. Mesoporous support synthesis	96
2.1.8. Plasma cleaning.....	97
2.2 Experimental	97
2.2.1. Nanoparticles/catalytic materials.....	97
2.2.1.1. Platinum/PVP nps.....	97
2.2.1.1.1. Preparation.....	97
2.2.1.1.2. Further Characterisation	98
2.2.1.2. Platinum/oleylamine nanoparticles (platinum/OAm nps).....	98
2.2.1.3. Cobalt/oleic acid nanoparticles (cobalt/OAc nps)	99
2.2.1.3.1. Oleylamine mass spectrometry and vacuum distillation	100
2.2.1.4. Silver/oleylamine/oleic acid nanoparticles (silver/OAm/OAc nps) synthesised from Ag perchlorate	100
2.2.1.5. Copper nanoparticles	101

2.2.1.5.1. Calculation of the amount of oleylamine capping agent required to give full coverage of copper surface	101
2.2.1.5.2. Standardised preparation	104
2.2.1.5.2.1. Reducing agent	105
2.2.1.5.2.2. Oleylamine and metal complexation	105
2.2.1.5.2.3. Full list all preparation conditions trialled	106
2.2.1.5.3. Silver nanoparticles from silver(I) acetylacetonate	106
2.2.1.6. Bimetallic silver and copper nanoparticles	106
2.2.1.6.1. List of preparation conditions used for bimetallic silver and copper nanoparticles	107
2.2.1.7. Copper nanoparticles doped with platinum to give a material with the following molecular structure of platinum _{0.18} copper ₁₅ /alumina	109
2.2.1.8. Palladium/oleylamine nanoparticles (palladium/OAm nps)	109
Palladium nanoparticles were synthesised from adaptation of the preparation from Mazumder and Sun,	109
2.2.2. Attempted purification of fluorescent species from polyvinylpyrrolidone	110
2.2.2.1. Purification-Soxhlet extraction	110
2.2.3. Catalyst supports	111
2.2.3.1. SBA-15 mesoporous silica	111
2.2.3.1.1. The synthesis of hierarchically ordered mesoporous-macroporous SBA-15	112
2.2.3.2. Cerium (IV) oxide mesoporous ceria	113
KIT-6 mesoporous silica preparation	113
Subsequent cerium (IV) oxide preparation	113
2.2.3.3. Supporting nanoparticles/ catalytic materials	114
2.2.3.3.1. Supporting of platinum and palladium nanoparticles upon bimodal ordered SBA-15	114
2.2.4. Raman and TIR Raman spectroscopy	115
2.2.4.1. System 1: 532 nm	115

2.2.4.1.1 Bulk Raman spectroscopy.....	116
2.2.4.2. System 2: 532 nm / 660 nm.....	116
2.2.4.3. System 3: TIR Raman spectroscopy at 660 nm	117
2.2.4.4. Bulk and TIR Raman spectroscopy: An overview of the Raman systems used and sample preparation	119
2.2.4.4.1. TIR Raman spectroscopy.....	119
2.2.4.4.2. Sample deposition using drop cast method	119
2.2.4.5. Cell design	119
2.2.4.6. Plasma cleaning of LB deposited monolayers of nanoparticles upon a silica hemisphere	121
2.2.5. Analytical/ characterisation techniques	122
2.2.5.1. ¹³ C and ¹ H, and ¹¹ B NMR.....	122
2.2.5.2. IR spectroscopy	122
2.2.5.3. Gas chromatography – mass spectrometer (GCMS).....	122
2.2.5.4. PXRD.....	123
2.2.5.5. XPS.....	123
2.2.5.6. UV–vis spectroscopy.....	123
2.2.5.7. ICP-OES.....	124
2.2.5.8. Nitrogen porosimetry measurements: BET, and BJH analysis	124
2.2.5.9. LB deposition of nanoparticles	124
2.2.5.9.1. Sample preparation and substrate cleaning	125
2.2.5.9.2. Experimental protocol	125
2.2.5.10. TEM	127
2.2.5.10.1. Microscope details	127
2.2.5.10.2. Sample preparation	128
2.2.5.10.3. Particle size analysis	128
2.2.5.11 SEM	129
2.2.5.11.1. Microscope details	129

2.2.5.11.2. Sample preparation	129
2.2.6. <i>In situ</i> studies and catalytic testing.....	129
2.2.6.1. Ethylene hydrogenation studied in situ using TIR Raman.....	129
2.2.6.2. Silver catalysts for amide bond synthesis	130
2.2.6.2.1. Synthesis of supported silver catalysts.	130
2.2.6.2.2. Calcination and reduction procedures for supported silver catalysts.	131
2.2.6.2.3. Direct dehydrogenative amide synthesis.....	133
2.2.6.2.4. Analysis of product stream by GC.....	135
2.2.6.3. Platinum doped copper catalysts for furfural hydrogenation	136
2.2.6.4. Palladium nanoparticles for use in hierarchical structured materials	137
2.3. Bibliography	138
Chapter 3. Nanoparticle synthesis, deposition, and initial studies by confocal and TIR	
Raman	143
3.1. Nanoparticle synthesis, for use in initial TIR Raman experiments.....	143
3.1.1. Platinum/polyvinylpyrrolidone nanoparticles (platinum/PVP nps) for proposed	
use as a hydrogenation catalyst	144
3.1.1.1. TEM imaging.....	144
3.1.2. Silver/oleylamine/oleic acid nanoparticles (silver/OAm/OAc nps) for proposed	
use as an epoxidation catalyst.....	145
3.1.2.1. TEM imaging.....	146
3.1.2.2. Investigation of the nature of the capping agent for silver/OAm/OAc nps	
3.1.2.2.1. TEM analysis of silver nanoparticle supernatant	153
3.1.3. Palladium/oleylamine nanoparticles (palladium/OAm nps).....	155
3.1.4. Investigation of oleylamine capping agent purity	156
3.2. LB trough deposition, of nanoparticles onto silicon wafers and silica hemispheres for	
bulk and TIR Raman spectroscopy.....	157
3.2.1. Platinum/PVP nps.....	158

3.2.1.1. TEM imaging of platinum/PVP nps deposited onto a TEM grid via LB trough methods	161
3.2.1.2. XPS investigation of platinum/PVP nps LB deposited onto substrates	162
3.2.1.3. SEM investigation of platinum/PVP nps method LB deposited onto substrates.....	166
3.2.2. Silver/OAm/OAc nps	167
3.2.2.1. TEM silver/OAm/OAc nps deposited via standard and LB trough methods	168
3.3. Confocal Raman studies of platinum/PVP nps	169
3.4. Polyvinylpyrrolidone characterisation and purification.....	174
3.4.1. ¹³ C and ¹ H nuclear magnetic resonance (NMR) spectroscopy	174
3.4.2. UV-visible (UV-vis) spectroscopy	175
3.4.3. Gel permeation chromatography (GPC) analysis.....	179
3.4.4. Soxhlet purification	181
3.5. Proof of concept detection of nanoparticle capping agent using TIR Raman spectroscopy	182
3.5.1. TIR Raman spectroscopic studies of platinum/PVP nps	183
3.5.2. TIR Raman studies of silver/OAm/OAc nps	185
3.5.3. TIR Raman studies of palladium/OAm nps	190
3.6. Development of plasma cleaning protocol for capping agent removal.....	193
3.6.1. Platinum/PVP nps	193
3.6.1.1. SEM investigation of LB deposited materials.....	195
3.6.2. Silver/OAm/OAc nps	196
3.6.3. Palladium/OAm nps	198
3.7. Conclusions	200
3.8. Bibliography	201

Chapter 4. Development of a synthesis procedure for copper/oleylamine/oleic acid

nanoparticles (copper/OAm/OAc nps)	205
4.1. Results and discussion - monometallic copper nanoparticles	205
Monometallic copper nanoparticles by solvent reduction method (no additional reducing agent)	206
Monometallic copper nanoparticles with additional reducing agent	206
Monometallic copper nanoparticles with complexation of the capping agent and metal precursor	207
4.1.1. Monometallic copper nanoparticles by solvent reduction method (no additional reducing agent)	207
4.1.1.1. Temperature and time variation	207
4.1.1.1.1. Temperature variation (1 h ripening time)	209
4.1.1.1.2. Temperature variation (10 min, and 30 min ripening times).....	214
4.1.1.1.2.1. Comparison with Mott <i>et al.</i> procedure	218
4.1.1.2. Capping agent investigation	220
4.1.1.2.1. Variation of oleylamine capping agent concentration.....	220
4.1.1.2.2. Variation of capping agent: using combination of oleylamine and oleic acid	224
4.1.1.2.3. Comparison of oleylamine and octadecylamine capping agents	227
4.1.2. Monometallic copper nanoparticles by use of a separate reducing agent	230
4.1.2.1. Morpholine borane reducing agents	230
4.1.2.1.1. Mechanistic studies of morpholine borane reducing agent <i>via</i> DSC and ¹¹ B nuclear magnetic resonance (NMR) spectroscopy	234
4.1.2.1.2. Morpholine borane reducing agent with octadecylamine capping agent	237
4.1.2.2. 1,2-tetradecandiol reducing agent	241
4.1.3. Infrared (IR) studies into the role of pyridine in the reduction of copper(II) acetylacetonate.....	244
4.2. Results and discussion - bimetallic copper/silver nanoparticles.....	247

4.2.1. Silver nanoparticles from optimised copper nanoparticle conditions	247
4.2.2. Bimetallic copper/silver nanoparticles	248
4.2.3. Further characterisation.....	251
4.2.3.1. Ultraviolet-visible (UV-vis) spectroscopy.....	251
4.2.3.2. ICP-OES analysis	255
4.2.4. Chapter 4 conclusions	256
4.3. Bibliography	257

Chapter 5. *In situ* studies of ethylene hydrogenation using total internal reflection (TIR)

Raman spectroscopy	263
5.1. Ethylene hydrogenation	263
5.1.1. Calculation for variation of reaction conditions upon proportion of free and absorbed molecules probed.....	263
5.1.2. Ethylene hydrogenation studies over a platinum/polyvinylpyrrolidone nanoparticle (platinum/PVP np) catalyst	265
5.2. Raman setup, alignment and testing.....	271
5.2.1. White light and neon lamp calibrations	273
5.3. TIR Raman spectroscopic investigations using System 3	275
5.3.1. Reference spectra: Bulk spectra of capping agents	275
5.3.1.1. Comparison of bulk and drop cast spectra: dodecanethiol	276
5.3.2. Sensing nanoparticles: <i>ex situ</i>	279
5.3.2.1. Transmission electron microscopy (TEM) imaging and particle size analysis of cobalt nanoparticle system	279
5.3.2.2. TIR Raman spectroscopic results	280
5.3.3. Plasma cleaning of platinum/OAm nps	285
5.3.4. Sensing nanoparticles: <i>in situ</i>	286
5.3.4.1 Blank hemispheres with gas feeds	286
5.3.4.2. In situ measurements for plasma cleaned platinum/OAm nps	287

5.4. Conclusions and future work.....	288
5.5. Bibliography	289
Chapter 6. Catalytic applications of supported nanoparticle systems	292
6.1. Silver nanoparticles for amide bond synthesis, kinetics and reaction data	292
6.1.1. Catalytic testing of the reaction of two differing amines with benzyl alcohol for the direct creation of an amide bond.....	292
6.1.2. The investigation of silver nanoparticle catalysts for use in the direct formation of an amide bond from reaction of benzyl alcohol and piperidine	304
6.2. Furfural hydrogenation using platinum and copper Single Atom Alloys (SAAs)	310
6.2.1. Introduction	310
6.2.1.1. Early work of Single Atom Alloys (SAA), using low-temperature scanning tunnelling microscopy (LT-STM) and Density function theory (DFT) computational modelling	312
6.2.1.2. Scanning tunnelling microscopy (STM), temperature programmed desorption (TPD) spectroscopy and initial catalytic studies for further understanding of the SAA	312
6.2.1.3. Development of the SAA strategy for the synthesis of a heterogeneous hydrogenation catalyst for use under more realistic operating conditions.....	313
6.2.1.4. Synthesis of copper-platinum SAA type catalysts by GR.....	314
6.2.2. Characterisation of copper nanoparticles with small amounts of platinum.....	314
6.2.2.1. TEM imaging of supported and un-supported platinum and copper Single Atom Alloys (SAAs).....	314
6.2.2.2. ICP-OES analysis of platinum and copper Single Atom Alloys (SAAs).....	315
6.2.2.2.1. ICP-OES for platinum ₁ copper ₈₃ nanoparticles	315
6.2.2.3. Catalytic testing of supported platinum and copper Single Atom Alloys (SAAs).....	318
6.3. Palladium nanoparticles for use in hierarchical structured materials	319

6.3.1. TEM of palladium nanoparticles.....	320
6.3.2. ICP-OES of palladium nanoparticles	321
6.3.3. Catalytic data from application of palladium nanoparticles.....	321
6.4. Conclusions	323
6.5. Bibliography	324
Overall conclusions	331
Future work.....	334
Bibliography.....	337
Appendix: Chapter 1	339
The calculation of probing distances for infrared (IR) and Raman spectroscopy	339
Appendix: Chapter 3	340
Calculation of the amount of oleylamine capping agent required to give full coverage of the silver surface.....	340
Langmuir Blodgett (LB) trough deposition, of nanoparticles onto silicon wafers or silica hemispheres for bulk and total internal reflection (TIR) Raman spectroscopy	342
X-ray photoelectron spectroscopy (XPS) investigation of platinum/polyvinylpyrrolidone nanoparticles (platinum/PVP nps) LB deposited onto substrates	343
Pt/PVP np and polyvinylpyrrolidone in ethanol concentration calculation.....	358
Polyvinylpyrrolidone characterisation and purification: Nuclear magnetic resonance (NMR) spectroscopy.....	360
Bibliography	362
Appendix: Chapter 4	363
Full list all preparation conditions trialled.....	363

Inductively coupled plasma-optical emission spectrometry (ICP-OES)	370
Appendix: Chapter 5	371
Total internal reflection (TIR) Raman spectra recorded for platinum/polyvinylpyrrolidone nanoparticle (platinum/PVP np) samples both before and after plasma cleaning	371
TIR Raman spectra for platinum/oleylamine nanoparticles (platinum/OAm nps) taken at the beginning (the first 50 frames of data) and towards the end of the exposure (the last 50 frames)	373
Division spectra for TIR Raman spectroscopy of monolayer deposited nanoparticle samples	374
Sensing nanoparticles <i>in situ</i> , blank hemispheres with gas feeds unprocessed data	375
Appendix: Chapter 6	376
KIT-6 X-ray diffraction (XRD)	376
Worked calculation-response factor and yield calculations	377
Effective carbon number (ECN) for products and internal standard	377
Response factors for products	377
Amount of product measured by gas chromatography (GC).....	377
Bibliography	378