

THE APPLICATION OF ORGANICALLY MODIFIED HETEROGENEOUS CATALYSTS IN CONTINUOUS FLOW HYDROGENATION REACTIONS

by

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and Science which requires the thesis to be formatted:*

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As the candidate's supervisor I have approved this thesis for submission

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SYNOPSIS OF THE THESIS

This thesis is written as a series of original research articles which have either been published, submitted for publication, or prepared as a manuscript for submission for publication. Each paper has its own abstract, introduction, experimental section, results and discussion as well as tables, figures and schemes.

Chapter 1 gives an overall introduction to catalysis and its importance, including examples of industrial processes and methods of catalyst deactivation and modification. It ends off with a discussion on ionic liquids and its potential application as modifiers to traditional heterogeneous catalysts.

Chapter 2 explores the applicability of ionic liquids as nickel catalyst modifiers in the competitive hydrogenation between 1-octene and 1-octyne, as well as 1,7-octadiene and 1-octyne under trickle bed conditions. It also proposes potential reasons for the effects observed with these catalysts.

Chapter 3 expands on the catalytic work presented in Chapter 2 on the competitive hydrogenation between 1-octene and 1-octyne. It also discusses the problems associated with *ex situ* prepared catalysts intended for modification by ionic liquids and attempts to provide reasons (derived from surface studies) for the encountered problems.

Chapter 4 discusses the application of ionic liquid modified palladium catalysts in the competitive hydrogenation between 1-octene and octanal in comparison to palladium catalysts modified by traditional nitrogen containing organic modifiers. It also explores some of the surface properties of these catalysts and attempts to relate them to catalyst performance.

Chapter 5 discusses the application of ionic liquid modified copper catalysts in the competitive hydrogenation between 1-octene and octanal, in comparison to a strongly discriminating silver catalyst and copper catalysts modified by traditional nitrogen containing organic modifiers. A discussion on some of the surface properties of these catalysts is also included.

Chapter 6 is a summary of the prepared original research papers and discusses some of the more speculative reasons for the phenomena observed with the different catalytic systems. It ends off with a short discussion on the potential future of ionic liquid modified catalyst research.

Chapter 7 is a final conclusion of the results obtained from the investigation.

PREFACE

All catalytic work and the majority of the characterisation studies were carried out at the School of Chemistry & Physics, University of KwaZulu-Natal, Westville Campus under the supervision of Professor Holger B. Friedrich. XPS analysis was carried out at the National Metrology Institute of South Africa. Some of the HRTEM analysis of nickel catalysts was carried out at the *National Centre for High Resolution Electron Microscopy; NMMU*. Additionally, some IR and TGA-DSC analysis was conducted at the Department of Chemistry, University of Johannesburg, Kingsway Campus.

The research in this thesis embody original work by the author and have not otherwise been submitted in any form, degree or diploma to any national or international tertiary institution. Where use has been made of the work by others, it is referenced in the text.

DECLARATION 1 - PLAGIARISM

I, Stuart Frank Miller, declare that

1. The research reported in this thesis, except where otherwise stated, is my original research.
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DECLARATION 2 - PUBLICATIONS

Publication 1: The effects of SCILL catalyst modification on the competitive hydrogenation of 1-octyne and 1,7-octadiene versus 1-octene. First Author: Stuart F. Miller, Other Authors: Holger B. Friedrich and Cedric W. Holzapfel. Published in ChemCatChem: **2012**, 4, 1337-1344

Publication 2: Activity and selectivity of a nickel SCILL catalyst in the competitive hydrogenation between 1-octene and 1-octyne. First Author: Stuart F. Miller, Other Authors: Holger B. Friedrich and Cedric W. Holzapfel. Submitted for publication.

Publication 3: Effects of organic modifiers on a palladium catalyst in the competitive hydrogenation of 1-octene versus octanal. First Author: Stuart F. Miller, Other Authors: Holger B. Friedrich and Cedric W. Holzapfel. Prepared manuscript for submission.

Publication 4: First Author: Stuart F. Miller, Other Authors: Holger B. Friedrich and Cedric W. Holzapfel. Prepared manuscript for submission.

Contributions by co authors:

Paper 1: co authors provided research advice

Paper 2: co authors provided research advice

Paper 3: co authors provided research advice

Paper 4: co authors provided research advice

Excluding the contributions of people/organisations acknowledged, the author of this thesis conducted all the experimental work (i.e. reactor and associated electronics construction as well as catalysis/data collection/interpretation).

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LIST OF ABBREVIATIONS

BET	Brunauer, Emmet and Teller
BJH	Barrett, Joyner and Halenda
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
GC-FID	Gas Chromatography - Flame ionisation detection
GHSV	Gas hourly space velocity
GSV	Gas space velocity
HAAD	High angle annular dark field
HRTEM	High resolution transmission electron microscopy
ICP-OES	Inductively coupled plasma - optical emission spectroscopy
JCPDS	Joint committee on powder diffraction standards
LHSV	Liquid hourly space velocity
LSV	liquid space velocity
NEXAFS	Near edge X-ray absorption fine structure
NMR	Nuclear magnetic resonance
SCILL	Solid catalyst with an ionic liquid layer
SILP	Supported ionic liquid phase
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TGA-DSC	Thermal gravimetric analysis - differential scanning calorimetry
TGA-DSC-MS -	Thermal gravimetric analysis - differential scanning calorimetry mass spectrometry
TPR	Temperature programmed reduction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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CHAPTER 1

THE IMPORTANCE OF CATALYSIS, CATALYST DEACTIVATION AND MODIFICATION, AND THE ROLE OF IONIC LIQUIDS: A BRIEF LITERATURE SURVEY

1.1 The Importance of Catalysis: an Overview

The modern definition of a catalyst describes the catalyst as a substance that increases the rate of a reaction without itself being consumed in that reaction.^[1] In effect a catalyst lowers the activation energy by providing an alternative pathway which avoids the rate-limiting step of the reaction.^[2]

Human knowledge in the use of catalysis dates back to around the origin of civilisation, through the use of fermentation to produce alcohol. However, it was only in 1835 that a formal definition of a catalyst was given.^[1] Modern catalysis began to emerge in the early 1800's with demonstrations of catalytic activity by metals such as platinum^[3] and processes such as the Schtitzbach quick vinegar method.^[1] Catalytic knowledge was further enhanced by the development of the Fischer-Tropsch,^[4] Haber-Bosch^[5] and Wacker^[6] processes and investigations into these reactions which produced, for example, the hydroformylation or “oxo” process (Fischer-Tropsch research).^[7]

One noticeable aspect about catalysts is in their physical nature compared to the substrates intended for reaction. A catalyst can be in the same phase as the reactants and thus be homogeneous, or in a different phase and exist as a heterogeneous catalyst. The two different types of catalysts have distinct advantages and disadvantages compared to each other. Examples of which can be seen in Table 1.^[8]

Table 1. Properties of homogeneous and heterogeneous catalysis.

Property	Homogeneous Catalysis	Heterogeneous Catalysis
Activity (rel. to metal content)	High	Variable
Selectivity	High	Variable
Reaction conditions	Mild	Harsh
Service life of catalyst	Variable	Long
Sensitivity towards poisons	Low	High
Diffusion problems	None	High
Catalyst recycling	Expensive	Relatively unnecessary
Catalyst property optimisation	Possible	Limited

As can be seen, the use of homogeneous catalysts in general has a noticeable advantage over heterogeneous catalysts, except in catalyst recycling and service life. These two parameters are often highly desirable and as a result, heterogeneous catalysis is the preferred option in bulk chemical synthesis of commodity chemicals and refinery processes. Indeed, approximately 75% of all catalytic processes occur by heterogeneous catalysts.^[9]

Since the early use of fermentation, the chemical industry has broadly developed into five main areas which all utilise heterogeneous and/or homogeneous catalysts. These are: refining, petrochemical, polymer, environmental and pharmaceutical.^[9] In 2001 alone, the world wide merchant catalysis market was estimated to be worth 25 billion US dollars, with 20-25% of the value each belonging to: refining, petrochemical, polymer and environmental, with approximately 11% belonging to the pharmaceutical catalytic market.^[9]

However, the worth of catalysts cannot be judged alone on its worldwide annual value of sales. The value of the product it produces must also be taken into consideration, as the product of many of these processes would either be impossible to produce, expensive or even economically unviable without the application of catalysts. For example, the refining of crude oil into petrol (which accounts for an annual production in the region of a billion tons) has an approximate yield of 50 % thanks to improvements in the refining processes including catalytic cracking.^[9,10] It is easy to see that without these improvements, the cost of petrol production would be much higher. An additional example is with the polymerisation of alkenes, where the original methodology used a radical catalysed process to produce linear low density polyethylene. This process used severe conditions (3000 bar, 200 °C) which greatly contributed to the cost of

production.^[11] The discovery of Ziegler-Natta catalysts strongly reduced this cost due to the mild conditions required for the polymerisation of alkenes (1 bar, 25 °C).^[11] Furthermore, a greater variability and quality of polymerised product are also possible with these catalysts, allowing for fine tuning of the polymer to meet specifications required by consumer demands. These vary from highly flexible polymer materials such as for food wrapping and plastic bags to relatively hard and durable material for plumbing and electrical conduits.^[11]

Sometimes the value of a catalytic process (as a result of the application of the product it produces) is more difficult to quantify; such as the emotional value placed on the increased standard of living and/or life expectancy brought about by an affordable pharmaceutical product. Moreover, the catalytic process responsible for the affordable nature of the pharmaceutical may not necessary lie in one of the final steps in its production, as the main chemical areas tend to lead into each other. For example, refineries produce the raw materials for the petrochemical industries, which in turn provide the basic commodity chemicals used for the synthesis of fine chemicals. Indeed, optimisation of a catalytic process in the final steps of synthesis of a pharmaceutical might not be economically worthwhile, as it may only represent a fraction of the cost of production. This is especially so if the volume of the pharmaceutical produced is small.^[9]

On the other hand, due to the volume of product produced by refinery and petrochemical industries, even a small increase in the performance of a catalyst can translate into an economic advantage, enlarging profit margins. These slight improvements on catalytic performance in these industries form the basis of research into catalyst modification. However, performance increases of existing catalytic reactions are not the only area open to catalytic improvements. Research into producing a valuable commodity chemical from a different feedstock (i.e. one that is at least as cheap and readily available) can have a dramatic effect. For instance, the production of acrylonitrile initially occurred by the relatively expensive catalytic addition of hydrogen cyanide to ethylene and the ethylene cyanohydrin process before the Standard Oil of Ohio company discovered the ammoxidation of propene in ca. 1960.^[12] Today acrylonitrile is almost exclusively produced by this process.

Although the optimisation of an existing catalytic reaction or even the development of a new one can be attractive methods of increasing the profits of a process, developing catalysts for ancillary cost reduction are an alternative means of increasing the economic attractiveness of the process. For example, if a catalyst has been optimised for the production of a certain product but

does, however, catalyse small amounts of undesirable side product, then development of a different catalyst for the removal of the side product can be attractive, as this may lead to the production of a far more valuable chemical. This is exemplified in the production of terephthalic acid (PTA), whereby the process used in the oxidation of *p*-xylene PTA can form small amounts of 4-carboxybenzaldehyde as by-product.^[9,13] 4-Carboxybenzaldehyde is known to interfere in the polymerisation of terephthalic acid with ethylene glycol to form poly-ethylene terephthalate (PET, commonly found as plastic bottles) by inducing premature chain termination.^[9,14] To overcome this, the product feed containing 4-carboxybenzaldehyde is hydrogenated with a palladium catalyst to form 4-methylbenzoic acid, which aids in the purification process.^[9,15]

Ultimately the success of a catalytic process also depends on several additional aspects. These include the thermodynamic and kinetic feasibility of the reaction investigated and the total economic viability. Evaluation of the thermodynamic feasibility is one of the initial steps in determining if the catalytic reaction is worth pursuing and one of the thermodynamic properties investigated is the change in Gibbs free energy of the reaction or ΔG_0 , which essentially determines the relative extent between concentrations of product and reactant. In general, if a free energy of around + 40 kJ/mol or greater is found, the reaction is not deemed practical enough to pursue as the equilibrium concentrations would be too far in favour of the reactants.^[9] However, as $\Delta G = \Delta H - T\Delta S$, altering the temperature of the process may bring the free energy into a favourable range. Nevertheless, the kinetic rate caused by the catalyst is also dependant on the temperature and it is not uncommon where a compromise temperature needs to be found where both the kinetic rate and free energy are acceptable. An example of this occurred with the hydrogenation of carbon monoxide to methanol by a (now obsolete) $\text{ZnO-Cr}_2\text{O}_3$ catalyst.^[9,16] The catalyst required a high temperature (327 °C) for an acceptable conversion but the free energy at this temperature is 45 kJ/mol. Consequently, the process ran at high pressures of the reactants to "force" the production of methanol^[9]

In addition to this, the enthalpy of the reaction needs to be considered to determine the energy cost of supplying or effectively removing heat, as both exothermic and endothermic processes occur. Indeed, the total cost around the catalytic process needs to be evaluated for economic viability, such as: the variable nature in the price of feedstock and utilities, the cost of construction and maintenance of the reactor and associated plant components (a catalyst requiring harsh and/or corrosive environments will require a more expensive reactor and plant components) and the cost of reactant/product delivery as liquids/solids are easier to transport

than gasses. This is all in addition to the traditional financial considerations such as the return on capital/investment.

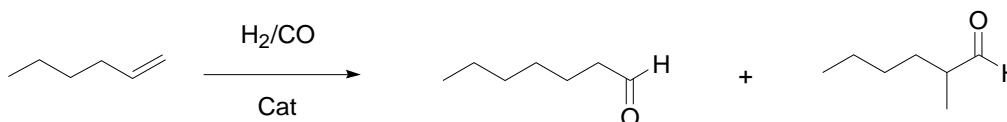
These financial considerations highlight the importance of an in-depth understanding of the catalytic reaction, especially in the refinery and commodity chemicals sector where slight improvements can increase profits and/or reduce costs. In general, the elucidation of a catalytic reaction begins with an empirical investigation, where a potential catalyst is added to set reactants with the hopes of producing a desired product. If successful, the conditions of the reaction are varied to determine the primary performance ranges for the reaction. These include parameters such as temperature, pressure and concentration. Further investigations lead to speciation determination and their interrelated kinetics, which begin to reveal a mechanistic catalytic cycle. This is the beginning point for reaction modelling, which may provide supplementary insights. However, the path from preliminary investigations to mechanistic understanding is tedious, as, in general, only one variable at a time is altered to reveal potential factors. Furthermore, the conclusions drawn from an investigation can be contested. This is especially so with heterogeneous catalysis, as surface species elucidation and kinetics, as well as the factors affecting them, are far more difficult to directly identify than for homogeneous catalysis. As a result, homogeneous processes are generally better understood. Examples of industrial homogeneous and heterogeneous catalysis relevant to the refinery and commodity chemical sectors are now briefly discussed.

1.1.1 Examples of industrial homogeneous catalysis

A few homogeneous catalysis reactions are currently used on a large scale in industry. Most notably are: the rhodium catalysed acetic acid process with capacities in the region of 1200 kilo-tons of acetic acid per year, the rhodium and cobalt hydroformylation reactions with ca. 3700 and 2500 kilo-tons of aldehyde respectively per year, the SHOP ethylene oligomerisation process with a capacity of ca. 870 kilo-tons of product per year and the hydrocyanation reaction with a capacity of approximately 1000 kilo-tons of product per year.^[17] A brief explanation of these processes and their mechanisms follow.

1.1.1.1 *The Hydroformylation reaction*

The hydroformylation reaction is an elegant process whereby an alkene is reacted with carbon monoxide and hydrogen to form an aldehyde with a one carbon extension to the molecule.^[18] The two main metals used in this industrial catalysis reaction are cobalt and rhodium.^[17] With linear alkenes, both linear and branched products, according to Scheme 1, are possible.^[19]



Scheme 1. Potential reaction products of the hydroformylation reaction.

Each metal has a specific advantage over the other depending on the nature of the alkene used in the reaction. In general, long chain internal alkenes are hydroformylated using cobalt. This is due to the cobalt process having a higher selectivity towards linear products as well as resistance to catalyst degradation (occurring as a result of higher temperatures needed to remove long chain products from the reaction medium). Catalyst degradation is also financially more tolerable with cobalt based catalysts than rhodium catalysts.^[20-22] Cobalt also has the propensity to produce alcohols (hydrogenation of the aldehyde) whereas rhodium generally produces only the aldehyde.^[20-22] The proposed general mechanism for CO ligated cobalt hydroformylation is shown in Figure 1.^[7,23,24]

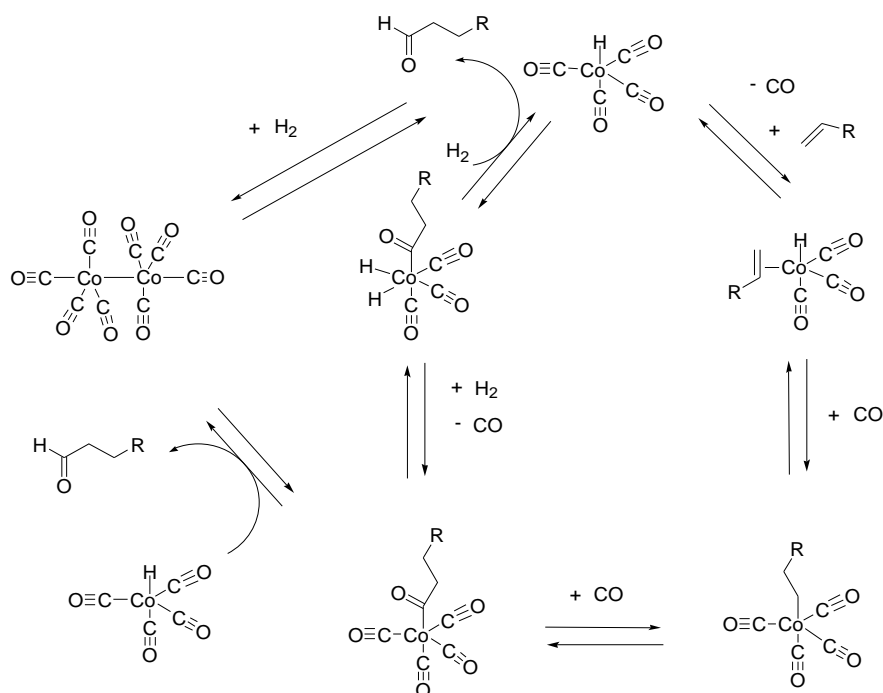


Figure 1. A proposed general mechanism for CO ligated cobalt hydroformylation.

Originally, no ligands apart from CO were used in this reaction, however, it was found that by the addition of electron rich trialkylphosphines such as tributylphosphine, the selectivity of the reaction to linear aldehydes could be increased.^[25] In addition to this, the phosphine ligand stabilises the catalyst preventing cobalt metal deposition, however, due to the relative cheapness of the metal and higher activity with increased temperature, the benefits of this are somewhat mitigated.^[25]

Phosphine ligands nevertheless feature quite prominently in rhodium catalysed hydroformylation reactions. Rhodium hydroformylation has in general, greater activity than cobalt hydroformylation; however, it suffers from decreased selectivity and activity to linear products from long chain internal alkenes. This coupled with the high cost of rhodium usually direct its application to smaller alkenes such as ethene, the products of which being easier to separate by distillation from the catalyst.^[20-22] Phosphorous based ligands in rhodium hydroformylation have exhibited the ability to prevent metal deposition as well as dramatically alter the linear to branched ratio and even the ability to induce asymmetric catalysis.^[25-27] To aid

in explanation, the proposed mechanism of ethene hydroformylation with triphenylphosphine as a ligand is presented in Figure 2.^[26]

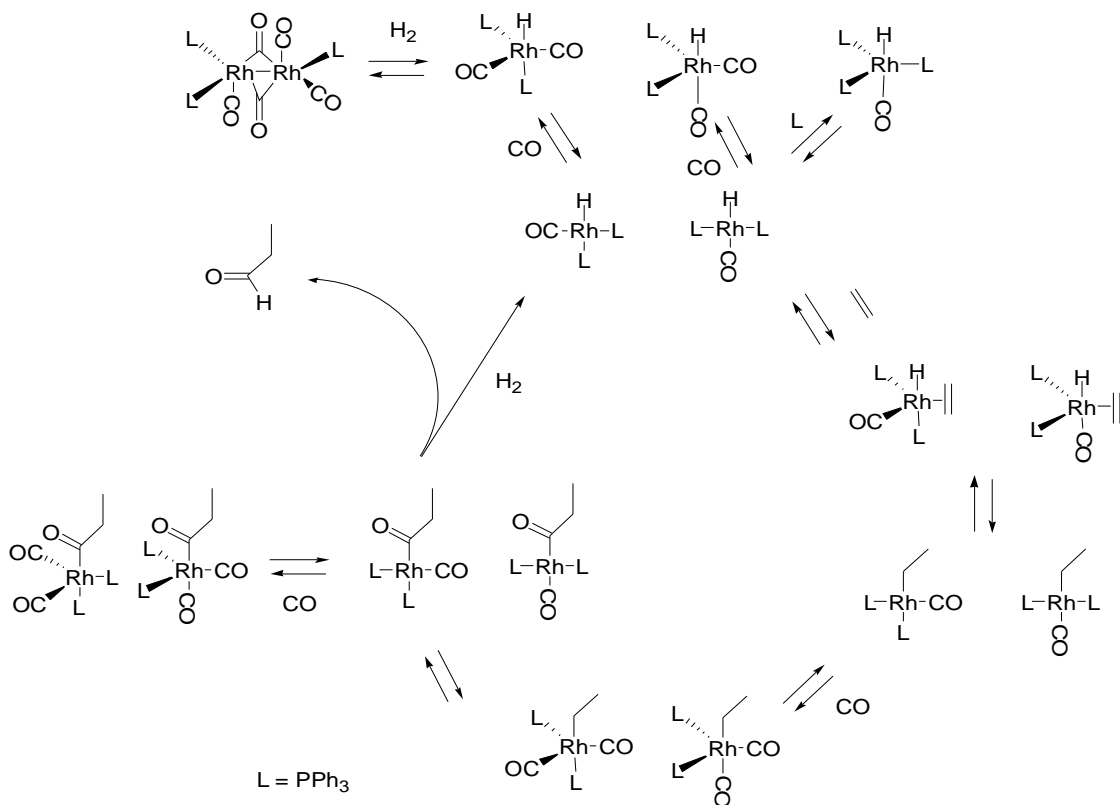


Figure 2. A proposed mechanism for rhodium catalysed hydroformylation of ethene with PPh₃.

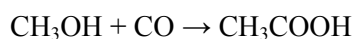
An in-depth review of the potential reasons for the altered ratios of the linear to branched products and other effects by phosphorus based ligands have been conducted by P.W.N.M van Leeuwen and others.^[27] The general consensus of the effects of ligand interaction with the rhodium catalyst are the following:

- Electron withdrawing phosphines increase the activity of the reaction as a result of decreased electron density on the rhodium atom. This weakens the metal CO bond and increases the rate of CO loss which is considered the rate determining step.

- Bidentate ligands of a certain range of bite angle preferentially occupy the bis-equatorial configuration of the rhodium complex (Figure 2), which is responsible for the increased linear product ratio.
- The steric constraints of the chiral phosphorous based ligands influence the stereo-specific insertion of carbon monoxide and hydrogen.

1.1.1.2 *Acetic Acid Production*

With a worldwide demand for acetic acid in the region of 10 million tonnes,^[28] several artificial methods for its synthesis has been developed. Traditionally the synthesis of acetic acid has relied on the aerobic fermentation of ethanol. However, with the abundant supply of fossil fuel based hydrocarbons, such as methanol from synthesis gas and CO from natural gas, catalytic carbonylation of methanol has become economically viable (Scheme 2).



Scheme 2. The carbonylation of methanol.

Several different metals have been employed as catalysts, notably from group VIII transition metals.^[28,29] The first commercial process used a cobalt catalyst promoted with iodine.^[29] The iodine is required for the formation of methyl iodide which is further carbonylated.^[30] This prevents the CO insertion into the O-H bond of methanol. A proposed reaction cycle is shown in Figure 3.^[29]

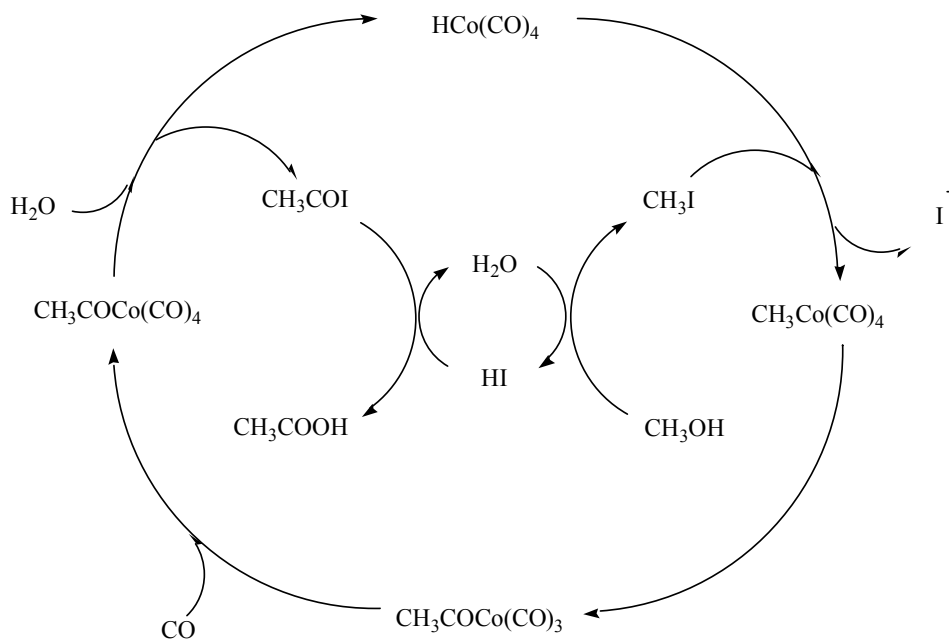


Figure 3. The proposed reaction cycle of cobalt catalysed methanol carbonylation.

Although the cobalt based synthesis of acetic acid has seen application in an industrial setting with up to 90% selectivity to acetic acid, the process requires relatively high temperatures and pressures in the region of 230 °C and 600 bar.^[29] These harsh conditions can potentially be overcome by a nickel based catalyst with high concentrations of iodine and the presence of stabilising compounds such as phosphines and other metals such as tin.^[29] However, Ni(CO)_4 is a toxic compound and the process has not seen commercialisation.^[29] A milder process involving rhodium has seen commercialisation and is known as the Monsanto acetic acid process.^[28,29,31] This process requires conditions in the region of 45 bar CO and 175 °C and has methanol carbonylation selectivities up to 99%.^[31] Iodine is still used as a promoter, however, ligand addition (such as phosphines) to this process has resulted in an increased rate of reaction.^[29] This is thought to occur by the increased electron density on the rhodium atom (from the phosphines complexed in a trans position) increasing the rate of oxidative addition of methyl iodide, which is the rate determining step (Figure 4).^[29,31,32]

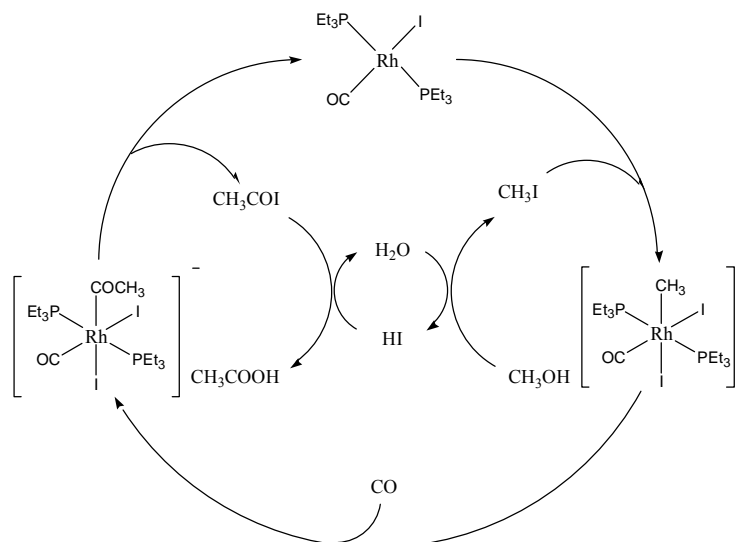
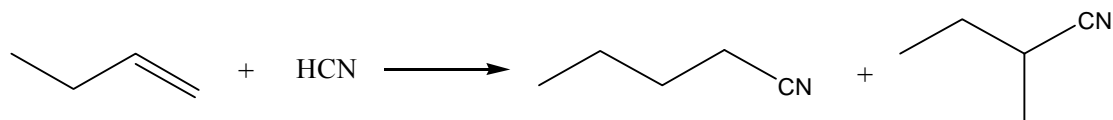


Figure 4. The reaction cycle for the rhodium catalysed methanol carbonylation.

In addition to the rhodium catalysed process, an iridium based process has also seen commercialisation and is known as the Cativa process.^[31] This process offers the advantage of increased catalyst stability in comparison to the rhodium analogues.^[29] However, the rate is slower but does become comparable with the addition of promoter metals such as ruthenium.^[29] These iridium based catalysts exhibit higher solubility than rhodium catalyst in the reaction medium and therefore higher rates may be achieved due to increased catalyst concentrations.^[29] This is especially so if lower concentrations of iodine are used, as the oxidative addition of methyl iodide is no longer the rate determining step. Instead, the rate of CO replacement of ligated iodine is the limiting factor.^[31]

1.1.1.3 Hydrocyanation

In many ways, hydrocyanation is similar to hydroformylation. Both involve the reaction of a terminal alkene with hydrogen and a functionalised carbon atom. Like hydroformylation, hydrocyanation can result in a linear or branched product (Scheme 3).



Scheme 3. The potential products of 1-butene hydrocyanation.

Commercially, DuPont's manufacture of adiponitrile occurs by this process, whereby butadiene is reacted twice with hydrogen cyanide.^[33-35] The product can be further reacted to form nylon 6,6. In addition to this, nitriles are valuable precursors in the synthesis of esters, isocyanates, amides, amines and carboxylic acids.^[35] The process typically involves a nickel complex with phosphines, phosphonites, phosphinites and phosphites.^[35] A proposed mechanism can be seen in Figure 5.^[35-38]

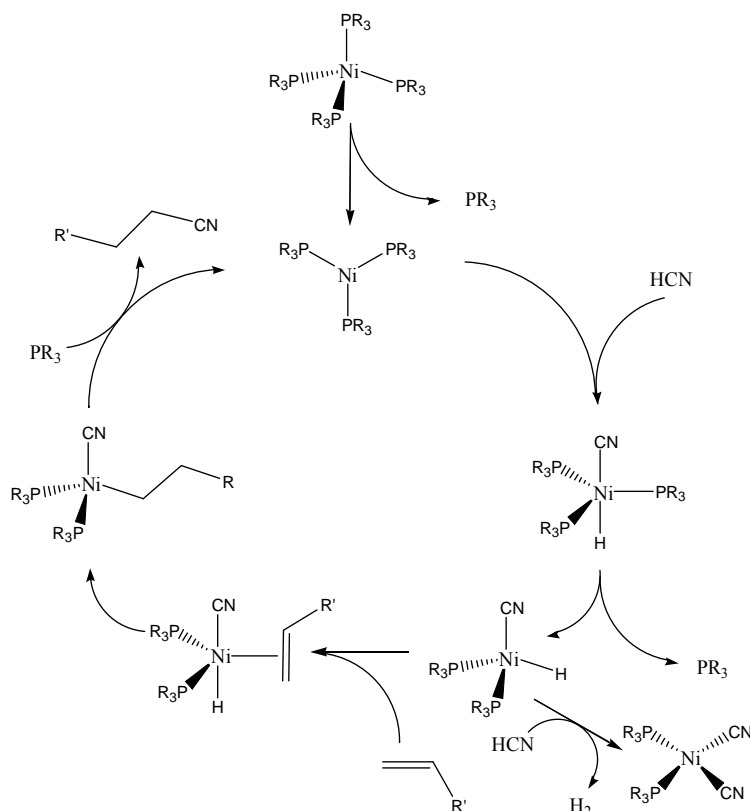


Figure 5. A proposed reaction mechanism for the hydrocyanation process.

As with the hydroformylation reaction, control over the regio-selectivity is desirable.^[35] To this effect, several different ligand types and designs have been employed to achieve an excess of linear or branched products. This is often effected by modifying the steric parameters of the ligand, which is generally measured by the cone angle, bite angle in the case of bidentate ligands and the solid angle (the area projected by the ligand on a unit sphere, measured in steradians Ω).^[39] For example, an increased regio-selectivity to linear product has been shown with bidentate phosphine ligands with a bite angles in the region of 101-131 °.^[39] In addition to this, the electronic parameter “ χ ” of the ligand can play a major role in the rate of the reaction, as the rate determining step is believed to be the reductive elimination to form the nitrile molecule.^[39] Therefore ligands with increased electron withdrawing capacity tend to accelerate the reaction.

1.1.1.4 Shell Higher Olefin Process

In addition to the nickel catalysed methanol carbonylation and hydrocyanation reactions, the Shell Higher Olefin Process (SHOP) uses a nickel phosphine complex for olefin metathesis.^[40] A typical catalyst can be seen in Figure 6.^[41] In this process, ethelene is oligomerised by the nickel catalyst to form a mixture of linear even numbered α -olefins ranging from C₄-C₄₀ with a Schulz-Flory type of distribution.^[42] The C₆-C₁₈ olefins are removed by distillation for use in the formation of a number of different products such as detergents, lubricants, plasticisers and fatty acids.^[42] The remaining higher and lower fractions are further purified and undergo isomerisation to form internal olefins for cross metathesis.^[42] The cross metathesis reaction produces a range of odd and even linear internal olefins which are separated by distillation.^[42] The C₁₁-C₁₄ alkenes are kept for further reactions, while the remainder are recycled again for the cross metathesis reaction.^[42]

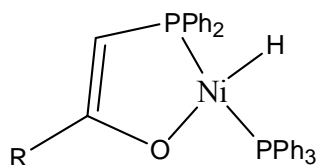


Figure 6. A typical catalyst used in the Shell Higher Olefin Process.

As the initial oligomerisation reaction is effected by a complex nickel phosphine catalyst (Figure 6), fine tuning of the catalyst performance is possible by several parameters. These included the character of the backbone in the chelating P, O, molecule, the nature of the R group and the nature of the phosphine amongst others.^[41] For example, since the non-cyclised phosphine ligand is replaced by ethylene during the oligomerisation steps, it therefore stands to reason, experimental evidence that a strongly binding phosphine ligand in high concentrations will result in reducing the rate to oligomerisation and thus a shift in the distribution of olefins to shorter chain lengths.^[43]

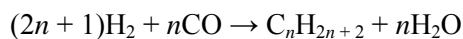
This brief overview of some of the well known homogeneous reactions highlight a few interesting aspects of homogeneous catalysis. In particular, modifications of the catalyst by altering the supporting ligands can dramatically enhance the selectivity and/or activity of the reaction to very high enantiomeric/regio-specific excess, turn over frequency (TOF) and turn over numbers (TON). However, as mentioned previously, the relative lifetime of homogeneous catalysts can be short in comparison to heterogeneous catalysts, and separation of homogeneous catalysts from the product is more problematic. These two aspects are of significant importance in commercial applications, especially with the synthesis of commodity chemicals. As a result, heterogeneous catalysis is often desirable and many economically important chemicals are produced by it. A few examples of heterogeneous catalysis are described below.

1.1.2 Examples of industrial heterogeneous catalysis

1.1.2.1 Fischer-Tropsch Process

The Fischer –Tropsch reaction is used for the production of hydrocarbons from synthesis gas ($2\text{H}_2:\text{CO}$). First described in 1926,^[44] the reaction has typically been industrially applied in conditions where oil availability has been relatively limited, for example, by Germany during WW2 as a result of limited access to oil, and the South African Republic as a result of oil sanctions and the availability of cheap domestic coal.^[45,46] However, with the dwindling supply of oil and the relative abundant supply of coal and natural gas, the process is becoming more important in the supply of liquid hydrocarbons.^[46] Several metals are active in this process, namely iron, cobalt, nickel and ruthenium.^[45,46] The reaction generally occurs by the adsorption of CO and H_2 onto the metal surface, followed by reduction of CO and oligomerisation. Chain

growth occurs with the formation of water and a desorption step produces the oligomerised hydrocarbon, according to Scheme 4.^[47]



Scheme 4. Oligomerisation of syngas by the Fischer-Tropsch process.

Although nickel and ruthenium are active for Fischer-Tropsch synthesis, the high cost of ruthenium and the ease of catalyst deactivation with nickel have prevented these metals from being used in industrial settings.^[46] Iron and cobalt catalysts, however, have seen considerable commercial implementation. For example, iron based catalysts have been used for the production of light olefinic hydrocarbons by SASOL's high temperature Fischer-Tropsch process.^[48] Indeed, at least 6 million tonnes per annum of light olefinic hydrocarbons (C₂-C₇) can be produced by SASOL with iron based catalysts.^[46] However, the iron based catalysts do require the addition of an alkali metal (e.g. K₂O) for high activity and stability, copper for ease of reduction, manganese for increased selectivity to olefins, as well as potential structural promoters such as alumina or silica.^[46]

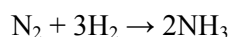
In addition to high temperature iron based Fischer-Tropsch reactions, low temperature versions are used to produce paraffin waxes. These waxes can be cleanly cracked for the production of high quality diesel fuel low in sulphur.^[46] Indeed, the temperature of the reaction strongly influences the molecular weight distribution of the hydrocarbons, typically governed by an Anderson-Schulz-Flory type distribution.^[45]

Although iron based catalysts are effective at producing linear α -olefins, they do suffer from increases in water concentrations, as these catalysts are active for the water-gas shift reaction and an increase in water concentration would increase the consumption of CO to form CO₂ and H₂.^[46] Cobalt catalysts on the other hand seem not suffer from this problem. As a result, cobalt catalysts are used to produce paraffin waxes with higher conversions and selectivities. These are further cracked to produce high quality diesel fuel.^[46] Cobalt catalysts have traditionally been prepared by the quick precipitation of hot solutions of cobalt and zirconium salts with suspended silica. This method, after calcination and reduction, produces a cobalt catalyst with a

high dispersion of cobalt and a large pore framework.^[46] However, due to potential diffusion issues with these catalysts, egg shell catalysts have been developed which have the active metal close to the surface of the catalyst particle.^[49] In addition to this, bi-metallic catalysts are possible, for example, the addition of small amounts of ruthenium to cobalt based Fischer-Tropsch catalysts has shown to increase catalyst activity.^[50] However, the majority of described Fischer-Tropsch catalysts have been restricted to laboratory investigations. Although many academic studies into Fischer-Tropsch reactions have not seen commercialisation, investigations into its mechanism has resulted in some important discoveries, such as the hydroformylation reaction.^[51]

1.1.2.2 *Haber-Bosch Process*

The hydrogenation of nitrogen to ammonia is one of the most important industrial reactions due to the further use of ammonia in fertilizer production and explosives.^[52] Developed in the early 20th century by Fritz Haber and others,^[52] the reaction (Scheme 5) follows a dissociative mechanism whereby nitrogen and hydrogen adsorb onto the catalyst surface, their intermolecular bonds are broken and reformed as N-H bonds.^[53] This is in contrast to enzymatic production of ammonia which occurs by a hydrogenation of nitrogen via an associative mechanism.^[53,54]

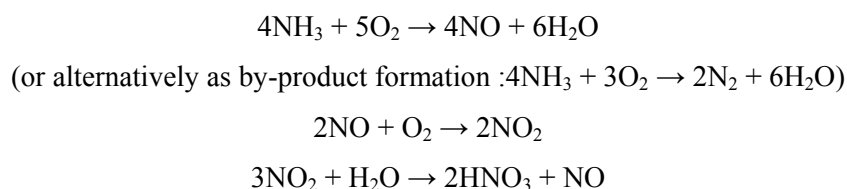


Scheme 5. The hydrogen fixation of nitrogen to form ammonia.

The reaction typically uses conditions in the region of 500 °C and 300 bar with an iron based catalyst.^[17] Other metal based catalysts are known to be active, such as osmium and ruthenium, but their high cost can be prohibitive.^[55] Nevertheless, commercial ruthenium catalysts have found industrial application in this process.^[56] In addition to these, the ternary nitrides Fe₃Mo₃N, Co₃Mo₃N and Ni₂Mo₃N have shown promising activity, with caesium promoted Co₃Mo₃N demonstrating greater activity than commercial iron based catalysts.^[55]

1.1.2.3 Ostwald Process

The combustion of ammonia is a follow through from the production of ammonia from the Haber-Bosch process to form nitric acid, which is the basis for the manufacture of fertilizers and explosives.^[57] Originally demonstrated in 1789 by Isaac Milner, it was more thoroughly investigated with the use of a platinum catalyst by Frédéric Kuhlmann for which he obtained a patent in 1838.^[57] However, it was Wilhelm Ostwald who thoroughly developed the process.^[57] The reaction proceeds according to Scheme 6,^[58] whereby ammonia is first converted into nitric oxide. The nitric oxide is further oxidised to nitrogen dioxide which is then dissolved in water to form nitric acid. However, one of the limiting factors of this process is that during the catalytic conversion of ammonia to nitric oxide, the formation of dinitrogen is possible.^[58]

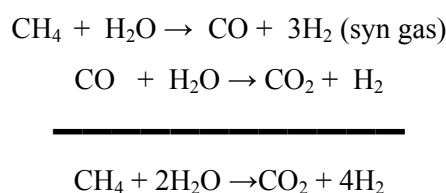


Scheme 6. The Ostwald combustion of ammonia to form nitric acid.

As the cost of ammonia accounts for approximately 90 % of the cost of the process, the efficiency of the oxidation of ammonia is a key factor in the production of nitric acid.^[59] This has led to some development in the catalysts used in this process. The original industrial catalyst used was a pure platinum gauze, however, this has now been largely replaced by platinum-rhodium and even platinum-palladium-rhodium alloys where the rhodium content is between 5 and 10%.^[59] These catalysts exhibit 92-98 % efficiency in the production of nitrogen oxides.^[59] Nonetheless, research into catalyst development continues,^[60] mainly to produce cheaper catalysts as catalyst metal loss is still a major concern in this process.^[59] As a result, metal oxide catalysts such as Co_3O_4 are beginning to show promising results.^[59]

1.1.2.4 Steam Reforming

Steam reforming is a process whereby hydrogen is generated by the oxidation of hydrocarbons by water (Scheme 7)^[61] and is responsible for the production of ~50 % of the world's supply of hydrogen.^[62] The carbon monoxide and/or hydrogen from this process is used in a variety of further chemical processes, such as the Haber-Bosch and Fischer-Tropsch (syn gas) processes, as well as for hydrogen fuel cells.^[63,64]



Scheme 7. The steam reforming and water gas shift of methane.

The most cost effective and industrially efficient method of hydrogen production is via the steam reforming of natural gas.^[62] However, gasification of coal is also a common method for the production of hydrogen, especially where cheap domestic coal is available.^[62,65] Indeed, this method finds use with SASOL's Fischer-Tropsch process in South Africa as a source of synthesis gas (CO:2H₂).^[46] In addition to these methods, studies into ethanol steam reforming are increasing due to its "green credentials" from the renewable nature of ethanol; as well as the advantage of decreased levels of catalyst poisons relative to fossil fuel based sources.^[62,66]

There are numerous catalysts that are active in steam reformation. For example, in ethanol reforming, metal oxide, reduced transition metals and multi metallic catalysts have found use.^[62] Indeed the metal oxide catalyst zinc oxide gives ~ 97% yield of H₂ and CO at 450 °C under atmospheric pressure and a gas hourly space velocity of 22000 h⁻¹.^[67] However, with industrial natural gas steam reforming, as well as with other commercial sources of hydrocarbons, supported nickel catalysts are used; such as nickel supported on an alumina-magnesia spinel. This is mainly due to the relative cost versus activity/stability of nickel catalysts compared to other active catalysts, such as those based on ruthenium and rhodium.^[68,69]

1.1.2.5 *Hydrodesulphurisation*

Hydrodesulphurisation is a catalytic process whereby sulphur is removed from fossil fuel sources of hydrocarbons such as natural gas, coal and refined oil products, by reduction with H_2 to form H_2S .^[70] Sulphur containing compounds are known catalyst poisons for a number of catalysts employed in many different industrially important reactions. For example, the catalysts employed in methanol formation from synthesis gas and skeletal reformation of naphtha (C_5 - C_{12}) are easily deactivated by sulphur.^[71] However, there can be beneficial effects on selectivity with a controlled partial poisoning of catalysts by sulphur. For example in the Fischer-Tropsch reaction, selective poisoning of cobalt based catalysts can increase catalyst lifetime and the selectivity to heavier hydrocarbons.^[72] However, due to the catalyst poisoning aspect and other environmental concerns over sulphur dioxide formation in combustion processes, hydrodesulphurisation is a common process in many industrial applications.^[58,73]

The common catalysts used for hydrodesulphurisation are based on molybdenum disulphide or tungsten disulphide with additional metals such as nickel and cobalt which promote higher activities.^[74] The exact mechanisms of hydrodesulphurisation are still debatable, but the basic mechanism is believed to start with the creation of a sulphur vacancy on the catalyst and adsorption of the sulphur containing compound to the vacant catalyst site.^[73,75] This is followed by a substitution of the sulphur in the compound with adsorbed hydrogen. The sulphur is then combined with adsorbed hydrogen to form H_2S which leaves the catalyst.^[75] The H_2S can be converted to elemental sulphur or combusted to form SO_2 for sulphuric acid production.

Although the mechanisms are still debated, the activities of the un-promoted catalysts are believed to be related to the sites on the edges of the catalysts.^[76] With promoted catalysts, the promoter-metal edge atoms are believed to play a key role.^[74,76] In addition to this, the nature of the catalyst support can influence reaction activity.^[77] For example, CoMoS deposited on SiO_2 has been shown to exhibit 1.7 times the hydrodesulphurisation activity than CoMoS deposited on Al_2O_3 , TiO_2 and ZrO_2 which has been ascribed to the formation of CoMoS(II) species versus CoMoS(I) respectively.^[78] On the other hand, CoMoS deposited on Al_2O_3 results in increased hydrogenation activity.^[78] These aspects highlight some of the major areas of investigation into heterogeneous catalysis, namely deactivation, geometric and electronic effects of bimetallic catalysts and catalyst-support interactions.

1.1.2.8 Ziegler-Natta catalysis

The polymerisation of α -olefins by Ziegler-Natta catalysts represents one of the largest chemical processes globally, with a worldwide production in the range of 100 million metric tonnes.^[79] Ziegler-Natta catalysts exist as both homogeneous and heterogeneous versions, however, the heterogeneous catalysts are the predominantly used industrial catalysts.^[79, 80] In the 1950's Karl Ziegler discovered that a mixture of Et_3Al , TiCl_4 and ethylene under atmospheric pressure at room temperature resulted in a polymerisation of ethylene up to 3 million Daltons.^[81] This being in contrast to the standard radical polymerisation procedure by ICI which required conditions in the region of 200 °C and 2000 atm.^[81] Later, amongst controversy over the origin of the intellectual knowledge, Giulio Natta "independently" discovered the stereo regular polymerisation of polypropylene with TiCl_3 and Et_3Al .^[81]

The majority of the homogeneous Ziegler-Natta catalysts are based on sandwich compounds similar to that shown in Figure 7 and are activated by the addition of methylaluminoxane.^[80] However, the heterogeneous catalysts still use tri-ethyl aluminium as a co-catalyst with titanium tetra-chloride supported on magnesium chloride,^[80] with the polymerisation process simply involving a coordination of the unsaturated bond to a titanium site and insertion of an alkyl group into this bond to form a new alkyl group.^[79,82] Several types of arrangements of these insertions are possible, for example: isotactic, syndiotactic, atactic, isoblock and stereoblock^[80] and it is possible to influence the predominant type of arrangement in the polymerisation by the addition of other reagents, such as a Lewis base.^[79,80,82,83]

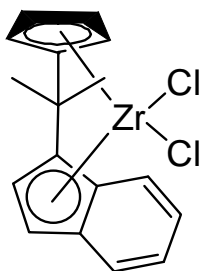


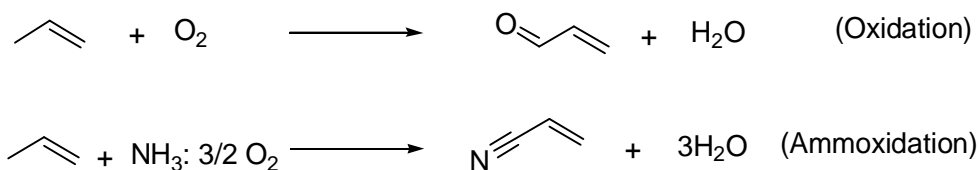
Figure 7. A typical Ziegler-Natta catalyst.

As with many heterogeneous catalysts, Ziegler-Natta catalysts have multiple active sites which make their design and mechanistic understanding difficult. However, it is generally believed that the coordinatively unsaturated magnesium cations in the 110 and 104 planes (of the supporting magnesium chloride) play host to the active titanium chloride species.^[79,82] The nature of these species are influenced by the nature of the host site. For example, the 104 plane is believed to contain stereo-specific sites with coordinated Ti_2Cl_8 .^[79] These sites are presumably responsible for stereo-specific polymerisation (e.g. isotactic or syndiotactic). As the addition of a Lewis base can also enhance stereo-selectivity, it is believed that the Lewis base modifies the catalyst surface by activating stereo-specific sites.^[79]

1.1.2.9 *SOHIO Process*

The Standard Oil of Ohio process or SOHIO process involves the ammoxidation or oxidation of propene to acrylonitrile and acrolein respectively (Scheme 8, Figure 8).^[84,85] Discovered in 1955, a commercial plant based on this process was operational by 1960 and today acrylonitrile is mainly produced by this process.^[86] The original catalyst used for acrylonitrile production was bismuth phosphomolybdate, however, modern catalysts are more complex formulations with additional metals (such as iron and cerium) which improve yields and selectivities.^[85,86] The general steps in the reaction are believed to be:^[85]

- Chemisorption of propene to an active site
- Activation of propene at a bismuth site to form a π allylic species
- C-O bond formation (acrolein) or (C-N) bond formation (acrylonitrile)
- Hydrogen abstraction to form acrolein or acrylonitrile and water
- Reoxidation of the catalyst from diffused oxygen species



Scheme 8. The oxidation and ammonoxidation of propene to acrolein and acrylonitrile.

Although there have been several investigations into the mechanistic steps of the SOHIO process, unfortunately, they have revealed conflicting results.^[85] However, for the simple bismuth molybdate oxides, the generally accepted mechanism can be seen in Figure 8. In both acrolein and acrylonitrile pathways, the allylic species formation is seen as the rate determining step.^[85]

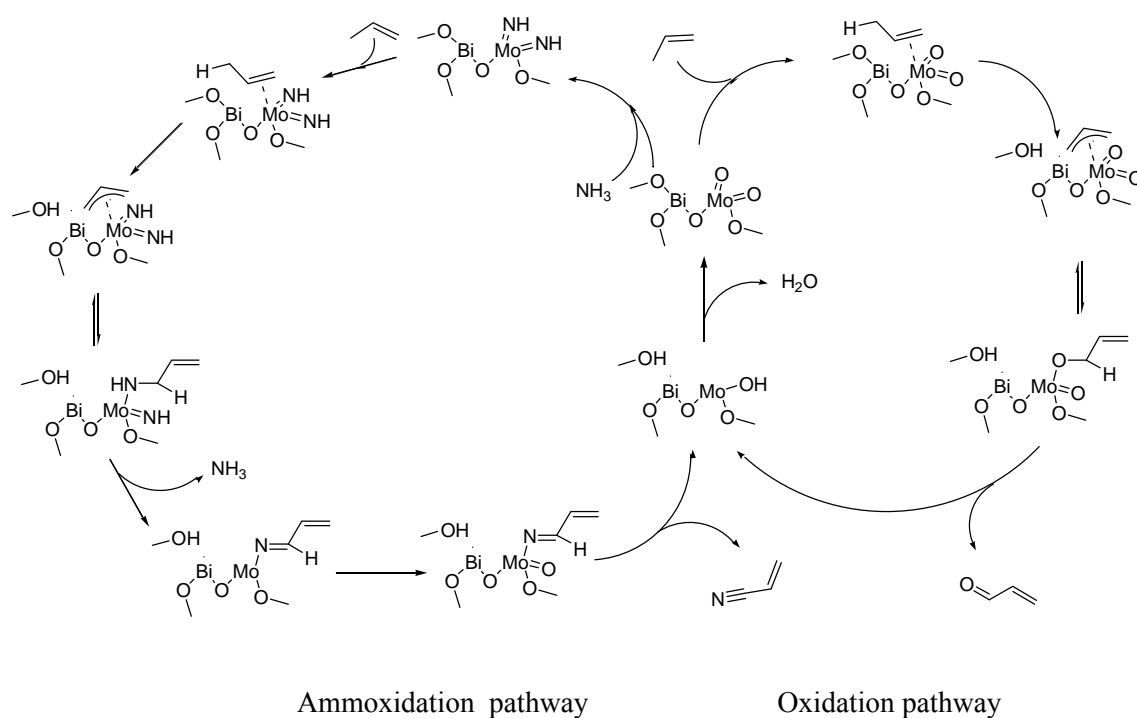


Figure 8. A general mechanism for the SOHIO process using bismuth molybdates.

As the world wide demand for acrylonitrile alone is in the region of 5 million tonnes per annum, and the major method for its production is by the SOHIO process, research into improvements of yield and selectivity has obvious economic advantages.^[85] This has led to a number of investigations into the effects of adding promoters, such as other metals to form multi metallic catalysts, as well as using propane as a starting material.^[84] For example, with the addition of iron and equal amounts of bismuth, the yield of acrylonitrile improves from ~55 % to ~65%.^[86] This is followed by a uranium antimony oxide catalyst which further improves yields to ~70 %; a rare example of an industrially used catalyst free of bismuth.^[86] Further additions to the bismuth based catalyst of: potassium, nickel, cobalt, manganese, chromium, caesium and magnesium in different ratios eventually leads to a catalyst, namely $(K,Cs)_y(Ni,Mg,Mn)_{7.5}(Fe,Cr)_{2.3}Bi_{0.5}Mo_{12}O_x/SiO_2$ capable of greater than 80 % yields of acrylonitrile.^[86]

The reasons for the increased yields over these multi metallic catalysts are complex, but in almost all cases bismuth is believed to be responsible for the hydride abstraction to form the allylic species of the rate determining step.^[85] It seems that bismuth alone performs this role as the majority of other components alone or together are inactive.^[85] Other aspects of importance in these catalysts include the strength and type of the metal oxygen bond and properties of the catalyst host structure.^[86] Too strong a metal oxygen bond or too weak a bond will either produce no reaction or decreased selectivity respectively, and the host structure needs to be able to combine high oxygen diffusion, anionic vacancies and rapid electron transfers with structural integrity.^[86] These requirements are invariably part of the reason for the success of the multi metallic catalysts.^[86]

1.2 Deactivation of catalysts and catalyst modifications

Apart from the efforts into developing new catalysts for novel reactions, research into improving the yields and selectivity of existing catalysed reactions as well as to prevent their deactivation (of both homogeneous and heterogeneous catalysts), forms one of the largest areas of catalysis research. As such, the body of literature on these subjects is vast. Therefore only a general summarisation on catalyst deactivation and modification is discussed, with emphasis on catalyst deactivation and modification relevant to the body of this research.

1.2.1 Catalyst deactivation

Catalyst deactivation may occur via several different mechanisms, which depends on the reaction conditions and type of catalyst used. For example, a heterogeneous catalyst exposed to high temperatures may well suffer from deactivation via sintering of the catalyst crystallites into larger agglomerates. The general mechanisms of catalyst deactivation can be found in Table 2.^[87]

Table 2. The general mechanisms of catalyst deactivation.

Mechanism	Type	Catalyst	Description
Reduction/oxidation	Chemical	Homo/Heterogeneous	Reduction or oxidation of an active species to an inactive version
Degradation	Chemical/Thermal	Homo/Heterogeneous	Destruction of the supporting matrix (i.e. ligand/Homogeneous; support surface area/Heterogeneous)
Fouling	Mechanical	Heterogeneous	Deposition of a species (i.e. carbon) onto the catalyst surface and pores
Attrition	Mechanical	Heterogeneous	Loss of catalytic material due to friction or impact force
Vapour formation	Chemical	Heterogeneous	Reaction of a gas with the catalyst to form a volatile catalyst/gas species (i.e. CO and Ni to form nickel carbonyls)
Fluid-solid/ solid-solid reactions	Chemical	Heterogeneous	Reaction of the reactant fluid, support or promoter with the catalytic phase to produce an inactive phase
Poisoning	Chemical	Homo/Heterogeneous	Strong chemisorption of species blocking catalytic sites

The deactivation of a catalyst by either oxidation or reduction to an inactive species is a problem found with both heterogeneous and homogeneous catalysts. For example, in the well known homogeneously catalysed Wacker oxidation process of ethene to ethanal, deactivation of the palladium catalyst can occur by reduction of the cationic palladium species to palladium black (Pd(0)).^[25] In the heterogeneously catalysed preferential oxidation of CO to CO₂ in hydrogen

gas, it stands to reason that a metal/metal oxide catalyst can be converted to an inactive state depending on the temperature and gas compositions^[88] Indeed, the SOHIO process requires gaseous oxygen to replenish the oxygen of the metal oxide catalyst, without which the catalyst would be reduced to an inactive state.^[85]

Deactivation of a catalyst by degradation occurs when the supporting matrix of the catalyst undergoes damage or the catalyst is directly affected. For example, it is known that silica, a common support for heterogeneous catalysts, is unstable at high temperatures in the presence of water.^[89] Indeed many supports can lose surface area and pore volume under harsh conditions which can directly affect the catalytic activity, i.e. by structural degradation encapsulating the active crystallite particles.^[87] In addition to this, sintering of the active crystallites into larger agglomerates can cause a reduction in activity due to the loss of metal surface area.^[87,90] This loss in surface area directly affects the numbers of active sites which may, for example, exist at the crystallite edges. There are many factors affecting the rate of crystallite sintering, however, temperature increase is one of the principal, as an increase in temperature results in increased atomic and crystallite motion.^[87,90] Other factors include the strength of the metal-support interaction and chemical environment of the reaction.^[87,90] With regards to homogeneous catalysts, degradation of the supporting ligands by side chemical reactions can result in either a poisoning of the catalyst or an inability to prevent its deactivation.^[25] For example, in the cobalt catalysed hydroformylation reaction, a loss in the effective concentration of the supporting ligand results in the precipitation of cobalt metal which is inactive.^[25]

Fouling is another means by which heterogeneous catalysts can deactivate. It is caused by the mechanical blocking of the pores of the support and a deposition onto the support and catalyst surface.^[87] A common form of fouling is the deposition of carbon, or coke formation. For example it is well known that catalysts used for hydrotreating heavy oils in oil refineries undergo a rapid initial deactivation by coke formation, with further fouling occurring by heavy metal deposition from heavy metals present in the feed.^[91] Regeneration of coke fouled catalysts is however possible by calcination with an oxidising agent.^[92] Regeneration of heavy metal fouled catalysts is unfortunately far more difficult.

Along with fouling, mechanical attrition is another method of catalyst deactivation. It occurs when the frictional or impact force of the reactants wears away the mass of the heterogeneous catalyst.^[87] Common occurrences of this are found with the catalysts used in the Fischer-

Tropsch and sulphuric acid Contact processes.^[58,93] As with the other methods of catalyst deactivation, research into the prevention of attrition is an active area of investigation.

Vapour formation, fluid-solid and solid-solid reactions are chemical methods of heterogeneous catalyst deactivation. For example, volatile metal halides of platinum catalysts (such as those used in the Ostwald process) are readily formed under low temperatures and low concentrations of halogen in the reactant feed.^[87] In addition to this, volatile PtO_2 is formed at high temperatures with oxygen which leads to a loss of up to 0.3g of platinum per ton of HNO_3 produced by the Ostwald process.^[51,87] Phase transition of alumina to aluminium sulphate, which blocks the pores of automotive catalytic converters, occurs via the fluid-solid deactivation method;^[87] while the phase transformation of active carbides to inactive oxides with iron based Fischer-Tropsch catalysts is an example of a solid-solid reaction deactivation pathway.^[87] These last two methods of deactivation are almost identical to the oxidation/reduction mechanism, except these methods include phase transitions (i.e. space group) with no changes in the oxidation state of the metal.

Poisoning of both homogeneous and heterogeneous catalysts can represent a significant challenge to the long term use of industrial catalysts. It can occur via both reversible and irreversible methods and may induce electronic and geometric changes to the catalyst, in addition to blocking the active site.^[87] For example, sulphur species are poisons for all heterogeneous catalytic processes using reduced metals as the active phase.^[94] However, the relative effects and mechanism of sulphur poisoning depend on the species concentration, reaction conditions and the type of catalyst metal.^[87] There are two deactivation pathways for sulphur poisoning, namely surface sulphidation and bulk sulphidation. Surface sulphidation occurs more readily than bulk sulphidation and initially creates a surface barrier for bulk sulphidation.^[94] With regards to surface sulphidation, the sulphur atom, in addition to blocking a reactant adsorption site, may influence the electronic characteristics of the nearest atoms up to 5 a.u. and affect their binding abilities towards the reactants.^[87] Furthermore, the sulphur atom may rearrange the structure of the surrounding atoms to a geometry which is unfavourable for the adsorption of reactants adjacent to the sulphur atom.^[87] Surface diffusion of the reactants may also be altered by the sulphur atom which may in effect block access between the reactants.^[87] Sulphur is not the only element to cause catalyst poisoning. Indeed, group VA-VIIIA elements are known poisons. The strength of their poisoning and mechanism by which it occurs depends on the type of species that the poison is present in and the way in which the electrons from the catalyst poison interact with the catalysts.^[87] For example, hydrogen sulphide

is generally a stronger poison than thiophene. Table 3 reveals some of these poisons and the type of electronic interaction with the catalyst.^[87]

Table 3. Known catalyst poisons and their electronic interactions with the catalyst.

Chemical type	Examples	Electronic interaction
Groups 15 and 16	N, P, As, Sb, O, S, Se, Te	σ and π bonds
Group 17	F, Cl, Br, I	σ and π bonds
Heavy metals and ions	As, Pb, Hg, Bi, Sn, Zn, Cd, Cu, Fe	d orbital interaction
Multiple bonding poisons	CO, NO, HCN, some unsaturated hydrocarbons	σ and π bonds, potentially with back-bonding

In general, the relative strength of these poisons increases with atomic or molecular size as well as electronegativity.^[87] However, the strengths of these poisons can be mitigated if the poison can be gasified by molecular oxygen, water or hydrogen present in the reactant feed.^[87] Another aspect of catalyst poisoning is the relative trends of the inactivity versus concentration of the poison. For example, a selective poisoning will result in a sharp initial deactivation with a decreasing level of deactivation with increasing levels of poison concentration.^[87] This is ascribed to highly active reaction sites being preferentially blocked by the poison until their numbers have decreased to a level where the poison starts binding to less active sites, i.e. the poison has a similar affinity trend to the different catalyst sites as the reactant(s).^[87] The converse of this has been described as an "anti-selective" poisoning while a linear trend in poison concentration versus deactivation is known as non-selective poisoning.^[87] In addition to the poisoning-activity trends, other parameters exist to characterise the nature of the poisoning event, these include: catalyst poisoning susceptibility, poison toxicity, catalyst poison resistance and poison tolerance.

An example of a non-selective trend would be where there is only one active site and the poison has a strong affinity for this site. Although single catalytic sites generally do not occur in heterogeneous catalysis, it is the norm amongst homogeneous catalysis as single atom catalysts are common in literature. For instance, alkynes and dienes present in the hydrocarbon product feed from the Fischer-Tropsch process strongly deactivate the catalysts used in the hydroformylation reaction.^[95] This is of particular industrial concern if hydroformylation of an

alkenes (produced by Fischer-Tropsch) is required to increase the value of the product.^[95] Indeed, it has been found that with the addition of alkynes, dienes and enones to a typical rhodium hydroformylation catalyst, rapid formation of stable rhodium complexes occur.^[96] As a result, these catalyst poisons present in the feed require removal before introduction to the catalyst. Hydrocarbon poisons are not only poisons for metal catalysed reactions. They may also interfere with other types of reactions. For example, in radical processes with aldehydes/alkenes, the presence of an alkene/aldehyde can dramatically influence the outcome.^[97] Mixtures of alkenes and alcohols can potentially be found in the products from hydroformylation. For exemplification of the relevance of catalyst poisoning with heterogeneous catalysts, Table 4 reveals some of the industrial catalysts (and the reactions they catalyse) with the poisons which strongly deactivate them.^[87]

Table 4. Industrial catalysts and their deactivating poisons.

Catalyst	Reaction	Poisons
Silica-alumina, Zeolites	Cracking	Organic bases, some hydrocarbons, heavy metals
Nickel, platinum, palladium	Hydrogenation, dehydrogenation	S, P, As, Zn, Hg, halides, Pb, NH ₃ , C ₂ H ₂
Nickel	Steam reforming of methane, naphtha	H ₂ S, As
Iron, ruthenium	Ammonia synthesis	O ₂ , H ₂ O, CO, S, C ₂ H ₂ , H ₂ O
Cobalt and iron	Fischer-Tropsch	H ₂ S, COS, As, NH ₃ , metal carbonyls
Noble metals on Zeolites	Hydrocracking	NH ₃ , S, Se, Te, P
Silver	Ethylene oxidation to ethylene oxide	C ₂ H ₂
Vanadium Oxide	Oxidation, selective catalytic reduction	As, Fe, K, Na from fly ash
Platinum, Palladium	Oxidation of CO and hydrocarbons	Pb, P, Zn, SO ₂ , Fe
Cobalt and molybdenum sulphides	Hydrotreating of refinery residue	Asphaltenes, N compounds, Ni, V

As mentioned before, heterogeneous catalyst poisoning may not necessarily be completely negative. For example, a selective initial poisoning of a catalyst may be intentionally undertaken to reduce highly exothermic initial catalyst activities, which may result in a runaway thermal event if left untreated.^[98] Selective poisoning may also enhance the selectivity of a reaction, potentially by the blockage of an active site responsible for undesirable side reactions or influencing the steric environment.^[98] This particular aspect of selective poisoning forms part of the investigations into heterogeneous catalyst modification which are discussed below.

1.2.2 Catalyst modification

Catalyst modification revolves around three main aspects important to catalysis, namely catalyst activity, longevity or stability and selectivity. Within homogeneous catalysis, major focus is given to the supporting structure of the catalyst or ligands. However, other aspects are considered too. For example, in the Wacker oxidation process, copper is added to re-oxidise the palladium catalyst as it is easier to oxidise copper with molecular oxygen than palladium.^[25] This addition transforms the process from stoichiometric to continuous. Ligand modifications are however, quite effective in stabilising reactions and increasing selectivity. For instance, the addition of tri-alkyl phosphines to cobalt hydroformylation catalysts;^[25] and the bidentate, as well as chiral, phosphorus ligands which increase regio- and stereo-selectivity in many homogeneous reactions.^[21,26]

Heterogeneous catalysts enjoy two fields of catalyst modification which can increase the stability, selectivity and/or activity; namely metallic/metalloid and organo main group modifiers.^[99] With regards to selectivity, an ideal catalyst modifier should be able to enhance the selectivity at modifier concentrations between ppm levels and 1 mol% of the catalyst.^[99] The mechanism of selectivity enhancement can be generally classified into the following categories:^[99]

- Steric blocking of a fraction of active sites, or competitive adsorption
- Electronic effects on the metal or metal oxide catalyst
- Stereo directing interaction between adsorbed modifier and reactant
- Formation of a bi-functional or synergistic catalyst

The blockage of a fraction of active sites is in effect selective poisoning which can occur irreversibly or reversibly. For example, in the Fischer-Tropsch reaction, irreversible selective sulphur poisoning of cobalt on alumina results in a decrease in the activity of the reaction but with an increased selectivity towards light hydrocarbons, i.e. a reduction in the content of waxes.^[100] This increase in selectivity has been ascribed to the interfering effect of sulphur on the surface oligomerisation of the hydrocarbons.^[100] An example of a reversible poisoning or competitive adsorption which results in selectivity enhancement, is ethyne and propyne hydrogenation to ethene and propene by the addition of carbon monoxide.^[101,102] It is believed that the carbon monoxide reduces the concentration of surface hydrogen, thereby decreasing the rate of hydrogenation to ethane.^[101,102]

Electronic modification of a catalyst upon addition of a modifier to enhance selectivity can in principle be difficult to isolate from geometric effects resulting from atomic rearrangement of the catalyst.^[87] This is primarily due to the associated electronic differences between different atomic arrangements. However, the addition of modifiers (or dopants) to alter the electronic band gaps of crystals or to provide electronic holes is an established area of research, primarily in semiconductor technology. A common method of introducing electronic modifications of a catalyst is by the addition of a different metal salt, such as sodium or potassium. For example, it has been shown that the addition of alkali metals to silver catalysts for NO_x reduction can have a noticeable effect on the activity, which has been linked to the concentration of Ag⁺ atoms.^[103] Besides metal catalyst crystallite modification, the addition of alkali metals can also enhance the performance of a reaction by interacting with the catalyst support.^[104,105] Alkali metals are not the only metals which can be used as promoters, indeed even other transition metals can be used.^[106] There are, however, several ways in which metal addition can interact with the catalyst. For instance: as adatoms (single atom additions) on the surface of the catalyst, as diffused atoms within the metal crystallite to form alloys and as multilayer deposits on both the crystallite and support.^[99] Furthermore, the conditions of the metal promoter addition can affect the relative levels of the different types of interaction, which potentially alters the intensity of promotion.^[99] It has been demonstrated that with the addition of copper sulphate to a palladium on carbon catalyst, the media can have a direct effect on the type of deposition.^[99,107] In the presence of citric acid, deposition resulted in the formation of multilayered deposits while formic acid resulted in a high level of adatom formation.^[99,107] The two structures have linked to selectivity differences in the hydrogenation of *para*-chloronitrobenzene.^[99,107]

Stereo directing interaction between adsorbed modifier and reactant can perhaps be best demonstrated by the addition of a Lewis base to heterogeneous Ziegler-Natta catalysts to increase the selectivity to stereo-specific polymers.^[79,80,82,83] It is believed that the base complexes with stereo-specific sites aiding in its activity as well as rearranging non specific sites to stereo-specific ones.^[79] In addition to Lewis acid modification, another well known stereo-directing modifier is cinchonidine. Cinchonidine is a nitrogen containing chiral compound (Figure 9) which has been used to enhance the enantiomeric excess in several types of reactions, such as the asymmetric hydrogenation of α - β unsaturated acids and ketones.^[108, 109]

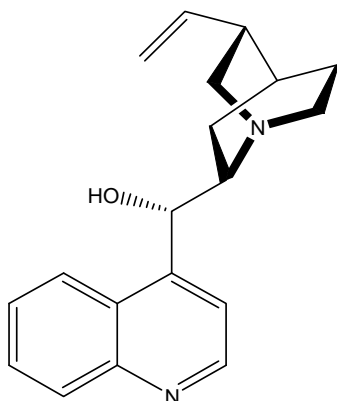


Figure 9. An example of cinchonidine.

Cinchonidine however, is not the only nitrogen containing chiral organic modifier, as several others have been reported.^[99] It seems that the requirement for this class of modifier is the presence of a nitrogen containing group, a chiral centre and an “anchoring” aromatic moiety which interacts with the catalyst surface.^[99] These examples highlight the potential application and effectiveness of organic bases catalyst modifiers.

Another example of the effectiveness of organic modifiers is the addition of a thin layer of ionic liquid to a platinum catalyst to form a bi-functional version which enhances the skeletal isomerisation of linear octane to iso-octane, thereby increasing the octane rating.^[110] The Lewis acidic ionic liquid acts in tandem with the heterogeneous catalyst to promote isomerisation activity and to prevent the side product formation of octene.^[110] This class of modification is relatively new and is known as a Solid Catalyst with an Ionic Liquid Layer or SCILL.^[111] Indeed, SCILL catalysts have been shown to promote the selectivity of many different hydrogenation reactions, which forms the basis of this study and is discussed in the next section.

1.3 Ionic liquids

Ionic liquids are liquids that are exclusively composed of ions; in essence they are molten salts. However, the use of the name is normally in reference to salts which are molten at or near room temperature and are typically composed of an organic cation with an inorganic or organic anion.^[112] The first known indirect description of an ionic liquid was published in 1877 with the description of the Friedel-Crafts alkylation reaction, which was later identified as an alkylated aromatic cation with a chloroaluminate anion.^[112,113] Since then there was little research into ionic liquids until the late 1990's.^[112] Now a cursory search of the literature concerning them will reveal a vast amount of research in their application. This is due in part to several properties that are inherent in the nature of the ionic liquid. These are:^[112]

- Very low vapour pressures which causes the ionic liquid to be resistant to evaporation
- Multiple variations in the nature of the cation and anion which result in a vast number of possible permutations, all of which have different properties. These differences allow for a fine tuning or tailoring of applications such as the separation of gasses based on differing solubilities in the ionic liquid.
- Low flammability and high stability at elevated temperatures
- Wider liquid ranges compared to traditional solvents
- Wide range of solubilities and miscibilities for both polar and non polar compounds
- Wide electrochemical windows
- Can be used as reaction media and/or catalysts for a wide variety of chemical reactions
- Used for separations and extractions
- Tailored applications with changes in their physical, chemical or biological properties by changing the cation or anion

As a result of these and other reasons, ionic liquids have been the subject of investigation for many green chemistry applications in the hopes of replacing toxic, flammable volatile organic solvents; reducing pollution and improving the safety of chemical processes and products.^[112] Furthermore, designer ionic liquids are possible, whereby the chemical nature of the ionic liquid is altered to produce a functionalised or task specific ionic liquid.^[112] Examples of these include ionic liquids incorporating acidic sites for acid catalysed reactions.^[110,112] Another interesting class are the chiral ionic liquids, where the cation or anion or both possess chiral centres. These have been applied as solvents to induce asymmetric catalysis, with several examples existing in literature.^[112] Due to the wide variation of applications that ionic liquids can lend themselves to, it comes as no surprise that ionic liquids have been used as reaction mediums for a large number of homogeneously catalysed reactions. As the literature is replete with examples, and comprehensive reviews already exist,^[112] only supported ionic liquid phase catalysis (SILP) will be discussed as a comparison to SCILL catalysis.

1.3.1 Supported Ionic Liquid Phase

Supported ionic liquid phase (SILP) catalysis is a concept aimed at combining some of the advantages of heterogeneous and homogeneous catalysis, namely the ease of catalyst separation of heterogeneous systems and the activity and selectivity of homogeneous catalysis. These outcomes are achieved by coating a support such as silica or alumina with an ionic liquid containing a homogeneous catalyst, such as those based on rhodium for hydroformylation (Figure 10).^[114]

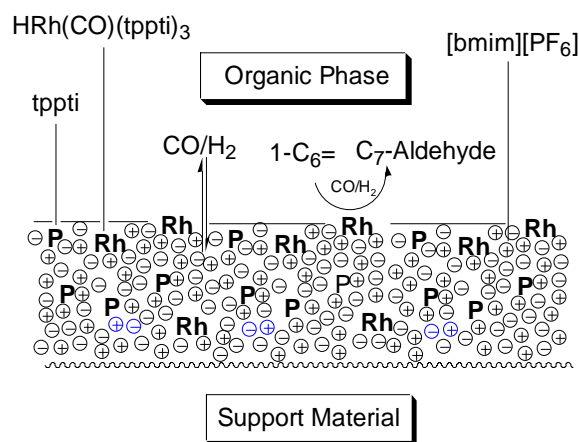


Figure 10. Supported Ionic Liquid Phase (SILP) catalysis.

Due to the low vapour pressure and ionic nature of these liquids, they invariably form a different phase to the substrates and diluents used in the reaction forming, at least, a tri-phasic system. However, the substrate intended for the reaction generally forms an equilibrium concentration, between the ionic liquid and organic phase, which reacts with the homogeneous catalyst before leaving the ionic liquid.^[114] However, to avoid possible catalyst and ionic liquid leaching, the reactions tend to be conducted in the gas phase.^[115] Nevertheless, ionic liquids can have high decomposition temperatures enabling the use of high pressures and temperatures. Indeed SILP catalysis has been applied to hydroformylation,^[116] asymmetric hydrogenation,^[117] Heck reactions,^[118] Suzuki reactions,^[119] and Friedel-Crafts acylation^[115] amongst others. The most notable aspect of this type of catalysis is the layer of ionic liquid containing catalyst on a support; although there are many examples of homogeneous catalysis within this layer, relatively little research has been conducted into the heterogeneous version.^[111]

1.3.2 *Heterogeneous reactions in ionic liquids*

In general there exist two types of heterogeneous catalysis in ionic liquids, namely supported nano-particles in a bulk ionic liquid medium and the supported catalyst with an ionic liquid layer. The supported nano-particle system offers similar advantages as the homogeneous system (i.e. ease of catalyst-reactant separation and increased activity as a result of increased metal surface area). However, in SCILL catalysis, bulk separation advantages of ionic liquids are of no consequence, as the system resides on a solid support. Nano-particle catalysis in ionic liquids has received relatively greater attention.^[120] It has been shown that ionic liquids are quite effective in the formation and stabilisation of small metal nano-particles.^[120] These nano-particles can be quite small, when formed in an ultrasonic bath, and exhibit high catalyst activities, potentially as a consequence of the smaller sizes.^[120] Indeed, nano-particle catalysis in ionic liquids have been successfully applied to palladium,^[121] iridium,^[122] rhodium^[123] and gold^[124] amongst other, as well as bimetallic catalysts.^[125] The results from some of these studies suggest that the ionic liquid stabilises the particles by a carbene-metal interaction, which is supported by investigations with nuclear magnetic resonance spectroscopy.^[126] This implies that the ionic liquid's role is more than that of a spectator and may be able to modify the catalyst both electronically and morphologically.^[112,126] In effect, the ionic liquid may potentially act as a new class of organic modifier of heterogeneous catalysts, which may well be the origin of performance enhancement in some of the recently described SCILL catalysts.

1.3.3 Solid catalyst with an ionic liquid layer

The original motivation for the solid catalyst with an ionic liquid layer (SCILL) was centred on using the ionic liquid as a means of increasing the selectivity of a reaction by taking advantage of the differences in the solubility of the reactant and an intermediary product.^[111] For example, if the intermediary product has a lower solubility in the ionic liquid than the initial reactant and/or final product, (compared to the organic phase) then it would have a lower concentration in the ionic liquid and thus potentially a slower rate of reaction, causing an increase in selectivity for the intermediate product.^[111] Although increases in selectivity in the hydrogenation of cyclooctadiene to cyclooctene have been ascribed to this, the level of enhancement cannot be attributed to it alone.^[111] Furthermore, increases in chemo-selectivity with the use of SCILL catalysts have been reported, most notably in the selective hydrogenation between intra-molecular alkene and α - β unsaturated carbonyls.^[110,127-130] In addition to this, selectivity enhancements have been achieved in the competitive hydrogenation between linear alkynes and alkenes and dienes and alkenes; which have been related to the chemo-selective nature of carbon modified catalysts in alkyne hydrogenation.^[131]

Several potential reasons have been put forward to explain this, such as: modification of the catalyst by the ionic liquid causing a change in the chemical nature of the active sites of the catalyst; site specific blockage of active sites on the catalyst by either the cation or anion of the ionic liquid and changes in the surface diffusion of reactants on the catalyst surface.^[131,132] The site specific interaction between the ionic liquid and catalyst as well as modification of the catalyst surface by ionic liquid fragments, has been demonstrated by XPS and *in situ* I.R. studies.^[133,134] Although diffusion effects through the ionic liquid have been ruled out by some studies,^[111] the none involvement of surface diffusion has been questioned as this is an inherent property in supported heterogeneous catalysis.^[131,132] However, SCILL catalysis is still in its infancy and many questions over the origin of the enhancements with the addition of an ionic liquid layer still need to be comprehensively answered. Furthermore, no examples of asymmetric catalysis with a SCILL catalyst using a chiral ionic liquid have been reported. As a result, a systematic study with a range of different ionic liquids and reactions needs to be conducted.

1.4 Conclusions

Catalysis is a large area of research within the field of chemistry; it encompasses theoretical physical chemistry to biochemical enzymatic catalysis. However, some of the largest impacts on society reside with industrial catalysis to produce bulk chemical products such as fuels, fertilizers, plastics and acids as well as the large scale (worldwide) removal of pollutants which greatly enhance humanity's standard of living.

At such large volumes of production, the slightest improvement of yield from increased selectivity, activity or longevity of these industrial catalysts, due to catalyst modification, can translate into large profits. As a result, research into improving catalyst properties with respect to these areas is ongoing in both industrial and academic laboratories. However, due to the plethora of potential heterogeneous catalyst modifications and the limited and contested understanding of the mechanisms behind the modification, empirical research into catalytic properties remains the basis of industrial and academic investigations.

Of the different types of heterogeneous catalyst modifications, organic modifiers exhibit interesting and mechanistically complex interactions with heterogeneous catalysts. From chiral induction to suppression of side reactions and potential alterations to reactant surface diffusion. Within organic catalyst modification, ionic liquids seem to be the least investigated, especially the solid catalyst with an ionic liquid layer which was formally described in 2007. From the limited studies conducted so far, ionic liquid modified catalysts seem to hold some promise for increased selectivity which may be applicable in industrial settings. However, understanding of ionic liquid modified heterogeneous catalysts is still in its infancy, providing ample scope for investigation.

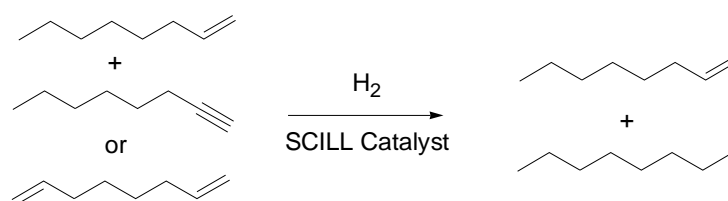
Although SCILL catalysts may find applications in many of the industrial processes described above (where increased selectivity to a certain product is desirable); due to the nature of the current commodity chemical industry in South Africa (mainly based on Fischer-Tropsch technologies) and its relatively large presence, it would be specifically relevant to investigate SCILL applications in the following two areas:

- Selective removal of dienes and alkynes from α -olefin feedstocks in the C₆-C₁₂ range with a relatively cheap metal such as nickel.

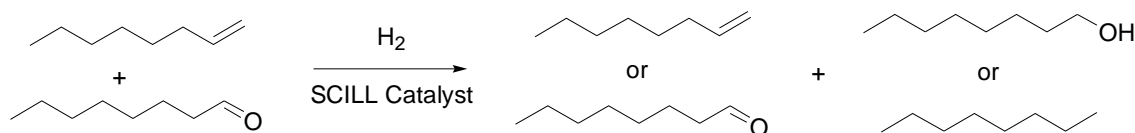
- Selective hydrogenation of potential hydroformylation products (un-reacted alkenes and aldehydes in the C₆-C₁₂ range) with metals such as copper and palladium (which traditionally have opposite chemo-selectivities for alkene and aldehyde hydrogenation).

To compliment these investigations, low concentrations of liquid phase reactants would be desirable so as to prevent aniso-thermal conditions over the catalysts and increase flow rates to ranges which are easily controllable.

Graphically these two areas of potential application are represented in Scheme 9 and 10 below. The rational of these reactions is to remove homogeneous catalyst poisons (such as alkynes or dienes) from Fischer-Tropsch based α -olefin feedstocks; and to selectively hydrogenate either an alkene or aldehyde in the presence of each other. Aldehydes may be produced by the hydroformylation reaction with alkenes (Scheme 1, p 6) and selective hydrogenation of the aldehyde allows for the dehydration of the resultant alcohol to a higher value (longer chain) α -olefin, while recycling the starting α -olefin back into the hydroformylation reaction through easier separation of alcohols from alkenes. Selective hydrogenation of alkenes in the presence of aldehydes would purify the feedstock for radical reactions, where traces of alkene may have adverse effects on the reaction.



Scheme 9. Potential reaction product of the selective hydrogenation of 1-octene versus 1-octyne or 1,7-octadiene.



Scheme 10. Potential reaction products of the selective hydrogenation of 1-octene versus octanal.

With regards to organic modifiers such as ionic liquids and nitrogen containing organic bases, the following compounds in Figure 11 would be useful in the proposed investigations.

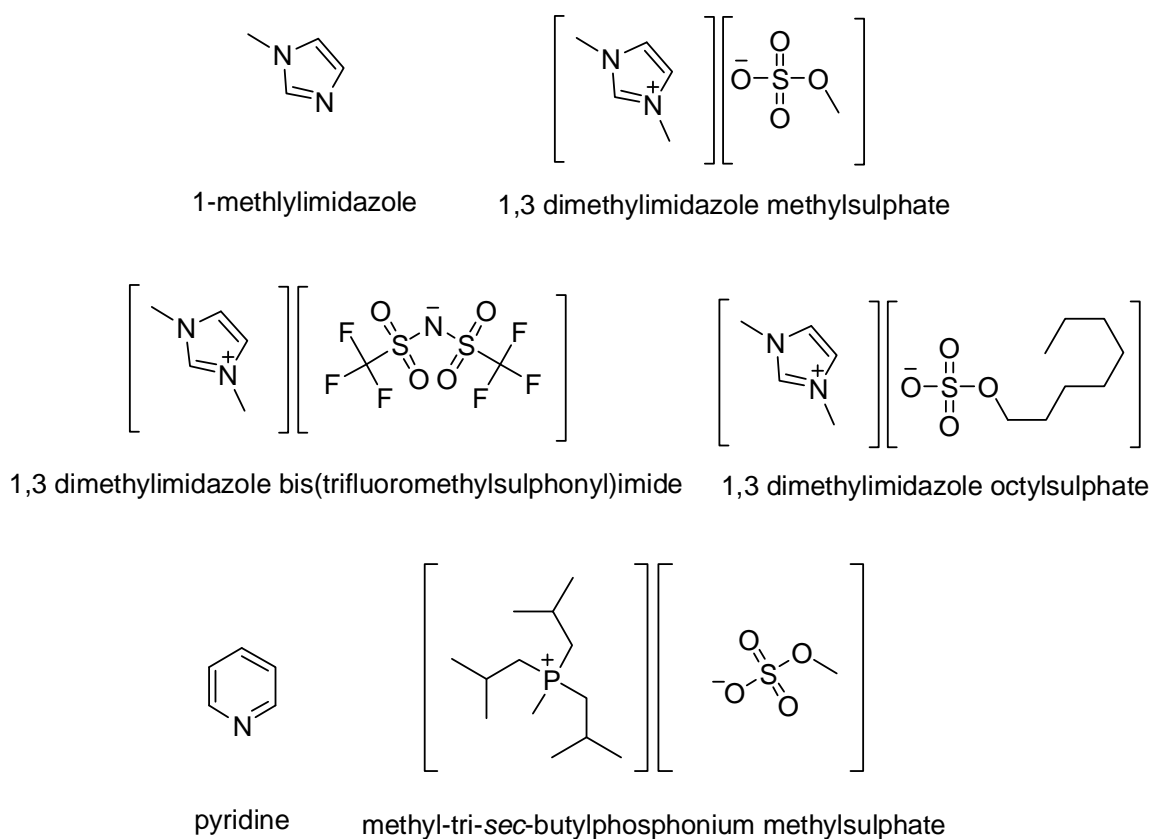


Figure 11. Structures for the different organic molecules which will find use in the following investigations.

1-Methylimidazole based ionic liquids are readily available, commercially made ionic liquids. They are also the predominantly used ionic liquids within the small body of literature which currently exists on SCILL catalysis. However, to aid in the understanding of SCILL catalysis, ionic liquids based on 1-methylimidazole should be used with variations in the anion and perhaps one variation in the cation. 1-Methylimidazole on its own and pyridine as organic

modifiers would be useful to determine any relative effects of nitrogen containing organic bases, as these are commonly available and structurally relevant compounds.

As can be anticipated, the stability of the modifiers on the heterogeneous catalyst would be of importance, as the relative thickness of the modifying layer may influence properties such as diffusion and solubility of the reactants,^[135-137] as well as the structure of the modifying layer on the catalyst.^[138-142] Monitoring the content of modifier remaining after a reaction (either by ICP analysis or TGA-DSC) would help determine if any alteration of selectivity/activity is the result of physical processes or chemical modification (which would not require a large layer of modifier).

The potential for physical processes (mediated by the modifying layer) influencing the catalyst does need to be emphasised, as ionic liquids do find use in the synthesis and stabilisation of metal nano-particles with particular characteristics (via the interaction of the ionic liquid and metal surface).^[120-126] In addition to this, the specific properties of ionic liquids with respect to catalysis (excluding chemical interactions) may have an effect. For example, the ionic nature of ionic liquids is the defining characteristic of these "solvents" and may influence the relative concentrations of surface species important in the mechanism of the catalytic action, thereby potentially influencing product distributions.

1.5 Aim of the present study

The broad aspect of this study is to evaluate the application of ionic liquid modified heterogeneous catalysts under continuous flow and trickle bed conditions. To the best of our knowledge no examples of ionic liquid modified heterogeneous catalysts applied under these conditions existed in literature at the commencement of this research. More concisely, the following is investigated:

- Determining the modified catalysts effectiveness at removing homogeneous catalyst poisons such as alkynes and dienes from alkene products (typical of Fischer-Tropsch product feeds) with an extreme case of 1:1 poison to alkene ratio at c.a 98 % poison conversion through hydrogenation. Utilising an extreme case allows for any potential limitations of SCILL catalysts and its applicability to be quickly ascertained.

- Evaluation of different ionic liquid effects compared to the base catalyst by varying the nature of both the cation and anion as well as the loading of the ionic liquids to determine any empirical trends and possible mechanistic reasons for improved selectivity.
- Assessing the effects of SCILL catalyst modification on the competitive hydrogenation of an alkyne and alkene under different iso-conversion levels; and exploring any problems encountered with *ex situ* SCILL catalyst preparation.
- Extending the reactant substrates to include aldehydes with alkenes (typical of hydroformylation product feeds) which provide a closer comparison to substrates used in the bulk of SCILL catalyst research.
- Changing the base metal to those that allow for *in situ* SCILL catalyst formation and exploring any problems encountered by this method of formation.

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CHAPTER 2

THE EFFECTS OF SCILL CATALYST MODIFICATION ON THE COMPETITIVE HYDROGENATION OF 1-OCTYNE AND 1,7-OCTADIENE VERSUS 1-OCTENE

2.1 Abstract

Competitive hydrogenation of mixtures of related unsaturated compounds remains a challenging problem. Recently solid catalysts with an ionic liquid layer (SCILL) have shown potential for increased catalyst selectivity under batch conditions. Our results on the continuous flow competitive hydrogenation of 1-octyne and 1,7-octadiene versus 1-octene under trickle bed conditions with a nickel SCILL catalyst indicate improved catalyst selectivity under trickle bed conditions. Different ionic liquids ([MMIM][MeOSO₃], [MMIM][OcOSO₃], [MMIM][NTf₂], [MeP*sec*-Bu₃][MeOSO₃] and [Et₃S][NTf₂]; MMIM=1,3-dimethylimidazole and Tf=trifluoromethanesulfonyl of varying catalyst loadings were investigated. The results highlight the importance of potential site specific interactions by the ionic liquid. They also indicate the importance of the cation for these effects.

2.2 Introduction

Despite extensive hydrogenation studies, competitive hydrogenation of higher alkenes, alkynes and dienes is still an important topic of research. In addition, research into the hydrogenation of longer chain compounds is receiving greater attention;^[1] as they are present in chemical feed stocks.^[2a] Alkynes and dienes can be catalyst poisons for homogenous catalytic processes for the conversion of alkenes into higher value products.^[2a,b] Frequently the desired component is the alkene which can be, for example, hydroformylated into the corresponding aldehyde with an extension of the carbon chain.^[3] It is therefore necessary to selectively reduce the catalyst poisons without affecting the alkene before the feed is introduced to the catalyst.^[4] A number of catalysts have found use in this application; however, they normally contain expensive metals

such as palladium,^[4] which are themselves vulnerable to poisoning.^[5] Although their selectivity can be high, their cost could be prohibitive for general widespread use. It would be therefore advantageous to find an inexpensive catalyst for continuous flow processes which can offer the same selectivity.

In 2007 the first example of a solid catalyst with an ionic liquid layer (SCILL) showed improved selectivity in the hydrogenation of cyclo-octadiene to cyclo-octene with a SCILL nickel catalyst, compared to the uncoated version.^[6] The idea behind the study was to see if the ionic liquid could increase selectivity based on differences of solubility of the cyclo-octadiene versus cyclo-octene in the ionic liquid. The authors found increased selectivity at partial conversion but could not account for the increase by solubility differences of these substrates alone and postulated that the ionic liquid must act as a co-catalyst by modifying the catalyst in some way. Since then a few other studies using SCILL catalysts have been undertaken which show marked increases in selectivity^[7a,b] in the hydrogenation of other functional groups. More recently the first example of a continuous process using a palladium SCILL catalyst for citral hydrogenation showed 100% selectivity (at approximately 50% conversion) towards citronellal^[8] and a related microwave assisted version of this selective hydrogenation has also been reported.^[9] The potential reasons for these selectivity increases have only recently been investigated by studies into the surface changes of metals by ionic liquids.^[10a,b] It has also been shown that in the surface modification of catalysts by ionic liquids, the 1-alkyl-3-methyl imidazolium cation can occupy different catalyst sites, resulting in site specific modification. Furthermore, upon heating the ionic liquid decomposition can occur and result in the formation of metal-carbon species,^[10b] which may show different catalytic properties.

It is therefore possible that these site specific modifications can cause a change in selectivity in the following ways: 1) with substrates that react at different sites the ionic liquid may increase selectivity by blocking one site preferentially; 2) in substrates that share an active site the ionic liquid may discriminate between them by its relative ability to compete for adsorption on the active site; 3) the catalyst may also be chemically modified by decomposition products from the ionic liquid. In addition, the relative solubility and thus concentrations of the reactants in the ionic liquid can play a role. For continuous flow processes there is also the possibility of initial kinetic effects influencing the selectivity. For example, it stands to reason that differences in the rate of reactant transfer across the liquid-liquid boundary to obtain a local saturation, as well as any differences in the diffusion rates through the ionic liquid to reach overall saturation (all potentially influenced by temperature and the concentration of the reactants) may lead to an initial selectivity which can change until a steady state is achieved. This is assuming that the

ionic liquid layer is sufficiently thick to cause this effect. These ideas are incorporated in Figure 1.

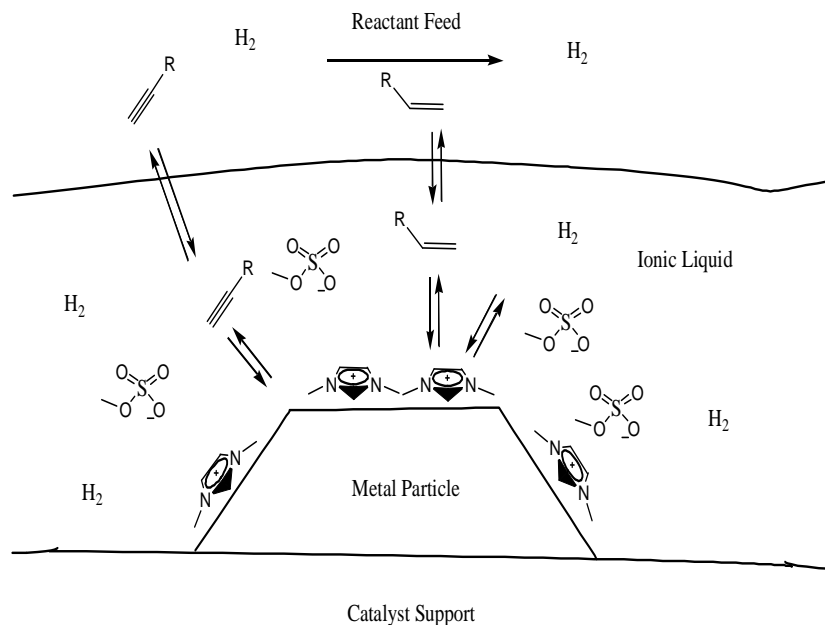


Figure 1. A model of the potential effects in a SCILL catalyst.

Finally attention should be given to the properties of the SCILL catalyst as a function of the type of ionic liquid used. Evidence for the interactions of both the cation and anion of the ionic liquid with the metal catalyst has been reported.^[9,10a,b,11]

Part of an investigation into the selective removal of alkyne and diene poisons in SASOL Fischer-Tropsch alkene streams by (chemo) selective hydrogenation involves the evaluation of SCILL catalysts. In this regard we have selected an extreme case of a 1:1 alkyne-alkene (or 1:1 diene-alkene) mixture with the object to see whether SCILL catalysts could assist in the reduction of the alkyne (or diene) with a minimal loss in the alkene content. A positive result would demonstrate the beneficial effect of (chemo) selective reduction of an alkyne (or diene) over the reduction of an alkene. More specifically we now report the results of competitive hydrogenation studies in continuous flow processes of the hydrogenation of a 2% (v/v) 1,7-octadiene or 1-octyne versus a 2% (v/v) 1-octene solution in hexane at a constant conversion

[illegible]

In the data in Table 1, there is no major difference in the surface area, pore volume and pore size between the catalysts coated to the same degree with the different ionic liquids, which indicates similar ionic liquid layer thicknesses,^[6] even though there are variations in the molar amounts of the ionic liquids used. This has been found in previous studies investigating different ionic liquids with SCILL catalysts.^[9] Changes in catalyst performance (between the different ionic liquids) due to these surface parameters should therefore be similar. There is, however, a difference between the 10 and 25% coated catalysts; as well as between the coated and uncoated catalysts. This shows that the presence and increasing mass of ionic liquid has an effect on these parameters which is consistent with literature.^[6]

2.3.2 Hydrogenation of 1-octyne with 1-octene in hexane

The reaction profile for the hydrogenation of the 2% 1-octyne and 2% 1-octene in hexane system ($GSV = 4.43 \times 10^{-1} s^{-1}$; $LSV = 3.33 \times 10^{-2} s^{-1}$) using the uncoated catalyst can be seen in Figure 2a. It is interesting to note that as the reaction time progresses; there is an increase in the octene content. Similar results with related substrates have been described before for palladium and nickel catalysts and have been attributed to the build up of carbonaceous deposits on the metal particles and the concomitant formation of selective Pd-C and Ni-C species.^[12a,b] Also, the catalyst seems to undergo deactivation after 20 hours and this is likely to be the result of continuous carbonaceous build up. The profile for the identical reaction with the 10% [MMIM][OcOSO₃] ionic liquid coated catalyst can be seen in Figure 2b. The GSV and LSV were halved to obtain constant conversion ($GSV = 2.22 \times 10^{-1} s^{-1}$; $LSV = 1.66 \times 10^{-2} s^{-1}$). Similar observations have been attributed to the coating of the ionic liquid retarding accessibility to the active catalyst sites.^[6] In this experiment the reaction time was increased (effectively doubled) to equal the amount of feed processed by the uncoated catalyst. While the octene content increases with time over both the coated and uncoated catalyst, the initial octene content is considerably higher with the coated catalyst, moreover catalyst deactivation with regards to 1-octyne hydrogenation occurs after 20 hours in the uncoated catalyst reaction, while there is no such deactivation with the coated catalyst. However, if the coated catalyst is left in the reactor under hydrogen for 7 hours before the start of the hydrogenation, instead of the usual 15-20 hours, the initial reaction profile in the first 10 hours is difficult to reproduce. Nevertheless, the octene content is initially less but with time attains values identical to those of the catalyst left under H₂ for 15-20 hours. These results suggest that the increased octene content caused by the ionic liquid may be due to the slow formation of Ni-C species and/or of “ligand molecules” resulting from the decomposition at the catalyst-ionic liquid interface under the reaction

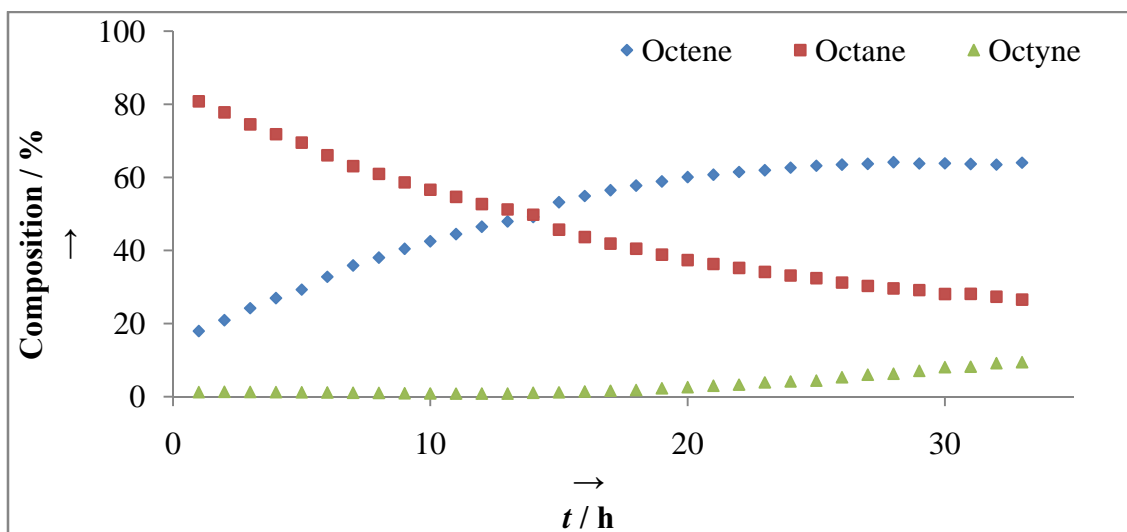
conditions. Indeed, XPS studies have shown that heating a palladium on alumina catalyst coated with an ionic liquid to 300 K results in decomposition fragments, primarily from the methyl imidazolium cation, which preferentially binds to the active metal particles.^[10a,b]

Comparison of Figures 2a and 2b shows the differences in the alkene content both initially (from ca. 20% to 65%) and eventually (≥ 10 hours, from ca. 63% to 75%). These differences are significant, particularly since the results pertain to a bigger or equal to ca. 93% alkyne conversion. This is comparable to, if not better than, the selectivity obtained for citronenall at high conversions.^[8]

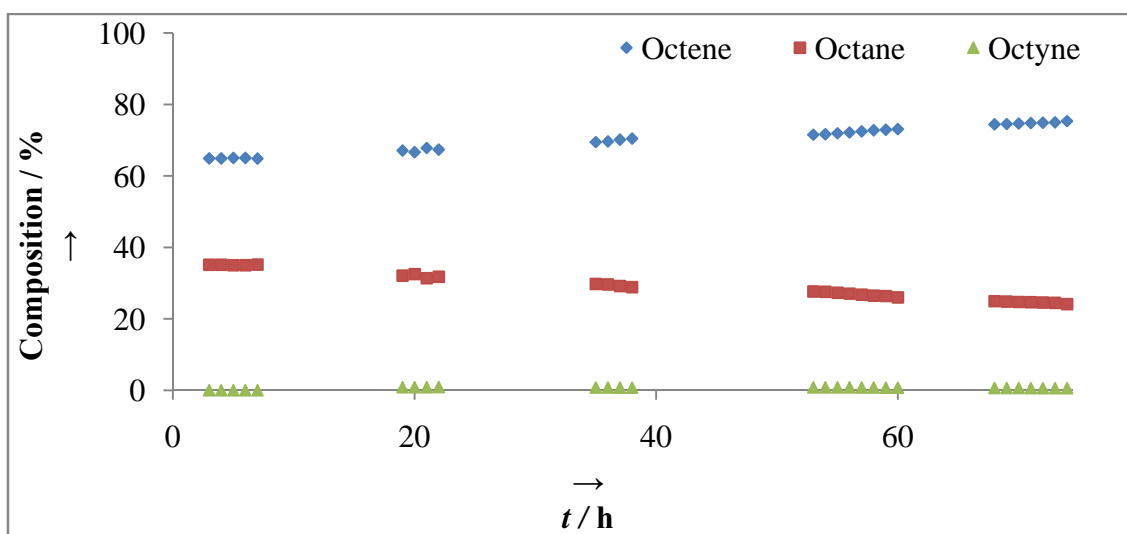
To see any potential effects on the octene content and activity by polarity and general anion changes in the ionic liquid, the ionic liquids [MMIM][MeOSO₃] and [MMIM][NTf₂] were used and compared to [MMIM][OcOSO₃] over the first 10 hours. Additionally the ionic liquids [MeP_{sec}-Bu₃][MeOSO₃] and [Et₃S][NTf₂] were used to show any influence by the cation; both the anions [NTf₂] and [OcOSO₃] have been previously used in SCILL catalysts.^[6,7b] The effects of the various ionic liquids can be seen by comparing Figures 2c-h.

From the reaction profiles for the 10% ionic liquid loaded catalysts it appears that the octene content is the same after 10 hours. This indicates that the anion does not play a major role in this regard. An effect of loading can be seen in the 25% ionic liquid loaded catalysts, whereby there seems to be a slight increase in octene content ($\geq 80\%$ in the first 2 hours). There was however a decrease in both activity and octene content with the [MMIM][NTf₂] coated catalysts compared to the other ionic liquids. While these results confirm that the use of SCILL catalysts improves selectivity, the increase in selectivity was not dramatic. The effect of lower conversion of 1-octyne on octene content is presently under investigation.

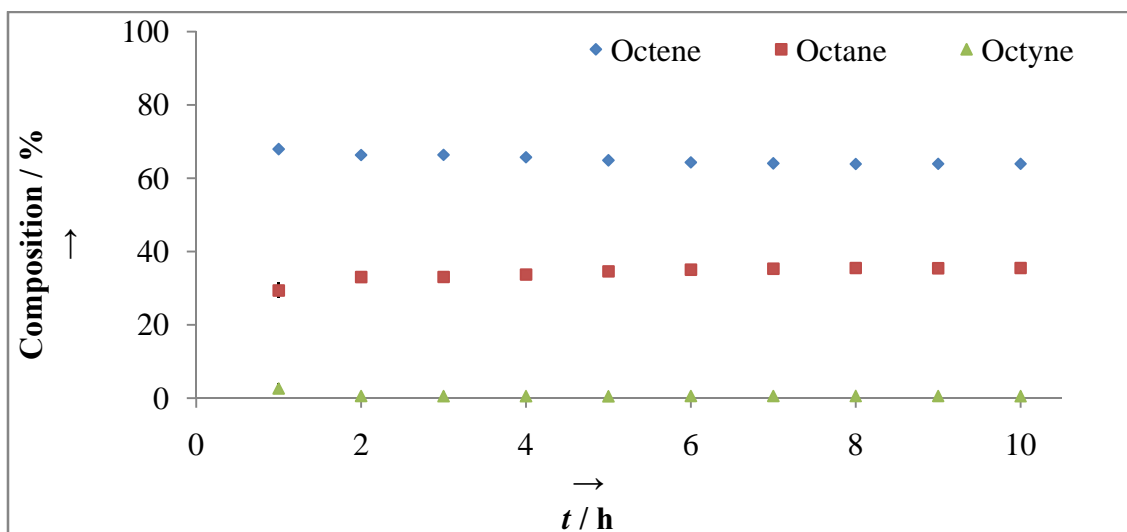
The catalysts coated with the [MeP_{sec}-Bu₃][MeOSO₃] and [Et₃S][NTf₂] ionic liquids were found to be inactive, which may be a result of a potential poisoning of the catalyst by the ionic liquid. This inactivity was also found in the competitive hydrogenation of the 2% 1,7-octadiene with 2% 1-octene in hexane reactions.



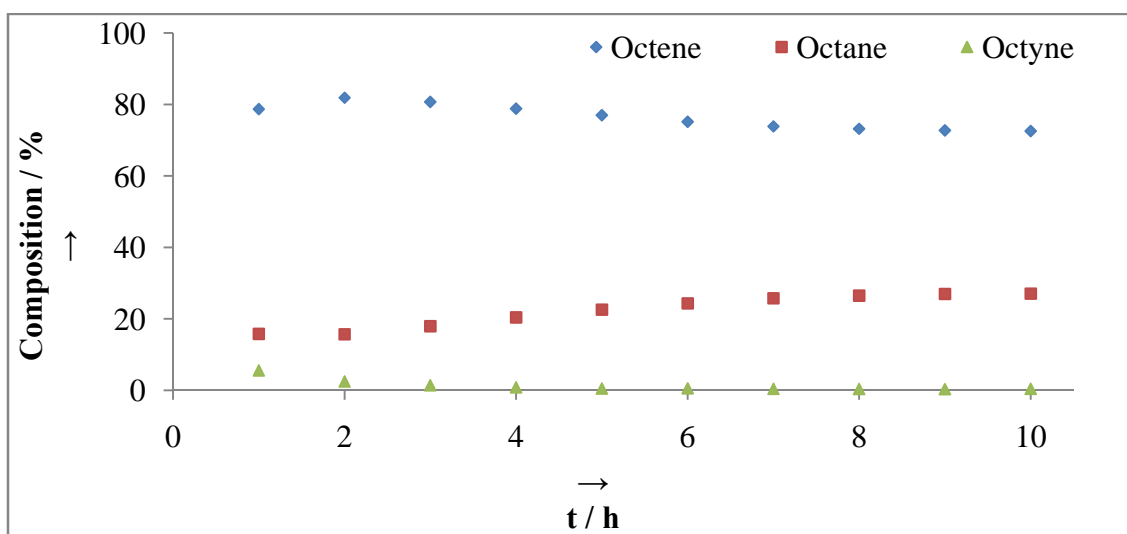
2a. uncoated catalyst ($\text{GSV} = 4.43 \times 10^{-1} \text{s}^{-1}$; $\text{LSV} = 3.33 \times 10^{-2} \text{s}^{-1}$)



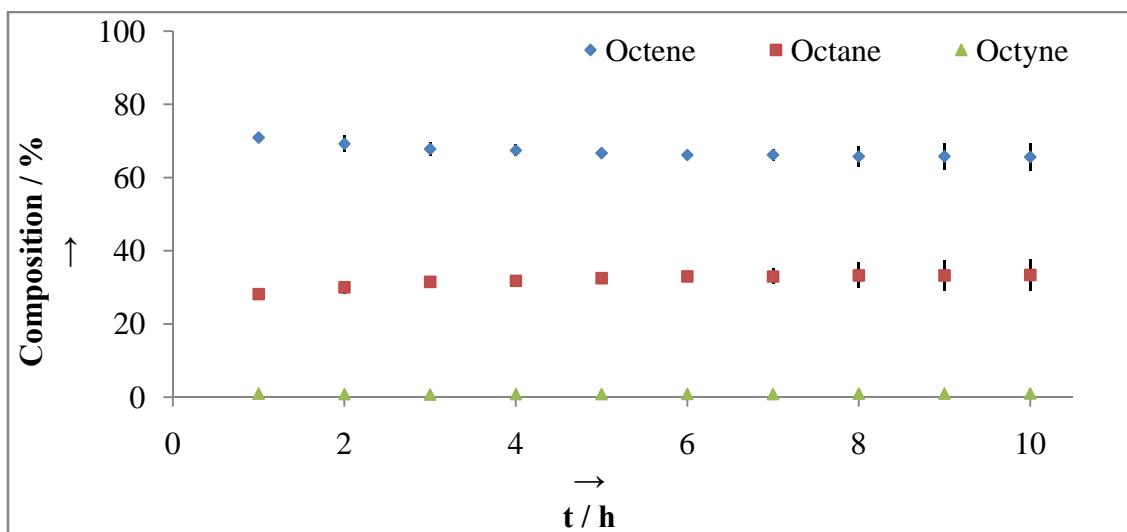
2b. 10% [MMIM][OcOSO₃] coated catalyst ($\text{GSV} = 2.22 \times 10^{-1} \text{s}^{-1}$; $\text{LSV} = 1.66 \times 10^{-2} \text{s}^{-1}$)



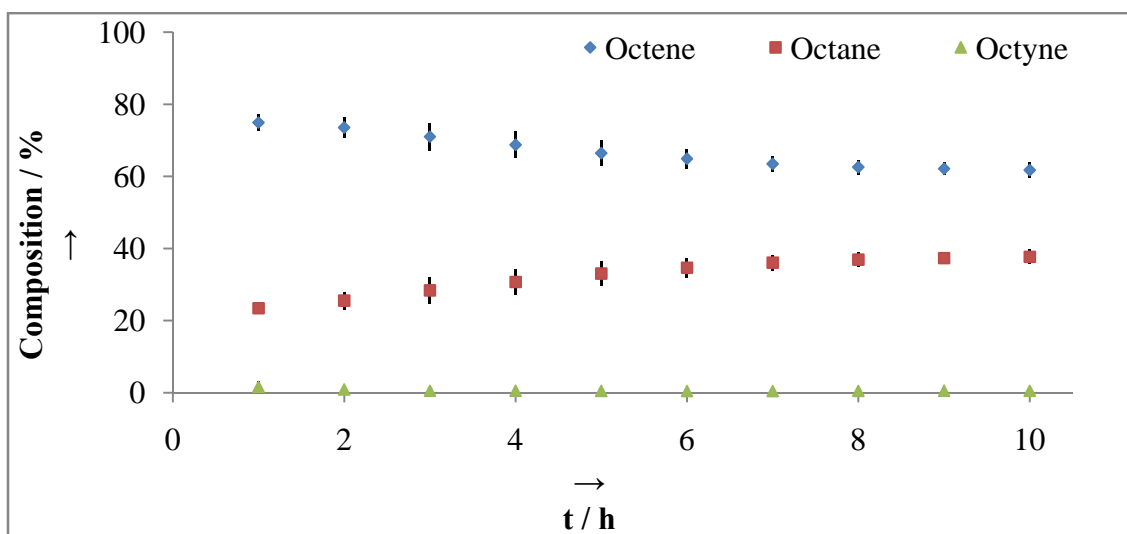
2c. 10% [MMIM][OcOSO₃] coated catalyst (GSV = $2.22 \times 10^{-1} \text{ s}^{-1}$; LSV = $1.66 \times 10^{-2} \text{ s}^{-1}$)



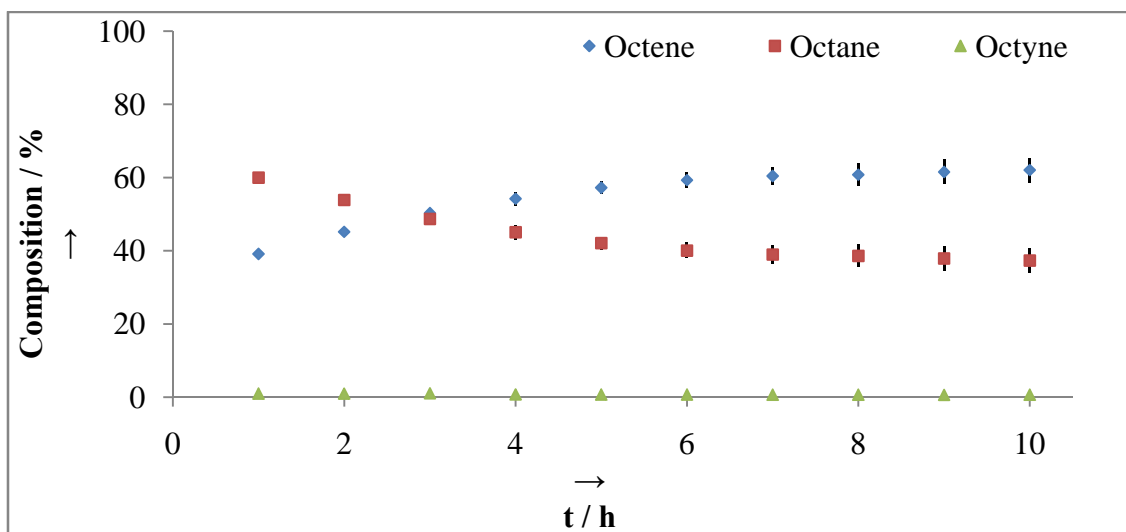
2d. 25% [MMIM][OcOSO₃] coated catalyst (GSV = $2.22 \times 10^{-1} \text{ s}^{-1}$; LSV = $1.66 \times 10^{-2} \text{ s}^{-1}$)



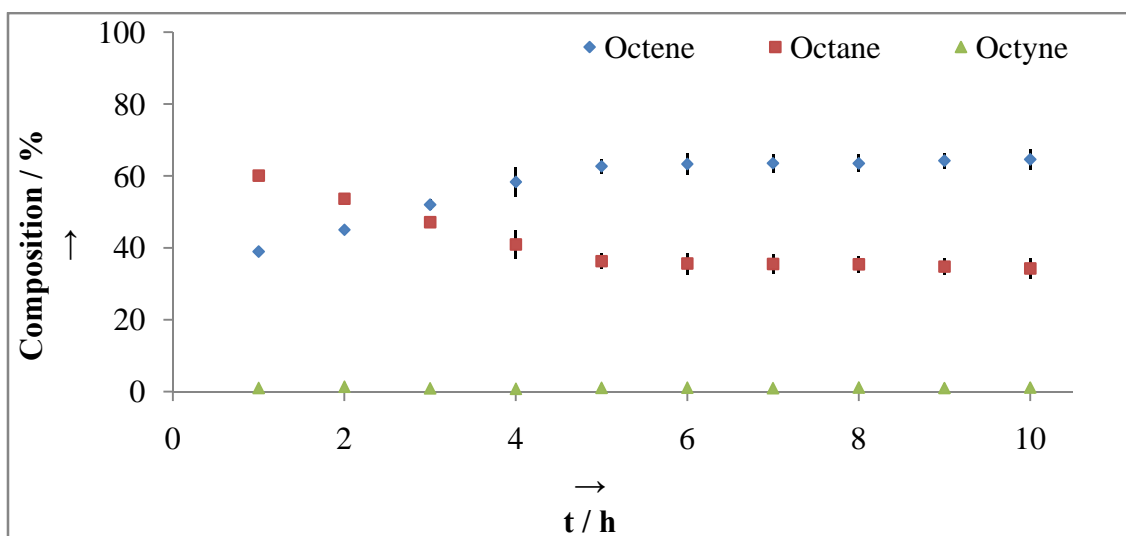
2e. 10% [MMIM][MeOSO₃] coated catalyst (GSV = $2.22 \times 10^{-1} \text{ s}^{-1}$; LSV = $1.66 \times 10^{-2} \text{ s}^{-1}$)



2f. 25% [MMIM][MeOSO₃] coated catalyst (GSV = $2.22 \times 10^{-1} \text{ s}^{-1}$; LSV = $1.66 \times 10^{-2} \text{ s}^{-1}$)



2g. 10% [MMIM][NTf₂] coated catalyst (GSV = $1.67 \times 10^{-1} \text{ s}^{-1}$; LSV = $1.25 \times 10^{-2} \text{ s}^{-1}$)



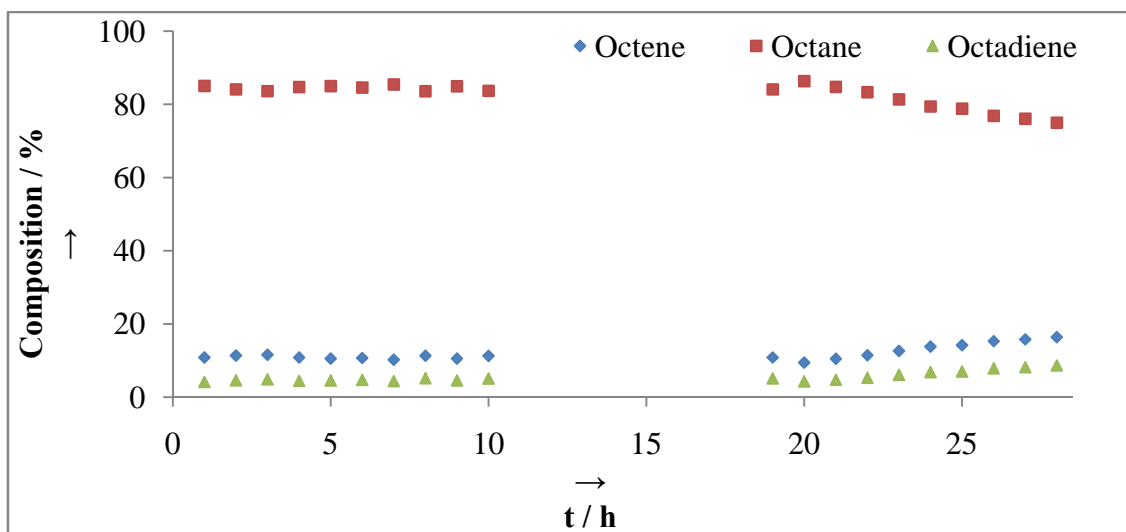
2h. 25% [MMIM][NTf₂] coated catalyst (GSV = $1.67 \times 10^{-1} \text{ s}^{-1}$; LSV = $1.25 \times 10^{-2} \text{ s}^{-1}$)

Figure 2a-h. Competitive hydrogenation between 1-octyne and 1-octene, error bars represent standard deviation.

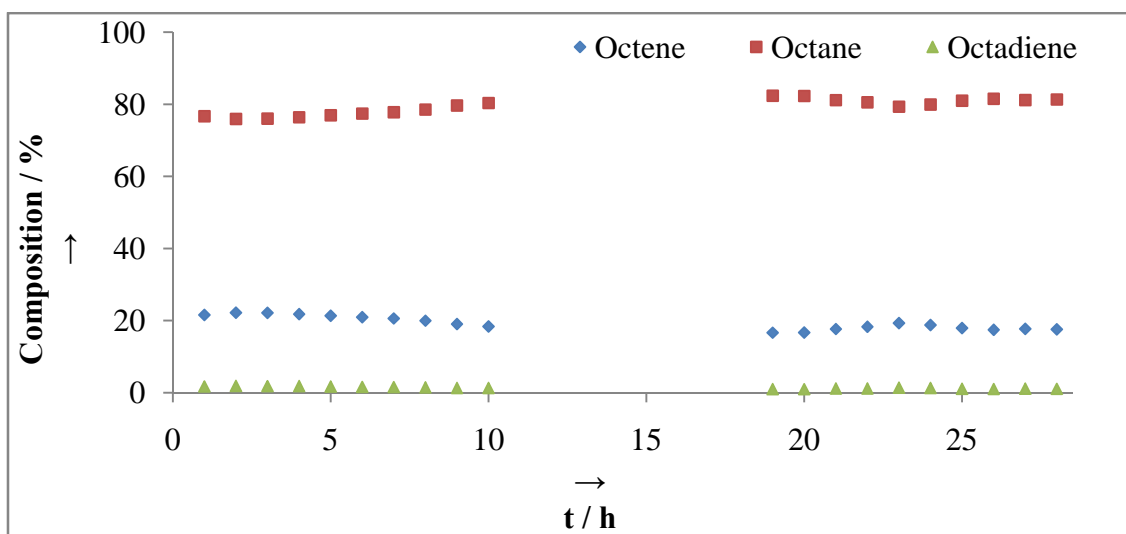
2.3.3 Hydrogenation of 1,7-octadiene with 1-octene in hexane

From the reaction profile for the competitive hydrogenation using the uncoated catalyst (Figure 3a), it is noticeable that there is a relatively low octene content. This is understandable since the reducible groups of the reactants are essentially the same and compete for reaction at the same sites. Catalyst deactivation, with regards to 1,7-octadiene hydrogenation, is observed after 20 hours. This was also observed in the competitive hydrogenation of 1-octyne. In both cases this could be due to carbonaceous build up inhibiting the availability of reaction sites. The reaction profile of the catalyst coated with 10% [MMIM][OcOSO₃] (Figure 3b) showed an approximate doubling of the octene content which is in agreement with observations reported in literature for the reduction of 1,5-cyclooctadiene using a nickel SCILL catalyst in a batch process.^[6] However, the space velocity of the reaction to bring about constant conversion of the 1,7-octadiene was approximately a quarter that of the uncoated catalyst, rather than the half as seen in the 1-octyne system. The rate of the reaction with 10% of [MMIM][MeOSO₃] (Figure 3e) was even slower, requiring a space velocity of one seventh that of the uncoated catalyst. This indicates the (potential) effects of polarity (and therefore solubility of the reactants) of the ionic liquid on reaction rates with a SCILL catalyst.

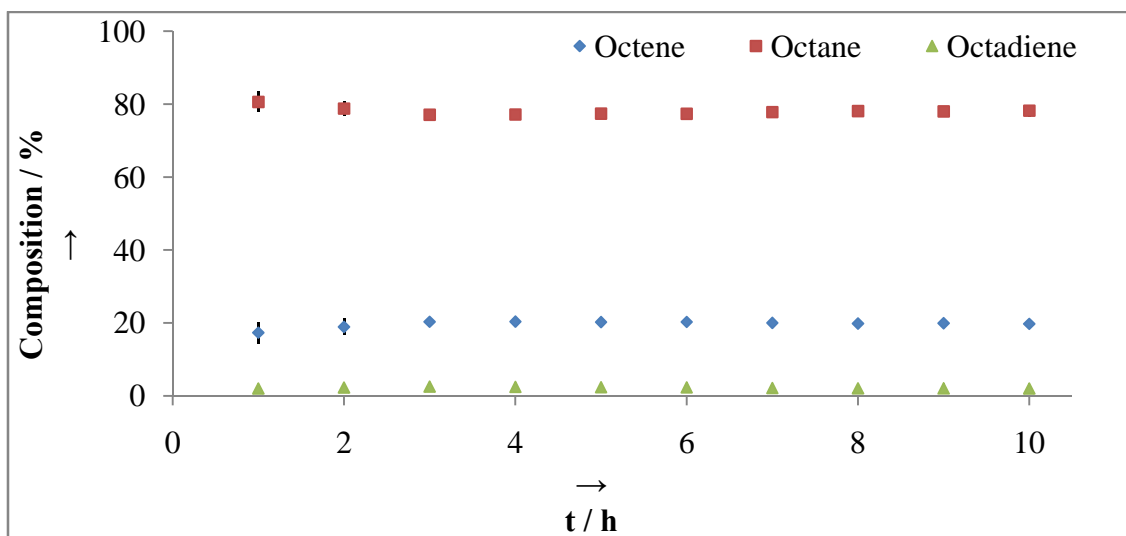
Interestingly, the reactions with the [MMIM][NTf₂] ionic liquid required 1.7 times the GSV and LSV needed for the [MMIM][OcOSO₃] ionic liquid system to obtain constant conversion with the same octene content, even though the solubilities of these reactants, which were determined experimentally, are less in [MMIM][NTf₂]. The solubility of the reactants in the ionic liquid is discussed later. Additionally, by more than doubling the amount of the ionic liquid of the differently coated ionic liquid catalysts, the GSV and LSV of the reactions were more than halved, but remained in the same order of magnitude. This decrease in activity was not seen in the competitive hydrogenation of 1-octyne and 1-octene. Additionally the change of ionic liquid to [MMIM][NTf₂] causes an opposite effect in activity with respect to the earlier reaction (1-octyne versus 1-octene). These results lend experimental evidence to the possibility of site specific interaction of the ionic liquid with the metal catalyst.



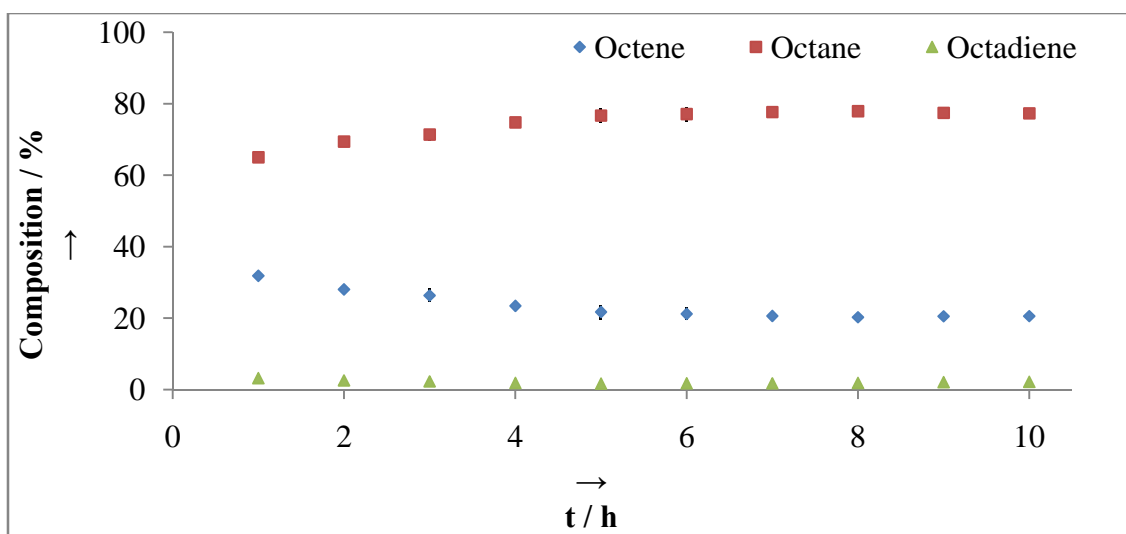
3a. uncoated catalyst ($GSV = 2.77 \times 10^{-1} s^{-1}$; $LSV = 2.08 \times 10^{-2} s^{-1}$)



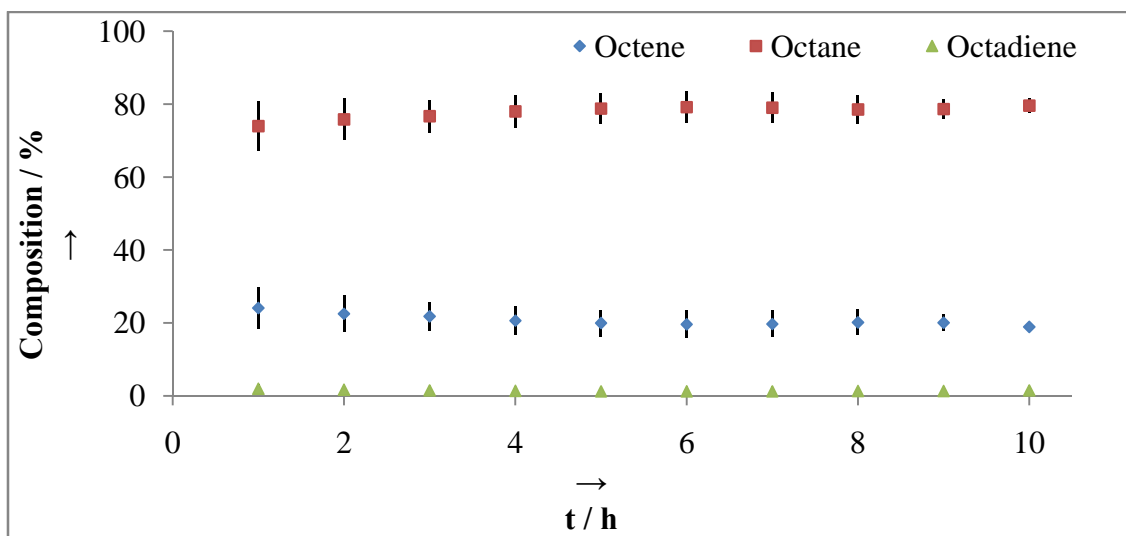
3b. 10% $[MMIM][OcOSO_3]$ coated catalyst ($GSV = 6.92 \times 10^{-2} s^{-1}$; $LSV = 5.21 \times 10^{-3} s^{-1}$)



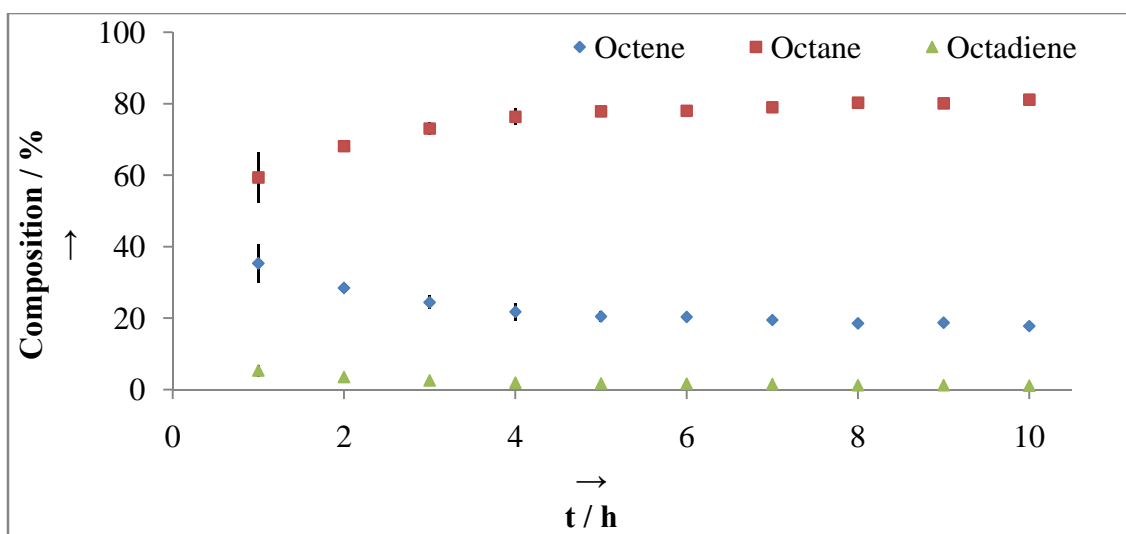
3c. 10% [MMIM][OcOSO₃] coated catalyst (GSV = $6.92 \times 10^{-2} \text{ s}^{-1}$; LSV = $5.21 \times 10^{-3} \text{ s}^{-1}$)



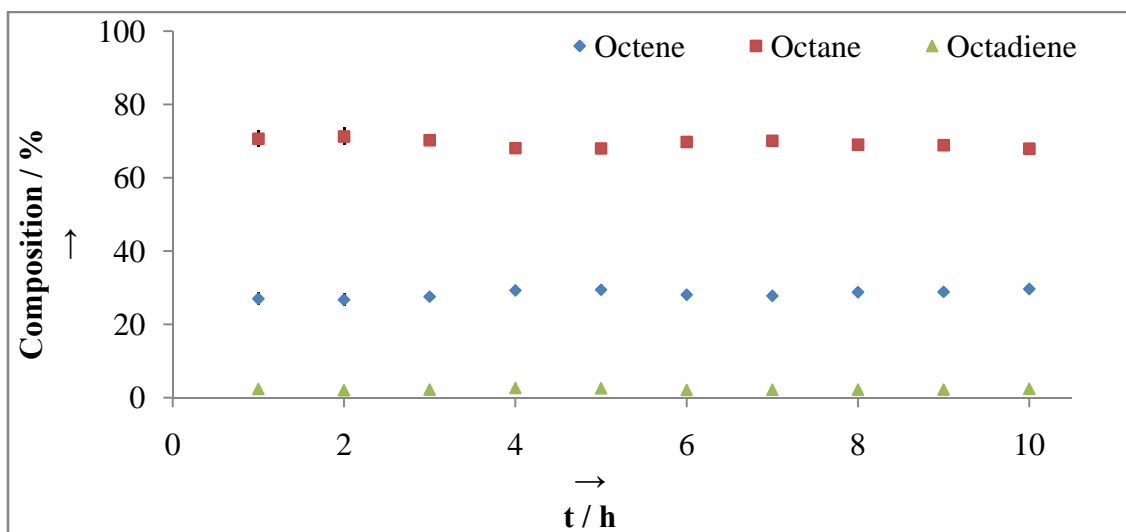
3d. 25% [MMIM][OcOSO₃] coated catalyst (GSV = $1.86 \times 10^{-2} \text{ s}^{-1}$; LSV = $1.39 \times 10^{-3} \text{ s}^{-1}$)



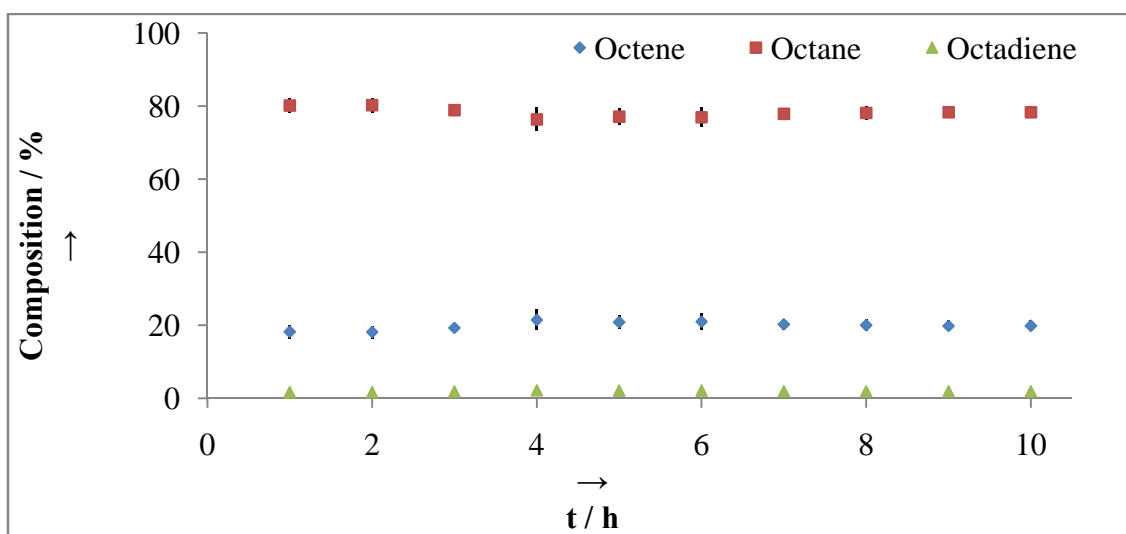
3e. 10% [MMIM][MeOSO₃] coated catalyst (GSV = $4.17 \times 10^{-2} \text{ s}^{-1}$; LSV = $3.13 \times 10^{-3} \text{ s}^{-1}$)



3f. 25% [MMIM][MeOSO₃] coated catalyst (GSV = $9.17 \times 10^{-3} \text{ s}^{-1}$; LSV = $6.94 \times 10^{-4} \text{ s}^{-1}$)



3g. 10% [MMIM][NTf₂] coated catalyst (GSV = $1.18 \times 10^{-1} \text{ s}^{-1}$; LSV = $8.83 \times 10^{-3} \text{ s}^{-1}$)



3h. 25% [MMIM][NTf₂] coated catalyst (GSV = $4.17 \times 10^{-2} \text{ s}^{-1}$; LSV = $3.13 \times 10^{-3} \text{ s}^{-1}$)

Figure 3a-h. Competitive hydrogenation between 1,7-octadiene and 1-octene, error bars represent standard deviation.

2.3.4 *A summary of results between the 1-octyne and 1,7-octadiene with 1-octene systems*

Our results show that, not surprisingly, the use of SCILL catalyst can have a dramatic effect on reaction rates. In addition the results also show that even at high conversions of 1-octyne there is a significant increase in octene content with SCILL catalysts. This increase in octene content is less apparent in the 1,7-octadiene system and suggests that high selectivity requires substantial differences in functional groups, at least in the case of hydrogenation over nickel catalysts.

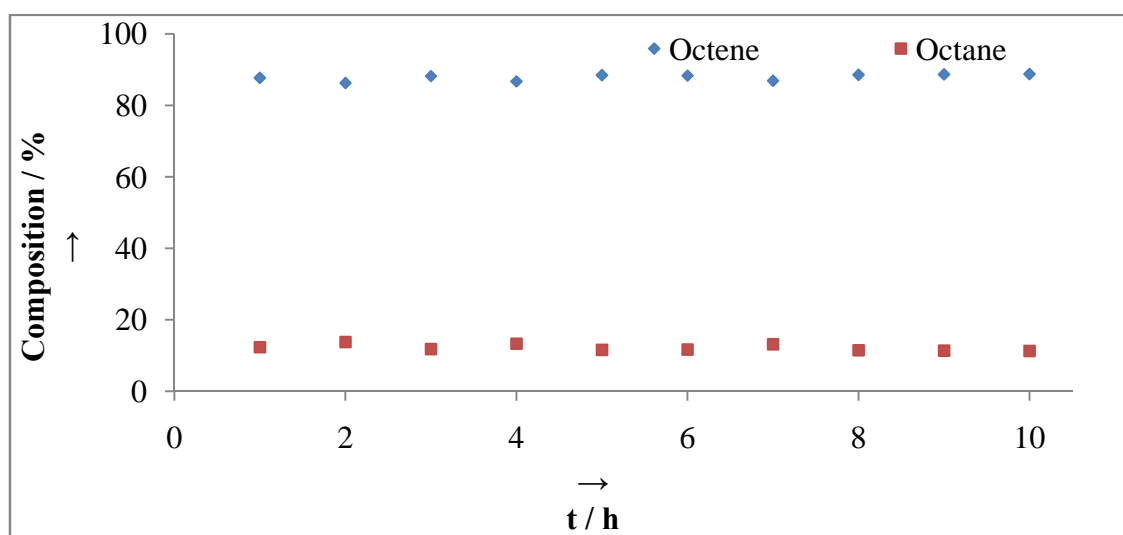
The effects observed can be viewed as a combination of effects mentioned by other authors including selective blockage of active sites and/or chemical modification of the active sites.^[10a,b] To further demonstrate the possibility of a site specific interaction by the MMIM cation, reactions containing the individual components were conducted under the same conditions as the mixed reactant reactions. The result can be seen in Figure 4a-e. The reaction profile for the 2% octene feed shows that under the same conditions as the mixed reactant feed for the 1-octyne system there is relatively low conversion to octane; whereas the 2% 1-octyne reaction shows complete reduction of 1-octyne to octene as well as a large amount of octane. If this is compared to the uncoated catalyst in the mixed feed reactions then it appears that the ionic liquid is blocking sites specific to octene hydrogenation, which may be unblocked by the alkyne. Additionally, if the absolute values of the components are added together they approximately equal the composition of the mixed feed reactions.

Figure 4e shows the reaction profile for 2% 1,7-octadiene in hexane; the octene content and space velocity for constant conversion of 1,7-octadiene remain the same as the 2% 1,7-octadiene with 2% 1-octene in hexane (Figure 3h), which is surprising since under competitive reaction conditions for two competitors it is easy to assume that a decrease in the concentration of one competitor for an active site will cause an increase in the rate of reaction for the other (i.e. an increase in the space velocity for constant conversion of 1,7-octadiene). This experimental observation lends additional evidence to site-specific interaction by the ionic liquid if there is complete coverage by the MMIM cation of the active sites, with two competitors displacing the MMIM cation.

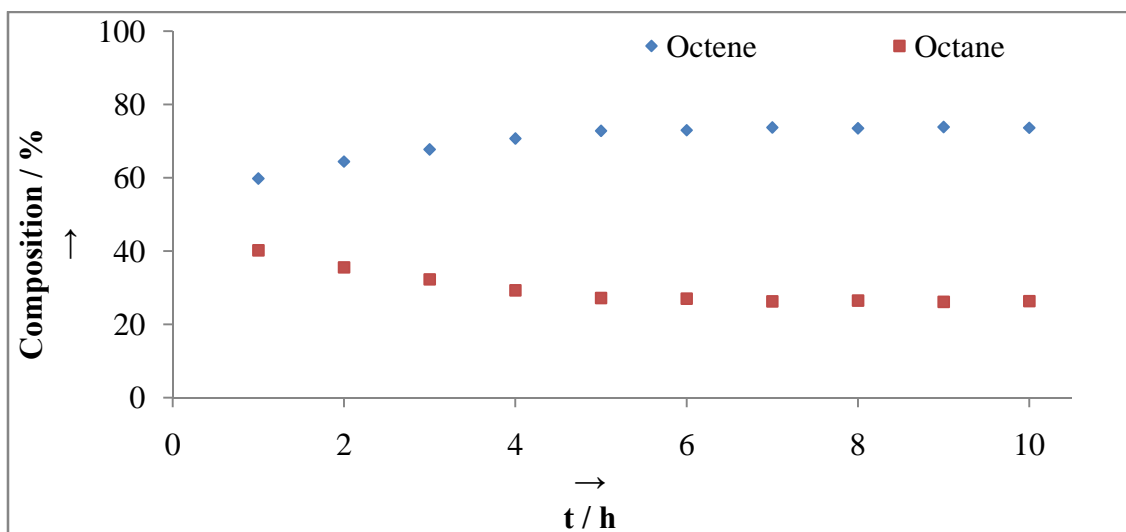
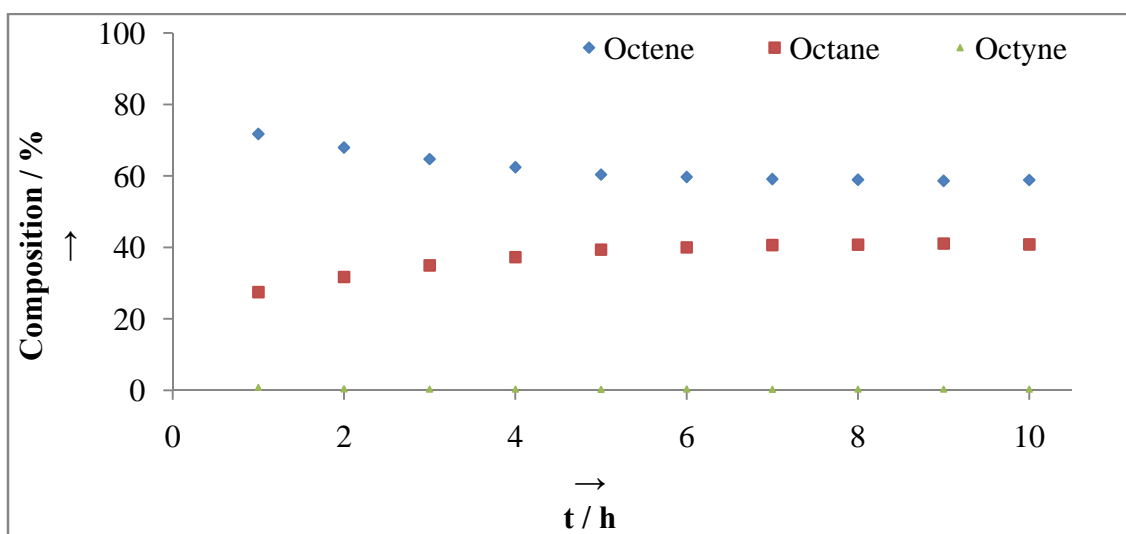
However, it may be that some of the results pertaining to the effect of different loadings suggest, at least to a small extent and in addition to other effects previously described in literature, that

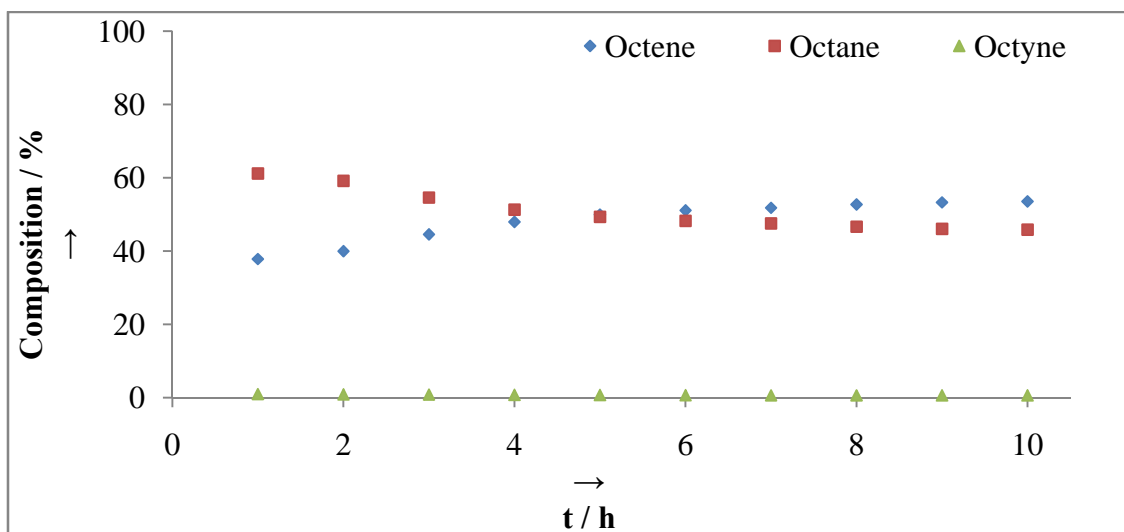
the ionic liquids could be influencing the surface diffusion of one or more of the reactants on the catalyst interface. It is well known that the surface diffusion of adsorbed species is an important aspect which can influence the performance of heterogeneous catalysts, and that the chemical properties of the support (and modifications thereof) play a role in these processes; such as the spill over effect of reactants including oxygen, hydrogen and hydrocarbons.^[13] However, it may well be that the differences in solubility of the reactants in the ionic liquids is a more important cause for the observed differences in activity between the SCILL catalysts.

The solubility of 1-octyne, 1,7-octadiene and 1-octene in the various ionic liquids at 50 °C were experimentally determined to be (51.88 g/100 g, 24.89 g/100 g, 15.69 g/100 g) in [MMIM][OcOSO₃], (0.35 g/100 g, 0.10 g/100 g, relatively insoluble) in [MMIM][MeOSO₃] and (3.12 g/100 g, 2.17 g/100 g, 1.08 g/100 g) in [MMIM][NTf₂], respectively. However, these trends in solubility do not seem to precisely match the trends in activity observed between the different SCILL catalyst reactions. It could possibly be that the variations in the molar amounts of ionic liquid used to coat the catalysts are influencing the observed activities, but this may also be an aspect of surface diffusion effects. We are now engaged in studies to determine the credibility and extent of surface diffusion effects influenced by ionic liquids, as well as to ascertain with theoretical models the influence of solubility differences and how they change under reaction conditions, compared to the effects of any potential site specific interaction by the ionic liquid.

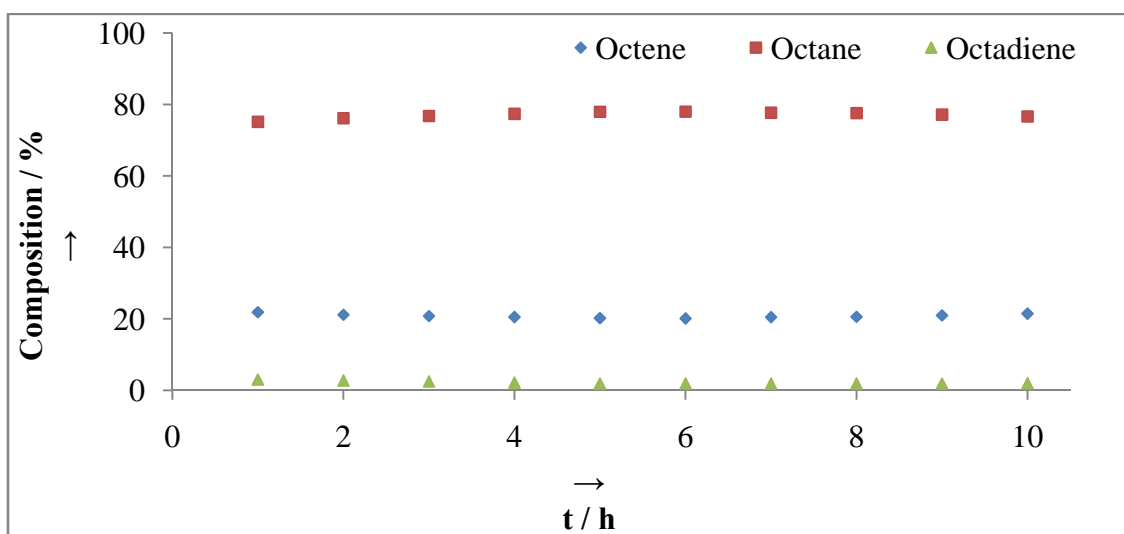


4a. 2% 1-octene using 25% [MMIM][OcOSO₃]

4b. 2% 1-octene using 25% [MMIM][NTf₂]4c. 2% 1-octyne using 25% [MMIM][OcOSO₃]



4d. 2% 1-octyne using 25% [MMIM][NTf₂]



4e. 2% 1,7-octadiene using 25% [MMIM][NTf₂]

Figure 4a-e. Reaction profiles of the individual components using the same SV's of the mixed component reactions.

2.3.5 The ionic liquids $[Et_3S][NTf_2]$ and $[MePsec-Bu][MeOSO_3]$

The catalysts coated with the ionic liquids $[Et_3S][NTf_2]$ and $[MePsec-Bu][MeOSO_3]$, unexpectedly, were inactive in the hydrogenation reactions, even though the solubility of 1-octyne, 1,7-octadiene and 1-octene were experimentally determined to be (6.07 g/100 g, 3.69 g/100 g, 1.56 g/100 g) in $[Et_3S][NTf_2]$ and (33.88 g/100 g, 9.38 g/100 g, 6.00 g/100 g) in $[MePsec-Bu][MeOSO_3]$, respectively. This may possibly be ascribed to a strong binding of the cations to all active sites. Alternatively, decomposition products of the ionic liquids could be involved, where the possibility of the formation of nickel sulphides or phosphides cannot be excluded. However, XPS spectra did not show the presence of NiP and NiS (see Appendix). Indeed literature has shown that NiP and NiS oxidises to nickel oxide, nickel hydroxide, nickel phosphate, nickel phosphite and nickel sulphate in the presence of oxygen.^[14a,b] The phosphorus and sulphur from these ionic liquids may therefore be unlikely to form NiP and NiS from a catalyst particle which has a layer of nickel oxide, common for finely divided nickel particles. The XPS analysis did reveal the presence of nickel oxide.

2.4 Conclusion

It has been shown that with the use of a SCILL nickel catalyst in the hydrogenation of a 1-octene/1-octyne mixture, substantial increases in the octene content can be attained even at high conversions of 1-octyne.

There have been several potential reasons described for the effects of coating a catalyst with an ionic liquid.^[6,10a,b] Some have been dismissed,^[6] whereas others need further investigation. Ultimately the results of this study suggest that the enhanced octene content can be ascribed to site specific interactions on one hand and, in addition to solubility differences, potential surface diffusion effects on the other which can influence activity. The MMIM cation is likely to be partially blocking the sites specific for 1-octene and 1,7-octadiene hydrogenation on a nickel catalyst and not 1-octyne hydrogenation. Furthermore coating a nickel catalyst with the ionic liquids $[Et_3S][NTf_2]$ and $[MePsec-Bu][MeOSO_3]$ resulted in inactivity in the hydrogenation reactions, highlighting the importance of the cation in SCILL catalysts.

The possibility and extent of altered solubility of the reactants under reaction conditions in the ionic liquids, and the potential change in surface diffusion processes caused by the ionic liquids is currently being explored.

2.5 Experimental Section

The ionic liquids [MMIM][MeOSO₃] and [MMIM][OcOSO₃] were prepared by methods already described in literature by the alkylation of 1-methylimidazole with dimethylsulphate followed by a trans-esterification reaction with octanol.^[15a,b] The [MePsec-Bu₃][MeOSO₃] ionic liquid was obtained from SASOL R&D and the [Et₃S][NTf₂] ionic liquid from Sigma Aldrich. The ionic liquid [MMIM][NTf₂] was synthesised by an anion exchange of [MMIM][MeOSO₃] with [Na][NTf₂]. NMR analysis was used to confirm of the purity and identity of the synthesised ionic liquids.

A nickel on alumina catalyst (ca. 29% w/w) was prepared by wet impregnation of a crushed gamma alumina support with nickel nitrate at 70 °C for 4 hours. The resultant paste was dried in an oven at 110 °C for an additional 2 hours before being calcined at 500 °C for 8 hours. The catalyst was then pelletized to a size distribution between 300 and 600 µm before reduction under hydrogen for 4 hours at 525 °C with a hydrogen flow rate of 10 ml/min. The resultant catalyst was then coated with the following ionic liquids [MMIM][OcOSO₃], [MMIM][MeOSO₃], [MMIM][NTf₂], [MePsec-Bu₃][MeOSO₃] and [Et₃S][NTf₂] by dissolving the required amounts of ionic liquid in either methanol or dichloromethane in a pill vial before introducing the parent catalyst. The mixture was allowed to evaporate slowly in a fume hood to obtain a dry powder which was then placed under high vacuum for 60 minutes to ensure the complete removal of the organic solvent.

Temperature programmed reduction (5% H₂ in Ar) (Micromeritics Autochem II 2029) and powder XRD analysis (Bruker D2 Phaser) were used to confirm the reduction of the catalyst and the average particle size of the nickel particles was determined by the use of a JEOL 2100 HRTEM counting approximately 300 particles under high angle annular dark field (HAAD) conditions. The average particle size was found to be approximately 14 nm and did not vary significantly between new and used catalysts. Inductively coupled plasma optical emission spectroscopy (Perkin Elmer DV5300) was used to confirm the weight percent loading of the

nickel and that the ionic liquid remains intact on the catalyst after the reaction which is consistent with previously reported findings.^[6,8] BET and pore size distribution were determined on a Micromeritics ASAP 2020 to determine the extent of the reduction in pore volume and surface area of the different ionic liquid coated catalysts compared to the parent catalyst. XPS analysis was performed on a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. For the analyses of catalysts requiring high vacuum techniques, the catalysts were washed five times with the solvent used to dissolve the ionic liquid and coat the catalyst.

Hydrogenation experiments were carried out in a concurrent down flow trickle bed reactor with an inner diameter of 14 mm and a length of 250 mm to give a volume of 38.5 cm³. The catalyst (1-6 cm³) was diluted with carborundum (grit size 24) to give a total volume of 8 cm³ which also served to prevent aniso-thermal conditions as well as a large pressure drop across the column. The rest of the reactor was packed with carborundum and quartz wool was used as a plug at the ends of the carborundum and the catalyst bed which served as an efficient dispersant of the liquid phase.^[16] A 2% 1-octyne or 1,7 octadiene mixture with 2% 1-octene in hexane was introduced into the reactor by means of an HPLC pump and the hydrogen introduced by means of mass flow controllers at a constant substrate to hydrogen ratio of 1:2. A hexane feed was used to provide a non polar liquid phase to prevent any stripping of the ionic liquid present on the catalyst surface as well as to prevent any potential interference with the product analysis by a gas chromatograph with a flame ionisation detector (GC-FID). The feed was dried with molecular sieves^[17] and degassed with argon^[18] to eliminate water and oxygen from the system. An argon feed was supplied to the head space of the feed bottle to give a slight positive pressure. The temperature and pressure of the reaction system was kept at 50 bar and 50 °C (to emulate the conditions first described for these catalysts^[6]) by a temperature controlled heating jacket with an internal sliding thermocouple. The gas space velocity (GSV) and liquid space velocity (LSV) were adjusted to produce a conversion of 93% (\pm 2%) of either the 1-octyne or 1,7-octadiene for each respective catalyst type and the C₈ product composition was analysed off line by means of a GC-FID. In the 1,7-octadiene reactions isomerisation products were detected, but only amounted to ca 1% and are not shown. In almost all of the reactions the reactor was charged with fresh catalyst and kept under hydrogen for 15-20 hours at 50 °C before use. All mixed reactant reactions up to 10 hours were done in duplicate.

The solubilities of 1-octyne, 1,7-octadiene and 1-octene in the different ionic liquids were determined by NMR techniques using a Bruker 600 MHz NMR spectrometer. The substrates were stirred at 50 °C for 30 minutes with the various ionic liquids and left unstirred for 10

minutes (which formed a bi-layer) before a portion of the ionic liquid phase was transferred to an NMR tube for analysis. A proton NMR spectrum was obtained and the ratio of signals between the ionic liquid and substrate was determined. This was compared to two standards with known ionic liquid and substrate content.

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CHAPTER 3

ACTIVITY AND SELECTIVITY OF A NICKEL SCILL CATALYST IN THE COMPETITIVE HYDROGENATION BETWEEN 1- OCTENE AND 1-OCTYNE

3.1 Abstract

Competitive hydrogenation of mixtures of unsaturated compounds is still a topical area of research, mainly due to their continued presence in industrial feed stocks. Previously we have shown some advantages to using SCILL (solid catalyst with an ionic liquid layer) catalysts in the hydrogenation of 1-octyne and 1,7-octadiene versus 1-octene with various ionic liquids and levels of coating. Here we investigate the effects of coating a catalyst with the ionic liquid 1,3-dimethylimidazole methylsulphate [MMIM][MeOSO₃] at various iso-conversions in the competitive hydrogenation of 1-octyne versus 1-octene. Our results indicate that SCILL catalysts do offer advantages over this iso-conversion range (ca. 10-98%) compared to the uncoated versions. We also investigated some of the difficulties in creating SCILL catalysts which can lead to catalyst deactivation, with crystallite morphologies appearing to play a role in catalyst deactivation with time on exposure to the atmosphere.

3.2 Introduction

SCILL catalyst modification is a relatively new concept in modifications of traditional heterogeneous catalysts, which involves coating the heterogeneous catalyst with a thin film of ionic liquid. The original thought behind this modification was to increase selectivity based on differences of solubility between reactants in the ionic liquid.^[1] However, reports in literature suggest that there may be other processes occurring which may influence the selectivity and activity of the reaction.^[1,2a-d] For example, in the hydrogenation of molecules containing multiple reducible groups, changes in the selectivity of hydrogenation between these groups have been demonstrated.^[2a-d] It has also been shown by infrared studies that the cation of an

ionic liquid can occupy and potentially block specific sites on a catalyst surface, which vary depending on the metal used, and may be responsible for these changes in selectivity.^[3a,b] Recently, we showed potential catalytic evidence for site specific interactions (by the ionic liquid) affecting selectivities in the competitive hydrogenation of 1-octyne and 1,7-octadiene versus 1-octene, in which surface diffusion effects may also be occurring.^[4]

Alkyne and diene hydrogenation studies have been the focus of much attention in literature, but have traditionally been restricted to short chain molecules such as C₂ and C₄ compounds.^[5a-e] However, relating the behaviour of these short chain compounds to longer chain versions is fraught with difficulties.^[5c,6a,b] For example, small differences in the structure of the molecule intended for hydrogenation, such as a *cis* or *trans*-alkene, can dramatically influence the behaviour of the catalysts used; and their subsequent reactions with different molecules.^[6b] This is thought to occur through modification of the catalyst by different types of carbonaceous build up, with carbon depositions altering selectivity.^[6b,7a-d] This also shows that even within classes of different organic catalyst modifiers, small structural differences may have a noticeable effect on the selectivity of the reaction. As a result of this, alkyne and diene hydrogenation studies remain a topical area of research, especially with the increasing supply and demand of longer chain hydrocarbons.

Alkynes and dienes are potential catalyst poisons for a number of homogeneous catalytic reactions and are consequently removed, often by hydrogenation, before being introduced to the susceptible homogeneous catalyst.^[8a-c] As part of a study into removing these compounds from SASOL feed stocks, we investigated a series of nickel SCILL catalysts and an uncoated nickel catalyst using an extreme case of hydrogenation with a 1:1 1-octyne to 1-octene mixture at close to a 93% conversion of the alkyne.^[4] It was hoped that the SCILL catalyst could offer increased selectivity to alkyne hydrogenation over alkene hydrogenation. We were able to show an advantage of the SCILL catalyst over the uncoated version, with octene contents in the reacted feed at up to 80%. We now present the results of our investigation with a 10% (m/m) [MMIM][MeOSO₃] (1,3-dimethylimidazole methylsulphate) coated nickel on alumina (27% m/m) SCILL catalyst with lower conversion levels of the alkyne, to further elucidate any additional effects of coating a nickel heterogeneous catalyst with an ionic liquid.

We also report on some of the difficulties experienced with preparing SCILL catalysts as these catalysts are generally prepared by reduction and may, in the absence of special conditions, be exposed to the atmosphere during the ionic liquid coating procedure. Such exposure may have a

detrimental effect on catalyst activity and selectivity. It is well known that finely divided reduced metal particles can be pyrophoric,^[9] and as a result the catalyst properties can be affected on exposure to the atmosphere. Catalyst pacification of susceptible catalysts is normally used to prevent this. However, to the best of our knowledge, no catalyst pacification has been described in the preparation of SCILL catalysts. Furthermore, the method of the catalyst reduction can play a role in the performance of the catalyst. Reduction at too low a temperature may result in an incomplete reduction resulting in decreased activity. This may be of concern for SCILL catalyst preparation where complete catalyst reduction from the metal oxide occurs at a temperature higher than that of the decomposition temperature of the ionic liquid.

3.3 Results and Discussion

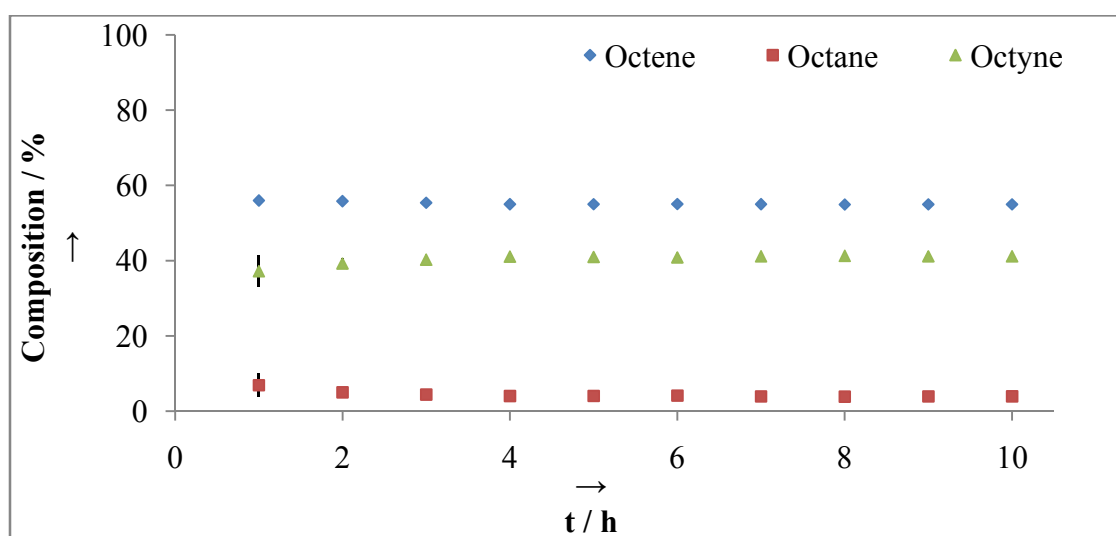
3.3.1 *Activity/selectivity relationships*

From Figure 1a-d an interesting pattern can be seen emerging from the changes in the conversion of 1-octyne in a 1:1 (v:v) feed mixture of 1-octyne and 1-octene, brought about by changes in the gas space velocity (GSV) and liquid space velocity (LSV). It is noticeable that as the 1-octyne undergoes greater conversion with decreasing space velocity, the octane content increases while the octene content remains the same. This suggests that the 1-octyne is predominantly converted directly to octane while 1-octene is unaffected, leaving the 1-octene content unchanged (a similar result is achieved with the relevant additions of the composition levels of Figure 4a-e).

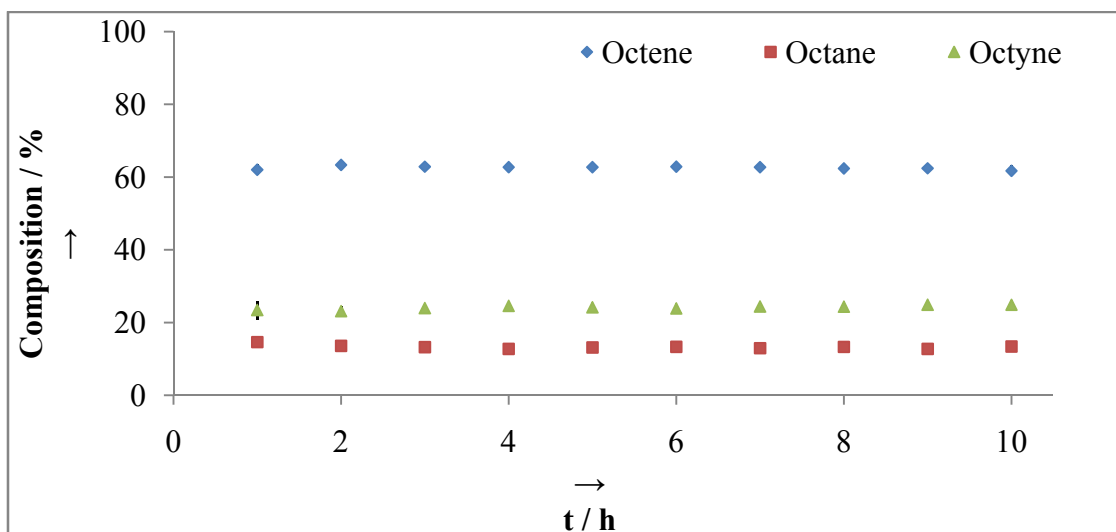
Although an isotopic study would be required for confirmation, this proposal is consistent with the possibility that the ionic liquid may be blocking active catalytic sites specific for alkene hydrogenation, while the alkyne is undergoing complete hydrogenation to the alkane. However, the possibility that an alkyne would hydrogenate straight to the alkane may appear doubtful, particularly since the literature is replete with examples of heterogeneous catalysis where an alkyne is first hydrogenated to the alkene before reacting again to form the alkane.^[10] However, in this case, it is likely that the octene content of the reaction under investigation would rise as the content of octyne decreases, which is not observed.

An alternate possibility is that the 1-octene from the feed saturates the ionic liquid, thus preventing 1-octyne from disassociating from the active site. In this circumstance it would then appear as if the alkyne is converted straight to the alkane. In effect, this could be a result of a solubility phenomenon. Alternatively, a sequential hydrogenation of the alkyne to the alkane before the alkene can disassociate from the active site, may occur naturally with an uncoated catalyst and the only effect the ionic liquid has, is the ability to hinder the hydrogenation of free alkene; with solubility effects not playing a major role. In effect, the major result that the ionic liquid would have on the catalyst is its ability to modify the active sites, possibly in a similar manner as alkynes do^[5c-e], to form species selective for alkyne hydrogenation over alkene hydrogenation.

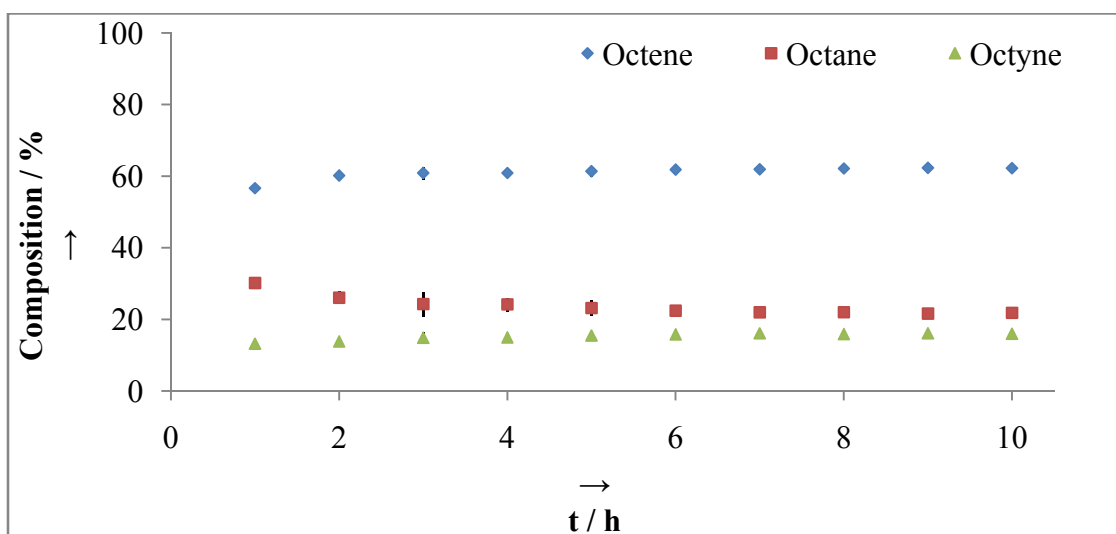
To determine the possibility that the sequential hydrogenation of the alkyne straight to the alkane is a phenomenon inherent in the uncoated catalyst, the hydrogenation of the mixed feed was carried out over this catalyst at different conversion levels of 1-octyne, brought about by changes in the GSV and LSV. These can be seen in Figure 2a-d.



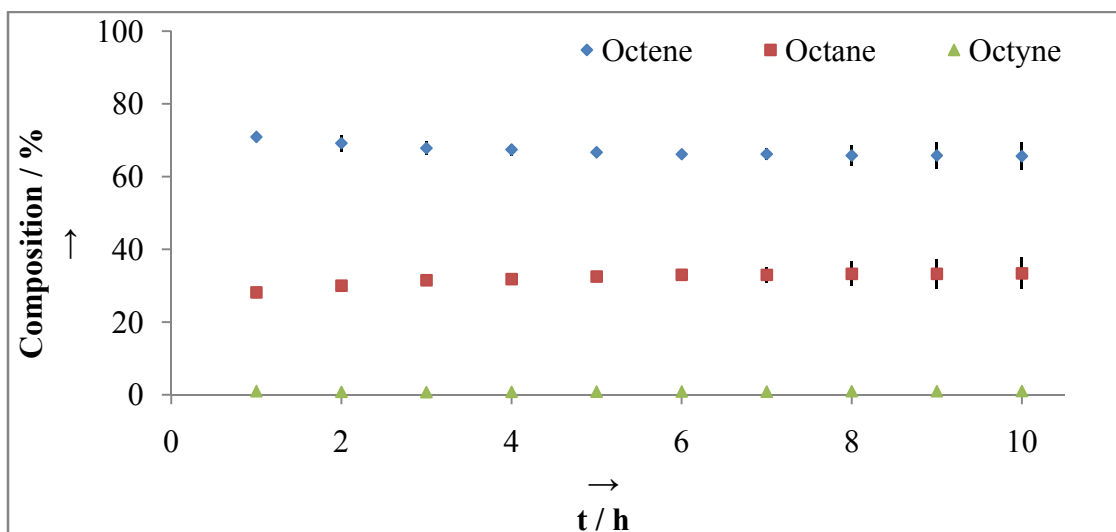
1a. I.L. coated catalyst (GSV = 1.66 s^{-1} ; LSV = $1.25 \times 10^{-1} \text{ s}^{-1}$)



1b. I.L. coated catalyst (GSV = 1.38 s^{-1} ; LSV = $1.04 \times 10^{-1} \text{ s}^{-1}$)

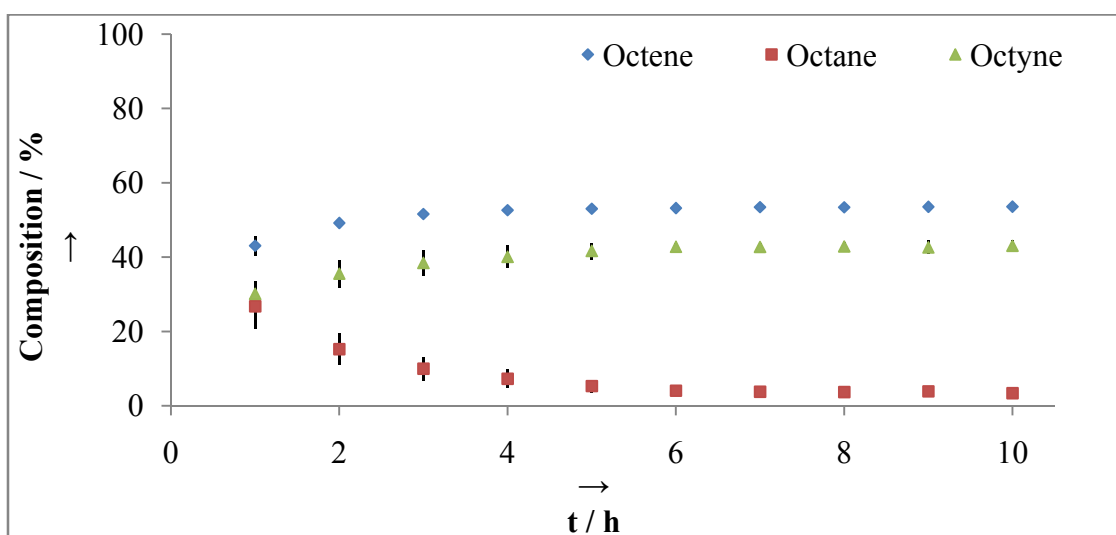


1c. I.L. coated catalyst (GSV = 1.11 s^{-1} ; LSV = $8.33 \times 10^{-2} \text{ s}^{-1}$)

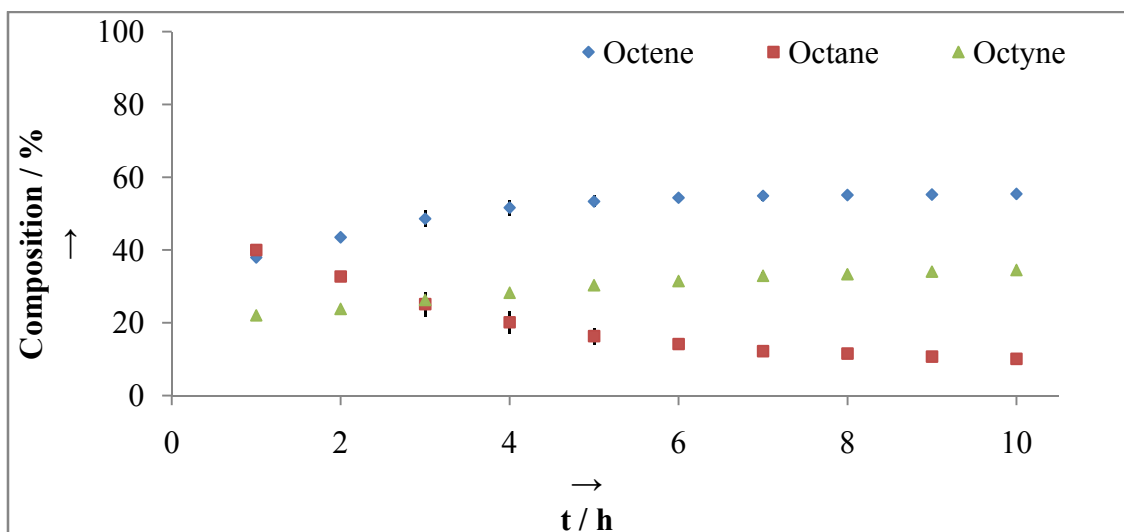


1d. I.L. coated catalyst ($GSV = 2.22 \times 10^{-1} \text{ s}^{-1}$; $LSV = 1.66 \times 10^{-2} \text{ s}^{-1}$)

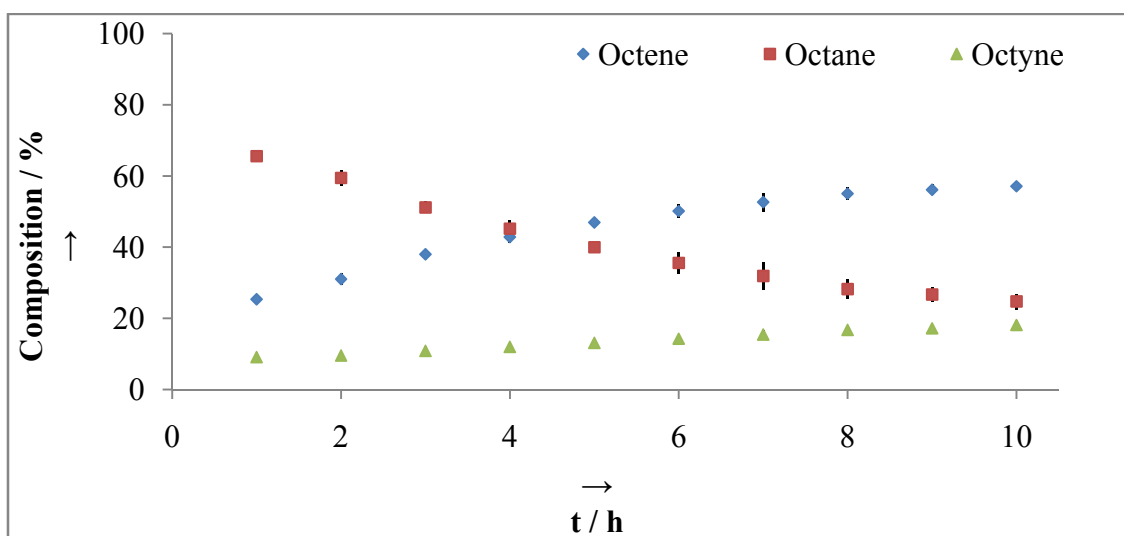
Figure 1a-d. Reaction profiles for the 10% [MMIM][MeOSO₃] coated catalyst at various LSV and GSV. Error bars represent standard deviation. The feed before reaction is composed of 1:1 (v/v) 2% each 1-octyne and 1-octene in hexane.



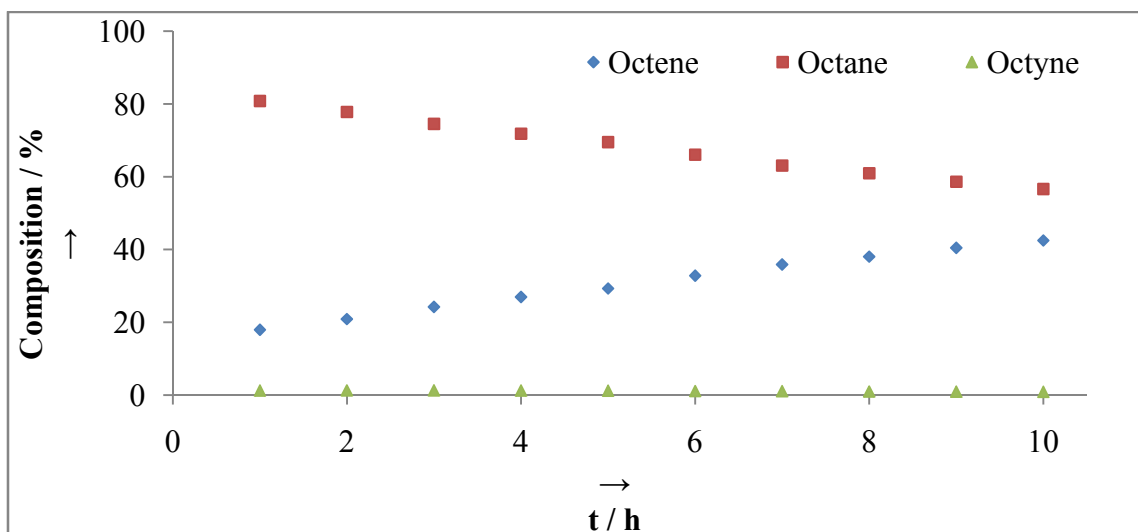
2a. uncoated catalyst ($GSV = 4.43 \text{ s}^{-1}$; $LSV = 3.33 \times 10^{-1} \text{ s}^{-1}$)



2b. uncoated catalyst ($GSV = 3.33 \text{ s}^{-1}$; $LSV = 2.50 \times 10^{-1} \text{ s}^{-1}$)



2c. uncoated catalyst ($GSV = 1.66 \text{ s}^{-1}$; $LSV = 1.25 \times 10^{-1} \text{ s}^{-1}$)



2d. uncoated catalyst ($GSV = 4.43 \times 10^{-1} \text{ s}^{-1}$; $LSV = 3.33 \times 10^{-2} \text{ s}^{-1}$)

Figure 2a-d. Reaction profiles for the uncoated catalyst at various LSV and GSV. Error bars represent standard deviation. The feed before reaction is composed of 1:1 (v/v) 2% each 1-octyne and 1-octene in hexane.

From Figure 2a-d it can be observed that the general trend with regards to the octyne, octene and octane content at different conversion levels of octyne, shows similarities to that of the ionic liquid coated catalyst. However, in the case of the uncoated catalyst, there is an increase in the octene content with time. The rate of reduction of 1-octyne decreases within the first few hours of operation. This could be explained in terms of carbon deposition onto the catalyst sites responsible for the hydrogenation of an alkyne.^[7a-d] The figure also shows that as the 1-octyne content decreases over these first few hours, there is an increase in the octene content. This could well be evidence that the alkyne is hydrogenating preferentially over the alkene. However, comparing the reaction profiles towards the end of the reactions, when a steady state appears to have been reached, reveals that as the conversion of 1-octyne increases, the octane content increases, while the octene content tends to remain constant with decreasing space velocity.

These observations suggest that the sequential hydrogenation of the alkyne to the alkane before the disassociation of the alkene from the catalyst does indeed occur. This phenomenon appears to be inherent in the catalyst irrespective of the presence or absence of ionic liquid. This

observation that 1-octyne can directly hydrogenate to octane without octene disassociating from the catalyst surface has also recently been shown with an iron nanoparticle catalyst.^[11] This interesting behaviour may provide evidence that hydrogenation of C-C pi bonds on metal surfaces occurs by the commonly accepted stepwise addition of hydrogen atoms rather than the concerted addition of H₂.^[12a-g]

However, additional confirmation that the ionic liquid does not alter the fundamental mechanism of alkyne hydrogenation can be seen with a plot of LSV versus the conversion of 1-octyne at 10 hours over the ionic liquid coated and uncoated catalysts (Figure 3). The rate of 1-octyne conversion seems to follow a linear trend which indicates a first order reaction. A first order reaction rate is quite common and has been demonstrated before with octyne conversion.^[13a,b] It can be seen from the plot that the ionic liquid reduces the LSV required to bring about a comparable conversion with the uncoated catalyst. This is in effect a deactivation of the nickel catalyst. Interestingly, the slope of the trend (which can be seen as a measure of the intrinsic reactivity of the reaction)^[13a] is steeper and therefore more intrinsically reactive.

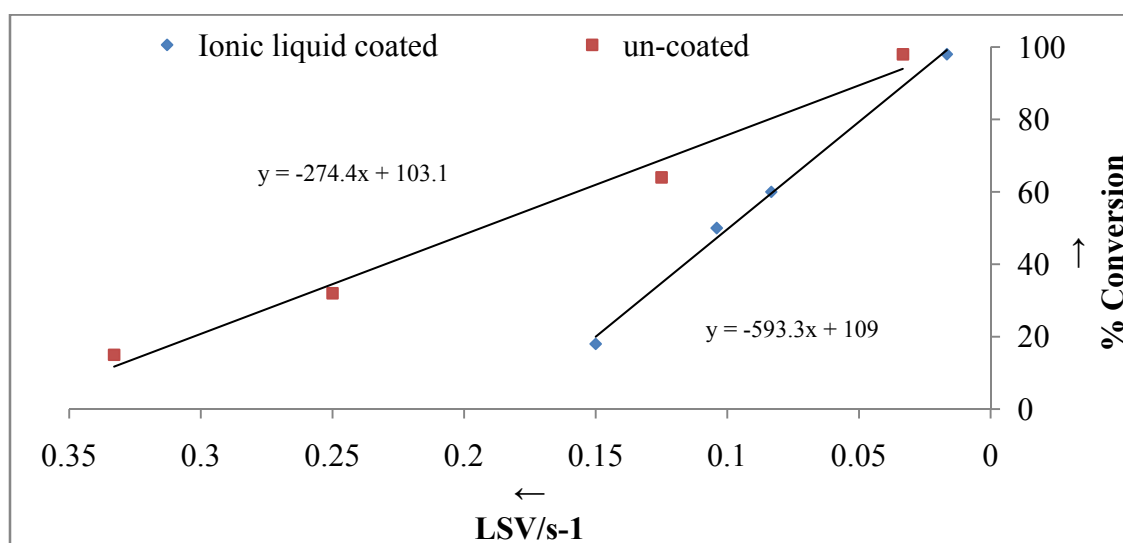
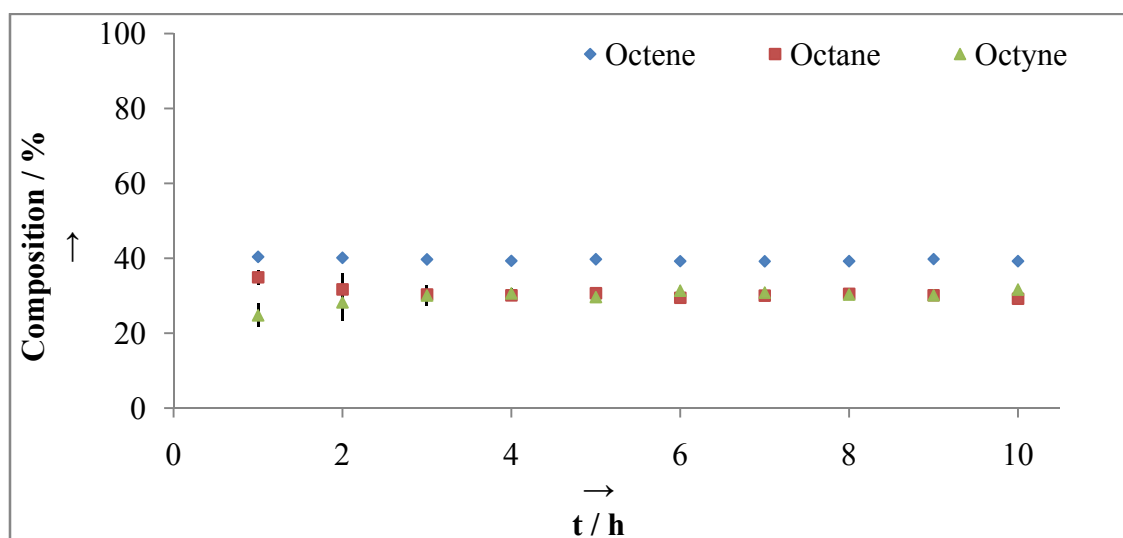


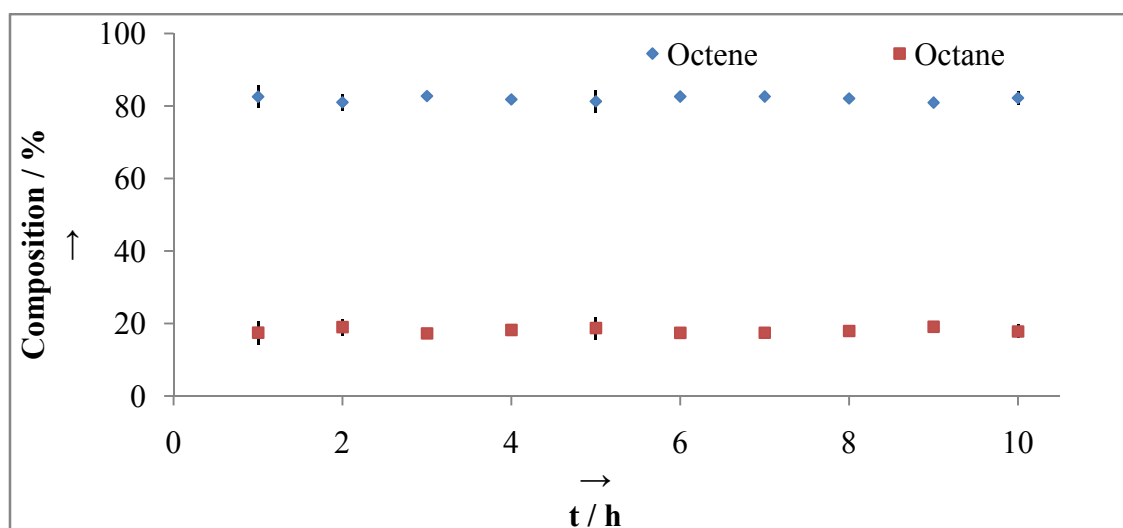
Figure 3. LSV versus conversion of 1-octyne over the [MMIM][MeOSO₃] ionic liquid coated and uncoated nickel catalyst. The "x" coordinate represents LSV, while the "y" coordinate represents % conversion.

To further determine if the major effect of the ionic liquid in this type of reaction is to modify the catalyst in a similar fashion as alkynes do, the individual components of the feed (i.e. 1-

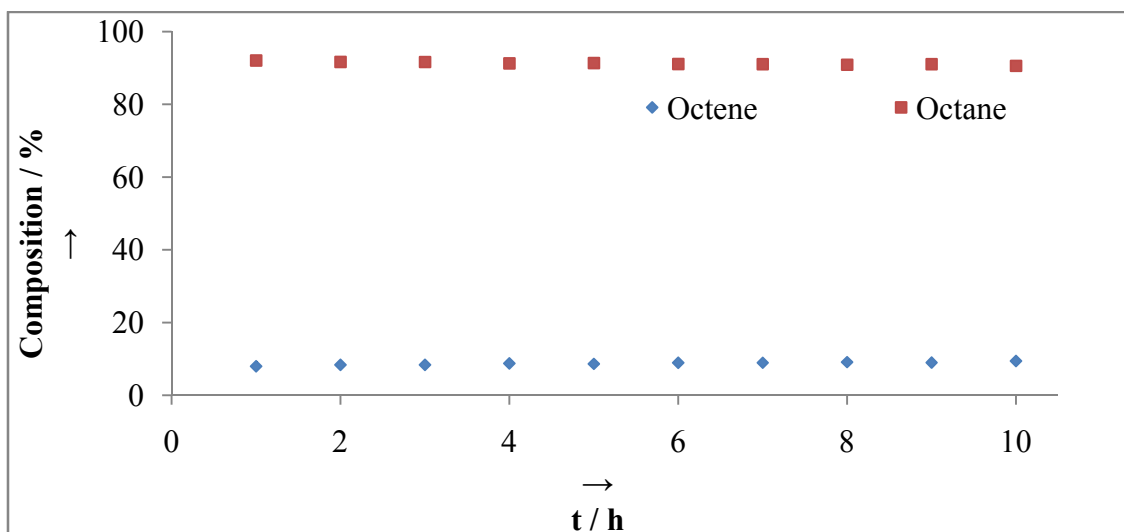
octyne and 1-octene) were run separately over an uncoated and ionic liquid coated catalyst with the same GSV's and LSV's as those in Figures 2c and 1c respectively. Additionally, the single component feed of 1-octyne was hydrogenated over an uncoated catalyst using the same conditions as shown in Figure 4d, before the feed was switched to the single component feed of 1-octene. The results can be seen in Figure 4a-e.



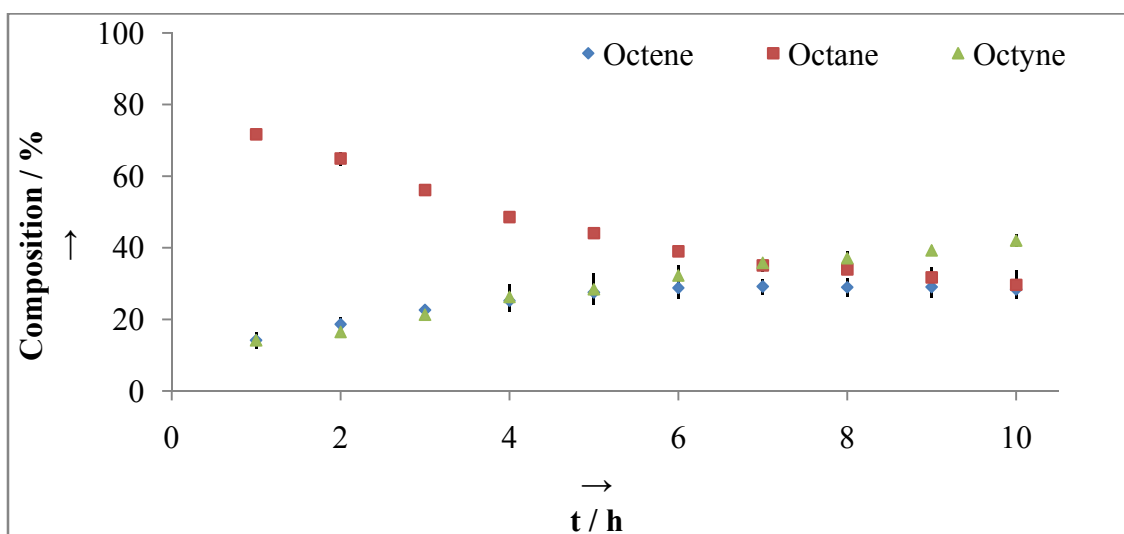
4a. I.L. coated catalyst (GSV = 1.11 s^{-1} ; LSV = $8.33 \times 10^{-2} \text{ s}^{-1}$) 1-octyne only



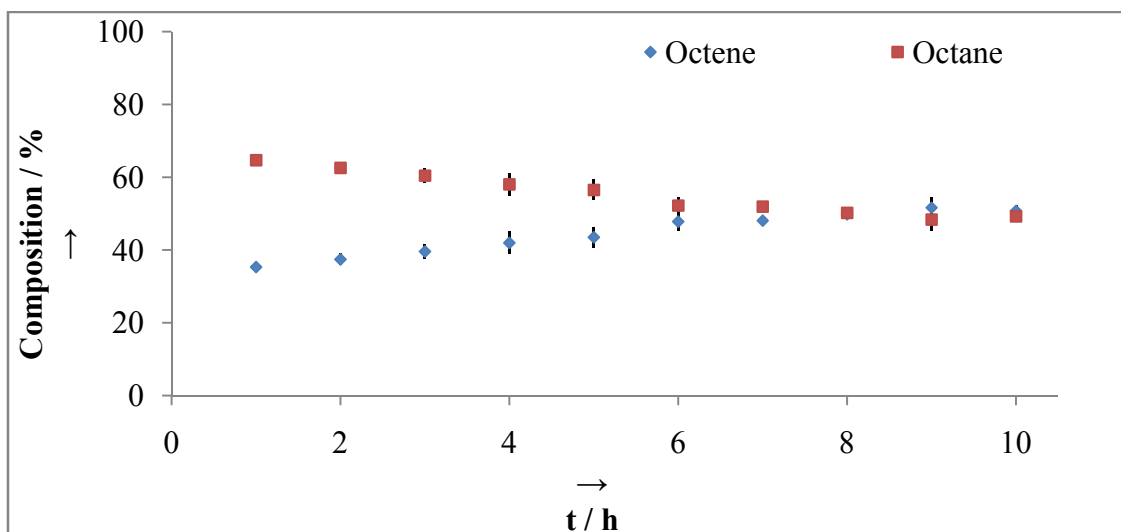
4b. I.L. coated catalyst (GSV = 1.11 s^{-1} ; LSV = $8.33 \times 10^{-2} \text{ s}^{-1}$) 1-octene only



4c. uncoated catalyst ($\text{GSV} = 1.66 \text{ s}^{-1}$; $\text{LSV} = 1.25 \times 10^{-1} \text{ s}^{-1}$) 1-octene only



4d. uncoated catalyst ($\text{GSV} = 1.66 \text{ s}^{-1}$; $\text{LSV} = 1.25 \times 10^{-1} \text{ s}^{-1}$) 1-octyne only



4e. uncoated catalyst ($GSV = 1.66 \text{ s}^{-1}$; $LSV = 1.25 \times 10^{-1} \text{ s}^{-1}$) pre reacted with 1-octyne then reacted with 1-octene

Figure 4a-e. Reaction profiles for the components of the feed with the 10% [MMIM][MeOSO₃] coated catalyst, uncoated catalyst and an uncoated catalyst modified by a reaction with 1-octyne for 10 hours.

From Figure 4a-e it can be seen that the conversion of 1-octyne remains approximately the same as that in the mixed feed reactions over both the uncoated and ionic liquid coated catalysts. With regards to the 1-octene hydrogenation, it can be seen that the ionic liquid coated catalyst does not readily hydrogenate 1-octene to octane, and that if the reaction compositions of 1-octene and 1-octyne each individually (for the ionic liquid coated catalyst) are combined it results in the composition levels of the mixed feed reaction. However, in the hydrogenation of 1-octene with the uncoated catalyst, the conversion of 1-octene to octane was approximately 90%. Combining the conversions of the individual component reactions for the uncoated catalyst does not result in the compositions present for the mixed feed reaction.

This observation can be explained by the growing formation of sites specific to the hydrogenation of 1-octyne, which is particular to the presence of 1-octyne.

From the conversion levels observed in Figure 4e, it is quite evident that treating the uncoated catalyst with the single component feed of 1-octyne for 10 hours before switching to the 1-octene feed has a noticeable effect on the conversion of 1-octene, compared to the virgin uncoated catalyst. The lower conversion level of 1-octene is readily explained by the formation of sites specific to 1-octyne hydrogenation and not 1-octene hydrogenation by the pre-treatment of the catalyst with 1-octyne. In comparison with the effects observed by coating the catalyst with an ionic liquid, it is evident that the effect of coating a catalyst with an ionic liquid is mainly due to an immediate catalyst modification. Furthermore, from our previous studies on this catalyst in conjunction with other ionic liquid SCILL catalysts, the 1,3-dimethylimidazole cation may be responsible for the modification effect.^[4] This may occur by a potential site specific interaction with the metal crystallite, or decomposition fragments on the metal crystallite from this cation.^[3a,b] However, a surface study by near edge X-ray absorption fine structure (NEXAFS) will be required to determine the mechanism of ionic liquid modification.

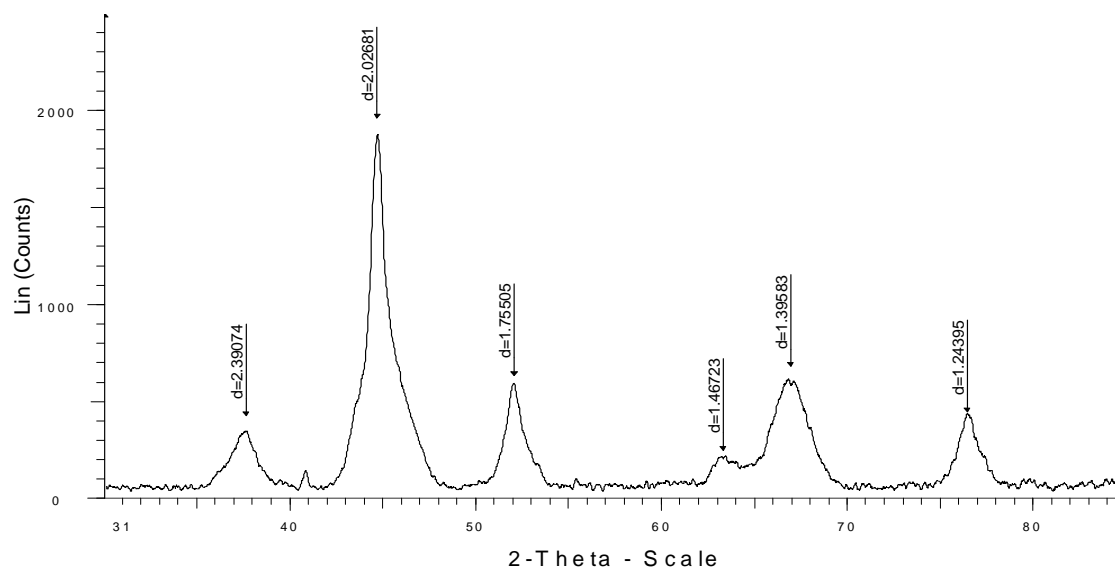
3.3.2 Deactivation studies

The current literature dealing with the preparation of SCILL catalysts *ex situ* does not specifically state the length of time between reduction of the catalyst and the start to the subsequent coating of the ionic liquid. However, we have found that an uncoated nickel catalyst is rapidly deactivated on exposure to air which results in complete deactivation after 2 days. In addition to this, the activity of the catalyst is critically influenced by the method of preparation, for example the length of time allowed for cooling under hydrogen.

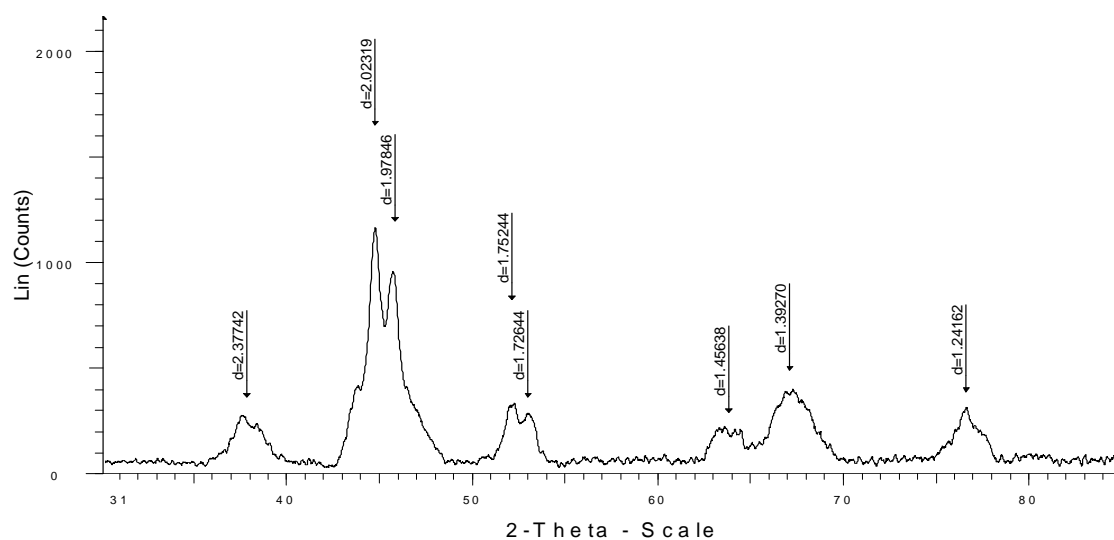
More specifically, catalyst reduction according to method A, which had a hydrogen flow of 10 ml/min and was cooled at 1.5 °C/min from 525 °C, resulted in an active catalyst which lost its activity with storage time, even when stored under H₂, but could be regenerated by a pre-treatment with H₂ at 100 °C for 4 hours.

Method B, which had a hydrogen flow of 60 ml/min and was cooled at 5 °C/min from 525 °C, resulted in a catalyst which was completely inactive. Considering that the temperature of the reduction between the two methods was identical, as was the length of time spent at this temperature, it seems incongruous how the two catalysts can exhibit such differences in activity, especially as typical characterisation techniques (BET surface area, ICP-OES, see Appendix) revealed no major differences between the catalysts.

However, XRD analysis did reveal a difference in the signature nickel peaks between the catalysts. Figure 5a-b shows the X-ray diffractograms of the inactive and active nickel catalysts.



5a. XRD diffractogram of the active catalyst

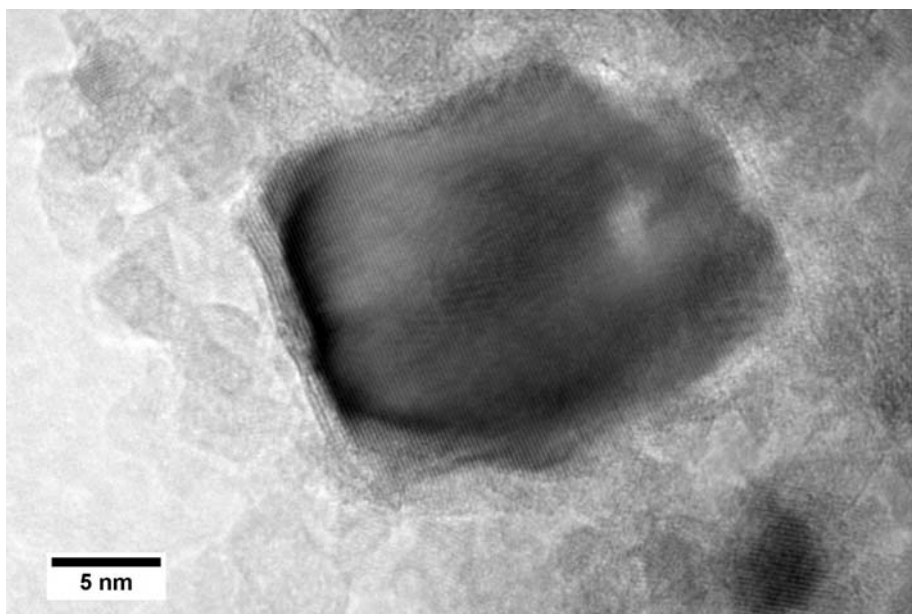


5b. XRD diffractogram of the inactive catalyst

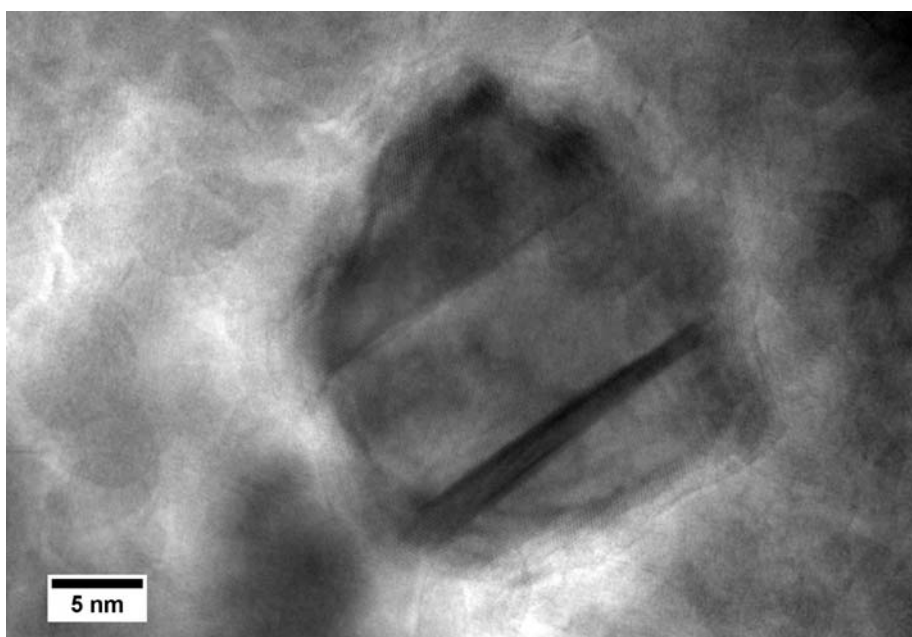
Figure 5a-b. XRD diffractograms of the inactive and active catalysts.

The key difference is in the region of $2\Theta \approx 45^\circ$ and 54° . Alumina peaks overlap many nickel/nickel oxide peaks (including the 45° peak) but, of the elements present (namely Al, O, Ni), the d spacing of around 1.72 ($2\Theta \approx 53^\circ$) is unique to reduced nickel metal, which corresponds to the 200 plane. Twin peaks are found in this area for the inactive metal catalyst, while only one exists for the active catalyst (Rietveld refinement suggests that only one nickel species is present in the active catalyst, or the contribution of a second species is very low. See Appendix). The twin peaks (found for the inactive catalyst) both correspond to nickel, but with two different JCPDS file entries (01-087-0712 and 01-088-2326, peaks left and right respectively). The two entries both list the space group to be cubic Fm-3M (225), but their unit volumes and therefore cell lengths are different ($v = 43.76 \text{ \AA}^3$, $a = 3.5438 \text{ \AA}$; $v = 41.06 \text{ \AA}^3$, $a = 3.45 \text{ \AA}$ respectively). The same argument can be applied to the twin peaks at around 45° . This indicates that the inactive catalyst contains a sizable mixture of different nickel crystallite morphologies (mainly two, with larger and smaller atom to atom lengths respectively), potentially caused by defects in the crystallites. This is in contrast to the active catalyst which displays in its diffractogram (Figure 5a) single peaks in the region of $2\Theta \approx 45^\circ$ and 54° , corresponding to one JCPDS file entry, namely 01-087-0712 (i.e. there is mainly one nickel species present, namely the species with the larger atom to atom length).

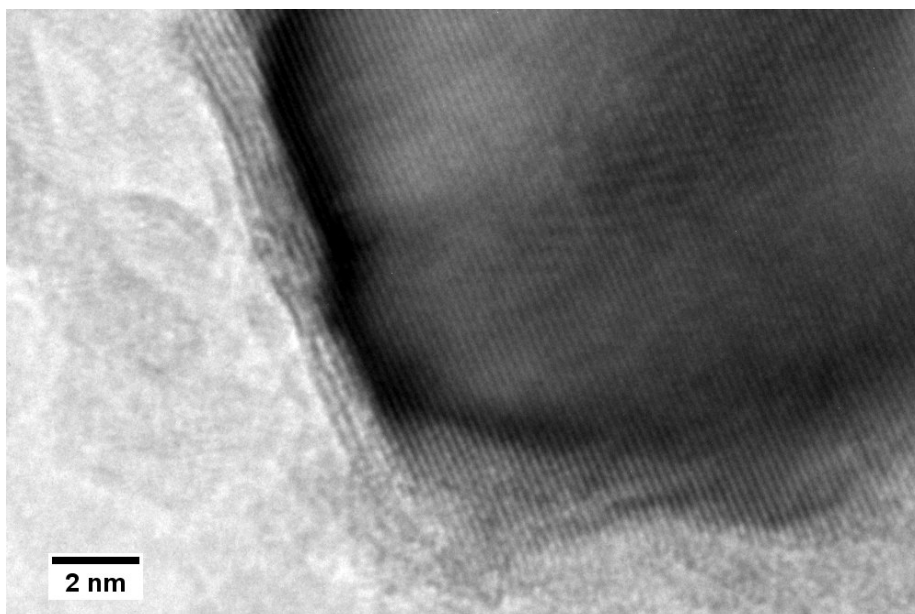
It is well known that structural defects of crystallites such as twinning, stacking faults, microstresses and changes in lattice parameters can alter the shape and position of a diffraction peak (related to the distances between atoms).^[14] In order to directly determine if defects may be occurring in the inactive catalyst, which may provide a potential reason as to why the differences in the two methods of preparation can cause such dramatic differences in activity, HRTEM analysis of the two catalysts was performed. Images from this analysis can be seen in Figure 6a-d.



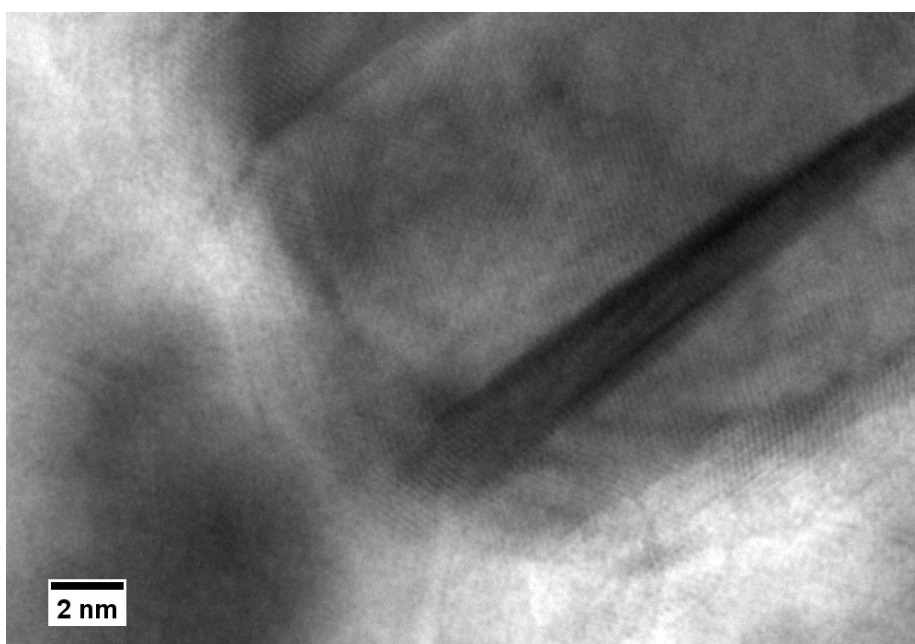
6a. Nickel crystallite from the active catalyst



6b. Nickel crystallite from the inactive catalyst



6c. Expanded view of 5a



6d. Expanded view of 5b

Figure 6a-d. HRTEM images of nickel crystallites in the active and inactive catalysts.

It is noticeable (Figure 6a-d) that the crystallites formed from method A exhibit whole crystallites with uniform planes of nickel atoms; this was seen with all the crystallites observed during the analysis (ca. 30 image acquisitions over 7 grid squares). Method B resulted in crystallites of similar size to those found in Method A, except that many had defects. There are multiple sections of close packing nickel atoms within the crystallite which interface each other with different orientations of planes, consistent with domain boundaries.^[15]

The results from these images support the differences seen in the XRD diffractograms between the two catalysts, namely, that there are relatively large numbers of nickel crystallites with structural defects present in the inactive catalyst. However, it is difficult to explain how these defects could result in the inactivity observed in the hydrogenation reactions, as large numbers of crystallite defects are normally associated with increased activity and/or selectivity in hydrogenation reactions (for example, in reactions with CO and acetylene).^[16a-c]

The inactivity in the hydrogenation reactions could be a result of an effective crystallite size. It is known in the related Fischer-Tropsch process that crystallite size is an important property in the activity and product distribution of the reaction. For example, Co crystallites smaller than 10 nm are considerably less active than larger versions.^[17a,b] The reasons for this effective crystallite size are still disputed, but it has been shown that smaller crystallites are easily oxidised under conditions tolerated by larger crystallites and resist reduction under conditions used to reduce the larger crystallites.^[17a,b]

It may be that the domain boundaries observed in the crystallites from Method B, effectively “break up” the crystallites as a whole and cause it to be below a size threshold needed for a reduction of surface oxide under the conditions the catalyst is subjected to prior to commencement of a reaction (50 bar H₂, 50 °C, 15h). Alternatively, the domain boundaries, resulting in changes to the orientation of crystal planes, could be disrupting the dynamic processes of the reaction which occur over the crystallite as whole, i.e. geometric effects and associated strong metal-support interactions.^[14]

With regards to the active catalyst prepared by method A, as mentioned before, we have found that the length of time between the reduction of the active catalyst and coating of the ionic liquid can be a critical parameter in the *ex situ* preparation of active SCILL catalysts, where an increased delay results in a deactivation of the catalyst. This is in addition to an observation that a coated nickel SCILL catalyst can deactivate over several weeks when stored under argon.^[1]

These observations suggest that over an extended period of time of exposure to the atmosphere, (either before or during the coating phase of a nickel SCILL catalyst), surface oxidation of the nickel crystallites takes place to such an extent that reduction is not possible under the conditions that the catalyst is subject to prior to a reaction (50 bar H_2 , 50 °C, 15h). This may be responsible for the observed inactivity found with the catalyst prepared by method B (supporting an effective crystallite size) and the deactivation over storage time found with the catalyst prepared by method A, as it is well known that exposure to the atmosphere can cause adsorption of oxygen species to, and subsequent oxidation of, finely divided reduced metal particles.^[9]

In order to determine if significant crystallite surface oxidation of the nickel crystallites is occurring during the time intervals between reduction and the commencement of the reaction, and whether there is any variation in the extent of oxidation over time (as well as variations between the two catalyst prepared by the different methods), a series of temperature programmed reductions on the active and inactive catalysts was carried out. These included (from method A) a freshly reduced uncoated catalyst, an uncoated catalyst exposed to air for 2 hours, an uncoated catalyst which had been exposed to air for 48 hours and a deactivated uncoated catalyst which had undergone regeneration by treating the catalyst with 5% hydrogen in Argon at 100 °C for 4 hours, as well as an uncoated catalyst (from method B) exposed to air for 2 hours. These results can be seen in Figure 7a-e.

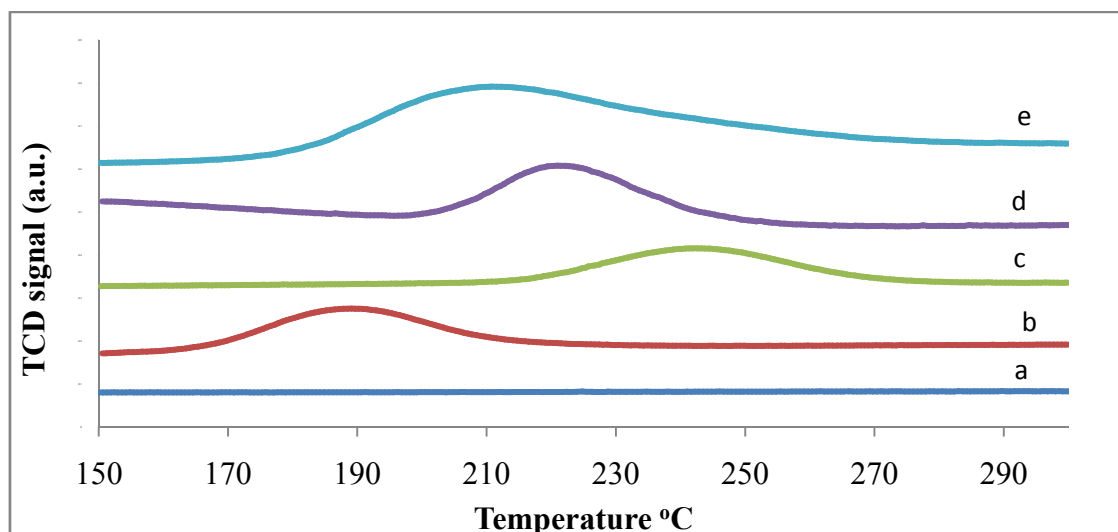


Figure 7a-e. TPR (under H_2): Thermal conductivity detection (TCD) in arbitrary units (a.u.) versus temperature of the different catalysts exposed to air with varying time and pre-treatment procedures. 7a. Freshly prepared nickel catalyst (method A), 7b. Nickel catalyst exposed to air for 2 hours (method A), 7c. Nickel catalyst exposed to air for 48 hours (method A), 7d. Nickel catalyst exposed to air for 48 hours and then treated with 5% hydrogen in argon at 100 °C for 4 hours (method A), 7e. Nickel catalyst exposed to air for 2 hours (method B).

The temperature programmed experiments, represented in Figure 7a-c, show that with an initial and continued exposure to the atmosphere, oxidation of the nickel crystallites does indeed occur. Between 2 and 48 hours there is a shift in the peak temperature at which reduction takes place (Figure 7b-c), from 187 °C to 242 °C. This change in the reduction temperature is associated with an increased difficulty in reducing the nickel crystallites. In turn this indicates that a bulk chemical change in the nature of bonding of the metal-oxygen species present on the crystallite has occurred.

This increased difficulty in the reduction of the catalyst exposed for a longer period provides evidence as to why the catalyst (from method A) becomes inactive when there is an extended delay between reduction and coating to form the SCILL catalyst. It is likely that the conditions which the catalyst is subjected to prior to the reaction are insufficient to reduce the nickel oxide to an active state for hydrogenation. However, it was found that regeneration of the catalyst is possible by treating the uncoated deactivated catalyst with 100% H_2 at 100 °C under

atmospheric pressure for 4 hours before an immediate coating of the ionic liquid. Unfortunately, treating the deactivated ionic liquid coated catalysts with this method gave irreproducible conversion levels (in the hydrogenation reaction), which is further compounded by the risk of decomposing the ionic liquid at elevated temperatures. It may be that the coating of ionic liquid on the deactivated catalyst inhibits the reduction of the stronger surface metal-oxide, as it is known that hydrogen has a low solubility in ionic liquids.^[18a,b]

Figure 7d shows the effects of a treatment with hydrogen (5% H₂ in argon for 4 hours at 100 °C) on the reducibility of a deactivated catalyst (from method A). It is quite apparent that treating the catalyst at 100 °C results in a lower reduction peak temperature in the TPR profile (221 °C). This implies an increased ease in reduction of the crystallite surface oxide and suggests that the pre-treatment procedure changes the nature of the metal-oxygen species to a state which can be reduced by the conditions that the catalyst is subjected to prior to the reaction, even with the presence of an ionic liquid coating.

Figure 7e shows the TPR profile for the catalyst prepared by method B and exposed to the atmosphere for 2 hours. The profiles (not shown) for the catalyst exposed for 48 hours and subsequent treatment with H₂ at 100 °C for 4 hours were similar to the profiles for the catalysts prepared by method A (Figure 7c-d). However, in this profile (Figure 7e) the reduction peak occurs at 210 °C instead of 187 °C found for the catalyst prepared by method A (Figure 7b). This suggests that the catalysts prepared by method B undergo a more rapid surface oxidation of the nickel crystallites than the catalysts prepared by method A. This may be the result of the defects observed in the crystallites from the HRTEM analysis, as defects are associated with increased reactivity.^[16a-c] This could explain why the catalysts prepared by method B are inactive in the hydrogenation reactions, as the catalysts prepared by method B are rapidly oxidised after exposure to the atmosphere. The time required for coating the catalyst with ionic liquid and/or charging the reactor with this catalyst might therefore be longer than the time required for the catalyst to reach a level of oxidation that cannot be reduced under the conditions the catalyst is exposed to before the commencement of a reaction.

To help determine if rapid oxidation is responsible for the inactivity observed with the catalyst prepared by method B, the catalyst was coated with the ionic liquid [MMIM][MeOSO₃] under anaerobic and anhydrous conditions using standard Schlenk techniques, before being applied in the competitive hydrogenation between 1-octyne and 1-octene. The reaction profile for this SCILL catalyst preparation method can be seen in Figure 8 below.

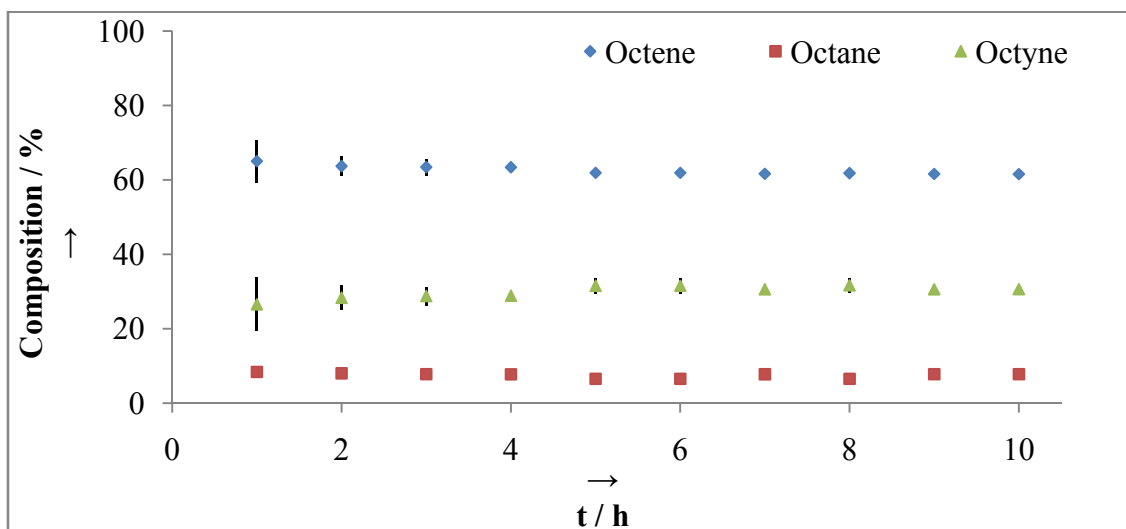


Figure 8. Reaction profile for the competitive hydrogenation between 1-octene and 1-octyne (1:1 v/v 2% each in hexane) with an I.L. coated catalyst prepared by method B and coated under anhydrous and anaerobic conditions ($GSV = 1.11 \text{ s}^{-1}$; $LSV = 8.33 \times 10^{-2} \text{ s}^{-1}$).

It is interesting to note that the catalyst is active in the competitive hydrogenation between 1-octyne and 1-octene which indicates that rapid oxidation of the catalyst prepared by method B (on exposure to the atmosphere) is responsible for the observed inactivity. However, the activity of this catalyst is far less than that prepared by method A (Figure 8a compared to Figure 1c). Although this suggests that the defects present in the crystallites are detrimental to the reaction (either inherently or by catalyst site – ionic liquid interaction), oxidation effects cannot be ruled out completely due to the inevitable, although slight, exposure of the coated catalyst to the atmosphere while handling and charging the reactor.

3.4 Conclusion

From these results it can be seen that the addition of the ionic liquid [MMIM][MeOSO₃] has a dramatic effect on the hydrogenation of 1-octyne versus 1-octene over the range of iso-conversion conditions. This is substantiated by the immediate decrease in octene hydrogenation activity, compared to the reaction over the uncoated catalyst.

A comparison between the two sets of reaction data (uncoated vs. coated) reveals that the hydrogenation of 1-octyne to octane can occur directly and is not the result of any influence by the ionic liquid. The influence that the ionic liquid appears to exert is an immediate modification effect on the catalyst similar to the modification effects caused by carbon deposition by alkynes over time, and a slight overall decrease in activity.

This highlights that although the SCILL catalyst may provide an immediate beneficial modification affecting the selectivity of a reaction, with time on stream other methods can produce similar results. The application of SCILL catalysts to alkyne hydrogenation in the presence of alkenes might therefore be best under batch conditions, where immediate enhanced selectivity is paramount, rather than continuous flow processes which may tolerate a relatively gradual change to enhanced selectivity. However, these results do confirm that ionic liquids provide a relatively instant method for catalyst modification, potentially by transport effects and/or crystallite modification.

Furthermore, the preparation of nickel SCILL catalysts needs care, both in the synthesis of the virgin catalyst and in the coating procedure. In particular, attention must be given to ensure the formation of catalyst crystallites with uniform atomic close packing. Also, active nickel catalysts tend to deactivate over a short period of time before and during the coating procedure. Therefore, an immediate coating must be applied after the reduction step. The deactivated catalysts can, however, be reactivated by a short pre-treatment with 100% H₂ at 100 °C for 4 hours. Nevertheless, it may be that the best reduced metal catalysts to use with the SCILL concept are metals whose reduction temperatures are below the decomposition temperature of the ionic liquid, so that *in situ* generation of a SCILL catalyst occurs before the commencement of a reaction.

3.5 Experimental Section

The ionic liquid [MMIM][MeOSO₃] was prepared via methods described in literature, namely by the alkylation of 1-methylimidazole with dimethylsulphate.^[19] NMR analysis was used to confirm of the purity and identity of the synthesised ionic liquid.

A nickel on alumina catalyst (29% m/m) was prepared by wet impregnation of a crushed gamma alumina support with nickel nitrate at 70 °C for 4 hours. The resultant paste was dried in an oven at 110 °C for an additional 2 hours before being calcined at 500 °C for 8 hours. The catalyst was then pelletized to a size distribution between 300 and 600 µm before being reduced under hydrogen.

Method A for reduction under hydrogen: The catalyst underwent an initial temperature ramp from 30 °C to 525 °C^[20] over 3 hours and this temperature was maintained for 4 hours before cooling at a rate of 1.5 °C per minute. The hydrogen flow rate was 10 ml/min.

Method B for reduction under hydrogen: The catalyst underwent an initial temperature ramp from 30 °C to 525 °C^[20] over 3 hours and this temperature was maintained for 4 hours before cooling at a rate of 5 °C per minute. The hydrogen flow rate was 60 ml/min. Apart from the differences in Method A and Method B, catalyst treatment (i.e. storage and handling) was identical.

The resultant active catalyst was then coated with the ionic liquid [MMIM][MeOSO₃] by dissolving the required amount of ionic liquid in methanol within a pill vial before introducing the parent catalyst. The mixture was allowed to evaporate slowly in a fume hood over 2 hours to obtain a dry powder which was then placed under high vacuum for 60 minutes to ensure the complete removal of the organic solvent.

Temperature programmed reduction experiments (5% H₂ in Ar) were performed in a Micromeritics Autochem II 2029 and powder XRD analysis with a Bruker D8 Advance. All other catalyst characterisation techniques have been described previously, as well as the hydrogenation experimental setup in a concurrent down flow trickle bed reactor.^[4] A 2% 1-octyne with 2% 1-octene in hexane mixture was used in the mixed substrate reactions, while a 2% 1-octyne in hexane mixture and a 2% 1-octene in hexane mixture were used in the single substrate reactions.

Regeneration of the deactivated catalyst for subsequent hydrogenation reactions was performed by treating the deactivated catalyst with 100% hydrogen at 100 °C for 4 hours. Analysis of the pre-treatment procedure was conducted on a Micromeritics Autochem II 2029 using 5% H₂ in argon.

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CHAPTER 4

EFFECTS OF ORGANIC MODIFIERS ON A PALLADIUM CATALYST IN THE COMPETITIVE HYDROGENATION OF 1-OCTENE VERSUS OCTANAL

4.1 Abstract

Competitive hydrogenation between 1-octene and octanal has been investigated with a ca. 5% palladium on alumina catalyst prepared *in situ* with the following organic modifiers: pyridine, 1-methylimidazole, 1,3-dimethylimidazole methylsulphate [MMIM][MeOSO₃], 1,3-dimethylimidazole bis(trifluoromethylsulphonyl)imide [MMIM][NTf₂] and methyl-tri-*sec*-butylphosphonium methylsulphate [MeP*sec*-Bu₃][MeOSO₃]. The result of these investigations indicate that the ionic liquid modifiers have significant and specific effects on catalytic performance, for example, certain systems can completely suppress octanal conversion. In addition to this, analytical techniques reveal the matrix and quantity of organic species on the used catalysts are different between the different ionic liquids used as modifiers. Surface studies also reveal that the modifiers have a noticeable effect on crystallite size and chemisorption properties of the catalysts.

4.2 Introduction

Competitive hydrogenation between inter-molecular functional groups is a relatively unexplored area compared to intra-molecular versions. Due to current methods in the industrial production of hydrocarbons, downstream industrial feedstocks may contain several species of unsaturated molecules.^[1a-c] For example, in the hydroformylation of alkenes by homogeneous rhodium catalysts, the product may well contain un-reacted alkenes with aldehydes.^[1c] Further chemical manipulations of such product streams often require the removal of one or more minor constituents, either to prevent undesired side reactions or catalyst poisoning.^[1c,2a,b] Hydrogenation by heterogeneous catalysts is often used to remove catalyst poisons such as

alkynes and dienes.^[2a,b] As a result, a catalyst selective in the hydrogenation of one or related components versus others in a multi component feed is desirable.

Heterogeneous catalyst modifications by either inorganic or organic modifiers have been used to either increase the "intrinsic activity" of a catalyst or its selectivity. For example, cinchonidine has been used to promote asymmetric catalytic hydrogenations^[3a-e] and site modification by CO has been used to enhance reaction selectivity.^[4a-c] Pyridine has also found use as a modifier of heterogeneous catalysts.^[5a,b] Indeed, nitrogen containing organic compounds have found widespread use as organic modifiers of traditional heterogeneous catalysts.^[6]

The additions of other metals are also seen as modifiers of traditional monometallic catalysts. They form multi-metallic catalysts with enhanced selectivity and increase catalyst stability, due to a variety of reasons; both electronic and morphological.^[6, 7a-e] As a result of this, a potential plethora of catalytic performance modifications exist with both inorganic and organic modifiers. Investigations with ionic liquids in continuous flow processes have traditionally focused on the supported ionic liquid phase (SILP) catalysis, whereby a homogeneous catalyst is dissolved into an ionic liquid which is itself supported on common porous and non porous heterogeneous supports such as alumina and other metal oxides.^[8a-e] These reactions are typically performed under gas phase conditions.

Recently, a new concept with ionic liquids and heterogeneous catalysis has emerged. The solid catalyst with ionic liquid layer (SCILL) has shown to be effective in altering the selectivity and "intrinsic activity" of a number of different reactions including competitive hydrogenation between two different substrates.^[9a-e] In particular, the selective hydrogenation of citral to citronellal with palladium based catalysts have been investigated (Figure 1), with improved selectivities towards citronellal.^[10a-c]

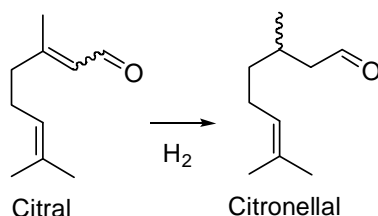


Figure 1. Hydrogenation of citral to citronellal.

The SCILL catalysts described so far have shown that the ionic liquid layers remain intact on the catalyst in both batch and trickle bed conditions. However, it is still unknown to what relative extent transport effects (if any) and crystallite modification effects contribute to the SCILL catalyst behaviour. Diffusion effects have been claimed to have no effect,^[9e] however, the idea that diffusion effects do not play any role has been challenged.^[9a,c] In addition to this, no relation or comparison has been made with traditional organic catalyst modifiers such as pyridine.

In the hope that palladium SCILL catalysts may have differing effects on the hydrogenation performance with respect to industrially important alkenes and aldehydes in competitive modes, a series of ionic liquid modified palladium on alumina catalysts (ca. 5% w/w) were used in the competitive hydrogenation between 1-octene and octanal (1:1 v/v, 2% each in hexane) under continuous flow conditions. A comparison with the effects of some traditional organic modifiers, such as pyridine and 1-methylimidazole, are also included in this study.

The following compounds were used as modifiers in the *in situ* preparation of these catalysts: pyridine, 1-methylimidazole, 1,3-dimethylimidazole methylsulphate [MMIM][MeOSO₃], 1,3-dimethylimidazole bis(trifluoromethylsulphonyl)imide [MMIM] [NTf₂], methyl-tri-*sec*-butylphosphonium methylsulphate [MeP*sec*-Bu₃][MeOSO₃]. The structures of these modifiers are shown in Figure 2.

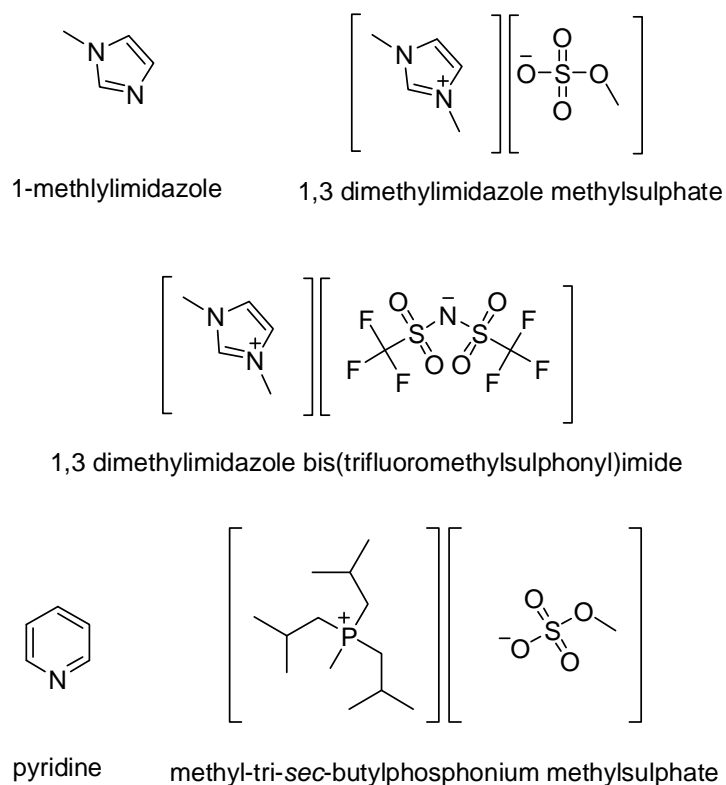
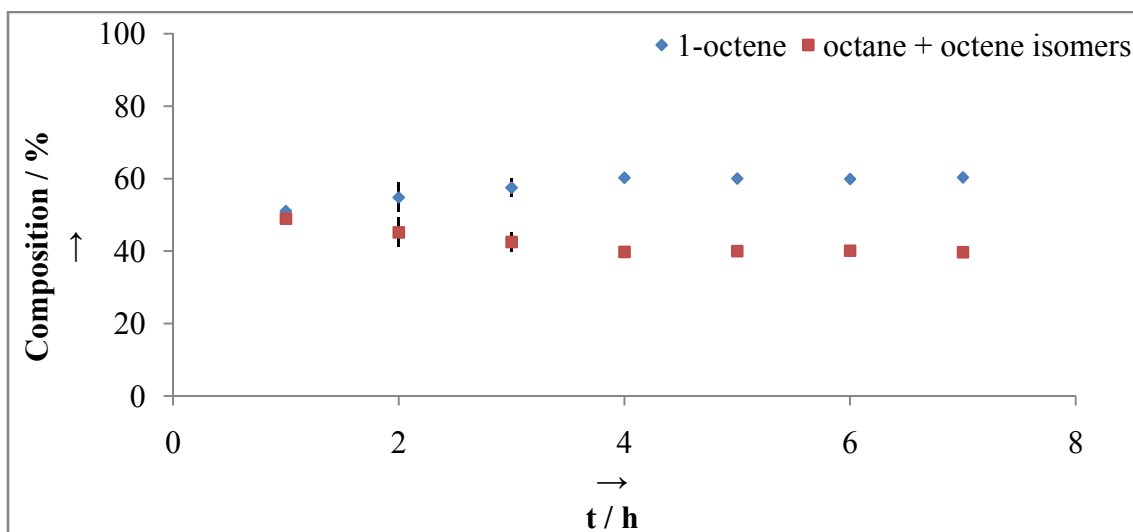


Figure 2. Structures for the different organic molecules used to modify the 5% Pd on alumina catalyst.

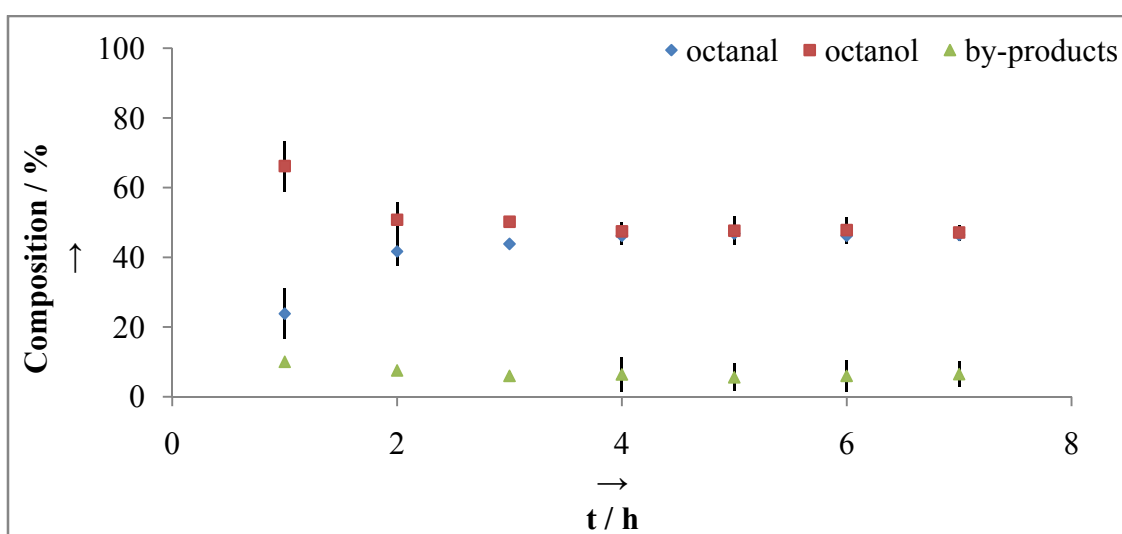
4.3 Results and Discussion

4.3.1 Hydrogenation of 1-octene and octanal over a 5% Pd on alumina catalyst

In order to determine the effects of the modifiers in question on the competitive hydrogenation between 1-octene and octanal, the performance of the uncoated catalyst at different iso-conversion points was first established. For the purpose of this discussion, iso-conversion is defined as the constant conversion attained once steady state has been achieved in the continuous flow reactions. A typical reaction profile for the 40% conversion of 1-octene can be seen in Figure 3a-b. To avoid confusion, the reader should note that the un-reacted mixture, before passing over the catalyst bed, contains a 100% 1-octene and 100% octanal composition. However, for a meaningful comparison we would like to focus on the conversion (obtained at steady state with a minimum time of 7 hours on stream) versus liquid hourly space velocity (LHSV) plots which are shown in Figure 4a.

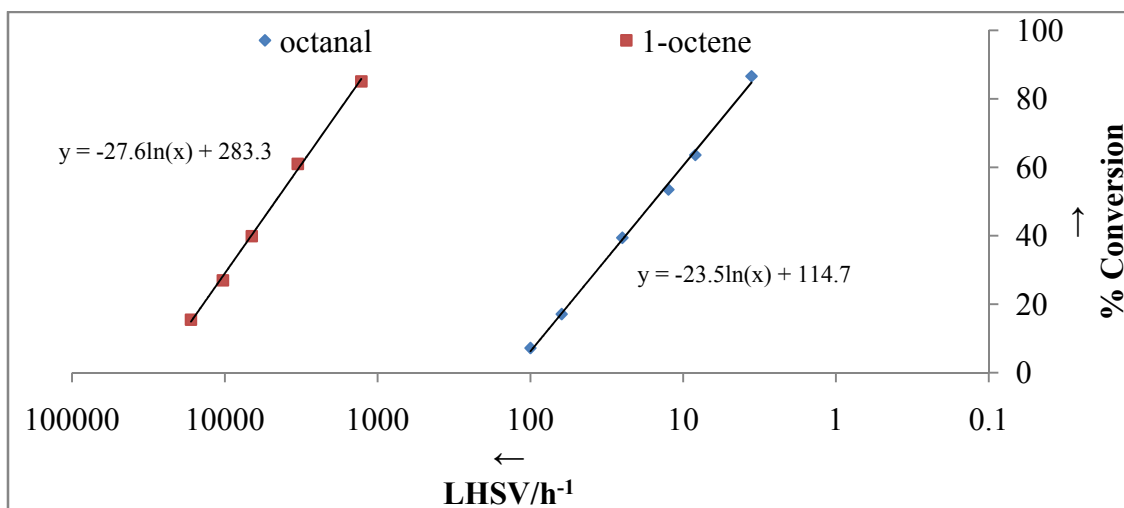


3a. A typical reaction profile for the hydrogenation of 1-octene to octane with the uncoated catalyst condition

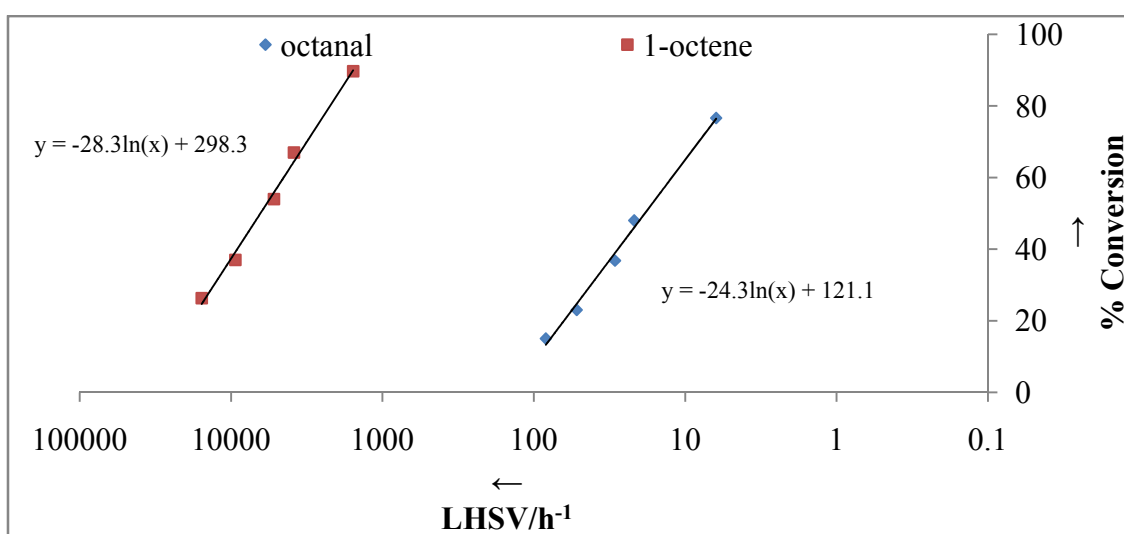


3b. A typical reaction profile for the hydrogenation of octanal to octanol with the uncoated catalyst conditions

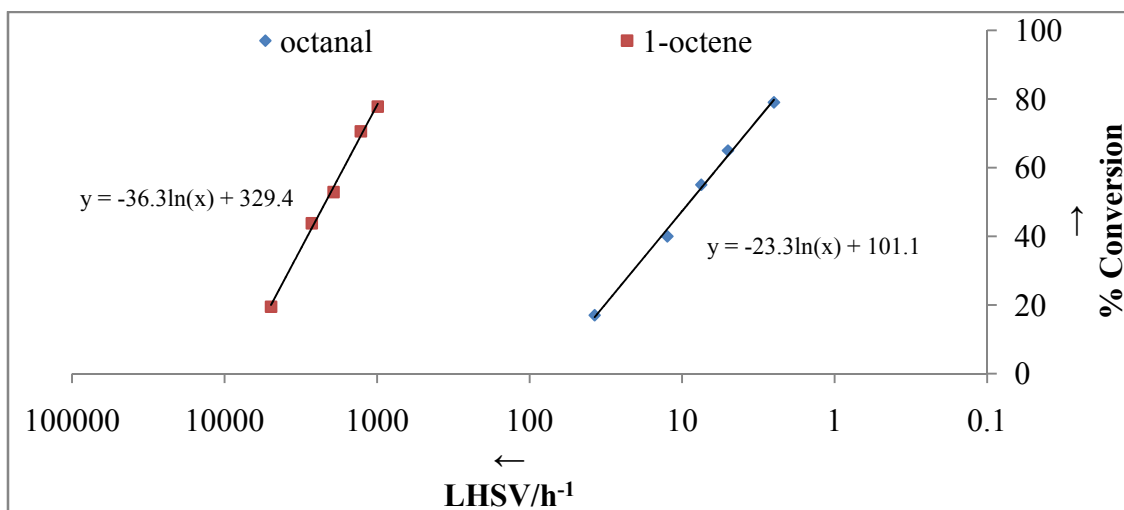
Figure 3a-b. Reaction profiles for the hydrogenation of 1-octene to octane and octanal to octanol. Error bars represent standard deviation between a minimum of 2 runs. By-products include diols and acetyls amongst others. The increase in octanal and 1-octene content over time, until steady state is reached, is due to a decrease in the catalyst's ability to convert the respective substrates (initial catalyst deactivation).



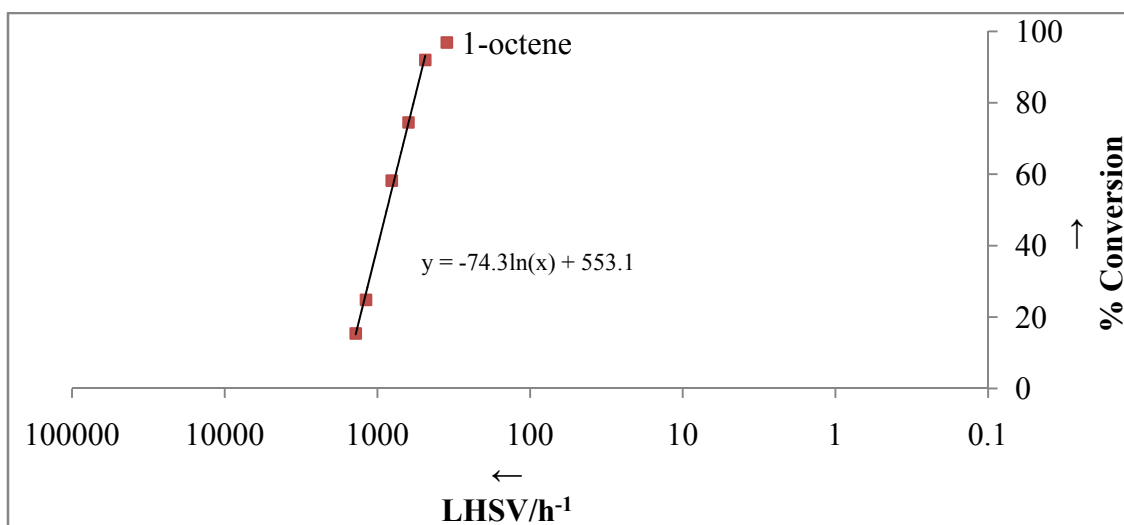
4a. Iso-conversion points of both 1-octene and octanal plotted to the LHSV's required to obtain them with the uncoated catalyst



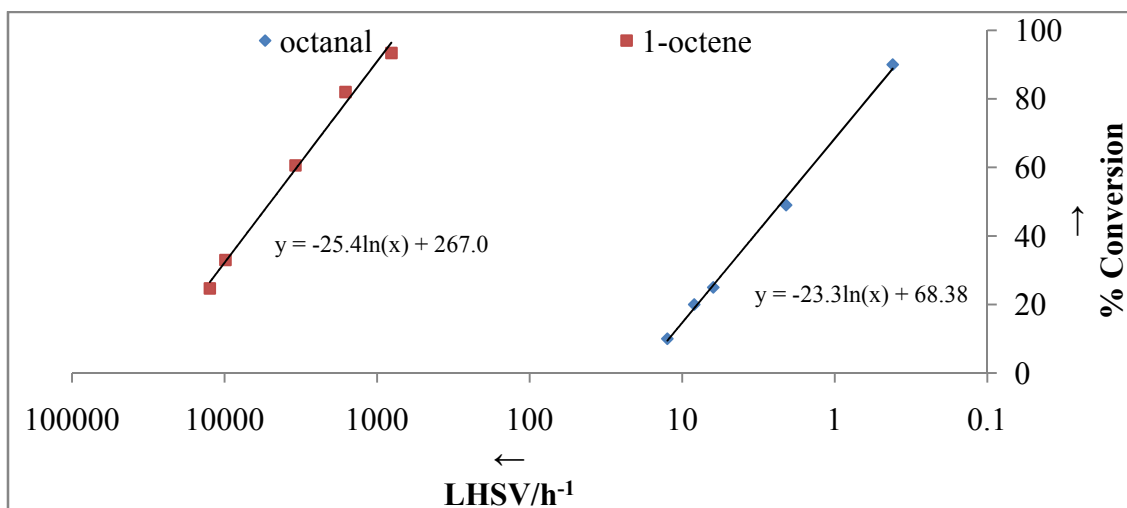
4b. Iso-conversion points of both 1-octene and octanal plotted to the LHSV's required to obtain them with the pyridine modified catalyst



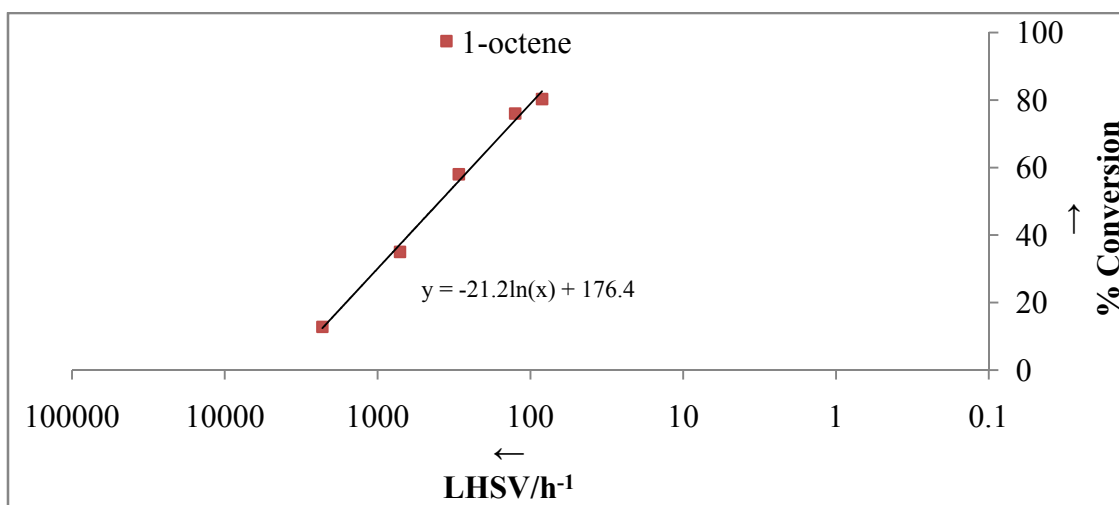
4c. Iso-conversion points of both 1-octene and octanal plotted to the LHSV's required to obtain them with the 1-methylimidazole modified catalyst



4d. Iso-conversion points of 1-octene plotted to the LHSV's required to obtain them with the [MMIM][MeOSO₃] modified catalyst, no octanal conversion was observed



4e. Iso-conversion points of both 1-octene and octanal plotted to the LHSV's required to obtain them with the [MMIM][NTf₂] modified catalyst



4f. Iso-conversion points of 1-octene plotted to the LHSV's required to obtain them with the [MePsec-Bu₃][MeOSO₃] modified catalyst, no octanal conversion was observed

Figure 4a-f. LHSV versus iso-conversion of octanal and/or 1-octene with the 5% palladium on alumina catalysts modified by the different organic compounds. The LHSV is represented as a log scale and corresponds to the "x" coordinate. The "y" coordinate corresponds to % conversion.

Table 1. A summary of "intrinsic reactivity and activity" of conversion of 1-octene and octanal, respectively, with the differently modified catalysts.

Coating	1-octene conversion		octanal conversion	
	reactivity ^[a] (%.h)	activity ^[b] (LHSV, h ⁻¹)	reactivity ^[a] (%.h)	activity ^[b] (LHSV, h ⁻¹)
uncoated	-27.6	4688	-23.5	16
Pyridine	-28.3	6463	-24.3	19
1-methylimidazole	-36.3	2201	-23.3	9
[MMIM][MeOSO ₃]	-74.3	872	~0	~0
[MMIM][NTf ₂]	-25.4	5132	-23.3	2
[MeP _{sec} -Bu ₃][MeOSO ₃]	-21.2	388	~0	~0
[a] Defined as the gradient of the logarithmic function. ^[11] [b] Defined as the LHSV required to bring about 50% conversion. Values listed as ~0 are below the detection limit.				

Figure 4a shows the conversion data for the uncoated catalyst. It is evident that the liquid hourly space velocity versus conversion follows a logarithmic trend. The ranges of the octanal and 1-octene conversions do not overlap (LHSV values where both 1-octene and octanal convert) each other and the catalyst is more active towards 1-octene conversion than octanal conversion. This is in agreement with palladium being known as an effective catalyst for C-C bond transformations.

Figure 4b shows the conversion data for the pyridine modified catalyst. Pyridine is a known catalyst modifier^[5a,b] and it is noticeable that the modification by pyridine has resulted in the formation of a slightly more "intrinsically active" catalyst (intrinsic activity defined as the LHSV required to bring about 50% conversion, Table 1) in the conversion of both 1-octene and octanal. Additionally there seems to be a slight increase in the "intrinsic reactivity" of the catalyst (defined as the gradient or slope of the logarithmic function,^[11] Table 1) for both 1-octene and octanal conversion, implying an improvement on the numbers or efficiency of the catalyst sites responsible for the conversions.

Figure 4c shows the conversion data for the palladium catalyst coated with 1-methylimidazole. There is a larger effect on the "intrinsic activity and reactivity" of both 1-octene and octanal

conversion compared to the pyridine modified catalyst. However, the effect is different from the pyridine modification. The "intrinsic reactivity" of 1-octene conversion is greater (larger gradient) but the "intrinsic activity" has diminished (lower LHSV) compared to both the uncoated and pyridine modified catalysts. With regards to octanal conversion, the "intrinsic reactivity" is similar to the uncoated catalyst but the "intrinsic activity" has decreased. Structurally (the geometric arrangement of atoms), 1-methylimidazole is in many respects similar to pyridine, as they are both planar and contain nitrogen in their ring system (Figure 2), it is therefore surprising that they exhibit such different effects as catalyst modifiers. This may be related to the basicity of the organic modifiers with the pK_b of pyridine at 8.78 ^[12a] and 1-methylimidazole at 6.95 ^[12b] which may have an effect on the metal crystallite formation or surface support properties. However, 1-methylimidazole is a known precursor to many different ionic liquids, some of which have been shown to noticeably modify the "intrinsic activity" and selectivity of catalysts used in several different hydrogenation reactions.^[9a-e]

Figure 4d shows the conversion data for [MMIM][MeOSO₃], an ionic liquid based on 1-methylimidazole. There is a dramatic change in the "intrinsic activity and reactivity" in the conversion of 1-octene, compared to the uncoated catalyst. There is a drop in "intrinsic activity", while there is an increase in "intrinsic reactivity", as evidenced by the slope of the trend line. With regards to the 1-octanal hydrogenation, the ionic liquid completely inhibits the reaction, at least within the limits of the reactor capabilities. This shows that the ionic liquid strongly discriminates between 1-octene and octanal hydrogenation, increasing the catalyst's selectivity to 1-octene conversion and increasing its "intrinsic reactivity".

To investigate what effect a change in the anion would have on the "intrinsic activity and reactivity" of 1-octene and octanal conversion, the ionic liquid [MMIM][NTf₂] was used as a modifier. The results can be seen in Figure 4e. There is a slight increase in the "intrinsic activity" of 1-octene conversion with a decrease in the "intrinsic reactivity", compared to the uncoated catalyst. There is also a strong effect on the octanal conversion. Although there is no outright inactivity as compared to the [MMIM][MeOSO₃] modified catalyst, there is a large decrease in the "intrinsic activity" compared to the uncoated catalyst, the pyridine modified catalyst and the 1-methylimidazole modified catalyst.

Figure 4f shows the effects of coating the catalyst with the ionic liquid [MeP_{sec}-Bu₃][MeOSO₃]. There is a significant change to both the "intrinsic activity and reactivity" of 1-octene conversion, with both the "intrinsic reactivity and activity" of the reaction decreasing the most out of all the modified catalysts. As with the [MMIM][MeOSO₃] modified catalyst, the [MeP_{sec}-Bu₃][MeOSO₃] modified catalyst was inactive in the conversion of octanal.

The results of the conversion data of 1-octene and octanal show that the ionic liquid modified catalysts have a massive effect on the "intrinsic reactivity and activity" of the reaction, a summary of which can be found in Table 1. Especially, the selectivity of the product obtained from the conversion of a particular reactant is an important aspect which ionic liquid modified catalysts have been shown to alter in a number of related hydrogenation reactions. The product selectivity of the hydrogenation reactions versus their corresponding iso-conversion level for both 1-octene and octanal can be seen in Tables 2 and 3.

Table 2. Iso-conversion of 1-octene versus the mol fraction of converted 1-octene to octane, over the range of iso-conversion points with the differently modified catalysts.

Coating	% conversion : selectivity to octane (mol fraction)				
uncoated	10 : 0.60	30 : 0.71	40 : 0.67	60 : 0.73	80 : 0.76
Pyridine	27 : 0.57	40 : 0.56	50 : 0.55	65 : 0.53	75 : 0.58
1-methylimidazole	20 : 0.53	45 : 0.58	50 : 0.60	70 : 0.65	78 : 0.69
[MMIM][MeOSO ₃]	10 : 0.30	25 : 0.41	50 : 0.43	75 : 0.53	90 : 0.69
[MMIM][NTf ₂]	25 : 0.50	33 : 0.46	60 : 0.57	80 : 0.66	93 : 0.75
[MeP _{sec} Bu ₃][MeOSO ₃]	10 : 0.47	35 : 0.44	60 : 0.47	75 : 0.43	80 : 0.45

Table 3. Iso-conversion of octanal versus the mol fraction of converted octanal to octanol, over the range of iso-conversion points with the differently modified catalysts.

Coating	% conversion : selectivity to octanol (mol fraction)				
uncoated	7 : 1.0	17 : 0.89	39 : 0.86	54 : 0.89	87 : 0.87
Pyridine	13 : 0.94	23 : 0.97	37 : 0.92	47 : 0.98	86 : 0.94
1-methylimidazole	16 : 0.71	36 : 0.91	46 : 0.92	75 : 0.94	82 : 0.92
[MMIM][MeOSO ₃]	~0	~0	~0	~0	~0
[MMIM][NTf ₂]	9 : 1.0	19 : 1.0	26 : 0.90	49 : 0.87	91 : 0.89
[MeP _{sec} -Bu ₃][MeOSO ₃]	~0	~0	~0	~0	~0

This selectivity versus iso-conversion of 1-octene hydrogenation data for the uncoated catalyst reveals that as the conversion level increases, there is an increase in the selectivity towards octane. This can potentially be explained by an increase in residence time of the unsaturated alkene with the catalyst resulting in a relative increase in alkene saturation. The selectivity versus iso-conversion of octanal reveals that as the iso-conversion increases there is a decrease in the selectivity towards octanol. This is understandable as alumina is known to catalyse side reactions with oxygen containing groups (i.e. aldol condensation) by its basic and acidic sites.^[13a-d] It stands to reason that a decrease in LHSV and an increase in the concentration of octanol will result in an increase in by-product formation.

The pyridine modified catalyst provides a lower but constant level of selectivity to octane versus iso-conversion. This implies that the pyridine has modified the catalyst in a manner which lowers the relative rate of H₂ addition to the unsaturated C-C bond. Interestingly, the selectivity to octanol is also relatively constant but at a much higher average level compared to the uncoated catalyst. As it is known that acidic sites on alumina are in part responsible for by-product formation,^[13a] it is to be expected that the basicity of pyridine is reducing the numbers of these acidic sites.^[6,13a]

The 1-methylimidazole modified catalyst exhibits a similar trend to the uncoated catalyst with regards to the product selectivity versus iso-conversion of 1-octene, except, the product selectivity to octane is less, this suggest that the modification effect on the catalyst is different from that of pyridine but that it still has a depressive effect on the relative rate of unsaturated C-C bond hydrogenation. The trend in selectivity versus iso-conversion of octanal is, however, different from that of the uncoated catalyst and is similar to the pyridine modified catalyst, the potential reasons for this being alike to the pyridine modified catalyst.

The [MMIM][MeOSO₃] modified catalyst also shows a trend in selectivity versus iso-conversion of 1-octene similar to the uncoated catalyst. However, the general level is far lower than that of the uncoated catalyst (as much as half the selectivity at lower conversion levels), the pyridine modified catalyst and the 1-methylimidazole modified catalyst. Furthermore, the catalyst is inactive in the hydrogenation of octanal.

The [MMIM][NTf₂] modified catalyst reveals a trend that is also similar to the uncoated catalyst with regards to 1-octene hydrogenation (increasing selectivity with increasing iso-conversion). As with the [MMIM][MeOSO₃] coated catalyst the general selectivity to octane is lower than

that of the uncoated catalyst but not to the same extent. However, in contrast to the [MMIM][MeOSO₃] modified catalyst, this catalyst was active in octanal hydrogenation and its selectivity to octanol decreases with increasing levels of iso-conversion. Although the selectivity at lower levels of iso-conversion is higher than that of the uncoated catalyst, it drops after 39% conversion. This implies there may be an effective concentration level after which by-product formation starts to occur.

The [MeP_{sec}-Bu₃][MeOSO₃] modified ionic liquid shows a constant and reduced level of selectivity, compared to the uncoated catalyst, with increasing levels of iso-conversion of 1-octene. This trend is similar to the pyridine modified catalyst, albeit at a lower level of selectivity to octane, and in addition to this, the catalyst is inactive in the hydrogenation of octanal to octanol.

4.3.2 Catalyst characterisation

In order to help reveal some of the reasons as to why these organic modifiers can have such dramatic differences in modification effects on the uncoated Pd catalyst, a series of surface and analytical experiments were conducted. These included BET surface area analysis between the used and freshly prepared catalyst, diffuse reflectance infrared transmittance spectroscopy (DRIFTS), inductively coupled plasma optical emission spectroscopy (ICP-OES), thermal gravimetric analysis with differential scanning calorimetry (TGA-DSC), high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) under high angle annular dark field conditions (HAAD) of the used catalysts, as well as chemisorption with H₂ and CO.

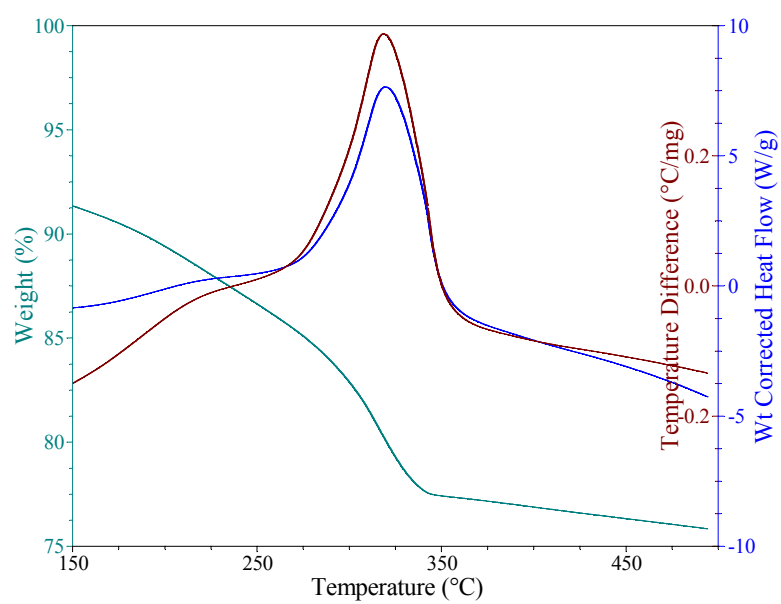
The results of the BET analysis can be seen in Table 4. It is quite apparent that with the uncoated catalyst there is a drop in the surface area, pore volume and pore width of the catalyst from the freshly prepared catalyst to the used catalyst. This is most likely the result of strongly adsorbed carbonaceous deposits produced during the hydrogenation reaction. The pyridine modified catalyst also reveals lower values for the used catalyst compared to the freshly prepared catalyst. However, the difference is less than that between the uncoated catalysts. The 1-methylimidazole modified catalyst also follows this trend; however, the values are similar to those of the pyridine modified catalyst.

Interestingly, the ionic liquid modified catalyst all show an increase in surface area from the freshly prepared catalysts to the used catalysts. This is also the case for the pore volumes of these catalysts, but the opposite trend occurs with the pore widths. This in general suggests that there may be a loss in the content of the ionic liquid layer during the reaction process.

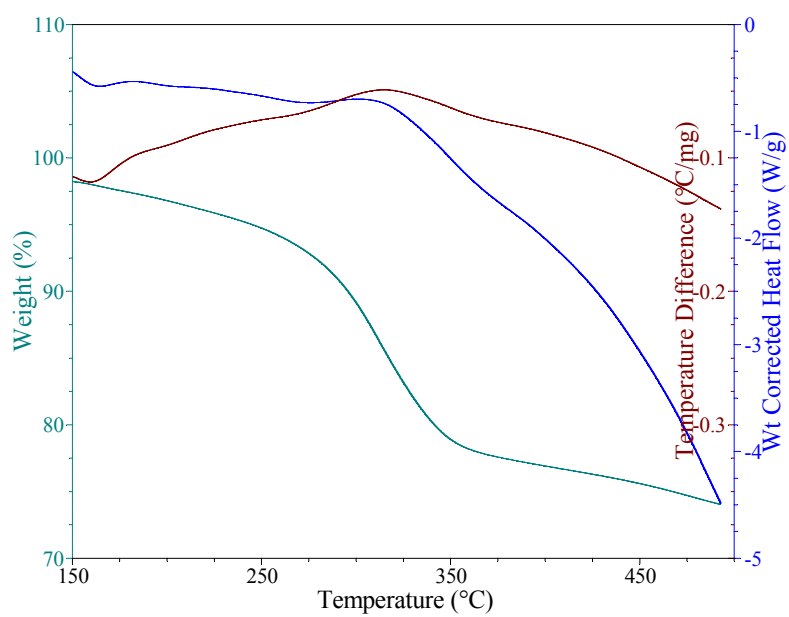
Table 4. BET surface area, pore volume, pore width and sulphur content analysis of the freshly prepared and used catalysts.

Coating	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore width (Å)	S content (weight %)
Uncoated fresh	190	0.62	131	-
Uncoated used	142	0.39	110	-
Pyridine fresh	177	0.54	121	-
Pyridine used	160	0.48	120	-
1-methylimidazole fresh	175	0.57	126	-
1-methylimidazole used	153	0.40	106	-
[MMIM][MeOSO ₃] fresh	87	0.29	132	4.7
[MMIM][MeOSO ₃] used	106	0.36	134	4.2
[MMIM][NTf ₂] fresh	56	0.25	182	8.6
[MMIM][NTf ₂] used	101	0.36	142	0.0
[MePsec-Bu ₃][MeOSO ₃] fresh	42	0.21	199	4.7
[MePsec-Bu ₃][MeOSO ₃] used	85	0.27	128	2.0

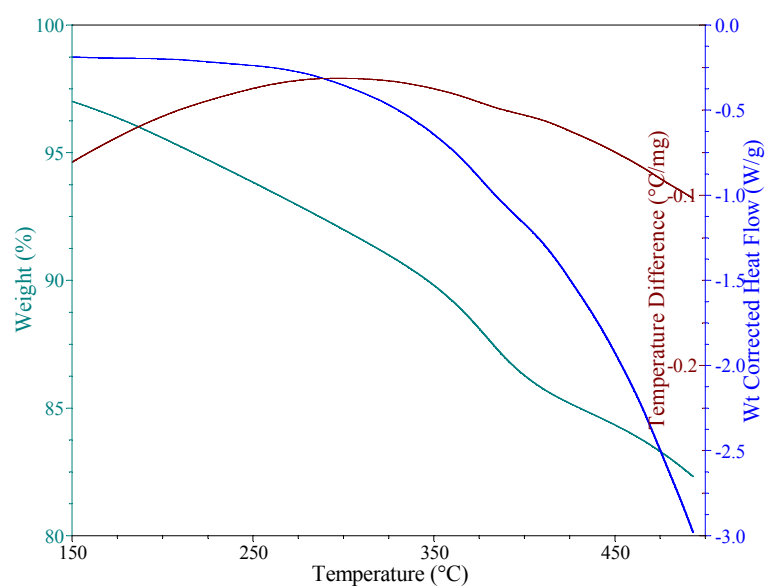
To determine if the ionic liquid layers of the ionic liquid modified catalyst were being removed from the catalyst surface, TGA-DSC, DRIFTS and ICP-OES were used to analyse the used catalysts. The TGA-DSC analysis and DRIFTS spectra for the ionic liquid modified catalysts are shown in Figure 5.



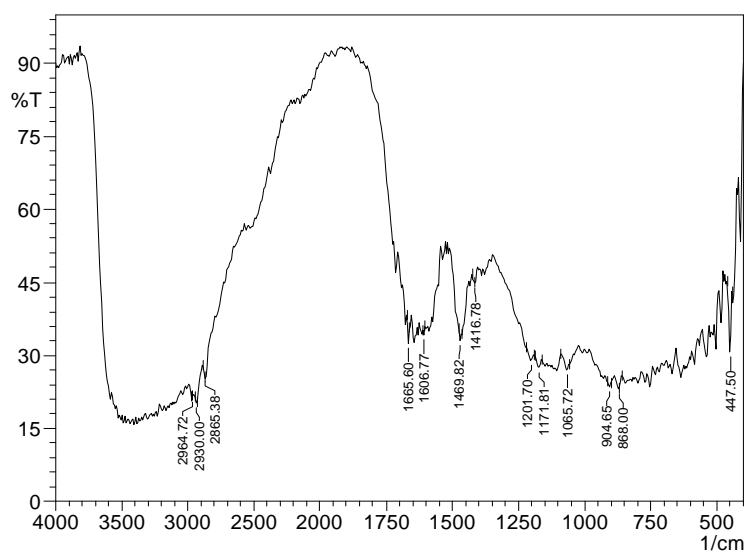
5a. The TGA-DSC profile for the used [MMIM][MeOSO₃] modified catalyst



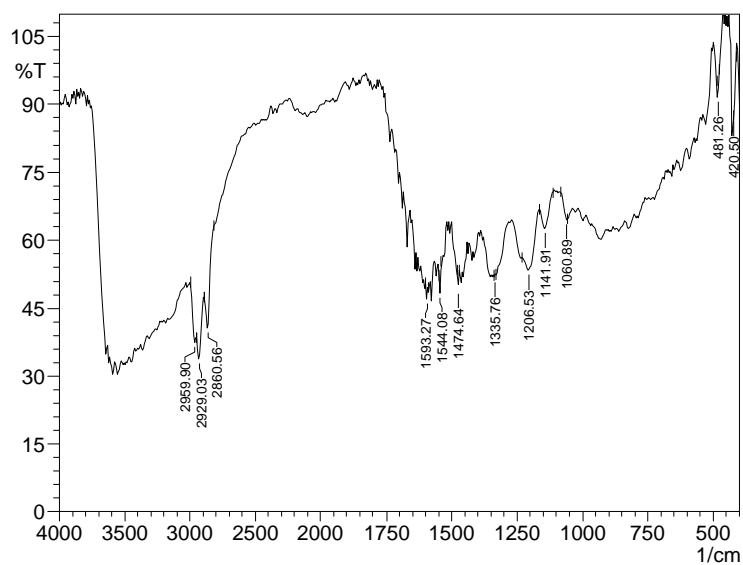
5b. The TGA-DSC profile for the used [MMIM][NTf₂] modified catalyst



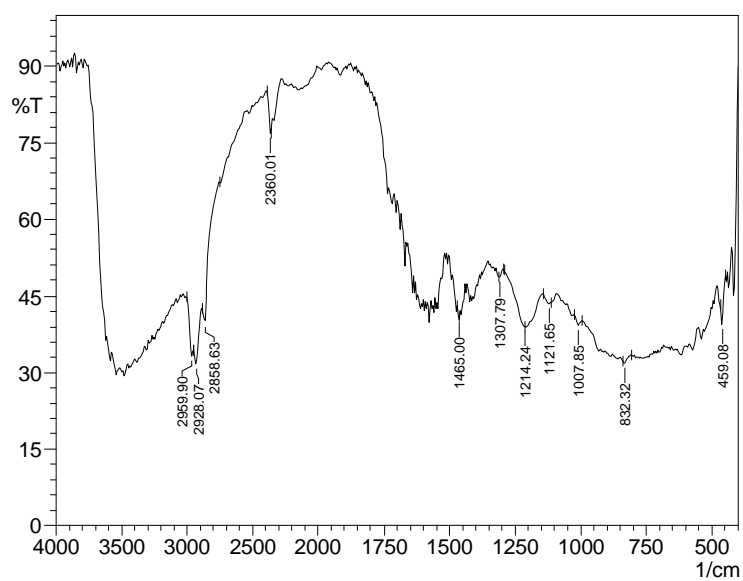
5c. The TGA-DSC profile for the used $[\text{MePsec-Bu}_3][\text{MeOSO}_3]$ modified catalyst



5d. The DRIFTS spectra for the used $[\text{MMIM}][\text{MeOSO}_3]$ modified catalyst



5e. The DRIFTS spectra for the used [MMIM][NTf₂] modified catalyst



5f. The DRIFTS spectra for the used [MeP_{sec}-Bu₃][MeOSO₃] modified catalyst

Figure 5a-f. TGA-DSC profiles and DRIFTS spectra for the used ionic liquid modified catalysts.

Absorption bands in the region of 1060 cm^{-1} and 1000 cm^{-1} are characteristic of S-O and S=O groups. The spectra for the ionic liquid modified catalysts do reveal some peaks in these areas and they may well originate from the ionic liquid. The absorption bands in the region of $2960\text{--}2850\text{ cm}^{-1}$ and 1470 cm^{-1} are characteristic of CH_n stretching frequencies, which are most likely present due to the reaction products and reactants adsorbed onto the catalyst surface; as well as the ionic liquid substituents or decomposition products thereof. These results suggest that the ionic liquid, or remnants of it, may still be present on the catalyst surface, at least as a thin molecular layer.

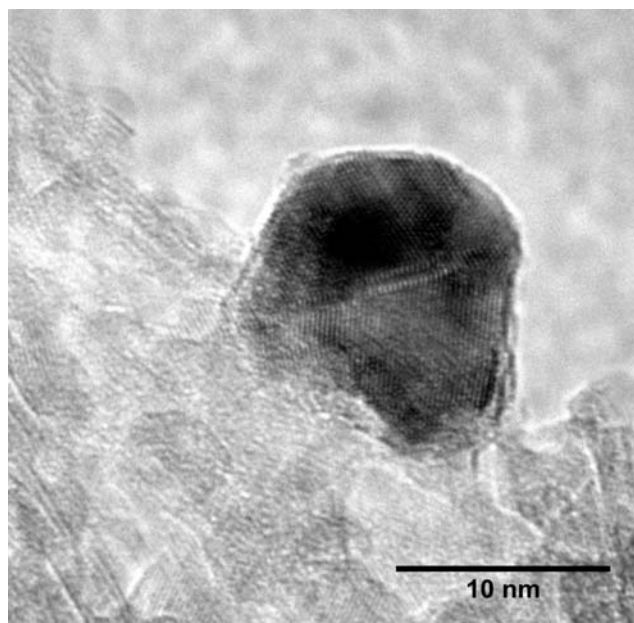
However, the TGA-DSC analysis for these catalysts (Figure 5) revealed dramatic differences between them. The $[\text{MMIM}][\text{MeOSO}_3]$ modified catalyst reveals a weight loss of approximately 18 % with an associated exothermal peak at $323\text{ }^\circ\text{C}$. The exothermal peak is characteristic of a decomposition and the corresponding temperature is fairly close to that reported for the decomposition temperature of pure $[\text{MMIM}][\text{MeOSO}_3]$.^[14] This indicates that the ionic liquid is still intact and that a significant amount of it has remained. This is confirmed by the sulphur content analysis by ICP-OES (Table 4). The TGA-DSC analysis for the $[\text{MMIM}][\text{NTf}_2]$ modified catalyst reveals a slight exotherm at $312\text{ }^\circ\text{C}$ with an associated weight loss of around 17 %. However, the sulphur content analysis (Table 4) indicates that the ionic liquid has not remained intact; this is supported by the relatively small exotherm found with the DSC. The weight loss may simply be due to carbonaceous material formed by an *in situ* decomposition or alteration of the ionic liquid. It is relevant to note that the gradual loss of weight between 150 and $500\text{ }^\circ\text{C}$ with an associated gradual endotherm has been attributed to a gradual loss of carbonaceous materials.^[15] The TGA-DSC analysis for the $[\text{MePsec-Bu}_3][\text{MeOSO}_3]$ reveals no exotherms characteristic of ionic liquid decomposition, there is, however, a slight differential weight loss starting at approximately $350\text{ }^\circ\text{C}$. The sulphur content analysis (Table 4) reveals that a fair amount of sulphur has remained on the catalyst. This implies that the ionic liquid layer has not survived intact and that an *in situ* decomposition has taken place with sulphur fragments remaining on the catalyst. These results reveal that *in situ* preparation of ionic liquid modified catalysts can result in dramatic differences in the surface characteristics of the catalysts, depending on the type of ionic liquid used, which may translate into differences in catalyst performance.

HRTEM analysis, particle size analysis by STEM and chemisorptions techniques of the used catalysts were conducted to determine if the *in situ* preparation and use of organically modified catalysts have any effect on the morphological and chemical properties of the Pd crystallites. The results of these analyses can be seen in Table 5 and Figure 6.

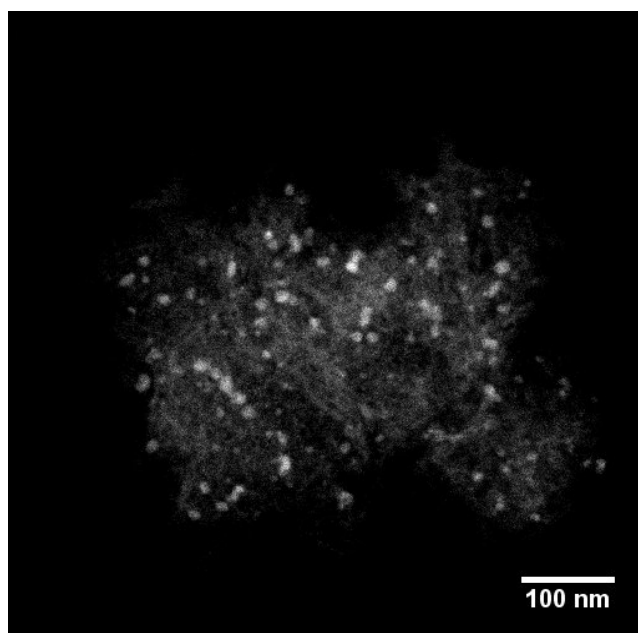
An example of an image obtained by HRTEM can be seen in Figure 6a. It can be seen that the crystallites present are of a uniform nature, i.e. whole crystallites with no observable defects, apart from plane interfaces. This was found with all catalysts analysed. Furthermore, an image obtained for STEM analysis under HAAD conditions can be seen in Figure 6b, a minimum of 300 particle measurements over 20 images were used to calculate the average particle size (Table 5).

Table 5. Crystallite size and metal surface area analysis by STEM and chemisorption techniques.

Coating	STEM (nm)	CO chemi- sorption (nm)	H ₂ chemi- sorption (nm)	CO chemi- sorption (m ² /g)	H ₂ chemi- sorption (m ² /g)
uncoated	10 ±3 ^[a]	26 ±4 ^[b]	10 ±3 ^[b]	19 ±4 ^[b]	49 ±3 ^[b]
Pyridine	7 ±2 ^[a]	18 ±4 ^[b]	7 ±2 ^[b]	48 ±4 ^[b]	72 ±2 ^[b]
1-methylimidazole	7 ±4 ^[a]	21 ±2 ^[b]	9 ±3 ^[b]	24 ±2 ^[b]	59 ±3 ^[b]
[MMIM][MeOSO ₃]	10 ±3 ^[a]	39 ±5 ^[b]	15 ±3 ^[b]	13 ±5 ^[b]	34 ±3 ^[b]
[MMIM][NTf ₂]	7 ±2 ^[a]	28 ±5 ^[b]	7 ±4 ^[b]	18 ±5 ^[b]	69 ±4 ^[b]
[MePsec-Bu ₃][MeOSO ₃]	10 ±4 ^[a]	35 ±4 ^[b]	13 ±1 ^[b]	14 ±4 ^[b]	38 ±1 ^[b]
[a] Standard deviation [b] Percentage error					



6a. HRTEM image of a palladium crystallite from a 5% palladium on alumina catalyst



6b. STEM image under HAAD conditions of a 5% palladium on alumina catalyst

Figure 6a-b. Image examples from the TEM analysis techniques.

Chemisorption studies of SCILL palladium on silica catalysts have been conducted before,^[16] however, these were unused *ex situ* prepared catalysts (pre-reduced catalysts, followed by a coating of ionic liquid) with intact ionic liquid layers, analysed to confirm the assumption that a layer of ionic liquid (known for their low solubilities of H₂ and CO) will reduce the amount of absorbed H₂ and CO on the catalyst. To the best of our knowledge, this is the first time a comparison has been made between used *in situ* prepared (coated catalysts reduced *in situ*) SCILL palladium on alumina catalysts and those modified by traditional organic modifiers; with the hope of correlating catalyst performance. As part of our investigation, we use a standard model for crystallite size determination, (for ease of comparison between H₂ chemisorption, CO chemisorption and STEM analysis) using an assumption of complete coverage by the gasses and a stoichiometry factor of 1 for CO and 2 for H₂. These factor values are commonly used values despite the most accurate values being disputed.^[17a-g,18]

The crystallite size analysis by STEM for the uncoated catalyst reveals an average size of around 10 nm. This is supported by the H₂ chemisorption analysis, revealing a good correlation between the two techniques. CO chemisorption, however, gave a much larger average crystallite size at approximately 26 nm, the ratio between the STEM analyses being 1 : 2.5. CO has multiple bonding conformations to transition metals, for example linear on top, bridged or hollow bonding using 5d and 2π* orbitals.^[17a] The different energies associated with these bonding modes result in the amount of CO bonded being dependant on coverage (i.e. relative pressure of CO).^[17b] In addition to this, the relative numbers of different sites of bonding (i.e. plateau, hollow, terrace or steps; Figure 6a reveals some of these sites) affects the amount of CO bonded.^[17b] The electronic state of the metal due to modifications may also have a direct influence on the bonding of CO.^[17c] This, along with the data obtained, suggest that a stoichiometry factor of 2 for CO is a more accurate value. However, as there are already many in-depth investigations into the nature of CO chemisorption on palladium catalysts,^[17a-g,18] we will focus on the differences in chemisorption of CO (seen as changes in crystallite size) between the different catalysts as a potential measure on the catalytic performance of the catalysts, with regards to the binding and reaction of carbonyl compounds.

Interestingly, the pyridine and 1-methylimidazole modified catalyst have an average crystallite size (by STEM analysis) of around 7 nm. This suggests that these modifiers may have an effect on the formation size of the Pd crystallites. The H₂ chemisorption analysis confirms this for the pyridine modified catalyst. However, the H₂ chemisorption results for the 1-methylimidazole modified catalyst reveals a larger average crystallite size which is potentially the result of a hindrance in H₂ adsorption due to a chemically modified surface, and may be in part responsible

for the differences in the "intrinsic activity" observed between these two catalysts. A similar observation can be seen with the CO chemisorption analysis, with the ratio of STEM analysis to CO chemisorption analysis being 1 : 2.6 and 1 : 2.9 respectively. Taking the directly measured crystallite sizes (STEM analysis) into account, the ratio of these and the uncoated catalyst tend to follow the trend in "intrinsic activity" of octanal conversion.

The [MMIM][MeOSO₃] modified catalyst revealed an average crystallite size of around 10 nm, which is similar to the uncoated catalyst. However, the H₂ chemisorption analysis revealed an average particle size of around 14 nm. This suggests that the H₂ molecules used in the chemisorption analysis are hindered in their chemisorption to the Pd crystallites, possibly due to the ionic liquid molecular layer or decomposition products. This, in general, correlates with the catalytic results of "intrinsic activity" and selectivity versus iso-conversion of 1-octene, between the uncoated and [MMIM][MeOSO₃] modified catalysts. The crystallite size determined by CO chemisorption shows a crystallite size of approximately 39 nm, with the ratio to STEM analysis being 1 : 3.9. It is interesting to note that the catalyst was inactive in the conversion of octanal to octanol.

The [MMIM][NTf₂] modified catalyst reveals an average crystallite size of 7 nm by STEM analysis, which confirms the H₂ chemisorption analysis. Interestingly, this also correlates with the catalytic "intrinsic activity" of this catalyst compared to the uncoated catalyst with regards to 1-octene conversion and crystallite size. The CO chemisorption analysis reveals a larger crystallite size compared to the uncoated catalyst. The ratio of STEM analysis to CO chemisorption analysis gives a value of 1 : 3.6. These data fit well with both the 1-octene and octanal conversion results where there was a noticeable decrease in the "intrinsic activity" of octanal conversion compared to the uncoated catalyst, but not inactivity, with a slight increase in "intrinsic activity" for 1-octene conversion.

The [MeP_{sec}-Bu₃][MeOSO₃] modified catalyst reveals an average crystallite size (by STEM analysis) of approximately 10 nm. This is similar to the uncoated and [MMIM][MeOSO₃] modified catalysts. As with the [MMIM][MeOSO₃] modified catalyst, the H₂ chemisorption analysis reveals a larger Pd crystallite size and the "intrinsic activity" of the 1-octene conversion is depressed compared to the uncoated catalyst. As with the [MMIM][MeOSO₃] and [MMIM][NTf₂] modified catalysts, the CO chemisorption analysis reveals a larger Pd crystallite size compared to the uncoated catalyst, with the ratio of crystallite size to STEM analysis being 3.6; the catalyst was inactive in the conversion of octanal to octanol.

These results show an interesting pattern emerging between the catalytic results and the chemisorption analysis, and it may be possible to anticipate the general catalytic results of ionic liquid modified catalysts by chemisorption techniques together with STEM analysis.

4.4 Conclusion

The catalytic results from this study reveal that ionic liquid modified catalysts have dramatic and specific effects and indicate that they have a place alongside traditional organic modifiers. They also have the ability to selectively alter the catalytic performance between different types of substrates.

Catalyst characterisation studies reveal that BET surface area analysis of these catalysts can give an indication to a possible loss in the content of ionic liquid, but cannot be used as a means to predict the behaviour of the catalyst's "intrinsic activity or reactivity".

DRIFTS, TGA-DSC and ICP-OES analyses of these catalysts reveal that a relatively thick ionic liquid layer can survive the reaction conditions. However, this is not a universal rule and ionic liquid decomposition or removal can indeed occur. The decomposition of the ionic liquid can potentially lead to a very different matrix of surface modification, depending on the ionic liquid used. In addition to this, *in situ* preparation of the catalysts with different organic modifiers can have an effect on the formation size of the palladium crystallites. However, chemisorption techniques coupled with STEM analysis can reveal the size of the crystallites and potentially give a general method for the anticipation of catalytic results.

These results highlight that the effects of ionic liquid modification of traditional heterogeneous catalysts are many and varied. In addition to any transport and/or modification effects, crystallite size modification may also potentially be a factor. As these varied effects are also dependent on the type of ionic liquid used and the substrate catalysed, a large scale investigation is required to fully appreciate the trends and modifications of SCILL catalysts. This is especially so if different metals and combinations of them are to be considered, as ionic liquid modified catalysts from this study and others with different metal catalysts, have shown to be effective in altering reaction product selectivity, "intrinsic reactivities" and "intrinsic activities" (compared to the uncoated catalyst).

4.5 Experimental Section

The ionic liquid [MMIM][MeOSO₃] was prepared by methods already described in literature, by the alkylation of 1-methylimidazole with dimethylsulphate.^[14] Pyridine and 1-methylimidazole were obtained from Sigma-Aldrich, while the [MeP_{sec}-Bu₃][MeOSO₃] ionic liquid was obtained from SASOL R&D. The ionic liquid [MMIM][NTf₂] was synthesised by an anion exchange of [MMIM][MeOSO₃] with [Na][NTf₂]. NMR analysis was used to confirm the purity and identity of the synthesised ionic liquids.

A palladium on alumina catalyst (ca. 5% w/w) was prepared by wet impregnation of a crushed gamma alumina support with palladium acetate in dichloromethane at 50 °C for 4 h. The resultant paste was dried in an oven at 110 °C for an additional 2 h before being calcined at 350 °C for 8 h. The catalyst was then pelletized to a size distribution between 300 and 600 µm. The resultant catalyst was then coated with the following organic modifiers: pyridine, [MMIM][MeOSO₃], [MMIM][NTf₂], [MeP_{sec}-Bu₃][MeOSO₃] and 1-methylimidazole, to the equivalent molar amount of 25 weight % of [MMIM][MeOSO₃], by dissolving the required amounts of modifier in either methanol or dichloromethane in a pill vial before introducing the parent catalyst. The mixture was allowed to evaporate slowly in a fume hood to obtain a dry powder. The reduced metal catalysts were then generated *in situ* in the reactor (50 bar H₂, 15ml/min H₂, 180 °C, 4 h) before commencement of the reaction.

The average Pd crystallite size and crystallite morphology of the organically modified catalysts were determined by the use of a JEOL 2100 HRTEM, counting approximately 300 particles under HAAD and STEM conditions for the crystallite size analysis. ICP-OES (Perkin Elmer Optima DV2100) was used to confirm the weight percent loading of the palladium as well as the sulphur content of the freshly prepared and used catalysts. BET and pore size distribution and width were determined on a Micromeritics TRISTAR 3020 to resolve the extent of change in pore volume, pore width and surface area between the freshly prepared and used organically modified and uncoated catalysts, all catalyst were placed under vacuum until a stable 70 Tor was reached. Chemisorption experiments were performed on a Micromeritics ASAP 2020C using volumetric techniques. Calculation of crystallite size and metal surface area was performed on the Micromeritics ASAP 2020C software using established formula.^[18] DRIFTS spectra were obtained using a Shimadzu IRAffinity-1 FTIR spectrophotometer and TGA-DSC profiles of the used catalysts were obtained using a TA SDT Q600.

Hydrogenation experiments were carried out in a concurrent down flow trickle bed reactor with an inner diameter of 14 mm and a length of 250 mm to give a volume of 38.5 cm³. When required, the catalyst was diluted with carborundum (grit size 24) to maintain a constant catalyst bed volume and served to prevent aniso-thermal conditions with strongly active catalysts (high LHSV's). The grit size is sufficient to prevent a large pressure drop across the reactor tube. The rest of the reactor was packed with carborundum and quartz wool was used as a plug at the ends of the carborundum and the catalyst bed, which serves as an efficient dispersant of the liquid phase.^[19] A 2,5 % (v/v) 1-octene with 2,5% (v/v) octanal mixture in hexane was introduced into the reactor by means of an HPLC pump. The hydrogen was introduced by means of mass flow controllers at a constant substrate to hydrogen ratio of 1:2. The feed was dried with molecular sieves^[20] and degassed with argon^[21] to eliminate water and oxygen from the system. An argon feed was supplied to the head space of the feed bottle to give a slight positive pressure. The temperature and pressure of the reaction system was kept at 50 bar and 130 °C by a temperature controlled heating jacket with an internal sliding thermocouple. The gas hourly space velocity (GHSV) and liquid hourly space velocity (LHSV) were concurrently adjusted to produce the different iso-conversion of 1-octene and octanal for each of the differently modified catalysts. The product composition was analysed off line by means of a GC-FID (Perkin Elmer Clarus 500).

4.6 References

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CHAPTER 5

APPLICATION AND CHARACTERISATION OF MODIFIED COPPER CATALYSTS IN THE COMPETITIVE HYDROGENATION BETWEEN 1-OCTENE AND OCTANAL

5.1 Abstract

Selective hydrogenation of different reducible molecules, found in common industrial feedstocks, remains a challenging area of investigation. Recently, SCILL catalysts (Solid Catalyst with an Ionic Liquid Layer) have shown to be potentially applicable in this regard. However, the majority of SCILL catalysis has focused on group 10 metals (Pt, Pd, Ni). Herein we report the use of group 11 metal (Cu) SCILL catalysts in the competitive hydrogenation between 1-octene and octanal. Our results indicate that a (Cu) SCILL catalyst (in contrast to the uncoated version) can effectively suppress the hydrogenation of 1-octene over octanal, to a similar extent of a strongly discriminating uncoated silver catalyst. However, the potential to deactivate the catalysts with regards to both 1-octene and octanal hydrogenation also exists, which may be related to an effect of the ionic liquid on the average metal crystallite size of the modified catalysts.

5.2 Introduction

Selective hydrogenation of different reducible molecules remains a topical field for investigation, especially in competitive inter-molecular hydrogenation of commercially important hydrocarbon feed stocks.^[1a,b]

Problems associated with mixed reducible compounds is, for example, encountered when Fischer-Tropsch feedstocks (mainly mixtures of alkenes together with aldehydes and ketones)^[2]

are used in further downstream reactions. Thus, the rhodium catalysed hydroformylation of such alkene feedstock would furnish product aldehydes contaminated with aforementioned oxygenates. This could pose serious separation troubles. Selective reduction of the oxygenates present in the alkene feed could therefore help circumvent this problem. It is in this context that the competitive hydrogenation between octanal and 1-octene reported in this study was undertaken.

The benefits of such selective hydrogenation of mixtures of this kind range from increased ease of product separation to removal of potential poisons and inhibitory compounds of further chemical reactions.^[3a-b]

A relatively new class of organically modified catalysts has been described which provide enhanced selectivity in a number of competitive hydrogenation reactions. The Solid Catalyst with an Ionic Liquid Layer (SCILL) has been shown to provide enhanced selectivity in both inter- and intra-molecular functional groups under both batch and continuous flow conditions.^[1a,4a-f] For example, the hydrogenation of Citral to Citronenal has been enhanced with the application of a palladium SCILL catalyst in both batch and continuous flow processes.^[4a-d] The application of a nickel SCILL catalyst has also shown to increase the selectivity towards cyclooctene in the hydrogenation of 1,4-cyclooctadiene and towards 1-octene in the competitive hydrogenation between 1-octene and 1-octyne as well as 1-octene and 1,7-octadiene.^[1a,4f] More recently, a bi-functional platinum SCILL catalyst has been successful in enhancing the skeletal isomerisation of octane to iso-octane.^[5] However, a decrease in activity is generally associated with these enhanced selectivities, which is akin to the effects of other organic modifiers such as quinoline.^[6]

The exact reason for this enhanced selectivity is still uncertain, and a number of possibilities exist which may singularly or in tandem be responsible. These include surface diffusion, solubility effects and site specific interaction by both the cation and anion.^[1a] Although there is evidence of both cation and anion association with surface sites on the catalyst crystallite, we have found that in general, the nature of the cation seems to have the stronger influence.^[1a] In addition to this, the nature of the metal catalyst used for SCILL catalysts also appears to play a role in site specific interaction with ionic liquids. It has been demonstrated with platinum and palladium metal crystallites that after coating with an ionic liquid, there is a difference between them in the nature of site bound CO molecules (i.e. edge or plateau).^[7] Additionally, site modification by degradation products may also occur and be at least partially responsible for

changes in selectivity and activity.^[7] These intertwined possibilities so far described, provide a large capacity for the study of ionic liquid modification on traditional heterogeneous catalysts and its effects on various substrates.

To date, the majority of literature concerning the application of SCILL catalysts has been focused on group 10 elements (Ni, Pd, Pt). Herein we describe the application of a group 11 (Cu) SCILL catalyst compared to an uncoated group 11 (Ag) catalyst in the competitive hydrogenation between 1-octene and octanal over a range of iso-conversion conditions. The results now reported indicate that the objective of the selective hydrogenation of the aldehyde in the presence of the alkene can be achieved, with both an uncoated silver catalyst and a copper SCILL catalyst. However, the copper SCILL catalyst may be economically advantageous. An additional effect of ionic liquid modification, namely alteration of crystallite size is also reported. We also compare the effects of ionic liquid modifiers with two traditional organic modifiers, namely pyridine and 1-methylimidazole.

5.3 Results and Discussion

5.3.1 Catalytic hydrogenation of 1-octene and octanal

Of the group 11 elements, silver has been shown to be an active and selective catalyst in the hydrogenation of acrolein to allyl alcohol and citral to nerol/geraniol.^[8a,b] The application of a silver based catalyst in the competitive hydrogenation between 1-octene and octanal may therefore provide at least a partially selective, although expensive, means of reducing octanal in preference to 1-octene.

Figure 1 below shows the conversion range of octanal at two different temperatures (180 °C, 250 °C) from a feed containing 2.5% (v/v) octanal and 2.5% (v/v) 1-octene in hexane. Under these conditions, the silver catalysts were found to be inactive in the hydrogenation of 1-octene. The conversion data which is shown for the hydrogenation of octanal is derived from reaction runs with a minimum of 7 hours on stream to achieve an approximate steady state. For meaningful comparison the conversion versus the liquid hourly space velocity (LHSV) required to effect the conversion are shown. For the purpose of this discussion, the conversion range is defined as the scope of LHSV required to bring about a ≥ 0 % to ≤ 100 % conversion.

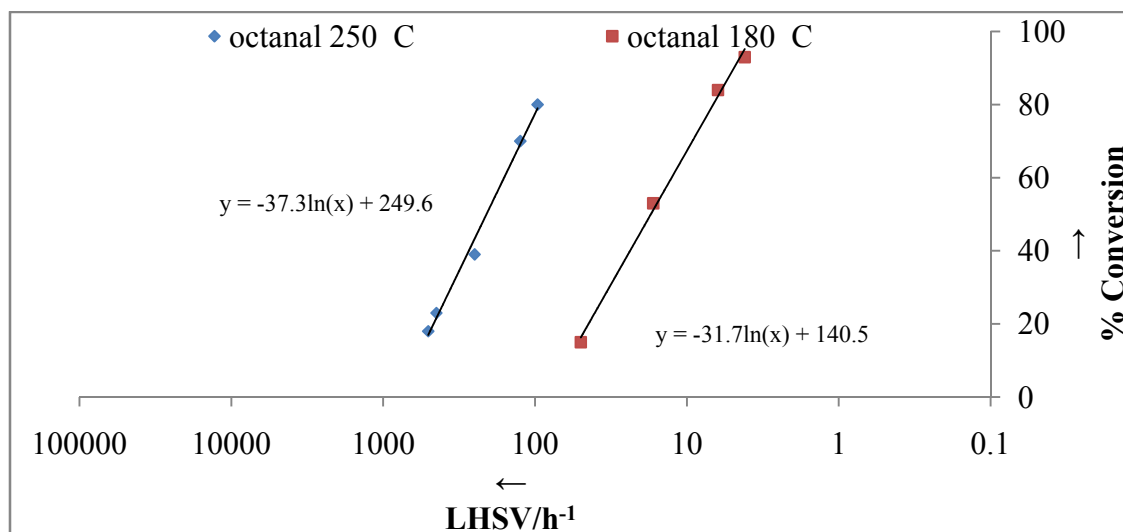


Figure 1. Iso-conversion points versus LHSV in the competitive hydrogenation between 1-octene and octanal at 180 °C and 250 °C with a 5% silver on alumina catalyst. The LHSV is represented as a log scale and corresponds to the "x" coordinate. The "y" coordinate corresponds to % conversion. Iso-conversion is defined as the constant conversion attained once steady state has been achieved in the continuous flow reactions. No octene conversion was observed.

The conversion data versus LHSV (Figure 1) reveals a logarithmic relationship between the conversion and LHSV required to bring about the conversion. To aid in the comparison of the data, the gradient or slope of the relationship is defined as a measure of "intrinsic reactivity" (a steeper slope indicating a more reactive catalyst),^[9] while the specific LHSV at 50% conversion is defined as a measure of the intrinsic activity (greater LHSV's indicating a more active catalyst). Intuitively it can be seen that with an increase in temperature, the silver catalyst becomes more "intrinsically active" in the conversion of octanal, while the "intrinsic reactivity" remains approximately the same for the conversion data of the different temperature reactions.

In both ranges for the different temperatures, the catalyst exhibited remarkable selectivity for octanal conversion to octanol (Table 2). Indeed, even at 250 °C the catalyst completely produces octanol without any significant formation of by-products, (e.g. aldol condensation products amongst others) which can occur with alumina based catalysts.^[10a-d] In addition to this the catalyst was found to be inactive in the hydrogenation of 1-octene even at 250 °C, providing an efficient means of hydrogenating octanal in the presence of 1-octene. However, silver is an expensive metal and its cost may be prohibitive in the use of large scale applications.

Copper is, however, a relatively cheap metal in comparison to silver. A cursory glance of current market prices place it at least two orders of magnitude cheaper. In addition, copper based catalysts have also been shown to be at least partially selective towards the hydrogenation of oxygen containing reducible groups.^[11a-c] Figure 2 shows the conversion profiles in the competitive reaction between 1-octene and octanal at 180 °C for the uncoated copper catalyst.

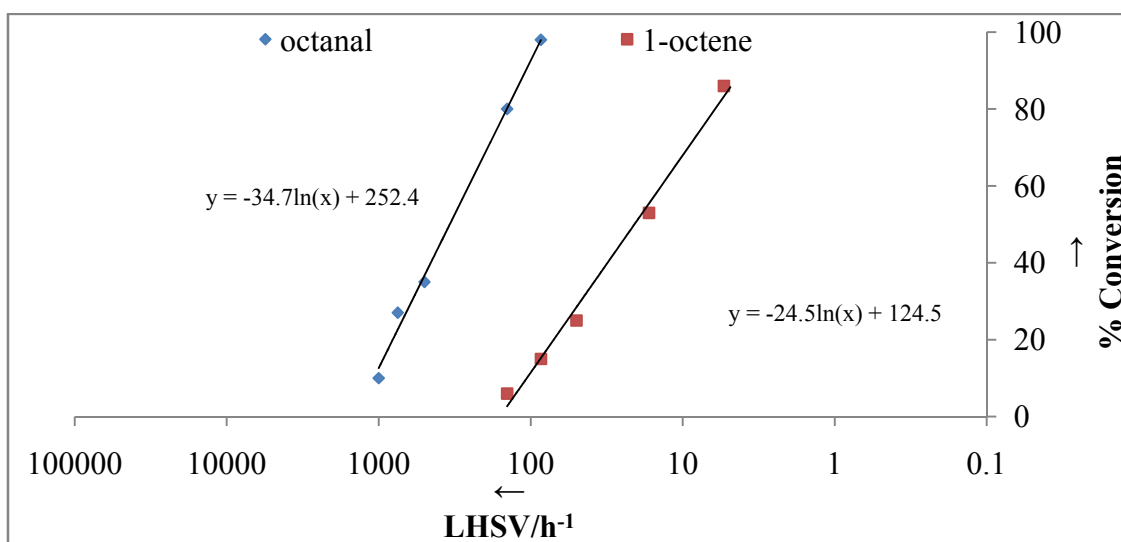


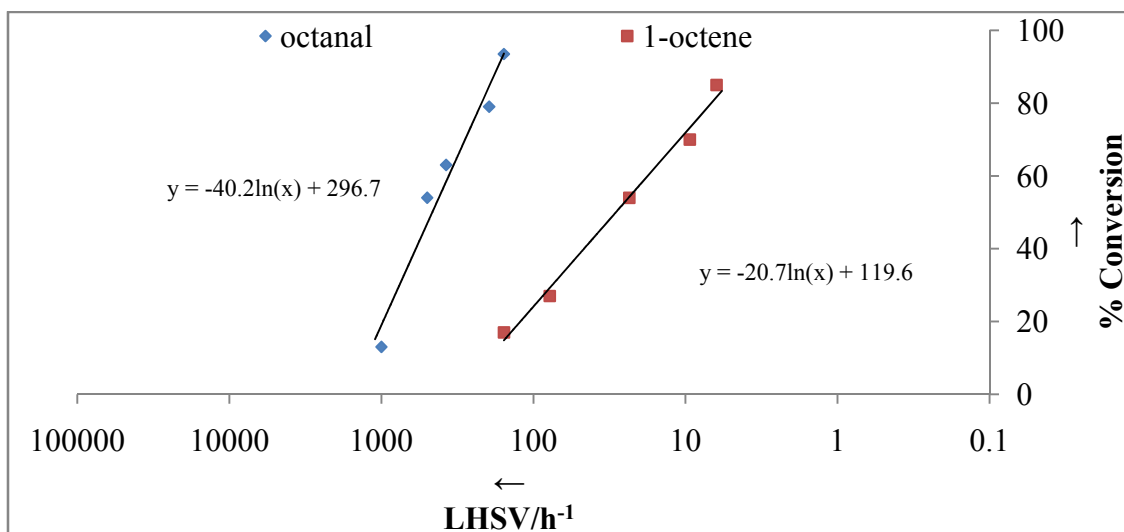
Figure 2. Iso-conversion points versus LHSV in the competitive hydrogenation between 1-octene and octanal at 180 °C with a 5% copper on alumina catalyst. Iso-conversion is defined as the constant conversion attained once steady state has been achieved in the continuous flow reactions.

The conversion versus LHSV for octanal and 1-octene also follow a logarithmic relationship and the "intrinsic activity and reactivity" of octanal conversion at 180 °C seems to be similar to that brought about by the silver catalyst at 250 °C. However, the copper catalyst also hydrogenates 1-octene, with the conversion range of octanal partially overlapping the conversion range of 1-octene. This occurs at the higher conversions of octanal (lower LHSV of the conversion range) and lower conversions of 1-octene (higher LHSV of the conversion range). In addition to this, the "intrinsic reactivity" of octanal and 1-octene conversion are dissimilar; the octanal conversion exhibiting greater "intrinsic reactivity" over 1-octene conversion.

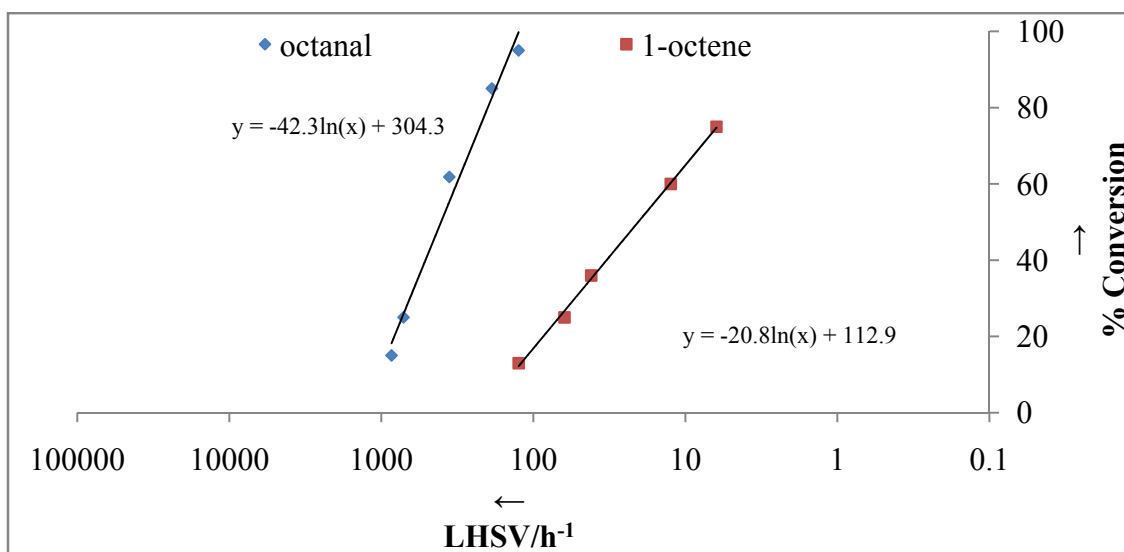
As mentioned previously, the unmodified copper catalyst also hydrogenates 1-octene within the range of octanal conversion. Ionic liquids have demonstrated the ability to suppress conversion in a selective manner depending on the type of substrate used,^[1a,4a-f] and, in the expectation that these organic modifiers might be able to selectively alter the "intrinsic activities and/or reactivities" of octanal and 1-octene conversion, a series of copper catalysts were coated with the ionic liquids: 1,3-dimethylimidazole methylsulphate [MMIM][MeOSO₃], 1,3-dimethylimidazole bis(trifluoromethylsulphonyl)imide [MMIM][NTf₂] and methyl-tri-*sec*-butylphosphonium methylsulphate [MeP*sec*-Bu₃][MeOSO₃]. The coatings contained an equimolar quantity based on the molar content of 1,3-dimethylimidazole methylsulphate in a 25% (w/w) 1,3-dimethylimidazole methylsulphate coated catalyst. To investigate the relative effects of traditional organic modifiers, the copper catalyst was coated with an equivalent molar content of pyridine and 1-methylimidazole. The conversion data for these modified catalysts can be seen in Figure 3a-c and Table 1.

Table 1. A summary of "intrinsic reactivity and activity" of conversion of octanal and 1-octene, respectively, with the different catalysts.

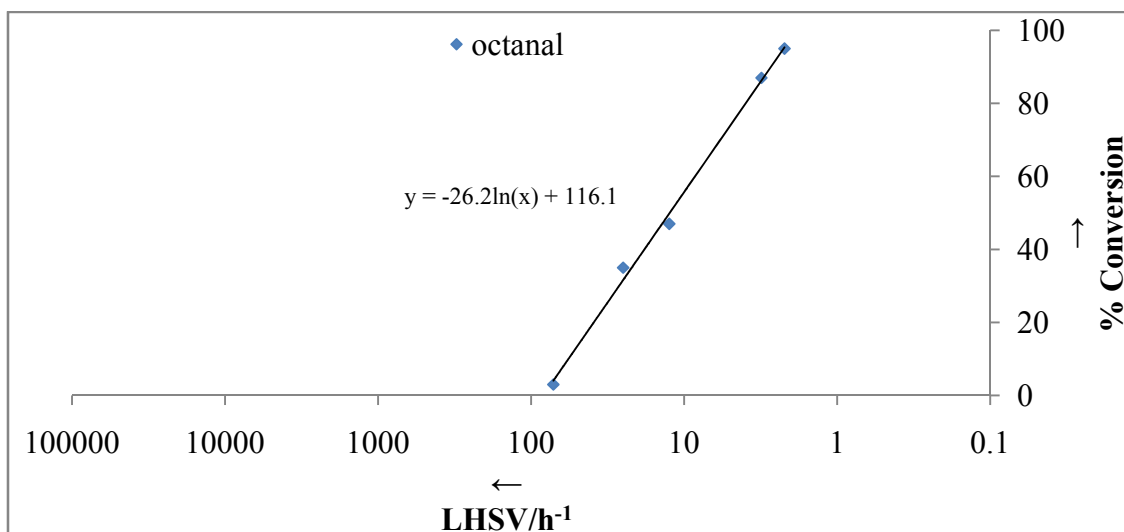
Coating	octanal conversion		1-octene conversion	
	reactivity ^[a] (%.h)	activity ^[b] (LHSV, h ⁻¹)	reactivity ^[a] (%.h)	activity ^[b] (LHSV, h ⁻¹)
uncoated Ag (180 °C)	-31.7	17	~0	~0
uncoated Ag (250 °C)	-37.3	211	~0	~0
uncoated Cu	-34.7	341	-24.5	21
Pyridine	-40.2	463	-20.7	29
1-methylimidazole	-42.3	408	-20.8	21
[MMIM][MeOSO ₃]	-26.2	12	~0	~0
[MMIM][NTf ₂]	~0	~0	~0	~0
[MeP <i>sec</i> -Bu ₃][MeOSO ₃]	~0	~0	~0	~0
[a] Defined as the gradient of the logarithmic function. ^[9] [b] Defined as the LHSV required to bring about 50% conversion. Values listed as ~0 are below the detection limit.				



3a. Iso-conversion points versus LHSV in the competitive hydrogenation between 1-octene and octanal at 180 °C with a pyridine modified 5% copper on alumina catalyst



3b. Iso-conversion points versus LHSV in the competitive hydrogenation between 1-octene and octanal at 180 °C with a 1-methylimidazole modified 5% copper on alumina catalyst



3c. Iso-conversion points versus LHSV in the competitive hydrogenation between 1-octene and octanal at 180 °C with a [MMIM][MeOSO₃] modified 5% copper on alumina catalyst, no octene conversion was observed

Figure 3a-c. Conversion versus LHSV relationship plots for the pyridine, 1-methylimidazole and [MMIM][MeOSO₃] modified copper catalysts. Iso-conversion is defined as the constant conversion attained once steady state has been achieved in the continuous flow reactions.

Figure 3a reveals the conversion data for the copper catalysts modified by pyridine. It is quite noticeable that the modified catalyst exhibits an increase in the "intrinsic reactivity" of the octanal conversion compared to the uncoated catalyst, with a slight increase in the "intrinsic activity". This indicates that the traditional catalyst modifier has a positive effect on the copper catalyst, at least for this substrate and these reaction conditions. However, there is an unexpected decrease in the "intrinsic reactivity" of the 1-octene conversion, with an associated increase in the "intrinsic activity".

Figure 3b shows the conversion data for the copper catalyst coated with 1-methylimidazole. It follows a similar trend to the pyridine modified catalyst with regards to an increase in the "intrinsic reactivity" of octanal conversion; however, the "intrinsic activity" of this conversion has remained similar to the uncoated catalyst. Interestingly, the "intrinsic reactivity" of 1-octene conversion has remained similar to the uncoated catalyst, while the "intrinsic activity" has decreased, which is contrasting to the pyridine modified catalyst.

Figure 3c shows the conversion data for the catalyst coated with 1,3-dimethylimidazole methylsulphate. It is quite apparent that the ionic liquid has a dramatic effect on both the "intrinsic activity and reactivity" of octanal conversion. Comparing the uncoated catalyst to the [MMIM][MeOSO₃] modified catalyst, it is evident that the ionic liquid modified catalyst is less active and less efficient in the conversion of octanal. However, the catalyst was inactive for the conversion of 1-octene, effectively separating out the conversion range overlap in 1-octene and octanal conversion seen with the uncoated, pyridine and 1-methylimidazole modified catalysts. In addition to this, the range of LHSV for octanal conversion with the [MMIM][MeOSO₃] modified catalyst is similar to the silver catalyst at 180 °C, which potentially provides an economically viable alternative catalyst.

Unexpectedly, the catalysts modified by the ionic liquids [MeP_{sec}-Bu₃][MeOSO₃] and [MMIM][NTf₂] were both inactive in the hydrogenation of 1-octene and octanal. This is in stark contrast to results we have obtained for analogous hydrogenation reactions using a palladium on alumina catalyst. In an effort to identify potential reasons behind such a dramatic difference in results, several surface studies were carried out and are discussed shortly. However, to further investigate the effects of the organic modifiers on the copper catalyst with regards to reaction performance, the selectivity of product formation with the conversion data are compared and shown in Tables 2 and 3.

Table 2. Conversion of octanal versus the mol fraction of converted octanal to octanol, over the range of conversion points with the different catalysts.

Coating	% conversion : selectivity to octanol (mol fraction)				
uncoated Ag (180 °C)	15 : 1	54 : 0.99	-	84 : 1	93 : 1
uncoated Ag (250 °C)	17 : 0.99	22 : 0.98	39 : 1	70 : 1	78 : 0.99
uncoated Cu ^[a]	8 : 1	27 : 0.93	39 : 1	79 : 0.99	97 : 0.99
Pyridine ^[a]	11 : 0.98	56 : 0.99	67 : 1	79 : 0.98	93 : 1
1-methylimidazole ^[a]	16 : 0.95	25 : 1	62 : 0.99	85 : 0.97	95 : 0.98
[MMIM][MeOSO ₃] ^[a]	4 : 0.65	35 : 0.93	46 : 0.90	87 : 0.95	98 : 0.88
[MMIM][NTf ₂] ^[a]	~0	~0	~0	~0	~0
[MeP _{sec} -Bu ₃][MeOSO ₃] ^[a]	~0	~0	~0	~0	~0
[a]: Reactions were carried out at 130 °C					

Table 3. Conversion of 1-octene versus the mol fraction of converted 1-octene to octane, over the range of conversion points with the differently modified copper catalysts.

Coating	% conversion : selectivity to octane (mol fraction)				
uncoated	6 : 0.62	15 : 1.67	25 : 0.67	53 : 0.69	86 : 0.72
Pyridine	17 : 0.78	27 : 0.77	54 : 0.72	70 : 0.74	85 : 0.73
1-methylimidazole	15 : 0.76	25 : 0.76	37 : 0.74	57 : 0.69	74 : 0.72
[MMIM][MeOSO ₃]	~0	~0	~0	~0	~0
[MMIM][NTf ₂]	~0	~0	~0	~0	~0
[MeP _{sec} -Bu ₃][MeOSO ₃]	~0	~0	~0	~0	~0

In general, the catalysts exhibit remarkable selectivity to octanol formation which is consistent over almost all the iso-conversion points. However, there is a slight decrease in the average selectivity with the [MMIM][MeOSO₃] modified catalyst at higher conversions. These data further confirm the applicability of group 11 catalysts with regards to carbonyl bond hydrogenation, and that an ionic liquid modified copper catalyst may provide a cheaper alternative to silver based catalysts.

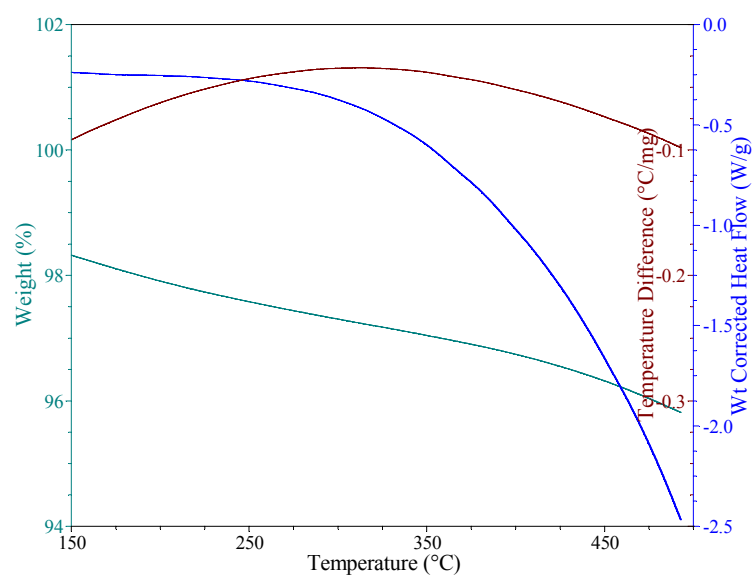
With regards to the selectivity towards octane, the uncoated copper catalyst exhibits a slight increase in selectivity with increasing conversion, which may be attributable to an increase in the relative contribution of the hydrogenation of octene isomers.

Unexpectedly, the modification by both pyridine and 1-methylimidazole resulted in an increase in selectivity to octane formation compared to the uncoated catalyst. However, it is associated with a slight trend of decreasing selectivity with increasing conversion. This increase in selectivity with modification is in contrast to results we have obtained with an analogous palladium on alumina catalyst, where the modification by pyridine and 1-methylimidazole resulted in a decrease in the selectivity to octane. An understanding of the reasons behind these observed trends is difficult without a detailed isotopic mechanistic study, but it might be possible that the organic modifiers interfere with the rate determining step of the reaction, which is perhaps different between palladium and copper.^[12]

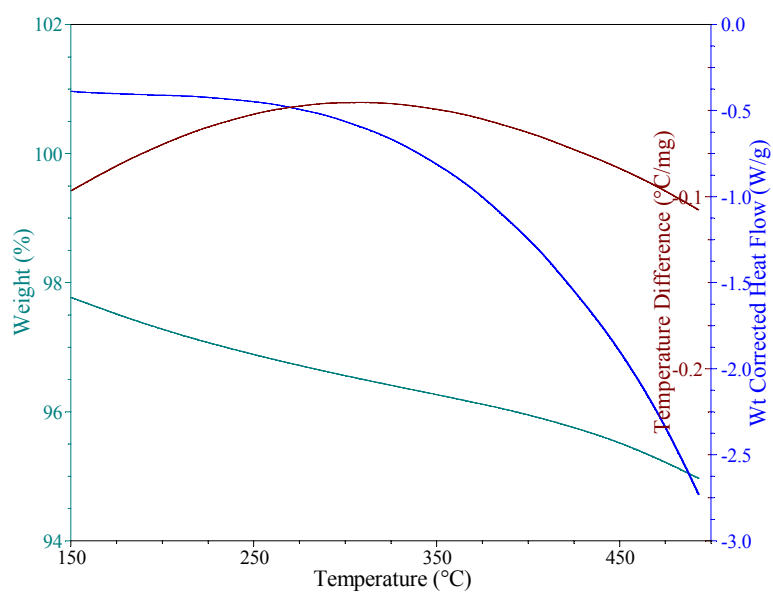
5.3.2 Catalyst characterisation

Due to the differences observed in the competitive hydrogenation between 1-octene and octanal with the different copper catalysts, a series of surface investigations were conducted to assist in the elucidation of potential reasons for the differences. These included BET surface area analysis of the used and freshly prepared catalyst, diffuse reflectance infrared transmittance spectroscopy (DRIFTS), inductively coupled plasma optical emission spectroscopy (ICP-OES), thermal gravimetric analysis with differential scanning calorimetry (TGA-DSC) and high resolution transmission electron microscopy (HRTEM) of the used catalysts.

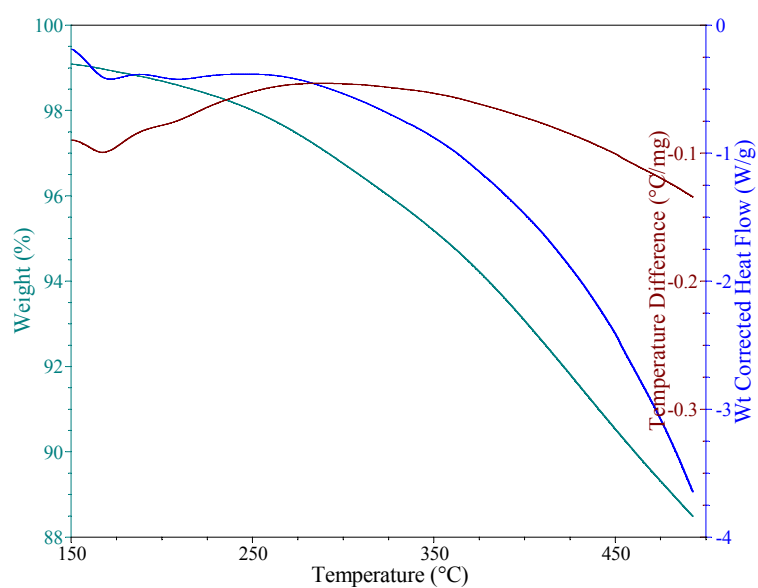
The BET surface area results are shown in Table 4. The uncoated and pyridine coated catalysts exhibit a loss of surface area, pore volume and pore width from the freshly prepared to the used catalysts. As pyridine has a low boiling point and would most likely be removed during the analysis and reaction conditions, the reduction in surface area is likely due to strongly adsorbed reaction products binding on the catalyst and support surfaces, which would decrease the measurable surface area. The ionic liquid and 1-methylimidazole modified catalysts all exhibit an increase in surface area and pore volume from the freshly prepared to the used catalysts. The boiling points of the ionic liquids and 1-methylimidazole are relatively high. They would likely survive the analysis conditions, causing a decrease in the measurable surface area. An increase in surface area would therefore be an indication that the coating has been removed during the course of the reaction. Interestingly, the pore width of these catalysts increases from the freshly prepared to the used entities. Unfortunately, the general trends of these data do not reflect the trends of the catalysis results. However, to further investigate the surface matrix of the used catalysts, ICP-OES, DRIFTS, and TGA-DSC techniques were applied. These data are shown in Table 4 and Figure 4.



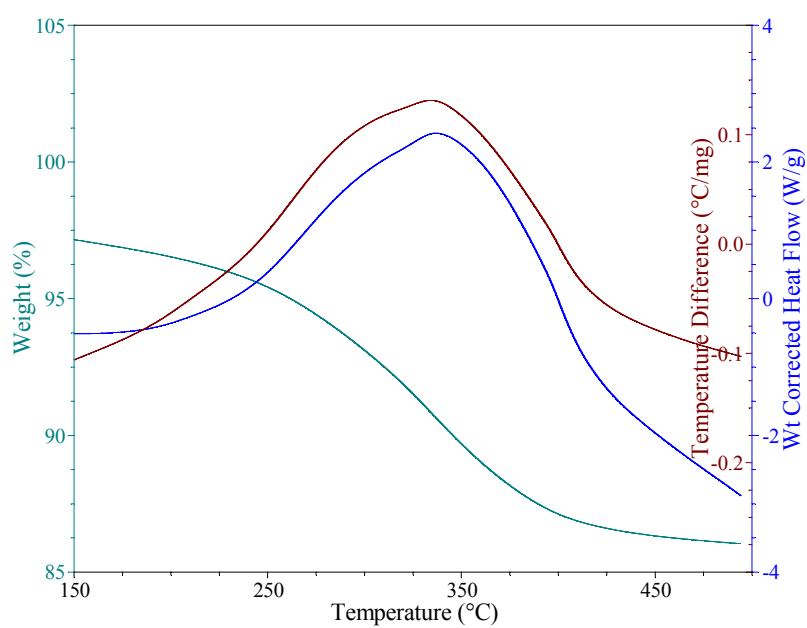
4a. DSC-TGA analysis of the used unmodified copper catalyst



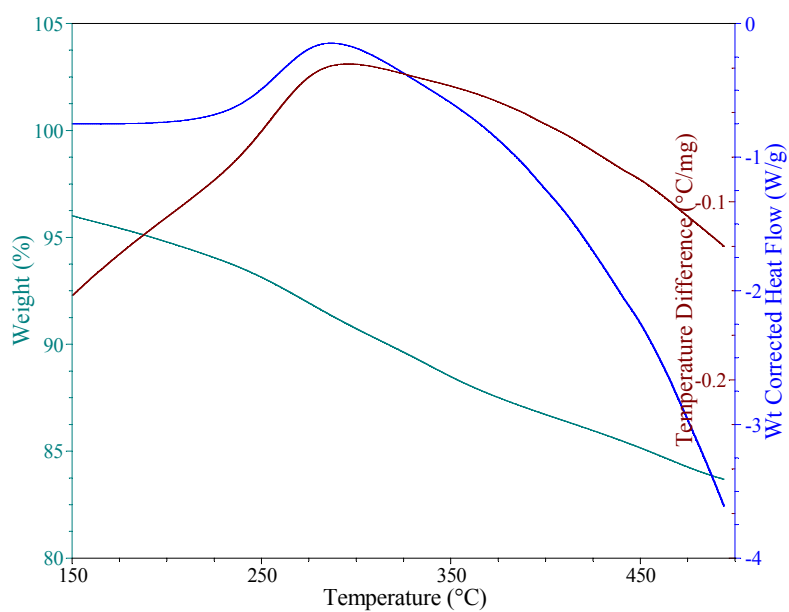
4b. DSC-TGA analysis of the used pyridine modified copper catalyst



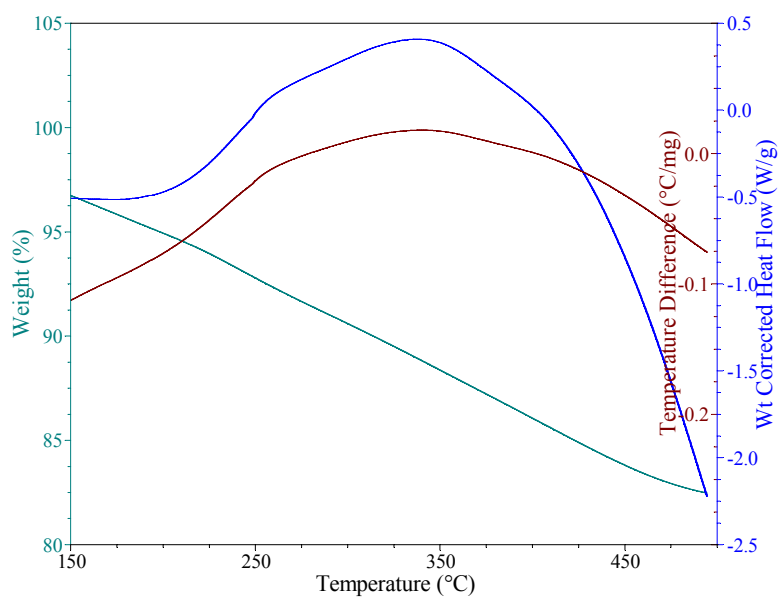
4c. DSC-TGA analysis of the used 1-methylimidazole modified copper catalyst



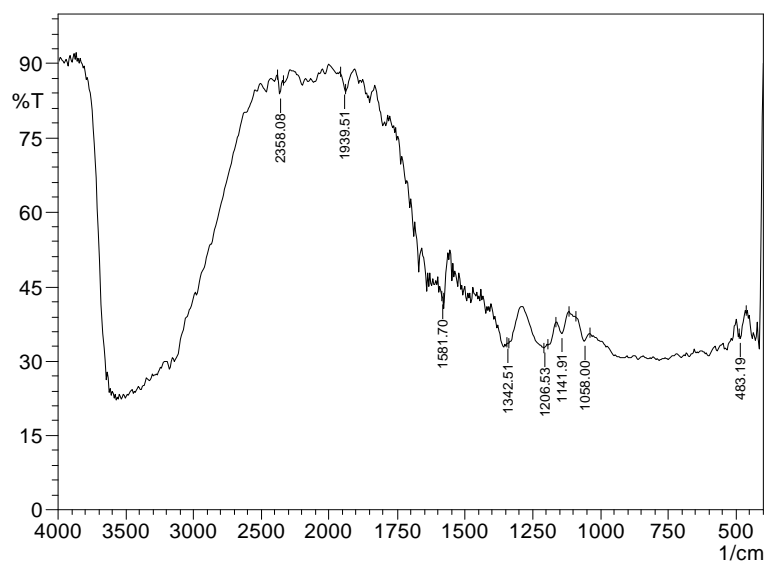
4d. DSC-TGA analysis of the used [MMIM][MeOSO₃] modified copper catalyst



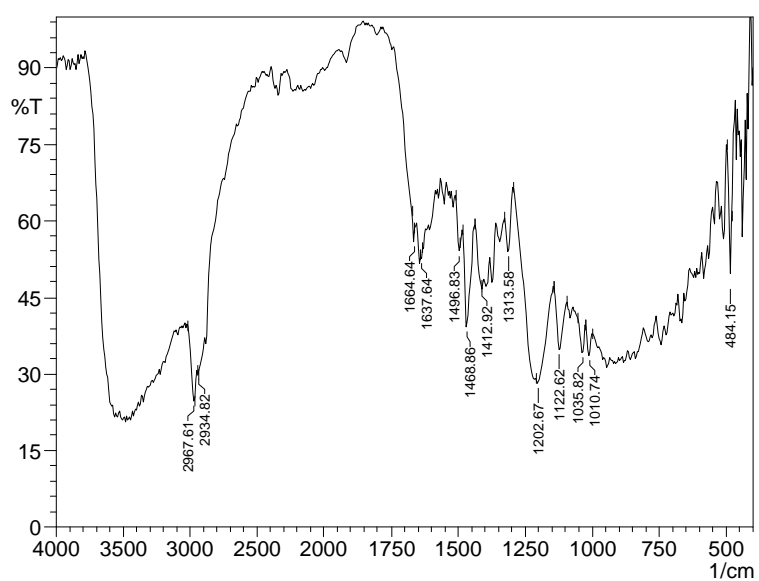
4e. DSC-TGA analysis of the used [MMIM][NTf₂] modified copper catalyst



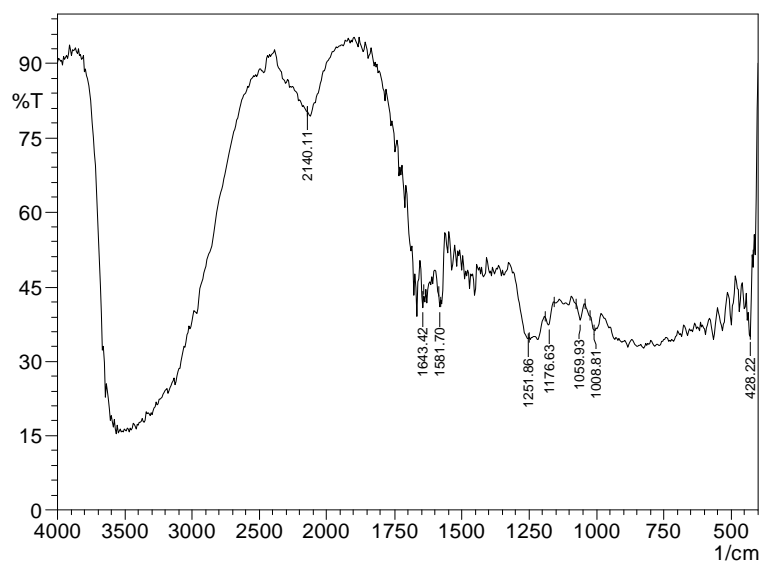
4f. TSC-TGA analysis of the used [MeP-*sec*Bu₃][MeOSO₃] modified copper catalyst



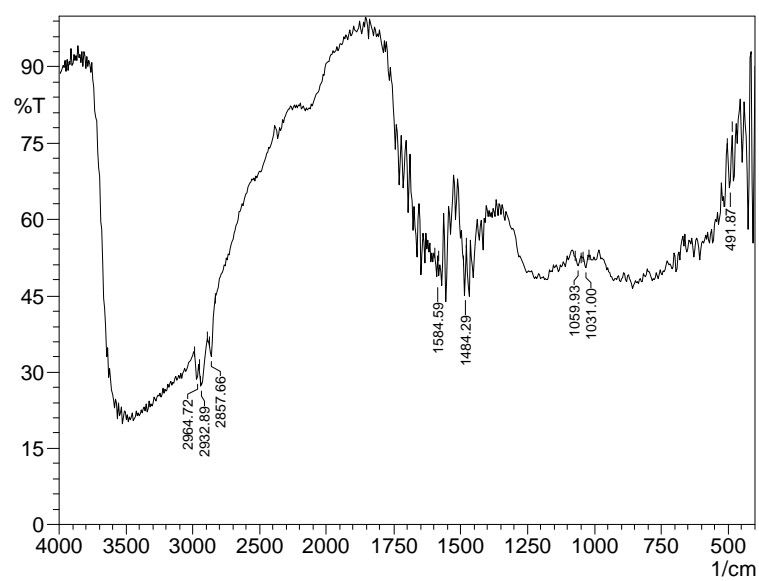
4g. DRIFTS analysis of the freshly prepared [MMIM][MeOSO₃] modified copper catalyst



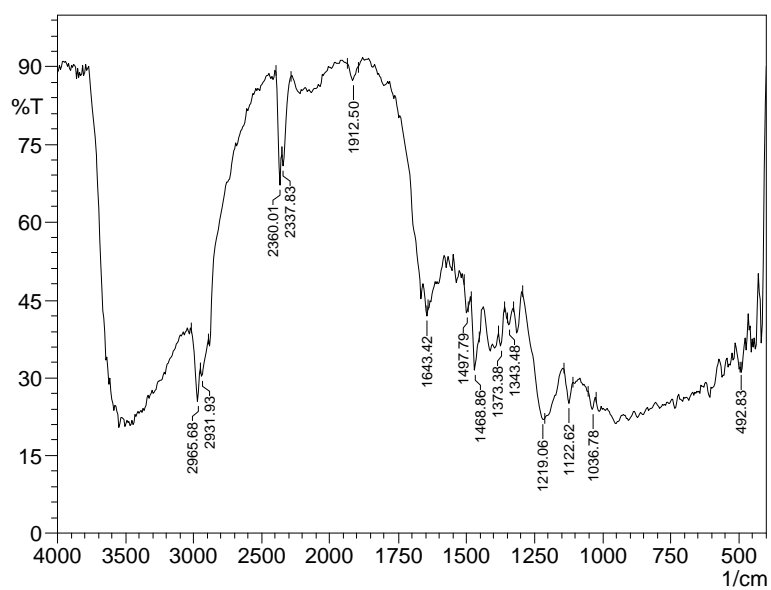
4h. DRIFTS analysis of the used [MMIM][MeOSO₃] modified copper catalyst



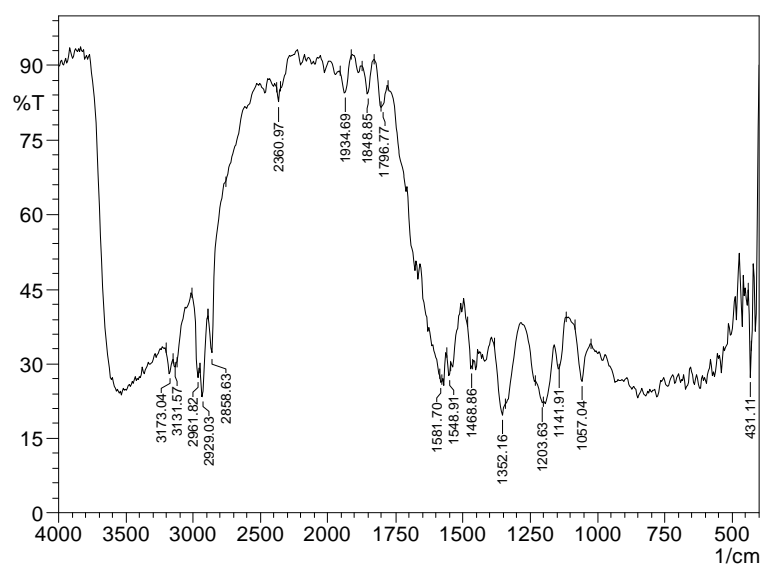
4i. DRIFTS analysis of the freshly prepared [MMIM][NTf₂] modified copper catalyst



4j. DRIFTS analysis of the used [MMIM][NTf₂] modified copper catalyst



4k. DRIFTS analysis of the freshly prepared [MeP-secBu₃][MeOSO₃] modified copper catalyst



4l. DRIFTS analysis of the used [MeP-secBu₃][MeOSO₃] modified copper catalyst

Figure 4a-i. DSC-TGA analysis of the different used copper catalysts and DRIFTS spectra of the freshly prepared and used ionic liquid modified copper catalysts.

Table 4. BET surface area, pore volume, pore width and sulphur content analysis of the freshly prepared and used copper catalysts.

Coating	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore width (Å)	S content (weight %)
Uncoated fresh	165	0.51	123	-
Uncoated used	157	0.42	108	-
Pyridine fresh	172	0.48	112	-
Pyridine used	156	0.42	107	-
1-methylimidazole fresh	61	0.23	149	-
1-methylimidazole used	141	0.42	120	-
[MMIM][MeOSO ₃] fresh	63	0.24	143	3.6
[MMIM][MeOSO ₃] used	114	0.33	115	3.4
[MMIM][NTf ₂] fresh	33	0.14	171	7.4
[MMIM][NTf ₂] used	97	0.30	123	0.34
[MePsec-Bu ₃][MeOSO ₃] fresh	61	0.23	148	3.7
[MePsec-Bu ₃][MeOSO ₃] used	96	0.30	123	3.4

The sulphur content data from Table 4 reveal that there is a noticeable loss of sulphur between the freshly prepared and used [MMIM][NTf₂] ionic liquid modified catalyst, while both the [MMIM][MeOSO₃] and [MePsec-Bu₃][MeOSO₃] ionic liquid modified catalysts seem to retain their contents. This observation is, in general, similar to results we have obtained in previous studies with a 5% palladium on alumina catalyst.

The DRIFTS spectra for the used [MMIM][MeOSO₃] modified copper catalyst (Figure 4g) qualitatively identifies sulphate stretching frequencies in the region of 1000 cm⁻¹ for both the freshly prepared and used catalysts, while the DSC-TGA data for the used catalyst (Figure 4d) reveals an exothermic peak and associated weight loss typical of the decomposition of ionic liquids. These data suggest that the ionic liquid [MMIM][MeOSO₃] has survived the reaction conditions and remains intact as a layer on the catalyst surface.

The DSC-TGA data for the used [MMIM][NTf₂] modified copper catalyst (Figure 4e) reveals a slight exothermal peak with associated weight loss in the region of 275 °C, while the DRIFTS spectra still qualitatively reveals the presence of sulphate groups. These data in combination with the ICP-OES sulphur content analysis appear to confirm the loss of ionic liquid and that the ionic liquid does not survive the reaction conditions.

The DRIFTS spectra for the used [MeP_{sec}-Bu₃][MeOSO₃] modified copper catalyst also reveals the presence of sulphate groups. However, the DSC-TGA data (Figure 4f) discloses a broad exothermal peak (reaching a maximum at approximately 350 °C) with no identifiable characteristic differential weight loss typical of pure organic species decomposition. This suggests that the matrix of organic material present on the catalyst surface is a complex mixture of various organic species.

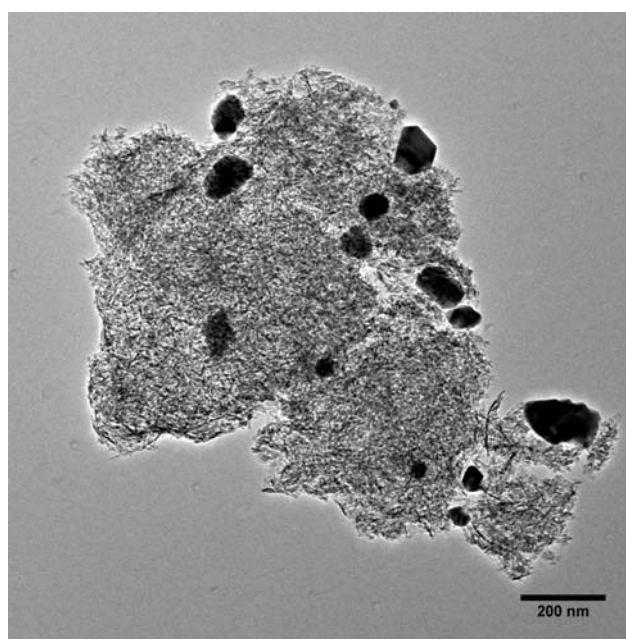
On the other hand, a relatively consistent loss in catalyst mass with a decreasing heat flow in DSC-TGA analysis is typical of the loss in adsorbed carbonaceous material. This description is representative of the data obtained for the uncoated, pyridine and 1-methylimidazole modified catalysts where the carbonaceous material may originate from the modifiers and/or reaction products/media. These data in comparison to the ionic liquid modified catalyst data suggest that the ionic liquids do, in some form, modify the organic matrix present on the catalyst surface which may potentially affect the catalyst performance.

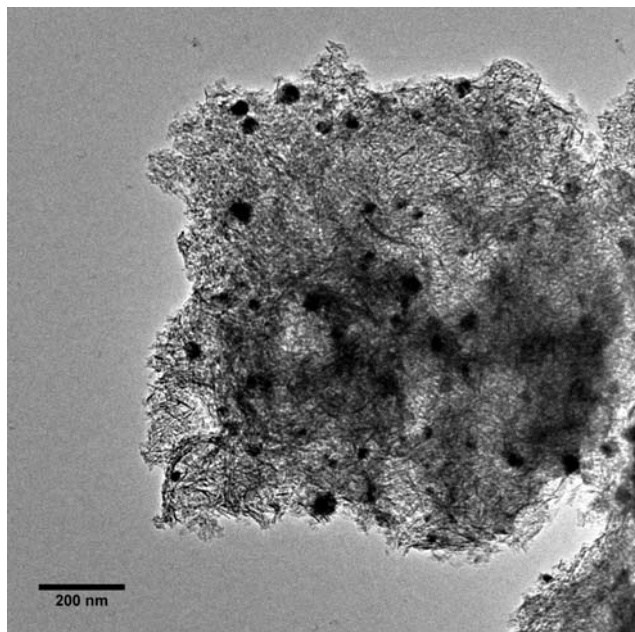
Furthermore, the results obtained from the TGA-DSC, ICP-OES and DRIFTS analysis suggest that there is a variation in these carbonaceous matrixes, which was initially hinted at by the BET surface area, pore volume and pore width analyses. Nonetheless, they do not provide a comprehensive reason as to why the differently coated ionic liquid catalysts would exhibit such dramatic differences in catalytic performance in comparison to the unmodified, pyridine and 1-methylimidazole modified catalysts.

In an effort to further provide potential reasons for these catalytic observations, the average crystallite sizes of the different catalysts were determined by electron microscopy using at least 150 measurements over a minimum of 15 images. The results of this study can be found in Table 5, while examples of some of the images obtained can be seen in Figure 5a-b.

Table 5. Average crystallite sizes of the differently modified copper catalysts.

Coating	uncoated	Pyridine	1-methyl imidazole	[MMIM] [MeOSO ₃]	[MMIM] [NTf ₂]	MeP _{sec} -Bu ₃ [MeOSO ₃]
Crystallite size (nm) ^[a]	11±3 ^[b]	7±3 ^[b]	8±2 ^[b]	34±17 ^[b]	101±39 ^[b]	109±36 ^[b]
[a] Determined by a minimum of 150 measurements over 15 images. [b] Standard deviation						

5a. A typical TEM image of the freshly prepared [MMIM][NTf₂] modified copper catalyst



5b. A typical TEM image of the freshly prepared [MMIM][MeOSO₃] modified copper catalyst

Figure 5a-b. Examples of images obtained for crystallite size analysis of the different copper catalysts. Dark areas represent copper crystallites.

An observation that immediately stands out is the large differences in crystallite size between the uncoated, pyridine and 1-methylimidazole modified catalysts and the ionic liquid modified catalysts. There is a tenfold increase in the average crystallite size between the uncoated and [MeP_{sec}-Bu₃][MeOSO₃] modified catalysts. This would cause an approximate tenfold decrease in the crystallite surface area (61 m²/g to 6 m²/g using a simplified spherical model), which would undoubtedly strongly and adversely affect the relative rates of hydrogenation. This is in addition to any potential decrease in the rates of hydrogenation associated with carbonaceous modification of catalyst surfaces, or site specific interaction by ionic liquids.

The concept that nitrogen containing organic modifiers can alter morphologies and crystallite sizes of catalysts is not uncommon. Indeed, this has been a subject of investigation for palladium catalysts.^[6] However, to the best of our knowledge, this is the first reported observation that ionic liquids used for *in situ* preparation of SCILL catalysts can so dramatically affect the activity of the catalyst potentially by the relative sizes of the metal crystallites.

An interesting observation occurs with the average crystallite size of the [MMIM][MeOSO₃] modified catalyst (34 nm) and the increase in selectivity to octanal conversion over 1-octene conversion (compared to the uncoated, pyridine and 1-methylimidazole modified catalysts). The average crystallite size for this modified catalyst is greater than the uncoated, pyridine and 1-methylimidazole catalysts, but less than the [MMIM][NTf₂] and [MeP*sec*-Bu₃][MeOSO₃] modified catalysts. It has been shown that an increase in copper crystallite size is associated with an increased selectivity for carbonyl hydrogenation.^[11b] It may therefore be that the increased crystallite size is at least partly responsible for the increased selectivity. This is in addition to any potential effects brought about by the ionic liquid still present on the catalyst (i.e. site specific interaction and carbonaceous modification of the metal crystallite surface). This provides a new and interesting angle of the role of the ionic liquid in SCILL catalysts, whereby the ionic liquid may affect selectivities based on an effect it might have on crystallite size.

5.4 Conclusion

Silver is clearly an effective catalyst for the selective hydrogenation of octanal in the presence of 1-octene. However, with the application of a ionic liquid modified copper SCILL catalyst, a similar outcome may be achieved. This would be highly desirable if the cost of a catalyst is an important consideration. This is in contrast to the catalysts modified by traditional organic modifiers. Although the modifiers were able to alter the activity and reactivity of the hydrogenation of 1-octene and octanal, they were unable to effectively separate out the LHSV overlap in their respective conversion ranges.

However, ionic liquid modification of the copper catalyst has the potential to deactivate both 1-octene and octanal hydrogenation. These observations may be due to a potential influence the ionic liquid has on the average crystallite size, as the ionic liquid modified catalysts all exhibited much larger crystallite sizes compared to the other catalysts. This is in addition to any effects that the ionic liquid may have through site specific interaction and/or carbonaceous modification of the catalyst surface.

BET surface area, pore volume and pore area analysis together with DSC-TGA, DRIFTS and ICP-OES analysis reveal the intricacy in the organic matrix (remaining on the catalyst after reaction) between the different catalysts. With regards to the ionic liquid modified catalysts, the

ionic liquid [MMIM][MeOSO₃] seems to survive the reaction conditions, while the ionic liquids [MMIM][NTf₂] and [MeP_{sec}-Bu₃][MeOSO₃] appear to be (at least partly) decomposed.

These results highlight the complexity of potential factors governing the modification effects by ionic liquids in SCILL catalysts.

5.5 Experimental Section

The ionic liquid [MMIM][MeOSO₃] was prepared by methods already described in literature, by the alkylation of 1-methylimidazole with dimethylsulphate.^[13] Pyridine and 1-methylimidazole were obtained from Sigma-Aldrich, while the [MeP_{sec}-Bu₃][MeOSO₃] ionic liquid was obtained from SASOL R&D. The ionic liquid [MMIM][NTf₂] was synthesised by an anion exchange of [MMIM][MeOSO₃] with [Na][NTf₂]. NMR analysis was used to confirm the purity and identity of the synthesised ionic liquids.

The silver and copper on alumina catalysts (ca. 5% w/w) were prepared by wet impregnation of a crushed gamma alumina support with silver or copper nitrate respectively in water at 80 °C for 4 hours. The resultant paste was dried in an oven at 110 °C for an additional 2 hours before being calcined at 500 °C for 8 hours. The catalyst was then pelletized to a size distribution between 300 and 600 µm. The resultant catalyst was then coated with the following organic modifiers: Pyridine, [MMIM][MeOSO₃], [MMIM][NTf₂], [MeP_{sec}-Bu₃][MeOSO₃] and 1-methylimidazole, to the equivalent molar amount of 25 weight % of [MMIM][MeOSO₃], by dissolving the required amounts of modifier in either methanol or dichloromethane in a pill vial before introducing the parent catalyst. The mixture was allowed to evaporate slowly in a fume hood to obtain a dry powder. The reduced metal catalysts were then generated *in situ* in the reactor (50 bar H₂, 15 ml/min H₂, 250 °C, 4h for Ag 8h for Cu) before commencement of the reaction.

The average Cu crystallite size and crystallite morphology of the organically modified catalysts were determined by the use of a JEOL 2100 HRTEM, counting approximately 300 particles under HAAD and STEM conditions for the crystallite size analysis. ICP-OES (Perkin Elmer Optima DV2100) was used to confirm the weight percent loading of the copper as well as the sulphur content of the freshly prepared and used catalysts. BET and pore size distribution and

width were determined on a Micromeritics TRISTAR 3020 to resolve the extent of change in pore volume, pore width and surface area between the freshly prepared and used organically modified and uncoated catalysts. Chemisorption experiments were performed on a Micromeritics ASAP 2020C using volumetric techniques. DRIFTS spectra were obtained using a Shimadzu IRAffinity-1 FTIR spectrophotometer and TGA-DSC profiles of the used catalysts were obtained using a TA SDT Q600.

Hydrogenation experiments were carried out in a concurrent down flow trickle bed reactor with an inner diameter of 14 mm and a length of 250 mm to give a volume of 38.5 cm³. When required, the catalyst was diluted with carborundum (grit size 24) to maintain a constant catalyst bed volume and served to prevent aniso-thermal conditions with strongly active catalysts (high LHSV's). The grit size is sufficient to prevent a large pressure drop across the reactor tube. The rest of the reactor was packed with carborundum and quartz wool was used as a plug at the ends of the carborundum and the catalyst bed, which serves as an efficient dispersant of the liquid phase.^[14] A 2,5 % (v/v) 1-octene with 2,5% (v/v) octanal mixture in hexane was introduced into the reactor by means of an HPLC pump. The hydrogen was introduced by means of mass flow controllers at a constant substrate to hydrogen ratio of 1:2. The feed was dried with molecular sieves^[15] and degassed with argon^[16] to eliminate water and oxygen from the system. An argon feed was supplied to the head space of the feed bottle to give a slight positive pressure. The temperature and pressure of the reaction system was kept at 50 bar and 130 °C by a temperature controlled heating jacket with an internal sliding thermocouple. The gas hourly space velocity (GHSV) and liquid hourly space velocity (LHSV) were concurrently adjusted to produce the different iso-conversion of 1-octene and octanal for each of the differently modified catalysts. The product composition was analysed off line by means of a GC-FID (Perkin Elmer Clarus 500).

5.6 References

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CHAPTER 6

SUMMARY

6.1 Ionic liquids as catalyst modifiers

Selective transformation of specific molecules in competitive modes remains a challenging problem in the commodity chemicals industry. The main body of research into this problem will not only reside in removing poisons and increasing the ease of purification, but also in the potential of transforming undesirable molecules into value added commodity chemicals. Undoubtedly, research into catalysts able to bring this about will focus on the development of new heterogeneous catalysts and modifications of existing ones. Within modification research, both inorganic and organic modifiers seem to be effective in altering the reaction performances of traditional heterogeneous catalysts.^[1]

Traditional organic modifiers have generally encompassed (but have not been restricted to) nitrogen containing organic compounds such as quinoline, cinchonidine, ethylene diamine, pyridine and pyrrole derivatives.^[1] The mechanisms of their modification effects range from electronic modification and active site restructuring to steric influences on the catalyst surface.^[1] Although organic modifiers have been the subject of much research, only recently (2007) has a new class come to be the focus of research, the solid catalyst with an ionic liquid layer or SCILL catalyst.^[2] This new class of organic modifier brings, in addition to the mechanisms inherent in traditional organic modifiers, further potential reasons for the effects of modification. These include (but may not be restricted to) surface diffusion and concentration effects on the reactants, site specific interaction by the anion or cation or both with catalyst sites, site specific modification by fragments of decomposition products, dramatic crystallite size modification and variation of these effects based on the elemental metal used for the catalyst.^[3-5]

Although the rate of diffusion through the ionic liquid has been ruled out as a mechanism by which ionic liquids are able to alter the selectivity of a reaction (considered to be faster than the

rate determining step),^[2] this may be a premature conclusion. The reasons for this are based on the following:

- The experimental investigations into the rates of diffusion of hydrocarbons in ionic liquids related to SCILL catalysis have been based on the rate of diffusion according to Fick's law in 1 dimension ($J = -D(\delta\phi/\delta x)$, J = diffusion flux, D = diffusion coefficient, ϕ = concentration, x = distance) for a maximum concentration gradient ($\delta\phi$) which may not necessarily be the case in the reaction environment.
- Ionic liquids have been shown to have site specific interactions on metal crystallites and if the site of interaction coincides with the site of the substrate adsorption then a competitive environment potentially exists.
- If a competitive environment does indeed exist between an ionic liquid component and the substrate intended for reaction, then, depending on adsorption/desorption kinetics, the relative concentrations between the ionic liquid and reactant affects the adsorption coverage of these molecules on the metal crystallite site.
- If such a case existed in a reaction with a SCILL catalyst, then the concentration of the reactant at the catalyst surface cannot be approaching zero as this would allow the site to be effectively blocked by the ionic liquid component. The rates of diffusion through the ionic liquid cannot therefore be based on a maximum concentration gradient. Rather, the rates would be based on a much smaller gradient which reduces the rate of diffusion.

Under such a scenario a situation might arise where the rate of diffusion is the rate determining step of the reaction. Assuming a set concentration gradient, an increase in the ionic liquid layer thickness of a SCILL catalyst would decrease the rate of reaction. If a catalyst has more than one type of site for adsorption/reaction and the ionic liquid interacts with only one type, then in the competitive reaction between two substrates (which differ in their adsorption/reaction site preferences), a relative increase in reaction selectivity for one of the substrates may be achieved with an increase in the ionic layer thickness.

Although several studies need to be conducted into the feasibility of such a scenario (such as gas phase spectroscopic studies into potential site specific competitive adsorption between ionic liquids and molecules intended for reaction), this mechanism of selectivity may in part explain why there was no decrease in the activity of 1-octyne hydrogenation with an increase in the ionic liquid content of the SCILL catalysts, while a decrease was observed in the hydrogenation activity of 1,7-octadiene.

However, some of the results in this study indicated that the ionic liquid layer need not remain as an intact, pure, unadulterated layer to bring about effects on catalyst performance. This was found in the competitive hydrogenation between 1-octene and octanal over copper and palladium SCILL catalysts, where the organic surface matrix was considerably different between the used catalysts. Indeed, a study of surface matrix species of SCILL catalysts under several reaction applications and conditions needs to be conducted to identify key species and any trends in catalyst performance with these species. This may be done by TGA-DSC-MS and other spectroscopic methods.

In a broader sense and due to the infancy of this area of research, a deep mechanistic study on the relative contributions of the possible reasons for selectivity increases with SCILL catalysts needs to be conducted. This may be achieved by methods which involve molecular modelling supported by empirical observations with techniques such as *in situ* XPS/TEM/DRIFTS. Indeed, the need for a mechanistic study has been increased, now that the applicability of ionic liquid modified catalysts in key industrial processes have been demonstrated. These range from increases in the skeletal isomerisation of octane to increases in the selective hydrogenation of alkynes, dienes, aldehydes and alkenes, as well as their successes under continuous flow trickle bed conditions.^[2,3,6] It does seem that the next major challenge in this area of research is to determine a rational (complex structure)-activity relationship over a range of ionic liquids, reaction conditions and reaction types. However, empirical studies will still prove valuable in contributing to and guiding this challenge.

6.2 Nickel SCILL catalysts in the competitive hydrogenation of unsaturated hydrocarbons and the potential mechanism of 1-octyne hydrogenation

From the results of the study into *ex situ* prepared nickel SCILL catalysts, it can be concluded that nickel SCILL catalysts provide an appreciable increase (over the uncoated version) in octene content (of the reaction media) with the competitive hydrogenation of 1-octyne versus 1-octene and 1,7-octadiene versus 1-octene, even under extreme conversion conditions of 1-octyne and 1,7-octadiene and increased time of stream.

However, the presence of the ionic liquid coating was found to adversely affect the activity of both 1-octyne and 1,7-octadiene hydrogenation. This decrease in activity for 1,7-octadiene hydrogenation (as mentioned previously) depended on the amount of ionic liquid present, while a variance in the content of ionic liquid (apart from its presence) had no effect on the hydrogenation activity of 1-octyne. This may be related to site specific interaction by the ionic liquid causing diffusion effects and/or changes in the adsorption abilities of the reactants. In addition to this, the type of ionic liquid used also seems to play a role as ionic liquids not based on the 1,3-dimethylimidazole cation ([MeP*sec*-Bu₃][MeOSO₃] and [Et₃S][NTf₂]) were associated with complete catalytic inactivity. The most likely reason for this is still under investigation; however, poisoning by sulphur and phosphorus is doubtful due to the lack of evidence of sulphur- and phosphorus-metal surface species, which was determined by XPS.

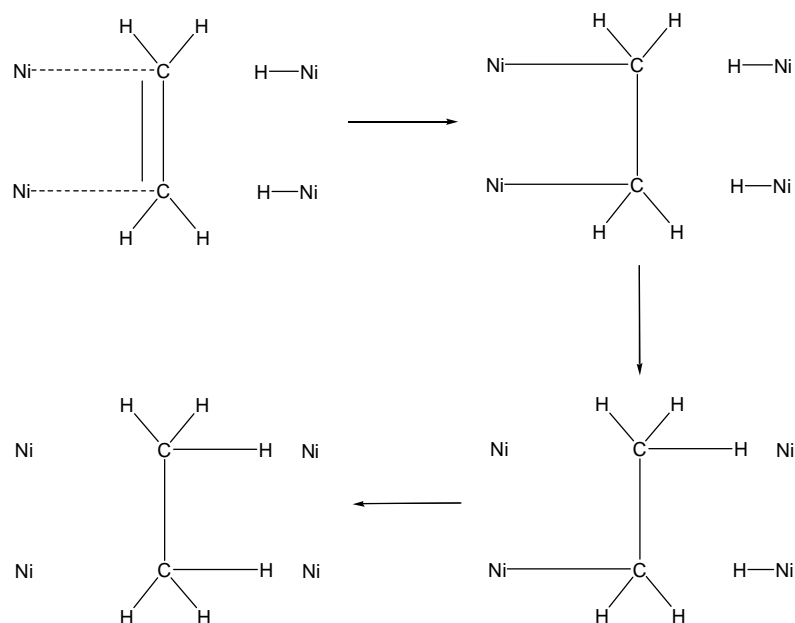
Competitive hydrogenation between 1-octyne and 1-octene with the nickel [MMIM][MeOSO₃] SCILL and uncoated catalyst (over a range of iso-conversion of 1-octyne) reveals that the SCILL catalyst provides an additional advantage; as a strong prevention of octane formation in the beginning stages of time on stream was observed. However, with an extension of time on stream, the uncoated catalyst begins to give a more comparable octene content (in the reaction mixture) as that for the SCILL catalyst.

Interestingly, with the variations in iso-conversion of 1-octyne in both the SCILL and non-SCILL nickel catalyst, it is observed that (after several hours) the octene content generally remains the same while the relative contents of 1-octyne and octane change. This suggests that the general mechanism of the hydrogenation of 1-octyne with the SCILL catalyst may be the same as that for the uncoated nickel catalyst (i.e. the modification by ionic liquids may have no effect on mechanistic action). Although a detailed mechanistic study with *in situ* spectroscopy

techniques and isotopic methods would be required for confirmation, it is plausible that the addition of hydrogen occurs via a multi step sequential action, with the formation of an octene intermediate which may dissociate. This is supported by the fact that the octene content (of the reaction mixture) for all reactions after several hours was greater than 50 %. This possibility of dissociation would also cause a ratio between the amounts of octene and octane formation from the site responsible for 1-octyne hydrogenation. Indeed the hydrogenation of 1-octyne only on a SCILL catalyst (at ca 70% conversion of 1-octyne) produced an almost equimolar mixture of octene to octane (4:3). Furthermore, the concept of a formation ratio between octene and octane (from a site responsible from 1-octyne hydrogenation), is supported by the fact that the equivalent reaction conditions applied to the hydrogenation of 1-octene only resulted in a higher octene to octane ratio (17:3). These results also suggest that 1-octyne binds to, and is hydrogenated by, the nickel catalyst more readily than 1-octene.

These results also support an assumption that the origin of octane in the competitive hydrogenation between a mixture of 1-octyne and 1-octene occurs primarily through a continuous multi step sequential hydrogenation of 1-octyne to octane. Any changes in the ratio of octene to octane may therefore be specific to factors affecting this multi step sequential hydrogenation of 1-octyne. To support this reasoning, an isotopic study on these catalysts with ^2H or ^{13}C labelled reactants may prove to be beneficial, where the relative amounts of deuterium or ^{13}C in octene and octane can be determined by GC-HRMS. Additional empirical studies which may provide evidence for this mechanism include variations in the absolute and relative concentrations of 1-octyne and octene as well as hydrogen pressure and reaction temperature; as these factors have the potential to alter complex equilibria of species and their associated kinetics.

However, the assumptions made on the mechanism of 1-octyne hydrogenation in this study are based on the well-known Horiuti-Polanyi model,^[7] which has been used in the interpretation of results in the hydrogenation of many unsaturated hydrocarbons and seems to be the dominant mechanism of hydrogenation.^[8-12] It is therefore unlikely that the hydrogenation of 1-octyne and 1-octene will be different. To expand on the general steps of this mechanism, the Horiuti-Polanyi model described for ethylene hydrogenation over nickel is given in Scheme 6-1 and begins with the dissociative adsorption of hydrogen to form nickel hydride.^[7] Ethylene adsorbs onto the nickel surface which undergoes a bond transformation to form nickel carbon species. The nickel hydride then sequentially bonds to the nickel carbon species, breaking the nickel carbon bonds to form ethane.



Scheme 1. The proposed mechanism of ethylene hydrogenation over nickel.

One of the main factors in this model is the dissociative adsorption of hydrogen molecules to form nickel hydride species. A non dissociative adsorption would cause a mechanism different from that shown in Scheme 6-1. However, recent density functional theory (DFT) calculations on the dissociation of hydrogen on nickel in the hydrogenation of propyne shows that the activation energy required for the dissociation step is quite low and the overall reaction is quite exothermic.^[13] These results support the assumption that hydrogen dissociatively adsorbs on nickel crystallites. Interestingly, the same study found that there is a strong thermodynamic drive for the adsorption of propyne over propene, with propene adsorption having almost no thermodynamic gain. This finding, through functional group association, supports the possibility of octene desorption discussed in the hydrogenation of 1-octyne. Furthermore, the authors of the study also found that nickel is strongly prone to over hydrogenate an alkyne to an alkane.^[13]

Assuming the same factors exist for 1-octyne and 1-octene hydrogenation as they do for propyne and propene hydrogenation, this interpretation explains why 1-octyne is preferentially hydrogenated in the presence of 1-octene to form more octene as well as octane. With regards to the increase in octane formation with an increase in 1-octyne conversion, an increase in the local concentration of octene near the catalyst surface (as a result of dissociation after 1-octyne

hydrogenation, or intentional addition of octene) would decrease the rate of octene dissociation. This in turn would increase the extent of over hydrogenation to octane. The reasons for this would be in part due to the slight thermodynamic gain in octene adsorption, and that species concentrations affect the kinetics of adsorption and desorption at a particular site. Indeed, it is known that simple Langmuir-Hinshelwood kinetic models (where all elementary reactions are assumed to be much faster than the rate determining step) do fail and the kinetics of adsorption and desorption of reaction species needs to be considered.^[14]

6.3 SCILL catalyst preparation with associated problems and the competitive hydrogenation between 1-octene and octanal over modified palladium and copper catalysts

The *ex situ* preparation of SCILL catalysts can be problematic, especially with metals that are prone to oxidation and are difficult to reduce under mild conditions. Indeed, the differences in the reduced nickel catalyst preparation exemplifies this, as the method of preparation which resulted in numerous crystallite defects was associated with increased levels of crystallite oxidation and reaction inactivity. Indeed, a detailed study involving *in situ* TEM/XPS monitoring of the metal crystallite formation, *in situ* TEM/XPS monitoring of the reaction between oxygen and the metal crystallites and molecular modelling (including the influence of ionic liquids) should be conducted to provide strong evidence for a complex structure - activity relationship. This is particularly important as a study on the influence and extent of oxidation over time on reduced metal crystallites for SCILL catalysts (with various metals and metal crystallite morphologies) will reveal the practical limitations of *ex situ* prepared SCILL catalysts. Furthermore, it would also provide a comparative study for *in situ* prepared SCILL catalysts.

The *in situ* preparation of SCILL and non-SCILL catalysts circumvents the problem of crystallite oxidation with exposure to the atmosphere. This method of preparation was applied to the formation of SCILL and non SCILL palladium and copper catalysts in the competitive hydrogenation between 1-octene and octanal. As with *ex situ* prepared SCILL catalysts, the different ionic liquids used in these investigations had varying effects on catalyst performance, including both the intrinsic activity and reactivity of hydrogenation of 1-octene and octanal.

However, regarding the copper catalysts, complete inactivity was observed with some of the ionic liquid modified versions.

In addition to ionic liquid modified catalysts, catalysts modified by traditional nitrogen containing organic compounds were applied in the competitive hydrogenation between 1-octene and octanal. The comparative results reveal that the effects of ionic liquids on catalyst performance are far greater than that for traditional organic modifiers. For example, the [MMIM][MeOSO₃] modified copper catalyst strongly increased the preference for octanal hydrogenation over 1-octene which was not achieved with the traditionally modified catalysts.

The assumption that ionic liquids may induce greater modification effects is further supported by the greater increase in isomerised octene content (associated with the conversion of 1-octene in the competitive hydrogenation between 1-octene and octanal over palladium) with ionic liquid modified palladium catalysts in comparison to the traditionally modified catalysts. This increase in isomerised octene indicates that the rate of hydrogen addition to 1-octene is depreciated to a greater extent than the overall rate of 1-octene adsorption, isomerisation and desorption. A decrease in the rate of hydrogen addition may well be the result of a decreased hydrogen surface concentration relative to 1-octene, as hydrogen is known to have low solubilities in ionic liquids.

However, as mentioned previously, DSC-TGA, ICP-OES, and DRIFTS analysis revealed that the ionic liquid does not necessarily have to remain as an intact layer for modification effects to occur, and that the matrix of organic surface species on the catalyst can vary quite dramatically between different SCILL catalysts. The destruction of the ionic liquid layer is especially pertinent for SCILL catalysts prepared by *in situ* methods, where the temperature required for the formation of active metal crystallites (in addition to the temperature of the reaction) is relatively close to or higher than the decomposition temperature of the ionic liquid.

Nevertheless, hydrogen chemisorption studies with the palladium catalysts revealed a decrease in the amount of chemisorbed hydrogen (in comparison to the uncoated catalyst) with all the ionic liquid modified catalysts, regardless if their ionic liquid layers had remained intact or not. Interestingly, the chemisorption studies with these palladium catalysts also revealed a relationship between catalyst performance and the chemisorption properties of the catalyst, when used in conjunction with TEM techniques. It appears that the ratios of average crystallite size (obtained from chemisorption methods with various gasses and compared to TEM

techniques), follows a pattern similar to the changes in the intrinsic activity of 1-octene and octanal hydrogenation brought about by the differently modified catalysts. The large values in the crystallite size ratio of ionic liquid modified catalysts (compared to the traditional modifiers) provides additional evidence towards the concept of strong modification effects by ionic liquids, and may be useful for predicting the performance of numerous SCILL catalysts. Indeed, a study on the chemisorption properties of SCILL catalysts (in relation to TEM techniques) may well provide an easy contributory method for the creation of a (complex structure)-activity relationship database.

Nonetheless, TEM analysis alone on both the copper and palladium catalysts presented an interesting observation with regards to their average crystallite size, as there was a variance in the average crystallite size of the differently modified catalysts. Although this variance was not dramatic for the palladium catalysts, it was noticeable and is in agreement with literature reports that nitrogen based organic modifiers affect palladium crystallite sizes.^[1] In contrast to the palladium crystallites, the effect on the copper crystallites was remarkable. This is revealed by the fact that there was a variance of a few nanometres for the palladium catalysts, while there was a variance of tens or even hundreds of nanometres with the copper catalysts (particularly observed with the ionic liquid modified versions). Although elucidating the mechanism (which brings about these large differences) would be a study on its own, it is possible that the ionic liquid may increase the ease of crystallite sintering. This could potentially occur by a reduction in the strength of the crystallite to support bond (mainly through metal-oxide bonds) brought about by the ionic nature of the ionic liquid. It is well known that copper has an affinity towards oxygen in oxygen containing organic compounds. For example, the hydrogenation of furfural to furfuryl alcohol over copper is believed to occur via a sequential addition of hydrogen to a perpendicularly bonded η^1 (O)-aldehyde species.^[15] Although the following is quite speculative, it might be possible that the oxygen containing anion of the ionic liquids complex with the copper crystallites to form a type of micelle with "solubilising" properties. The crystallite to support bond would be relatively weakened (with a slightly "solubilised" crystallite) increasing its ease of mobility on the support surface. This ease of mobility would lead to amplification in the level of sintered crystallites, thereby increasing the average crystallite size.

Anecdotal evidence for copper having an affinity for oxygen in oxygen containing organic compounds comes from the fact that copper was observed to have a preference towards octanal hydrogenation over 1-octene, while palladium had a preference for 1-octene hydrogenation over octanal. Furthermore, with palladium, there is no overlap in the LHSV's required to convert 1-

octene and octanal, which existed with the copper catalysts. This suggests that octanal strongly competes against 1-octene for active copper catalyst sites and that only after a sizable amount of octanal has been removed, does the 1-octene begin to hydrogenate. Indeed, DFT studies on crotonaldehyde and acrolein on Cu (111) suggest that both the C=O and C=C groups can bind to the metal surface, but with increasing chain length the preference is for C=O adsorption.^[16] Furthermore, with the modification of the copper surface by sulphur, the bonding/adsorption mode of crotonaldehyde becomes more like that for furfural due to steric interactions.^[16] In the case of acrolein hydrogenation over Ag (111), even an increase in hydrogen coverage (as a result of increased hydrogen pressure) causes the molecular adsorption to be preferentially through C=O.^[17] This is in contrast to palladium (111) where the adsorption preference of unsaturated aldehydes increases towards C=C adsorption with increasing chain length and steric bulk.^[18] These studies provide a potential reason and mechanism (through functional group association) for the hydrogenation trends of 1-octene and octanal observed for the uncoated palladium and copper catalysts, whereby the different adsorption preferences of the metals for C=O and C=C dictate which molecule is hydrogenated first through the sequential addition of hydrogen. Indeed, perhaps one of the methods by which the ionic liquid may increase the selectivity of hydrogenation is through a steric influence by its interaction with the metal crystallite, increasing the inherent adsorption preference that a metal has for a particular functional group. This would be in addition to any of the other reasons by which the ionic liquid may affect selectivity, such as alterations to the average crystallite size. However, vapour phase coating of the metal catalyst with an ionic liquid (to produce an extremely thin layer) followed by a subsequent introduction of the reactants, all monitored by *in situ* spectroscopy such as near edge X-ray absorption fine structure or NEXAFS, will be required to provide evidence for a steric based mechanism of selectivity increases.

Regardless of the method by which ionic liquids increase selectivity, the ionic liquid modified catalysts showed strong alterations to the intrinsic reactivity and activity of hydrogenation (both 1-octene and octanal) over copper and palladium in comparison to the uncoated catalyst, which were far greater than that brought about by the traditional modifiers. As mentioned previously, the overlap in the LHSV's required for 1-octene and octanal conversion over the uncoated copper catalyst, was effectively separated out by the application of a copper [MMIM][MeOSO₃] SCILL catalyst (inhibiting the hydrogenation of 1-octene), which was not achieved by the traditional modifiers. Comparable results to the selective [MMIM][MeOSO₃] copper SCILL catalyst may be obtained with an uncoated silver catalyst. However, the copper SCILL catalyst may prove to be more economically viable in an industrial setting due to the lower cost of the

metal. Prolonged time on stream studies need to be conducted first to ascertain the relative extents of deactivation between these catalysts before the financial viability can be confidently determined. Unfortunately, the other ionic liquid modified copper catalysts were completely inactive. Although several reasons may exist for this, the average crystallite size for these inactive catalysts were very large compared to the active catalysts. This suggests that the available crystallite surface area (per mass of copper) had reduced to a level which results in the relative inactivity. Interestingly, the selective [MMIM][MeOSO₃] copper SCILL catalyst had an intermediate average crystallite size compared to the other ionic liquid modified catalysts and those modified by traditional organic modifiers. In addition to contributing to a reduction in intrinsic activity, this may have also contributed to the increased selectivity, as larger copper crystallites are associated with increased selectivity in hydrogenation reactions.^[19]

These results seem typical of the tendency that may be occurring with ionic liquid modifiers in comparison to traditional organic modifiers, namely a larger and stronger modification effect. It would therefore be interesting to see the result of a chemisorption study on the copper SCILL catalysts. However, due to the complexity and difficulty of chemisorption studies with copper, it may not prove to be as useful a study as that on palladium based catalysts. An appealing and less arduous investigation, which may further reveal a stronger modification effect by ionic liquids, is the application of an ionic liquid version of cinchonidine in a system that requires the continuous addition of cinchonidine to maintain high enantiomeric excesses.

6.5 The future of SCILL catalysis research

Ultimately, the results from this study and others show (in addition to the applicability of SCILL catalysis) that the scope of application and research into SCILL catalysis is much larger than previously anticipated, with more questions arising with each investigation. No single study can hope to encompass the breadth of all the questions that now exist. Rather, research into SCILL catalysis appears to be best suited for research teams and collaborations. Where in-depth characterisation studies and volumous screening can be quickly conducted. Undoubtedly though, it seems that SCILL catalysis will continue to be the subject of much interesting research in the foreseeable future.

6.4 References

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CHAPTER 7

CONCLUSION

From the results of this study, the following conclusions may be drawn:

- With the use of a SCILL nickel catalyst in the hydrogenation of a 1-octene/1-octyne mixture, substantial increases in the octene content can be attained even at high conversions of 1-octyne.
- The addition of the ionic liquid has a dramatic effect on the hydrogenation of 1-octyne versus 1-octene over a range of iso-conversion conditions.
- The enhanced octene content can be ascribed to site specific interactions on one hand and, in addition to solubility differences, potential surface diffusion effects on the other which can also influence activity.
- The MMIM cation is likely to be partially blocking the sites specific for 1-octene and 1,7-octadiene hydrogenation on a nickel catalyst and not 1-octyne hydrogenation.
- The hydrogenation of 1-octyne to octane can occur directly and is not the result of any influence by the ionic liquid. The influence that the ionic liquid appears to exert is an immediate modification effect on the catalyst similar to the modification effects caused by carbon deposition by alkynes over time, and a slight overall decrease in activity.
- The preparation of nickel SCILL catalysts needs care, both in the synthesis of the virgin catalyst and in the coating procedure. In particular, attention must be given to ensure the formation of catalyst crystallites with uniform atomic close packing.
- Ionic liquid modified catalysts have dramatic and specific effects and indicate that they have a place alongside traditional organic modifiers.

- DRIFTS, TGA-DSC and ICP-OES analyses of the palladium catalysts reveal that a relatively thick ionic liquid layer can survive the reaction conditions. However, this is not a universal rule and ionic liquid decomposition or removal can indeed occur. The decomposition of the ionic liquid can potentially lead to a very different matrix of surface modification, depending on the ionic liquid used.
- *In situ* preparation of the catalysts with different organic modifiers can have an effect on the formation size of the palladium crystallites.
- Chemisorption techniques, of the palladium catalysts, coupled with STEM analysis can reveal the size of the crystallites and potentially give a general method for the anticipation of catalytic results.
- Silver is clearly an effective catalyst for the selective hydrogenation of octanal in the presence of 1-octene. However, the application of an ionic liquid modified copper SCILL catalyst can produce a similar effect.
- BET surface area, pore volume and pore area analysis together with DSC-TGA, DRIFTS and ICP-OES analysis of the copper catalysts reveals the intricacy in the organic matrix remaining on the catalysts after reaction. They confirm that the ionic liquid [MMIM][MeOSO₃] seems to survive the reaction conditions with the competitive hydrogenation between 1-octene and octanal, while the ionic liquids [MMIM][NTf₂] and [MeP^{sec}-Bu₃][MeOSO₃] appear to be (at least partly) decomposed.
- Ionic liquid modification of copper catalysts has the potential to deactivate both 1-octene and octanal hydrogenation. These observations may be due to a potential influence the ionic liquid has on the average crystallite size.

APPENDIX

XPS data




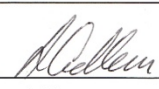
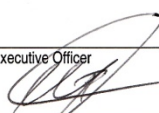
Certificate of Analysis

Private Bag X34, Lynnwood Ridge, Pretoria, 0040
 Calibration office: +27 12 841 4623
 Reception: +27 12 841 4152
 Fax: +27 12 841 4458
 E-mail enquiries: info@nmisa.org
 www.nmisa.org

Analysis of:	The surface composition of catalysts
Description of sample:	Powders
Identification of sample:	P, S
Analysed for:	University of Kwazulu-Natal, Westville
Analysis procedure:	See paragraph 1
Location of analysis:	NMISA, CSIR Campus, Meiring Naude Road, Pretoria, 0184
Date samples received:	09 December 2011
Date/s samples analysed:	09 December 2011

1 PROCEDURE

Scanning X-ray photoelectron spectroscopy (SXPS) consists of irradiating a surface with X-rays in order to extract photo-electrons. Knowing the energy of the X-ray photons and measuring the kinetic energy of the extracted electrons, one can determine the binding energy of the extracted electrons. This quantity is unique and can be used to identify the elements from which the electrons were extracted. The technique can detect all of the elements except hydrogen and helium, as well as compounds, because the binding energy of an element differs from compound to compound. It is primarily a surface technique, as the escape depth of the photo-electrons ranges from 2 to 5 nm. The detection limit of XPS is approximately 0,1at%. Information from subsequent layers beneath the outer surface can be obtained by sputtering the surface with energetic argon ions, while monitoring the binding energy regions of specific elements. The sample(s) was/were analysed as received.

Analysed by  Werner Jordaan Metrologist (Technical Signatory)	Checked by  Loukie Adlem Metrologist	For Chief Executive Officer 
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ANALYSIS OF THE SURFACE COMPOSITION OF CATALYSTS

2 EXPERIMENTAL SETUP

Instrument Brand: Physical Electronics
 Instrument Model: Quantum2000
 X-rays: Al K α (1486eV)
 X-ray Power: 20 W
 Beam Diameter: 100 μ m
 Pass Energy (Wide): 117,4 eV
 Pass Energy (Narrow): 29,35 eV

3. RESULTS

From the data collected, the following results have been obtained:

For more information please visit the NIST database at: <http://srdata.nist.gov/xps/>

Sample	Element	Atomic Concentration (%)	Binding Energy (eV)	Probable Bond(s)/Compound(s)
P	Al	22.3	74.3	Al ₂ O ₃
	C	7.9	284.4 (77%) 286.1 (11%) 288.6 (12%)	C-(C,H) C-O O-C=O
	Ni	6.3	853.6 (12%) 855.6 (88%)	NiO Ni ₂ O ₃
	O	63.6	531.3	O-(C,H), Metal Oxides

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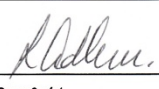
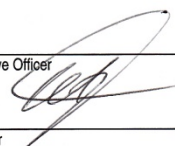
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Sample	Element	Atomic Concentration (%)	Binding Energy (eV)	Probable Bond(s)/Compound(s)
S	Al	22.6	74.4	Al ₂ O ₃
	C	6.3	284.4 (76%) 286.1 (9%) 288.6 (15%)	C-(C,H) C-O O-C=O
	Ni	6.5	853.3 (19%) 855.8 (81%)	NiO Ni ₂ O ₃
	O	64.4	531.4	O-(C,H), Metal Oxides
	S	0.2	169.3	Sulfate, Sulfone

4. COMMENTS

- 4.1 The signal to noise ratio of the sulphur peak (sample S) is very low and hence the determined binding energy value should not be considered to be accurate.

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ANALYSIS OF THE SURFACE COMPOSITION OF CATALYSTS

5. REMARKS

- 5.1 The results in this report relate only to the sample(s) mentioned herein.
- 5.2 Certain of the NMISA certificates are consistent with the capabilities that are included in appendix C of the MRA (Mutual Recognition Arrangement) drawn up by the CIPM. Under the MRA, all participating institutes recognise the validity of each other's calibration and measurement certificates for the quantities and ranges and measurement uncertainties specified in Appendix C. For details see <http://www.bipm.org>.
- 5.3 The analyses were carried out at an ambient temperature of $20\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ and a relative humidity of $50\text{ \%RH} \pm 25\text{ \%RH}$.
- 5.4 The final report will be the property of the client and may be published by him, provided that it is published in full, or where only extracts there from or a summary or an abridgement thereof is published, the NMISA's prior written approval of the extracts, summary or abridged report are to be obtained.

end of certificate

Analysed by Werner Jordaan Metrologist (Technical Signatory)	Checked by Loukie Adlem Metrologist	For Chief Executive Officer
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Further information (expanded spectra and curve fitting) may be obtained from NMISA.

GC-FID information

Column type: PONA

Column width: 0.53 μm

Column length: 50 m

Flow rate of H_2 : 1 ml/min

Sample volume: 1 μl

Mass of reactants and selected products in 1 μl obtained by calibration curves (ng/mV)

Oven programs:

1-octene, 1-octyne, 1,7-octadiene, octane mass determination from the competitive hydrogenation between (1-octene and 1-octyne) and (1-octene and 1,7-octadiene)

Initial temperature: 80 $^{\circ}\text{C}$ for 5 min

Ramp 1: 10 $^{\circ}\text{C}/\text{min}$ to 110 $^{\circ}\text{C}$ hold for 0 min

Ramp 2: 5 $^{\circ}\text{C}/\text{min}$ to 145 $^{\circ}\text{C}$ hold for 0 min

1-octene, octane, octanal, octanol mass determination from the competitive hydrogenation between 1-octene and octanal

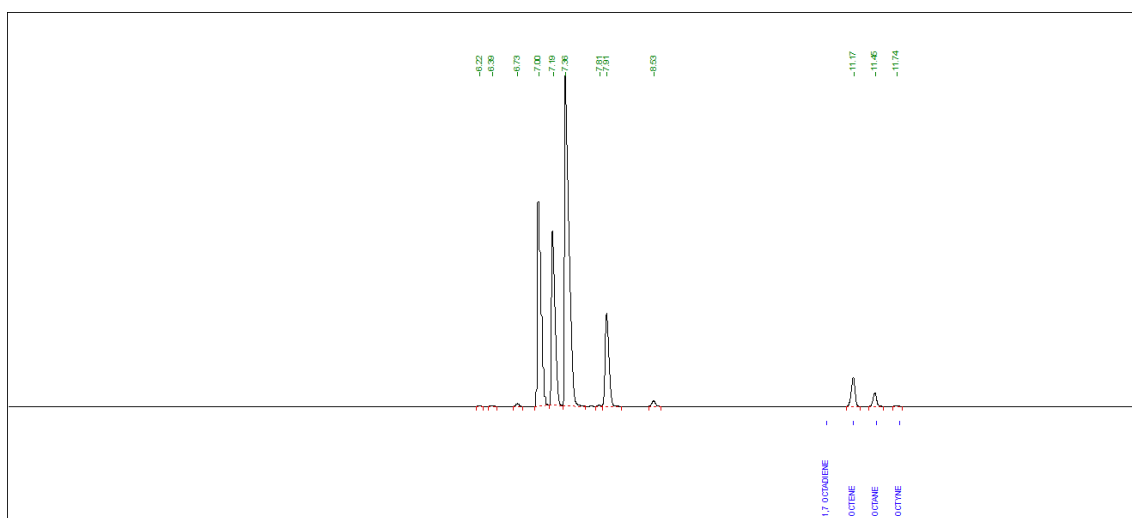
Initial temperature: 80 $^{\circ}\text{C}$ for 5 min

Ramp 1: 3 $^{\circ}\text{C}/\text{min}$ to 156 $^{\circ}\text{C}$ hold for 0 min

By-product identification from the competitive hydrogenation between 1-octene and octanal

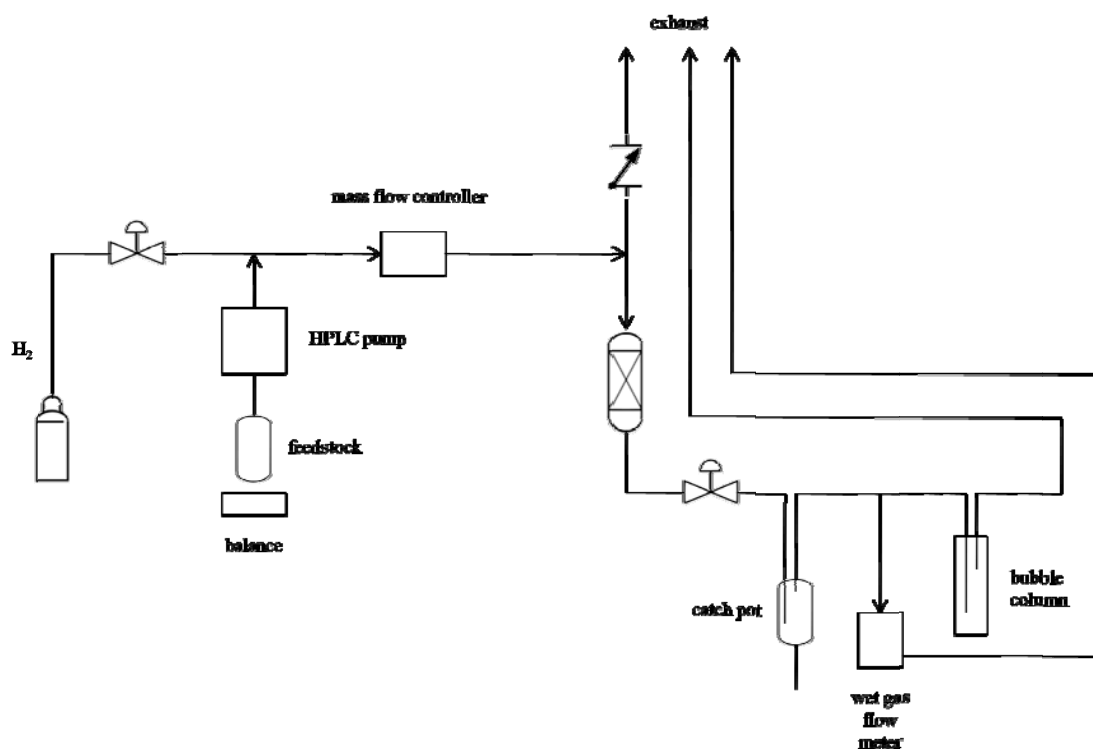
Initial temperature: 40 $^{\circ}\text{C}$ for 5 min

Ramp 1: 3 $^{\circ}\text{C}/\text{min}$ to 240 $^{\circ}\text{C}$ hold for 20 min

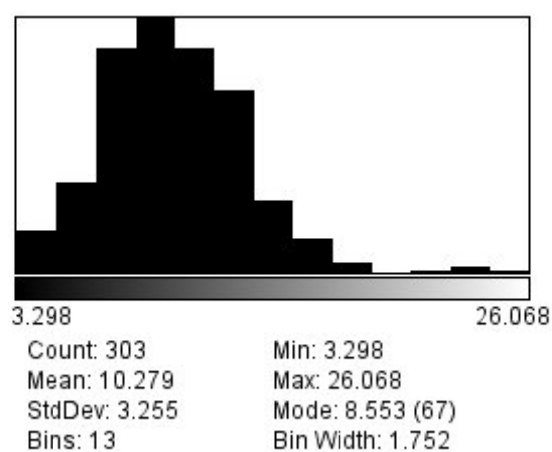


An example of a GC-FID trace

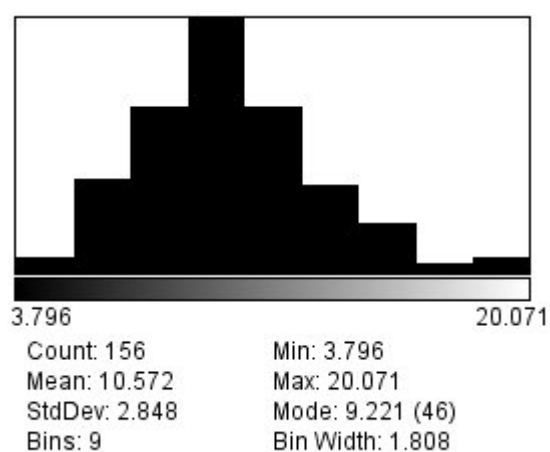
Process flow diagram for the continuous flow fixed bed reactor



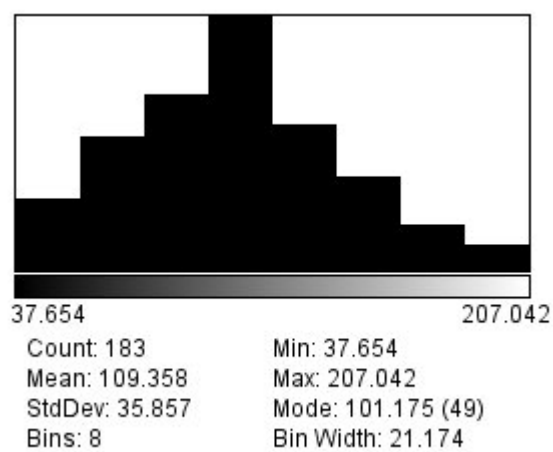
(HR)TEM, STEM particle size distribution (selected examples)



un-coated palladium catalyst



un-coated copper catalyst



[MePsec-Bu₃][MeOSO₃] modified copper catalyst

Definitions and calculations

Competitive hydrogenation between (1-octene and 1-octyne) and (1-octene and 1,7-octadiene)

% Composition of 1-octene, octane and (1-octyne or 1,7-octadiene)

((mass of individual component)/total mass of all components) X 100 %

Total mass of all components calculated by:

(mass octane + mass 1-octene + mass (1-octyne or 1,7-octadiene))

% Conversion of (1-octyne or 1,7-octadiene)

100 % - (2 X % composition of 1-octyne or 1,7-octadiene)

Competitive hydrogenation between 1-octene and octanal

% Composition of 1-octene, octene isomers and octane

(1-octene equivalent volume of the particular component/1-octene equivalent volume of all components) X 100%

Volume of 1-octene remaining calculated by:

(mass determined by GC - FID)/(density of 1-octene)

1-Octene equivalent volume of octene isomers calculated by:

(mass determined by GC - FID)/(density of 1-octene)

1-Octene equivalent volume of 1-octene converted to octane calculated by:

(mass determined by GC - FID) X (Fw 1-octene/Fw octane)/(density of 1-octene)

% Conversion of 1-octene

100% - (((volume of 1-octene remaining)/(volume of 1-octene remaining + volume of octene isomers + volume of octene converted to octane)) X 100 %)

Selectivity of octane formation

(1-octene equivalent volume of octane/1-octene equivalent volume of all products)

% Composition of octanal, octanol and by-products

(octanal equivalent volume of component / octanal equivalent volume of all components) X 100%

Volume of octanal remaining calculated by:

(mass determined by GC-FID) / (density of octanal)

Volume of octanal converted to octanol

(mass determined by GC - FID) X (Fw octanal / Fw octanol) / (density of octanol)

Volume of octanal converted to by-products

volume of octanal present if no conversion occurred - (volume of octanal remaining + volume of octanal converted to octanol)

Volume octanal present if no conversion occurred calculated by:

(volume of 1-octene remaining + volume of 1-octene converted to isomers + volume of 1-octene converted to octane) x (the ratio of the volume of octanal to 1-octene present in the pre-reaction mixture (i.e. volume of octanal / volume of 1-octene))

% Conversion of octanal

100 % - ((volume of octanal remaining / volume octanal present if no conversion occurred) X 100%)

Selectivity of octanol formation

(octanal equivalent volume of octanol / octanal equivalent volume of all products)

Solubility of 1-octyne, 1-octene and 1,7-octadiene in the various ionic liquids

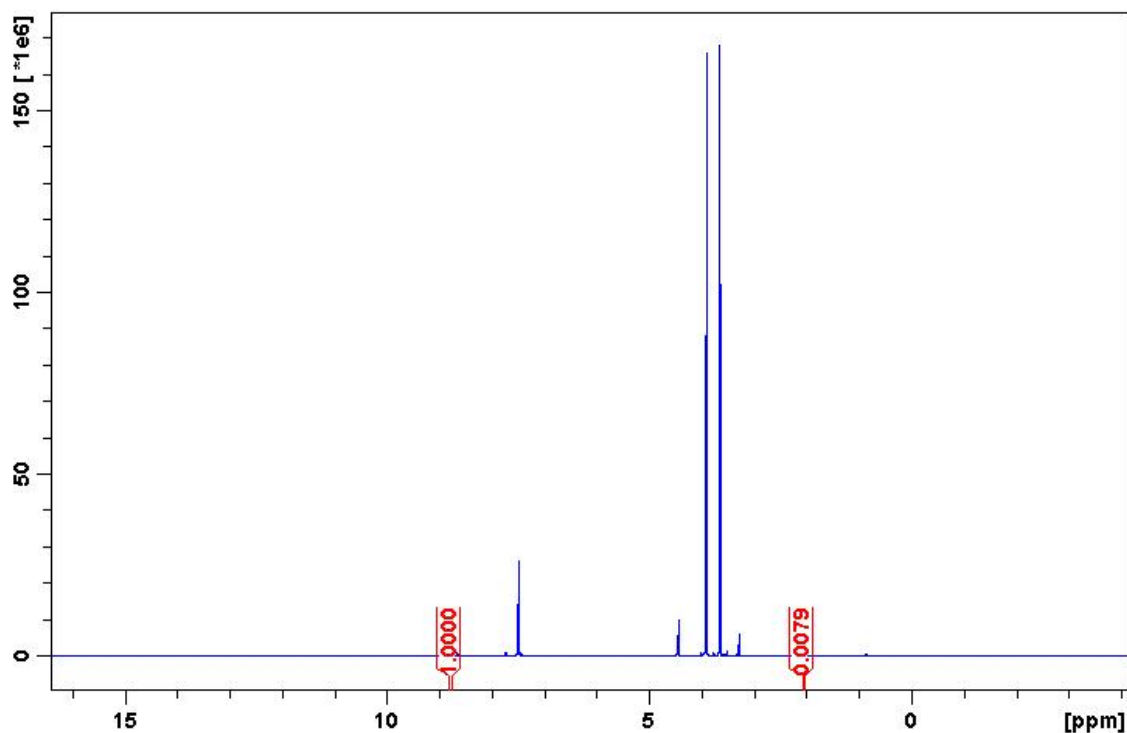
Maximum (saturated) solubilities at 50 °C were determined by:

Obtaining the ratio of the integrated ¹H NMR values (peak(s) specific to the ionic liquid: peak(s) specific to either 1-octyne, 1-octene or 1,7-octadiene) in an ionic liquid singularly saturated with these hydrocarbons.

Comparing this value to a 3 point calibration curve of the integrated ¹H NMR ratio versus the known mass of either 1-octyne, 1-octene or 1,7-octadiene. Values obtained were within the range of the curve.

The following calibration data were obtained:

Ionic liquid:	[MMIM][MeOSO ₃]	Ionic liquid:	[MMIM][MeOSO ₃]
Hydrocarbon:	1-octyne	Hydrocarbon:	1-octene
Trend:	Linear	Trend:	Linear
Trend equation:	$y = 0.4413(x)$	Trend equation:	$y = 0.2264(x)$
R ² value:	0.999	R ² value:	1
Ionic liquid:	[MMIM][MeOSO ₃]	Ionic liquid:	[MMIM][OcOSO ₃]
Hydrocarbon:	1,7-octadiene	Hydrocarbon:	1-octyne
Trend:	Linear	Trend:	Linear
Trend equation:	$y = 0.116(x)$	Trend equation:	$y = 0.3551(x)$
R ² value:	0.9997	R ² value:	0.9998
Ionic liquid:	[MMIM][OcOSO ₃]	Ionic liquid:	[MMIM][OcOSO ₃]
Hydrocarbon:	1,7-octene	Hydrocarbon:	1,7-octadiene
Trend:	Linear	Trend:	Linear
Trend equation:	$y = 0.1908(x)$	Trend equation:	$y = 0.0888(x)$
R ² value:	0.9997	R ² value:	0.9996
Ionic liquid:	[MMIM][NTf ₂]	Ionic liquid:	[MMIM][NTf ₂]
Hydrocarbon:	1-octyne	Hydrocarbon:	1-octene
Trend:	Linear	Trend:	Linear
Trend equation:	$y = 0.2888(x)$	Trend equation:	$y = 0.1446(x)$
R ² value:	0.9999	R ² value:	0.9999
Ionic liquid:	[MMIM][NTf ₂]	Ionic liquid:	[MePsec-Bu ₃][MeOSO ₃]
Hydrocarbon:	1,7-octadiene	Hydrocarbon:	1-octyne
Trend:	Linear	Trend:	Linear
Trend equation:	$y = 0.0725(x)$	Trend equation:	$y = 0.6334(x)$
R ² value:	0.9999	R ² value:	0.9995
Ionic liquid:	[MePsec-Bu ₃][MeOSO ₃]	Ionic liquid:	[MePsec-Bu ₃][MeOSO ₃]
Hydrocarbon:	1-octene	Hydrocarbon:	1,7-octadiene
Trend:	Linear	Trend:	Linear
Trend equation:	$y = 0.3128(x)$	Trend equation:	$y = 0.1503(x)$
R ² value:	0.9995	R ² value:	0.9987
Ionic liquid:	[Et ₃ S][NTf ₂]	Ionic liquid:	[Et ₃ S][NTf ₂]
Hydrocarbon:	1-octyne	Hydrocarbon:	1-octene
Trend:	Linear	Trend:	Linear
Trend equation:	$y = 1.8227(x)$	Trend equation:	$y = 0.8957(x)$
R ² value:	0.9997	R ² value:	0.9999
Ionic liquid:	[Et ₃ S][NTf ₂]		
Hydrocarbon:	1,7-octadiene		
Trend:	Linear		
Trend equation:	$y = 0.4548(x)$		
R ² value:	0.9999		

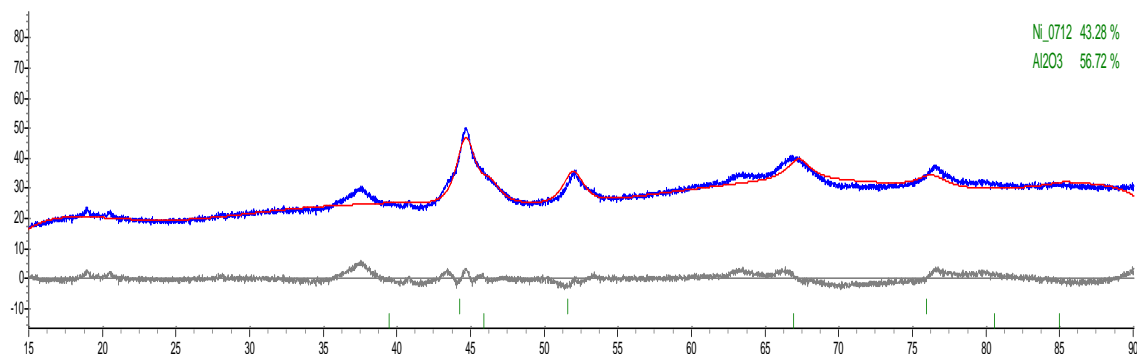


An example of an integrated ^1H NMR spectrum used for the determination the maximum solubility of 1-octyne in $[\text{MMIM}][\text{MeOSO}_3]$ at $50\text{ }^\circ\text{C}$

ICP and BET values for the nickel catalysts prepared by Method A and Method B in Chapter 3

Catalyst	Ni catalyst prepared by Method A	Ni catalyst prepared by Method B
% Ni content by ICP	29	31
surface area (m^2/g) ^[a]	133.0	147.7
Average pore volume (cm^3/g) ^[b]	0.42	0.46
[a] determined by BET analysis. [b] determined by BJH analysis		

Rietveld refinement Data



R-Values

Rexp : 3.49 Rwp : 9.08 Rp : 7.25 GOF : 2.60
Rexp' : 1.49 Rwp' : 3.88 Rp' : 4.37 DW : 0.29

Quantitative Analysis - Rietveld

Phase 1 : Ni₀₇₁₂ 43.284 %
Phase 2 : Al_{2O3} 56.716 %

Background

One on X 52433.23
Chebyshev polynomial, Coefficient 0 -740.3712
1 1519.464
2 -579.293
3 134.8078
4 -122.6132
5 57.28025
6 -2.931753
7 -14.24175
8 -79.88059

Instrument

Primary radius (mm) 217.5
Secondary radius (mm) 217.5

Corrections

Zero error -0.2049318
Specimen displacement -1.184877
LP Factor 90

Structure 1

Phase name Ni₀₇₁₂
R-Bragg 4.121
Spacegroup Fm-3m
Scale 0.00927880963
Cell Mass 234.761
Cell Volume (Å³) 44.36186
Wt% - Rietveld 43.284
Crystal Linear Absorption Coeff. (1/cm) 428.543
Crystal Density (g/cm³) 8.788
PVII peak type
FWHM = a + b/Cos(Th) + c Tan(Th)

a 0.02983087
b 0.1583576
c 0.9999979
Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)

ma 0.2727462
mb 0.6485447
mc 0.2164412

Lattice parameters
a (Å) 3.5400000

Site	Np	x	y	z	Atom	Occ	Beq
Ni1	4	0.00000	0.00000	0.00000	Ni	1	1

Structure 2

Phase name Al_{2O3}
R-Bragg 0.902
Spacegroup Fm-3m
Scale 0.0151168766
Cell Mass 135.909
Cell Volume (Å³) 61.62988
Wt% - Rietveld 56.716

Crystallite Size
Cry size Lorentzian (nm) 5.6
Crystal Linear Absorption Coeff. (1/cm) 116.221
Crystal Density (g/cm³) 3.662
PVII peak type

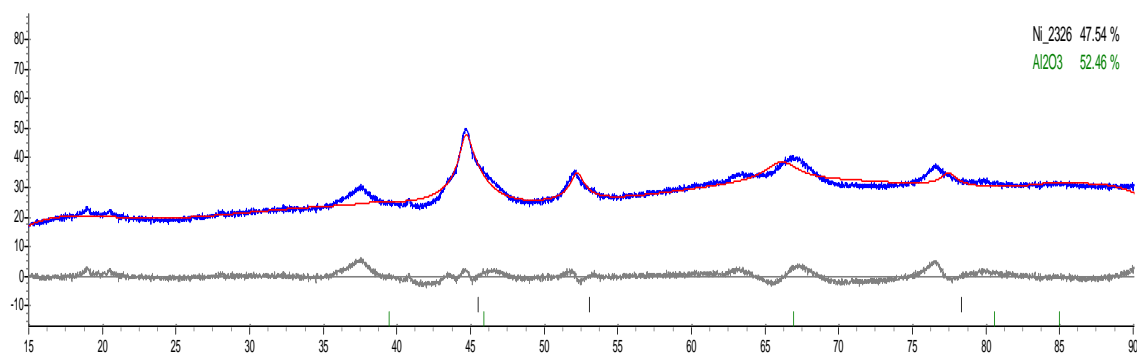
FWHM = a + b/Cos(Th) + c Tan(Th)
a 0.0001005823
b 0.001882069
c 0.0001904257

Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)

ma 2.904531
mb 0.2199163
mc 2.465763

Lattice parameters
a (Å) 3.9500000

Site	Np	x	y	z	Atom	Occ	Beq
O1	4	0.00000	0.00000	0.00000	O-2	1	0
Al1	4	0.50000	0.50000	0.50000	Al+3	0.4665	0
Al2	8	0.25000	0.25000	0.25000	Al+3	0.0999	0



R-Values

R_{exp} : 3.49 R_{wp} : 9.39 R_p : 7.20 GOF : 2.69
 R_{exp}' : 1.48 R_{wp}' : 3.97 R_p' : 4.22 DW : 0.27

Quantitative Analysis - Rietveld

Phase 1 : Ni₂₃₂₆ 47.544 %
 Phase 2 : Al₂O₃ 52.456 %

Background

One on X 51961.52
 Chebychev polynomial, Coefficient 0 -764.1673
 1 1510.46
 2 -535.2572
 3 126.6105
 4 -132.006
 5 72.06586
 6 8.355166
 7 -18.37945
 8 -71.86292

Instrument

Primary radius (mm) 217.5
 Secondary radius (mm) 217.5

Corrections

Zero error -1.293416
 Specimen displacement -0.952055
 LP Factor 90

Structure 1

Phase name Ni₂₃₂₆
 R-Bragg 0.846
 Spacegroup Fm-3m
 Scale 0.0229587564
 Cell Mass 234.761
 Cell Volume (Å³) 41.06363
 Wt% - Rietveld 47.544
 Crystallite Size
 Cry size Lorentzian (nm) 10000.0
 Crystal Linear Absorption Coeff. (1/cm) 462.964
 Crystal Density (g/cm³) 9.493
 PVII peak type

$$\text{FWHM} = a + b/\cos(\text{Th}) + c \tan(\text{Th})$$

a 0.245769
 b 0.2075634
 c 0.17962
 Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)
 ma 0.0001053921
 mb 0.01846126
 mc 0.0001

Lattice parameters

a (Å) 3.4500000

Site	Np	x	y	z	Atom	Occ	Beq
Ni1	4	0.00000	0.00000	0.00000	Ni	1	1

Structure 2

Phase name Al₂O₃
 R-Bragg 1.052
 Spacegroup Fm-3m
 Scale 0.0291536261
 Cell Mass 135.909
 Cell Volume (Å³) 61.62988
 Wt% - Rietveld 52.456
 Crystallite Size
 Cry size Lorentzian (nm) 3.9
 Crystal Linear Absorption Coeff. (1/cm) 116.221
 Crystal Density (g/cm³) 3.662
 PVII peak type

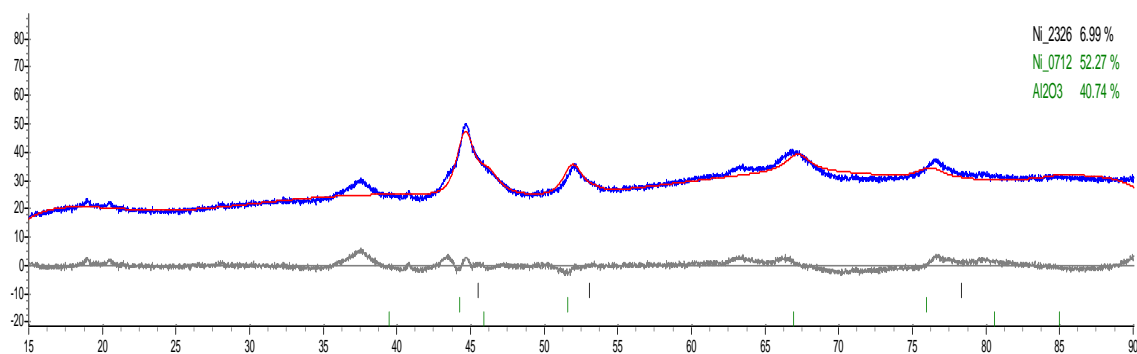
$$\text{FWHM} = a + b/\cos(\text{Th}) + c \tan(\text{Th})$$

a 0.0001
 b 0.0001000025
 c 0.006596395
 Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)
 ma 0.0001002106
 mb 0.0001000035
 mc 4.991628

Lattice parameters

a (Å) 3.9500000

Site	Np	x	y	z	Atom	Occ	Beq
O1	4	0.00000	0.00000	0.00000	O-2	1	0
Al1	4	0.50000	0.50000	0.50000	Al+3	0.4665	0
Al2	8	0.25000	0.25000	0.25000	Al+3	0.0999	0



R-Values

Rexp : 3.49 Rwp : 9.32 Rp : 7.15 GOF : 2.67
 Rexp' : 1.48 Rwp' : 3.97 Rp' : 4.23 DW : 0.28

Quantitative Analysis - Rietveld

Phase 1 : Ni_2326 6.993 %
 Phase 2 : Ni_0712 52.270 %
 Phase 3 : Al2O3 40.738 %

Background

One on X 52208.99
 Chebychev polynomial, Coefficient 0 -734.7663
 1 1514.044
 2 -577.192
 3 134.5297
 4 -122.5131
 5 58.33276
 6 -0.6114342
 7 -12.5969
 8 -81.76842

Instrument

Primary radius (mm) 217.5
 Secondary radius (mm) 217.5

Corrections

Zero error -0.2662644
 Specimen displacement -1.238374
 LP Factor 90

Structure 1

Phase name Ni_2326
 R-Bragg 1.989
 Spacegroup Fm-3m
 Scale 0.00117990234
 Cell Mass 234.761
 Cell Volume (Å³) 41.06363
 Wt% - Rietveld 6.993
 Crystallite Size
 Cry size Lorentzian (nm) 7.6
 Crystal Linear Absorption Coeff. (1/cm) 462.964
 Crystal Density (g/cm³) 9.493
 PVII peak type
 FWHM = a + b/Cos(Th) + c Tan(Th)
 a 0.003690293
 b 0.0001
 c 0.0001
 Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)

ma 0.0001
 mb 0.08920245
 mc 0.0001

Lattice parameters

a (Å) 3.4500000

Site	Np	x	y	z	Atom	Occ	Beq
Ni1	4	0.00000	0.00000	0.00000	Ni	1	1

Structure 2

Phase name Ni_0712
 R-Bragg 4.354
 Spacegroup Fm-3m
 Scale 0.00816406816
 Cell Mass 234.761
 Cell Volume (Å³) 44.36186
 Wt% - Rietveld 52.270
 Crystallite Size
 Cry size Lorentzian (nm) 10000.0
 Crystal Linear Absorption Coeff. (1/cm) 428.543
 Crystal Density (g/cm³) 8.788
 PVII peak type
 FWHM = a + b/Cos(Th) + c Tan(Th)
 a 0.0001
 b 0.1386397
 c 1
 Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)
 ma 0.3856562
 mb 1.120509
 mc 0.1918725

Lattice parameters

a (Å) 3.5400000

Site	Np	x	y	z	Atom	Occ	Beq
Ni1	4	0.00000	0.00000	0.00000	Ni	1	1

Structure 3

Phase name Al2O3
 R-Bragg 1.713
 Spacegroup Fm-3m
 Scale 0.00791133521
 Cell Mass 135.909
 Cell Volume (Å³) 61.62988
 Wt% - Rietveld 40.738
 Crystallite Size
 Cry size Lorentzian (nm) 5.3
 Crystal Linear Absorption Coeff. (1/cm) 116.221

Crystal Density (g/cm³) 3.662

PVII peak type

FWHM = a + b/Cos(Th) + c Tan(Th)

a 0.0006696021

b 0.0001000383

c 0.0001

Exponent m = 0.6+ma+mb/Cos(Th)+mc/Tan(Th)

ma 0.0001

mb 0.4775168

mc 0.0001

Lattice parameters

a (Å) 3.9500000

Site	Np	x	y	z	Atom	Occ	Beq
O1	4	0.00000	0.00000	0.00000	O-2	1	0
Al1	4	0.50000	0.50000	0.50000	Al+3	0.4665	0
Al2	8	0.25000	0.25000	0.25000	Al+3	0.0999	0