



**A Fundamental Perspective on the Effects of Sulfur
Modification for Transition Metal Nanocatalysts**

By

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**A dissertation submitted for the degree of Doctor of Philosophy at the
Inorganic Chemistry Laboratory, Department of Chemistry,
University of Oxford**

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DECLARATION

I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

Amy Louise Kolpin

DEDICATION

To my lovely husband, Nick, and to my parents and my family.

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Abstract

The application of heterogeneous catalysts to industrial processes is a key factor in the synthesis of nearly all chemicals currently produced, however billions of pounds are lost every year due to unplanned reactor shutdowns and catalyst replacement as a result of catalytic deactivation processes. Poisoning of heterogeneous catalysts by sulfur compounds is a particularly prominent class of deactivation processes, affecting a wide range of catalytic materials and catalytic reactions, including the industrially-prominent Haber-Bosch process for the synthesis of ammonia and steam reforming of methane for the synthesis of hydrogen. However, while the effects of sulfur adsorption on catalytic behaviour are often unmistakably apparent, the fundamental interactions leading to these effects are not yet well understood.

The work presented in this thesis uses a combination of model systems, novel and traditional characterization techniques, and methods of modifying catalyst geometric and electronic structure to approach the topic of sulfur poisoning from a fundamental perspective. Particular focus is placed on using selective decoration of active sites to develop a system of model hydrogenation reactions to relate changes in catalytic behaviour to changes in geometric and electronic structure. Application of these model reactions to investigate the sensitivities of palladium- and ruthenium-based catalytic systems to modification by sulfur shows contrasting effects for the two metals. While both systems exhibit similar geometric effects of modification, the palladium-based catalysts are far more sensitive than the ruthenium-based catalysts to modification of electronic structure. Additionally, controlled variation in particle size for the palladium-based catalysts demonstrates that catalytic behaviour is dominated by electronic structure for small nanoparticles and geometric structure for large nanoparticles. This leads small nanoparticles to show increased sensitivity to electronic modification effects resulting from sulfur adsorption.

Ultimately, the research presented within this thesis provides a basis for the intelligent design of heterogeneous catalysts for improving tolerance for sulfur poisoning, and for utilizing the effects of sulfur modification to optimize catalytic activity and selectivity for the synthesis of fine chemicals.

Keywords: Heterogeneous catalysis, Catalyst deactivation, Sulfur poisoning, Catalytic hydrogenation, Electronic modification, Geometric modification

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List of abbreviations and symbols

ATR – Attenuated total reflectance

BE – Binding Energy

CCD – Charge coupled device

DFT – Density functional theory

DOS – Density of states

E_a – Activation energy

EDX – Energy dispersive X-rays

E_F – Energy of the Fermi level

EtOH – Ethanol

fcc – Face centred cubic

FFT – Fast Fourier transform

FID – Flame ionization detector

FTIR – Fourier transform infrared

FWHM – Full width at half maximum

ΔG – Change in Gibb's free energy

GC – Gas chromatography

GGA – Generalized gradient approximation

GNP – Gross national product

HAADF – High angle annular dark field

hcp – Hexagonal close packed

HRTEM – High resolution transmission electron microscopy

LDOS – Localized density of states

m – Shell number

MBA – 3-Methyl-2-butan-3-ol

MBE – 3-Methyl-2-buten-3-ol

MBY – 3-Methyl-2-butyne-3-ol

MEA – 2-Mercaptoethanol

MHA – Mercaptohexanol

ML – Monolayer

MPT – Methylpropanethiol

MSI – Metal support interaction

MW – Molecular weight

NMR – Nuclear magnetic resonance

PAW – Projector-augmented wave

Pd(PVP) – Polyvinylpyrrolidone stabilized Pd nanoparticles

Pd+Te(PVP) – Tellurium decorated palladium nanoparticles supported by Polyvinylpyrrolidone

PGM – Platinum group metal

PVP – Polyvinylpyrrolidone

RMSE – Root mean square error

RPBE – revised Perdew-Burke-Ernzerhof

rpm – rotations per minute

Ru(PVP) – Polyvinylpyrrolidone stabilized Ru nanoparticles

SAM – Self-assembled monolayer

SG – Seed growth

SPARG – Sulfur passivated reforming

STEM – Scanning transmission electron microscopy

T – Temperature

TEM – Transmission electron microscopy

TGA – Thermogravimetric analysis

TPD – Temperature programmed desorption

TPO – Temperature programmed oxidation

TPR – Temperature programmed reduction

TOF – Turn over frequency

TON – Turn over number

UPS – Ultra-violet photoelectron spectroscopy

UV – Ultra violet

XPS – X-ray photoelectron spectroscopy

XRD – X-ray diffraction

WGSR – Water-gas shift reaction

List of publications

1. T. Jia, A. Kolpin, C. Ma, R. C. T. Chan, W. M. Kwok, S. C. E. Tsang, Chemical Communications, **2014**, 50, 1185-1188.
2. S. Jones, S. M. Fairclough, M. Gordon-Brown, W. Zheng, A. Kolpin, B. Pang, W. C. H. Kuod, J. M. Smith, S. C. E. Tsang, Chemical Communications, **2014**, Accepted.
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Chapter 1

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1.1 Principles of catalysis

Since the concept of catalysis was first proposed by Berzelius in 1836, the world has seen an exponential increase in the application of catalysts to chemical processes¹. This is particularly true for developed nations, and approximately 25% of the gross national product (GNP) for these industrialized societies is currently derived from processes involving catalysis¹. With the incorporation of these materials into a vast range of industrial processes including petroleum refining², the production of pharmaceuticals and fine chemicals³, ammonia synthesis, and green technologies such as solar cells and automotive catalytic convertors⁴, it is no surprise that catalysts are a crucial component in approximately 90% of all industrial processes^{1,5}. And while the applications for catalysts span nearly the full spectrum of chemical technologies, the basic principles of catalysis remain constant regardless of the application.

Generally speaking, a catalyst is defined as any material which increases the rate of a chemical reaction whilst also being regenerated in its original form upon completion of the reaction cycle⁶. This second condition is particularly important and allows true catalysts to be distinguished from simple promoters, which also increase reaction rates but are consumed or fundamentally altered during the process. In fact, it is the reusability of these materials that provides one of the biggest driving forces behind the commercial success of catalytic processes, and has enabled the development of catalysts from the full range of chemical elements including expensive precious metals which would be impractical for use as simple reaction promoters.

From a fundamental standpoint, the rate at which a chemical reaction occurs is governed by the Arrhenius Equation (Equation 1.1):

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad \text{Equation 1.1}$$

where k is the rate constant for a chemical reaction, T is the temperature (in K), A is the pre-exponential factor, R is the universal gas constant, and E_a is the activation energy. In the absence of a catalyst, the activation energy for a chemical reaction remains constant and thus the rate is dependent on the reaction temperature, where an increase in temperature leads to an increase in the reaction rate. For many industrially relevant chemical processes, the activation energy is sufficiently high that it is not practical or economically viable to control the reaction rate simply through increasing the reaction temperature. Additionally, this method of rate control also has the potential to introduce thermodynamic complications that affect the equilibrium of the reaction. In these cases, it is necessary to include a catalyst which functions to lower the activation barrier for the process, leading to an increase in the reaction rate without the requirement of increasing reaction temperature.

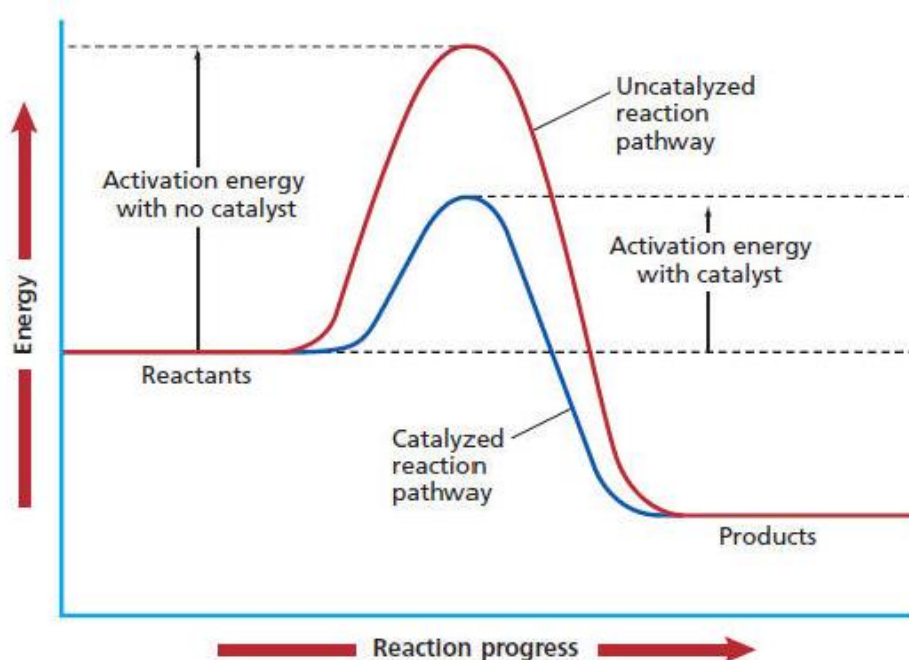


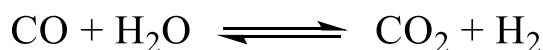
Figure 1.1 – Reaction pathways for a chemical process in the absence and presence of a catalyst. Reproduced from reference¹¹⁷.

Figure 1.1 above illustrates the decreased activation energy for a catalysed reaction pathway over the uncatalysed pathway for a chemical process resulting from lowering the energy of the transition state. The decreased energy requirement for catalytic processes has made the application of these materials of even greater economic importance in today's energy conscious world, and with the rising costs of energy production it is no surprise that further improvements are continually being sought. A particularly illustrative example is the Haber-Bosch processes for the synthesis of ammonia, a key component in fertilizers for agricultural use. The production of this single chemical currently consumes 1% of the world's total energy output on an annual basis⁷, and with the rate of production increasing at approximately 4% every year it is clear that the drive to develop more efficient catalytic materials will only increase in the near future⁸.

While the use of a catalyst affects the kinetics for a chemical reaction by modifying the reaction pathway, the unaltered initial and final energy states for the reactants and products in Figure 1.1 indicate that the reaction thermodynamics are not similarly affected. The thermodynamic favourability of each reaction is still governed the Gibb's free energy for the system, expressed as a function of temperature in Equation 1.2:

$$\Delta G = \Delta H - T\Delta S \quad \text{Equation 1.2}$$

where ΔG is the change in Gibb's free energy for a reaction, ΔH is the enthalpy change, ΔS is the entropy change, and T is the reaction temperature. If the ΔG term is negative, the reaction equilibrium will favour formation of products, while the reverse is true if the ΔG term is positive. As both Equations 1.1 and 1.2 are dependent on temperature, it is unsurprising that the ideal temperatures for optimal kinetic and thermodynamic favourability will be in conflict for certain reactions. A clear example of this principle lies in the water-gas shift reaction (WGSR), an important step in the production of hydrogen for ammonia synthesis and purification of hydrogen feedstocks through the removal of CO⁹.



$$\Delta H_{298} = -41 \text{ kJ mol}^{-1}; \Delta G_{298} = -28 \text{ kJ mol}^{-1}$$

Scheme 1.1 – General mechanism for the water gas shift reaction⁹.

A general mechanism for the reaction, along with the change in Gibb's free energy and enthalpy at room temperature, is given in Scheme 1.1 above. Under typical circumstances, the desired products are H_2 and CO_2 and the reaction thermodynamics favour their formation at room temperature⁹. However, kinetic factors cause the rate of reaction to be extremely low under these conditions, and any attempt to improve the rate by increasing the temperature results in an unfavourable shift in the thermodynamics for the reaction, leading to a decrease in conversion. In order to carry out the reaction under conditions suitable for the formation of CO_2 and H_2 (less than 600 °C), a catalyst is used to lower the activation energy for the reaction¹⁰. However, the prevailing thermodynamics combined with insufficient reaction rates fuels continued efforts to develop new and improved catalysts with higher activities to enable the process to be carried out at lower temperatures¹¹. The independence of thermodynamics in catalytic processes is one of the many reasons why catalysts must be carefully selected to achieve optimal activity and selectivity for each reaction, with the end result being that most industrial processes involve the use of highly specialized catalytic materials and carefully tailored reaction conditions.

1.2 Types of catalysis

As the previous section demonstrated, the principles of catalysis including reaction thermodynamics and kinetics dictate that the optimal catalyst for a reaction will often be highly specific, resulting in almost as many different catalysts as there are reactions to be catalysed. In

order to somewhat simplify the consideration of different systems, the field of catalysis is generally broken down into three subcategories: homogeneous, enzymatic, and heterogeneous.

In homogeneous catalysis, the reactants and catalyst are contained within the same phase (generally liquid), and catalysts are usually in the form of organometallic complexes with a single metal atom comprising the active site. The properties of these catalysts are easily tailored by modifying the nature of the supporting ligands, enabling their use in reaction processes requiring a high degree of selectivity, particularly when chirality of the products is important¹². For this reason, homogeneous catalysts are most commonly employed in the synthesis of pharmaceuticals where each synthesis processes often requires a tailor-made catalyst and the purity of the products is of the utmost importance.

Enzymes are difficult to strictly classify as either homogeneous or heterogeneous catalysts, as even though they generally operate freely dispersed in solution, the organic framework of the material is significantly larger than typical molecular homogeneous catalysts. In enzymatic catalysis, catalytic activities tend to be extremely high, reaching levels of up to 600,000 conversions per second¹³. They are also among the most selective catalysts, as the 3-dimensional structure of the active site strongly disfavours any side reactions¹⁴. However, these systems tend to be highly sensitive to changes in temperature and pH, making them unsuitable for use in most industrial processes¹⁵.

The final classification is heterogeneous catalysis, where the catalyst and the reactants are contained in separate phases with the most common arrangements being gas/solid and liquid/solid systems¹⁶. The ease of separating heterogeneous catalysts from the reaction media was recognized early on as the principle benefit of these systems, and has lent itself well to the

design of high-throughput flow-through reactors for gas-phase industrial synthesis and portable technologies such as automotive catalytic converters¹⁷. There have been attempts to merge the types of systems together, for instance the process of immobilizing a homogeneous catalysts or enzymes on a heterogeneous support¹⁸, however in actuality traditional heterogeneous catalysts make up 85-90% of the market share for all catalysts sold¹⁹.

The catalytic active site is central to all three forms of catalysis, and ever since the concept of a specific active site for catalytic reactions was first proposed by Taylor in 1925 research in this area has sought a complete understanding of its properties¹. All three main types of catalyst hinge on the concept of an active site. In homogeneous and enzymatic catalysis, the catalytic active site is generally a single metal atom within an organic complex, and each mole of catalyst is assumed to have one mole of active sites²⁰. For these systems, catalytic activity is thus generally expressed in terms of turnover number (TON) calculated as the number of moles of reactant converted per mole of catalyst per unit time²⁰. However, in the case of heterogeneous catalysis occurring at surfaces, this is no longer true. In these systems, only a fraction of the atoms in the active phase are located at the surface of the material and available to act as active sites for catalysis. In this case, it is more appropriate and informative to express catalytic activity in terms of turnover frequency (TOF) calculated as the number of moles of reactant converted per mole of surface active sites per unit time²⁰.

Referring back to Figure 1.1 in Section 1.1, it should be appreciated that the pathway for a catalysed reaction depicting a single transition state between the free reactants and products is only a simplified illustration. In reality, the catalysed reaction pathway will be composed of multiple steps including the adsorption of reactants, activation of the adsorbed species/conversion to products, and the desorption of said products²¹. Each of these reaction

steps will exhibit its own activation energy dependent on the thermodynamics of the free/adsorbed species relative to the energy of the transition state, and the step with the highest activation energy barrier will generally become the rate determining step (assuming the reaction does not operate under diffusion control)²². As it is highly likely one or more reaction steps in this catalysed pathway will possess activation energies greater than the apparent activation energy depicted in Figure 1.1, determining the suitability of a catalyst for a particular reaction is more complicated than simply minimizing this apparent activation energy.

When determining how the various processes of a catalytic reaction affect the observed activity of a particular catalyst, it is useful to start by considering the adsorption processes separately from desorption processes and the activation energy for the transition state.

1.2.1 The Sabatier principle

In order for a heterogeneous catalyst to be effective for a particular reaction, one or more reactants must be chemisorbed to the surface of the catalyst, and if this is the only process considered it logically follows that the stronger the adsorption between the catalyst and reactants, the higher the catalytic activity. It is generally accepted that adsorption strength of molecules to the surface of transition metals where the d-band is more than half filled decreases by moving right across the periodic table due to increased filling of antibonding states in the surface-reactant bond resulting from lowering the metal d-band centre relative to the Fermi level²³. If this was the only factor in determining catalytic activity for a reaction, one would expect earlier transition metals such as Fe and Ru to consistently be the best choice in the design of catalysts.

However, if the activation energy for the transition state is the only process considered, the opposite trend is observed. In this case the energy of the transition state is fixed, but the energy

required to reach the transition state is dependent on the thermodynamics of the adsorbed reactants. Increasing the adsorption strength by moving left across the transition metals stabilizes the adsorbed reactants, thereby widening the energy difference with the transition state and increasing the activation energy¹². The minimal activation energy for the reaction is thus achieved when reactants are only weakly chemisorbed to the catalyst surface, as is the case for late transition metals such as Au and Ag. This same rationale also applies to the process of product desorption from the metal surface, which will occur most readily when the adsorption strength is low.

Given that the conditions for optimizing the favourability of reactant adsorption, activation energy for the transition state, and product desorption are in conflict with each other, it is logical to focus on a set of optimal conditions that provides a balance between the favourability of all three processes. This realization is the basis for the Sabatier Principle, which states that optimal catalytic activity for a reaction will be reached when all species possess intermediate adsorption strengths^{1,24}. The concept can be represented visually by a plot of reaction rate versus the heat of adsorption for a reactant on a range of transition metal surfaces where the interplay between the favourability of the various processes results in a typical volcano-shaped curve (Figure 1.2 below). Sabatier's conditions of intermediate adsorption strength are met by elements at the apex of the curve, while elements to the right of this point limit catalytic activity due to adsorption strengths too weak to ensure sufficient interaction between reactants and the surface and elements to the left exhibit adsorption strengths too high to allow the resulting products to rapidly desorb from the surface^{12,24}.

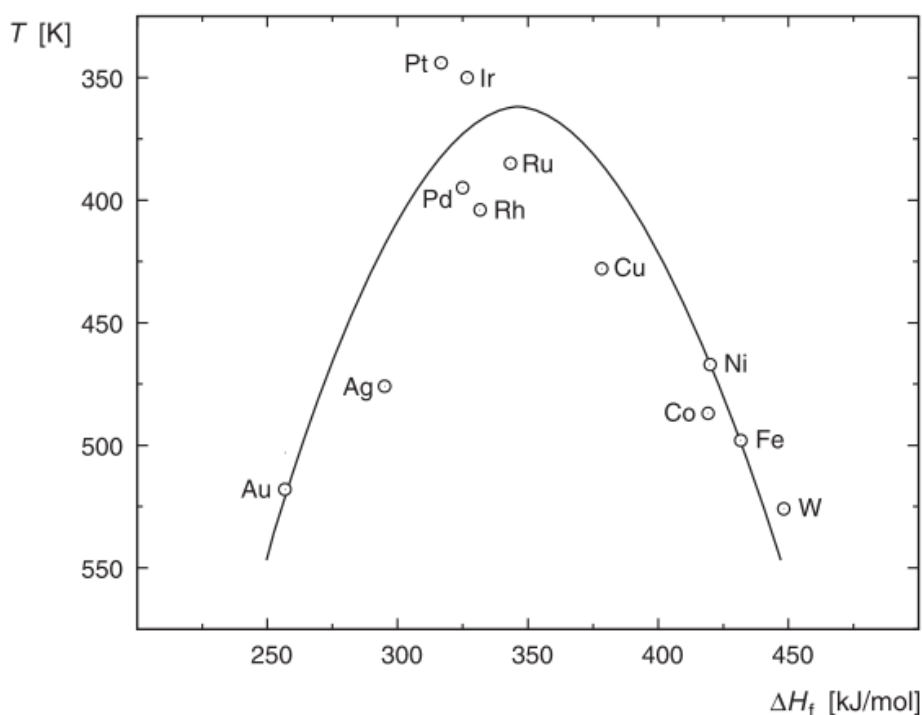


Figure 1.2 – Volcano plot for the adsorption of formic acid on various transition metals. Reproduced from reference¹⁹.

As Figure 1.2 demonstrates, there are generally only a few metals with the potential to act as catalysts for a given reaction by adequately balancing the processes of adsorption, conversion, and desorption, however fine tuning the favourability of these processes to optimize catalytic performance requires more subtle techniques than simply changing the catalyst metal. The most common methods include changing reaction conditions, alteration of supporting materials, use of catalyst modifiers, alloying, and design of catalysts with highly specific structures¹. Fine tuning catalytic performance *via* these methods creates a branching effect along the path of catalyst development, with the end result being a wide range of highly specialized materials that are often as complex as they are diverse.

1.2.2 Adsorption and reaction kinetics

When dealing with adsorption of reactants at active sites on heterogeneous surfaces, the Langmuir adsorption model is most often used to define the relationship between the equilibrium

for adsorption of a reactant and the partial pressure or concentration of that reactant²⁵. In the simplest case where only a single reactant and the catalyst surface are considered, the mechanism for adsorption can be expressed as:



where A is the adsorbing species, M^* are unoccupied active sites, and MA are occupied active sites. When the system is at equilibrium, the equilibrium constant for the adsorption of reactant A (K_A) can be expressed by Equation 1.4:

$$K_A = \frac{[MA]}{[A][M^*]} \quad \text{Equation 1.4}$$

where [MA], [A], and $[M^*]$ are the equilibrium concentrations of the various species. From these two equations, the Langmuir adsorption isotherm can be derived (Equation 1.5) which expresses the fraction of surface sites occupied by reactant A (θ_A) as a function of the adsorption constant and the reactant concentration:

$$\theta_A = \frac{K_A[A]}{1 + K_A[A]} \quad \text{Equation 1.5}$$

Under the assumptions that all active sites are equivalent and no site can simultaneously adsorb multiple reactants, this equation can easily be expanded to account for competitive adsorption between multiple reactants by adding terms to the denominator to represent each additional reactant concentration and adsorption constant. The Langmuir adsorption model is clearly a simplified model as it is well known that the assumption of equivalent active sites does not hold for many heterogeneous catalytic systems²⁵. Nevertheless, this remains one of the most commonly applied methods for expressing the adsorption behaviour of reactants.

When considering the kinetics of a heterogeneous catalytic reaction, most reactions are found to proceed *via* either an Eley-Rideal type mechanism or a Langmuir-Hinshelwood type mechanism²⁶. In an Eley-Rideal mechanism multiple molecules are involved in the reaction,

however the reaction progresses with only one of the reactants chemisorbed to the surface of the catalyst. Conversion of the activated adsorbed species relies on collision with a secondary reactant molecule contained in the gas or liquid phase. However in the Langmuir Hinshelwood reaction model, conversion occurs only when both participating reactants are adsorbed to the catalyst surface. Most heterogeneous catalytic reactions, including hydrogenation reactions, are found to operate *via* this second type of mechanism²⁶.

In the case of a reaction proceeding *via* the Langmuir-Hinshelwood model, the most general mechanism involving multiple reactants can be expressed as:



and if the Langmuir adsorption isotherm is assumed to relate the overall reactant concentrations to the concentration of adsorbed species, the corresponding reaction rate can be calculated from Equation 1.7:

$$r = k\theta_A^x\theta_B^y \quad \text{Equation 1.7}$$

where r is the reaction rate, k is the rate constant, x is the reaction order for species A, and y is the reaction order for species B. From this equation, the Arrhenius Equation, and the Langmuir adsorption isotherm, it is apparent that the rate for a reaction will be sensitive to multiple variables including reaction temperature, pressure, and the catalyst employed. It is therefore essential to ensure that these variables are accounted for when determining the kinetics of a chemical reaction²⁷. It is also essential to ensure that the reaction is not carried out in the realm of diffusion control where the rate is inhibited by processes surrounding the diffusion of reactants or products to/from the catalyst surface²⁷. When these conditions are met, the study of reaction kinetics forms a key component in the determination of reaction mechanisms and other detailed studies of catalytic properties.

1.3 Nanoparticle catalysis

By far the most common form for heterogeneous catalysts is as highly dispersed metallic particles with sizes in the nanoscale range deposited on a high surface area support¹. These systems have been used extensively in industrial processes for over 100 years, however it was not until much more recently that synthesis and characterization techniques advanced to a point where detailed investigations of these systems were possible¹. These advances have increased the focus on continued development of nanoparticles as catalytic systems, leading to a dramatic increase in the number of publications relating to the study of nanocatalysts since the early 1990's (Figure 1.3).

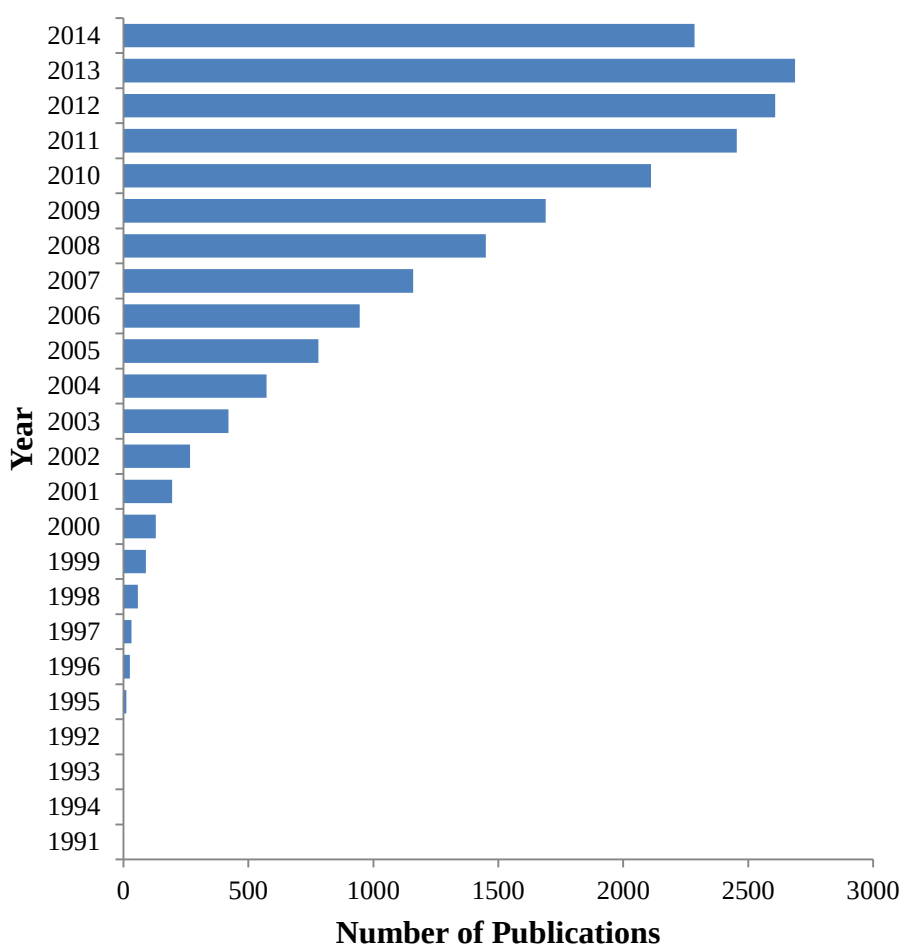


Figure 1.3 – Number of publications pertaining to nanoparticle catalysis per year from 1991 to partway through 2014. Obtained from searching for the phrase “nanoparticle catalysis” in SciFinder.

One of the clearest advantages of the active phase of heterogeneous catalysts being composed of highly disperse nanoparticles is the dramatic increase in active surface area over systems comprised of metallic thin films, with surface areas in nanocatalytic systems typically ranging from 10 to 100 m² per gram of active phase²⁴. And given that approximate costs for Pt and Pd (common materials for the active phase of heterogeneous catalysts) were £814.84 and £490.77 per ounce, respectively, at the time this thesis was produced, there is clear economic motivation to decrease the amount of metal required to make up the active phase for a catalyst²⁸. However, the advantages of nanocatalytic systems over their bulk counterparts are not derived solely from considerations of relative active surface areas as the inherent catalytic properties of the system also change dramatically when bulk materials approach the nanoscale.

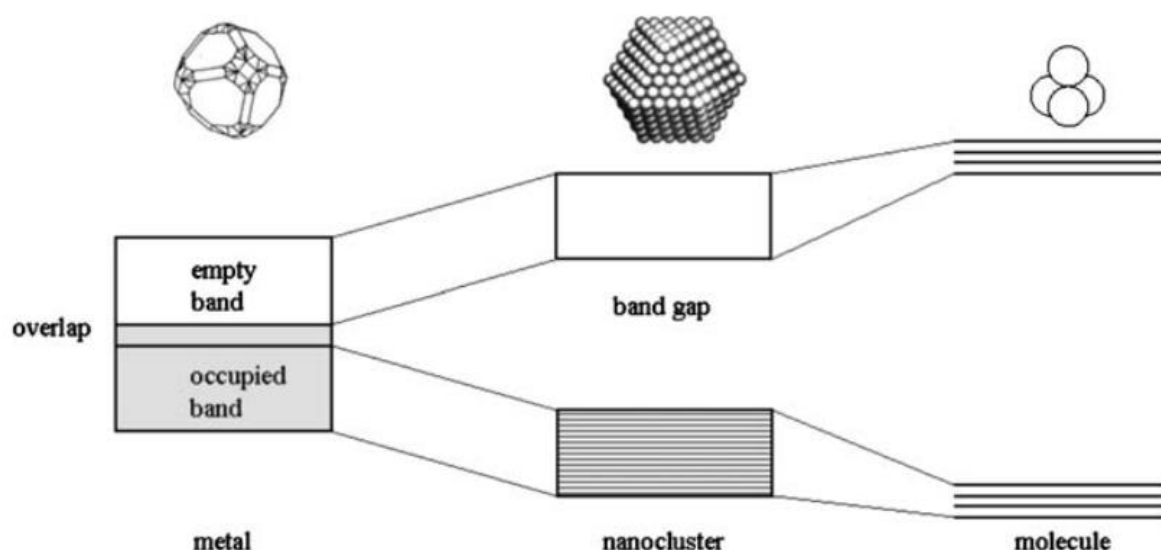


Figure 1.4 – Illustration demonstrating the differences in band structure for bulk metals, metal nanoclusters, and isolated molecules. Reproduced from reference²⁹.

The properties of metallic nanoparticles represent something of a transition state between the physical and electronic structures of bulk metals and individual molecules (Figure 1.4). When a metal is in the form of a bulk crystal, overlapping atomic d-orbitals from an extremely large

number of metal atoms result in the formation of a complete, continuous band structure where the spacing between energy levels (δ) can be calculated from Equation 1.8:

$$\delta = \frac{E_f}{n} \quad \text{Equation 1.8}$$

where n is the number of atoms in the particle and E_f is the energy of the Fermi level for the metal²⁹. In a bulk metal where the number of atoms in the crystal approaches infinity, the spacing between energy levels essentially becomes non-existent and the density of states (DOS) is high. However, as the number of atoms in the crystal is decreased, contributions from atomic orbitals to the band structure are reduced leading to an increase in the spacing between energy levels within the band. When the number of atoms present is small enough that the system resembles individual molecules, the band structure devolves completely resulting in the formation of discrete molecular orbitals³⁰. The unusual catalytic properties of nanoparticles arise from gradual changes in d-band structure and energy level spacings/DOS in the transitional region between bulk and molecular systems as electrons become more localized to individual atoms whilst still maintaining a degree of the band structure inherent to metallic systems³⁰. These intermediate properties allow nanoparticles to exhibit higher activity for catalytic processes than their bulk counterparts, but without requiring individual surface atoms to undergo a formal change in oxidation state typical of isolated atoms in homogeneous catalytic systems.

The most often invoked example of the changing reactivity for nanosized metallic particles is the case of nanogold, which has been studied extensively ever since pioneering experiments into the catalytic properties were conducted by Haruta *et al.* in the early 1980's³¹. When gold is present in the bulk state, its chemical reactivity is so low it is considered to be inert. However, changes to the d-band structure as gold particles transition from the bulk state to the nanoscale drastically enhance the catalytic properties of the system to the point where gold nanoparticles smaller than

approximately 5 nm become highly active catalysts for numerous reactions including CO oxidation and propene epoxidation^{26,32}.

The upper size boundary for “nanoscale” systems is typically placed around 100 nm, although it is generally accepted that d-band structure does not deviate substantially from the bulk in nanoparticles larger than approximately 10 nm^{26,33}. An estimate for the lower boundary of traditional nanoscale systems is placed at approximately 1 nm, as decreasing the number of atoms beyond this point leads to a complete loss in metallic character^{34,35}. As the band structure transitions toward the discrete energy levels of a molecule, the spacing between energy levels increases to a value greater than the thermal energy ($k_B T$) of the system, and the particles begin to behave as insulators²⁹. Particles in this size range are more appropriately referred to as “nanoclusters”, and their properties are rarely characterized by the same principles that are applied to standard nanoparticle systems³⁶.

1.4 Size effects

The previous section confined metal nanoparticles to a specific size region that covers a portion of the band structure continuum arising from the transition of systems from a bulk metal down to a single isolated atom. However, this begs the question of how do the specific properties of metal nanoparticles change when the size is varied within this nanoscale regime?

The simplest consequence of changing the average size of metal nanoparticles is a corresponding change in the number of surface atoms per particle relative to the number of atoms contained within the bulk, which was already discussed as one of the biggest advantages to the use of highly disperse nanoparticles in heterogeneous catalysis. However, a second and slightly more subtle consequence of changing particle size is a corresponding change in the relative prevalence

of surface atoms with a specific coordination number³⁷. When working with nanoscale systems, it is important to realize that the surface structure of particles is not uniform, instead resulting from a combination of different crystal facets and defect sites. This concept is most easily visualized by considering an idealized geometric representation of a metal nanoparticle, such as the model truncated cubooctahedron depicted in Figure 1.5 below.

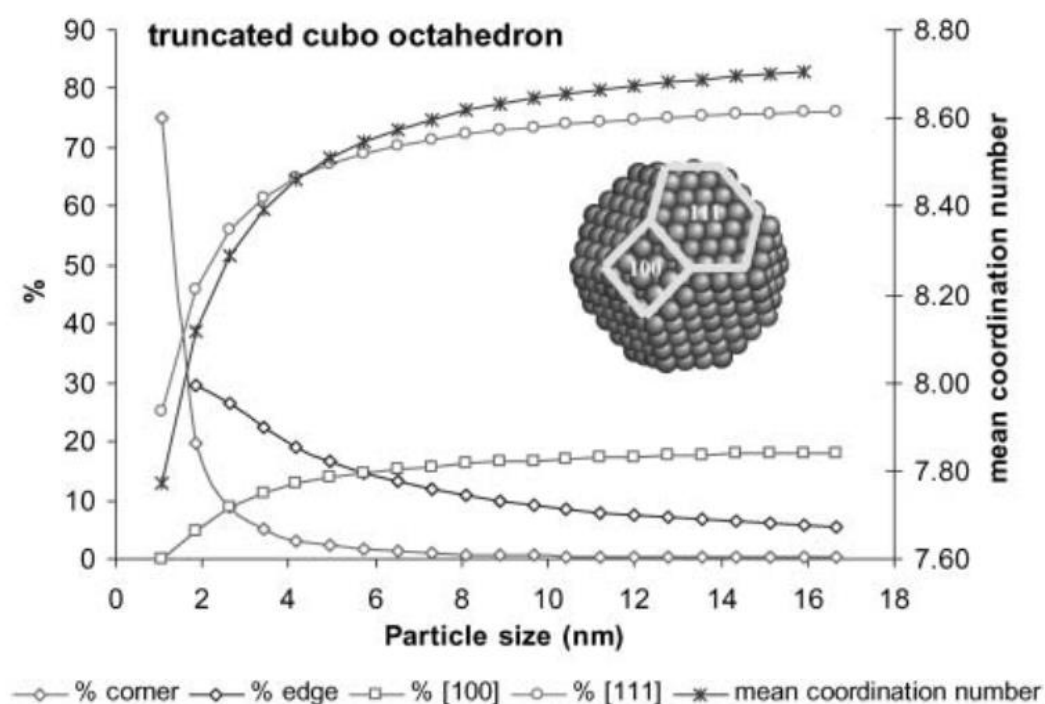


Figure 1.5 – Relationship between particle size and the relative prevalence of surface atoms in different types of active sites along with the mean coordination number for surface atoms. Reproduced from reference⁴⁷.

As Figure 1.5 illustrates, the surface of a cubooctahedral nanoparticle is comprised of both (111) and (100) crystal planes and the atoms present demonstrate a range of coordination numbers. Surface atoms contained entirely within the (111) facets are the most coordinatively saturated with a coordination number of 9, followed by surface atoms within the (100) facets with a coordination number of 8³⁸. Edge atoms located at the boundary between two planes and corner atoms at the boundary between three planes are the most coordinatively unsaturated with

coordination numbers of 7 and 6, respectively³⁸. When the particle size is large, the surface is dominated by high-coordinate atoms located within the (111) and (100) crystal planes with very few edge and corner atoms present. However, decreasing the particle size changes the relative prevalence of the different types of surface atoms until the surface is eventually dominated by low-coordinate edge and corner atoms, with the most rapid transition in surface structure occurring for nanoparticles smaller than approximately 5 nm in diameter²⁶. Shifts in surface geometry resulting from changes in particle size can be expressed more concisely in terms of the average coordination number for atoms on the particle surface calculated based on the Benfield geometric model³⁹. As Figure 1.5 illustrates, this value provides an effective summary of the size-dependent geometric surface structure where increasing particle size to approximately 5 nm rapidly increases the average coordination number, after which point the values begin to level off while approaching the maximum surface coordination number of 9. While the specific arrangement of surface atoms will be different depending on the particle shape under consideration, the general concepts discussed for the example cubooctahedral nanoparticles hold for all systems³⁸.

Moving on from these relatively simple changes in surface geometric structure allows for consideration of the more subtle alterations in the electronic band structure of metal nanoparticles that accompany changes in particle size. Some of these effects were touched upon previously in Section 1.3 during the discussion of changes in band structure resulting from the bulk/nano/molecular transition, and the same general concepts can be applied to particles within the nano size range. In general, a decrease in nanoparticle size leads to a narrowing of the metal d-band and a corresponding shift in the energy of the d-band centre to a level closer to the Fermi level⁴⁰. The transition to lower average coordination numbers also leads to a decrease in the DOS near the Fermi level⁴⁰.

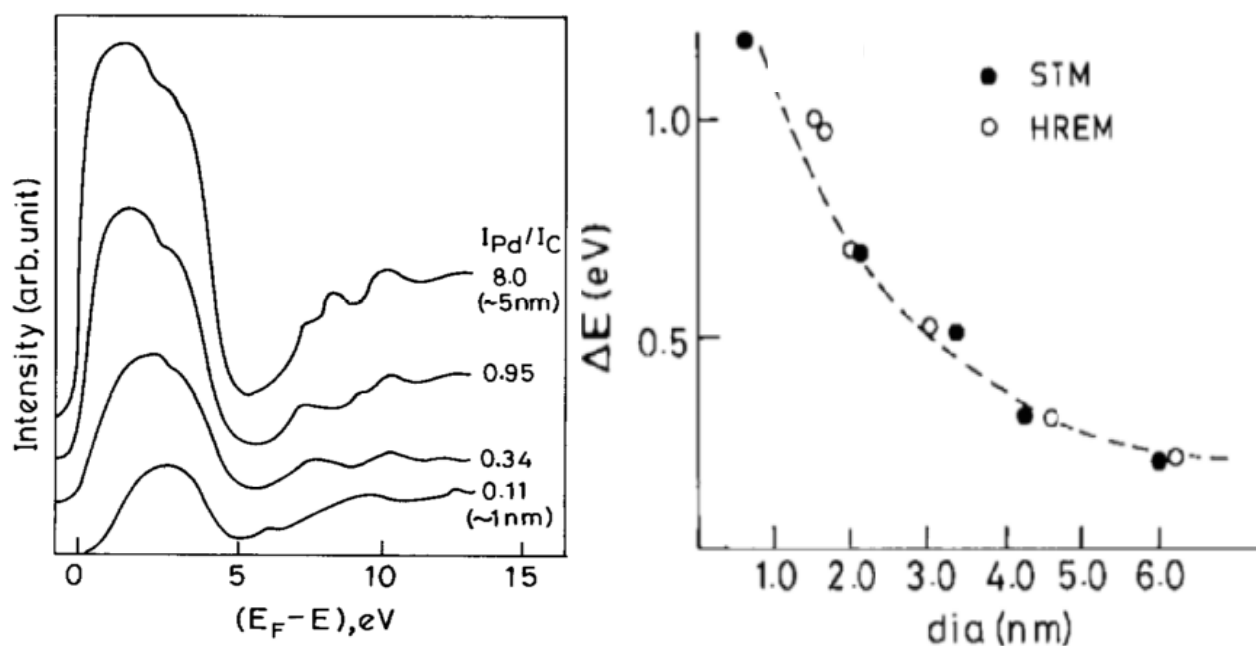


Figure 1.6 – Summaries of (a) UPS and (b) XPS results for Pd nanoparticles supported on graphite with a range of average sizes. XPS results show the position of the Pd 3d 5/2 peak with respect to the binding energy for Pd in the bulk state. Reproduced from reference⁴¹.

These concepts were demonstrated experimentally in a report by Aiyer *et al.* studying the effects of changing particle size on the d-band properties for Pd nanoparticles supported on graphite with average diameters ranging from 1.0 to 6.0 nm⁴¹. From the ultra-violet photo electron spectroscopy (UPS) measurements shown in Figure 1.6(a) above, the authors were able to conclude that decreasing particle size leads to a reduction in the DOS near the Fermi level and a narrowing of the spectral features attributed to the 4d states. A shift in maximum peak intensity to higher binding energies was also observed, and was confirmed by XPS results showing an increase in binding energy for the Pd 3d_{5/2} peak from the bulk value of 335.1 eV to 336.3 eV when particle size is decreased from 6.0 nm to 1.0 nm (Figure 1.6(b)). These results were taken as an indication of the progressive transition from metallic to insulating character as particle size is decreased. Similar increases in binding energy for core electrons as particle size is decreased

have also been reported for a range of other transition metal nanoparticles including Au, Ag, Ni, and Cu^{42,43}.

Given that the properties of d-band width, d-band centre, and DOS near the Fermi level all vary concurrently with particle size, it is generally sufficient to only consider one of them when comparing the size-related electronic structures of nanoparticles. Selecting the position of the d-band centre relative to the Fermi level as the parameter for comparison is a popular choice as it allows a direct relationship to be drawn between particle size and surface adsorption properties by application of the Norskov adsorption model. According to this theory, the position of the d-band centre relative to the Fermi level is a strong factor governing the filling of antibonding states for an adsorbate molecule and therefore correlates strongly with reactant adsorption strength²³. In large particles where the d-band is broad and the d-band centre is located well below the Fermi level, the antibonding states of an adsorbate are mostly filled leading to repulsion between the adsorbate and the metal surface, weak adsorption strength, and generally decreased reactivity. However, when the d-band narrows and the d-band centre shifts up as a result of decreasing particle size, decreased filling of the antibonding states for adsorbates results in increased adsorption strength. This change in adsorption behaviour with changing d-band structure is one of the key reasons small nanoparticles tend to exhibit higher reactivity than large nanoparticles⁴⁴.

The question that now must be addressed in greater detail is whether the changes in electronic d-band structure as a result of changing particle size are primarily due to changes in the total number of atoms in the particle or to changes in the average coordination number of atoms within the particle.

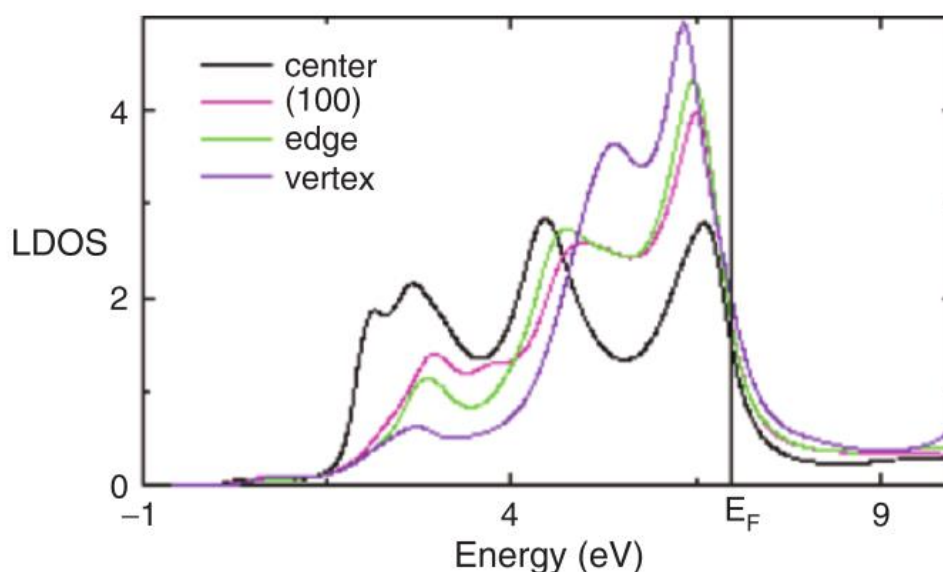


Figure 1.7 – Calculations of the LDOS for atoms in various bulk and surface positions in a Pd nanoparticle with 3874 atoms (approximately 5.7 nm diameter). Reproduced from references^{26,45}.

The relationship between the coordination number for an atom and the localized electronic structure was investigated in a report by Mottet *et al.* where the localized density of states (LDOS) was calculated for atoms located within the bulk structure and on the surface in low-coordinate (edge and corner) and high-coordinate (within the (100) crystal facet) positions (Figure 1.7)⁴⁵. From the clear decrease in LDOS that occurs when the coordination number decreases from 12 for atoms contained within the bulk structure to 6 or 7 for atoms present in low-coordinate sites, Mottet's calculations are able to clearly demonstrate a lack of uniform electronic structure throughout all atoms within a metal nanoparticle of catalytically relevant size. A corresponding narrowing of the d-band is also observed for atoms in low-coordinate positions, leading to a localized shift in the d-band centre towards the Fermi level at these sites⁴⁵. By again invoking the Norskov model, it is apparent that adsorption strength will be highest on surface atoms with highly unsaturated coordination numbers²³. Additional evidence of differing localized electronic structures for surface atoms with different coordination numbers is provided from a report by Zilm *et al.* detailing the study of CO adsorption to small Pd nanoparticles by ¹³C NMR⁴⁶. In this report, the authors noted that Knight shift effects resulting from coupling of the

active nucleus to surface electrons in the metal conduction band were much less significant for CO adsorbed to low-coordinate sites than high-coordinate terrace sites. This was attributed to low-coordinate sites being electronically decoupled from the bulk structure in good agreement with the previous report demonstrating a decrease in the LDOS near the Fermi level for these surface atoms.

It is not difficult to extend the principles just presented to explain the changes in overall d-band structure and DOS that occur upon changing particle size as a simple consequence of average coordination number. This argument is also supported by the simple observation that electronic properties only vary significantly over the same size region where average coordination varies significantly^{41,47}. However, while this explanation makes it tempting to interpret the general d-band structure as a simple average of the local electronic structure for each atom in the particle, there is some debate in the literature as to how influential the average coordination number is in determining electronic structure when coordination number and particle size are not varied concurrently. In a report by van Bokhoven *et al.*, theoretical calculations performed on gold nanoclusters did demonstrate that d electrons are not distributed evenly amongst atoms with differing coordination numbers in agreement with the results discussed previously⁴⁸. However, the same calculations also showed that localized electronic structure is not solely dependent on the coordination number. When only the properties of coordinatively saturated atoms were considered, increasing particle size still led to a broadening of the d-band, a lowering of the d-band centre relative to the Fermi level, and an increase in the LDOS⁴⁸. From these findings, the authors concluded that varying the particle shape would have a slight effect on the electronic structure due to changing average coordination number for the particles, however this effect was expected to be relatively insignificant compared to the effects resulting from changing the number of atoms in a particle.

It is clear from the discussion presented in this section that changes in particle size lead to changes in both the geometric and electronic structures for metal nanoparticles. These changes are most significant for nanoparticles in the 1-5 nm size range, and are virtually non-existent once nanoparticles exceed a size of 10 nm^{41,47}. Nanoparticles that fall within this size range are therefore the most interesting when investigating the catalytic behaviour of these systems. And when it comes to determining whether the effects of changing geometric or electronic structure dominate for a particular size range, literature reports indicate that small particles are dominated by electronic effects⁴⁹. However, for nanoparticles containing more than 2000-3000 atoms (approximately 3 nm in diameter), changes in geometric surface structure were found to be the main determiner of catalytic behaviour^{30,49}.

1.5 Surface sensitivity and surface modification

From the discussion of localized electronic structure on the surface of metal nanoparticles presented in Section 1.4, it is logical to expect that not all surface atoms will show uniform catalytic behaviour for all reactions. Reactions where the catalytic activity varies depending on the arrangement of atoms on the surface of a catalyst are termed “surface sensitive”. The concept of surface sensitivity in heterogeneous catalytic reactions was pioneered in 1966 when Boudart and his colleagues first expressed catalytic activity in terms of TOF, rather than TON⁵⁰. By first titrating the active surface area of Pt catalysts with different dispersions, the authors were able to demonstrate that TOF for the hydrogenation of cyclopropane was insensitive to the particle size, and thus likewise insensitive to the specific geometric arrangement of surface atoms⁵¹. This concept of considering the availability of surface active sites independently from the total amount of catalyst in a system has become central to a fundamental understanding of heterogeneous catalysis, however it wasn't until more than a decade later that the first report of a

surface sensitive reaction was made for the synthesis of ammonia over supported Fe nanoparticles⁵². This particular reaction is an excellent example of the important role surface sensitivity plays in the intelligent design of catalytic systems, as it was later discovered from studies over single crystals that the (111) facets of Fe are the most catalytically active surface by more than two orders of magnitude⁵³. Since this time, many reactions have been reclassified as surface sensitive and the methods for investigating and classifying the nature of this surface sensitivity have grown in sophistication and precision. Traditionally speaking, the surface sensitivity of a reaction is only stated with regard to the specific geometric surface structure of the catalyst. However, as it is clear that these effects are also tied to the electronic structure of specific surface active sites, methods of investigating surface sensitivity by varying both geometric and electronic structure of the catalyst will be discussed in the following sections.

1.5.1 Geometric effects

The study of the relationship between catalytic activity and geometric structure essentially boils down to the question of which surface sites are most active or selective for certain reactions, and why? Experimental methods of answering this question rely on modifying catalysts in such a way as to change the number of available active sites in order to observe the effects on catalytic behaviour. These “geometric effects” can be achieved by altering the size and/or shape of nanoparticles to control the prevalence of surface atoms with a particular coordination number. They can also be achieved by simply blocking surface active sites as a result of depositing nanoparticles on a support or addition of modifying ligands, supporting polymers, or decorating adatoms⁵⁴. Once the relationship between catalytic behaviour and geometric structure is understood, it can be utilized to design catalysts with properties tailored to the activity and selectivity requirements of specific reactions.

The ability to control particle size has long been present in the field of heterogeneous catalysis, and as such it is one of most commonly employed methods for modifying the geometric structure of metal nanoparticles⁵¹. The groundwork for this type of research was provided by the calculations of van Hardeveld and Hartog, which determined the distributions of surface atoms for nanoparticles of various morphologies and also demonstrated how the prevalence of these surface atoms changes with particle size³⁸. Since their development, the van Hardeveld and Hartog equations have been one of the most oft invoked methods for comparing the relative prevalence of different types of surface atoms in nanoparticles⁵⁵.

When using changes in particle size to determine the relationship between catalytic behaviour and geometric structure, it is also important to consider possible complications from corresponding changes in electronic structure. As Section 1.4 clearly indicated, the geometric and electronic properties of metal nanoparticles are inherently linked within the size range most relevant to catalytic applications, and separating the competing influences on catalytic behaviour has historically proven to be a difficult challenge⁴⁰. As such, many current studies attempting to isolate the geometric sensitivity of a particular reaction employ catalysts composed of relatively large metal nanoparticles, as these systems tend to exhibit bulk properties and are less sensitive to electronic variation³⁰. However this was not taken into account in many of the early studies where changes in particle size were used to determine surface sensitivity, and as a result the conclusions reached in early literature reports are often conflicting⁵⁶.

Recently, colloidal nanoparticles have been shown to be promising for use as model systems due to ease of synthesizing nanoparticles with narrow size distributions and excellent size control^{57–59}. And while it is more challenging to prepare stable dispersions of large nanoparticles, studies

do exist that have successfully used variations in particle size above the realm of dominant electronic effects to examine the relationship between changing geometric properties and catalytic behavior⁴². For example, Semagina *et al.* investigated the hydrogenations of 1-hexyne and 2-methyl-3-butyne-2-ol over cubooctahedral Pd nanoparticles with average diameters ranging from 6-14 nm and found that the reactions exhibited structure sensitivity without complications from additional underlying size effects^{60,61}. The increase in TOF with increasing particle size led the authors to conclude that extended terrace sites on the catalyst surface were the active sites for both alkyne hydrogenations. Of course, determining geometric effects by varying particle size still presents challenges even when the particles are large enough to eliminate complications from electronic modification because changes in the relative prevalence of surface sites also become relatively minor³⁸. In a study comparing particle size effects for the gas-phase hydrogenations of 2-methyl-3-butyne-3-ol and 2-methyl-3-buten-1-ol over silica-supported cubic Pd nanoparticles, no change in activity was observed when the particle size was increased from 10 to 18 nm despite previous literature reports indicating both reactions are surface sensitive⁶². Given the large sizes of the two particles being compared, the lack of activity change was attributed to the only minor difference in active site distribution on the particle surfaces (surface is 90% terrace atoms for 18 nm cubes versus 83% for 10 nm cubes).

To overcome some of these challenges, additional colloidal techniques have recently been developed that also allow for accurate control of particle shape. Synthesis methods have been tailored to selectively produce a vast range of nanoparticle morphologies for various transition metals, including cubes, octahedrons, hexagonal and trigonal plates, and pentagonal rods achieved by specific combinations of stabilizers, reducing agents, synthesis conditions, and shape directing agents⁶³⁻⁶⁵. The arrangement of atoms on the surface of a nanoparticle is highly dependent on the morphology, with some shapes showing a mixture of crystal facets while others

display a nearly uniform surface³⁸. For example, the model cubooctahedral nanoparticle shown in Figure 1.8 below is composed of both (111) and (100) crystal facets, while the surfaces of the model cubic and octahedral nanoparticles are composed exclusively of (100) and (111) facets, respectively. By comparing the catalytic behaviour of particles with different morphologies, conclusions can therefore be drawn about the surface sensitive nature of a particular reaction.

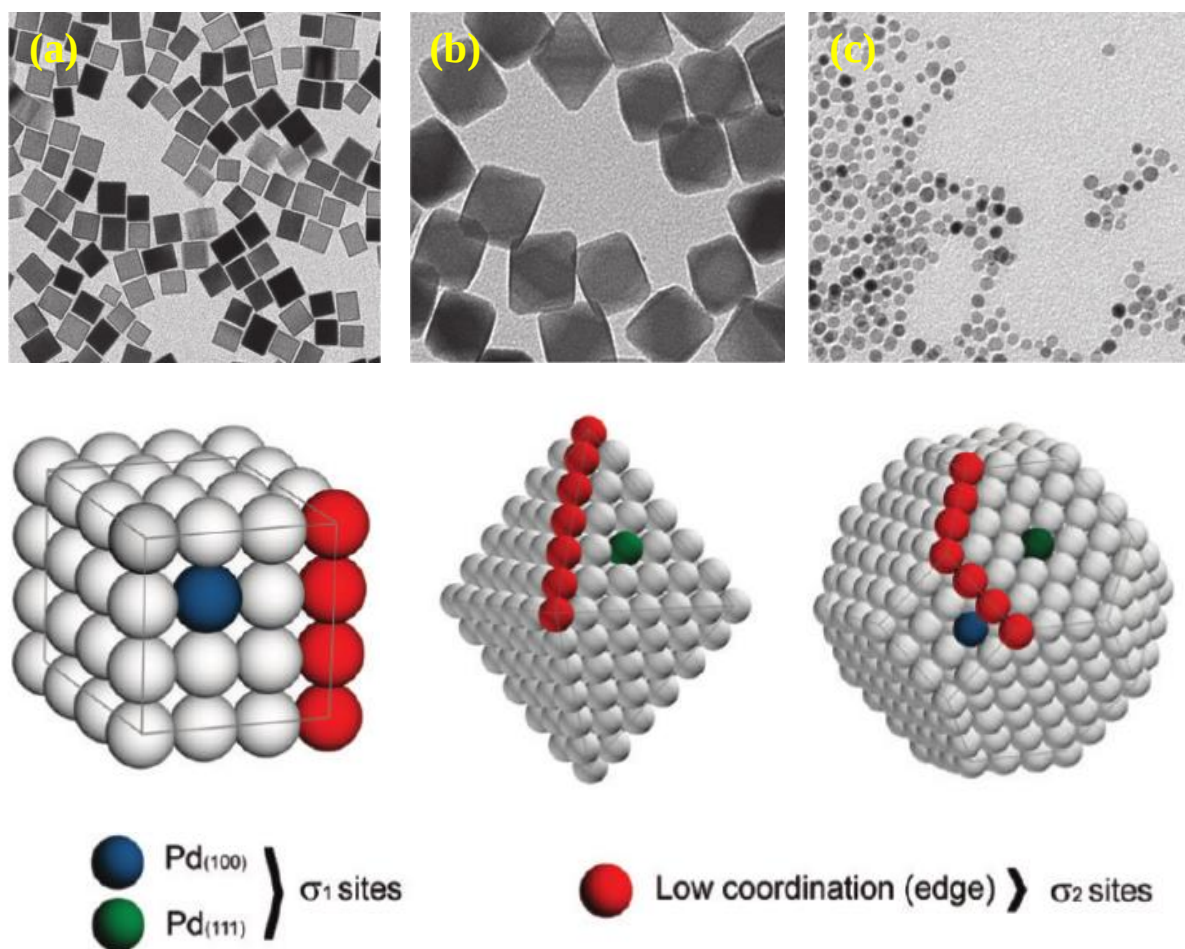


Figure 1.8 – TEM images from the shape controlled synthesis of nano-sized Pd (a) cubes, (b), octahedrons, and (c) cubooctahedrons along with corresponding model particles showing the prevalence of surface atoms in terrace (σ_1) and low coordination (σ_2) sites. Modified from reference⁶⁶.

An excellent example of this geometric modification technique can be found in a report by Crespo-Quesada *et al.*, where the authors employed shape controlled synthesis methods to create model systems of cubic, octahedral, and cubooctahedral Pd nanoparticles with sizes large enough

to minimize any uncertainties in electronic structure (Figure 1.8 above). Catalytic properties of the different morphologies were then compared in order to determine structure sensitivity for the catalytic hydrogenation of 2-methyl-3-butyn-2-ol⁶⁶. By comparing results for the cubic and octahedral systems displaying exclusively (100) and (111) crystal facets, respectively, the authors were able to demonstrate a slightly higher TOF for alkyne hydrogenation over the more coordinatively unsaturated (100) facets (19.2 sec^{-1} versus 15.6 sec^{-1}). However, selectivity to the desired alkene intermediate was shown to be independent of these crystal facets for all three systems, instead correlating solely with the number of low-coordinate atoms present on the surface. Aside from simply determining the surface sensitivity of the target reaction, the authors were also able to use these results to predict the ideal Pd nanoparticle size and shape required in order to achieve optimal catalytic activity and selectivity for 2-methyl-3-butyn-2-ol conversion⁶⁶.

A less common but also promising technique for investigating surface sensitivity is the control of surface geometric properties through the selective decoration of active sites. This enables small particles with more interesting geometric and electronic structures to be studied without the potential complications of changing particle size. Anderson *et al.* utilized this surface modification technique to investigate surface sensitivity for the hydrogenations of 1-hexene and 2-hexene over supported Pd nanoparticles by selectively blocking low-coordinate surface sites with Bi adatoms⁶⁷, and similar systems of Bi and Te decorated Pd nanoparticles were recently used by Jones *et al.* to demonstrate active site preferences for the dehydrogenation and dehydration mechanisms of formic acid decomposition on Pd nanoparticles (Figure 1.9 below)⁶⁸. In this second case, the authors were able to take advantage of differences in the surface sensitivity for the two mechanisms to decrease poisoning effects from CO by geometrically modifying the catalyst to limit decomposition of formic acid *via* the dehydration reaction pathway. Selective decoration of the metal surface has also been employed to determine the

prevalence of specific active sites on the metal surface. In a report by Rodriguez *et al.*, the authors used the specific redox potential for adsorption of Te adatoms to (111) planes on the surface of a platinum electrode to quantitatively estimate the number of terrace active sites⁶⁹.

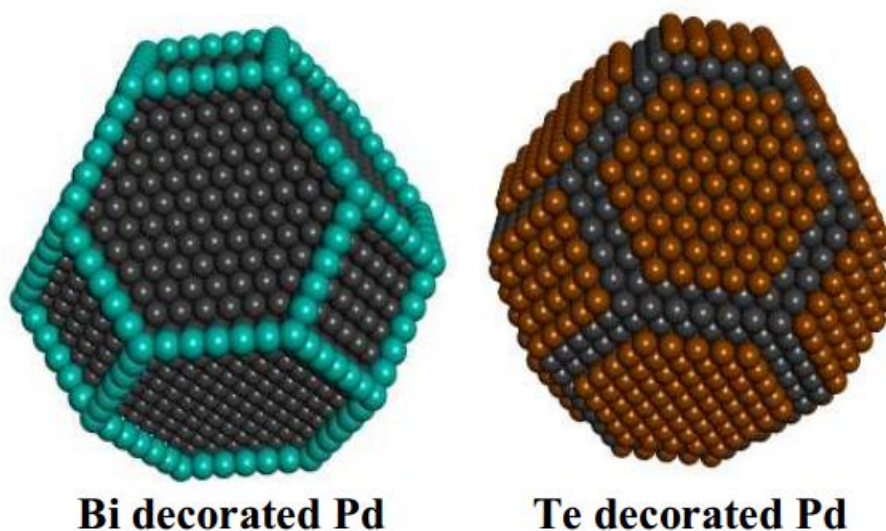


Figure 1.9 – Cubooctahedral Pd nanoparticles with (a) selective decoration of low-coordinate active sites by Bi adatoms and (b) selective decoration of terrace active sites by Te adatoms. Modified from reference⁶⁸.

1.5.2 Electronic effects

When the topic of investigating surface sensitivity by using changes in particle size to control geometric structure was addressed in Section 1.5.1, it was mentioned that particle sizes tend to be large in order to avoid complications from simultaneous changes in electronic structure. However, for nanoparticles in the size range most relevant for catalytic applications, changes in particle size do noticeably affect the electronic structure resulting in “electronic effects” which lead to a change in the affinity of one or more types of active site for a particular substrate⁵⁴. Unlike geometric effects, electronic effects are not specifically tied to the surface sensitivity of a particular reaction as they have the potential to affect catalytic behaviour for surface sensitive and surface insensitive reactions alike. As a result, changing the particle size and/or shape in

order to tune electronic properties is rarely used as a method for investigating surface sensitivity for a reaction. Even specifically addressing the relationship between catalytic behaviour and electronic structure is relatively uncommon in the literature due to difficulties in separating the electronic and geometric effects of changing particle size⁴⁰.

However, these challenges and the lack of literature directly addressing electronic effects should not give the impression that consideration of these effects is a new concept. In fact, in the first paper to report a particle size effect for hydrogenation reactions published by Boitiaux *et al.*, the authors addressed an electronic component to changing particle size which they believed was responsible for increased selectivity in the hydrogenation of 1-butyne towards the 1-butene intermediate over Pd due to a decrease in adsorption strength for the alkyne⁷⁰. However, this study also serves to highlight some of the common complications that plague literature reports of this type. When investigating particles with dispersions ranging from 20% to 100%, the authors used synthesis processes requiring three different metal precursors and three different supports (α -alumina, γ -alumina, and silica) with vastly different surface areas and metal loadings, however subsequent studies have since demonstrated that all of these parameters have the potential to affect catalytic behaviour^{1,40}. Additionally, lack of precision in the synthesis methods makes it difficult to fully exclude the influence of geometric effects on the observed catalytic behaviour.

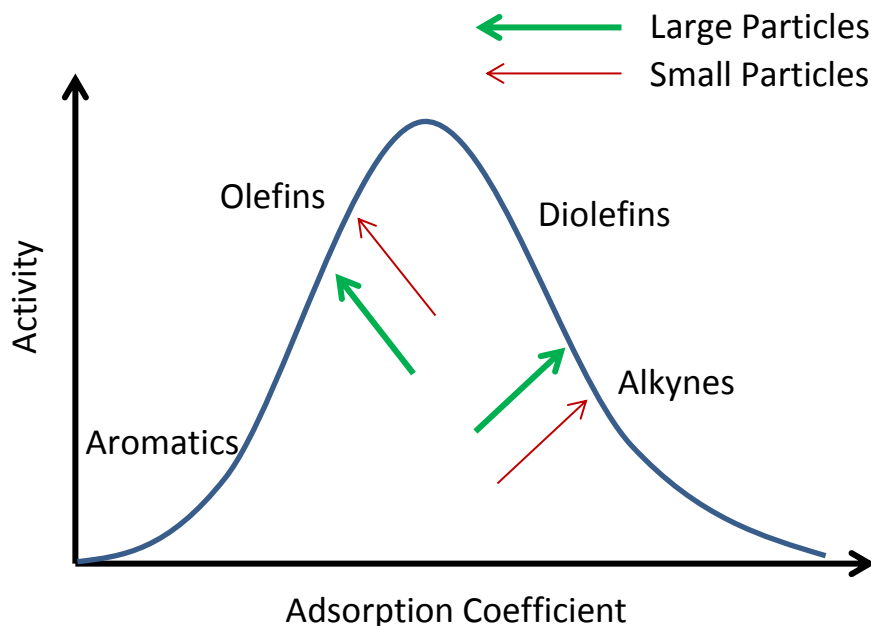


Figure 1.10 – Relationship between the catalytic activities of Pd nanoparticles for alkyne and alkene hydrogenations, the adsorption coefficient of the reactants, and the particle size. Modified from reference⁷¹.

In a later report by Hub *et al.*, electronic effects of changing particle size were again observed for heterogeneous catalysts composed of alumina-supported Pd nanoparticles with dispersions ranging from 26% to 97%⁷¹. In this case, the authors found that changing particle size had differing effects on the hydrogenation activity for the Pd catalysts, with highly dispersed, electron-deficient nanoparticles exhibiting increased activity for the hydrogenation of 1-butene but reduced activity for the hydrogenation of 1-butyne. The contrasting results were explained from a derived volcano plot for the adsorption of reactants with unsaturated carbon-carbon bonds to Pd shown in Figure 1.10. According to this plot, the differing effects on hydrogenation activity for the two reactants can both be traced to decreased reactant adsorption strength, with the seemingly conflicting results arising from the activity for 1-butyne hydrogenation being desorption limited whilst activity for 1-butene hydrogenation is adsorption limited. However, the authors' exclusion of possible geometric influences for the observed effects was contingent upon the hydrogenations of both 1-butyne and 1-butene requiring the same surface active sites, a

conclusion which has been subject to debate in other literature reports where similar reactants are considered^{66,70}.

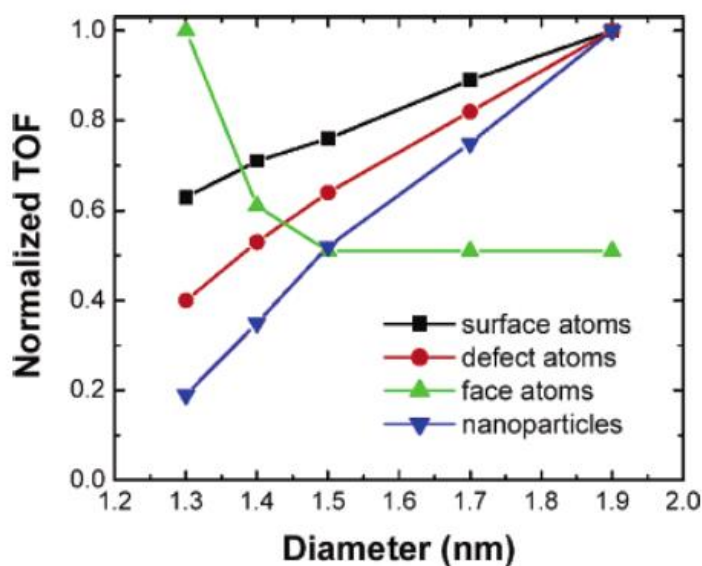


Figure 1.11 – TOF's for the hydrogenation of allyl alcohol catalysed by dendrimer-stabilized Pd nanoparticles of varying sizes. TOF's are normalized to the number of surface atoms, defect (edge and corner) atoms, face atoms, and total number of nanoparticles present. Reproduced from reference⁷².

A more recent report by Wilson *et al.* represents one of the few studies that report electronic effects of modification after systematically addressing and dismissing the geometric variations that occur as a result of changing particle size⁷². In this case, the relationship between particle size for a series of dendrimer-stabilized cubooctahedral Pd nanoparticles and activity for allyl alcohol hydrogenation was investigated. By reporting TOF's relative to the number of low-coordinate (defect), terrace (face), and surface atoms along with the total number of nanoparticles present, the authors were able to show that catalytic activity was directly proportional to the number of available terrace atoms for nanoparticles between 1.5 and 1.9 nm in diameter (Figure 1.11). Therefore, deviation from this relationship for nanoparticles below 1.5 nm in diameter was able to be attributed to the changes in electronic structure that result from decreasing particle size⁷².

1.5.3 Reaction modifiers

The topics just discussed in Section 1.5.2 highlight the potential for controlling catalytic activity and selectivity for a given reaction through tailoring the specific electronic structure of a catalyst. However, given the complications that arise when attempting to modify electronic structure by controlling particle size, it is a much more common practice to accomplish this goal through the use of catalyst modifiers which may take many forms including traditional heterogeneous supports, polymeric supports, or organic ligands. All three modifier types can be used to alter the electronic properties of metal nanoparticles, and some levels of geometric modification may also be possible due to selective blocking of active sites or changes in particle morphology due to strong interactions between nanoparticles and the modifier^{73,74}.

Changes in electronic properties resulting from interaction between metal nanoparticles and traditional heterogeneous supports are perhaps the most well-known and widely researched form of modification⁵⁵. This “metal-support interaction” (MSI) can be utilized to tune the electronic characteristics of small metal nanoparticles to improve activity and/or selectivity for catalytic reactions depending on specific properties of the support such as acid/base character or surface free energy^{1,75}. More recently, similar principles for modifying the electronic structure of metal nanoparticles have also been applied to polymer-supported systems by controlling the acid/base character of functional groups on the polymer chain⁷⁶.

The use of organic ligands as catalyst modifiers to control the electronic properties of metal nanoparticles is also widely reported in the literature⁷⁷. The concept is borrowed from traditional homogeneous systems, where the catalytic properties of active sites in coordination complexes can be finely tuned through the choice of ligands with different functional groups. The

relationship between the catalyst and ligand-type modifiers is very similar to that of a polymer support, however the interaction is easier to tailor as the catalyst need not be synthesized in the presence of the modifier⁷⁷. Amines are among the most common ligand modifiers, and are purported to act as electron donors, increasing the electron density of the catalyst surface and stabilizing electron deficient metal centres^{78–80}. These effects have been observed *via* XPS measurements and shifts in vibrational frequency for probe molecules adsorbed to the metal surface. Utilizing these effects to improve catalytic activity and selectivity is a common practice in the design of alkyne hydrogenation catalysts, where an increase in electron density on the metal surface helps to destabilize adsorption of desirable alkene intermediates⁷⁷. For example, a report by Sakai *et al.* showed that modification of Ni catalysts with ethylenediamine led to improvement in final selectivity for the *cis* intermediates in the hydrogenations of 1-octyne and 2-octyne⁸¹, and similar modification of Pd catalysts led to enhanced initial selectivity in the hydrogenation of 1-hexyne to 1-hexene⁸². Probably the best known case of using amine ligands to modify the electronic properties of metal nanoparticles is Lindlar's catalyst, where CaCO₃ supported Pd-Pb nanoparticles are modified with quinoline in order to decrease activity for the isomerization and over hydrogenation of alkenes^{77,83}.

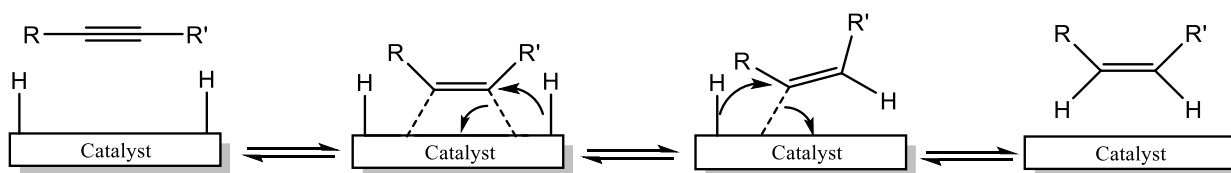
1.6 Catalytic hydrogenation of hydrocarbons

The catalytic hydrogenation or partial hydrogenation of unsaturated hydrocarbons is an economically important class of reactions in the chemical industry^{40,84}. These processes form an important step in the purification of feedstocks for polymerization reactions, where removal of alkyne impurities from the alkene reactant stream is required to prevent the deactivation of polymerization catalysts and/or defects in the structure of resulting polymers⁸⁴. Catalytic hydrogenation reactions are also used in approximately 20% of all processes for fine chemical production, including the syntheses of vitamins A, E, and K, and chemicals important to the

fragrance industry^{85,86}. The majority of late transition metals exhibit catalytic activity for the hydrogenation of unsaturated hydrocarbons, however heterogeneous catalysts with Pd as the active phase are considered to be the most versatile, particularly for reactions requiring the selective hydrogenation of alkynes to *cis*-alkenes⁸⁴.

1.6.1 Mechanisms of alkyne and alkene hydrogenations

The catalytic hydrogenation of alkynes over most heterogeneous catalysts initially results almost exclusively in the formation of *cis*-alkenes through the syn addition of 1 molar equivalent of hydrogen⁴⁰. In order to fully appreciate the origins of catalytic activity and selectivity for these partial hydrogenation reactions, it is necessary to consider the process in some detail and a general mechanism for the reaction is illustrated in Scheme 1.2 below.



Scheme 1.2 – General mechanism for alkyne hydrogenation over a heterogeneous catalyst via syn addition of one molar equivalent of H_2 .

Prior to adsorption to the catalyst surface, the R groups of the free alkyne are in a linear conformation imposed by the structure of the triple bond. However, adsorption to the catalyst surface formally breaks this triple bond, allowing the molecule to adopt a planar structure with the R groups directed away from the metal surface in a *cis* conformation in order to reduce steric hindrance. The presence of a double bond in the structure of the adsorbed alkyne throughout the addition of hydrogen prevents the molecule from undergoing a conformational change to form the more thermodynamically stable *trans* isomer⁴⁰. As long as this alkene intermediate desorbs from the catalyst surface after addition of a single molar equivalent of H_2 , the resulting products

will show high selectivity for the cis isomer. However, prolonged adsorption of the alkene intermediate formally breaks the double bond, allowing free rotation of the R groups upon further addition of hydrogen and potentially leading to isomerization of the alkene or complete hydrogenation to the alkane^{40,87}.

This mechanism has important implications for controlling the activity and selectivity of partial alkyne hydrogenation reactions, the goal of which is typically high selectivity for cis alkenes. As cis alkenes are the initial product of alkyne hydrogenation, the key to achieving high selectivity lies in limiting over-hydrogenation and isomerization processes by promoting desorption of the alkene intermediate and preventing its re-adsorption to the catalyst surface⁴⁰. This occurs in systems where alkyne adsorption is much stronger than the alkene intermediate. Competitive adsorption effects allow the alkyne reactant to both displace the alkene intermediate from the catalyst surface immediately after its formation and prevent its re-adsorption. In some systems, such as those employing Pd-based catalysts, the differences in relative adsorption strength for alkynes and alkenes are high enough to maintain nearly 100% selectivity for cis alkenes as long as there is alkyne present in the reaction mixture⁸⁷. However, this relationship between relative adsorption strengths and reaction selectivity also implies that altering the inherent selectivity of a system will require changing the thermodynamics for alkyne and/or alkene adsorption⁴⁰.

At present, almost 90% of literature reports relating to catalytic hydrogenation concern ethylene, with relatively little attention paid to the investigation of higher order alkenes and alkynes^{40,88}. However, the well-established surface insensitivity of ethylene hydrogenation makes it difficult to apply the findings of these studies to the hydrogenations of other alkene and alkyne reactants^{89–92}. Previous discussions throughout Section 1.5 concerning surface sensitivity and surface modification should provide an idea of the important role surface sensitive catalytic

hydrogenations of alkynes and alkenes plays in evaluating the geometric and/or electronic structure of a catalyst. However, this relationship can also be viewed from the opposite perspective, where controlled geometric or electronic modification of a catalytic system by changing particle size and/or shape can be utilized to determine the surface sensitivity of hydrogenation reactions. The following sections will thus focus on providing a brief review of literature reports concerning surface sensitivity for the hydrogenations of higher order alkynes and alkenes as determined by controlling a catalyst's geometric and/or electronic structure.

1.6.2 Surface sensitivity of alkyne hydrogenations

When investigating the surface sensitivity of alkyne hydrogenation reactions, reactants can be grouped into either internal alkynes or terminal alkynes based on the location of the triple bond. Both types of system were investigated in a report by Jackson *et al.* where the catalytic behaviour of palladium catalysts supported on alumina, silica, and zirconia was compared for the hydrogenations of 1-pentyne and 2-pentyne⁹³. In this study, the authors found that large particles exhibited the highest activity for internal alkyne hydrogenation, however the differences in activity for terminal alkynes resulting from changes in particle size were less pronounced. These results led to the conclusion that the hydrogenation of internal alkynes is surface sensitive, occurring primarily on extended terrace sites, whilst the hydrogenation of terminal alkynes is surface insensitive. It was later proposed that terminal alkyne hydrogenation should, in fact, be less surface sensitive than internal alkyne hydrogenation because terminal alkynes can adsorb in either parallel or perpendicular configurations to the surface of a catalyst, whereas internal alkynes can only adsorb in a perpendicular fashion⁹⁴. However, there are a number of reports in the literature with conclusions that contradict both of these generalizations. A study conducted by Papp *et al.* on the hydrogenations of various internal and terminal alkynes over supported Pd catalysts of differing sizes concluded that extended terraces on the catalyst

surface are the preferred active sites regardless of the triple bond location⁹⁵. This surface sensitivity for terminal alkyne hydrogenation is also supported by Crespo Quesada's work on the hydrogenation of 2-methyl-3-butyne-2-ol, which demonstrates a four-fold preference for hydrogenation over terrace active sites⁶⁶. These reports clearly indicate a level of disagreement in the literature when it comes to the surface sensitivities of alkyne hydrogenation, and this is perhaps best exemplified by considering the case of 2-butyne-1,4-diol hydrogenation. In literature reports by Joannet *et al.* and Telkar *et al.*, three separate systems of supported Pd catalysts were employed to study the hydrogenation of this internal alkyne, and three different conclusions were reached as to the surface sensitivity of the reaction^{80,96}. It should be noted that many of the literature reports mentioned in this section use variations in particle size and/or shape to control catalyst electronic and geometric structure. Therefore, a partial explanation for the contradictions between these reports may relate to the complications that arise when electronic and geometric structure are varied simultaneously, as was discussed previously in Sections 1.4 and 1.5. Additionally, the use of a wide variety of catalyst support materials and synthesis methods may further contribute to the differences in conclusions.

1.6.3 Surface sensitivity of alkene hydrogenations

Considerably more agreement is found between literature reports when the hydrogenations of internal and terminal alkenes are considered, and the general surface sensitivities for the reactions are clearly illustrated in a report by Anderson *et al.* concerning the hydrogenations of 1-hexene and 2-hexene. In this study, the authors compared catalytic behaviour of the Lindlar catalyst to unmodified Pd supported on calcium carbonate for the hydrogenation of 1-hexene and saw no difference in catalytic activity despite geometric blocking of surface terrace sites (Figures 1.12(a) and (b)), leading the authors to conclude that terminal alkene hydrogenation is specific to low-coordinate sites⁶⁷. However, when the same catalysts were tested for the hydrogenation of 2-

hexene, a clear loss in alkene hydrogenation activity was observed for the Lindlar catalyst in comparison to the unmodified Pd supported on calcium carbonate (Figures 1.12(c) and (d)), demonstrating that the hydrogenation reaction could not proceed without the presence of extended terrace sites.

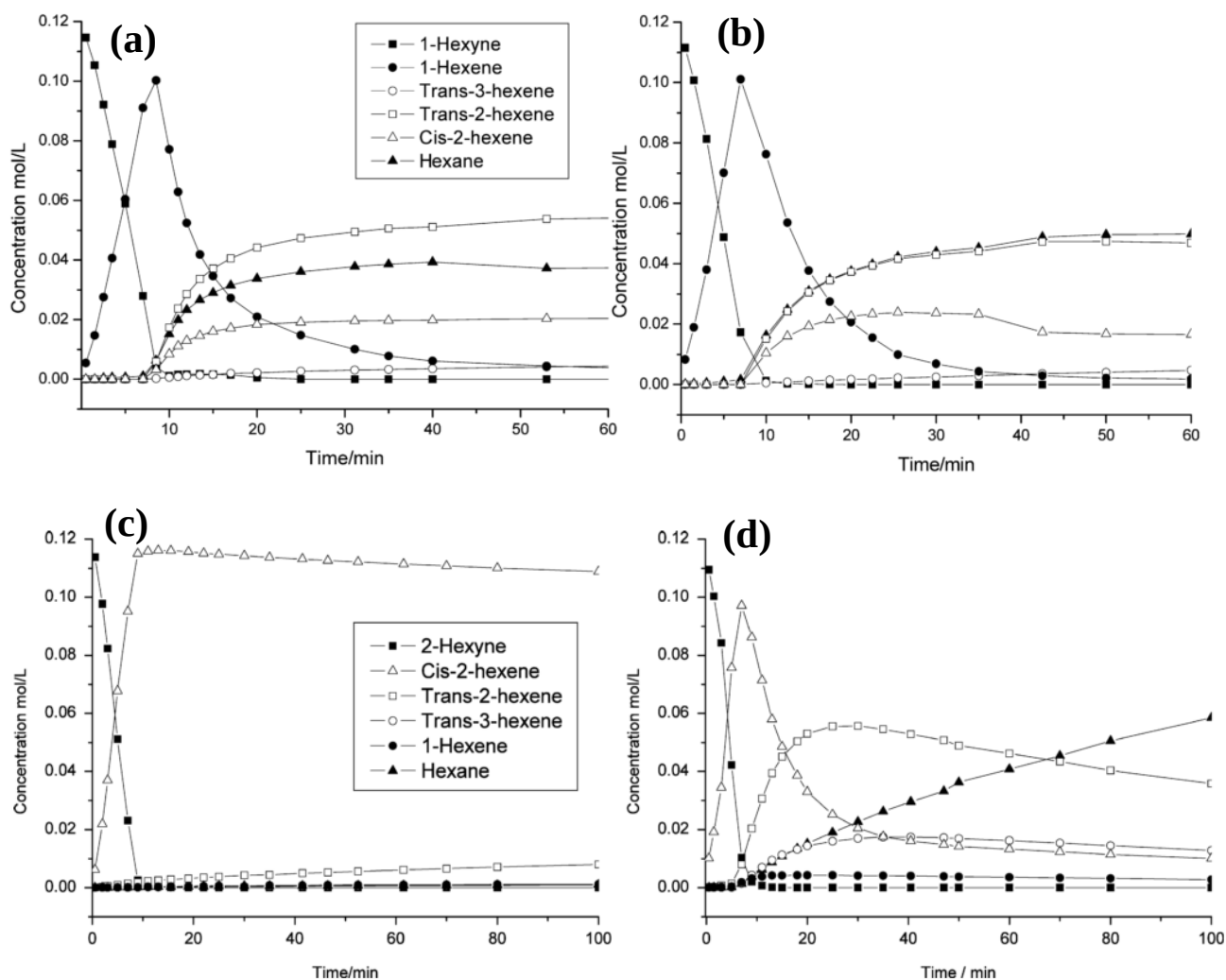


Figure 1.12 – Reaction profiles for the catalytic hydrogenations of 1-hexyne/hexene and 2-hexyne/hexene over (a) and (c) Lindlar's catalyst and (b) and (d) 5% Pd/CaCO₃. Reproduced from reference⁶⁷.

In the case of terminal alkene hydrogenation, these findings are supported by much earlier studies on the hydrogenation of propene over silica supported Pt catalysts conducted by Wachter

et al., where the authors observed that TOF for the reaction was directly proportional to the number of low-coordinate surface atoms⁹⁷. Additional literature reports concerning the surface sensitivity of terminal alkene hydrogenations have also come to similar conclusions^{74,98,99}. However, reports detailing the mechanisms of hydrogenation for internal alkenes are less common, with most of the focus in the literature directed toward more general studies on the activity and selectivity of these reactions.

1.7 Catalyst deactivation

The material presented thus far in this chapter has clearly demonstrated the significant impact the field of catalysis has made on industrial chemical processes dating back to the concept's first proposal over 150 years ago. However, it has only been relatively recently that experimental and characterization techniques have advanced to the point where catalytic processes can begin to be understood from a fundamental perspective. Sections 1.4, 1.5, and 1.6 of this introduction sought to provide insight into some these current topics in heterogeneous catalysis by exploring the fundamental relationships between catalyst structure, both geometric and electronic in nature, and catalytic behaviour for particular reactions. However, it should be noted that any discussion of the effects of deactivation processes for catalysts is conspicuously absent from these earlier sections. This is primarily because the current state of research into deactivation processes in heterogeneous catalysis lacks the level of depth and detail typically encountered when reports focus solely on catalytic processes. However, catalyst deactivation is still an extremely widespread phenomenon in industrial catalysis, resulting in the loss of billions of pounds each year due to reactor shutdown and catalyst replacement¹⁰⁰. This provides a strong economic incentive to increase understanding of deactivation processes to a level that is on par with current understanding of catalytic processes.

Catalyst deactivation is a broad term generally applied to any and all processes which lead to a loss in activity and/or selectivity of a catalyst for a given reaction¹⁰¹. Timescales for these processes are extremely varied, ranging from only a few minutes before the majority of catalytic activity is lost to thousands of hours of reaction time before significant effects are observed¹⁰². Types of catalyst deactivation also vary widely, and in order to consider these processes in detail they are typically grouped into five main categories: sintering, vapour transport, phase transformation, fouling or coking, and poisoning^{100,103,104}. Sintering is perhaps the most intuitive form of catalyst deactivation, as the loss in catalytic activity can be attributed to a simple decrease in active surface area due to agglomeration of the metal particles making up the active phase. Sintering is a common process in heterogeneous catalysts, particularly for systems where interactions between the metal and the support are weak or the active phase is comprised of highly-disperse, thermodynamically unstable nanoparticles. Deactivation as a result of vapour transport is also a relatively intuitive concept involving a loss of material comprising the active phase of a catalyst to the surrounding system. Phase transformation involves fundamental changes in the crystalline structure of a catalyst that occur when the metal is exposed to high temperatures. This type of deactivation process affects surface sensitive reactions, where the preferred active sites are related to a specific crystal plane. Deactivation through coking is a more narrowly defined process, resulting from the deposition of carbonaceous compounds onto the catalyst surface which prevents reactant molecules from interacting with the catalyst by blocking active sites or clogging pores in the support structure. However, catalyst deactivation through coking is widespread enough in industrial reactions to merit its own consideration as a separate deactivation process. The final class of catalyst deactivation processes, poisoning, results from chemisorption of a species to the surface of a catalyst in such a manner as to change the activity or selectivity the catalyst exhibits for a particular reaction.

1.7.1 Catalyst poisoning

Of the five categories of deactivation processes, poisoning is considered to be one of the most complicated to understand and the reasons for this can be understood by revisiting some of the principles of catalysis discussed previously in this chapter.

Firstly, the Sabatier principle was used in Section 1.2.1 to describe the ideal balance of adsorption strengths between a particular reactant and the catalyst surface, leading to optimal catalytic activity due to interactions which are not significantly limited by either adsorption or desorption processes²⁴. However, in practice most reaction mixtures contain a range of potential reactants, including reaction intermediates, products, impurities, and solvents or carrier gases, each of which will exhibit a unique interaction with the catalyst surface. If any one of these components adsorbs more favourably to the catalyst than the target reactant for a particular reaction, competition for active sites may become significant leading to a reduction in activity for the desired process. If this interaction becomes strong enough, adsorption becomes irreversible and the strongly adsorbing species is said to have “poisoned” the metal surface from further catalytic reactions¹⁰⁰. The term “poison” thus only carries an operational definition based entirely on the conditions, reactants, and catalyst present in the system being considered. Unfortunately, this also implies that each combination of catalyst, reactants, and reaction conditions may be poisoned by a different set of compounds. This results in a wide range of common poisons (including the group VA to VIIA elements, small molecules such as CO and NH₃, and numerous heavy metals) and a wide range of affected reactions (including ammonia synthesis, hydrogenation/dehydrogenation reactions, steam reforming, methanol synthesis, and oxidation of CO and hydrocarbons)¹⁰³.

Secondly, additional complications are introduced when the varying adsorption and reactive properties of different active sites present within a single system are also considered. These effects, which are the basis for surface sensitivity of catalytic reactions, were addressed in detail in Sections 1.4 and 1.5. When applied to catalyst poisoning, the concept of specific active sites means that understanding the mechanisms for these processes may be more complicated than simply examining the relative adsorption strengths of components present within the reaction mixture. If either the desired reaction or the poisoning process is surface sensitive, effects of deactivation will only be observed if the potential poison possesses high affinity for the same type of active site required to carry out the desired reaction.

Finally, the measurable effects of poisoning processes for a particular reaction may be further complicated by the fact that not all catalytic reactions, particularly those used in industry, operate under kinetic control¹⁰⁵. In cases where reaction rate and/or selectivity is controlled by diffusion processes, a decrease in catalytic activity as a result of poisoning may be sufficient to shift the reaction from diffusion control to kinetic control. This shift may have implications for catalytic activity and selectivity that are entirely independent of those related to the specific catalyst-poison interaction. This added complication also presents the possibility that the apparent influence a poison has on catalytic behaviour for a particular system will be dependent on the conditions under which that system is examined¹⁰⁵.

1.7.2 Sulfur as a catalyst poison

Sulfur containing molecules represent a particularly prominent class of catalyst poisons which exhibit strong deactivation tendencies for a wide range of heterogeneous transition metal catalysts employed for industrial processes¹⁰⁰. While the poisoning properties of sulfur have long been recognized in the field of heterogeneous catalysis, the interactions between sulfur and metal

catalysts which can result in drastic alterations of catalytic activity and/or selectivity are still not clearly understood¹⁰⁶. However, research into achieving a clearer understanding of the fundamental basis for the poisoning effects of sulfur has received increasing attention in recent years, partially due to steadily increasing concentrations of sulfur contaminants in feedstocks for energy production¹⁰⁶. These contaminants can lead to serious and irreversible deactivation for catalysts employed for processes such as steam reforming, hydrocracking, and catalytic conversion of automotive exhaust¹⁰⁰. It has also become increasingly expensive to replace poisoned catalysts where the active phase is composed of precious metals such as Pt, Pd, or Rh²⁸.

The negative effects of deactivation through sulfur poisoning can occur as a result of both geometric and electronic modification of the catalyst surface^{105,107}. In the case of geometric modification effects, the standard concepts of decreasing catalytic activity through the blocking of active sites discussed previously in Section 1.5 still apply and are still the most straightforward consequence of catalyst poisoning. However, sulfur poisoning of metal catalysts can also lead to several additional, and more complicated, geometric modification effects. For a number of transition metals including Ni, Fe, Mo, Cu, and Pd, strong interactions between adsorbed sulfur and the metal surface have been shown to cause reconstruction of the localized crystal structure over a range of approximately 2-3 atomic layers¹⁰⁸. These effects are particularly relevant for surface sensitive reactions, where extended distortions in the catalyst's surface structure may alter the geometric structure of required active sites beyond the adsorption site, resulting in significant deactivation effects even at relatively low coverages. Reaction conditions involving high temperature or pressure may also exacerbate these effects to the point where bulk sulfidation of the metal occurs¹⁰⁵. Geometric modifications of this type may also indirectly modify the electronic structure of the metal surface through strain effects, where localized compressions or expansions of the crystal structure affect d-band width, position of the

d-band centre, and DOS near the Fermi level²³. However, the electronic effects of poisoning by sulfur are more traditionally attributed to the interaction between the metal surface and unshared electrons on the adsorbing sulfur species¹⁰³. The strength of poisoning effects for various sulfur species can thus be roughly classified by considering how “shielded” or “unshielded” the sulfur atom is (ie, how many free lone pairs are available to interact with the metal surface), for example, H₂S is considered a stronger catalyst poison than SO₂¹⁰³.

1.7.3 Methods of preventing sulfur poisoning

Whilst it is impossible to completely avoid the poisoning effects of sulfur adsorption for catalysts used in industrial processes where sulfur is present as a contaminant, techniques for controlling the deactivation processes can help to prolong catalyst lifetimes¹⁰⁹. Currently, targeted removal of potential poisons remains the primary method for dealing with sulfur contaminants, however these processes are not completely effective and build-up of poisoning species will still occur over time^{103,109,110}. An alternative approach to the problem revolves around the regeneration of poisoned catalysts. As demonstrated by the high-temperature treatment of vehicle-aged catalysts, binding of sulfur to the metal surface can be considered reversible, however harsh conditions employed in the treatment processes may negatively impact catalytic performance in the regenerated systems¹¹¹. In the case of exhaust-treatment catalysts, the regeneration conditions permanently disrupt the oxygen storage capacity of the support¹¹¹. Currently, one of the most promising areas of research concerning prevention of catalyst deactivation by sulfur lies in the design of poison-resistant catalysts. These catalysts often include a scavenger component in their design that preferentially binds sulfur, such as ZnO in Cu-based catalysts for the synthesis of methanol. Supports can also be selected to preferentially convert highly toxic sulfur species to a less toxic form prior to interaction with the catalytically active phase¹⁰⁶. More general efforts to control the effects of sulfur poisoning can also be

undertaken by using changes in reaction temperature and pressure to alter the thermodynamic favourability of poisoning processes¹¹².

1.7.4 Sulfur modification to control catalytic behaviour

Despite the classical definition of sulfur as a catalyst poison, it is possible to take advantage of the significant changes in catalytic activity and/or selectivity that result from adsorption of sulfur to a catalyst. A long-standing example of utilizing the effects of sulfur modification to control catalytic activity is the sulfur passivated reforming (SPARG) process, where partial poisoning of Ni catalysts is used to limit the availability of active site ensembles required for the synthesis of carbon filaments that lead to coking in steam reforming reactions^{106,113}. Pre-treatment with sulfur is also commonly used in the case of Pt catalysts for reforming reactions. In this case, the high activity of the unmodified catalyst can result in undesirable side reactions such as hydrocracking and dehydrogenations¹⁰⁹. Controlling the catalytic activity by partially poisoning the catalyst with sulfur prior to the reaction also helps to prevent thermal runaway from occurring. Much more recently, Marshall *et al.* demonstrated the use of thiolate self-assembled monolayers (SAM's) to dramatically increase the selectivity of Pd catalysts for the hydrogenation of epoxybutene¹¹⁴. Additional reports have since appeared in the literature using similar ligand-type thiol-based systems to geometrically and/or electronically modify Pd catalysts to control catalytic activity and selectivity for the hydrogenations of *o*-chloronitrobenzene and α,β -unsaturated aldehydes^{115,116}.

The topics discussed in Sections 1.7.2, 1.7.3, and 1.7.4 serve to provide an introduction to the complex nature of the interaction which results from the adsorption of sulfur to the surface of transition metal nanocatalysts. And whether the effects of this interaction are considered detrimental or beneficial to the catalytic properties of a given system, it is clear that optimizing

the system benefits from a more fundamental understanding of principles governing sulfur poisoning. In some cases, this involves prolonging catalyst lifetime for catalytic processes where contamination by sulfur is problematic, potentially through modifying catalyst structure, support, or reaction conditions to improve sulfur tolerance. In others, a clearer understanding of the underlying principles may enable metal-sulfur interactions to be tuned in order to achieve optimal catalytic activity and/or selectivity for a given process.

1.8 Aims and objectives

As the previous sections in this introduction have clearly illustrated, the field of heterogeneous catalysis is a complex and continually evolving area of research. This has particularly strong implications for research into the nature of catalyst poisoning, where the large number of different catalytic systems leads to highly individualized deactivation processes due to complex relationships between potential poisons and the reaction conditions. Sulfur-based poisoning of heterogeneous catalysts is a particularly prominent topic in catalyst deactivation, however a fundamental understanding of the interactions between sulfur and transition metals which lead to deactivation is still lacking.

As such, the primary aim of this thesis was focused on exploring the fundamental interactions that result when sulfur adsorbs to the surface of transition metal nanocatalysts, with the overall objective of providing a foundation for the intelligent design of catalysts with increased tolerance for sulfur poisoning. These aims were addressed by investigating key aspects of the metal sulfur relationship, including metal-dependent and size-dependent interaction effects.

Recently-developed complimentary experimental techniques employing nanoparticles with clearly defined morphologies and structure sensitive hydrogenation reactions have been

instrumental to the investigation of the geometric and electronic properties of nanocatalysts under reaction conditions. In order to accomplish the aims of this thesis, the principles of these concepts were taken and carefully modified to allow the techniques to be applied to a detailed investigation of the effects of sulfur modification on metal nanoparticles.

1.9 Thesis overview

This thesis is divided into seven chapters, with Chapters 4-7 detailing the experimental work I have undertaken over the course of my DPhil degree.

Chapter 1 – Provides an introduction to the principles of catalysis, with particular emphasis on heterogeneous systems and more recent developments in the field of nanocatalysis. Focus is directed toward the fundamental properties of these systems including the relationship between electronic/geometric structure and the size, shape, or modification of the particles considered. Additionally, a summary of the literature pertaining to the mechanisms and surface sensitivity of alkyne/alkene hydrogenation reactions is given. Finally, an introduction to the principles of catalyst poisoning by sulfur is provided including an overview of the complexities of poisoning mechanisms, common strategies for minimizing deactivation effects, and recent developments in the field.

Chapter 2 – Summarizes key concepts relating to the background, theory, and application of experimental techniques employed for the characterization of systems and materials throughout this thesis.

Chapter 3 – Provides detailed descriptions of the experimental conditions required for the synthesis and characterization of materials investigated in this thesis. Experimental conditions under which catalytic reactions were carried out are also provided in detail.

Chapter 4 – Develops the methodology required to enable the fundamental effects of sulphur modification to be investigated. Focus is placed on the development and use of model catalytic systems, the experimental conditions required to precisely evaluate catalytic properties, and a detailed characterization of the principles and mechanisms of 3-hexyn-1-ol hydrogenation in order to provide a basis for its use as a model test reaction.

Chapter 5 – Compares the effects of sulphur modification on model catalytic systems of Ru and Pd in order to determine which metal is more sensitive to the effects of modification by sulphur, and why. Geometric and electronic effects of modification are determined and compared for both metals using multiple characterization techniques including the model hydrogenation reaction developed in Chapter 4.

Chapter 6 – Builds on the concepts developed in Chapter 5 to answer the question of how the sensitivity of Pd nanoparticles to geometric and electronic effects of sulphur modification is affected by changes in the average particle size.

Chapter 7 – Summarizes the primary conclusions presented throughout this thesis and ends with a brief discussion of the future perspectives for the research topics addressed.

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Chapter 2

Analytical Techniques

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2.1 Introduction

The last 150 years of scientific development have seen an exponential increase in the range of analytical techniques available for the characterization of chemical systems¹. With the economic importance of catalytic processes, much of the focus in recent years has been on developing and improving methods for the characterization of heterogeneous catalytic materials¹. A wide range of techniques have been developed to directly evaluate bulk and/or surface properties of catalysts including evaluation of adsorbed probe molecules, probing crystal, molecular, or atomic properties using broad spectrum radiation techniques, and indirect imaging of the material surface. Such techniques can be combined to comprehensively characterize the structural and electronic properties of a catalytic material, along with providing information on interactions with substrates.

Characterization methods are generally classified as either bulk or surface techniques, where analysis with surface techniques is limited to the top 0.5-3 nm of material (approximately 2-10 atom layers) while bulk techniques indiscriminately probe the entirety of a sample². In the characterization of heterogeneous catalysts, these classifications can become blurred as many surface techniques essentially function as bulk techniques when evaluating highly disperse samples.

2.2 X-ray diffraction

Powder X-ray Diffraction (XRD) is one of the most broadly applied analysis techniques for probing the crystal structure of heterogeneous catalytic materials. X-ray radiation is high-energy with a wavelength on the scale of angstroms, similar to the interatomic spacings within a crystal lattice. These properties, along with relatively weak interactions between X-rays and the atoms

of a crystal, allow XRD to function as a bulk probe through deep penetration of X-ray radiation into the structure of a solid sample².

In a typical laboratory instrument, X-rays are generated by bombarding a source (usually Cu) with high-energy electrons, resulting in ejection of electrons from core energy levels (typically the K-shell) of the source. Electrons from higher level shells then transition to fill holes left behind by the ejected electrons, resulting in a release of energy in the form of X-rays with a range of characteristic energies. The X-rays are then subjected to a collimator and a monochromator to focus and filter the radiation. The result is a semi-coherent beam of parallel X-ray photons with only one or two different wavelengths.

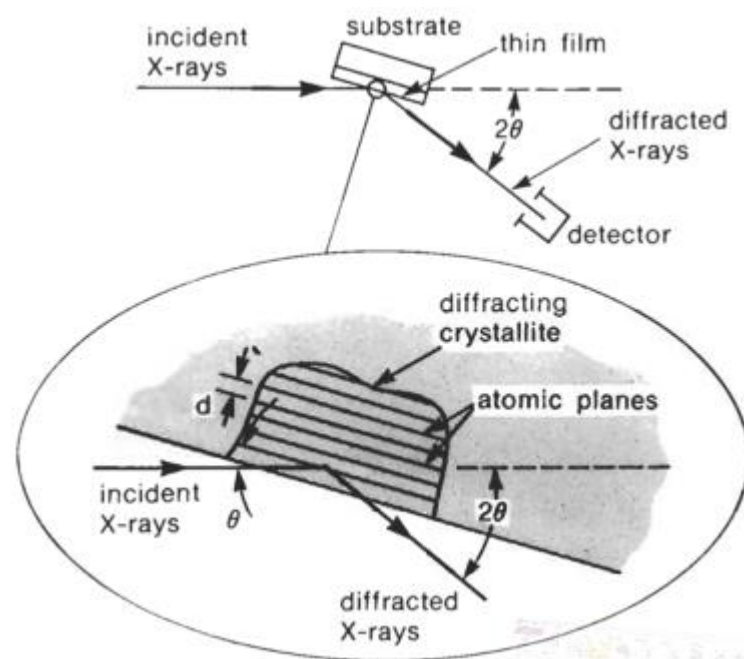


Figure 2.1 – Diagram of a typical XRD experiment on a thin film sample depicting diffraction of incident X-rays by atomic planes of a crystallite, where d is the interplanar spacing and θ is the diffraction angle (Bragg angle). Reproduced from reference³.

When a solid sample (typically a powder or thin film) is subjected to the X-ray beam, diffraction occurs through elastic scattering of photons by atoms in the material. If a sample comprises an extended structure of ordered crystallographic planes, constructive interference between

diffracted photons will occur at angles characteristic for the material (Figure 2.1). The measured diffraction angles can be used to calculate interlayer spacings for the crystal lattice through Bragg's Law (Equation 2.1):

$$n\lambda = 2d \sin \theta \quad \text{Equation 2.1}$$

where λ is the wavelength of the incident radiation, θ is the diffraction angle (also called the Bragg angle), d is the interplanar spacing, and n is an integer representing the order of reflection. In the investigation of heterogeneous catalysts, diffraction patterns are regularly used to identify materials through comparison of peak positions and intensities to a reference database⁴. Additionally, slight shifts in the diffraction angles relative to a standard can be used to monitor subtle lattice changes, including expansion, contraction, or alloy formation. For metals such as Pd with a cubic unit cell, the lattice parameter can be calculated from Equation 2.2:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{Equation 2.2}$$

where d is the interplanar spacing calculated from Bragg's Law, h , k , and l are the Miller indices of the Bragg plane, and a is the lattice parameter.

In samples with an extended crystal structure, destructive interference between diffracted photons at all angles other than the Bragg angles leads to sharp peaks. However, as a crystal's long-range order becomes limited, due to loss in sample crystallinity or a decrease in crystallite size, the angles at which constructive and destructive interference from diffracted photons occurs is significantly widened. This results in peak broadening, the degree of which can be used to determine the average length of crystal planes within the sample through the use of the Scherrer Equation (Equation 2.3).

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad \text{Equation 2.3}$$

where τ is the average crystallite size, λ is the wavelength of the incident radiation, θ is the diffraction angle (also called the Bragg angle), β is the peak broadening at FWHM, and K is a dimensionless shape factor. The Scherrer Equation is often used to provide an estimate of nanoparticle size in supported metal catalysts, however there are limits and uncertainties associated with its application. Only crystallite sizes in the range of 1-100 nm can be determined, and particle size is often overestimated because the average is weighted by particle volume, not by particle number, leading to overcounting of large crystallites⁴. However, underestimation can also occur due to the assumption that each particle is a single crystal with a well-ordered lattice, which is likely not the case in a bulk sample⁵. Finally, additional uncertainties arise for very small particles due to difficulty accurately determining and subtracting a baseline when the intensity between broad diffraction peaks does not reach zero⁶. It is thus most appropriate to use XRD in combination with additional characterization techniques (such as transmission electron microscopy) when determining particle size for supported metal catalysts.

2.3 X-ray photoelectron spectroscopy

Like XRD, X-ray photoelectron spectroscopy (XPS) utilizes X-ray photons for the study of solid materials. Both techniques are routinely used in characterization of heterogeneous catalysts and can be considered complimentary, for while XRD provides information on bulk crystal structure, XPS is a surface technique only capable of probing the uppermost 2-5 nm of a sample's surface⁷. The primary function of XPS is to provide information on the elemental composition of a surface along with additional detail concerning electronic states for atoms of a particular element. Typical laboratory instruments are able to identify all elements present in a sample at concentrations greater than 0.1 atom %, with quantitative determination of surface composition to approximately +/- 10%².

X-rays used for XPS are generated in a similar manner to that described for XRD in Section 2.2, though the source is typically aluminium or magnesium instead of copper, resulting in radiation of much lower energy (1486.3 eV for Al versus 8027.8 eV for Cu). When an X-ray photon impinges on an atom, it can either pass through without interacting, become scattered resulting in partial energy loss, or completely transfer its energy to a core level electron, causing it to be ejected from the atom as depicted in Figure 2.2(a). This final process, referred to as “photoemission”, is the basis for XPS. The kinetic energy of photoemitted electrons is relatively low, accounting for the shallow sampling depth (2-5 nm) as electrons emitted from the bulk will have insufficient energy to escape due to inelastic collisions within the sample⁷. In this thesis, XPS essentially functions as a bulk technique as the materials investigated typically consist of nanoparticles less than 5 nm in diameter. Photoemitted electrons leave behind holes in the core energy levels of the surface atoms, resulting in unstable ions. Auger processes relax the unstable ions by transitioning electrons from higher energy shells to fill the core vacancies (Figure 2.2(b)). This process results in an energy release sufficient to either eject another electron from a higher energy shell (an Auger electron), or emit a characteristic X-ray (Figure 2.2(c)). The characteristic X-rays are not monitored by XPS, although Auger electrons can be monitored in addition to the photoemitted electrons.

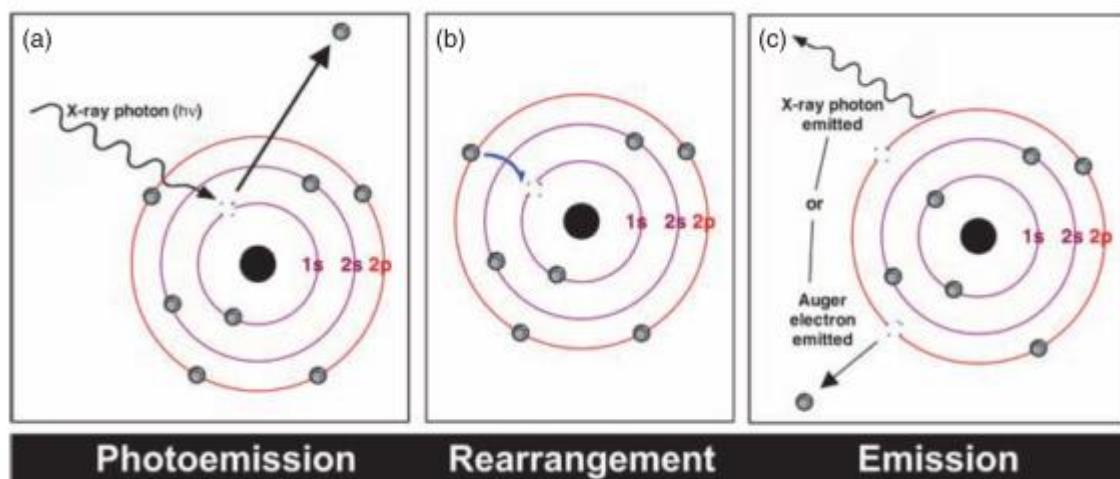


Figure 2.2 – Summary of the processes undergone by an atom when an X-ray photon is absorbed consisting of (a) photoemission of a core electron followed by (b) rearrangement of an electron from a higher energy level to fill the vacancy resulting in (c) emission of an X-ray photon or an Auger electron. Reproduced from reference².

The kinetic energy of ejected electrons is related to their binding energy in the unexcited state by

Equation 2.4:

$$E_k = h\nu - E_b - \varphi \quad \text{Equation 2.4}$$

where E_k is the kinetic energy of the photoemitted electron, h is Planck's constant, ν is the frequency of incident radiation, E_b is the binding energy of the photoemitted electron, and φ is the work function of the spectrometer. Binding energies are characteristic to specific elements, and peaks detected by low resolution scans are typically used to qualitatively and quantitatively determine elemental composition of a surface⁷. High resolution scans to measure small shifts in binding energy can also be used to investigate the oxidation state, chemical bonds, or crystal structure of a specific element⁷. Shifts in binding energy for specific peaks are typically within the range of 0-3 eV⁴. When determining oxidation states for elements, peaks shifting to a higher binding energy indicate an increase in an element's oxidation state.

Large shifts in binding energy for specific peaks can be caused by charging effects. When a conducting sample cannot be in electrical contact with the spectrometer (for example, a catalyst sample coated in a polymeric support) or is not sufficiently electrically conductive on its own, charging effects occur through the build-up of positive charge in the sample due to loss of photoelectrons. This results in a consistent shift in binding energy for elements of the sample to higher energy, obscuring the true values. Ideally, this would be corrected for by showering the sample with low-energy electrons to maintain charge neutrality, but as this is not always possible normalization of the binding energy of a component peak to a standard value is also a valid correction method². When evaluating catalytic materials, this is often the C1s peak of the carbon or polymeric support.

2.4 Transmission electron microscopy

Since the initial development of nanoscale materials for use in heterogeneous catalysis, there has been a persistent desire to directly image the catalyst surface. However optical microscopes are of no use for studying nanoscale features of catalysts, as the wavelength of visible light limits resolution to approximately $1\text{ }\mu\text{m}$ ⁴. Development of microscopes utilizing a high energy electron beam with a wavelength below $1\text{ }\text{\AA}$ increases image resolution by four orders of magnitude (to 0.1 nm)⁴. These electron microscopes allow for magnification up to 10^6 times that of the original sample, sufficient to directly observe particle dispersion, morphology, and even atomic structure for most heterogeneous catalysts. Over the last 40 years, basic electron microscopy has evolved into a subset of more specialized techniques, including scanning electron microscopy (SEM), scanning tunnelling microscopy (STM), transmission electron microscopy (TEM), and combinations thereof³. Materials in this thesis are primarily characterized by TEM, an imaging technique based on the detection of electrons transmitted through a thin-film sample (less than 200 nm thick).

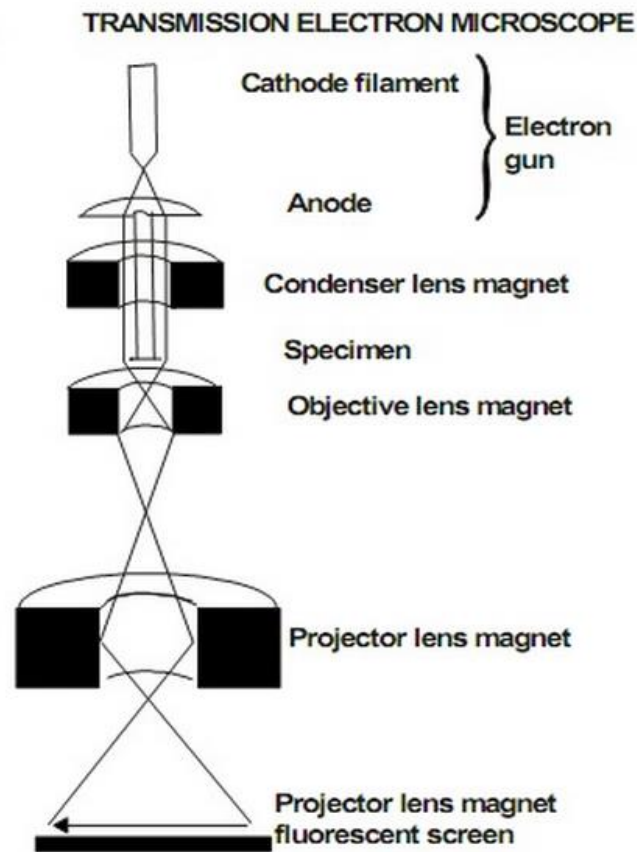


Figure 2.3 – General schematic showing the arrangement of basic components in a TEM. Modified from reference²⁶.

Generally speaking, a transmission electron microscope consists of an illumination system, specimen stage, objective lens system, magnification system, and image analysis system⁶. A basic schematic detailing the arrangement of components within the microscope is shown in Figure 2.3. The illumination system consists of an electron gun and one or more condenser lenses. To generate the electron beam, a current is passed through the cathode filament (typically tungsten or LaB₆) sufficient to overcome the work function for the material, resulting in emission of electrons which are accelerated toward the anode. The beam is converted to parallel rays of electrons by focusing through a series of electromagnetic condenser lenses, and an aperture is often applied to filter out high-angle electrons. The result is a highly coherent beam of parallel

electrons with very small wavelength. These electrons illuminate material on the specimen stage perpendicular to the sample surface. Electrons that are transmitted or diffracted are refocused by an objective lens before magnification takes place. The objective lens is primarily responsible for determining the resolution of a microscope⁶. A series of apertures located below the objective lens allows for improved image resolution through exclusion of diffracted electrons. A 2-D projection of the image is then displayed on a fluorescent screen where data is recorded, often using a charge-coupled device (CCD) camera.

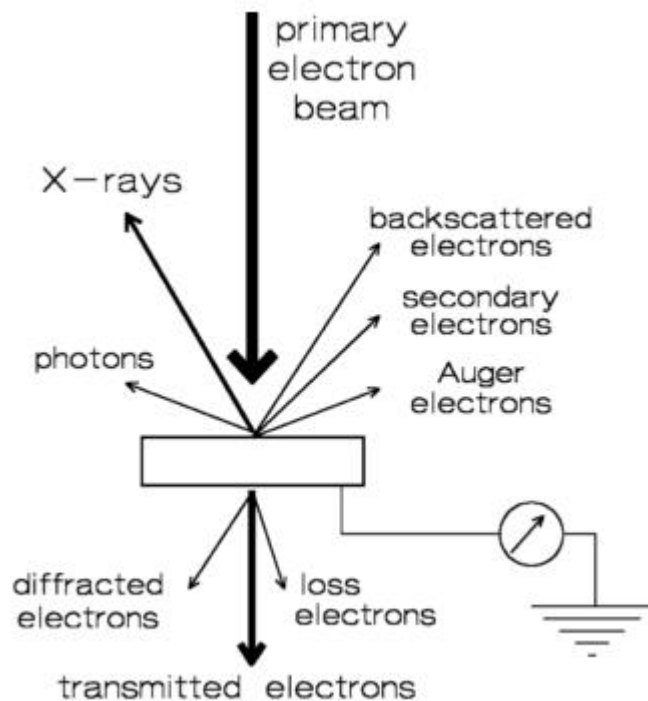


Figure 2.4 –Illustration depicting the range of processes resulting from interactions between the electron beam and a thin-film sample in TEM. Reproduced from reference⁴.

Figure 2.4 summarises the range of possible interactions between the electron beam and the illuminated sample. In standard TEM (bright field imaging), only transmitted electrons are used to form the projected image where areas of sample appear dark against a bright background. Attenuation of the transmitted beam occurs from a number of processes, particularly electron diffraction and backscattering. These processes are more common for electrons interacting with

heavier nuclei or thicker areas of the sample, causing these regions of the image to appear darker (higher Z-contrast). Dark field imaging uses only those electrons which are diffracted by the sample to form the image. As more electrons are diffracted by heavier elements, this imaging method causes these areas of the sample to appear brighter than areas containing light elements. Bright field and dark field imaging are typically used in parallel to clarify structural features of complex materials, such as those composed of multiple elements.

2.5 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDX) is a technique for elemental analysis often performed in parallel with TEM. In contrast to XPS, which is used to analyse a wide sample area, EDX is capable of qualitatively and quantitatively determining the surface elemental composition of specific sample areas⁸. Coupling with TEM imaging makes the technique particularly powerful by directly relating elemental distributions to localized sample structure⁸.

EDX spectroscopy uses characteristic X-rays produced by interaction between the electron beam in TEM and the sample (Figure 2.4) for elemental analysis. The mechanisms by which the X-rays are generated are intimately related to the fundamental processes of XPS and are described in detail in Section 2.3. Briefly, high energy electrons from the beam strike surface atoms of the sample causing electrons from core energy levels to be ejected (Figure 2.2.a). Electrons from higher energy states in the atom then fill the vacant states (Figure 2.2.b), resulting in emission of Auger electrons or X-rays with characteristic energies (Figure 2.2.c).

Emission of Auger electrons is the prominent process for light elements, but X-ray emission increasingly dominates for elements heavier than magnesium giving EDX an enhanced sensitivity toward these elements⁴. Quantitative analysis is carried out by monitoring counts of

energy-specific charge/voltage pulses created by emitted X-rays interacting with a solid-state detector⁷. A comparison between the energy spectrum of X-rays emitted from the sample and a spectral database of elements allows for determination of sample surface composition. However, truly quantitative results are difficult to obtain without the use of internal standards of similar structure to the unknown sample due to sensitivities in sampling depth⁷.

2.6 Fourier transform infrared spectroscopy

Infrared (IR) spectroscopy is one of the oldest and most frequently applied spectroscopic techniques in catalysis⁴. IR radiation generated by the instrument is absorbed by the sample at characteristic frequencies corresponding to the vibrational states of intramolecular bonds within the sample. While classically used to characterize metal complexes in homogeneous catalysis, the most common application of IR spectroscopy in heterogeneous catalysis is the study of chemisorbed surface molecules, such as carbon monoxide, to provide information on electronic and geometric properties of catalyst adsorption sites⁴. The major drawback of classical IR spectroscopy is the low sensitivity relative to the high vacuum spectroscopic techniques such as XPS⁸. However, coupling IR spectroscopy with Fourier transform (FT) significantly improves the sensitivity of the technique, and modern Fourier transform infrared spectroscopy (FTIR) is sensitive enough to be used for surface characterization of materials⁸.

The behaviour of intramolecular bonds excited by absorption of IR radiation can be approximated by two oscillating spheres joined by a spring (a simple harmonic oscillator) and described using Hooke's law (Equation 2.5):

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}} \quad \text{Equation 2.5}$$

where ν is the vibrational frequency in cm^{-1} , k is the force constant of the bond, c is the speed of light, and m_1 and m_2 are the masses of the vibrating atoms. Equation 2.5 directly relates the force constant for a bond to the oscillation frequency, allowing the measured vibrational frequency to be taken as an indication of bond strength. It also indicates that, as the mass of the constituent atoms decreases, or as the bond strength increases, the vibrational frequency increases. This is an important relationship when considering changes in vibrational frequency for probe molecules. It also allows for direct prediction of frequency shifts caused by isotopic substitutions.

When selecting a probe molecule, characterization of metal active sites by IR spectroscopy of chemisorbed CO is particularly effective because changes in vibrational frequency and binding configuration can both be used to monitor surface changes in a catalyst⁹. Depending on localized surface geometry, CO adopts different binding configurations, such as linear and bridging, which are easily monitored and compared due to differences in vibrational frequency¹⁰. As CO bound in a linear configuration formally contains a triple bond, the vibrational frequency ($2000\text{--}2130\text{ cm}^{-1}$) is significantly higher than for CO in a bridging configuration with only a double bond ($2000\text{--}1880\text{ cm}^{-1}$)¹¹. The precise vibrational frequency observed for each binding mode is dependent on adsorption strength to the metal surface and the degree of back donation from the metal d-orbitals into the $2\pi^*$ anti-bonding orbitals of the CO bond. If the metal surface experiences a decrease in electron density, less back donation from the d-orbitals occurs and the CO bond strength increases, resulting in a shift in vibrational frequency to higher energy⁴. As such, shifts in vibrational frequency for chemisorbed CO can be used to monitor changes in the electronic properties of a metal surface, however care must be taken when interpreting frequency changes in terms of changing bond strength alone. The bond frequency is also strongly affected by dipole-dipole interactions when the probe molecule is surrounded by others in the same configuration, and a decrease in these interactions through reduction in surface coverage will

lower the vibrational frequency¹². However it is possible to discount these interactions through calibration using isotopic mixtures of CO because dipoles of the different isotopes do not resonate with one another¹³.

Many heterogeneous catalytic materials absorb IR radiation too strongly to be characterized using classic transmission FTIR experiments. When this is the case, or when the material to be analysed is highly scattering, attenuated total reflectance (ATR) FTIR is a more appropriate technique⁸. In ATR FTIR, a thin film of substrate is deposited on the sample window composed of an IR transparent prism with a higher refractive index than the substrate. IR radiation enters this prism and strikes the surface at an angle greater than the critical angle for the sample-prism interface, resulting in total internal reflectance of the radiation as depicted in Figure 2.5. At the points of total internal reflectance, a small fraction of the IR radiation passes through the boundary between the prism and the substrate establishing an evanescent field. Absorption of radiation from this field causes attenuation of the reflected radiation (attenuated total reflectance) which is monitored to produce a spectrum similar to standard absorption spectra.

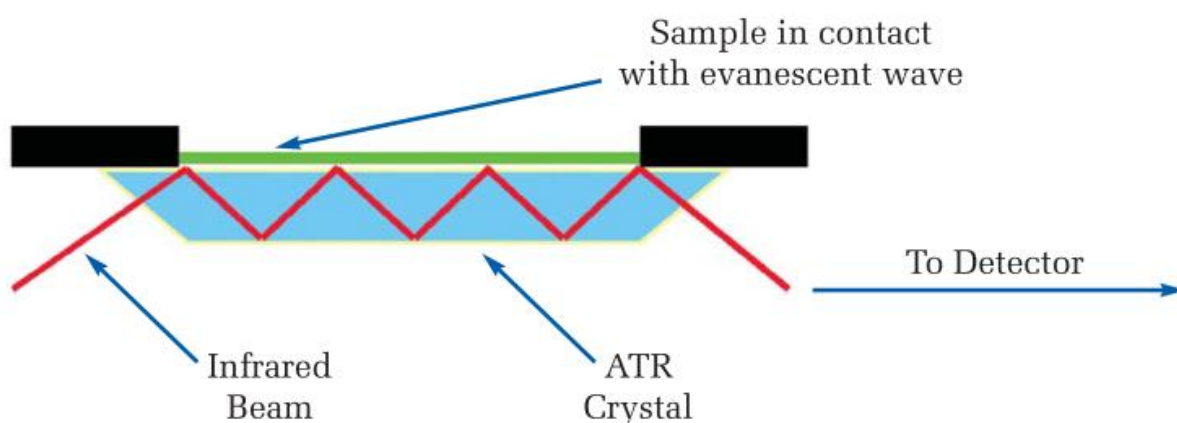


Figure 2.5 – Diagram of the sample window for an ATR FTIR spectrometer depicting total internal reflectance of the IR beam and the resulting interaction with the sample via an evanescent field. Reproduced from reference¹⁴.

2.7 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy encompasses a broad range of specialized techniques capable of probing the localized electronic environments of active nuclei. Like XRD, NMR is a bulk technique but with the significant advantage of being element specific. This allows for investigation of chemical bonding and electronic structure for isolated atoms located well below the sampling depth of surface techniques such as XPS. Line widths for signals obtained by NMR are also much narrower than for most spectroscopic techniques, and the high degree of resolution allows for sensitive monitoring of perturbations in the environment surrounding active nuclei¹⁵.

NMR operates by principles similar to those found in FTIR, except that instead of measuring the frequency of IR radiation required to excite the vibrational states of a bond, the radio frequency required to change the orientation of nuclear spins aligned in a magnetic field is monitored. When an external magnetic field is applied to a sample, the spins of nuclei with a permanent magnetic dipole (NMR active nuclei with nonzero nuclear spins) will align either parallel or antiparallel to the direction of the field creating low and high energy states. The sample is subjected to a radio frequency (RF) pulse and radiation is absorbed by the sample at frequencies corresponding to the energies required to reverse nuclear spin alignment in the magnetic field.

Isotopes of different elements resonate over a wide range of radio frequencies, while changes in electronic environment for a nucleus shift the resonance frequency only slightly³. This allows individual isotopes to be probed with little to no overlap from resonance frequencies of other nuclei. The frequency of absorbed radiation for each isotope is displayed in terms of chemical shift, which is essentially a measure of how strongly the nucleus “feels” the effects of the applied magnetic field. Chemical shift is affected by the electronic environment surrounding a nucleus,

and changing this environment will change the chemical shift. If the environment surrounding a nucleus becomes more electron rich, the nucleus is said to be shielded from the magnetic field and will resonate at a lower frequency (lower chemical shift) as less energy is required to reverse spin alignment. Conversely, a nucleus surrounded by an electron poor environment is deshielded from the magnetic field and will resonate at a higher frequency (higher chemical shift).

NMR experiments are typically classified as either solution state or solid state techniques. Solution state techniques are characterized by superior resolution, good intensities and narrow peak widths when compared with solid state experiments and are the more commonly used of the two types¹⁶. Solution state NMR is a crucial tool in the evaluation and characterization of catalysts, although it is almost exclusively employed in the investigation of homogeneous metal complexes¹⁷. Attempts to use probe molecules such as ^{13}CO to characterize heterogeneous catalysts by this technique are severely limited by peak broadening introduced by restricting the molecular motion of the probe through chemisorption to a solid surface¹⁶. Solid state NMR experiments are more common for the investigation of heterogeneous catalysts, where use of magic angle spinning (MAS) narrows resonance signals for probe molecules. However, peak broadening cannot be completely eliminated and resolution of neighbouring peaks is limited as peak widths are still often larger than the difference in chemical shift between adsorbed species¹⁶. Chemical shifts of probe molecules are also strongly influenced by external factors such as Knight Shift effects, often to the point of no longer being useful for active site characterization¹⁶. Knight Shift effects are caused by coupling of the chemisorbed probe to conduction electrons on the metal surface often resulting in a severe downfield shift in resonance frequency.

2.8 CO Pulse chemisorption

Materials of catalytic importance are often highly-disperse supported metal nanoparticles with large surface areas. When measuring activities for these catalysts, an accurate determination of active surface area is vital. Catalyst surface area can be calculated from simple measurements of particle size by TEM or XRD, but it is difficult to account for surface area loss due to localized aggregation or interaction between the metal and support, particularly for highly-disperse metals. Additionally, the specific surface area (surface area per gram) of a catalyst changes rapidly with dispersion for very small nanoparticles, creating large uncertainties in the calculated values. These challenges can be largely overcome through the use of chemisorption techniques which indirectly measure the active surface area through adsorption of a titrant gas (typically CO or H₂). CO was chosen as the titrant gas for surface area characterization in this thesis to avoid the complications of subsurface absorption which can occur when using H₂ for metals such as Pd³.

In a typical CO chemisorption experiment using the pulse flow method, a precise volume of the titrant gas is injected into a carrier gas stream (typically He) which flows through a pre-reduced catalyst bed. A thermal conductivity detector (TCD) monitors the signal produced by titrant gas remaining in the carrier gas stream after interaction with the catalyst bed, and comparison between signals from pulses with adsorbed titrant gas and signals with no adsorbed titrant gas (reference) allows for quantitative determination of the adsorbed titrant molecule¹⁶. Reference peaks are established after saturation of the sample surface by the probe. A typical chemisorption profile is displayed in Figure 2.6 where pulses 1-4 show complete uptake of the titrant gas and pulse 5 shows partial uptake as the surface saturation point is reached. Pulses 6-8 with no titrant gas uptake are used as a reference to calculate uptake volume.

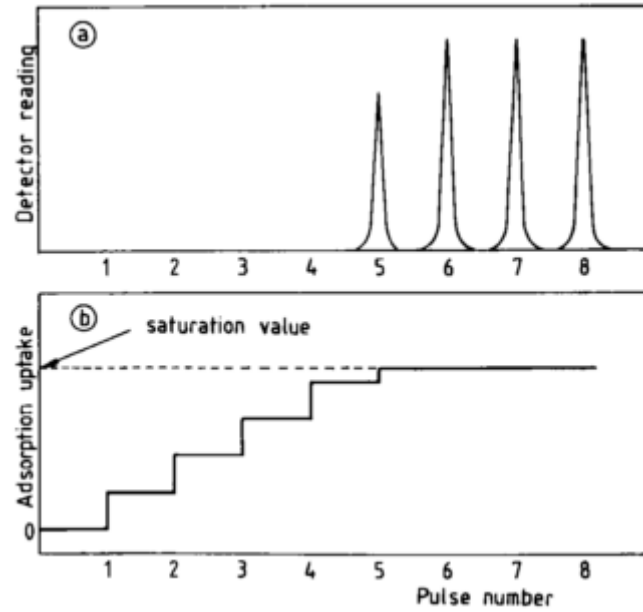


Figure 2.6 – Profiles for a typical CO pulse chemisorption experiment showing (a) pulses resulting from complete uptake (1-4), partial uptake (5) and no uptake (6-8) of the titrant gas and (b) the resulting uptake of titrant gas plotted relative to the pulse number. Reproduced from reference¹⁶.

Quantitative determination of adsorbed molecules of titrant gas allows for calculation of metal dispersion (Equation 2.8) and the active metal surface area relative to both metal and sample mass (Equations 2.6 and 2.7)¹⁸.

$$A_s = N_A n_{ads} F_s a_m 10^{-23} \quad \text{Equation 2.6}$$

$$A_m = A_s \frac{100}{X_m} \quad \text{Equation 2.7}$$

$$D = \frac{10 n_{ads} F_s M_m}{X_m} \quad \text{Equation 2.8}$$

where A_s and A_m are the metal surface area per gram of sample or metal, respectively, N_A is Avogadro's number, n_{ads} is the moles of adsorbed gas per gram of sample, F_s the stoichiometric factor relating moles of adsorbed gas to moles of metal, a_m is the cross sectional area for a metal atom, X_m is the percent metal loading in the sample, D is the metal dispersion, and M_m is the

metal atomic weight. Average particle size can also be calculated from the active surface area using Equation 2.9:¹⁸

$$d = \frac{S_f 10^3}{A_m \rho_m} \quad \text{Equation 2.9}$$

where S_f is a dimensionless shape factor, ρ_m is the metal density, and d is the average particle size, although it is usually more accurate to use a direct measurement method such as TEM.

One drawback to the pulse chemisorption method is that it assumes strong chemisorption interactions between the titrant gas and all atoms of the active surface without accounting for weaker physisorption interactions¹⁶. This can be corrected for by monitoring any time delays for the titrant gas when flowing through the catalyst bed. By adding a second, non-interacting gas to the carrier gas stream which can be monitored by the TCD (such as Ar), residence time of the titrant gas in the catalyst bed can be determined¹⁶. If physisorption effects are not taken into account, the measured catalyst surface areas will tend to be lower than the true value. Additionally, as CO does not always bind in a linear conformation on the catalyst, assuming a 1:1 relationship between the adsorbed probe and the surface atoms can result in underestimation of catalyst surface area³.

2.9 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is one of the most powerful thermoanalysis techniques for obtaining quantitative data¹. The principle of the technique is simple: properties of materials are determined by measuring weight changes as a sample is heated or cooled in a controlled manner. Changes in sample weight with changing temperature can be used to indicate solvent loss, oxidation/reduction processes, or volatilization or decomposition of sample components. A schematic for the TGA instrument used in this thesis is shown in Figure 2.7. When performing

TGA, a small mass of sample (1-50 mg) in a sample pan (typically platinum) is loaded into a furnace, and the environment within the furnace is controlled with an inert or reactive purge gas. The weight of the sample is constantly monitored with a microbalance by comparison to a tare pan to measure changes in sample weight with changing temperature and/or time if the sample is kept isothermal. When analysing a range of similar samples, it is important to use a consistent heating rate and sample mass, as variations in these factors can change peak resolution and observed decomposition temperatures¹.

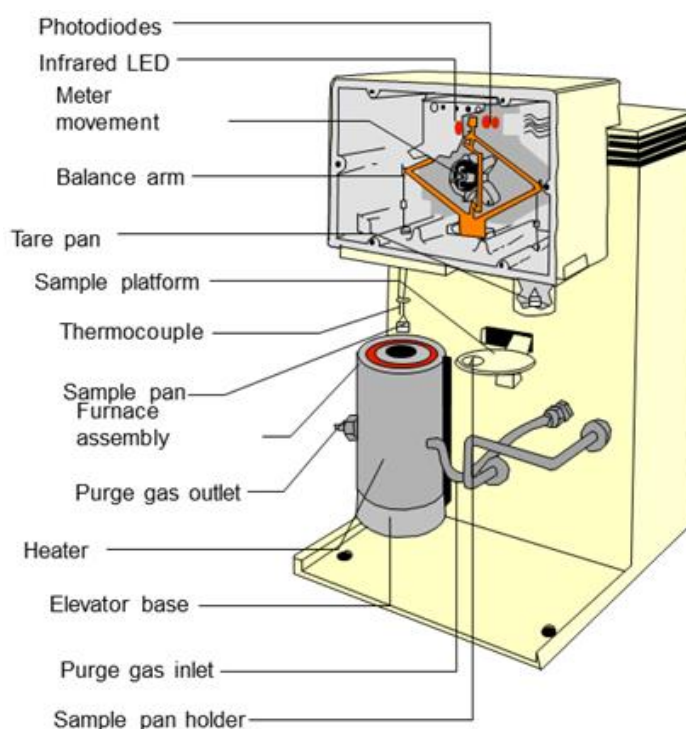


Figure 2.7 – Schematic for a TA instrument TGA Q50. Reproduced from reference¹⁹.

2.10 Gas chromatography

Gas chromatography (GC) is a powerful method for separating mixtures of volatile compounds. GC operates on the principle of differing adsorption/desorption properties between analytes within a sample and the stationary phase of the column. During analysis, a sample is injected into a heated chamber to ensure vaporization of all components. The mobile phase, or carrier

gas, transports the sample through a column containing a stationary phase (often a high-molecular weight polymer coating). Molecules of a particular analyte interact similarly with the stationary phase and thus have similar retention times, resulting in uniform elution from the column. The resulting peak recorded by the detector can be used to quantitatively determine the analyte concentration. Separation of multiple analytes is achieved by optimizing differences in interaction strength between sample components and the stationary phase of the column.

Maximizing efficiency for the separation process is carried out by optimizing column resolution as determined by the number of theoretical “plates”. The plate number for a column is based on the number of plates that would theoretically be required to carry out the same separation process using a standard distillation column. Theoretical plate height is determined by calculating the length of column equal to one theoretical plate. The resolving power of a column is optimized by minimizing plate height based on the van Deemter Equation (Equation 2.10):

$$H = A + \frac{B}{v} + Cv \quad \text{Equation 2.10}$$

Where H is the plate height and v is the velocity of the carrier gas flow through the column. The A term relates to mixing between analytes and the carrier gas due to non-uniform column packing, and does not depend on carrier gas flow. The B term is governed by diffusion between analytes and the carrier gas and is minimized by increasing carrier gas flow rate. The C term is governed by the equilibrium between adsorbed and gas phase analytes, and is minimized by decreasing the carrier gas flow rate²⁰. As B and C involve equilibrium and diffusion processes, they will both also show temperature dependence. Choosing an optimal combination of temperature and flow rate to balance the three terms and minimize plate height is generally achieved experimentally through trial and error.

GC for this thesis was performed using a capillary column with a solid stationary phase. Capillary columns are preferable to packed columns because the data obtained is more reliable¹. Additionally, there is no *A* term in the van Deemter Equation for capillary columns, giving them a greater resolving power²⁰. Use of a solid stationary phase allows for a wide range of analysis temperatures without column bleeding presenting a major issue. After separation, analytes were detected using a flame ionization detector (FID). FID's are universal detectors, responding to all components present in the mobile phase that ionize in a flame. The minimum detectability is 10 pg sec⁻¹ of carbon with a linear range of 10⁷, making them ideal for analyte quantification¹. They function by mixing the carrier gas containing the analyte with hydrogen, which is then combusted in air. The combustion produces ions which are collected at an electrode and produce a current proportional to the analyte concentration.

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Chapter 3

Experimental and Characterisation Methods

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3.1 Synthesis of PVP stabilized metal nanoparticles

3.1.1 Synthesis of Ru(PVP)

Polyvinylpyrrolidone (PVP) supported Ru nanoparticles were prepared by a polyol reduction method modified from the procedure used by Bonet *et al.*¹. In a typical synthesis, 240 mg (2.148 mmol) of 40K molecular weight (MW) PVP was dissolved in 30 mL of diethylene glycol, followed by 50 mg (0.2023 mmol) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$. The solution was flushed with N_2 and stirred for 1 hour to ensure complete dissolution of the metal precursor and then heated at 160°C under N_2 for 2 hours, reducing Ru^{3+} to form dark brown colloidal nanoparticles. Once the reaction was complete, the sample was cooled to room temperature under N_2 and the nanoparticles were precipitated with acetone by centrifugation (5000 rpm, 5 min). The nanoparticles were washed twice with acetone by alternating sonication and centrifugation before being left to dry in air.

3.1.2 Synthesis of Pd(PVP)

PVP supported Pd nanoparticles were prepared by a polyol reduction method modified from the procedure used by Bonet *et al.*¹. In a typical synthesis, 240 mg (2.148 mmol) of 40K MW PVP was dissolved in 30 mL of ethylene glycol, followed by 56 mg (0.2142 mmol) of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The solution was flushed with N_2 and stirred for 1 hour to ensure complete dissolution of the metal precursor and then heated at 120°C under N_2 for 2 hours, reducing Pd^{2+} to form dark brown colloidal nanoparticles. Once the reaction was complete, the sample was cooled to room temperature under N_2 and the nanoparticles were precipitated by centrifugation (5000 rpm, 5 min) with a mixture of acetone and hexane (7:3 acetone:hexane). The nanoparticles were washed twice with acetone by alternating sonication and centrifugation before being left to dry in air.

3.1.3 Size control of Pd(PVP)

Size control of PVP supported Pd nanoparticles was achieved by a stepwise growth method modified from the procedure used by Teranishi *et al.*². Seed particles were synthesized as described previously in Section 3.1.2 however the procedure was stopped prior to precipitation in acetone and hexane, yielding a colloidal solution of PVP supported nanoparticles in ethylene glycol. In order to achieve stepwise growth of the seed particles, an additional 56 mg (0.2142 mmol) of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ dissolved in 2 mL ethylene glycol was added to the colloidal seed solution. The solution was flushed with N_2 and stirred for 1 hour, and then heated at 90°C under N_2 for 2 hours to encourage particle growth through slow reduction of the Pd precursor onto the seed. The solution was then heated at 120°C for a further 1 hour to ensure complete reduction and then cooled to room temperature under N_2 . This represented one growth step. The stepwise growth procedure was repeated until the desired nanoparticle size was achieved, at which point the particles were precipitated, washed, and dried as described previously in Section 3.1.2.

3.1.4 Tellurium decoration of Pd(PVP)

Tellurium decoration of PVP supported Pd nanoparticles was achieved by a redox method modified from the procedure used by Gauthard *et al.*³. Seed particles were synthesized as described previously in Section 3.1.2 however the procedure was stopped prior to precipitation in acetone and hexane, yielding a colloidal solution of PVP supported nanoparticles in ethylene glycol. N_2 flow was stopped and the solution was bubbled with H_2 for 1 hour with vigorous stirring to ensure complete coverage of the metal surface by a Pd-H species. N_2 flow was then replaced and 8.19 mg (31.4 μmol) TeCl_4 dissolved in 5 mL ethylene glycol was added dropwise to the seed solution and stirred for a further 1 hour to allow Te^{4+} to reduce onto the metal surface. In order to ensure complete reduction of Te^{4+} to Te^0 , an additional reduction step was carried out by adding 4.75 mg (125.6 μmol , 4 molar equivalents) NaBH_4 dissolved in 3 mL ethylene glycol.

The solution was stirred under N₂ for a further 1 hour before the particles were precipitated, washed, and dried as described previously in Section 3.1.2.

3.2 Thiol modification of metal nanoparticles

3.2.1 Thiol modification of PVP stabilized metal nanoparticles

Colloidal dispersions of PVP stabilized metal nanoparticles were achieved by sonicating the dried particles synthesized in Sections 3.1.1-3.1.3 with a desired volume of polar solvent (typically water or ethanol) for 30 minutes. Thiol modification of the colloids was carried out by adding a volume of thiol solution (typically aqueous or ethanolic) calculated to give the desired surface coverage. Modified samples were sonicated for 60 minutes and allowed to age for 24 hours before characterisation and testing was carried out.

3.2.2 Thiol modification of commercial carbon supported metal nanoparticles

Thiol modification of commercial carbon supported metal nanoparticles was achieved by first sonicating the supported catalyst (typically 25 mg) in 6 mL of ethanol for 1 hour until the sample was well-dispersed. An ethanolic solution of thiol was then added at a volume calculated to give the desired level of surface coverage. Samples were sonicated for a further 4 hours and then stirred for 24 hours before being transferred to a 100°C oven overnight to remove the solvent.

3.3 Catalyst testing

3.3.1 High pressure 3-hexyn-1-ol hydrogenation

High pressure hydrogenation of 3-hexyn-1-ol was carried out in a High Pressure HEL Chemsan reactor (Figure 3.1 below) at the Johnson Matthey Technology Centre in Sonning Common. The Chemsan was equipped with 8 parallel stainless-steel hastelloy reactors with independent control and monitoring of temperature, pressure, and stirring rate. Each reactor was equipped with a Teflon stirrer and lined with a glass reaction vessel. In a typical reaction, 5 mL of 3-hexyn-1-ol reagent (0.5 M, 2.5 mmol) and 1,4-dioxane (0.5 M, 2.5 mmol) in ethanol and 2.5 μ mol metal catalyst were added to each glass reaction vessel. Reaction temperature was set at 40°C and stirring rate at 1200 rpm. Reaction pressure was set at 3 bar and 15 bar of H₂ for Pd and Ru catalysts, respectively. Prior to hydrogenation, each reactor was subjected to an inert gas purge with N₂, heated to the desired reaction temperature, and then purged twice with H₂ at the reaction pressure. Hydrogen uptake was monitored throughout the reaction and samples taken after the reaction was stopped were analysed by GC.



Figure 3.1 – High Pressure HEL Chemsan with 8 parallel stainless steel hastelloy reactors used at Johnson Matthey Technology Centre in Sonning Common.

3.3.2 Ambient pressure hydrogenation of alkynes and alkenes

Ambient pressure hydrogenation of alkynes and alkenes (3-hexyn-1-ol, *cis*-3-hexen-1-ol, 2-methyl-3-butyn-2-ol, 2-methyl-3-buten-2-ol) was carried out in a 250 mL 3-necked round bottom flask as depicted in Figure 3.2. The flask was equipped with a silicon oil bubbler and two rubber septa, one for bubbling H₂ through a stainless steel needle and the other for withdrawing sample. All appropriate components were cleaned with aqua regia prior to catalyst testing. The reaction was stirred at 750 rpm with a Teflon-coated stir bar and temperature was maintained at 30 °C by a 1 L water bath. H₂ was bubbled at a rate of 30 mL min⁻¹. In a typical reaction, 50 mL of ethanol was added to the reaction vessel and bubbled with H₂ at 30 °C under stirring for 15 min. Successive injections of 1.015 mL 1,4-dioxane (15 mmol), concentrated alkyne/alkene reagent (approximately 15 mmol), and finally PVP supported colloidal metal catalyst in ethanol were then added under continued stirring and bubbling with H₂. The catalyst concentration was varied to maintain a reactant hydrogenation rate below 220 μmol min⁻¹ to avoid limitations from H₂ solubility. Reaction conditions for the various reagents are summarized in Table 3.1. Samples of approximately 0.3 mL were taken at regular intervals throughout the reaction and subsequently analysed by GC.



Figure 3.2 – Reactor setup for the ambient pressure hydrogenation of alkynes and alkenes.

Table 3.1 – Summary of reaction conditions for the ambient-pressure hydrogenation of assorted reagents.

Reagent	Reactant injection volume (mL)	Metal catalyst (μmol)	Reactant:Catalyst
3-hexyn-1-ol	1.64	0.30	50,000:1
<i>cis</i> -3-hexen-1-ol	1.77	3.75	4,000:1
3-methyl-2-butyl-3-ol	1.45	0.10	150,000:1
3-methyl-2-buten-3-ol	1.57	0.94	16,000:1

3.4 Characterisation

3.4.1 Powder X-ray diffraction

Powder X-ray diffraction was performed on a PANalytical X'Pert PRO Diffractometer with $\text{CuK}\alpha$ radiation (wavelength $\lambda = 1.5406 \text{ \AA}$) produced by a generator operating at 40 kV and 40 mA. Profiles were measured from $\theta = 20\text{-}90^\circ$. Colloidal samples were prepared by depositing a concentrated ethanolic dispersion of PVP supported nanoparticles on the surface of a glass slide. The solvent was evaporated in air, leaving a thin film of sample with an even thickness and smooth surface. Supported samples were prepared by covering a glass slide in a thin, even layer of finely powdered sample. The powder was gently pressed with a metal spatula to ensure a smooth surface.

3.4.2 TEM, HRTEM, and EDX

TEM was performed using a JEOL 2010 microscope operating at 200 kV. EDX analysis was performed with the same microscope equipped with an Oxford Instruments LZ5 windowless EDX spectrometer. HAADF STEM was performed at Birmingham University on a JEOL 2100 aberration-corrected microscope operating at 200 kV. Samples for TEM/EDX analysis were prepared by dispersing a small amount of material (typically 1 mg) in approximately 1 mL of ethanol. One drop of this dispersion was placed onto a copper grid (holey carbon supported on copper, 400 mesh) and the solvent evaporated in air prior to analysis. Average particle size distributions were calculated from the measurement of at least 200 individual particles.

3.4.3 FTIR

FTIR was performed using a Nicolet 6700 ATR-IR spectrometer equipped with a Smart Golden Gate Accessory, a ZnSe window, and an MCT-B detector. Spectra were obtained by averaging

the result of 128 scans typically performed from 4000 to 650 cm^{-1} with an aperture setting of 32. For the analysis of chemisorbed CO by FTIR, colloidal samples of PVP supported metal nanoparticles were used. In a typical procedure, approximately 200 μmol of metal catalyst was dispersed in 1 mL H_2O and bubbled with 1% CO in argon for 20 minutes. A drop of the sample was then deposited on the ZnSe window and dried to form a thin film. Spectra were analysed after subtraction of a blank spectrum.

3.4.4 Thermogravimetric analysis

Thermogravimetric analysis of samples was performed using a TA instrument TGA Q50. Analysis was conducted under air with a furnace flow rate of 12 mL min^{-1} . In a typical procedure, 5-10 mg of finely powdered material was placed on a platinum analysis pan within the TGA and accurately weighed by comparison to a reference pan. Samples were held isothermal for 5 min before heating to 800 $^{\circ}\text{C}$ with a ramp rate of 10 $^{\circ}\text{C min}^{-1}$, followed by a further isothermal period of 60 min before cooling to room temperature. Changes in sample weight were monitored over time and with increasing temperature.

3.4.5 Gas chromatography

Samples from hydrogenation reactions were analysed by gas chromatography using a Perkin Elmer AutoSystem XL Gas Chromatograph equipped with an FID. Samples obtained from reactions detailed in Section 3.3.3 were separated using an Agilent DB-1701 low/mid polarity column (30 m x 0.025 mm) with nitrogen as the carrier gas. Samples obtained from hydrogenation of 3-hexyn-1-ol detailed in Section 3.3.1 were separated using an Agilent CP-SIL-19-CB medium polarity column (10 m x 0.53 mm) with helium as the carrier gas.

3.4.6 CO Pulse chemisorption

CO pulse chemisorption for the determination of sample surface area was performed using a Quantachrome Instruments ChemBET Pulsar TPR/TPD Automated Chemisorption Analyzer. In a typical procedure, 30 mg of sample was accurately weighed and loaded into a quartz analysis tube between two quartz wool plugs. The analysis tube was equipped with a thermocouple probe. Helium was used as the carrier gas with a flow rate of 20 mL min⁻¹ and 100% CO was used as the titrant gas. The sample was reduced under H₂ for 40 min at 40 °C followed by 40 min of room temperature carrier gas flow before automated titration was carried out. Titration consisted of at least 7 pulses with an injection volume of 72 µL per titration pulse. At least 4 pulses were used for calibration. Detector current was set to 150.0 mA with an attenuation of 1.

3.4.7 Solution state NMR

All spectra were recorded on either a Bruker Avance III HD nanobay 400 MHz NMR or Varian Mercury 300 MHz NMR Spectrometer. ¹H spectra were the result of 16 scans with a 1 second cycle delay. ¹³C spectra were the result of 2000 scans with a 5 second cycle delay. Chemical shifts for all peaks were normalized to an internal standard, typically 1,4-dioxane or hexane. Samples for the analysis of chemisorbed ¹³C formic acid were prepared by dispersing a sample of the PVP supported nanoparticles with approximately 0.2 mmol metal content in 500 µL of D₂O. Thiol modification was conducted as outlined in Section 3.2.1. ¹³C labelled formic acid (1 M, 200 µL) was added followed by 10 µL 1,4-dioxane as the internal standard. The sample was then sonicated for 30 minutes before the ¹³C NMR spectrum was measured.

3.4.8 XPS

XPS analysis was performed on a VG Escalab XPS Spectrometer operating under ultra-high vacuum (1 x 10⁻⁹ torr) using aluminium K_α radiation with an energy of 1486.3 eV. Samples were

prepared by depositing a thin layer of finely ground powder onto a double-sided sticky carbon tab attached to each sample holder. Wide scan spectra were acquired from 0 to 1200 eV to identify elements present in the sample, and were compiled from 4 scans with a 0.1 sec dwell time, a 1 eV step interval, and a pass energy of 50 eV. Spectra of specific regions were obtained for elements of interest and were compiled from 15 scans with a 0.4 sec dwell time, a 0.1 eV step interval, and a pass energy of 20 eV. Data was processed using CasaXPS peak fitting software and binding energies were referenced to the C 1s peak corrected to a value of 284.50 eV to eliminate charging effects in accordance with the method by Jansen and van Bakkum⁴.

3.6 Computational details

3.6.1 Kinetic modelling

Experimental profiles for the hydrogenation reactions were fit using a Langmuir-Hinshelwood kinetic model. A root mean square error (RMSE) was determined by the model based on mismatch between the calculated and experimental concentration profiles. (Note: the output error value is not a percentage deviation between calculated and experimental profiles). A least squares method was used to determine unknown rate constants. A RMSE cost function, f (Equation 3.1), was defined to quantify the mismatch between the experimental and calculated reaction profiles:

$$f = \sqrt{\frac{1}{n - nk} \sum_{i=1}^{ns} \frac{([P_i]_{\text{exp}} - [P_i]_{\text{cal}})^2}{[P_i]_{\text{exp}}}} \quad \text{Equation 3.1}$$

where n = number of experimental data points, nk = number of rate constants to be fit, and ns = number of species. The calculation renders to a non-linear least squares optimization of the unknown rate constants (depending on the model used) to minimize f . The calculated rate

constant k was treated as a constant in the optimization calculation. The SIMPLEX method was utilized for this purpose⁵. All data reported in this thesis returned a mismatch (f) value of 0.08 or less, and all calculations were performed using Matlab (R2013b) in a Linux cluster. Initial values for rate constants were set based on the values obtained from the kinetic fitting of the experimental profile for the previous sample in a series. For example, initial rate constants for Pd(PVP) with 12% MEA coverage were taken from the fitted rate constants for Pd(PVP) with 0% MEA coverage, and initial rate constants for Pd(PVP) seed growth 2 were taken from the fitted rate constants for Pd(PVP) seed growth 1. No initial rate constants were set at zero, even if this value appeared in the fitted rate constants for the previous sample.

3.6.2 DFT calculations

All DFT calculations were performed by Dr. Glenn Jones of the Johnson Matthey Technology Centre in Pretoria, South Africa. Grid based calculations were carried out using the GPAW (projector-augmented wave) code^{6,7}, and electron-electron interactions were described at the revised Perdew-Burke-Ernzerhof (RPBE)/generalized gradient approximation (GGA) exchange-correlation functional level⁸. A grid spacing of 0.18 was used and the Brillouin zone was sampled by a Monkhorst-Pack mesh with dimensions of $4 \times 4 \times 1$ ⁹. The electronic cores were described using PAW setups, and the atomic geometry was described using periodic slabs consisting of 2×4 Pd(111) unit cells comprised of 3-atomic layers. A vacuum region of 10 Å was used. Effects of sulfur adsorption were simulated by introducing two sulfur atoms per unit cell, equivalent to 0.25 ML coverage. Post-processing of the electronic structural properties was facilitated through the use of the Atomic Simulation Environment¹⁰.

3.7 References

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Chapter 4

3-Hexyn-1-ol hydrogenation as a model test reaction for liquid-phase catalysis

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4.1 Background

The partial-catalytic hydrogenation of alkynes is a vast class of reactions, many of which play vital roles in industrially important processes such as petrochemical operations, the production of fine chemicals, and the purification of feedstocks for polymer synthesis^{1,2}. Given the economic importance of these reactions, considerable research has been devoted to tailoring individual catalysts to achieve an optimal combination of activity and selectivity. The effects of variations in catalyst support, catalyst metal, particle shape and size, and use of organic ligands or heavy metals as modifiers are all widely reported in the literature³⁻⁶. However, the body of work focused on systematically linking the effects of these variations on activity and selectivity to a mechanistic understanding of the target reaction is limited. The main notable exceptions are the gas-phase hydrogenations of acetylene and ethylene, which have been thoroughly characterized using a combination of experimental and theoretical techniques¹. This detailed understanding of the sensitivity of both activity and selectivity to variations in the catalyst makes this system a useful test reaction for evaluating the catalytic properties of new materials. However, as many of the industrially relevant alkyne hydrogenation reactions take place in the liquid-phase, there is motivation to develop an analogous liquid-phase test reaction that would allow for assessment of a catalyst's geometric and electronic structure by monitoring reaction activity and selectivity.

4.2 Objectives

The aim of this chapter is to develop a liquid-phase alkyne hydrogenation test reaction to evaluate the characteristics of catalytic materials by monitoring reaction activities, selectivities, and kinetics. This will be accomplished through the use of Pd(PVP) as a model catalyst for the hydrogenation of 3-hexyn-1-ol. Careful consideration will be given to development of experimental conditions with the goal of achieving maximum accuracy in measurements of catalytic activity and selectivity. Most importantly, the reaction mechanism will be explored in

detail with emphasis on determining individual mechanisms and surface sensitivities for the various reaction processes. This work will enable subsequent chapters to utilize these model systems to explore the modification effects that result from the adsorption of sulfur to transition metal nanocatalysts.

4.3 Experimental details

A detailed discussion of experimental methods can be found in Chapter 3. In brief, the synthesis of PVP supported palladium nanoparticles was achieved through a polyol reduction method modified from that used by Bonet *et al.*⁷. In a typical synthesis, PVP and $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (10:1 monomer units to moles of metal) were dissolved in ethylene glycol and heated under a nitrogen atmosphere to form a colloidal dispersion of polymer-stabilized nanoparticles. The nanoparticles were precipitated by centrifugation in a mixture of acetone and hexane, washed with acetone, and dried under nitrogen. Tellurium decoration was achieved by a redox method modified from the procedure used by Gauthard *et al.*⁸. Synthesis of PVP supported Pd nanoparticles was carried out as detailed above. Prior to precipitation, the colloidal dispersion was bubbled with H_2 to ensure surface coverage by a Pd-H species. A solution of TeCl_4 in ethylene glycol sufficient to give a Pd:Te ratio of 1:0.15 was then added, followed by treatment with NaBH_4 to ensure complete reduction of the tellurium. The decorated nanoparticles were then precipitated, washed, and dried as described above.

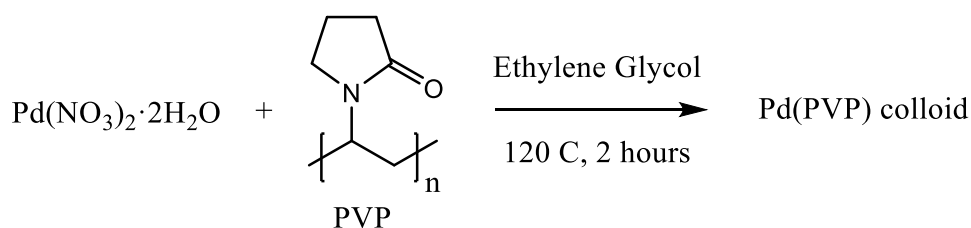
4.4 PVP stabilized palladium as a model catalyst

The initial aim of this chapter is to develop a model palladium catalyst suitable for detailed kinetic analysis of liquid-phase hydrogenation reactions. Ideally, such a catalyst would be composed of small, monodisperse metal nanoparticles of uniform morphology in order to limit uncertainty when determining the relationship between catalyst characteristics and reaction

dynamics. A colloidal synthesis method utilizing a polyol reduction process and a polymer stabilizer was chosen. This method has been shown to provide the desired level of particle size and morphological control through slow reduction of the metal precursor and allows for tailoring of these characteristics by varying the polyol reducing agent, stabilizing polymer, or polymer to metal ratio⁷.

4.4.1 Synthesis

The model palladium catalyst was synthesized using ethylene glycol as the solvent/reducing agent and PVP as the polymer stabilizer with a monomer to metal ratio of 10:1, depicted in Scheme 4.1.



Scheme 4.1 – Preparation of PVP stabilized Pd via the polyol reduction method with ethylene glycol as solvent and reducing agent.

Both PVP and the palladium precursor were thoroughly dispersed in ethylene glycol prior to the reduction step in order to minimize particle size variation. Upon heating, formation of the colloidal nanoparticles was characterized by a slight colour change from a dark red/brown solution to a dark brown/black colloidal suspension signifying the reduction of Pd^{2+} to Pd^0 . When the reaction was complete, the resulting nanoparticles were isolated as described in Section 4.3.

While the stabilizing polymer plays a debatable role in determining catalytic activity and selectivity for a given reaction^{5,9-11}, removal of the stabilizing polymer was not attempted to limit variation in sample quality and/or physical characteristics such as particle size and shape introduced through a multitude of deposition and cleaning steps. In particular, standard techniques for removal of the polymer often involve high-temperature treatments, which can induce morphological changes in the nanoparticles or result in aggregation^{12,13}. A promising alternative method for polymer removal *via* UV ozone cleaning has recently been developed by Crespo-Quesada *et al.* which avoids these issues¹⁴. However, this technique results in a partial poisoning of the catalyst surface through chemisorption of CO which cannot be easily controlled, making it unsuitable for use on the model catalysts required for this thesis. Instead, polymer to metal ratios were carefully controlled across all experimental methods, and systems were characterized in the presence of the stabilizer.

4.4.2 Characterization

XRD Characterization

The as-synthesized Pd(PVP) nanoparticles were characterized by XRD. A typical profile is displayed in Figure 4.1 below, with four clear peaks assigned to the (111), (200), (220), and (311) crystal planes. A fifth peak corresponding to reflections from the (222) crystal plane is included in the reference spectrum, but is not clearly observed in the experimental profile due to insufficient intensity. No additional peaks signifying the formation of palladium oxides are present.

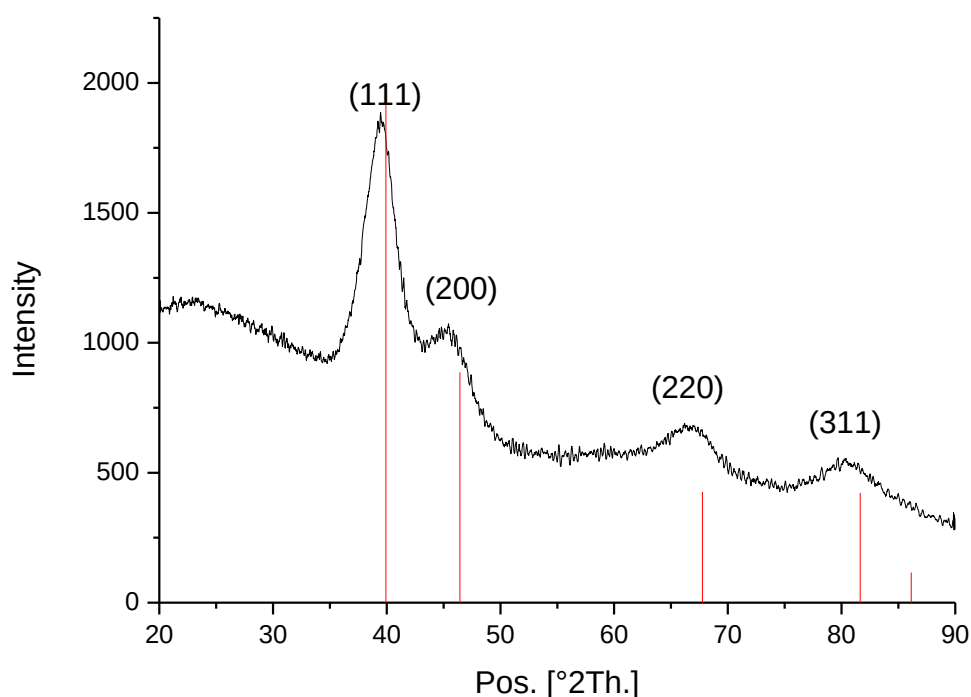


Figure 4.1 – XRD profile of Pd(PVP) with peak positions for bulk palladium indicated in red.

Due to significant overlap between the (111) and (200) peaks, the (220) peak was selected for the calculation of average particle size. Application of the Scherrer Equation (Equation 2.3) to the fitted peak gives an average particle size of 2.5 nm. A slight shift to lower angles is observed for all Pd(PVP) peaks when compared to the reference peaks for bulk palladium resulting from an increase in lattice parameter from the bulk value of 3.8907 Å to 3.9393 Å for Pd(PVP). This increase in lattice parameter is typical for highly-disperse PVP-stabilized nanoparticles as properties transition away from those of the bulk system¹⁵.

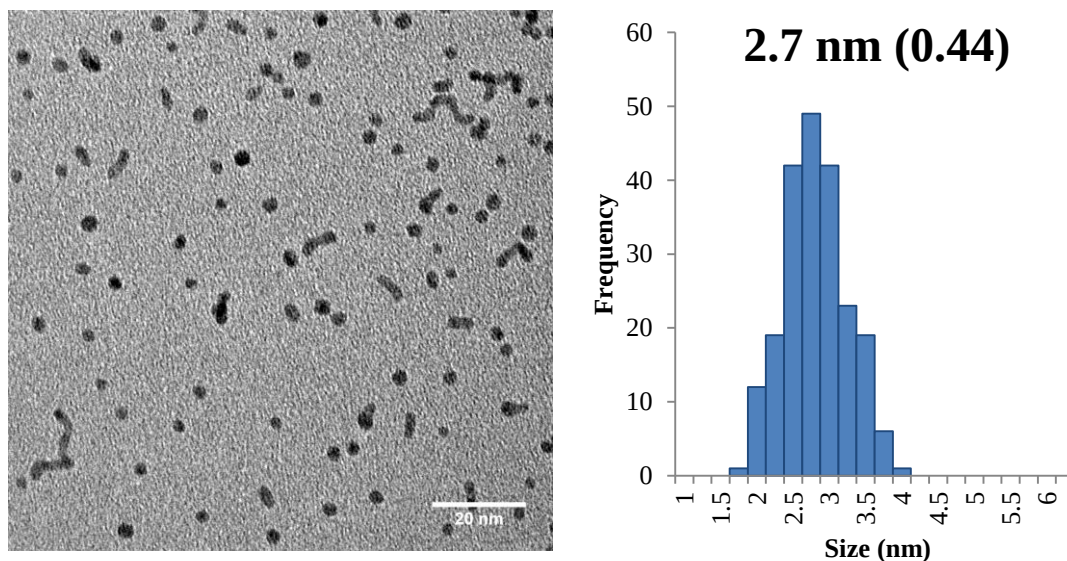
TEM Characterization

Figure 4.2 – TEM micrograph for Pd(PVP) with corresponding particle size distribution histogram.

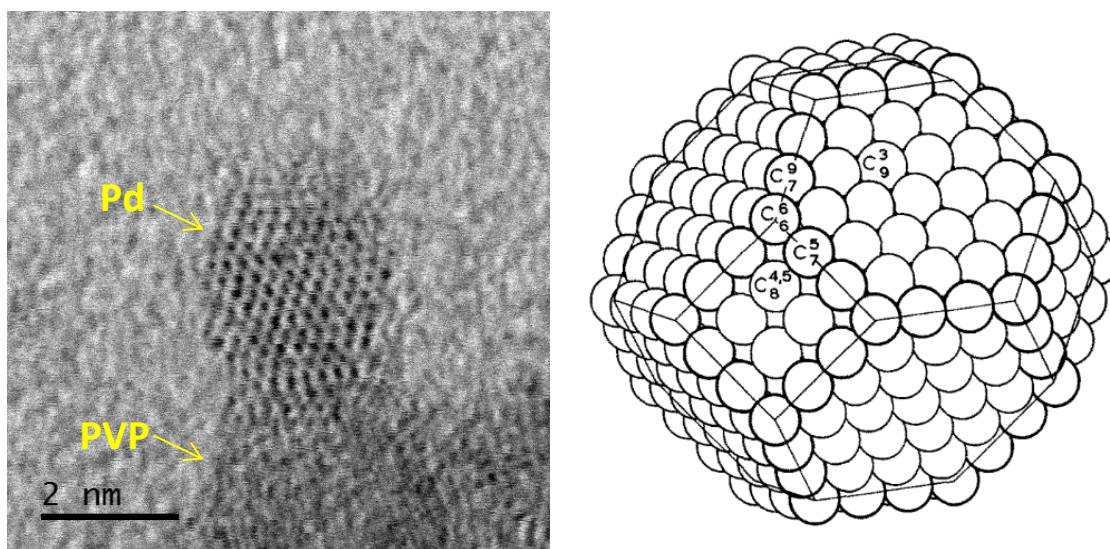


Figure 4.3 – (a) HRTEM micrograph for a representative Pd(PVP) nanoparticle with cubooctahedral structure and (b) a model cubooctahedral nanoparticle reproduced from reference²².

Additional characterization of the Pd(PVP) nanoparticles was performed by TEM and a typical image along with corresponding particle size distribution is displayed above in Figure 4.2. The TEM results show no significant aggregation and the particles are nearly mono-disperse with an

average particle size of 2.7 nm (standard deviation 0.44 nm). This result is in good agreement with the average particle size determined from XRD (2.5 nm). There are, however, a small number of particles that appear to be joined into longer, chain-like structures. While it was not possible to determine their composition by low-resolution TEM, similar structures have previously been reported for highly disperse, polymer-supported nanoparticles^{9,16,17}. These “beads on a string” type structures result when multiple nanoparticles are supported on a single polymer chain¹⁸.

A high resolution (HR) TEM image of the terminus of one of these structures is displayed in Figure 4.3(a) above, and two distinct regions are clearly visible. The region at the end of the structure (designated “Pd”) displays clear lattice fringes corresponding to one of the model Pd particles, which is shown to have the cubooctahedral structure typical of PVP-stabilized nanoparticles synthesized by polyol reduction¹⁹. The second region (designated “PVP”) displays an amorphous structure and was thus assigned to the polymer stabilizer, supporting the conclusion that the chain-like features observed from low-resolution TEM are an artefact of the polymer rather than a deviation from the typical structure for model Pd nanoparticles.

Surface Statistics

In contrast to typical heterogeneous catalytic systems, catalytic activities for colloidal systems are often reported relative to total moles of metal catalyst with little consideration for effective surface area²⁰. However any study aiming to compare catalytic properties of materials with differing particle surface geometries or dispersions must account for changes in relative surface area across the systems. Accurate determination of effective surface area for colloidal systems is a challenge as standard techniques, such as chemisorption measurements or CO stripping cyclic voltammetry, are inhibited by the polymer support²¹. In order to best address these challenges, an

alternative theoretical approach was employed for the determination of surface area for the model Pd(PVP) catalyst. Based on the average particle size and cubooctahedral structure demonstrated by TEM, surface statistics were calculated in accordance with the method by van Hardeveld and Hartog²² using Equations 4.1-4.5:

$$\text{Total atoms} = 16m^3 - 33m^2 + 24m - 6 \quad \text{Equation 4.1}$$

$$\text{Surface atoms} = 30m^2 - 60m + 32 \quad \text{Equation 4.2}$$

$$\text{Terrace atoms} = 30m^2 - 96m + 80 \quad \text{Equation 4.3}$$

$$\text{Edge atoms} = 36m - 72 \quad \text{Equation 4.4}$$

$$\text{Corner atoms} = 24 \quad \text{Equation 4.5}$$

where m is the number of cubooctahedral shells comprising the particle. Terrace atoms are defined as surface atoms located within the (111) or (100) crystal facets, depicted in Figure 4.3.b as atoms C^3_9 and $C^{4,5}_6$, respectively. Edge atoms are defined as surface atoms located at the junction between two terrace planes, depicted in Figure 4.3.b as atoms C^9_7 and C^5_7 . Corner atoms are surface atoms located at the junction between three terrace planes, and are depicted in Figure 4.3.b as atom C^6_6 . For the purposes of this work, edge and corner atoms are grouped together and referred to collectively as “low-coordinate” atoms. An average particle diameter of 2.7 nm corresponds to a 4 shell cubooctahedral structure (as depicted in 4.3.b). Approximate calculations of atom distribution statistics give 46% of the particle as surface atoms, 54% as bulk atoms, 35% of the surface atoms in low-coordinate sites, and 65% of the surface as terrace sites. Additional calculations based on the total number of surface atoms and a reference value for the Pd surface packing density of $1.27 \times 10^{19} \text{ atoms m}^{-2}$ yields a theoretical surface area of $184.8 \text{ m}^2 \text{ g(Pd)}^{-1}$.²³

4.5 Hydrogenation of 3-hexyn-1-ol

The catalytic hydrogenation of 3-hexyn-1-ol was selected as a test reaction in order to investigate the catalytic properties of the Pd(PVP) nanoparticles. This reaction is of economic importance to the fine chemicals industry through the synthesis of leaf alcohol (*cis*-3-hexen-1-ol), a valuable chemical used for the production of fragrances².

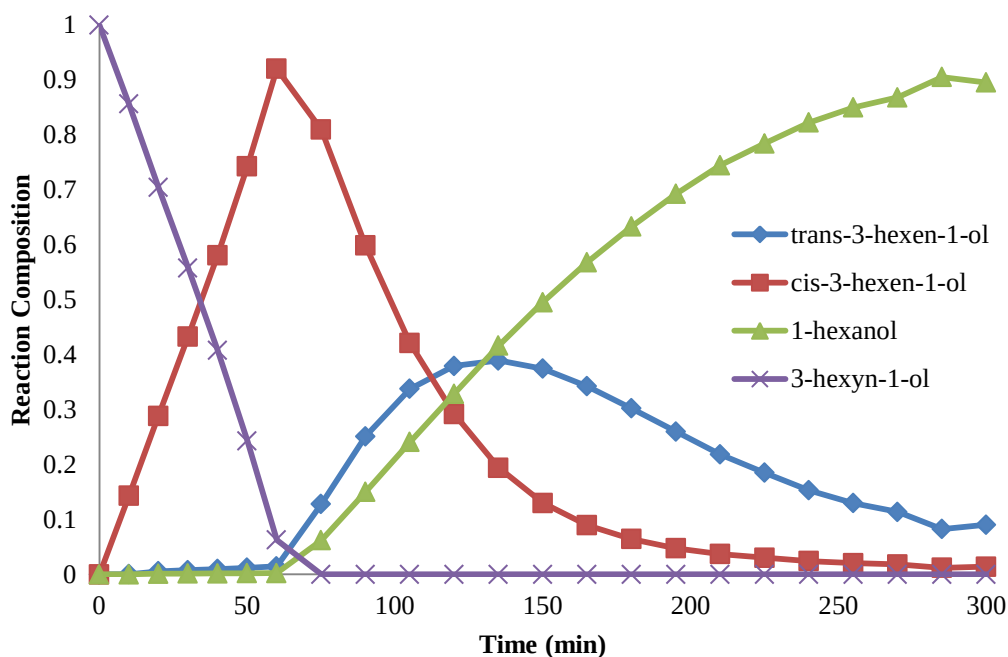
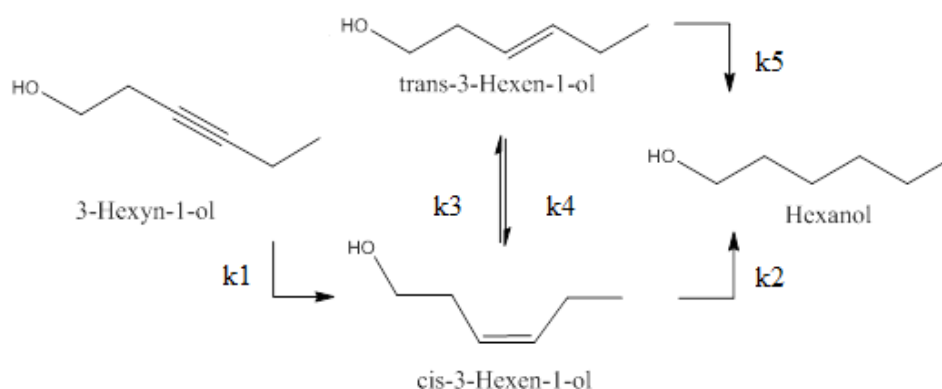


Figure 4.4 – Reaction profile for the Pd(PVP) catalysed hydrogenation of 3-hexyn-1-ol.

Hydrogenation was carried out in the liquid phase at 30 °C and ambient pressure using the reaction setup described in Section 3.3.3. A typical reaction profile is shown in Figure 4.4 above and is characterized by two distinct reaction steps. The initial step involves the hydrogenation of 3-hexyn-1-ol to *cis*-3-hexen-1-ol due to *cis*-addition of hydrogen atoms to the triple bond *via* the metal surface. The high initial selectivity of this step (97.4% selectivity to the *cis* product) is characteristic of Pd catalysed alkyne hydrogenation reactions where the high relative binding strength of the alkyne effectively blocks the surface from catalysing additional reactions whilst 3-hexyn-1-ol remains present in the reaction composition. Once this initial hydrogenation step is complete, rapid conversion of the *cis*-3-hexen-1-ol intermediate occurs through hydrogenation

and/or isomerisation to further products. The reaction rate for the initial hydrogenation step was found to be independent of the 3-hexyn-1-ol concentration, while the rate for the secondary reaction step was found to depend linearly on the *cis*-3-hexen-1-ol concentration, indicating zero and first order reactions, respectively. This behaviour is typical for the catalytic hydrogenations of internal alkynes and alkenes over palladium catalysts, and numerous literature reports exist in agreement with these results^{24–27}. A general mechanism for the reaction is given by Scheme 4.2.



Scheme 4.2 – General mechanism for the hydrogenation of 3-hexyn-1-ol, where *cis*-3-hexen-1-ol is the initial product with others resulting from isomerization (k_3 and k_4) and over-hydrogenation (k_2 and k_5).

4.5.1 Optimization of reaction conditions

An important aspect of this thesis is the detailed kinetic analysis of palladium catalysed hydrogenations of alkynes and alkenes, however these reactions occur with extremely high turnover frequencies, necessitating the careful design of experimental conditions in order to avoid effects from mass transfer limitations and blank contributions due to possible palladium contaminations in the reaction setup. In a review of the literature pertaining to the kinetics of liquid-phase hydrogenation reactions over supported metal catalysts, Singh and Vannice found that reliable quantitative kinetic information could only be obtained after contributions from these effects are accounted for²⁸.

In the case of the ambient pressure hydrogenation of 3-hexyn-1-ol, a blank reaction performed using the cleaning procedures outlined in Section 3.3.2 resulted in only 0.52% conversion after 4 hours. This level of conversion indicates blank contributions are unlikely to significantly impact further measurements of catalytic behaviour. In liquid phase reactions, mass transfer limitations often result from low rates of hydrogen transfer from the gas phase²⁸. Hydrogen solubility and rates of phase transfer vary a great deal depending on temperature, pressure, stirring rate, and nature of the solvent, and are difficult to determine theoretically^{29–31}. Hydrogen solubility, along with any additional contributions to mass transfer limitations from polymer effects, were therefore determined experimentally through a variation on the Madon-Boudart test where the reaction rate relative to catalyst concentration was monitored with all other parameters held constant³². The results are displayed in Figure 4.5 below, with corresponding reactant to catalyst ratios given in Table 4.1.

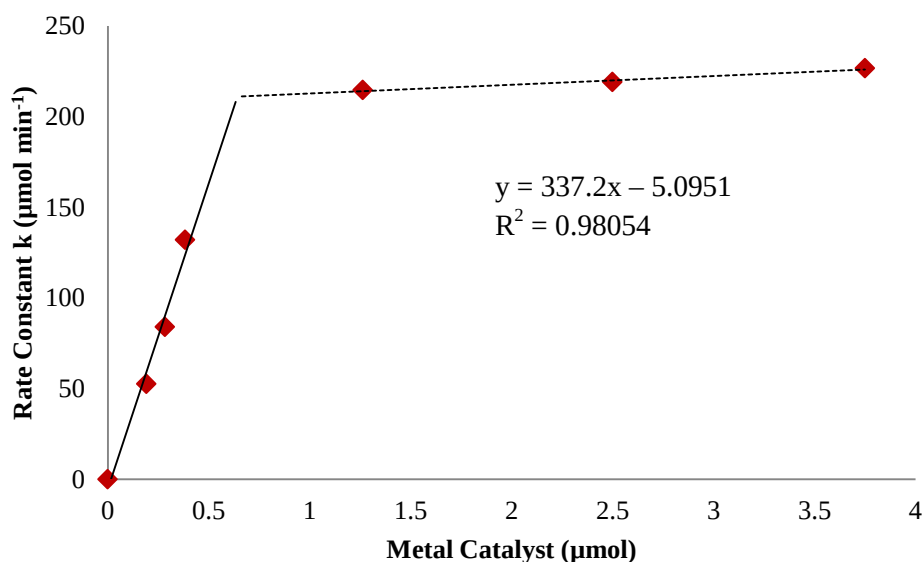


Figure 4.5 – Relationship between the zero order rate constant for hydrogenation of 3-hexyn-1-ol to *cis*-3-hexen-1-ol and catalyst concentration. The solid trend line corresponds to the region free from mass transfer limitations, while the dashed trend line indicates the region where these effects dominate. Conditions: 15 mmol 3-hexyn-1-ol, 50 mL EtOH, 30°C, ambient pressure H₂, and stirring rate 750 rpms.

Table 4.1 – Summary of reactant:catalyst ratios for the various catalyst concentrations plotted in Figure 4.5.

Catalyst metal (μmol)	3-Hexyn-1-ol (μmol)	Reactant: catalyst
0	15000	-----
0.191	15000	78410
0.283	15000	53020
0.383	15000	39220
1.263	15000	11880
2.500	15000	6000
3.750	15000	4000

A reaction free of mass-transfer limitations will maintain a linear relationship between reaction rate and catalyst concentration with a zero intercept. This criterion is met when catalyst concentrations below $0.668 \mu\text{mol}$ Pd metal are used, corresponding to a maximum hydrogenation rate of $220 \mu\text{mol min}^{-1}$. In order to ensure a reaction rate below the mass transfer limited region, a catalyst concentration of $0.300 \mu\text{mol}$ Pd metal was chosen for further hydrogenation experiments using this reaction setup.

With a catalyst concentration of $0.300 \mu\text{mol}$ and a reactant to catalyst ratio of 50000:1, the completion time for the initial 3-hexyn-1-ol hydrogenation step was found to be 178 min. In an effort to decrease the time required to complete both this and the subsequent reaction step without altering the reaction rate, a series of experiments were conducted with decreased reactant to catalyst ratios achieved through lowering the initial reactant concentration. A comparison between calculated and measured completion times for the reaction at the various reactant to catalyst ratios is given in Table 4.2 below.

Table 4.2 – Predicted and measured completion times for the initial reaction step in the hydrogenation of 3-hexyn-1-ol at different reactant to catalyst ratios.

Catalyst metal (μmol)	3-Hexyn-1-ol (μmol)	Reactant: catalyst	Calculated 1 st step completion time (min) ^a	Measured 1 st step completion time (min)
0.300	15000	50000:1	N/A	178.00
0.300	3000	10000:1	35.60	23.56
0.300	1200	4000:1	14.24	7.93

^aCalculated based on the measured first step completion time for a reactant:catalyst of 50000:1. Conditions: 0.300 μmol Pd metal, 50 mL EtOH, 30°C, ambient pressure H_2 , and stirring rate 750 rpms.

The data shows a discrepancy between the predicted and measured completion times that increases in significance as reactant:catalyst is decreased. This is attributed to partial evaporation of the reactant as a result of the hydrogen bubbling reaction setup, and results in artificially fast completion times (and thus hydrogenation rates). Minimizing contributions from this effect can be achieved by maximizing initial reactant concentration. In order to achieve a suitable compromise between optimizing reaction time and minimizing contributions from reactant loss, the initial conditions of 0.300 μmol Pd metal and a reactant to catalyst ratio of 50000:1 were chosen for evaluation of reaction rate for the initial 3-hexyn-1-ol hydrogenation step.

However this choice of reaction conditions introduces a complication when measuring the successive reaction steps present in the hydrogenation of 3-hexyn-1-ol, namely that the same partial evaporation that occurs for 3-hexyn-1-ol will also affect the concentration of all other reactants present in the system, particularly *cis*-3-hexen-1-ol as it is the primary reaction intermediate. As such, the concentration of reaction intermediates present in the system when the

initial hydrogenation step is complete will be dependent on the time required to complete this step.

In order to eliminate the possibility of uncertainties in the initial reaction step affecting the kinetics of subsequent steps, a separate hydrogenation experiment using *cis*-3-hexen-1-ol as the starting reactant was used to determine all reaction rates pertaining to the isomerization and over-hydrogenation of *cis*-3-hexen-1-ol. The same high initial reactant concentration used for 3-hexyn-1-ol hydrogenation (15000 μmol) was also chosen for these experiments in order to minimize error contributions due reactant evaporation. However, as the reaction rate for *cis*-3-hexen-1-ol conversion was found to be significantly slower than the rate for hydrogenation of 3-hexyn-1-ol under equivalent reaction conditions, the possibility of increasing catalyst concentration to decrease reaction completion time and thus further minimize error contributions was also investigated. The highest catalyst concentration tested in Figure 4.5 (3.75 μmol Pd metal, reactant:catalyst of 4000:1) resulted in a *cis*-3-hexen-1-ol hydrogenation rate of 164 $\mu\text{mol min}^{-1}$, and as this rate is still sufficiently below the previously established limit of 220 $\mu\text{mol min}^{-1}$ to ensure no adverse effects from mass transfer limitations, the higher catalyst concentration of 3.75 μmol was chosen for all further reactions measuring the conversion of *cis*-3-hexen-1-ol.

4.6 3-Hexyn-1-ol hydrogenation surface sensitivity

The reaction mechanism for 3-hexyn-1-ol hydrogenation given in Scheme 4.2 consists of three distinct processes: the hydrogenation of 3-hexyn-1-ol to *cis*-3-hexen-1-ol, the hydrogenation of *cis*-3-hexen-1-ol to 1-hexanol, and the isomerization of *cis*-3-hexen-1-ol to *trans*-3-hexen-1-ol. While literature reports of similar liquid-phase alkyne hydrogenations suggest all three processes are sensitive to the relative prevalence of terrace and low-coordinate sites on the catalyst surface, it is preferable to confirm specific active site preferences experimentally^{25,33}. Measuring the site

dependency of these processes will provide a detailed understanding of the overall mechanism for the reaction, ultimately allowing the Pd(PVP)/3-hexyn-1-ol hydrogenation system to be used as a tool for connecting reaction kinetics to changes in catalyst surface structure.

4.6.1 Tellurium decoration of Pd(PVP)

Synthesis

In order to investigate the specific site selectivity of the 3-hexyn-1-ol hydrogenation reaction, geometric modification of the Pd(PVP) nanoparticles was carried out through selective deposition of tellurium adatoms onto terrace sites of the metal nanoparticles. Given the surface statistics determined in Section 4.4.2, a Pd:Te ratio of 1:0.15 was chosen for modification to give approximately 39% total surface coverage while selective blocking approximately 59% of terrace sites. The standard Pd(PVP) nanoparticles were synthesized as described previously in Section 4.4.1, but without the precipitation steps. Instead, the colloidal suspension of Pd(PVP) nanoparticles in ethylene glycol was bubbled with hydrogen in order to cover the metal in surface-bound Pd-H species. A solution containing Te^{4+} was then added, resulting in a redox reaction with the bound hydrogen and partial reduction of the Te ions onto the metal surface. The particles were further treated with NaBH_4 to ensure complete reduction of the Te adatoms before the particles were precipitated, washed, and dried as described previously for the unmodified catalyst.

Characterization

The resulting Pd+Te(PVP) nanoparticles were characterized by TEM, and a typical image along with size distribution histogram is given in Figure 4.6 below.

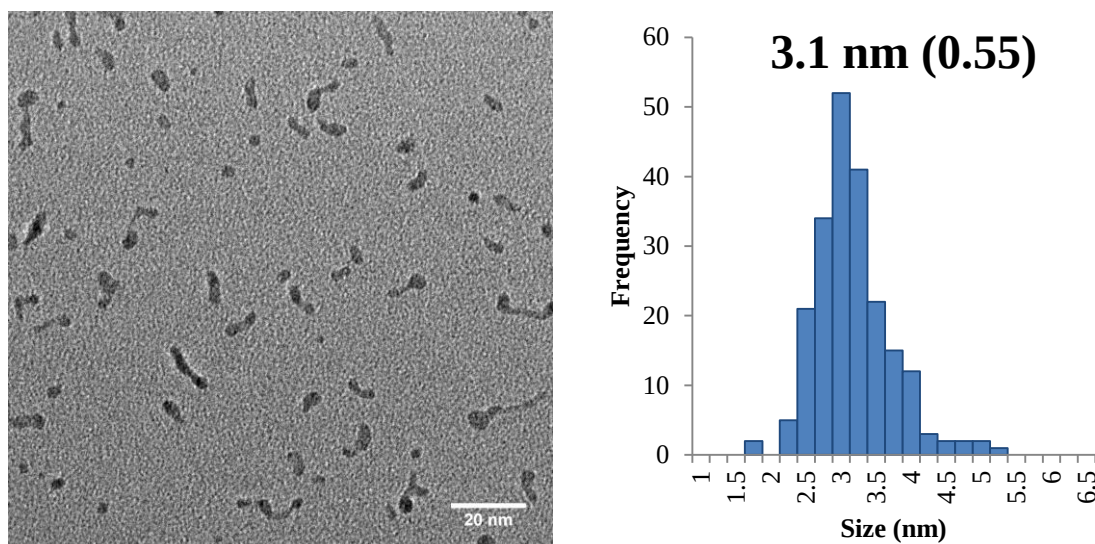


Figure 4.6 – TEM micrograph for Pd+Te(PVP) with corresponding particle size distribution histogram.

The overall sample characteristics appear similar to those for the unmodified Pd(PVP) nanoparticles, and no significant aggregation is observed. Analysis of average particle size shows a slight increase over the unmodified particles, from 2.7 nm (standard deviation 0.44 nm) to 3.1 nm (standard deviation 0.55 nm), consistent with the Te adatoms forming an additional partial shell on the Pd surface. Standard deviation in the particle size relative to the average is very similar for both samples (16.3% for Pd(PVP), 17.7% for Pd+Te(PVP)), suggesting the size increase is the result of uniform decoration rather than complete coverage of a small portion of the particles. EDX analysis of the sample performed on four separate regions gave an average measured Pd:Te ratio of 1:0.166, in good agreement with the experimentally targeted value of 1:0.15. A typical spectrum is shown below in Figure 4.7.

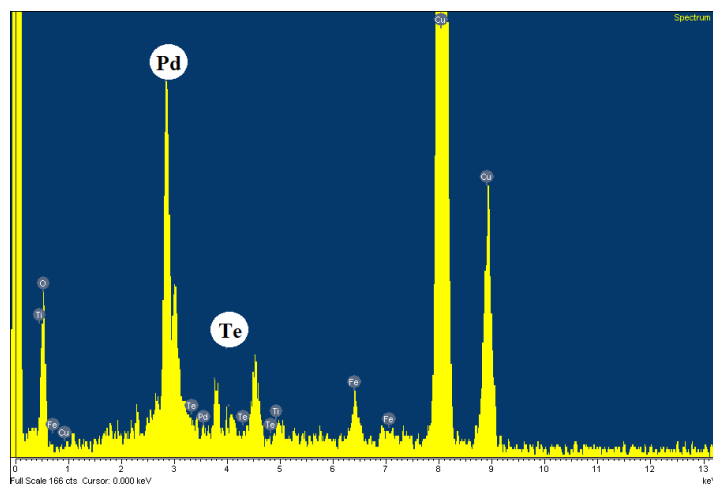


Figure 4.7 – EDX spectrum for Pd+Te(PVP) with peaks corresponding to Pd and Te indicated.

In an effort to confirm selective deposition of the Te adatoms onto terrace sites of the metal surface, high-angle annular dark field scanning transmission electron microscopy (HAADF STEM) was performed on the modified particles and the results for a representative particle with size and shape typical for the Pd+Te(PVP) system are displayed in Figure 4.8 below.

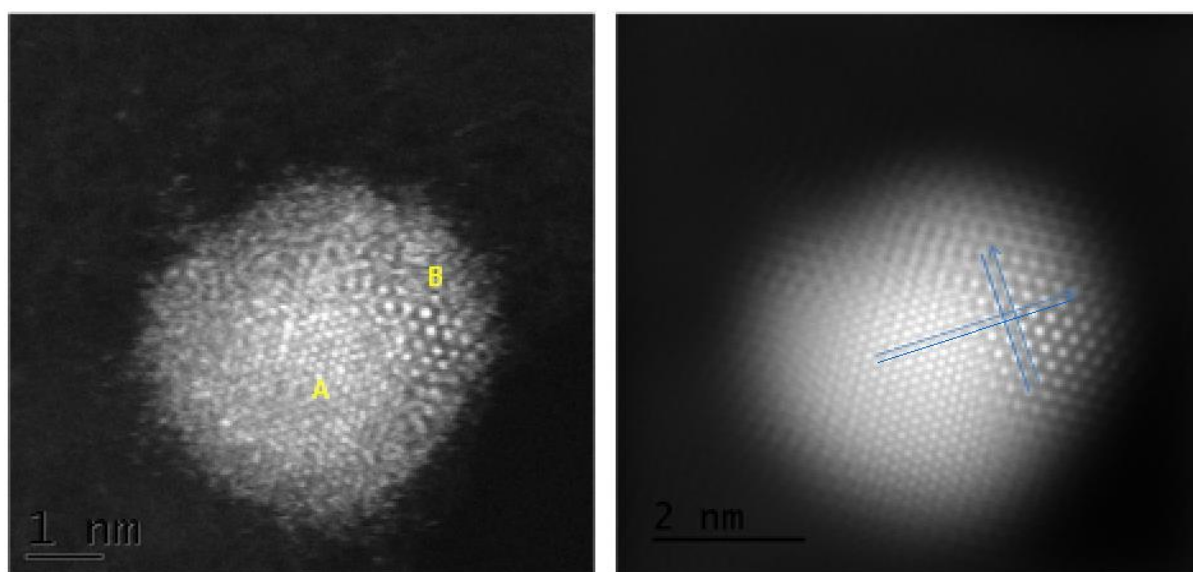


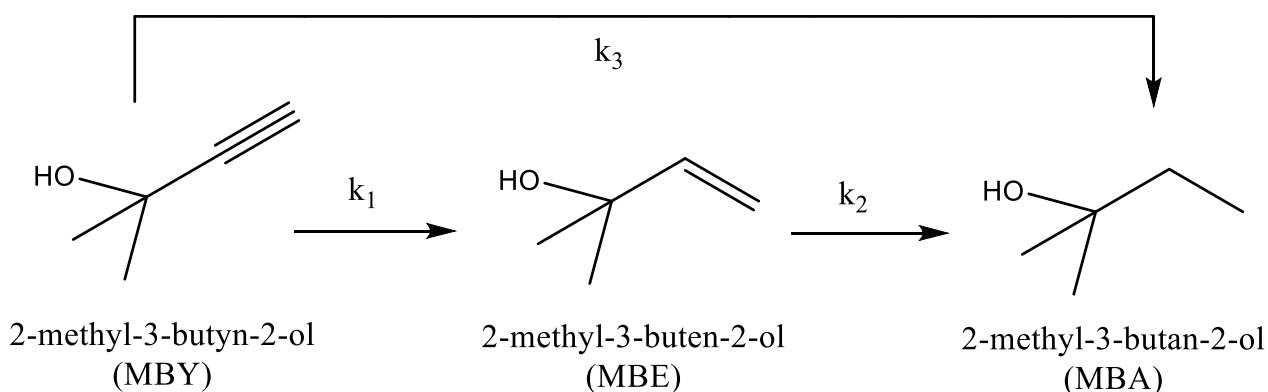
Figure 4.8 – (a) Original HAADF image of a Pd+Te(PVP) nanoparticle where the lattice region designated A corresponds to Pd and the lattice region designated B corresponds to Te. (b) FFT filtered image of the same nanoparticle with relative lattice spacings for regions A and B indicated.

Similar to bright field imaging techniques, image contrast in HAADF STEM is dependent on the number of atoms in a specific area of the sample and the atomic number of the elements present³⁴. However in this case, the image is generated by monitoring electrons diffracted by the sample and thus areas with greater atomic density or elements with higher atomic numbers appear brighter³⁴. The use of HAADF STEM also eliminates additional contributions to image contrast that occur in bright field imaging, allowing the resulting image contrast to be directly interpreted in terms of elemental composition and sample thickness³⁵.

Two distinct lattice regions are clearly visible on the particle shown in Figure 4.8(a), designated as region A and region B. A simple visual analysis of this image shows that the atoms located in region B appear slightly brighter than those in region A, and as image contrast for different elements is proportional to Z^2 (where Z is the atomic number), region B was provisionally assigned to Te atoms and region A to Pd atoms (areas of the particle containing Te are expected to be approximately 1.3 times brighter than areas containing Pd). From the fast Fourier transform (FFT) filtered image in Figure 4.8(b), the lattices for both regions are shown to be coherent but the atoms in region B have a measured spacing 1.62 times greater than those in region A. This value is in good agreement with the calculated relative spacings for Te versus Pd (given a lattice parameter for Pd (fcc) of 3.89 Å and an a lattice parameter for Te (hcp) of 4.46 Å), indicating the particle consists of a Pd core (region A) decorated by a partial Te shell (region B). Furthermore, the extended lattice of region B is consistent with Te primarily decorating terrace planes on the metal surface rather than the more scattered deposition expected for unselective decoration or selective decoration of low-coordinate sites.

4.6.2 Hydrogenation of 2-methyl-3-butyn-1-ol

Given the selective geometric modification of Pd(PVP) by Te discussed above, it was proposed that comparing catalytic properties of Pd(PVP) to those of the modified Pd+Te(PVP) system could present an effective method for determining active site preferences for liquid-phase hydrogenation reactions. A similar technique was reported by Anderson *et al.*, where the authors used bismuth selectively deposited on low-coordinate sites of small palladium nanoparticles to compare mechanisms for the catalytic hydrogenations of 1-hexyne and 2-hexyne²⁵. In order to confirm the validity of this method of determining active site preferences, the hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE) and 2-methyl-3-butan-2-ol (MBA) was initially selected as a test reaction.



Scheme 4.3 – Mechanism for the hydrogenation of 2-methyl-3-butyn-2-ol.

While the mechanism for this reaction (Scheme 4.3 above) is analogous to that for the hydrogenation of 3-hexyn-1-ol, the absence of an alkene isomerization step simplifies the measurements by eliminating the need to determine site selectivity of competing processes. This mechanism has also been extensively studied by Crespo-Quesada *et al.*, who employed an alternative method of geometric modification to determine site-specific TOF's for each hydrogenation process by comparing the catalytic behaviour of model cubic, octahedral, and

cubooctahedral palladium nanoparticles stabilized by PVP^{33,36–38}. Comparison of these findings from the literature to results obtained with the modified Pd+Te(PVP) catalyst will provide an additional check on the validity of determining active site preferences for hydrogenation reactions by this method of selective geometric modification.

A typical profile for the reaction (Figure 4.9 below) demonstrates the same two-step hydrogenation process observed for the hydrogenation of 3-hexyn-1-ol discussed previously.

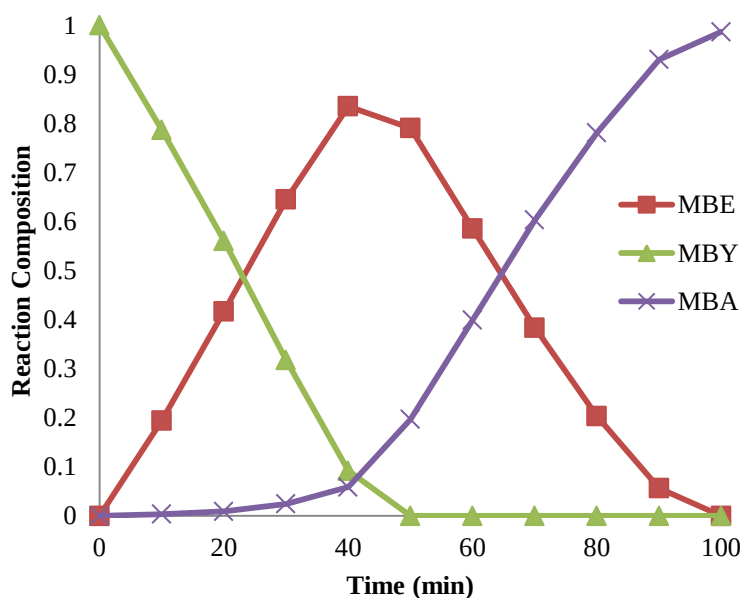


Figure 4.9 – Reaction profile for the Pd(PVP) catalysed hydrogenation of 2-methyl-3-buten-2-ol.

Table 4.3 – Activities of various Pd(PVP) catalysts for the hydrogenations of MBY to MBE and MBE to MBA.

	Hydrogenation of MBY to MBE ^b		Hydrogenation of MBE to MBA ^c	
	TOF (sec ⁻¹)	Activity loss ^a	TOF (sec ⁻¹)	Activity loss ^a
Pd(PVP)	38.56	-----	11.19	-----
Pd+Te(PVP)	3.01	92.2%	7.37	34.1%
Pd+NaBH ₄ (PVP)	30.54	20.8%	8.86	20.8%

^aCalculated relative to TOF for unmodified Pd(PVP). ^bConditions: 0.103 μ mol Pd metal, 15 mmol MBA, 50 mL EtOH, 30°C, ambient pressure H₂, and stirring rate 750 rpms. ^cConditions: 0.938 μ mol Pd metal, 15 mmol MBE, 50 mL EtOH, 30°C, ambient pressure H₂, and stirring rate 750 rpms.

Table 4.3 above lists the measured TOF's for the hydrogenation of MBY to MBE and MBE to MBA for both the Pd(PVP) and Pd+Te(PVP) catalysts. When determining active site preference for each reaction step, Crespo-Quesada *et al.* found that hydrogenation of MBY to MBE showed a four-fold preference for terrace sites over low-coordinate sites, while hydrogenation of MBE to MBA was exclusive to low-coordinate sites³³. Assuming deposition of Te is selective to terrace sites of Pd(PVP) as shown by HAADF STEM, a Pd:Te ratio of 1:0.15 as confirmed by EDX, and the Pd surface statistics calculated previously, the Pd+Te(PVP) catalyst would have a 59% reduction in available terrace sites with no reduction in the number of low-coordinate sites. Based on literature values for the relative activities of MBY and MBE hydrogenations catalysed by terrace and low-coordinate sites, this is expected to reduce the TOF for hydrogenation of MBY to MBE by 53% while leaving the TOF for hydrogenation of MBE to MBA unaffected. However, the measured activity losses for the Pd+Te(PVP) hydrogenation were higher than

expected for both reaction steps (92.2% and 34.2% reduction in TOF for MBY to MBE and MBE to MBA hydrogenations, respectively). It should be noted that while overall activity loss was higher than expected, the TOF for hydrogenation of MBY to MBE showed 58% greater loss in activity than the TOF for hydrogenation of MBE to MBA. This activity difference between the two steps is quite close to the predicted relative decrease in TOF of 53%, and therefore suggests an additional source of non-site-specific deactivation may be responsible for the overall reduced activity.

As literature reports have shown that employing NaBH_4 as a reducing agent can result in the formation of B_xO_y species on the surface of Pd nanoparticles that remain even after extensive washing procedures have been carried out³⁹, the NaBH_4 reduction step during the Te decoration process was investigated as a possible source of the additional deactivation observed in the previous section. For these experiments, all steps of the Pd(PVP) decoration method except the addition of Te were performed on the original Pd(PVP) system. The resulting NaBH_4 modified Pd(PVP) catalyst was then tested for MBY and MBE hydrogenation and was found to be 20.8% less active than the unmodified Pd(PVP) catalyst for both reactions. This uniform activity loss indicates treatment with NaBH_4 leads to a degree of nonselective blocking that is likely responsible for discrepancies between the predicted and measured TOF's, and further supports attributing the loss in activity for MBY hydrogenation relative to MBE hydrogenation to selective blocking of terrace sites by Te.

As additional confirmation of selective Te decoration, the direct over-hydrogenation of MBY to MBA was monitored as literature reports state this process is catalysed exclusively by terrace sites³³. With Pd(PVP) as the catalyst, selectivity to MBA was found to be 7.05% at 95% MBY

conversion. This decreased to 1.43% for the Pd+Te(PVP) catalyst, confirming that modification of Pd(PVP) with Te results in blocking of terrace active sites.

4.6.3 Hydrogenation of 3-hexyn-1-ol

The method of determining active site selectivity through selective geometric modification of Pd(PVP) by Te was also applied to the hydrogenation of 3-hexyn-1-ol. As in the previous example, both Pd(PVP) and Pd+Te(PVP) were used as catalysts in order to determine changes in TOF for the various reaction processes resulting from partial blockage of terrace sites. A summary of the results is presented in Table 4.4 below.

Table 4.4 – Activities of various Pd(PVP) catalysts for the conversion of 3-hexyn-1-ol to *cis*-3-hexen-1-ol and the conversion of *cis*-3-hexen-1-ol to *trans*-3-hexen-1-ol and 1-hexanol.

	3-Hexyn-1-ol conversion TOF (sec ⁻¹) ^c	<i>cis</i> -3-Hexen-1-ol conversion TOF (sec ⁻¹) ^d
Pd(PVP)	12.37	4.74
Pd+Te(PVP)	2.31	2.27
Observed activity loss ^a	81.3%	53.0%
Corrected activity loss ^b	60.5%	32.2%

^aCalculated relative to TOF for unmodified Pd(PVP). ^bCorrected to account for 20.8% reduction in active sites due to NaBH₄ treatment. ^cConditions: 0.300 μmol Pd metal, 15 mmol 3-hexyn-1-ol, 50 mL EtOH, 30°C, ambient pressure H₂, and stirring rate 750 rpm. ^dConditions: 3.75 μmol Pd metal, 15 mmol *cis*-3-hexen-1-ol, 50 mL EtOH, 30°C, ambient pressure H₂, and stirring rate 750 rpm.

In order to account for general activity loss resulting from treatment with NaBH₄, reductions in TOF were corrected to account for non-selective blockage of 20.8% of the surface active sites as demonstrated in Section 4.6.2. As shown in Table 4.4, modification of Pd(PVP) with Te resulted in a 60.5% reduction in TOF for the initial 3-hexyn-1-ol conversion. This is in excellent agreement with 59% reduction in available terrace sites for this catalyst, and indicates the hydrogenation of 3-hexyn-1-ol occurs solely on terrace sites.

In the case of *cis*-3-hexen-1-ol conversion, modification of Pd(PVP) with Te resulted in a 32.3% reduction in TOF. This activity loss is similar to the total level of surface blockage resulting from Te decoration (39% total surface coverage including both terrace and low-coordinate sites) and suggests *cis*-3-hexen-1-ol conversion is a surface insensitive process. However, as this process encompasses *cis*-3-hexen-1-ol conversion resulting from both isomerization and over hydrogenation reactions, it is necessary to examine both contributions independently in order to accurately determine surface sensitivity.

A kinetic modelling approach was used to separate the isomerization and hydrogenation processes contributing to the overall *cis*-3-hexen-1-ol conversion. Experimental reaction profiles were fitted with a Langmuir-Hinshelwood kinetic model using the method described in Chapter 3. Rate equations (Equations 4.6-4.10 below) were derived based on the mechanism presented in Scheme 4.2, and rate constants were grouped into isomerization processes (k_3 and k_4) or hydrogenation processes (k_2 and k_5).

$$\frac{dA}{dt} = -\theta_A k_1$$

Equation 4.6

$$\frac{dB}{dt} = k_1\theta_A + k_4\theta_C - \theta_B(k_2 + k_3) \quad \text{Equation 4.7}$$

$$\frac{dC}{dt} = k_3\theta_B - \theta_C(k_4 + k_5) \quad \text{Equation 4.8}$$

$$\frac{dD}{dt} = k_2\theta_B + k_5\theta_C \quad \text{Equation 4.9}$$

$$\theta_i = \frac{K_i P_{(i)}}{1 + \int_D^A K_i P_{(i)}} \quad \text{Equation 4.10}$$

Equations 4.6-4.10 – Rate equations for the mechanism presented in Scheme 4.2, where A = 3-hexyn-1-ol, B = *cis*-3-hexen-1-ol, C = *trans*-3-hexen-1-ol, D = 1-hexanol, K_i = adsorption constant of species i , $P_{(i)}$ = equilibrium concentration of species i , and θ_i = probability of a surface site being occupied by species i .

Fitted reaction profiles for the Pd(PVP) and Pd+Te(PVP) catalysed hydrogenations are shown in Figure 4.10 and a summary of the results is given in Table 4.5.

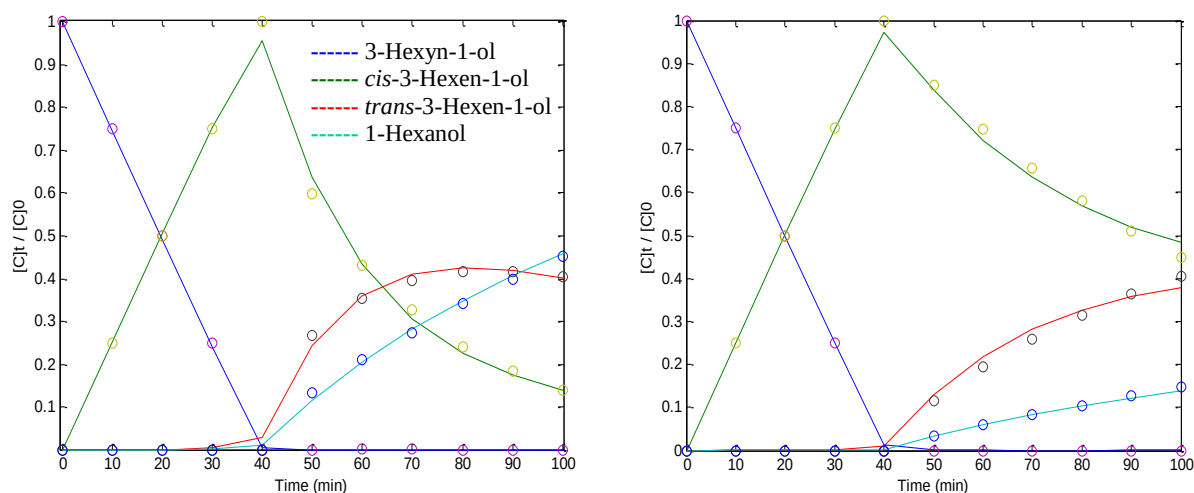


Figure 4.10 – Kinetic fittings for the hydrogenations of 3-hexyn-1-ol and *cis*-3-hexen-1-ol catalysed by (a) Pd(PVP) and (b) Pd+Te(PVP). Open circles correspond to experimental data points and solid lines to fitted profiles.

Table 4.5 – Activities of various Pd(PVP) catalysts for the hydrogenation and isomerization of *cis*-3-hexen-1-ol.

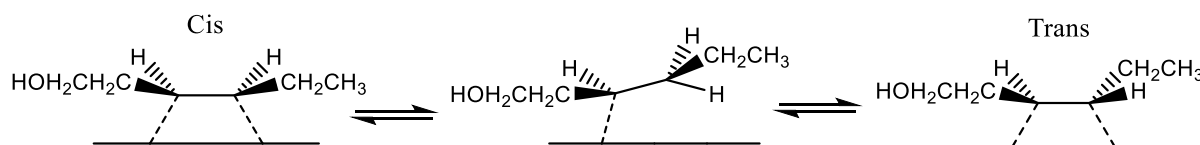
	<i>cis</i> -3-Hexen-1-ol hydrogenation TOF (sec ⁻¹) ^c	<i>cis</i> -3-Hexen-1-ol isomerization TOF (sec ⁻¹) ^c
Pd(PVP)	3.98	7.67
Pd+Te(PVP)	0.678	5.81
Observed activity loss ^a	82.9%	24.3%
Corrected activity loss ^b	62.1%	3.5%

^aCalculated relative to the TOF for unmodified Pd(PVP).

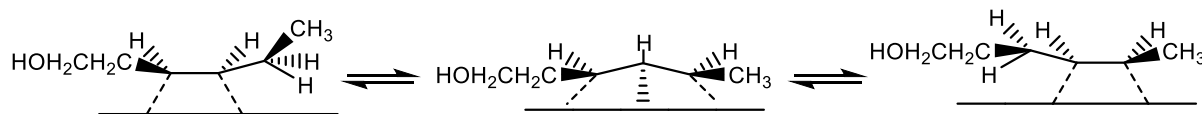
^bCorrected to account for 20.8% reduction in active sites due to NaBH₄ treatment. ^cConditions: 3.75 μmol Pd metal, 15 mmol *cis*-3-hexen-1-ol, 50 mL EtOH, 30°C, ambient pressure H₂, and stirring rate 750 rpm.

As the results in Table 4.5 demonstrate, when the conversion of *cis*-3-hexen-1-ol is separated into hydrogenation and isomerization processes, it becomes apparent that the 32.2% reduction in overall TOF reported previously is due almost exclusively to attenuation in activity for the hydrogenation of *cis*-3-hexen-1-ol to 1-hexanol. The 62.1% loss in TOF for this reaction upon modification of Pd(PVP) with Te is very close to the activity loss reported for the hydrogenation of 3-hexyn-1-ol (60.5%), indicating this reaction is also catalysed by terrace sites on the metal surface. In contrast, only a 3.5% reduction in the TOF for *cis*-3-hexen-1-ol isomerization is observed, indicating this reaction occurs exclusively on low-coordinate sites.

These findings are supported by the mechanism proposed by Ulan *et al.* for the catalytic hydrogenation of internal alkenes. In this report, the authors used deuterium uptake measurements to demonstrate that *cis/trans* isomerization occurs through non-stereoselective, reversible addition of a single H *via* an alkyl intermediate, whereas double bond hydrogenation occurs through progressive bond shift toward decreasingly stable alkenes, resulting in a highly-reactive terminal alkene which is subsequently reduced to produce the saturated alkane²⁶. Based on this report, and our experimentally determined active site preferences for *cis*-3-hexen-1-ol conversion, mechanisms for each process are proposed where *cis/trans* isomerization occurs reversibly on a single active site (Scheme 4.4) and hydrogenation occurs as the result of bond shifting *via* π -allyl intermediates, requiring multiple active sites on the metal surface (Scheme 4.5).



Scheme 4.4 – Mechanism for the reversible isomerization of *cis/trans*-3-hexen-1-ol over a single active site.



Scheme 4.5 – Mechanism for the hydrogenation of *cis*-3-hexen-1-ol over multiple active sites. Progressive bond shifting *via* π -allyl intermediates results in a highly-reactive terminal alkene, which is subsequently reduced to yield 1-hexanol.

4.7 Conclusions

This chapter focused on developing the catalytic hydrogenation of 3-hexyn-1-ol by Pd(PVP) as a model reaction system suitable for use as a tool to investigate changes in catalyst surface structure. Pd(PVP) was chosen as a model catalyst, and synthesis *via* a polyol reduction method yielded highly-disperse cubooctahedral nanoparticles with a narrow size distribution. The hydrogenation of 3-hexyn-1-ol was chosen as a model alkyne hydrogenation reaction, and the experimental conditions were optimized to ensure maximum accuracy for measured hydrogenation activities and kinetic analyses. Most notably, it was found that conducting separate experiments for alkyne and alkene hydrogenations improved overall accuracy by allowing experimental conditions to be tailored for the individual reactions. Geometric modification of Pd(PVP) was achieved through selective decoration of terrace active sites by Te adatoms. Mechanisms detailing the active site preferences for the various reaction processes in 3-hexyn-1-ol hydrogenation were then determined by comparing the catalytic characteristics of the Pd(PVP) and Pd+Te(PVP) catalysts. It was shown that reactions for the hydrogenation of 3-hexyn-1-ol to *cis*-3-hexen-1-ol and the hydrogenation of *cis*-3-hexen-1-ol to 1-hexanol both occur exclusively on terrace sites, while the isomerization of *cis*-3-hexen-1-ol to *trans*-3-hexen-1-ol only occurs on low-coordinate sites. In accordance with literature reports²⁶, mechanisms for the two reactions of *cis*-3-hexen-1-ol were proposed where isomerization occurs as the result of non-stereoselective, reversible addition of H over a single active site while hydrogenation requires multiple active sites to progressively shift the double bond to a highly-reactive terminal position *via* a series of π -allyl intermediates. These detailed characterizations of both the model Pd(PVP) nanocatalysts and the model 3-hexyn-1-ol hydrogenation reaction clearly establish the combined use of these systems for monitoring modifications to the catalyst structure, allowing subsequent chapters to utilize this method to characterize the effects of sulfur modification for transition metal nanocatalysts.

4.8 References

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Chapter 5

Metal-dependent effects of sulfur modification

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5.1 Background

In recent industrial practises, catalysts are involved in the production of over 60% of all chemicals, with 90% of all chemical processes relying on catalysis in some way^{1,2}. However, billions of pounds are lost every year due to reactor shutdown and catalyst replacement as a result of deactivation processes³. Some of this cost is unavoidable, as all industrial catalysts will eventually need to be replaced, but this decay is often dramatically accelerated due to catalyst poisoning by reactant stream contaminants^{3,4}.

Sulfur compounds represent a particularly problematic class of poisons for catalysts in industrial reactions, affecting a wide range of processes including ammonia synthesis, steam reforming, methanol synthesis, and CO hydrogenation⁵. The most potent poisons encountered are generally small sulfur containing molecules such as H₂S, COS, and elemental sulfur⁵, with molecules such as H₂S of particular concern for industrial reactions as their high toxicity means that even very low concentrations in the reactant feed stream can cause significant deactivation. For example, sulfur will adsorb strongly and irreversibly to Ni catalysts, resulting in half coverage at H₂S concentrations of only 1-10 ppb in the reactant stream, and near complete coverage at only 100-1000 ppb⁶. These concentrations represent sulfur levels typically encountered in a reactant stream after efforts have already been undertaken to remove the contaminants, and the lower range includes concentrations which fall below the detection limits of most modern analytical techniques⁴. Results such as this are typical when considering the poisoning of transition metal catalysts by sulfur⁶. For instance, Ni, Co, Fe, and Ru all suffer a 3-4 magnitude loss in activity towards methanation at H₂S levels as low as 15-100 ppb, demonstrating an extremely low sulfur tolerance for these metals⁷. This dramatically illustrates one of the main challenges encountered when managing catalyst poisoning: it is difficult to avoid deactivation purely through removal of the target poison. This example also highlights the wide range of transition metals catalysts that

are strongly affected by sulfur poisoning, including Pt, Pd, Ru, Fe, Ni, Co, and Cu⁵. As such, the focus in recent years has shifted toward redesigning catalysts and catalytic systems to improve sulfur tolerance. However, if this area of research is to be successful, a more fundamental understanding of how poisons interact with a catalyst's surface is first required.

In the past, research often focused on a two-pronged approach for the investigation of catalyst deactivation by sulfur poisoning from both a system level and a component level. As this area of research is motivated by an economic drive to prolong catalyst lifetimes for industrial processes, reactions are most often addressed on a case by case basis in order to optimize sulfur tolerance for a specific combination of catalyst, reactant, poison, and reaction conditions. This system-level approach focuses on observations of poisoning under reaction conditions, often through observing losses in catalytic activity and/or selectivity. However, this presents a particular challenge when attempting to draw general conclusions about the fundamental causes of sulfur poisoning, as catalysts and reaction conditions employed for the most commonly studied industrial processes are extremely varied. For example, sulfur compounds are a common poison for ruthenium catalysts used in ammonia synthesis and biomass conversion, both of which typically take place at high temperature and pressure^{3,8}. However, the poisoning of palladium catalysts used for catalytic hydrogenations takes place at low temperature and low pressure. From a component level, theoretical modelling and ultra-high vacuum studies provide a wealth of detailed information on the fundamental interactions between poisons and the metal surface, allowing for comparisons to be drawn across systems. Literature reports detail theoretical studies of sulfur adsorption on a range of transition metals including W⁹, Mo¹⁰, Rh^{10,11}, Ru¹², Pd^{13,14}, Pt¹⁵, Cu¹⁶, and Ni¹⁷. However, limitations on theoretical modelling still exist and such results often prove difficult to apply to complex reaction systems¹⁸.

Attempts to bridge these two methods of investigating catalyst poisoning have been reported in the literature, but with varying degrees of success. In a study by Nasri *et al.*, the authors compared deactivation and regeneration behaviour for a series of H₂S modified Pd, Pt, and Rh catalysts supported on alumina for the combustion of methane¹⁹. All catalysts were modified and evaluated under identical experimental conditions and there were no significant variations in particle morphology, however the extensive pretreatment with H₂S (100 ppm for 90 min) meant no useful comparisons could ultimately be drawn from the deactivation behaviour as only the Pd catalyst showed any activity after modification. This study highlights one of the biggest challenges when attempting to use gaseous sulfur compounds common to industrial reactions: it is often necessary to fully saturate the catalyst in order to ensure uniform coverage levels as sulfur tends to adsorb rapidly and irreversibly to a catalyst surface. This makes any detailed studies of sulfur poisoning extremely challenging. In a more recent report, Badano *et al.* overcame this limitation through controlled modification of a series of alumina supported Ru, Rh, Pd, and Pt catalysts using a dilute solution of thiophene²⁰. In this study, effects of modification on catalytic activity were compared using the hydrogenation of styrene as a test reaction, however difficulties encountered in controlling particle size for the catalysts meant no usable data was obtained for the Ru catalyst. Additionally, while it was proposed that sensitivities to thiophene modification relate to the d-electron configuration of a metal, no attempt was made to address additional effects of modification such as competitive binding or blocking of specific active sites.

While these reports illustrate the potential of using systems with minimal experimental variation to directly compare the fundamental effects of sulfur modification across catalytic systems, it is clear that the methods employed must be modified if the challenges discussed previously are to be overcome. This is particularly true if detailed investigations of the separate geometric and

electronic effects of modification are to be undertaken. The use of colloidal catalysts as model systems offers a promising alternative to standard heterogeneous materials for studying these fundamental effects. These systems are already frequently used as model catalysts to study hydrogenation reactions due to their easily controlled size and morphology, and these properties have been utilized to investigate electronic and geometric modifications to the catalyst^{21–23}.

5.2 Objectives

The research presented in this chapter aims to determine and compare the specific electronic and geometric effects of sulfur modification on a range of transition metal nanocatalysts. Palladium and ruthenium systems are chosen as representative transition metals, and focus will be directed toward designing a model PVP supported ruthenium system analogous to the Pd(PVP) system developed in Chapter 4. Numerous techniques will be used in combination to investigate the specific effects of sulfur modification, including novel surface characterization by ¹³C NMR, FTIR of chemisorbed CO, and analysis of the model 3-hexyn-1-ol hydrogenation test reaction developed in Chapter 4. The results are expected to provide a basis for the intelligent design of nanocatalysts with controlled effects of sulfur modification.

5.3 Experimental details

A detailed discussion of experimental methods can be found in Chapter 3. In brief, the synthesis of PVP supported palladium or ruthenium nanoparticles was achieved through a polyol reduction method modified from that used by Bonet *et al.*²⁴. In a typical synthesis, PVP and the metal precursor (10:1 ratio moles of monomer units to moles of metal) were dissolved in ethylene or diethylene glycol and heated under a nitrogen atmosphere to form a colloidal dispersion of polymer-stabilized nanoparticles. The nanoparticles were precipitated by centrifugation in a mixture of acetone and hexane, washed with acetone, and dried under nitrogen. Sulfur

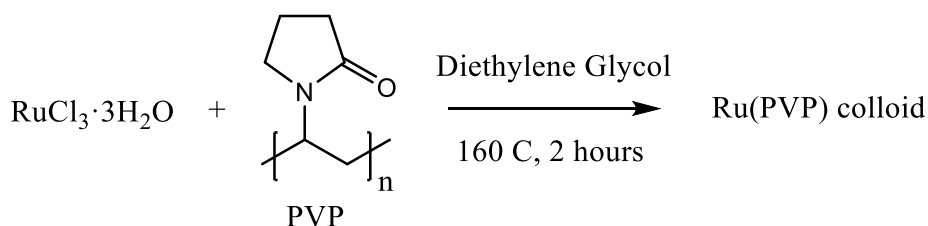
modification was achieved by first redispersing the dried nanoparticles in ethanol, followed by addition of an ethanolic solution of an appropriate thiol (2-mercaptoethanol (MEA), mercaptohexanol (MHA), or 2-methyl-2-propanethiol (MPT)) sufficient to provide the desired level of surface coverage. The modified particles were then thoroughly sonicated and left to age for 24 hours prior to characterization or catalytic testing.

5.4 PVP stabilized ruthenium nanoparticles

The primary aim of this chapter is determining and comparing the effects of sulfur modification of equivalent palladium and ruthenium catalysts. The model Pd(PVP) catalyst discussed in Chapter 4 was chosen as a starting point for the development of a suitable system. In order to keep experimental variations between the systems to a minimum, the methods employed for the synthesis of Pd(PVP) were used as a template for the synthesis of an equivalent Ru(PVP) model catalyst.

5.4.1 Synthesis

The ruthenium catalyst was synthesized with a PVP monomer to ruthenium metal ratio of 10:1 to maintain consistency with the Pd(PVP) system. A polyol reduction process was again employed, and the ruthenium precursor and PVP were both thoroughly dispersed in diethylene glycol prior to reduction resulting in a dark amber colored solution. Upon heating, a series of color changes were observed for the solution indicating the progressive reduction of ruthenium from Ru^{3+} (dark amber), to Ru^{2+} (light orange), to Ru^+ (dark green), to Ru^0 (black), finally yielding the fully reduced PVP-stabilized ruthenium nanoparticles (dark brown colloid). The resulting Ru(PVP) nanoparticles were precipitated, washed, and dried as described previously. A summary of the synthesis is shown in Scheme 5.1.



Scheme 5.1 – Preparation of PVP stabilized Ru *via* the polyol reduction method with diethylene glycol as solvent and reducing agent.

5.4.2 Characterization

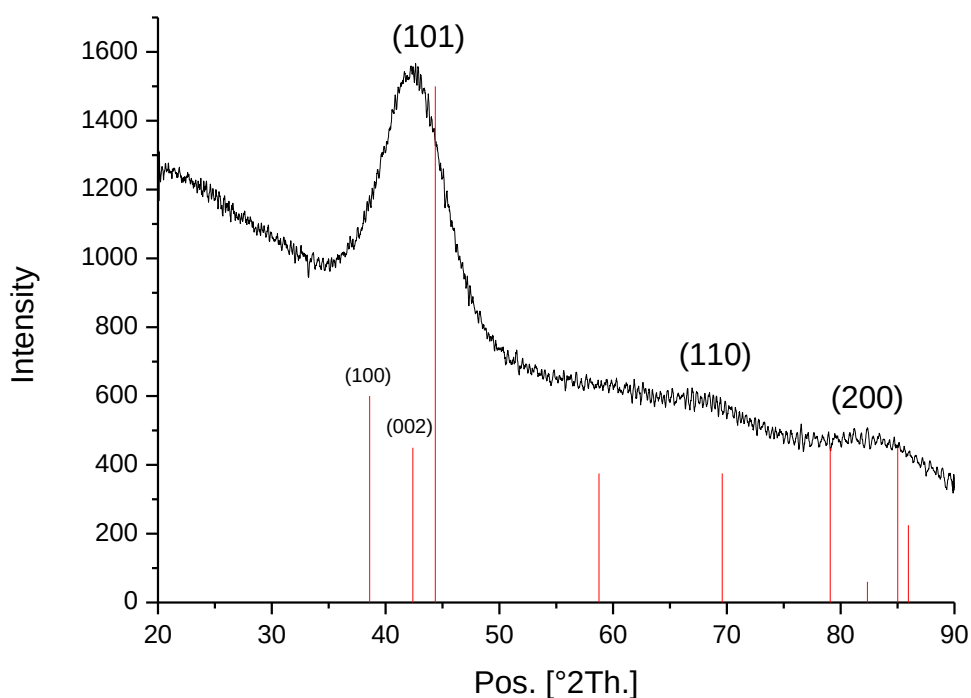


Figure 5.1 – XRD profile of Ru(PVP) with peak positions for bulk ruthenium indicated in red.

The as-synthesized Ru(PVP) nanoparticles were initially characterized by XRD, and a typical profile with reference peaks for bulk ruthenium is given in Figure 5.1 above. Only one prominent peak is visible in the experimental profile corresponding to reflections from the (101) plane, and a further two peaks assigned to reflections from the (110) and (200) planes are just discernible.

All peaks present are severely broadened, indicating the system is composed of highly-dispersed nanoparticles. However, additional broadening of the (101) peak is likely the result of overlap with the (100) and (002) peaks, which are not distinguishable in the experimental profile but are indicated in the reference pattern. As the broadening contributions from peak overlap cannot easily be eliminated for the only clearly visible peak, estimation of average particle size *via* the Scherrer equation was not possible.

The Ru(PVP) nanoparticles were further characterized by TEM in order to determine average particle size and shape. Figure 5.2 below shows a typical TEM micrograph along with the corresponding size distribution histogram. The results demonstrate the Ru(PVP) nanoparticles are similar in shape to the Pd(PVP) nanoparticles discussed in Chapter 4, and there is similarly no evidence of aggregation. Average particle size is found to be 2.0 nm, with a standard distribution of 0.30 nm indicating the Ru(PVP) nanoparticles are monodisperse and similar in size and shape to the 2.7 nm Pd(PVP) nanoparticles synthesized in Chapter 4.

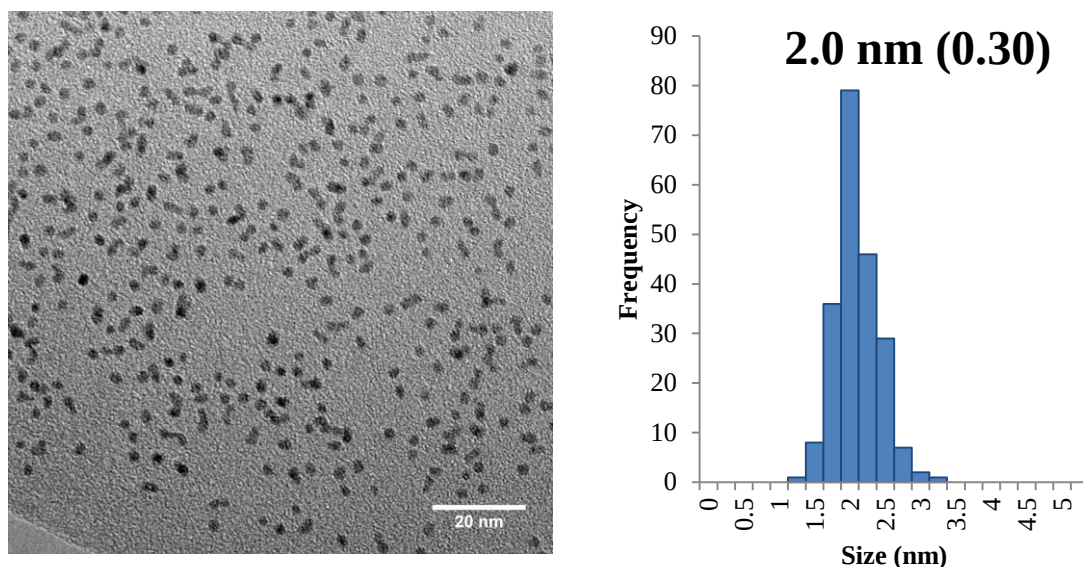


Figure 5.2 – TEM micrograph for Ru(PVP) with corresponding particle size distribution histogram.

Based on an average particle size for Ru(PVP) of 2.0 nm, surface statistics were calculated in accordance with the method by van Hartog and Hardeveld as described in Chapter 4 for particles with cubooctahedral structure²⁵. A slightly higher surface packing density for Ru ($1.63 \text{ atoms m}^{-2}$)²⁶ than Pd ($1.27 \text{ atoms m}^{-2}$)²⁶ results in the same number of surface atoms and the same 4-shell particle structure for both systems despite the differences in average particle size. This means the Ru(PVP) nanoparticles possess the same surface statistics as the Pd(PVP) nanoparticles, with approximately 46% of the atoms located on the surface, 35% of these surface atoms in low-coordinate sites, and 65% in terraces as determined from Equations 4.1-4.5.

5.5 Modification of Pd(PVP) and Ru(PVP) by MEA

The most common sulfur poisons encountered in an industrial setting are small, gaseous molecules such as H_2S , SO_2 , or CS_2 , which cause measureable changes in catalytic behavior for many transition metal catalysts when present in reactant streams at concentrations as low as 10 ppb^{4,5}. This extreme sensitivity presents numerous practical challenges for experiments attempting to systematically investigate the modification of heterogeneous catalysts by gas-phase sulfur compounds. First, it is difficult to control the concentration of gaseous sulfur-containing molecules in a reactant stream with enough accuracy to achieve precise levels of surface coverage. Second, introduction of sulfur to a catalyst bed *via* a reactant stream often leads to location-dependent coverage effects, where initial areas of the bed are saturated due to strong metal-sulfur interactions while the rest of the catalyst remains unmodified²⁷. Finally, small sulfur-containing molecules often decompose on the surface of transition metal catalysts, resulting in complex structures of molecular sulfur and varying degrees of surface or bulk sulfidation of the metal, depending on reaction conditions³.

In order to avoid many of these challenges, modification of the model PVP-stabilized catalysts was carried out in the liquid phase. As the PVP stabilized catalysts require the use of polar solvent systems, the short-chain thiol 2-mercaptoethanol (MEA) was selected as a model sulfur-containing compound. Ru(PVP) and Pd(PVP) nanoparticles were modified with dilute MEA solutions of variable concentration by the method described in Section 5.3 in order to precisely control coverage levels, and the reported coverages are calculated based on the previously-determined surface statistics for the systems.

The MEA modified Ru(PVP) and Pd(PVP) particles were characterized by TEM and the results are displayed in Figures 5.3 and 5.4 below. Neither system shows any signs of particle growth resulting from the addition of MEA (2.0 nm and 2.6 nm post-modification versus 2.0 nm and 2.7 nm pre-modification for Ru(PVP) and Pd(PVP), respectively), and the particles remain nearly mono-dispersed. In the case of metal nanoparticles synthesized with alkanethiols as the stabilizer, literature reports commonly demonstrate the formation of hexagonal superlattices due to van der Waals interactions between the ligands when particles are deposited on a TEM grid²⁸⁻³². The modified PVP-stabilized nanoparticles show no evidence of such superlattice formation, even when near monolayer coverage is achieved. This result suggests the stabilizing polymer remains present in the system even at high coverages, and is sufficient to prevent aggregation or direct interactions between the modified particles.

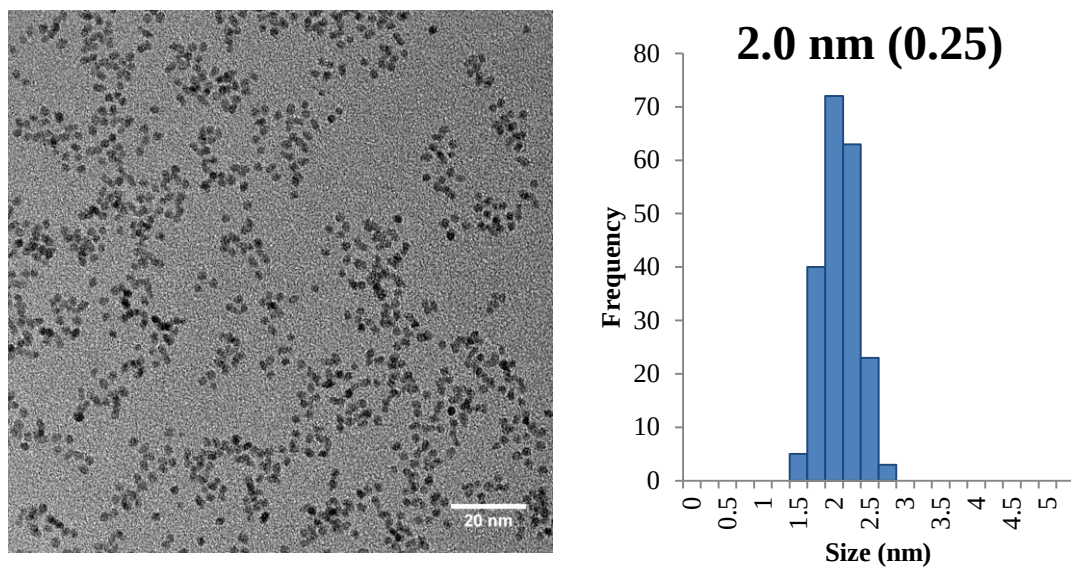


Figure 5.3 – TEM micrograph and corresponding particle size distribution histogram for Ru(PVP) with 89% surface coverage by MEA.

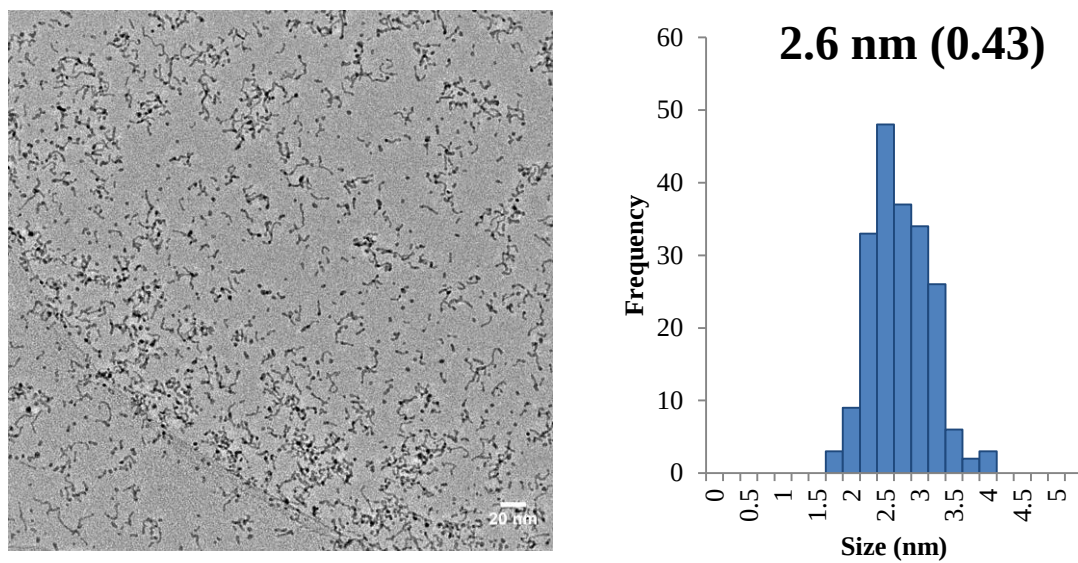


Figure 5.4 – TEM micrograph and corresponding particle size distribution histogram for Pd(PVP) with 30% surface coverage by MEA.

EDX analysis was performed on the Ru(PVP) and Pd(PVP) nanoparticles with various MEA coverage levels. The results displayed below in Table 5.1 of relative metal and sulfur content show good agreement between the measured and targeted values, confirming the modification method allows for precise control of surface coverage for both systems. Furthermore, it is interesting to note that targeted metal to sulfur ratios were in agreement with the measured values even at coverages exceeding 100% of the surface. As surface coverages are calculated with the assumption of one molecule of MEA per metal surface atom, one explanation for this observation is that additional sites, such as 3 and 4-fold hollow sites on (111) and (100) surface planes, may also be available for the adsorption of MEA.

Table 5.1. Summary of EDX results for M:S ratios for PVP supported metal nanoparticles where M is Pd or Ru.

MEA Surface Coverage	M:S Targeted ^a	Pd:S Measured ^b	Ru:S Measured ^b
30%	1:0.14	1:0.16	1:0.14
89%	1:0.41	nd	1:0.45
118%	1:0.55	1:0.44	nd
236%	1:1.10	1:0.80	1:1.24

^aRatios of metal (Ru or Pd) to sulfur content calculated from the targeted coverage levels. ^bMeasured ratios of metal to sulfur content determined by EDX.

Additional characterization of the modified Ru(PVP) and Pd(PVP) nanoparticles was performed by XRD, and typical profiles of both the modified and unmodified systems are shown in Figure 5.5 below. Neither system shows the presence of additional peaks or significant shifts in peak position for the MEA modified nanoparticles, indicating bulk sulfidation is not a significant factor in the modification process.

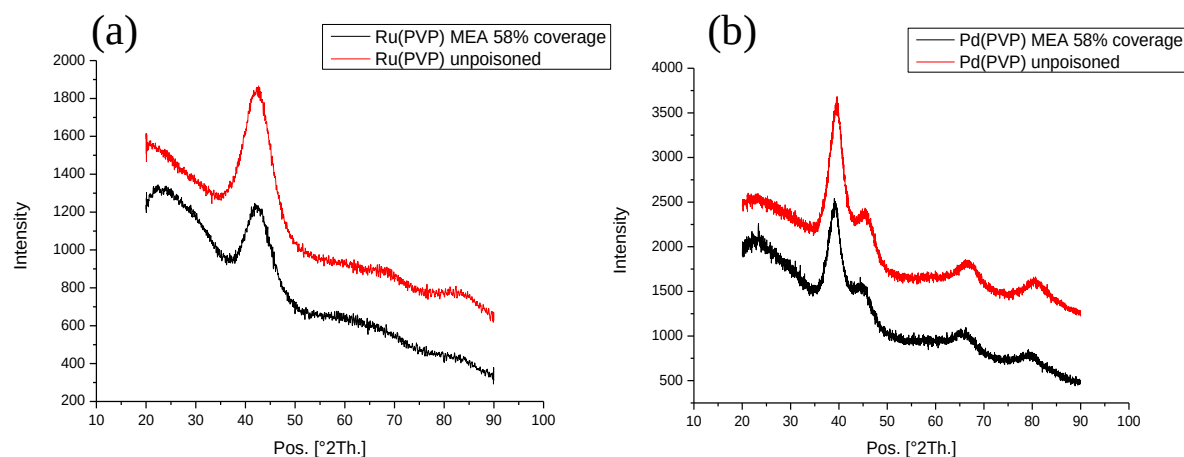


Figure 5.5 – XRD profiles demonstrating the results of MEA modification on (a) Ru(PVP) and (b) Pd(PVP).

Results presented in Sections 5.4 and 5.5 of this chapter and Section 4.4 from Chapter 4 provide a solid foundation for the use of MEA modified Ru(PVP) and Pd(PVP) nanoparticles as a model system for determining and comparing the effects of sulfur modification on the two different transition metals. In the case of the unmodified particles, both systems were synthesized *via* a polyol reduction method with a PVP to metal ratio of 10:1, resulting in particles with similar size, shape, and surface statistics. Modification by MEA in the liquid phase allowed for precise control of surface coverage for both metals with no evidence of particle growth or aggregation. The following sections will focus on using these model systems to separate the overall effects of surface modification into electronic and geometric components. As geometric modification is the simpler of the two effects, this component of MEA modification will be established before the electronic effects are investigated.

5.5.1 Geometric effects of MEA modification

FTIR of chemisorbed CO is a widely reported technique for investigating the surface structure of metallic nanoparticles, and the basic principles of the method were outlined in Chapter 2^{33,34}. Essentially, this technique relates the various binding modes of CO chemisorbed on the metal

surface to localized surface geometry, including the relative prevalence of terrace and low-coordinate sites. Examples of its application from literature include monitoring changes in surface structure resulting from changing particle size^{35,36}, and determining site-selective blocking of active sites by decorating metals^{34,37}. This second example is of particular relevance to the aims of this section and serves as a basis for applying this technique to study the geometric effects of MEA modification on the Ru(PVP) and Pd(PVP) nanoparticles.

In the case of CO adsorbed on the unmodified Ru(PVP) nanoparticles, three bands are observed in the FTIR spectrum at 2050 cm^{-1} , 1999 cm^{-1} , and 1955 cm^{-1} assigned to mono, multi, and bridge-bound CO (Figure 5.6(a))³⁸. These binding modes are assigned to CO adsorbed on low-coordinate (multi and mono) and terrace (bridge) surface sites³⁵. Monitoring the relative intensities of these bands as surface coverage by MEA is progressively increased allows any site selectivity of the modification to be determined. As Figure 5.6(a) illustrates, progressive modification by MEA results in a general decrease in intensity for peaks corresponding to adsorbed CO. Normalization of peak areas to the multi-carbonyl peak demonstrates a clear loss in intensity for the band corresponding to the terrace bound species, with the ratio of available terrace site to low-coordinate sites decreasing from 2.8:1 in the un-poisoned sample to 1.1:1 at 30% surface coverage by MEA (Table 5.2 below). This result clearly indicates a geometric preference for adsorption of MEA to terrace sites on the surface of Ru(PVP) nanoparticles.

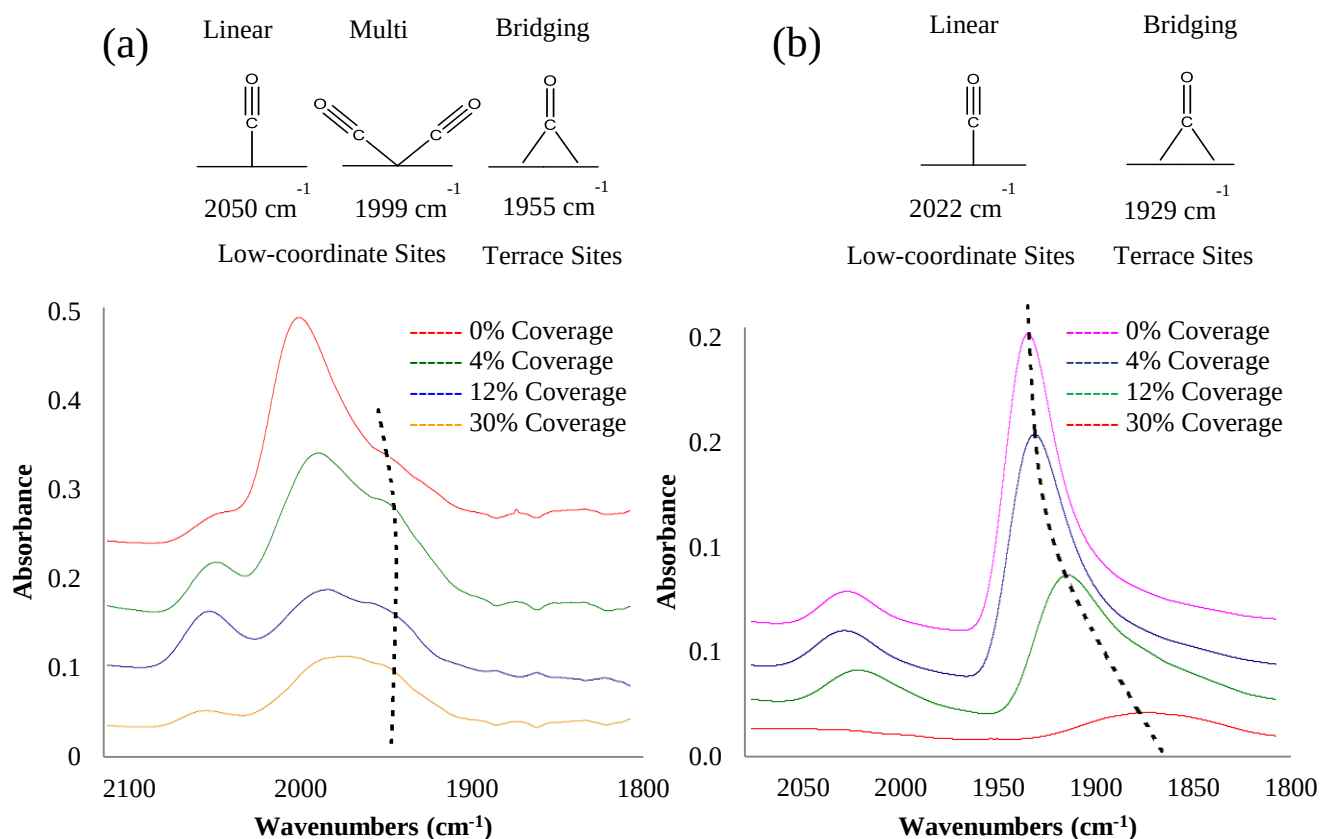


Figure 5.6 – FTIR of CO chemisorbed on (a) Ru(PVP) and (b) Pd(PVP) progressively modified with MEA. Illustrations of CO adsorption modes assigned to specific active sites are shown in insets.

Table 5.2 – Ratios between corrected CO peak intensities for terrace and low-coordinate sites

MEA Surface Coverage	Ru(PVP) Terraces ^a : Low-Coordinate Sites ^b	Pd(PVP) Terraces ^a : Low-Coordinate Sites ^c
0%	2.8: 1	8.4: 1
4%	1.5: 1	5.4: 1
12%	1.3: 1	4.6: 1
30%	1.1: 1	N/A

^aCalculated from the CO bridging peak assuming two terrace atoms per adsorbed CO. ^bCalculated from the linear and multi CO peaks assuming 1 atom (linear) and 0.5 atoms (multi) per adsorbed CO. ^cCalculated from the linear CO peak assuming 1 atom per adsorbed CO.

When the same CO adsorption technique is applied to the unmodified Pd(PVP) nanoparticles, two adsorption bands are observed in the FTIR spectrum at 2022 cm^{-1} and 1929 cm^{-1} corresponding to linearly and bridge-bound CO adsorbed on low-coordinate and terrace sites, respectively (Figure 5.6(b))³⁴. When the Pd(PVP) nanoparticles are modified with progressively increasing MEA surface coverages, normalization to the linearly bound species again shows a steady decrease in intensity for bridge bound CO (Table 5.2). A corresponding decrease in the ratio of terrace sites to low-coordinate sites from 8.4:1 in the unpoisoned sample to 4.6:1 at 12% surface coverage (Table 5.2) confirms a geometric preference for the adsorption of MEA to terrace sites on the surface of Pd(PVP) nanoparticles. This geometric preference is in agreement with the results of Marshall *et al.*, who demonstrated the formation of stable assemblies of short-chain alkanethiols similar to MEA on extended terraces of a Pd surface³⁹. Additionally, theoretical calculations by Makkonen *et al.* confirm a preference for sulfur adsorption at hollow sites of terraced surfaces, where the increase in coordination number is sufficient to overcome any preference for binding to more energetically favorable low-coordinate sites⁴⁰.

As the observed geometric effects of modification are very similar for both model catalysts, further experiments will be able to disregard geometric influences when comparing the catalytic behavior of the two systems. This also simplifies the determination of electronic effects of MEA modification for Ru(PVP) and Pd(PVP), as the equivalent geometric component can be ignored.

Previous work has demonstrated FTIR of CO adsorption to be an effective technique for investigating electronic modification of the metal surface by monitoring shifts in band frequency for bound CO³⁴. However, coverage effects must be discounted in order to accurately determine electronic modification of the catalyst as CO surface coverage strongly influences band frequency⁴¹. The black dashed lines on the spectra in Figures 5.6(a) and 5.6(b) above illustrate

the band frequencies for bridge-bound CO in the Ru(PVP) and Pd(PVP) systems, respectively, and the relationship between band frequency and surface coverage by MEA is shown in Figure 5.7 below. In the case of Ru(PVP), no clear trend is observed between the vibrational frequency of bridge-bound CO and MEA coverage on neighboring terrace sites, suggesting MEA adsorption on surface sites does not result in long-range electronic modification of adjacent atoms. In contrast, the Pd(PVP) system shows a strong shift to lower frequency for the bridge-bound CO species at progressively higher MEA coverages (from 1931 cm^{-1} for the unmodified catalyst to 1869 cm^{-1} with 30% MEA coverage). However, such a shift is a well-documented result of decreased CO surface coverage as dipole-dipole interactions between adjacent adsorbate molecules become disrupted, making it extremely difficult to discern any electronic modification of the surface using this technique⁴².

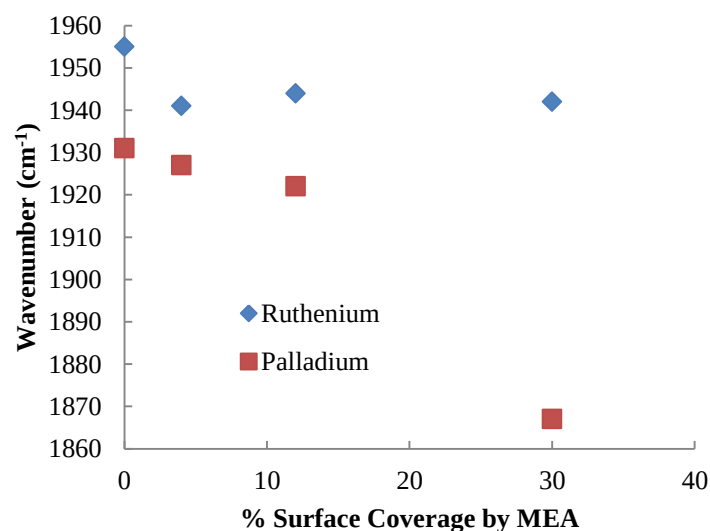


Figure 5.7 – Vibrational frequency for the bridging CO peak at increasing surface coverages by MEA for both Pd(PVP) and Ru(PVP).

5.5.2 Electronic Effects of MEA Modification

Solution state ^{13}C -NMR using ^{13}C labelled formic acid as a surface probe was employed as an alternative technique to investigate the electronic effects of MEA modification on the Ru(PVP)

and Pd(PVP) systems. This recently-developed technique, first reported by Tedsree *et al.* in 2011⁴³, effectively eliminates many of the challenges inherent to typical NMR investigations of probe molecules on heterogeneous materials highlighted in Chapter 2. Firstly, peak broadening due to restricting the molecular motion of the probe molecule is largely eliminated by the use of highly-disperse, polymer-supported metal nanoparticles in a colloidal suspension³⁶. These colloidal particles retain the electronic and geometric properties of traditional supported materials whilst overcoming the motion limitations of heterogeneous systems. The second and most important advantage of this technique is the elimination of Knight shift effects. This effect is particularly problematic for typical probe molecules such as ^{13}CO , where direct contact between the metal surface and the active nucleus results in strong coupling to s electrons of the conduction band, which overwhelms slight perturbations in electronic environment that usually impact chemical shift⁴⁴. Changing the probe molecule to ^{13}C labeled formic acid removes this direct contact, as adsorption occurs through oxygen rather than the active ^{13}C nucleus. In Tedsree *et al.*⁴³, the authors used DFT calculations of the formic acid system to prove that introduction of this oxygen spacer between the metal surface and active nucleus substantially decreases overlap between the tightly held 5s orbitals of the metal and the C 2s and 2p orbitals of the probe. However, the same calculations also show that indirect adsorption of the active nucleus still allows for overlap between the C 2s and 2p orbitals and the more diffuse 4d orbitals of the metal surface, indicating the environment surrounding the active nucleus remains sensitive to the electronic state of the metal surface even with the oxygen spacer present. The overall result is a solution-state technique with high resolution, narrow peak widths, and coupling between the active nucleus and metal d-orbitals sufficient to indirectly monitor changes in electronic structure of the metal surface reflected by shifts in resonance frequency for formic acid.

A typical ^{13}C NMR spectrum obtained from application of this technique to the MEA modified Ru(PVP) and Pd(PVP) systems is shown in Figure 5.8 below, with peaks corresponding to formic acid, carbon dioxide, and dioxane which functions as an internal standard to normalize chemical shifts for the probe. No peaks were observed for MEA, likely due to broadening effects similar to those reported by Zelakiewicz *et al.* for octanethiol-stabilized palladium nanoparticles due to transmission of Knight shift effects through the adsorbed sulfur atom^{45,46}.

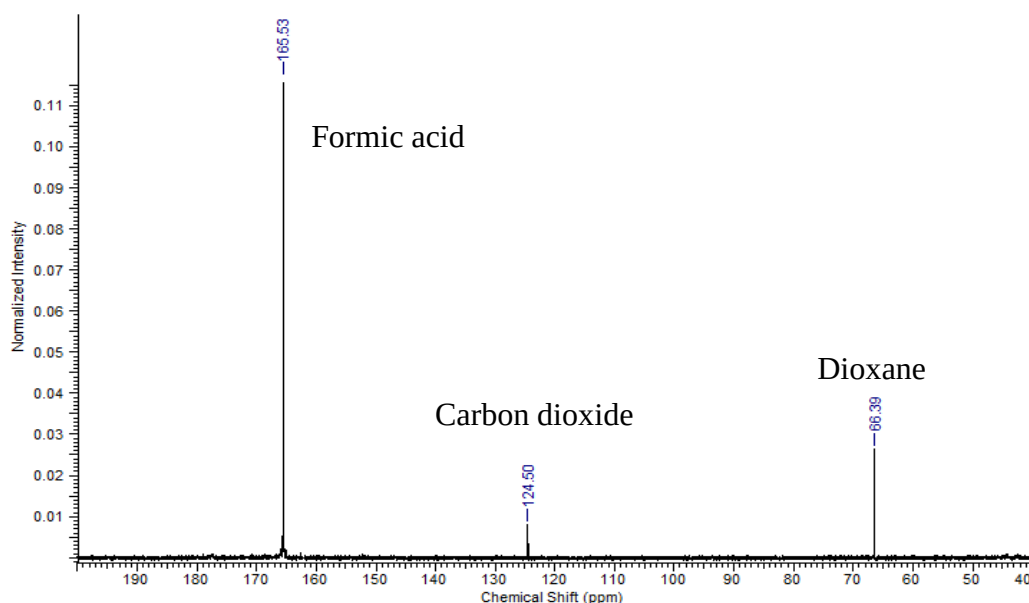


Figure 5.8 – ^{13}C NMR spectrum for Pd(PVP) with 58% surface coverage by MEA with dioxane as an internal standard and ^{13}C labelled formic acid as a surface probe.

Figure 5.9 below illustrates the relationships between chemical shift of the formic acid probe and progressive surface coverage by MEA for the Ru(PVP) and Pd(PVP) systems. When both systems are investigated without MEA modification, a clear downfield shift in resonance frequency for formic acid is observed relative to the unbound state, confirming a strong surface-probe interaction for both systems. Progressive coverage of the Pd(PVP) surface by MEA results in a steady decrease in chemical shift for the probe, from 166.17 ppm with no modification to 165.58 ppm with 54% surface coverage. However, no such change in chemical shift is observed

for Ru(PVP) modified by MEA. As both systems show similar geometric modification by MEA (Section 5.5.1), the contrasting behaviour of the formic acid probe is attributed to differences in electronic modification effects on the metal surfaces. In the case of Ru(PVP), the lack of relationship between formic acid chemical shift and MEA coverage indicates adsorption strength of the probe is not significantly altered by increasing modification by MEA. From this result it can be concluded that Ru is relatively insensitive to electronic modification effects resulting from the adsorption of sulfur. However, the strong dependence of formic acid chemical shift on MEA surface coverage for Pd(PVP) indicates Pd is highly sensitive to electronic modification effects, resulting in decreased adsorption strength for the probe as the surface is increasingly modified by MEA.

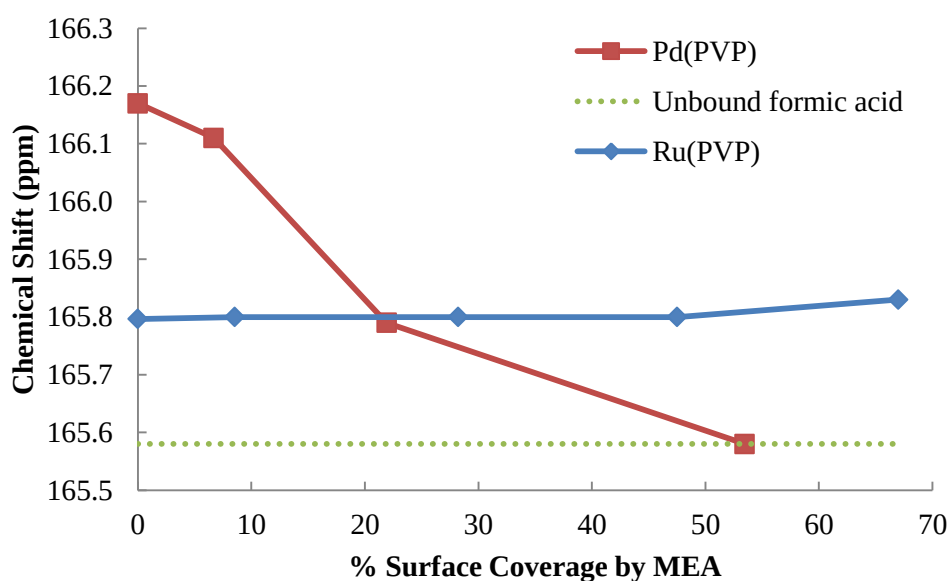


Figure 5.9 – Chemical shift of the formic acid probe with increasing surface coverage by MEA for Pd(PVP) and Ru(PVP) plotted along with the chemical shift for unbound formic acid.

In a comparative study of sulfur modification on palladium, platinum, and rhodium, Rodriguez *et al.* demonstrated an important relationship between metal d-band filling and the influence of sulfur adsorption¹³. The authors found that metals with more complete d-band fillings, like palladium (d^{10}), experience a much greater reduction in density of states near the Fermi level due

to sulfur adsorption than metals like platinum (d^9) and rhodium (d^8) where the d-band is less full. It is therefore proposed that the electronic effects of MEA modification on Pd(PVP) are caused by a lowering of the d-band centre relative to the Fermi level for the metal surface, resulting in decreased adsorption strength for the formic acid probe as coverage is increased. Extension of this argument to ruthenium (d^7) suggests MEA adsorption has little influence on d-band centre position relative to the Fermi level, which is in good agreement with the lack of electronic modification observed by NMR.

It is interesting to note that, at 54% MEA surface coverage, the chemical shift for the probe converges with that of free formic acid, suggesting this level of coverage is sufficient for complete electronic deactivation of the Pd(PVP) surface. This level of surface coverage is approximately that required to fully block terrace sites of the catalyst, which make up approximately 65% of the metal surface. Given that low-coordinate sites are electronically decoupled from the bulk, it is logical to expect that electronic modification of the catalyst will only result when MEA is adsorbed to electronically coupled terrace sites on the metal surface. Further modification effects observed at higher coverages when MEA is forced to adsorb to less favourable low-coordinate sites are thus expected to be purely geometric in nature.

5.6 Hydrogenation of 3-hexyn-1-ol

The sensitivities of Ru(PVP) and Pd(PVP) to geometric and/or electronic modification by MEA as determined by FTIR and ^{13}C NMR were verified using the model 3-hexyn-1-ol hydrogenation reaction discussed at length in Chapter 4. Hydrogen uptake profiles for the reaction catalysed by both systems with varying levels of MEA surface coverage are given in Figure 5.10 below. In accordance with the 2-step hydrogenation mechanism presented in Chapter 4, hydrogen uptake of less than 1 molar equivalent (60 mL) was attributed to conversion of 3-hexyn-1-ol to *cis*-3-

hexen-1-ol, and any further uptake up to a maximum of 2 molar equivalents (120 mL) was attributed to subsequent conversion of *cis*-3-hexen-1-ol. As *cis*-3-hexen-1-ol is typically considered the desired product of this reaction, measuring the uptake rates over these two regions thus provides approximate measurements of catalyst activity and selectivity.

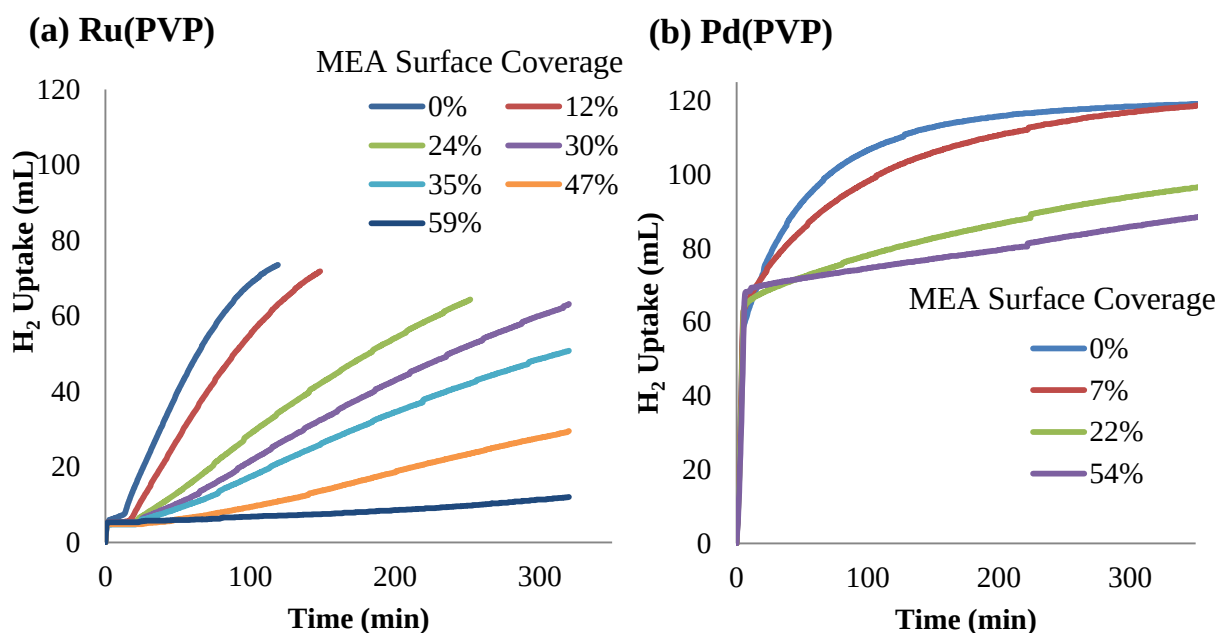


Figure 5.10 - Hydrogen uptake profiles of 3-hexyn-1-ol conversion over MEA modified (a) Ru(PVP) and (b) Pd(PVP). Half- and full-uptakes occur at approximately 60 mL and 120 mL of H₂, respectively, corresponding to consumption of 1 and 2 molar equivalents of H₂. Conditions: 2.5 mmol reagent, 2.5 μ mol metal catalyst in EtOH, 40 $^{\circ}$ C, 3 bar H₂ (Pd) and 15 bar H₂ (Ru).

Comparison of the catalytic behaviour for the two systems prior to modification demonstrates that initial selectivity for the *cis* isomer is strongly dependent on the catalyst metal, with Pd(PVP) showing 98.0% *cis*-3-hexen-1-ol and 99.7% total alkene selectivities versus only 53.9% *cis*-3-hexen-1-ol and 61.3% total alkene selectivities for Ru(PVP) at 82% conversion. The initial selectivity of Pd(PVP) is in good agreement with the results presented in Chapter 4, indicating weak alkene adsorption strengths relative to the alkyne. However, the much lower initial selectivity of Ru(PVP) suggests a substantial increase in alkene adsorption strength, enabling

alkenes to compete more effectively with the alkyne for reactive sites during the initial hydrogenation step. This explanation for the differences in initial selectivity between the two systems is supported by the well-accepted tendency for reactants to adsorb more strongly to early transition metals such as Ru, where lower d-band filling leads to a higher d-band centre relative to the Fermi level (-1.41 eV for Ru versus -1.83 eV for Pd)⁴⁷. The same reasoning can also be employed to explain the overall decrease in initial hydrogenation activity for unmodified Ru(PVP) versus unmodified Pd(PVP) (Figure 5.10 above), because in the case of strongly adsorbed reactants such as alkynes, initial hydrogenation activity is often governed by the rate the reactant desorbs from the catalyst surface^{48,49}. Increasing this adsorption strength by changing the metal from Pd to Ru only further decreases the alkyne desorption rate, leading to the observed reduction in hydrogenation activity for Ru(PVP) versus Pd(PVP).

Contrasting catalytic behaviour for the two systems is also observed upon modification with MEA. In the case of Ru(PVP), the initial rate of hydrogen uptake, and thus activity for 3-hexyn-1-ol hydrogenation, is progressively attenuated with increasing surface coverage until near total deactivation is achieved (Figure 5.10(a)). A comparison between TOF for 3-hexyn-1-ol hydrogenation and MEA surface coverage shows the deactivation response is linear (Figure 5.11), suggesting the relatively strongly adsorbed MEA decreases alkyne hydrogenation activity through blocking of active sites on the metal surface (geometric modification) without altering the alkyne adsorption strength (electronic modification). However, no attenuation in the initial rate of hydrogen uptake is observed for Pd(PVP) with increasing surface coverage by MEA, indicating the relative alkyne adsorption strength is high enough to displace MEA from the metal surface in this system (Figure 5.10(b)).

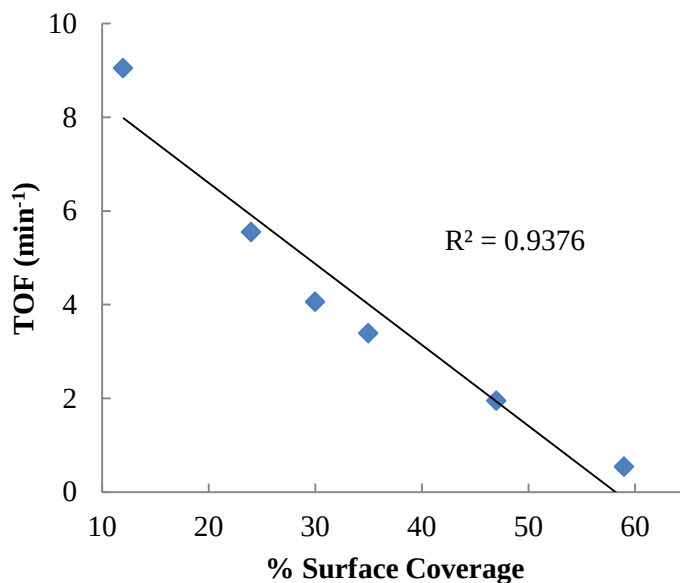


Figure 5.11 – Plot demonstrating the linear relationship between TOF for 3-hexyn-1-ol hydrogenation over Ru(PVP) and surface coverage by MEA.

Analysis of completion times for the conversion of 3-hexyn-1-ol over Pd(PVP) with a broader range of MEA surface coverages shows this behaviour is maintained until coverage exceeds 1 ML, where completion time increases from approximately 70 min to 104 min with 118% surface coverage and 267 min with 236% surface coverage (Table 5.3 below). However, no significant change is observed in the maximum TOF for the reaction even at MEA coverages above 1 ML (TOF's of 12.10, 13.74, and 11.62 sec⁻¹ at 0%, 118%, and 236% MEA coverage, respectively), indicating adsorbed MEA is eventually completely displaced by the alkyne even at these high levels of surface coverage. In contrast, the much weaker adsorption strength of alkenes on Pd(PVP) does not appear sufficient to displace adsorbed MEA, as evidenced by progressive attenuation in hydrogen uptake rates above 60 mL, for the second-step hydrogenation, as MEA surface coverage is increased (Figure 5.10(b)).

Table 5.3 – Maximum TOF's and reaction completion times for the conversion of 3-hexyn-1-ol over Pd(PVP) with various levels of MEA surface coverage.

MEA Surface Coverage	3-Hexyn-1-ol Conversion	
	Maximum TOF (sec ⁻¹)	Completion time (min)
0%	12.10	67.27
12%	11.05	68.81
30%	12.09	66.59
58%	11.25	72.10
89%	15.35	69.47
118%	13.74	103.91
236%	11.62	267.45

A compilation of reaction profiles for the production and subsequent conversion of *cis*-3-hexen-1-ol over Pd(PVP) at various MEA surface coverages (Figure 5.12 below) provides a clear summary of the contrasting effects of MEA modification for the two reaction steps. Catalytic activity for the hydrogenation of 3-hexyn-1-ol to *cis*-3-hexen-1-ol is unaffected by MEA modification due to displacement of adsorbed MEA by the alkyne until conversion of 3-hexyn-1-ol is complete. MEA then re-adsorbs to the metal surface, effectively blocking alkene adsorption and thereby decreasing activity for conversion of *cis*-3-hexen-1-ol to further products as the level of modification is increased.

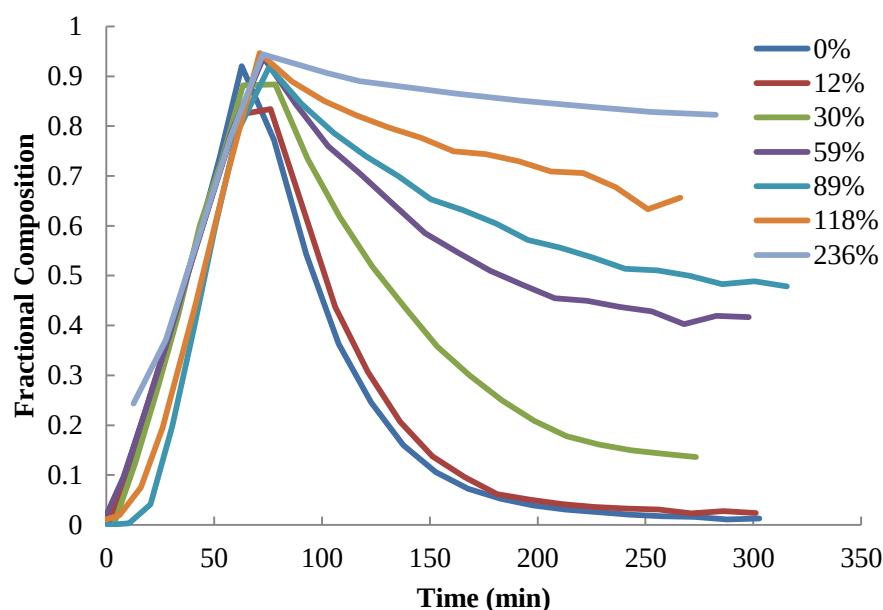


Figure 5.12 – Production and subsequent conversion of *cis*-3-hexen-1-ol by progressively modified Pd(PVP) expressed as a fractional composition of the total reactant/products. Completion time for the reaction profiles has been normalized to that for Pd(PVP) with 0% MEA (67.27 min).

As the activity for 3-hexyn-1-ol conversion was shown to depend solely on competitive binding effects (geometric modification) for both the Ru(PVP) and Pd(PVP) systems modified with MEA, the key remaining question is whether these same effects or a combination of geometric and electronic modifications govern catalytic behavior for the subsequent conversion of *cis*-3-hexen-1-ol. Based on the mechanism for this reaction presented in Chapter 4, hydrogenation of *cis*-3-hexen-1-ol to 1-hexanol occurs only on terrace sites of the metal surface and isomerization to *trans*-3-hexen-1-ol is specific to low-coordinate sites. Changes in activity for these two processes can thus be used to indicate site-selective geometric modification of the metal surface. Electronic modification can be similarly monitored as the prolonged surface adsorption over multiple active sites required for the bond-shifting hydrogenation reaction is expected to be more sensitive to changes in adsorption strength than the rapid, single site isomerization reaction. The low-coordinate active sites required for isomerization are also less susceptible to electronic

effects of modification than the terrace sites required for hydrogenation, due to electronic decoupling from the bulk⁵⁰.

Contributions to overall modification by MEA from both geometric and electronic effects were therefore investigated by monitoring the two reactions for *cis*-3-hexen-1-ol conversion. Results are expressed as a ratio of hydrogenation to isomerization products in order to more clearly compare effects between the two systems (Figure 5.13 below). It is important to note that, as MEA demonstrates similar site-specific adsorption preferences for both Ru(PVP) and Pd(PVP), geometric modification effects can be discounted and differences in behavior for the two systems are attributed to contrasting effects of electronic modification.

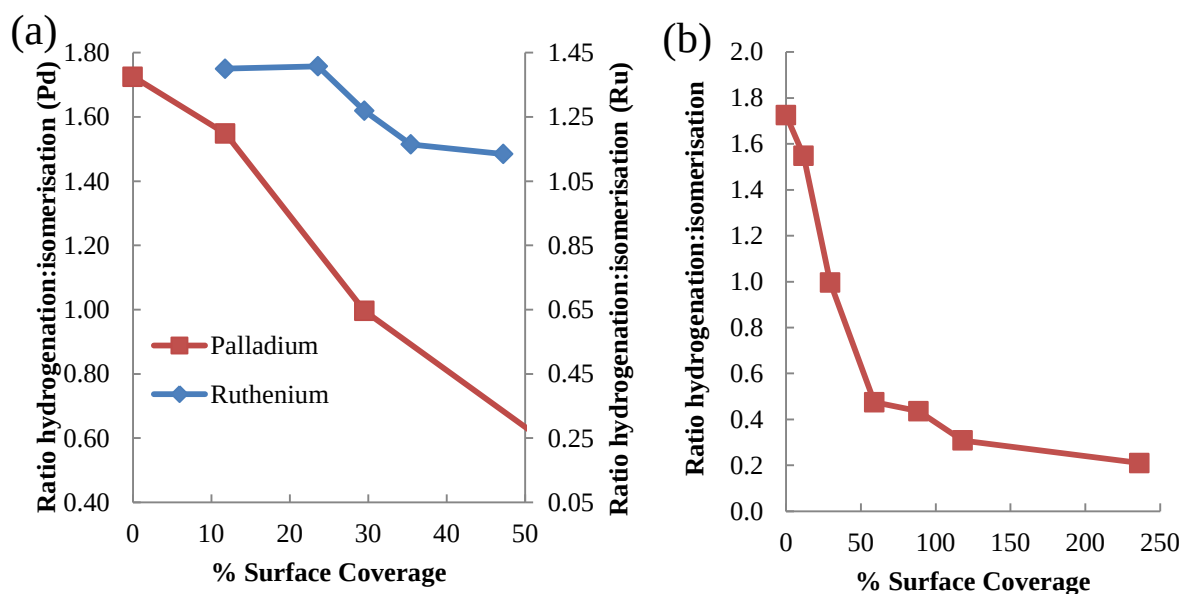


Figure 5.13 – Ratios of hydrogenation:isomerisation for the hydrogenation of *cis*-3-hexen-1-ol for (a) Ru(PVP) (y-axis right) and Pd(PVP) (y-axis left) at MEA surface coverages below 60% and (b) Pd(PVP) at MEA surface coverages up to 236%.

Ru(PVP) modified with MEA shows only a slight decrease in hydrogenation:isomerization (1.4 to 1.1) at increasing levels of surface coverage compared to Pd(PVP) (1.5 to 0.5) at similar coverage levels (Figure 5.13(a)). These results demonstrate that, while both systems show a

geometric component to modification, the electronic component is much more significant for Pd(PVP) than Ru(PVP). This conclusion is in good agreement with the previous results from both FTIR and NMR. Additionally, the significant shift in reaction mechanism from hydrogenation toward isomerization for the Pd(PVP) system at increasing coverage by MEA supports the argument that modification weakens reactant adsorption strength by lowering the d-band centre of Pd relative to the Fermi level, causing hydrogenation of *cis*-3-hexen-1-ol to be preferentially disrupted.

Closer examination of the MEA modified Pd(PVP) system reveals two distinct regions in the plot for hydrogenation:isomerization versus MEA surface coverage (Figure 5.13(b)). The first region (0%-59% coverage) was addressed in the comparison with Ru(PVP), where attenuation in *cis*-3-hexen-1-ol hydrogenation relative to isomerization results primarily from electronic modification effects. However, in the second region where surface coverage exceeds 59%, only a slight decrease in hydrogenation relative to isomerization is observed (hydrogenation:isomerization decreases from 0.5 to 0.2), suggesting modification above 59% coverage is primarily due to geometric effects. This result is in excellent agreement with the previous ^{13}C NMR experiments, which showed complete electronic deactivation of Pd(PVP) at 54% surface coverage.

5.7 MEA modified Pd(PVP)

Given the relatively straight-forward geometric modification of Ru(PVP) by MEA, focus is shifted toward exploring the more complex relationship between MEA and Pd(PVP) in greater detail.

5.7.1 Further characterization of MEA modified Pd(PVP)

In order to eliminate the possibility that previously observed effects result from sulfidation of the metal surface, the MEA modified Pd(PVP) catalysts were further characterized by both XRD and XPS.

XRD Characterization

When Pd(PVP) modified with a wide range of MEA surface coverages is characterized by XRD, no relationship is observed between the Pd lattice parameter (calculated from Equation 2.1 in Chapter 2) and the level of surface coverage by MEA even above 1 ML coverage (Table 5.4 below), suggesting modification does not result in significant formation of either PdS or PdO.

Table 5.4 – Pd lattice parameters for Pd(PVP) progressively modified by MEA.

MEA Surface Coverage	Pd Lattice Parameter (Å)
0%	3.9163
30%	3.9263
58%	3.9184
89%	3.9241
118%	3.9139

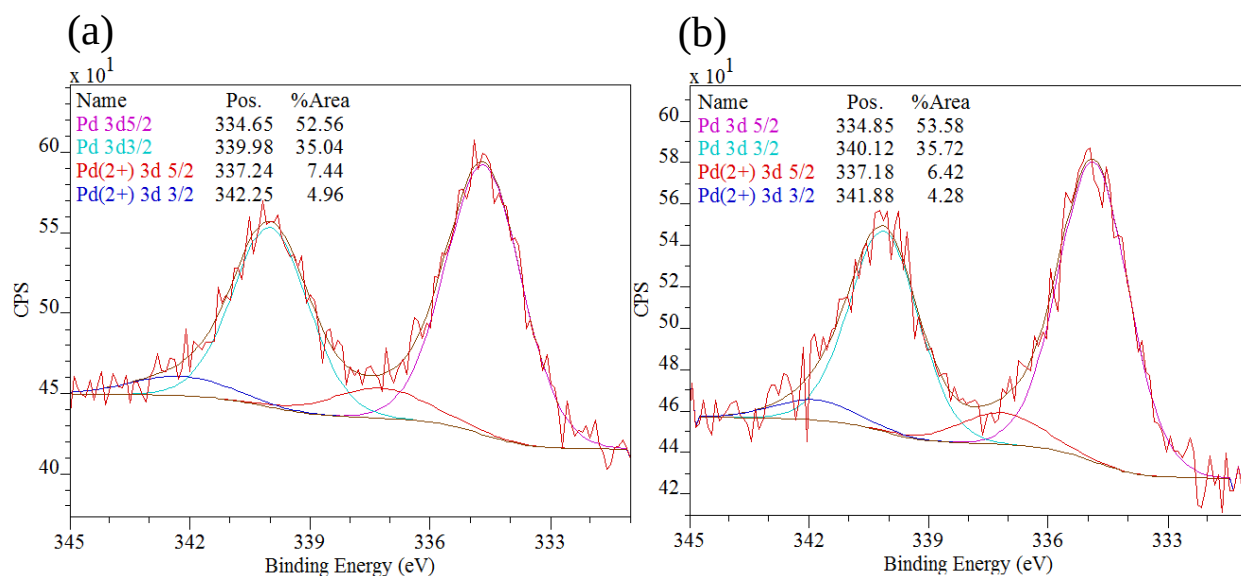
XPS Characterization

Figure 5.14 – XPS spectra of the Pd 3d region for (a) unmodified Pd(PVP) and (b) Pd(PVP) with 30% surface coverage by MEA.

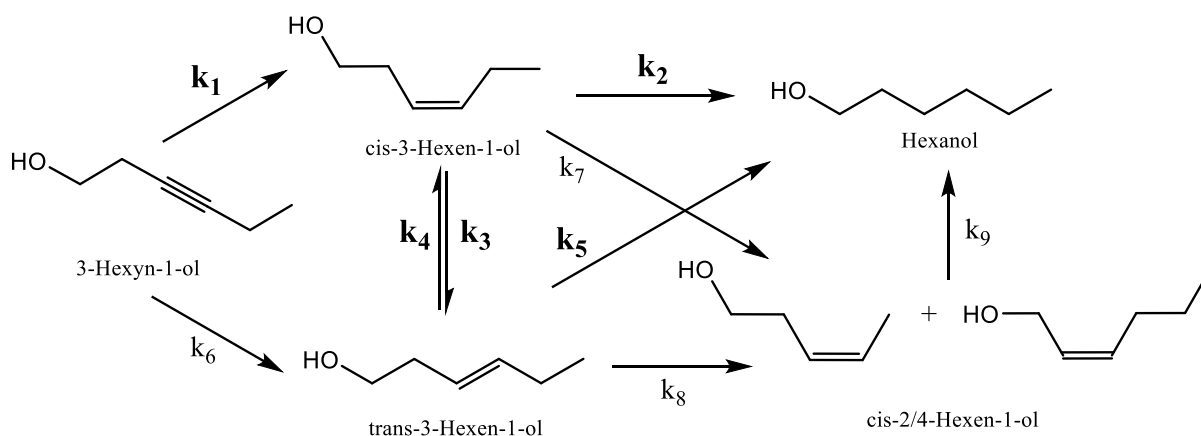
XPS spectra of the Pd 3d region for the MEA modified Pd(PVP) catalysts show the presence of a slight shoulder on the main Pd⁰ peaks, indicating some Pd²⁺ is present in the sample (Figure 5.14 above). A recent literature report by Chang *et al.* attributed this feature to the formation of surface PdS upon thiol adsorption⁵¹, however as no correlation was found between the area of this peak and the level of surface coverage by MEA (Pd²⁺:Pd⁰ is 0.14 for 0% MEA and 0.12 for 30% MEA, Table 5.5 below), the presence of Pd²⁺ was attributed to a small amount of PdO present on the metal surface. It is also interesting to note a steady increase in binding energy for the Pd 3d_{5/2} peak (from 334.65 eV to 335.04 eV) until MEA surface coverage reaches 58%, above which no further shift is observed (Table 5.5 below). This electronic modification indicates MEA adsorption decreases Pd electron density and further supports the previous conclusion from both ¹³C NMR and 3-hexyn-1-ol hydrogenation that electronic effects dominate the modification of Pd(PVP) by MEA at surface coverages below approximately 60%.

Table 5.5 – Summary of XPS results for Pd(PVP) progressively modified with MEA

MEA Surface Coverage	Pd ⁰ 3d _{5/2} BE (eV)	Pd ²⁺ :Pd ⁰
0%	334.65	0.14:1
12%	334.68	0.04:1
30%	334.85	0.12:1
58%	335.04	-----
89%	335.06	0.06:1
118%	335.02	-----

5.7.2 Kinetic modelling

Kinetic analysis of the 3-hexyn-1-ol hydrogenations was performed based on a detailed reaction mechanism accounting for reaction intermediates resulting from the bond-shifting hydrogenation processes (Scheme 5.2), from which expanded rate equations were derived (Equations 5.1-5.6). In order to simplify the analysis, rate constants were grouped into semi-hydrogenation (k_{semi} : k_1 and k_6), isomerization (k_{isom} : k_3 and k_4), and full-hydrogenation processes (k_{full} : k_2 , k_5 , k_7 , k_8 , and k_9).



Scheme 5.2 – Detailed mechanism for the hydrogenation of 3-hexyn-1-ol over Pd(PVP).

$$\frac{dA}{dt} = -\theta_A(k_1 + k_6) \quad \text{Equation 5.1}$$

$$\frac{dB}{dt} = k_1\theta_A + k_4\theta_C - \theta_B(k_2 + k_3 + k_7) \quad \text{Equation 5.2}$$

$$\frac{dC}{dt} = k_6\theta_A + k_3\theta_B - \theta_C(k_4 + k_5 + k_8) \quad \text{Equation 5.3}$$

$$\frac{dD}{dt} = k_7\theta_B + k_8\theta_C - k_9\theta_D \quad \text{Equation 5.4}$$

$$\frac{dE}{dt} = k_2\theta_B + k_5\theta_C + k_9\theta_D \quad \text{Equation 5.5}$$

$$\theta_i = \frac{K_i P_{(i)}}{1 + \int_E^A K_i P_{(i)}} \quad \text{Equation 5.6}$$

Equations 5.1-5.6 – Rate equations for the mechanism presented in Scheme 5.2, where A = 3-hexyn-1-ol, B = *cis*-3-hexen-1-ol, C = *trans*-3-hexen-1-ol, D = *cis*-2/4-Hexen-1-ol, E = 1-hexanol, K_i = adsorption constant of species i , $P_{(i)}$ = equilibrium concentration of species i , and θ_i = probability of a surface site being occupied by species i .

Reaction profiles for a range of the MEA modified Pd(PVP) catalysts (Figure 5.15 (a) 0%, (b) 59%, and (c) 118% surface coverages) demonstrate good agreement between the experimental and fitted profiles across all coverage levels investigated, and a complete summary of kinetic data is presented in Table 5.6.

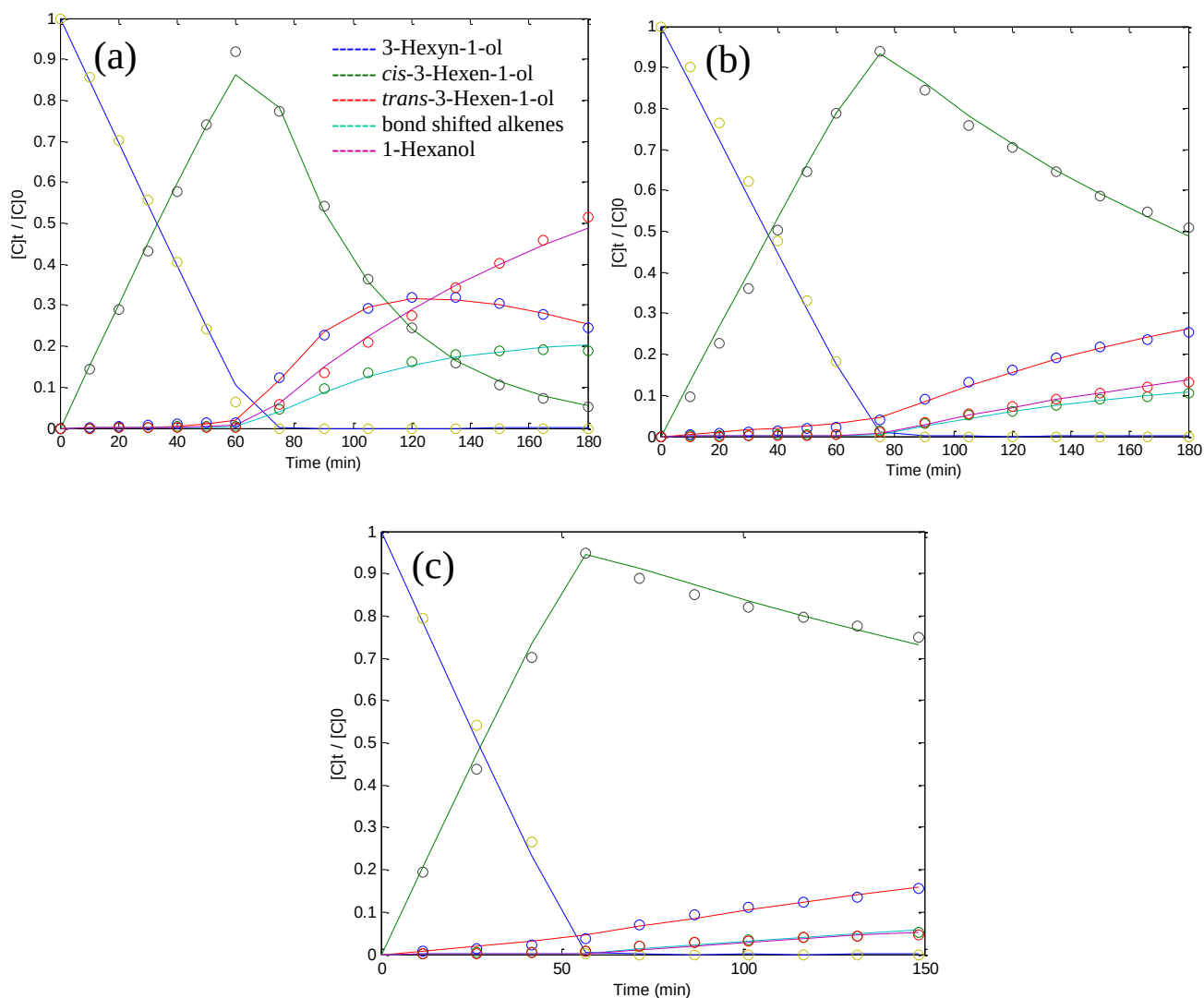


Figure 5.15 – Kinetic fittings for the hydrogenations of 3-hexyn-1-ol and *cis*-3-hexen-1-ol catalysed by Pd(PVP) with MEA surface coverages of (a) 0%, (b) 59%, and (c) 118%. Open circles correspond to experimental data points and solid lines to fitted profiles.

Table 5.6 – Complete summary of fitted kinetic data for the hydrogenation of 3-hexyn-1-ol over Pd(PVP) at various MEA surface coverages.

	Surface Coverage by MEA (%)						
	0%	12%	30%	58%	89%	118%	236%
k_1	730.83	648.43	716.78	644.16	948.97	862.16	638.73
k_2	214.91	155.85	97.18	53.18	35.77	20.51	5.36
k_3	458.92	396.09	184.58	92.59	67.19	46.01	13.97
k_4	23.78	0.00	0.14	0.28	1.37	1.26	3.23
k_5	176.98	212.88	134.76	0.00	0.00	0.05	0.12
k_6	0.00	1.67	2.46	4.79	8.11	7.28	6.89
k_7	140.80	165.43	85.20	46.86	35.43	21.77	6.62
k_8	117.36	155.70	32.46	27.00	17.47	0.00	0.00
k_9	98.76	67.99	0.00	0.02	0.02	0.04	0.06
Σk_{semi}	730.83	650.10	719.24	648.95	957.08	869.44	645.62
Σk_{full}	748.80	757.85	349.59	127.06	88.69	42.38	12.16
Σk_{isom}	482.69	396.09	184.72	92.87	68.56	47.28	17.19
$\Sigma k_{\text{full}}/\Sigma k_{\text{isom}}$	1.55	1.91	1.89	1.37	1.29	0.90	0.71

k_n is expressed as TOF in units of min^{-1} , $k_{\text{semi}} = k_1 + k_6$, $k_{\text{isom}} = k_3 + k_4$, and $k_{\text{full}} = k_2 + k_5 + k_7 + k_8 + k_9$.

Results of the kinetic modelling confirm that the high TOF's for the conversion of 3-hexyn-1-ol to *cis*-3-hexen-1-ol are maintained for all MEA modified catalysts (k_1 , Table 5.6 above), with no apparent relationship between activity and surface coverage. This result is in good agreement with the displacement of adsorbed MEA by 3-hexyn-1-ol observed previously. However it is

interesting to note that direct conversion of 3-hexyn-1-ol to *trans*-3-hexen-1-ol (k_6) is increasingly favoured at higher coverages (TOF is 0 for unmodified Pd(PVP) versus 8.11 min^{-1} with 89% surface coverage). While even the highest value for k_6 doesn't significantly contribute to k_{semi} , this result may indicate that MEA is not completely displaced from all surface active sites, resulting in a slight electronic modification effect that shifts initial selectivity towards the *trans* isomer. However, strong MEA adsorption relative to the alkene intermediates results in attenuated activity for nearly all further reaction processes as coverage is increased (k_{full} and k_{isom}). The one notable exception is the isomerization of *trans*-3-hexen-1-ol back to the initial *cis* product (k_4) which becomes an increasingly favored reaction pathway at high coverages, supporting the previous argument that MEA modification preferentially disrupts alkene hydrogenation processes. Further confirmation of this effect is provided when a comparison of TOF's for the combined hydrogenation and isomerization processes ($\Sigma k_{\text{full}}/\Sigma k_{\text{isom}}$) at different MEA coverages yields the same trend observed previously, with the relative activity for full hydrogenation decreasing until the reaction is eventually dominated by *cis/trans* isomerization (Table 5.6).

5.7.3 DFT calculations

Calculations were performed to determine the specific influence of sulfur adsorption on the DOS for the Pd d-band at both nearest and next-nearest sites, and the results are displayed in Figure 5.16 below.

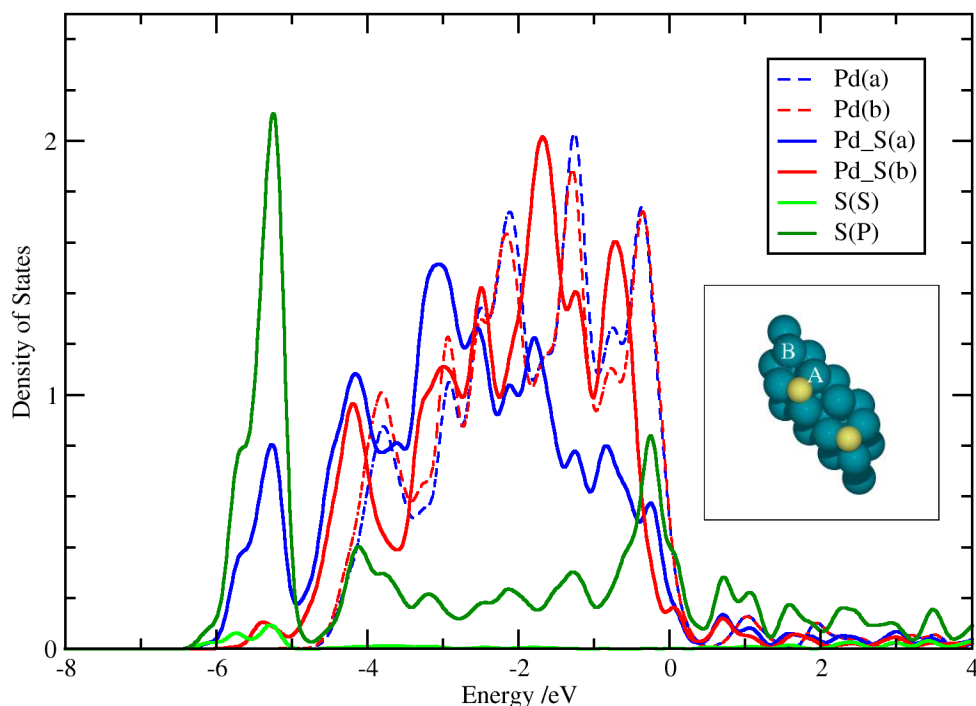


Figure 5.16 – Projected density of states for the Pd d-band in the presence of, and absence of, a 0.25 ML of adsorbed sulfur for two different Pd sites along with projected density of states for the s and p-orbitals of adsorbed sulfur. Inset illustrates the placement of sulfur on the Pd surface along with positions of Pd atoms A and B.

As Figure 5.16 illustrates, adsorption of sulfur to the surface of Pd results in a significant broadening of the d-band (0.3 eV) at the nearest surface site (Pd A) due to interaction between the d-orbitals of Pd and the p-orbitals of sulfur. This stabilization of the d-band at lower energies shifts the d-band centre away from the Fermi level by approximately 0.5 eV and leads to a corresponding reduction in the DOS near the Fermi level. These results are in excellent agreement with the findings by Rodriguez et al.¹³ for the effects of sulfur adsorption on the Pd DOS discussed previously in Section 5.5.2, and further support the conclusions regarding significant electronic effects for the modification of Pd by MEA presented throughout this chapter thus far. Similar effects of sulfur adsorption on the width of the Pd d-band, position of the d-band centre, and DOS near the Fermi level also extend to the next-nearest surface site (Pd B), confirming long-range electronic modification effects of sulfur adsorption, although the

changes in d-band structure are less pronounced than for the nearest site (Figure 5.16). Additional analysis of the surface electron density was also performed using the Bader method in order to quantify the level of charge transfer from Pd that results when the surface is modified with sulfur. However, at the 0.25 ML coverage level investigated, the charge transfer from Pd was found to be only 0.02 electrons per Pd atom, suggesting the electronic effects of sulfur modification result primarily from covalent interactions rather than the typical electron donating/withdrawing effects that are more often invoked for reaction modifiers.

This model was then applied to a simulation of the 3-hexyn-1-ol hydrogenation reaction in order to determine the effects that changing the Pd d-band structure through sulfur adsorption would have on the catalytic behavior of the system. Reaction pathways for the conversions of 3-hexyn-1-ol to both *cis*-3-hexen-1-ol and *trans*-3-hexen-1-ol were considered, and the results are displayed below in Figure 5.17.

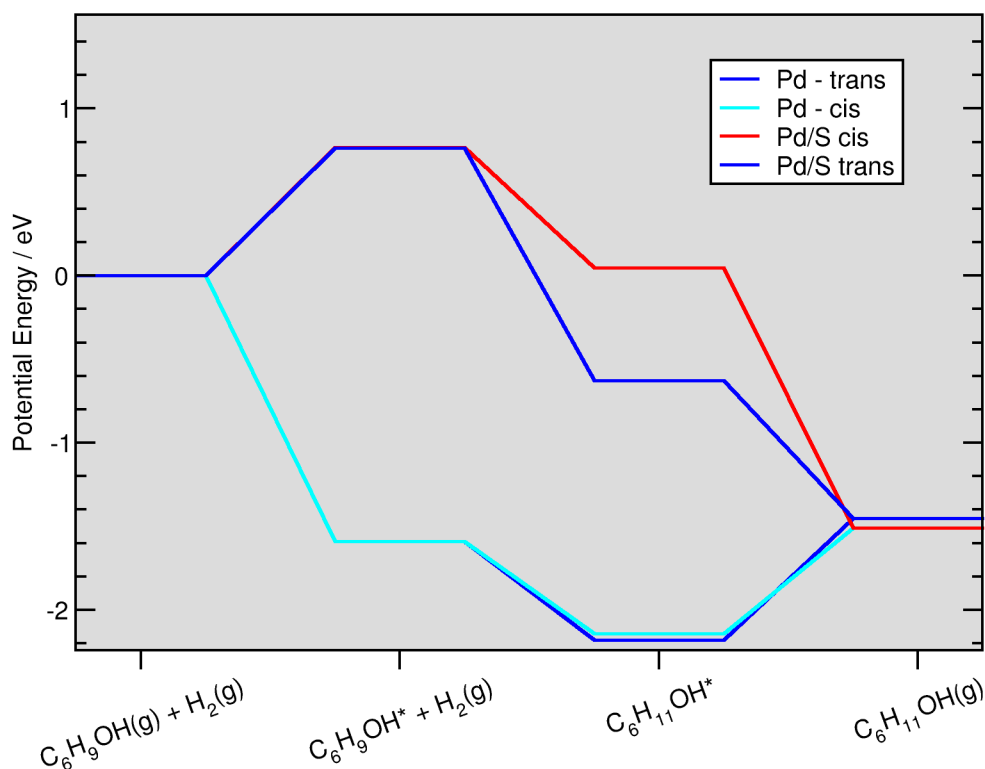


Figure 5.17 – Potential energy profiles for the hydrogenation of 3-hexyn-1-ol to *cis*-3-hexen-1-ol and *trans*-3-hexen-1-ol over clean and sulfur modified Pd surfaces.

The potential energy profiles for conversion of 3-hexyn-1-ol over the unmodified Pd surface displayed in Figure 5.17 indicate that adsorption of 3-hexyn-1-ol is an energetically favourable processes, and there is virtually no difference in the energy profiles for either of the hydrogenation pathways. However, when the Pd surface is modified with sulfur, a substantial destabilization in the adsorption of 3-hexyn-1-ol is observed and direct hydrogenation to the trans isomer becomes the more energetically favourable reaction pathway. This shift in selectivity for the reaction towards the trans isomer mirrors that observed from the kinetic modelling discussed previously in Section 5.7.2, however it should be noted that the impact of sulfur adsorption on the pathway of 3-hexyn-1-ol is likely more significant in these theoretical models than in the laboratory experiments as there is no potential for competitive adsorption between sulfur and 3-hexyn-1-ol in the modelled systems.

5.8 Additional thiol modifiers

Given the specific geometric preference for adsorption of MEA to terrace sites on the surface of Pd(PVP) demonstrated previously in Section 5.5.1, and the implications of this site-selective adsorption on selectivity in the hydrogenation of *cis*-3-hexen-1-ol, the possibility of tailoring reaction selectivity by using alternative thiol modifiers with different site-selective adsorption properties was investigated. Literature reports have suggested that the geometric preferences thiols exhibit for adsorption to metal surfaces are at least partially influenced by the ability of the adsorbing thiols to form an ordered monolayer structure^{32,39}. In systems where the thiol tail group consists of an extended carbon chain, steric properties make it possible to tightly pack adsorbed molecules on extended terrace sites of the metal surface. In fact, additional stabilization effects result when thiols are adsorbed in this conformation due to van der Waals interactions between the carbon chains of the molecules. However, increasing the steric hindrance of the

organic tail group decreases stabilization effects between adjacent molecules, which is expected to make adsorption to extended terraces through formation of ordered monolayers less favourable.

Based on these arguments, two additional thiol modifiers with differing organic tail groups were selected for comparison to the original MEA modified Pd(PVP) system (Figure 5.18). With its relatively short alkyl tail group, MEA was treated as an intermediate case when considering the influence of steric effects on the site selective adsorption properties of thiols. Mercaptohexanol (MHA) was chosen with the prediction that the longer alkyl chain would provide additional stabilization of the thiol monolayer on terrace sites of the metal surface, and 2-methyl-2-propanethiol (MPT) was also selected with the expectation that the bulky end group would discourage monolayer formation on the surface terrace sites, instead directing adsorption to the more electron deficient low-coordinate sites.

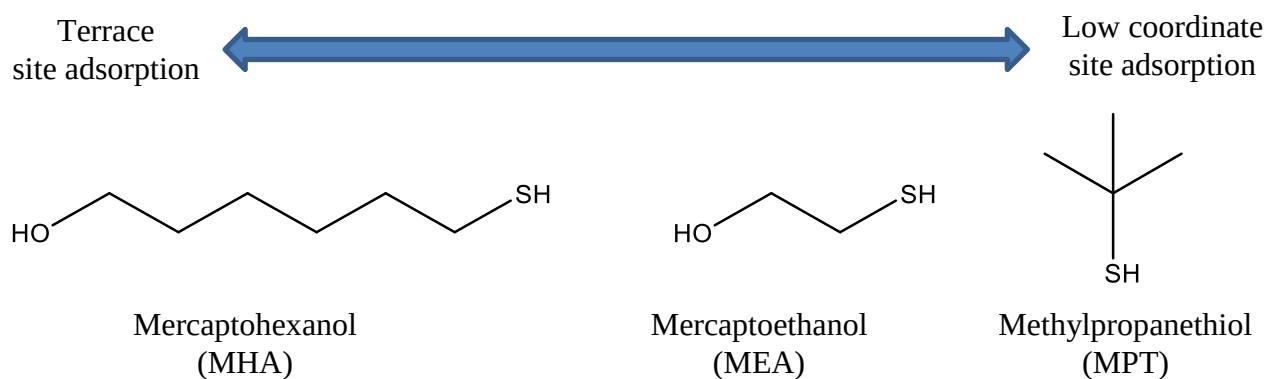


Figure 5.18 – Expected relative site adsorption preferences for MHA, MEA, and MPT.

Given that the surface of the model Pd(PVP) particles consists of approximately 35% low coordinate sites and 65% terrace sites as determined in Section 4.4.2 of Chapter 4, a surface coverage level of 30% was chosen for comparing the systems modified with MEA, MHA, and MPT to avoid complete coverage of any specific class of active site. The model 3-hexyn-1-ol

hydrogenation reaction was again employed to monitor the effects of modification, however as differences in the electronic effects of modification are not expected to be significant, changes in the relative activity for conversion of *cis*-3-hexen-1-ol *via* over hydrogenation processes versus isomerization processes was attributed to changes in the geometric modification effects between the three systems. The same methods and equations for kinetic modelling used in Section 5.7.2 were also employed for this analysis, and fitted reaction profiles are shown below in Figure 5.19 with a complete summary of kinetic results given in Table 5.7.

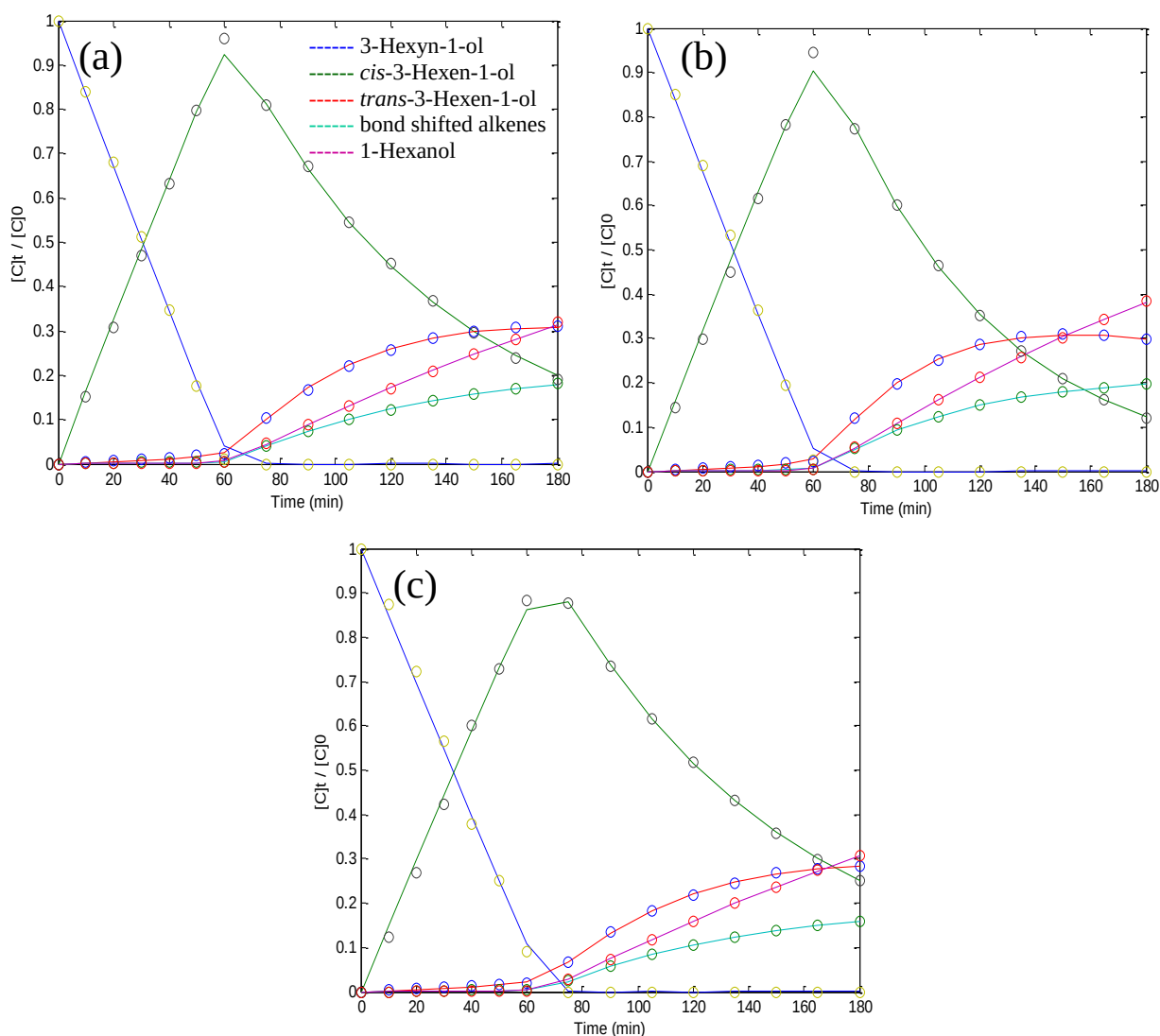


Figure 5.19 – Kinetic fittings for the hydrogenations of 3-hexyn-1-ol and *cis*-3-hexen-1-ol catalysed by Pd(PVP) with 30% surface coverages of (a) MHA (b) MPT, and (c) MEA. Open circles correspond to experimental data points and solid lines to fitted profiles.

Table 5.7 – Complete summary of fitted kinetic data for the hydrogenation of 3-hexyn-1-ol over Pd(PVP) modified with various thiols.

	MHA	MEA	MPT
k_1	781.87	716.78	764.73
k_2	95.99	97.18	128.28
k_3	225.61	184.58	283.86
k_4	0.00	0.14	0.00
k_5	146.73	134.76	180.16
k_6	2.05	2.46	3.15
k_7	89.74	85.20	121.92
k_8	12.25	32.46	6.88
k_9	0.22	0.00	0.43
Σk_{semi}	783.92	719.24	767.88
Σk_{full}	344.93	349.59	437.68
Σk_{isom}	225.61	184.72	283.86
$\Sigma k_{\text{full}}/\Sigma k_{\text{isom}}$	1.53	1.89	1.54

k_n is expressed as TOF in units of min^{-1} , $k_{\text{semi}} = k_1 + k_6$,
 $k_{\text{isom}} = k_3 + k_4$, and $k_{\text{full}} = k_2 + k_5 + k_7 + k_8 + k_9$.

Unfortunately, no clear difference in reaction profiles for the hydrogenation of *cis*-3-hexen-1-ol is observed for the three different thiol modified Pd(PVP) systems, and no clear trend is present in the ratios of activity for hydrogenation processes relative to isomerization processes calculated from kinetic fittings of the reaction profiles (Figure 5.19 and Table 5.7). These results appear to suggest that the primary factor governing the site-selective adsorption of thiol modifiers is the

preference for adsorption in 3 and 4-fold hollow sites of terrace surfaces frequently reported in theoretical studies, rather than any significant influence from steric effects of the thiol chain^{40,52}.

5.9 Optimization of MEA modification

Given the dramatic effects MEA modification has on the catalytic behavior of Pd(PVP) for 3-hexyn-1-ol hydrogenation, it is logical to extend the work presented in this chapter thus far toward optimization of the model system for production of the valuable *cis*-3-hexen-1-ol intermediate. An ideal catalyst for this process will show high TOF and initial selectivity for *cis*-3-hexen-1-ol production combined with low activity for further conversions.

Initial activity and selectivity for *cis*-3-hexen-1-ol

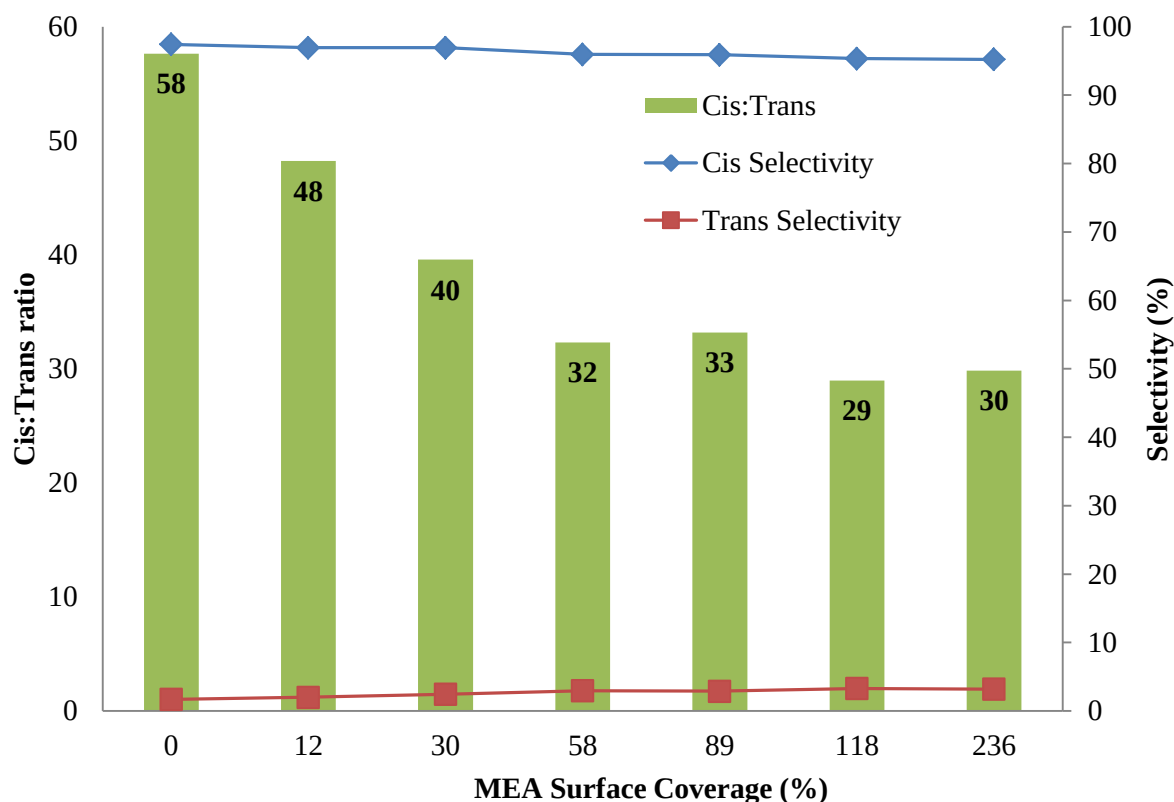


Figure 5.20 – Initial selectivities for *cis*-3-hexen-1-ol and *trans*-3-hexen-1-ol in the catalytic hydrogenation of 3-hexyn-1-ol by Pd(PVP) progressively modified with MEA.

The effects of MEA modification on initial activity have already been discussed previously in Sections 5.6 and 5.7, and will not be further addressed here. As Figure 5.20 above demonstrates, initial selectivity toward the *cis* isomer is adversely affected when Pd(PVP) is modified by MEA in agreement with the previous kinetic modelling results, with the ratio of *cis*-3-hexen-1-ol to *trans*-3-hexen-1-ol decreasing from 58:1 for the unmodified catalyst to only 32:1 at 58% surface coverage. Above this level of MEA surface coverage, no relationship is observed between initial selectivity toward the *cis* isomer and the degree of modification, further suggesting the changes in initial selectivity are governed by electronic modification of the catalyst by MEA. However the actual loss in selectivity across the full range of surface coverages tested is relatively minor, decreasing from 97.4% for the *cis* isomer and 99.1% total alkenes with no modification to 95.2% for the *cis* isomer and 98.4% total alkenes for the highest coverage case. Given these consistently high values for initial selectivity at all levels of modification, the most important parameter to optimize is likely the rates of further conversions which determine final selectivity for the desired product.

Final selectivity for *cis*-3-hexen-1-ol

Figure 5.21 below summarizes final relative selectivities for both the *cis* isomer and total alkenes (expressed as product ratios for *cis*:*trans* and alkene:alkane) for a series of commercial and MEA modified Pd(PVP) catalysts determined immediately after conversion of 3-hexyn-1-ol was complete.

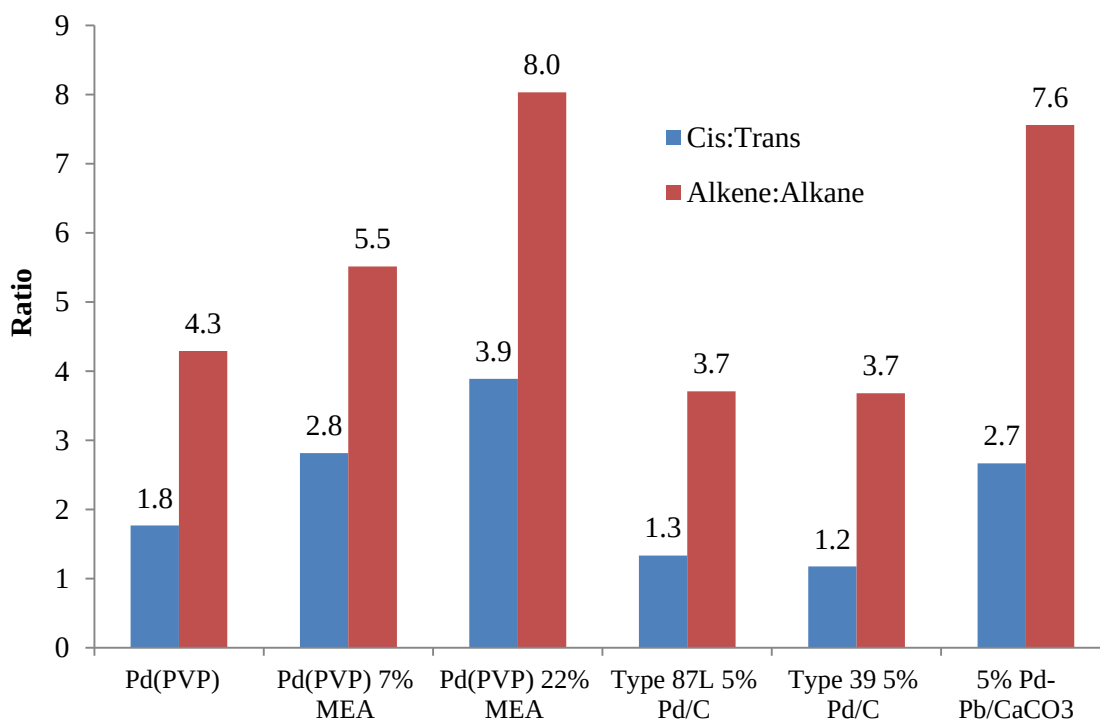


Figure 5.21 – Final relative selectivities for *cis*-3-hexen-1-ol and total alkenes (expressed as product ratios of *cis*:*trans* and alkene:alkane) for the hydrogenation of 3-hexyn-1-ol by assorted Pd catalysts. Reactions were analyzed immediately after 3-hexyn-1-ol conversion was complete.

Final selectivity to both the *cis* isomer and total alkenes is shown to be higher for Pd(PVP) than the commercial Type 87L and Type 39L catalysts, and only improves further upon modification with MEA. Most significantly, Pd(PVP) with 22% MEA coverage showed better selectivity than the Lindlar catalyst (5% Pd-Pb/CaCO₃), which is typically considered an industry standard for selective alkyne hydrogenation²³. Expanding the analysis to include high coverage cases (Figure 5.22 below) shows final selectivities continue to improve dramatically as the level of modification is increased beyond this point, particularly for total alkenes.

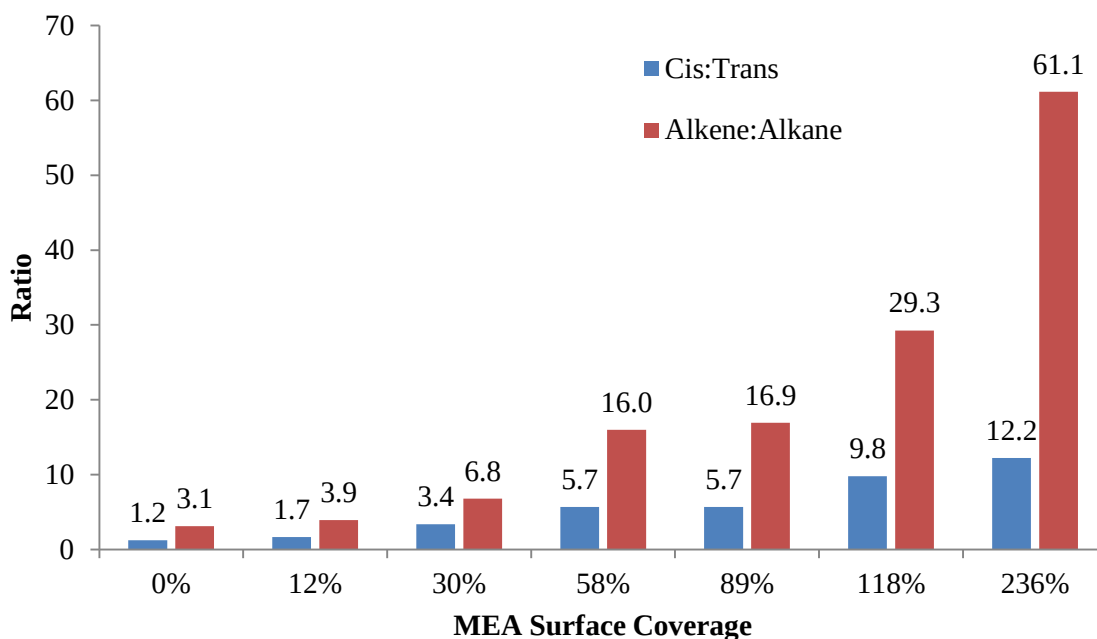


Figure 5.22 – Final relative selectivities for *cis*-3-hexen-1-ol and total alkenes (expressed as product ratios of *cis*:*trans* and alkene:alkane) for the hydrogenation of 3-hexyn-1-ol by Pd(PVP) modified with MEA. Reactions were analyzed 40 min after 3-hexyn-1-ol conversion was complete.

As high initial selectivity is achieved with low modification levels, and high final selectivity is achieved with high modification levels, optimization of the system requires balancing these competing effects. Based on these results and the previous measurements of initial activity, the optimal catalyst for production of *cis*-3-hexen-1-ol is Pd(PVP) with 89% MEA surface coverage. This level of modification does not adversely affect the maximum TOF for 3-hexyn-1-ol conversion or the completion time for this initial conversion (TOF 15.35 sec⁻¹ and completion time 69.47 min for Pd(PVP) with 89% MEA surface coverage versus TOF 12.10 sec⁻¹ and completion time 67.27 min for unmodified Pd(PVP)). Initial selectivity for the *cis* product is slightly decreased (97.4% to 95.9%), however final selectivity is significantly increased for both the *cis* product (36.4% to 76.2%) and total alkenes (65.6% to 89.6%) 40 min after the conversion of 3-hexyn-1-ol is complete.

5.10 Conclusions

This chapter focused on comparing the effects of MEA modification on equivalent palladium and ruthenium catalysts. Ru(PVP) was developed as a model system comparable to the model Pd(PVP) catalyst developed in Chapter 4. MEA was chosen as a model sulfur compound and modification of both the Ru(PVP) and Pd(PVP) model systems was achieved without significantly altering the physical characteristics of the model systems. Modification in the liquid phase allowed for precise control of surface coverage across the model systems.

Geometric and electronic effects of modification were compared for the two systems using a combination of techniques including FTIR of chemisorbed CO, ^{13}C NMR with formic acid as a probe, and the hydrogenation of 3-hexyn-1-ol model test reaction developed in Chapter 4. The results of these experiments established that Ru(PVP) is primarily sensitive to the geometric effects of modification by MEA with little influence from electronic effects, however Pd(PVP) is sensitive to both geometric and electronic effects of modification. Further characterization of the MEA modified Pd(PVP) system eliminated the possibility that changes in catalytic behavior are significantly influenced by sulfidation of the metal surface, as no evidence of PdS formation in the modified catalysts was found by XPS or XRD. These differences in sensitivity to electronic modification effects between the two systems are therefore proposed to originate from a greater sensitivity to changes in d-band width, and position of the d-band centre, for metals with more complete d-band fillings (such as Pd) when sulfur is adsorbed to the metal surface. These effects were confirmed by DFT calculations in the case of Pd. In the case of Pd(PVP), it was also interesting to find that results from monitoring hydrogenation:isomerization ratios for *cis*-3-hexen-1-ol conversion, initial selectivity for 3-hexyn-1-ol conversion, and surface analysis by both XPS and the ^{13}C NMR formic acid technique all demonstrate that electronic effects of MEA modification are only dominant at surface coverages below approximately 60%. This finding is

expected to relate to the geometric preference for adsorption of MEA to electronically coupled terrace sites which make up approximately 65% of the metal surface. Further modification at higher surface coverages requires adsorption to electronically decoupled low-coordinate sites, which results in a primarily geometric modification effect.

In the case of Pd, an interesting competitive binding effect was also observed during hydrogenation of 3-hexyn-1-ol for Pd(PVP) modified with MEA. Strong adsorption by the alkyne reactant was shown to effectively displace MEA pre-adsorbed to the metal surface, leading to no significant changes in maximum TOF for the reaction, and no change in completion time for the conversion of 3-hexyn-1-ol until MEA coverage was increased to over 1 ML. However a slight decrease in initial selectivity toward the *cis* isomer at increased MEA surface coverage demonstrated by kinetic modelling and analysis of reaction compositions may suggest displacement of MEA from the catalyst surface is not complete, leading to a slight modification effect for alkyne hydrogenation. However final selectivity to both the desired *cis*-3-hexen-1-ol product and total alkenes was shown to increase markedly with increasing surface coverage by MEA. Analysis of these effects led to selection of Pd(PVP) modified with 89% MEA surface coverage as the optimal system for synthesis of *cis*-3-hexen-1-ol, with excellent activity and a higher selectivity for the desired products than all commercial catalysts investigated, including the industry standard Lindlar catalyst.

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Chapter 6

Size-dependent effects of sulfur modification

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6.1 Background

The effect of nanoparticle size on the activity and selectivity for catalytic reactions has long been a topic of great interest in the literature¹. From an industrial standpoint where many catalysts are composed of costly platinum group metals (PGM's), it is economically advantageous to reduce the amount of metal required by maximizing the active surface area of the material². This is most easily accomplished by decreasing the average particle size of the active phase, leading to an increase in the surface area to volume ratio and a higher proportion of the metal atoms located on the catalytically active surface³. However, the properties of nanoparticles do not scale directly from bulk materials as the particle size is decreased, and for small nanoparticles, changes in both electronic and geometric properties of the materials occur when particle size is varied⁴. The effects of changing particle size in the region of approximately 1-50 nm on catalytic behaviour have been extensively reported in the literature, with particular emphasis directed toward the relationship between particle size and the activity and selectivity of catalytic hydrogenation reactions^{1,5-9}. However, comparatively little information is available on the size-dependent sensitivities of small nanoparticles to deactivation processes such as catalyst poisoning, and even less information is available regarding specific sensitivities to modification by sulfur.

Of the limited reports that do attempt to detail the relationship between particle size and modification by sulfur, most are found to suffer from the same experimental challenges that plague the comparisons of all systems modified with gaseous sulfur species. Namely, as it is very difficult to accurately control coverage levels of strongly adsorbed sulfur species when modification takes place in the gas phase, complete coverage of the metal surface is often the only option that enables comparison between systems^{10,11}. This results in attempts to compare modification effects on materials that are almost completely deactivated by the sulfur adsorbate. For example, a recent report by Baldyga *et al.* focused on determining the size dependent

sensitivity of Pt nanoparticles supported on silica with diameters of 2-7 nm to poisoning by thiophene¹². While the authors did observe a decrease in sensitivity to sulfur poisoning as particle size increased, extensive pretreatment with thiophene during the modification process lead to almost complete coverage of the catalyst surface for all samples investigated. As a result, the smallest observed decrease in catalytic activity for ethylene hydrogenation after modification was still 99.7%, and the largest was 99.9%. While the arguments presented in studies such as this raise interesting questions about size-dependent modification by sulfur, the experimental conditions employed do not allow for detailed analysis of contributions from geometric or electronic effects.

Another report by Király *et al.* overcame many of these challenges by studying the size-dependent relationship between supported cubooctahedral nanoparticles and modification by CS₂ in the liquid phase¹³. In this study, particle sizes ranging from 1.5 to 4.6 nm were progressively modified with CS₂ up to 100% surface coverage to determine the effects on catalytic activity for the hydrogenation of styrene. The authors found that adsorption of CS₂ and hydrogenation of styrene both took place exclusively on low-coordinate sites of the metal surface, however the only modification effects observed were geometric in nature as catalytic activity was directly proportional to the number of available low-coordinate sites. No electronic modification was evident, and no changes in sensitivity were observed for the different particle sizes. While it is likely that the lack of electronic modification results from adsorption of CS₂ to low-coordinate sites electronically decoupled from the bulk structure¹⁴, this type of study provides a promising template for further investigations into size-dependent sensitivities of metal nanoparticles to both geometric and electronic effects of sulfur modification.

6.2 Objectives

This chapter aims to determine and compare the size-dependent modification effects of MEA adsorbed to Pd(PVP) over a range of catalytically relevant particle sizes. As the previous chapter highlighted an interesting combination of geometric and electronic effects when MEA is adsorbed to small Pd nanoparticles, the focus of this chapter will be directed toward exploring how these effects are altered when the geometric and electronic properties of the surface are simultaneously varied by changing particle size. The model reaction of 3-hexyn-1-ol hydrogenation will once again be employed to monitor these effects, along with the novel ^{13}C NMR formic acid probe technique employed in Chapter 5. The results of this chapter will hopefully establish which Pd(PVP) particle sizes have the greatest sensitivity toward modification by MEA, with the ultimate goal of providing a basis for improving the sulfur tolerance for Pd catalysts.

6.3 Experimental details

A detailed discussion of experimental methods can be found in Chapter 3. In brief, the synthesis of PVP supported palladium nanoparticles was achieved through a polyol reduction method modified from that used by Bonet *et al.*¹⁵. In a typical synthesis, $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and PVP were completely dissolved in ethylene glycol under a nitrogen atmosphere. Upon heating, reduction of the metal precursor occurred resulting in formation of PVP-stabilized nanoparticles in a colloidal suspension. These particles then served as a seed for the synthesis of larger particles *via* a stepwise growth method modified from the procedure outlined by Teranishi *et al.*¹⁶. For each step in the stepwise growth procedure, additional $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ calculated to give the desired level of growth was thoroughly dispersed with a colloidal suspension of seed particles in ethylene glycol. The reaction was then heated at low temperature (90 °C) to encourage slow reduction of the additional precursor onto the seed surface, followed by an increase in

temperature (120 °C) to ensure complete reduction of the grown particles. This procedure was repeated until the desired level of growth was attained, after which the nanoparticles were precipitated by centrifugation in a mixture of acetone and hexane, washed with acetone, and dried under nitrogen. Modification with MEA was achieved by first re-dispersing the dried nanoparticles in ethanol, followed by addition of an ethanolic solution of MEA sufficient to provide the desired level of surface coverage. The modified particles were then thoroughly sonicated and left to age for 24 hours prior to characterization or catalytic testing.

6.4 Pd(PVP) size variation

In order to begin addressing the size-dependent modification effects of sulfur adsorption on palladium as outlined in the aims for this chapter, it was first necessary to synthesize a series of palladium nanocatalysts covering a range of particle sizes. Given the extent to which results and discussion presented in Chapters 4 and 5 focused both on developing Pd(PVP) as a model catalyst system and providing a detailed understanding of effects resulting from MEA modification, it was logical to use the same system as a starting point from which variation of particle size could be achieved. Synthesis methods were chosen with the aim of preserving key characteristics of the original model Pd(PVP) system, namely that the resulting nanoparticles are well-dispersed with a narrow size distribution and no variation in the relative amounts or nature of the stabilizing polymer. The range of particle sizes investigated was also carefully selected to provide variation in both geometric and electronic properties of the metal surface, as both were shown to be important factors on the effects of MEA modification for Pd(PVP) in Chapter 5.

6.4.1 Synthesis

According to literature reports by Teranishi *et al.*, size control of Pd(PVP) nanoparticles can be achieved through two main synthesis methods¹⁶. For particles less than 3.0 nm in diameter, the

authors found that size could be controlled *via* a one-step synthesis by varying the ratio of stabilizing polymer to Pd metal, where increasing the PVP:metal from 0.1:1 to 40:1 resulted in a reduction in average particle size from approximately 3.0 to 2.0 nm. As the 2.7 nm Pd(PVP) model catalyst introduced in Chapter 4 was synthesized with a PVP to metal ratio of 10:1, the results of Teranishi *et al.* suggest that a relatively slight changes in particle size would require substantially changing the amount of stabilizing polymer present in the system. Despite literature reports indicating that the geometric and electronic structure of small metal nanoparticles varies most rapidly in the region of approximately 1-5 nm^{3,6,17}, it was concluded that the increase in the PVP:metal ratio required to synthesize Pd(PVP) nanoparticles smaller than the original 2.7 nm model catalyst introduced too much uncertainty to allow the resulting systems to be fairly compared. However, Teranishi's results also demonstrated that Pd(PVP) nanoparticles larger than 3.0 nm in diameter could be synthesized *via* a stepwise growth method without significantly altering the PVP to metal ratio¹⁶. In this method, small Pd(PVP) nanoparticles are used as seeds, and growth is achieved by reducing small amounts of additional metal precursor onto the surface of the seed particles. The size of the resulting nanoparticles can be predicted using Equation 6.1¹⁸:

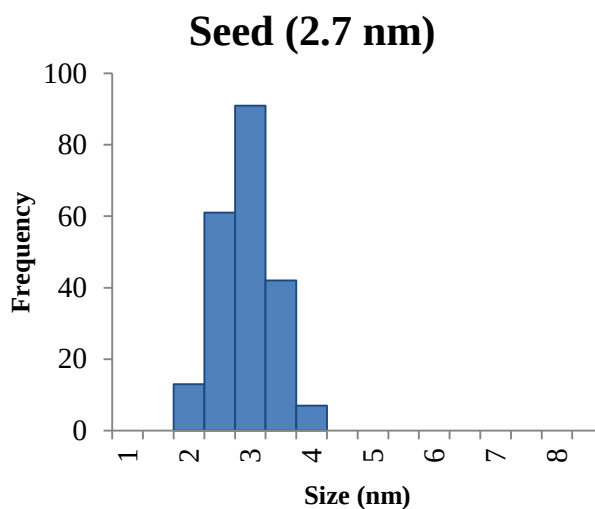
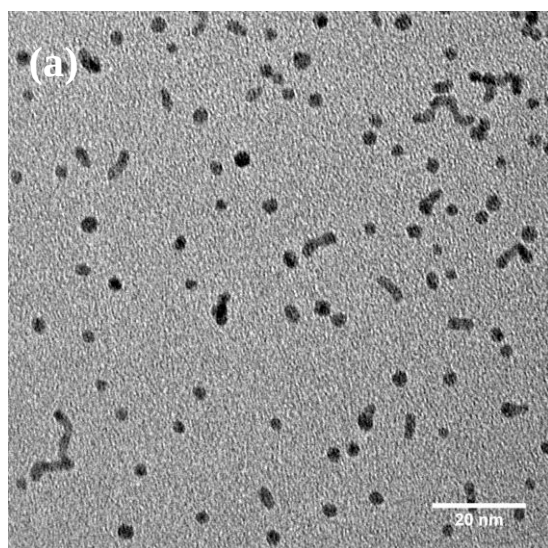
$$d = d_0 \sqrt[3]{\frac{n_i + n_m}{n_m}} \quad \text{Equation 6.1}$$

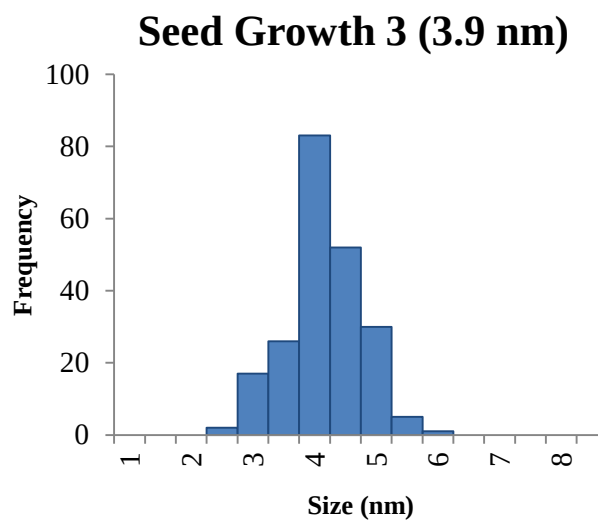
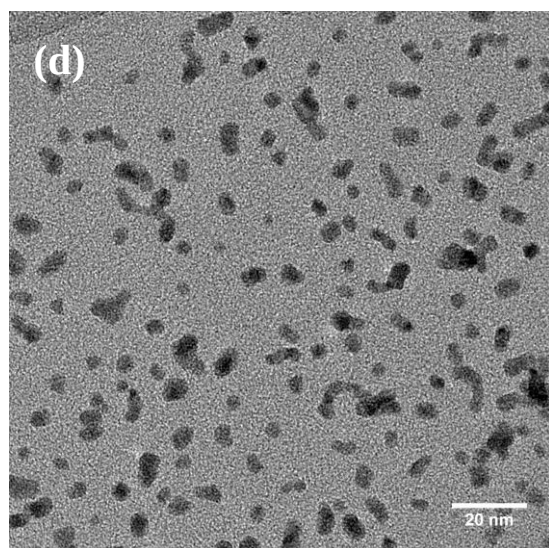
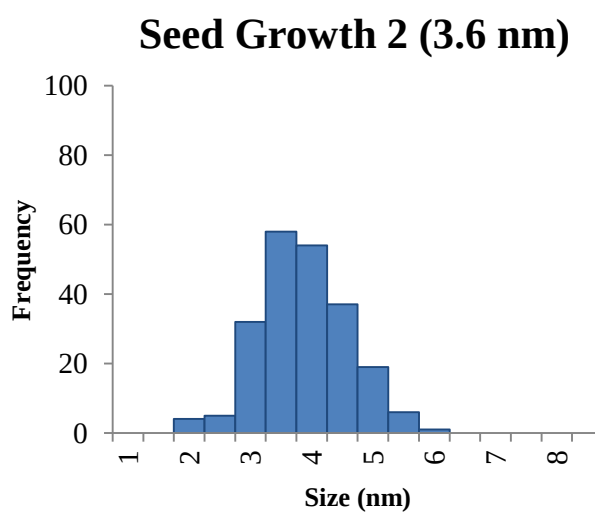
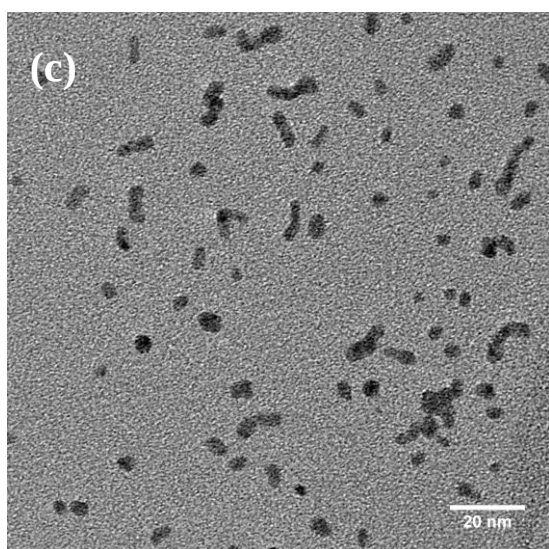
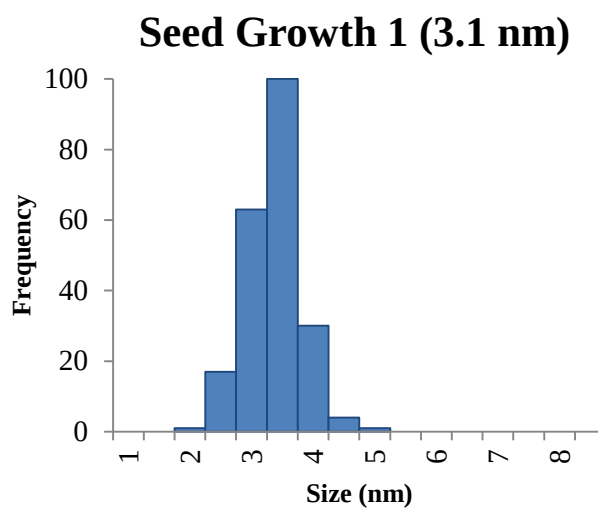
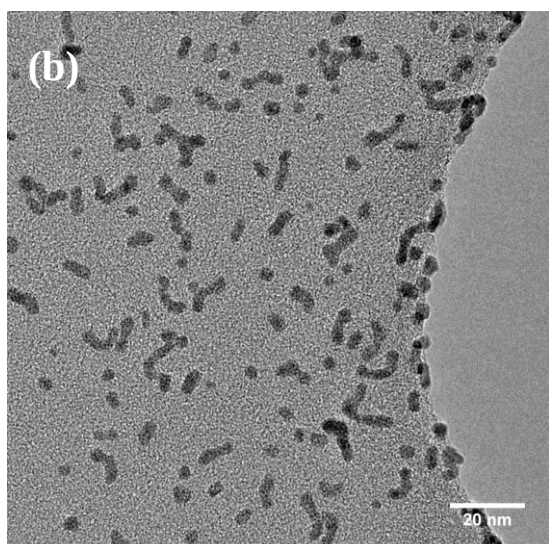
where d is the diameter of the grown particles, d_0 is the diameter of the seed, n_m is the moles of metal in the seed, and n_i is the moles of additional metal precursor. Growth is carried out in steps through reduction of the metal precursor onto increasingly larger seeds until the desired particle size is attained. The only main drawback of this stepwise method for achieving particle size variation compared to a one-step synthesis is the tendency for the size distribution to broaden as the number of successive growth steps is increased¹⁶.

Taking into account the advantages and disadvantages of both methods, the stepwise growth method was chosen for the synthesis of additional systems with varying particle sizes in order to best maintain the characteristics of the model Pd(PVP) nanoparticles. Experimental parameters were modified slightly from those used in Teranishi *et al.* to include ethylene glycol as the solvent/reducing agent and a multi-step reduction process carried out at two different temperature levels. The original 2.7 nm Pd(PVP) nanoparticles synthesized in Chapters 4 and 5 were used as seeds and each growth step was carried out with an additional 1 molar equivalent of metal precursor. Four repetitions of this growth step were performed to yield four sets of Pd(PVP) nanoparticles with expected average particle diameters (calculated from Equation 6.1) of 3.4 nm (one growth step), 3.9 nm (two growth steps), 4.3 nm (three growth steps), and 4.6 nm (four growth steps) in good agreement with the sub 5 nm target range for maximum changes in geometric and electronic structure mentioned previously.

6.4.2 Characterization

TEM Characterization





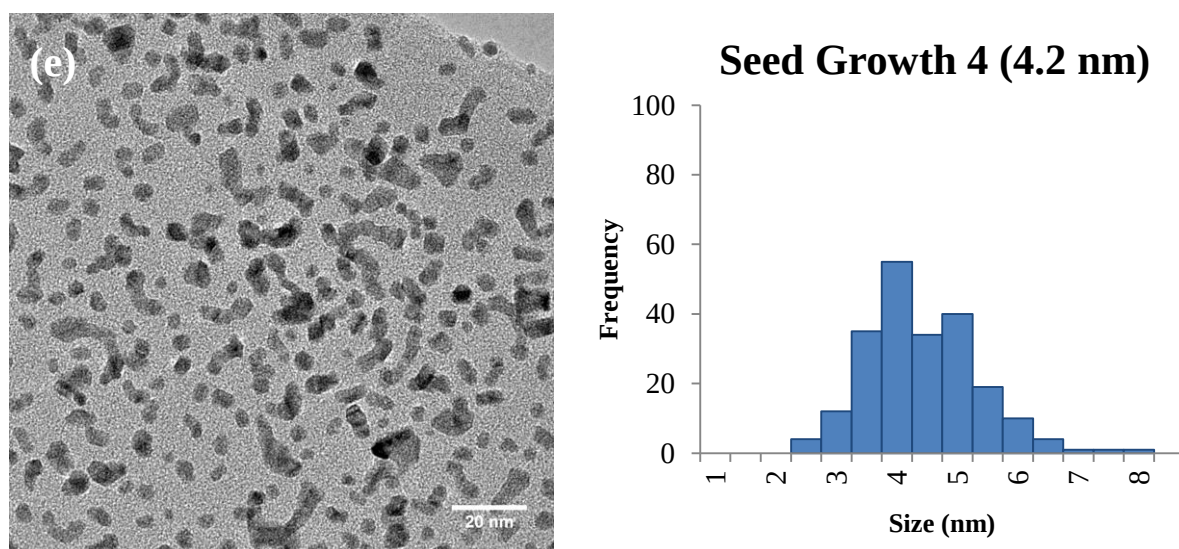


Figure 6.1 - TEM micrographs and corresponding particle size distribution histograms for Pd(PVP) (a) Seed, (b) Seed Growth 1, (c) Seed Growth 2, (d) Seed Growth 3, and (e) Seed Growth 4.

The five particle sizes (designated Pd(PVP) Seed and Pd(PVP) Seed Growth (SG) 1-4) were characterized by TEM and the results are displayed above in Figure 6.1 and below in Table 6.1. Analysis of the TEM micrographs shows the resulting particles are relatively well-dispersed and that average particle size does in fact increase with successive growth steps, attaining a maximum of 4.2 nm for SG4, although the resulting growth is slightly less than predicted from Equation 6.1 (4.6 nm for SG4). In fact, a comparison between predicted and measured particle sizes (Table 6.1) shows that the grown particles are consistently smaller than expected. Since the calculated particle sizes assume all additional metal precursor is reduced onto the surface of the seed particles in each growth step, deviation from this value suggests a small portion of the additional precursor is diverted toward formation of new seed particles, resulting in incomplete particle growth. With this in mind, predicted particle sizes were recalculated based on the measured size for the previous growth step and the results are also given in Table 6.1.

Table 6.1 – Summary of calculated and measured particle sizes for a range of Pd(PVP) systems synthesized by a stepwise growth method.

	Initial Calculated Size ^a (nm)	TEM Measured Size ^b (nm)	TEM Calculated Size ^c (nm)	XRD Measured Size ^d (nm)	Lattice Parameter (Å)
Seed	-----	2.7 (0.44)	-----	2.5	3.9412
Seed Growth 1	3.4	3.1 (0.43)	3.4	3.0	3.9002
Seed Growth 2	3.9	3.6 (0.70)	3.5	3.3	3.8975
Seed Growth 3	4.3	3.9 (0.61)	4.0	3.8	3.8952
Seed Growth 4	4.6	4.2 (0.92)	4.2	4.4	3.8952

^aInitial calculated sizes are determined from Equation 6.1 where d_0 is the calculated size from the previous growth step. ^bStandard deviations in the average particle sizes obtained from TEM are given in parentheses. ^cTEM calculated sizes are determined from Equation 6.1 where d_0 is the particle size from the previous step as measured by TEM. ^dMeasured sizes from XRD are determined by applying the Scherrer Equation to the Pd (220) peak.

Comparing these new predicted sizes with those measured from TEM now shows that the only significant discrepancy exists for the first seed growth sample (SG1, 3.4 nm predicted versus 3.1 nm measured). Two possible reasons exist for the behaviour of this particular sample. Firstly, the degree of growth expected for the synthesis of SG1 from the seed sample (0.7 nm) is the highest of all the growth steps (0.4-0.3 nm for SG2-4) due to the relatively high ratio of additional metal precursor to Pd(PVP) seed for this initial step ($\text{Pd}^{2+}:\text{Pd}$ is 1:1 for SG1 versus only 1:4 for SG4). This excess of metal precursor is likely to favour the formation of additional seed particles through self-nucleation rather than purely growth of the original seed. Secondly, as no additional

PVP stabilizer was added to any of the growth steps to compensate for the increasing metal content, this initial step contains the highest PVP to Pd ratio. It is likely that any PVP not directly bound to the surface of the seed particles will act as a stabilizer for additional self-nucleation, further encouraging the formation of new seed particles from the excess metal precursor.

In addition to well-dispersed nanoparticles with average particle sizes controlled over the 2.7-5.0 nm range, it is essential that the model Pd(PVP) stepwise growth particles show narrow size distributions in order to allow precise comparisons between the systems. While the original seed particles are nearly monodisperse with a standard deviation in average particle size of 16.3% (0.44 nm), the formation of additional seed particles during the synthesis of SG1 would be expected to adversely affect particle size distributions for subsequent growth steps. Table 6.1 does show that particle sizes are more widely distributed for these larger particles, however standard deviations in average particle size remain below 20% in all cases except for SG4 (21.9%), allowing the seed through SG3 systems to be classified as “narrowly-distributed” with the final SG4 system also nearly meeting this qualification.

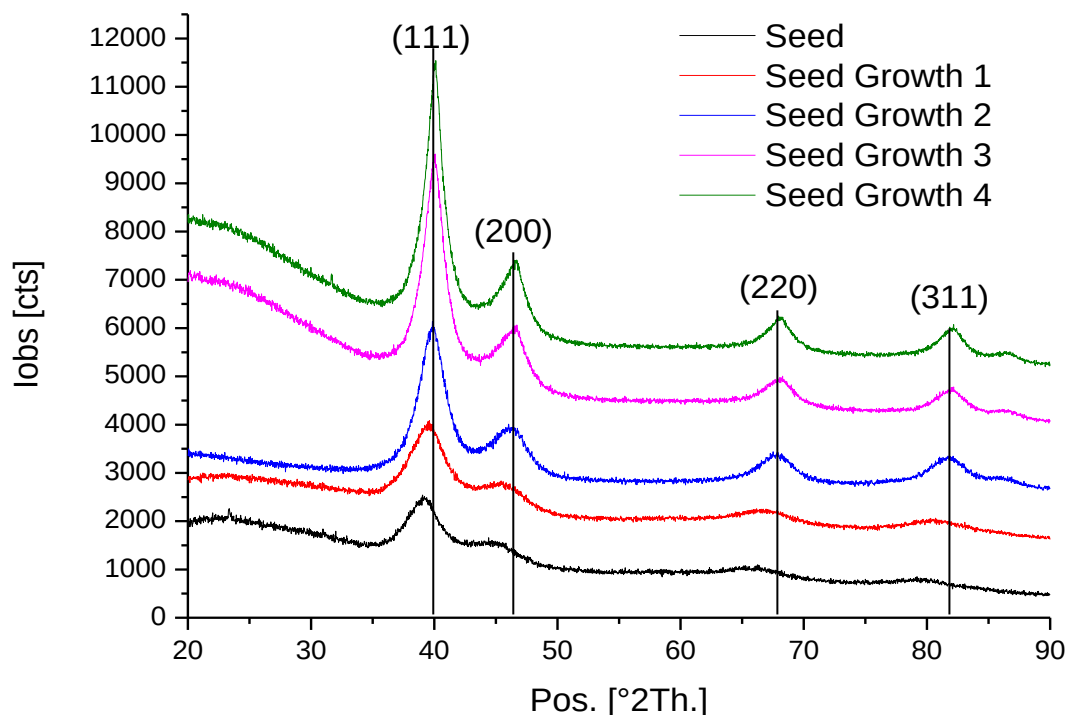
XRD Characterization

Figure 6.2 – XRD profiles for the Pd(PVP) stepwise growth systems (seed, SG1, SG2, SG3, and SG4). Peak positions for the SG4 profile are indicated by black lines.

The stepwise growth systems were further characterized by XRD, and typical profiles are shown in Figure 6.2 above. Peaks corresponding to the (111), (200), (220), and (311) crystal planes of metallic Pd are present in all five samples, and a clear sharpening of these peaks is observed as growth progresses from the Pd(PVP) Seed to SG4 resulting from the increase in particle size. Average crystallite sizes calculated from application of the Scherrer Equation (Equation 2.2) to the Pd (220) peak (Table 6.1) are slightly smaller than those obtained from TEM, indicating the samples may not be entirely crystalline. However, the generally good agreement between the two values suggests this is only a minor effect. Figure 6.2 also shows that particle growth leads to a gradual shift in peak positions to higher angles, and determination of lattice parameters for these systems (Table 6.1) shows this shift corresponds to a gradual lattice contraction as particle size is

increased. While the lattice parameter for the Pd(PVP) seed is 3.9412 Å, this value decreases steadily for all subsequent samples until SG3 (3.8952 Å) when the lattice parameter approaches the value for bulk palladium (3.8907 Å). Multiple accounts in the literature report a similar effect of lattice expansion due to decreasing palladium particle size^{16,19,20}, even though it is generally accepted that a decrease in particle size should be accompanied by contraction of the metal lattice due to increased surface stress^{21–23}. It has therefore been proposed that the lattice expansion for small Pd(PVP) nanoparticles is related to an enhanced ability for highly-disperse palladium nanoparticles to form surface oxides under ambient conditions²⁴. This explanation is supported by the XPS results for 2.7 nm Pd(PVP) presented in Chapter 5, which showed a small degree of the palladium surface was composed of PdO. However, given the ease with which PdO nanoparticles of less than 5 nm are reduced to Pd⁰ when treated with hydrogen under ambient conditions²⁵, no PdO is expected to be present in the Pd(PVP) catalysts used for the alkyne and alkene hydrogenation reactions investigated in this thesis.

6.4.3 Stepwise growth surface statistics

Surface statistics for the stepwise growth nanoparticle systems were calculated in accordance with the methods of Hardeveld and Hartog³ for cubooctahedral nanoparticles using Equations 4.1-4.6, and the results are summarized in Table 6.2 below. Growth of the nanoparticles from 2.7 nm (Seed) to 4.2 nm (SG4) causes the surface population of low-coordinate sites to decrease from 35.3% to 23.0% with a corresponding increase in terrace sites from 64.7% to 77.0%. However, it is expected that true surface statistics for the stepwise growth particles may differ somewhat from these calculated values, as all systems except for the Pd(PVP) seed were found to possess incomplete shell structures. This will likely result in a higher occurrence of low-coordinate sites in the samples with incomplete shells, and may be a source of uncertainty when determining geometric properties of the systems.

Table 6.2 – Surface statistics for the Pd(PVP) stepwise growth systems.

	Shell Structure (<i>m</i>)	Total Atoms	% Surface Atoms	% Low-coordinate Sites	% Terrace Sites
Seed	4.00	586	46.4	35.3	64.7
Seed Growth 1	4.56	934	40.9	30.4	69.6
Seed Growth 2	5.13	1409	36.5	26.6	73.4
Seed Growth 3	5.48	1768	34.2	24.7	75.3
Seed Growth 4	5.84	2196	32.1	23.0	77.0

6.5 Polymer effects

Discussions of the Pd(PVP) stepwise growth systems up until this point have ignored variations in the ratio of stabilizing polymer to palladium metal introduced during the synthesis process. While the initial Pd(PVP) seed was synthesized with a monomer to metal ratio of 10:1, subsequent growth steps increased the metal concentration without simultaneously increasing the amount of PVP stabilizer. As a result, the monomer to metal ratios present during the synthesis of these systems decreased to 5.0:1 (SG1), 3.3:1 (SG2), 2.5:1 (SG3), and 2.0:1 (SG4). As minimal variation in concentration of the supporting polymer was one of the requirements for accurately comparing these model systems, it is necessary to address this issue before any detailed analysis of catalytic properties is carried out.

6.5.1 Polymer content

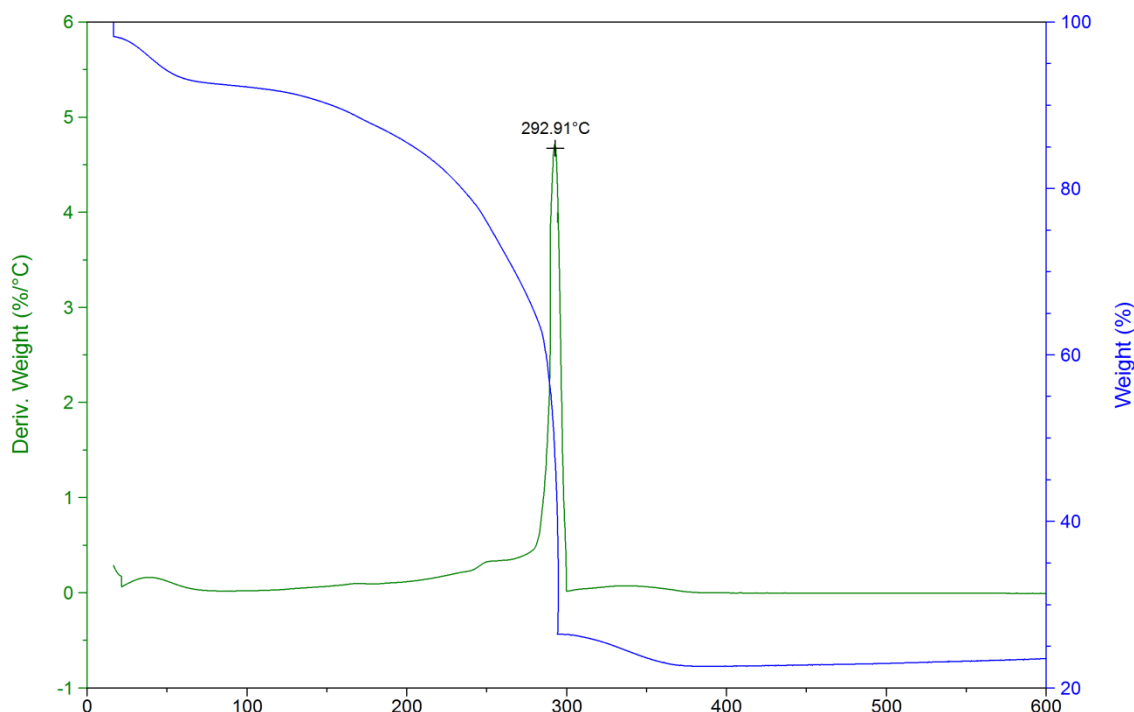


Figure 6.3 – TGA profile for the thermal decomposition of Pd(PVP) Seed.

TGA was performed on each of the five stepwise growth samples in order to quantify the amount of PVP in the final systems (i.e. after synthesis, precipitation, washing, and drying procedures were all complete), and a typical profile for thermal decomposition of the Pd(PVP) seed is shown in Figure 6.3 above. The dominant feature in the profile is a marked drop in sample weight, accompanied by a sharp peak in the derivative weight, at approximately 293°C corresponding to the decomposition of PVP. A slight decrease in sample weight is also observed at low temperature, and was attributed to evaporation of residual moisture or solvent left over from the synthesis process. No further change in sample weight is observed above 500°C, and this remaining mass is assigned to palladium still present in the sample after thermal decomposition of PVP is complete. In accordance with the report by Yeh and Wang

demonstrating the formation of bulk oxides (in the form of PdO for nanoparticles larger than 2.0 nm in diameter) at temperatures greater than approximately 430 °C²⁴, all Pd remaining in the sample at 500 °C was assumed to be in the form of PdO. As such, the relative mass of PVP in each sample was determined by measuring % weight loss in the region of 100-500 °C, and the relative mass of Pd was determined from the % weight remaining in the sample at 500 °C with both calculations accounting for the formation of bulk PdO. The results, expressed in terms of PVP:Pd weight ratios, are summarized in Table 6.3 below.

Table 6.3 – Summary of polymer loadings for the Pd(PVP) stepwise growth systems.

	PVP:Pd Calculated ^a	PVP:Pd Measured ^b	PVP Decomposition Temp. ^c (°C)	Surface Area ^d (m ² g(Pd) ⁻¹)	PVP: Surface Area ^e (mg m ⁻²)
Seed	10.73:1	3.54:1	292.91	184.83	19.153
Seed Growth 1	5.37:1	2.98:1	283.06	160.98	18.512
Seed Growth 2	3.58:1	2.57:1	260.40	138.62	18.540
Seed Growth 3	2.68:1	1.52:1	276.44	127.96	11.879
Seed Growth 4	2.15:1	1.39:1	269.82	118.82	11.698

^aCalculated based on masses of PVP and Pd used in the synthesis of the stepwise growth systems. ^bCalculated from TGA based on weight remaining in the sample at 100 °C (total PVP+Pd content) and 500 °C (total PdO content). ^cMeasured from the point of most rapid weight loss during the decomposition of PVP. ^dCalculated based on surface statistics determined in Section 6.4.3. ^eCalculated from the PVP:Pd ratios determined by TGA and the calculated surface areas.

As the results in Table 6.3 demonstrate, the measured PVP:Pd weight ratios for the stepwise growth systems decrease with increasing particle size as expected, however the ratios are all smaller than those calculated based on the polymer to metal ratios used for the synthesis of these systems. This likely indicates the washing step in the synthesis procedure removes a significant portion of the stabilizing polymer, and further confirms the need to determine these PVP:Pd weight ratios experimentally. When considering the effects of variations in the amount of supporting polymer on catalytic behaviour, it is expected that the key factor is actually the ratio of PVP to metal surface area, not the ratio of PVP to total metal. With this in mind, theoretical surface areas for the stepwise growth systems were calculated based on the total number of surface atoms (Section 6.4.3) and a reference value for the Pd surface packing density of 1.27×10^{19} atoms m^{-2} (Table 6.3)²⁶. These values were then used to calculate the mass of PVP relative to the metal surface area (mg m^{-2}) for each system. When expressed in these terms, Table 6.3 shows that the amount of PVP per unit surface area is actually quite close for the three smallest samples (approximately 19 mg m^{-2} for the Pd(PVP) seed, SG1, and SG2), however this value drops significantly for both Pd(PVP) SG3 and SG4 (approximately 12 mg m^{-2}). In order to eliminate these variations, the amount of PVP relative to the metal surface area in all systems was normalized to the highest value (Pd(PVP) seed, 19.193 mg m^{-2}) by adding additional PVP to the systems once the synthesized nanoparticles were re-dispersed prior to characterization.

Aside from the amount of PVP present in each system, it is also interesting to note the PVP decomposition temperatures, which generally decrease as the Pd(PVP) particle size increases (Table 6.3). While it is possible these temperatures simply relate to the amount of PVP present in the sample, it is also possible that the decrease results from a weakening of PVP adsorption strength as average particle size increases.

6.5.2 Effects of PVP on activity for 3-hexyn-1-ol hydrogenation

While normalizing the amount of PVP relative to the metal surface is expected to eliminate most of the variation between the stepwise growth systems, it is unlikely that all samples will contain exactly the same amount of stabilizing polymer. Literature reports indicate that the amount of stabilizing polymer in a system can have an effect on catalytic activity. For example, Telkar *et al.*²⁷ demonstrated that changing the ratio of PVP to Pd from 1:1 to 40:1 increased TOF for 2-butyne-1,4-diol hydrogenation from $3.0 \times 10^{-5} \text{ hr}^{-1}$ to $5.7 \times 10^{-5} \text{ hr}^{-1}$, while Vu *et al.*²⁸ observed a decrease in activity for 1-octene hydrogenation of almost 80% when PVP loading was increased from 40:1 to 80:1. Given these results, it is pertinent to discount any remaining influence PVP concentration might have on activity of the Pd(PVP) catalysts for the primary reactions considered in this thesis: the catalytic hydrogenations of 3-hexyn-1-ol and *cis*-3-hexen-1-ol. For these experiments, the effects of varying the concentration of PVP were determined for both Pd(PVP) seed and Pd(PVP) SG4 to ensure any size-dependent effects were accounted for. The range of PVP concentrations investigated in these experiments is much narrower than typically reported in the literature, as only variations that might result from experimental errors are relevant to this work. As such, the PVP:Pd weight ratio originally used for the synthesis of the Pd(PVP) seed (10.73:1) was established as a maximum value for both catalysts, as it is unlikely that any experimental errors could result in a higher PVP:Pd ratio. A summary of the results is given below in Table 6.4.

Table 6.4 – Activities of Pd(PVP) stepwise growth catalysts for the conversions of 3-hexyn-1-ol and *cis*-3-hexen-1-ol with various loadings of PVP.

PVP:Pd	3-Hexyn-1-ol conversion TOF (sec ⁻¹)		<i>cis</i> -3-Hexen-1-ol conversion TOF (sec ⁻¹)	
	Seed	Seed Growth 4	Seed	Seed Growth 4
1.21:1	-----	3.16	-----	1.75
3.08:1	12.37	3.20	4.74	2.55
10.73:1	11.04	4.86	5.56	2.28

3-Hexyn-1-ol conversion

In general, TOF's for the Pd(PVP) seed are higher than those for Pd(PVP) SG4 for all PVP:Pd weight ratios investigated. For the Pd(PVP) seed, an increase in PVP:Pd from 3.08:1 to 10.73:1 results in a slight decrease in TOF for the conversion of 3-hexyn-1-ol from 12.37 sec⁻¹ to 11.04 sec⁻¹. However, the opposite effect is observed for Pd(PVP) SG4, where increasing PVP:Pd from 1.21:1 to 10.73:1 causes the TOF to increase from 3.16 sec⁻¹ to 4.86 sec⁻¹. While it is possible that addition of PVP results in opposing promotional and deactivating effects for these two catalysts, the effects are not particularly significant for either system and are unlikely to affect future measurements of 3-hexyn-1-ol hydrogenation activity. This conclusion is also supported by the results of Telkar *et al.*²⁷, who found that varying PVP:Pd over a similar range of loadings to those investigated above (1:1 to 10:1) had very little effect on catalytic activity for 2-butyne-1,4-diol hydrogenation as increasing PVP:Pd from 1:1 to 10:1 only increased TOF from 3.0x10⁻⁵ hr⁻¹ to 3.2x10⁻⁵ hr⁻¹.

cis-3-Hexen-1-ol conversion

In the case of *cis*-3-hexene-1-ol conversion, TOF's for the Pd(PVP) seed are again higher than those for Pd(PVP) SG4 for all PVP:Pd weight ratios investigated. However, in contrast to the conversion of 3-hexyn-1-ol, both catalysts now show a slight increase in catalytic activity when higher concentrations of PVP are present. When PVP:Pd is increased from 3.08:1 to 10.73:1 for the Pd(PVP) seed, TOF increases from 4.74 sec⁻¹ to 5.56 sec⁻¹. A similar effect is observed for Pd(PVP) SG4, where increasing PVP:Pd from 1.21:1 to 10.73:1 leads to an increase in TOF from 1.75 sec⁻¹ to 2.28 sec⁻¹. This slight promotion effect is in line with literature reports that indicate adsorption of nitrogen-containing ligands increases the activity of palladium for catalytic hydrogenation of alkenes²⁷, however the effects are again shown to be quite mild and are not expected to significantly impact future results.

6.6 Size-dependent hydrogenation of 3-hexyn-1-ol

It is generally accepted that an increase in nanoparticle size leads to electronic modification of the system through broadening of the d-band to lower energy states, causing the d-band centre to shift further away from the Fermi level²⁹⁻³². Transitioning to a larger particle size also leads to a corresponding increase in the density of states near the Fermi level, as the band structure becomes more similar to that of a bulk metal³⁰. These effects are particularly prominent for nanoparticles in the 1-5 nm size range, and generally result in decreasing adsorption strength for nucleophilic reactants, such as alkynes and alkenes, due to an increase in electron density on surface atoms as the average coordination number is increased. However, this increase in average coordination number is also directly linked to geometric modifications of the metal surface that result when particle size is varied over the same size region^{3,32}. For surface sensitive reactions, any resulting shift in the prevalence of surface active sites can lead to additional changes in apparent catalytic activity that are completely independent from changes in activity

caused by electronic modification⁶. This relationship between geometric and electronic structure makes it virtually impossible to electronically modify a system through changing particle size without simultaneously modifying the geometric structure of the metal surface. As such, any study aiming to investigate changes in particle size must ensure both effects are taken into account.

After the model Pd(PVP) stepwise growth systems were thoroughly characterized and sources of possible variation were addressed, focus was turned toward a detailed investigation of how geometric and electronic properties of the catalyst vary as particle size is changed across the model Pd(PVP) stepwise growth systems. The catalytic hydrogenations of 3-hexyn-1-ol and *cis*-3-hexen-1-ol were again employed as model test reactions to study these effects as described previously in Chapters 4 and 5. Kinetic modelling was conducted based on the rate equations derived in Chapter 5 (Equations 5.1-5.6) from the reaction mechanism presented in Scheme 5.2, and a full summary of results is presented in Table 6.5 below. Analysis of these results was again simplified by grouping rate constants into semi hydrogenation (k_{semi} : k_1 and k_6), isomerization (k_{isom} : k_3 and k_4), and full hydrogenation processes (k_{full} : k_2 , k_5 , k_7 , k_8 , and k_9).

Table 6.5 – Complete summary of fitted kinetic data for the hydrogenation of 3-hexyn-1-ol over the Pd(PVP) stepwise growth systems.

	Seed	SG1	SG2	SG3	SG4
k_1	721.55	609.75	282.41	194.09	186.26
k_2	144.26	150.71	123.84	84.24	65.18
k_3	344.75	351.71	249.48	177.50	133.83
k_4	137.56	152.31	108.35	79.24	59.83
k_5	20.47	39.08	1.98	3.56	5.45
k_6	13.00	10.62	4.93	3.25	3.35
k_7	122.90	135.51	88.33	65.32	47.20
k_8	38.19	17.81	59.75	40.00	33.81
k_9	101.89	71.09	114.12	89.42	76.16
Σk_{semi}	734.55	620.37	287.34	197.34	189.61
$\Sigma k_{\text{full}} + \Sigma k_{\text{isom}}$	910.02	918.22	745.85	539.28	422.13
$\Sigma k_{\text{full}} / \Sigma k_{\text{isom}}$	0.89	0.82	1.08	1.10	1.18
% k_{full}	47.00%	45.11%	52.02%	52.39%	54.05%
% k_{isom}	53.00%	54.89%	47.98%	47.61%	45.95%

k_n is expressed as TOF in units of min^{-1} , $k_{\text{semi}} = k_1 + k_6$, $k_{\text{isom}} = k_3 + k_4$, and $k_{\text{full}} = k_2 + k_5 + k_7 + k_8 + k_9$.

3-Hexyn-1-ol hydrogenation activity

Literature reports are generally in agreement that electronic and geometric modifications resulting from an increase in particle size function cooperatively to increase catalytic activity for

the hydrogenation of alkynes⁵. When particle size is confined to the range in which electronic effects vary significantly, a lowering of the d-band centre relative to the Fermi level as particle size increases leads to a corresponding decrease in alkyne adsorption strength. As alkyne hydrogenation reactions catalysed by palladium tend to be desorption limited, any destabilization of the strongly adsorbed alkyne leads to an increase in catalytic activity³³. Changes in geometric surface structure at increasing particle size have also been shown to promote alkyne hydrogenation activity. When investigating the catalytic behaviour of PVP-stabilized Pd nanocubes, Crespo-Quesada *et al.* observed an increase in TOF for the hydrogenation of 2-methyl-3-butyne-2-ol from 15.3 sec⁻¹ to 17.5 sec⁻¹ when particle size was changed from 6 nm to 18 nm³⁴. The resulting activity effects were attributed to an increase in the relative prevalence of terrace sites (from 72.1% to 90.0% of the surface), which were shown to be favoured active sites for catalysing the hydrogenation. Chapter 4 of this thesis demonstrated a similar active site preference for the hydrogenation of 3-hexyn-1-ol, suggesting a similar increase in TOF should be observed when average particle size is increased across the model Pd(PVP) systems. Additional promotional effects are expected to result from a decrease in adsorption strength for 3-hexyn-1-ol.

However contrary to these predictions, a clear trend of decreasing catalytic activity for the hydrogenation of 3-hexyn-1-ol (k_{semi}) is observed as average particle size is increased, with TOF decreasing from 734.55 min⁻¹ for the Pd(PVP) seed to 189.61 min⁻¹ for Pd(PVP) SG4 as shown in Table 6.5 above. This loss of activity is far too substantial to result solely from uncertainties in the polymer content of the samples, and effects from mass transfer limitations are unlikely as the range of particle sizes investigated is quite narrow. A similar result was reported in the literature by Anderson *et al.*, where the authors observed a decrease in TOF from 6.3 sec⁻¹ to 3.2 sec⁻¹ for

the hydrogenation of 1-hexyne over Pd supported on silica when the average particle size was increased from 3.4 to 8.0 nm, however the cause of this behaviour was not identified³⁵.

A possible explanation for the unexpected behaviour of 3-hexyn-1-ol hydrogenation may arise from the fact that all of the stepwise growth systems excluding the initial Pd(PVP) seed possess an incomplete shell structure (Section 6.4.3). While the equations derived by Hardeveld and Hartog³ allow for calculation of surface statistics for a continuum of m values, they are only truly accurate for systems possessing a complete outer shell structure¹⁷. Particles with incomplete shells (such as the Pd(PVP) SG1-SG4 systems) will have significantly more surface atoms in low-coordinate sites than the number calculated from Equations 4.4 and 4.5 as partial shells with additional low-coordinate sites develop on terraces. This effectively results in a loss of catalytically-active terrace surface area for the systems with incomplete shells, as low-coordinate sites were shown in Chapter 4 to be inactive for 3-hexyn-1-ol hydrogenation due to strong adsorption between the nucleophilic alkyne and the electron deficient low-coordinate atoms³⁶. And even though adsorption strength of 3-hexyn-1-ol bound to the remaining terrace sites is still expected to decrease with increasing particle size, no similar effect is expected for adsorption to low-coordinate sites which are electronically decoupled from the bulk structure¹⁴. The ultimate result is an overall increase in the average alkyne adsorption strength and a corresponding drop in hydrogenation activity.

cis-3-Hexen-1-ol conversion activity

The incomplete shell structure for the Pd(PVP) SG1-SG4 systems is not expected to similarly affect the overall catalytic activity for conversion of *cis*-3-hexen-1-ol. In this case, both terrace and low-coordinate sites were shown in Chapter 4 to be catalytically active for conversion of the alkene, albeit *via* separate reaction pathways. Changes in *cis*-3-hexen-1-ol conversion activity

are thus expected to result primarily from electronic modification of the surface as particle size is varied without significant contribution from geometric effects.

As Table 6.5 demonstrates, a reduction in total activity for the conversion of *cis*-3-hexen-1-ol ($\Sigma k_{\text{full}} + \Sigma k_{\text{isom}}$) is observed as particle size is increased (TOF is 910.02 min⁻¹ for Pd(PVP) seed versus 422.13 min⁻¹ for Pd(PVP) SG4). This result agrees with the expected decrease in adsorption strength for the already weakly bound alkene as the d-band centre shifts further from the Fermi level with increasing Pd(PVP) particle size. Similar effects were observed by Goetz *et al.*³⁷ for the hydrogenation of 1-butene over Pd nanoparticles supported on alumina, where an increase in average particle size from 2.7 to 4.5 nm resulted in a 64.5% decrease in TOF for alkene conversion (activity for the Pd(PVP) stepwise growth systems is reduced by 53.6% for nearly identical size variation).

***cis*-3-Hexen-1-ol conversion selectivity**

The effects of varying particle size on selectivity for the conversion of *cis*-3-hexen-1-ol are expected to be more complicated than the effects on activity. If the Pd(PVP) stepwise growth systems possessed the ideal surface geometries calculated in Section 6.4.3, geometric and electronic effects resulting from varying particle size should have opposing influences on selectivity. In terms of geometric effects, an increase in particle size should favour hydrogenation to 1-hexanol over isomerization to *trans*-3-hexen-1-ol due to increasing prevalence of the terrace sites required for the bond-shifting hydrogenation mechanism demonstrated in Chapter 4. However, the accompanying decrease in alkene adsorption strength resulting from electronic effects should favour isomerization over hydrogenation, as the latter pathway is preferentially affected by changing surface electronic structure (as discussed in Chapter 5).

With these influences in mind, the relative levels of catalytic activity for *cis*-3-hexen-1-ol conversion resulting from hydrogenation (k_{full}) and isomerization (k_{isom}) processes given in Table 6.5 were compared to the theoretical number of terrace sites on the metal surface for the Pd(PVP) stepwise growth systems (Figure 6.4 below).

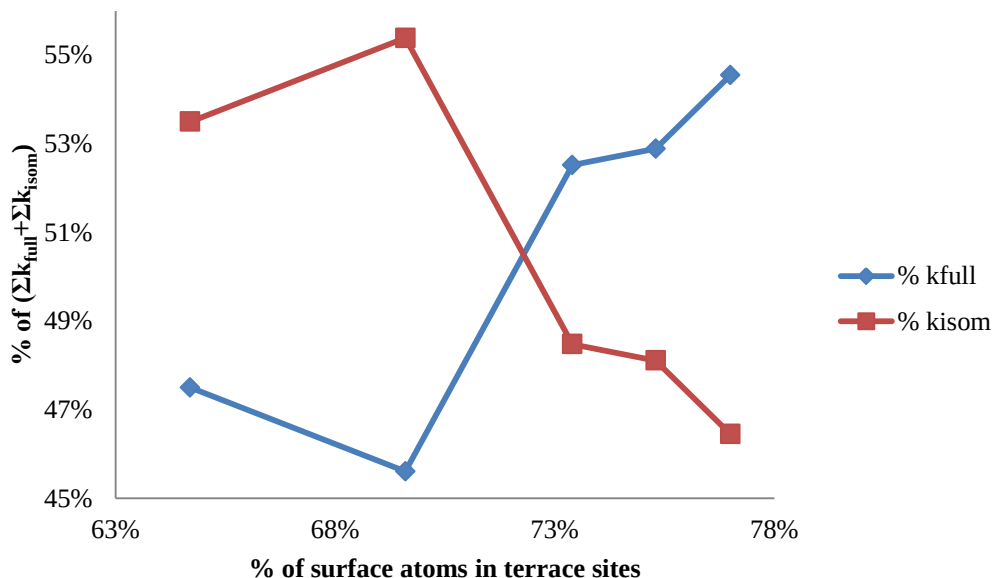


Figure 6.4 – Relationship between the population of surface active sites and relative activities for the isomerization and hydrogenation processes of *cis*-3-hexen-1-ol conversion.

As Figure 6.4 demonstrates, the relative activity for the hydrogenation process initially shows a negative correlation with the prevalence of terrace sites on the particle surface, decreasing from 47.0% of the total conversion activity for the Pd(PVP) seed to 45.1% for Pd(PVP) SG1. This result suggests that changes in electronic effects play a dominant role in determining selectivity over this size range (2.7-3.1 nm). However, further increasing particle size results in a positive correlation between relative activity for the hydrogenation process and the prevalence of terrace sites (45.1% for Pd(PVP) SG1 versus 54.1% for Pd(PVP) SG4), suggesting changes in geometric effects become the dominant factor in determining selectivity for larger particles (3.1-4.2 nm).

The observed differences in sensitivities of small and large nanoparticles to changes in electronic and geometric structure are in good agreement with literature reports, where changes in catalytic behaviour for alkene hydrogenation due to varying particle size were attributed to electronic effects for small particles and geometric effects for large particles^{6,34}. However, it should be noted that the above analysis has ignored the likelihood that more surface atoms are in low-coordinate sites than originally predicted for most of the systems, which may complicate the results.

6.7 Size-dependent MEA modification effects

Given the uncertainties in geometric surface structure for many of the Pd(PVP) stepwise growth systems, investigations into the sensitivity of the different particle sizes to modification by MEA will focus primarily on the electronic sensitivities of the particles. In Chapter 5, the original Pd(PVP) model system was shown to be sensitive to both electronic and geometric effects of MEA modification at surface coverages below approximately 56%. Above this level, catalytic behaviour was dominated by geometric effects. To ensure electronic effects could be observed and compared for the stepwise growth systems, a surface coverage of 30% was chosen for the MEA modified Pd(PVP) stepwise growth systems.

6.7.1 Hydrogenation of 3-hexyn-1-ol

Catalytic behaviour of the MEA modified Pd(PVP) stepwise growth systems was investigated using the model 3-hexyn-1-ol hydrogenation reaction to allow for comparison with the unmodified systems. Kinetic analysis was performed in an identical manner to Section 6.6, and a complete summary of the results is given in Table 6.6 below. Results from comparison of reaction kinetics for the stepwise growth systems before and after modification with MEA are given in Table 6.7.

Table 6.6 – Complete summary of fitted kinetic data for the hydrogenation of 3-hexyn-1-ol over the Pd(PVP) stepwise growth systems modified with 30% MEA surface coverage.

	Seed	SG1	SG2	SG3	SG4
k_1	686.13	652.16	323.01	254.09	248.43
k_2	99.73	104.26	137.38	68.06	58.36
k_3	191.70	185.66	205.30	106.39	89.26
k_4	79.08	98.61	128.69	72.22	102.42
k_5	42.11	22.61	3.26	2.28	0.00
k_6	12.93	11.65	5.67	5.61	5.44
k_7	65.69	68.58	89.38	44.00	33.10
k_8	0.00	0.00	0.00	16.41	0.91
k_9	38.26	53.87	67.15	83.61	56.57
Σk_{semi}	699.06	663.81	328.68	259.7	253.87
$\Sigma k_{\text{full}} + \Sigma k_{\text{isom}}$	516.57	533.59	631.16	392.97	340.62

k_n is expressed as TOF in units of min^{-1} , $k_{\text{semi}} = k_1 + k_6$, $k_{\text{isom}} = k_3 + k_4$, and $k_{\text{full}} = k_2 + k_5 + k_7 + k_8 + k_9$.

Table 6.7 – Changes in reaction kinetics for the Pd(PVP) stepwise growth systems after modification with MEA at 30% surface coverage.

	Seed	SG1	SG2	SG3	SG4
Change in Σk_{semi}	-4.91%	+7.00%	+14.38%	+30.91%	+33.38%
Change in $\Sigma k_{\text{full}} + \Sigma k_{\text{isom}}$	-43.24%	-41.89%	-15.38%	-27.13%	-19.22%

3-Hexyn-1-ol hydrogenation activity

When MEA modification of the original Pd(PVP) model system was investigated in Chapter 5, no effects on the activity for 3-hexyn-1-ol hydrogenation were observed regardless of the level of surface coverage by MEA. This result was attributed to alkyne adsorption strength being high enough to enable 3-hexyn-1-ol to almost completely displace MEA pre-adsorbed to the catalyst surface (activity loss was only 1.93% at 30% MEA surface coverage). When the same experiments were conducted for analysis of the stepwise growth systems, a similar result is obtained for the Pd(PVP) seed, with modification by MEA resulting in only a slight loss of catalytic activity (4.9%, Table 6.7). However, when the Pd(PVP) SG1-SG4 samples are modified with MEA, activity for 3-hexyn-1-ol hydrogenation (k_{semi}) is found to increase relative to the unmodified systems. The magnitude of this promotional effect is positively correlated with the particle size, as the relative increase in activity after MEA modification was 7.0% for Pd(PVP) SG1 versus 33.3% for Pd(PVP) SG4. A possible explanation for this trend relates to the decrease in adsorption strength for 3-hexyn-1-ol adsorbed to terrace sites on the catalyst surface as particle size is increased, due to lowering of the d-band centre relative to the Fermi level³⁰. When alkyne adsorption strength is weakened, MEA is able to compete more effectively for active sites on the metal surface, essentially leading to increased modification effects for the larger particles. In Chapter 5 it was demonstrated that adsorption of MEA to Pd(PVP) leads to a broadening of the Pd d-band and a lowering of the d-band centre relative to the Fermi level³⁸. As such, increased modification by MEA due to higher effective surface coverage is expected to affect the d-band centre position most significantly for larger particles, leading to destabilization of the strongly adsorbed alkyne and a corresponding increase in activity for 3-hexyn-1-ol hydrogenation.

3-Hexyn-1-ol hydrogenation selectivity

The effects of MEA modification on the Pd(PVP) stepwise growth systems for 3-hexyn-1-ol hydrogenation activity are also mirrored by measurements of the initial selectivity to *cis*-3-hexen-1-ol. Ratios of the selectivities for *cis*-3-hexen-1-ol and *trans*-3-hexen-1-ol determined prior to complete 3-hexyn-1-ol conversion for the different stepwise growth systems with and without modification by MEA are shown in Figure 6.5 below, and the corresponding selectivity data is given in Table 6.8.

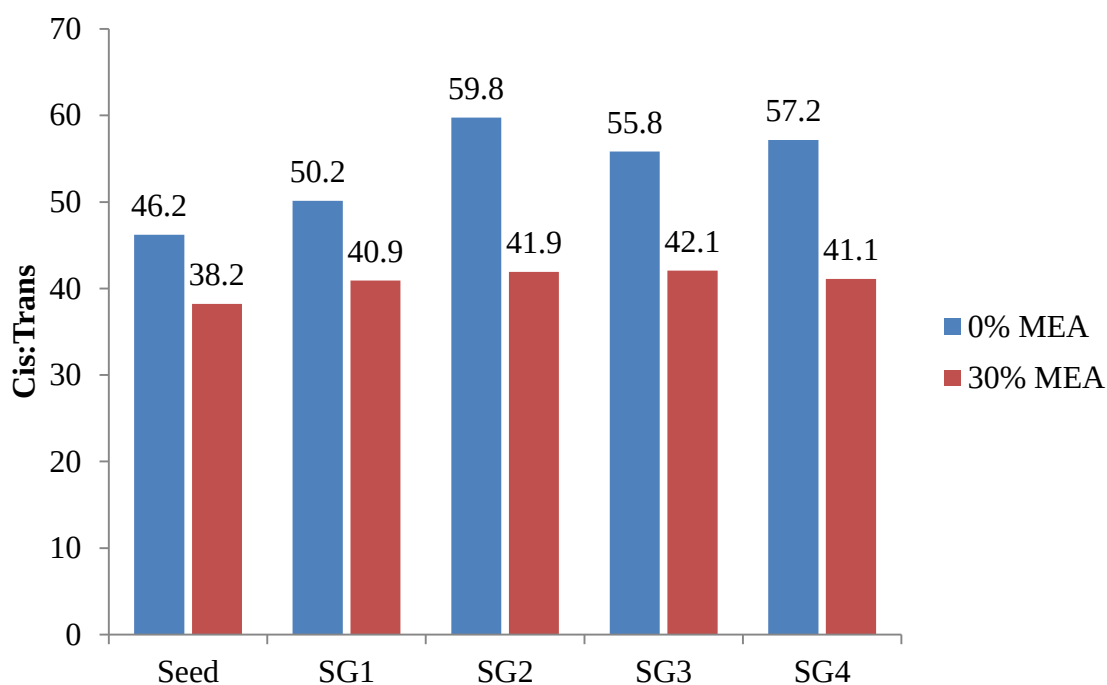


Figure 6.5 – Relative initial selectivities for *cis*-3-hexen-1-ol and *trans*-3-hexen-1-ol in the catalytic hydrogenation of 3-hexyn-1-ol by the Pd(PVP) stepwise growth systems before and after modification with MEA.

Table 6.8 – Initial selectivities for the hydrogenation of 3-hexyn-1-ol catalysed by the Pd(PVP) stepwise growth systems.

	<i>cis</i> -3-Hexen-1-ol Selectivity		<i>trans</i> -3-Hexen-1-ol Selectivity	
	0% MEA	30% MEA	0% MEA	30% MEA
Seed	96.60%	96.28%	2.09%	2.52%
Seed Growth 1	96.79%	96.53%	1.93%	2.36%
Seed Growth 2	97.40%	96.38%	1.63%	2.30%
Seed Growth 3	97.12%	96.32%	1.74%	2.29%
Seed Growth 4	97.17%	96.20%	1.70%	2.34%

Selectivity values determined prior to the completion of 3-hexyn-1-ol conversion.

Similar to results presented in Chapter 5, modification of the Pd(PVP) seed system with MEA leads to a slight decrease in initial selectivity for *cis*-3-hexen-1-ol (Figure 6.5, Table 6.8). This loss of selectivity becomes more prominent as particle size is increased, and likely results from increased competitive adsorption of the alkene intermediates due to weakening alkyne adsorption strength. However, selectivity changes for the different stepwise growth systems resulting from MEA modification are quite minor, with losses in *cis*-3-hexen-1-ol selectivity for the Pd(PVP) seed and SG4 systems of 0.32% and 0.97%, respectively. This result is further evidence of the substantial difference in adsorption strengths for the alkyne and alkene reactants, as a reduction

in adsorption strength for 3-hexyn-1-ol large enough to significantly affect reaction activity still has little effect on reaction selectivity.

cis-3-Hexen-1-ol conversion activity

When MEA modification of the original Pd(PVP) model system was investigated in Chapter 5, a significant reduction in activity for the conversion of *cis*-3-hexen-1-ol was observed as surface coverage was progressively increased. This was in contrast to the effects on activity for 3-hexyn-1-ol hydrogenation, and was attributed to the significant difference in adsorption strengths for alkynes versus alkenes. While the strongly adsorbed 3-hexyn-1-ol was capable of displacing pre-adsorbed MEA, the weakly adsorbed *cis*-3-hexen-1-ol was not.

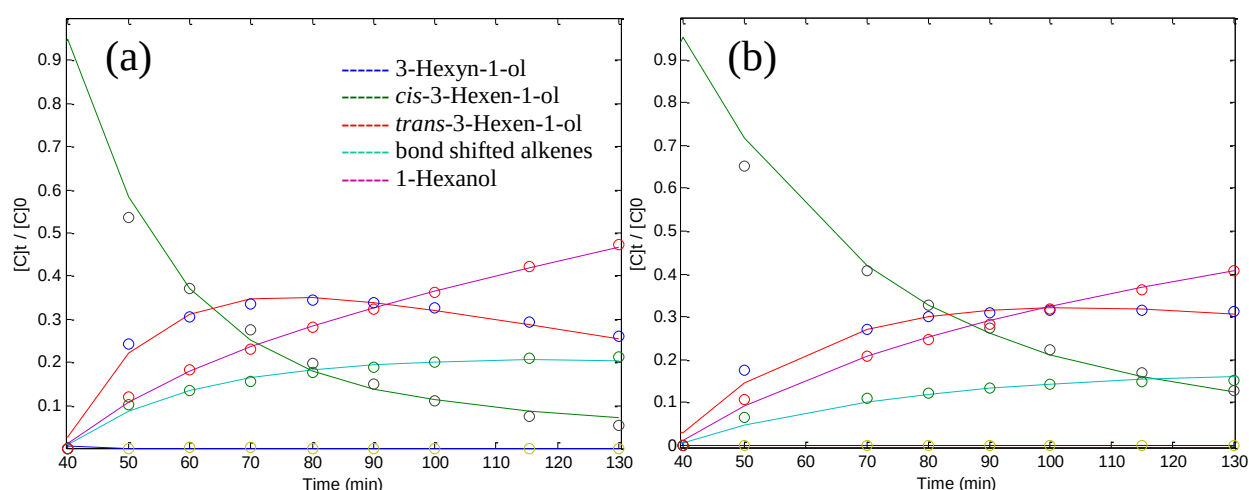


Figure 6.6 – Kinetic fittings for the hydrogenation of *cis*-3-hexen-1-ol catalysed by Pd(PVP) seed with MEA surface coverages of (a) 0% and (b) 30%. Open circles correspond to experimental data points and solid lines to fitted profiles.

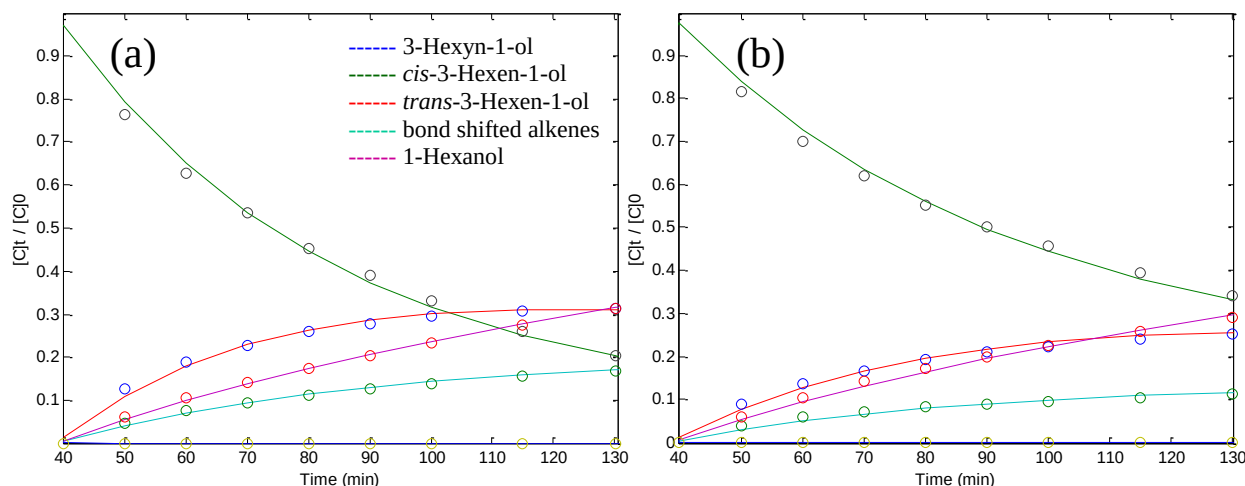


Figure 6.7 – Kinetic fittings for the hydrogenation of *cis*-3-hexen-1-ol catalysed by Pd(PVP) SG4 with MEA surface coverages of (a) 0% and (b) 30%. Open circles correspond to experimental data points and solid lines to fitted profiles.

Similar results are obtained when the Pd(PVP) seed is modified with MEA, with the fitted reaction profiles shown in Figure 6.6 demonstrating a clear loss in conversion activity after modification. Analysis of changes in reaction kinetics shows a loss of *cis*-3-hexen-1-ol conversion activity ($\Sigma k_{\text{full}} + \Sigma k_{\text{isom}}$) of 43.2% (Table 6.7) for the modified Pd(PVP) seed. However as particle size is increased, the activity for *cis*-3-hexen-1-ol conversion is less affected by modification of the systems with MEA, with the Pd(PVP) SG4 system only showing a loss in activity of 19.2% (Figure 6.7, Table 6.7).

While at first glance these results would appear to contradict the conclusions from the previous section that larger particles are more sensitive to modification by MEA, the same general arguments can be used to rationalize both sets of results. In both cases, there are essentially two components in the system: MEA and either an alkyne or alkene reactant. When average particle size increases, adsorption strength for the most strongly adsorbed component in the system is preferentially weakened. For 3-hexyn-1-ol hydrogenation, MEA is the weakly adsorbed component and thus the most significant modification effects are observed for large particles.

However, as MEA is the strongly adsorbed component for conversion of *cis*-3-hexen-1-ol, the most significant modification effects are observed for small particles. For these small Pd(PVP) particles, adsorption of MEA electronically modifies the system by broadening the Pd d-band and lowering of the d-band centre relative to the Fermi level, weakening alkene adsorption strength and leading to reduced conversion activity. However, as particle size increases, adsorption strength for MEA decreases as does its ability to modify the Pd d-band structure, resulting in less significant changes in *cis*-3-hexen-1-ol conversion activity for larger particles.

6.7.2 ^{13}C Formic acid NMR

The results of the previous section appear to demonstrate that the electronic effects of MEA modification become less significant as average particle size is increased. In order to confirm this finding, the same ^{13}C formic acid NMR technique employed to investigate electronic effects of MEA modification in Chapter 5 was applied to the stepwise growth systems, and the results are shown in Figure 6.8 below.

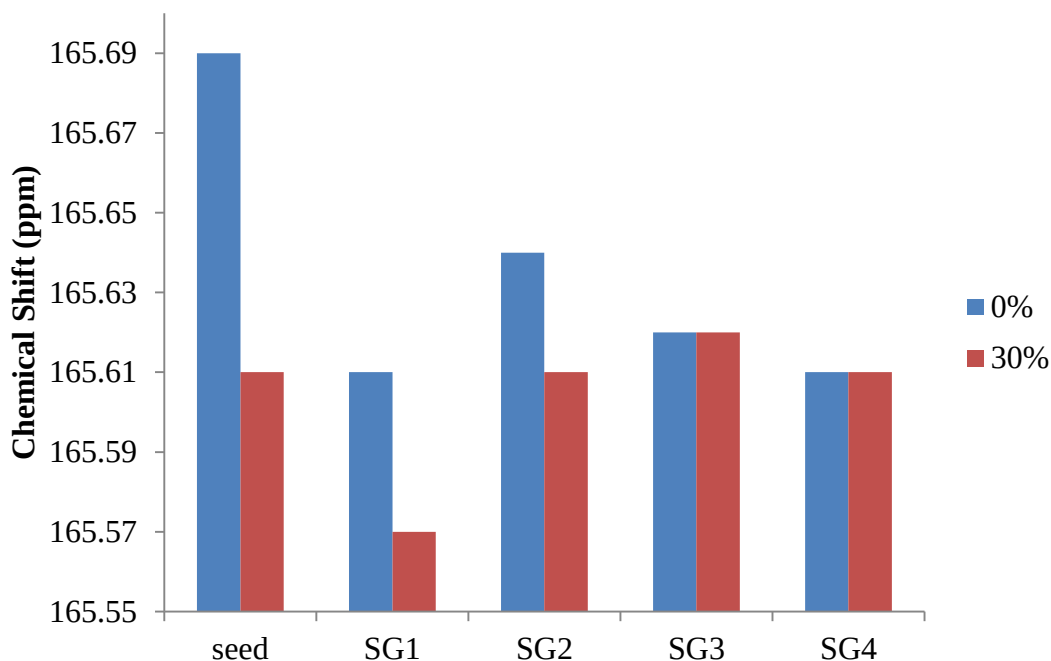


Figure 6.8 – Chemical shifts of the formic acid probe for the Pd(PVP) stepwise growth systems with and without modification by MEA.

Prior to modification by MEA, the highest chemical shift for the formic acid probe is observed with the Pd(PVP) seed, indicating adsorption of the probe is strongest for this system. As particle size increases, a general upfield shift is observed in line with decreased adsorption strength for the formic acid probe as the d-band widens and the d-band centre shifts further from the Fermi level. A similar trend was observed by Tedsree *et al.* when the same technique was applied to Pd(PVP) nanoparticles with average particle sizes spanning 2.3 to 5.2 nm³⁹. However in this report the authors attributed the decrease in adsorption strength of the probe to decreasing prevalence of low-coordinate sites on the surface as particle size is increased. Given that the same trend is observed even with the uncertain surface geometry of the Pd(PVP) stepwise growth systems, it would appear that position of the d-band centre, rather than surface geometry, plays the dominant role in determining chemical shift of the formic acid probe.

When the Pd(PVP) seed system is modified with MEA, an upfield shift in resonance frequency for the formic acid probe is observed indicating electronic modification of the Pd surface similar to the results presented in Chapter 5. However, as particle size is increased, the magnitude of the upfield shift observed for the modified systems decreases in prominence until a diameter of 3.9 nm is reached (Pd(PVP) SG3). After this point, no relationship is observed between modification by MEA and the chemical shift of the formic acid probe. There are several conclusions that can be drawn from these results. Firstly, the influence of electronic effects due to modification by MEA is shown to decrease with increasing particle size in support of the results of the previous section. Secondly, the lack of relationship between chemical shift of the formic acid probe and modification by MEA for the Pd(PVP) SG3 and SG4 systems suggests modification of these systems is governed primarily by geometric, rather than electronic effects. This conclusion is supported by the effects of changing particle size on the selectivity of *cis*-3-hexen-1-ol

conversion, where small particles were shown to be dominated by electronic effects while larger particles were dominated by geometric effects.

6.8 Conclusion

The primary aim of this chapter was to determine and compare the size-dependent modification effects of MEA adsorbed to Pd(PVP) over a range of catalytically relevant particle sizes. In order to accomplish this goal, a stepwise growth method was employed to synthesize a series of model Pd(PVP) nanoparticles with sizes ranging from 2.7 to 4.2 nm. Particles in this range were expected to show changes in both geometric and electronic structure as particle size was varied. Additional experiments were carried out to ensure equal polymer loadings for all of the stepwise growth systems, and measurements of catalytic activity for 3-hexyn-1-ol and *cis*-3-hexen-1-ol conversions demonstrated that any remaining uncertainty in polymer content would not significantly affect further measurements of catalytic behaviour.

The question of which particle size is the most sensitive to sulfur modification was then approached by investigating the size-dependent effects of MEA modification on the Pd(PVP) stepwise growth systems using the model 3-hexyn-1-ol hydrogenation reaction. However, results from the two steps of the reaction appeared to lead to conflicting conclusions. In the case of 3-hexyn-1-ol hydrogenation, the catalytic activity of larger particles was shown to be the most strongly affected by modification with MEA. However, the reverse was true for conversion of *cis*-3-hexen-1-ol, where the catalytic activity of larger particles was shown to be the least affected by modification with MEA. These results would seem to suggest that the relationship between particle size and sensitivity to modification by MEA is complicated, although the resulting effects are in fact governed by the same underlying principles. In both cases, modification of the metal surface by MEA resulted in decreased adsorption strength for the

alkyne and alkene reactants due to broadening of the d-band and lowering of the d-band centre relative to the Fermi level. However, due to competitive binding effects in the 3-hexyn-1-ol system, adsorption of MEA was most favourable on larger particles and thus the modification effects were also more prominent for these systems. For the conversion of *cis*-3-hexen-1-ol where competitive binding effects were not significant, adsorption of MEA was most favourable on small particles due to their higher d-band centre and thus the modification effects were most apparent for these systems.

This chapter also aimed to answer the question of which modification effects are dominant for the different particle sizes. Results from measurements of lattice constants from XRD, selectivities for the conversions of 3-hexyn-1-ol and *cis*-3-hexen-1-ol, and comparisons of formic acid chemical shift by ^{13}C NMR all indicate that modification of small particles (Pd(PVP) seed and SG1) by MEA is dominated by electronic effects, while modification of large particles (Pd(PVP) SG3 and SG4) is dominated by geometric effects.

The results presented in this chapter demonstrate that the sweeping statements often made in literature reports regarding the size-dependent sensitivities of metal nanoparticles to modification by sulfur are likely gross oversimplifications of the complicated relationship between particle size and the effects of modification. In particular, the manifestation of these modification effects on catalytic activity was shown to depend entirely on the mechanisms of the reaction under investigation. It is therefore difficult to say conclusively what the optimal particle size should be for designing a more sulfur-tolerant Pd catalyst, as the answer would likely change depending on the specific requirements the system under consideration. However for catalytic reactions where sulfur adsorption is strong and irreversible, the conclusions of this chapter would suggest that modification could be limited to simple geometric effects through the use of larger nanoparticles.

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Chapter 7

Conclusions and future perspectives

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7.1 Conclusions

Throughout this thesis, the primary objective of the research conducted has been to explore the fundamental basis for modification effects resulting from the adsorption of sulfur to transition metal nanocatalysts.

In furtherance of this objective, colloidal synthesis methods were employed in order to design well-characterized model catalytic systems suitable for comparing and contrasting the modification effects of sulfur adsorption across systems of varying composition and particle sizes. The hydrogenation of 3-hexyn-1-ol was developed as a model test reaction by selectively modifying the geometric surface structure of the model nanocatalysts in order to determine the surface-sensitive reaction mechanisms. Application of this model reaction to characterize sulfur-modified transition metal nanocatalysts allowed both geometric and electronic effects of the modification to be monitored under reaction conditions, offering significant advantages over standard evaluation techniques.

Use of these model systems for the determination of metal-dependent effects of sulfur modification demonstrated a clear difference in the sensitivities of different transition metals to geometric and electronic modification effects. The activity of ruthenium-based catalysts was shown to be strongly affected by adsorption of a model sulfur compound, however the modification effects were shown to be primarily geometric in nature with little to no electronic component. In contrast, the catalytic behaviour of palladium-based systems was shown to be strongly influenced by both geometric and electronic effects of sulfur adsorption. Differences in the sensitivities of the two systems to electronic modification effects were proposed to result from an enhanced ability for adsorbed sulfur to modify the d-band structures of transition metals

with higher d-band fillings, leading to broadening of the d-band, lowering of the d-band centre, and a reduction in the DOS near the Fermi level upon interaction with sulfur.

The relationship between geometric and/or electronic structure of nanocatalysts and sensitivity to modification effects of sulfur adsorption were further investigated by varying particle size for the palladium-based catalytic systems. For small nanoparticles where catalytic behaviour is governed by both geometric and electronic structural properties, modification effects from sulfur adsorption were shown to be primarily electronic in nature. In contrast, larger nanoparticles where electronic structure approaches that of a bulk material were shown to be influenced primarily by the geometric effects of sulfur adsorption.

7.2 Future perspectives

The research presented in this thesis provides a basis for understanding how changes in catalytic behaviour resulting from modification of transition metal nanocatalysts by sulfur are tied to fundamental interactions between the adsorbate and the metal surface. It is expected that further research in this area will be able to apply these concepts to the intelligent design of catalysts for specific reaction systems by tailoring sensitivities to sulfur modification effects through choices concerning catalyst metal, particle size, and particle morphology.

Additionally, this thesis briefly illustrated the potential for utilizing the modification effects of sulfur adsorption to palladium-based systems to optimize catalytic activity and selectivity for fine chemical production, with sulfur-modified catalysts demonstrating stronger catalytic performance than prominent industrial heterogeneous catalysts. However, the colloidal model systems employed in this thesis are not practical for application to industrial processes. It is thus expected that further research into this area will focus on adapting the concepts presented in this

thesis for the modification of traditional supported heterogeneous catalysts, with the ultimate goal of developing a convenient, easily separated, and reusable system with excellent activity and selectivity for catalytic hydrogenation reactions.