



**Development of silver nanocatalyst for propylene
selective oxidation reaction**

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DECLARATTION

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

Bin Yu

DEDICATION

To my family.

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Development of Silver Nanocatalysts for Selective Propylene Oxidation

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Abstract

Propylene is the second most important starting chemical in the petrochemical industry after ethylene. Unlike ethylene, propylene readily undergoes substitution reactions including polymerisation, oxidation, halogenation, hydrohalogenation, alkylation, hydration, oligomerization and hydroformylation, which lead to a wide variety of important downstream products. One of the principal uses of propylene is to produce key chemicals from selective oxidation. In 2016, the world annual production of propylene is about 94 million tonnes, and the global proportion used to produce selective oxidation product is over 18%. They constitute a key part of the chemical industry and contribute towards substantial economic benefits. The application of Ag based heterogeneous catalysts to selective propylene oxidation is a key factor in the synthesis of nearly all downstream chemicals, however billions of pounds are lost every year due to unplanned reactor shutdown, safety control and environment unfriendly emission control as a results of inefficiency catalytic selectivity and activity. Despite, both theoretical and experimental research works

have been intensively involved, the fundamental reason leading to these effects are not yet well understood.

The work presented in this thesis explores a range of novel modification techniques that alter the activity of Ag nanocatalysts for selective propylene oxidation, especially in propylene epoxidation. Particular focus is placed on developing surface modified Ag catalysts through morphology control, surface architecture engineering with another sublayer metal. Using a combination of modelling, novel and traditional materials characterisation methods, it is found that these modification result in some significant electronic and/or geometric alterations to the Ag nanoparticles surface. The Ag-Ag bond distance can be dramatically enlarged by exposing a high-index Ag surface or a core-shell structure with monolayer Ag shell. When interacting with molecular oxygen, the molecular oxygen adsorption and dissociation behaviour is sensitive to the geometric changes in Ag surface. This leads to an enhanced selectivity toward propylene epoxidation than combustion resulting from preventing a C-H bond cleavage.

Finally, by creating atomically dispersed Ag on zeolite, a completely different interaction between molecular oxygen and single atom Ag were discovered comparing to on an extensive silver surface. This leads to the observation of an excitingly new propylene oxidation reaction producing ethanol and CO₂ resulting from C=C bond cleavage. Overall, the research presented within this thesis demonstrated a number of methods for the intelligent design of novel heterogeneous Ag catalysts with remarkable activity and selectivity toward specific selective

propylene oxidation. These modification methods are believed to be potentially applicable to a wide range of other catalytic reactions.

Keywords: Heterogeneous catalyst, Single atom silver catalyst, Geometric modification, Molecular oxygen adsorption, Selective oxidation, Propylene oxide, Ethanol production.

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1.1 Principles of catalysis

1.1.1 Definition of catalysis

The word catalysis comes from two Greek words, the prefix *cata-*, meaning down, and the verb *lysein*, meaning to split or break.^[1] In the early 19th Century, it was noticed that many chemical reactions were affected by trace amounts of substances that were involved in, but not consumed by the reactions. J. W. Döbereiner demonstrated that platinum was able to induce the oxidation of hydrogen; Michael Faraday discovered that a platinum sponge could bring the oxidation of ethanol vapour; Peregrine Philips demonstrated and patented the oxidation ability of platinum for sulphur dioxide, which later sustained the sulphuric acid manufacture.^{[2–}

^{4]} However, at that time, none of these observations was bringing to what was later known as chemical reactivity. It is not surprising that none of the rates of reaction have ever been available to be accurately measured and calculated. In 1836, J. J. Berzelius first attempted at a rational definition of these unconventional findings.^[2] In his comment on this extraordinary chemical effect, he named it ‘the catalytic power of substances’, which he used to describe the chemical forces driving the chemical processes. Ever since the concept of catalysis has been proposed, an exponentially increased research works have been reported in the new field. Today, approximately 25% of the gross national product (GNP) for these industrialized societies is currently derived from processes involving catalysis.^[5] It is of no doubt that catalysts are a crucial component in a vast range of industrial processes, including petroleum refining,^[6] Fisher-Tropsch process,^[7] ammonia synthesis,^[8] the production of pharmaceuticals and fine chemicals^[9] and green technologies such as biomass transformation,^[10] solar cell^[11] and sustainable energy utilisation.^[12] Therefore, an understanding of the principles of catalysis must be regarded as an essentially

chemical phenomenon for the development of modern chemical technologies.

Developed from the original concept of catalysis, the generally accepted definition of a catalyst is that it is any kind of substance that increases the rate of a chemical reaction at which the chemical system approaches equilibrium, whilst being regenerated in its original form upon completion of the reaction cycle.^[13] The second part of the definition distinguished catalysts from promoters, which also increased the rate of reaction yet are consumed in the process.^[1,2] Catalysis is the phenomenon of a catalyst in action. The properties of catalysts enabled the utilization of full range of chemical elements including expensive precious metals because of its reutilization comparing to normal promoters.^[14]

1.1.2 Kinetics of catalysed reactions

From a fundamental standpoint, the primary effect of a catalyst is to increase the reaction rate. Theoretically, a chemical reaction and rate coefficient can be described by transition state theory or the Arrhenius equation.^[15] The transition state theory assumes a special chemical equilibrium between the reactants and activated transition state and is successfully calculates the activation energy. Based on the classic mechanics, the transition state theory can be expressed in the terms of the absolute rate theory, and the rate coefficient k is given by Equation 1.1:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad \text{Equation 1.1}$$

where k_B is the Boltzmann constant, h is the Planck's constant, T is the absolute temperature, R is the gas constant and $\Delta G^\ddagger$ is the Gibbs free energy of activation which is defined by Equation 1.2:

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

Where $\Delta H^\ddagger$ is the enthalpy of activation and $\Delta S^\ddagger$ is the entropy of activation.

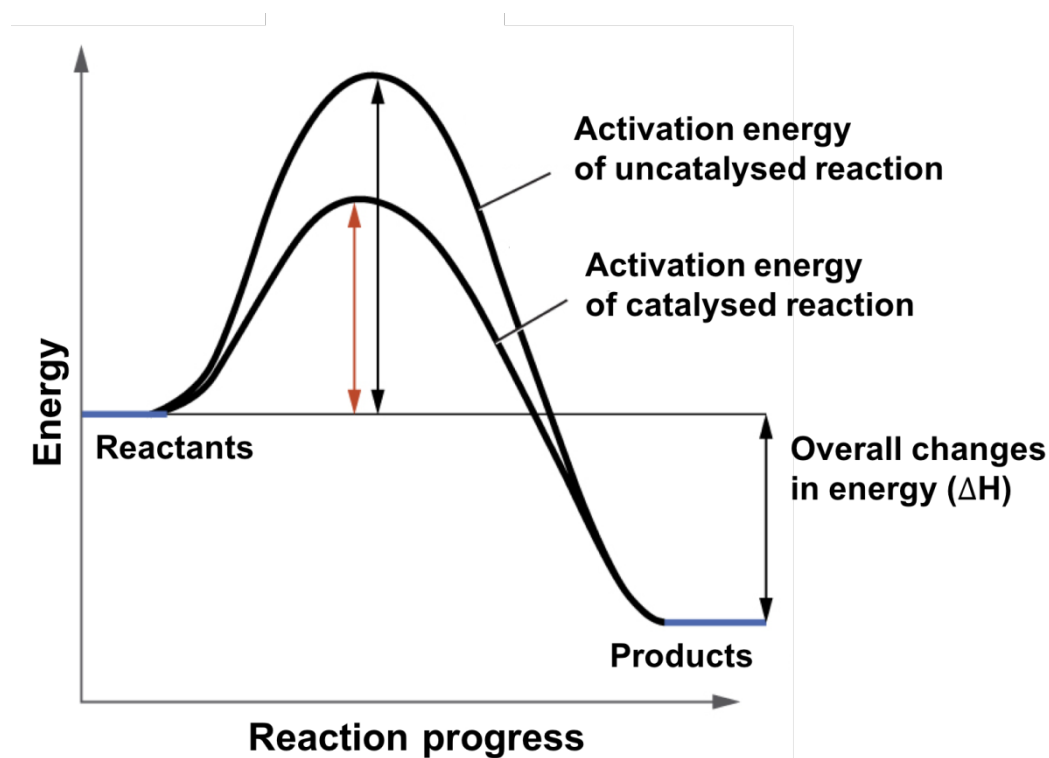


Figure 1.1 Potential energy profile for an exothermic reaction, showing the lower activation energy of the catalysed reaction. Reproduced from reference.^[16]

According to the absolute rate theory, to increase the rate of a reaction, the effect of a catalyst is to decrease the free energy of activation of the reaction, which is composed of both the entropy and the enthalpy of activation. The reactants are usually immobilized on the catalyst surface with consequent loss of translational freedom, resulting in a lower entropy of activation in a catalysed reaction pathway over an uncatalysed reaction pathway. Therefore, there must be a corresponding decrease in the enthalpy of activation to compensate when an efficient catalysis is applied. According to the definition of Gibbs free energy, the activation energy for a catalysed reaction is less than for a uncatalysed reaction as shown in Figure 1.1.

Some experimental values of activation energy for catalysed and uncatalysed reactions are given in Table 1.1.

Table 1.1 Activation energies (kJ mol⁻¹) for catalysed and uncatalysed reactions.^[17]

Reaction	E(catalysed)	E(uncatalysed)	Catalyst
2HI → H ₂ + I ₂	-	184	-
	105	-	Au
	59	-	Pt
2N ₂ O → 2N ₂ + O ₂	-	245	-
	121	-	Au
	134	-	Pt
Pyrolysis of	-	224	-
	144	-	I ₂ vapour

The Arrhenius equation (Equation 1.3) is a formula for the temperature dependence rate of reaction:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad \text{Equation 1.3}$$

where A is the pre-exponential factor (A constant for each chemical reaction that defines the rate due to frequency of collision in the correct orientation). According to the Arrhenius equation, when taking the temperature into consideration, the Arrhenius diagram in Figure 1.2 illustrates that the effect of a catalyst is either to increase the rate coefficient at a given temperature or to decrease the temperature at which it achieves a given value. There is a notable comparison between homogeneous and heterogeneous reaction from the Arrhenius diagram, which is resulting from the difference in dimensions of the rate coefficients and the pre-exponential factor. For a catalysed reaction, the value of the later one depends on the active surface area of the catalyst. The Arrhenius equation illustrates that

decreasing the activation energy is a fundamental principle of catalysis, and it applies to all forms of it.

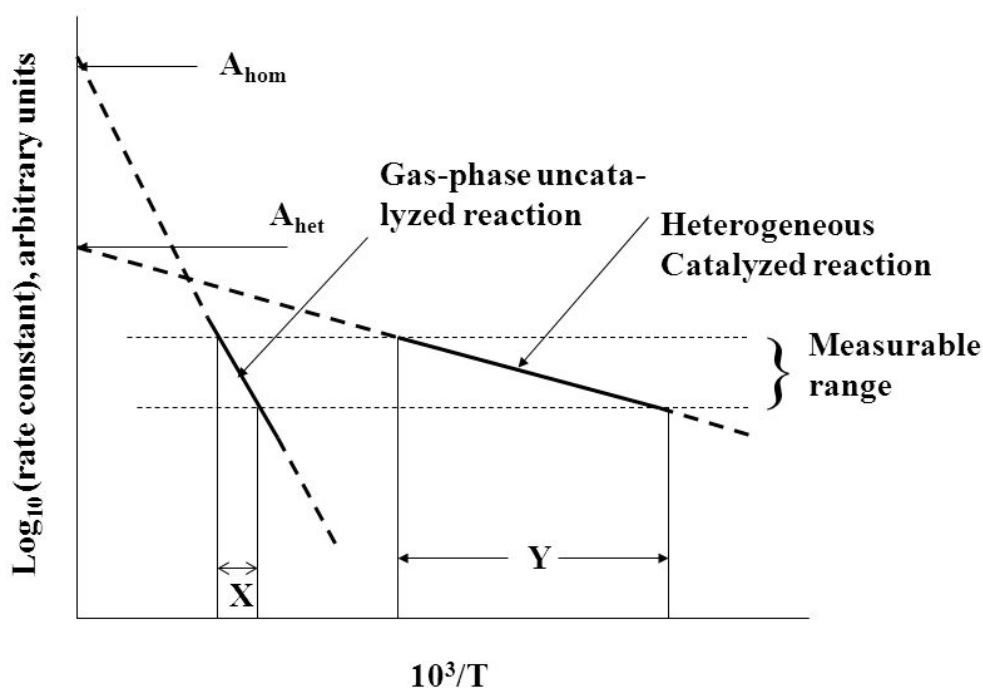


Figure 1.2 Arrhenius diagram for catalysed and uncatalyzed reaction: X and Y are the range of $1/T$ in which the respective reactions can be observed. Reproduced with permission from reference.^[15]

1.1.3 Classification of catalytic systems

As previously demonstrated, the principle of catalysis applies indiscriminately to all different forms of catalysts for variety of reactions. However, the kinetics and thermodynamics derivation of the optimal catalysts for a reaction are often highly specific. In order to simplify the consideration of different systems, the forms of catalytic systems can be generally divided into three distinct categories: homogeneous catalysis, enzymes catalysis and heterogeneous catalysis.

Homogeneous catalysis is defined as when the catalysts are of the same phase as the reactants, and no phase boundary exists. They can be both a) in gas phase, as, for example, when nitrogen oxide catalyses the oxidation of sulphur dioxide; or b) more generally in liquid phase, as when the catalysts are usually in the form of organometallic complexes with a single metal atom comprising the active site. The properties of these catalysts are normally tailored by modifying the nature of the supporting ligands, which enables the enhancement of the target products selectivity in reaction processes.^[18] It is particularly applicable when chirality of the products is important, and the disadvantage of homogeneous catalysts is in the separation of products. For these reasons, homogeneous catalysts are mainly used in the synthesis of pharmaceuticals and refine chemical productions.^[19]

Enzymes are one extremely important group of substances that are difficult to be accommodated within the homogeneous and heterogeneous classification. Enzymes are neither homogeneous or heterogeneous catalysts. They are complex organic molecules, usually a protein formed a lyophilic colloid which are significantly larger than the typical homogeneous catalysts. In enzymatic catalysis, catalytic activities tend to be extremely high, reaching levels of up to 600,000 conversions per second.^[20] For example, P450 is one of the most selective catalysts for partial oxidation reactions.^[21] However, these systems are highly sensitive to changes in temperature and pH, making them less suitable for most industrial processes.

Heterogeneous catalysis, which is within the main scope of the research work in this thesis, is defined as when a phase boundary separates the catalyst from the reactant. A number of phase combination can then occur, as shown in Table 1.2.

Solid/liquid and solid/gas are the two main phase combinations being studied in the thesis. The ease of separating heterogeneous catalysts from the reaction medium was recognized early on as the principle benefit of these system, 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 convertors.^[5] There have been attempts to merge the types of systems together, for instance, the process of immobilizing a homogeneous catalysts or enzymes on the heterogeneous supports.^[22] However, in actuality, traditional heterogeneous catalysts make up 85 – 90% of the market share for all catalysts sold.^[23] More details of the solid-state catalysts will be given in the following session.

Table 1.2 Phase combinations for heterogeneous catalysis.^[17,24]

Catalyst	Reactant	Example
Liquid	Gas	Polymerization of alkenes catalysed by phosphoric acid
Solid	Liquid	Decomposition of hydrogen peroxide catalysed by gold
Solid	Gas	Ammonia synthesis catalysed by iron
Solid	Liquid + Gas	Hydrogenation of nitrobenzene to aniline catalysed by Palladium

1.1.4 Classification of heterogeneous catalysts

When industrial scientists are called upon to devise a catalyst for a new application, they must have the basic information they need in a readily accessible form. As the process of catalysts design becomes progressively more sophisticated with

increasing standards that are placed on a successful catalyst, the chemical and physical complexity of the finished product become greater. If we know the most important capabilities of various classes of substances, it becomes easier to select the ingredients for an effective catalyst.

Catalysis is essentially a chemical phenomenon. The ability of a substance to act as a catalyst in a specified system depends on its chemical nature. With heterogeneous catalysts, we are concerned with the specific chemical properties of the surface of the chosen substance. These of course reflect the chemistry of the bulk solid, and some useful insight into the catalytic activities of a surface is gained from knowledge of the bulk properties of the solid.

Table 1.3 presents a preliminary and somewhat superficial classification of solid into a group depending on their catalytic abilities. Fine structure of specific examples will be discussed later.

Table 1.3 Classification of heterogeneous catalysts.^[1,3,14,25–30]

Class	Functions	Examples
Metal	Hydrogenation Dehydrogenation Oxidation	Fe, Ni, Pd, Pt, Ag, Au, Cu
Semiconducting oxides and sulphides	Oxidation Dehydrogenation desulphurization	NiO, ZnO, TiO ₂ , CdS, MnO ₂ , Cr ₂ O ₃ , WS ₂ , Bi ₂ O ₃ - MoO ₂
Insulator oxides	Dehydration	Al ₂ O ₃ , SiO ₂ , MgO
Acids	Polymerization Isomerization Cracking Alkylation	H ₃ PO ₄ , H ₂ SO ₄ , Zeolite, SiO ₂ -Al ₂ O ₃ , ZrO ₂

It shows that transition metals are especially good catalysts for reactions involving hydrogen and hydrocarbons.^[27,28] This is because these substances readily adsorb on the metal surface, in a manner to be described in more detail below, and except for a few cases, the reaction does not proceed below the surface. Base metals are less useful as catalysts for oxidation because at the necessary temperature they are rapidly oxidized throughout their bulk. Only those 'noble' metals (such as palladium, platinum and silver) that are resistant to oxidation at the relevant temperature may be used as oxidation catalysts.^[14] Many oxides on the other hand are excellent oxidation catalysts because they interact with oxygen together with other molecules, but with some important exceptions, i.e. copper chromium oxide, they are not well suited for hydrogenation because of the likelihood of reduction to a metal.^[31] Those oxides which may be used for hydrogenation or dehydrogenation are of course immune to reduction by hydrogen at the temperature at which they are active.^[29] Similarly, metal sulphides catalyse reaction of molecules containing sulphur. If oxides are used, they rapidly become sulphided.^[32] Those oxides such as alumina, silica, and magnesia, which do not interact much with oxygen, are poor oxidation catalysts, but they easily adsorb water and thus may be used to catalyse dehydration.^[30] The concept emerges that we must first understand the adsorption of molecules at solid surfaces before we can proceed to a deeper knowledge of catalysis.

1.1.5 Adsorption on the solid surface

1.1.5.1 The Sabatier principle

The adsorptions of molecules on the solid surfaces is the early steps of the catalysed processes. French chemist, Paul Sabatier, proposed that the strength of a molecules' chemisorption to a catalyst surface is a key factor in determining the activity of a catalysts, and for a given reaction, the adsorption of a molecule must be just the right strength.^[1]

When the energy of the transition state is fixed, and the activation energy for the transition state is the only process being considered, 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 energy.^[33] The minimal activation energy for the reaction is thus achieved when reactants are only weakly chemisorbed to the catalysts surface. If the molecule adsorbs too weakly, then it will desorb and not be present in high enough quantities to provide an activated surface intermediate for further reactions. If adsorption is too strongly, these species will not be able to react or desorb from the catalysts surface resulting in blockage of the catalyst surface, and decrease the reaction active sites.

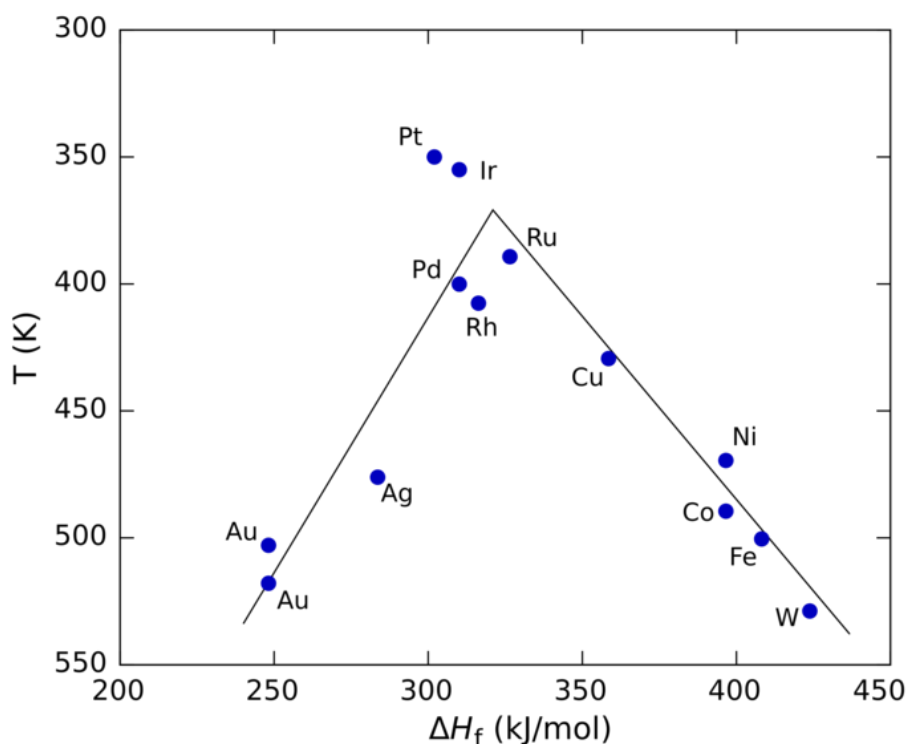


Figure 1.3 Volcano plot of formic acid decomposition temperature against enthalpy of formation of various transition metals. Reproduced with permission from reference.^[5]

The Sabatier principle, based on the qualitative concept, states the interaction property related to the stability of the surface intermediate on a catalyst, and is represented graphically in the volcano curves by plotting the reaction rate against the heat of adsorption for a reactant on a range of transition metal surfaces. Figure 1.3 shows a typical volcano plot for the decomposition of formic acid.^[5] During the decomposition process, a formic acid molecule is adsorbed dissociatively to adsorbed on the catalyst surface, which then forms either carbon dioxide and hydrogen or carbon monoxide and water. Over a wide range of metal surfaces, the ‘not too weak and not too strong’ adsorption strength appears when a maximum activity is found at an intermediate value of the heat of formation of the metal.^[33,34] However, many advanced techniques have been developed to optimize the catalytic

performance rather than simply changing the metal. More details on catalytic design will be discussed in section 1.3 Nanoparticle catalyst.

1.1.5.2 Langmuir- Hinshelwood kinetics

The Langmuir adsorption model is often used to define the relationship between the equilibrium for adsorption of a reactant and partial pressure or concentration of that reactant, when dealing with adsorption of reactants at active sites on heterogeneous surfaces.^[35] In a simplified case, for a single reaction when only the catalyst surface is considered, the adsorption can be expressed as Equation 1.4:



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 1.5:

$$K_A = \frac{[MA]}{[A][M^*]} \quad \text{Equation 1.5}$$

where $[MA]$, $[A]$ and $[M^*]$ are the equilibrium concentrations or partial pressures of the various species. Given the amount of a certain species adsorbed at a given pressure is x , and the maximum amount that can adsorb to the entire surface is x_{max} , which gives a fractional surface coverage, θ . On a partially covered surface it can be defined by Equation 1.6:

$$\theta = \frac{x}{x_{max}} \quad \text{Equation 1.6}$$

The Langmuir adsorption isotherm can be derived by combining Equation 1.5 and Equation 1.6, which expresses the fraction of surface sites occupied by reactant A (θ_A) as a function of the adsorption constant and the reactant concentration, as shown in Equation 1.7:

$$\theta_A = \frac{K_A[A]}{1+K_A[A]} \quad \text{Equation 1.7}$$

For a unimolecular reaction, Scheme 1.1, the rate of product formation can be described by Equation 1.8:



$$\text{Rate} = k_2\theta_A = \frac{k_2K_Ap_A}{1+K_Ap_A} \quad \text{Equation 1.8}$$

The key assumption of Langmuir isotherm is that the surface consists of identical non-interacting sites so adsorption can be treated with equal probability at each site and at all coverages.^[35] For a real catalysed system, not all adsorptions obey the Langmuir isotherm, especially for many real heterogeneous catalytic systems. Nevertheless, this simplified model allows to help understand the adsorption behaviours of reactants.^[36]

Real catalyst surfaces consist of different sites such as corners, edges, kinks, and terraces; these sites have different atomic arrangements leading to different catalytic abilities toward specific chemical reactions.^[37] Some chemical reactions can only be active on specific surface sites, so for different reactions the amount of catalytically active surface can be vary significantly.^[37] The sites that are catalytically active for a specific reaction are termed 'active sites'. With an increased amount of active site, the catalytic performance can be dramatically enhanced for a chemical reaction.^[38]

Whilst high activity is an important factor for a catalyst, ensuring the formation of the desired product is clearly another highly important factor. The ratio of a specified product to all other products gives the selectivity to the specified product. Highly selective catalysts are desired to reduce the production of unwanted products. The trace number of unwanted products on an industrial scale will resulting in extra

efforts on separation and purification and have some significant negative economic effects.^[5]

The development of better catalysts with increased activity and selectivity is a key area of catalysis research. Through knowledge of the rate determining step, adsorbed intermediates and active sites - obtained from fundamental studies of reactions and based on the theory presented above - the ability to engineer catalyst surfaces resulting in catalysts with desired catalytic properties has been demonstrated.^[39] A wide range of methods have been utilised to provide more active and/or selective catalysts. A number of these methods will be discussed in detail in later Section 1.3.^[40–42]

1.2 Computational methods

In recent times, the ability of computational methods to model catalysts and catalytic reactions has increased dramatically, due to the increasing speed and availability of powerful computers. Computational techniques have been widely used to model the adsorption strength of molecules on catalyst surfaces and the stability of the transition state/intermediates on catalyst surfaces.^[43] The effects of modifying the electronic and geometric properties of catalyst surfaces through morphology control, alloying, lattice expansion and other modifications, have been examined on the adsorbed species and reaction paths.^[44] The results have both been used to explain experimental data and to independently predict new catalysts. Density functional theory (DFT) is commonly used for the description of adsorbate-surface interactions, as it allows for modelling of relatively large systems without being too computationally expensive, making it ideal for catalytic systems that may involve many atoms.^[43,45,46]

DFT calculations describe the properties of a system using a set of one-electron Schrödinger equations.^[43] These Kohn-Sham equations are solved to describe the electron density and total energy of the system. Catalysts are modelled as small sections of the surface, as performing calculations on the huge number of atoms and sites present in real catalysts is often not practical. Two models are widely used to represent heterogeneous catalysts, as illustrated in Figure 1.4, they are the cluster model and the Slab model. In the cluster model, a limited number of atoms around the adsorption site is used to model the catalyst. It is assumed that the surface atoms further away are not important. In the Slab model, a repeating unit, a few atomic layers deep, with a surface area large enough to prevent interactions between adsorbates in adjacent units is used to model the catalyst surface, defined as the super cell.

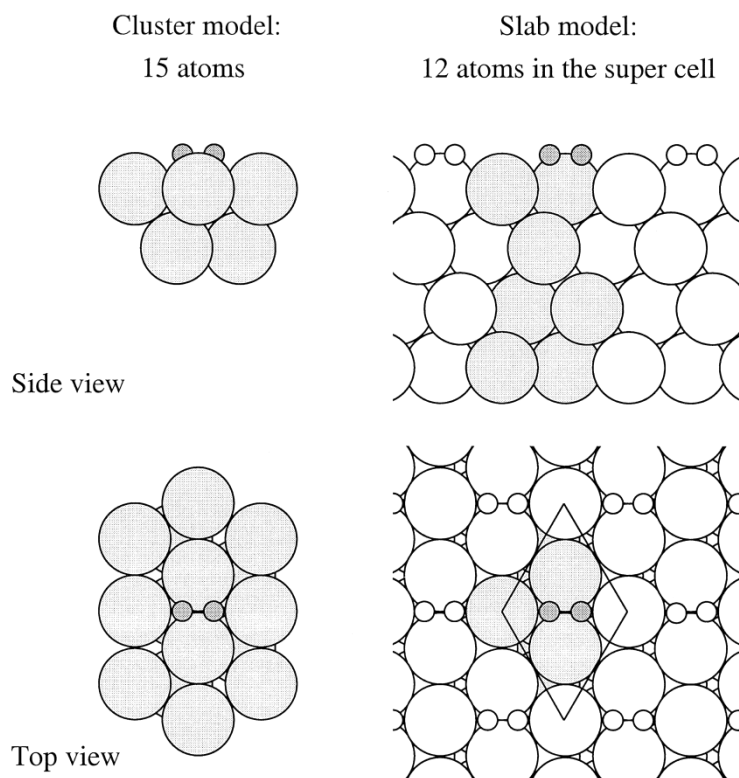


Figure 1.4 A illustration of cluster and slab representation of H_2 molecule (shown as small circles) on a semi-infinite surface. Shaded and un-shaded circles represent atoms in the super cell and in repeating cells, respectively. Reproduced with permission from reference.^[43]

The other key parameters of DFT models are the basis set and the exchange – correlation function.^[43] The basis set is an approximation used to simplify the Khon-Sham equations of the electronic orbitals of the system. Generally, for catalyst surfaces a pseudo-potential method is used to separate core and valence electrons. Dominated bonding interactions are modelled as a free electron gas in an infinite solid, mathematically described as a plane wave. The main approximation in DFT is due to the exchange-correlation function, which is used to approximate the interactions between one-electron wavefunctions, and is used to reduce the impact of errors caused by the limitations of the slab and basis set.

As the Sabatier principle explains, the strength of adsorption on the surface of heterogeneous catalysts is a key factor in determining their reactivity.^[38] As DFT calculations give the electronic properties of the system the position of the d-band centre and the position of the Fermi level – the maximum energy of an electron at zero Kelvin – relative to an adsorbates bonding and anti-bonding orbitals can be used to determine the strength of an adsorbate surface bond.^[43]

Similar to the adsorption strength of a single species, the reactions mechanisms can be computationally modelled from the relative stability of different adsorbed species on the catalyst surface and finding the lowest energy path from reactants to products.^[47] The large number of variables determines the adsorption strength of each intermediate and transition state, such as surface site, adsorbate orientation, dissociation, etc., makes this a computationally heavy technique.^[48–52]

1.3 Nanoparticle catalyst

These classic metal-supports heterogeneous catalysis systems have been used as a ‘black art’ for over 100 years without a clear fundamental understanding.^[24] However, with the development of advanced high-resolution characterization techniques - e.g. electron microscopy, energy-dispersive X-ray spectroscopy and extended X-ray absorption fine structure; nanoscience and nanotechnology have become popular fields for research and development in the last few decades.^[53–55] According to the U.S. National Nanotechnology Institute, nanotechnology encompasses research and development to synthesize, control, and manipulate structures, devices, and systems of novel properties and functions.^[56] The development of heterogeneous catalysts

has significantly benefitted from the advances in nanotechnology.^[56] Significant amount of research has been dedicated to both the fundamental and applied aspects of heterogeneous catalysis, from the structure, size and composition of catalysts.^[42,57,58] By far the most common form for heterogeneous catalysts is as highly dispersed metallic particles with sizes in the nanoscale (range from approximately 1-100 nm) deposited on a high surface area support.^[59,60] From the most basic level, metal in nanoscale is attractive for use as catalysts because of their high surface-to-volume ratios which can minimize the costs associated with their use.^[60]

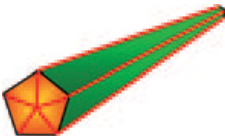
It has been found that, for most heterogeneous catalysts containing precious metal particles on the nanoscale, the catalytic active sites are generally the small crystallites or domain of the active phase.^[14] The catalytic performance can be altered by the chemical and physical properties of the active surface.^[61] The importance of small particles to the performance of catalyst has stimulated extensive efforts to their characterization.^[61] Coupling with theoretical DFT calculations, advances in nanoscience have contributed to detail understanding of the effects of particle morphology, size and composition on catalysts performance.^[56] Additionally, nano-engineering gives us the access to a new level of control in nanoparticle synthesis. Therefore, the catalytic performance can be enhanced by modification of metal particles morphology, sizes and composition from both geometric and electronic effects. The following session will discuss how the local morphology, size and composition of metal particles affect their catalytic performance and the common methods of modifying nanoparticles.

1.3.1 Morphology effects

With the development of nanoengineering, the last decade has witnessed the successful synthesis of metal nanocrystals in a variety of shapes with similar crystalline structure (particularly metal of fcc structure).^[63] In Table 1.4, it presents a summary of different shapes of that have been achieved for various metal nanocrystals, including spheres; spheroids; cubes; cuboctahedra; octahedra; tetrahedra; right bipyramids; decahedra; icosahedra; thin plates with a triangular, hexagonal, or circular profile; and rods or wires with a circular, square, rectangular, pentagonal, or octagonal cross-section.^{[63][64][62][60]}

Table 1.4 summary of different morphologies that have been achieved for various metal nanocrystals. Reproduced with permission from reference.^[63]

Structures	Shapes	Schematic drawings		Metals
Single-crystal	Perfect/truncated cube			Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe
	Perfect/truncated octahedron			Pd, Ag, Au, Pt
	Perfect/truncated tetrahedron			Ag, Au, Pt, Rh
	Rectangular bar			Pd, Ag, Pt
	Octagonal rod			Pd, Au, Fe, Co, Ni
	Rectangular or Octagonal wire			Pb, In, Sn, Sb, Fe, Co

Single twinned	Right bipyramid		Pd, Ag
	Beam		Ag
Multiply twinned	Decahedron		Pd, Ag, Au
	Icosahedron		Pd, Au
	Five-fold twinned pentagonal rod		Pd, Ag, Au, Cu
	Five-fold twinned pentagonal wire		Ag, Au, Cu
	Triangular/hexagonal plate		Pd, Ag, Au, Cu, Pb, Bi, Co, Ni
	Disc		Sn, Co

Ever since the 1850s, when Michael Faraday first prepared Au colloids by a reduction process in water with phosphorus,^[65] the solution-phase methods have been well developed and widely used in preparation of metal colloids.^[63,64,66–69] In a typical synthesis of metal nanocrystals, a precursor compound is either decomposed or reduced to generate zero-valent atoms, the building blocks of a metal nanocrystal. The following evolution pathways will be then divided into three distinct stages: 1) nucleation, 2) evolution of nuclei into seeds, and 3) growth of seeds into nanocrystals.^[63] (The mechanism of nucleation and evolution of nuclei into seeds has been discussed in detail later in section 1.3.2 Size effects.)

Once a seed is formed, it can grow in size through the addition of metal atoms, and the growth of a crystal is controlled by the competition between a decrease in bulk

energy (favouring growth) and an increase in surface energy (favouring dissolution).^[70] This dynamic interplay of growth and dissolution dictates the evolution of seeds into nanocrystals. Figure 1.5 summarizes the correlation that has been established between different types of seed and the final nanocrystals of an fcc metal. The nanocrystal is driven to adopt to different shapes described in Figure 1.5 through the introduction of a selective capping agent.^[63] The evolution of nanomorphology was first observed in some catalytic processes in which the chemisorption of atomic or molecular species onto a metal nanoparticles can lead to morphology changes.^[71,72] For example, Pt nanocrystals will evolve into nanocubes with {100} dominated when exposed an environment contaminated by trace amount of H₂S.^[71] The {100} facets are formed preferentially over {111} facets in the H₂S because the {100} interacts more strongly with sulphur.^[71]

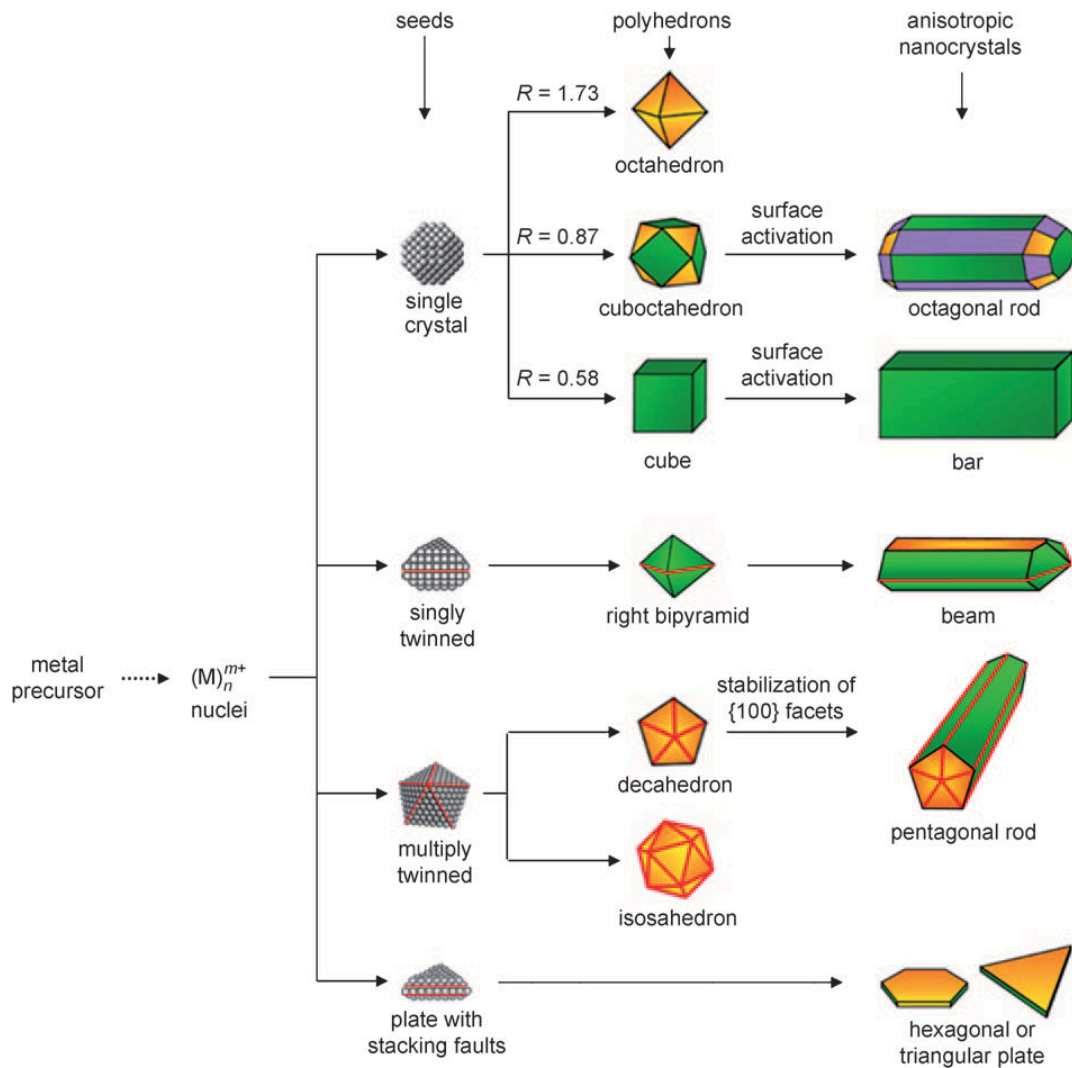


Figure 1.5 Reaction pathways leading to fcc metal nanocrystals with different shapes. First, a precursor is reduced or decomposed to form the nuclei (small clusters). Once the nuclei have grown past a certain size, they become seeds with a single-crystal, singly twinned, or multiply twinned structure. The green, orange, and purple colours represent the $\{100\}$, $\{111\}$, and $\{110\}$ facets, respectively. Reproduced with permission from reference.^[63]

Inspired by a morphology change effects during catalytic reactions, in materials synthesis, capping agent is introduced purposely to a solution-phase synthesis to control shape. The binding affinity of a capping agent can vary from one crystal facet

from one crystal facet to another, and such preferential capping can effectively hinder the growth of a particular facet.^{[73][74,75]} Through chemical interaction with a metal surface, the presence of a capping agent can change the order of free energies for different crystallographic planes, and thus the relative growth rates. For example, PVP is a polymeric capping agent whose oxygen atoms bind most strongly to the {100} facets of Ag and Pd.^{[75][76]} This preferential capping can drive the addition of metal atoms to the other crystal facets when crystal seeds are suitably large. Thus, for single crystal seeds terminated with only {111} and {100} facets, metal atoms will add preferentially to the poorly passivated {111} facets; these additional-atoms then migrate to the face edges, resulting in an elongation of {100} facets and the formation of nanocubes.^{[76][77][78]}

By controlling the shape of a nanocrystal, the reactivity and selectivity of a catalyst can be both tailored. As previously mentioned, the shape determines which crystal facets comprise the surface of a nanocrystal, resulting in different surface atomic arrangement.^[79] For example, the {111} faces are represented by a hexagonal array of metal atoms, and the {100} facets are represented by a square array of metal atoms.^[62] Somorjai and co-workers in 2007 looked at the shape effects of cubic and cuboctahedra Pt nanocrystals in the hydrogenation of benzene, and the differences in selectivity were observed.^[80] When cuboctahedra Pt bound by both {111} and {100} facets were used as the catalyst, both cyclohexane and cyclohexene were produced.^[80] However when cubic nanocrystalline Pt bound by only {100} facets was used as a catalyst, only cyclohexane was produced.^[80] It was found that for cubic Pt the apparent activation energy for cyclohexane production was $10.9 \pm 0.4 \text{ kcal mol}^{-1}$, whilst for cuboctahedra Pt the apparent activation energy for cyclohexene production

and cyclohexane were 8.3 ± 0.2 kcal mol⁻¹ and 12.2 ± 0.4 kcal mol⁻¹, respectively.^[80]

These significant differences in activation energies for the formation of different Pt facets were attributed to the different adsorption strength of benzene on different atomic arrangement.

1.3.2 Size effects

The physical properties of metallic nanoparticles, in general, also change with size range.^[43] 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 1.9:

$$\delta = \frac{E_f}{n} \quad \text{Equation 1.9}$$

where n is the number of atoms in the particle and E_f is the energy of the Fermi level for the metal.^[81] In a bulk metal where the number of atoms in the crystal approaches infinity, the spacing between energy levels essentially becomes no-existent and the density of states (DOS) is high.^[44] However, as the number of atoms in the crystal is decreased, contribution from atomic orbitals to the band structure are reduced leading to an increase in the spacing between energy levels within the band, as shown in Figure 1.6.^[82] 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 orbitals.^[83] The surface electrons become more localized to individual atoms as the d-band structure and energy level spacing/DOS in the transitional region gradually changed with material size.^[83] These changes in physical electronic properties allow nanoparticles to exhibit higher activity for catalytic processes than their bulk counterparts.

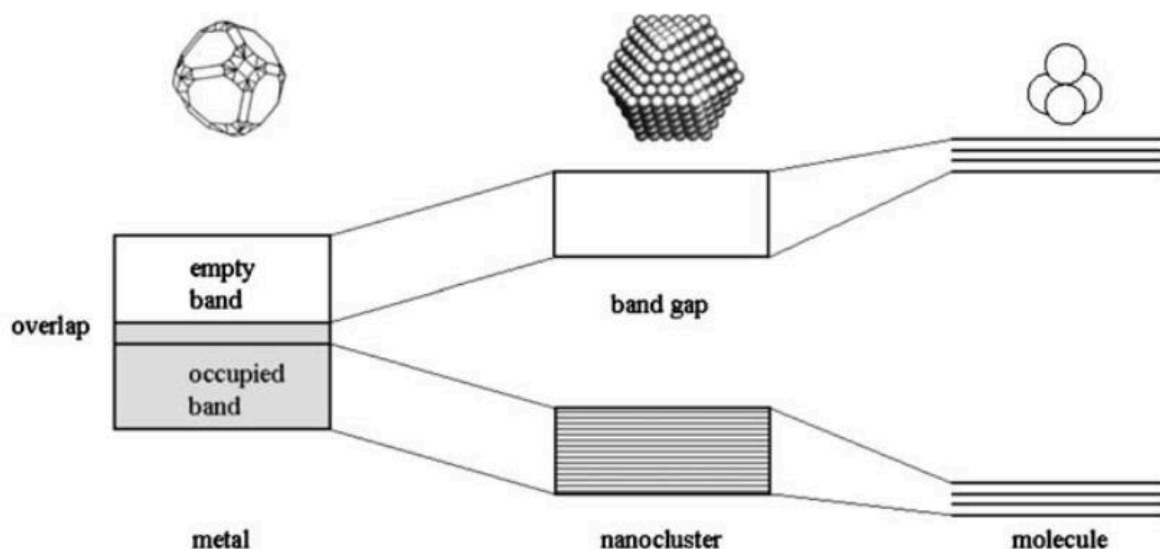


Figure 1.6 Illustration demonstrating the differences in band structure for bulk metal, metal nanoparticles, and isolated molecules. Reproduced with permission from reference.^[82]

The consequence of changing the average size of metal nanoparticles leads to a corresponding change in the geometric structure of the nanoparticles surface and surface area.^[82] Compared to bulk metal, a nanoparticle contained higher number of surface atoms per particle, and the atoms locate on different sites of the surface correspond to different coordination number with different catalytic activity.^[84] Fundamental studies on an idealized geometric representation of nanoparticles with different sizes have been conducted by van Hardeveld and Hartog to produce mathematical models for the number of atoms with a given coordination number.^[85] Figure 1.7 (a) shows a typical cubooctahedral particle with different atom coordination numbers (CN) as marked. It can clearly be seen that the different coordination numbers correlate with different sites on the catalyst surface, i.e. corner, edge, terrace.^[85] From the model, the ratio of atoms in each site can be

calculated for a given metal at a specified size. Figure 1.7 (b), displays the change in corner, edge, terrace, and total surface atoms as a percentage of total atoms of cubooctahedral Pd particles with increasing sizes.^[85]

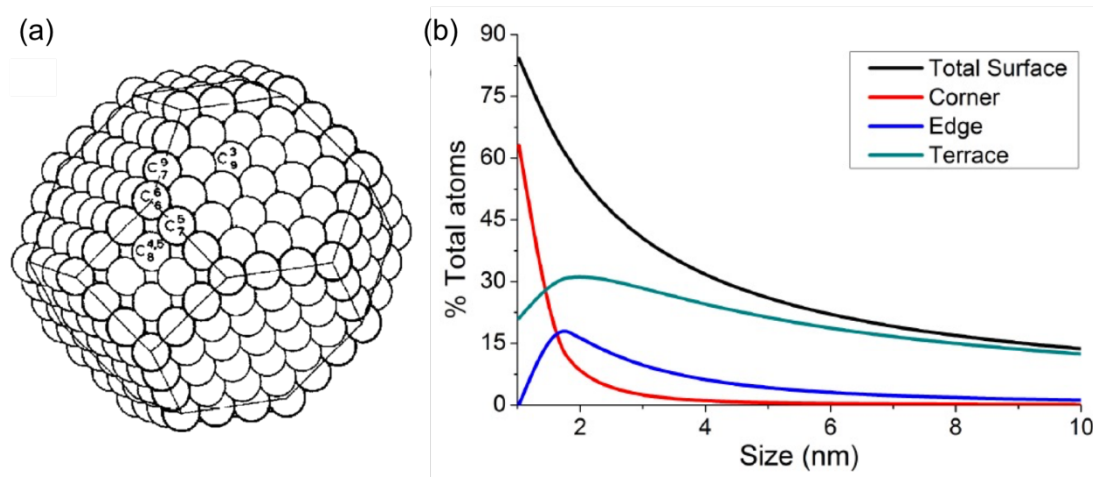


Figure 1.7 Relationship between particle size and the relative prevalence of surface atoms in different types of active sites along with the mean coordination number for surface atoms. Reproduced with permission from reference.^[85]

Both concepts were demonstrated by Crooks and co-workers with studying on the size effect of Pd on the hydrogenation of allyl alcohol ($\text{CH}_2=\text{CHCH}_2\text{OH}$) to propanol.^[84] They discovered that for Pd particles with size between 1.5-1.9 nm, the face sites are the preferred site for allyl alcohol hydrogenation, making the reaction structure sensitive. However, for the smaller Pd particles (<1.5 nm), electronic effects were dominant rather than relative number of catalytic sites.

1.3.3 Composition effects

Composition modified metal particles as a novel class of materials, usually have better catalytic efficiency than their corresponding single component particles.^[86–88] Generally, bimetallic nanoparticles are the most commonly used composition

modified metal particles. Although the structures of bimetallic nanoparticles are complicated and in multiform, they can be mainly categorized into three main groups: core-shell, heterojunction/intermetallic and alloys structures as shown in Figure 1.8.^[89] Both geometric and electronic effects of metal nanoparticles can be modified by introducing a second metal, which can induce significant impact on the catalytic activity.

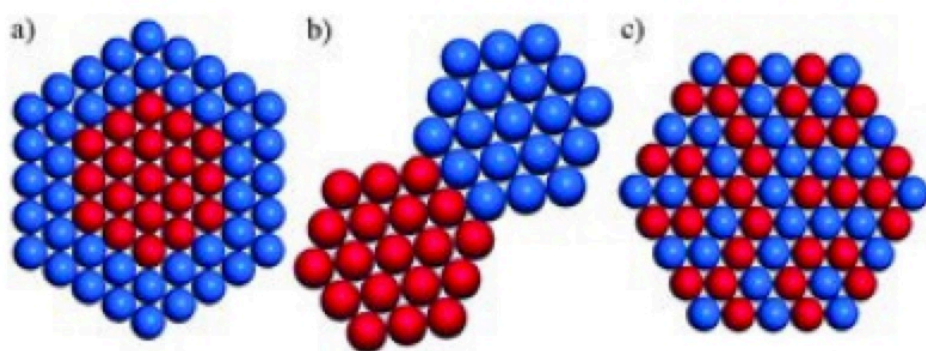


Figure 1.8 Illustration of bimetallic nanoparticles structures: (a) core-shell; (b) heterojunction/intermetallic; (c) alloy. Reproduced with permission from reference.^[89]

For bimetallic particles with a core-shell structure (Figure 1.8a), the average bond lengths between the metal atoms in the up-layer shell (guest) and the sublayer core (parent) are generally different. The difference in atomic size and energy potential of two metal atoms would introduce lattice mismatch and charge transfer due to the difference in d-band energies of two monometallic phases at the interface of the core-shell.^[45] Both theoretical and experimental studies have demonstrated that a compression should be expected with a larger atoms in the shell, and in contrast a smaller atoms would lead to an expansion (isomorphic effects).^[90–93] The modification on the particle surface atoms arrangement will ultimately affect the

adsorption and catalysis, as demonstrated by numerous surface science studies.^[94,95]

Bimetallic particles with a core-shell composition (Figure 1.8a) have also been used to modify the electronic properties of metal surfaces, with minimal geometric modification to the surface. Tsang and co-workers reported a range of PVP stabilised nanoparticles consisting of a Pd shell with different transition metal cores (M@Pd), using ^{13}C NMR to monitor the electronic effects exhibited on a formic acid probe molecule by the surface of core-shell nanoparticles and a strong correlation between the work function of the core and the NMR shift was observed.^[96] The difference in work function between the core and shell was shown to determine electron donation to or withdrawal from the surface, with associated modification of formic acid adsorption. This highlights the potential for the electronic properties of surface to be tailored by a second metal. However, the lack of stability is a significant problem with core-shell particles.

1.3.4 Metal support interaction

All metal nanoparticles discussed so far are naturally unstable due to the high surface energy caused by the high surface area to volume ratio and have a tendency to agglomerate into larger, and more stable particles.^[2] This is often prevented by attaching ligands to the surface of the particles that keep them separated through steric or electrostatic repulsion.^[96] The stability of these particles is limited especially at high temperatures, where the ligands decompose or come off. In addition, the activity of ligand stabilised particles is often greatly reduced because the ligands block the surface sites.^[97] Another method to keep the metal particles apart is to

attach them to a support, which is the most common approach with numerous studies on a wide range of metals and support materials.^[98] Metal nanoparticles can be added to the metal support by addition of pre-formed particles stabilised by ligands followed by removal of the ligands or more commonly, by addition of a metal precursor to the support followed by reduction to form metal particles.^[58,99] The interaction between the particle and support reduces particle mobility, preventing agglomeration.

A wide range of materials are used as catalyst supports depending on the properties required of the catalyst and the conditions that it will operate under. Typically supports have high surface areas, 300-1000 m²/gram, so the active metal species are highly dispersed.^[2] However, for catalysts operating under very harsh conditions, more stable and lower surface area supports are used (i.e. α -alumina in ethylene epoxidation).^[100] For industrial applications other factors are also important for the catalyst support (mechanical strength, etc.) to ensure a long lifetime with limited loss of the catalyst during usage.^[5]

The strength of the interaction between metal and support has a large effect on the size and stability of metal particles on its surface. For example, Zeng and co-workers observed the catalyst deactivation due to agglomeration of Ag particles on an activated carbon fibres, indicating the interaction between the particles and the support is not sufficient to overcome the high surface energy.^[101] In contrast to activated carbon fibres, TiO₂,^[102] SiO₂,^[103] Al₂O₃^[104] and zeolites^[105] supported Ag nanoparticles could maintain their stability without aggregating under similar conditions.

The interaction between the metal nanoparticles and the support can also modify the electronic properties through charge transfer, which has been important in explaining activity differences upon changing supports.^[106] Particularly, a dramatic electronic modification is seen with reducible metal oxides, such as TiO_2 and CeO_2 , referred to as the Strong Metal- Support Interaction (SMSI).^[1] This phenomenon occurs when the metal ion of the support is partially reduced at high temperatures (i.e. M^{4+} to M^{3+}), leading to electron donation from electronically rich metal oxide support to the metal particles.^[1] The SMSI effect may also result in geometric alterations to the metal surface, as the high temperature reduction has been reported to cause a thin coverage of the metal particle by the partially reduced support.^[1]

1.4 Selective catalytic oxidation

A large segment of the modern chemical industry is based on selective catalytic oxidation processes.^[107] Selective catalytic oxidation is one of the major areas of industrial petrochemical production, and more than 69% of the chemicals and intermediates synthesized via catalytic processes are products of oxidation.^[108] Rough estimates place the worth of world products that have undergone a catalytic oxidation step at \$20 to \$40 billion.^[108] Figure 1.9 shows the global share of selective oxidation processes with respect to the total organic chemical production in 1991. Considering catalysts alone, the value of oxidation catalyst produced commercially in the United States was \$105 million (in 1990), second only to polymers.^[109]

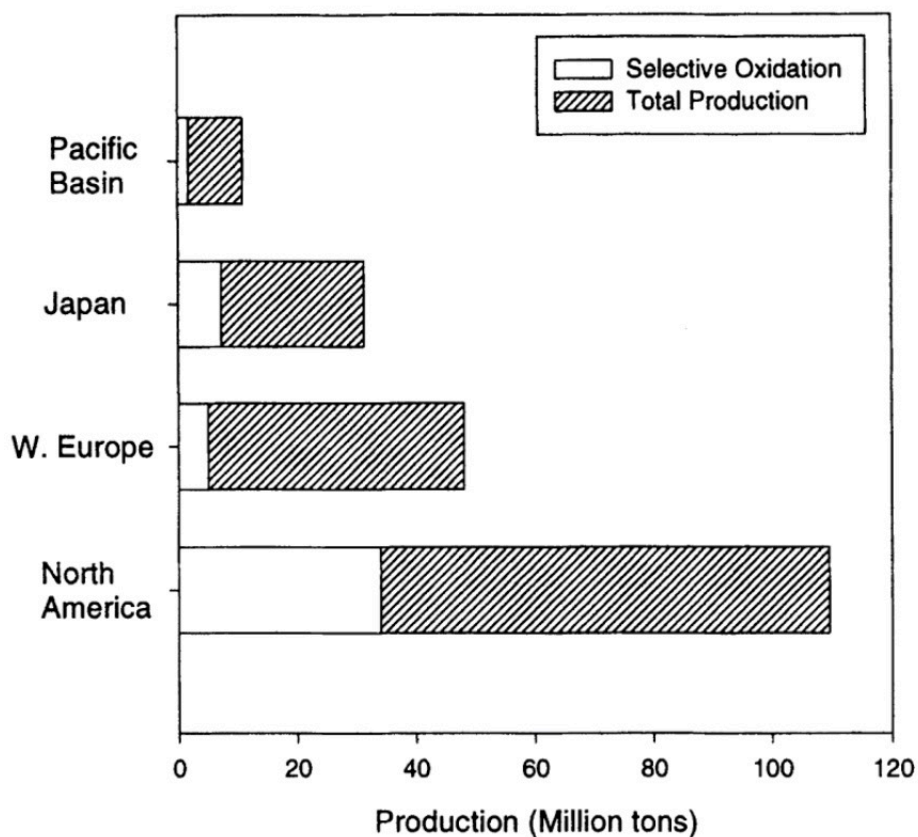


Figure 1.9 World organic chemical production in 1991. Reproduced from reference.

[109]

One of the most important applications of selective oxidation catalysis is the functionalization of hydrocarbons.^[110] Catalytic oxidation is the basis for the synthesis of large percentage of the monomers or modifiers used for the production of fibres and plastic.^[111] The major industrial applications of catalytic oxidation for the synthesis of monomers are listed in Table 1.5.^[112]

Table 1.5 Major catalytic oxidation process for the synthesis of monomers.

Reproduced from reference.^[112]

Reactants	Products/coproducts	Catalysts	Conversion,	Selectivity,
-----------	---------------------	-----------	-------------	--------------

			%	%
Methanol/Air	Formaldehyde	Heterogeneous	99	94
Ethylene/O ₂	Ethylene oxide	Heterogeneous	90	80
Ethylene/air/HCl	1,2-Dichloroethane	Heterogeneous	>95	>95
Ethylene/O ₂ /HCl	1,2-Dichloroethane	Heterogeneous	>95	>97
Propylene/air	Acrolein	Heterogeneous	>90	80-85
Propylene/H₂O₂	Epoxide/Alcohol	Heterogeneous/ Homogeneous	10	90
<i>n</i> -Butane/air	Maleic anhydride	Heterogeneous	70-80	65-70
Benzene/air	Maleic anhydride	Heterogeneous	98	75
Isobutene/air	Methacrolein	Heterogeneous	>97	85-90
Cumene/air	Phenol/acetone	Homogeneous	35-40	90
Cyclohexane/air	Cyclohexanone	Homogeneous	5-15	85-90
Acrolein/air	Acrylic acid	Heterogeneous	>95	90-95
<i>o</i> -Xylene/air	Phthalic anhydride	Heterogeneous	100	79

The data in Table 1.5 indicate some important limitations in catalytic oxidation, which can be summarized as follows:

- With the formation of undesired by-products, none of the reactions runs at maximum selectivity, and few reactions attain total or close-to-total conversion.
- Processes can generate coproducts that are not always of economic interest.
- Some raw materials and products are suspected or proven to be carcinogens.
- Some processes require expensive oxidizing agents.

Ideally, molecular oxygen is the most desirable oxidant. The use of stoichiometric oxidants such as permanganates or chromium salts is also a common practice in

fine chemicals production, and catalytic oxidation is always an environmentally more acceptable alternative to these stoichiometric oxidations.^[9] Other oxidants are also widely used in industry, for example, hydrogen peroxide is also relatively inexpensive, has a high active oxygen content, and is environmentally friendly as the coproduct is mainly water.^[113] Table 1.6 characterizes the commonly used oxidants.

Table 1.6 Oxygen donor oxidants. Reproduced from reference.^[114]

Donor oxidant	Active oxygen, %	By-product	Comments
O ₂	100	None	No by-product is generated if reducing agent-free, nonradical chain aerobic oxygenation can be achieved
H ₂ O ₂	47	H ₂ O	Environmentally attractive
O ₃	33	O ₂	Potentially environmentally attractive
NaClO	21.6	NaCl	Inorganic salt by-products are to be avoided in general; in some cases, ClO ⁻ can produce toxic and carcinogenic chlorocarbons by-products
<i>tert</i> -BuOOH	17.8	<i>tert</i> -BuOH	Commercially important in catalysed oxygenations
KHSO ₅	10.5	KHSO ₄	Water-compatible, but generates a marginally toxic salt
C ₆ H ₅ IO	7.3	C ₆ H ₅ I	Metal-catalyzed oxidations are often quite selective, but the cost is prohibitive

In today's petrochemical industry, most of the available technologies are considered 'mature', and even considerable research effort is not expected to yield significant improvements.^[5] However, as profit margins can sometimes be increased by improving selectivity by one percentage point or less, it is still desirable to invest in

improving catalyst performance. Technological innovations in catalytic oxidation processes are thus expected from:

- a. Introducing substantial modifications in technology: New raw materials and catalysts are being used, and new process technologies, new machinery, and new equipment are being developed.^[108]
- b. Fine-tuning existing processes: work continues on optimizing all the process components, eliminating bottlenecks, and revamping exiting plants.^[115]
- c. Complying with new requirements and regulations: processes are being developed that have a less severe environmental impact, which translates into lower pollutant emissions, less waste, and greater safety. There is also an increasing demand for purer products for the production of high-quality polymers.^[116]

1.5 Propylene epoxidation

Among all the selective oxidation products, epoxides are versatile intermediates of great value to the chemical industry.^[117] However, the heterogeneous epoxidation of alkenes are extremely difficult processes. The silver-catalyzed, gas phase epoxidation of ethylene using molecular oxygen is one of the most successful examples of heterogeneous catalysis to date.^[99] In this process, selectivity towards epoxide production (vs. CO₂ and H₂O formation) is about 85%.^[118] Ethylene oxide is produced on a very large scale by the direct silver catalysed heterogeneous partial oxidation process. The world production of ethylene oxide was 18 million tonnes in 2008 with an annual production growth of 4.4% from 2008 to 2013, and 3% during 2013 to 2016. This places ethylene oxide 14th most produced organic chemical.^[119]

Propylene oxide, which is also known as propene oxide, methyloxirane, or 1, 2-epoxypropane, is another one of the most important starting materials in the chemical industry.^[120] Comparing to ethylene oxide, propylene oxide is an epoxide with much higher added value. The production of propylene oxide consumes over 10% of all propylene production. In 1999, the total production for propylene oxide amounted to about 5.8 million tons per year.^[121] As shown in Figure 1.10, the globally market demand for propylene production has continuously increased from 1992 to 2007.^[122]

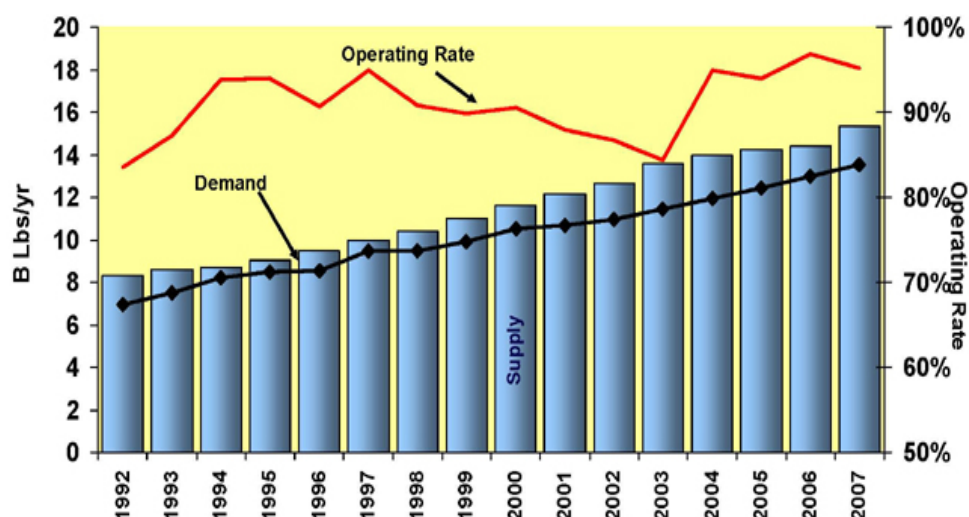


Figure 1.10 Propylene oxide global annual production from 1992 to 2007.

Reproduced from reference.^[122]

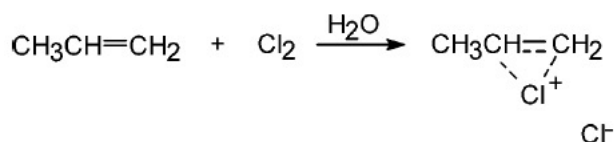
The major application of propylene oxide is in the production of polyether polyols which are mainly used for the production of polyurethane (foams), with about 65% of all propylene oxide consumption. The second largest application is in the production of propylene glycol, with about 30% of all propylene oxide consumption and the third largest application is in the production of propylene polycol ethers with about 4% of

all propylene oxide consumption.^[123] For the other applications, propylene oxide is also commonly used in the preparation of biological samples for electron microscopy, to remove residual ethanol previously used for dehydration; and from September 2007, the United States Food and Drug Administration has approved the use of propylene oxide to pasteurize raw almonds in response to two incidents of contamination by Salmonella in commercial orchards, one incident occurring in Canada and one in the United States.^[123]

1.5.1 Industrial production processes

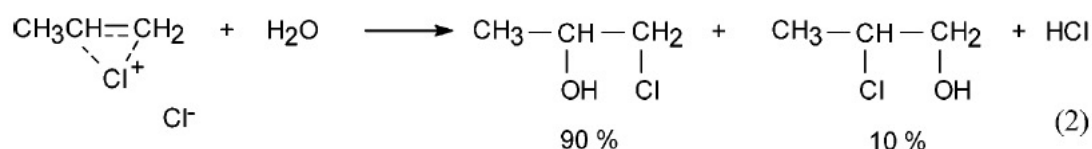
Industrially, propylene oxide is currently produced in three different types of commercial processes: the chlorohydrin process, the propylene oxide/styrene monomer (PO/SM) process and the hydroperoxide process.

Chlorohydrin Process: The synthesis of propylene oxide using the chlorohydrin route was first described in 1859 by Wurtz.^[124] In this route, propylene and chlorine in the presence of water are reacted to form propylene chlorohydrin, which is further reacted with sodium hydroxide or calcium hydroxide to obtain PO.^[125] This traditional route has long been the main process for producing propylene oxide; although, at the moment, it is gradually being replaced by other more advanced processes. The chlorohydrin process is schematically demonstrated in Figure 1.11.^[126] In the first hypochlorination reactor, the propylene reacts with chlorine to produce the propylene chloronium complex,^[126] as shown in Scheme 1.2:



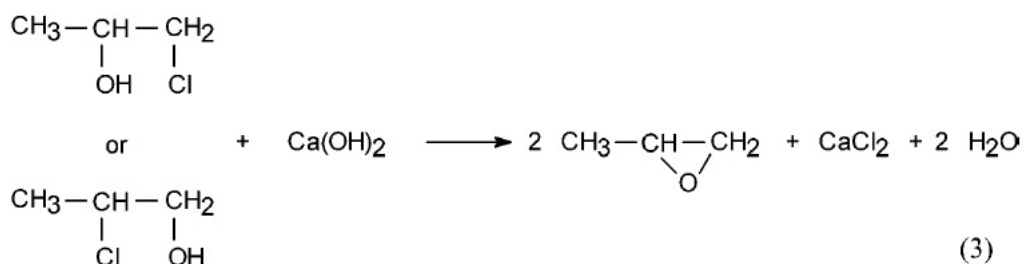
Scheme 1.2

The propylene chloronium complex further reacts with water to produce two propylene chlorohydrin isomers,^[127] as shown in Scheme 1.3:



Scheme 1.3

The selectivity of these reactions to the chlorohydrin isomers is about 90 to 95%.^[127] The by-products formed are primarily 1,2-dichloropropane (from the reaction of propylene with chlorine), smaller amount of dichloropropanols (from reaction of propylene with chlorine) and dichloroisopropyl ethers (from reaction of chloronium complex with propylene chlorohydrin).^[127] The reaction condition is normally at a pressure of 1.5 bar and temperature of 323 K. The propylene chlorohydrin further converted to propylene oxide through a dehydrochlorination reaction in the epoxidation reaction in the presence of a base (calcium hydroxide),^[125] as shown in Scheme 1.4:



Scheme 1.4

The CaCl_2 is normally discharged in this process, as it has very low commercial value. However, the amount of CaCl_2 produced is usually about 40 times larger than the amount of propylene oxide produced.^[127] Alternatively, sodium hydroxide can be used instead of calcium hydroxide.^[126] The by-product sodium chloride can then be used in the production of chlorine. In this case, these plants are often integrated with chlor-alkali plants which consume a large amount of power to make the chlorine.^[124] The relatively large amount of 1,2-dichloropropane (about 10%) is another main by-product with little commercial value, which also induces the environmental disposal problem.^[127] The disadvantages of the chlorohydrin process are the two disposal problems described above.

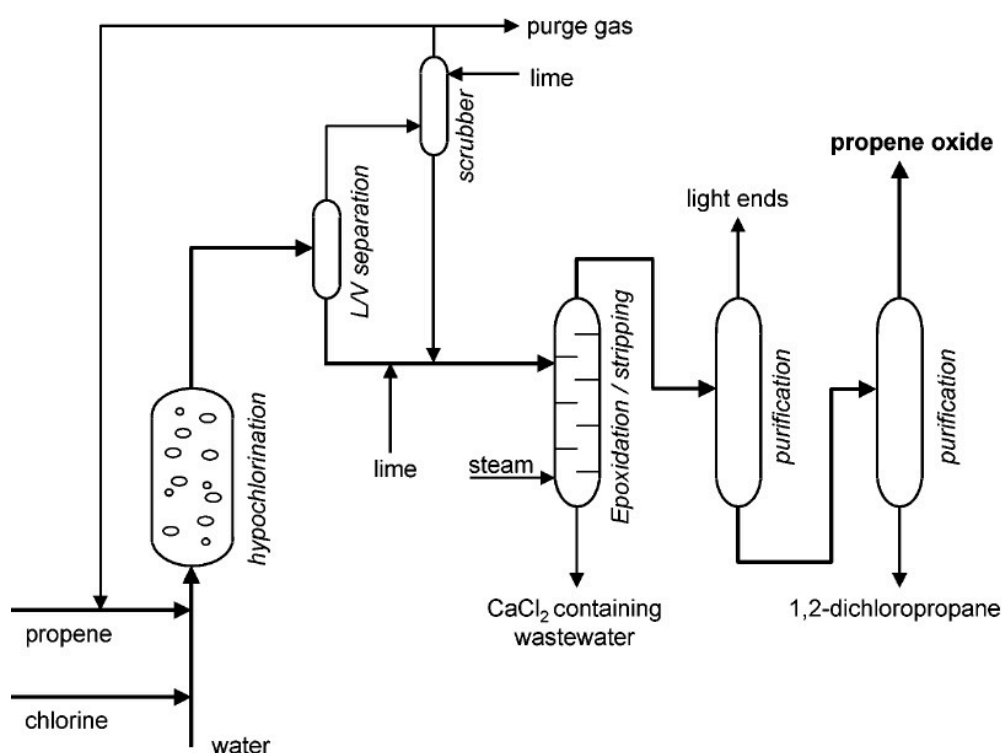
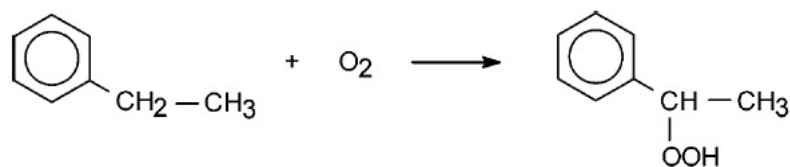


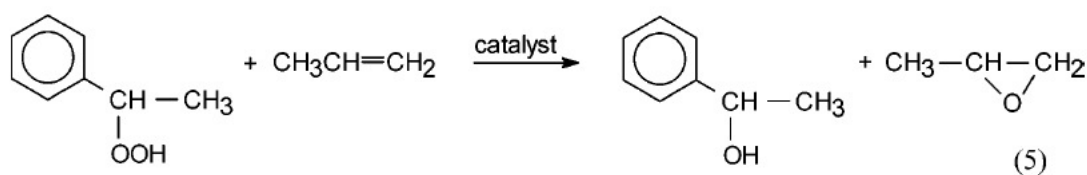
Figure 1.11 Schematic representation of the chlorohydrin process for the production of propylene oxide. Reproduced with permission from reference.^[126]

The PO/SM process:^[128–130] In this process, ethylbenzene is peroxidised to ethylbenzene hydroperoxide by direct liquid phase oxidation using oxygen or air, as shown in Scheme 1.5:



Scheme 1.5

The ethylbenzene hydroperoxide further catalytically reacts with propylene to produce propylene oxide and an alcohol, as shown in Scheme 1.6:



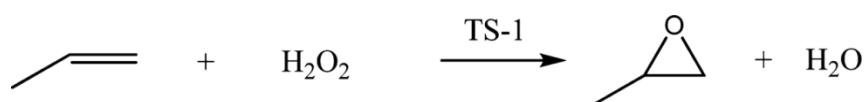
Scheme 1.6

The alcohol can be further converted to the high commercial value compound styrene through dehydration reaction.

During the PO/SM process, homogeneous tungsten, molybdenum, or vanadium catalysts are generally used to catalyse the epoxidation reaction.^[131] The total conversion in this process is over 95%, and at over 95% selectivity to propylene oxide.^[121] However, the oligomerization of styrene being produced in the dehydration reaction is an important side reaction which results in a loss of catalyst activity and reduces the catalyst lifetime.^[132] Moreover, it also has the potential disadvantage of coproducing 2.25 tonnes of styrene for every tonne of PO.^[121,124] This can present difficulties in balancing the markets for PO and styrene, leading to volatility in

economic performance of the operation over time, and the capital costs can also be high.

The HPPO process^[120] The HPPO process is the direct route to convert propylene to propylene oxide. In this process, hydrogen peroxide (H_2O_2) is used as oxidizing agent to oxidize propylene to propylene oxide with the presence of catalyst (normally TS-1), as shown in Scheme 1.7:



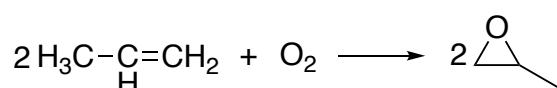
Scheme1.7

Heterogeneous titanium silicate catalysts (TS-1) are generally used in the HPPO process.^[120] The catalyst was invented by Enichem in Italy at the end of the 1970s, that patented as TS-1 catalysts for the direct epoxidation of propylene with hydrogen peroxide in liquid phase.^[133] TS-1 is a zeolite with an MFI structure that can be synthesized by isomorphous substitution of Ti for Si in the framework of silicalite-1. The TS-1 catalyst opened the possibility to use of hydrogen peroxide as an oxidizing agent.^[120] It is generally believed that titanium atoms existing in TS-1 lattice positions, replacing silicon atoms, are the active sites in the selective oxidation reactions. By using the TS-1 catalyst, the reaction can be carried out under a mild reaction condition at a pressure of 30 bar and temperature of 40 °C, and theoretically the only by-product is water.^[134] Though this process, the final conversion of propylene in a finishing reactor can achieve over 96%, and the total PO selectivity is about 94%.^[124] In 2008, Evonik (formerly Degussa) and the German engineering contractor Uhde developed the HPPO technology, and SKC build the first HPPO plant in Ulsan, South Korea, with 100,000 tonnes per year capacity after 25 years

from the first Enichem TS-1 patent.^[120] In 2009, Dow and BASF started up their joined HPPO plant based on the Dow-BASF HPPO technology at Map Ta Phut, Thailand with 300,000 tonnes per year capacity.^[135] Compared to the traditional chlorohydrin process, the HPPO process reduces the wastewater by about 70% and the energy consumption by about 35%.^[135] Since then, many research works have been focusing on developing the next generation TS-1 based catalysts.^[136] Haruta and co-worker reported an Au/TS-1 catalysts, which catalysed propylene selective oxidation to form PO in a gas phase reaction with the presence of oxygen and hydrogen.^[137] However, even considering the advantages and development of HPPO process, the usage of either high concentration of hydrogen peroxide or hydrogen still remains an increased raw material cost and massive safety problems associated in the industrial plants. An environmental friendly and more economically efficient solution for propylene oxide production is still in an extremely high demand in the modern industry.

1.5.2 Direct propylene epoxidation with molecular oxygen

Oxygen is one of the cheapest, most abundant green oxidants. The gas-phase epoxidation of propylene by molecular oxygen is the most ideal one step reaction process to produce high quality propylene oxide with low economic cost. In this process, propylene directly reacts with oxygen to produce propylene oxide in a catalytic gas-phase reaction, as shown in Scheme 1.8:



Scheme 1.8

Theoretically, propylene oxide will be the only product through this process and nothing environmental unfriendly by-product need to be discharged. A successful reaction will open a way to a direct method of PO production that does not form coproducts or use expensive reagents. However, the direct epoxidation of propylene with molecular oxygen is suffered a very low conversion and extremely poor propylene oxide selectivity for a long time, which remains this reaction as one of the most difficult catalytic reactions.^[138] In the last two decades, many research works have been focused on the study of direct epoxidation of propylene from both experimental and theoretical aspects to attain higher PO selectivity and have a deep understanding of the reaction mechanism.^[78,139–143] In Figure 1.12, a summary of some main types of catalysts that are being studied for this process is presented.

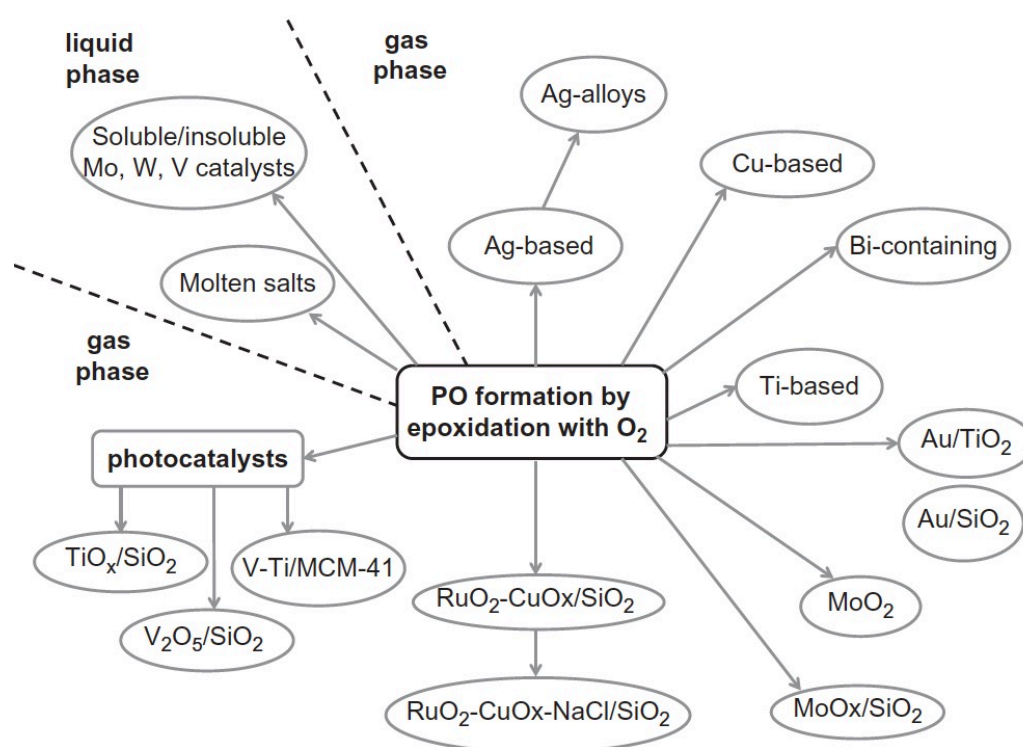


Figure 1.12 Summary of classes of catalysts investigated for propylene epoxidation with molecular oxygen. Reproduced with permission from reference.^[138]

Among all these catalysts, IB group elements, Cu,^[144] Ag^[145] and Au,^[143] based catalysts show promising catalytic activity toward propylene epoxidation. Copper recently has drawn an increased attention as it is cheaper than gold and silver for use as an industrial catalyst.^[78] Both metallic copper and copper based catalysts have been examined for the selective oxidation of propylene with O₂.^{[146][147]} In 2013, Linic and co-workers demonstrated using visible light source to manipulate the oxidation state of Cu nanoparticle with an average size of 41 nm supported on an inert SiO₂ support.^[144] Under the visible light source, the copper material undergoes a dramatic surface phase change from an oxide to a metal on atomic level. The light induced change in atomic structure of the copper surface causes a dramatic noncontinuous change in the rate of propylene consumption and the intrinsic product selectivity. As shown in Figure 1.13, over the copper oxide surface, it mainly contributes to CO₂ production with a PO selectivity about 18%, and accompanied by an increased CO₂ selectivity at higher rates of propylene consumption, and the increase in the CO₂ selectivity. On the other hand, on the Cu metal surface, the selectivity to PO rapidly increases to about 50%.^[144] Although a drop of PO selectivity has been observed at a higher rate of propylene consumption, the findings show the possibility for direct epoxidation of propylene without expensive sacrificial agents.

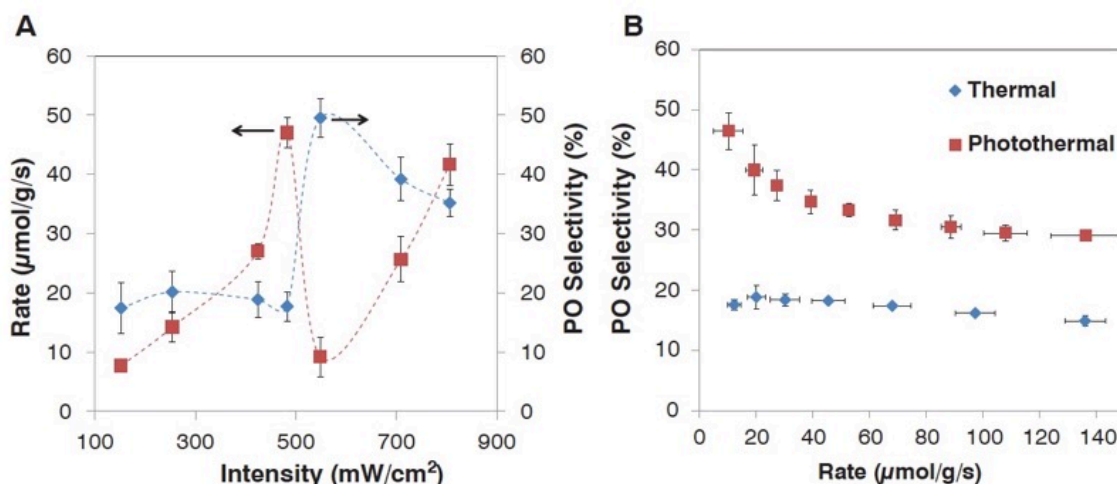


Figure 1.13 (A) Rate of propylene consumption (left axis, red squares) and the selectivity to propylene oxide (right axis, blue diamonds) at 200 °C. (B) Selectivity to propylene for thermal (light off) and photothermal (light on) processes as function of the reaction rate. Reproduced f with permission from reference.^[144]

Ever since then, the Cu-based catalysts have become more attractive for propylene epoxidation by eliminating the need for H_2 addition. Among all the Cu-based catalysts, $\text{RuO}_2\text{-CuO-NaCl/SiO}_2$, as shown in Figure 1.14, was the most active catalyst for PO production with 5 to 8% of PO yield (about 40-50% of PO selectivity and 10 to 20% of propylene conversion).^[148] It has been suggested that the vital role in the epoxidation route is provided by crystalline CuO.^[148] In the proposed mechanism, O_2 favourably adsorbs onto the catalyst, specifically on the RuO_2 surface, which is subsequently dissociated into O-atom and transferred onto the CuO surface for PO synthesis.^[147] The addition of combustion-inhibiting promoter such as NaCl, shows the further enhancement of PO selectivity by reducing acidity of the active surfaces, possessing an electronic effect to the adsorbed oxygen species to become electrophilic.^[149] However, even the Cu based catalysts have been shown to have a promising activity, the PO selectivity reported hardly exceed

50% at a wide range of C_3H_6 conversion (0.24 to 20%,^{[148][78,146]} and 0.08% to 8%^[138,150] PO yield).

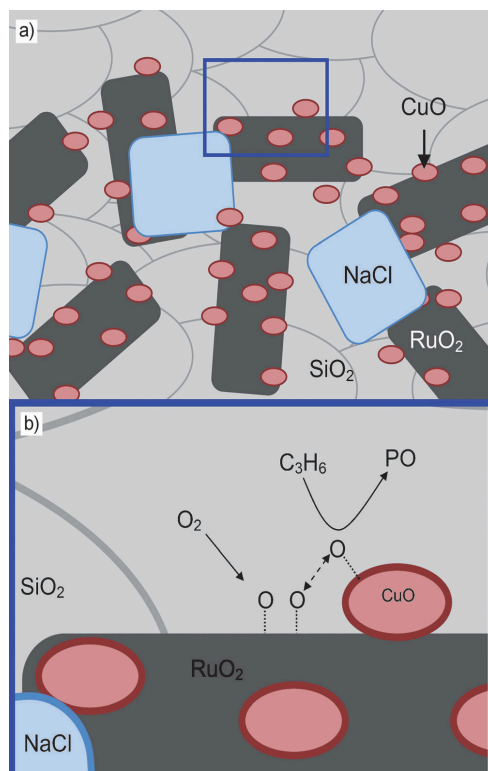


Figure 1.14 a) Schematic structure of the RuO_2 - CuO - $NaCl/SiO_2$ catalyst. b) proposed mechanism for the epoxidation of propylene, showing the dissociative adsorption of O_2 onto the RuO_2 surface, surface migration of adsorbed oxygen to CuO surface, and the formation of PO. Reproduced with permission from reference.^[148]

1.5.3 Silver based catalysts for direct propylene epoxidation

Silver catalysts have been long studied for selective oxidation reactions, especially for epoxidation reactions. Ag nanoparticles are the only practical catalyst available today for converting ethylene to ethylene oxide. Many studies have been focused on gas-phase reaction using conventional Ag based catalysts for propylene epoxidation because of their great catalytic performance for the ethylene epoxidation. The

conventional silver catalysts for ethylene epoxidation generally have a high metal loading on a low surface area support, typically α -alumina.^[3] Other low surface area support, such as silicon carbide, glass wool, and quartz can also be used as substitution in commercialised processes.^{[151][118]} Microporous materials generally yield poor selectivity due to further oxidation of the epoxide products in the pores.

Early propylene epoxidation research work has focused on the usage of those silver catalysts in ethylene oxide production for the propylene epoxidation. The most widely studied catalyst is a 10-20 wt % silver catalyst supported on low surface area ($<1 \text{ m}^2/\text{g}$) α -alumina. The SEM image of the catalysts (Figure 1.15) shows that the silver nanoparticles (light coloured particles) with about 100-150 nm diameter were evenly distributed on the support.^[126] However, most results show a very poor propylene oxide production activity over this catalyst. It is because that silver particles are very active in allylic oxidation, in the case of propylene oxide production, it is very effective to form an allylic intermediate which will continuously lead to a complete oxidation route.^[126] The details will be later described in the Reaction Mechanism sub-heading.

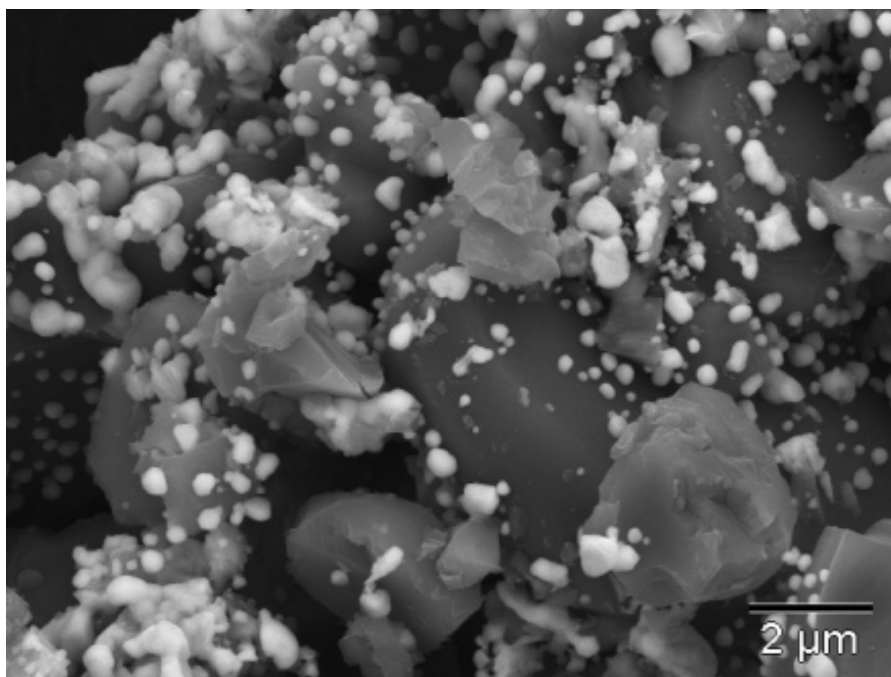


Figure 1.15 Scanning electron microscopy (SEM) image of the Ag based catalysts used in ethylene epoxidation process - 18 wt% silver on an α -alumina catalysts. Reproduced with permission from reference.^[126]

1.5.3.1 The promoter effects

To reduce the allylic oxidation, the silver catalysts have been modified with a variety range of promoters. Alkali metals together with Ca and Ba have been initially used as the promoter on the catalysts itself to reduce the catalysts acidity.^[138] In 1999, Lu and Li reported the promoter effects on unsupported Ag as shown in Table 1.7.^[152] The silver catalysts containing alkali or alkaline earth chloride salts were tested for the propylene epoxidation with air under a wide range of reaction temperatures. It shows that the cation in chloride salt has a great influence on the efficiency of the silver catalysts.^[152] Using NaCl or BaCl₂ as a promoter, the silver catalyst exhibited an enhanced propylene conversion and PO selectivity.^[152] With a highest catalytic activity observed at 350 °C over Ag-NaCl, the conversion of propylene was reported

to be 18.6% and selectivity of PO was 33.4%.^[152] Over Ag-LiCl at the same temperature, the selectivity of PO was 27.5%, but the conversion of propylene was very poor with 8.2% only. It can be seen that both NaCl and BaCl₂ can promote the silver catalysts activity for PO production.^[152] The promotion effects can be explained from the inductive effect of the ions on nearby oxygen atoms adsorbed on the silver surface. As reported by Lambert, the ions, Cl⁻ are moderately electronegative and withdraw only a partial charge from the oxygen, rendering it sufficiently electrophilic for attack of the propylene double bond.^[153] The alkali metal counteractions also have an effect on the reaction, with Na⁺ being more effective than Ba²⁺ and K⁺.^[153] Although the mechanistic role of alkali metals is still unclear, it is proposed that the inductive effect produced by these ions is probably felt through the silver atoms in a similar way to that of the surface oxygen.

Table 1.7 Effect of Na, Ba and Li promoter on the efficiency of silver catalyst.

Reproduced from reference.^[152]

Catalyst		Temperature (°C)			
		280	310	350	390
Ag-NaCl	conversion of propylene (%)	4.2	7.8	18.6	29.9
	Selectivity of PO (%)	34.5	25.0	33.4	11.9
Ag-BaCl ₂	conversion of propylene (%)	3.4	5.3	24.6	30.6
	selectivity of PO (%)	15.5	19.0	26.1	14.7
Ag-LiCl	conversion of propylene (%)	2.3	5.1	8.2	14.1
	selectivity of PO (%)	0	12.1	27.5	18.0

X. Liu and co-workers reported a different promotion effect for an unsupported silver catalysts modified with MoO_3 .^[154] Both pure Ag and Ag- MoO_3 catalysts were tested for a gas-phase propylene epoxidation with molecular O_2 , while the pure Ag catalysts had a PO selectivity of only 0.8% at a propylene conversion of 11%, with the addition of MoO_3 the PO selectivity was progressively increased to 34% with a decline in propylene conversion to 4.6% at a reaction temperature of 400 °C.^[154] At such a high temperature, it is normally expected a high propylene conversion and very low PO selectivity, which is because at high temperature the surface adsorbed oxygen (O_{ad}) is more favourable to interacted with propylene through the allylic oxidation and the complete oxidation of propylene is thermodynamically more favourable.^[141] The decreased in conversion of propylene indicated a surprised inhibiting of the allylic oxidation induced by MoO_3 . X-ray photoelectron spectroscopy indicated the formation of Ag^+ and $\text{Mo}^{(6-\delta)+}$, consistent with electron transfer from Ag to Mo. The authors suggest that Mo^{6+} can compete with the O_{ad} to acquire electrons from Ag weakening the effective charge of the O_{ad} on the silver sites.^[154] Consequently, O_{ad} would have a stronger electrophilic property which inhibits the attack of the allylic hydrogen of propylene on the O_{ad} .^[141] Therefore, the olefinic bond of propylene has more chances to be attacked by the O_{ad} on the silver to form PO. The promoter effects demonstrated an important role of the electrophilic surface oxygen in the propylene epoxidation reaction route. However, the supported silver particles are normally with large sizes between 576 and 738 nm.^[149] The naked silver will also suffer from a sintering process as the reaction carried on which dramatically reduces the catalytic activity and stability.^[154]

1.5.3.2 The size effects

As previously mentioned, the metal particle size could induce both geometric and electronic effects on the catalytic properties. The influence of the silver particle size on propylene oxidation has also been considered in several interesting studies. For the alkali metal promoted naked silver catalysts, although the promoter can have an electronic effect on the surface adsorbed oxygen, which can inhibit the allylic reaction, the activity is limited by both large size of silver particles and a further sintering of silver metal.^[154] Lambert and co-workers comparatively study the effect of Ag particle size induced by supports on catalysed direct propylene epoxidation.^[155] The properties of two support materials, namely α -alumina, K-promoted CaCO_3 were carefully investigated. With a consistent Ag loading, Ag/ α -alumina was found to be dominated by very large Ag particles (>150 nm) whereas the size of Ag particles on Ag/ CaCO_3 was much smaller (< 50 nm).^[155] The reaction results showed that with very large Ag particles, the Ag/ α -alumina exhibited very poor selectivity towards propylene epoxidation; however, reducing the particle size dramatically increased the selectivity of PO over the K-Ag/ CaCO_3 .^[155]

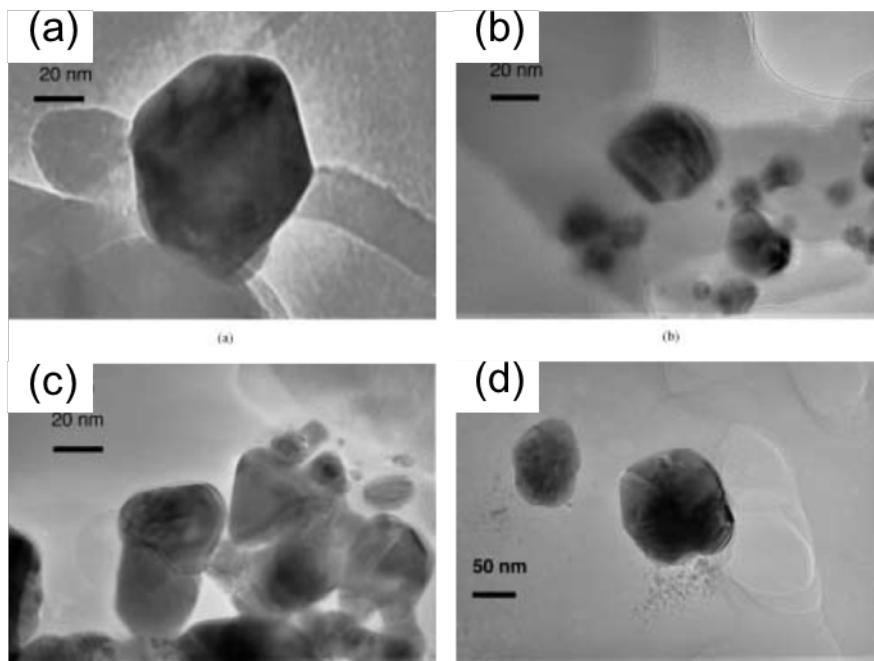


Figure 1.16 (a), (b), (c), (d) are representative high-resolution electron microscopy (HREM) images of K-Ag/ CaCO_3 containing, respectively, 0.0, 1.7, 2.5, 4.2 w/w% K. Note different magnifications. Reproduced with permission from reference.^[155]

With a relatively high PO selectivity, the effect of potassium loading on catalysts performance was also studied. Four CaCO_3 -supported Ag catalysts (45% w/w Ag loading) were prepared with increasing potassium loadings 0% (C1), 1.7% (C2), 2.5% (C3) and 4.2% (C4). The HREM of the K-Ag/ CaCO_3 with variety of potassium loading, in which the (a) is the Ag/ CaCO_3 without K, and from the (b) to (d) with an increased K loading, was shown in Figure 1.16.^[155] It has been reported that both the Ag/ CaCO_3 catalyst without K loading (a) and with highest K loading (d) have a narrow particle size distribution, which is about 70nm, and 100nm respectively. For the (b) and (c) catalysts, images showed two distinctly different group of Ag particles: larger Ag particles size of about 20-40 nm, and very small Ag crystallites with particles size about 5 nm. Comparing (b) and (c), increasing in K loading resulted in

a dominant Ag particle size of 20-40 nm. The effect of varying potassium loading on PO selectivity and propylene conversion is shown in Figure 1.17.^[155] At 210 °C, both (a) and (d) gave a very low selectivity of PO, with 3.7% and 6.1%, respectively, whereas over catalysts (b) and (c), the increased selectivity of PO was observed to be much higher. A similar trend was also obtained for the propylene conversion. The authors concluded that the change in catalytic activity is more likely due to the geometric effect rather than promoter effect of the K-Ag/CaCO₃ for catalysis propylene epoxidation.^[155] They proposed that the optimal crystallite size was the result of a balance between the exposures of low index planes which favoured epoxidation by stabilizing oxygen adatoms in the most electrophilic state, but also disfavoured epoxidation by interacting most strongly with the product epoxide.^[155] However, in the case of C2 and C3 catalysts exhibiting better propylene conversion and PO selectivity, the samples had a mixture of particles of different size. To verify this conclusion, a study with samples having narrow particle size distribution would be desirable.

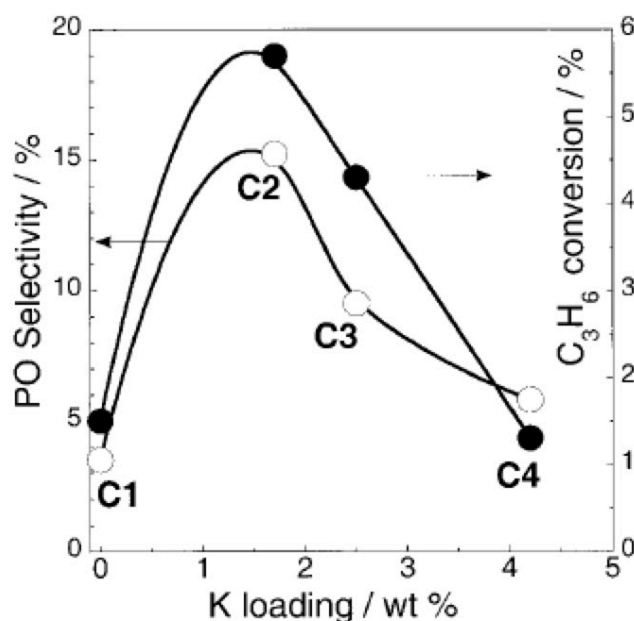


Figure 1.17 Effect of potassium loading on PO selectivity and propylene conversion.

Reproduced with permission from reference.^[155]

More recently, two scientists Lei and Vajda demonstrated a strong subnanometer size effect of Ag catalysts for direct propylene epoxidation.^[145] To investigate the catalytic properties of supported Ag clusters for direct propylene oxidation, the size-selected Ag trimers (Ag₃) supported on amorphous alumina film was prepared by a physical mass selection method.^[145] In addition to that, very small Ag nanoparticles with average size of about 3.5 nm (2 nm in height and 4 nm in diameter) resulting from agglomeration of the silver trimers at high temperature has also been tested.^[145] In Figure 1.28 (A), in-situ grazing incidence small-angle x-ray scattering (GISAXS) revealed that the sintering of Ag₃ cluster begins around 110 °C, and a uniform Ag particles with an average size of 2.5 nm can be obtained at 200 °C. The catalytic tests over the supported silver trimers (Figure 1.20 (B) and (C)) showed that propylene oxide, acrolein, and carbon dioxide were identified as the dominating

reaction products. The rate of both propylene oxide and acrolein formation increased sharply with temperature, starting from room temperature. The formation of CO₂ could be observed at 60 °C coincided with the decrease of acrolein production, which indicates that the production route of CO₂ and acrolein are competitive. The main products were propylene oxide and acrolein below 60 °C with a propylene oxide selectivity of about 40%. A much higher propylene oxide to acrolein product ratios (3:1) were achieved at higher temperature range (between 70 °C and 100 °C), but the improvement was realized together with an increase in CO₂ formation.

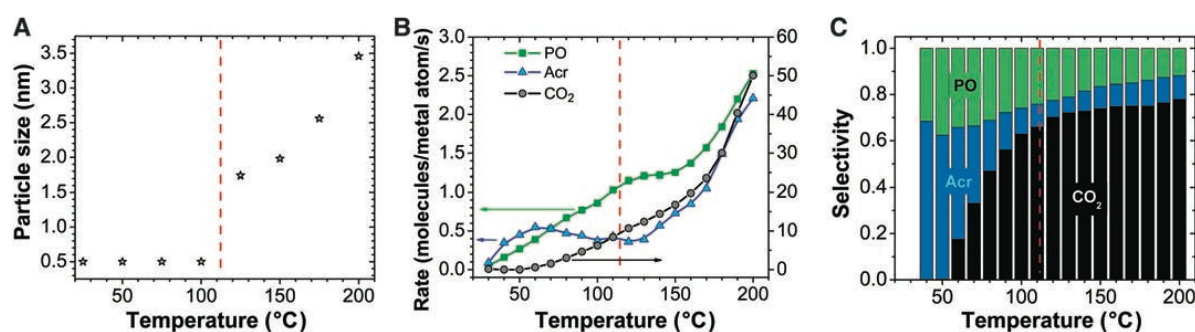


Figure 1.18(A) Temperature dependent average cluster size from GISAXS. B) Rate of propylene oxidation towards PO, acrolein (Acr), and CO₂ per surface silver atom over supported silver trimers. C) Selectivity of propylene oxide, acrolein, and CO₂ versus temperature over supported silver trimers. The vertical dashed lines indicate the temperature at which the sintering of the silver trimers begins. Reproduced with permission from reference.^[145]

On the other hand, the silver aggregates exhibited superior selectivity toward propylene oxide at temperature up 120 °C as shown in Figure 1.19.^[145] Both the PO selectivity and the formation rate over silver aggregates were higher than over Ag₃ clusters, and most reported promoted Ag catalysts. Their XPS results revealed a

significant electronic structure effect being induced by the geometric changes.^[145] The silver aggregated particles were mostly metallic during propylene oxidation with any oxidized contribution below 5%, whilst the Ag₃ clusters were partially oxidized.^[145] The catalytic activity of those silver catalysts is likely controlled by both the geometric and electronic structure of the silver surface. The reaction results for the first time demonstrated that it is possible to use unpromoted silver particles for propylene epoxidation.

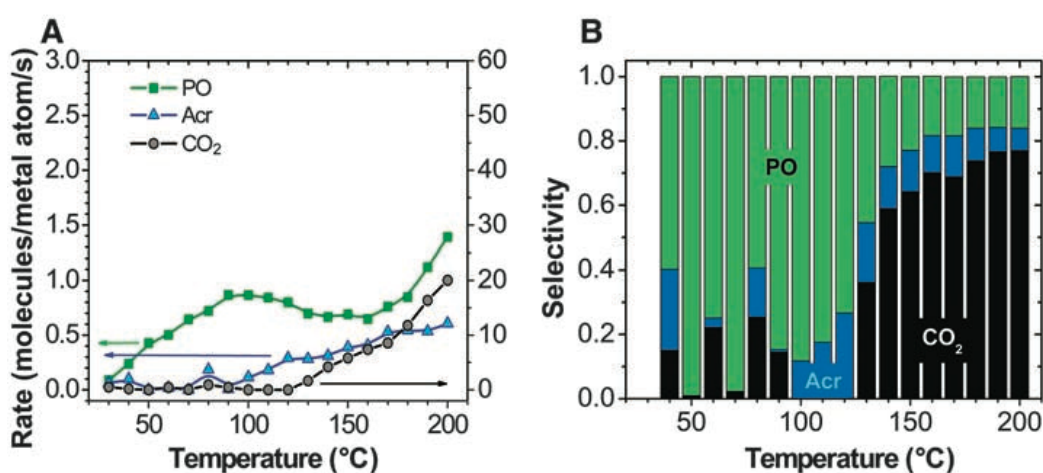
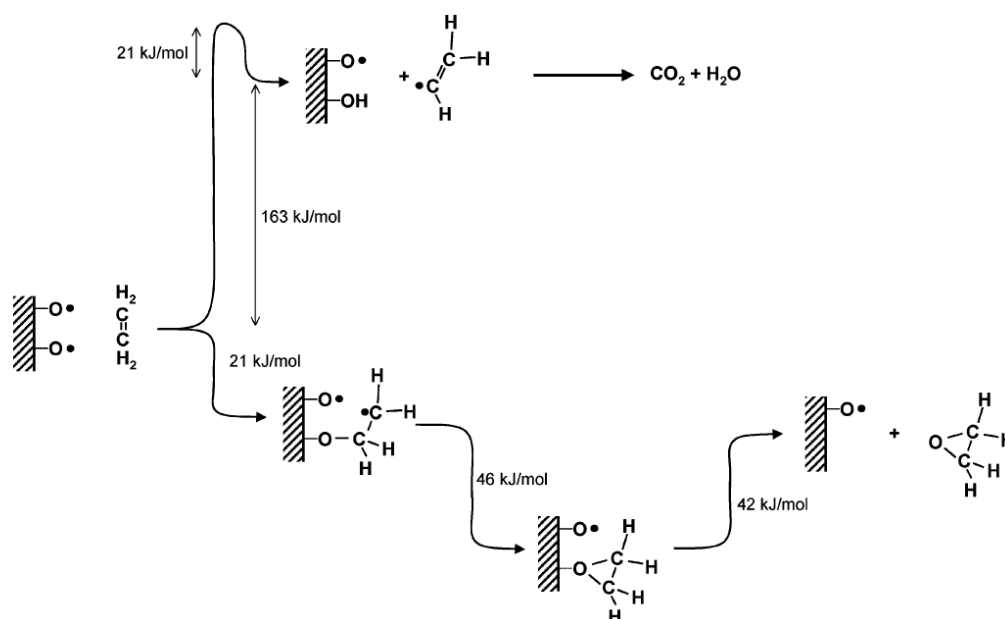
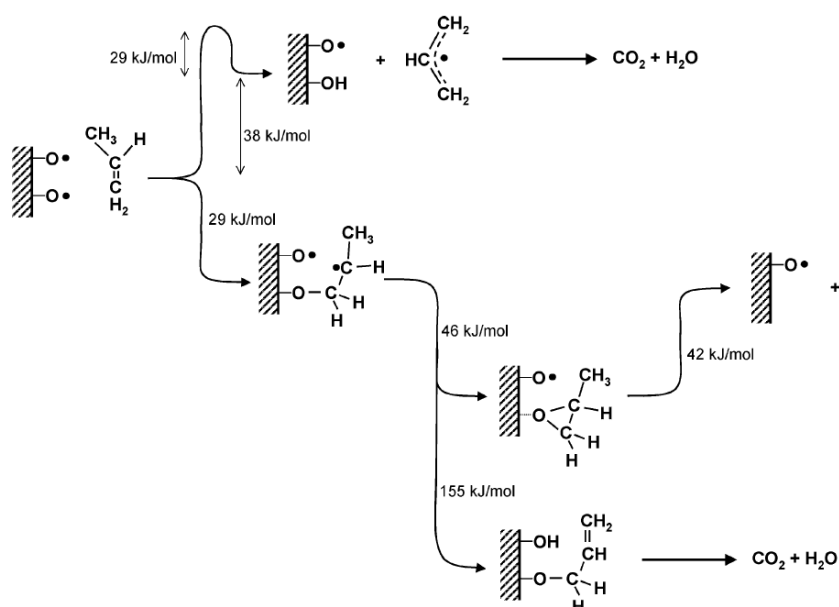


Figure 1.19 (A) Rate of propylene oxidation toward PO, acrolein (Acr), and CO₂ per surface silver atom over supported silver aggregates (about 3.5 nm). (B) Selectivity of propylene oxide, acrolein, and CO₂ versus temperature over supported silver aggregates (about 3.5 nm). Reproduced with permission from reference.^[145]

1.5.3.3 Reaction mechanism in propylene epoxidation as compared to ethylene over silver surface



Scheme 1.8 A reaction scheme for the epoxidation and total oxidation reaction pathways for ethylene over a silver catalyst. Reproduced with permission from reference.^[126]



Scheme 1.9 A reaction scheme for the epoxidation and total oxidation reaction pathways for propylene over a silver catalyst. Reproduced with permission from reference.^[126]

Schemes 1.8 and 1.9 show the proposed oxyradical mechanisms for both ethylene and propylene. It is generally believed that surface atomic oxyradical (adsorbed atomic oxygen with its unpaired electron pointing out from the surface) is the active oxygen specie for the oxidation. As seen from Scheme 1.8, when ethylene reacts with oxygen, the reaction can proceed in two ways. The first is the C-H cleavage due to the abstraction of a H atom. According to the calculations from Cater and Goddard,^[156] this reaction has a relatively high activation energy (+184 kJmol⁻¹) from the stabilized adsorbed oxygenated reaction intermediate (-29 kJmol⁻¹) which is produced from the O-insertion into the C=C bond caused by the attack of oxyradical. Once this reaction step has occurred by overcoming the high activation barrier, the only reaction steps would result in the complete combustion of ethylene. On the other hand, the oxygenated reaction intermediate can produce even more stable adsorbed ethylene epoxide (-46 kJmol⁻¹) which forms the gas phase ethylene epoxide product with a small barrier energy (42 kJmol⁻¹). This scheme is consistent with the general experimental observation that a decrease in ethylene epoxide selectivity at higher reaction temperatures when the kinetic barrier is overshoot.^[157]

However, one can appreciate the main challenges in getting comparable epoxide selectivity as ethylene in the case of propylene by referring to Scheme 1.9.^[126] Despite the fact that the two schemes are largely analogous to each other, the calculated activation energy for H- abstraction of propylene is much favourable (67

kJmol^{-1}) than that of ethylene due to the formation of energetically favourable allylic intermediate, which will undergo uncontrolled combustion to CO_2 .^[156] Instead of the formation of propylene epoxide at low temperature as that of ethylene case, a further challenge is that there exists an alternative and more energetically favourable route for H-abstraction from oxygen adsorbed intermediate (-201 kJmol^{-1}) by the second oxyradical (formed from dioxygen activation over extended silver surface) hence forming similar to allylic intermediate to lead to combustion at low temperature. The degree of γ -H abstraction from the neighbour adsorbed oxygen atom is believed to critically dependent on the geometric and electronic effects on the underneath silver atoms, which in turn are affected by the atomic morphology, size and structure (electronic impurities) of the silver nanoparticles.

1.6 Aims and objectives

In this thesis, three novel approaches of modifying both the geometric and electronic properties of Ag nanocatalysts will be investigated with the aim of improving selectivity for partial oxidation of propylene under various reaction conditions, namely: (i) controlled silver nanoparticle morphology and exposed facets with different interatomic Ag distances and their metal-support interactions over supported silver catalysts (ii) M-Ag core@shell nanoparticle approach by deposition of a second metal nanoparticle (M) with Ag atoms to control surface interatomic Ag distance and to influence the electronic structure of Ag in porous SBA-15 template; (iii) atomically isolated Ag atom anchored to the internal surface of HZSM-5 in order to avoid the formation of neighboured di-oxyradicals (two close neighboured oxygen atoms).

The objective of this thesis will be two-fold: firstly, demonstration the modification of Ag catalysts and exploring the performance of modified Ag catalysts for propylene selective oxidation with molecular oxygen under various conditions. Secondly, characterisation of the Ag materials with advanced techniques to understand how the modifications can affect the catalysts surfaces and how molecular oxygen adsorption with and without dissociation can be influenced by the surface geometric and electronic changes of the surface, and ultimately develop a comprehension on how all the factors can be modified to enhance the selectivity and activity of propylene selective oxidation.

1.7 Thesis overview

This thesis consists of seven chapters. Chapter four to six inclusive, detail the research performed during my study for this DPhil degree.

Chapter One – Catalysis principles and associated basic theories used in heterogeneous catalysis are introduced. Specifically, the backgrounds in proposed mechanisms, challenges in carrying out selective propylene oxidation reaction and our approaches (controlled in Ag morphology/facet, M-Ag core-shell catalysts, size effect from nanoparticle to isolated Ag atom) are presented and discussed.

Chapter Two – The background and theory of the analytical techniques used to characterise developed heterogeneous catalysts throughout this thesis are presented.

Chapter Three – A detailed description of the experimental methods used for synthesising, characterising and testing of the developed catalysts in this thesis.

Chapter Four – The performances of morphology/facet controlled Ag nanoparticles on lanthanide series metal oxides for direct propylene oxidation are given, and the assistance in molecular oxygen dissociation by the support at Ag-support interface is discussed with the support of DFT calculations.

Chapter Five – Surface tailoring of geometric and electronic effects of Ag atoms on Ni metal nanoparticle surface through the formation of Ni-Ag core@shell structure, on the activity and selectivity of selective propylene epoxidation are described.

Chapter Six – The influence of atomically but isolated Ag atom supported on the interior wall of HZSM-5 on selective propylene selective oxidation in liquid phase is reported.

Chapter Seven – Conclusions and future outlooks of the work are presented.

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Chapter 2 Analytical Techniques

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2.1 X-ray powder diffraction

X-ray powder diffraction (XRD) is one of the most widely applied analytical techniques primarily used to study the crystalline structure of catalytic materials. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction grating for X-ray wavelengths similar to the spacing of planes in a crystal. Based on the constructive interference of monochromatic X-ray and a crystalline sample, the X-ray diffraction provides information on the phase identification, crystal structure, size, unit cell dimensions and atomic spacing of crystalline materials.^[1]

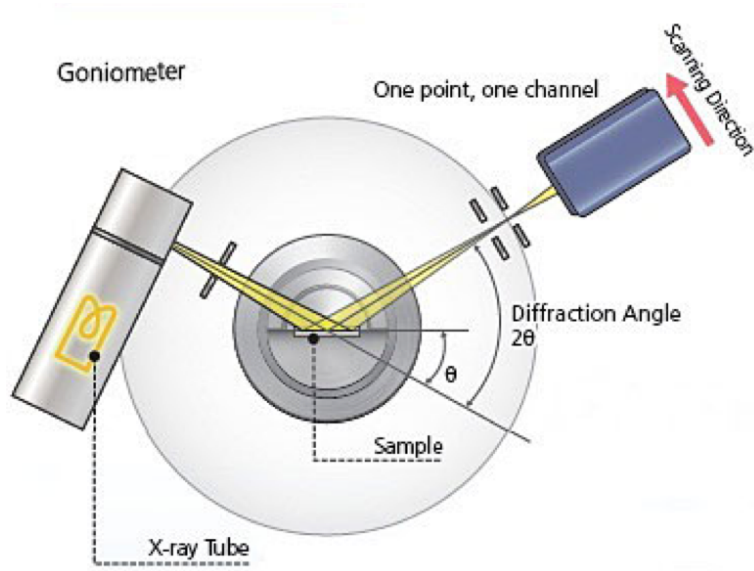


Figure 2.1 Diagram of a typical XRD experiment on a thin film sample, where θ is the diffraction angle (Bragg angle). Reproduced from reference.^[2]

Typically, X-ray diffractometers consist of three main elements: an X-ray tube, a sample holder, and an X-ray detector as shown in Figure 2.1. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons from the K shell.^[3] The X-ray spectra consist of several components, the most common being K_α and K_β . K_α consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. The

monochromatic X-rays are produced by filtering with foils or crystal monochrometers. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Copper is used as target material for XRD diffraction in this thesis, with CuK_α radiation $\lambda = 1.5418 \text{ \AA}$.^[1] These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-ray is collected and recorded by the detector.

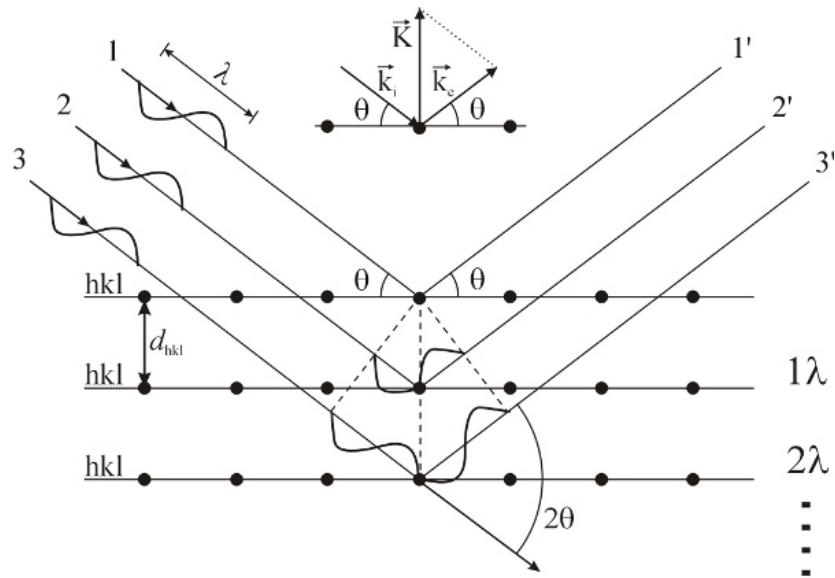


Figure 2.2 Illustration of diffraction of incident X-ray by atomic planes of a crystallite, where d is the interplanar spacing and θ is the diffraction angle (Bragg angle). Reproduced from reference.^[2]

The geometrical picture in Figure 2.2. shows the elastic scattering of an X-ray beam by planes of atoms in a crystal.^[4] The X-ray beam of wavelength λ , incident on the crystal at an angle θ with respect to equidistant hkl lattice-planes, with interplanar spacing d_{hkl} . Constructive interference will be observed for X-rays that are reflected from the lattice planes at the specular angle, if the path length difference between X-

rays scattered from different hkl-planes is an integer times the wavelength. This condition is summarized by the Bragg law:

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

Diffraction (i.e. constructive interference of the scattered X-rays) will occur if the Bragg condition (Eq. 2.1) is fulfilled and of the scattering vector K is parallel to the normal of the hkl-planes. By scanning crystalline samples in search of interference peaks, the crystal information on the lattice parameters, strain, etc. can be obtained. The interplanar spacing d_{hkl} , can be used to calculate the lattice parameter, a , of a crystalline material by relating the spacing with Miller indices, h , k , and l of particular lattice planes. For cubic structure crystals, such as silver, Equation 2.2 can be applied.

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad \text{Equation 2.2}$$

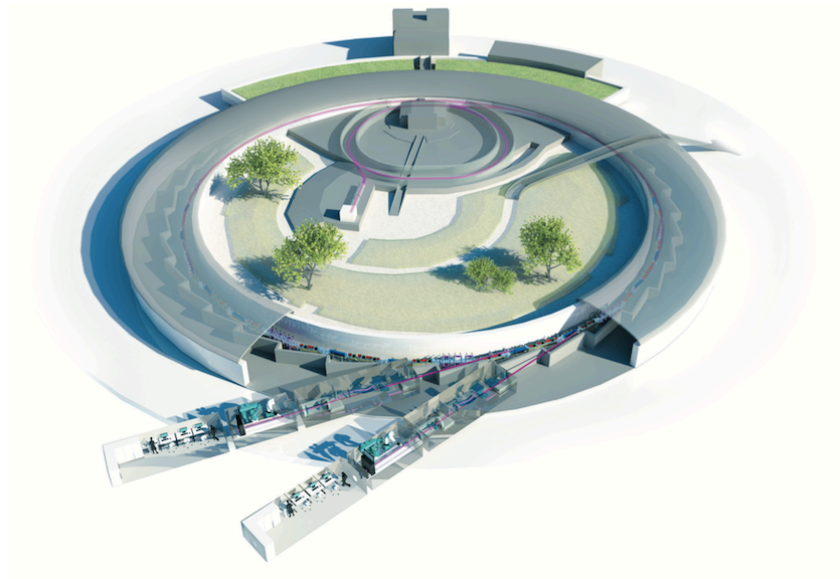
The determination of the interplanar distance also makes it possible to determine stress and strain epitaxial or implanted in the specimen. In core-shell structural nanoparticles studies in particular, stress and/or strain results in the deviation of the interplanar distances within a crystal.^[5] This stress can be induced by the presence of shell with a core of slightly different lattice parameter, etc. Not only the peak position contains valuable information on the specimen under investigation, the width or full width at half maximum of the diffraction peak contains information on the as well. In case of a perfect crystal, the width of the interference peak (as a function of θ) is inversely proportional to the thickness of the crystalline layer.^[5] The full width at half maximum (FWHM) of the peak is given by the Scherrer formula, Equation 2.3:

$$\text{FWHM} = 0.9\lambda/t \cos \theta \quad \text{Equation 2.3}$$

where the FWHM is expressed in radians, λ is the wavelength of the X-rays, t is the thickness of the layer and θ is the Bragg angle of the reflection. A core-shell

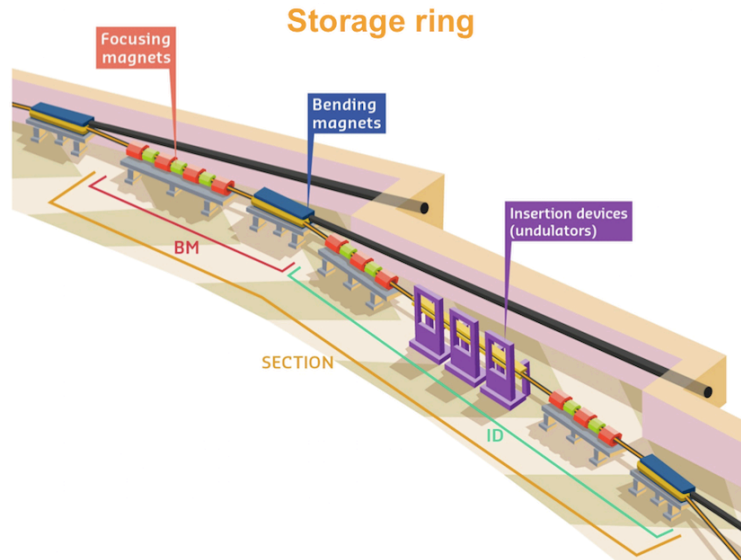
structural particles can be divided into different crystalline domains (crystallites) that all have a slightly different orientation. The thickness t in the Scherrer formula will, in that case, be related to the core particle size, and thickness of the shell.

2.2 Synchrotron Light Source and Synchrotron X-ray



Scheme 2.1 The illustration of Diamond Light Source. (UK's national synchrotron light source). Reproduced from reference.^[6]

Synchrotron light source is an electromagnetic radiation usually produced by a storage ring or more typically accelerating electrons.^[7] Once the high energy electron beam has been generated, it is directed into auxiliary components. These supply magnetic fields perpendicular to the beam. The synchrotron light source is an extremely powerful source of X-rays. When a moving electron changes direction, it emits energy. If the electron is moving fast enough, the emitted energy is at X-ray wavelength. The resulting X-rays are emitted as dozens of thin beams, and each directed toward a beamline.



Scheme 2.2 The illustration of storage ring at Diamond Light Source. Reproduced from reference.^[6]

The storage ring (Scheme 2.2) is a tube with 844 metres in circumference where the electron circle for hours close to the speed of light.^[6] The tube is maintained at low pressure (about 10^{-9} mbar).^[6] As the electrons travel in the ring, they pass through different types of magnets and in the process producing X- rays. The X-ray beams emitted by the electrons are directed toward “beamlines” that surround the storage ring in the experimental hall. Each beamline is designed for use with a specific technique or for a specific type of research. The synchrotron X-ray has higher brilliance comparing to X-ray source produced in conventional way. It typically has a brilliance larger than 10^{18} photons/s/mm²/mrad²/0.1 % BW, where 0.1% BW denotes a bandwidth $10^{-3} w$ centred around the frequency w , which allows for better materials characterisation of the nanostructure.^[7]

2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), based on the detection of ejected electrons, is a technique for the analysis of solid state surfaces. It is only capable of probing 2-5 nm depth of a sample surface.^[4] Heterogeneous catalysis reactions occur mainly on active sites located at the surface of the catalyst. The primary function of XPS in characterisation of heterogeneous catalysts is to investigate the elemental composition of a surface, and electronic states for the atoms of a particular element. The advanced utility of XPS can also provide information on the changes of the surface electronic, chemical and structural properties during a particular catalysis process. This makes it possible to study the key elementary steps of a reaction, including adsorption, surface diffusion, chemical rearrangement of the adsorbed intermediates and etc.

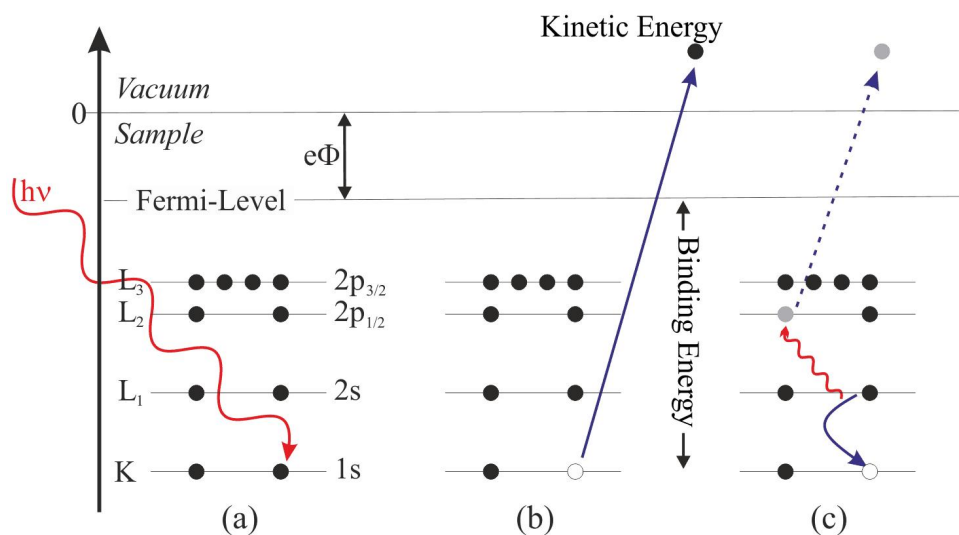


Figure 2.3 Principle of photoelectron emission and the Auger relaxation effect. (a) the incident X-ray photon is absorbed, (b) the absorbed photon energy induced the ejection of a core electron, and (c) an electron at higher energy level relaxes down to

fill the vacancy, and results in the emission of a photon (Auger electron).
Reproduced from reference.^[3]

The X- rays used for XPS are generated in a similar manner to that described for XRD, with an aluminium source substituted for copper, resulting in lower radiation energy (1486.3 eV for Al). When high energy photons impinge on an atom, they can either pass through without interacting, become elastically scattered resulting in partial energy loss, or completely release the energy to a core energy level electron, resulting in ejection of an electron from the atom as depicted in Figure 2.3 (a). This consequent emission of electrons (photoelectrons) is photoemission. XPS is based on this photoemission effect. The photoelectron kinetic energy is given by Einstein's law

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

where E_k is the kinetic energy of the photoelectron, $h\nu$ is the energy of the incident radiation, and E_b is the binding energy of the electron in a particular level. If the incident photon is sufficiently energetic, many different levels in the sample may be ionized and thus a spectrum is produced displaying all accessible energy levels as a distribution of photoelectrons. Photoelectron peaks are labelled according to the quantum numbers of the level from which the electron originates. The presence of these types of peaks is very useful for chemical state determinations. As a consequence of the primary ionization process, a hole in the core level is created as shown in Figure 2.3 (b), and an electron from an external level fills the vacancy created in the core level and the difference between the two energy levels is carried away by the ejected Auger electron.

In this thesis, all the XPS is represented by the high vacuum environment, resulting in a modified Einstein's law

$$E_k = h\nu - E_b - \varphi \quad \text{Equation 2.5}$$

where φ is the work function of the spectrometer. Binding energies are characteristic to specific elements, and can give information on the chemical environment of the emitting atom. XPS yields both quantitative and qualitative information. The quantitative information arises from the element specificity of the binding energies and the relation between the intensity of the photoelectron peaks and the element concentration. Qualitative information is obtained from the energy position of a photoelectron peak. Chemical shifts of binding energies of a certain element level determine different oxidation states and different chemical environments. They are interpreted in terms of a simple electrostatic theory, called the "charge potential model".^[4] According to the model, the energy of the atom is divided into two terms, one associated with the net charge on the probe atom and the other term associated with the charge distribution of the surrounding atoms. The binding energy chemical shift of a level of the atom i in a molecule with respect to a reference can then be expressed as

$$\Delta E_b = \frac{\Delta q_i}{r_v} - \frac{\sum \Delta q_j}{r_{ij}} - \Delta R \quad \text{Equation 2.6}$$

The first term on the right represents the electrostatic potential due to the valence charge on atom i with an average valence orbital radius r_v . The summation term is the sum of the potentials at *atom i* due to the surrounding atoms j considered as point charges. ΔR is the relaxation term. A Chemical shifting to a higher binding energy indicates an increase in an element's oxidation state.^[4]

For a typical XPS characterization, the kinetic energy of the outgoing electron is affected by the charge accumulated on the sample during the ejection of photoelectrons, resulting in large shifts in binding energy. Calibration with respect to the energy of a reference peak is needed. In this thesis, when evaluating supported catalysts, the correction is done by normalization of C1s binding energy to a reference value, set at 284.4 eV.^[8]

2.4 Transmission electron microscopy

Transmission electron microscopy (TEM) is a very powerful technique for catalysts characterisation. It operates on the same basic principles as the conventional optical microscopy. However, the electrons are used instead of a light source for TEM. The utility of a high energy electron beam leads to a lower wavelength comparing to light source, which increases the imaging resolution by four orders of magnitude (to 0.1 nm).^[3] These electron microscopes allow for magnification up to 10^6 times that of the original sample. It is capable to observe the catalyst features such as the crystal structure, size and morphology. Chemical synthetic analysis can also be performed. It can be used to study the growth of nanocrystal, their composition and defects on the surface. 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 thereof.^[2] Materials in this thesis are primarily characterized by TEM and HRSTEM.

A TEM consists of an illumination system (lamp, electron gun, and condenser lens), specimen stage, objective lens system, magnification system, and image analysis

system Figure 2.4 (left).^[5] The beam of electrons is generated from the electron gun, focused into a small, thin, coherent beam by the condenser lens, and restricted by the condenser aperture, which excludes high angle electrons. The highly coherent beam of parallel electrons then illuminates the specimen and parts of it are transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion is focused by the objective lens into an image on phosphor screen or charge coupled device camera. Optional objective apertures are used to enhance the contrast by blocking out high angle diffracted electrons. The image is passed down the column through the intermediate and projector lenses, is enlarged.

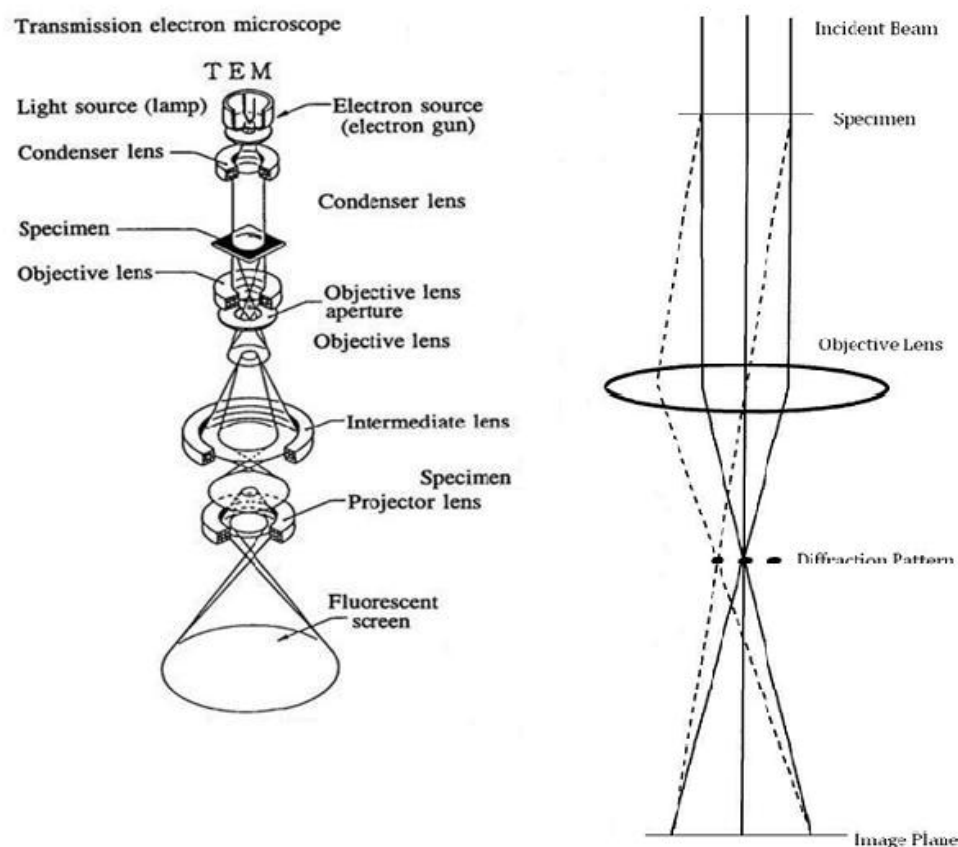


Figure 2.4 (left) General schematic of the arrangement of major components and describing the path of electron beam in a TEM (from JEOL 2010 Handbook); right) A ray diagram for the diffraction mechanism in TEM. Reproduced from reference.^[5]

Figure 2.4 (right) shows a simple sketch of the path of a beam of electrons in a TEM from just above the specimen and down the column to the phosphor screen. As the electrons pass through the sample, they are scattered by the electrostatic potential set up by the constituent elements in the specimen. After passing through the specimen they pass through the electromagnetic objective lens which focuses all the electrons scattered from one point of the specimen into one point in the image plane. Also, shown in Figure 2.4 (right), a dotted line is where the electrons scattered in the same direction by the sample are collected into a single point. This is the back focal plane of the objective lens and is where the diffraction pattern is formed.

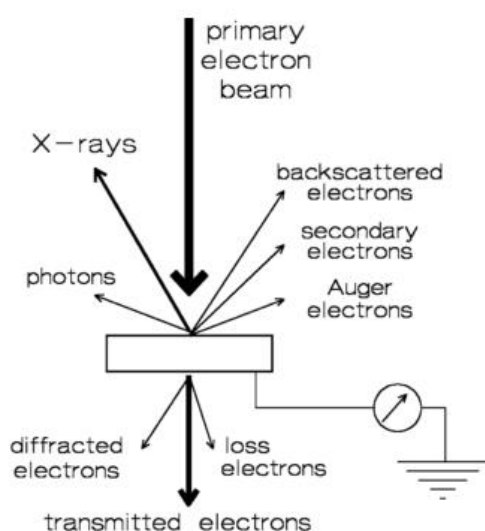


Figure 2.5 General schematic showing fundamental interactions of primary electron beam. Reproduced from reference.^[3]

Figure 2.5 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).^[3] Dark field imaging uses only those electrons which are diffracted by the sample to form the image.^[5] 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 an analytical technique used for elemental analysis and it is commonly used in conjunction with electron microscopy. EDX is capable of qualitative and quantitative analysis of the surface element composition of specific sample areas.^[9] For catalyst characterisation, coupling with TEM, it can provide chemical composition information on a certain particle, and elements distribution over the surface.^[9]

As previously described, the incident high energy electrons beam used in TEM can result in core electron ejection of the atoms and leave an energy hole. An outer electron moves down to fill the hole resulting in release the excess energy in the form of X-rays. The number and energy of the X-rays emitted from the specimen can be measured by an energy-dispersive spectrometer. The elemental composition can then be determined as the energy of the emitted X-ray is related to the energy of the orbitals and is characteristic for each element.

Compared to XPS where Auger emission is the prominent process for light elements, the X-ray emission increasingly dominates for elements heavier than magnesium giving EDX an enhanced sensitivity toward these elements.^[9] Quantitative analysis is carried out by monitoring counts of energy-specific charge/voltage pulses created by emitted X-rays interacting with a solid-state detector. 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 depth.^[9]

2.6 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is the most commonly used method of thermal analysis for quantitative data.^[4] The principle of TGA is to monitor the weight changes of the sample during a temperature programmed process, under a controlled atmosphere, and the change of sample weight is recorded. The properties of sample can be determined by the weight changes as a function of temperature.^[4] It can provide information about physical phenomena, including vaporization, sublimation, absorption, desorption, and chemical phenomena, including chemisorption, decomposition, oxidation, reduction and decomposition reactions.

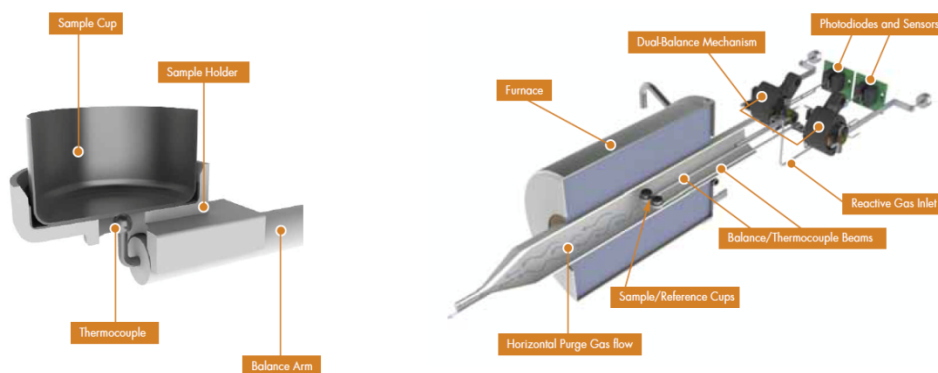


Figure 2.6 Schematic representation of major components of a TA instrument SDT Q600. Reproduced from reference.^[10]

The schematic for the major components of the TGA instrument used in this thesis is shown in Figure 2.6. For a typical TGA measurement, a small amount of sample (1-50 mg) was loaded into the sample pan. The temperature is controlled by the furnace and the environment is controlled with a reactive gas inlet. The weight of the sample is constantly monitored with a dual-balance system by comparing to a tare pan. The TGA is mainly used for catalysts stability analysis under stimulated reaction condition.

2.7 High-sensitivity low-energy ion scattering (HS-LEIS)

Low-energy ion scattering (LEIS) is a unique analytical technique that provides quantitative information on the composition of the outermost atomic layer of a solid-state surface.^[11] A problem of LEIS is that the bombarding ions can damage the sample surface. The development of High-Sensitivity LEIS (HS-LEIS) has enabled the use of low energy ions that the damage to surface is negligible. Comparing favourably to XPS, where the detection depth is several nanometres, HS-LEIS is specific for the detection of the outermost atomic layer.^[4] In heterogeneous catalysis,

reactions take place at the outer most atomic layer of solid catalysts.^[12] The utility of HS-LEIS can provide information on chemical composition of this layer, which is crucially important for the fundamental studies of catalysts.

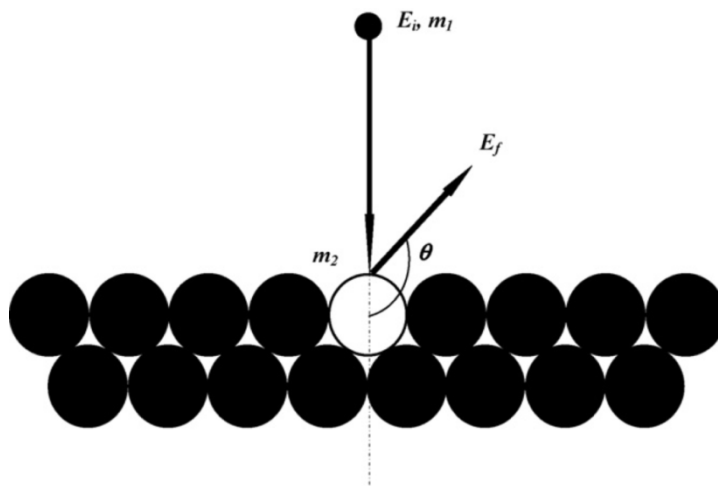


Figure 2.7 Schematic representation of the ion scattering process, where the energy, E_i , and mass m_1 of the primary ion are controlled in the experiment. The scattering angle, θ , is fixed for the instrument geometry. The final energy, E_f , is measured, which yields the mass of the surface atom, m_2 . Reproduced from reference.^[11]

The schematic representation of the principle of the HE-LEIS technique is depicted in Figure 2.7. Typically, a primary noble gas ion with a known energy, E_i , is aimed at the surface. The primary ion collides with the surface atom in a binary collision with a backscattered ion.^[11] The energy of the backscattered ion, E_f , is measured and can be summarized by the classic law of mechanics, Equation 2.7:

$$E_f = k^2 \left(\frac{m_2}{m_1}, \theta \right) E_i \quad \text{Equation 2.7}$$

where m_1 is the mass of the primary ion, m_2 is the mass of the scattering surface atom, and θ is the scattering angle (determined by the geometry of the instrument). θ , m_1 , and E_i are with known value, and E_f is measured with an energy analyser in a

standard experiment. The factor k^2 is a known function of $\frac{m_2}{m_1}$ and θ . The mass of the scattering surface atom can then be calculated from Equation 2.7. Only surface atoms with a mass lighter than the primary ion can be measured as the primary ion will scatter in the forward direction if it scatters from very light atoms. In many applications, the HE-LEIS spectra are measured with different primary ions. With 4He^+ , it gives the highest mass resolution and sensitivity for lighter surface atoms such as oxygen ($m = 16$ amu), aluminium (27 amu) and vanadium (51 amu).^[11] For identification of heavier surface atom, like molybdenum (96 amu) and tellurium (118 amu), the mass resolution can be improved by using 20Ne^+ ions. 40Ar^+ ion can be used if even heavier surface atom need to be discriminated.^[11] However, with a higher energy, 40Ar^+ ion will result in damaging the detected atomic layer. In this thesis, 4He^+ is used as initial primary ions for outermost atomic layer measurement and 40Ar^+ is used for characterization of core-shell structure nanoparticles layer by layer.

2.8 Atom probe tomography (APT)

Atom probe tomography (APT) is a microscopy technique provides extensive capabilities for 3D imaging and chemical composition analysis at the atomic scale (around 0.1-0.3 nm resolution in depth).^[13] The technique is a natural complement to other major microscopy techniques such as TEM and SEM, and APT provides the highest available spatial resolution for chemical analysis.

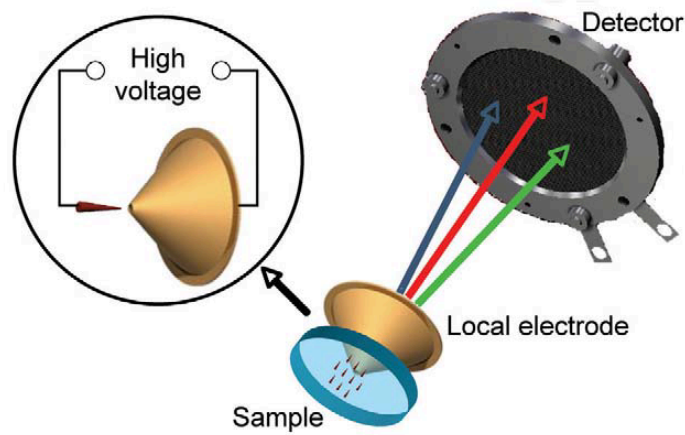


Figure 2.8(a) Schematic representation of a 3D local electrode atom probe. The atoms are field evaporated from the apex of a needle-shaped specimen by application of a high electric field between the counter (local) electrode and the specimen (as shown inset). (b) View of the LEAP™ 3000XSi in Oxford. Reproduced from reference.^{[14][13]}

The atom probe (AP) is consisted with a time-of-flight mass spectrometer and a point projection microscope capable of atomic-scale imaging.^[13] Combining this with position sensing, it permits full 3D reconstruction capabilities of APT. The principle of APT is based on the pulsed field evaporation of surface atoms and the identification of field evaporated ions by time-of-flight mass spectrometry.^[13] As shown in Figure 2.8(a), the sample is prepared in the form of a very sharp tip (< 100 nm radius). By

applying a high voltage (3-15 kV), a high electric field (10^{10} V/m) is created on the apex of the sharp specimen.^[13] Atoms on the specimen apex are field evaporated as ion and accelerated toward the imaging detector. It can be summarized by a simple point projection law:

$$F = \frac{V}{\beta R} \quad \text{Equation 2.8}$$

where F is the electric field, V is the applied electric voltage to the specimen, R is the tip radius and β is the field factor. The evaporation process is mostly thermally activated, considering the rate of evaporation for a given surface atom submitted to a field F , by the following Arrhenius equation:

$$K_e = v_0 \exp\left(-\frac{Q_n(F)}{k_B T_0}\right) \quad \text{Equation 2.9}$$

where T_0 is the operating temperature in APT, v_0 is the frequency of vibration of the surface atoms, of the order of 10^{12} - 10^{13} s⁻¹, k_B is the Boltzmann constant, and $Q_n(F)$ is the energy barrier that must overpass the atom to become an ion and be ejected from the tip surface.^[15] This energy barrier is strongly dependant on the field F present at the surface, and the height of the barrier continuously decreased with the applied field F . At a '*0 K evaporation field*', the barrier completely disappears.^[15] This law describes a critical field is required for efficient field evaporation and ion tunnelling is observed at a very low temperature, especially for low-mass atoms. APT is normally operated at cryogenic temperatures in range 20-150 K.^[13]

By pulsing the evaporation, the flight time of each ion can be measured and used to calculate the mass to charge ratio and thus determine its chemical nature. A 100 nm diameter area on the apex is projected onto the roughly 100 mm diameter detector, giving magnification of 10^6 .^[13] The original position of atoms on the specimen apex is determined from the hit position of the ions on the detector, while the sequence of

evaporation events is used to provide depth information. This combination of data allows 3D images of the element distribution to be reconstructed with near-atomic resolution.^[15]

2.9 Gas Chromatography

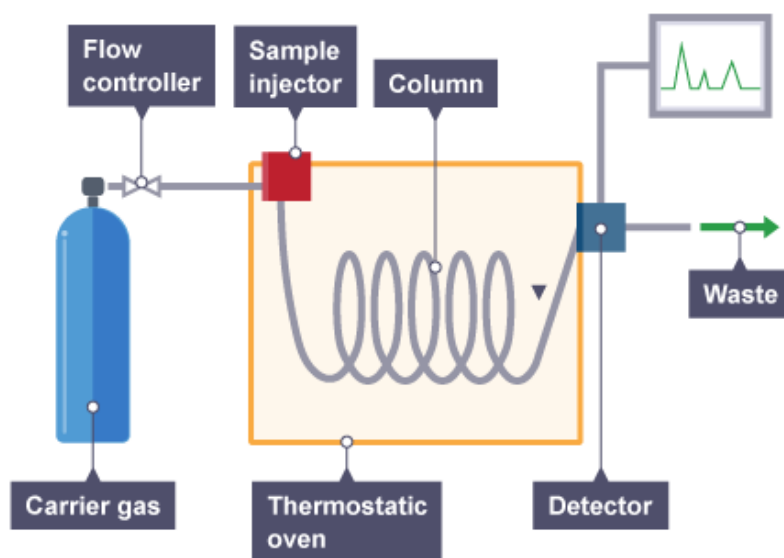


Figure 2.9 The illustration of Gas Chromatography. Reproduced from reference.^[16]

Gas chromatography is an analytical technique for separating and analysing various gases and volatile compounds from gas or liquid phase mixture. GC operates on the principle of differing adsorption/desorption properties between analyte within a sample and the stationary phase of the column. As shown in Figure 2.9, in a standard GC testing, the sample is injected from the sample injector and immediately heated to a certain temperature by a heating chamber to ensure vaporization of all components. The mobile phase is the carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. Helium remains the most commonly used carrier gas in about 90% of instruments although nitrogen is preferred for improved separation.^[17] The carrier gas transports sample through a column coated

with the stationary phase (often a high-molecular weight polymer coating). The gaseous compounds interact with stationary phase. Different compounds have different interaction performance, resulting in each compound to elute at different retention times.^[17] The identification peaks recorded by the detector connect to the column. The peak area can be used to quantitatively determine the analyte concentration. Separation of multiple compound can be achieved by optimizing differences in interaction strength between sample components and the stationary phase of the phase of the column.

The separation efficiency can be maximized by optimizing column resolution as determined by the number of theoretical plates.^[17] The plates number for a column is based on the number of plates that would theoretically be required for the separation process using a standard distillation column. Theoretical plates height is determined by calculating the length of column equal to single theoretical vector.^[17] The resolving power of a column is optimized by minimizing vector height based on the van Deemter equation (Equation 2.10):

$$H = A + \frac{B}{u} + (C_s + C_m) \cdot u \quad \text{Equation 2.10}$$

where H is height equivalent to a theoretical plate which is a measure of the resolving power of the column (m), u is the linear velocity of the carrier gas flow through the column. A is Eddy-diffusion parameter, which related to channelling the mixture of analyses and the carrier gas through a non-ideal column packing (m). B is the diffusion coefficient of eluting particles in the longitudinal direction, resulting in dispersion and is minimized by increasing the carrier gas flow rate. C is resistance to mass transfer coefficient of analyse between mobile and stationary phase and is minimized by decreasing the carrier gas flow rate. Both B and C have temperature

dependence. As a result, optimization of the column temperature and the carrier gas flow rate can balance all the three terms and minimize plate height, which is normally achieved experimentally through trial.

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3.1 Synthesis of Ag /Ln₂O₃ catalysts

The Ag/Ln₂O₃ catalysts were prepared in a one-pot polyol method.^[1] The catalytic supports are pre-treated at 600 °C for 4 hrs in N₂. In a standard synthesis, 20 mL ethylene glycol (EG) (99.8 purity, Sigma-Aldrich) was added into a 100 mL round bottom flask and heated to 130 °C under magnetic stirring. 5 mL of PVP solution (1 M in EG), 0.5 mL AgNO₃ solution (1 M in EG) and 5mL Ln₂O₃ solution (40 M in EG) were immediately added to the reactor respectively when the temperature reached 130 °C. The mixture was reacted for 1hr at 130 °C, then cooled down to room temperature. All the samples were collected by centrifugation (5000 rpm, 15 mins), then washed with acetone (once) and water (five times) to remove the excess amount of EG and PVP and dried in vacuum.

3.2 Synthesis of morphology-controlled Ag catalysts

3.2.1 Synthesis of Ag nanocubes

Ag nanocubes were synthesised using a polyol process reported by Xia and co-workers.^[2,3] In a standard synthesis, 5 mL ethylene glycol (EG) (99.8 purity, Sigma-Aldrich Cat No.324558) was added into a 50 mL round bottom flask and heated under magnetic stirring for 30 mins in an oil bath pre-set to 150 °C. 0.06 mL NaSH (3mM in EG, Sigma-Aldrich) was quickly injected into the solution when the temperature reached 150 °C. Two minutes later, 0.5 mL HCl solution (3mM in EG, 37% by weight, Sigma-Aldrich) was quickly injected into the heated solution followed by the addition of 1.25 mL poly(vinyl pyrrolidone) solution (PVP, 20mg/mL in EG, MW≈55,000, Sigma-Aldrich). A 30 mM HCl solution was prepared by adding HCl (37% by weight) into 5 mL EG first. The prepared solution was further diluted into a 3 mM

HCl solution. After another 2 min, 0.4 mL silver trifluoroacetate solution (282 mM in EG) was quickly added into the heated mixture. During the entire process, the flask was capped with a glass stopper except during the addition of reagents. The Ag nanocubes were achieved after 35 min reaction time. The reaction solution was quenched by placing the reaction flask in an ice-water bath. All the samples were collected by centrifugation (2200 rpm, 20 mins). The Ag nanocubes were then washed with acetone for 5 times to remove the remaining precursor, EG and excess PVP and stored in acetone solution in the dark.

3.2.2 Synthesis of Ag nanospheres

The Ag nanospheres were prepared using a similar method to Ag nanocube synthesis without the addition of capping agents (NaHS and HCl). In a standard synthesis, 5 mL ethylene glycol (EG) (99.8 purity, Sigma-Aldrich Cat No.324558) was added into a 50 mL round bottom flask and heated under magnetic stirring for 30 mins in an oil bath pre-set to 150 °C. 1.25 mL poly(vinyl pyrrolidone) solution (PVP, 20mg/mL in EG, MW $\approx$ 55,000, Sigma-Aldrich) was quickly injected into the solution when the temperature reached 150 °C. 2 min later, 0.4 mL silver trifluoroacetate solution (282 mM EG, $\geq$ 99.99% Sigma-Aldrich) was quickly add into the heated mixture. During the entire process, the flask was capped with a glass stopper except during the addition of reagents. The Ag nanospheres were achieved after 35 min reaction time. The reaction solution was quenched by placing the reaction flask in an ice-water bath. All the samples were collected by centrifugation (2200 rpm, 20 mins). The Ag nanospheres were then washed with acetone for 5 times to remove the excess PVP and stored in acetone solution in the dark.

3.2.3 Synthesis of morphology-controlled Ag /La₂O₃ and Ag /Al₂O₃ catalysts

The morphology controlled Ag catalysts were prepared using a volumetric impregnation method.^[4] The morphology-controlled Ag nanoparticles prepared as previously described were centrifuged and washed with dry-acetone for 5 times. The concentrated solutions of Ag nanoparticles in acetone were ready to be used as impregnation solution. The catalytic supports are pre-treated respectively. The La₂O₃ ($\geq 99\%$ purity, Sigma Aldrich) was calcined at 600 °C for 4 hrs in N₂ in a tubular furnace. The Al₂O₃ (activated, neutral, Brockmann Activity, Sigma-Aldrich) was calcined at 500°C for 4 hrs in air in a tubular furnace. In a typical preparation, a known amount of concentrated Ag nanoparticles solution was mixed and stirred with a certain amount of pre-treated supports. The obtained products were aged at room temperature under N₂ environment in dark for 4 hrs then dried at 100 °C. All the prepared catalysts were stored under N₂ environment in dark to prevent further oxidation or interaction with environmental water vapour.

3.3 Synthesis of the bimetallic catalysts

3.3.1 Synthesis of SBA-15

The ordered silica-block copolymer mesoporous SBA-15 was synthesized by a modified method according to Zhao & Stucky's work.^[5] In a standard preparation, 2 g of poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, $M_{av} = 5800$) was dissolved into 15 g of Milli-Q water and 60g of 2M HCl aqueous solution under stirring at 35-40 °C. 4.15 g of tetraethoxysilane (TEOS) was then added into the homogeneous solution. The mixture was stirred at 35-40 °C

for 20 h and crystallized at 100 °C for 2 days. The obtained solid product was then collected by filtering. The excess amount of P123 triblock copolymer was finally removed by calcination at 550 35-40 °C under air for 6 h to obtain Cal-SBA-15.

3.3.2 Synthesis of Ni@Ag/SBA-15 catalysts

The core@shell bimetallic Ni-Ag/SBA-15 catalysts with a silver loading of 5 wt% were prepared using a co-impregnation method according to our previous report.^[6] In a typical preparation, known amounts of AgNO₃ and Ni(NO₃)₂·6H₂O were dissolved in Milli-Q water. SBA-15 was then added to the prepared solution under vigorously stirred at room temperature, then the mixtures were subjected to aging for 12 h in dark and dried in oven at 100 °C overnight. The obtained sample was calcined at 350 °C in N₂ for 4 h and further reduced in dilute H₂ for 3 h to produce the Ni-Ag/SBA-15 catalyst. Ni-Ag/SBA-15 catalysts with variety of Ni Ag content, monometallic Ag/SBA-15 and Ni/SBA-15 were all prepared using the previously described method. The higher Ag content bimetallic catalysts were denoted as Ni_x-Ag₁/SBA-15, where x (0.2 and 0.4) represents the atomic ratio of Ni to Ag; and the low Ag content bimetallic catalysts were denoted as Ni₁-Ag_y/SBA-15, where y (0.4 and 0.2) represents the atomic ratio of Ag to Ni. Similarly, monometallic Ag/SBA-15 and Ni/SBA-15 were also prepared for the comparison testing.

3.4 Synthesis of the Ag zeolite catalysts

3.4.1 Zeolite pre-treatment

H-ZSM-5 zeolite (Al₂O₂:SiO₂=1:38.5) was obtained from SRIFT-Sinopec, China. The sample was first calcined in air at a ramp rate of 1 °C min⁻¹ to 450 °C for 2hrs upon

received. The sample was then cooled in dry air and stored under vacuum for further use.

3.4.2 Synthesis of the ion-exchanged AgZSM-5

The ion-exchanged AgZSM-5 samples with a silver loading of 2 wt% were prepared by a conventional ion-exchange method.^[7] In a typical preparation, a known amount of AgNO₃ was dissolved in 30 mL Milli-Q water. 1.5 g pre-treated ZSM-5 was then added to the prepared solution under vigorously stirred at 30 °C for 24 hrs in the dark. The sample was collected and washed by filtering. The obtained sample was calcined in N₂ at a ramp rate of 1 °C min⁻¹ to 450 °C for 2hrs, then cooled and stored under vacuum in dark for further use.

3.5 Catalytic testing

All the gas-solid phase fixed bed reactions were performed in a vertical tubular fixed bed reactor that allowed a three stages of temperature control throughout the whole reactor which delivers evenly distributed temperature. The gas flow was controlled and mixed by mass flow controller (Brooks SLA5850s mass flow controller) with an error range of ± 0.05 mL/min. The reactants and products were analysed online by a gas chromatograph equipped with a methanizer and a flame ionization detector (FID).

The conversion and selectivity results reported here for the gas-solid phase reactions were measured under steady state reaction conditions. Propylene oxide (PO) and carbon dioxide (CO₂) were observed as the principal products. The reaction conversion was calculated using the formula, $1 - C_P / (C_{PO} + C_{CO_2} / 3 + C_P)$, where C_{PO}, C_{CO₂} and C_P denoted the concentration of products PO and CO₂ and unreacted

propylene. The PO and CO₂ selectivity were calculated using the formulae $C_{PO}/(C_{PO}+C_{CO_2}/3)$ and $C_{CO_2}/3/(C_{PO}+C_{CO_2}/3)$, respectively. All the gas-solid phase reaction results reported in this thesis have calculated the carbon balance all over 92%. For all the reaction data presented in this this thesis has been repeated at least once to make sure that the results were repeatable.

3.5.1 Catalytic performance of metal oxides supported Ag catalysts

3.5.1.1 Direct propylene epoxidation with 5% Ag/Ln₂O₃

In a standard reaction, 100 mg of catalysts were packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The catalysts were pre-reduced at 250 °C for 2 hrs in 10% hydrogen in helium at a constant flow rate of 30 mL/min in the reactor before starting the reaction. For the propylene epoxidation reaction, the composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/min, which was delivered from the top of the reactor. A temperature program was used, beginning at 100 °C; at each reaction temperature, the reaction time test was held for 1 h allowing the GC to analyse the reaction products.

3.5.1.2 Direct propylene epoxidation with morphology controlled

Ag/La₂O₃ and Ag/Al₂O₃

In a standard reaction, 100 mg of catalysts were packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The catalysts were pre-reduced at 250 °C for 2 hrs in 10% hydrogen in helium at a constant flow rate of

30 mL/min in the reactor before starting the reaction. For the propylene epoxidation reaction, the composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/mins, which was delivered from the top of the reactor. A temperature program was used, beginning at 100 °C, at each reaction temperature, the reaction time test was held for 1 h allowing the GC to analyse the reaction products

3.5.2 Catalytic performance of Ni@Ag/SBA-15

3.5.2.1 Temperature effect on Ni_{0.4}-Ag₁/SBA-15 activity

In a standard reaction, 50 mg of Ni_{0.4}-Ag₁/SBA-15 was packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/mins, which was delivered from the top of the reactor and the reaction pressure was at 1 bar. A temperature program was used, beginning at 100 °C to 350°C, at each reaction temperature point (every 10 °C from 100-350 °C), the reaction was held for 1 h allowing the GC to analyse the reaction products.

3.5.2.2 Catalysts loading amount effect on the catalysts activity

The Ni_{0.4}-Ag₁/SBA-15 catalyst was tested for an isothermal reaction at optimised temperature 220 °C with 5 different loadings, namely: 50 mg, 100mg, 200mg 300mg and 500mg over Ni_{0.4}-Ag₁/SBA-15. In a standard reaction, a known amount of Ni_{0.4}-Ag₁/SBA-15 was packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20

mL/mins, which was delivered from the top of the reactor and the reaction pressure was at 1 bar. The isothermal reaction test was kept at 220 °C for 1 h allowing the GC to analyse the reaction products.

3.5.2.3 Catalytic performance of bimetallic Ni-Ag/SBA-15 catalysts

The catalysts performances, including Ag/SBA-15, Ni_{0.2}-Ag₁/SBA-15, Ni_{0.4}-Ag₁/SBA-15, Ni₁-Ag_{0.4}/SBA-15 and Ni₁-Ag_{0.2}/SBA-15, were tested for an isothermal reaction at optimised temperature 220 °C. In a standard reaction, 500 mg of catalyst was packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/mins, which was delivered from the top of the reactor and the reaction pressure was at 1 bar. The isothermal reaction test was kept at 220 °C for 1 h allowing the GC to analyse the reaction products

3.5.2.4 Catalyst stability of bimetallic Ni-Ag/SBA-15 catalysts

Catalysts stability tests, including Ag/SBA-15, Ni_{0.2}-Ag₁/SBA-15, Ni_{0.4}-Ag₁/SBA-15, Ni₁-Ag_{0.4}/SBA-15 and Ni₁-Ag_{0.2}/SBA-15, were conducted to evaluate the stability of the Ag structure during the selective oxidation reactions. In a standard reaction, 500 mg of catalyst was packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/mins, which was delivered from the top of the reactor and the reaction pressure was at 1 bar. The stability test was kept at 220 °C for 10 h, and the reaction products were analysed by GC every hour.

3.5.3 Catalytic performance of AgZSM-5

3.5.3.1 Gas-solid phase propylene oxidation reaction

Both AgZSM-5 and HZSM-5 were tested for the gas-solid phase propylene oxidation reaction. All the gas-solid phase reactions were performed in a vertical tubular fixed bed reactor that allowed a three stages of temperature control throughout the whole reactor which delivers evenly distributed temperature. The gas flow was controlled and mixed by mass flow controller (Brooks SLA5850s mass flow controller) with an error range of ± 0.05 mL/min. The reactants and products were analysed online by a gas chromatograph equipped with a methanizer and a flame ionization detector (FID).

In a standard reaction, 50 mg of catalyst was packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/min, which was delivered from the top of the reactor and the reaction pressure was at 1 bar. A temperature program was used, beginning at 100 °C to 350°C, at each reaction temperature point (every 10 °C from 100-350 °C), the reaction was held for 1 h allowing the GC to analyse the reaction products.

3.5.3.2 Liquid-solid phase propylene oxidation reaction

The liquid-solid phase batch reactions were conducted in a pressurized autoclave reactor.

3.5.3.2.1 Temperature effect

In a typical experiment, 20 mL of the Milli-Q water and 50 mg AgZSM-5 were mixed in the autoclave with a magnetic stirring bar. The Milli-Q water was saturated with a mixture of propylene and O₂ gas with a mixing ratio of 2:1. The reaction vessel was then sealed and flushed with gas mixture of 5% C₃H₆ in helium and 5% O₂ in helium with a mixing ratio of 2:1 to build up a high-pressure reaction condition (30 bar). The reaction tests were performed at various of reaction temperature (50°C, 100°C, 150°C and 200°C, respectively). For each temperature controlled reaction, the test was kept for 1h. After the reaction, the autoclave was cooled down to room temperature. The gas phase products were collected by 'downward displacement of water' method, and the volume of gas was measured by graduated cylinder. The liquid phase products were separated from the catalysts by filtration. Both the gas phase and liquid phase products were identified and quantified using a gas chromatograph (Agilent 7890) equipped with two TCD detectors and one FID detector calibrated with pure standards.

3.5.3.2.2 Catalyst Loading Effect

In a typical experiment, 20 mL of the Milli-Q water and a known amount of AgZSM-5 (50mg, 75mg, 100mg, 125mg and 150mg, respectively) were mixed in the autoclave with a magnetic stirring bar. The Milli-Q water was saturated with a mixture of propylene and O₂ gas with a mixing ratio of 2:1. The reaction vessel was then sealed and flushed with gas mixture of 5% C₃H₆ in helium and 5% O₂ in helium with a mixing ratio of 2:1 to build up a high-pressure reaction condition (30 bar). The reaction tests were performed at 50°C for 1h. After the reaction, the autoclave was

cooled down to room temperature. The gas phase products were collected by 'downward displacement of water' method, and the volume of gas were measured by graduated cylinder. The liquid phase products were separated from the catalysts by filtering. Both the gas phase and liquid phase products were identified and quantified using a gas chromatograph (Agilent 7890) equipped with two TCD detectors and one FID detector calibrated with pure standards.

3.5.3.2.3 Reaction Time effect

In a typical experiment, 20 mL of the Milli-Q water and 100mg of AgZSM-5 were mixed in the autoclave with a magnetic stirring bar. The Milli-Q water was saturated with a mixture of propylene and O₂ gas with a mixing ratio of 2:1. The reaction vessel was then sealed and flushed with gas mixture of 5% C₃H₆ in helium and 5% O₂ in helium with a mixing ratio of 2:1 to build up a high-pressure reaction condition (30 bar). The reaction tests were performed at 50°C for various of reaction time (1h, 5h, 10h, 15h, 20h, 25h and 30h, respectively). After the reaction, the autoclave was cooled down to room temperature. The gas phase products were collected by 'downward displacement of water' method, and the volume of gas were measured by graduated cylinder. The liquid phase products were separated from the catalysts by filtering. Both the gas phase and liquid phase products were identified and quantified using a gas chromatograph (Agilent 7890) equipped with two TCD detectors and one FID detector calibrated with pure standards.

3.6 Characterisation

3.6.1 Powder X-ray diffraction (XRD)

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

3.6.2 TEM and EDX

TEM was performed using the JEOL 2010 and JEOL 300 operating at 200 kV. EDX analysis was performed with the same microscope equipped with an Oxford instruments LZ5 windowless EDX spectrometer. Samples for TEM/EDX analysis were prepared by dispersing a small amount of material (typically 1 mg) in approximately 1 mL of ethanol. For the morphology controlled Ag nanoparticles, it was dispersed in acetone. One drop of the dispersion was placed onto a copper grid (holey carbon supported on copper, 400 mesh) and the solvent evaporated in air prior to analysis. Average particles size distributions and the histogram were calculated from the measurement of at least 150 individual particles.

3.6.3 High-resolution HAADF STEM

High-resolution electron microscopy of WO_x/USY was carried out using an aberration-corrected JEOL ARM200F. The microscope was operated at 200 kV in HAADF-STEM mode with HAADF detector collection semi-angles from 73 to 236 mrad. The convergence semi-angle was 31.48 mrad with probe array sizes of 1024 by 1024 and a dwell time of 0.8 μ s per pixel. The probe current was 11 pA.

3.6.4 Thermogravimetric analysis

Thermogravimetric analysis of samples was performed using a TA instruments TGA Q 50. 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 weighted by comparison to a reference pan. Samples were held isothermal at 35 °C for 5 min before heating to 600 °C with a ramp rate of 10 °C min⁻¹, followed by a further isothermal period of 30 min before cooling to room temperature. Changes in sample weight were monitored over time and with increasing temperature.

3.6.5 XPS

XPS analysis was performed on a VG Escalab XPS Spectrometer operating under ultra-high vacuum (1×10^{-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 1 to 1200 eV to identify elements present in the sample, and were compiled from 4 scans with 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 Bakkum.^[8]

3.6.6 APT

To prepare the APT sample, a drop of diluted Ag@Ni/SBA-15 colloidal dispersions was first placed onto a Si wafer. A 150 nm thick protective Cr-layer was then coated on top of the samples in the Cressington sputter coater. Needle-shaped APT specimens were prepared by means of a site-specific lift-out procedure using a FEI Helios G4 CX Nanolab focused ion beam (FIB)/scanning electron microscope. The APT experiments were conducted on a CAMECA LEAP 5000XR instrument equipped with an ultraviolet laser with a spot size of 2 μm and a wavelength of 355 nm. The detection efficiency of this state-of-the-art microscope is ~52%. Data was acquired in laser pulsing mode at a specimen temperature of 60 K, with a target evaporation rate of 5 ion per 1000 pulses, a pulsing rate of 120 kHz, laser pulse energy of 80 pJ. The APT data were reconstructed and analysed using the commercial IVAS 3.6.14TM software by Dr Tong Li of Ruhr-Universität Bochum.

3.6.7 SXRD

SXRD measurements were conducted on Beamline I11, Diamond Light Source (Diamond, Harwell, UK by Dr Ben Lo of our group. The energy of the incident X-ray flux was set at 15keV, the wavelength and the 2 θ -zero point were refined using a diffraction pattern obtained from a high-quality silicon powder (SRM640c),

corresponding to $\lambda=0.826617(4)$ Å and $2\theta_{ZP} = -0.000254(10)^\circ$. High resolution SXRD data were obtained from the zeolite samples using the multi-analyser crystals (MAC) detectors. The patterns were collected in the 2θ range $0-150^\circ$ with 0.001° data binning.

3.6.8 EXAFS

EXAFS measurements at the Ag K-edge and Ni K-edge were conducted on the B18 beamline at Diamond Light Source (Diamond, Harwell, UK) to obtain information about the local structure of the Ni-Ag catalysts by Ms Molly Meng-Jung Li of our group. Diamond installation comprises a 3 GeV electron storage ring with typical currents of 200mA, and B18 is a bending magnet beamline which has been designed to deliver monochromatic X-ray in the energy range of 2 to 35 keV. A Si (311) double crystal monochromator was used for energy selection with a resolution of 1 eV. Prior to the measurement, the samples were reduced in 5% H_2 - 95% N_2 . The reduced monometallic Ag/SBA-15, Ni/SBA-15 samples and bimetallic Ni-Ag/SBA-15 samples were loaded in the capillary tubes with the diameter of 3 mm. X-ray absorption spectroscopy data were collected at ambient temperature in transmission mode for the Ag K-edge measurements, while fluorescence spectra were acquired for the Ni K-edge measurements. Several scans were collected for each sample to get satisfactory data. The EXAFS data analysis was calibrated with foils as a reference to avoid energy shifts of the samples. The amplitude parameter was obtained from EXAFS data analysis of the foils, which was used as a fixed input parameter in the data fitting to allow the refinement in the coordination number of the absorption element. In this work, the first shell data analyses under the assumption of single scattering were performed with the errors estimated by R-factor.

3.6.9 HS-LEIS

All the experiments were performed in a combined elevated-pressure reaction cell-ultrahigh vacuum (UHV) system by Dr Jianwei Zheng of Xiamen University, China. Both sample preparation and testing were conducted in the primary UHV chamber (base pressure, 2×10^{-9} Torr). HS-LEIS were measured by IONTOFQtac100 using $^{20}\text{Ne}^+$ (5 keV) as ion source. The scattering angle was 145° .

3.7 Computational details

Density functional theory (DFT) calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) by Mr Zhi Qiang Wang of East China University at Shanghai.^[9] The exchange-correlation energy and potential were described by the generalized gradient approximation (GGA-PW91).^[10,11] The kinetic energy cut-off for the wave function expanded in the plane-wave basis was set as 400 eV. To optimize the structures, the calculation was performed until the maximum force upon each relaxed atom was less than 0.05 eV/Å. The vacuum height was set as 15 Å to eliminate the interaction between neighboring slabs. For bulk silver, the calculated lattice constant is 4.15 Å in better agreement with the experimental lattice constant (4.09 Å). The high-temperature A-form of La_2O_3 crystallizes in the experimental lattice constants are $a = b = 3.939$ Å and $c = 6.136$ Å.^[12] The optimized bulk lattice constants for La_2O_3 are $a = b = 3.920$ Å and $c = 6.093$ Å, in good agreement with the experimental values.

The adsorption energy (E_{ads}) was calculated as follows:

$$E_{\text{ads}} = -(E_{\text{total}} - E_{\text{substrate}} - E_{\text{gas-phase adsorbate}})$$

where E_{total} is the calculated total energy of the adsorption system, $E_{\text{substrate}}$ is the energy of the clean substrate and $E_{\text{gas-phase adsorbate}}$ is the energy of the gas-phase molecule.

The oxygen vacancies energy (E_{vac}) was calculated as follows:

$$E_{\text{vac}}(f) = E_{\text{vac}} + E_{\frac{1}{2}\text{O}_2} - E_{\text{st}}$$

where E_{vac} is the energy of the surface with one vacancy per supercell, $E_{\frac{1}{2}\text{O}_2}$ is half the energy of an O_2 molecule in the gas phase and E_{st} is the energy of the same supercell with no vacancy.

In order to study the adsorption of oxygen on gold surfaces, we used the following models: a 4×4 surface cell was used to construct a six-layer Ag(100) and Ag(111) slab. The top three layers of the Ag(100) and Ag(111) slab were allowed to relax. In addition, In order to study the oxygen vacancies energy on polar and nonpolar La_2O_3 surfaces, we used the following models: a 4×4 surface cell was used to construct a three-layer $\text{La}_2\text{O}_3(001)$ slab. The top two layers of the $\text{La}_2\text{O}_3(001)$ slab were allowed to relax.

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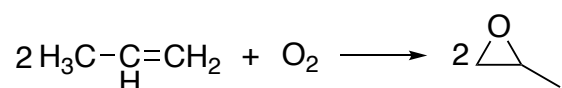
Chapter 4 Propylene epoxidation over La₂O₃ supported cubic silver

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4.1 Background

Propylene oxide is an important precursor to produce high value-added commodity chemicals. The current methods to produce propylene oxide with an industrial scale are the chlorohydrin process and hydroperoxide process.^[1] However, these two processes involve environment unfriendly substrates and side products with increasing production costs. Thus, the employment of direct heterogeneously catalysed epoxidation of propylene with molecular oxygen as an alternative route (Scheme 4.1) has been received considerable attentions.^[2-7]



Scheme 4.1 Direct propylene epoxidation with molecular oxygen.

Given the profound economic importance of these reactions, considerable research has been devoted to tailoring individual catalysts to achieve an optimal combination of activity and selectivity for this heterogeneous catalytic reaction. Silver based catalysts have been widely investigated and has been successfully used for ethylene oxide production on an industrial scale.^[8] Although the effects of catalyst support, metal particle shape and size on catalytic performance have been empirically studied in the past ^[9-11], the absence of a rational and systematic approach to develop direct propylene epoxidation catalysts prohibits their development. For direct propylene epoxidation, the use of silver catalysts always gives a very poor propylene oxide selectivity at extremely low conversions as compared to ethylene.^[2,10-12] In the last few decades, although numerous attempts have been made, the progress on improving catalytic activity for propylene epoxide is still not significant to approach to

industrial interest. A detailed understanding on the relationships between activity and selectivity to the variations in the Ag catalyst structure is therefore urgently required.

4.2 Objectives

This chapter will present a systematical study on the geometric and electronic effects of selected exposed specific Ag facets and supports towards the direct propylene epoxidation reaction. The study of the Ag catalyst support effect is accomplished by comparing conventional Al_2O_3 with the chosen series of lanthanide oxides (Ln_2O_3) as supports for Ag catalysts of controlled morphologies. Careful consideration will be given to experimental conditions with the goal of achieving maximum catalytic activity and selectivity. Most importantly, the reaction mechanism will also be elucidated from both experimental and theoretical studies to reveal some elementary reaction steps including molecular oxygen adsorption, dissociation and diffusion on specific Ag facets and Ag-oxide support interfaces. Thus, the findings from this chapter could therefore underpin the further works and discussions on subsequent chapters in developing a generic rational approach to optimise structure and morphology of Ag catalysts for improved catalytic performance.

4.3 Experimental details

Extensive experimental details of the synthesis procedures, characterisation methods and catalysis testing are given in chapter three, a brief summary of catalysts synthesis is given here.

The conventional Ag catalysts with different supports were prepared in a one-pot polyol method.^[13] A chosen series of commercially available Sigma-Aldrich

lanthanide oxides (Ln_2O_3) of few m^2g^{-1} surface areas were used as metal oxide supports for the Ag based catalysts, which include La_2O_3 from early lanthanide series, Gd_2O_3 , Eu_2O_3 from middle lanthanide series and Yb_2O_3 , Lu_2O_3 from late lanthanide series. A commercial high surface area $\gamma\text{-Al}_2\text{O}_3$ ($150\text{m}^2\text{g}^{-1}$)^[14] was used as the standard metal support for comparison. In a standard synthesis, 20 mL ethylene glycol (EG) was added into a 100 mL round bottom flask and heated to 130 °C under magnetic stirring. The EG was used as a reducing agent for the syntheses of Ag and was pre-heated to 130 °C to ensure the reduction rate is consistent for all syntheses. To prepare 5 wt% Ag catalysts, a known amount of PVP solution (1 M in EG), AgNO_3 solution (1 M in EG) and Ln_2O_3 solution (40 M in EG) were quickly added to the reactor respectively when the temperature reached to 130 °C (PVP to Ag molar ratio is 10 to 1). The mixture was reacted for 1hr at 130 °C to allow all AgNO_3 be reduced to Ag^0 , then cooled down to room temperature in ice-water bath to prevent further sintering. All the samples were collected by centrifugation (5000 rpm, 15 mins), then washed with acetone (once) and water (five times) to remove the excess amount of EG and PVP and dried in vacuum.

Morphology controlled Ag nanoparticles were synthesised using a modified polyol process reported by Xia and co-workers.^[15,16] For Ag nanocube preparation, in a standard synthesis, 5 mL ethylene glycol (EG) was added into a 50 mL round bottom flask and heated under magnetic stirring for 30 mins in an oil bath pre-set to 150 °C. 0.06 mL NaSH (3mM in EG) was quickly injected into the solution when the temperature reached to 150 °C. Two minutes later, 0.5 mL HCl solution (3mM in EG) was quickly injected into the heated solution followed by the addition of 1.25 mL PVP solution (20mg/mL in EG, $\text{MW}\approx 55,000$). Both NaSH and HCl were used as capping

agent to enable a more favourite growth of Ag(100).^[17] After another 2 min, 0.4 mL silver trifluoroacetate solution (282 mM EG, $\geq 99.99\%$) was quickly added into the heated mixture. During the entire process, the flask was capped with a glass stopper except during the addition of reagents. The Ag nanocubes were achieved after 35 min reaction time. The reaction solution was quenched by placing the reaction flask in an ice-water bath to prevent further reaction. All the samples were collected by centrifugation (2200 rpm, 20 mins). The Ag nanocubes were then washed with acetone for 5 times to remove the remaining precursor, EG, excess capping agent and PVP. The Ag nanospheres were prepared using a similar method to Ag nanocubes synthesis but without the addition of capping agents (NaHS and HCl). All the morphology-controlled Ag nanoparticles were kept in acetone for further use. It was found that Ag particles have maintained a stable morphology in acetone for at least 3 months. The morphology controlled Ag catalysts were then prepared using a volumetric impregnation method. The obtained products were aged at room temperature under N₂ environment in dark for 4 h then dried at 100 °C. All the prepared catalysts were stored under N₂ environment in dark to prevent further oxidation or interaction with environmental water vapour.

4.4 Results and Discussion

4.4.1 Support effect of Ln₂O₃

Many previous research works were experimentally attempted to explore the catalyst support effects for direct propylene epoxidation.^{[18][5,19]} Conventional metal oxides, semiconductor materials and a range of zeolites were all studied.^[20] Most of them gave an extremely low selectivity for selective oxidation product. As far as we are aware, lanthanide metal oxides (Ln₂O₃) have not been systematically studied due to

their generally low surface areas. As a result, chosen elements of Ln_2O_3 were herein used as catalyst supports for the systematic screening reaction tests. Ln_2O_3 was chosen from early, middle and late lanthanide series elements, and conventional $\gamma\text{-Al}_2\text{O}_3$ was used as industrial support for comparison. The $\text{Ag/Ln}_2\text{O}_3$ and $\text{Ag/Al}_2\text{O}_3$ with a Ag loading of 5 wt% were synthesised by a one-pot polyol method;^[13] this preparation method is commonly used for the synthesis of narrow distributed metal nanoparticles with a good metal-support interaction over the support.

The catalytic selective propylene oxidation tests of all as prepared 5 wt% Ag catalysts were performed in a vertical tubular fixed bed reactor at 1 bar with a total gas flow rate of 20 mLmin^{-1} . The composition of the gas mixture was 5% C_3H_6 in helium and 5% O_2 in helium with a mix ratio of 2:1. The reaction products were analysed by a gas chromatograph equipped with a methanizer and a flame ionization detector (FID), as described in Chapter 3. All the selected metal oxide supports were initially tested under the same reaction condition. The results show that none of the supports exhibit activity towards propylene oxidation.

The catalytic performance of all catalysts is shown in Figure 4.1 with a form of selectivity of PO and rate of PO versus support being tested at 250°C . Very interestingly, it can be seen that both the selectivity and production rate of PO can be significantly influenced by the catalyst support. Among as-prepared $\text{Ag/Ln}_2\text{O}_3$ catalysts, a higher activity towards PO can be observed when early and middle lanthanide series metal oxides were used. However, we observe both combustion and epoxidation reaction products, CO_2 and propylene oxide, respectively, over $\text{Ag/La}_2\text{O}_3$, $\text{Ag/Gd}_2\text{O}_3$ and $\text{Ag/Eu}_2\text{O}_3$. $\text{Ag/La}_2\text{O}_3$ is catalytically more active than the

Ag/Gd₂O₃ and Ag/Eu₂O₃. According to Figure 4.1, at 250 °C, the highest PO selectivity of 15% is observed on Ag/La₂O₃, followed by 11% on Ag/Gd₂O₃ and 7.6% on Ag/Eu₂O₃. The selectivity of PO from Ag/Ln₂O₃ is ranked according to the order Ag/La₂O₃ > Ag/Gd₂O₃ > Ag/Eu₂O₃. The production rate of PO normalized to the specific surface area of Ag nanoparticles also follows the order Ag/La₂O₃ > Ag/Gd₂O₃ > Ag/Eu₂O₃. A remarkably high production rate of 0.96 μmol/g/s is observed from the figure over Ag/La₂O₃, which is 2 times higher than over Ag/Gd₂O₃ and nearly 8 times higher than over Ag/Eu₂O₃. However, when late lanthanide series metal oxides were used as catalyst supports, no epoxidation reaction could be observed. Production rate of PO was 0 over both Ag/Yb₂O₃ and Ag/Lu₂O₃. Thus, Ag/Yb₂O₃ and Ag/Lu₂O₃ showed no activity in catalysis of propylene to propylene oxide in the presence of O₂. When the conventional industrial catalyst Ag/Al₂O₃ was used both combustion and epoxidation products were observed at 250 °C. As seen in Figure 41, the selectivity for the formation of propylene oxide is 4% over Ag/Al₂O₃, and the rate of propylene oxide formation is only 0.02 μmol/g/s. Thus, the Ag/Al₂O₃ showed an extremely low activity in propylene epoxidation with O₂ regarding both the selectivity and production rates, despite its apparently much higher surface area of this support. Compared to Ag/Al₂O₃, all the Ag/La₂O₃, Ag/Gd₂O₃ and Ag/Eu₂O₃ were more active in catalysing propylene oxide formation. The screening test over various metal oxides supported Ag nanoparticles clearly shows that the propylene epoxidation with O₂ depends sensitively on the nature of catalyst support used. Amongst all the five catalysts, the La₂O₃ supported Ag catalyst gives the best selectivity and productivity toward the epoxide product. But, both early and middle lanthanide series metal oxides deliver better catalytic activity than Al₂O₃ when used

as the catalyst support. Thus, we have demonstrated Ln_2O_3 as a novel class of potential support for Ag nanoparticles in selective propylene epoxidation reaction.

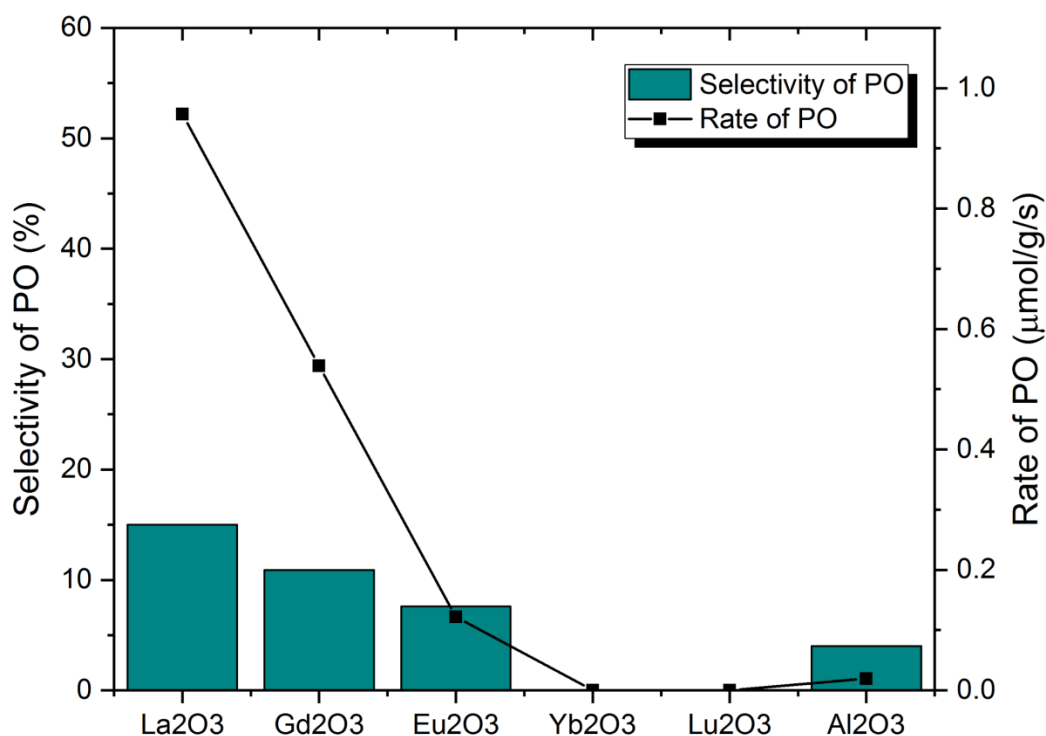


Figure 4.1 Selectivity of propylene oxide (PO) and productivity rate of propylene oxide (per gram of silver) on Ln_2O_3 ($\text{Ln} = \text{La}, \text{Gd}, \text{Eu}, \text{Yb}, \text{Lu}$) and Al_2O_3 supported Ag catalysts (catalysts loading amount of 50mg for all reactions) at 250 °C.

To further rationalize the support effect, the surfaces of $\text{Ag/Ln}_2\text{O}_3$ catalysts were characterized using X-ray photoelectron spectroscopy (XPS). The obtained XPS spectra for O are shown in Figure 4.2. The broadened peak after deconvolution fitting suggests that there are three types of oxygen species on all the materials surfaces. The details of peak deconvolution can be found in Chapter 3. According to

the literature, a satisfactory deconvolution of the O 1S spectra of lanthanide oxides is also achieved with three components: two well defined peaks on low binding energies (BEs) and one component with a broad shoulder on high BE.^[21] For Ag/La₂O₃, the lowest intense peak labelled as O_γ is located at 534.2 eV BE, which is close to literature values reported for the characteristic of OH⁻^[22] and CO₃²⁻^[23,24] on lanthanide surface. This can be attributed to the interaction between environmental water/carbon dioxide from air with the La₂O₃ surface, resulting in the formation of hydroxyl groups or carbonate groups. The O_α peak at 528.5 eV BE is fitted well inside the notably wide range of energies reported for lattice oxygen in lanthanum oxide (following BE have for example been reported: 528.4-532.8 eV,^[25] 528.4 eV,^[23] 529.8 eV,^[22] 529.9 eV,^[24] 530.5 eV^[26]). Thus, this region can be comfortably assigned to the lattice oxygen peak of lanthanide. It is interesting to reveal an intense O_β peak at about 531.6 eV BE which has been attributed to surface adsorbed oxygen species.^[22] Their quantifications caused a large deviation from the expected surface stoichiometry in our measurements. Thus, from the XPS study, one can see the presence of a significant amount of surface oxygen species existed at the interface of Ag-lanthanide oxide catalysts. La₂O₃ as an example, according to the literature, La₂O₃ has a hexagonal structure in which all the lanthanum atoms have equivalent positions with a seven-fold coordination to lattice oxygens.^[27] However, the oxygen atoms are distributed on two different sites, a four-coordinated position with the La-O bond lengths being between 2.36 and 2.42 Å and a six-coordination position with La-O bond lengths equal to 2.72 Å.^[21,27] The surface structure of La₂O₃ is not stable which may host some surface oxygen vacancies for the both two oxygen positions. Molecular oxygen or water from air can adsorb and dissociate on the vacancy of the lanthanide surface.^[28] Previous bond valence

calculations performed on La_2O_3 indicated a significantly lower negative charge on surface oxygen than lattice oxygen, and thus, leading to its higher BE.^[29–31] This surface adsorbed oxygen specie as a higher BE also indicates the nature of oxygen is approaching towards more electrophilic rather than the nucleophilic nature of lattice oxygen.^[31] As previously mentioned, an adequate peak deconvolution could be achieved with three well separated oxygen components for all the other $\text{Ag/Ln}_2\text{O}_3$ materials (see Table 4.1). Particularly, the amount of electrophilic surface O_β follows the order $\text{Ag/La}_2\text{O}_3 > \text{Ag/Gd}_2\text{O}_3 > \text{Ag/Eu}_2\text{O}_3 > \text{Ag/Yb}_2\text{O}_3 > \text{Ag/Lu}_2\text{O}_3$, which correlates with the order of their catalytic performances (decreasing selectivity and production rate of PO).

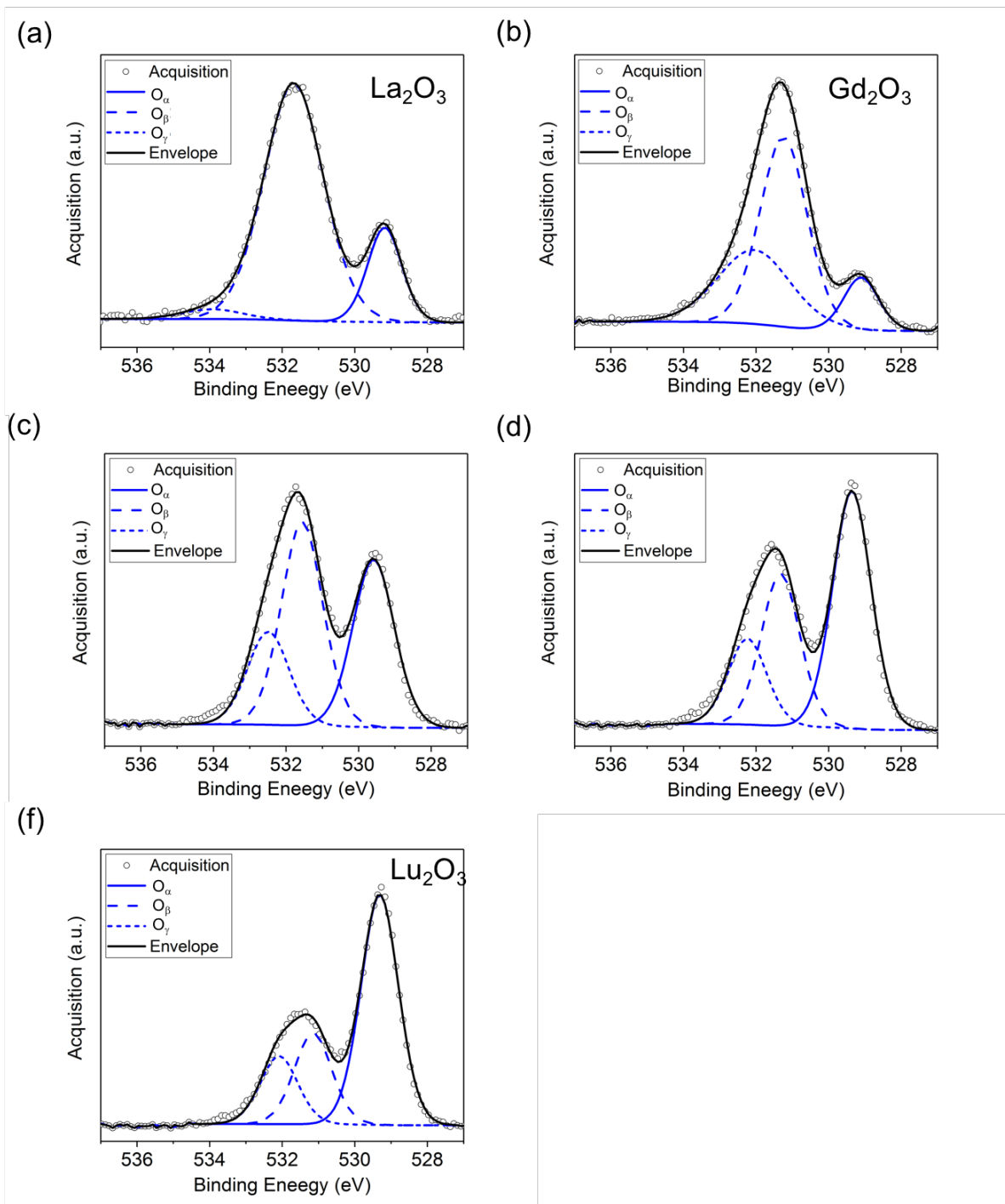


Figure 4.2 XPS of O 1s region for Ag/Ln₂O₃ (From top to bottom: Ln= La, Gd, Eu, Yb and Lu) with the peak fitting components. O_α: lattice oxygen, O_β: mobile surface oxygen, and O_γ oxygen from the hydroxyl groups or carbonate groups. Details in attribution of the different oxygen chemical states were discussed in the text.

Table 4.1 Deconvolution of oxygen peaks over the Ln₂O₃-supported Ag catalysts

Oxygen species	La ₂ O ₃	Gd ₂ O ₃	Eu ₂ O ₃	Yb ₂ O ₃	Lu ₂ O ₃
O _α	21.6	12.3	35.5	45.7	54.2
O _β	74.2	55.3	42.6	31.1	25.2
O _γ	4.2	32.4	21.9	23.2	20.6

To have a clear illustration of the relationship between the electrophilic O_β species and the selective propylene oxidation reaction, Figure 4.3 shows the plots of production rate of PO against O_β (%) over all the Ag/Ln₂O₃ surfaces.

As shown in Figure 4.3, The amount of O_β on Ag/Ln₂O₃ surface is found to decline dramatically decreased from early lanthanide oxide to late lanthanide oxide support. According to Table 4.1, Ag/La₂O₃ gives 74% O_β of all oxygens, followed by 55% of Ag/Gd₂O₃, 42% of Ag/Eu₂O₃, 31% of Ag/Yb₂O₃, and 25% of Ag/Lu₂O₃. It can be clearly seen that the production rate of propylene oxide from Figure 4.3 is also decreased following the same order that Ag/La₂O₃ > Ag/Gd₂O₃ > Ag/Eu₂O₃ > Ag/Yb₂O₃ > Ag/Lu₂O₃. The nucleophilic C=C in propylene can be more selectively attracted by electrophilic species. Combining with the experimental results, it is thus logical to believe that the production rate of propylene oxide can be significantly influenced by the amount of electrophilic O_β presented on the Ag/Ln₂O₃ surface with lower BE than that of nucleophilic lattice oxygen. The highest O_β content on Ag/La₂O₃ matches with the best propylene oxide productivity measured from the experiment. Similarly, when O_β decreases, the propylene oxide productivity is also decreased from Ag/La₂O₃ to Ag/Lu₂O₃, Ag/Yb₂O₃ and Ag/Lu₂O₃ accordingly.

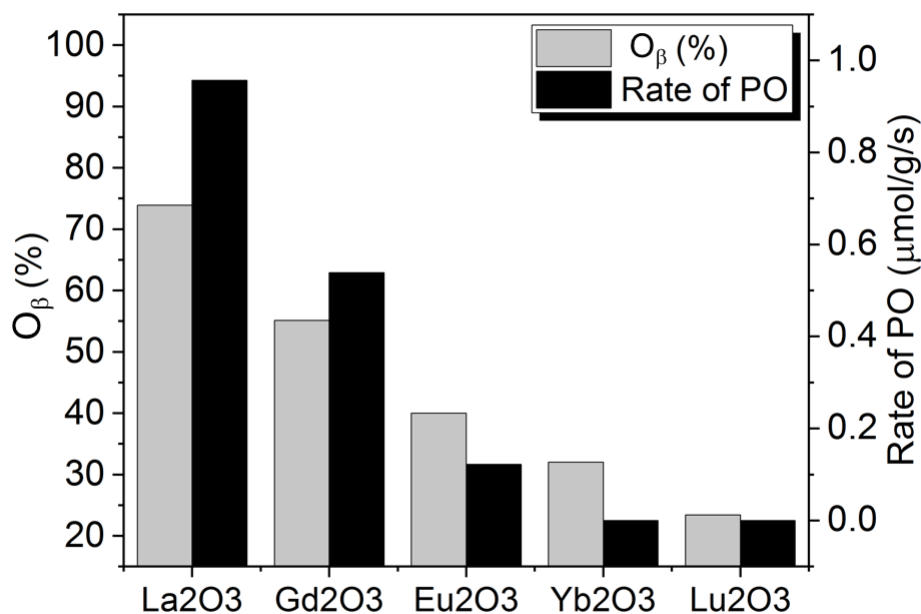


Figure 4.3 Production rate of PO and O_{β} (%) on the series of Ag/ Ln_2O_3 catalysts (Ln= La, Gd, Eu, Yb and Lu).

4.4.2 Shape effects of Ag nanoparticles

It is generally accepted that the catalytic performance of nano-catalyst can be altered by the morphology of metal nanocrystal being used.^[32] Different shapes of Ag nanoparticles could affect the selectivity of ethylene oxide in direct ethylene epoxidation on aluminium oxide supported Ag catalysts.^[12,33] DFT calculations also revealed that enhanced selectivity can be attributed to the use of higher Ag(100) content from other facets ^[12] Recently, Corma and co-workers reported the effect of

different Ag facet in selective propylene oxidation based on theoretical calculations.^[34] They concluded that Ag(100) provides a more active and selective surface in the activation of dioxygen for the formation of propylene oxide in partial air oxidation of propylene as compared to Ag(111).^[34] However, further experimental proof and a systematic comparison of supported Ag nanoparticles of controlled morphologies for the direct propylene epoxidation are required.

To study the shape effects of Ag nanoparticles, two different kinds of Ag nanoparticles with unique morphologies have been carefully prepared. The challenge in syntheses was to produce uniform Ag nanoparticles with controlled morphologies for their comparison. We have thus modified a polyol method reported by Xia and co-workers^[15,16] to prepare high quality of Ag nanocubes and Ag nanospheres, respectively. La_2O_3 has been selected as the catalyst support as this support phase gives propylene epoxide in good selectivity. Al_2O_3 has also been used as support for the direct comparison. Their catalytic performances were tested followed the method as described in Chapter 3.

The morphology-controlled Ag nanoparticles were characterized by XRD. The XRD pattern with reference peaks from bulk silver is given in Figure 4.4. The XRD pattern of Ag nanoparticles confirms that both as-prepared Ag nanocubes and nanospheres are in the form of highly crystalline fcc silver structure (JCPDF 87-0597). According to the figure, the XRD pattern of Ag nanospheres shows a most intense Ag(111) peak, which indicates the nanospheres were overwhelmed by the lower energy {111} facets. For single crystalline Ag nanocubes, a significant change in the relative intensity of (111) and (200) peaks in the XRD pattern corresponding to a change in

morphology can be clearly seen. The most intense (200) peak (the higher ratio of (200) to (111)) can be ascribed to the texturing effect of the ordered nanocubes on the flat substrate. With the preferential orientation, $\langle 200 \rangle$ is perpendicular to the substrate, it is indicative that most cubes were aligned on the substrate with $\{100\}$ facets being oriented upward.

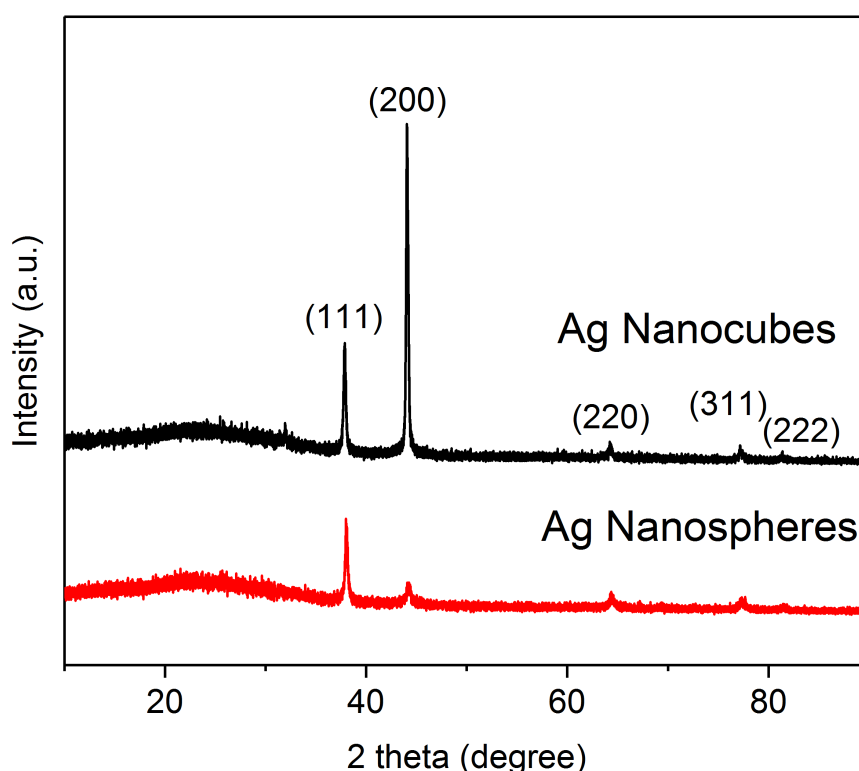


Figure 4.4 XRD patterns of morphology-controlled Ag nanocrystals a) upper black solid line represents the Ag nanocube sample, b) lower red solid line represents Ag nanospheres.

As mentioned earlier, the La_2O_3 surface is normally unstable and non-stoichiometric when exposed to air. To ensure a high quality La_2O_3 phase the materials were calcined and annealed at 600 °C for 4h and kept in dry N_2 environment before use.

The XRD pattern of pre-treated La_2O_3 is shown in Figure 4.5. It confirms the distinctive hexagonal La_2O_3 (JCPDF 02-0688). The La_2O_3 (100) peak indirectly indicates the existence of this polar surface on La_2O_3 as a part of the crystal terminated facets.

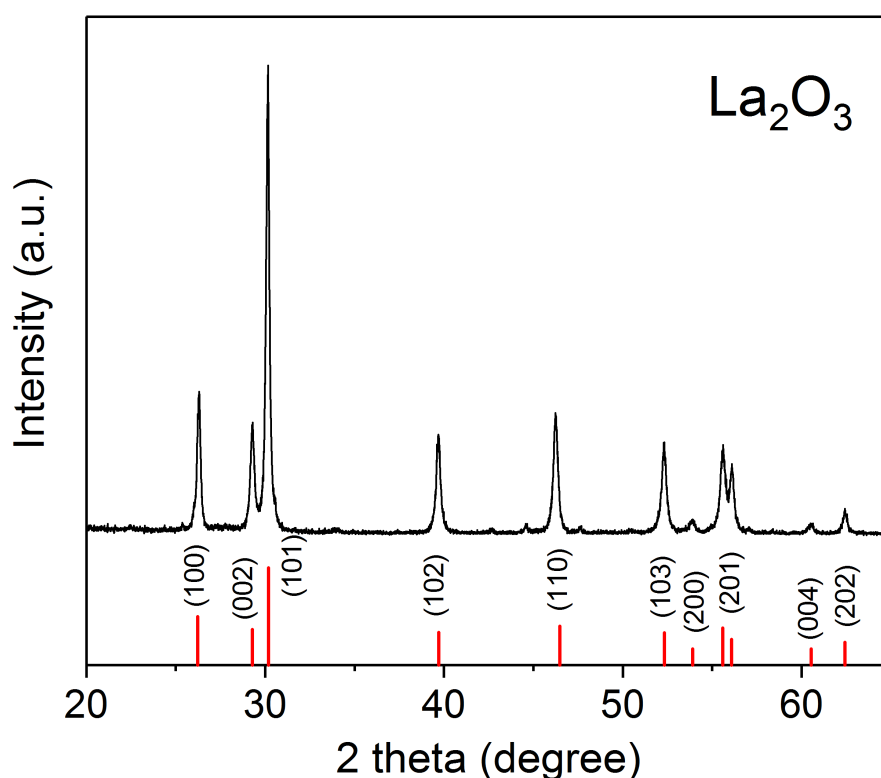


Figure 4.5 XRD patterns of pre-treated La_2O_3 (calcined at 600 °C, 4h).

The morphology controlled Ag nanoparticles were further characterized by TEM in order to determine average particle size and morphology. Figure 4.6 shows a typical TEM micrograph along with the corresponding size distribution histogram for morphology-controlled Ag nanoparticles. The TEM images results show no significant aggregation for both Ag nanocubes and nanospheres, and the particles

are nearly mono-disperse such that majority of cubes were aligned on the TEM grid being oriented upward, which is in agreement with the XRD results. More than 80% of the Ag nanocubes sample have an identical cubic shape with round corners. According to the histogram of particle size distribution, the Ag nanocubes have an average edge length of 45 nm. There are, however, very few number of particles that appear to be in a short rod shape. The Ag nanosphere samples are also present a narrow size distribution with an average particle diameter of 42.3 nm, and a narrow size distribution. The sample presented particles of nearly identical spherical morphology. The similar average size of Ag nanocubes and nanospheres may eliminate the complex size effect when tested for the catalytic reaction.

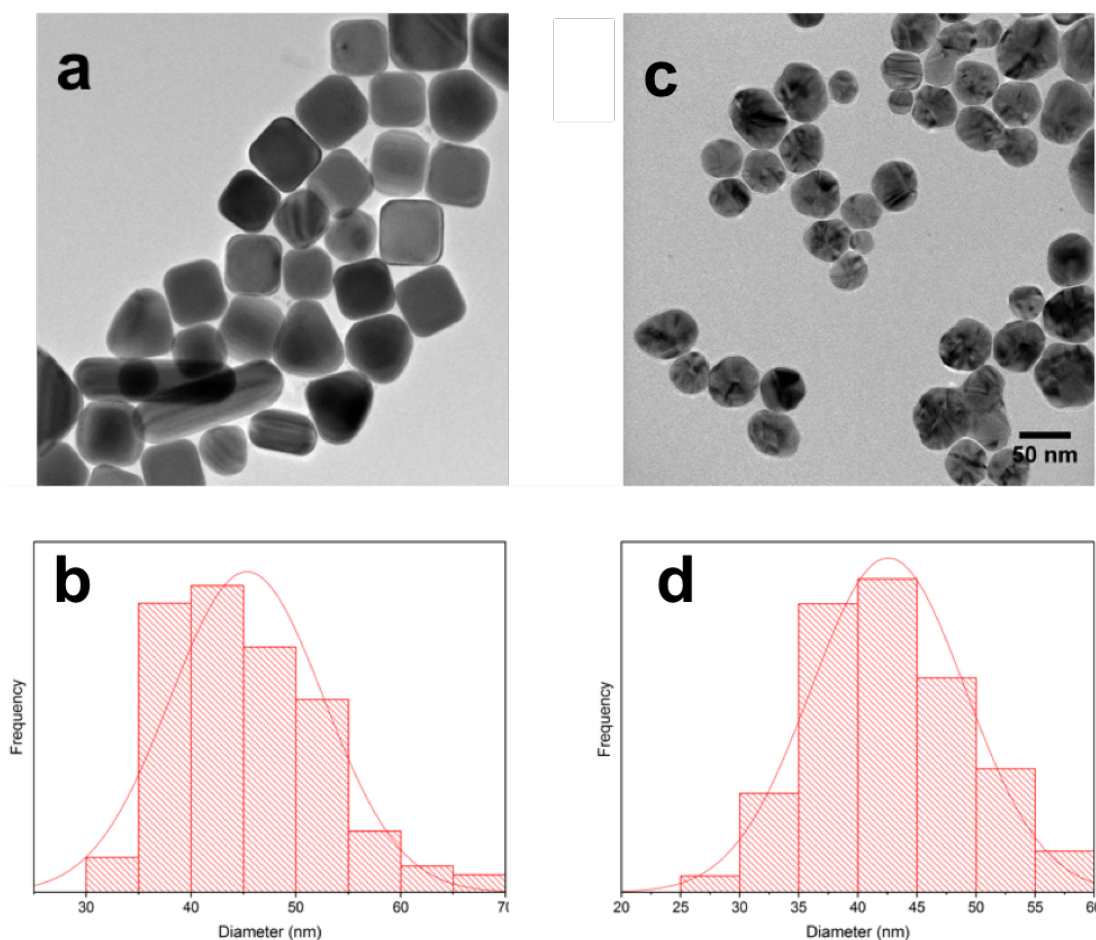


Figure 4.6 TEM images of a) Ag nanocubes (average edge length of 45nm); b) size distribution of Ag nanocubes; c) Ag nanospheres (average diameter of 42.3 nm size; d) distribution of Ag nanospheres.

A STEM image of a representative Ag nanocube is displayed in Figure 4.7. It shows that the average d-spacing values of $2.0 \text{ \AA}$ for Ag nanocube, which can be assigned to the d-spacing of $\{200\}$ facets within experimental error for (fcc) Ag.^[15] This measured crystal plane to plane distance agrees with our XRD results as well as the literature. The $\langle 200 \rangle$ indicates that the Ag nanocubes surfaces are all bounded by $\{100\}$ facets.^[35–37] Accordingly, the conventional polycrystalline Ag nanospheres are mostly terminated with more energetically favourable Ag(111), which suggests that the exposed facets are mainly in forms of Ag(111).^[38]

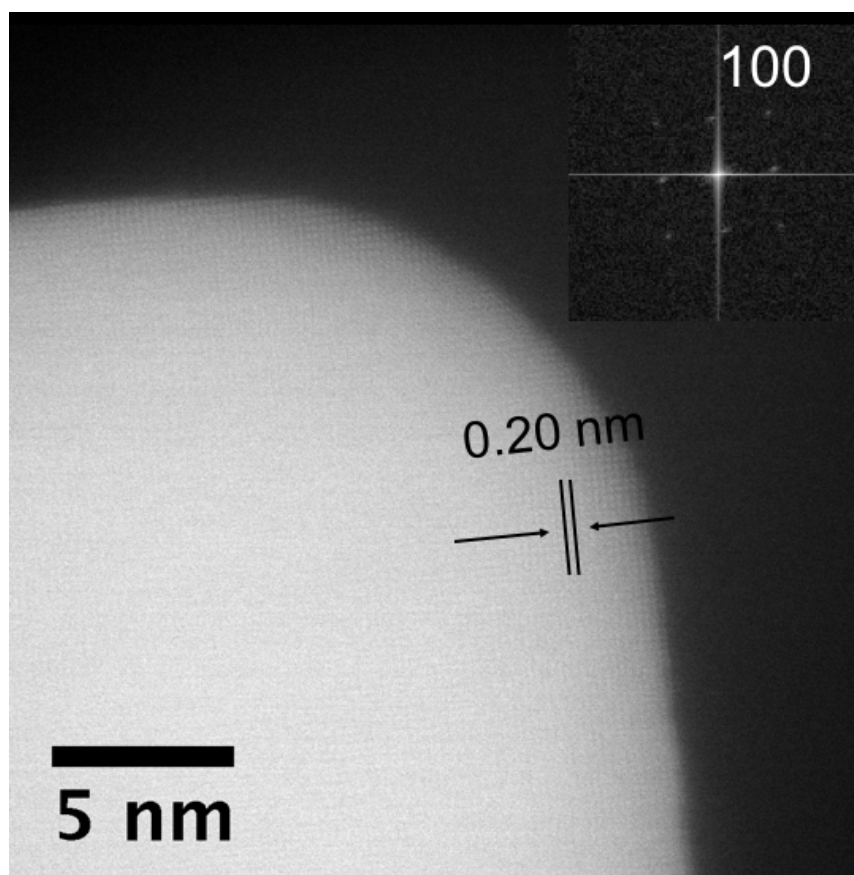


Figure 4.7 HAADF-STEM micrograph (dark field mode) of Ag nanocube showing corresponding d-spacing: the inner image on top right-hand corner shows corresponding Fourier Transform (FT) pattern.

The shape-controlled Ag nanoparticles were then deposited onto La_2O_3 and Al_2O_3 using a wet impregnation method. The overall characteristics of the Ag nanoparticles appeared similar to those of the as-synthesised Ag nanoparticles. The Ag nanoparticles maintained their morphologies and sizes unchanged after impregnation. Both Ag nanocubes and nanospheres gave good distributions over the two supports. The TEM results depicted in Figure 4.8 show that the as-prepared catalysts contain the morphology-controlled Ag nanoparticles allowing direct comparison in propylene-air epoxidation.

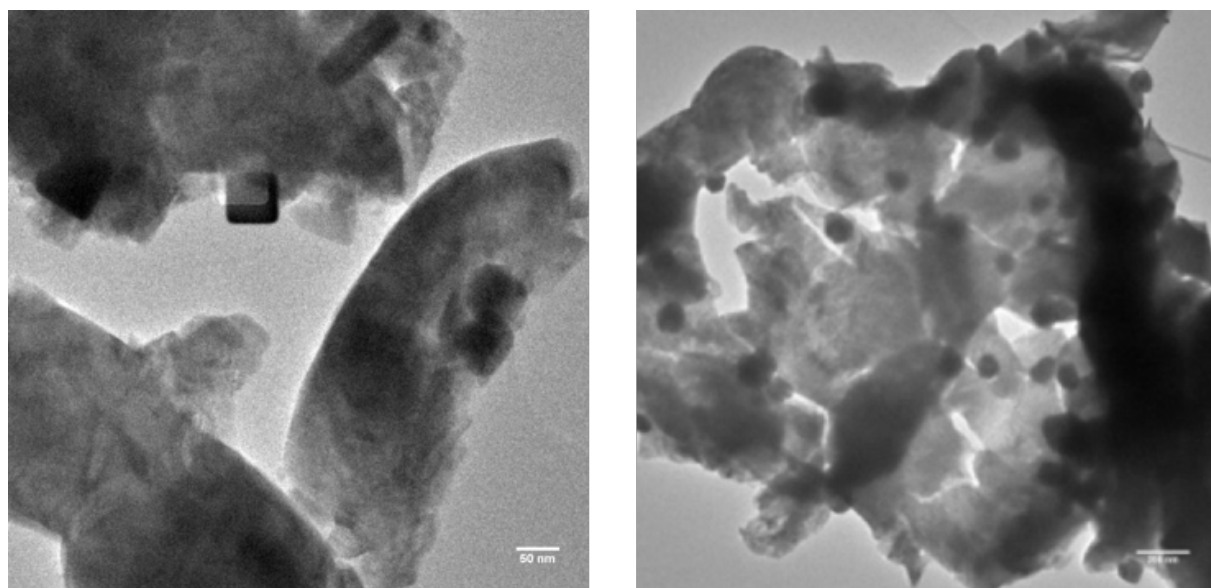


Figure 4.8 TEM images of left: Ag nanocubes/La₂O₃, right: Ag nanospheres/La₂O₃

The catalyst performance was evaluated under temperature programmed reaction conditions and the results were presented in Figure 4.9. The formation of propylene oxide starts to be observed at 250°C for all catalysts. The highest PO selectivity on Ag nanospheres/Al₂O₃ is 4% at 250°C. On the other hand, the selectivity of propylene oxide is slightly increased to 8% when using Ag nanocubes/Al₂O₃ at the same temperature. For both Al₂O₃ supported Ag catalysts, the selectivity of propylene oxide decreases as the temperature increases, and at higher temperature (290 °C) the selectivity towards propylene oxide nearly drops to 0%, which indicates the formation of combustion product CO₂ as majority. Both Al₂O₃ supported Ag catalysts show a very poor production rate of propylene oxide, although a slightly increase in PO production rate of 0.04 μmol/g/s has been observed on Ag nanocube/Al₂O₃ as compared to 0.02 μmol/g/s on Ag nanospheres/Al₂O₃. The

production rate of propylene oxide also decreases as the temperature increases in a similar trend with the selectivity.

It is notable that a remarkable enhancement of propylene oxide selectivity is observed in Figure 4.9 when La_2O_3 supported Ag catalysts was studied. As shown in Figure 4.9 for Ag nanospheres/ La_2O_3 , the selectivity towards propylene oxide is 15% at 250 °C, and slightly drop to 11% when the temperature increases to 290 °C. On the other hand, the propylene oxide selectivity is dramatically enhanced by Ag nanocubes/ La_2O_3 with a 36% at 250°C, which is two times higher than over Ag nanospheres/ La_2O_3 . As the temperature is raised, the selectivity of propylene oxide continuously increases to the highest value of 50% at 270 °C and maintains at around 47% at 280 and 290 °C over the Ag nanocubes/ La_2O_3 . It is also noticed that unlike Al_2O_3 support, the productivity of PO over La_2O_3 supported Ag catalysts increases with increasing temperature. The measured PO production rate increases from 16.23 $\mu\text{mol/g/s}$ to 26.53 $\mu\text{mol/g/s}$ when the temperature is raised from 250 °C to 290 °C over the Ag nanocubes/ La_2O_3 . Similarly, the PO production rate increases from 0.95 $\mu\text{mol/g/s}$ (250 °C) to 5.00 $\mu\text{mol/g/s}$ (290 °C) over the Ag nanospheres/ La_2O_3 .

Based on these results, it is clear that both Al_2O_3 and La_2O_3 supported Ag nanocubes show a better propylene oxide selectivity and productivity as compared to Ag nanospheres. The results also indicate that a degree of Ag(100) facet exposure in the supported Ag nanocubes sample is more favourable for the propylene oxide formation when compared with Ag nanospheres. This experimental result appears to support the conclusions from the theoretical calculations of Corma and co-

workers.^[34] However, according to their calculations, the Ag(100) or Ag(111) surfaces can activate di-oxygen molecules in air to generate mono-atomic active oxygen species spontaneously for the conversion of propylene to propylene oxide, intermediates and combustion products. On the other hand, we note that the activity and selectivity of our Ag catalysts depend critically on the nature of the oxide support used. Al₂O₃ as a support for Ag on its own gives much lower selectivity and productivity for propylene epoxidation formation as compared to La₂O₃. As a result, the Ag nanoparticles in whatever shape with either (111) or (100) facets do not seem to possess the ability to activate the dioxygen from air and propylene spontaneously as predicted by the DFT without the strong contributing roles of the support under kinetic controlled conditions.^[34] It is possible that the size of Ag particle plays a significant role in the activation of di-oxygen (normally the rate limiting step) particularly, the use of large size Ag nanoparticles in our supported catalysts. A specific oxide support such like La₂O₃ appears to strongly assist the dioxygen activation to the required surface atomic oxygen at the Ag-support interface for the propylene oxide production. The XPS analysis suggests that the electrophilic O_β surface oxygen, presumably generated by di-oxygen molecular interaction with the lanthanide oxide surface can spill over to the Ag surface to assist the generation of atomic oxygen species at their interface. Clearly, the Ag(100) facet with the electrophilic atomic oxygen will act as the active site for the propylene oxidation to corresponding epoxide than that of Ag(111) facet.

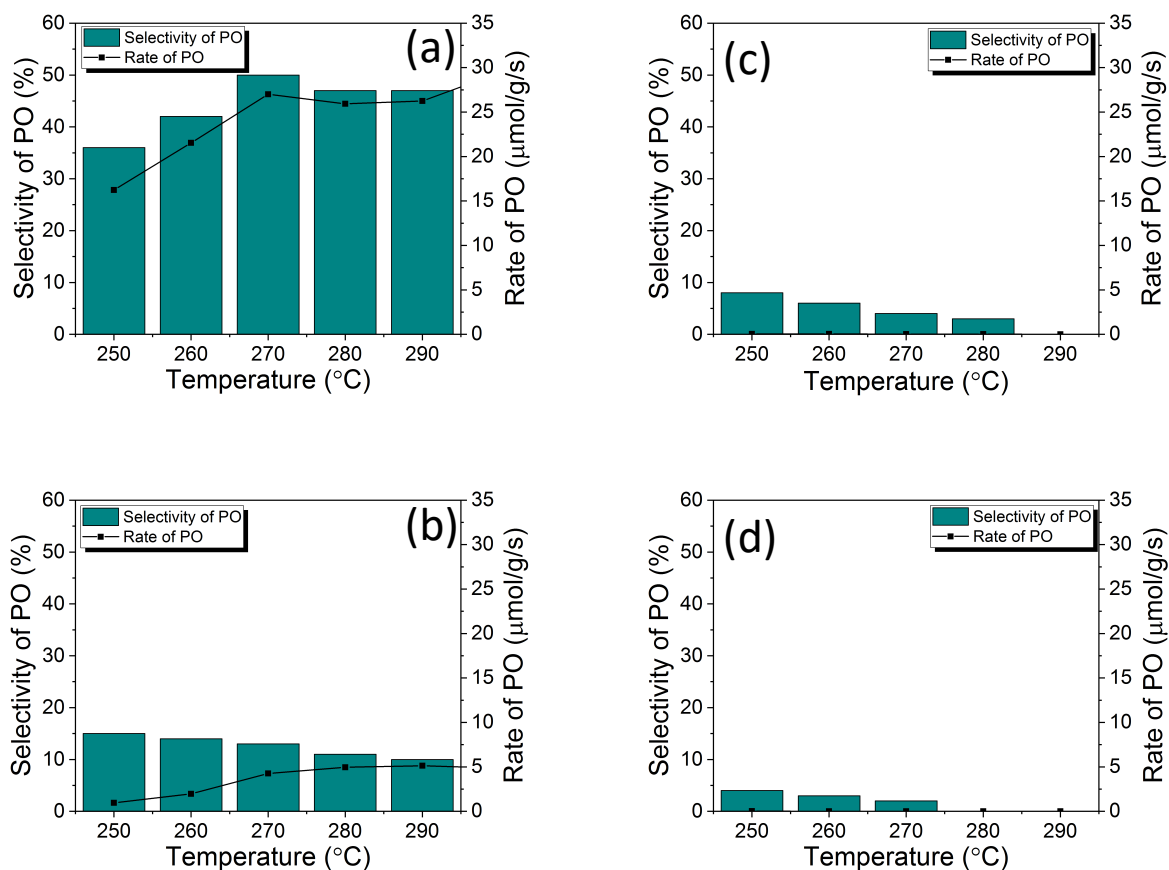


Figure 4.9 Selectivity of propylene oxide (PO) and Production rate of PO vs temperature (°C) on a) Ag nanocubes/La₂O₃; b) Ag nanospheres/La₂O₃; c) Ag nanocubes/Al₂O₃; d) Ag nanospheres/Al₂O₃

4.4.3 DFT calculations

Theoretical calculations were therefore performed to reveal the processes of molecular oxygen adsorption and dissociation on Ag (111) and (100) surfaces and to appreciate the specific roles of support effect of La₂O₃ in assisting the formation of propylene oxide.

In order to study the adsorption of oxygen on silver surfaces, the following models: a 4×4 surface cell was used to construct a six-layer Ag(100) and Ag(111)slab were

used. The top three layers of the Ag(100) and Ag(111) slabs were allowed to relax. In addition, in order to study the oxygen vacancy energy on polar and nonpolar La_2O_3 surfaces, we used the following models: a 4×4 surface cell was used to construct a three-layer $\text{La}_2\text{O}_3(001)$ slab. The top two layers of the $\text{La}_2\text{O}_3(001)$ slab were allowed to relax.

Table 4.2 Calculated adsorption energies of oxygen molecules and atoms at Ag(111) and Ag(100).

Adsorption energies at different Ag facets				
	Ag(111)-O ₂ - ads1(a)	Ag(111)-O ₂ - ads2(b)	Ag(111)-O ₂ - ads3(c)	Ag(111)-2O- ads1(d)
E _{ads} /eV	0.29	0.17	0.16	1.14
	Ag(111)-2O- ads2(e)	Ag(111)-2O- ads3(f)	Ag(100)-O ₂ - ads1(g)	Ag(100)-O ₂ - ads2(h)
E _{ads} /eV	1.12	1.03	0.62	0.19
	Ag(100)-O ₂ - ads3(i)	Ag(100)-2O- ads1(j)	Ag(100)-2O- ads2(k)	Ag(100)-2O- ads3(l)
E _{ads} /eV	0.10	1.58	1.51	1.26

The three calculated adsorption energies of oxygen molecules and atoms at Ag(111) and Ag(100) surfaces were listed in Table 4.2 above. The calculated results in Table 4.2 indicate that O₂ was adsorbed more strongly on Ag(100) than on Ag(111), and the O₂ dissociation is more favourable on Ag(100) than Ag(111) that can spontaneously happen as similar to the calculations of Corma and coworkers.^[34] The most stable O₂ adsorption complex on the Ag(111) surface with respect to gas phase O₂ and the silver surface is only 0.29 eV. After dissociation, the energy of two oxygen atoms adsorbed on Ag(111) is 1.14 eV and the O₂ dissociation is exothermic by 0.85 eV. The relative energy of the most stable O₂ adsorbed complex on the

Ag(100) surface is 0.62 eV and the O₂ dissociation is exothermic by 0.96 eV, which is higher than on Ag(100) surfaces.

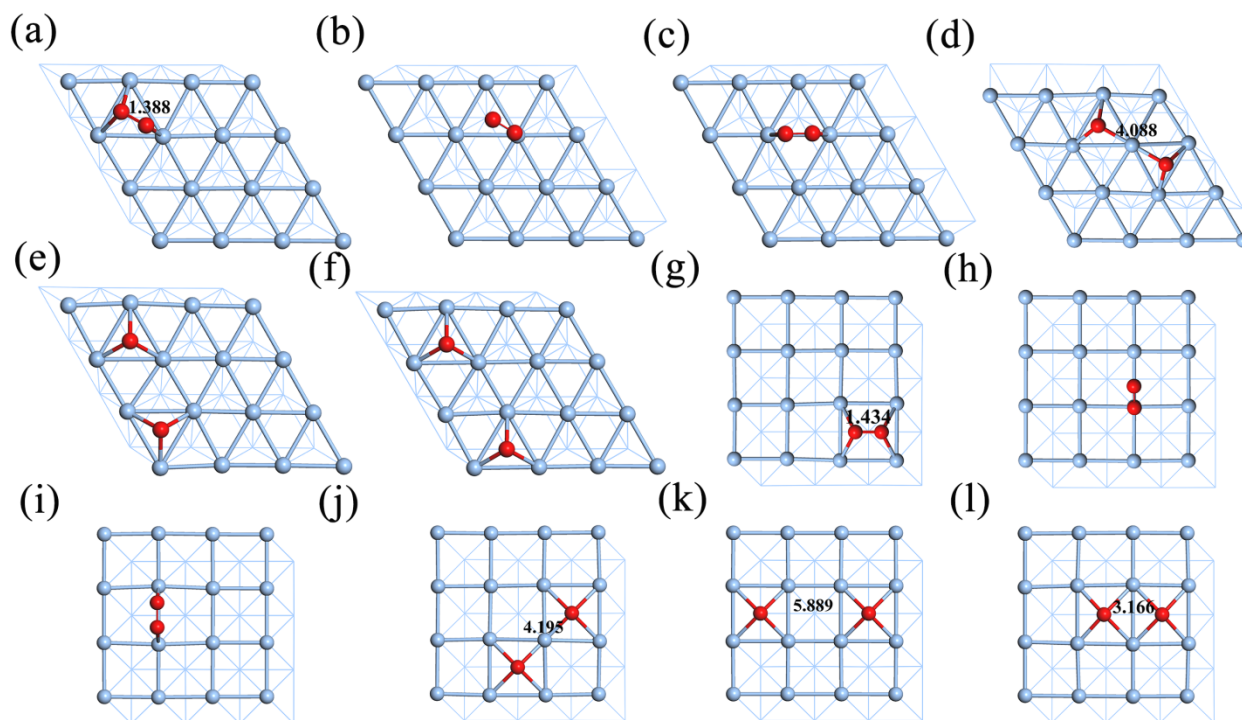


Figure 4.10 The calculated favourable structures of the oxygen molecules and atoms being adsorbed at Ag(111) and Ag(100) facets. (a-c, the top view of adsorbed O₂ on Ag(111); d-f, the top view of O₂ dissociation adsorbed on Ag(111); g-i, the top view of adsorbed O₂ on Ag(100); j-l, the top view of O₂ dissociation adsorbed on Ag(100).)

Besides, from the calculated three favourable structures of the adsorbed molecules and atoms at Ag(100) and Ag(111) surfaces (Figure 4.10), one can notice that the most stable molecular O₂ adsorption appears on the hollow site of Ag(111) surface. After oxygen dissociation, there forms a pair of two surface silver atoms with one O atom of Ag-O-Ag bridge structure. The interatomic O-O distance of two well-separated adsorbed atomic oxygens of 4.08 Å is obtained. On the other hand, the

most stable O₂ adsorbed complex on Ag(100) surface shows each of the two oxygen atoms bridged bonded between two silver atoms (Figure 4.10 (g)), and the most stable of O-O bond (1.434 Å) is larger than on the Ag(111) surface (1.388 Å) due to the particular geometric atomic arrangement on this facet. Notably, one can find that the energetically favourable O₂ dissociation can form a pair of Ag-O-Ag structures, which is also in good agreement with previously reported results of Corma and co-workers.^[34] Our DFT calculation predicts a lower energy barrier for oxygen activation on the Ag(100) than on the Ag(111) surface, which results in a higher active oxygen atom coverage on Ag(100) than on Ag(111). The surface separated atomic oxygens located on Ag(100) with an apparently even longer interatomic O-O distance of 4.195 Å (Fig. 4.10j) than that of Ag(111) will be more favourable towards the formation of propylene oxide. It is because of lower activation energies to generate the oxametallacycle intermediates which lead to an epoxide production route.^[12,20,34,39] With reference to Scheme 2 of Chapter 1 which depicts that the alternative low temperature route of γ-H abstraction of oxametallacycle intermediate by neighboured oxyradical (atomic oxygen) can cause total combustion over a silver catalyst,^[20] the geometrically longer interatomic O-O distance of 4.195 Å on the Ag(100) facet is anticipated to reduce the combustion extent significantly, giving higher selectivity of PO of over 50%. As a result, tailoring surface geometric distance of two atomic oxygens from activation of di-oxygen seems to be very important in enhancing propylene epoxide selectivity over Ag nanocube surface.

Table 4.3 Oxygen-vacancy formation energy (E_{vac(f)}, eV) needed for removing an oxygen atom O₄ or O₆ to form an oxygen vacancy and 1/2 molecule of O₂ in gas.

	Non-polar surface (001)		Polar surface (100)	
	O _{4V}	O _{6V}	O _{4V}	O _{6V}
E _{vac(f)} /eV	6.725	6.045	-0.875	-1.195

The geometric structures of a typical non-polar La₂O₃(001) surface^[40] are shown in Figure 4.11. In the La₂O₃(001) non-polar surface (Figure 4.11 a-b), the top layer consists of O₄ atoms (coloured in yellow), the O₆ atoms (coloured in green) located in the third layer, and the structure is symmetrical. Also, we have found that the La₂O₃ structure has nine oxygen atoms layers and these layers consist of six O₄ atoms layers and three O₆ atoms layers. In contrast, in La₂O₃(100) polar surface^[40,41] (Figure 4.11 e-f), the top layer consists O₆ atoms and the bottom layers consist La atoms, and the bond distance of La-O₆ (2.427 Å) is clearly shorter than that of non-polar surface (2.634 Å).

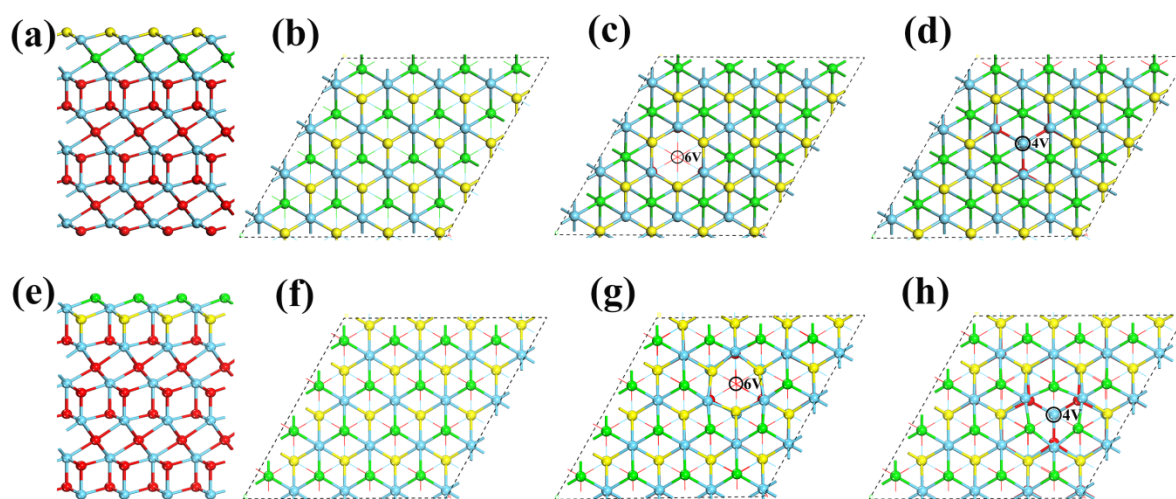
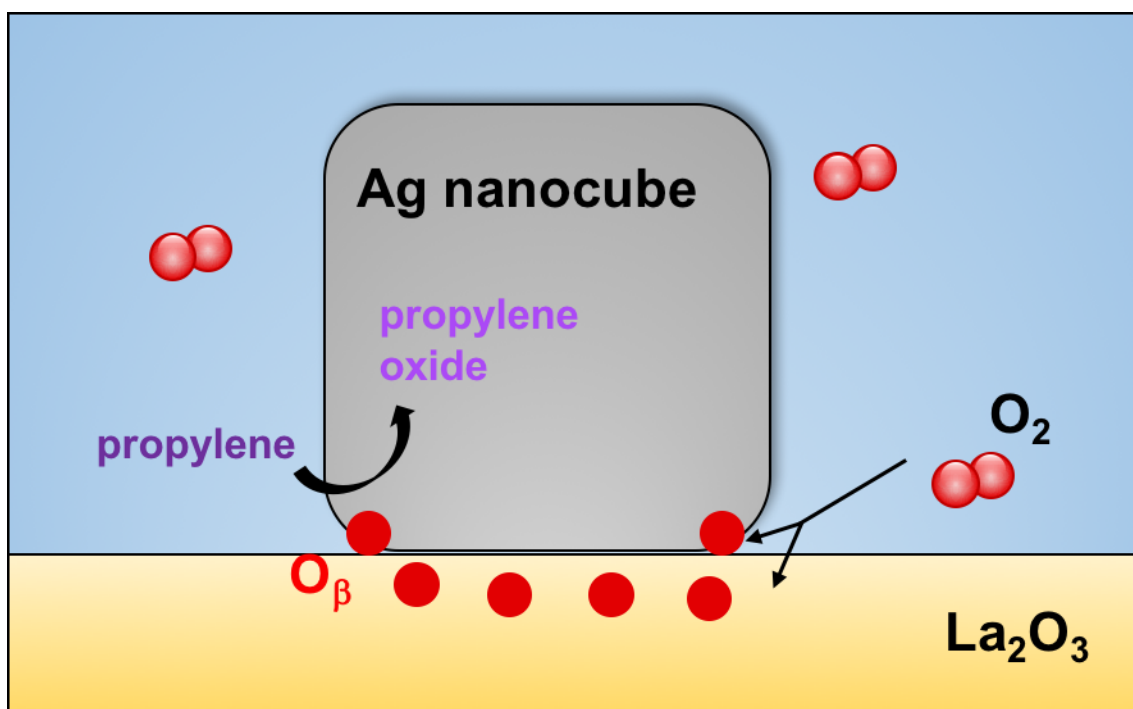


Figure 4.11 Geometric structure of La₂O₃(001) surface. (a-d, the La₂O₃(001) non-polar surface; a, the side view of La₂O₃(001); b, a, the top view of La₂O₃(001); c, the six-coordinated oxygen-vacancy of La₂O₃(001); d, the four-coordinated Oxygen-vacancy. e-h, the La₂O₃(100) polar surface; e, the side view of La₂O₃(100); f, the top

view of $\text{La}_2\text{O}_3(100)$; g, the six-coordinated oxygen-vacancy of $\text{La}_2\text{O}_3(100)$; h, the four-coordinated Oxygen-vacancy. Red, oxygen atoms; yellow, the surface of four-coordinated oxygen atoms; green, the surface of six-coordinated oxygen atoms; sky blue, La atoms)

It is interesting to note that from our calculated oxygen-vacancy formation energies for forming an O6V and O4V for the $\text{La}_2\text{O}_3(001)$ non-polar and corresponding polar $\text{La}_2\text{O}_3(100)$ surface given in Table 4.3, for the non-polar surface, we can find that the values of 6.725 and 6.045 eV, for the O4 and O6 removal, respectively, which appears to be prohibitively very large. This is consistent with the fact that the $\text{La}_2\text{O}_3(001)$ non-polar surface is kinetically very stable.^[40] However, $\text{La}_2\text{O}_3(001)$ polar surface is kinetically very unstable, presumably due to surface polarity. The calculated oxygen-vacancy formation values for O4 and O6 are -0.875 and -1.195 eV, respectively. The negative oxygen formation energy indicates that on the polar surface a more stable state can be reached by forming oxygen vacancy. Notably, we have also found that forming O6 vacancy is easier than O4 vacancy in this polar surface with the surrounding vacancy to lead to reconstruction in $\text{La}_2\text{O}_3(100)$. As a result, we envisage that dioxygen from air can be easily dissociated and form the active oxygen species on this surface structure upon using La_2O_3 as the Ag catalyst support. Thus, it is possible that the corresponding higher BE of atomic oxygen species O_β from the XPS analysis of La_2O_3 supported Ag catalyst represents the active oxygen site for propylene epoxide formation over Ag/ La_2O_3 at the materials interface.

4.5 Conclusions



Scheme 4.2. Proposed reaction profile for direct propylene epoxidation at Ag nanocube/La₂O₃ interface where dioxygen is preferably dissociatively activated by (100) La₂O₃ due to its surface polarity and form the active atomic oxygens with long interatomic O distance over (100) surface at its interface for the propylene epoxidation.

In conclusion, we have shown for the first time that La₂O₃ supported Ag nanocube catalysts exhibit dramatically higher selectivity (>50%) at higher conversion comparing to other Ag catalysts in propylene epoxidation reaction. As summarised in

Scheme 4.2, with La_2O_3 , the molecular oxygen will be preferably dissociated into active O_β on the La_2O_3 although it is thermodynamically favourable on silver surface with a high kinetic barrier. Thus, the contributing role of La_2O_3 support is clearly demonstrated. The active O_β will then migrate or spillover to the $\text{Ag}(100)$ at proximity in materials interface. The electrophilic atomic oxygen on Ag surface with higher binding energy will interact with propylene and form the oxametallacycle intermediates and finally generate the propylene oxide (refer to Scheme 1.9 of Chapter 1)^[20] without much of surface species directing to total combustion route due to longer interatomic oxygen distance to disfavour γ -H abstraction, as in contrast to the case of Ag (111) surface. The enhancement of selectivity and productivity of La_2O_3 supported Ag nanocube catalysts can be attributed to a lower apparent activation energy for dioxygen dissociation on La_2O_3 polar surface and the characteristic geometric feature of surface $\text{Ag}(100)$ leading to a more favourable formation of the epoxide product.

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Chapter 5 Ni@Ag core@shell nanoparticles in mesoporous SBA-15 for direct propylene epoxidation with molecular oxygen

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5.1 Background

It was shown in Chapter 4 that the study of direct propylene epoxidation with molecular oxygen over La_2O_3 supported silver catalysts exhibits a strong support effect for the molecular oxygen activation. With a higher degree of oxygen vacancy on the polar surface of La_2O_3 , the La_2O_3 supported silver catalysts exhibits a higher rate of propylene oxide production than that of a conventional alumina supported silver catalyst due to the assistance of active oxygen species production from the metal-support interface. DFT calculation also shows a much lower energy barrier of O_2 dissociation at the oxygen vacant site on La_2O_3 surface, which allows the O_2 activation to take place at mild temperature. In addition to that, both the experimental and theoretical works give mechanistic understanding of the nature and reaction pathway of surface-active oxygen on rate of propylene oxide production and selectivity of propylene oxide. It is clearly indicated that when the active oxygen adsorbed on a longer Ag-Ag atomic distance on typical Ag(100) surface rather than Ag(111), the chance of propylene-oxygen complex on surface via the reaction pathways towards combustion route could be effectively reduced. However, the average particle size of the shape-controlled Ag nanoparticles (about 45 nm) used is considerably large, which prohibits the direct activation of dioxygen over Ag metal for this catalysis.

Many research have demonstrated that the size effect of metal nanoparticle can significantly influence the catalyst activity as mentioned in Chapter 1. Therefore, there is a motivation to develop the use of smaller silver nanoparticles as catalyst (< 10 nm), it is however, difficult to tailor its exposure of a specific facet in this size

dimension. On the other hand, our group have previously demonstrated the preparation of surfactant-free small silver-shell and nickel-core nanoparticles where it may be possible to engineer the thickness of the silver shell using mesoporous SBA-15 as template.^[1] Herein, a systematic work to develop this type of catalysts may give the possibility for further improvement of the direct propylene epoxidation by architecting the shell atoms with a longer interatomic Ag distance in the core@shell configuration. Combining the experiment work by monitoring reaction activity and selectivity with material characterisation, the direct propylene selective oxidation over engineered Ag shell atoms was achieved.

5.2 Objective

The aim of this chapter is to develop a series of surfactant-free nickel-silver core@shell nanoparticles using mesoporous SBA-15 as template for the direct propylene-oxygen epoxidation. A systematic testing of the Ag@Ni/SBA-15 catalysts under a variety reaction conditions, including temperature, metal loading amount, catalyst loading amount will be conducted to achieve the optimized catalytic activity and selectivity. The material structures and properties will be characterised using advanced techniques including Atomic Probe Tomography (APT), Extended X-ray Atomic Fine Structure (EXAFS), Synchrotron X-Ray Powder Diffraction (SXRD) in combined with Transmission Electron Microscopy (TEM). Most importantly, a deeper understanding of the surface oxygen adsorption effect on Ag shell atoms will be explored in detail by surface tailoring the average interatomic Ag distances on Ni@Ag/SBA15 catalysts. This work will demonstrate the advanced surface tailoring approach used in this catalysis reaction, which may open up future capabilities in many selective oxidation reactions.

5.3 Experimental details

A detailed discussion of experimental methods can be found in Chapter 3. A brief summary of catalyst syntheses is given here.

The ordered silica-block copolymer mesoporous SBA-15 were synthesized by a modified method according to Zhao & Stucky's work.^[2] The core@shell bimetallic Ni-Ag/SBA-15 catalysts with a silver loading of 5 wt% were prepared using a co-impregnation method according to our previous report but this time more fine control in Ag shell thickness was conducted.^[1] In a typical preparation, known amounts of AgNO₃ and Ni(NO₃)₂·6H₂O were dissolved in 0.25 mL of Milli-Q water, respectively. 500 mg SBA-15 was then added to the prepared solution under vigorously stirring at room temperature, then the mixtures were subjected to aging for 12 h in dark and dried in oven at 100 °C overnight. The obtained sample was calcined at 350 °C in N₂ for 4 h and further reduced in diluted H₂ for 3 h at 420 °C to produce the Ni-Ag/SBA-15 catalyst. Ni-Ag/SBA-15 catalysts with a variety of Ni/Ag contents, monometallic Ag/SBA-15 and Ni/SBA-15 were all prepared using the same method described above, for all samples with a constant Ag loading of 5 wt% and various of Ni loading. The bimetallic catalysts were denoted as Ni_xAg_y/SBA-15, where x and y represents the nominal atomic ratio of Ag to Ni.

The reactions were performed in a vertical tubular fixed bed reactor that allowed a three-stage of temperature control throughout the whole reactor which delivers evenly distributed temperature. For a typical propylene epoxidation reaction, the composition of the reactant gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium

with a mix ratio of 2:1 at a total flow rate of 20 mL/min, which was delivered from the top of the reactor. The reactants and products were analysed online by a gas chromatograph equipped with a methanizer and a flame ionization detector (FID).

5.4 Results and Discussion

5.4.1 Catalytic performance

The aim of this chapter is to evaluate catalytic performance of the Ag-Ni bimetallic nanoparticles catalysts for the direct propylene epoxidation with molecular oxygen. To address the bimetallic composition effect, a series of Ni-Ag/SBA-15 with a variety of Ag/Ni contents were prepared. The higher Ag content bimetallic catalysts were denoted as Ni_x-Ag₁/SBA-15, where x (0.2 and 0.4) represents the atomic ratio of Ni to Ag; and the low Ag content bimetallic catalysts were denoted as Ni₁-Ag_y/SBA-15, where y (0.4 and 0.2) represents the atomic ratio of Ag to Ni. Similarly, Monometallic Ag/SBA-15 and Ni/SBA-15 were also prepared for the comparison testing. All the catalysts were initially tested under the reaction conditions reported in Chapter 4. To further investigate the reaction parameters on catalytic performance, several reaction conditions, including the catalyst loading amount, reaction temperature and catalyst stability, were all carefully studied in this chapter.

The catalytic selective propylene oxidation tests of all as prepared Ag catalysts were performed in a vertical tubular fix bed reactor at 1 bar with a total gas flow rate of 20 mLmin⁻¹. The composition of the gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1. The reaction products were analysed by a gas chromatograph equipped with a methanizer and a flame ionization detector (FID) as described in Chapter 3.

5.4.1.1 Temperature effect on the catalyst activity

The $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$ was selected as a catalyst for direct propylene epoxidation with molecular oxygen at a variety of reaction temperatures to study the temperature effect. The catalytic performance of $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$ catalyst with the loading of 50mg is shown in Figure 5.1. It can be seen that propylene oxide and CO_2 are the two major products over $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$ catalyst. Started from 220 °C the rate of propylene oxidation increases sharply with temperature from 0.2 $\mu\text{mol/g/s}$ at 220 °C to 39.3 $\mu\text{mol/g/s}$ at 300 °C. The formation of propylene oxide is observed at 220 °C with a remarkable 70.6% selectivity, which is considerably higher than that of the best Ag nanospheres / La_2O_3 catalyst reported in Chapter 4. It should be noted that direct activation of dioxygen and propylene to propylene oxide over this core-shell catalyst is clearly evident without adding La_2O_3 support. The selectivity of propylene oxide progressively decreases as the temperature increases, and it drops to only 11.1% when the temperature is at 300 °C. In contrast, the selectivity of combustion product CO_2 increases sharply with temperature from 29.4% at 220 °C to 88.9% at 330 °C. The observation for the formation of CO_2 at the expense of the partial oxidised product, propylene oxide at elevated temperature, which supports the findings from calculations presented in Scheme 2 of Chapter 1 (their formation routes are temperature dependent and competitive).^[3] Although at high temperature, the kinetics favours the increase in rate of propylene oxidation, the combustion is more favourable over the partial propylene oxide formation to produce CO_2 as the major product.

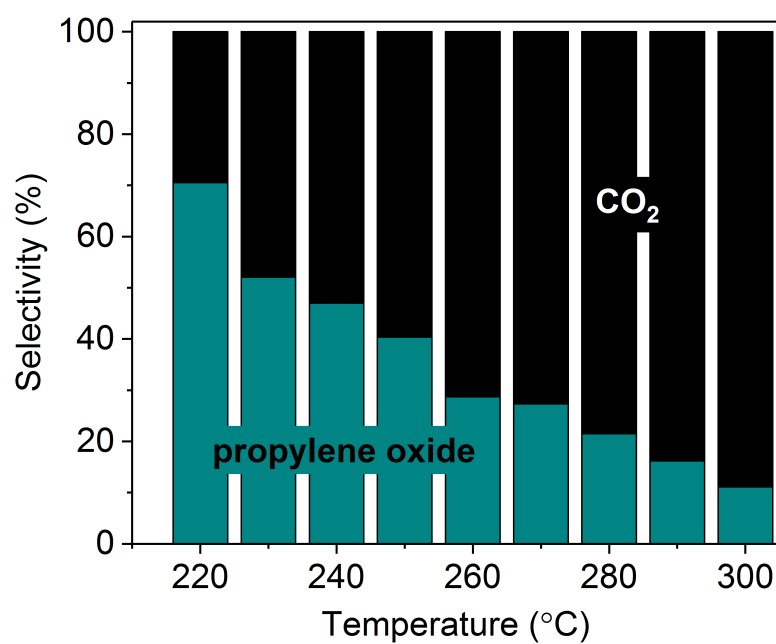


Figure 5.1 Selectivity of propylene oxide and CO₂ versus temperature over Ni_{0.4}-Ag₁/SBA-15.

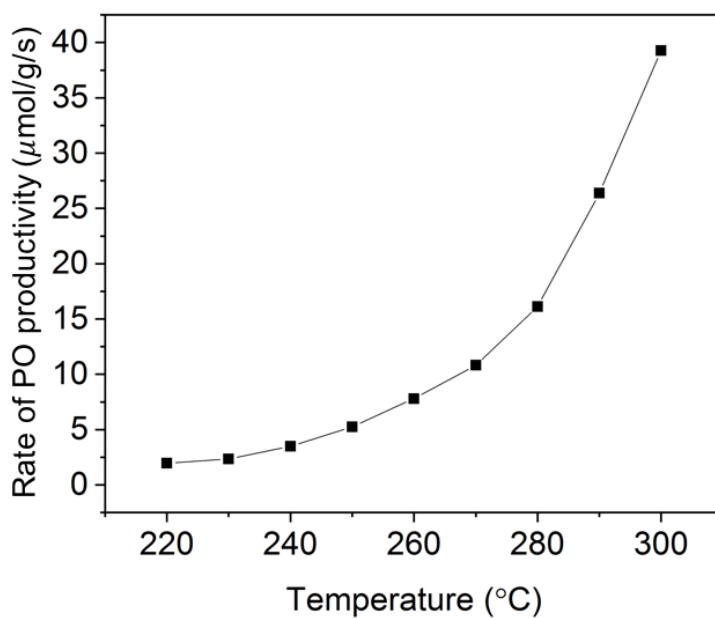


Figure 5.2 Rate of propylene oxidation versus temperature over Ni_{0.4}-Ag₁/SBA-15.

5.4.1.1.1 Effect of catalysts loading amount on the catalytic activity

Although the $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$ catalyst exhibited a promising selectivity towards propylene oxide at 220 °C, the rate of propylene oxidation remained at a very low value. In order to improve the rate of propylene oxidation, the $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$ catalyst was tested for an isothermal reaction at the optimised temperature 220 °C with 5 different loadings, namely: 50 mg, 100mg, 200mg 300mg and 500mg over $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$.

The reaction results are shown in Figure 5.3. The rate of production (rate calculated per gram catalysts per second) shows a nearly constant value for all 5 different loadings. However, the total propylene conversion is dramatically changed with different catalyst loadings. With 50 mg, the total propylene conversion is only 0.2% at 220 °C. The total conversion progressively increases from 50 to 500 mg. When the loading reaches 300 mg, the conversion peaks at 0.76%, a nearly 4 times more than that of 50 mg used. As the catalysts loading amount continuously increases to 500mg the conversion increases to nearly 1%. The selectivity of propylene oxide shown in Figure 5.4, on the other hand, gives a strikingly different trend. The selectivity of propylene oxide sharply drops from 70.6% to 56.7%, when the loading is increased from 50 to 100mg. As the loading increases to 300mg, only a slight decrease in propylene oxide selectivity of 52.1% is observed. However, as the loading increases to 500 mg, the selectivity of propylene oxide slight drops to 41.4%. In general, higher catalyst loading will lead to longer reaction residence time or contact time for the partial oxidised products to be in touch with oxygen over the same catalyst. Thus, the oxide product will be further oxidised to the combustion

product as the secondary product resulting in a decrease in selectivity. However, the relationship between catalyst loading with the residence time or contact time may not be linear due to the contribution of direct combustion from unselective sites of the catalyst, flow characteristics and packing of the catalyst bed, etc.^{[4][5][6]} The optimization shows that 500mg loading gives the highest propylene oxide yield, and this will be used as the optimized reaction conditions for further tests.

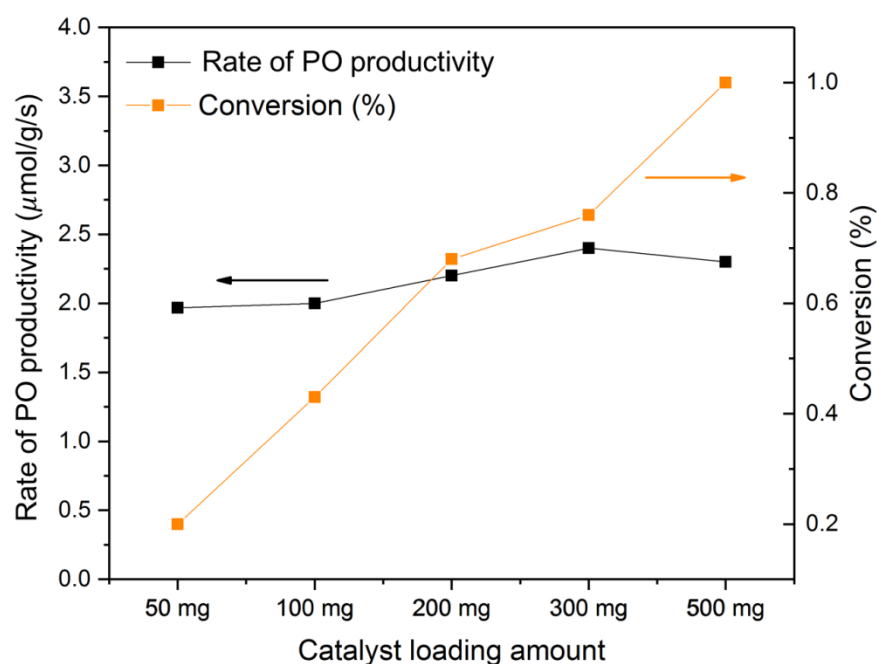


Figure 5.3 Rate of propylene oxidation and conversion of propylene versus catalyst loading amount over $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$.

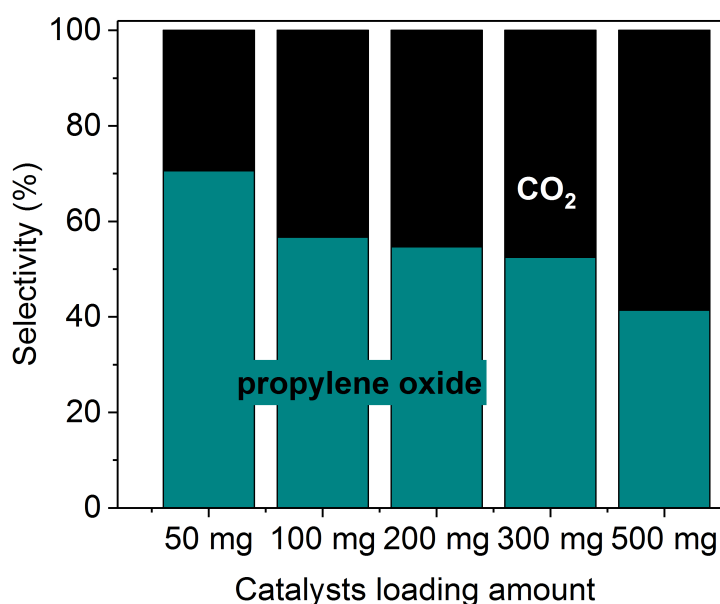


Figure 5.4 Selectivity of propylene oxide and CO₂ versus catalyst loading amount over Ni_{0.4}-Ag₁/SBA-15.

5.4.1.2 Catalytic performance of bimetallic Ni-Ag/SBA-15 catalysts

Table 5.1 Catalytic performance of Ni-Ag/SBA-15 catalysts (500mg) for direct propylene epoxidation at 220 °C, 1 bar, 20mL/min (5% C₂H₆ to 5% O₂= 2:1). (Ag/SBA-15 and Ni/SBA-15 for comparison).

Catalyst	Rate of PO productivity (10 ⁻⁵ mol/g/s)	Selectivity (%)	
		Propylene oxide	CO ₂
Ag/SBA-15	1.78	9.9	87.3
Ni _{0.2} -Ag ₁ /SBA-15	2.01	28.5	71.5
Ni _{0.4} -Ag ₁ /SBA-15	2.30	41.4	58.6
Ni ₁ -Ag _{0.4} /SBA-15	4.40	70.7	29.3
Ni ₁ -Ag _{0.2} /SBA-15	3.85	60.2	39.8
Ni/SBA-15	0	0	0

We reported in Chapter 4 that the selectivity of propylene epoxidation depends on the geometric structure of Ag facet exposed. Herein, in order to modify the surface structure of Ag atoms, we tested a series of Ni/Ag core-shell catalysts with a variation of Ag to Ni atomic ratios. Table 5.1 shows the catalytic performances of Ni-Ag/SBA-15 catalysts for the direct propylene epoxidation at 220 °C. It can be seen that Ni/SBA-15 catalyst displays no activity towards the formation of propylene oxide, presumably the Ni particles might have been fully oxidised to NiO in air.^{[7][8]} Over all silver containing Ni-Ag/SBA-15 samples, the propylene oxide and CO₂ are the two major products at 220 °C. For the Ag/SBA-15, the selectivity of propylene oxide is kept at only 9.9% with the rate of production of 1.78×10^{-5} mol/g/s while CO₂ selectivity of 87.3% is recorded. At higher ratios of Ni to Ag (smaller Ag shell thickness, assuming that the particle adopted the SBA-15 channel size of 4.6nm)^[9], the selectivity of propylene oxide is dramatically enhanced and reached a maximum of 70.7%. Comparing to the monometallic Ag/SBA-15, the bimetallic Ni-Ag/SBA-15 is more selective to epoxidation, and the propylene oxide becomes the dominated product. The selectivity of propylene oxide for Ni-Ag/SBA-15 is much higher than the reported supported silver catalysts mentioned in Chapter 1.^[10–13] The measured propylene oxide rates are 2.3×10^{-5} mol/g/s and 4.4×10^{-5} mol/g/s for Ni_{0.4}-Ag₁/SBA-15 and Ni₁-Ag_{0.4}/SBA-15, respectively, which are higher than that of the monometallic Ag/SBA-15. The results are significant from two important perspectives. First, it demonstrates that the Ni₁-Ag_{0.4}/SBA-15 catalyst possesses a dramatically enhanced activity and selectivity for the direct oxidation of propylene to propylene oxide, and to our knowledge, such core-shell catalysts have not yet been reported for the propylene epoxidation reaction. Most importantly, it is shown that, by

changing the Ni: Ag ratios, the catalytic routes on Ag atoms as catalysts can be modified from combustion favoured to epoxidation favoured pathways. In order to gauge the structural modifications of Ag shell atoms, detailed characterisations of the catalyst materials were conducted, and will be discussed in later paragraphs. Before that, we would like to test the stability of selected catalysts under our reaction conditions.

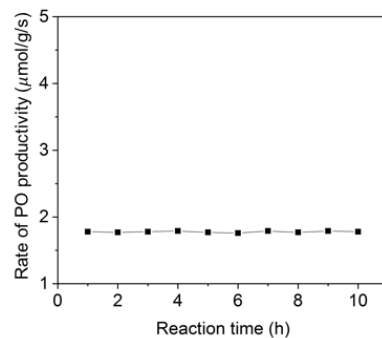
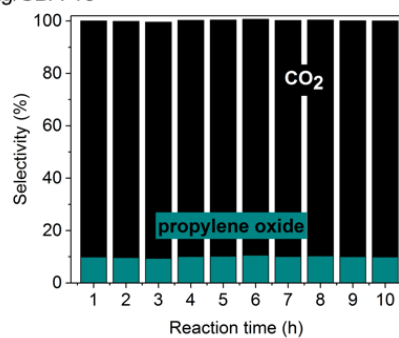
5.4.1.3 Catalyst stability

Catalysts stability tests were conducted to evaluate the stability of Ag structure during the selective oxidation reactions. The reaction results over bimetallic Ni_{0.4}-Ag₁/SBA-15, Ni₁-Ag_{0.4}/SBA-15, and monometallic Ag/SBA-15 are shown in Figure 5.5. The stability test was kept at 220 °C for 10 hours with 500mg catalyst, and the products were monitored for every hour. According to the results in Figure 5.5, all the catalysts maintain their stable catalytic performances over the 10 hours reaction time. Conventionally, supported Ag metal can suffer from a rapid time-deactivation, due to facile aggregation of thermal labile Ag atoms at elevated temperature.^[11] However, in our case, using SBA-15 catalysts, Ag atoms as shell on Ni nanoparticle core do not suffer from rapid aggregation, which may be related to the strong interactions between Ag and Ni on the SBA-15 template. In addition, the narrow walls with strong wall effect of SBA-15 channels^[14] may also reduce the extent of Ag or AgNi aggregation.^[15]

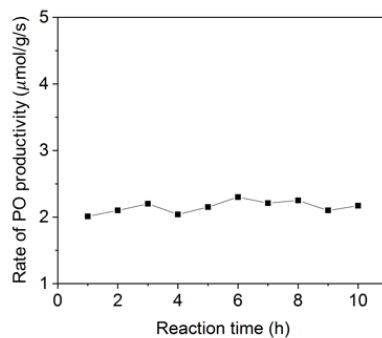
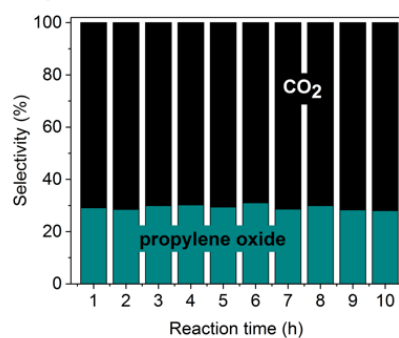
It is interesting to note that the selectivity of propylene oxide over the catalysts follows the increasing order: Ag/SBA -15 < Ni_{0.2}-Ag₁ /SBA-15 < Ni_{0.4}-Ag₁ /SBA-15 < Ni₁-Ag_{0.4}/SBA-15 (decreasing Ag: Ni ratios). The same order for the rate of

propylene oxide formation is also obtained, in which Ag/SBA-15 displays the lowest rate while Ni₁-Ag_{0.4}/SBA-15 shows the highest rate. This means that the thinner Ag shells on Ni nanoparticles with lower Ag: Ni ratios synthesised in a size-fixed 4.6±0.5nm channel^[9] can give higher propylene oxide selectivity and activity. Figure 5.6 shows the volcano relationship where mono-metallic Ni and Ag show poor PO selectivity while the optimal selectivity peaks at Ni₁-Ag_{0.4}/SBA-15.

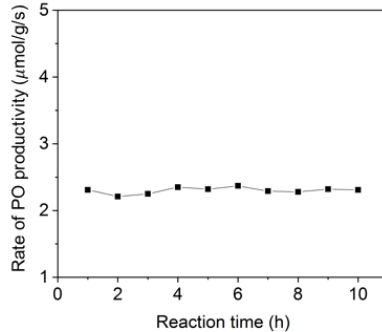
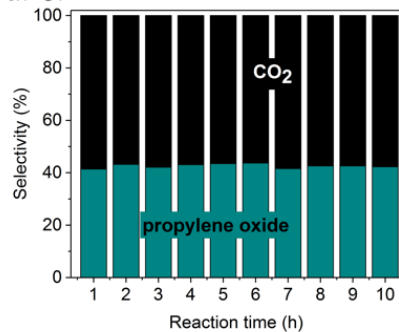
Ag/SBA-15



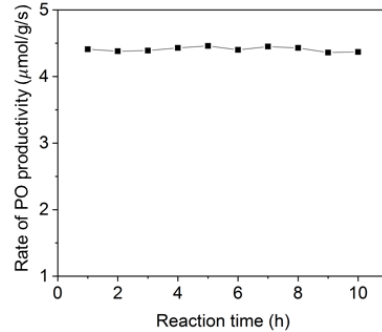
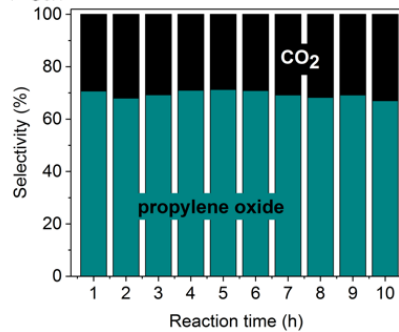
Ni_{0.2}Ag₁/SBA-15



Ni_{0.4}Ag₁/SBA-15



Ni₁Ag_{0.4}/SBA-15



Ni₁Ag_{0.2}/SBA-15

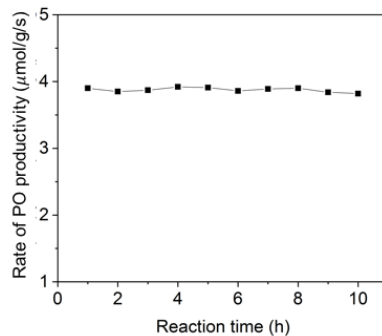
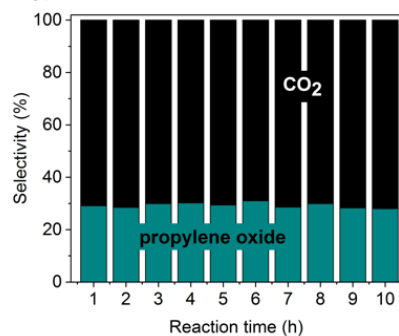


Figure 5.5 Stability test results: left) from top to bottom, selectivity of propylene oxide and CO₂ over Ag/SBA-15, Ni_{0.2}-Ag₁/SBA-15, Ni_{0.4}-Ag₁/SBA-15, Ni₁-Ag_{0.4}/SBA-15 and Ni₁-Ag_{0.2}/SBA-15; right) from top to bottom, rate of propylene oxide formation over Ag/SBA-15, Ni_{0.2}-Ag₁/SBA-15, Ni_{0.4}-Ag₁/SBA-15, Ni₁-Ag_{0.4}/SBA-15 and Ni₁-Ag_{0.2}/SBA-15. All catalysts were tested at 220 °C, 1 bar, 20mL/min (5% C₂H₆ to 5% O₂= 2:1).

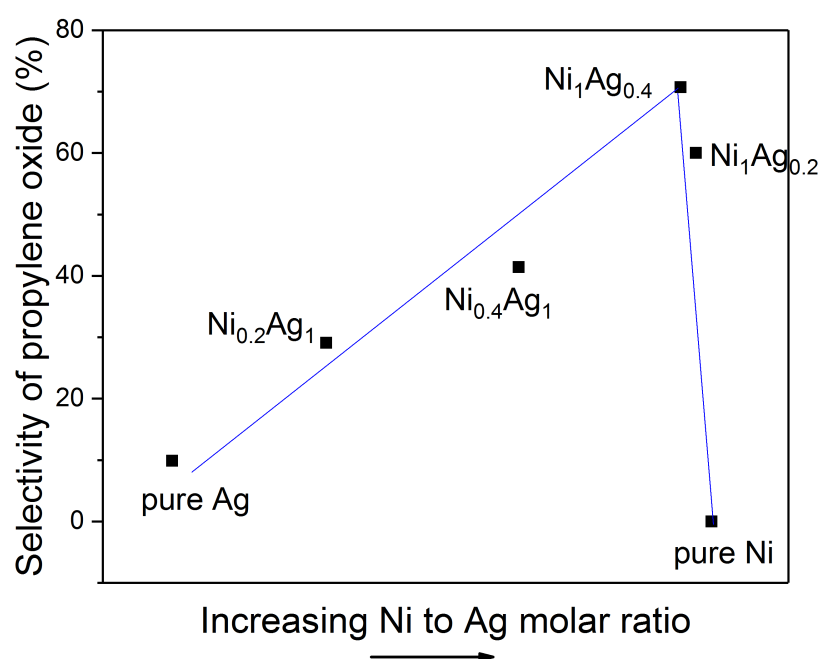


Figure 5.6 Propylene oxide selectivity versus Ni: Ag ratio over Ni-Ag bimetallic nanoparticles.

In order to understand structure-activity relationships the structures of all catalytic materials of Ni-Ag/SBA-15 were characterised using advanced techniques including TEM, HS-LEIS, SXRD, EXAFS and APT and XPS.

5.4.2 Materials characterisations

5.4.2.1 TEM

The structural details of SBA-15, Ni-Ag/SBA-15 and isolated Ni-Ag bimetallic nanoparticles were analysed using high resolution transmission microscopy (TEM). The TEM images of the as-prepared SBA-15 are first shown in the Figure 5.7. The images were taken at four randomly chosen areas. All the images depict the well-defined mesoporous silica channels of 4.6 ± 0.5 nm, as previously reported.^[2,9] It confirms the porous ordered structure of SBA-15 with typical cylindrical pore channels with no amorphous region. Thus, SBA-15 offers the high-quality porous template for the preparation of nanoparticles.

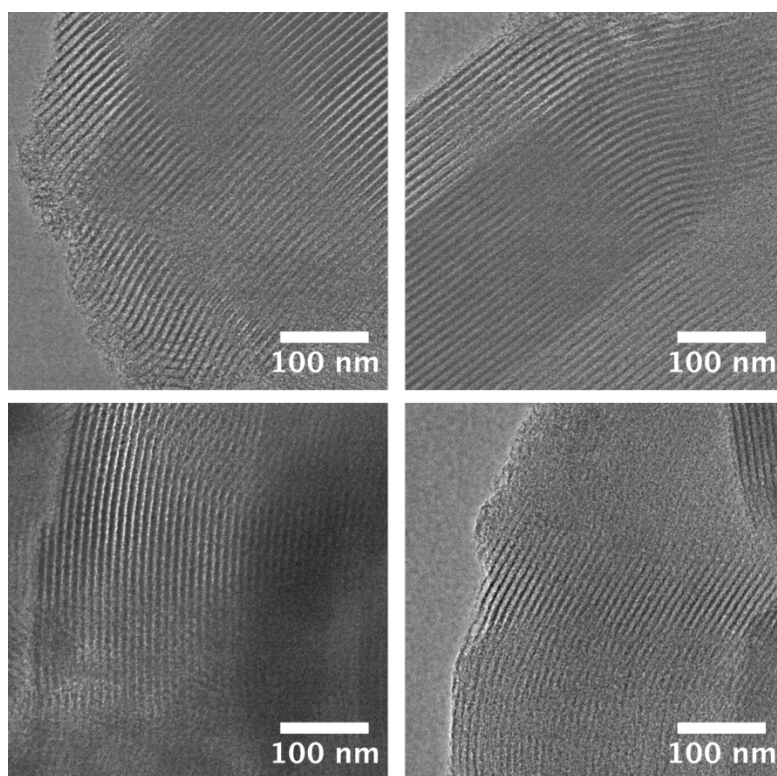


Figure 5.7 TEM images of pure SBA-15 showing the 4.6 ± 0.5 nm cylindrical porous channels alongside with the structure.

The TEM images of Ni-Ag/SBA-15 are shown in Figure 5.8. They confirm the on and off filling of cylindrical pore channels with nanoparticles over all these catalysts. The preparation procedure including high temperature calcination and reduction did not seem to induce any structural damage to the mesoporous material. Metal nanoparticles are clearly incorporated into the porous silica matrix and encapsulated by the ordered channel structure. All the metal nanoparticles are uniformly distributed throughout the entire SBA-15 framework with no significant agglomeration. Comparing $\text{Ni}_{0.4}\text{Ag}_1$ /SBA-15 (Figure 5.8 a) and b)) with $\text{Ni}_1\text{Ag}_{0.4}$ /SBA-1 (Figure 5.8 c) and d)), the average size of nanoparticle is similar, which appears to have adopted the SBA-15 channel dimension (4.6 ± 0.5 nm) despite the variation in Ag to Ni ratios.

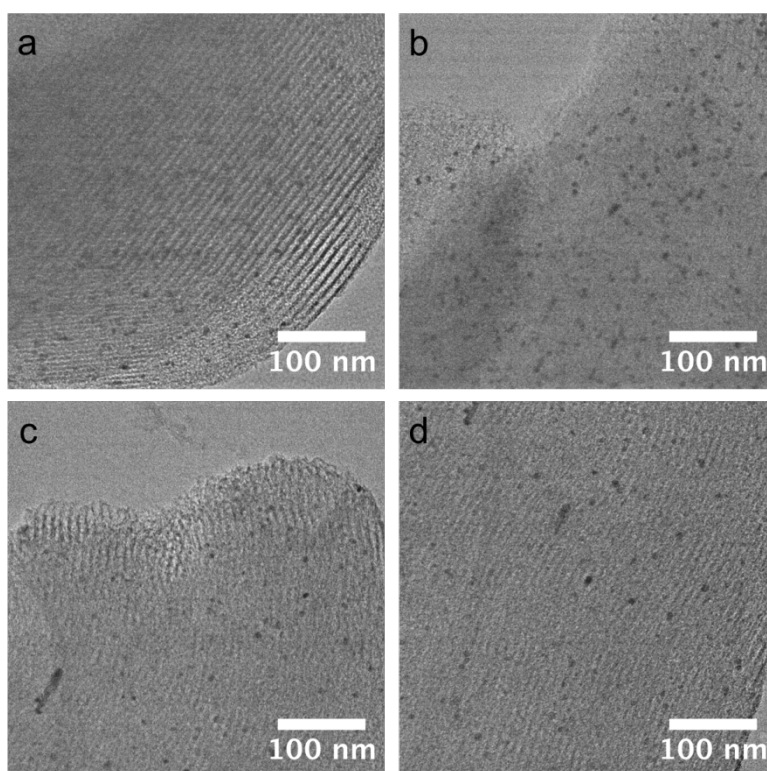


Figure 5.8 TEM images of SBA-15 showing the $4.6 \pm 0.5\text{\AA}$ parallel porous channels filled up with a, b) $\text{Ni}_{0.4}\text{Ag}_1$ /SBA-15 nanoparticles c, d) $\text{Ni}_1\text{Ag}_{0.4}$ /SBA-15 nanoparticles of same size where the particles adopt the dimension of the channels.

The Ni-Ag nanoparticles were isolated by the selective removal of SBA-15 silica using chemical dissolution method (see Chapter 2). The TEM images of isolated nanoparticles obtained from $\text{Ni}_{0.4}\text{Ag}_1/\text{SBA-1}$ and $\text{Ni}_1\text{Ag}_{0.4}/\text{SBA-15}$ are shown in Figures 5.9 and 5.10, respectively. The mean particles sizes of these Ni-Ag nanoparticles are 4.0 ± 1.0 nm. There are two sets of lattice fringes can be observed, the outer but lighter fringe separation corresponds to $\text{Ag}(111)^{[16]}$ and the inner, darker fringe separation corresponds to $\text{Ni}(111)^{[17]}$ of their cubic structures. This may indicate the formation of Ni@Ag core-shell structure. It is well accepted that Ni^{2+} will prone to reduction to Ni metal by H_2 prior to Ag^+ . Once the Ni^0 phase is formed, it will rapidly catalyse the Ag^+ reduction to give Ni core- Ag shell structure.^[18–20] Due to the limited resolution of the TEM images, the thickness of Ag shell of the two nanoparticles was unable to determine. As a result, further characterisations were conducted.

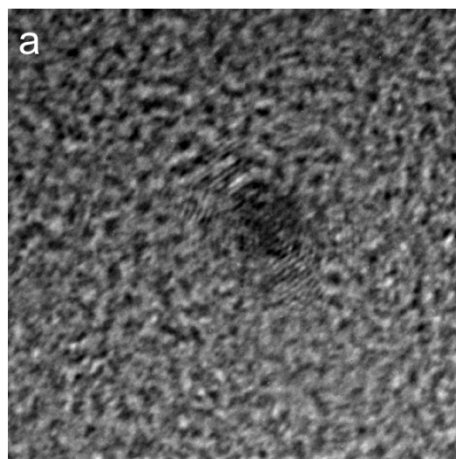


Figure 5.9 TEM image of a Ni core@Ag shell nanoparticle from $\text{Ni}_{0.4}\text{-Ag}_1/\text{SBA-15}$.

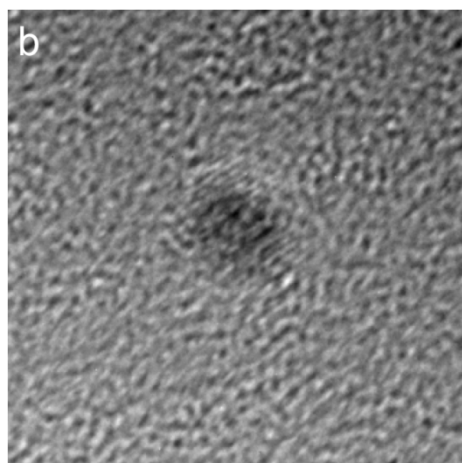


Figure 5.10 TEM image of a Ni core@Ag shell nanoparticle from $\text{Ni}_1\text{-Ag}_{0.4}$ /SBA-15.

5.4.2.2 High-sensitivity low-energy ion scattering (HS-LEIS)

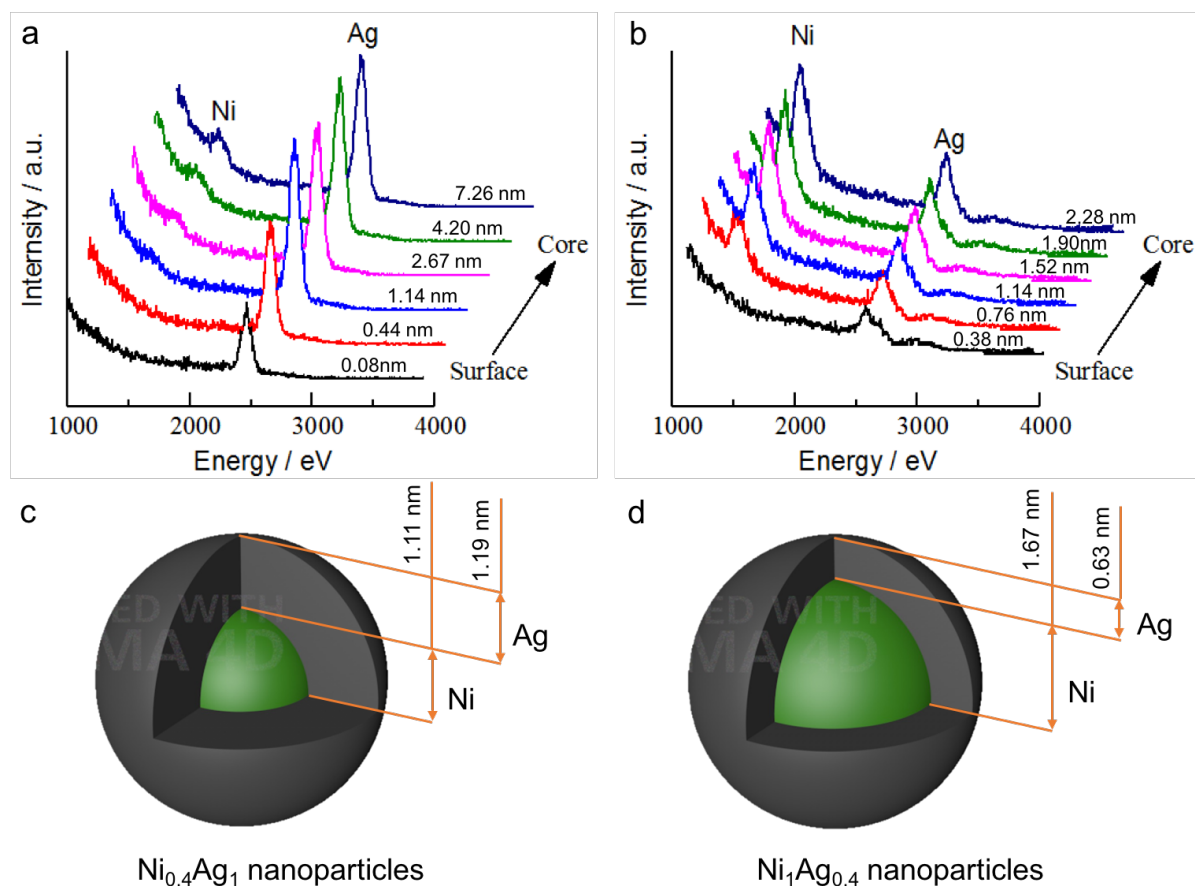


Figure 5.11 HS-LEIS spectra of $\text{Ni}_{0.4}\text{-Ag}_1$ and corresponding structural model (a, c-left); HS-LEIS spectra of $\text{Ni}_1\text{-Ag}_{0.4}$ and corresponding structural model (b, c-right).

The high sensitivity low-energy ion scattering (HS-LEIS) is a technique which is able to reflect the composition of a material in the function of depth from the surface. The HS-LEIS spectra are recorded with both Ar^+ and He^+ . The high energy Ar^+ beam was used to strip off surface atoms of known thickness (see Chapter 2) to give the HS-LEIS depth profiles of $\text{Ni}_{0.4}\text{-Ag}_1$ and $\text{Ni}_1\text{-Ag}_{0.4}$ as depicted in Figure 5.11. At each depth, the spectra are then recorded with He^+ ions to give the information in term of mass resolution for elements identification. The feature peak at region between 2500 to 2750 eV is Ag, and Ni is between 2250 to 2500 eV. The O and Si signals are always detected from the SBA-15 top layers. Upon further stripping, only Ag peaks can be first observed before the inner Ni peaks, evidencing the Ag shell and Ni core nanoparticle configuration. Notice that the Ni peak appears of about ca. 1.14nm after the Ag peak in the case of $\text{Ni}_{0.4}\text{-Ag}_1$ nanoparticle as shown in Figure 5.11a. This matches with the model in Figure 5.11b based on the theoretical calculated Ag thickness of 1.11nm from the given Ag: Ni ratio by assuming the formation of homogeneous core-shell particles of 4.6nm diameter which adopt the dimension of the SBA-15 channel. Similarly, the Ni peak appears of between ca. 0.38 to 0.76 nm after the Ag peak in the case of $\text{Ni}_1\text{-Ag}_{0.4}$ nanoparticle as shown in Figure 5.11c. This also matches with the model in Figure 5.11d based on the theoretical calculated Ag thickness of 0.63 nm from the given Ag: Ni ratio. Their relative peak intensities reflect the chemical compositions of these core-shell nanoparticles. Clearly, Ag atoms are more favourable to segregate on the surface to form Ag shell and Ni atoms are embedded in the core without the formation of alloy under our mild synthesis conditions.^[1,20] For the Ni@Ag core@shell nanoparticles of different Ag: Ni ratios, we demonstrate the tailoring of Ag shell thickness in this synthesis.

5.4.2.3 Synchrotron X-ray diffraction (SXRD)

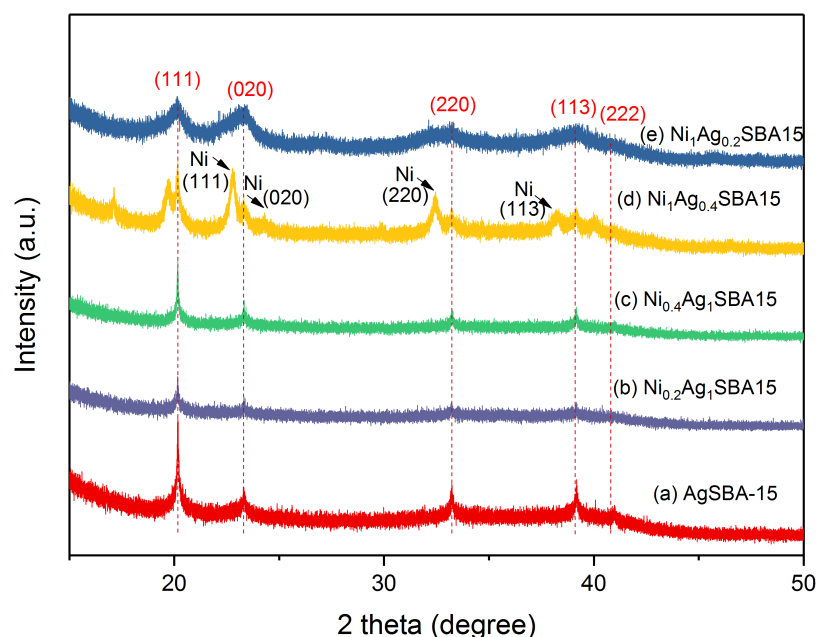


Figure 5.12 SXRD patterns of (a) Ag/SBA -15, (b) $\text{Ni}_{0.2}\text{Ag}_1$ /SBA-15, (c) $\text{Ni}_{0.4}\text{Ag}_1$ /SBA-15, (d) $\text{Ni}_1\text{Ag}_{0.4}$ /SBA-15 and (e) $\text{Ni}_1\text{Ag}_{0.2}$ /SBA-15 showing that the derived lattice parameter of Ag (Fm-3m) with samples (marked in red) maintains as $4.08719 \pm 0.00040 \text{ \AA}$ ($R_{\text{wp}}\% = 17.7$, $G_{\text{of}} = -0.3$) for all particles; the derived lattice parameter of Ni (Fm-3m) with samples containing Ni (marked in black) also maintains as $3.52761 \pm 0.00010 \text{ \AA}$ ($R_{\text{wp}}\% = 15.8$, $G_{\text{of}} = -0.2$).

High sensitivity synchrotron XRD patterns of Ag/SBA-15 and Ni-Ag/SBA-15 were collected from I11 beamline using Diamond Light Source, UK and are shown in Figure 5.12. From the SXRD patterns, all the Ag peak positions despite the severe broadening due to small crystalline sizes as Ag shell atoms, are remained

unchanged. The derived lattice parameter of Ag (Fm-3m) with the samples (marked in red) maintains as $4.08719 \pm 0.00040 \text{ \AA}$ ($R_{wp}\% = 17.7$, $G_{of} = -0.3$) as that of pure Ag phase. For those Ni containing samples (marked in black), the derived lattice parameter of Ni (Fm-3m) also maintains as $3.52761 \pm 0.00010 \text{ \AA}$ ($R_{wp}\% = 15.8$, $G_{of} = -0.2$) as that of pure Ni phase. On the other hand, it has been reported the compression of the lattice parameter of Ag to $4.02 \text{ \AA}$ if alloy $\text{Ni}_{0.2}\text{Ag}_1$ is formed at high temperature,^[21] while our core-shell $\text{Ni}_{0.2}\text{-Ag}_1/\text{SBA-15}$ gives the same lattice parameter of $4.08719 \pm 0.00040 \text{ \AA}$ in our SXRD pattern. As a result, we have ruled out the significant alloy formation between the two well-segregated core-shell metallic phases.

5.4.2.4 Atom probe tomography (APT)

Atom probe tomography (APT) was also employed to further confirm the core-shell structure, which gave a more detailed information about the shell thickness of a selected Ag-Ni nanoparticle. This method has successfully been employed to resolve the core-shell structure of Ag-Pd,^[22] Pt-Co,^[23] and CdTe-ZnO nanoparticles or nanocrystals^[24] in previous work. APT data takes the form of a three-dimensional point cloud, in which every point represents a single atom detected and identified by arrays of positional mass spectroscopy in projected screen. Figure 5.13 clearly shows that the $\text{Ni}_1\text{-Ag}_{0.4}/\text{SBA-15}$ (the best selectivity towards PO as shown in Fig.5.6) indeed displays a core-shell structure with the shell thickness of 1-3 atomic layers (errors in measurements were encountered due to the preferential evaporation of Ag atoms and mixed phases)^[25]. This corresponds well to the calculated Ag average thickness of 0.63 nm from the given Ag: Ni ratio by assuming

the formation of homogeneous core-shell particles of 4.6nm diameter that adopt the dimension of the SBA-15 channel (refer to Figure 5.11d).

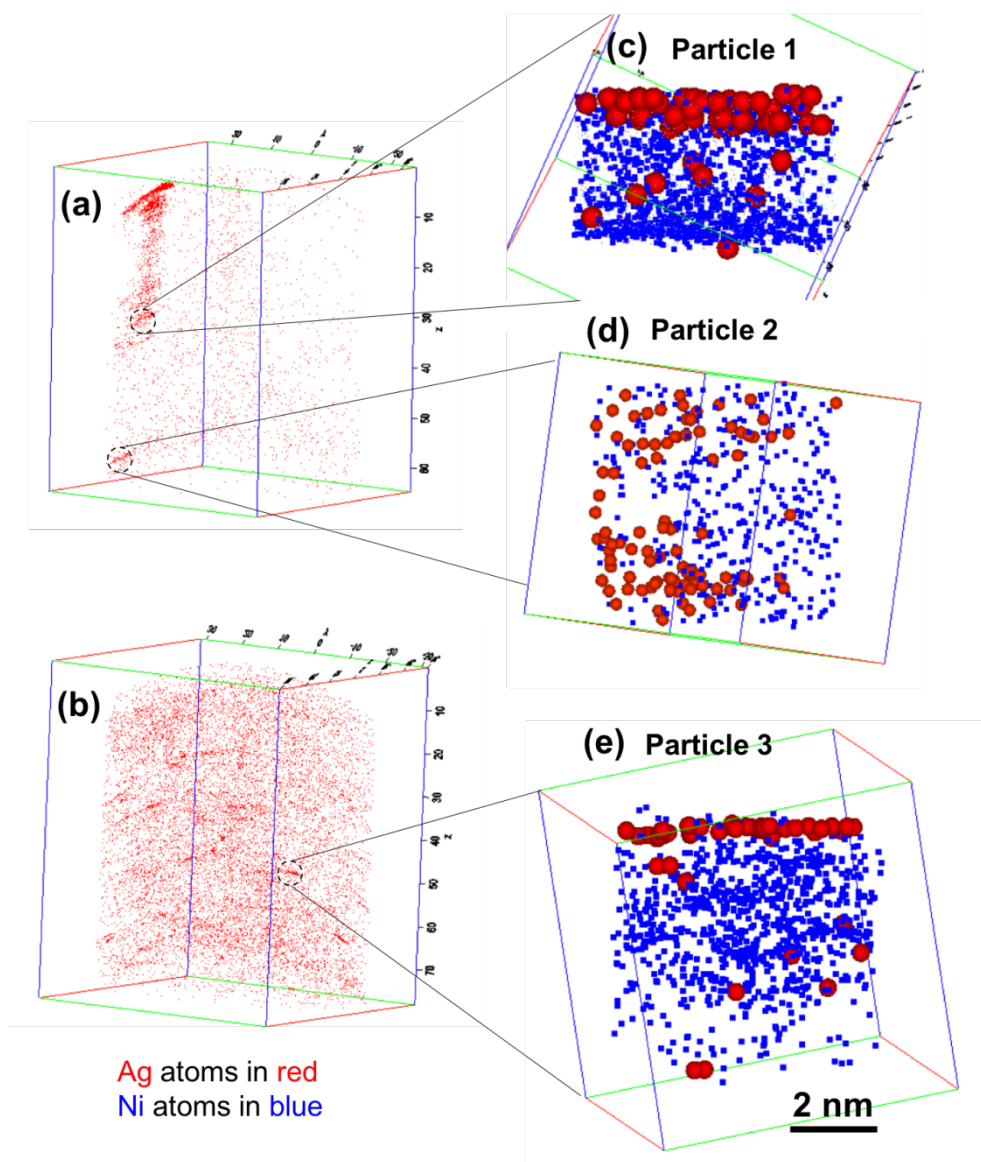


Figure 5.13 Atomic Probe Tomography (APT) data from $\text{Ni}_1\text{-Ag}_{0.4}/\text{SBA-15}$ Atom maps on the left measured the Ag distributions in selective areas of the sample. The enlarged atom maps show both the Ni and Ag with condensed atom regions (in silica matrix), which suggest approximately 1-3 atomic shell thickness of Ag atoms (slightly contaminated with Ni atoms) on Ni rich particles.

5.4.3 Surface feature of Ag atoms on Ni@Ag bimetallic nanoparticles

Thus, the above characterisations confirm that Ni-Ag nanoparticles are in core@shell bimetallic structure, which are distributed uniformly inside the SBA-15 channels. It also shows that the core-shell structure is related to the Ag: Ni loading ratios used. With a high Ag to Ni atoms ratio, such as Ni_{0.4}-Ag₁ after the reduction, a thicker Ag shell of 1.11nm (refer to Figure 5.11b) corresponding to the poor PO activity (2.3×10^{-5} mol/g/s) and PO selectivity of 41.4% (refer to Table 5.1). In contrast, with a thinner Ag shell using Ni₁-Ag_{0.4}/SBA-15, a relative more superior PO activity (4.4×10^{-5} mol/g/s) and PO selectivity of 70.7% (refer to Table 5.1) can be obtained. To further investigate the geometric and electronic features of local surface structure of Ag shell atoms with respect to catalytic performance, EXAFS and XPS were employed.

5.4.3.1 Geometric modification of Ag shell atoms by EXAFS

To analyse the local bonding structures of Ag shell atoms and Ni core atoms, X-ray absorption spectroscopy (XAS) was carried out at Ag and Ni K-edges for the Ag/SBA-15, Ni/SBA-15, Ni_{0.2}Ag₁/SBA-15, Ni_{0.4}Ag₁/SBA-15, Ni₁Ag_{0.4}/SBA-15 and Ni₁Ag_{0.2}/SBA-15, respectively. The extended X-ray adsorption fine structure (EXAFS) results for Ni₁-Ag_{0.4}/SBA-15 are selectively shown in Figure 5.14 and all data are summarised in Table 5.2 and 5.3.

The first shell analysis has been performed, taking the systematic errors of coordination number and the inter distances between the absorbing atom and neighbouring atoms into consideration. For the Ag and Ni K-edge data, to perform the EXAFS fitting, Ag and Ni metals with standard face centred cubic (fcc) structures were taken from National Chemical Database Service (NCDS) as the primary models to generate the scattering paths of Ag-Ag^[26] and Ni-Ni,^[27] respectively. The scattering paths were applied to calculate the average number of neighbouring atoms for absorbing Ag or Ni. The corresponding $k^3\chi$ intensity and $k^3\chi$ phase corrected Fourier transform fitting curves for the samples were also derived. The experimental data for all the samples were recorded and satisfactory R fitting were achieved. As seen from Table 5.2, each sample is fitted with a R factor of below 2.1% with the coordination number (CN) found to be around 7.7 to 8.2. Ag-Ni signal cannot be fitted due to the large scattering parameter of Ag. This CN value is typical for 3-5 nm nanoparticles with significant numbers of surface non-coordination sites (derivate from CN of 12 of bulk number).^[22,28] It is interesting to notice the difference in the average Ag-Ag bond distance. For the Ni_{0.2}-Ag₁/SBA-15 and Ni_{0.4}-Ag₁/SBA-15 with thicker Ag shells, their average Ag-Ag bond distance is comparable to that of the monometallic Ag/SBA-15 of 2.83 ± 0.01 Å. With the dramatic increase in Ni to Ag atom ratios, as in the cases of Ni₁-Ag_{0.4}/SBA-15 and Ni₁-Ag_{0.2}/SBA-15, there is a clear expansion of the Ag-Ag bond of 2.85 ± 0.01 Å beyond the statistical errors although the value is very small (Figure 5.14 and Table 5.2). Regarding the differences in atomic size and energy potential of Ni and Ag atoms, there should have lattice mismatches and charge transfer due to difference in d-band energies of these two monometallic phases at the interface in Ag-Ni binary core-shell system.^[19,29] Ideally, one should expect a compression in Ag lattice parameter exerted by the underlying

Ni lattice, which has the same fcc crystal structure as Ni but with a larger lattice parameter (isomorphic effect).^[30] In contrast, an expansion in Ag-Ag interatomic distance is observed. This expansion is thought to be due to loosely packed surface Ag atoms from bulk phase since the percentage of surface atoms is overwhelmingly high (see Chapter 1) in such thin atomic over-layers.

As can be seen in Table 5.3, each Ni K-edge fitting has also an R-factor below 2.6%, which shows the average coordination number of Ni-Ni in the samples is also around 8 indicative of nanoparticle size of the similar size created in SBA-15. However, for the Ni K-edge analysis, the additional Ni-Ag coordination signals are evident, giving the total coordination numbers of 10-11. This high-coordination characteristic of Ag-Ni/SBA-15 samples clearly implies the Ni is in pseudo bulk-like position where the surface unsaturated Ni sites are in contact with Ag shell atoms in bimetallic core-shell structure, as agreeable to the data from advanced surface analyses.^[19,31] This observation also matches with general higher CN of core atoms of core-shell structures.^[19,31–34] It is interesting to note that the Ni-Ni bond of 2.48 ± 0.01 Å in Ni core nanoparticle this time, remains totally unchanged within the experimental error.

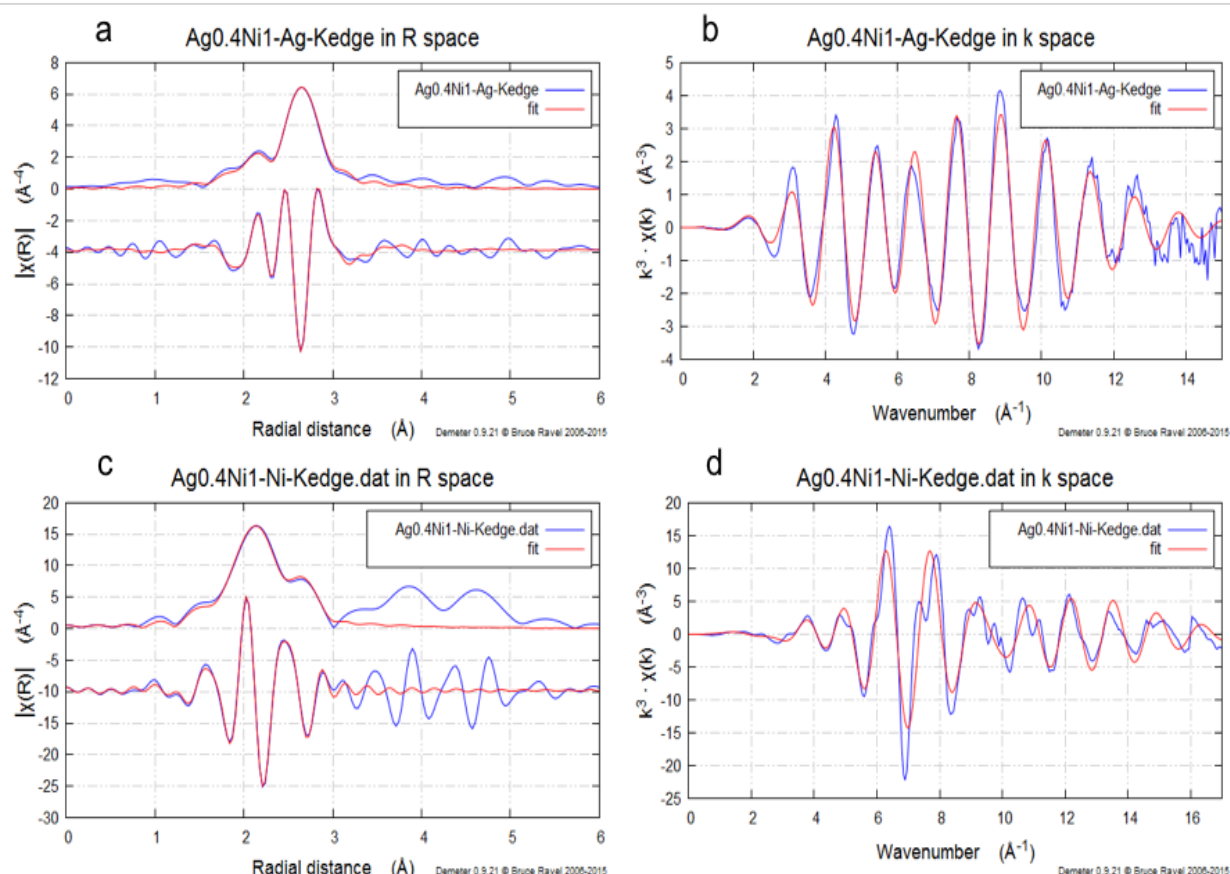


Figure 5.14(a) Raw and fitted Ag K-edge EXAFS for selected $Ni_1-Ag_{0.4}/SBA-15$; (b) Ag K-edge $k^3·χ$ phase corrected Fourier transform of experimental and fitted data for selected $Ni_1-Ag_{0.4}/SBA-15$; (c) Raw and fitted Ni K-edge EXAFS for selected $Ni_1-Ag_{0.4}/SBA-15$; (d) Ni K-edge $k^3·χ$ phase corrected Fourier transform of experimental and fitted data for selected $Ni_1-Ag_{0.4}/SBA-15$

Table 5.2 Ag K-edge EXAFS for Ag/SBA-15 and NI-Ag/SBA-15; (Enot is difference in absorption energy between experiment and calculation).

Catalysts	CN	D-W factor	Bond length	Enot	R-factor/%
	(Ag-Ag)	(Ag-Ag)	(Ag-Ag)/ $Å$		
Ag/SBA-15	8.0(3)	0.013(1)	2.83(1)	-0.3	1.9

Ni _{0.2} -Ag ₁ /SBA-15	7.7(4)	0.014(1)	2.83(1)	-0.7	2.1
Ni _{0.4} -Ag ₁ /SBA-15	7.8(3)	0.014(1)	2.83(1)	-1.4	2.0
Ni ₁ -Ag _{0.4} /SBA-15	8.1(2)	0.012(1)	2.85(1)	1.8	0.8
Ni ₁ -Ag _{0.2} /SBA-15	8.2(2)	0.013(1)	2.85(1)	1.9	0.7

Table 5.3 Ni K-edge EXAFS for Ni/SBA-15 and Ni-Ag/SBA-15; (Enot is difference in absorption energy between experiment and calculation).

Catalyst (Old)	Enot	CN (Ni-Ni)	D-W factor (Ni-Ni)	Bond length (Å) (Ni-Ni)	CN (Ni-Ag)	D-W factor (Ni-Ag)	Bond length (Å) (Ni-Ag)	R- factor
Ni _{0.2} Ag ₁ /SBA-15	-5.6	7.2(3)	0.005(1)	2.48(1)	4.2(6)	0.011(2)	2.78(1)	2.3%
Ni _{0.4} Ag ₁ /SBA-15	-4.8	7.7(3)	0.005(1)	2.48(1)	3.7(5)	0.010(1)	2.79(1)	1.5%
Ni ₁ -Ag _{0.4} /SBA-15	-5.4	7.3(2)	0.005(1)	2.48(1)	3.0(3)	0.010(2)	2.79(2)	0.3%
Ni ₁ -Ag _{0.2} /SBA-15	-5.5	7.6(2)	0.005(1)	2.48(1)	1.7(2)	0.011(2)	2.78(1)	0.4%
1Ni/SBA-15	-5.1	8.0(4)	0.005(1)	2.48(1)	-	-	-	2.6%

5.4.3.2 Geometric/electronic modification by XPS

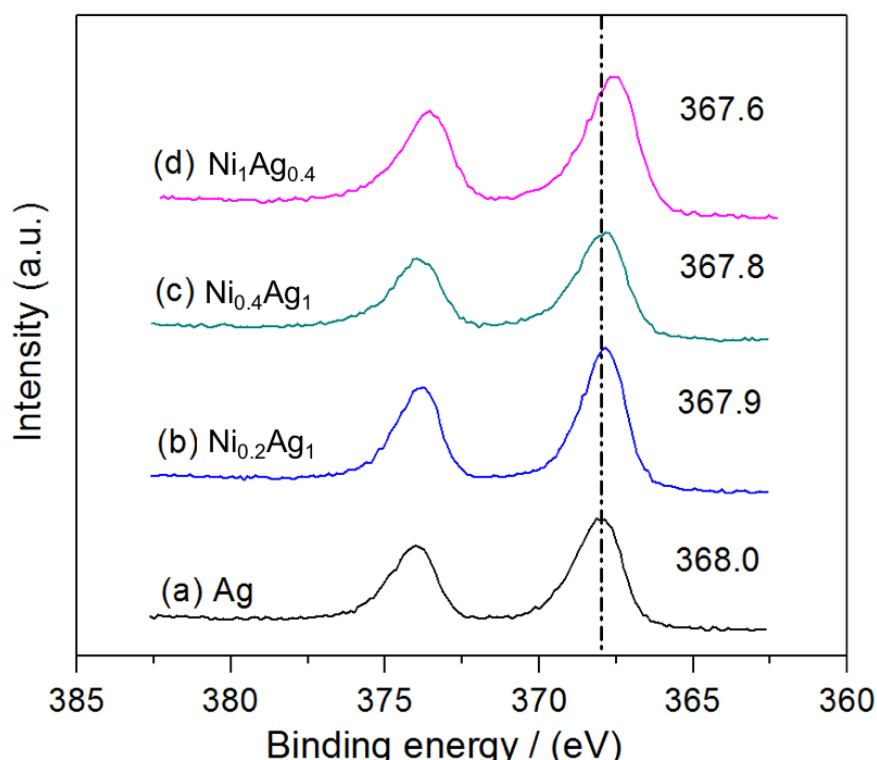
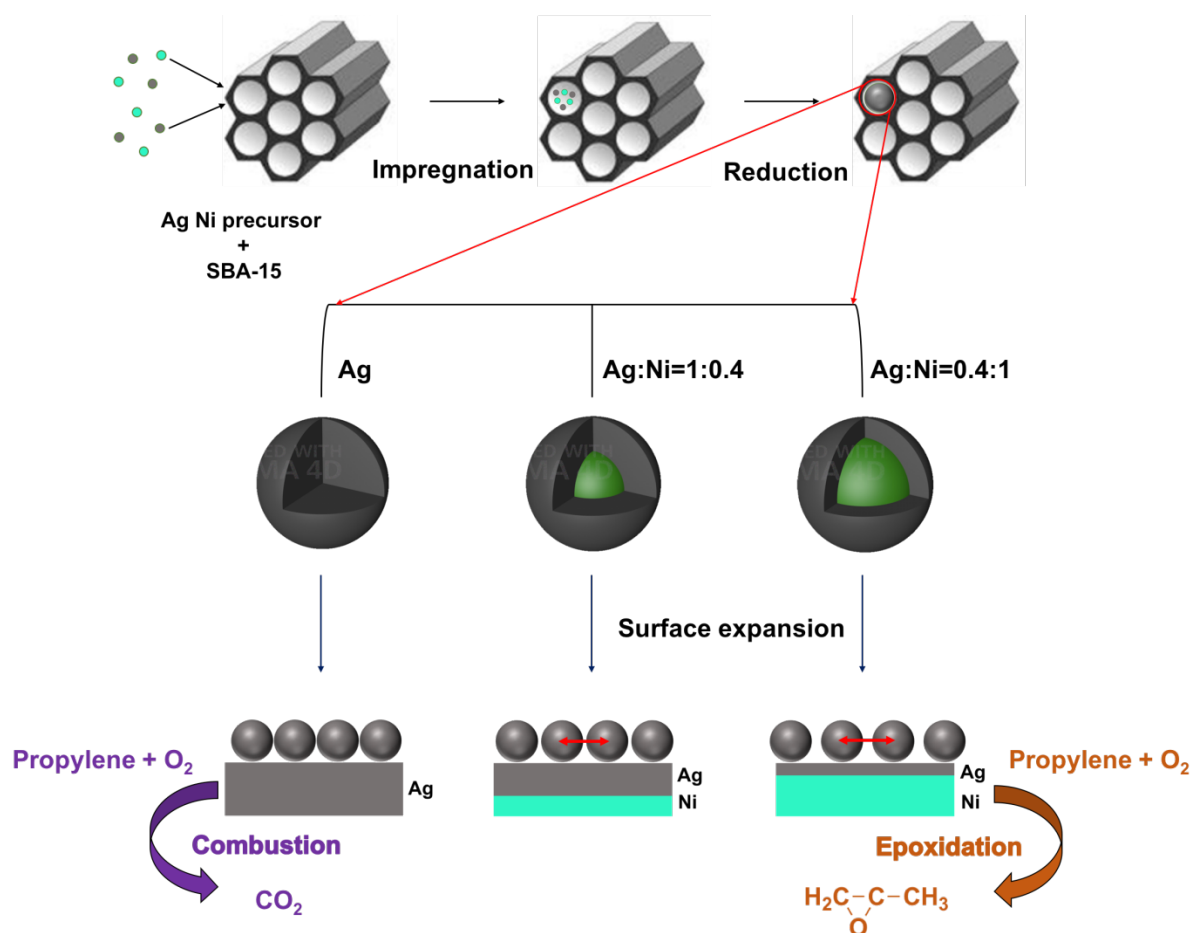


Figure 5.15 XPS spectra of decreasing Ag content (upwards) showing the progressive peak shift (in particular for Ni_{0.4}-Ag₁/SBA-15) in binding energy (B.E.) of Ag 3d_{5/2}.

XPS was employed to monitor the chemical state of Ag in these samples. Figure 5.15 shows Ag 3d XPS spectra of the (a) Ag/SBA-15, (b) Ni_{0.2}Ag₁ /SBA-15, (c) Ni_{0.4}Ag₁ /SBA-15, (d) Ni₁Ag_{0.4}/SBA-15, respectively. Two strong and distinct peaks at *ca.* 367.6 and 373.6 eV are observed from the Ag 3d XPS spectra, which can be attributed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively.^[35] Compared to Ag/SBA-15, the Ag 3d_{5/2} peak is progressively shifted to lower binding energies from 368.0 to the highest value of 367.6 eV of Ni₁Ag_{0.4}/SBA-15. This shift to lower BE may reflect the upshift of the surface d-band centre due to the geometric loosely packed interatomic Ag atoms in the shell.^[36] On the other hand, considering the electronegativity (EN) values of Ag

(1.93) and Ni (1.92), respectively, a slight tendency for an electron transfer may occur from the Ni phase to Ag phase leading to an increase in charge density of the Fermi level of Ag hence also accounting for the lower BE.



Scheme 5.1 Summarises the synthetic protocol in making controlled dimension of Ni core@ Ag shell nanoparticle (4.6 ± 0.5 nm). Propylene oxide selectivity is found critically dependent on the inverse thickness relationship of Ag shell atoms.

5.4.4 Discussion

As discussed in Chapter 4, the selectivity of propylene oxide over Ag(100) is much higher than Ag(111). This is attributed to the isolated active oxygen adsorbed on this facet with longer Ag-Ag interatomic distance for the effective epoxidation reaction.

The neighbored oxyradical formed from dioxygen molecule on this facet does not catalyse the γ -H abstraction from the surface adsorbed oxygenated species in a favourable position to lead to the total combustion. Similarly, the synthesis of Ni-Ag core shell nanoparticle and tailoring of Ag-Ag interatomic distance on Ag shell atoms as summarised in Scheme 5.1 may also provide a new way to create a longer Ag-Ag distance to reduce the total combustion route. Such longer interatomic Ag distance resulted from lesser surface packing can raise the surface d-band centre to promote higher activity as according to the d-band theory.^[37–40] This can account for the higher propylene oxide activity and selectivity observed for the first time on Ni-Ag core-shell catalysts. It is also shown that the ultra-thin Ag shell atoms with 0.63nm in the case of the Ni₁Ag_{0.4}/SBA-15 (see Figure 5.11 and Figure 5.13) can also activate the dioxygen directly without the assistance of La₂O₃ as support to give an optimal 70% selectivity to PO in the propylene-oxygen oxidation. The interesting question is that how the lattice expansion in Ag shell-atoms of the Ni@Ag core-shell nanoparticle can directly enhance the PO activity and selectivity. We do not anticipate a blunt ‘epitaxial like’ interface between the two metal phases in multifaceted core-shell nanoparticle morphology but rather in the interface region which contains inter-exchanged atoms from both sides (as shown by the Ag shell contaminated with Ni atoms in APT in Figure 5.13), as similar to our previous characterization of CdTe-ZnO nano-interface by atom probe tomography.^[24] Besides, the small but finite solubility (diffusion) between Ni and Ag phases and their difference in thermal expansion coefficient would make somehow irregular interface as contrast from that of single-crystals studies.^[31] Apart from the possible lattice expansion effects, hetero-metallic bonding interactions, termed the “ligand effect”, between Ag atoms of lower Fermi energy and core Ni atoms of higher Fermi energy

can result in charge transfer from Ni to Ag (also predicted by their difference in EN), and hence decreasing the activity of Ag atoms.^[36,41,42] It is difficult to assess the relative lattice strain and ligand effects because they occur simultaneously.^[29] We believe both these strain and ligand effects play the role to activate the Ag shell atoms.

5.5 Conclusions

The introduction of Ni nano-core to host Ag atoms offers a new way to create lattice expansion (geometric) and charge transfer (electronic) modification of Ag phase, which shows synergistic effect for enhanced catalytic performance on propylene oxidation reaction. These new core-shell catalysts present excellent stability over prolonged stability test, which can maintain the conversion and selectivity for at least 10h in our small-scale laboratory testing. The local structure of Ag-Ni was also confirmed in this study. It is evident bimetallic Ag-Ni forms a core-shell structure, which generates both geometric and electronic charge transfer effects for the greatly improved catalytic performance in this important reaction.

5.6 References

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Chapter 6 Atomically dispersed Ag in ZSM-5 for C=C bond cleavage

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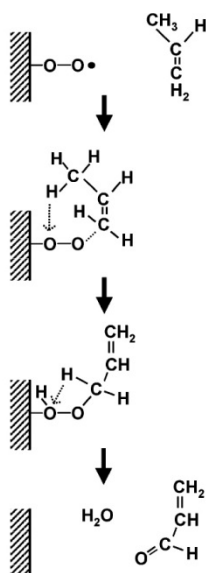
6.1 Background

In supported metal catalysts, metal components are generally in the form of finely dispersed nanoparticles on a high surface area support. In a typical catalysis reaction, only a small fraction of the metal atoms on the surface is actually involved. When the particle size of a catalyst is reduced, the ratio of surface metal atoms to bulk metal atoms is substantially increased. As a result, size of metal particles is one of the most important factors, affecting the efficient utilization of metal active sites towards a specific product. Size reduction of metal particles also benefits the performance of catalysts in other aspects: (1) unsaturated-coordination environment of metal at the surface,^{[1][2]} (2) quantum size effects,^{[3][4]} and (3) stronger metal-support interactions^{[5][6]} as mentioned in both Chapters 1 and 4. The use of specific nanosized catalysts has brought about breakthroughs in some heterogeneous catalysts by providing abundant and well-designed active sites. In Chapter 5, our study on the Ni-Ag/SBA-15 has already demonstrated the small size Ag@Ni core shell nanoparticles of improved catalytic activity and selectivity for propylene epoxidation.

Despite the small particle size effect, the study also revealed that the selectivity of propylene oxidation is critically affected by the surface arrangement of Ag atoms. The Ag@Ni core shell nanoparticles with a larger interatomic Ag-Ag distance on Ag shell atoms exhibit higher selectivity to PO in propylene oxidation due to the lower chance for the γ -H abstraction by neighbouring oxyradical (atomic oxygen) to channel to total combustion route. If the Ag atoms can be reduced to single isolated atoms, one would expect to eliminate the low temperature route of oxidising the

adsorbed oxygenated species to combustion in propylene epoxidation due to the extended distance between Ag sites.^[7]

This type of catalyst can be created by alloying the silver with an inert material. In a study by Geenen et al. propylene epoxidation over supported silver-gold alloy catalysts were examined.^[8] They observed an increasing amount of acrolein when more gold was added and proposed the catalysis mechanism shown in Scheme 6.1 over isolated Ag atoms.^[8]



Scheme 6.1 A proposed reaction scheme for the conversion of propylene to acrolein over isolated Ag atom.^[8]

In fact, the concept of using single-atom catalysts (SACs) for catalytic reactions is currently receiving intense attention from the catalysis community. SACs can be defined as the catalysts accommodating individual and isolated metal atoms or ions (prior reduction) that are anchored to a specific support and can behave as active centres for heterogeneous catalysis.^[9] Through a precise design of catalytic active sites at atomic level, it enables the utmost utilization of supported metals, and

processes fascinating prospects, such as drastic cost reduction, high catalytic activity and selectivity toward specific product. Therefore, in recent years, many research works have focused on the design and investigation of SACs.^[9] To date, some examples of single-atom catalysts using metal oxides,^[5] metal nanoparticles,^[5] and carbon materials^[10] as supports have been reported. Herein, in this chapter, we will demonstrate the preparation of practical isolated Ag catalyst in a crystalline porous material, the zeolite through an ion-exchanged method.^[11]

In fact, the characterisation of atomically dispersed metal or metal ion on supports has always remained challenge. Recently, the significant advancement of modern diffraction facilities with bright synchrotron radiation has provided scientists with powerful tool for porous but crystalline material characterisation. The high-resolution synchrotron X-ray powder diffraction (SXRD) has already been successfully employed for the structure determination of various zeolites.^[12,13] From our research group, we have also reported the use of SXRD combined with Rietveld refinement to elucidate the structure of organic adsorbates in zeolites.^[12–14] In this chapter, the Ag environment of the as prepared Ag SACs will also be elucidated by SXRD in combination with EXAFS and advanced electron microscopy in comparison with other isolated metal ions.

The Ag SACs will be systematically studied in propylene partial oxidation reaction under variety reaction conditions. These studies will hopefully help to understand the new molecular oxygen dissociation mechanism on active but isolated silver sites in propylene selective oxidation.

6.2 Objective

The aim of this chapter is to design Ag based SACs by ion-exchange method, and investigate its catalytic utilities in propylene oxidation. As highlighted in the previous chapters, we have discovered the surface arrangement and size effects for the crucial molecular oxygen activation step involved in the catalysis propylene epoxidation process. In this chapter, we will focus on exploring a potentially new molecular oxygen activation mechanism on the isolated silver site. As stated, the interaction between molecular oxygen with isolated Ag atoms without encountering neighbour absorbed active oxygen radical is the key factor for a potential high selectivity toward the epoxidation product. To study this effect, we have created a catalyst with an atomic dispersed Ag in H-ZSM-5 and employed it for the propylene selective oxidation. The reaction result may help to establish a deeper understanding of how the molecular oxygen interacts with a silver atom, to further design the required active site for propylene epoxidation.

6.3 Experimental details

A detailed discussion of experimental method can be found in Chapter 3; a brief summary of catalyst synthesis is given here.

In brief, the synthesis of Ag SACs was prepared via an ion-exchange method^[11] using H-ZSM zeolite as the support. H-ZSM-5 zeolite ($\text{Al}_2\text{O}_3:\text{SiO}_2=1:38.5$) was obtained from SRIFT-Sinopec, China. The sample was first calcined in air at a ramp rate of $1\text{ }^\circ\text{C min}^{-1}$ to $450\text{ }^\circ\text{C}$ for 2hrs upon received. To prepare AgZSM-5 a silver loading of 2 wt%, a known amount of AgNO_3 was dissolved in 30 mL Milli-Q water. 1.5 g pre-treated ZSM-5 was then added to the prepared solution under vigorously

stirring at 30 °C for 24 h in dark. The sample was collected and washed with DI and filtered. The obtained sample was calcined in N₂ at a ramp rate of 1 °C min⁻¹ to 450 °C for 2h, then cooled and stored under vacuum in dark to prevent further reduction. The AgZSM-5 was tested in both gas phase fixed bed reactor and in liquid batch reactor under comparable conditions.

The fixed bed reactions were performed in a vertical tubular fixed bed reactor that allowed a three-stage of temperature control throughout the whole reactor which delivered evenly distributed temperature. In a standard reaction, a known amount of AgZSM-5 was packed in the middle stage of the reactor with quartz wool on the top and bottom of the catalysts. The composition of the feeding gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1 at a total flow rate of 20 mL/min, which was delivered from the top of the reactor. A temperature program was used, beginning at 100 °C, at each reaction temperature, the reaction time last for 1 h allowing the GC to analyse the reaction products.

The batch reactions were conducted in a pressurized autoclave reactor. In a typical experiment, 20 mL of Milli-Q water and a known amount of AgZSM-5 were mixed in the autoclave with a magnetic stirring bar. The Milli-Q water was saturated with a mixture of propylene and O₂ gas with a mixing ratio of 2:1. The reaction vessel was then sealed and flushed with gas mixture of 5% C₃H₆ in helium and 5% O₂ in helium with a mixing ratio of 2:1 to build up to a certain high-pressure reaction condition (30 bar). After the reaction, the autoclave was cooled down to room temperature. Both the gas phase and liquid phase products were identified and quantified using a gas

chromatograph (Agilent 7890) equipped with two TCD detectors and one FID detector calibrated with pure standards.

6.4 Results and Discussion

6.4.1 Ag single-atom catalysts (AgZSM-5)

While SACs are of great interest and potential in heterogeneous catalysis, experimental preparation and characterization of SACs still remain challenge. Highly dispersed isolated single metal atoms are with huge surface-free-energy, and have tendency of aggregation when higher surface-loading is achieved.^[9] On the other hand, even when these isolated atoms/ions dispersed finely on the support, stabilisation of these surface single atoms remains as a challenge owing to high mobility and ease of sintering. These single atoms are generally not capable of withstanding practical use, especially at higher temperature.^[3] Therefore, obtaining a robust anchoring site through a strong metal support interaction (SMSI) is the key to resolving these issues. However, on a flat and common surface an individual guest atom is usually in very weak bonding hence facilitated mobilization. For example, the activation energy for self-diffusion of gold atoms on a gold surface was found to be only about 30 kJmol⁻¹.^[3] Porous materials are normally used in catalyst preparation as supports because of their high surface areas. Among all these porous materials, HZSM-5 is commonly used as a solid acid as the internal surface gives a high density of Brønsted acid sites.^[14] The difference in valence of Si and Al from the framework atom substitution results in an unbalanced surface charge. H⁺ is normally bonded to the Al site to balance the surface charge to form a Brønsted acid site. As a result, isolated M⁺ can be used to immobilize on this internal surface acid site

through ion-exchange with H^+ or Na^+ form. In this chapter, we have synthesised AgZSM-5 as well as CuZSM-5 and ZnZSM-5 through ion exchange method.

6.4.1.1 Synthesis

According to literature reports, SACs can be synthesised by ion-exchange of metal ion with the cation of the porous materials,^[11] as well as using organometallic complexes^[10,15] to anchor to the supports. The method we reported in this chapter is to ion-exchange H^+ with Ag^+ to the Brønsted acid sites on HZSM-5 in order to achieve isolation and stabilization. The ion-exchange reaction was carried out under room temperature for 24 h to allow the maximum ion-exchange capacity. Ag^+ can easily be reduced by visible light in a mild condition. To avoid reduction and further aggregation into small Ag nanoparticles, the whole ion-exchange process was conducted in a dark environment, and no further reduction was required. The exceeded amount of Ag^+ was washed with plenty MQ water followed by centrifuging. CuZSM-5 and ZnZSM-5 were also synthesized in the same manner for comparison.

6.4.1.2 TEM Characterization

The structural detail of HZSM-5, AgZSM-5 and calcined AgZSM-5 were characterized by visible inspection, TEM. First, from the visual inspection, we saw that the pre-treated HZSM-5 is in the form of a white powder. After ion-exchange with Ag with or without calcination at high temperature (450 °C), the samples maintain as the same white powders. In contrast, the colour of any Ag nanoparticles containing samples with sufficient loading normally is highly intense, ranging from a light ruby yellow colour at very small size (under 4 nm) to a dark black colour (over 100 nm) because of the surface plasmon resonance effect.^[16,17] Particularly, our 2%

Ag loading after calcination with the thermal reduction should have created stained colour in the samples if Ag nanoparticles were formed. Thus, the absence of colour in both AgZSM-5 samples with and without calcination strongly indicated that Ag remains isolated on ZSM-5 during the syntheses.

The TEM image of HZSM-5 is shown in Figure 6.1. This HZSM-5 sample was made up of small cubic-like crystals with the size ranging from 40-100 nm range.

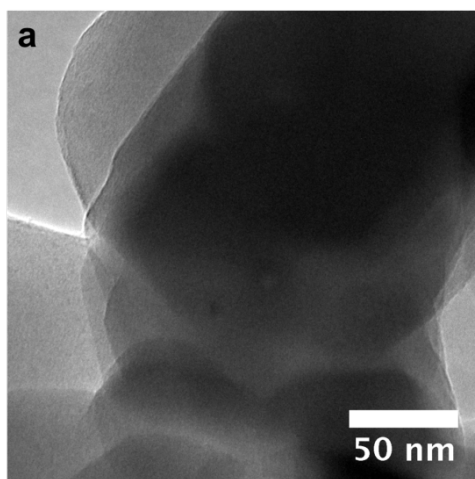


Figure 6.1 A TEM image of selected area of the commercial HZSM-5

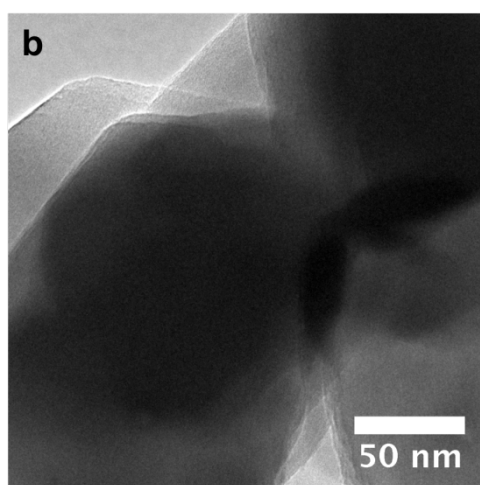


Figure 6.2 A TEM images of as-synthesised AgZSM-5 prior to calcination.

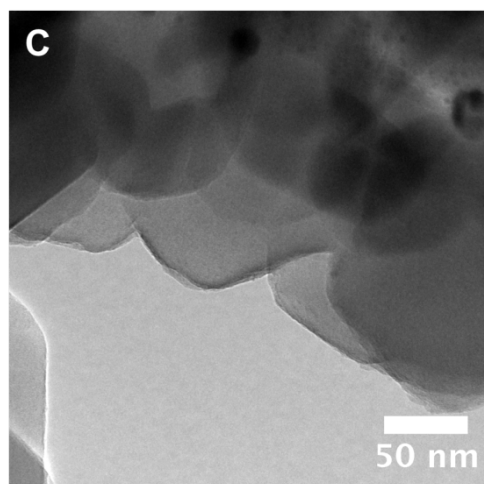


Figure 6.3 A TEM image of AgZSM-5 after calcination.

The TEM images of AgZSM-5 and calcined AgZSM-5 are shown in Figure 6.2 and 6.3, respectively. As shown in Figure 6.2, no obvious Ag metal particles can be found over the HZSM-5 phase, and the HZSM-5 appears to maintain a consistent structure after the ion-exchange process. For the calcined AgZSM-5 as shown in Figure 6.3, again a stable zeolite structure without detecting any metal particles after the high temperature treatment. On the other hand, for the synthesis of silver nanoparticles, thermal reduction and aggregation processes can be initiated from 60-80 °C. These results again indicate that Ag or Ag⁺ is in a stable environment, which appears to prevent aggregation at 450 °C.

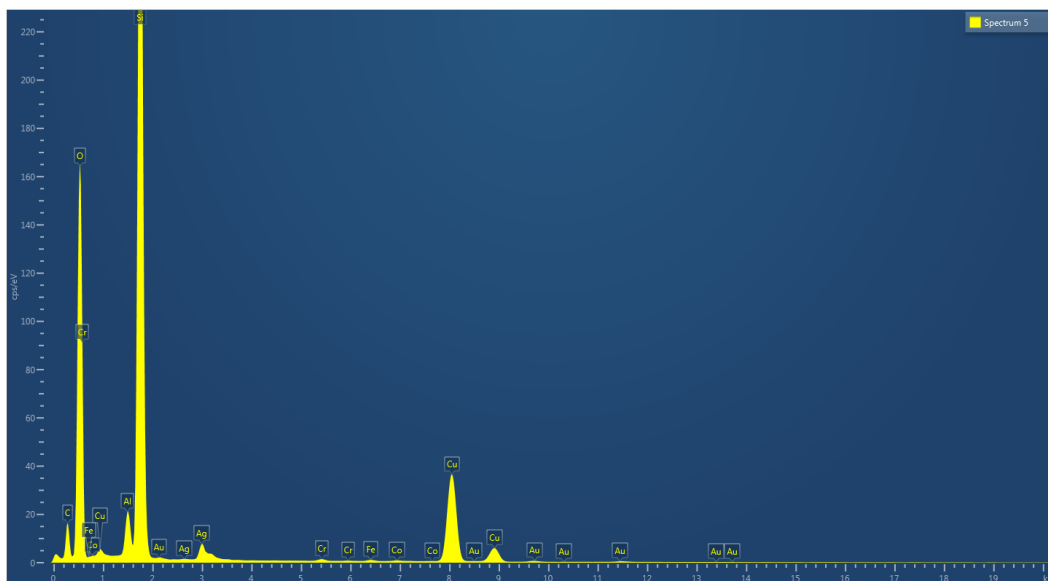


Figure 6.4 Energy Dispersive X-ray (EDX) spectrum of calcined AgZSM-5.

The EDX analysis of calcined AgZSM-5 sample is shown in Figure 6.4, which illustrates that the Ag to Al ratio is 1: 3.5. In this H-ZSM-5 ($\text{H}_{4.48}\text{Al}_{4.48}\text{Si}_{91.52}\text{O}_{192}$), a proton is generated for each Al site in order to balance the surface charge. It is therefore anticipated that the ion-exchange process takes place only at the proton sites, where Ag^+ ions substitute them. After ion-exchange with the substitution Ag to proton ratio kept at 1:1, the EDX result then corresponds to 28% of the proton sites replaced by Ag^+ . As such, the calculated actual silver loading is about 0.6 wt% on HZSM-5 instead of the nominated 2wt%.

6.4.2 Identification of AgZSM-5 structure

To collect the essential structural information of AgZSM-5, especially the local environment of silver sites on HZSM-5, we have conducted several characterisation techniques, including SXRD, EXAFS and STEM. This commercial HZSM-5 sample ($\text{H}_{4.48}\text{Al}_{4.48}\text{Si}_{91.52}\text{O}_{192}$) was previously characterized by our group.^[14] The atomic

location of Al^{3+} has been identified at framework T6 site (connected between two oxygens, O5 and O18) as determined by SXRD in combination with theoretical calculations. Thus, there is one Al^{3+} per asymmetric unit with the space group of Pnma.

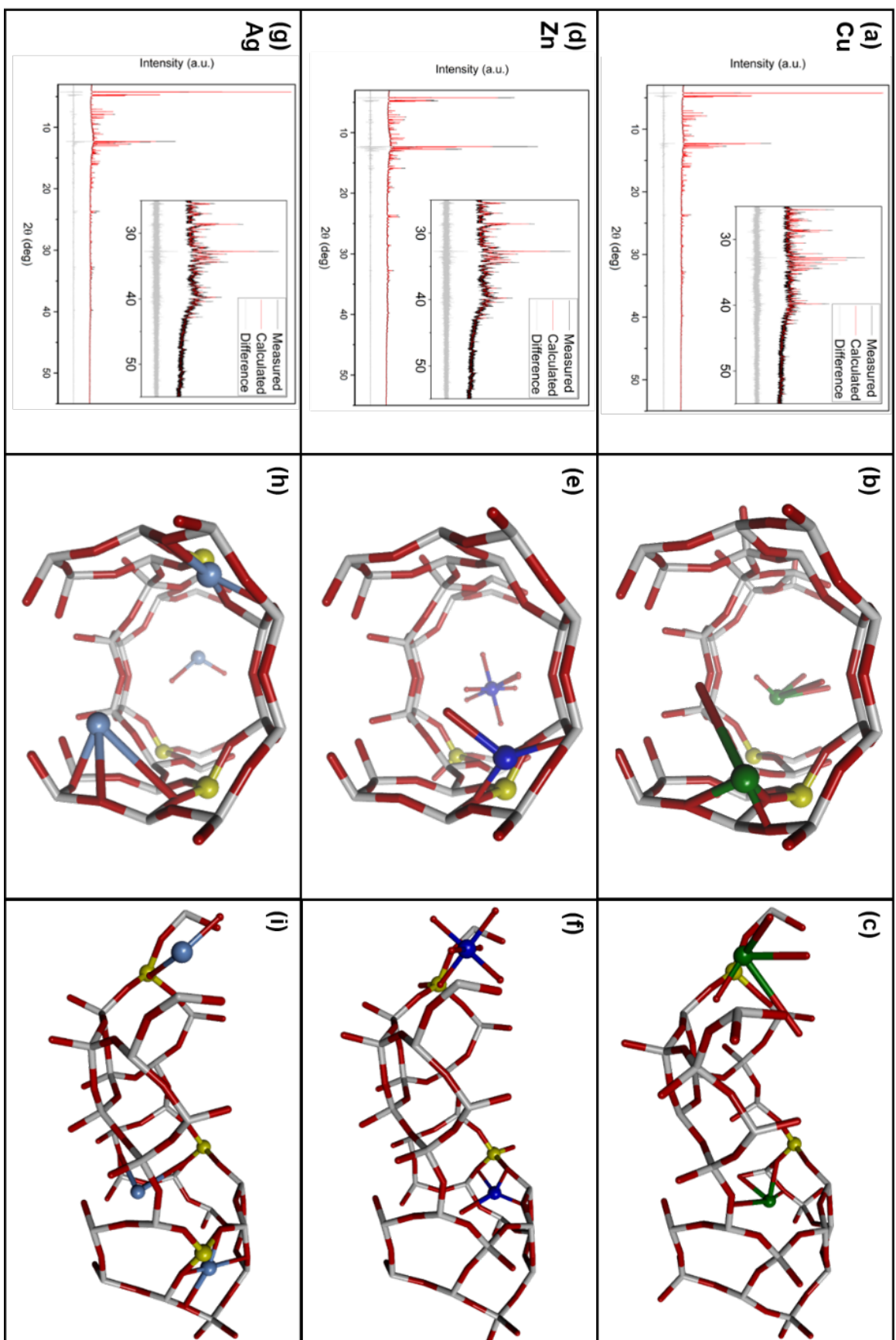


Figure 6.5 SXRD and Rietveld refinement measured at 25 °C of (a) CuZSM-5, ($R_{wp} = 7.956\%$, $\chi^2 = 1.581$) (d) ZnZSM-5, ($R_{wp} = 7.896\%$, $\chi^2 = 2.237$), and (g) AgZSM-5, ($R_{wp} = 7.212\%$, $\chi^2 = 2.181$). Their corresponding Rietveld derived crystal structure showing two asymmetric units are also shown viewing from the sinusoidal channel and from the straight channel, (b,c) CuZSM-5, (e,f) ZnZSM-5, and (h,i) AgZSM-5. The atomic and crystallographic parameters are summarized in Table A1 of Appendix. Atoms are represented in ball/sticks: grey = Si, yellow = Al (T6), red = O, green = Cu, blue = Zn, and light blue = Ag. Some symmetry is disregarded for clarity. See main text for the detailed bond distance description.

6.4.2.1 SXRD and Rietveld refinement

The SXRD and Rietveld refinement profiles for calcined Cu^{2+} , Zn^{2+} and Ag^+ samples are displayed in Figure 6.5. All the data were refined by the Rietveld method using TOPAS Academic refinement software (Bruker AXS, version 5). Analytical details were described in Chapter 3. In brief, all the SXRD data have been refined well with low R-factors and excellent data fittings. All the Rietveld refinement results show that the space group of *Pnma* maintained upon the addition of these metal ions as in a typical H-ZSM-5. A slight alteration in volume (*ca.* $\pm 0.05\%$) was observed for all the samples when compared to the unmodified H-ZSM-5. No additional peak was observed, which suggests the absence of metal clustering or alteration in structure. The corresponding derived crystal structures for the three metal ions are also summarized in Figure 6.5 (and the appendix), with showing the modified asymmetric unit. In our previous report, we have detected two isolated metal ion sites within the H-ZSM-5 framework. One metal ion site (site 1) is located in a straight channel, while another metal ion site (site 2) is anchored onto the wall of the H-ZSM-5 framework

(by coordinating with the oxygen atoms in proximity to the Al T6 site). Typically, as seen in Figure 6.5, ZnZSM-5 shows 0.42 (statistical occupancy value) of hexa-aqua Zn (Zn-1) in site 1 and 0.57 tetrahedral-coordinated Zn (Zn-2) species in site 2. The entrapped Zn-1 species in straight channel with the 6 equivalent water ligands with an average Zn-O(H)₂ distance of 2.12(3) Å. It is likely maintained by the surrounding negatively charged framework oxygen atoms through electrostatic interaction by ion-exchange with the Brønsted acid sites. For tetrahedral Zn-2, it is identified that it is held by three framework oxygen atoms (O6, O9 and O18) on the wall of H-ZSM5, with a remaining non-framework coordination with oxygen in the form of 'Zn-OH' ($r_{\text{Zn-OH}} = 2.32(2)$ Å).^[18] For CuZSM-5, there is 0.77 (occupancy value) of distorted hexa-aqua Cu (Cu-1) in site 1 in the straight channel and 0.54 tetrahedral coordinated Cu-2 site in site 2. The Cu-2 is also held by three framework oxygen atoms (O1 of 1.75(2) Å, O2 of 2.19(2) Å and O6_(acid site with Al) of 2.52(2) Å) on the wall of H-ZSM5, with the remaining longer non-framework coordination with oxygen of 2.52(2) Å presumably also in the form of 'Cu-OH' (will be confirmed by H¹ NMR shortly). As a result, both Cu²⁺ and Zn²⁺ are found in the ZSM-5 internal surface in a similar structure.

From the Rietveld refinement of the AgZSM-5 sample shown in Figure 6.5, 0.51(1) is occupied in site 1 by a slightly bended di-aqua Ag-1 species, while 0.35(1) Ag-2 site is also coordinated with three framework oxygen atoms (O2 ($r_{\text{Ag2-O2}} = 2.69(2)$ Å), O3 ($r_{\text{Ag2-O3}} = 2.43(2)$ Å) and O20 ($r_{\text{Ag2-O20}} = 2.64(2)$ Å)) through electrostatic interaction. Unlike the Zn-2 or Cu-2 site in ZSM-5, the Ag-2 site is not connected to any non-framework oxygen atom. Therefore, the Ag-2 site is not in the form of 'Ag-OH' or 'Ag-OH₂'. Excitingly, there is an extra Ag-3 site located on another 10-membered ring

adjacent to the Al T6 acid site. The population of the Ag-3 site is 0.18(1). It is coordinated with four framework oxygen atoms (O1 ($r_{\text{Ag3-O1}} = 2.41(2) \text{ \AA}$), O6 ($r_{\text{Ag3-O2}} = 1.69(2) \text{ \AA}$), O9 ($r_{\text{Ag3-O2}} = 2.24(2) \text{ \AA}$) and O18 ($r_{\text{Ag3-O2}} = 2.04(2) \text{ \AA}$)).

6.4.2.2 EXAFS

The EXAFS results are shown in Figure 6.6 and Table 6.1. The best –fit EXAFS average M-O bond distances for calcined Cu^{2+} , Zn^{2+} and Ag^+ and average coordination numbers (CN) are comparable with the structures derived by the SXRD and refinements. For AgZSM-5, the average Ag-O bond distance from EXAFS fit is 2.31(2) and the average CN is 2.9(2).

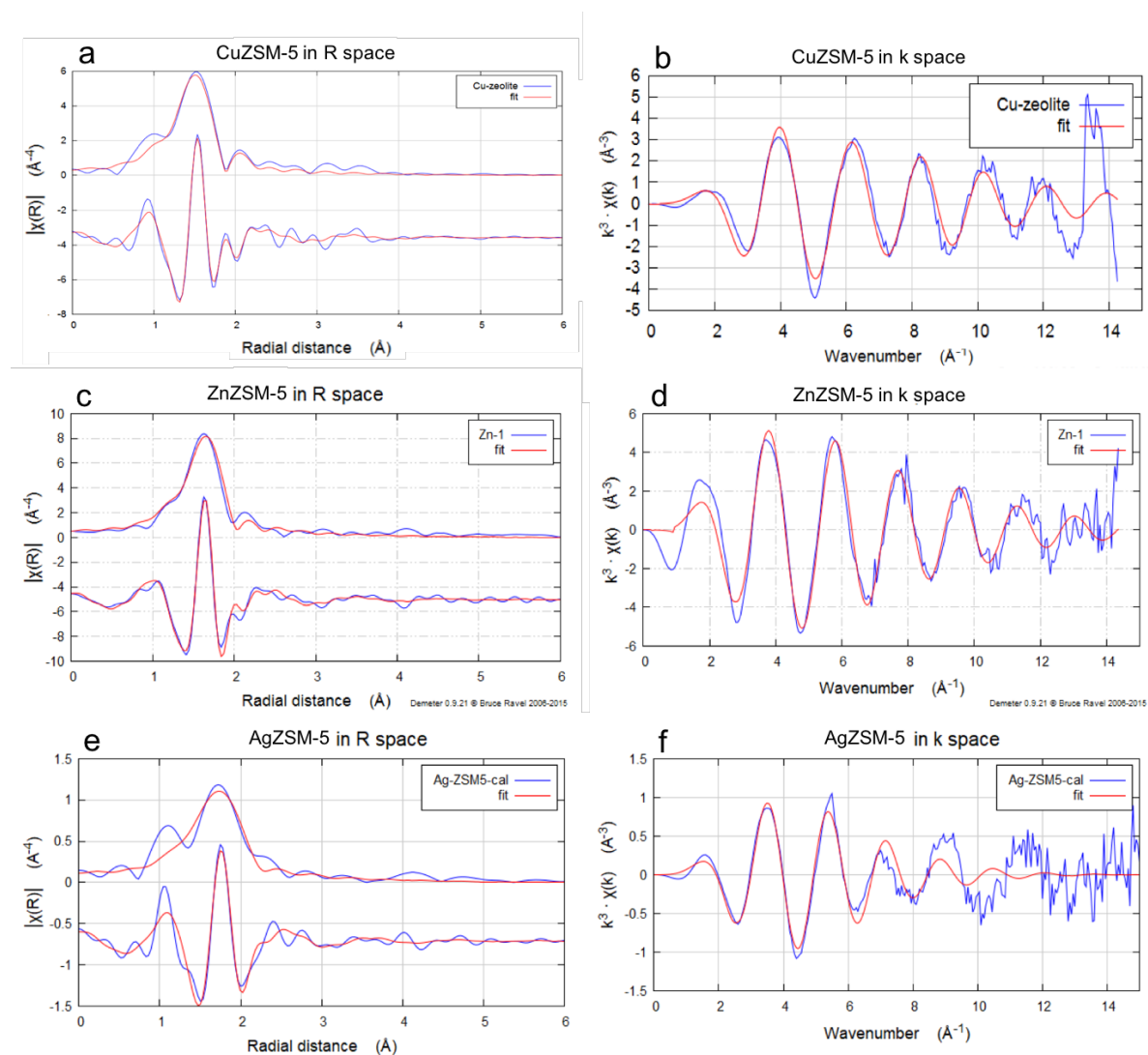


Figure 6.6 Extended X-ray Absorption Fine Structure (EXAFS) results and fittings for the three Cu^{2+} , Zn^{2+} and Ag^+ ion-exchanged H-ZSM-5 catalysts.

Table 6.1 Comparison between the derived structural models from the best-fit EXAFS and SXRD data for the three calcined Cu²⁺, Zn²⁺ and Ag⁺ ion-exchanged H-ZSM-5 catalysts.

Catalyst	Bond	CN ^{EXAFS}	CN ^{SXRD}	r _{M-O} ^{EXAFS} (Å)	r _{M-O} ^{SXRD} (Å)	Debye-Waller	E _{not}	R-factor (%)
CuZSM-5	Cu-O	3.8(1)	4.0(1)	1.96(1)	2.15(2)	0.006(1)	-5.4	1.1
ZnZSM-5	Zn-O	5.2(2)	4.8(1)	2.07(1)	2.11(2)	0.007(1)	3.4	1.4
AgZSM-5	Ag-O	2.9(2)	2.7(1)	2.31(2)	2.27(2)	0.015(2)	-0.2	1.5

For AgZSM-5, from the derived crystal structures by combining SXRD with EXAFS, two striking features are revealed, (i) about 1/3 of the Ag metal species have been successfully made anchored onto the framework 10-membered ring, i.e. immobilised by three or four framework oxygen atoms; (ii) these anchored Ag metal species are quite different in nature comparing to Zn in ZnZSM-5 or Cu in CuZSM-5. Instead of forming 'M-OH', Ag species are present in the form as 'Ag'. The charge and chemical properties of the metal ions seem to be crucial as catalyst precursors.

6.4.2.3 High-resolution HAADF STEM

High-resolution electron microscopy of calcined AgZSM-5 was carried out using an aberration-corrected JEOL ARM200F. The microscope was operated at 200 kV in HAADF-STEM mode with HAADF detector collection semi-angles from 73 to 236 mrad. The convergence semi-angle was 31.48 mrad with probe array sizes of 1024 by 1024 and a dwell time of 0.8 μ s per pixel. The probe current was 11 pA.

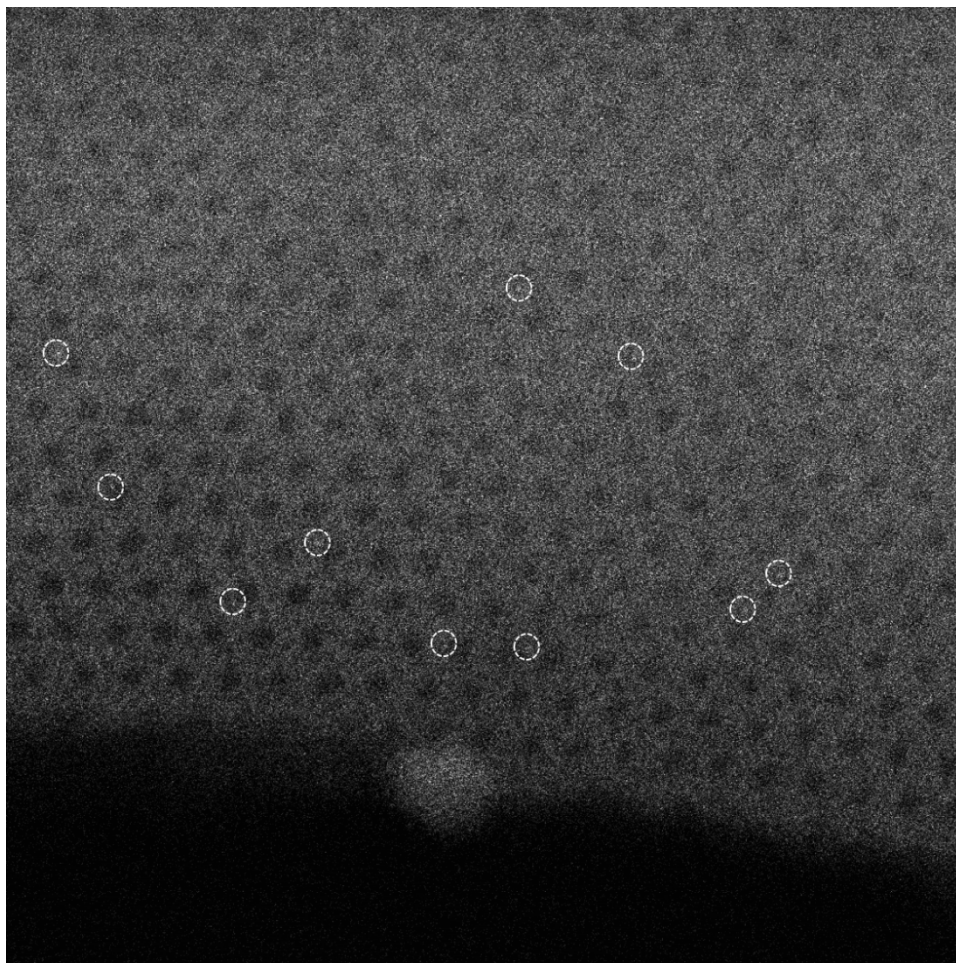


Figure 6.7 HAADF-STEM image of AgZSM-5 with pores projected along the zone axes $[1\ 0\ 0]$, the pore walls are decorated with isolated atomic Ag-containing species (circled). Corresponding crystallographic model of AgZSM-5 from Rietveld refinement (see Fig.6.4) matches with observed isolated Ag sites in the structure.

From the STEM image (Figure 6.7), the corresponding crystallographic model of AgZSM-5 (Fig. 6.4) appears to match with observed isolated Ag sites (marked in circle) immobilised on Brønsted acid sites on the inner surface of ZSM-5, which did not seem to suffer from rapid aggregation even under strong electron beam heating. This clearly suggests that isolated Ag sites are strongly anchored on the wall of the internal ZSM-5 structure.

6.4.3 Catalytic performance of AgZSM-5

6.4.3.1 Gas-solid phase propylene oxidation reaction

The AgZSM-5 catalyst was particularly tested under the same reaction conditions as mentioned in Chapters 4 and 5. The AgZSM-5 was packed in a vertical tubular fixed bed reactor at 1 bar with a total gas flow rate of 20 mL/min. The composition of the gas mixture was 5% C₃H₆ in helium and 5% O₂ in helium with a mix ratio of 2:1. The reaction products were analysed by a gas chromatograph equipped with a methanizer and a flame ionization detector (FID) as described in Chapter 3.

The gas phase reaction products over AgZSM-5 at 250 °C and 300 °C were tested, analysed and are shown in Figures 6.8 and Table 6.2. From the product analysis by GC, AgZSM-5 catalyst seems to be extremely reactive under the reaction conditions, giving about 19 main products. However, as labelled in the GC trace, both CO₂ and propylene oxide were not formed. The wide range of hydrocarbon products has posed a significant difficulty for us to carry out product identifications. Despite, we have found that the majority of products are in forms of higher hydrocarbons or aromatic products. The conversion of propylene at 250 °C is displayed in Table 6.2,

which is found to be 44.76%. In addition, we have found that this AgZSM-5 was deactivated very quickly and its colour rapidly changed from white to dark black, suggesting a serious carbon deposition. According to literature, acidic HZSM-5, is well known for catalysing acid reforming of hydrocarbons (isomerisation, oligomerization, fragmentation, aromatisation and polymerization, etc)^[19–24] to give a range of saturated and unsaturated hydrocarbons and aromatics of different carbon chain lengths and structures. This can also lead to macroscopic carbon deposition.^[24] Therefore, under the reactive gas phase conditions, the acid sites on AgZSM-5 is thought to contribute these activities while masking off any catalytic role of supported Ag atom in gas phase propylene-oxygen reaction.

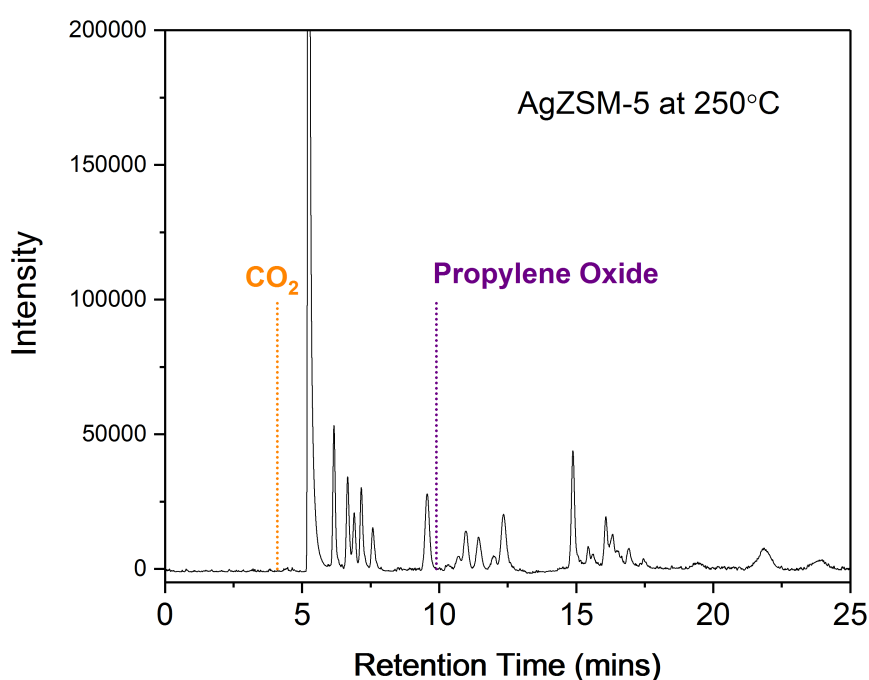


Figure 6.8 A wide range of hydrocarbons and aromatics formed but with no production of CO₂ and propylene oxide over AgZSM-5 under oxygen-propylene feed at 250°C.

In order to confirm our hypothesis, we tested the pure HZSM-5 instead of AgZSM-5, and the result is presented in Figure 6.9. Similarly, no CO₂ and propylene oxide was detected. There were also 19 products detected and the GC trace remained nearly unchanged comparing to Figure 6.7, despite a slight decrease in propylene conversion from 44.7% to 43.8%. It seemed that, even without silver atoms on HZSM-5, a similar reaction results were obtained.

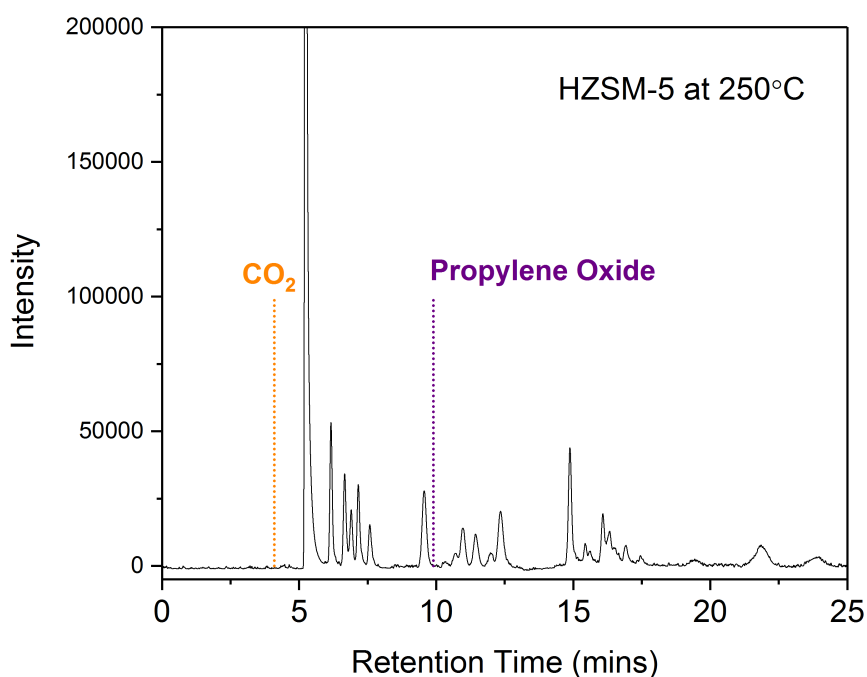


Figure 6.9 A similar range of hydrocarbons and aromatics formed but with no production of CO₂ and propylene oxide over HZSM-5 under oxygen-propylene feed at 250°C.

Table 6.2 Gas phase propylene oxidation reaction over zeolite catalysts.

	AgZSM-5		HZSM-5	
Temperature (°C)	250	300	250	300

Conversion (%)	44.7	1.7	43.8	1.0
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From the gas phase reaction, two striking features can be revealed, (i) the atomic dispersed silver atoms does not seem to contribute to the overall hydrocarbon reforming reactions and there is neither CO₂ nor propylene oxide production until 300 °C; (ii) acidic HZSM-5 on its own is extremely active to catalyse propylene reforming reactions such that the acidic sites appear to compete for hydrocarbons or intermediates more successfully than that of isolated Ag sites.

6.4.3.2 Liquid phase batch reaction

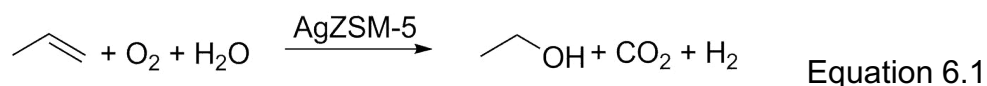
In this part, AgZSM-5 catalyst was tested under milder reaction conditions, with higher applied pressure and lower reaction temperature (< 200 °C) in order to reduce the reforming reactions induced by acid sites from the HZSM-5 phase. The catalyst was placed in a liquid phase-batch reactor, and the experimental details are presented in Chapter 3.

In brief, the liquid phase reactions were conducted in a pressurized autoclave reactor. In a typical experiment, 20 mL of the Milli-Q water and specific amount of AgZSM-5 were mixed in the autoclave with a magnetic stirring bar. The liquid mixture was saturated with a mixture of diluted propylene and O₂ with N₂. The reaction vessel was then sealed and flushed with diluted gas mixture of C₃H₆ (5% in helium) and O₂ (5% in helium) in a mixing ratio. This allowed the reaction pressure to be build up with a certain value (30 bar for all experiments mentioned in this thesis). The isothermal reaction was conducted at certain reaction temperature for a specific reaction time. Fresh catalyst was used for individual test under a specific reaction

condition. Once the experiments finished, the autoclave was cooled down to room temperature in iced-water bath. Both the gas phase and liquid phase products were identified and quantified using a gas chromatograph (Agilent 7890) equipped with two TCD detectors and one FID detector pre-calibrated with pure standards. The propylene conversion and selectivity for each reaction products were calculated based on the quantitative data obtained from GC analysis.

6.4.3.2.1 Temperature effect

The catalysis performance of AgZSM-5 was initially tested under various reaction temperatures. The results are summarised in Figure 6.10 and Table 6.3. Among all the reaction products, no epoxidation products can also be observed. However, excitingly, ethanol and CO₂ were two main reaction products, with nearly equal selectivity about 46.4% (stoichiometric produced). To our best knowledge, there is no report on the synthesis of ethanol from propylene. Industrial ethanol is mainly produced from catalytic hydrogenation of acetic acid, which in turn is formed from methanol carbonylation (synthesis gas technology).^[25] Alternatively, biological fermentation processes can also produce ethanol^[26] but no significant ethanol is obtained from the petro-chemical route. Equation 6.1 summarises the catalytic cleavage of propylene in oxygen to produce ethanol and CO₂.



According to Equation 6.1, for every mole of propylene, equal mole of ethanol and CO₂ can be produced over the AgZSM-5 in oxygen. To produce C1 and C2 species

from a C3 alkene, there must have undergone a selective catalytic C=C cleavage step. Noticeably, pure HZSM-5 did not produce CO₂ or ethanol under the same reaction conditions. Therefore, we attributed the atomically dispersed Ag in HZSM-5 to provide active sites for selective C=C bond cleavage in presence of O₂. The highest carbon selectivity of this reaction was about 91.1% at 50 °C. In addition, a small quantity of higher hydrocarbons/aromatics was detected according to GC-MS over both AgZSM-5 and pure HZSM-5. These higher hydrocarbons/aromatics although formed at low temperature were assigned to be the products from propylene reforming, as previously reported. As the temperature increased from 50 to 200 °C, the selectivity of hydrocarbons (i.e. naphthalene was identified by GC-MS) was also increased from 8.8% to 37.5%.

The conversions of propylene at various reaction temperatures were systematically studied and are summarised in Table 6.3. It is shown that a conversion of 5.7% can be obtained with high selectivity to ethanol/CO₂ as low as 50 °C. At 200 °C, the propylene conversion reaches 8.3%, although the contribution from propylene reforming to higher hydrocarbons/aromatics at the higher temperature decreases the selectivity towards ethanol/CO₂ products.

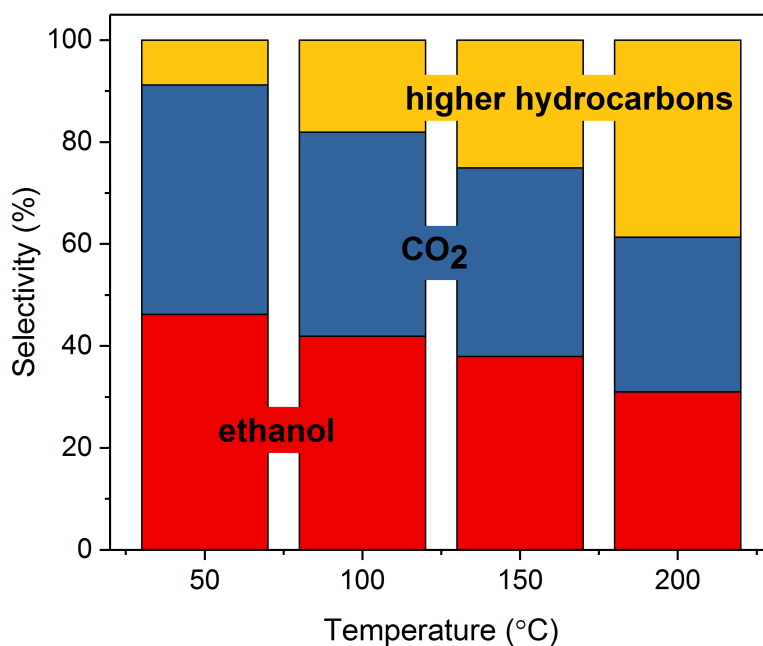


Figure 6.10 A plot of propylene oxide selectivity versus temperature over 50mg AgZSM-5 in a batch reactor for 1 h under 1:1 molar ratio of C₃H₆ to O₂ at 30 bar.

Table 6.3 A table to show the change in conversion of propylene versus temperature in a batch reactor for 1 h under 1:1 molar ratio of C₃H₆ to O₂ at 30 bar.

Catalysts	AgZSM-5 (50 mg)			
Reaction Temperature (°C)	50	100	150	200
Propylene Conversion (%)	5.7	6.4	7.5	8.3

It is interesting to note that the findings from the liquid phase propylene oxidation with AgZSM-5 are quite remarkable for at least two features: (i) It demonstrates that isolated Ag shows activity at low temperature while Brønsted acid sites in HZSM-5 are more active for propylene reforming reactions at high temperature. The liquid

phase reaction provides the possibility to study catalytic performance of isolated Ag atom. (ii) Comparing to Ag cluster or nanoparticles, isolated Ag in ZSM-5 exhibits completely distinctive catalytic properties. Instead of producing total or partial oxidation products, it catalyses C=C bond cleavage of propylene under molecular oxygen to give ethanol and CO₂.

6.4.3.2.2 Catalyst Loading Effect

The product selectivities and propylene conversions under various catalyst loadings in a batch reactor are shown in Figure 6.11 and Table 6.4. As shown in the figure, for all different AgZSM-5 loadings, ethanol/CO₂ and higher hydrocarbons/aromatics are the three main reaction products. There is a marginal effect on the selectivity when the catalyst loading is changed. The total selectivity to CO₂ and ethanol is 91.14% at 50 mg loading, and it slightly changes to 90.45% when the loading is increased to 150 mg. Therefore, the catalyst loading does not seem to affect the catalysis selectivity. However, a distinctive increasing of conversion with catalysts loading can be observed according to Table 6.4. The conversion of propylene is 5.7% at 50mg loading but is sharply increased to 13.3% at 100mg loading. Conversion appears to be in linear trend with the catalyst loading for the range of 50 to 100 mg, which means increasing the quantity of active sites causes an increase in conversion. However, at higher loadings of 125 and 150mg, the rate of increase declines, where the propylene conversions are 15.4% and 16.2%, respectively. This probably resulted from some degree of mass transfer problems.

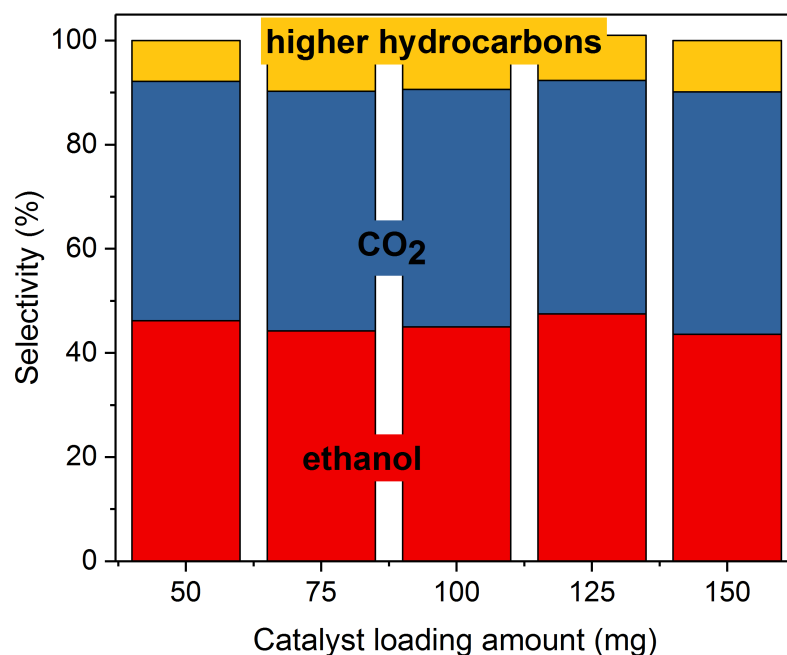


Figure 6.11 A plot of propylene oxide selectivity versus temperature over different loading of AgZSM-5 in a batch reactor for 1 h under 1:1 molar ratio of C₃H₆ to O₂ at 30 bar.

Table 6.4 Conversion of propylene in a batch reactor for 1 h under 1:1 molar ratio of C₃H₆ to O₂ at 30 bar.

Catalysts	AgZSM-5 (at 50 °C)				
Catalyst Loading (mg)	50	75	100	125	150
Propylene Conversion (%)	5.7	9.1	13.3	15.6	16.2

6.4.3.2.3 Reaction Time effect

In order to optimize the reaction time, 7 individual controlled experiments were designed. All experiments were conducted with 100 mg AgZSM-5 at 50 °C under 30

bar but with various reaction times. Similarly, ethanol, CO₂ and higher hydrocarbons/aromatics were the reaction products and no significant change in selectivity was observed at longer reaction times. Figure 6.12 and Table 6.5 show that the reaction time appears to give a significant effect on propylene conversion. Excitingly, no catalytic deactivation was noted. Instead, progressively enhanced conversions are demonstrated at longer reaction times. From the figure and the table, the highest reaction conversion observed after 30 h is 32.1%. Comparing all AgZSM-5 catalysts after reaction, no obvious colour change in the samples occurred. Apart from the side products from propylene reforming, at comparable long reaction times, the activity towards the main products maintains. In addition, under a longer reaction time, the propylene conversion is dramatically enhanced, which may possibly due to constant and continuous propylene catalysis over AgZSM-5 during the whole reaction process. Therefore, the AgZSM-5 exhibits a very stable catalytic performance.

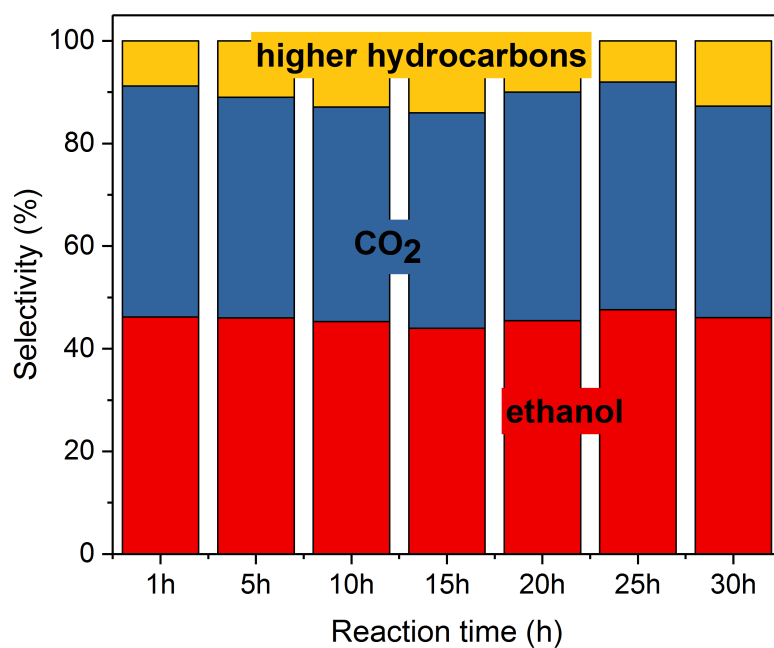


Figure 6.12 A plot of propylene oxide selectivity versus reaction time over 150mg AgZSM-5 in a batch reactor under 1:1 molar ratio of C₃H₆ to O₂ at 30 bar.

Table 6.5 Conversion of propylene versus reaction time over 100mg AgZSM-5 in a batch reactor under 1:1 molar ratio of C₃H₆ to O₂ at 30 bar.

Catalysts	AgZSM-5 (100 mg, 50 °C)						
Reaction Time (h)	1	5	10	15	20	25	30
Propylene Conversion (%)	13.3	16.7	20.2	24.1	26.7	29.4	32.1

6.4.4 Proposed Reaction Mechanism

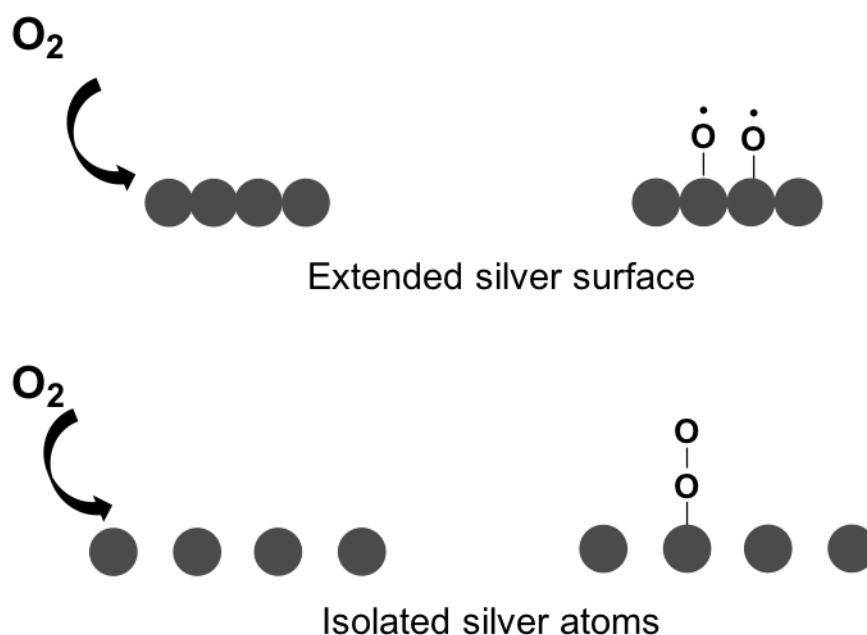
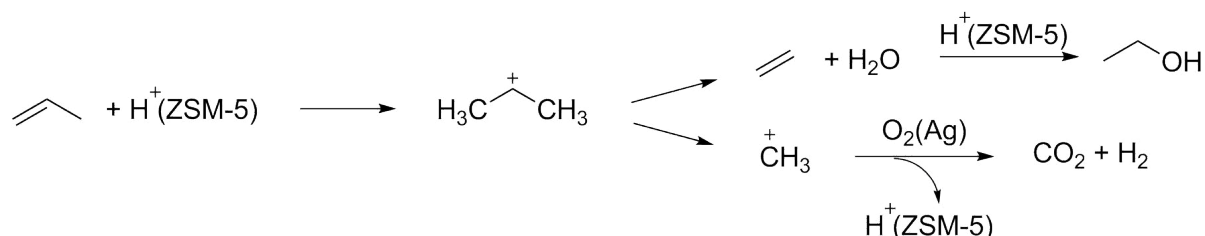


Figure 6.13 O_2 adsorption and dissociation on extended silver surface and isolated silver atoms, respectively.

As illustrated in Figure 6.13, for silver nanoparticle based catalysts, the molecular oxygen can adsorb on extended silver surface. The electron rich Ag surface can also donate to the antibonding orbitals of molecular oxygen to weaken $O=O$ bond leading to O_2 dissociation. This is thermodynamically favourable route as shown from our DFT calculations (see Chapter 4). As a result, the O_2 dissociation on metal surface will generate two surface atomic oxygen species (two neighbour oxyradicals) on Ag surface lattice. We have already demonstrated in Chapter 4 and 5 that the interatomic distance of Ag-Ag on (100) Ag lattice or ultrathin Ag over-layer on Ni nanoparticle can be slightly prolonged to reduce the low temperature combustion route hence improving propylene oxide selectivity (refer to Scheme 2 of Chapter 1). The isolated Ag site if created may show a totally different adsorption mode, as demonstrated in Figure 6.12. The dioxygen will not be dissociatively adsorbed on

neighbouring Ag metal sites but will be forced to align head-on to the isolated Ag site. According to our experimental results we have found a new reaction route for propylene oxidation over AgZSM-5 at low temperature.



Scheme 6.2 A proposed reaction scheme for the Brønsted acid induced cleavage of propylene over isolated Ag atom

We believe that this anchored but isolated Ag site in H-ZSM-5 structure as demonstrated from SXRD/refinement and STEM image, can take up the dioxygen in up-right manner for selective oxidation under reaction conditions. Without the formation of extremely active oxyradicals (atomic oxygens), this type of adsorbed dioxygen cannot oxidise propylene to the fragile allylic intermediate to lead to total combustion (see Chapter 1). The isolated Ag-O₂ in ZSM-5 structure does not even oxidise propylene to acrolein as shown in Scheme 6.1 due to their mild oxidising properties. On the other hand, the cleavage of propylene is mainly catalysed by the protonation of Brønsted acid site (BAS) in zeolite,^[27,28] as shown in Scheme 6.2. This will assist the selective cleavage over the BAS to generate adsorbed methyl (CH₃⁺)^[29] and ethylene^[30], which are the important intermediates identified from BAS-catalysed hydrocarbon reforming reactions.^[12] At elevated temperature, oligomerization/polymerization of adsorbed methyl to produce higher hydrocarbons/aromatics is favourable from ZSM-5 structure. It can also cause severe catalyst deactivation if the hydrocarbon pools (HCP) in zeolite further react to

form macroscopic carbons.^[31,32] It is however, in the presence of isolated Ag site-O₂ in the ZSM-5 structure at low temperature within few atomic distances, which may create a mild oxidation site to oxidise these facile hydrocarbons or oxygenated intermediates, in this case, methyl to CO₂/H₂ and ethylene/H₂O (H₂O is a solvent) to ethanol over the BAS.

6.5 Conclusions

In summary, isolated Ag site in ZSM-5 structure demonstrates a new catalytic capability for selective C=C bond cleavage of propylene in molecular oxygen in a liquid phase. This has led a discovery of a new reaction route to produce ethanol and CO₂ from propylene/O₂. Under optimised reaction conditions, the selectivity of this reaction can reach nearly 92% at 25.7% propylene conversion over the AgZSM-5. Excitingly, the single but isolated silver site as demonstrated from our STEM and SXRD/refinement can exhibit mild oxidation when interacting with molecular oxygen as compared to silver cluster or silver nanoparticles with extended Ag surface. The cooperative way to activate molecular oxygen for oxidative cleavage of C=C of alkene over isolated Ag in acidic ZSM-5 phase may offer new opportunities in selective oxidation of organic molecules.

6.6 References

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Chapter 7 Conclusion and Future Perspectives

7.1 Conclusions

Within this thesis, a range of advanced methods have been developed to tune the geometric and electronic properties of Ag catalysts. Polyol synthesis methods were employed in order to design uniform morphology or facet controlled Ag nanocrystal catalysts. Lanthanide series metal oxide was employed as substituted catalyst support to conventional Al_2O_3 . The activity and selectivity of lanthanide oxides supported silver catalysts were dramatically enhanced for propylene epoxidation with molecular oxygen, among which Ag-nanocube/ La_2O_3 shown a remarkable activity and selectivity towards propylene oxide. Fundamental studies revealed that molecular oxygen adsorption and dissociation are the key steps toward epoxide route. With a high concentration of oxygen vacancy, the molecular oxygen can be dissociated into active atomic oxygen species with lower energy barrier. When the activated oxygen species take residence on longer Ag-Ag sites of (100) facet, they can effectively reduce γ -H cleavage for combustion, leading to a favourable epoxide route.

The Ag nanoparticles surface can also be tailored by forming a core@shell structure. A lattice extension was observed on the very small NiAg core@shell particles when the Ag shell thickness was reduced to a 1-3 atomic layers. The selectivity of propylene oxide appeared to be very sensitive to the average Ag-Ag interatomic distance, on the surface with longer Ag-Ag as similar to (100) facet, higher propylene oxide selectivity was observed again. In addition to that, a strong size effect was also discovered. Compared to the morphology controlled Ag nanoparticle, the core-shell structure Ag nanoparticle with only a few nanometre sizes can directly activate the

dioxygen without the assistance from oxide support and can further improve the selectivity for epoxidation reaction.

As discovered that a silver surface with longer Ag-Ag interatomic distance is more favourable for epoxidation route, in order to totally eliminate another oxyradical (atomic oxygen) from the neighbour site, atomically dispersed Ag on HZSM-5 was developed. However, surprisingly, the interaction between single atom Ag and molecular oxygen is very different from those of silver nanosurface. Instead of linear -O-O adsorption, the single atom Ag has a weak coordination with the O=O bond. When those reacted with propylene, it resulted in C=C bond breakage and leading to stoichiometric production of ethanol and CO_2 .

7.2 Future perspectives

The modifications Ag nanoparticles presented in this thesis allow tuning of the surface features of the Ag catalysts. Thus, several novel Ag catalysts have been discovered with a remarkable selectivity towards propylene epoxidation. However, the limitation of these Ag catalysts is still at a relatively low propylene conversion due to the challenging low activation energies for combustion routes for favoured allylic intermediate formation. Apart from using conventional thermal means, it may be expected the use of other excitation sources such like tunable surface plasma resonance may offer some new directions for further improvement in activity.

The interesting role of lanthanide oxide support in offering activation of dioxygen molecule is depicted in this thesis. The enhancement of oxygen vacancies by dopants on lanthanide or mixed oxides may be the way forward. Additionally, further

tuning of geometric and electronic or ligand effect of Ag shell surface atoms by using different core atoms of various lattice parameters and electronegativities could lead to more effective core-shell catalysts.

The activity difference of single atom Ag and Ag nanoparticle have drawn a great interest in recent catalysis community, although the proposed mechanism is yet to be proven on various types of alkenes produced in the pathways. It demonstrated the unexpected properties of single atom catalysts, and the potential utility of other metal single atom catalysts in a vast range of important reactions. Whilst the significant advances are still required for further investigation, the demonstrated abilities of single atom catalysts displayed in this thesis may provide insights for further catalysts development.

Appendix

Table A1 Crystallographic data for CuZSM-5, ZnZSM-5 and AgZSM-5

Samples	CuZSM-5	ZnZSM-5	AgZSM-5
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
Chemical formula	H_{4.74}Al_{4.74}Si_{91.26}O₁₉₂ · Cu	H_{4.74}Al_{4.74}Si_{91.26}O₁₉₂ · Zn	H_{4.74}Al_{4.74}Si_{91.26}O₁₉₂ · Ag
2θ range refinement (°)	3 – 55	3 – 55	3 – 55
Detector	Multi-analyser crystals crystals	Multi-analyser crystals crystals	Multi-analyser crystals crystals
Number of parameters	148	148	148
Number of hkl's	4186	4186	4186
Refinement methods	Rietveld	Rietveld	Rietveld
<i>a</i> (Å)	20.13218(3)	20.12885(3)	20.12649(2)
<i>b</i> (Å)	19.95908(2)	19.95555(3)	19.92968(2)
<i>c</i> (Å)	13.42682(2)	13.43143(3)	13.42841(2)
<i>V</i> (Å ³)	5395.162(31)	5395.172(27)	5386.330(37)
<i>R_{wp}</i> / <i>R_p</i> / <i>R_{exp}</i> (%)	7.962/6.237/3.837	7.896/6.086/3.529	7.328/5.928/3.208
Wavelength (Å)	0.825900(2)	0.825900(2)	0.825900(2)
2θ Zero point (°)	-0.004944(2)	-0.004944(2)	-0.004944(2)
Gof χ^2	2.538	2.237	2.122

Table A2 Structural data for CuZSM-5

Species	Atom	X	Y	Z	SOF	B _{eq} (Å ²)	Wyckoff
Zeolite framework	O1	0.3791(4)	0.0428(2)	0.7428(4)	1	2.614(49)	8d

O2	0.3084(2)	0.0596(1)	0.9243(5)	1	2.614(49)	8d
O3	0.1994(1)	0.0630(5)	0.0212(2)	1	2.614(49)	8d
O4	0.0969(1)	0.0632(1)	0.9117(2)	1	2.614(49)	8d
O5	0.1137(7)	0.0505(9)	0.7283(5)	1	2.614(49)	8d
O6	0.2469(2)	0.0596(2)	0.7540(4)	1	2.614(49)	8d
O7	0.3732(8)	0.8479(5)	0.7628(9)	1	2.614(49)	8d
O8	0.3079(5)	0.8471(3)	0.9304(4)	1	2.614(49)	8d
O9	0.1914(8)	0.8468(2)	0.0331(7)	1	2.614(49)	8d
O10	0.0881(7)	0.8359(3)	0.9217(3)	1	2.614(49)	8d
O11	0.1192(3)	0.8426(8)	0.7376(3)	1	2.614(49)	8d
O12	0.2432(1)	0.8445(4)	0.7603(5)	1	2.614(49)	8d
O13	0.3080(5)	0.9486(3)	0.8187(8)	1	2.614(49)	8d
O14	0.8187(8)	0.9533(5)	0.8256(6)	1	2.614(49)	8d
O15	0.4204(6)	0.1296(8)	0.6093(9)	1	2.614(49)	8d
O16	0.4087(9)	1.0041(7)	0.5821(3)	1	2.614(49)	8d
O17	0.4013(2)	0.8693(7)	0.5748(9)	1	2.614(49)	8d
O18	0.1919(4)	0.1269(7)	0.6152(5)	1	2.614(49)	8d
O19	0.2036(9)	-0.0018(8)	0.5996(6)	1	2.614(49)	8d
O20	0.2010(1)	0.8680(2)	0.5781(5)	1	2.614(49)	8d
O21	0.9970(8)	0.0535(4)	0.7947(6)	1	2.614(49)	8d
O22	0.9991(4)	0.8502(3)	0.7946(1)	1	2.614(49)	8d
O23	0.4204(6)	0.1296(8)	0.6093(9)	1	2.614(49)	4c
O24	0.4087(9)	1.0041(7)	0.5821(3)	1	2.614(49)	4c
O25	0.4013(2)	0.8693(7)	0.5748(9)	1	2.614(49)	4c
O26	0.1919(4)	0.1269(7)	0.6152(8)	1	2.614(49)	4c
Si1	0.4226(5)	0.0582(8)	0.6618(8)	1	1.307(24)	8d
Si2	0.3096(4)	0.0313(1)	0.8139(2)	1	1.307(24)	8d
Si3	0.2787(6)	0.0596(1)	0.0349(3)	1	1.307(24)	8d
Si4	0.1200(2)	0.0638(4)	0.0276(5)	1	1.307(24)	8d
Si5	0.0696(2)	0.0294(2)	0.8147(7)	1	1.307(24)	8d
Si6	0.1876(4)	0.0555(6)	0.6757(2)	1	1.307(24)	8d
Si7	0.4251(6)	0.8303(1)	0.6730(8)	1	1.307(24)	8d
Si8	0.3076(5)	0.8704(2)	0.8177(5)	1	1.307(24)	8d

	Si9	0.2750(3)	0.8272(8)	0.0324(3)	1	1.307(24)	8d
	Si10	0.1217(3)	0.8257(8)	0.0305(2)	1	1.307(24)	8d
	Si11	0.0717(6)	0.8708(8)	0.8187(8)	1	1.307(24)	8d
	Si12	0.1891(4)	0.8254(2)	0.6823(7)	1	1.307(24)	8d
Copper	Cub	0.3568(7)	0.3931(1)	0.7938(2)	0.0690(48)	5	4c
	Cuc	0.5979(2)	0.1891(8)	0.7437(9)	0.0963(53)	5	4c
Oxygen water	Ow1	0.2488(4)	0.2705(5)	0.9080(3)	0.1321(12)	6	8d
	Ow2	0.5092(6)	0.2583(1)	0.6442(1)	0.0963(56)	6	8d
	Ow3	0.5946(3)	0.2872(7)	-0.4414(9)	0.09635(36)	6	8d
	Ow4	0.6500(5)	0.2382(2)	-0.1845(8)	0.09635(36)	6	8d

Table A3 Structural data for ZnZSM-5

Species	Atom	X	Y	Z	SOF	B _{eq} (Å ²)	Wyckoff
Zeolite framework	O1	0.37534(41)	0.05998(44)	0.75634(51)	1	3.162(33)	8d
	O2	0.30852(41)	0.06392(34)	0.92286(51)	1	3.162(33)	8d
	O3	0.19936(37)	0.06248(34)	0.02036(36)	1	3.162(33)	8d
	O4	0.09660(32)	0.05942(42)	0.91524(55)	1	3.162(33)	8d
	O5	0.11409(39)	0.04755(49)	0.73157(53)	1	3.162(33)	8d
	O6	0.24562(38)	0.04613(50)	0.75403(52)	1	3.162(33)	8d
	O7	0.37129(43)	0.84717(42)	0.76213(58)	1	3.162(33)	8d
	O8	0.30718(44)	0.84727(30)	0.92797(51)	1	3.162(33)	8d
	O9	0.19298(41)	0.84592(25)	0.02861(41)	1	3.162(33)	8d
	O10	0.08869(36)	0.84006(36)	0.92130(63)	1	3.162(33)	8d
	O11	0.11853(44)	0.84122(40)	0.73403(56)	1	3.162(33)	8d
	O12	0.24445(46)	0.84050(43)	0.76023(62)	1	3.162(33)	8d
	O13	0.31172(38)	0.95176(40)	0.82323(37)	1	3.162(33)	8d
	O14	0.07629(30)	0.95320(44)	0.82288(44)	1	3.162(33)	8d
	O15	0.41756(37)	0.12185(39)	0.59787(57)	1	3.162(33)	8d
	O16	0.40306(40)	0.99571(40)	0.59239(60)	1	3.162(33)	8d
	O17	0.40119(40)	0.86793(37)	0.57318(62)	1	3.162(33)	8d
	O18	0.18991(48)	0.12994(34)	0.61613(47)	1	3.162(33)	8d
	O19	0.20092(49)	0.00283(36)	0.59363(51)	1	3.162(33)	8d

	O20	0.19764(48)	0.87069(35)	0.58273(48)	1	3.162(33)	8d
	O21	0.99607(40)	0.04867(50)	0.79614(47)	1	3.162(33)	8d
	O22	0.99711(44)	0.85163(43)	0.79477(49)	1	3.162(33)	8d
	O23	0.42002(54)	0.7500	0.64499(66)	1	3.162(33)	4c
	O24	0.19445(68)	0.7500	0.65775(59)	1	3.162(33)	4c
	O25	0.28290(48)	0.7500	0.05561(70)	1	3.162(33)	4c
	O26	0.10353(54)	0.7500	0.05963(80)	1	3.162(33)	4c
	Si1	0.42180(20)	0.05861(27)	0.66258(31)	1	1.309(15)	8d
	Si2	0.30903(28)	0.02941(17)	0.81279(32)	1	1.309(15)	8d
	Si3	0.27978(17)	0.06190(22)	0.03485(29)	1	1.309(15)	8d
	Si4	0.12177(18)	0.06289(23)	0.02602(31)	1	1.309(15)	8d
	Si5	0.06889(21)	0.02935(20)	0.81760(34)	1	1.309(15)	8d
	Si6	0.18615(22)	0.05581(23)	0.67469(28)	1	1.309(15)	8d
	Si7	0.42467(22)	0.82990(20)	0.67103(34)	1	1.309(15)	8d
	Si8	0.30720(26)	0.86994(20)	0.81691(29)	1	1.309(15)	8d
	Si9	0.27366(20)	0.82692(19)	0.02870(32)	1	1.309(15)	8d
	Si10	0.11940(21)	0.82681(21)	0.03012(36)	1	1.309(15)	8d
	Si11	0.07193(22)	0.87211(23)	0.81566(33)	1	1.309(15)	8d
	Si12	0.18877(27)	0.82612(17)	0.68528(32)	1	1.309(15)	8d
Zinc 1	Translate	0.9290(8)	0.7173(11)	0.1885(10)			
	Zn1	0.9290	0.7173	0.1885	0.104(2)	8.1(12)	4c
	Zn1O _w 1	0.9060	0.6164	0.1529	0.104(2)	12.1(19)	4c
	Zn1O _w 2	0.8513	0.7182	0.2951	0.104(2)	12.1(19)	4c
	Zn1O _w 3	0.9963	0.6840	0.2994	0.104(2)	12.1(19)	4c
	Zn1O _w 4	1.0066	0.7164	0.0819	0.104(2)	12.1(19)	4c
	Zn1O _w 5	0.8616	0.7506	0.0777	0.104(2)	12.1(19)	4c
	Zn1O _w 6	0.9519	0.8181	0.2242	0.104(2)	12.1(19)	4c
Zinc 2	Zn2	0.7774(11)	0.1209(12)	0.8225(17)	0.071(3)	16.3(21)	8d
O2	Zn2O _w 1	0.7858(12)	0.3052(17)	0.6895(21)	0.071(3)	24.4 (31)	8d

Table A4 Structural data for AgZSM-5

Species	Atom	X	Y	Z	SOF	B _{eq} (Å ²)	Wyckoff
Zeolite framework	O1	0.374(78)	0.048(81)	0.758(84)	1	1.934(38)	8d

O2	0.312(25)	0.060(44)	0.922(56)	1	1.934(38)	8d
O3	0.200(07)	0.061(87)	0.021(66)	1	1.934(38)	8d
O4	0.097(79)	0.062(22)	0.914(18)	1	1.934(38)	8d
O5	0.114(58)	0.06(12)	0.733(54)	1	1.934(38)	8d
O6	0.245(16)	0.047(74)	0.752(03)	1	1.934(38)	8d
O7	0.377(03)	0.837(09)	0.757(15)	1	1.934(38)	8d
O8	0.304(45)	0.846(88)	0.934(45)	1	1.934(38)	8d
O9	0.193(10)	0.848(93)	0.026(53)	1	1.934(38)	8d
O10	0.086(01)	0.840(99)	0.926(19)	1	1.934(38)	8d
O11	0.121(77)	0.846(97)	0.734(09)	1	1.934(38)	8d
O12	0.252(26)	0.842(82)	0.770(31)	1	1.934(38)	8d
O13	0.317(06)	0.951(99)	0.818(85)	1	1.934(38)	8d
O14	0.081(51)	0.951(16)	0.820(92)	1	1.934(38)	8d
O15	0.418(55)	0.121(96)	0.598(74)	1	1.934(38)	8d
O16	0.409(36)	0.997(58)	0.586(77)	1	1.934(38)	8d
O17	0.402(89)	0.866(74)	0.570(49)	1	1.934(38)	8d
O18	0.190(76)	0.131(89)	0.621(54)	1	1.934(38)	8d
O19	0.206(14)	-0.0002(2)	0.603(07)	1	1.934(38)	8d
O20	0.200(48)	0.868(25)	0.588(29)	1	1.934(38)	8d
O21	0.994(2)	0.0483(3)	0.797(6)	1	1.934(38)	8d
O22	0.998(91)	0.852(42)	0.794(27)	1	1.934(38)	8d
O23	0.419(71)	0.75(4)	0.644(51)	1	1.934(38)	4c
O24	0.193(13)	0.75(8)	0.656(35)	1	1.934(38)	4c
O25	0.285(02)	0.75(5)	0.053(53)	1	1.934(38)	4c
O26	0.106(92)	0.75(6)	0.072(06)	1	1.934(38)	4c
Si1	0.420(86)	0.057(61)	0.663(41)	1	0.967(69)	8d
Si2	0.309(49)	0.030(2)	0.813(44)	1	0.967(69)	8d
Si3	0.278(93)	0.061(65)	0.033(21)	1	0.967(69)	8d
Si4	0.119(58)	0.064(05)	0.030(84)	1	0.967(69)	8d
Si5	0.069(62)	0.029(52)	0.815(29)	1	0.967(69)	8d
Si6	0.187(66)	0.056(76)	0.677(56)	1	0.967(69)	8d
Si7	0.426(06)	0.827(53)	0.672(57)	1	0.967(69)	8d
Si8	0.309(21)	0.873(08)	0.821(45)	1	0.967(69)	8d

	Si9	0.274(56)	0.828(1)	0.036(52)	1	0.967(69)	8d
	Si10	0.121(31)	0.824(35)	0.029(77)	1	0.967(69)	8d
	Si11	0.073(8)	0.867(28)	0.818(73)	1	0.967(69)	8d
	Si12	0.188(91)	0.827(62)	0.687(7)	1	0.967(69)	8d
Silver	Aga	0.25965	0.82707	0.44013	0.04363(62)	5	8d
	Agb	0.279(79)	0.095(68)	-0.334(03)	0.02278(91)	5	8d
	Agc	0.043(62)	-0.206(57)	0.317(48)	0.06361(59)	5	8d
Oxygen from water	Ow1	0.411(16)	0.80065(88)	0.2595(94)	0.26314(11)	6	8d
	Ow1	0.5078(46)	0.05660(29)	0.02144(17)	0.04399(76)	6	8d