SYNTHESIS AND CHARACTERIZATION OF BIMETALLIC PtNi PARTICLES FOR THE APPLICATION OF CATALYSTS

by

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LIST OF ABBREVIATIONS

A	Pre-exponential factor
AAS	Atomic Adsorption Spectroscopy
Ar	Argon
ASA	Silica-Alumina
Bz	Benzene
C	Classical
C_o	Initial conversion
CI	Co-impregnation
CP	Co-precipitation
D	Dispersion
D_F	Fractal dimension
d	diameter
d_{at}	Atomic diameter
$d_{rel(VS)}$	Relative volume surface mean diameter
Ea	Energy of activation
EDAX/EDS	Energy dispersive x-ray spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
H_2	Hydrogen
He	Helium
I	Impregnation
k	Rate constant
K_B	Chemisorption constant for benzene
K_E	Equilibrium constant

K_H	Chemisorption constant for hydrogen
$NaBH_4$	Sodium borohydride
m	Partial order of hydrogen
MCM-41	Mesotructured aluminosilicate
n	Partial order of benzene
N_A	Avogadro number
Ni	Nickel
O_2	Oxygen
OA	Oleic acid
P	Precipitation
P_{Bz}	Partial pressure of benzene
P_H	Partial pressure of hydrogen
Pt	Platinum
R	Gas constant
r	Rate
S	Total surface area
SiO_2	Silica
SEM	Scanning Electron Microscopy
SI	Step-impregnation
TEM	Transmission Electron Microscopy
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

**Sintesis dan Pencirian Zarah Dwi-Logam PtNi untuk
Aplikasi Sebagai Mangkin**

Abstrak

Sintesis mangkin zarah dwi-logam PtNi yang disokong oleh silika, disediakan melalui kaedah bukan klasik, dengan menggunakan natrium borohidrat ($NaBH_4$) sebagai agen penurun, telah dikaji secara terperinci. Penyokong silika yang digunakan bagi penyelidikan ini dihadkan kepada silika berhablur dan aluminosilikat mesoporos (MCM-41). Pelbagai teknik penyediaan dan parameter penurunan dikaji bagi memahami bagaimana faktor-faktor ini mempengaruhi struktur akhir zarah PtNi yang disokong oleh silika serta reaktiviti pemangkinan terhadap penghidrogenan benzena kepada sikloheksana. Didapati bahawa kaedah penurunan ini dapat menurunkan sepenuhnya garam-garam logam semasa peringkat penyediaan mangkin. Penggunaan hidrogen ditentukan menggunakan analisis H_2-TPR, yang mana sebahagian besarnya disebabkan oleh permukaan fasa logam yang teroksida semasa penyimpanan.

Kajian terhadap kesan daripada teknik penyediaan menunjukkan bahawa permukaan dan sifat pemangkinan adalah sangat dipengaruhi oleh nisbah PtNi serta kaedah bagaimana garam logam diperkenalkan ke atas penyokong. Mangkin yang disediakan melalui teknik ko-impregnasi umumnya mempamerkan reaktiviti pemangkinan yang lebih baik berbanding yang disediakan melalui teknik ko-pemendakan dan impregnasi berperingkat. Seterusnya, mangkin yang mengandungi kandungan Ni yang tinggi menunjukkan kecenderungan terhadap reaktiviti yang rendah berbanding dengan mangkin yang mengandungi kandungan Pt yang tinggi. Beberapa mangkin mempamerkan reaktiviti yang lebih baik berbanding dengan mangkin monologam Pt. Kajian menunjukkan bahawa reaktiviti yang lebih baik ini disebabkan oleh pengaloian Pt dan Ni serta diikuti pemisahan permukaan oleh Pt.

Bagi memperbaiki reaktiviti pemangkinan, zarah PtNi yang distabilkan oleh asid oleik telah disintesis sebelum diterap ke atas penyokong silika. Kajian ini bertujuan untuk mendapatkan kawalan yang lebih baik ke atas penyelerakan dan pengaloian antara zarah PtNi. Keputusan menunjukkan bahawa walaupun penyelerakan aloi yang lebih baik diperolehi, aktiviti yang sangat rendah diperhatikan. Pemisahan permukaan oleh Ni besar kemungkinan disebabkan oleh kehadiran oksigen daripada asid oleik.

Kesan daripada pelbagai parameter juga dikaji untuk meningkatkan reaktiviti pemangkinan. Suhu penurunan, kepekatan $NaBH_4$ dan medium di mana penurunan dilakukan dipelbagaikan. Kepelbagaian parameter ini mempengaruhi morfologi zarah dan penyelerakan zarah PtNi. Reaktiviti pemangkinan yang optimum diperolehi apabila zarah PtNi yang kecil berselerak terbentuk pada suhu 273 K menggunakan 0.3 M $NaBH_4$ di dalam medium etanol.

Kaedah klasik juga digunakan untuk mensintesis mangkin PtNi yang disokong. Dalam kajian ini, zarah PtNi terbentuk menggunakan H_2 sebagai agen penurun. Beberapa mangkin menunjukkan reaktiviti yang meningkat. Kajian menunjukkan ia disebabkan oleh kesan penambatan ion Ni^{2+} yang menambat Pt kepada penyokong lalu membentuk zarah Pt yang halus dan berselerak yang dapat digunakan bagi tindak balas pemangkinan.

Secara umumnya, adalah jelas bahawa zarah aloi dan bukan aloi dwi-logam yang disokong oleh silika boleh meningkatkan tindak balas penghidrogenan jika dibandingkan dengan masing-masing mangkin mono-logam. Namun demikian, nisbah PtNi, teknik penyediaan, persekitaran di mana zarah diturunkan dan penyokong mempengaruhi struktur fasa logam mangkin ini. Oleh itu pemahaman yang menyeluruh ke atas parameter ini adalah penting untuk mensintesis mangkin dengan ciri-ciri tertentu yang diingini.

**Synthèse et Caractérisation de Particule Bi-métallique PtNi
pour l'Application de la Catalyse**

Abstrait

La synthèse des catalyseurs bi-métalliques de PtNi supportées sur silice préparés par une méthode non-classique a été étudiée de manière approfondie en utilisant le borohydrure de sodium (NaBH$_4$) comme réducteur du précurseur métallique. Les supports silice utilisés ont été limités à la silice cristallisée et à l'aluminosilicate mesoporeux MCM-41. Diverses techniques de préparation et divers paramètres de réduction ont été étudiés pour déterminer l'effet de structure des particules bi-métalliques PtNi supportées, ainsi que leurs propriétés catalytiques pour l'hydrogénation du benzène en cyclohexane en phase gazeuse. On a montré que cette méthode permettait la réduction totale des sels métalliques pendant l'étape de préparation des catalyseurs. La consommation de l'hydrogène par ces catalyseurs, mesurée par réduction en température programmée, a été attribuée à l'oxydation de la surface de métal pendant leur stockage.

Les études de l'effet des différentes techniques de préparation, ont montré que les propriétés de la surface et les propriétés catalytiques sont influencées par le rapport de PtNi et par la méthode de dépôt des précurseurs métalliques sur la surface du support. En général, les catalyseurs qui ont été préparés par la technique de co-imprégnation donnent une meilleure réactivité catalytique comparée à celles donnée par la co-précipitation et par l'imprégnation par étapes. Par ailleurs, les catalyseurs qui contiennent plus de Ni ont montré une plus faible réactivité, contrairement aux catalyseurs plus riches en Pt, plus réactifs. Plusieurs catalyseurs bimetalliques ont démontré une meilleure réactivité que le catalyseur mono-métallique Pt. Les recherches ont prouvé que l'amélioration de la réactivité peut être attribuée à la formation d'alliage de Pt et Ni accompagnée de la ségrégation du Pt sur l'alliage.

Pour l'amélioration de la réactivité, des particules bi-métallique PtNi stabilisées d'acide oléique ont été synthétisées avant l'incorporation sur le support de silice. Cette méthode a pour but une meilleure dispersion pour la fabrication de l'alliage PtNi. Les résultats montrent, en effet, une meilleure dispersion des particules dans les alliages formés mais la réactivité est très faible. La ségrégation du Ni sur la surface de la particule d'alliage, qui se produit en raison de la présence des oxygènes de l'acide oléique, est la cause de la faible réactivité de l'hydrogénation du benzène.

L'effet de plusieurs paramètres de réduction a été également étudié pour augmenter la réactivité catalytique. Trois paramètres ont été étudiés, la température de la réduction, la concentration de NaBH$_4$ et l'environnement dans lequel la réduction a été effectuée. Les variations de ces paramètres affectent la morphologie et la dispersion des particules PtNi. La réactivité catalytique optimum a été obtenue lors de la formation de petites particules PtNi dispersées à la température de 273 K avec 0.3 M de NaBH$_4$ en solution dans l'éthanol.

Les méthodes classiques aussi ont été utilisées pour la synthèse des catalyseurs PtNi supportés. Dans cette étude les particules de PtNi ont été formées la en phase gazeuse en utilisant un traitement thermique sous hydrogène du précurseur métallique calciné. Plusieurs des catalyseurs ont montré une meilleure réactivité que le platine. On a trouvé qu'elle est attribuable à l'effet d'ancrage des ions de Ni^{2+} sur le support et la fixation du Pt sur ces ions. Dans ce cas, les particules de Pt sont très petites, bien dispersées et disponibles pour la réaction catalytique.

En conclusion, il apparaît dans ce travail que les particules bimétalliques supportées, combinées en alliage ou non, peuvent donner lieu à une meilleure réactivité que les catalyseurs monométalliques. Cependant, le rapport de PtNi, la technique de préparation, l'environnement dans lequel les particules sont réduites et le support

affecter la surface de la phase métallique des catalyseurs. Par conséquent, nos résultats montrent qu'il est impératif de comprendre et de contrôler ces paramètres pour synthétiser les catalyseurs possédant les meilleures propriétés.

Synthesis and Characterization of Bimetallic PtNi
Particles for the Application of Catalysts

Abstract

The synthesis of PtNi bimetallic particles supported silica catalysts, prepared via non-classical methods using sodium borohydride ($NaBH_4$) as a reducing agent, was studied in detail. The silica supports employed in this work is limited to crystalline silica and mesoporous aluminosilicate (MCM-41). Various preparation techniques as well as reduction parameters were investigated to gain an insight on how these factors influenced the final structure of the PtNi particles on the silica support and their catalytic reactivity towards the hydrogenation of benzene to cyclohexane. It was found that this reduction method enabled total reduction of the metal salts during the preparation stage of the catalysts. Hydrogen consumptions which were detected using H_2-TPR analysis were mainly attributed to surface oxidation of the metal phase during storage.

Studies on the effect of preparation techniques showed that the surface and catalytic properties of the catalysts are largely affected by the PtNi ratio as well as the method in which the metal salts are introduced onto the support. Catalysts prepared via co-impregnation technique generally exhibited better catalytic reactivity when compared to those prepared via co-precipitation and step-impregnation techniques. Further, catalysts with higher Ni content showed a tendency towards lower reactivity in contrast to those with high Pt content. Several catalysts demonstrated enhanced reactivity when compared to the monometallic Pt catalysts. Investigations showed that the improved reactivity can be attributed to alloying of the Pt and Ni accompanied by surface segregation of Pt.

As a means to improve catalytic reactivity, PtNi stabilized oleic acid particles were synthesized prior to incorporation onto a silica support. The intention of this study is to allow better control of the dispersion and alloying between the PtNi particles. Results show that though better dispersed alloys were obtained, very low activity was observed. Nickel surface segregation is likely to be the cause of this due to the presence of oxygen from oleic acid.

The effect of several reduction parameters was also investigated to enhance catalytic reactivity. The reduction temperature, $NaBH_4$ concentration and medium in which reduction was carried out were varied. Variations in these parameters affected the particle morphology and dispersion of the PtNi particles. Optimum catalytic reactivity was obtained when small dispersed PtNi particles were formed at 273 K using 0.3 M $NaBH_4$ in a medium of ethanol.

Classical methods were also used for the synthesis of PtNi supported catalysts. In this study the PtNi particles were formed using H_2 gas as the reducing agent. Several catalysts showed improved reactivity. Investigations show that this is attributed to the anchoring effect of Ni^{2+} ions which anchors Pt to the support, forming fine dispersed Pt particles available for catalytic reaction.

In general, it is obvious that alloyed and non – alloyed bimetallic particles supported on silica can lead to the enhancement of hydrogenation reactions when compared to the respective monometallic catalysts. However, the PtNi ratios, preparation techniques, environment in which the particles are reduced and support influences the structure of the metallic phase of these catalysts. Therefore it is imperative to gain a thorough understanding on these parameters, in order to synthesize catalysts with desired properties.

CHAPTER 1

INTRODUCTION

1.1 A Brief Overview

The term 'catalyst' is not novel in today's society. In fact, the term was first used by Berzelius as early as in the 1800's [1]. Since then, numerous catalytic processes have been developed to meet the requirements of a particular era. From the production of bulk explosives during World War I to the generation of hydrogen to produce energy as well as environmental catalysts to reduce pollution in our modern civilization, the applications of catalysts has changed with time. Though without a doubt, catalysts are important necessities as they exist in every aspect of our lives, it is undeniable that the main reason research in this area has been kept alive until now, is its tremendous economic benefits.

In recent times, much attention has been devoted to understanding catalysts and their synthesis, to enable the development of catalysts with better efficiency. Increasing interest has been placed on heterogeneous catalysis as they can be regenerated and used frequently, indirectly making them cost effective. With this in mind, various metals, supports and synthesis conditions have been investigated. This has inadvertently brought about the increasing attention in supported bimetallic catalysts especially when in the nanoscale. Nevertheless, these catalyst materials still lack comprehensive fundamental understanding. For

this reason, much work has been focused on studying not only the properties of these materials but also on their synthesis conditions.

1.2 Problem Statements

- The synthesis of supported bimetallic nanoparticles has gained tremendous attention as catalysts as they are known to promote enhanced reaction rates when compared to their monometallic catalysts. Although extensive work has been carried out on PtNi supported catalysts for oxidation reduction reactions, very few have focused on PtNi supported catalysts for hydrogenation reactions.

- A very limited work on PtNi supported silica based catalysts prepared via non-classical techniques exists. The lack of understanding of this particular system disables the design of potential catalysts for hydrogenation reactions.

1.3 Research Objectives

To overcome the above problems, the aims of this study have been to focus on the following:

- To investigate the influence of preparation techniques on the properties and reactivity of the PtNi supported crystalline silica catalysts prepared via non-classical methods.

- To study the effect of pre-stabilized PtNi nanoparticles on the synthesis of supported PtNi catalysts.

- To gain a comprehensive understanding on how to manipulate the reduction parameters of the non-classical method, in order to control the morphology of the PtNi particles on the MCM-41 support.

- To comprehend the nature in which the PtNi exists when prepared via classical catalysts and to compare its characteristics and reactivity with those prepared via non-classical methods.

1.4 Scope of Study

This study has been limited to the synthesis of PtNi bimetallic nanoparticles on silica supports. Both low and high surface area supports namely crystalline silica and aluminosilicate, mesostructured hexagonal framework, MCM-41 were used. Although the main intention of these supports is to control the morphology and nature in which the PtNi bimetallic particles existed, the effect of oleic acid as a stabilizer for the synthesis of PtNi bimetallic particles which were then incorporated onto crystalline silica was also investigated.

Non-classical reduction methods were mainly employed in this study. Sodium borohydride ($NaBH_4$) was used as the reducing agent for the formation of the bimetallic PtNi nanoparticles. Several techniques in relation to how the metal salts were introduced onto the support as well as the influence of various reduction parameters were investigated. For comparison purposes, classical methods whereby hydrogen (H_2) acted as a reducing agent, was also studied.

The surface of the resulting catalysts were mainly characterized using flow methods such as H_2 temperature programmed reduction (H_2-TPR), H_2-chemisorption and H_2 temperature programmed desorption (H_2-TPD). X-ray photoelectron spectroscopy (XPS) was also employed. Other characterization techniques include the transmission electron microscopy (TEM) and scanning electron microscopy (SEM), both equipped with energy dispersive x-ray

spectroscopy (EDAX/EDS) and electron diffraction as well as powder x-ray diffraction (XRD).

1.5 Thesis Layout

This thesis consists of nine chapters. The first chapter is an overview of this thesis. It highlights the research justification, problem statements, research objectives and the scope of this thesis. Chapter two provides a literature survey, which will cover the development in the field related to the subject of this thesis. In chapter three, the detail experimental procedures and techniques are described. The findings of this research are divided into several chapters. Chapter 4 to 7 focuses on the catalysts prepared via non-classical methods while the sole chapter on catalysts prepared via classical methods is presented in Chapter 8. In Chapter 4 and 5, the synthesis, characterization and reactivity of the PtNi supported crystalline silica catalysts prepared via precipitation and impregnation techniques respectively are discussed in detail. The results and discussion in both these chapters have been published in Journal of Molecular Catalysis A and Journal of Catalysis respectively. The following chapter then focuses on the effect of oleic acid stabilized PtNi nanoparticles incorporated onto crystalline silica as potential catalysts. This is followed by a detailed study on the influence of several reduction parameters on the properties and reactivity of the PtNi bimetallic particles supported on MCM-41 in Chapter 7, which has been published in Catalysis Letters. For comparison purposes, the PtNi supported MCM-41 catalysts prepared via classical methods is then presented in Chapter 8. Finally, Chapter 9 provides a conclusion and recommendations for future work in this field.

1.6 References

1. R. A. van Santen, P. W. N. M. van Leeuwen, J. A. Moulijn, B. A. Averill, Studies Surf. Sci. Catal. Vol. 123. 1999, Netherlands: Elsevier Science B. V, pg 3-28.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanoparticles

Nanoparticles are particles that fall in the 'nano' regime which ranges between 1 - 100 nm. In terms of size, these particles bridge between atoms or molecules and bulk materials. Hence, their electronic and geometric properties differ from the two. Nanoparticles exhibit 'quantum effects' whereby the energy levels are an intermediate between both the atoms or molecules and bulk materials [1]. Therefore this creates a bandgap energy unlike the bulk material and atoms/molecules which are continuous and large correspondingly. Metal nanoparticles also posses' unique properties such as an increase in the number of kinks, corners and edges with dangling bonds (unattached atoms that extend out of a surface) [2, 3]. An example of this occurrence is seen in Figure 2.1, where the number of surface and defect atoms increase with the decrease in particle size while face atoms decrease with decreasing particle size [4]. Generally, both the changes in electronic and geometric properties when nanoparticles are formed can be beneficial in catalytic reactions. A demonstration on the influence of the geometric effect of nanoparticles is shown in Figure 2.2. Here it is observed that the hydrogenation of allyl alcohol to propanol on Pd nanoparticles, prefers face atoms of larger particles (1.5-1.9 nm) when compared to other active sites [4].
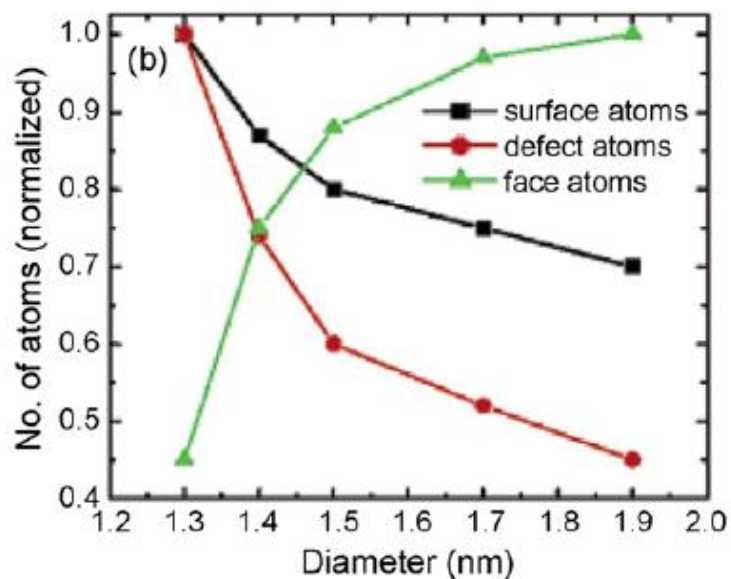
Figure 2.1: The influence of particle size on the number of surface, defect and face atoms [4].
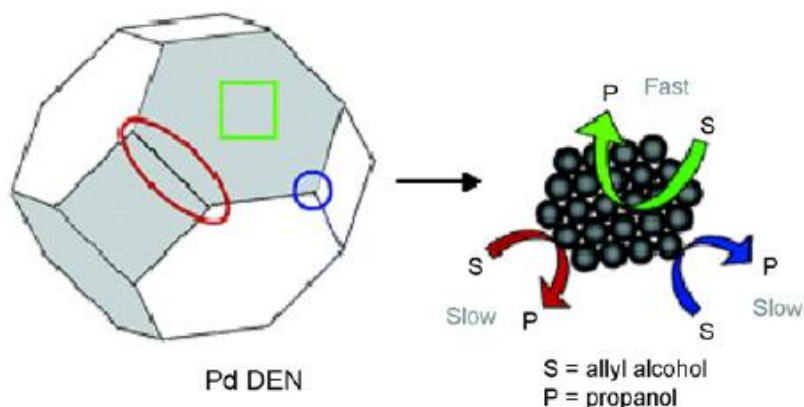
Figure 2.2: The effect of the various types of atoms on the conversion of allyl alcohol to propanol [4].

2.2 Bimetallic Nanoparticles

Bimetallic nanoparticles are formed via the incorporation of two or more metals in a system. Generally they can be categorized as alloyed or non-alloyed bimetallic nanoparticles. The alloyed particles may adopt a random alloy or intermetallic structure while non-alloyed particles result as, cluster in cluster

(atoms of a metal, grouping together) or core-shell structures [5]. A fine line exists between differentiating the existence of alloyed or non-alloyed bimetallic particles. Though several authors have attempted to clarify the differences between the two [6], the question whether a difference between the two exists, is still frequently debated upon.

2.2.1 Non-alloyed Bimetallic Nanoparticles

Generally, the formation of non-alloyed bimetallic particles is governed by the nucleation and growth rates of the metals involved. When two metals exist in a system, the energy required for nucleation of the metals to occur is minimized when compared to a system that contains only one metal. This is illustrated in Figure 2.3 which relates the free energy of a system containing either a type of metal (a homogeneous system) or more than one metal (a heterogeneous system) with the average particle size of the metal particles formed.
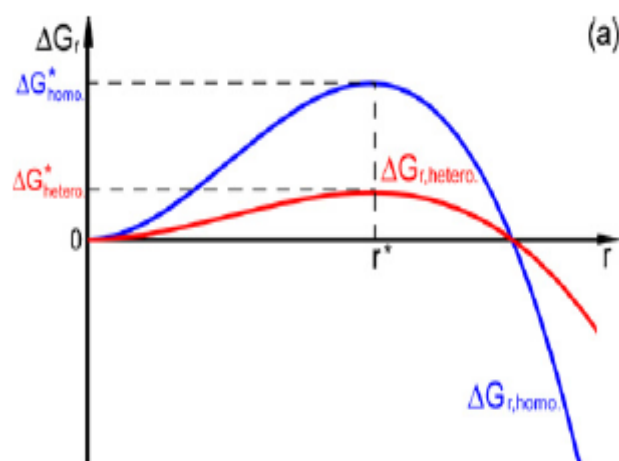
Figure 2.3: Graphical plot of the overall excess of free energy as a function of cluster size, r for heterogeneous and homogeneous nucleation [6].

Various structures of non-alloyed bimetallic particles have been reported. Among them are those that exhibit core-shell, random, separated as well as cluster in cluster morphologies. Some of these structures are illustrated in Figure 2.4.
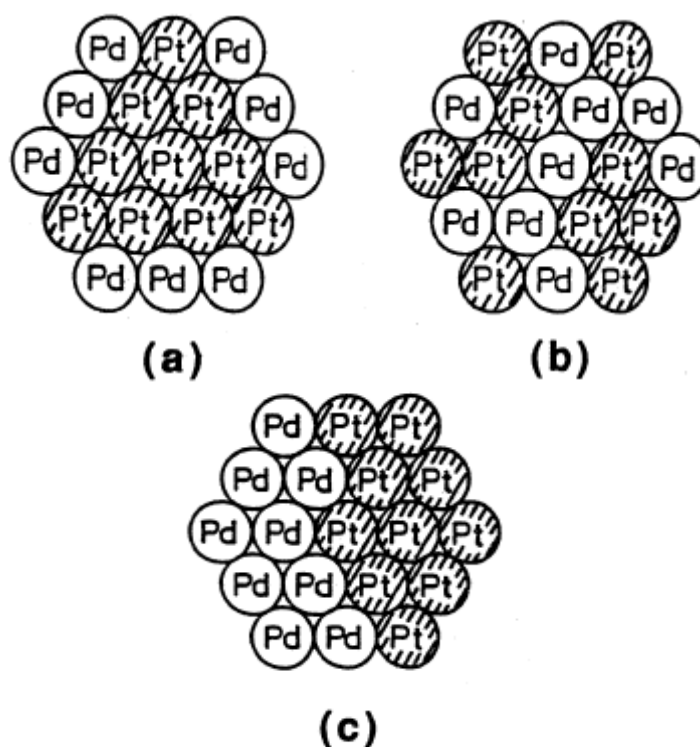
Figure 2.4:   Illustrations of typical bimetallic models (a) core-shell morphology; (b) random model and (c) separated model [5].

The formation of either of these structures depends on several factors such as the preparation method and metals involved. Typically, bimetallic particles which exhibit core-shell morphologies consist of a metal forming a core with another metal element surrounding the core to form a shell. A variety of factors influence its mechanism of formation. Among them are the reduction potential of the metals involved [7] as well as the method in which the metals are introduced into a system. Even so, a general mechanism of formation of this bimetallic

structure takes place in two steps. In the first stage, metal ions are reduced to form atoms, which subsequently aggregate into small clusters and grow at the expense of other metal ions. When metal ions of another metal are available, these ions will adsorb onto the surface of the first metal. Successive reduction in a suitable environment will result in a shell surrounding the first metal [8]. A schematic diagram of the growth mechanism is shown in Figure 2.5. Various techniques have been used to prepare bimetallic particles with these structures. Among them are the deposition technique used to prepare RePd and NiPt particles [9] and the chemical reduction technique to synthesize $PtFe_2O_3$ particles [10].
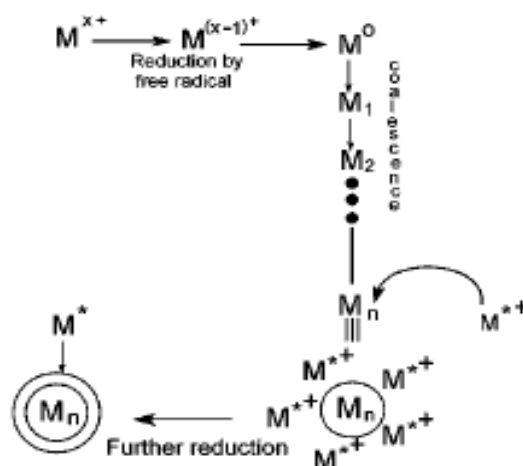
Figure 2.5: Schematic diagram of the growth mechanism of core shell bimetallic particles [8].

2.2.2 Alloyed Bimetallic Nanoparticles

Alloys have been identified as a metallic system consisting of two or more components irrespective of the nature in which the metals are mixed [11, 12]. The formation of these bimetallic particles can best be described in terms of thermodynamics. A simplified explanation is based on the understanding that

alloys occur when the excess of free energy, of the metals involved (ΔG), is negative. Therefore, the enthalpy and entropy of mixing for an alloy can take various values. Typically, most alloys occur spontaneously upon mixing of the metals. In this case, the system has a negative enthalpy of mixing ($\Delta H < 0$) and a positive entropy of mixing ($\Delta S > 0$) [6, 13]. In contrast when the mixing of metals is endothermic, in other words the enthalpy of mixing is positive ($\Delta H > 0$), alloys are formed only at high temperatures as this will lead to a higher contribution from the entropy when compared to the enthalpy of mixing [6, 13]. At low temperatures, the contribution of the entropy of mixing is lower than that of the enthalpy of mixing. Hence, the excess of free energy of mixing is positive. Under these conditions, alloys are not formed as the metals are immiscible [6,13].

The difference in the volume free energy of monometals and alloys formed from these monometals as a function of particle radius gives a good description of the effect of alloying. As shown in Figure 2.6, the volume free energy of alloys is lower than that of monometals.
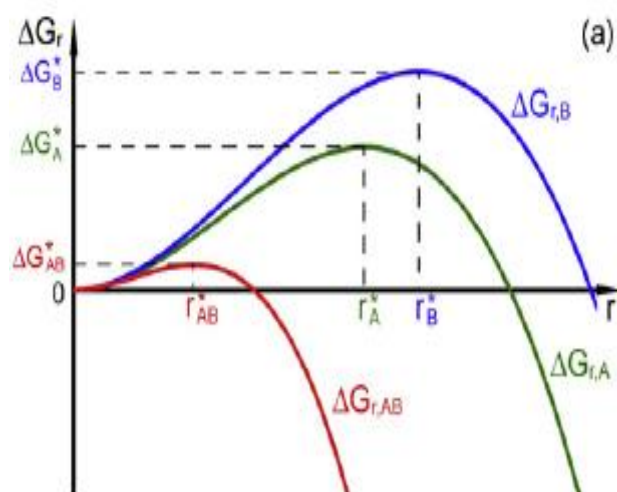
Figure 2.6: Graphical plot of the overall excess of Gibbs free energy, ΔG_r as a function of cluster size, r for alloys and the corresponding monometals [6]

Typically alloys can either take the form of monophasic or biphasic alloys. By definition, monophasic alloys are solid solutions whereby the metals involved exist as a homogeneous phase. In contrast, biphasic alloys occurs when the metals exist in two phases [11]. In this sense, only partial solid solutions are formed. An example of this type of alloy is the segregation of one of the metals to the surface of the alloy. This phenomenon has frequently been reported and its occurrence is dependent on factors such as the enthalpy of mixing, the atomic size of the metals as well as the surface free energies [14].

In addition, alloys can also be classified based on their crystalline order. Three different alloy structures which are known as random, clustered and ordered alloys exist [6]. Typical illustrations of the different types of alloys are presented in Figure 2.7.

(a)   (b)   (c)
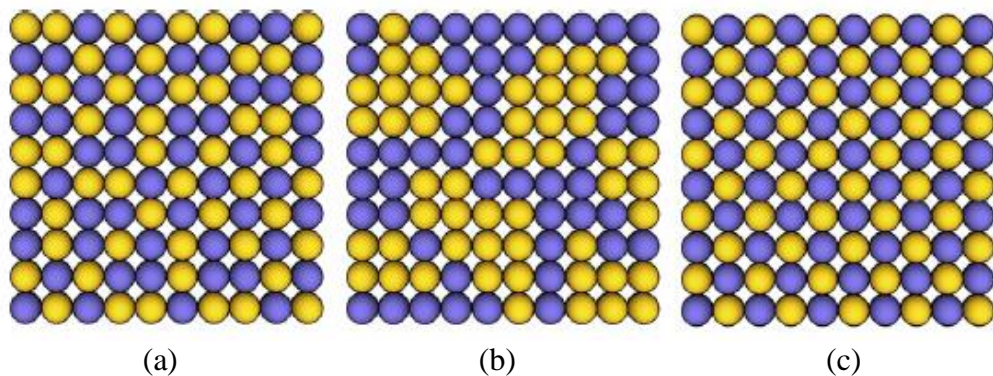
Figure 2.7: Schematic representation of three types of alloys, (a) random, (b) clustered and (c) ordered [6].

2.2.3 Ensemble and Ligand Effects of Bimetallic Particles

As catalysts, the formation of bimetallic particles has generated a lot of attention due to the benefits they present. Apart from the enhanced reactivity it can exhibit when compared to their respective monometallic catalysts [15], these particles may also demonstrate better selectivity [16] as well as resistance towards deactivation. Much interest has been given to understand how bimetallic nanoparticles influence these properties. Hence, the ensemble and ligand effects have been put forward to better explain these phenomenons.

The ligand effect which is also termed as the electronic effect refers to the modification in electronic interactions that occur between metals in bimetallic systems [17]. This involves electrons in the d band of transition metals. The ensemble effect (also known as the geometric effects) on the other hand explains the enhanced catalytic properties of alloys, in terms of the number of active sites on a surface that is necessary for a reaction to occur [17]. In other words, the selectivity of a reaction can be altered by blocking certain active sites that favor another reaction [14]. Some researches have expressed this as the dilution of actives sites in a metal with a second inert metal [18].

Several authors have attempted to ascribe the enhanced activity and selectivity of catalysts using the ligand and ensemble effects [19]. However, it has been established that the two effects correlate with each other [11, 20]. As an example, when an atom or several atoms of a metal A is placed in an environment of another metal B, such an occurrence cannot be considered solely as an ensemble effect as either metal may have an electronic effect on the other metal due to its close proximity [11].

2.3 Preparation of Catalysts

The preparation of supported metal catalysts can generally be prepared using one of two methods. These methods are widely known as the classical and non-classical methods. In both methods, the techniques in which the metal salts are introduced onto the supports are similar. The variation between the methods lies more in the reduction stage of the metal salts.

2.3.1 Classical Methods

The classical method is frequently used for its simplicity. It also has the advantage in eliminating chemical compounds such as sulfur and chlorine available in the metal salts, which can be poisonous in the final catalytic reaction. Generally, this method is a three step procedure that involves the incorporation of metal salts onto a support, calcinations and finally the reduction of the metal oxides to metal particles in a flow of hydrogen at elevated temperatures. Each step plays a significant role in determining the final properties of the catalyst. As an example, though the aim of the calcinations step is to oxidize the metal ions and to remove poisonous compounds, the temperature at which calcination is conducted can induce changes in the metal particle size as well as the support. In terms of the support, it has been reported that γ-Al_2O_3 changes to α-Al_2O_3 at calcination temperatures of 1300 K [21]. The reduction step can also influence the support. This particularly occurs when reducible oxides such as TiO_2 and CeO_2 are used as supports. For instance, CeO_2 can be reduced to Ce_2O_3 [22]. Even though the calcination and reduction steps are important when preparing catalysts via classical methods, it is no doubt that the technique in which the metal salts are introduced onto the support also plays a crucial role. Basically,

three types of techniques, the deposition, impregnation and precipitation are often employed.

2.3.1.1 Precipitation Technique

This technique entails the formation of an insoluble metal hydroxide or carbonate precipitate upon the addition of a solvent or an acid or base to a metal salt solution. The precipitate can then later be converted to metal oxides via calcinations [23]. One or more metals can be precipitated in a system. When two or more metals are involved, sequential or co- precipitation can occur. Sequential precipitation often arises as a result of a large difference in the solubility of the products formed from the original components concerned. Hence, co-precipitation requires a good solubility between the components. Though various metal salt solutions are mixed with the intention of carrying out co-precipitation, sequential precipitation may also occur [24]. This often leads to an inhomogeneity of the metal phase at a macroscopic level [24], which is the main disadvantage of the co-precipitation technique. Contrary to this, if co-precipitation is achieved, very small particles which are beneficial in catalytic reactions can be formed [23].

2.3.1.2 Impregnation Technique

The impregnation of metal salts into a support is typically carried out by mixing an excess of a metal salt solution with a support. The main objective is to occlude the solution into the pores or to allow it to adsorb onto the pore surface of the support [23]. After mixing for a certain duration of time, the catalysts are then dried and subsequently calcined.

The incorporation of large amounts of metal salts is preferable. However, several factors such as the mixing time, temperature, concentration of the metal salt solution and type of metal salt employed during impregnation can influence the final amount of metal salt incorporated into or onto the support. These preparation parameters have been studied extensively by various research groups.

Frequently, longer durations of impregnation time can increase the amount of impregnated metal salt. Though increasing the mixing time is effective, a major drawback of this technique is its extremely long preparation procedure. To overcome this, other researchers have carried out impregnation in several stages. In this technique, a metal salt solution is mixed with the support for a certain time before drying. This procedure is then repeated several times to increase the amount of impregnated metal salts [25]. Subsequently, to further optimize the amount of impregnated metal salt, higher temperatures have also been used during the mixing stage. Gayen et al. [26] used this technique in order to increase the solubility of the metal salt. As a result, they found that higher amounts of Ni nitrate can be impregnated indirectly reducing the number of impregnation stages required.

The impregnation of two or more metal salts onto a support can also be carried out simultaneously (co-impregnation) or subsequently (step-impregnation). In the prior technique, it is important to consider that the affinity of different metal salt solutions to adsorb onto a support varies. Therefore a consequence of utilizing this technique of impregnation is that the final ratio of the different components impregnated may not be the same as that in the metal salt solutions prepared [23].

2.3.2 Non - classical Methods

Non-classical preparation methods generally include those that do not involve calcinations followed by activations at high temperatures for long durations of time. This type of method includes those prepared via physical as well as chemical methods also known as the top-down and bottom-up methods correspondingly. Basically, the main purpose of these methods is to obtain an alternative route to synthesizing catalysts with small metal particles. A variety of non-classical methods have been put forward. However, methods which can be categorized as chemical methods remains the most popular.

2.3.2.1 Chemical Reduction

The chemical method usually involves the use of chemical reagents to reduce the metal salts. This may eliminate the need for a calcinations step and creates an opportunity to reduce the length of activation time. Several chemical reagents such as hydrazine [27], borohydride [28, 29] and alcohols [30] have been used for the preparation of bimetallic catalysts. The variation in reducing strength for the different chemical reagents results in different nucleation and growth rates of the metal particles [31]. This can indirectly influence the final properties of the catalysts formed.

2.3.2.2 Microwave Irradiation

The microwave irradiation technique is a potential reduction method for the formation of metallic particles. This is mainly due to its rapid and uniform heating nature which can lead to particle sizes with a narrow distribution [32]. This reduction technique has been used to prepare several catalysts such as Pd supported silica and alumina [33], PtRu [34] and PtNi [35] supported carbon

catalysts, as well as Pt supported carbon [36, 37]. Generally most of the studies show that metal supported catalysts prepared via microwave irradiation gave rise to small sized particles when compared to other reduction methods [35, 37]. Even so, there exist systems where the metal particles formed by microwave irradiation are larger than that formed via conventional heating [33]. Though the microwave reduction technique demonstrated contrary effects on the particle size, a general enhanced activity was observed for these catalysts when compared to those prepared via other techniques in these studies [33, 35].

2.3.2.3 Mechanical Attrition

This physical preparation method has commonly been employed to prepare alloys, hence is well known as the mechanical alloying technique. In this technique, the particles are formed via structural decomposition of coarser grained structures [38]. Examples of the application of this technique are the preparation of NiB-MgNi composites [39] and CoNi alloys for oxygen reduction reactions [40]. Though this method has been reported to be popular for the formation of nanocrystalline materials [38], one of its drawbacks is its difficulty in obtaining a narrow size distribution of the particles as well as controlling the particle size so that small sized particles are formed.

2.4 Supports

An early concept of typical supports is that this carrier for metal species is a non-reactive compound that is thermally stable even at high temperatures. Today, this perception of supports has altered. It is now well known that supports can also be involved in catalytic reactions. Generally, the choice of support can modify the behavior of a metal in numerous ways. It not only provides a means in

controlling particle morphology in terms of both shape as well as size, but also changes the reducibility of a metal. The use of mesoporous supports can lead to the synthesis of small sized particles provided that growth of the particles occurs in the pores of these supports [41]. In contrast, the reducibility of metal ions or oxides on the other hand is dependent on the strength of metal support interaction. It has been shown that reducible supports can lead to strong metal support interaction [42]. Furthermore, supports can also contribute to the selectivity and catalytic activity directly via spillover species on the support or by the availability of certain sites necessary for a reaction [43]. All these factors can indirectly influence catalytic activity.

2.4.1 Silicon (IV) Dioxide (SiO$_2$)

Silicon dioxide or better known as silica is composed of a silicon (Si), the second most available element on earth and two atoms of oxygen (O) [44]. It exists naturally in the form of quartz or sand. Silica can form both crystalline as well as amorphous structures. Among the various crystalline forms known are quartz, tridymite and cristobalite. The majority of the crystalline silica is composed of repeating tetrahedron SiO$_4$ units, which are bound together by their tops hence sharing an oxygen atom [45]. In contrast to crystalline silica, the amorphous state exists as anhydrous glass and hydrated colloidal silica [45].

Silica has long since been used as supports for metal particles as they are chemically inert and have high thermal stability. Among the numerous metals supported on this carrier are NiCu [46], Ni [47, 48] and NiB [49]. Though this support has been widely used due to its low cost, current trends are now turning

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to the use of mesoporous silica as this category of silica provides a larger surface area when compared to the traditional silica.

2.4.2 MCM-41

This mesoporous ordered silica material was discovered in 1992 by researches from the Mobile Central Research Laboratory [50, 51]. Its structure is composed of hexagonal shaped pore walls that are amorphous. Even so, the ordered nature of these pores results in the material adopting a long-range crystallinity characteristic [52]. Typically the pore sizes range in the nano regime of 1.5-10 nm, hence this provides the material with a high specific surface area of approximately 1000 m^2 g^{-1} [53]. Though this feature as well as its enhanced thermal stability is advantageous as a catalyst support, its poor acidity and redox properties limit its potential in several catalytic reactions [54]. Other established characteristics of siliceous MCM-41 is it's hydrophobic nature as well as its small amounts of OH sites on its surface including three types of silanol groups. These silanol groups are significant in surface modification reactions such as silylation [51]. These materials only show weak acidity hence are only promising for reactions that do not require strong acidity. This inconvenience has been overcome by incorporating metal species into the silica framework. Though this can cause deterioration in the long range ordered structure, it creates active centers which can improve catalytic behavior. For instance, incorporation of aluminium in the MCM-41 framework is known to form acid sites that can be advantageous for reactions that require strong acidity [55].

2.5 Characterization Techniques

In the early 1900s, a lack of fundamental understanding of the surface properties of supported metal catalysts especially bimetallic catalysts existed mainly due to the limitation in characterization tools. During this era, techniques such as magnetic moments and electrical conductivity measurements were mainly employed [12]. Better understanding of catalysts was only obtained from the 1950's when spectroscopic techniques were introduced as a means to investigate properties such as the surface of catalysts [56]. Since then, numerous characterization tools have been established, enabling researches to gain better insight on the properties of catalysts.

2.5.1 Temperature Programmed Reduction (TPR)

Temperature programmed reduction is a dynamic flow technique that provides information on the reducibility of metal oxides or metal ions in catalysts which are prepared via classical methods. It also gives an insight on the extent of reduction of the metal phase for catalysts synthesized using non-classical methods. The basic principle of this technique involves flowing diluted H_2 through a sample, while increasing its temperature at a predetermined rate. Metal oxides or metal ions available in the catalysts will consume hydrogen forming metal nanoparticles in a reduced state. Generally, the position of the peak at which H_2 consumption occurs, gives information on the temperature at which the metals can be reduced, the state in which the metals exist whether as ions or oxides, the strength of metal-support interaction as well as the size of the metal particles. For bimetallic supported catalysts, this surface characterization technique indirectly demonstrates how the addition of a second metal to a metal

supported catalyst, influences these characteristics. For instance, a study on silica-alumina (ASA) supported nickel catalysts demonstrates that the metal-support interaction decreases with increasing Ni content in the sample or as a result of the addition of Pd in the catalyst. This is elucidated by the decrease in temperature at which H_2 consumption for the NiO occurs [57]. Further, upon the addition of Li to the Ni/ASA catalyst, different metal species are observed. Peaks arising at 670, 720 and 820 K are indicative of various nickel oxides while the peak at 944 K corresponds to nickel in a cationic form [57]. Other research groups have also described the use of this characterization technique to comprehend similar characteristics of various catalysts [58, 59].

2.5.2 Temperature Programmed Desorption (TPD)

This dynamic flow method was originally applied to evaluate the strength of interactions between a surface and an adsorbed species as well as the reaction sites available on a catalyst [60, 61]. Its concept is based on the availability of sufficient thermal energy to break bonds between an adsorbent and its adsorbate. This is accomplished by applying a temperature ramp to the sample. Samples which are initially treated in a reactive gas such as H_2, desorbs the reactive gas into a passing non-reactive gas. The amount of adsorbate desorbed as a function of temperature is followed giving rise to desorption peaks. The peak positions and intensity are dependent on several factors such as the support and metal involved, the adsorbate as well as the pretreatment conditions [43]. The application of this technique to characterize the surface of catalysts has been demonstrated by Li and coworkers [62]. They described the desorption of H_2 from PtNi supported on carbon nanotube catalysts. It was shown that the

temperature at which desorption occurs shifted to lower temperatures with the addition of Ni to Pt. This is due to hydrogen spillover and suggests a strong interaction between Pt and Ni.

Further, the surface composition of bimetallic catalysts can also be evaluated using carbon monoxide (CO) TPD. This reactive gas is frequently employed to investigate the different surface adsorption sites available especially when Pd is involved. This is due to the fact that CO favors different adsorption sites on Pd when compared to other metals. As an example, this reactive gas has been employed for the investigations of PdCo bimetallic catalysts [63]. On Pd, CO adsorption mainly occurs on threefold hollow sites followed by bridge and atop sites. In contrast, adsorption of CO on Co occurs favorably on atop sites. Hence, the CO TPD for pure Pd/Al_2O_3 exhibits a desorption peak at 450 K (three fold hollow sites) while pure Co/Al_2O_3 gives rise to a peak mainly at 390 K (atop sites) with a shoulder at 280 K (bridge sites). When bimetallic $PdCo/Al_2O_3$ catalysts were formed by depositing Pd onto the support followed by Co, changes in the surface properties can clearly be seen with increasing deposition of Co. This is illustrated in Figure 2.8. Based on this knowledge, specific adsorption sites which promote a catalytic reaction can be identified.
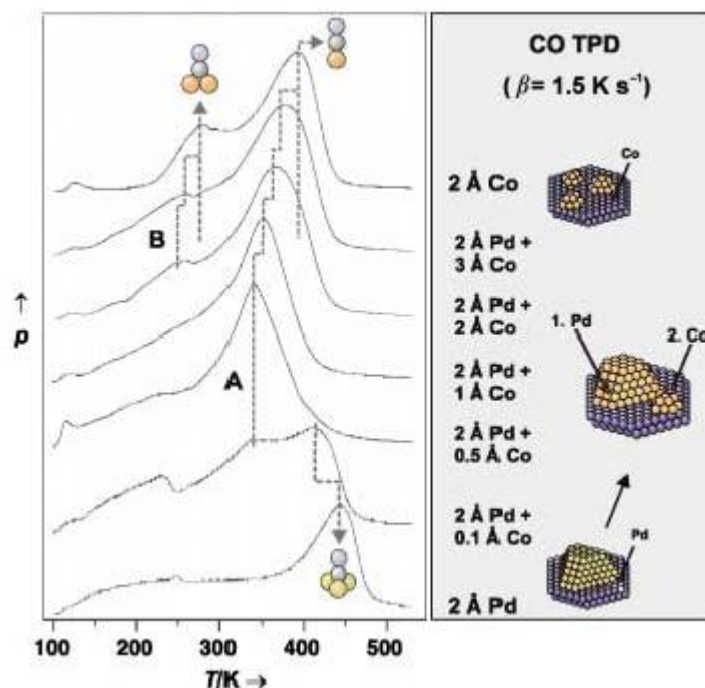
Figure 2.8: CO-TPD of PdCo supported Al_2O_3 catalysts prepared with various PdCo ratios [63].

This technique has also been expanded to characterize other characteristics. Among them is the acidity of the catalysts or their supports. Molecules such as pyridine are used as probes for the detection of acid sites due to their small size, good thermal stability and high basicity [64]. Other molecules such as ammonia [65, 66] and benzene have also been employed for similar purposes. This characterization technique gives an insight on the strength and number of acid sites available on a support or catalyst. However, its main disadvantage is its inability to differentiate Bronsted acid sites from Lewis acid sites. For this reason, this method has at times been supported by characterization methods such as pyridine FTIR.

The acidity of bimetallic catalysts has been studied by several research groups [65, 66]. As an example, valuable information on how the addition of Ni,

to Pt supported zeolite and modernite decreases the acidity of the catalysts irrespective of the preparation technique employed has been obtained [65]. Further, when the acidity of a range of alumina supports were investigated using ammonia TPD, studies showed that γ-alumina, extrudates and tablets show higher ammonia desorption when compared to α-alumina as well as trans-alumina. This is indicative of larger amounts of acid sites available on the earlier supports compared to the latter [67].

Furthermore this characterization tool can also be used to determine the distribution of activation energy for the desorption of hydrogen. This has been described for Ni supported silica catalysts using hydrogen as the probe molecule [68].

2.5.3 X-ray Diffraction

This x-ray technique is employed to comprehend the structure of nanoparticles and gain qualitative elemental information [5]. The basic principle of this characterization method is based on the generation of monochromatic x-rays from a cathode ray tube. These x-rays are directed to a sample resulting in the emission of scattered waves from the atoms. A diffracted radiation is formed when these waves interfere with each other. Its intensity is largely influenced by the structure of the elements analyzed [69]. Hence this enables the determination of the geometric structure of the particles as well as their average particle size.

In the case of bimetallic particles, this technique is advantageous as it enables discrimination between physical mixtures of different metal particles as well as alloys. In catalysts where mixtures of two or more types of metal particles are present, XRD patterns demonstrate the presence of diffraction peaks for both