SYNTHESIS AND CHARACTERISATION OF HALLOYSITE NANOTUBES SUPPORTED NICKEL CATALYSTS FOR HYDROGENATION OF BENZENE

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by

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LIST OF ABBREVIATIONS / SYMBOLS / UNITS

Å	Angstrom
AAS	Atomic Absorption Spectroscopy
BET	Brunaeur-Emmett-Teller
g	Gram
HNTs	Halloysite Nanotubes
H_2-TPD	Hydrogen Temperature Programmed Desorption
H_2-TPR	Hydrogen Temperature Programmed Reduction
HRTEM	High Resolution Transmission Electron Microscopy
K	Kelvin
kV	Kilovolt
mL	Mililiter
nm	Nanometer
NiO	Nickel Oxide
Ni-HNT/C	Halloysite Nanotubes Supported Nickel Catalyst Prepared via Classical Method
Ni-HNT/NC	Halloysite Nanotubes Supported Nickel Catalyst Prepared via Non-Classical Method
ppm	Parts per million
SEM	Scanning Electron Microscopy
wt%	Weight Percentage
XRD	X-Ray Diffraction
λ	Wavelength
μm	Micrometer
mg	Milligram
θ	Theta

SINTESIS DAN PENCIRIAN PEMANGKIN NIKEL YANG DISOKONG OLEH NANOTIUB HALLOYSIT UNTUK PENGHIDROGENAN BENZENA

ABSTRAK

Dua siri mangkin nikel yang disokong oleh nanotiub halloysit telah dihasilkan menerusi kaedah klasik dan tidak klasik menggunakan teknik impregnasi. Kandungan Ni dipelbagaikan antara 2-14 wt% dalam kedua-dua siri mangkin Ni-HNT. Mangkin tersebut telah dicirikan dengan menggunakan spektroskopi penyerapan atom (AAS), mikroskop elektron pengimbas (SEM), analisis N_2-penjerapan nyahpenyerapan, pembelauan X-ray (XRD), mikroskop elektron pancaran berpeleraian tinggi (HRTEM), penyahserapan suhu terprogram hidrogen (H_2-TPD), serapan kimia hidrogen dan pengurangan suhu terprogram hidrogen (H_2-TPR). Analisis SEM menunjukkan bahawa zarah-zarah logam nikel bertaburan dan bergantung pada wt% Ni yang berbeza tanpa dipengaruhi oleh kaedah penyediaan. Keputusan XRD menunjukkan kehadiran zarah-zarah logam Ni bagi teknik klasik dan kehadiran zarah-zarah NiO bagi teknik tidak klasik. Analisis SEM menunjukkan bahawa spesis Ni terenap di dalam lumen HNT serta di permukaannya. H_2-TPD dan analisis serapan kimia hidrogen mencadangkan bahawa tapak aktif yang berbeza dan saiz zarah Ni mungkin memberi kesan terhadap kedua-dua penyahjerapan dan penjerapan H_2. Selain itu, analisis H_2-TPR menunjukkan kekuatan interaksi yang berbeza bagi mangkin Ni-HNT serta kehadiran spesis Ni yang tidak dikurangkan. Bagi mangkin klasik, didapati bahawa 9.3 wt% Ni-HNT/C menunjukkan penukaran terbaik benzena kepada sikloheksana pada seluruh julat suhu yang dikaji. Hal ini adalah kerana taburan yang baik dan kurang aglomerasi oleh partikel Ni, seperti yang

ditunjukkan oleh keputusan SEM dan XRD. Ini menyediakan kawasan permukaan yang lebih besar bagi tindak balas berlaku. Keputusan penyahserapan suhu terprogram hidrogen (H_2-TPD) juga menunjukkan nilai penyahserapan tertinggi (0.3487 mmol g_{Ni}^{-1}) pada suhu rendah beranggaran ~360-550 K. Bagi mangkin tidak klasik, didapati bahawa 7.7 wt% Ni-HNT/NC menunjukkan prestasi penukaran terbaik benzena kerana memiliki nilai penyahserapan yang tertinggi (1.5109 mmol g_{Ni}^{-1}) pada suhu rendah beranggaran ~580-700 K dan nilai limpahan H_2 yang tinggi (0.7523 mmol g_{Ni}^{-1}) yang boleh mengekalkan kereaktifan penghidrogenan yang lebih tinggi di sepanjang julat suhu yang lebih besar.

SYNTHESIS AND CHARACTERISATION OF HALLOYSITE NANOTUBES SUPPORTED NICKEL CATALYSTS FOR HYDROGENATION OF BENZENE

ABSTRACT

Two series of halloysite nanotubes supported nickel catalysts (Ni-HNT) were prepared using classical and non-classical methods via impregnation technique. The Ni content was varied between 2-14 wt% in both series of Ni-HNT catalysts. Catalysts were characterized via Atomic Absorption Spectroscopy (AAS), Scanning Electron Microscope (SEM), N_2-adsorption desorption analysis, X-ray Diffraction (XRD), High Resolution Transmission Electron Microscope (HRTEM), Hydrogen Temperature-Programmed Desorption (H_2-TPD), Hydrogen Chemisorption and Hydrogen Temperature-Programmed Reduction (H_2-TPR) techniques. The SEM analysis showed that Ni particles were scattered depending on the different wt% of Ni regardless of the preparation methods. XRD results reveal the presence of NiO particles for the catalysts prepared via classical technique and the presence of Ni metal particles for the non-classical technique. The SEM analysis showed that the Ni species were deposited in the lumen of HNT as well as on its surface. The H_2-TPD and H_2 chemisorption analyses suggested that different active sites and Ni particle sizes may affect the desorption and adsorption of H_2 respectively. Besides, the H_2-TPR analysis indicates the different strength of interaction of the Ni-HNT catalysts as well as the availability of unreduced Ni species. For the classical catalysts, it was found that the 9.3 wt% Ni-HNT/C showed the best conversion of benzene to cyclohexane throughout the temperature range studied. This is due to the good

dispersion and less agglomeration of the Ni particles as confirmed by SEM and XRD results. This provides a higher surface area for the reaction to occur. The H_2-TPD results also showed that this catalyst exhibited the highest H_2 desorption value (0.3487 mmol g_{Ni}^{-1}) at lower temperatures of approximately ~360-550 K. For the non-classical catalysts, it was found that the 7.7 wt% Ni-HNT/NC showed the best performance for benzene conversion as it has the highest value of H_2 desorbed (1.5109 mmol g_{Ni}^{-1}) at lower temperatures of approximately ~580-700 K and a high value of H_2-spillover (0.7523 mmol g_{Ni}^{-1}) that can maintain the hydrogenation reactivity throughout a wider temperature range.

CHAPTER ONE

RESEARCH BACKGROUND

1.1   Brief Overview

Nanomaterials have received much attention since more than a decade. They are comprised of small sized materials whereby at least one dimension of the material has a measurement of 100 nm or less (Alagarasi, 2011). This means that a material with any one of its dimensions, such as length, width or height having a nanometer scale is considered as a nanomaterial (Finke, 2002). Nanomaterials have been applied in various fields such as electronics (Jariwala et al., 2013), optics (Kim et al., 2015), magnetic data storage (Gu et al., 2016), superadsorbents (Nechaev et al., 2009), sensors (Guo and Wang, 2011), separations (Zhang et al., 2006), pigments (Khanna, 2008) as well as catalysis (Parmon, 2013). For the purpose of catalysis, nanomaterials are widely applied in research studies and industries. This is due to the higher reactivity and selectivity characteristics of nanosized catalysts as compared to the bulk catalysts. These includes large surface areas and large surface energies (Cao, 2004). In catalysis, the properties of nanomaterials can be tuned by adjusting the size, shape, or extent of agglomeration (Cao, 2004). These features bring about the revolution for future science and technology.

1.2   Problem Statements

Increasing interest has been placed on metal supported catalysts as they can be regenerated and speed up reactions for industrial purposes. Various metals, supports, preparation methods and conditions have been studied. Nowadays, there has been a great deal of interest in the studies of nanotubes. Halloysite nanotube which is a unique and versatile nanotube has yet to be explored extensively especially as supports for catalytic purposes. Previous studies highlighted the use of HNT as supports for various metals such as Pd (Zhang et al., 2013), Co (Zhang and Yang, 2012) and Au (Fu et al., 2014). No study has reported the use of HNT as a support for monometallic Ni. A previous study focused on the use of Ni with Pt using MCM as a support (Abu Bakar et al., 2009b). Ni supported catalysts has the potential to be a good catalyst and is inexpensive (Abu Bakar et al., 2009b). At the same time, the production of hazardous compounds has created awareness among todays' community regarding the need to convert them into compounds which are more environmental friendly. So, based on these situations, the aim of this study is to synthesize suitable, cheap and an environmental-friendly HNT supported metal catalyst for the conversion of hazardous compounds to less toxic ones. To date, the number of works related to HNT supported metal catalysts for catalytic application is few. In fact no works on HNT supported monometallic Ni for hydrogenation reactions such as benzene is available. Hence it would be interesting to investigate this reaction in depth.

1.3   Objectives of Study

The objectives of this study are:

1. To synthesize HNT supported Ni catalysts via classical and non-classical methods.

2. To characterize and study the surface properties of the HNT supported Ni catalysts.

3. To investigate the effect of synthesis approach on the reactivity of Ni supported HNT catalysts for hydrogenation of benzene.

1.4   Scope of Study

This study has been limited to the synthesis of monometallic Ni nanoparticles on HNT as the support for the hydrogenation of benzene. In order to undergo the catalytic conversion of benzene into cyclohexane, HNTs were impregnated with Ni salt via wet impregnation technique and prepared using two different methods; the classical and non-classical methods. The classical method employed hydrogen (H_2) as a reducing agent whereas non-classical method employed hydrazine as a reducing agent. To compare the best performance of the catalysts, different weight percentages of the Ni-HNT catalysts were synthesized. The surface of the resulting catalysts were 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). Other characterization techniques investigated are the scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS) as well as the N_2 adsorption-desorption technique.

1.5   **Thesis Layout**

This thesis consists of five chapters. The first chapter is the introduction and a brief overview on this study. It highlights the research's introduction, problem statements, objectives of the study and the scope of study. Chapter two provides a literature review, which will cover recent studies related to the subject of this thesis. In chapter three, the materials and experimental procedures are discussed. In chapter four, the results and observations investigated are presented. Chapter five provides a conclusion and recommendations for future work in this field.

CHAPTER TWO

LITERATURE REVIEW

2.1   What are Clays?

Clays are phyllosilicates that are formed in the earth over millions of years, by surface weathering of aluminosilicate minerals (Barton, 2002). In general, clays are composed of individual layers that are made up of tetrahedral or octahedral sheets with a ratio of 1:1 or 2:1. Figure 2.1 demonstrates the different classes of clay based on this ratio.
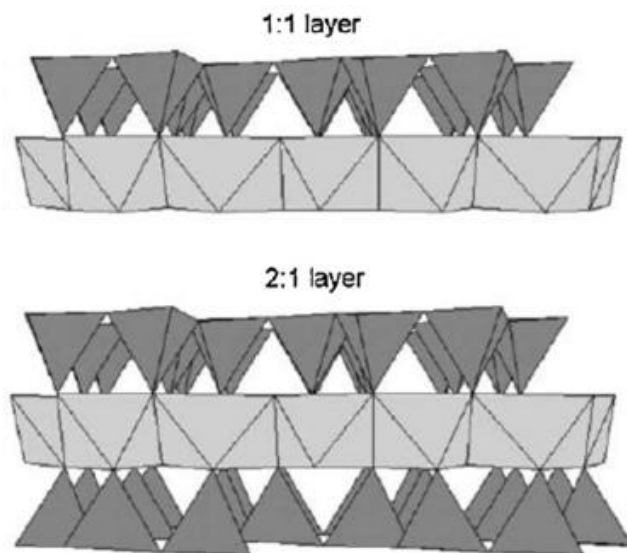
Figure 2.1: The clay mineral structure of 1:1 and 2:1 layer type (Brigatti et al., 2006)

The 1:1 clay minerals are composed of a two sheet mineral which combine a tetrahedral with an octahedral sheet in their basic structural unit. They are categorised as a kaolin group, with the general formula $Al_2Si_2O_5(OH)_4$ (Barton, 2002). Examples of these clay minerals are kaolinite, dickite, nacrite and halloysite nanotubes (Hussin et al., 2011). In contrast to the 1:1 clay minerals, the 2:1 clay minerals are composed of a three sheet mineral unit which joins two tetrahedral

sheets and one octahedral sheet. Some of the clay minerals which have this ratio of tetrahedral and octahedral sheets are known as smectite, micas, pyrophyllite, vermiculite and chlorite (Hussin et al., 2011). Among these, the most commonly used in various industries is the smectite (Hussin et al., 2011). In general, although there are numerous types of clays, these materials are similar in terms of their composition whereby most clays are composed of oxygen (O), silicone (Si), aluminium (Al) and magnesium (Mg). Apart from this, clays are similar because they are thermally stable up to temperatures of approximately 1173 K and these materials are also chemically inert towards a wide range of solvents (Vogels et al., 2005). To enhance its applicability in numerous fields, its surface can be modified (Barrientos-Ramírez et al., 2011; Leszczynskaa A et al., 2007) or incorporated into polymers (Du et al., 2007; Guo et al., 2008; Lecouvet et al., 2011; Ye et al., 2007) to impart different properties. As such, the possibilities for the use of clays in future are tremendous.

2.2 Halloysites

Halloysite is a 1:1 clay mineral with stoichiometry: $Al_2Si_2O_5(OH)_4.nH_2O$ (Joussein et al., 2005). The typical crystalline structure of halloysite is shown in Figure 2.2.
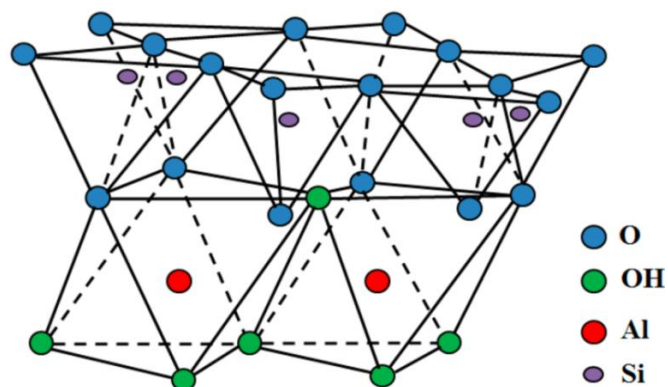
Figure 2.2: Crystalline structure of halloysite (Du et al., 2008)

It is a naturally occurring eco-friendly nanotube that is harmless to humans and the trendsetter for green technology (Joussein et al., 2005). There are three main shapes of halloysite, which are platy, tubular, and stack, as can be seen in Figure 2.3. The most common halloysite exhibit tubular shapes, but the use of stack and platy have also been reported (Saif and Asif, 2015).
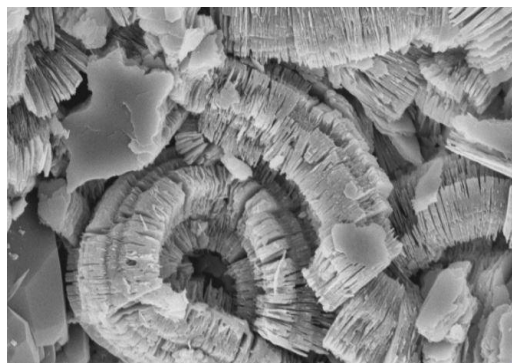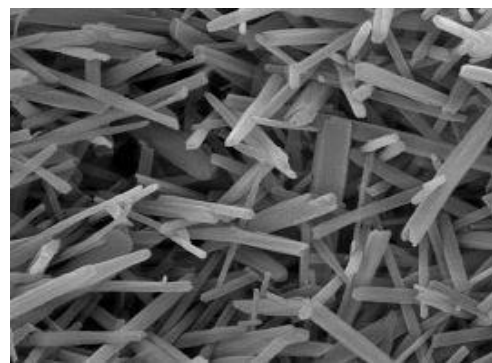
Platy HNTs   Tubular HNTs
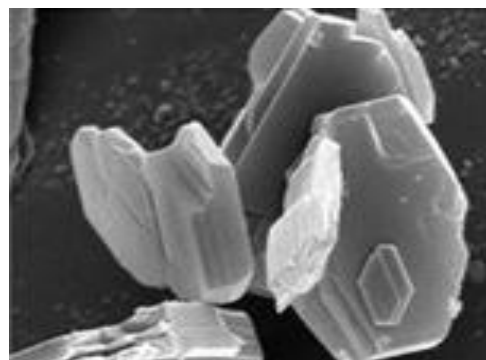
Stack HNTs

Figure 2.3: Various shapes of halloysite nanotubes (Saif and Asif, 2015)

Most HNT deposits are found in countries like America, Brazil, China, France, Belgium and New Zealand (Saif and Asif, 2015). In general, its chemical composition such as impurities as well as porosities are determined by various different deposits (Kamble et al., 2012). HNTs have a hollow nanotubular structure

which gives rise to its large surface area. In size, it ranges from 0.5-2 microns in length and 15-50 nm in diameter as shown in Figure 2.4.
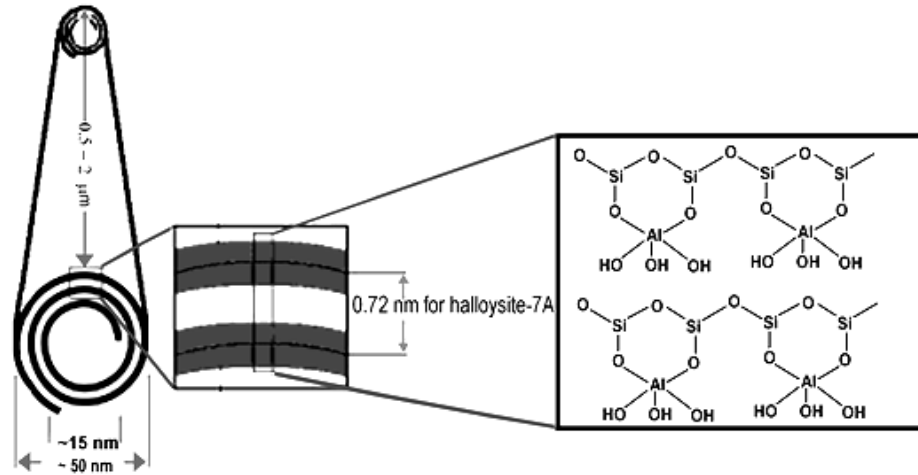
Figure 2.4: Structure of halloysite nanotube (HNT)(Abdullayev and Lvov, 2010)

It is normally described as a gibbsite octahedral sheet $(Al(OH)_3)$, which is modified by siloxane groups at the outer surface (Duarte et al., 2012). HNT contains two types of hydroxyl groups, which is located at the outer and the inner parts. The hydroxyl groups in the inner part is situated between layers and the outer part is situated on the surface of the nanotubes (Du et al., 2010). They can also be classified according to its hydration state that is either hydrated or dehydrated (Joussein et al., 2006). The hydrated form of HNT has a crystalline structure with a $d_{(001)}$ spacing of 10 Å, whereas the dehydrated one has a crystalline structure with a $d_{(001)}$ spacing of 7 Å. The dehydrated form of HNT may be obtained through the loss of the interlayer water molecules under mild heating and/or a vacuum environment (Joussein et al., 2005). The sublayers in halloysite nanotubes are divided with a monolayer of water molecules. Due to the fact that this interlayer of water is weakly held, the original form of HNTs with a hydrated crystalline structure of 10 Å can be

readily and irreversibly dehydrated to form the halloysite 7 Å (Joussein et al., 2005). It is impossible for the 7 Å HNTs to be treated to form the 10 Å HNTs, except by intercalation of organic compounds (Rawtani and Agrawal, 2012). To maintain the hydration state of HNTs, great care and suitable humidity conditions, for example, a well-humidified sealed container is required (Joussein et al., 2006).

2.3 Application of HNTs in Various Fields

As previously mentioned, HNTs occur naturally and are harmless to human. In addition, it has a unique morphology, stable in organic solvents and is inexpensive when compared to the other nanomaterials. As a result, these unique and versatile nanomaterials have been applied in a wide range of applications, ranging from the medical fields to support for catalysts, as highlighted in Figure 2.5. Reviews on recent applications of HNTs were published in 2010 (Du et al., 2010), 2012 (Kamble et al., 2012) and 2015 (Saif and Asif, 2015).
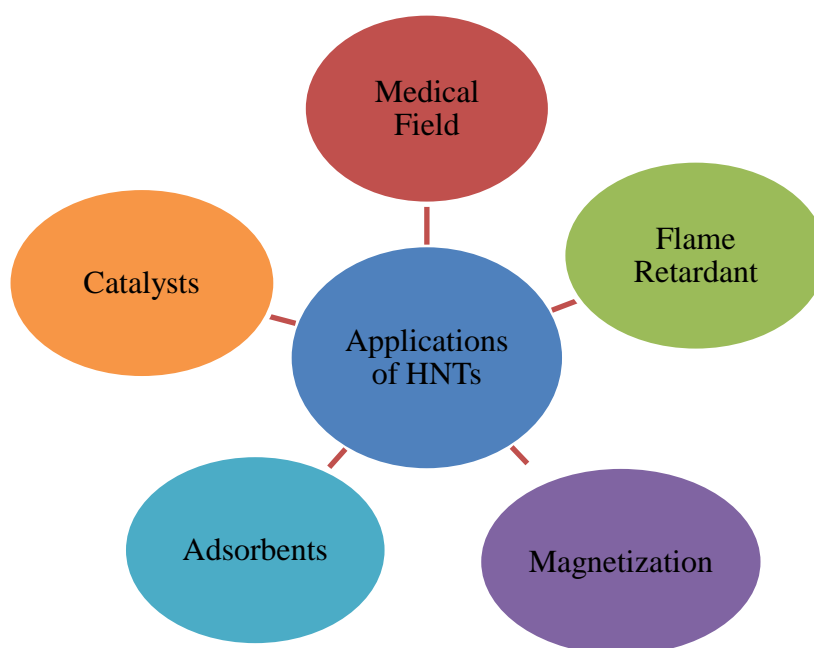
Figure 2.5: Various applications of HNTs.

2.3.1 Medical Field

In the medical field, HNTs have been investigated for the delivery of drugs, used to enhance the mechanical properties of the drug samples (Jiang et al., 2016; Tu et al., 2013). A previous study found the combination of HNTs with chitosan (CTS) to be successful for the delivery of Aspirin. For this purpose, the negatively charged HNT was introduced into the porous microspheres of CTS by the electrostatic self-assembly technique. The presence of hydrogen bonding as well as the physically coated HNT/CTS created an abundant of functional groups on the surface of the particles which enhances the loading amount of Aspirin. The results showed that the microspheres improved the amount of Aspirin loading from 2.1 wt% to 42.4 wt%. Furthermore, HalCTS/Aspirin nanocomposites released lower amounts of Aspirin in simulated gastric fluid as compared to intestinal fluid. This could help maintain an effective concentration of Aspirin in the body and reduces the side effects towards the stomach (Li et al., 2016).

In addition, HNTs have also been applied as dual-responsive nanocarriers. A recent study investigated the potential of HNTs as dual responsive nanocarriers for curcumin (Cur), where the samples are sensitive towards both intracellular glutathione (GSH) and pH conditions. Curcumin is a well-known antioxidant and anticancer compound which has been widely used in the medical field. HNTs was functionalized with cysteamine through disulphide linkages. The functionalized HNT was then conjugated to curcumin via the available amino groups of cysteamine, through the Schiff's base formation, also known as a pH-responsive imine bond. Based on the result, HNT-Cur showed positive response towards exposure to GSH-rich or acidic environment (Massaro et al., 2016).

Another study reported the use of HNTs to enhance the mechanical properties of a drug carrier samples. Tu et al. (2013) studied the uses of HNTs in nanocomposite hydrogels with tunable mechanical properties and drug release behavior. The nanocomposite hydrogels were prepared to study the performance of the release of bovine serum albumin (BSA). In this study, HNTs, oligo(trimethylene carbonate)–poly(ethylene glycol)–oligo(trimethylene carbonate) diacrylate (TPT), and alginate sodium (AG) were used to form hydrogels composed of TPT-HNT, TPT-AG and TPT-AG-HNT. The mechanical properties of the hydrogels were improved after the incorporation of HNTs (Tu et al., 2013)

2.3.2 Flame Retardant

HNTs have also been applied as flame retardants. HNTs have limited heat conduction and eventually reflects radiant heat, thus creating heat barrier properties which tend to retard the burning of composites. Studies reported the incorporation of HNTs into nylon 6 (Marney et al., 2008) and polyethersulfone (PES) (Lecouvet et al., 2013) via melt extrusion and water-assisted extrusion methods respectively. Researchers used different amounts of HNT loadings in order to compare the properties and performances of these nanocomposites.

For example, HNTs have been reported to improve thermal properties of polymers when used as an additive in nylon 6. In a study by Marney et al. (2008), nylon 6–HNT composites were prepared using 5–30 wt% of HNT loadings by a simple melt extrusion process. Based on the results obtained, HNTs inhibited the burning of nylon when the amount of HNTs is in the range of 15-30 wt%. With increasing loadings of HNTs, the rate of heat release is reduced. The flammability of the composites were investigated using the Oxygen Index (OI) test. Upon

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increasing the HNTs content from 15 wt% to 30 wt%, the OI test showed an increasing trend from 22% to 30% for the PA6-HNT composite. This signals the reduction in flammability of the composites (Marney et al., 2008).

Another study by Lecouvet et al. (2013) investigated the thermal resistant of polyethersulfone (PES)/HNT nanocomposites. Polyethersulfone is an amorphous thermoplastic resin with good thermal properties compared to other plastics. Other than that, it can withstand flame with a limiting OI of around 38 vol%. However, due to its amorphous characteristic, it easily reacts with some organic solvents. To limit this from occurring, the melt compounding process was conducted through a water-assisted extrusion procedure. During the extrusion process, the -OH chain ends of PES from the originally OH-terminated PES resins were covalently bonded onto the aluminosilicate surface. Results showed that the PES has improved thermal and thermo-oxidative stability as well as fire retardancy in the presence of HNTs. This is due to the presence of complex networks on the protective ceramic surface prevailed from the dispersed HNTs. It is summarized that the fire retardancy effect is attributed to the ceramic available (Lecouvet et al., 2013).

2.3.3 Magnetization

Recent studies reported that HNTs can be applied for magnetization purposes. For example, Co nanoparticles can be deposited on the surface of HNT via electroless deposition method (Zhang and Yang, 2012). Vibrating sample magnetometer (VSM) was used to determine the ferromagnetic or ferroelectric (coercivity) of Co, the residual magnetization as well as the saturated magnetization of the samples. Results showed that the coercivity (Hc) values of the Co-HNTs (1659 Oe) were higher than the coercivity (Hc) values of the pure Co nanoparticles

alone (580 Oe). So it can be concluded that Co-HNT are potential as magnetic devices. Eventhough HNTs have no magnetic properties but the deposition of Co nanoparticles on the surface of HNT enhances the performance of Co metals in magnetic field (Zhang and Yang, 2012).

2.3.4 Adsorbents

Cao et al. (2015) studied the hybrid materials of β-cyclodextrin decorated HNTs (HNTs-g-βCD) as a nano adsorbent for the removal of dye. The HNTs-g-βCD composites could be used as nano adsorbent for methylene blue (MB). For this purpose, the HNTs' surface were first modified with poly(glycidyl methacrylate) by using the reversible addition fragmentation chain transfer polymerization (RAFT) process. Then, β-cyclodextrin was prepared through a facile route. β-cyclodextrin is a natural product for the environmental treatment and catalysis. The modified HNTs and β-cyclodextrin were then conjugated together to produce the HNTs-g-βCD by grafting βCD onto the HNTs' surface. The HNTs-g-βCD showed better adsorbent characteristics compared to pristine HNTs, thus effectively removing MB from an aqueous solution. This is based on the result obtained, where 4 mg of HNTs-g-βCD adsorbed 79.6% of MB whereas the pristine HNT only adsorbed 73.1% (Cao et al., 2015).

Besides, HNTs have been used in hydrogels as an adsorbent. It is used as adsorbents for the removal of ionic dyes and hazardous metal ions. These hydrogels have large ionic groups and surprising affinity for pollutants. Recently, chitosan grafted with granular hydrogel composites has been developed and incorporated with HNTs, and used as an adsorbent for the removal of nitrogen (NH_4^+)-based pollutants which are responsible components for causing eutrophication. By introducing HNTs

into the polymeric networks, the resulting composite not only shows heightened adsorption behavior but also enhances the affinity towards the contaminates that is comparable to the pure polymer hydrogel for NH^{+4} removal (Zheng et al., 2007).

2.3.5   Catalysts and Catalysts' Support

Nowadays, metal or metal oxide nanoparticles and enzyme on various supports have attracted interest because they can be used in catalytic applications. Studies reported that catalytic performance are greatly enhanced by nanotube supports (Suib, 2013). HNT offers this characteristic. A thorough search reveals that numerous studies have been devoted to the incorporation of cobalt (Co) ((Zhang and Yang, 2012), palladium (Pd) (Zhang et al., 2013) and gold (Au) (Fu et al., 2014) or metal oxides, such as copper oxides and cobalt oxides (CuO and CoO) (Carrillo and Carriazo, 2015) as well as zinc oxide and titanium dioxides (ZnO and TiO_2) (Zhang et al., 2014) on HNT. Interestingly, these metals or metal oxides can be incorporated within the nanotubes or on its surface. For example, Zhang et al. (2013) studied the deposition of palladium (Pd) nanoparticles on the surface of HNTs after modification with organosilanes and their catalytic property. Modification prevented leaching of the metal nanoparticles during the hydrogenation of styrene. The Pd supported on HNT catalysts exhibits excellent activity for the hydrogenation of styrene because of the strong synergistic interaction between palladium nanoparticles and HNTs (Zhang et al., 2013) .

Besides the surface of HNT, incorporation of metal particles   inside the lumen of HNT has also been conducted. In a recent study, Pd metal was incorporated inside the tubular lumen of HNTs. K. Dedzo et al. (2016) decorated the lumen of

HNT via selective grafting of ionic liquid onto the aluminol surfaces. The reason behind the use of this technique was to preserve the amount and size of the immobilized nanoparticles in the lumen of the HNT support. As a result, the Pd nanoparticles were synthesized uniformly in the HNTs' lumen with average sizes ranging from 3 to 6 nm. In contrast to this grafting technique, the use of unmodified HNTs resulted in the position of Pd nanoparticles both inside and outside the tubes. Both types of Pd-HNT composites were tested for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), in the presence of borohydrate ions. The researchers observed that the modified HNTs showed faster conversion of 4-NP to 4-AP, that is within only 3 min when compared to unmodified HNTs, which took around 8 min for complete degradation of 4-NP. In addition, it was found that the catalysts could be used up to three times (K. Dedzo et al., 2016).

Interestingly, another recent study investigated the deposition of nanoparticles inside the lumen of HNTs and on its surface. The study was related to the fabrication of Ag/HNTs/Fe_3O_4 nanocatalyst and their catalytic performance in the reduction of 4-nitrophenol (4-NP). Here, Fe_3O_4 nanoparticles were loaded into the hollow lumen of HNTs, whereas Ag nanoparticles which was the active phase, was deposited on the surface of HNTs/Fe_3O_4. The incorporation of Fe_3O_4 nanoparticles into the lumen of HNTs prevented their oxidation to air, plus forming magnetic HNT. Upon decorating the magnetic HNT with Ag, the nanocatalysts exhibited excellent conversion of 4-NP to 4-AP in a duration of 38 min. The trend was enhanced by increasing the amount of active phase on the catalyst. Furthermore, the catalysts showed potential towards recoverability as well as reusability. This feature has great potential for efficient water treatment purposes (Gan et al., 2015).

Other metal oxides or semiconductors have also been incorporated on or in HNT. Among these are zinc oxide and titanium dioxide (ZnO and TiO_2) (Zhang et al., 2014), cadmium sulfide (CdS) (Xing et al., 2012) and lanthanum (La) (Meksi et al., 2016). These catalysts were mainly used for photocatalytic purposes. For instance, Li et al. (2015) studied the potential of HNTs as supports for crystalline TiO_2 synthesized at low temperatures. They prepared a series of polyaniline-crystalline TiO_2-HNT nanocomposites with different mass ratio of polyaniline (PANI) to TiO_2. It was observed that upon reaction in acidic environment, the initial anatase TiO_2 in the PANI-crystalline TiO_2–HNT composites changed to mix phases of rutile and anatase and different PANI redox states are obtained. Besides, it is observed that there were no morphological effects on the HNTs and TiO_2, but the e^- excitation range of TiO_2 was shifted towards visible-light regions. Based on the results obtained, the highest photocatalytic activity was obtained at pH 0.5 with 1% volume ratio of aniline (ANI) and titanium isopropoxide (TTIP). Plus, the PANI-crystalline TiO_2-HNTs nanocomposites possessed good stability and can be reused four times (Li et al., 2015).

HNT can also serve as good supports to immobilize enzymes, except that they are limited towards temperature and stability (Rawtani and Agrawal, 2012). Zhai et al. (2010) studied the immobilization of enzyme biocatalyst on HNTs. Using ionic adsorption binding, amylase and urease enzymes with different size were immobilized in the channels of HNTs. According to the zeta potential behavior of HNTs, they are negatively charged at pH 6–7 . Due to the isoelectric point of α-amylase and urease, both enzymes retained negatively charged during the immobilization process. They are immobilized inside the inner lumen of HNTs (at pH 6). Based on the result, it was observed that the immobilized enzymes possessed

good thermal and storage stabilities as well as efficient reusability. It was observed that the two immobilized enzymes obtained great percentage of activities which is more than 80 %. Even after storing for 15 days, they still showed huge percentage of activities, which is 90 %. Besides, after 7 cycles, almost 55% initial activity of the enzyme was retained. Plus, at 353 K, the immobilized α-amylase had a 19% loss in activity compared to the great loss of 87 % of the free α-amylase. Whereas for the immobilized urease, it had an optimum temperature of 343 K, compared to the optimum temperature of the free urease which was 333 K. These results showed that HNTs are good support materials for enzyme mobilization (Zhai et al., 2010).

Although HNTs have been well known mainly as supports in catalysts, Zhao et al. (2016) has reported that HNT itself can be used as a catalyst. Zhao and co-workers employed the HNTs as low cost solid acid catalysts for the alkenylation of diverse aromatics with phenylacetylene to alpha–arylstyrenes (Zhao et al., 2016). Alkenylation of aromatic compounds, which is also called as hydroarylation of alkynes, has attracted researchers' attention due to its potential to synthesize alpha–arylstyrenes, which are important organic intermediates for numerous industrial products (ie. dyes, medicines, natural products and agrochemicals). Based on the structure of HNTs, it is found that the acidic sites come from the internal Al_2O_3, the interface of SiO_2 and Al_2O_3, as well as the removal of Na and K salts from the HNT walls which cause an increase in acidic sites for the HNT structures (Zhao et al., 2016). Furthermore, it was also observed that the mesopores produced on the HNT walls due to dehydration via the calcination process can enhance the mass transfer and improve accessibility to acidic sites. Based on the results obtained, it was found that catalytic activity of alkenylation strongly depends on the appropriate acidic properties as well as textural features. For the alkenylation of p-xylene with

phenylacetylene, 95.6% of phenylacetylene conversion with 95.8% of selectivity toward -(2,5-dimenthylphenyl) styrene was achieved (Zhao et al., 2016).

Besides, HNTs were also applied as catalyst in esterification reactions. Zatta et al. (2011) studied the methylic and ethylic esterifications of lauric acid using HNTs as heterogenous catalysts. Esterification is crucial in industrial sectors due to the demand of ester products. Different molar ratios of alcohol:lauric acid were used with different proportions of catalyst. Based on the results obtained, the use of HNTs as a catalyst produced lauric acid conversion of 95.02% and 87.11% for the methylic and ethylic esterifications, respectively. This was better than the results obtained from thermal conversion (75.61% and 59.86% for methanol and ethanol, respectively). The most interesting part was, HNTs could be reused back after the reactions (Zatta et al., 2011).

2.4   Supported Metal Catalysts

Catalysts are divided into two types, which are heterogeneous and homogeneous catalysts. Catalysts which are in a different phase when compared to its reaction medium are called heterogeneous catalysts, whereas homogeneous catalysts comprise of catalysts in the same phase as its reactants, usually liquid (Cole-Hamilton and Tooze, 2006). Table 2.1 shows the differences in terms of advantages and disadvantages between these two types of catalysts. In general, supported metals are typically heterogeneous catalysts. These materials have received great attention because they can overcome the limitations of the homogeneous catalysts, such as increasing the production yields as well as minimizing side reactions (Ali et al., 2014). Nowadays, inorganic solid supports such

as silica, carbon, clay, zeolite and other mesoporous materials have catched researchers' attention (Corma et al., 2010). They are mostly inert, nontoxic, nonvolatile, and can be recycled (Gupta et al., 2009).

There exists several methods to prepare supported metal catalysts and several techniques to incorporate metals onto the supports. This results in a variety of characteristics such as metal particles with different sizes and morphologies, different interactions between the metal and the support, etc. These factors affect the catalytic process differently.

Table 2.1: Differences between homogeneous and heterogeneous catalysts
(Hartley, 1985)

Characterisation	Homogeneous Catalyst	Heterogeneous Catalyst
Phase(s)	Liquid	Gas/solid or liquid/solid
Temperature	Low (< 523 K)	High (523-773 K)
Thermal stability	Poor	Good
Diffusion	Facile	Can be difficult
Catalyst recycle	Expensive	Simple
Separation of the catalysts	Difficult. A very efficient distillation process is needed.	Easy to separate catalysts from the products at the end of the reaction by using a coarse filtration method
Selectivity	Good-single active site	Poor-multiple active sites
Controllability	Have a definite structure, so they are easier to be modified in order to control the reaction.	Due to the availability of several active sites, modification and further improvement of the structures is difficult.

2.4.1   Preparation of Metal Supported Catalysts

Generally, there are two methods for the preparation of metal supported catalysts which are classical and non-classical methods. There are three steps involved for the preparation of metal supported catalysts via classical methods, which are the incorporation of metal salts onto a support, calcination, and lastly the formation of metal particles via reduction of metal oxides, which is done by using hydrogen gas as reducing agent at elevated temperatures. Calcination helps to eliminate chemical compounds such as sulphur and chlorine available in the metal salts, which can be poisonous in the final catalytic reaction. However, calcination can oxidize metal ions and the temperature at which calcination is conducted can induce changes in the metal particle size as well as the support, depending on the support employed (Gao et al., 2008). Hence activation of the catalysts in pure H_2 is required prior to a catalytic reaction. Figure 2.6 illustrates possible occurrences for the surface compound formation of supported metal catalysts during low and high calcination temperatures (Sinfelt and H.Knozinger, 1997). Generally, metal nanoparticles are well dispersed on the surface of the support. At low-temperature calcination, the metal oxides are well dispersed (Olaf Deutschmann, 2009). When the metal nanoparticles are reduced at a low temperature, they are observed to be well dispersed, however the metal nanoparticles can be reoxidised back to the initial metal oxides. The process between metal nanoparticles and the support during a high-temperature calcination leads to two occurrences. Either agglomerates (cohesive forces) or pillbox (adhesive forces) are formed due to mobile metal particles. In addition, the high-temperature calcinations of metal nanoparticles-support results in sintering of the support (cohesive forces) as well as encapsulation or strong metal-support interaction (adhesive forces) (Olaf Deutschmann, 2009).
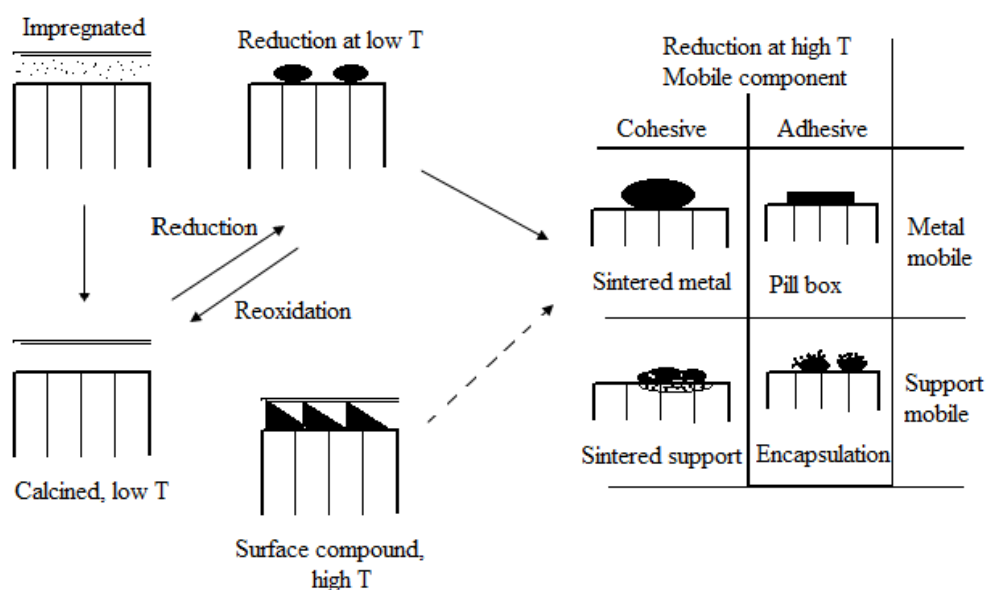
20

Figure 2.6: Schematic representation of metal-support interactions
(Sinfelt and H.Knozinger, 1997)

A recent study that highlights the preparation of HNT supported metal catalysts using the classical method was done by Fu et al. (2014). In their work, they studied gold nanoparticles supported on HNTs via homogeneous-precipitation method. They investigated the specific characteristics of the catalyst as well as its performance for solvent-free oxidation of benzyl alcohol. The results showed a high stable structure that exhibited a high catalytic activity as compared to other supported gold catalysts. This is due to the presence of a higher amount of Au^{1+} which was determined by XPS method (Fu et al., 2014).

Non-classical methods generally do not involve calcinations. This method is used as an alternative to the classical methods to prepare the catalysts in a short period of time. This method uses various reducing agents other than H_2. The reducing agents usually involve chemicals like hydrazine (Wojcieszak et al., 2008a) borohydrate (Abu Bakar et al., 2009a) and alcohol (Nitani et al., 2007). This method

is preferable in industrial sectors due to its faster preparation procedure as well as less aggregation of particles (as it only uses low temperature and shorter times for the pre-treatments) (Tan et al., 2016). Zhang et al. (2013) studied silanized HNTs to support Pd nanoparticles using the non-classical method for the liquid-phase hydrogenation of styrene to ethylbenzene. In this work, they used hydrazine as the reducing agent. It was observed that the deposition of Pd nanoparticles were uniform and the particle sizes were smaller than the Pd nanoparticles prepared using classical method. Plus, there was less aggregation of the particles, so the conversion of styrene was completed in just a short time of 30 minutes (Zhang et al., 2013).

2.4.2 Techniques to Introduce Metal Salts on Supports

2.4.2(a) Impregnation Technique

Impregnation method involves mixing of an excess of metal precursor, usually metal salt onto a support (Schwarz, 1995). This technique aims to adsorb the solution onto the pore surface of the support (C.N.Satterfield, 1991). Depending on the amount of the solution used, there are two types of impregnation method, which are wet impregnation and incipient wetness or also known as dry impregnation. In the wet impregnation method, an excess of solution is used. After a certain period of stirring time, the solid product is then filtered. The product is then dried and calcined (Pinna, 1998). In contrast, the incipient wetness method uses a spraying method, where the metal salt solution is sprayed on the surface of the support in order to decrease the volume of the metal salt as compared to the volume of the support (Schwarz, 1995). This method is considered to be economical especially when using costly metal precursors. There are many factors that should be taken into

consideration when using this technique, such as temperature, concentration and type of the metal salt, as well as mixing time. These factors may affect the final amount of the metal salt incorporated into or onto the support. It is important to consider that different metal salts have different ability and effectiveness to be adsorbed onto a support (Pinna, 1998).

2.4.2(b) Precipitation Technique

Precipitation involves the mixing of a metal salt with another solvent or an acid or base. This technique aims to convert the liquid form into solid precipitate products either as hydroxides or carbonates (Pinna, 1998). Coprecipitation occurs when there is two or more metals involved (Schwarz, 1995). In the coprecipitation method, the composition of the precipitate depends on the differences in solubility between the components. There are many variables that need to be highlighted, which are efficient mixing process, temperature, pH values etc. (Pinna, 1998). A highly dispersed solid metal product will be obtained on the surface of the supports when using this technique. Thus, precipitation is the preferred procedure for preparing supported catalysts in industrial fields (Pinna, 1998).

2.4.2(c) Deposition-Precipitation Technique

This method is similar to the precipitation method, except that it involves nucleation and growth of the metal hydroxide precipitates on the pores of the support (Pinna, 1998). This method has the limitation, where there might be large crystallites and inhomogeneous distribution of the particles during the nucleation and growth processes that will affect the deposition of particles into the pores. Therefore, in order to solve this problem, an alkali solution is added during the

mixing process. A study that investigated the effect of different alkali solutions on the homogeneous distribution of particles have also been reported (Geus, 1993). According to Geus (1993), urea promoted enhanced particle distribution.

2.5   Hydrogenation of Benzene

Benzene is a carcinogenic volatile organic compound which is found in various industries and appliances including tobacco smoke, paint, automobile exhaust emissions and printing industries (Duarte-Davidson et al., 2001). Realizing the poisonous effect of benzene, the release of benzene into the surrounding environment has been restricted. Strict regulations are made by government in order to discipline the factories to release only very low concentrations of this hazard. Hydrogenation of benzene is one of the most applied technology to convert benzene into more safer products such as cyclohexane or cyclohexene. It is important to highlight that the performance of catalytic activities is attributed to the characteristics of the supported metals, type of support and metal particle size. (Gallezot, 1979). There are two types of metallic systems used for the supported metals, which are monometallic and bimetallic. For the purpose of benzene hydrogenation, the monometallic system employs noble metals such as Pt (Bratlie et al., 2007; Sabbe et al., 2015), Pd (Zhang et al., 2004), base metals such as Ni (Chettibi et al., 2011; Mokrane et al., 2016; Savva et al., 2008; Wan et al., 2013; Wojcieszak et al., 2004) and Ru (Miao et al., 2006; Ronchin and Toniolo, 2001). Besides, there are also recent studies that employ multiple metals, which are Ni, Pt, Pd, Ru and Rh (Keypour et al., 2016) in order to compare their performance in the hydrogenation of benzene (Keypour et al., 2016). Whereas bimetallic systems