

SYNTHESIS OF POLYMER-STABILIZED METALLIC NANOPARTICLES AND
THEIR HYDROGENATION ACTIVITY FOR VEGETABLE OILS

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ABSTRACT

Hydrogenation of vegetable oils is an important method to modify oils. However, high content of trans fatty acid (TFA) formed during hydrogenation disqualify the application of these hydrogenated oils in food industries. With the aims of producing hydrogenated oils containing low or zero TFA, polymer-stabilized metallic nanoparticles were designed and used as catalysts in this research. The objectives of this study include the preparations of polymer stabilized metallic nanoparticles, the characterization of the newly prepared nanoparticles and the hydrogenation of vegetable oils with the newly prepared nanoparticles as catalysts. The catalytic activity and selectivity were investigated and the reaction path ways are suggested.

Chitosan (CTS) stabilized metallic nanoparticles were prepared with molar ratio of CTS to metal of 5:1. CTS-stabilized Pd nanoparticles were firstly investigated and the preparation conditions were optimized. Based on the optimum result, CTS-stabilized monometallic nanoparticles (CTS-Pd, CTS-Pt, CTS-Ru, CTS-Rh and CTS-Ir) were prepared at room temperature and atmosphere pressure, formic acid solution was used as both solvent and reducing agent. CTS-stabilized bimetallic nanoparticles were also prepared. CTS-Pd and CTS-Pt were selected as the first metals. The bimetallic nanoparticles were prepared by continual deposition of the second metals on the surface of the first metal. CTS demonstrated to be a good stabilizer for the preparation of nanoparticles in aqueous solution. The newly prepared nanoparticles can be stable in the colloidal solutions for more than half a year. Cyclodextrins (α , β and γ CDs) stabilized metallic nanoparticles were also prepared with molar ratio of CD to metal of 5:1. CD stabilized Pd nanoparticles (CD-Pd) can be prepared at room temperature and atmosphere pressure. 2-propanol was utilized as the optimum reducing agent. The nanoparticles can be stable for more than two weeks. However, CD-Pt cannot be prepared under the optimum condition.

The structures of the newly prepared metallic nanoparticles were characterized. The UV-vis spectra showed that the metallic ions were reduced during the preparation. The newly prepared nanoparticles were mainly in spherical shape as shown from the TEM images. The average diameters of Pd based nanoparticles were larger than that of the relative Pt based nanoparticles. CTS-stabilized Pt based nanoparticles and γ -CD-Pd were obtained with small size (<10 nm) and narrow sizes distribution. Based on the XPS analysis, Pd and Pt in CTS stabilized Pd or Pt based nanoparticles were mainly in zero-valent while most of the secondary metals were in oxidized form. The interaction between CTS and the metals were also observed. Meanwhile, the interaction between CTS or CD and Pd were observed through the FT-IR results.

The metallic nanoparticles were used as the catalysts for the hydrogenation of vegetable oils. The hydrogenation was conducted at room temperature and atmosphere pressure. 1-Propanol was used as a co-solvent to increase the solubility of oils. The results showed that the catalytic activity and selectivity for the hydrogenation was mainly influenced by the nature of the catalysts. Most of the CTS stabilized metallic nanoparticles and CD stabilized Pd show high activity while CD stabilized Pd achieve higher reaction rate. However, hydrogenation with CD-Pd based nanoparticles present higher selectivity for TFA under the same linoleate conversion. Thus, CTS stabilized Pd and Pt nanoparticles demonstrate as the optimum mono metallic nano catalysts. CTS stabilized Pt based nanoparticles produce lower TFA content under the same linoleate conversion. The additions of second metals show different influences to CTS-Pd and

CTS-Pt, CTS-Pd-Ru, CTS-Pd-Zn, CTS-Pt-Fe and CTS-Pt-Ir are four bimetallic catalysts with both higher activity for $C_{18:2}$ and lower selectivity for TFA. CTS-Pt-Fe demonstrates as the best catalyst which produced low TFA content (3.8%) at high conversion of $C_{18:2}$ (92.3 %). Polyvinyl pyrrolidone (PVP) stabilized Pd and Pt monometallic nanoparticles (PVP-Pd, PVP-Pt) were prepared based on literatures and used for comparison study. Comparing with the PVP stabilized metallic nanoparticles, the newly designed nanoparticles in this research presented lower selectivity for TFA under the same conversion of $C_{18:2}$.

Based on this research, the optimum CTS stabilized metallic nanoparticles were obtained. The catalysts which have high activity for $C_{18:2}$ and low isomerization of cis $C_{18:1}$ can be used to produce hydrogenated oils with high conversion of unsaturated double bonds and low content of TFA.

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LIST OF SYMBOLS AND ABBREVIATIONS

d	spacing between the planes in the atomic lattice
λ	Wavelength
σ	Standard deviation
AFM	Atomic force microscopy
AOCS	The american oil chemists' society
BE	Binding Energy
CD	Cyclodextrin
CD-Pd	Cyclodextrin stabilized Pd monometallic nanoparticles
CTS	Chitosan
CTS-Pd	Chitosan stabilized Pd monometallic nanoparticles
CTS-Pt	Chitosan stabilized Pt monometallic nanoparticles
CTS-Pd-M	Chitosan stabilized Pd-M bimetallic nanoparticles M=(Fe, Co, Ni, Cu, Zn, Ru, Rh, Ir)
CTS-Pt-M	Chitosan stabilized Pt-M bimetallic nanoparticles M=(Fe, Co, Ni, Cu, Zn, Ru, Rh, Ir)
DMF	N,N-dimethylformamide
EDX	Energy-dispersive X-ray
EXAFS	Extended X-ray absorption fine structures
EG	Ethylene glycol
E_k	The kinetic energy of the photoelectron
E_p	The energy of the X-ray photon
EtOH	Ethanol
FAME	Fatty acid methyl ester
FFT	First Fourier transformation

FTIR	Fourier Transform infrared spectrum
GC-FID	Gas chromatography equipped with FID detector
GC-MS	Gas chromatography equipped with mass detector
HRTEM	High-resolution transmission electron microscopy
IPA	2-propanol
MeOH	Methanol
rt.	Room temperature, room temperature in open lab Malaysia from 9:30 am to 6:30 pm (31-35 °C, measuring by mercury thermometer without calibration)
SEM	Scanning electron microscopy
STM	Scanning tunneling microscopy
TEM	Transmission electron microscopy
TFA	Trans fatty acid
TPR	Temperature programmed reduction
UV-VIS	Ultraviolet visible spectrophotometer
US	Ultrasonic irradiation
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence spectroscopy
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.0 Introduction

Nanostructures are structures with one of their dimensions about 100 nanometers or less. Materials with nanostructures have different properties and effects compared to that with larger particles. This is due to their high surface to volume ratio. Based on the special properties, nano materials and nanoparticles are widely used in electronic, optical, mechanical devices and chemical processes. The properties of nanoparticles are dependent on their shape, size, surface characteristics and inner structure (<http://ec.europa.eu/health/opinions2/en/nanotechnologies/>, Zeng et al, 2009). These features have been proven to be affected by the preparation conditions. Generally, the synthesis of nanoparticles involves the use of organic solvent and toxic reducing agent, which inevitably lead to serious environmental issues. In order to minimize the pollution to the environment, green methods are required for preparing metallic nanoparticles. During preparation, the utilization of nontoxic chemical, environmentally friendly solvent and renewable materials are considered as the key approach. Based on this approach, chitosan and cyclodextrins are selected as the polymer for the preparation of metallic nanoparticles in this research. Different metallic nanoparticles were prepared with water as solvent while environmentally friendly

reducing agent was utilized to reduce the metallic ions. The homogeneous colloidal solutions were formed with high stability.

After the preparation, it is important to characterize the structures of nanoparticles. In general, the dispersed metallic nanoparticles have no characteristic peak in UV-vis absorption spectra and present only the tailing reflection. However, UV-vis spectra can still provide information about the formation process from metallic ions to metallic nanoparticles (Okitsu, 2013). With the help of UV-vis spectra, the presence of precursors can be monitored by their ligand to metal charge transfer transition. Meanwhile, the formation of nanoparticles can be detected by their plasmon band or broad tailing absorption in the range from UV to visible (Corain et al, 2008). The most important information about nanoparticles is size and their size distribution. This can be obtained by calculation from enlarged TEM micrographs of the nanoparticles. Moreover, the crystal structure with lattices spacing values can be obtain with the assistance of HRTEM (Browning et al, 2000), which enable the structural identification of single particles. The particle size of a metallic catalyst can influence both the catalytic activity and selectivity. Beside the size effects, the catalytic activity and selectivity of metallic catalysts also depends on the individual metal and other additives. In the case of metallic nanoparticles, the information on valences of metals and the ratios of metals presence are important especially for bimetallic nanoparticles. The information can be provided by XPS analysis (Corain et al, 2008). FTIR can be used to monitor the formation of the nano structures. It can be used to indentify different materials and the formation of nanocomposites especially the interaction between the polymer and metals (Grundmeier and Stratmann, 2005). In this research, UV-vis, TEM including HRTEM, XPS and FTIR were used as the main techniques to characterize the newly prepared polymer stabilized metallic nanoparticles.

The unique properties of nano materials increase the application in both science and engineering. Nano materials have been widely applied in various fields, such as computer, electronics, communication, energy products, medicine, catalysis, food industries and the environment. As one of the most important fields, the application of

nano material in catalysis is attractive. In general, the catalytic activity of nanoparticles depends on their size, shape, composition and the surface atomic arrangement (Cuenya, 2010). During the catalysis, nano clusters and nanoparticles are key component of heterogeneous catalysts, which provide various specific sites that can bind with reactant molecules. It has been proven that nanotechnology improve the performance of catalysts because nano catalyst have much more surface area per unit mass to interact with the reactant and make the catalysts more effective. In this research, the newly prepared nanoparticles in aqueous solution were used for the hydrogenation of vegetable oils with the goal of producing hydrogenated vegetable oils with high conversion of $C_{18:2}$ and low TFA content under ambient conditions in aqueous solution.

1.1 Preparation of polymer-stabilized metallic nanoparticles

The properties of nanoparticles are size and shape dependent, which is in turn determined by the conditions of preparation. However, the high surface energy makes inorganic nanoparticles unstable. This increases the difficulties in their preparation and application. Many researchers have investigated different ways to overcome these problems and the most efficient way is to use polymer to fabricate metallic nanoparticles. Polymer inorganic nano composite materials have attracted particular attention because of their unique electronic, optical and mechanical properties. When the size is beyond the “nano” range, many atoms become part of the surface rather than fully bonded as “bulk” atoms. Surface atoms are distinguished by their reduced coordination to the crystal backbone. Thus, they are much easier to react with their neighbors and exhibits unusual physical and chemical phenomena (Corain et al, 2008).

Many methods were used for the production of nanoparticles. Particles coated by a polymer shell were found to be more stable against aggregation (Rozenberg and Tenne, 2008). Such a polymer shell can be obtained by synthesizing the nanoparticles first and dispersing the nanoparticles in a polymer solution which is known as the ex situ method. Alternatively, the formation of protective polymer coating and the

formation of nanoparticles can be combined in one step. During the preparation of nanoparticles, nano composites are formed inside a polymer matrix by the precursors. Then the precursors are transformed into the desired particles by reduction reaction. Comparing with the ex situ method, the second method attracted much more attention.

1.1.1 Synthesis and application of nanoparticles as catalysts

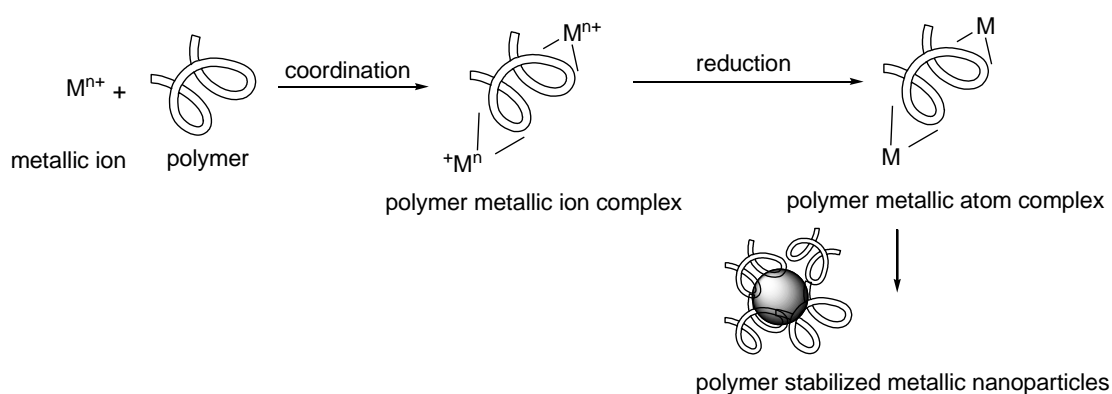
A catalyst can be defined as a reaction component that is essential to the pathway or mechanism of a reaction and often appear in the rate law, but not in the overall stoichiometric equation (Toshima et al, 2011). The materials used as a catalyst can be classified into five categories which are metals, metal oxides, metal complexes, special chemicals and biocatalysts. Since the catalysis by solid metallic catalysts occurs only on the surface of metal, the particles size is one of the major factors influencing the catalytic properties. The catalytic activity and selectivity of catalysts depend on their compositions and structures. Small metallic particles are favored for using as catalysts because of the existence of both large percentage of surface atoms and active atoms.

Metallic nano catalysts can be divided into homogenous and heterogeneous depended on the phases involved in the reactions. In the case of metallic nanoparticles, they can be used as both homogenous and heterogeneous catalysts. The homogeneous nano catalyst exists as colloidal dispersion in solution while the heterogeneous catalyst involves supported nanoparticles on inorganic supports. When metallic nanoparticles are used in a colloidal form, the stability of the colloid is the most important factor to ensure catalytic activity. The stabilization by polymer stabilizer is required to ensure the stable dispersion of metallic nanoparticles.

1.1.2 Preparation of polymer- stabilized metallic nanoparticles

The formation of metallic nanoparticles can be obtained through both physical and chemical methods. In general, chemical method has a significant advantage for the

preparation of structure controlled nanoparticles. In order to control the particle sizes and structure, it is very important to select the effective stabilizing polymers. During the preparation, the polymers coordinate with the metallic ions before reduction. The coordination to metal atoms and the metal nanoparticles continues after the reduction reaction as shown in scheme 1.1 (Toshima et al, 2011). This approach can be used to prepare nanoparticles with high stability. Different reducing agents and reaction conditions can be used during the reduction reaction.



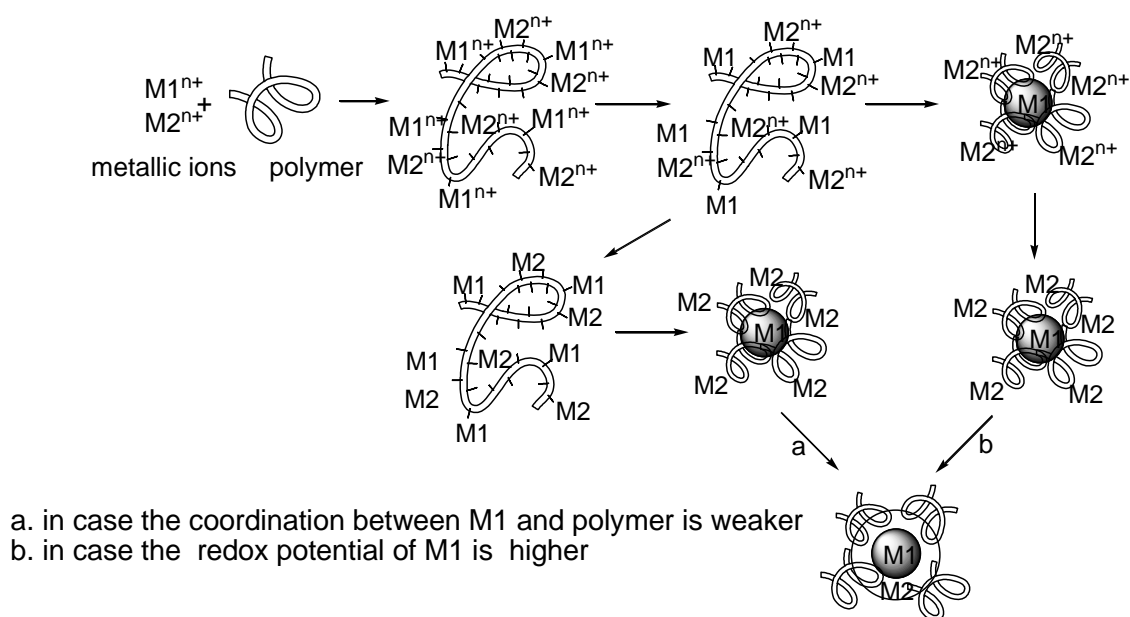
Scheme 1.1: Preparation of polymer stabilized metallic nanoparticles

(Toshima et al, 2011)

The catalytic activity and selectivity of nanoparticles depends on the nature of individual metals (Toshima et al, 2011) and novel catalytic properties were obtained from bimetallic nanoparticles. In the preparation of bimetallic nanoparticles, bimetallic nanoparticles with core-shell structures are attractive. The different methods for the preparation of bimetallic nanoparticles by chemical methods are described below:

1. Simultaneous or co-reduction.

The simultaneous reduction of two metallic ions can result in the mixture of two different monometallic nanoparticles or one bimetallic nanoparticles. The core-shell structures can also be obtained by simultaneous reduction in proper conditions whereby the metals of the core have lower redox potential or the presence of different coordination bond between the two metals. The mechanism for the formation of core-shell noble bimetallic nanoparticles is illustrated as in scheme 1.2 (Toshima et al, 2011). As shown in scheme 1.2, the polymer metallic ion complex forms before the reduction. Polymer stabilized bimetallic nanoparticles with core-shell structures can be obtained either when the coordination between M1 and polymer is weaker or the redox potential of M1 is higher.



Scheme 1.2: Formation of polymer stabilized core-shell bimetallic nanoparticles with simultaneous reduction
(Toshima et al, 2011)

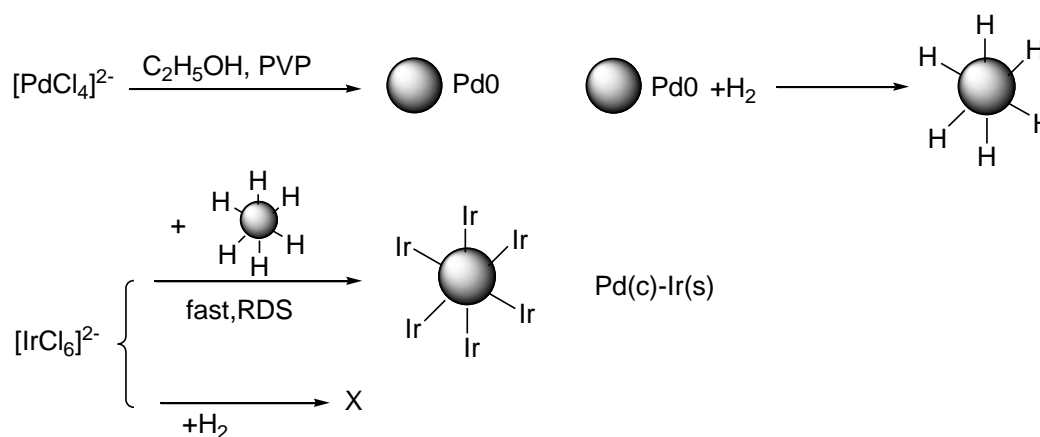
2. Successive or two-step reduction.

Successive reduction involves the reduction of first metal ions, following by the reduction of second metal ions. During this process, the second metals can deposit on the surface of the first metal and form bimetallic nanoparticles with core-shell structures.

However this method is not always successful. As in Harada's report for the preparation of Au-Pd bimetallic nanoparticles (Harada et al, 1993), the nanoparticles did not form bimetallic nanoparticles but the mixture of monometallic Au and Pd nanoparticles when the Pd ions were reduced in the present of Au nanoparticles. Bimetallic nanoparticles with cluster in cluster structure can be obtained by the reduction of Au ions in the presence of Pd nanoparticles. The presence of cluster in cluster structure is due to the reaction between Pd atoms and Au ions. On the other hand, Au nanoparticles surrounded with Pt or Pd shells were successfully prepared when the core size was 18nm (Schmid et al, 1996; Lee et al, 1995). Thus, it is not so easy to obtained core-shell structure with small particle sizes. The major problems are:

1. The oxidization of core metal by the second metal ions with high redox potentials.
2. The formation of large island of the shell on the core metal.

It has been found that a so called "hydrogen-sacrificial protective" method can be used to control the preparation with core-shell structures (Wang and Toshima, 1997). During the preparation, the colloidal dispersions of the core metals were treated with hydrogen first. Then the ions solutions of the second element were added to the dispersion slowly. Thus, the successive reduction method can be demonstrated as the easy way to prepare bimetallic nanoparticles with core-shell structures. Bimetallic nanoparticles with core (Pd)-shell (Ir) structure have been synthesized using hydrogen-sacrificial reduction method (Hessa et al, 2013). The result confirms that Ir was deposited on Pd nanoparticles following the hydrogen-sacrificial technique illustrated as in scheme 1.3.



Scheme 1.3: Formation of core (Pd)-shell (Ir) nanoparticles by hydrogen-sacrificial reduction method

(Hessa et al, 2013)

The 3d-transition metals are important for catalysis. However, the reduction of 3d-transition metallic ions is quite difficult due to their low redox potentials (Corain et al, 2008). The reductions of noble metal ions are not so difficult. Thus, bimetallic nanoparticles involving 3d-transition metals can be prepared by two-step reduction. During the preparation, noble metallic nanoparticles are produced first, which would catalyze the reduction of 3d-transition metal ions to produce the bimetallic nanoparticles in the second step.

1.2 The characterization of polymer-stabilized metallic nanoparticles

The current revolution in nanoscience has been driven by the development of technology. Along with the synthesis and fabrication process, the nano materials need to be characterized to identify their morphology, size, and defects. Typical characterization methods for nanoparticles include spectroscopy and microscopy.