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A Review on Chemical Synthesis Process of Platinum Nanoparticles

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ABSTRACT

Nanoparticles are key components in the advancement of future energy technologies; thus, strategies for preparing nanoparticles in large volume by techniques that are cost-effective are required. In the substitution of fossil-fuels by renewable energy resources, nanometersized particles play a key role for synthesizing energy vectors from varying and heterogeneous biomass feedstocks. They are extensively used in reformers for the production of hydrogen from solid, liquid, or gaseous energy carriers. Catalyst activities depend critically on their size-dependent properties. Nanoparticles are further indispensable as electrocatalysts in fuel cells and other electrochemical converters. The desire to increase the activity per unit area, and decrease the necessary amount of the expensive catalytic standard, It is clear that performance and commercialization of fuel cells depend on electrode materials performance. The application of pt nanomaterials as an electrode in the field of fuel cell has become a new, growing area of interest in recent years. We review chemical process for synthesis of pt nanoparticles. Recent developments in syntheses process of pure & mixed platinum nanoparticles has briefly reviewed specifically for applications in fuel cells. As the physicochemical properties of noble-metal nanostructures are strongly dependent upon shape and size, the development of reliable synthesis methods for the production of nanocrystals with well-defined size and morphology have been discussed briefly. The role of nanostructured supports for the nanoparticles, such as ordered mesoporous carbon, dendrimer have also discussed. And size of the nanoparticles obtained in deferent process and their temperature dependence has also discussed briefly.

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INTRODUCTION

The chemical method is relatively easy and inexpensive, with some difficulties to place and align the resulting nanostructures in desired configurations or patterns. Pt metal nanoparticles have been usually prepared by impregnation and reduction of Pt metal precursors in a micro porous support. In this paper, we will discuss recent advances made in the synthesis of platinum nanoparticles using chemical synthetic procedures on supporting materials.

General rout of chemical synthesis of Pt. nanoparticles is as:

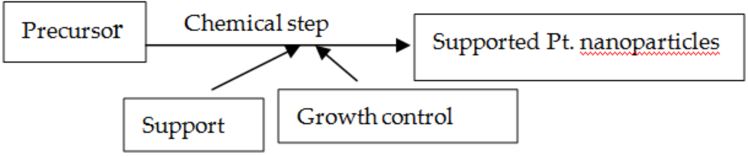

Fig. 1 Chemical synthesis process of supported metal nanoparticles.

In the synthesis process, the pt metal precursor, either in an ionic or a molecular state is taken. Chemical changes are initiated to convert the precursor to pt metal atoms by the reducing agent, these metal atoms then merge into suitable supported materials/or stabilizer to form nanoparticles. For example in chemical reduction, H_2PtCl_6 is reduced by $NaBH_4$ (Park and *et.al.* 2002) or Zn (Jiang and *et.al.*2003) to give rise to platinum nanoparticles;

$$H_2PtCl_6 + NaBH_4 \longrightarrow Pt + \text{Other reaction product.}$$

Particle growth is usually confined by the presence of a confining support or a protection agent/stabilizer,. Supported and size-controlled nanoparticles are then formed. For example in surfactant-stabilized colloidal method, in which H_2PtCl_6 was employed as the precursors of Pt nanoparticles, and zwitterionic surfactant 3-(N, N-dimethyldodecylammonio) propanesulfonate (SB 12) as the stabilizer and methanol as the reductant (Li and Hsing 2006).

PRECURSOR

The common precursor used in platinum nanoparticles synthesis is H_2PtCl_6.The precursor is usually dissolved in an aqueous or organic liquid phase. The chemical step to change the dissolved metal precursor to the solid metal is usually effected by the introduction of a reducing agent. Other chemical steps such as decomposition, displacement, or electrochemical reactions are also possible. In addition to initiation by physical mixing, the chemical step can be activated by radiolytic (Belapurkar and *et. al.*2001) sono-chemical (Chen and *et. al.* 2003) or electrochemical means (Zoval and *et. al.* 1998). In addition to the chemical steps, many additional physical steps are required between the initial precursor state to the final supported state in a working electrode (Chan and *et. al.* 2004).

In situations of mixed metal nanoparticles the different reactivities of two types of precursors, e.g. $RuCl_3$ and H_2PtCl_6 (Maiyalagan 2009, Yang and *et. al.* 2003, William and *et. al.* 2002) are usually used. Sometimes {$Pt(NH_3)_2(NO_2)_2$, $Ru_3(CO)_{12}$, $RuNO(NO_3)$}(Takasu and *et. al.* 2000), {$Na_6Pt(SO_3)_4$, $Na_6Ru(SO_3)_4$}(Friedrich and *et. al.* 2002), { $PtCl_2$ and $RuCl_3$}(Choi and *et. al.* 2003) etc. various complex precursors have been also used. Now we will discuss about supporting materials usually used in synthesis process of platinum nanoparticles.

SUPPORTING MATERIALS

The support for the metal nanoparticles turns out to be as important as the nanoparticles for providing their dispersion and stability. It also provides electrical conductivity when used as electrode for catalyst. The need for electrical conductivity has ruled out conventional catalyst supports such as molecular sieves and alumina (Rajesh and *et. al.* 2002).

In addition to electrical conductivity, supporting materials must have some important properties such as high surface area, hydrophobicity, morphology, porosity, corrosion resistance etc. for the choice as a good catalyst support. So that low surface area single crystal metals and graphite are undesirable as support materials. Based on these considerations, carbon is the best catalyst support material for low temperature fuel cells. Carbon black (Takasu and *et. al*. 2000), and activated carbons have been extensively used as catalyst supports, with Vulcan 72 being the most representative.(Yang and *et. al.* 2003, William and *et. al.* 2002, Dubau *et. al.* 2003). In the last decade, a number of new synthetic carbons with various mesostructures and nanostructures have been reported. These include carbon nanotubes, aerogel carbon and mesocarbon with or without a high degree of order(Yu and *et. al*. 2002). Our focus is on several new types of synthetic carbon materials as mixed metal nanoparticle catalysts in fuel cell electrodes. The family of carbon nanotubes is the most well known synthetic porous carbon. These carbon nanotubes may be semiconducting or metallic in behavior. In the synthesizing of carbon nanotubes, these require purification from amorphous carbon. In addition, uniform loading of metal into sub nanometer scale nanotubes is not a simple task. Metal nanoparticles are often adhered to the outside of nanotubes or in the inter-tubular space.

Aligned and monodispersed carbon nanotubes loaded with Pt, Pt–Ru abd Pt-WO3 nanoparticles showed good electrochemical activity for oxygen reduction and methanol oxidation which is evaluated through cyclic voltammetry (Rajesh and et al. 2002). At the same time the performance of multi wall carbon nanotube loade with Pt also was investigated and Pt loaded multi wall carbon nanotubes at 900 C shows a better Oxidation for methanol (Li and et al. 2003). Some researchers have walked around the loading method of noble metals (Ye and et al. 2003, Yu and et al. 1998). But we will lock up our discuss in a brief about mesocarbon and dendrimer which are hugely used as a supporting materials.

MESOCARBON

A recent important development is the synthesis of ordered carbon structures with tunable pore sizes on the order of 2 to 50 nm (mesopores). The mesopores are expected to offer better mass-transfer properties compared to carbon nanotubes (Warren and et al. 2008). The ordered mesoporous carbon is synthesized by a templating procedure starting with highly ordered mesoporous silica as shown schematically in Fig.2

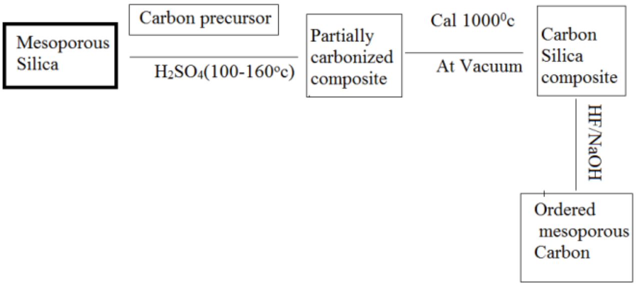

Fig. 2 Show the mesoporous silica preparation process

A variety of ordered but amorphous silica porous structures can be synthesized. Carbon replicas are made by filling up the porous silica with a carbon source such as sucrose and allowing carbonization to take place at an elevated temperature about 1000^0C. The silica template can be removed by dissolution in HF or NaOH. By using different silica templates corresponding different carbon structures can be made.

DENDRIMER

Dendrimers are good candidates for preparing metal nanoparticles because they can act as structurally and well-defined templates and robust stabilizers. Dendrimers are highly branched macromolecules and generally described to have a structure of spherical shape with a high degree of symmetry. In the field of catalysis, the hope is that dendrimer catalysts will retain the benefits of homogeneous catalysts (high activity, high selectivity, good reproducibility, accessibility of the metal site and so on) and, unlike most other polymeric species, they will be readily recoverable after reaction. In principle, dendrimer is one of the most promising candidates that can meet the needs for an ideal catalyst: persistent and controllable nanoscale dimensions, chemically reactive surface, favorable configuration in which all the active sites would always be exposed towards the reaction mixture so that they are easily accessible to migrating reactants, and soluble but can be easily recovered by filtration. These properties, or some combination of them, are what makes dendrimers so useful for application in catalysis. Dendrimers have also been considered as new types of host for accommodation of guest molecules by virtue of their three-dimensional structure having interior void space, and hence various metal nanoparticles have been successfully prepared using dendrimer as a template (Kim and *et al.* 2004). The driving force for guest encapsulation within dendrimers can be based on electrostatic interactions, complexation reactions, steric confinement, various types of weaker forces (van der Waals, hydrogen bonding, hydrophobic force, etc.), and their combinations. For example: Polyamidoamine (PAMAM) dendrimers, in particular, have been used as nano reactors with effective nanoparticle stabilization. In addition, encapsulated nanoparticles surfaces are accessible to substrates so that catalytic reactions can be carried out (Knecht and et al. 2004). The electrocatalytically activity for oxygen reduction of PAMAM dendrimer encapsulated Pt nanoparticles and Pt-Pd bimetallic nanoaparticles are studied (Ye and Crooks 2007). The dendrimer-encapsulation process of platinum nanoparticles also examined through the supported on carbon fiber (Ledesma and et et al. 2008) and nitrogendoped CNT as electrodes for oxygen reduction (Vijayaraghavan and Stevenson 2007). (Maiyalagan 2009) makes use of the fourth generation amine-terminated PAMAM dendrimers (G_4-NH_2) to anchor on the functionalized carbon nanofiber (CNF) as a substrate and then encapsulate Pt–Ru nanoparticles on dendrimers for the better dispersion of the electrode, which exhibited very good catalytic activity. Now we will focus our discussion on the growth process of platinum nanoparticles.

GROWTH CONTROL

It is the most important step for nano particles synthesis. During the chemical step, metal atoms formed will aggregate to form a nucleus. Nuclei that grow beyond a critical size will be stable, but a mechanism is needed to curb the growth of particles and to achieve a narrow size distribution. Different growth control mechanisms and strategies are used in the different types of nanoparticle synthesis. On base of growth control mechanism chemical process can be classified as (A) Colloidal method, (B)Microemulsion methods, (C) Impregnation method.

In the colloidal method, aggregation of nanoparticles is prevented either by electrostatic hindrance or the addition of a protecting agent, which will adhere onto the surface of the nanoparticles. In the microemulsion methods, surfactants are added and chemical reaction and mass-transfer processes are confined within the microdroplets engulfed by the surfactant molecules. A simpler strategy in the impregnation method is the early addition of the microporous support before the start of the chemical step. The support then acts as the confining medium to restrict reaction, diffusion, and aggregation processes.

Table 1 Reports of chemical methods for synthesis of supported pure pt. metal nanoparticles with their characterizations.

Nano particles	Size	Support/Loading	Preparation Method	Precursor	Characterization	Reference
Pt	2–3 nm	Vulcan XC-72R 20–60%	Radiolytic synthesis	H2PtCl6	TEM	Gratiet and et al. 1998
Pt	2.9 nm	Vulcan XC-72R 40%	Reduction by ethylene glycol at 1300 c	H2PtCl6	TEMTEM, CO-Chemisorption	Zhou and et al. 2003
Pt	9 nm		Reduction by sodium borohydride	H2PtCl6	XRD, XPS, SEM	Chen and and et al. 2001
Pt	3.5–13 nm	Vulcan XC-72R 10–50%	Reduction by formaldehyde	H2PtCl6	TEM	Umeda and et al. 2003
Pt	2.5 nm	Carbonised SBA15 20–50%	Impregnation H2 reduction at 300 uC	H2PtCl6	TEM, BET	Joo and et al. 2001
Pt	3-5nm	Mesoporous carbon microbeads	Liquid-phase reduction	H2PtCl6	SEM, XRD	Liu and et al. 2002
Pt	7.1 nm	Carbon nanotubes by CVD with alumina membrane as the template	Impregnation H2 reduction at 580 uC	H2PtCl6	TEM, SEM	Che and et al. 1998
Pt	1.2 nm	Template carbonisation of polypyrrole on a alumina membrane	Impregnation H2 reduction at 550 uC	H2PtCl6	SEM, XPS, HRTEM	Rajesh and et al. 2002
Pt	2-5nm	Multiwalled carbon nanotube	Liquid-phase reduction	H2PtCl6	HRTEM, XRD	Li and et al. 2003
Pt	2.6 - 3.7nm		Reduction by aqueous alcohol in the presence of polymeric stabilizer protector),	(H2PtCl6.nH2O)	TEM,XRD	Wang and et al. 2009
Pt	3· 6 ± 0· 6 nm		Thermolysis in hexadecylamine (HDA) at 210°C under argon atmosphere	[Pt2(μ-OR)2(C8H12OMe)2] (R = Me or Ac)	XRD, EDAX and TEM	Ghavale and et al. 2009
Pt	2–5 nm		ethanolic reduction stabilized by poly(N-vinyl-2-pyrrolidone) (PVP) in ionic liquids	H2PtCl6 .6H2O	(HRTEM)	Mu and et al. 2004
Pt	10nm	Vulcan XC-72 modified by hydrogen molybdenum bronze (HxMoO3, 0 ≤ x ≤ 2)	Reduction by formaldehyde	Solution of H2PtCl6,	SEM, XRD	Xiang and et al. 2010
Pt	2–4 nm	Multi-walled carbon nanotubes (MWNTs	Reduction by ethylene glycol & sodium citrate as the coordination reagent and stabilizer,	H2PtCl6	TEM, XRD	Li and Zhang 2008
Pt	~9 nm		Modified polyol process with the addition of silver ions	H2PtCl6 .6H2O,	TEM, HRTEM	Rioux and et al. 2006

Table 2 Reports of chemical methods for synthesis of supported mixed Pt. metal nanoparticles with their characterizations.

Nano particles	Size	Support/Loading	Preparation Method	Precursor	Characterization	References
Pt-Ru	2.6 nm	Functionalized carbon nanofibers (CNF)	Reduction by NaBH4	H_2PtCl_6 & $RuCl_3$	SEM, XRD, TEM	Maiyalagan 2009
Pt_3Ru	1.5 ± 0.5 nm	Vulcan XC-72,40% Pt	Impregnation H2 reduction at 120 0C	H_2PtCl_6, $RuCl_3$	HRTEM, XRD, EDAX, TGA/DTA	Yang and et al. 2003
Pt_xRu_y	2.7–3.9 nm	Carbon black	Thermal decomposition under H_2–N_2	$Pt(NH_3)_2(NO_2)_2$, $Ru_3(CO)_{12}$, $RuNO(NO_3)_x$	HRSEM, BET, HRTEM	Takasu and et al. 2000
PtRu	3–15 nm	Vulcan XC-72 10–90%	H2 reduction	$Na_6Pt(SO_3)_4$, $Na_6Ru(SO_3)_4$	HRTEM, XRD,TEM	Friedrich and et al. 2002
$Pt_{52}Ru_{48}$	1.7 ± 0.5 nm	HOPG, Vulcan XC-72 , 20%	Colloid		HRTEM, XPS, AFM, XRD	Schmidt and et al. 1998
Pt_xRu_y	2 nm	Vulcan XC-72 30%	Colloid	$PtCl_2$, $RuCl_3$	TEM, XRD, EDX	Dubau and et al. 2003
PtRu	2.5–5 nm	Carbon cloth electrode	Microemulsion	H_2PtCl_6, $RuCl_3$	XRD, XPS, TEM, PCS, EDX	Zhang and et al. 2003
Pt2Ru	4–20 nm	Vulcan XC-72 40%	Microemulsion	H_2PtCl_6, $RuCl_3$	TEM, XRD, XPS	Liu and et al. 2002
PtRu	2-6 nm	Vulcan XC-72	Thermal decomposition on Carbon	K_2PtCl_4,$RuCl_2$(2,2′-bipyridine), $Pt_2Cl_4(C_2H_4)_2$, $RuCl_3$	TEM, XRD, EDS	William and et al. 2003

Pt_2Ru	2.5 ± 0.5 nm	Vulcan XC-72	Decomposition on carbon	$Pt(CO)x$, $Ru_3(CO)_{12}$	TEM, EDX	Dickson and et al. 2002
$Pt_{1.06}Ru$	7 nm	Graphitic carbon nanofiber 42%	Thermal decomposition of bimetal complex	(η-C2H4)(Cl)Pt(μ-Cl)2Ru(Cl)-(η 3: η 3-2,7-dimethyloctadienediyl	TEM, XRD, EDS	Steigerwalt and et al. 2001
PtxRuy	2–5 nm	Vulcan XC-72 20%	Reduction by formic acid	H_2PtCl_6, $RuCl_3$	XRD, EDX	William and et al. 2002
PtRu	2–3 nm	Conducting polymer or Vulcan XC-72 60%	Reduction with LiBH4 in THF	$PtCl_2$ and $RuCl_3$	XRD, TEM, SEM	Choi and et al. 2003
PtRu	2–3 nm	Carbonised colloidal silica 20%	Borohydride reduction		TEM	Yu and et al. 2002
Pt3Ru	13.1 nm	Mesoporous carbon micro beads	Liquid-phase reduction	H_2PtCl_6 and $RuCl_3$	SEM, XRD	Liu and et al. 2002
PtRu	1.59 ±0.03 nm	Carbon nanotubes	H_2 reduction at 580^{0}C	H_2PtCl_6 and $RuCl_3$	SEM, TEM	Che and et al. 1998
PtRu	2 nm	Template carbonization of poly pyrrole	H2 reduction at 550o C	H_2PtCl_6	SEM, XPS, HRTEM	(Rajesh and et. al 2002).

IMPREGNATION METHOD

The impregnation method is characterized by a deposition step of Pt or other metal precursors followed by a reduction step. Deposition means soaking up of a dissolved metal precursor, e.g. $PtCl_6^{2-}$ into the pores of a support, e.g. Vulcan 72 carbon, before reduction of the metal precursor to metal nanoparticles.

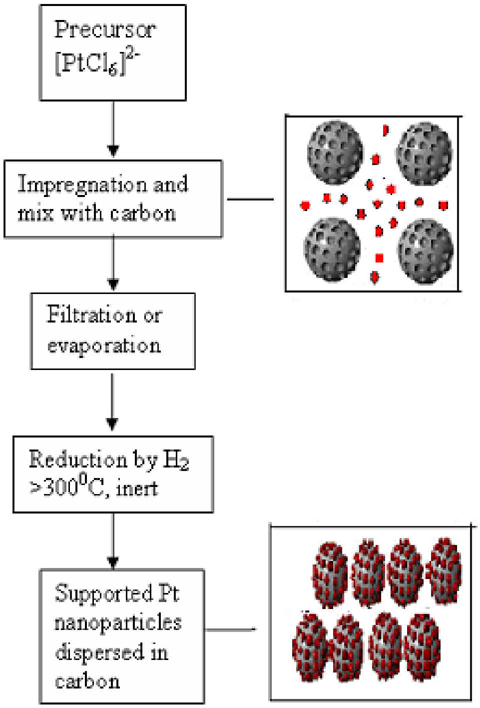

Fig. 3The impregnation procedure is shown schematically in the flow line

This method is simple and has been the most common method used for electrocatalyst preparation over the years. The reduction step can be chemical or electrochemical. The chemical reduction may be (liquid-phase reduction) (Park and et al. 2003) of the metallic catalysts slurry in solution by using reducing agents or gas-phase reduction of the metallic particles impregnated carbon using a flowing H_2 gas stream at a rather high temperature of about 250–600^{0}C (Arico and et al. 2004). The common reducing chemicals are hydrazine, borohydride, formic acid, and hydrogen. Borohydrides are mostly used for the reduction. In the case of hydrogen, temperature elevation to above 300^{0}C under an inert atmosphere is required. Control of the size and size distribution of particles depends on many factors. The morphology of the porous substrate and the pore size distribution will play a major role in terms of penetration and wetting of the precursor and also providing the confinement for nanoparticle growth.

Reaction time and kinetics and mass-transfer of reducing agent will also affect the nucleation and growth of the nanoparticles.

DRAWBACK OF IMPREGNATION METHOD

The major drawback of the impregnation method is the lack of size control of metal particles except when the porous substrate has a narrow pore size distribution, e.g. in highly ordered mesoporous carbon. A distribution of particle sizes from nanometer to micron scale is commonly observed. Hydrogen can penetrate better into the micropores of the porous matrix. By the modification of surface of the support materials e.g. Vulcan 72 carbon, the activity of platinum toward methanol oxidation can be improved, In literature reports (Li and et al. 2005), it has been found that the composite of platinum with hydrogen molybdenum bronze (HxMoO3, $0 \leq x \leq 2$) can improve significantly the activity of platinum toward methanol oxidation, and several Pt- H_xMoO_3 composite electrocatalysts have been prepared for methanol oxidation with the aim at the improvement of electrocatalytic activity of platinum and the reduction of platinum amount. Xingde Xiang and co workers (Xiang and et al. 2010) have developed a new composite of platinum with H_xMoO_3 by dispersing platinum nano-particles on the carbon modified with H_xMoO_3 and obtained a new electrocatalyst, dispersed platinum supported by hydrogen molybdenum bronze-modified carbon (Pt/H_xMoO_3-C), for methanol oxidation. The platinum supported with hydrogen molybdenum bronze-modified carbon exhibits better electrocatalytic activity toward methanol oxidation than the platinum supported with carbon without modification. The improved electrocatalytic activity is ascribed not only to the smaller particle size but also to the proton spillover effect between platinum and hydrogen molybdenum bronze. In addition to size, the shape of a nanocrystal may also provide another useful parameter to control when one needs to tailor the electronic, optical, magnetic, or chemical properties of a solid material.

COLLOIDAL METHOD

It is the most common and powerful method to synthesize metal nanopartcles In this method metal colloids are taken in organic media then reduction of transition metal salt carried in the presence of stabilizing agent. The pt nanoparticles are synthesized using colloid techniques by the reduction of a platinum precursor (H_2PtCl_6) in alcohol in the presence of a polymer capping agent to prevent aggregation (Humphrey and et al. 2007, Zhang and et al. 2007). As the particles nucleate and grow they are kept with a polymer that is porous enough to allow growth to various sizes from 1 to 8 nm. The particle size can be controlled by the monomer concentration and with suitable changes of the growth parameters, it can be changed the shape of these particles from hexagonal to cubic, as well as to an intermediate shape called cuboctahedra, which is a cube with truncated vertices (Bratlie and et al. 2007) because catalytic reactivity depends on the size and the shape of the nanoparticles. For this reason the colloidal method is widely used for synthesizing metal nanoparticles with various size control. In the presence of a protective agent, such as surfactant molecules, the metal precursor is chemically reduced or reacted to form metal nanoparticles. A narrow size distribution is achieved as the colloidal metal nanoparticles are stabilized either by steric hindrance or by electrostatic charges. Colloidal metals can form in the organic medium (organosols) or aqueous medium (hydrosols).

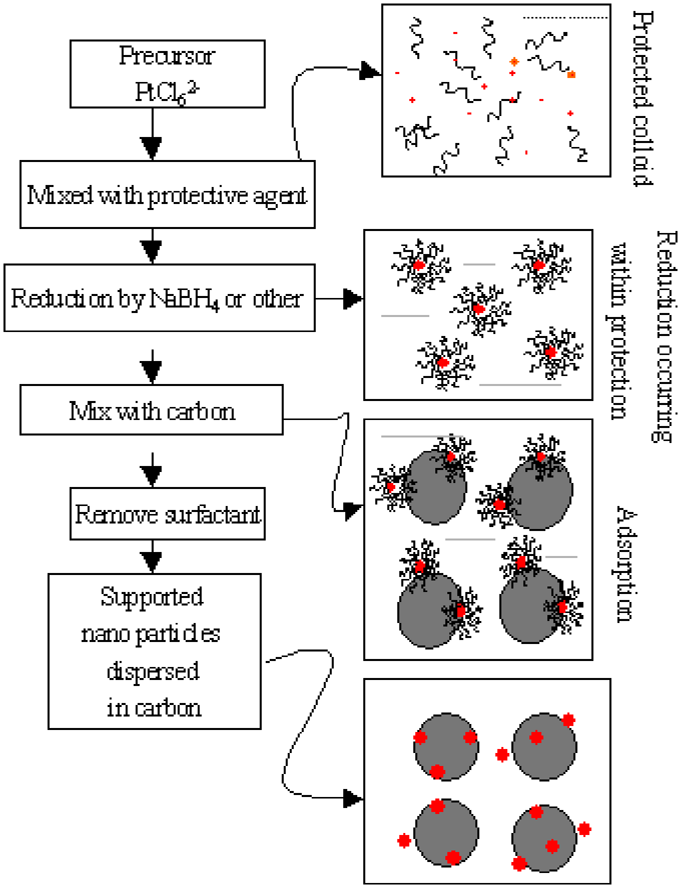

Fig .4 Colloidal method shown schematically the procedure in flow line

In the case of adsorbed ions or charged colloids, protection from merging into larger particles is provided by the electrostatic repulsion of like charges. On the other hand, coating the metal core with organic chain molecules can provide steric stabilization. Examples of common protecting ligands include NR_4^+, PPh_3, PVP, and PVA. Recently, this popular method has been widely used and PVP was introduced to stabilize the Pt nanoparticles in solution by preventing the particles from aggregating. In the presence of PVP, the reaction between alcohol and the metal precursor occurs. By FTIR spectroscopy, Bock and MacDougall (Bock and MacDougall 2003) suggested that the colloidal metal nanoparticles may be protected by glycol, which serves as both a solvent and the protecting agent. The glycol can be removed by electro-oxidation during usage as an anode.

The glycol colloidal process is very attractive for large-scale synthesis of metal nanoparticles and this type of solution syntheses of Pt particles yield monodisperse samples with tunable size and shape. Catalyst materials that are prepared by the combination of the proper support and monodisperse particles have unprecedented uniformity, which is difficult to achieve with conventional catalyst synthetic methods. The effect of metal nanoparticle size on catalytic activity is better understood than the influence of nanoparticle shape on catalytic activity, since size control of crystallites has generally been easier to achieve than shape control.

Many studies on colloidal particles have focused on the control of particle sizes and their growth kinetics and have related particle size and catalytic activity. Moreover, research has shown that the degree of polymerization and the concentration of the stabilizing polymer influence the size distribution, stability, and catalytic activity of colloidal particles. For example, a recent study has shown that a higher ratio of capping material to metal produces smaller metal particles. Recently, the morphologies of Pt colloidal particles were studied by means of ultraviolet-visible spectrophotometry and transmission electron microscopy (TEM) (Duff and et al. 1998).

Introduction of foreign ions during solution phase synthesis of metal nanoparticles is a major parameter for controlling particle shape. A study on morphology changes of noble metal nanoparticles (Ag, Pd, and Pt) by adding various foreign ions (Long and et al. 2010). It was observed that chloride ions and oxygen in the reaction mixture preferentially dissolved twinned particles initially formed during reduction and led to selective formation of single crystalline products such as truncated tetrahedra and cuboctahedra. In another study by Chen et al. (Chen and et al. 2004), trace amounts of iron chloride slowed the reduction of Pt(II) species, inducing optimal anisotropic growth condition during a polyol process to form agglomerates of single-crystalline Pt nanowires rather than small (<5 nm) Pt crystallites which formed without iron chloride. The addition of large amounts of $NaNO_3$ to a Pt salt solution led to the formation of branched nanostructures due to platinum nitrate formation, which alters the reduction kinetics of Pt. Addition of silver ions in a polyol synthesis of Pt nanoparticles results in lower nucleation temperatures, which favor anisotropic growth to form Pt multipods. Although several foreign ions have been reported to substantially affect particle morphologies, the exact mechanism has not been determined.

It is thought that selective adsorption of the additive ion on one or more crystal surfaces changes the selective growth rate of crystal faces leading to the change of shape. It was demonstrated the synthesis of Pt nanocrystals of well-defined shape (cubes, octahedra, and cuboctahedra) using the silver ions and poly (vinylpyrrolidone) (PVP) in solution (Song and et al. 2005).

However Pt nanoparticles of various sizes and shapes having the face-centered cubic structure are also synthesized by the alcohol reduction method. Alcohol also serves as both a solvent for dissolving metal precursors and surfactants and a reducing agent to produce Pt colloids.The synthesis of particulate pt metals by aqueous alcohol reduction of metal salts in the presence of polymeric stabilizer (or protector), in particular, has been reported to be an enabling technique toward a better control of the synthesized particle morphology and the aggregated structure. Hirai and co-workers (**Hirai and et al. 1979)** were the first to examine the catalytic activity and the formation mechanism of metal particles protected by polyvinyl alcohol or polyvinyl pyrrolidone (PVP) in methanol. Duff et al. (**Duff** et al. 1995) further confirmed that the aggregation of platinum particles was suppressed by a high [PVP]/[Pt] ratio which in turn facilitated the dispersion of platinum sols so that the particles with a more uniform morphology become attainable. Chen and Akashi (Chen and Akashi 1997) synthesized colloidal platinum nanoparticles that were protected by poly (N-isopropylacrylamide) in ethanol/water mixtures by the reduction of $[PtCl_6]^{2-}$. They reported that the protective polymer serves not only as a stabilizer, but also as a functional component conferring catalytic activity and selectivity. (Teranishi and et al. 1999) further revealed that the mean diameter of monodispersed Pt nanoparticles can be controlled from 1.9 to 3.3 nm by adjusting the kind of alcohol and the PVP concentration used in the sol process. The size of Pt particles with an ascending order, i.e., 1-propanol\ethanol\methanol, was found when various alcohols were used. This suggests that the reduction rate of $[PtCl_6]^{2-}$ ions in solution is critically important to the synthesized Pt particles. In addition, the synthesized particle size was found to decrease linearly with the alcohol concentration over the [PVP]/[Pt] ratio range from 10 to 40.

Though the colloidal method can provide a narrow size distribution of metal nanoparticles, the major drawback is the presence of the protecting agent, which may also hinder the catalytic function of the nanoparticles. The organic protecting shell can be removed by washing in an appropriate solvent or by decomposition at elevated temperature in an inert atmosphere. Before the removal of the protecting agent, adsorption into a protecting microporous catalyst support is necessary to prevent agglomeration into larger metal particles.

MICROEMULSION METHOD

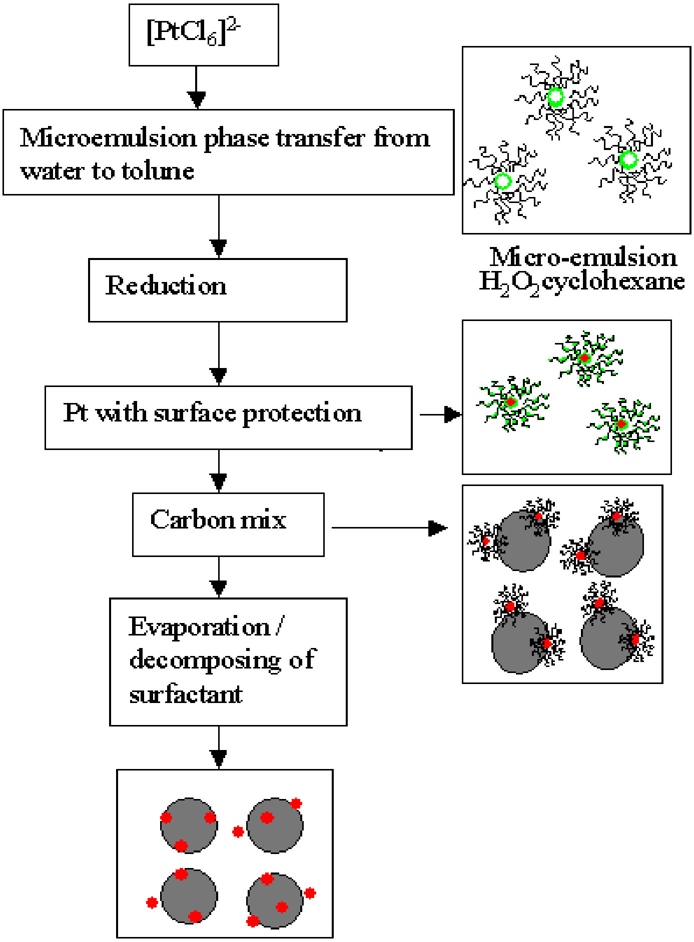

Fig.5 The microemulsion method shown schematically the procedure in flow line

By this method a better control of particle size, shape, size distribution, and chemical composition are possible, Although a number of techniques have been used for producing nanoparticles which include gas evaporation sol–gel methods sputtering and co-precipitation. It is well documented in the scientific and patent literature that combining a transition metal element with platinum gives enhanced catalytic activities for reactions such as oxygen reduction in fuel cells and direct oxidation of methanol. It is, however, difficult to control the size and size distribution, and gain a consistent nanoscopic chemical composition with these preparation techniques.

Microemulsion is a tiny drop of precursor containing liquid engulfed by surfactant molecules. This microemulsion is uniformly dispersed in a continuous liquid phase, which is immiscible to the precursor containing liquid phase. The chemical reaction is confined within a microemulsion. The size of the microemulsion is of the order of a few nanometers to hundreds of nanometers and is determined by the balance of surface free energy mediated by the surfactant molecules and the free energy difference arising from the immiscibility of the two liquid phases. Normally, the dispersed liquid phase is oil and water forms the continuous medium. The reverse microemulsion is the water-in-oil microemulsion can be possible. A co-surfactant is sometimes added to modify the size of the microemulsion. Supercritical carbon dioxide has also been used as the continuous medium for the microemulsion method and gives additional ease in separation of the nanoparticle from the medium. So the preparation of nanoparticles with water-in-oil (w/o) microemulsion has attracted increasing attention but systematic investigation is warranted (Ohde and et al. 2001). It has reported an alternative route to synthesize dodecanethiol-stabilized Pt NPs, with narrow and controllable size distribution, by a two-phase route by (Castro and et al. 2009). The synthesis was based on a phase-transfer (water to toluene) of $[PtCl_6]^{2-}$ followed by reduction and surface protection with dodecanethiol (DT). Since chemical steps are conducted within the microemulsion, which serves as a micro- or nano-scale reactor, a narrow particle size distribution can be obtained accordingly. The introduction of a reducing agent, e.g. hydrazine, into the miroemulsion is achieved by stirring and the reaction time is in the order of minutes. The size and distribution of the nanoparticle can be further controlled and improved by a two-microemulsion method with the reducing agent also confined in a separate emulsion. The two microemulsion technique has been applied to synthesize mixed metal nanoparticles of Pt–Co and Pt–Ru (Zhang and Chan 2002). The final composition of the mixed metal nanoparticles has been easily controlled by the ratio of the metal precursors solutions. Various parameters that control the size of particles in the microemulsion method such as water to surfactant ratio, the amount of surfactants, the concentration of precursor solution and temperature etc. After the reduction step, nanoparticles are protected from agglomeration by the surfactant molecules. Similarly to the colloidal method where protecting agents are used, they should be adsorbed onto a porous support before the surfactant molecules are removed. Nevertheless, the microemulsion method requires the use of costly surfactant molecules with extra washing steps and may not be economical for a large-scale synthesis.

EFFECT OF TEMPERATURE ON NANOPARTICLE'S SIZE

The nanoparticle size is one of the important factors to control the unique properties of nanomaterials. Usually, the smaller the nanoparticle size is, the more prominent the unique properties are. Therefore, people attempt to control the size of nanoparticles as small as possible in sample preparation. However, the nanoparticle size depends not only on the sample preparation, but also on the applied environment of nanomaterials including temperature and even radiation (Kluth and et al. 2006). It is well known that the nanoparticle size will become larger with temperature increasing for most free nanomaterials.

CONCLUSION AND OUTLOOK

Platinum stands as one of the most important metals for several industrial applications. We have reviewed the chemical synthesis process of platinum nanoparticles from the last decade. In the past few years, considerable progress has been made in the synthesis of monodisperse and well-defined structured pt nanoparticles with sizes ranging from 1.2 to several nm. From the work detailed in this review, it is clear that the chemical method is relatively easy and inexpensive, by microemulsion process pt nanoparticles with better control of particle size, shape, size distribution, and chemical composition can be produce. The outlook of such platinum nanoparticles is very promising because these materials will find many important applications including as a catalyst in Fuel cell, Bio sensor,etc.In fuel cell platinum nanoparticles are used in reformers for the production of hydrogen from solid, liquid, or gaseous energy carriers.

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