Pt–Cu BIMETALLIC NANOPARTICLES SYNTHESIZED BY POLYOL METHOD UNDER DIFFERENT REDUCTION CONDITIONS

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ABSTRACT

Platinum–copper (molar ratio 1:1) bimetallic nanoparticles were synthesized by polyol method using ethylene glycol (EG) as the solvent and PVP as the stabilisation agent under microwave conditions compare with reduction by using NaBH₄ at room temperature and combination both technique of reduction. The samples were characterised by UV-vis, transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron (XPS). UV-vis results show that formation of particles from colloid Pt-Cu bimetallic samples. TEM analyses confirm that the very fine and monodisperse with narrow size distribution particle with average particle size were 3.1 ± 1.0 nm for combination reduction technique, 3.3 ± 0.8 nm for microwave reduction and 4.1 ± 1.1 nm for NaBH₄ reduction. XRD results show that there is no peak in the pattern of bimetallic nanoparticles observed unless peak of carbon refer to PVP carbon content. However XPS illustrates resulted that both elements in the nanoparticles are obtain based on characteristic metallic binding energy. Moreover, besides the influencing of sizes Pt-Cu bimetallic nanoparticles due to technique of reduction, it is also influence the Pt to Cu atomic ratio whereas 1:2, 1:1.3 and 1:1.7 respective to Pt-Cu (1:1)-mw; Pt-Cu (1:1)-NaBH₄ and Pt-Cu (1:1)-comb.

KEYWORDS: Pt-Cu bimetallic nanoparticles; polyol method; microwave reduction; NaBH₄ reduction

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1.0 INTRODUCTION

Nanoparticles have received significant attention in the last several decades due to potential applications in photonics, electronics and catalysis. The nanoparticles are often defined as a material that having dimensions less than 100 nanometers in size or diameter and have the properties fundamentally different from their bulk counterparts. Application of nanoparticles material has attracted a lot of attention due to nanoparticles have the potential to be more active and selective than the current technology especially in catalysis.

Recently, lot of researches considerable efforts have been committed to bimetallic nanoparticles since they are of great interest from both scientific and technological perspective for the modification of physical and chemical properties of metallic nanoparticles according to Major et al. (2009). Mainly, Pt and Pt-containing bimetallic are important catalysts and have many interesting properties and practical applications especially in enhanced catalytic activity and selectivity, particularly as nanoparticles. For example, Pt nanoparticles are efficient catalysts for NOx reduction (Burch & Ramli, 1998; Balint et al., 2002) or in hydrogenation (Choo et al., 2003). Meanwhile, Pt-M (M= Cu, Fe, or Ni, etc.) bimetallic nanoparticles have also been studies for various purpose of catalytic activity such as electrocatalysis (Hsieh & Lin, 2009), CO oxidation (Liu et al 2009) hydrogenation (Gupta et al., 2008) and also for NOx reduction (Dimick et al., 2009).

Many methods for the preparation of bimetallic nanoparticles have been reported, such as chemical reduction (Liu et al., 2004), hydrothermal (Ueji et al., 2008), and reverse micelles (Hwang et al., 2004). The polyol method was used for the preparation of nanoparticles (Viau et al., 2001) in the past decade. In this technique, a polyol (for example, ethylene glycol (EG)) was used as both a reducing reagent and a solvent. Meanwhile, the presence of some protective compound (such as poly (Nvinyl-2-pyrrolidone), PVP) and the utilization of extra reducing agent likes NaBH₄, hydrazine and other, possibly will be influences of characteristics on nanoparticles obtained by the polyol technique.

The polyol method using conventional heating requires a relatively long preparation time (usually several hours or longer). Compared with the conventional heating, microwave heating is promising due to its unique effects, such as rapid volumetric heating, higher reaction rates and shorter reaction time, higher reaction selectivity and energy saving and leads to the formation of uniform nanoparticles with small particle size, narrow size distribution, and high purity.
The purpose of the present work is to report the synthesis of the Pt-Cu bimetallic nanoparticles using ethylene glycol (EG) and PVP as the stabilisation agent under microwave conditions compare with reduction by using NaBH₄ at room temperature. Subsequently, the morphology, size, structure and composition of the resultant bimetallic nanoparticles were characterized by UV-vis, transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectrum (XPS).

2.0 EXPERIMENT

2.1 Materials

Hydrogen hexachloroplatinate (IV) hexahydrate (Aldrich), Cooper (II) nitrate trihydrate and NaBH₄ (Merck) were used as received. Poly (N-vinyl-2-pyrrolidone) (PVP), whose average molecular weight was about 40,000, was purchased from Aldrich and used as received. Ethylene glycol (EG) (Aldrich, 99.5%) and distilled water was used.

2.2 Preparation of Pt-Cu nanoparticles

The Pt–Cu nanoparticles stabilised by poly-N-vinyl-2-pyrrolidone and ethylene glycol 50% v/v in water as solvent were prepared. In brief, certain amount of aqueous H₂PtCl₆, Cu(NO₃)₂ and PVP mixed together. Then, appropriate amount of ethylene glycol was added in to the solution prepared and also distilled water added to adjust the volume of solution containing EG to H₂O volume ratio of 1:1 for certain total volume solution. The final concentration of Pt ion in mixture solution was 2 mM. In the meantime, the molar ratio of Pt ions to Cu ions was 1:1, and molar ratio of PVP to Pt ions was 10:1 was stirred for 15 min at the room temperature. The mixture solution prepared used for differences technique of reduction. The samples were noted as Pt-Cu (1:1)-mw for microwave reduction, Pt-Cu (1:1)-NaBH₄ for sodium borohydride reduction and Pt-Cu (1:1)-comb for NaBH₄ and microwave reduction, based on samples reduction techniques used.

2.2.1 Microwave reduction

The microwave reduction apparatus used in this study was similar to that reported previously (Tsuji et al 2007). A commercial microwave oven (Samsung model MW71E, 2450 MHz, maximum 800 W) was modified by installing a condenser through holes of the ceiling. A volumetric flask (500 mL) was placed in the microwave oven and connected to the condenser. The Pt-Cu (molar ratio 1:1) solution
sample was irradiated by microwave in a continuous wave mode at 300 W for 2 min. The solution was rapidly heated after about 1 min and immediately the colour turned from yellow to dark without any precipitate after microwave irradiation.

2.2.2 Sodium borohydride reduction

Metal reduction using sodium borohydride was conducted according to a reported method (Chen et al., 2009). Typically, for Pt-Cu (molar ratio 1:1) solution prepared was added with amount of NaBH₄ (molar ratio NaBH₄ to Pt ions of 5:1) at room temperature under stirring for 15 min and immediately the colour turned from yellow to dark without any precipitate.

2.2.3 NaBH₄ and Microwave reduction

This technique due to the combination reduction method above, the Pt-Cu (molar ratio 1:1) solution was reduced by NaBH₄ same as sodium borohydride reduction technique, then sample was threatned with hydrothermal treatment by microwave irradiation for 2 min at 300 W.

2.3. Characterization

The disappearance of metal ions and the formation of metal particles were studied using a U-1800 UV–vis spectrophotometer. The size and morphology of Pt-Cu (molar ratio 1:1) nanoparticles were determined using a FEI Tecnai G20 transmission electron microscope (TEM) operated at 200 kV. The colloid samples were dropped onto a carbon-coated copper grid, and then excess solution was removed by adsorbent paper. The average particle size of the Pt-Cu particles was determined from more than 250 particles in randomly chosen areas in the enlarged micrographs using Digital Micrograph Demo software. X-ray diffraction measurements were carried out on a Bruker Advance D8 powder diffractometer using Cu Kα. Continuous X-ray scans were carried out from 10° to 80° of 2θ. The crystallite phase was estimated with the data of Joint Committee on Powder Diffraction Standard (JCPDS). The X-ray photoelectron spectrum measurements were performed on a Thermo VG scientific ESCA MultiLab-2000 spectrometer equipped with monochromatic Al Kα X-ray source. Samples for XRD and XPS measurements were prepared by precipitating the colloid Pt-Cu bimetallic nanoparticles, which were washed with ethanol, followed by drying at 50°C, and then crushing in a mortar.
3.0 RESULTS AND DISCUSSION

3.1. Spectrophotometry studies

The UV–VIS spectra of Pt-Cu (1:1)-mw, Pt-Cu (1:1)-NaBH₄ and Pt-Cu (1:1)-comb show monotony without a peak as shown in Figure 1, but for monometallic Pt ions and Cu ions in water as a comparison, obviously shows the peaks at 260 nm for Pt ion and 300 nm for Cu ions. From UV-vis spectra for all type of reduction technique, indicate that all Pt and Cu ions are completely reduced, the colour turned yellow to dark during reduction process, suggesting the formation of particles.

![Figure 1. UV-vis absorption spectra of (a) Pt ion, (b) Cu ion, (c) Pt-Cu (1:1)-mw, (d) Pt-Cu (1:1)-NaBH₄ and (e) Pt-Cu (1:1)-comb](image)

3.2. Particle size (TEM)

The size and morphology of the bimetallic nanoparticles were characterized by TEM. As displayed in Figure 2, the Pt-Cu (1:1)-mw, Pt-Cu (1:1)-NaBH₄ and Pt-Cu (1:1)-comb nanoparticles were very fine and monodisperse with narrow size distribution among reduction techniques used. But size particles are slightly different, the average particle size for Pt-Cu (1:1)-mw, Pt-Cu (1:1)-NaBH₄ and Pt-Cu (1:1)-comb were 3.3 ± 0.8 nm, 4.1 ± 1.1 nm, and 3.1 ± 1.0 nm respectively. From the TEM image result also might be suggesting that microwave treatment after reduction with NaBH₄ would be influencing metal particles formation process. Which is the nucleation and growth stage were influenced by assisted microwave irradiation, same as the other
influence experimental parameter such as reducing reagent, metal ion concentration, and reaction temperature (Chen et al., 2009).

3.2 Particle size (TEM)

The size and morphology of the bimetallic nanoparticles were characterized by TEM. As displayed in Figure 2, the Pt-Cu (1:1)-mw, Pt-Cu (1:1)-NaBH4 and Pt-Cu (1:1)-comb nanoparticles were very fine and monodisperse with narrow size distribution among reduction techniques used. But size particles are slightly different, the average particle size for Pt-Cu (1:1)-mw, Pt-Cu (1:1)-NaBH4 and Pt-Cu (1:1)-comb were 3.3 ± 0.8 nm, 4.1 ± 1.1 nm, and 3.1 ± 1.0 nm respectively. From the TEM image result might be suggesting that microwave treatment after reduction with NaBH4 would be influencing metal particles formation process. Which is the nucleation and growth stage were influenced by assisted microwave irradiation, same as the other influence experimental parameter such as reducing reagent, metal ion concentration, and reaction temperature (Chen et al., 2009).

Figure 2. The TEM image and particle size distribution of (a) Pt-Cu (1:1)-mw, (b) Pt-Cu (1:1)-NaBH4 and (c) Pt-Cu (1:1)-comb

3.3 XRD analyses

It is known that pure Pt has a face-centered cubic (FCC) structure, the peaks at 2θ ≈ 40° and 47° can be characterised with the (111) and (200) plane respectively of the fcc structure platinum. Figure 3 illustrates the XRD patterns of Pt–Cu bimetallic nanoparticles, there are no obviously peak detected to show that Pt or Cu particles, only broadly peak in region of 2θ ≈ 40°. It is because of nanoparticles formed are very fine particles, and it could be indicated of Pt (2θ ≈ 40°) or PtCu alloy (2θ ≈41.1°). Meanwhile, more apparent peak for all samples at 2θ ≈ 31.7° and 45.6°, indicate the carbon (2θ ≈ 31.6° and 45.5°) that may be formed from the PVP carbon contain, due to difficulty of removing the PVP as a protective agent, unless heating up sample until 350°C (Du et al., 2009).
Pt–Cu Bimetallic Nanoparticles Synthesized by Polyol Method Under Different Reduction Conditions

It is known that pure Pt has a face-centered cubic (FCC) structure, the peaks at $2\theta \approx 40^\circ$ and $47^\circ$ can be characterized with the (111) and (200) plane respectively of the fcc structure platinum. Figure 3 illustrates the XRD patterns of Pt–Cu bimetallic nanoparticles, there are no obviously peaks detected to show that Pt or Cu particles, only broadly peak in region of $2\theta \approx 40^\circ$. It is because of nanoparticles formed are very fine particles, and it could be indicated of Pt ($2\theta \approx 40^\circ$) or PtCu alloy ($2\theta \approx 41.1^\circ$). Meanwhile, more apparent peak for all samples at $2\theta \approx 31.7^\circ$ and $45.6^\circ$, indicate the carbon ($2\theta \approx 31.6^\circ$ and $45.5^\circ$) that may be formed from the PVP carbon contain, due to difficulty of removing the PVP as a protective agent, unless heating up sample until 350°C (Du et al., 2009).

3.4 Composition analyses (XPS)

The surface atomic ratio of the bimetallic nanoparticles was measured by XPS. XPS spectra of the Pt 4f and Cu 2p regions in the sample of Pt-Cu (molar ratio 1:1) are displayed in Figure 4. Corresponding binding energies (BE) have been presented in Table 1. The characteristic peak of Pt 4f7/2 BE for the metallic Pt appears at 71.05, 70.71 and 70.81 eV for the sample of Pt-Cu (1:1)-mw; Pt-Cu (1:1)-NaBH$_4$ and Pt-Cu (1:1)-comb respectively. Meanwhile, the Cu 2p3/2 peak in the Pt-Cu bimetallic nanoparticles can be observed at the BE of 932.25, 932.05 and 932.2 eV. This proved that Pt-Cu bimetallic sample existent already a platinum and copper metallic compared with XRD result that show no directly observation of Pt and Cu peaks. Additionally, the surface atomic ratios of elements in the sample could be obtained from the intensity of XPS peaks. The results show that the ratio of Pt to Cu is about 1:2, 1:1.3 and 1:1.7 are respective to Pt-Cu (1:1)-mw; Pt-Cu (1:1)-NaBH$_4$ and Pt-Cu (1:1)-comb which is difference to the feed ratio of Pt to Cu.

Figure 3. The XRD pattern of (a) Pt-Cu (1:1)-mw, (b) Pt-Cu (1:1)-NaBH$_4$ and (c) Pt-Cu (1:1)-comb
are respective to Pt -Cu (1:1) -mw; Pt-Cu (1:1)-NaBH₄ and Pt -Cu (1:1) -comb which is difference to the feed ratio of Pt to Cu.

Figure 4. XPS peaks of Pt 4f (A) and Cu 2p (B) for (a) Pt-Cu (1:1)-mw, (b) Pt-Cu (1:1)-NaBH₄ and (c) Pt-Cu (1:1)-comb

Table 1. XPS binding energy data of Pt, Cu and Pt:Cu atom ratio

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
<th>Sample</th>
<th>Pt-Cu (1:1)-mw</th>
<th>Pt-Cu (1:1)-NaBH₄</th>
<th>Pt-Cu (1:1)-comb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt4f</td>
<td>71.05</td>
<td>70.71</td>
<td>70.81</td>
<td></td>
</tr>
<tr>
<td>Cu2p</td>
<td>932.25</td>
<td>932.05</td>
<td>932.20</td>
<td></td>
</tr>
</tbody>
</table>

Atomic ratio

Pt:Cu ratio

|   | 1:2   | 1:1.3  | 1:1.7  |

4.0 CONCLUSION

The feasibility of different types reduction of Pt-Cu bimetallic nanoparticle has been synthesis using polyol method resulted nanoparticles size. Which the combination reduction by NaBH₄ with microwave assists, show the superior nanoparticles size compares with other. Although we don’t know about structure system whether core-shell or alloy it might be meaningful if resulting good performance in catalytic activity especially in NOx reduction by CH₄ when there are supported on mesoporous molecular sieves of the SBA type.

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Pt–Cu Bimetallic Nanoparticles Synthesized by Polyol Method Under Different Reduction Conditions

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