EFFECTS OF ETHYLENE GLYCOL, TEMPERATURE AND pH ON THE SIZE AND THE DISPERSION OF THE PLATINUM NANOPARTICLE CATALYST ON CARBON SUPPORT

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Abstract - Controlling the size and the dispersion of Pt nanoparticle structures seems to be one of the most important goals in improving the electrochemical activity and the durability of an electrocatalyst as a Platinum nanoparticle catalyst for fuel cells. In this paper, we introduce a simple method to address the effects of temperature, pH and ethylene glycol enhancers (EG) on the morphology, the size and the distribution of the Pt nanoparticle catalyst in the process of fabricating Pt nanoparticles on carbon support (Pt NPs/C). By means of a facile method, the Pt NPs/C catalyst was synthesized with and without the use of EG at room temperature and 60ºC in pH = 6.5 and 11 solutions. The morphology, the size and the dispersion of the platinum nanoparticle catalyst on carbon support were characterized via X-ray diffraction (XRD) and transmissionelectron microscopy (TEM). We have found out that the size, the morphology and the dispersion of Pt nanoparticles on carbon were strongly affected by adjusting the temperature, pH and that the presence of ethylene glycol could enhance the properties of the Pt/C catalyst for fuel cells application.

Key words - Pt/C; Platinum catalyst; Pt nanoparticles; Pt catalyst; PtNPs/C.

1. Introduction

Pt is catalytically active at room temperature under electro-oxidation reactions of interest to fuel cell applications. It is well known that the metal catalytic activity is strongly dependent on the particle shape, size and the particle size distribution. The conventional preparation techniques based on wet impregnation and the chemical reduction of metal precursors do not provide satisfactory control of the particles' shape and size as well as the distribution of Pt particles on carbon support [1]. The synthesis of highly dispersed supporting platinum with a uniform nanoparticle size still remains a challenge, especially for high metal loading. The conventional methods for the synthesis of Pt electrocatalyst are mainly impregnation and colloid methods such as the sulfite complex route and the colloidal route, the impregnation method usually produces NPs with large average particle sizes and broad size distribution while the colloidal route produces well-homogenized ultrafine Pt electrocatalysts, however, the complexity of the latter hinders its utilization [2]. Many investigators have contributed many efforts to search for alternative routes.

Recently, there has been an attempt to develop alternative synthesis methods based on microemulsions [3], sonochemistry [4a] and microwave irradiation [4b,c], all of which are in principle more conducive to the production of colloids and clusters on the nanoscale, resulting in greater uniformity.

In this paper, a simple procedure for preparing Pt metal nanoparticles supported on carbon is reported. The uniform platinum nanoparticles are supported on carbon with Pt loading up to 40 wt%, which is a standard amount in order to obtain higher dispersion and smaller crystallites [5]. This study lays the foundation for further inspections with a desire to create the best possible Pt/C catalyst. Through this work, we have found that the optimal preparation is simple and fast but it is capable of controlling the particle size and the distribution of Pt particles on the carbon support and could be predicted to enhance the activity of the catalyst for fuel cell applications.

2. Experimental section

2.1. Preparation of Pt/C catalysts

Vulcan XC-72R carbon with the particle size of ~ 60 nm using as a support was purchased from Fuel Cell Store (USA). All the chemicals were of analytical grade; Hydrogen hexachloroplatinate(IV) hexahydrate, 99.9%, (trace metal basis), 38 to 40% Pt ($H_2PtCl_6.6H_2O$), ethylene glycol (EG), acetone branded Acros (Belgium), sodium borohydride ($NaBH_4$), nitric acid (HNO_3) (65%-68%) (China) were used.

Pt/C catalysts particles were synthesized by means of the following route: first, Vulcan XC-72R carbon powder was treated to clean the contaminant in the commercial carbon. (Figure 1) For example, 0.5 g carbon was dispersed in a round bottom flask with 500 mL of the 5% HNO_3 solution, the mixture was refluxed for 16 hours at 105 ºC [6]. The treated carbons were centrifuged with 4500 rpm for several times with 5 minutes each for washing with the de-ionized (DI) water and acetone (15mL H_2O or Acetone for each centrifuge tubes), then were dried at 105 ºC in an oven for 10 hours. Second, the Pt particles were synthesized and dispersed on the carbon supports via the following process: 50 mg of the treated carbon was dispersed into the solvent (DI water with and without using EG), 3.39 mL $H_2PtCl_6.6H_2O$ with concentration 0.05M into the mixed precursor. The pH of this mixture was adjusted to 6.5 and 11 by dropping a wise addition of NaOH 0.1N solution. The mixture was stirred for 5 minutes and ultrasonicated for 15 minutes at room temperature. Then an excess amount of reduction agent 6.84 mL $NaBH_4$ 0.05M was added and the mixture was stirred by using a magnetic bar under atmospheric pressure at room temperature or 60 ºC for 2 hours (Figure 2).

Finally, the synthesized catalyst particles Pt/C were washed by DI water, centrifuged and dried for 12 hours at 100 ºC [7]. All samples were shown in Table 1.

The samples were characterized by using X-ray diffraction, transmissionelectron microscopy (TEM) in order to assess the effects of ethylene glycol and the temperature on

the morphology, the size and dispersion of platinum nanoparticles catalyst on carbon support for fuel cells.

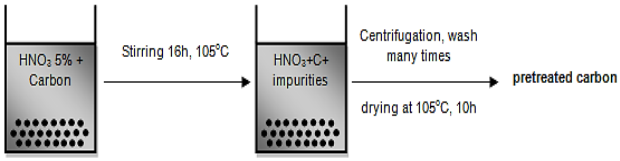

Figure 1. *Preparation procedure of pre-treated Vulcan XC-72R.*

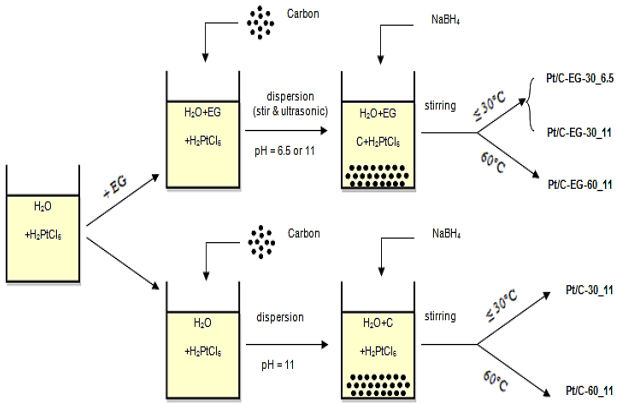

Figure 2. *The preparation of 40 wt% Pt/C with different conditions (pH, temperature, with and without EG).*

2.2. XRD and TEM Analysis

X-ray powder diffraction (XRD) patterns were recorded by using a Cu Kα radiation source on a D8 Advance Bruker powder diffractometer (University of Technology - VNU HCM City). The transmission electron microscope (TEM) were taken by JEM-1400 (*JEOL*, Japan), (University of Technology - VNU HCM City).

3. Results and discussion

Table 1 shows the samples of 40 wt% Pt/C catalysts prepared with various conditions. The effect of such parameters as EG, temperature as well as pH on the size and distribution of Pt NPs on carbon were examined. The samples were synthesized with and without using EG, carried out at room temperature (30℃) and 60℃. The influence of pH value was also examined at 6.5 and 11.

Table 1. *The samples of 40 wt% Pt/C catalysts were prepared with various conditions.*

Ethylene glycol (EG)	Temperature (°C)	pH	Catalysts
-	30	11	Pt/C-30_11
EG	30	11	Pt/C-EG-30_11
EG	30	6.5	Pt/C-EG-30_6.5
EG	60	11	Pt/C-EG-60_11
-	60	11	Pt/C-60_11

3.1. Effect of the presence Ethylene Glycol as a stabilizer for Pt/C preparation

Scherrer equation:

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

where L = average crystal size (angstrom or nm)

- B = the full width half maximum of the peak
- K = the Scherrer constant; depends on how the width is determined, the shape of the crystal, and the size distribution.
- λ = the wavelength of the radiation used to collect the data.

We used the Pt (111) plane to determine the average crystallite size. The FWHM are calculated from the (111) peak by means of Originlab software. The value of K is 0.9 due to the structure's Pt is face-centered cubic and the wavelength used to be λ_{Cu} = 1.54 Å.

Table 2. *Average crystallite size calculated from the Pt (111) using the Scherrer equation*

Sample	Average crystallite size (nm)
Pt/C-30_11	7.14
Pt/C-EG-30_11	3.84

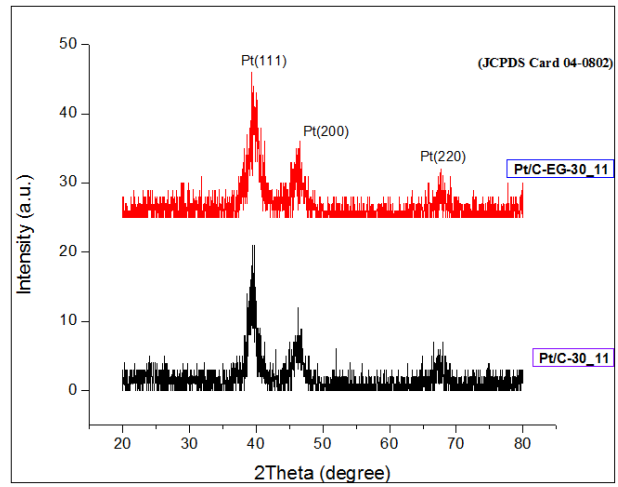

Figure 3. *X-ray diffraction (XRD) patterns of Pt-30_11 and Pt-EG-30_11 catalysts.*

The 40 wt% Pt/C samples are synthesized with or without the presence of EG at room temperature at pH=11. X-ray diffraction of these samples is shown in Figure 3. It indicates that all the broad diffraction peaks of the XRD patterns at 2θ = 39.6, 47.4, 67.1°, corresponding to the reflections (111), (200), (220), respectively, which are consistent with the face centered cubic (fcc) structure of platinum, can be assigned to (JCPDS Card 04-0802), thus demonstrating the presence of crystalline Pt [8]. In addition, a broad peak at 2θ ≈ 25° was observed but not clearly due to the fact that the (002) plane of the hexagonal structure of the carbon support (Vulcan XC-72R) is amorphous carbon with small regions of graphitic properties [9]. More importantly, the Pt/C sample with the presence of EG shows a wider peak than the sample without using EG in the preparation process, suggesting that the Pt particles size of sample using EG is smaller than the one without using EG (3.84 nm compare to 7.14 nm). (Table 2) The average crystalline sizes of the Pt catalysts were calculated by the Scherrer formula based on the diffraction peaks of the Pt (111) plane.

This result is supported by TEM measurement shown in Figure 4.

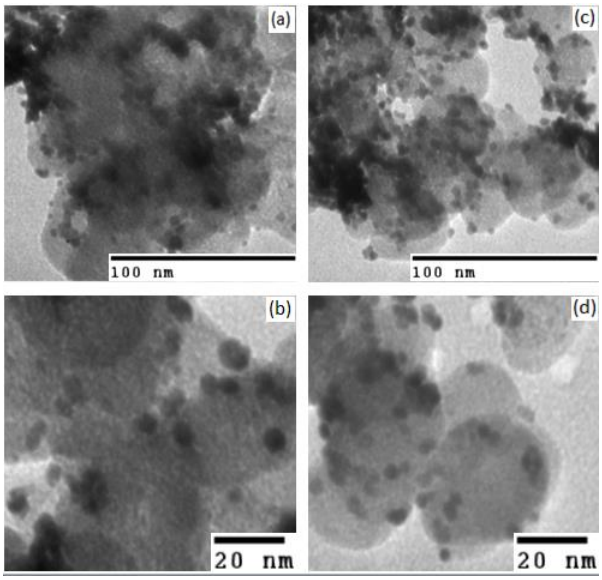

Figure 4. *(a), (b) are the TEM of Pt-30_11 catalyst; (c), (d) are the TEM of Pt-EG-30_11 catalyst.*

The Pt/C-EG-30_11 catalyst prepared using $NaBH_4$ as the reducing agent in EG solution at pH=11 has shown that its particles size is smaller than the size of Pt/C-30_11 (Figure 4. (d) compared to (b)). The presence of ethylene glycol (EG) supported Pt nanoparticles not only have a narrow size, but also distribute uniformly on carbon support (Figure 4. (c) compared to (a)). This has been reported that the reaction with the attendance of EG and $NaBH_4$ in a solution will form a complex reducing agent, and EG has performed roles both as a reducing agent for Pt reduction and a stabilizing for the reduced Pt nanoparticles [10].

3.2. Temperature effects on Pt/C preparation

Table 3. *Average crystallite size calculated from the Pt (111) using the Scherrer equation*

Sample	Average crystallite size (nm)
Pt/C-EG-30_11	3.84
Pt/C-EG-60_11	5.85

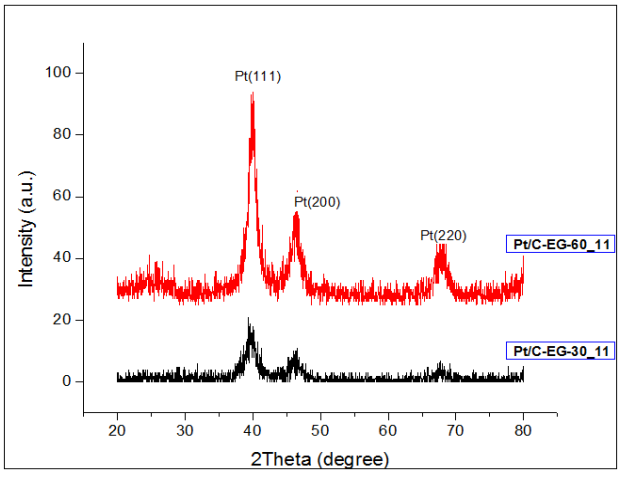

Figure 5. *X-ray diffraction (XRD) patterns of Pt-EG-30_11 and Pt-EG-60_11 catalysts.*

The effect of temperature is studied by preparing the sample 40 wt% Pt/C using EG at room temperature, pH=11 (denoting Pt-EG-30_11) and 40 wt% Pt/C sample using EG at 60ºC, pH=11 (denoting Pt-EG-60_11). We can clearly observe that all the samples show the reflections (111), (200), (220), respectively. However, when the temperature increases from room temperature to 60ºC, there is a significant difference in the crystallinity and the particle size of Pt on carbon. The Pt-EG-60_11 shows high crystallinity and a large particle size compared to Pt-EG-30_11. For example, the average crystallite size of Pt-EG-30_11 is about 3.84 nm and the average crystallite size of Pt-EG-60_11 is about 5.85 nm (estimated from the Scherrer formul at Pt (111) peak). (Table 3). This observation is then confirmed by TEM measurement (Figure 6). The sample Pt-EG-30_11 shows the good distribution as well as the small particle size compared to Pt-EG-60_11, indicates that the temperature strongly affected the distribution and the size of Pt on carbon. This phenomena could be explained by the fact that the degree of supersaturation of a solution decreases when the reaction temperature increases. At a lower temperature, the formation of crystal nuclei proceeds more rapidly than the growth. Therefore smaller Pt particles were obtained at 30ºC compared to those obtained at 60ºC [11].

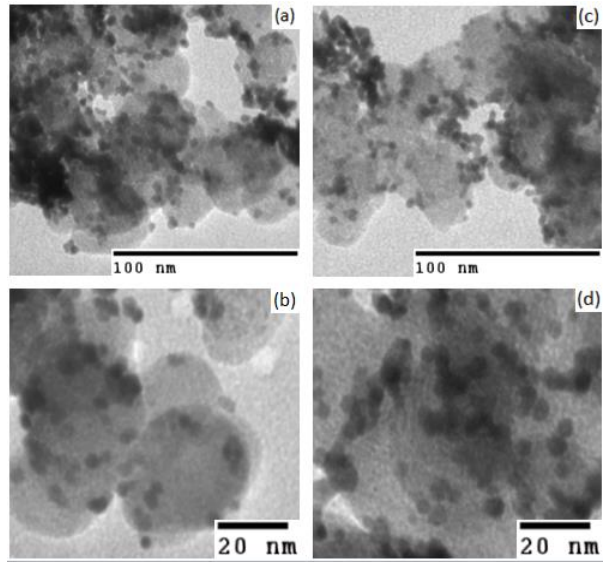

Figure 6. *(a), (b) are the TEM of Pt-EG-30_11 catalyst; (c), (d) are the TEM of Pt-EG-60_11 catalyst.*

3.3. Effect of the solution pH on Pt/C preparation

Table 4. *Average crystallite size calculated from the Pt (111) using the Scherrer equation*

Sample	Average crystallite size (nm)
Pt/C-EG-30_11	3.84
Pt/C-EG-30_6.5	7.72

The Pt/C-EG-30_6.5 sample is prepared in the same procedure as Pt/C-EG-30_11, but with a pH=6.5 solution differentiating from the pH=11 of Pt/C-EG-30_11 sample. Compared to Pt/C-EG-30_6.5, the Pt/C-EG-30_11 catalyst had highly dispersed Pt nanoparticles on the surface of the carbon support. Bonnemann et al. reported that Pt nanoparticles are stabilized via the electrosteric repulsion between the anionic surface of the Pt nanoparticle and the stabilizer [12]. In the acidic solution, a large number of H^+ ions interact with negatively charged Pt particles resulting

in the destruction of electrosteric repulsion and leading to the growth of Pt nanoparticles. In the basic solution, almost no species would directly interact with negatively charged Pt nanoparticles, which implied that the electrosteric stabilization is unbroken [13, 14]. A similar feature has also been observed in the synthesis of Pt-based metal nanoparticles using EG as a reducing agent [15]. In our case, the size of Pt nanoparticles of Pt/C-EG-30_6.5 sample is about 7.72 nm (Table 4) (estimated from the Scherrer formul at Pt (111) peak). The differences in Pt particles between Pt/C-EG-30_6.5 and Pt/C-EG-30_11 can be explained based on the effect of the electrosteric repulsion. Under high pH conditions, only minor interaction occurred between H^+ ions and stabilizer anions, yet the stabilizer strongly interacted with the reduced Pt nanoparticles. Therefore, the growth of Pt particles was significantly restrained, leading to the formation of Pt nanoparticles with a smaller size in the Pt/C-EG-30_11 than in the Pt/C-EG-30_6.5 catalyst (Figure 8).

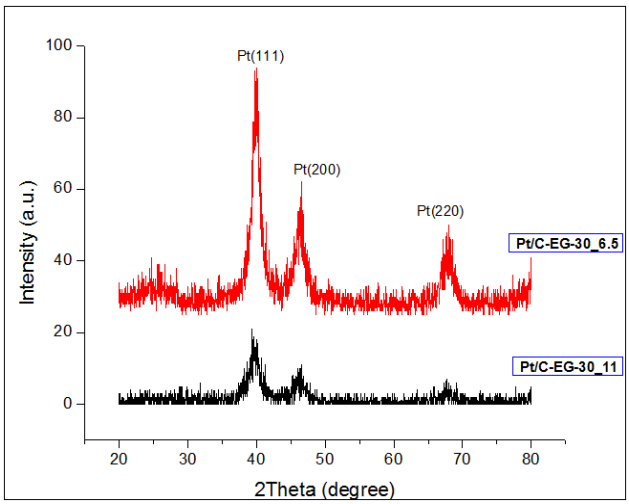

Figure 7. *X-ray diffraction (XRD) patterns of Pt-EG-30_11 and Pt-EG-30_6.5 catalysts*

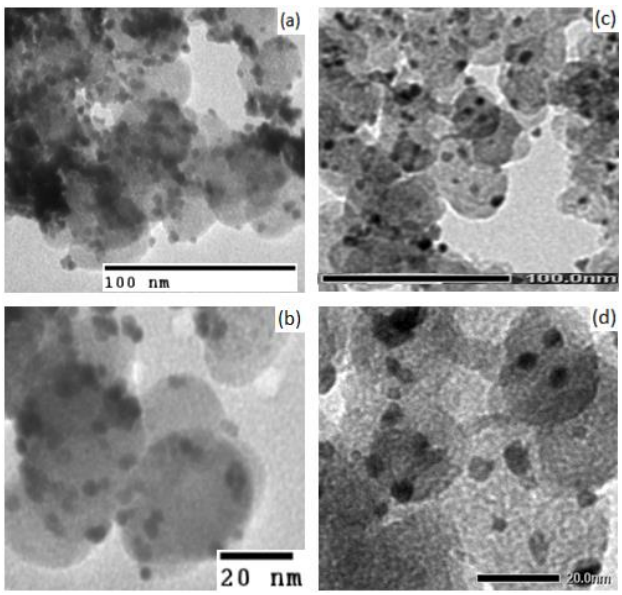

Figure 8. *(a), (b) are the TEM of Pt-EG-30_11 catalyst; (c), (d) are the TEM of Pt-EG-30_6.5 catalyst*

4. Conclusions

The effect of ethylene glycol and temperature on the size and the dispersion of platinum nanoparticles catalyst on carbon support has been examined in this research. We have found out that the temperature, EG agent as well as pH parameter strongly affected the particle size and the distribution of Pt on carbon support. The presence of EG functioning as a weak reducing agent and a stabilizer could enhance the distribution and make smaller Pt sizes compared to the sample without using EG. In addition, the effect of temperature on the Pt/C preparation was studied at room temperature and 60ºC. We also found that when the temperature increases from room temperature to 60ºC, there is a significant difference in the crystallinity and the particle size of Pt on carbon due to the degree of supersaturation of a solution that decreases with an increase in the reaction temperature. Finally, the effect of pH parameter on Pt/C preparation has also been examined in this work. The experimental results indicate that in the acidic solution (low pH value), a large number of H^+ ions interact with negatively charged Pt particles, which result in the destruction of electrosteric repulsion, leading to the growth of Pt nanoparticles. However, only minor interaction occurred between H^+ ions and stabilizer anions in high pH conditions. The results of this work showed the way to control the size and the distribution of Pt catalyst on carbon support that can be used to enhance the activity of the Pt/C catalyst with high loading for fuel cell applications.

Acknowledgment: This work was supported by Ho Chi Minh City University of Technology, Ho Chi Minh City University of Natural Resources and Environment.

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(The Board of Editors received the paper on 08/17/2015, its review was completed on 10/16/2015)