Chinese Chemical Letters Vol. 15, No. 7, pp 875-878, 2004
http://www.imm.ac.cn/journal/ccl.html

Preparation of Pt/C Catalyst with a New and Simple Organic Sol Method

Ya Wen TANG[1], Gang LI[1], Chang Peng LIU[2], Wei XING[2], Tian Hong LU[1,2]*

[1] Department of Chemistry, Nanjing Normal University, Nanjing 210097
[2] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022

Abstract: It is reported for the first time that the Pt/C catalyst can be prepared with a new and simple organic sol method using $SnCl_2$ as the reductant. It was found that the average size of the Pt particles in the Pt/C catalysts could be controlled with controlling the preparation conditions. The effect of the average sizes of the Pt particles in the Pt/C catalysts obtained with this method on the electrocatalytical activity of the oxidation of methanol was investigated.

Keywords: Pt colloid, Pt/C catalyst, particle size.

The colloidal Pt with largely uniform particles is interesting in the catalysis because it could improve the catalytic activity. In 1991, Bonnemann *et al*. reported for the first time that the preparation of colloidal Pt with a narrow particle size range using the organic sol method with $PtCl_2$ and NR_4BEt_3H (R=octyl, hexyl, decyl) reaction in the tetrahydrofunan solvent[1]. Thereafter, the researchers almost adopted their method to prepare the colloidal Pt/C catalyst. However, their preparation procedure is very complicated and the raw materials are very expensive. In this paper, it is reported for the first time that a new and simple organic sol method was used to prepare the Pt/C catalyst and the average size of the Pt particle in the Pt/C catalysts could be controlled with controlling the preparation conditions.

Stoichiometric H_2PtCl_6 and $SnCl_2$ were dissolved in the methanol solvent, respectively. Two solutions were ultrasonically mixed until the buff organic sol was formed. FT-IR difference spectroscopic measurement demonstrated that almost all of H_2PtCl_6 has been reduced to Pt. After Vulcan XC-72 carbon black was mixed with the Pt sol, the mixture was dried in the N_2 atmosphere at the different temperatures until the methanol solvent was completely evaporated. Then, the Pt/C catalyst obtained was aging-treated under the vacuum condition at 100°C for 12 h. Finally, it was washed with 6 mol/L NaOH solution and distilled water, sequentially, until no Cl^- was detected in the eluant. After dried at 90°C, the Pt/C catalyst with 20 wt% Pt was obtained. Energy dispersion spectra (EDS) measurements showed that there is no Sn in the Pt/C catalysts.

*E-mail: tianhonglu@263.net

The electrochemical measurements were performed with CHI 600 potentiostat (CHI Co.) and a traditional three-electrode cell at 30°C. The Pt/C catalyst modified glassy carbon electrodes were prepared using the method reported by Schmidt *et al.*[2]. The Pt loading was 28 μg/cm^2. The saturated calomel electrode (SCE) and Pt wire were used as the reference and auxiliary electrode, respectively. The solution used for the electrochemical measurements was 0.5 mol/L CH_3OH + 0.5 mol/L H_2SO_4 solution.

Figure 1 is the XRD patterns of the Pt/C catalysts prepared at the different evaporating temperatures of methanol. The characteristic diffraction peaks of Pt [111], [200], [220], [311] crystal face are observed at 2 θ values of *ca.* 39.9, 46.5, 67.8, and 81.2°, respectively. The average particle size can be calculated with Scherrer equation[3]. The relationship between the evaporating temperature and the average size of Pt particles was showed in **Figure 2**. It illustrated that the average size of Pt particles gradually decrease with increasing the evaporating temperature.

Figure 1 XRD of Pt/C catalysts prepared at (a) 65, (b) 60, (c) 50, (d) 40, (e) 30°C

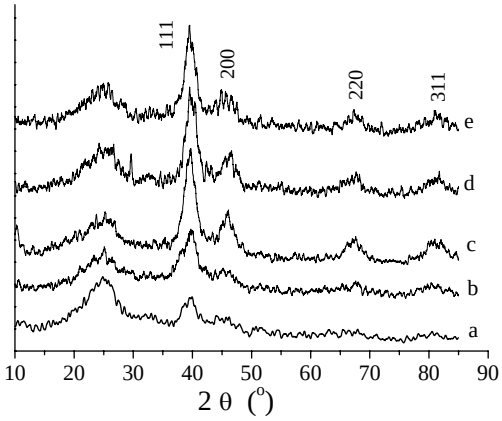


Figure 2 Effect of the evaporating temperatures of methanol on the size of Pt particle

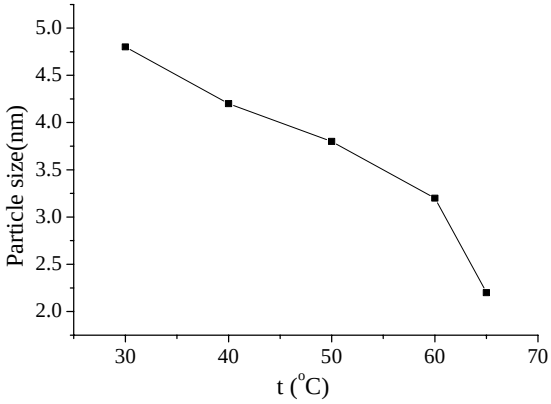


Figure 3 is the typical TEM image of the Pt/C catalyst prepared at the evaporating temperature of 50°C. It showed that Pt particles possess excellent dispersity and uniformity. The average size of the Pt particles measured from **Figure 3** is 3.8 nm, which is consistent with that calculated from the XRD data. The results of TEM and XRD illustrated that the average sizes of Pt particles in the Pt/C catalysts prepared with the organic sol method could be controlled with controlling the evaporating temperature of the solvent.

Figure 3 The TEM of Pt/C catalyst prepared at the evaporating temperature of 50°C

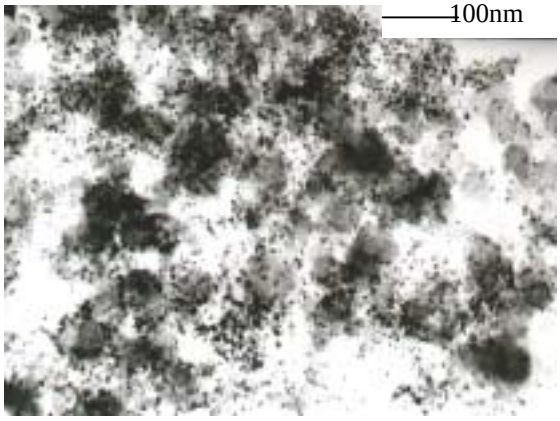
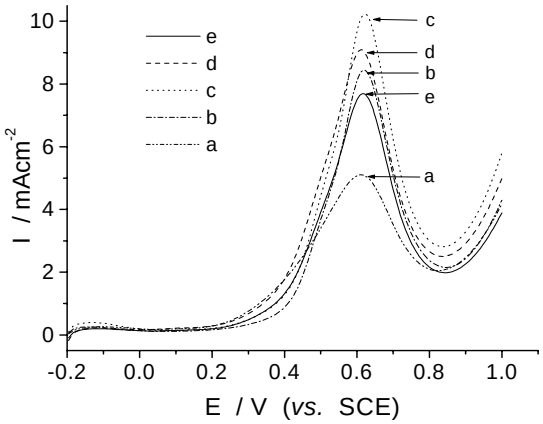


Figure 4 is the linear scan voltammograms of the Pt/C catalysts with the different average sizes of Pt particles in the 0.5 mol/L CH_3OH + 0.5 mol/L H_2SO_4 solution. It can be found from **Figure 4** that the oxidation peaks of methanol at all the Pt/C electrodes are located at 0.62 V and the peak current densities of the methanol oxidation

Figure 4 The linear scan voltammograms of the Pt/C catalysts in the 0.5 mol/L CH_3OH + 0.5 mol/L H_2SO_4 solution



(a) 2.2, (b) 3.2, (c) 3.8, (d) 4.2, (e) 4.8 nm Pt particle size. Scan rate: 50 mV/s

are 5.11, 8.45, 10.23, 9.07 and 7.69 mA/cm^2 for the average sizes of Pt particle of 2.2, 3.2, 3.8, 4.2 and 4.8 nm, respectively. It indicated that the optimal average size of Pt particles in the Pt/C catalyst for the oxidation of methanol is 3.8 nm. Frelink *et al*. has reported the effect of the average sizes of the Pt particles in the Pt/C catalysts on the electrooxidation of methanol[4]. However, they prepared the Pt/C catalysts with different Pt particle sizes using the different preparation methods and neglected their influence on the performance of the Pt/C catalyst. Obviously, the surface groups, the surface morphology and the metal-support interaction of Pt/C catalyst prepared in a various methods are different and these factors also affect the electrocatalytic activity of the Pt/C catalysts[5, 6]. Therefore, the results obtained in this study are accurate because the Pt/C catalysts with different average Pt particle sizes were prepared with the same method.

Acknowledgment

The authors are grateful for the financial supports of the "973" Project of China (G2000026408), the "863" Project of China (2001AA323060, 2003AA517060), the industrialization Project of Advanced Technique of Jiangsu Province (JH02-080), the study Project of Advanced Technique of Jiangsu Province (BG2003022) and National "211" Key Project.

References

1. H. Bonnemann, W. Brijoux, R. Brinkmann, *et al*., *Angew. Chem. Int. Ed. Engl.*, **1991,** *30*,1312.
2. T. J. Schmidt, Z. Jusys, H. A. Gasteiger, *et al.*, *J. of Electroanal. Chem.*, **2001**, *501*, 132.
3. E. Antolini, F. Cardelini, *J. of Alloys and Compounds*, **2001**, *315*, 118.
4. T. Frelink, W. Visscher, J. A. R. Van Veen, *J. Electroanal. Chem.*, **1995**, *385*, 65.
5. S. Mukerjee, *J. of Appl. Electroghem.*, **1990**, *20*, 537.
6. A. K. Shukla, A. Hamnett, A. Roy, *et al.*, *J. Electroanal. Chem*., **1993**, *352*, 337.

Received 23 June, 2003