



Comparison of Metal Cleaning Effect on Pt Particles Supported on Carbon and Pt Black Observed by NMR, CV, and TEM

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Abstract : 60% Pt on Vulcan XC-72 with similar Pt sizes to fuel cell grade Pt black was investigated by ¹³C nuclear magnetic resonance spectroscopy (NMR), cyclic voltammetry (CV), transmission electron microscopy (TEM). Experiments were carried out on electrochemically cleaned samples as well as as-received. The TEM and CV results showed that the average particle sizes were changed by cleaning. However, the chemical shift (δ_C) of ¹³C of ¹³CO absorbed on Pt surfaces did not show any appreciable variation with particle size change as did in Pt black. These results indicate that a combination of different analytic techniques is essential to understand the properties of the metal particle catalysts and that the presence of carbon black support strongly influences the NMR data, probably through metal-support interaction.

INTRODUCTION

Platinum supported on carbon is commonly used for catalysts in fuel cells, due to higher catalytic activity¹ than Pt black. Although one principal reason for high catalytic activity is thought to be the strong metal-support interaction,²⁻⁵ activity also depends on Pt particle size and surface morphology.^{4,5} These factors can be modified by sample preparation procedures, pretreatment, and the nature of the support materials.⁴⁻⁶ Typical cleaning procedures are: (1) applying extensive cyclic voltammetry (CV),^{2,7,8} (2) holding the potential at 250 mV (vs. 1 M Ag/AgCl),^{3,8} and (3) dipping into hot chromic acid.^{9,10} In previous work, we observed that the Pt particle size in Pt-black increases as a result of electrochemical cleaning.¹¹ Extensive CV treatment produces maximum growth, followed

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by cleaning with chromic acid, then by holding the potential at 250 mV. Extensive CV treatment is also known to increase the particle size in Pt.^{2,7,8,12} But the influence of a variety of cleaning methods on carbon-supported Pt has not been investigated yet. We have therefore examined 60% carbon-supported Pt catalysts, Pt sizes of which are known to be similar to Pt black in fuel cell grade, in order to investigate how the effects of different cleaning on the Pt are influenced by the presence of carbon black support.

We use transmission electron microscopy (TEM), ¹³C nuclear magnetic resonance (NMR) spectroscopy and cyclic voltammetry (CV) as probe techniques in this study. TEM has been proven to be very useful in determining Pt particle sizes of Pt/graphite catalysts,^{5,12} while NMR spectroscopy is well suited to study both the electronic and chemical bonding properties of Pt particles, as well as adsorbed species on Pt surfaces.^{2,3,6-10,13-22} Due to the high sensitivity of ¹³C as compared to ¹⁹⁵Pt NMR in these samples, we have employed here ¹³C NMR of CO adsorbed on carbon-supported Pt. In addition, we have used CV to investigate the CO stripping peak potentials in order to further probe platinum particle size and surface conditions.²³

EXPERIMENTAL

Sample Preparation

Carbon-supported Pt catalysts with Pt loadings of 60% Pt on Vulcan XC-72 were purchased (from E-Tek Inc., (Somerset, NJ, U.S.A.)) and are described below as 'as-received-60' samples (before any treatment), where 60 is the weight percent Pt in dry sample. Cleaning procedures employed in this work is essentially the same as in previous report on Pt black.⁸ However, samples cleaned by chromic acid were not prepared in this work because it proved to be difficult to prevent particles floating away during the cleaning process. Sample notation is also the same as previously reported except tagging with '-60'. All potentials were controlled by a model 362 Scanning Potentiostat (EG & G, U.S.A.) and measured versus a 1 M Ag|AgCl electrode.

For ¹³C NMR experiments, ¹³CO was adsorbed on the carbon-supported Pt catalysts by partial methanol oxidation,²⁴ then rinsed with 0.5 M H₂SO₄, to remove excess methanol just before the sample was transferred to an NMR tube, basically as reported previously.⁸

Characterization

TEM measurements were performed by using an EM912 Omega microscope (Carl Zeiss, Bruker, Germany) operating at 120 kV. ¹³C NMR experiments were performed using a 400MHz DSX spectrometer (Bruker, Germany) and a "home-built" probe. Acquiring ¹³C NMR spectra and the CO stripping CV of each sample were carried out in the same way as previously reported.⁸ Further details of all these experimental procedures can be found elsewhere.^{2,3,11}

RESULTS AND DISCUSSION

We show in Fig. 1 TEM images of 60% Pt on Vulcan XC-72 samples. The very small particles which are readily observable in the images of the as-received-60 and holding-at-250mV-60 samples are hardly observable in the extensive-CV-60 images. This result demonstrates that the Pt particle sizes vary depending on the cleaning procedures used, especially in extensive-CV-60.

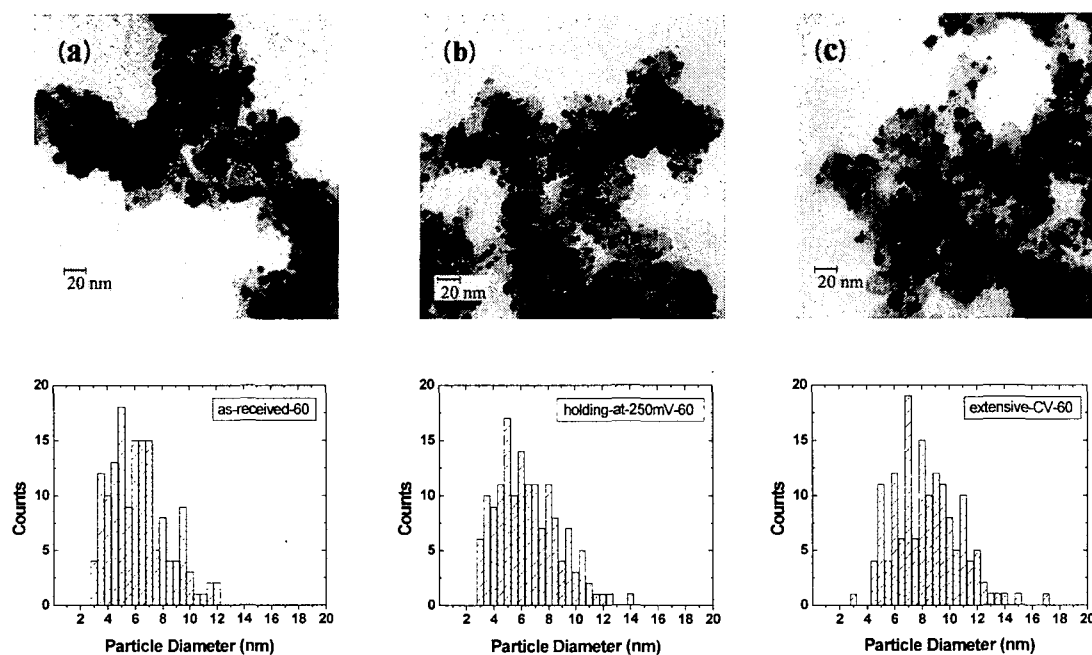


Fig. 1. TEM images and Pt particle size histogram of (a) as-received-60, (b) holding-at-250mV-60, (c) extensive-CV-60.

This TEM result agree with previous reports^{2,7,8,11,12} on the growth of in Pt particles by extensive CV treatment in both Pt supported on graphite/carbon samples^{2,7,8,12} and Pt black samples.¹¹ For a more quantitative analysis, individual Pt particle sizes were measured in each TEM image and the distributions are summarized as histograms in Fig. 1. The particle size distribution widths at half height of these samples are nearly the same and small particles appear in the as-received-60 samples and the holding-at-250mV-60 samples are absent in the extensive-CV-60 samples. However, the particle sizes with the highest population do not clearly change from those found in the as-received samples. This TEM result demonstrates that the average particle size (Table 1) change with cleaning procedure.

The effect is largest with the extensive-CV sample, as shown in Table 1, and can be taken to indicate some form of sintering, due to electrochemical cleaning just as in platinum black sample (Table 1).

Table 1. The average particle size (nm) from TEM.

| | 60% Pt | Pt black |
|------------------|---------------|---------------|
| As-received | 6.7 ± 0.2 | 6.7 ± 0.5 |
| Holding-at-250mV | 7.1 ± 0.5 | 7.1 ± 0.3 |
| Chromic-acid | | 8.3 ± 0.3 |
| Extensive-CV | 8.4 ± 0.4 | 9.1 ± 0.2 |

The ^{13}C NMR spectra of CO adsorbed on carbon-supported 60 % Pt samples and a blank reference (Pt on Vulcan XC-72, wetted with 0.5 M H_2SO_4 electrolyte) are shown in Fig. 2. The peaks on the right are from the carbon black in the supported catalyst while the peaks on the left are from ^{13}C CO on the surface of the Pt particles. The centers of gravity (δ_G) of the CO peaks, determined after subtracting the carbon black signal, are plotted in Fig. 3.

As can be seen from Fig. 3, δ_G for the carbon-supported samples do not show any appreciable effect of the cleaning procedure. The δ_G of the 60% Pt samples are all the same within the experimental error range (Fig. 3(a)). From fig. 3(b), it can be seen that the δ_G of supported Pt particles do not show any appreciable variation although TEM results clearly show particle growth due to cleaning. This is quite in contrast with the results of Pt black samples¹¹ in Fig. 3 which show a marked variation of Pt particle size and δ_G of ^{13}C NMR at the same time.¹¹

The CO-stripping cyclic voltammograms of the 60% Pt on Vulcan XC-72 samples in 0.5 M H_2SO_4 electrolyte solution are presented in Fig. 4. The center of gravity of the CO oxidation peak is highest for the as-received sample and smallest for the extensive-CV sample among the Pt samples as summarized in Table 2. As the particle is larger, its CO oxidation peak potential is known to be smaller.²³ Therefore, CO oxidation peak potential values suggest that the Pt particles grow mostly by extensive-CV treatment and moderately by holding-at-250mV. Thus the CO-stripping CV results agree well with our TEM results.

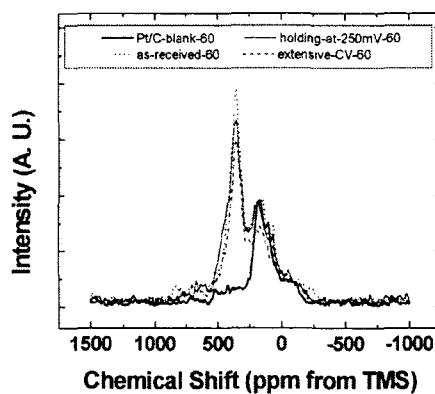


Fig. 2. ^{13}C NMR spectra of the 60% Pt samples.

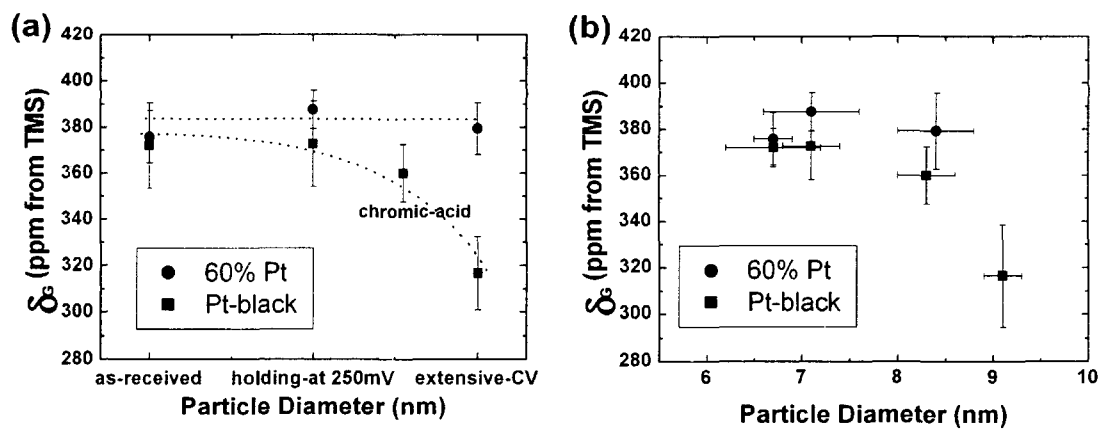


Fig. 3. The center of gravity (δ_G) plot of the ^{13}C NMR spectra with respect to (a) cleaning processes and (b) the average Pt particle sizes measured by TEM.

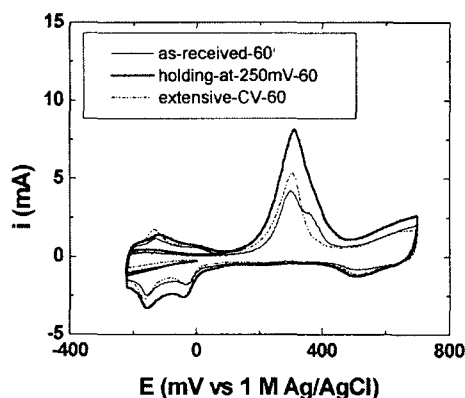


Fig. 4. CO-stripping CV of 60% Pt samples (scan-rate = 0.2 mV/s)

Table 2. Center of gravity of CO-oxidation peak potential in CO-stripping CV in 0.5 M $3\text{H}_2\text{SO}_4$ electrolyte solution in mV

| | 60% Pt | Pt black |
|------------------|--------|----------|
| As-received | 310 | 295 |
| Holding-at-250mV | 312 | 292 |
| Chromic-acid | N/A | 292 |
| Extensive-CV | 293 | 289 |

* The reading error of the peak potential is within ± 3 mV.

CONCLUSIONS

The influence of cleaning procedures on the Pt particle size in carbon-supported Pt, 60% Pt on Vulcan XC-72, were studied by TEM, ^{13}C NMR, and CO-stripping CV and compared with the results of Pt black to investigate the effect of carbon support. The cleaning procedures increase the Pt particle sizes in carbon-supported Pt and Pt black both, as detected by TEM. However, δ_G of ^{13}C NMR of ^{13}CO on Pt supported on carbon were not changed as much as that of Pt black. This could be due to metal-support interaction. This also implies that a combination of different analytic techniques is essential to understand the properties of the metal particle catalysts.

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