PtNi Alloy Nanoparticle-Supported MWCNTs Produced in a Nickel(II) Oxalate Dihydrate Dispersed Ionic Liquid with Pt(acac)2 by One-Pot Pyrolysis Method

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ABSTRACT

The novel one-pot pyrolysis method with ionic liquid (IL one-pot pyrolysis method) was developed in our previous study to prepare a PtNi alloy nanoparticle-supported multi-walled carbon nanotube (PtNi/MWCNT) composite. Herein, it was found that the PtNi/MWCNT composite could be prepared by IL one-pot pyrolysis method even if an insoluble nickel precursor with crystal water, nickel(II) oxalate dihydrate (NiC2O4·2H2O), was used. The Ni content and crystal structure of the resulting PtNi/MWCNT composites were similar to those of the composites produced under dehydrated and homogeneous conditions. It means that solubility of Ni precursor and existence of crystal water in the precursor had an insignificant effect on the production of the PtNi/MWCNT composite.

Keywords: PtNi Alloy Nanoparticle, Carbon Nanotube, Ionic Liquid, One-Pot Synthesis
diffraction (XRD) patterns of the as-prepared PtNi/MWCNTs were examined using a Rigaku Ultima IV X-ray diffractometer with a CuKα radiation source. The XRD patterns were collected from 20° to 80° at a scanning rate of 1° min⁻¹. The morphology of the PtNi/MWCNTs was observed through a Hitachi H-7650 transmission electron microscope (TEM). The composition of the PtNi nanoparticles was analyzed using a Shimadzu ICPS-7510 inductively coupled plasma atomic emission spectrometry (ICP-AES).

3. Results and Discussion

The thermal stability of Pt(acac)₂, NiC₂O₄·2H₂O, and [N₁,₁,₁,₃][Tf₂N] was examined by TG analysis before preparing the PtNi/MWCNT composite using the IL one-pot pyrolysis method (Fig. 1). For Pt(acac)₂ and [N₁,₁,₁,₃][Tf₂N], simple one-step thermal degradation was recognized. In contrast, NiC₂O₄·2H₂O was decomposed by a two-step process. The reactions at the first and second steps were attributed to anhydrous nickel(II) oxalate (NiC₂O₄) formation and NiC₂O₄ thermal decomposition, respectively, leading to Ni metal deposition.\(^{2,22}\) [N₁,₁,₁,₃][Tf₂N] IL was confirmed as a viable reaction medium for the IL-based pyrolysis method when the heating temperature was less than ca. 650 K. Considering these results and a recent finding,\(^{20}\) we applied a staircase heating process with three temperature plateaus at 373 K, 473 K, and 573 K to the one-pot pyrolysis method because the nanoparticle formation can be readily controlled by this approach. The heating conditions are graphically depicted in Fig. 2 and were employed for the TG analysis. As shown in Fig. 2, the weight loss for Pt(acac)₂ resulting from Pt deposition was initiated at 473 K, and with increasing heating time, it became clearer than that observed through the standard TG analysis (Fig. 1). Consequently, the weight loss was completed at the beginning of the plateau at 573 K.

Thermal decomposition of metal precursors in [N₁,₁,₁,₃][Tf₂N] mixtures with NiC₂O₄·2H₂O as the Ni precursor. The specimens were taken from the IL mixtures containing the metal precursors and MWCNTs at points A–J as shown on the top axis.

Figure 2. (—) Heating profile of the staircase heating process and TG analysis results of (——) Pt(acac)₂ and (—) NiC₂O₄·2H₂O obtained using the staircase heating process. Specimens were taken from the IL mixtures containing the metal precursors and MWCNTs at points A–J as shown on the top axis.

![Figure 2](image)

**Figure 2.** Heating profile of the staircase heating process and TG analysis results of (——) Pt(acac)₂ and (—) NiC₂O₄·2H₂O obtained using the staircase heating process. Specimens were taken from the IL mixtures containing the metal precursors and MWCNTs at points A–J as shown on the top axis.

Figure 3 shows TEM images of the specimens prepared in the [N₁,₁,₁,₃][Tf₂N] mixtures with NiC₂O₄·2H₂O as the Ni precursor. The specimens were taken from the IL mixture after different heating processes, labeled A–J in Fig. 2. Measurable nanoparticles (ca. 1 nm <) were confirmed only under the heating conditions at 573 K, i.e., conditions G–J. The mean particle sizes of the nanoparticles deposited on the MWCNTs are summarized in Table 1. A considerable number of nanoparticles with mean particle sizes of 3.7–4.4 nm were observed. Given the results of standard TG analysis for the metal precursors (Fig. 1), the Ni content of the specimens should be significantly lower than the Pt content. Contrary to our expectation, ICP-AES results of the specimens obtained under conditions G and J show that the Ni content of the specimens was >25 at%, which is identical to that of the Pt₃Ni alloy exhibiting considerably high catalytic activity.\(^{13}\) This unexpected result was also recognized when Ni[Tf₂N]₂ was employed as a nickel precursor.\(^{20}\) It seems to be a common thread in nickel precursors that have thermal stability over Pt(acac)₂. The PtNi/MWCNT prepared under condition G showed a higher Ni content than that under condition J, possibly because of the unreacted NiC₂O₄·2H₂O involved in the specimen.

![Figure 3](image)

**Figure 3.** TEM images of PtNi/MWCNTs prepared in [N₁,₁,₁,₃][Tf₂N] with 5.0 mmol L⁻¹ Pt(acac)₂, 5.0 mmol L⁻¹ NiC₂O₄·2H₂O, and 1.3 g L⁻¹ MWCNT. Samplings of the IL mixture were conducted at the sampling points of (a) G, (b) H, (c) I, and (d) J depicted in Fig. 2.
Figure 4. XRD patterns of the PtNi/MWCNTs prepared at sampling point (a, b) G and (c, d) J. The reflections from Pt metal (ICDD No. 00-04-0802), Ni metal (ICDD No. 00-04-0850) and carbon nanotube (ICDD No. 00-058-1638) are denoted at the bottom of the figure. (b) and (d) were the magnified figures for the light blue area in figures (a) and (c).

Table 1. Properties of PtNi/MWCNTs prepared in [N\textsubscript{1,1,1,3}[Tf\textsubscript{2}N] with 5.0 mmol L\textsuperscript{-1} Pt(acac)\textsubscript{2}, 5.0 mmol L\textsuperscript{-1} NiC\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O, and 1.3 g L\textsuperscript{-1} MWCNT.

| Sampling point | Condition | Mean particle size/\text{nm} | Pt loading amount/\text{wt\%} | Ni content of nanoparticles/\text{at\%} |
|---------------|-----------|------------------------------|-------------------------------|----------------------------------------|
| G             | 573 K     | 3.7 (0.7)\textsuperscript{a} | 25.5                          | 34.9                                   |
| H             | 573 K, 5 min | 3.9 (0.7)\textsuperscript{a} | —                            | —                                      |
| I             | 573 K, 1 h  | 4.1 (0.8)\textsuperscript{a} | —                            | —                                      |
| J             | 573 K, 4 h  | 4.4 (0.8)\textsuperscript{a} | 23.5                          | 25.6                                   |

\textsuperscript{a}The values in parentheses are standard deviations.

XRD patterns of the as-prepared PtNi/MWCNTs at point G and J are shown in Fig. 4 and are almost identical to those of the Pt metal. However, the XRD patterns shift very slightly to a higher angle (Fig. 4b and 4d), suggesting that the PtNi alloy nanoparticle with a face-centered cubic solid solution phase is formed under the experimental condition.\textsuperscript{23} Importantly, crystal water contained in the Ni precursor had an insignificant effect on the PtNi/MWCNT preparation through the IL one-pot pyrolysis method. This method did not need rigorous moisture control throughout the heating process because of the strong hydrophobicity of the [N\textsubscript{1,1,1,3}[Tf\textsubscript{2}N] IL.\textsuperscript{24} The electrocatalytic performance of the PtNi/MWCNT composite prepared in this study is being investigated. The result will be reported elsewhere.

4. Conclusion

PtNi/MWCNTs were successfully prepared by the IL one-pot pyrolysis method using the staircase heating process with an insoluble Ni metal precursor with crystal water, NiC\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O. The use of NiC\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O has negligible effect on the mean particle size, the Ni content of the nanoparticles, and crystal structure. This indicates that the solubility and existence of crystal water are not significant for a metal precursor used in the one-pot pyrolysis method to prepare metal and alloy nanoparticles. It is quite contrast to other chemical reactions in IL which require the homogeneous condition without contamination. Increase in the variety of metal precursors means expanding the application range of this one-pot pyrolysis method. Therefore, by making full use of this method, we will make attempts to prepare various metal and alloy nanoparticles, and their supported carbon materials, which are difficult to synthesize by the conventional methods.

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