Microwave Polyol Synthesis and Characterizations of Carbon-supported Pt and Ru Nanoparticles

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Carbon-supported platinum and ruthenium nanoparticles were synthesized by a microwave-assisted polyol heating process. TEM observations showed that the Pt and Ru particles prepared as such have uniform shapes and sizes, and well dispersed on the carbon surface. The average particle size was 3.1 nm for Pt and 2.9 nm for Ru.

Carbon-supported noble metal nanoparticles, such as Pt/C and Ru/C, have been receiving much attention as high performance catalyst. It is well known that the metal catalytic activity is strongly dependent on the particle shape and size.[1] The conventional preparation methods based on impregnation-reduction do not provide satisfactory control of particle shape and size. It is still challenge to synthesize highly dispersed supported metal particles with small and uniform size. As a fast, simple, uniform, and energy efficient heating method, microwave irradiation has been applied in chemical reactions[2] and nanomaterials synthesis.[3–6] There have been more reported successes in employing microwave irradiation to prepare high purity and uniform nanoparticles. For example, polymer stabilized Pt, Pd, Ru, and Ag colloids were synthesized by microwave assisted heating of ethylene glycol solution of dissolved metal salts.[7–9]

Herein, we report that the rapid synthesis of carbon-supported Pt and Ru nanoparticles by microwave heating of ethylene glycol solutions of H_2PtCl_6 and $RuCl_3$ in the presence of carbon. The products were characterized by EDX, XRD, XPS and TEM. It was found that a high dispersion of Pt and Ru nanoparticles with small and uniform sizes could be obtained on the carbon support.

A detailed description for the preparation of Pt/C is as follows. In a 100-mL beaker, 1.0 mL of an aqueous solution of 0.05 M $H_2PtCl_6{\cdot}6H_2O$ (Aldrich, A.C.S. Reagent) was mixed with 25 mL of ethylene glycol (Mallinckrodt, AR), 0.75 mL of 0.4 M KOH and 0.04 g of Vulcan carbon XC-72 with a specific surface area (BET) of 220 $m^2\ g^{-1}$ and an average particle size of 40 nm. The beaker and its contents were heated in a microwave oven (National NN-S327WF, 2450 MHz, 700 W) for 50 s. The product was collected by filter, and washed with acetone, then dried at 393 K over night in a vacuum oven. Ru/C was prepared likewise using $RuCl_3$ as the precursors. The starting material for Ru/C was a mixture of 25 mL ethylene glycol, 2 mL 0.05 M $RuCl_3$, 0.75 mL 0.4 M KOH, and 0.04 g carbon. The samples were characterized by TEM (JEOL JEM 2010), EDX (JEOL JSM-5600LV), XRD (A Philips PW 1710 diffraction meter, Cu Kα) and XPS (VG ESCALAB MKII spectrometer).

The metal content was calculated from EDX measurement to be 18.9 wt % for Pt/C and 19.1 wt % for Ru/C, which corresponded very well with 19.6 wt % for Pt/C and 20.1 wt % for Ru/C in the starting mixture. The above fact confirmed that Pt and Ru particles could also be efficiently supported on carbon using microwave-assisted polyol heating process in the presence of carbon.

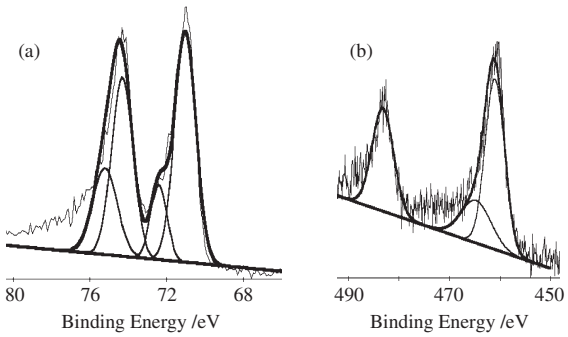

Figure 1. XPS of (a) Pt 4f of Pt/C and (b) Ru 3p of Ru/C.

Figure 1 shows Pt 4f and Ru 3p region of the XPS spectra of the microwave-synthesized Pt/C and Ru/C. As shown in Figure 1a, Pt 4f signal consists of two pairs of Pt peaks. The more intense peaks (71.0 and 74.3 eV) are due to metallic Pt (0). The second set of doublets (72.4 and 75.2 eV), could be assigned to the Pt(II) chemical state in PtO and $Pt(OH)_2$. The Pt(0):Pt(II) ratio can be calculated to be 80:20 according the relative intensity of the two Pt $3p_{7/2}$ photoemissions. As shown in Figure 1b, the binding energies of Ru $3p_{3/2}$ at 461.0 eV and Ru $3p_{1/2}$ at 483.2 eV correspond to photoemission from Ru metal, and the binding energies of Ru $3p_{3/2}$ at 464.7.0 eV correspond to photoemission from oxidized Ru (IV) surface species. The relative intensity of the two observed Ru $3p_{3/2}$ photoemissions gives a Ru(0):Ru(IV) atomic composition of about 72:28.

Figure 2 shows XRD pattern of the Pt/C and Ru/C. Figure 2a shows that Pt supported on XC-72 forms a face-centered cubic structure and has major peaks at about $2\theta = 39.7°$(111), 46.2° (200), 67.4°(220), and 81.2°(311). These peaks could be indexed using the standard powder diffraction file of Pt (JCPDS number 1-1311). The diffraction peak at $2\theta = 39.7°$ for Pt (111) corresponds well with the interplaner spacing of $d_{111} = 0.227$ nm. As shown in Figure 2b, the XRD pattern of Ru/C shows only a single diffuse peak at $2\theta = 43.1°$, although two more diffraction peaks at $2\theta = 42.1°$ and 44.0°, respectively are expected from the standard powder diffraction file (JPCDS number 6-663). The smallness of the Ru particles supported on

carbon probably makes it difficult to resolve the two closely spaced diffraction peaks because of peak broadening effects. The lack of distinct diffraction peaks was also previously reported by Yan et al. for polymer-stabilized Ru nanoparticles prepared by the microwave polyol process.[9]

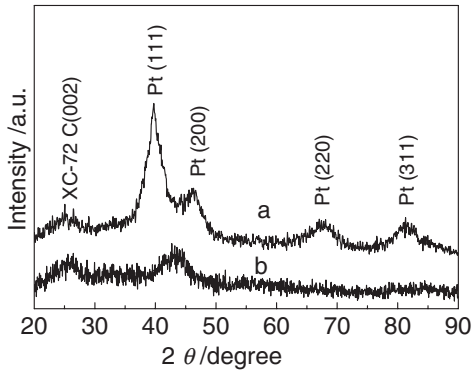

Figure 2. XRD patterns of (a) Pt/C and (b) Ru/C.

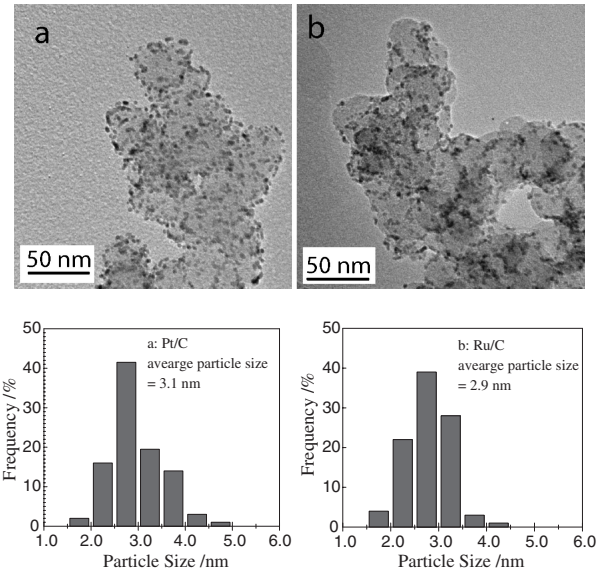

Figure 3. TEM images of (a) Pt/C, (b) Ru/C and their particle size distributions.

Repeated TEM observations showed that the Pt and Ru nanoparticles were uniformly distributed on the carbon surface. As shown in Figure 3a, microwave-synthesized carbon-supported Pt nanoparticles have a significantly small average diameter (3.1 nm) and a narrow particle size distribution. Most of Pt particles are between 2.0 and 4.0 nm, with only a few particles larger than 4.5 nm. The TEM image of carbon supported Ru nanoparticles in Figure 3b shows that the Ru particles are uniform in size with an average diameter of 2.9 nm. Most of Ru particles are between 2.0 and 3.5 nm, with only a few particles larger than 3.5 nm. Therefore, the microwave heating of the ethylene glycol solution of H_2PtCl_6 and $RuCl_3$ in the present of carbon had evidently promoted the uniform dispersion of Pt and Ru nanoparticles on the carbon surface.

The rate of metal precursor reduction is known to impose a deciding effect on the size of the metal nanoparticles. Ethylene glycol has a high dielectric constant (41.4 at 298 K) and carbon also is a good microwave absorber, so the mixture of the ethylene glycol and carbon can be rapidly heated by microwave irradiation. The temperature of the mixture was tested to be about 160–170 °C by microwave heating for 50 s. At high temperature, ethylene glycol would be decomposed to yield in-situ reducing species to reduce the metal ions to their zero valent state.[10,11] The fast microwave heating accelerates the reduction of the metal precursor and the nucleation of small metal clusters. The microwave heating of liquid samples also reduces the temperature and concentration gradients in the reaction medium, thereby providing a more homogenous environment for the nucleation and growth of metal particles. After platinum and ruthenium salt precursors were mixed with XC-72 carbon, the Pt and Ru ions would interact with and attach to the surface functional groups such as carboxyl, hydroxy, and carbonyl group on the carbon by a coordination reaction or an in-exchange reaction, thus functioning as a nucleation precursor that finally reduced to produce Pt and Ru nanoparticles on the carbon.[12] The presence of carbon support also interrupts Pt and Ru nanoparticle agglomeration. Therefore, the nearly monodispersed Pt and Ru with a sharp size distribution on the carbon could be prepared by the microwave assisted polyol heating process.

In summary, we have demonstrated that the microwave-assisted polyol process is a good technique for the synthesis of carbon-supported Pt and Ru nanoparticles. Since the metal nanoparticles prepared as such could be dispersed very well on carbon and had narrow particle size distributions, it would be expected that microwave-synthesized Pt/C and Ru/C should have very high catalytic performance.

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