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Sonochemical synthesis of tungsten carbide–palladium nanocomposites and their electrocatalytic activity for hydrogen oxidation reaction

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ABSTRACT

Nanocomposites between β-WC and Pd nanoparticles supported on carbon are synthesized and their electrocatalytic properties for the hydrogen oxidation reaction have been investigated. The Pd nanoparticles are obtained by a chemical reduction reaction of $PdCl_2$ and the β-WC nanoparticles by a sonochemical decomposition of $W(CO)_6$ on Pd-loaded carbon followed by heat-treatment. Depending on the relative amounts of W to Pd, the Pd nanoparticles can be reacted with W to form Pd–W alloy nanoparticles. The Pd–W alloy, whose composition is estimated to have W less than 18 at.% based on its lattice parameter, lost most of the catalytic activity of Pd. On the other hand, the nanocomposite between β-WC and pure Pd shows an enhanced activity compared with that of Pd nanoparticles alone. This enhancement can be explained with the H^+-spill-over to β-WC.

1. Introduction

Fuel cells constitute the alternative power sources that can answer the presently urgent concerns on the depletion of fossil fuels and the global warming [1]. However, several important technical and socio–economical issues need to be resolved before the fuel cells can find wide spread uses. The high cost, limited resources, and the CO poisoning of Pt, which most of the fuel cells rely on as the catalyst material, are at the top priority of the issues [2,3]. Numerous research works have been conducted to find alternative catalyst materials that can replace Pt partly or completely. Pd is one of them for its similarity to Pt in many aspects. However, Pd alone does not seem to be active enough for this purpose. Therefore, alloys and composites of Pd have been widely explored in hydrogen oxidation (HOR) and oxygen reduction reactions (ORR) [4–7].

Many researchers have considered early transition metal carbides such as tungsten carbide as alternative electrocatalyst or co-catalyst materials [8–11]. This is mainly because some of the metal carbides have been reported to have band structures similar to that of Pt [11]. Indeed, there have been reports on the electrocatalytic activity of tungsten carbides, but with much reduced activities compared with that of Pt [12]. Therefore, recent works on tungsten carbides are more focused on their co-catalyst effects with Pt. Recently we have reported that WC_{1-x} (also known as β-WC) nanoparticles can increase the electrocatalytic activity of Pt nanoparticles in the hydrogen oxidation reaction (HOR) through the H^+-spill-over effect [10].

There are three phases of tungsten carbides, namely W_2C, WC (or α-WC) and β-WC. The former two are thermodynamic phases and have been studied in many electrocatalysis systems [11,12]. On the contrary, the β-WC phase is a high temperature phase (stable above 2785 °C) and has not been studied until our recent report. On the other hand, according to a recent theoretical study on the electronic structures of the three tungsten carbides, the density of states at the Fermi level are in the order β-WC > α-WC > W_2C, suggesting that β-WC may be the most active among the three [13]. Therefore, it seemed worthwhile to study the co-catalyst effects of β-WC with metals other than Pt.

In the present study, we studied the effects of β-WC nanoparticles to the electrocatalytic activity of Pd in HOR. We used the sonochemical method to obtain β-WC nanoparticles on top of the Pd particles. We found that depending on the amount of W, Pd–W alloy nanoparticles are formed, which led us to study the catalytic properties of composites between β-WC and nanoparticles of Pd or Pd–W alloy. The details of the synthesis and characterization are discussed herein.

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2. Experimental

The materials in this study were synthesized through the chemical reduction of palladium(II) chloride ($PdCl_2$) and/or the sonochemical reaction of tungsten hexacarbonyl ($W(CO)_6$) on supports. Graphitic Ketjen Black (GKB), obtained through a high temperature heat-treatment of Ketjen Black (KB), was kindly donated by Dr. C. Pak at SAIT and was used as the support for all the syntheses.

Pd nanoparticles supported on GKB (Pd/C) were prepared by the borohydride reduction method. $PdCl_2$ (Aldrich, 99.9+%) was dissolved in a HCl solution with two equivalents of HCl per $PdCl_2$ to prepare a 10 mM H_2PdCl_4 precursor solution. 2 mmol of $Na_3C_6H_5O_7$ (0.588 g) was dissolved in 400 mL of de-ionized water and 100 mL of the H_2PdCl_4 precursor solution was added. 0.32 g of GKB was dispersed in 250 mL of de-ionized water for 1 h by sonication. These two solutions were mixed with vigorous stirring for 10 min and excess cold $NaBH_4$ solution was added rapidly into the mixture. The solution was stirred vigorously for 12 h at room temperature. After filtration and rinsing with ethanol for several times, the resultant black powder was placed in a vacuum desiccator for drying for 12 h.

Pd/C so-synthesized and GKB were used as the support for the sonochemical reaction of $W(CO)_6$. $W(CO)_6$ (Aldrich, sublimed, 99.9+ %) and a support were dispersed in 30 mL of *n*-hexadecane (Aldrich, anhydrous, ≥99%). The mixed solution was sonic-irradiated with a high-intensity ultra sonic horn (Sonic and Materials, model VC-500, amplitude 25%, 13 mm solid probe, 20 kHz) at 353 K for 3 h under an argon flow. The slurry was filtered and the resultant solid was washed with *n*-pentane (Aldrich, 98%) and dried under a vacuum. The black powder was heat-treated at 723 K for 12 h under a hydrogen gas flow at a flow rate of 70 mL min^{-1}.

Powder X-ray diffraction (XRD) patterns of these samples were recorded on a diffractometer (DC/max-2000, Rigaku, Cu Kα). The shape and size distribution of the nanoparticles were studied by a high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3011 300 kV). The elemental compositions were obtained with an energy dispersive X-ray spectroscopy (EDS) analyzer attached to a field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) with a × 5000 magnification. For each sample, five different locations were measured and their data were averaged. An EDS equipped on the TEM was also used to identify elements in small areas.

The electrocatalytic activity was investigated by a potentiostat (Ivium compactstat) and a standard three-electrode electrochemical cell equipped with a glassy carbon rotating disk electrode (RDE, AUTOLAB), a Ag/AgCl reference electrode and a Pt net counter electrode. 10 mg of an electrocatalyst was dispersed in 5 g of de-ionized water by sonication for 30 s. 5 μL of the slurry was dropped onto the top of the working electrode ($r = 1.5$ mm) and dried at room temperature. 5 μL of a 0.05 wt% Nafion solution was applied for mechanical protection of the electrode material during the rotation of RDE. The working electrode was pretreated with an electrochemical cleaning process, usually by a cyclic voltammetry (CV) at a rapid scan rate before each measurement. The CV measurements were carried out in a 0.1 M $HClO_4$ aqueous solution at a scan rate of 50 mV s^{-1} with N_2 purging. The electrocatalytic HOR activity was estimated with the linear sweep voltammetry in a H_2-saturated 0.1 M $HClO_4$ electrolyte. The measurements were performed under various rotation rates from 400 to 3600 rpm at a scan rate of 5 mV s^{-1}.

3. Results and discussion

In this study, we synthesized composite electocatalysts composed of Pd and β-WC nanoparticles in order to see the synergistic effects between them. The synthesis of β-WC nanoparticles was achieved by the sonochemical decomposition of $W(CO)_6$ in the presence of a support. In general, the mechanism in sonochemical synthesis is explained with the acoustic cavitation mechanism [14]. The high frequency oscillation of ultrasound generates bubbles which undergo oscillatory growth and, finally, collapse after reaching a critical size. This event of bubble collapse can generate extreme conditions of local temperature up to ∼5000 K and pressure up to ∼1800 atm. While the major part of the implosion energy is wasted, a part of it is converted into chemical energy and is used to break the chemical bonds of the $W(CO)_6$ precursor molecules to form β-WC nanoparticles.

The reaction on a carbon support produced β-WC nanoparticles dispersed on the support (β-WC/C). We used GKB as the carbon support, which is known to have a higher conductivity than KB. When a Pd-loaded GKB (Pd/C), obtained by reducing $PdCl_2$ with $NaBH_4$ in the presence of GKB, was used as the support, a nanocomposite composed of Pd and β-WC nanoparticles was obtained. By varying the amount of $W(CO)_6$ in the sonochemical reaction, two samples with different W-contents were synthesized. These will be denoted as β-WC(12)/Pd/C and β-WC(39)/Pd/C, where the numbers are the W-contents defined as W/(Pd + W), based on the elemental compositions from the EDS data as shown in Table 1.

According to the phase diagram of the W–C system, β-WC is a high temperature phase, stable above 2785 °C [15]. The conventional synthesis method such as carburization of tungsten oxide precursors cannot generate such high temperatures. Therefore, most of the studies on tungsten carbides have been restricted to W_2C or α-WC [11,12]. Probably because of this reason, β-WC has attracted less attention as a catalyst compared with the other two tungsten carbides. On the other hand, nanoparticles of β-WC can be synthesized by a sonochemical reaction method due to the aforementioned extreme conditions generated by this method [10,16,17]. Previously, we showed that the deposition of the W-precursor occurred preferentially on solid supports and the yield increased as the mass of the support increased. These observations agree well with the mechanism of the sonochemical decomposition process [10]. Therefore, in the present system, in which both the Pd nanoparticles and the exposed surface of GKB can function as the deposition sites, it is expected that the deposits are formed on the Pd nanoparticles preferentially.

Table 1
Characterization data of Pd and/or β-WC nanocomposite electrode materials.

Catalyst	Pd[a] (at.%)	W[a] (at.%)	C[a] (at.%)	Particle[b] size (nm)	Cell parameter[c] (Å)
β-WC(12)/Pd/C	2.40	0.34	97.26	10.6	3.894
β-WC(39)/Pd/C	2.62	1.70	95.68	12.4	3.879
Pd/C	2.46	0	97.54	5.3	3.940
β-WC/C	0	1.61	98.39	3.4	4.171

[a] From EDS.
[b] Calculated by the Scherrer's formula.
[c] Based on fcc structures.