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Radiochemical synthesis of a carbon-supported Pt–SnO_2 bicomponent nanostructure exhibiting enhanced catalysis of ethanol oxidation

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HIGHLIGHTS

- Ethanol oxidation catalysis was enhanced by Sn-addition, far less than ever reported.
- Pt–SnO_2 contact is crucial to the catalysis enhancement, alloying of Sn is not necessary.
- Nano-scaled intimate contact between Pt and SnO_2 was directly observed.

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ABSTRACT

Carbon-supported Pt–SnO_2 electrocatalysts with various Sn/Pt molar ratios were prepared by an electron beam irradiation method. These catalysts were composed of metallic Pt particles approximately 5 nm in diameter together with low crystalline SnO_2. The contact between the Pt and SnO_2 in these materials varied with the amount of dissolved oxygen in the precursor solutions and it was determined that intimate contact between the Pt and SnO_2 significantly enhanced the catalytic activity of these materials during the ethanol oxidation reaction. The mechanism by which the contact varies is discussed based on the radiochemical reduction process.

1. Introduction

Bicomponent nanoparticle materials containing two phases, such as a metal and a ceramic, have attracted significant attention from materials scientists due to their interesting and potentially important properties. Through the appropriate choice of the constituent phases and the morphology of the primary catalyst and its promoter, the catalytic activities of these materials may be significantly enhanced. Jiang et al. have reported that a structure composed of Pt and Sn showed enhanced catalysis of the ethanol oxidation reaction (EOR) occurring at the electrode of a direct ethanol fuel cell (DEFC) (Jiang et al., 2004; Jiang et al., 2005; Zhou et al., 2003). They attributed this increased catalytic activity to the contact between a SnO_2 phase and the Pt metal, which was partially alloyed with Sn. Li et al. (2010) reported a catalyst composed of PtRh–SnO_2 that also showed enhanced EOR activity. These improvements are believed to be associated with multi-valence states of the non-noble metal generated through the bicomponent contact. In these prior reports, the optimum composition of such materials is discussed, but the degree of contact obtained between the Pt and the SnO_2 is not made clear. It is important to both understand and control the extent of contact between the two components, although it is not an easy task to prepare samples with controlled bicomponent contact. Therefore, it is necessary to employ various methods of synthesis under a number of different conditions to assess the best means of producing appropriate samples.

In this work, we report the radiochemical synthesis of carbon-supported Pt–SnO_2 and its enhanced electrocatalytic activity in the EOR. The radiochemical synthesis of bimetallic alloy and core–shell nanoparticles has been reported by Belloni (2006). However, there have been only a few reports on radiochemical synthesis of

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nanoparticles containing different phases. We have previously succeeded in synthesizing bicomponent nanoparticles immobilized on supports, such as Pt–Cu alloy and CuO in close contact with one another supported on γ-Fe_2O_3 (Kugai et al., 2011; Yamamoto et al., 2010). We have also reported the application of this radiochemical method to the synthesis of Pt–SnO_2 nanoparticles (Okazaki et al., 2014). In the present study, we attempted to control the extent of contact between the Pt and SnO_2 phases by changing the dissolved gas in the precursor solution. The resulting degrees of contact were analyzed by scanning transmission electron microscopy (STEM) images and the synthetic process is discussed from a radiochemical point of view.

2. Experimental

2.1. Material synthesis

The procedure and mechanism associated with the electron beam irradiation method are described only briefly here, since the details have been previously reported (Seino et al., 2008). A 66.6 mg quantity of carbon powder (Vulcan XC-72R, Cabot) was dispersed in an aqueous solution containing the metal precursors $H_2PtCl_6 \cdot 6H_2O$ (Wako) and $SnCl_4 \cdot 5H_2O$ (Wako). Five different precursor mixtures, each 50 mL in volume, were prepared by varying the Sn concentration so as to produce Sn/Pt molar ratios from 0 to 4, keeping the Pt concentration constant at 0.5 mM. The resulting products are designated herein as "Pt1Sn*x*," where *x* is the molar ratio. The total metal concentration in each reaction mixture, Pt+Sn, ranged from 6.82 to 20.1 wt%. In addition, 1 vol% 2-propanol (Wako) was added to scavenge oxidative hydroxyl radicals formed during the irradiation. Dissolved air was removed from some reactant mixtures by purging with Ar gas for 10 min. Samples produced in a reaction mixture in which air remained dissolved are herein designated by appending "_air" to the sample name, while samples produced with Ar purging are designed with "_Ar." In each case, the reaction solution was well mixed and sealed in a 100 mL glass vial. As noted, each sample was denoted in accordance with its preparation conditions, and the samples are summarized in Table 1. Each vial was irradiated with a 4.8 MeV electron beam for several seconds at room temperature to a surface dose of 20 kGy. The Gy is a unit identifying the energy absorbed by a given mass of substance and is equivalent to 1 J/g. The irradiated samples were subsequently washed with pure water and dried at 60 °C overnight to obtain samples in powder form.

Table 1
Sn/Pt ratios in precursors and products, average particle sizes, and standard deviations of particle sizes of catalyst specimens.

Sample ID	Sn/Pt molar ratio		Average particle size (nm)	Standard deviation (nm)
	Precursor	Product		
Pt_air	–	–	4.0	1.0
Pt1Sn1_air	1	0.13	4.6	2.4
Pt1Sn2_air	2	0.18	5.0	2.2
Pt1Sn3_air	3	0.49	5.6	2.4
Pt1Sn4_air	4	0.67	4.6	1.6
Pt_Ar	–	–	3.1	1.1
Pt1Sn1_Ar	1	0.19	4.0	1.5
Pt1Sn2_Ar	2	0.62	4.0	1.4
Pt1Sn3_Ar	3	0.99	4.5	1.6
Pt1Sn4_Ar	4	1.3	4.2	1.6

2.2. Evaluation of materials and catalytic properties

The chemical compositions of the product powders were analyzed by inductively couple plasma atomic emission spectroscopy (ICP-AES, Shimadzu, ICPE-9000) and their microstructures were examined via TEM (Hitachi, H-8100, 200 kV). The nanoscale distributions of Sn and Pt in the samples were investigated by spherical aberration corrected STEM instrumentation (FEI, Titan[3] G2 60-300) equipped with units allowing energy dispersive X-ray (EDX) spectroscopy and high angle annular dark field (HAADF)

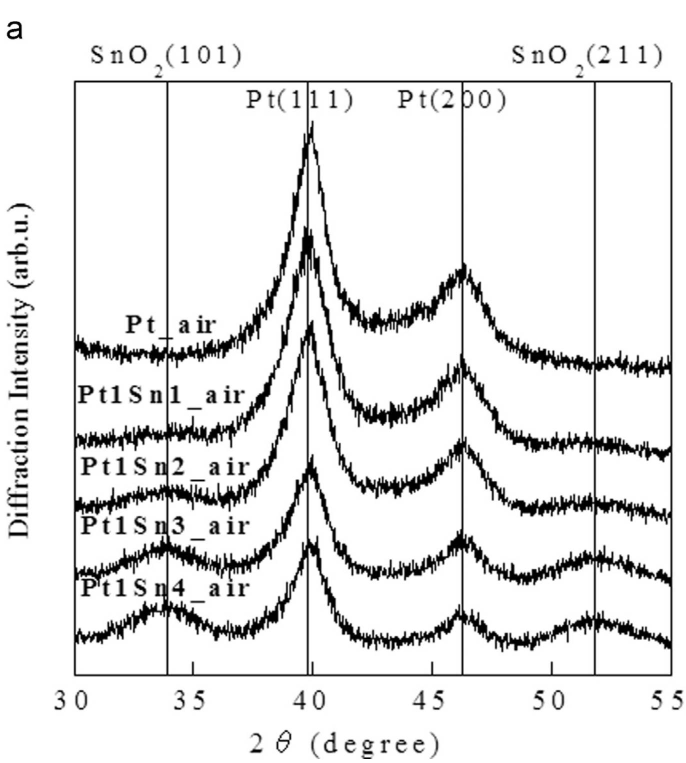

Fig. 1. X-ray diffraction patterns of catalyst samples with various Sn/Pt ratios: (a) air exposed samples and (b) samples with Ar gas purge.