

Novel Synthesis and Atomic Level Characterization of PtSn/C Nanocatalysts for Direct Ethanol Fuel Cell Applications

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Introduction

The depleting amount of fossil fuels and the recent concerns about global warming have been the driving force for developing alternative and renewable energy sources such as biomass-derived liquid fuels. For applications in transportation or portable devices, direct ethanol fuel cell (DEFC) has recently attracted attention because of its non-toxicity, higher power density and renewability. The PtSn/C nanocatalyst is now considered as the most effective catalyst for the anode performance of DEFC [1]. The optimum Pt/Sn ratio and their degree of alloying, however, still remain controversial; furthermore, the catalyst preparation procedure can significantly affect the catalyst's nature and performance [2-3]. To better control the composition profile as well as the size distribution of PtSn nanoparticles, we recently focused on developing precisely defined molecular complexes as precursor materials. We expect that uniform dispersion of such molecular complexes onto catalyst supports, such as carbon black powders, and the subsequent controlled reduction processes may provide a novel route to fabricate PtSn nanoparticle catalysts with better alloying, desirable stoichiometry, a narrow particle size distribution and a better spatial distribution.

Materials and Methods

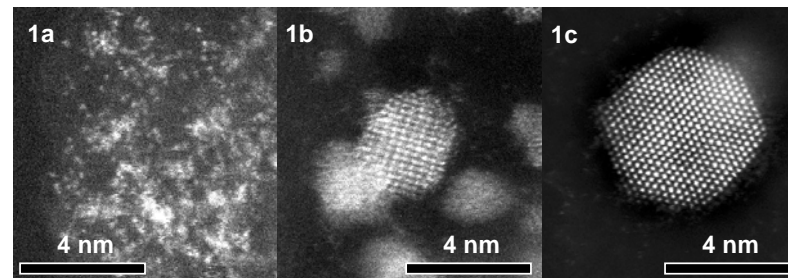
The molecular complex, $(\text{Ph}_3\text{P})_2(\text{H})\text{Pt}(\mu\text{-SnPh}_2)(\mu\text{-}\eta^2\text{-H-SnPh}_2)\text{Pt}(\text{PPh}_3)$ (**1**), was prepared by a 1:1 stoichiometry reaction between Ph_2SnH_2 and the Pt(0) complex, $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$ in toluene- d_8 solvent at room temperature under an argon atmosphere [4]. The dinuclear complex (**1**) was characterized by multinuclear ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectroscopy and elemental analysis. Molecules of complex (**1**) were then dispersed onto Vulcan XC-72 carbon black powders (10% of (**1**) by weight) via an impregnation method. The precursor materials were dried under inert gas environment and then were either reduced ex situ in a tube furnace or in situ inside an electron microscope. The final PtSn/C bimetallic nanocatalysts were characterized by sub-Ångström resolution electron microscopy techniques. High-angle annular dark-field (HAADF) images [5] were acquired using a JEOL 2200FS instrument equipped with a CEOS Co. aberration corrector which provides a nominal image resolution of about 0.07 nm. Catalyst precursor materials were heated in-situ, using a novel heater assembly provided by Protochips Inc. to understand the formation processes of the PtSn alloy nanoparticles and the structural evolution of the PtSn/C nanocatalysts.

Results and Discussion

The preparation of complex (**1**) involves the initial activation of one of the Sn-H bonds in Ph_2SnH_2 at the Pt(0) center in $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)$ to provide the initial mononuclear complex, $(\text{Ph}_3\text{P})_2\text{Pt}(\text{H})(\text{SnHPh}_2)$ which reacts further to produce the final bimetallic complex (**1**) [4]. The ^1H NMR and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra confirmed the molecular structure of the

synthesized complex (**1**) [4]. The loading of the molecular complex (**1**) onto E-TEK Vulcan XC-72 carbon black was accomplished by the impregnation method. Ex situ reduction of the above prepared precursor materials were performed in a tube furnace at different temperatures with a flowing gas mixture (5% H_2 + 95%Ar).

In situ heating of the precursor materials inside the JEOL 2200FS microscope provided insights into the diffusion processes of molecules and atomic clusters and how the PtSn nanoparticles evolved. Figure 1a shows a sub-Ångström resolution HAADF image of the molecular precursor material, clearly revealing individual metal-containing monomers and clusters finely dispersed onto the surfaces of the carbon black powders. Figure 1b shows an image of the same sample after in situ heating at 500°C for about 30 minutes, revealing the formation of small alloy crystallites. Figure 1c shows an image of the same sample after heating at 850°C for about 30 minutes, showing the arrangement of surface atoms; the 4-nm PtSn alloy nanoparticle primarily consists of {111} facets and surface steps. The image also reveals the presence of many individual monomers moving on the surfaces of the carbon black. Detailed phase analyses and structural evolution with temperature have been investigated.



Significance

The utilization of pre-formed and well-defined bimetallic/multimetallic clusters as catalyst precursors provides a novel route to develop desirable alloy nanoparticle catalysts and sub-ångström resolution electron microscopy techniques provide deep insights into the surface atomic arrangement of metal and alloy nanoparticles as well as their structural dynamics.

References

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