



Carbon nanofiber supports for the preparation of Pt-based metal nanoparticles with high tolerance to sintering

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ABSTRACT

Fishbone-typed carbon nanofibers (CNFs) that were formed by methane decomposition over silica-supported Ni catalysts were used as catalytic supports for Pt or Pt–Co alloy nanoparticles. The treatment of CNFs with concentrated HNO₃ led to the formation of porous structures as well as to the introduction of oxygen-containing functional groups. Pt metal particles of a few nanometers in diameter could be stabilized on the CNFs treated with HNO₃ and showed a high tolerance to sintering at high temperatures, whereas Pt metal particles supported on the CNFs without any treatment were seriously aggregated at high temperatures. The porous structures and functional groups in the CNFs worked as anchoring sites for Pt metal nanoparticles. Thus, Pt–Co alloy particles of a few nanometers in diameter could be prepared by using the CNF support since the CNFs inhibited the sintering of the alloy particles during the treatment at high temperatures to allow for alloy formation.

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1. Introduction

Precious metals such as Pt, Rh and Ru supported on carbon materials are widely used as active catalysts for various reactions. Pt metal supported on carbon black has been utilized as an electrocatalyst at the cathode for the oxygen reduction reaction (ORR), and utilized as an electrocatalyst at the anode for the hydrogen oxidation reaction in polymer electrolyte fuel cells (PEFCs). Pd, Pt or Ru catalysts supported on activated carbons catalyze the hydrogenation of ketones and aldehydes to form alcohols. Reducing the precious metal loading without compromising the catalytic activity is an important requirement because of the high cost of such precious metals and their limited resource. The catalytic performance of precious metals supported on carbon materials strongly depends on the morphology and surface structure of the carbon materials [1–4]. Recently, one-dimensional carbon materials such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been utilized as supports for precious metals [5–7]. Pt catalysts supported on CNTs and CNFs show a higher activity toward ORR when compared to Pt catalysts supported on carbon black, which are used in state of the art PEFCs [7–12]. The catalytic performance of Pt metal supported on CNTs and CNFs is enhanced by the interaction between the Pt metal and these carbon nanostructures. An

additional benefit of CNTs and CNFs as electrocatalyst supports is their potential to improve the electron conductivity and mass transport. Their one-dimensional structures allow effective fuel and oxidant access to the densely scattered triple phase boundaries. Thus, the use of CNTs and CNFs as supports has the potential to reduce precious metal loading in the catalysts. Precious metals supported on CNTs and CNFs also show a specific catalytic performance for the hydrogenation of α,β -unsaturated aldehydes such as cinnamaldehyde [13–16]. Pt or Pd catalysts supported on CNTs and CNFs catalyze the selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols, whereas saturated alcohols and aldehydes are inevitably formed on these metal catalysts supported on conventional carriers such as activated carbon, silica and alumina.

CNTs and CNFs can be formed by catalytic chemical vapor deposition [17–19]. Reactant molecules, such as CO, hydrocarbons and alcohols as carbon sources, are contacted with Fe, Co or Ni metal catalysts at high temperatures, to form CNTs and CNFs. The yields of CNTs and CNFs strongly depend on the reaction conditions such as the type of catalysts and reactant molecules, and reaction temperatures [20–22]. Nonetheless, the yields of CNFs are extremely higher than that of CNTs [23,24]. Thus, CNFs are promising supports for precious metals. CNFs formed by catalytic chemical vapor deposition are one of the fishbone-typed CNFs, meaning that graphene sheets are oriented at a uniform angle to the central axis of the nanofibers [17]. The edges of stacked graphene sheets form the outer walls of the CNFs. When metal particles are supported on

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