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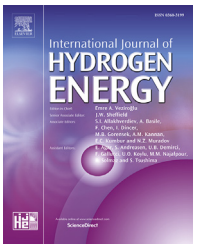

Enhancement of hydrogen storage capacity of multi-walled carbon nanotubes with palladium doping prepared through supercritical CO_2 deposition method

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ABSTRACT

Pd doped Multi-Walled Carbon Nanotubes were prepared via supercritical carbon dioxide deposition method in order to enhance the hydrogen uptake capacity of carbon nanotubes at ambient conditions. A new bipyridyl precursor that enables reduction at moderate conditions was used during preparation of the sample. Both XRD analyses and TEM images confirmed that average Pd nanoparticle size distribution was around 10 nm. Hydrogen adsorption and desorption experiments at room temperature with very low pressures (0 −0.133 bar) were conducted together with temperature programmed desorption (TPD) and reduction (TPR) experiments on undoped and doped materials to understand the complete hydrogen uptake profile of the materials. TPD experiments showed that Pd nanoparticles increased the hydrogen desorption activity at moderate temperatures around at 38 °C while for undoped materials it was determined around at 600 °C. Moreover, a drastic enhancement of hydrogen storage was recorded from 44 μmol/g sample for undoped material to 737 μmol/g sample for doped material through adsorption/desorption isotherms at room temperature. This enhancement, also verified by TPR, was attributed to spillover effect.

Introduction

Hydrogen Technologies, which enable the usage of hydrogen as one of the promising renewable and clean energy sources, are of great interest due to the decrease in fossil energy resources and also the environmental concerns related to fossil fuels [1,2]. In order to provide sustainability of Hydrogen Energy, efficient and safe storage conditions of Hydrogen are considered as one of the most important issues because of the high cost and risks of these technologies [3–7]. Currently, the disadvantages of conventional storage technologies increase the interest in nanomaterials which can be a good solution for hydrogen storage at ambient temperatures and moderate

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pressures rather than high cost high-pressure cryogenic systems. Carbon nanotubes (CNTs) are known as good candidates for this purpose with their low mass density, high surface area, narrow and nanometer pore size distribution [8–17]. However, when considering ambient temperatures and moderate pressures, it is necessary to improve their hydrogen adsorbing capacities. Doping certain transition metals on CNTs is one of the effective methods to improve these properties [18–23]. When compared to other transition metals, palladium (Pd) shows a strong hydrogen adsorption performance for hydrogen if well dispersed on CNTs [23–30]. It is attributed to the spillover process which is described in the literature as the dissociation of dihydrogen on the metal, resulting in migration of hydrogen atoms through the metal particles and diffusion on the multi-walled CNT (MW-CNT) supports which are composed of embedded layers of CNTs [23–38]. Hence, hydrogen uptake of CNTs can be improved effectively by employing this mechanism. In order to provide this strategy, the key step is to have uniformly dispersed Pd nanoparticles on MW-CNTs.

It is known that the degree of dispersion and consequently particle size distribution of metal atoms on carbon nanotubes is directly dependent on the deposition method [29]. So far different methods were reported to synthesize metal doped CNT or MW-CNTs [25–41]. Generally, most of these synthesis techniques such as wet impregnation, sputter coating, pyrolysis, thermal evaporation, and electrodeposition have disadvantages for obtaining well-dispersed structures due to poor adhesion, impurities from precursors or agglomeration of nanoparticles resulting in unsatisfactory size and shape control [20–30,39–42].

Supercritical carbon dioxide ($scCO_2$) deposition is relatively new, environmentally friendly and powerful method to prepare well-dispersed nanoparticles among these techniques [45–50]. Moreover, with other preparation routes, it is hard to control the nanoscale particle shape and size with desirable dispersion. In this method, a metal complex is dissolved within the $scCO_2$ fluid, followed by adsorption or sorption of the metal complex onto the support, and finally, the adsorbed complex is converted to metal species with either chemical or thermal reduction. Because $scCO_2$ has both gas and liquid phase properties at supercritical state (7.38 MPa and 304.2 K) such as excellent diffusivity, solvent capability, low viscosity, high density, zero surface tension, it is considered as a promising transport medium for nanomaterial preparation especially with complicated surfaces [44,45].

In literature, Pt [46,49], Ni [47] and Pd [46,48] doping was employed on MW-CNTs through $scCO_2$ deposition method and reported hydrogen storage enhancement of MW-CNTs up to 4–5 more than undoped CNTs. Chen et al. [48] showed 4 wt % Pd doping via $scCO_2$ deposition on CNTs had the best the hydrogen adsorption capacity due to spillover effect among different loadings of Pd ranging between 1 and 8 wt%. Besides, they prepared similar materials without $scCO_2$ deposition and showed the relation between effective nanoparticle size control and improvement of hydrogen storage as a function of triggered spillover mechanism.

On the other hand, hydrogen adsorption/desorption isotherms have an important place to understand the hydrogen storage behavior. Most of the studies reported in literature only worked on hydrogen adsorption isotherms under high pressures between 6 and 10 MPa which includes both chemisorption and physisorption effects. Moreover, especially for $scCO_2$ derived Pd/CNT nanoparticles, the desorption behavior was not clearly deliberated. It must be emphasized here that for hydrogen technology applications it is also important to understand the desorption behavior. Besides, estimations for spillover amounts from adsorption isotherms should also be verified by alternative techniques such as temperature programmed desorption (TPD) and temperature programmed reduction (TPR) tests.

In this work, 4 wt% Pd doped multi-walled carbon nanotubes (Pd/MW-CNTs) were targeted to obtain via $scCO_2$ deposition method in the presence of new precursors which enable moderate chemical reduction conditions to obtain controlled nanoparticle properties. Different from reports in the literature, the hydrogen uptake investigations were conducted under low hydrogen pressures up to 0.01 MPa at room temperature conditions to focus only on the chemisorption effect. Moreover, to have a complete hydrogen performance profile both adsorption/desorption tests of Pd/MW-CNTs at room temperature along with TPD and TPR tests were conducted.

Experimental study

Materials

All materials were used without further purification. Multi-walled carbon nanotube (MW-CNT) was purchased from Sigma Aldrich with a purity of ≥95%. The nanotubes have an outer mean diameter of 6–9 nm with a diameter distribution of 5.5–6.6 nm and the average length was reported as 5 μm in product specifications sheet. The carbon nanotubes were reported to be prepared by Catalytic Chemical Vapor Deposition Method in the presence of Co and Mo catalysts. The bulk density was specified as 0.22 g/cm^3. The BET surface area has been determined to be 176 $m^2\ g^{-1}$ with a pore size of 17.6 nm. Besides, wall number was estimated between 10 and 28 with an average of 21 according to TEM images taken at 10 and 5 nm as shown in Fig. 1.

In order to synthesize the Pd precursor, Palladium chloride and 2,2′bipyridyl materials were purchased from ABCR GmbH (both with a purity of 99%). Moreover, a buffer solution of sodium acetate/acetic acid ($NaCH_3COO/CH_3COOH$) with pH 4.5 was prepared via 36.5–37% hydrochloric acid (HCl) and acetic acid (CH_3COOH) (both purchased from Merck Millipore) with a purity of 99.8% in order to use during precursor synthesis.

For adsorption experiments, ultrahigh pure grade (99.999%) of Hydrogen (H_2), Argon (Ar) and Helium (He) gases (purchased from Linde) were used.

SCF deposition of bis(2,2′bipyridyl)palladium(II) chloride precursors

The deposition of Pd precursors on MW-CNTs was carried out with bis(2,2′bipyridyl)palladium(II) chloride ($[Pd(Pyr)_2]Cl_2$) precursor which was synthesized from 0.312 g $PdCl_2$ in 0.5 ml HCl (35%) with vigorous stirring at 70 °C. After dissolving, 3 ml DI water is added followed by addition of 40 ml $NaCH_3COO/CH_3COOH$ buffer solution. 0.529 g of 2,2′bipyridyl was added to

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