Fabricating series of controllable-porosity carbon nanofibers-based palladium nanoparticles catalyst with enhanced performances and reusability

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ABSTRACT

The porous carbon nanofibers-supported palladium nanoparticles hybrid catalyst was put forward. Highly porous, large specific surface area and uniform distribution without aggregating of palladium nanoparticles in the carbon matrix were achieved by combining eletrospinning, chemical reduction and subsequent calcination methods. Polystyrene and polyacrylonitrile acted as the thermal degradable polymer and the carbon precursor polymer, respectively. A series of characterization of catalyst were carried out to investigate the morphology and materials properties of the precursors and the final porous carbon nanofibers, which including simultaneous thermal analyzer, Brunauer–Emmett–Teller measurements, UV–vis diffuses reflectance spectra, Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, the field emission scanning electron microscope and the field emission transmission electron microscope. Foremost, when it was tested as catalyst for the Heck coupling reaction, the porous carbon nanofibers-loaded palladium nanoparticles catalyst exhibited enhanced activity, excellent stabilization and recyclability. Moreover, PS has the possibility of recycling which is important to develop green chemistry. Overall, the as-made carbon nanofibers-supported palladium nanoparticles catalyst with large porosity was prepared in an easy way and showed enhanced activity in comparision with the pure carbon nanofibers-supported palladium nanoparticles catalyst.

1. Introduction

As being known for the most prospect materials of the 21st century, nanomaterials with their superior functions and the extensive usages became the most investigative point in novel material science. Inorganic/organic composite nanomaterials, such as metals, metallic oxide, inorganic oxide, semiconductor and carbon nanotubes, were doped to polymer substrates to obtain composite nanomaterials with special functions [1–7]. They promised to access to a wide range of potential applications in diverse areas of material science and industry, such as electronics, photonics, mechanics, bioengineering, sensing, and so on [8].

Among many available and advanced multifunctional materials, one dimensional carbon nanofibers (CNFs) have attracted much attention in recent years, because nanostructured carbon provided high chemical stability, large specific surface area and excellent mechanical properties, which benefited that electrodes were used in high-power supercapacitors, composites, energy storages, water treatment system and catalyst support [9,10]. Nanostructure carbon-based fibers obviously offered better performance and more sustainable host materials for metal nanoparticles (NPs) (copper, platinum, Pd, lithium, stannum, ruthenium and so on) than traditional and most reported zeolite, molecular sieve and activated carbon, because they were able to be made directly out of biomass and their porosity [11,12]. Pd NPs have the reputation of being one of the most efficient metals in many fields due to their high catalytic activities to different types of reaction, especially for the formation of C—C bonds, for example, Suzuki and Heck coupling reactions, excellent economic benefits, good electrical conductivity and optical properties [13–16]. To date, Pd NPs with the size below 10 nm possessed remarkable properties because of their precise and ultrafine dimensions. Nevertheless, few reports involved Pd NPs with very small sizes; The most were larger than 10 nm. So far,

the facile and economical preparation of Pd NPs smaller than 10 nm is still challenging [17].

Novel and improved porous morphology polymeric materials have received an increased level of research interest, because they were in great demand for a wide range of applications such as adsorption and ultra-filtration materials, ion-exchange resins as well as supports or carriers for catalysts and reagents [18–20], especially, the preparation of highly porous carbon nanofibers (PCNFs) received significant attention because of their large surface area, well-defined porosity and relatively high electrical conductivity, which were useful to electrodes applied in high-power supercapacitors. The traditional preparation approaches included the phase separation technique (selective dissolution or solvent evaporation) [21–23], template methods [24,25], sol–gel synthesis and thermal treatment or photo degradation one component of blending polymers, for example, Demir et al. have demonstrated the use of this facile thermal treatment method in their fabrication of high specific surface area PCNFs with silicon-containing compounds [26]. Recently, electrospinning attracts immense attention as a versatile and an easy way to prepare a variety of functional polymers, metal oxides and CNFs successfully [27–30]. Porous or hollow fibers can be obtained employing electrospinning with highly volatile solvents or through special treatment following electrospinning [31]. Several research groups attempted to produce PCNFs by blending different components into electrospun fibers. For example, Peng et al. obtained submicrometer CNFs with a nanoporous structure [32]. Wang et al. obtained porous composite nanofibers by electrospinning polyacrylonitrile/polystyrene (PAN/PS) solutions, followed by stabilization and carbonization [33]. Consequently, if Pd NPs catalyst was incorporated into the electrospun PCNFs, the resulting of composite PCNFs would be exhibited the excellent performance and the important application values in future. Most of all, doping carbon with titanium, silicon, chromium, nickel, copper, magnesium, and/or iron initiates resulted in catalytic graphitization of carbon, and hence, highly graphitic structures were able to be produced at lower temperatures. Pd, another metallic element, was able to be used as a dopant for carbon to enhanced catalytic properties [34].

In our observation, there was no report about the preparation and application of PCNFs-supported Pd NPs composite catalyst by combining efficient and low-powered electrospinning and thermal treatment method. In our work, PS and PAN as thermal degradable polymer (TDP) and carbon precursor polymer (CPP) were determined, respectively, and electrospun composite nanofibers based on PAN, different PS contents and palladium chloride ($PdCl_2$) precursors. Based on the previous research work of our research group, some factors affecting the size and shape of Pd NPs were investigated, and the optimum reducing agent, dosage of $PdCl_2$ and the optimum carbonized temperature were determined. When they were employed in nanofabrication, thermal decomposition provided a simple one-step strategy for the creation of porous nanostructures with controlled porosity, which remained a challenge with other methods [35]. The nanopores/nanochannels in the fibers were continuous at about several tens of nanometers in widths and lengths. Most of all, the PCNFs-supported Pd NPs catalyst was almost completely conserved and easily separated from a reaction mixture system, which revealed that the PCNFs-supported Pd NPs catalyst showed excellent stability, good retrieval and reusability because the stable Pd NPs were able to be anchored both on the surface and in the interior of the PCNFs by electrospinning a mixture of polymer matrix and synergy between the metal nanoparticles and the supporting nanofibers in nanoscale. We believe this heterogeneous composite nanopores/nanochannels catalyst can be applied in many fields widely, such as reaction engineering, electrochemistry and aerospace industry.

2. Experimental

2.1. Materials

All the chemicals are of analytical grade and without further purification. Polyacrylonitrile (PAN, Mw = 80,000) was purchased from Kunshan hongyu plastics Co., Ltd. Polystyrene (PS, Mw = 110,000) was purchased from Xindahui chemical company in Tianjin. N,N-Dimethylformamide (DMF, C_3H_7NO, AR, 99.5%) was purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. Absolute ethyl alcohol (C_2H_6O, AR, 99.7%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Palladium chloride ($PdCl_2$, AR), iodobenzene (C_6H_5I, CP, 97%), methyl acrylate ($C_4H_6O_2$, CP, 98%), ethyl acrylate ($C_5H_8O_2$, CP, 98%), n-butyl acrylate ($C_7H_{12}O_2$, CP, 98%) and triethylamine ($C_6H_{15}N$, AR, 99%) were purchased from Sinopharm.

2.2. Fabrication of Pd NPs/PS/PAN composite nanofibers

In our experiments, the preparation process consisted of three steps. First, PAN was dissolved in DMF solution at a concentration of 8 wt% by stirring at room temperature for 12 h. Then, PAN/DMF and $PdCl_2$ powder were blended at mole ratio of 50 (n_{AN}:n_{PdCl2}) intensively stirred 24 h. In the end, the different contents doping of PS were mixed with $PdCl_2$/PAN/DMF to form kinds of blending solution, as well as wt% of PS was respected to PAN in the solution, and the molar ratio of PAN and PS was 10, 20, 30 and 40, respectively. The blending solution was loaded into a jet nozzle. The positive voltage was applied to the tip was 16 kV and the distance between the needle tip and the collector was 18 cm. The as-spun PAN fibers were collected on aluminum foil. The obtained $PdCl_2$/PS/PAN nanofibers were put into hydrogenated kettle and reduced by the hydrogen under 100 °C and 2.5 MPa after nitrogen and hydrogen gas were exchanged three times, respectively. After 5 h, the samples were taken out and characterized by UV–vis, FTIR, FESEM and etc.

2.3. An easy procedure for the preparation of Pd NPs/PCNFs catalyst

For stabilization process, all electrospun nanofibers substrates were placed in a tube furnace and stabilized in air at 250 °C for 2 h for the preoxidation of PAN in the carbonization process and the removing of PS. Then samples were annealed at 450 °C for 2 h under N_2 atmosphere to allow the forming of optimal Pd NPs on/in the carbonized nanofibers. Finally, the substrates were carbonized at 500 °C for 4 h under N_2 atmosphere (2°/min heating rate).

2.4. Characterization

UV–vis diffuses reflectance spectra (DRS) (UV-3600, Shimadzu Corporation) with a variable wavelength from 190 to 600 nm to detect if bivalent Pd was reduced to zerovalent Pd completely or not. Fourier transform infrared spectroscopy (FTIR, 670, Thermo Nicolet Corporation) confirmed the characteristic functional groups of as-spun PS/PAN, $PdCl_2$/PS/PAN, Pd NPs/PS/PAN and Pd NPs/PCNFs. Field emission scanning electron microscope (FESEM, FEG 650, Quanta) and scanning electron microscope (SEM, S-3400, Hitachi Ltd.) characterized the morphology of nanofibers of electrospun on aluminum foil and PCNFs. Field emission transmission electron microscope (FEITEM, F20 S-TWIN, Tecnai) observed the morphology and distribution of Pd NPs in/on the surface of PCNFs and porous structure which distributed in ethanol solution, and then they were dropped upon carbon-coated copper grids. Thermal performances of as-spun PS/PAN nanofibers were evaluated using a simultaneous thermal analyzer (STA PT1600, Linseis). Brunauer–Emmett–Teller measurements (BET,