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Facile one-pot synthesis and characterization of nickel supported on hierarchically porous carbon

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ABSTRACT

Described is a novel, facile route for the synthesis of nickel supported on hierarchically porous carbon (Ni/HPC) using a one-pot co-gelation sol–gel method. Ni/HPC with varying nickel loadings (0.5, 1, 2.5 and 5 wt % Ni) were synthesized and the materials characterized by nitrogen physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) and Raman spectroscopies. The results show a three-dimensional network of disordered carbon with fine nickel nanoparticles of sizes ranging from 8 nm to 13 nm at 0.5 wt% Ni loading which gradually increased with increase in the Ni loading. The carbon structure was retained at the macropore level, but not at the mesoscale where the ordered mesopores were lost on nickel addition. The nickel nanoparticles were observed to grow on the surface of the ligaments. This may make them particularly suitable for low pressure Ni-catalyzed organic transformations e.g., hydrogenations, C–C coupling, C-heteroatom coupling, etc.

1. Introduction

Hierarchically porous materials have garnered considerable attention in recent times due to the high surface area accessible through interconnecting pores at multiple length scales, which gives superior mass diffusion [1]. Owing to these unique properties this class of materials has potential applications in the fields of chromatography [2,3], medicine, electronics, optical switches, sensors, nanoelectronic devices [4], and heterogeneous catalysis [5,6]. Hierarchically porous materials are especially of interest in heterogeneous catalysis where better dispersion of metal particles is expected. Hierarchically porous materials as support for different active metals, including palladium (Pd) [7,8], platinum (Pt), niobium (Nb) [9], nickel (Ni) [10], silver (Ag) [11], have been of interest to catalyst scientists. In the reported literature these metals have been supported on various porous supports including SiO_2 [12], TiO_2 [5], ZrO_2 [7] and carbon [13]. Hierarchically porous carbon (HPC) has been used in applications including catalysis, adsorption, drug delivery, and energy storage as well as conversion [14–16]. Carbon is already widely used as a support for Pt group metals, which are the premium catalysts for many organic transformations such as hydrogenations, reductions, and dehalogenations. Pd supported on carbon is also used as a source of Pd for C–C couplings and C-heteroatom couplings. Because of the high prices of Pt and Pd, Ni is widely used for these reactions, when the activity is sufficiently high [17,18]. Various methods have been reported for the synthesis of Ni supported on carbon (Ni/C), for e.g., soft-template synthesis, [19], a one-step hydrothermal method [20], a solution phase chemical reduction method [21], and a sol–gel method [10].

Among various synthetic strategies reported for making Ni/C, only a few methods have been used to prepare hierarchically porous Ni/C in a monolithic form. Herein we report a facile one-pot, co-gelation sol–gel method for the synthesis of Ni nanoparticles supported on hierarchically porous carbon support (Ni/HPC) with the objective of studying the effect of incorporation of metal nanoparticles on the structural properties of the material. The Ni/HPC material obtained by this technique is suitable for use in catalytic microreactors for flow processes and electrocatalytic reactions, etc.

2. Experimental

2.1. Materials and chemicals

Ethyl alcohol (99%), and tri-block co-polymer Pluronic F127 (99.9%), were obtained from Aldrich, St Louis, MO, USA. Formalin (>99%) was purchased from Macron Chemicals, Philipsburg, NJ, USA. Resorcinol (99.9%) was purchased from Riëdel-De Haën Ag Seelze, Hannover, Germany. 1,6 diamino hexane (DAH, 99.5%) and

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Nickel (II) acetate, tetrahydrate ($Ni(CH_3CO_2)_2(H_2O)_4$, 99+%) were purchased from Acros Organics, New Jersey, USA.

2.2. Synthesis of Ni/C material

The Ni/HPC catalysts were synthesized using a novel co-gelation sol–gel technique. $Ni(CH_3CO_2)_2(H_2O)_4$ was used as Ni precursor. Ni/HPC catalysts with varying Ni loadings (0.5, 1. 2.5, 5 wt%) were prepared. A typical co-gelation synthesis of the 1 wt% Ni/HPC monolith is as follows. In a 250 mL beaker, resorcinol crystals (9 g), 3.75 g of F127, ethyl alcohol (27 g) and deionized (DI) water (27 g) were added to the same beaker and the solution was stirred until a transparent brown solution was observed. DAH (0.2314 g) was added, making the solution basic and the solution was stirred for 15 min (pH ~9.06). The $Ni(CH_3CO_2)_2(H_2O)_4$ salt (0.1415 g) was dissolved in 2 mL DI water and added to the transparent brown solution. The pH of the solution was observed to decrease to 8.79. Formalin solution (13.26 g) was added to the solution and stirred for 10 min. The resultant greyish, cloudy solution was degassed under vacuum for 10 min to remove the trapped air and transferred to cylindrical molds. The molds were sealed with lids and placed in a pressure cooker that contained 50 mL each of EtOH and DI water. The pressure vessel was placed in an oven at 80 °C for 24 h. After cooling to room temperature, the monoliths were removed from the pressure vessel and kept at 55 °C for two days in an oven (to allow maximum evaporation of the solvent). After being removed from the molds the resultant gel monoliths were dried at 100 °C in a tubular furnace under N_2 gas flow for 4 h. The dried monolithic columns were then simultaneously carbonized and the Ni was reduced by heating under 5% H_2/N_2 to 500 °C at a rate of 1 °C/min and then holding the temperature at 500 °C for 2 h. The resulting Ni/C monoliths were black. The remaining monoliths with 0.5, 2.5 and 5 wt% Ni loading were prepared using the same procedure described above. Hierarchically porous carbon (HPC) monoliths without Ni were also synthesized for comparison.

2.3. Material characterization

The nitrogen (N_2) physisorption measurements were recorded on a Quantachrome Nova 2200e pore size analyzer (Boynton Beach, FL) at −197 °C with He mode to determine surface area and void volume of the monoliths, respectively. Interpretation of the isotherms was done with Quantachrome NovaWin software version 11.1, using NL-DFT to obtain the surface area, and the BJH method was applied to the adsorption branch to calculate the pore size distribution. Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Discover with GADDS (General Area Detector Diffraction System) (wavelength Co Kα, 1.79 Å) and a Hi-Star area detector. Scanning electron microscope (SEM) images were taken on a JEOL 7000 FE-SEM (Tokyo, Japan) with diode based back scatter electron detector equipped with an Oxford Energy Dispersive Spectroscopy (EDS) detector for elemental analysis. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Bruker Vertex 70 FTIR, with software version Opus 5.5 and equipped with a Praying Mantis DRIFT attachment at ambient conditions with a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1} using 100 scans. The Raman scans were conducted using a Jobin-Yvon HR800 UV confocal microscope. The excitation line at 632.81 nm came from a He–Ne laser with approximately 12 mW of power at the sample. The shifts were detected using a Peltier cooled CCD detector. The image used a 10× objective lens and all scans were fixed using a 100× objective lens and scanned around the center of the as received monolith.

3. Results

Fig. 1 shows a schematic representation of the synthesis of the Ni/HPC monolithic material. The procedure used for preparation of Ni/HPC monoliths is similar to our earlier reported work describing the one-pot synthesis of palladium supported on carbon (Pd/C) monoliths [8]. The present procedure includes resorcinol-

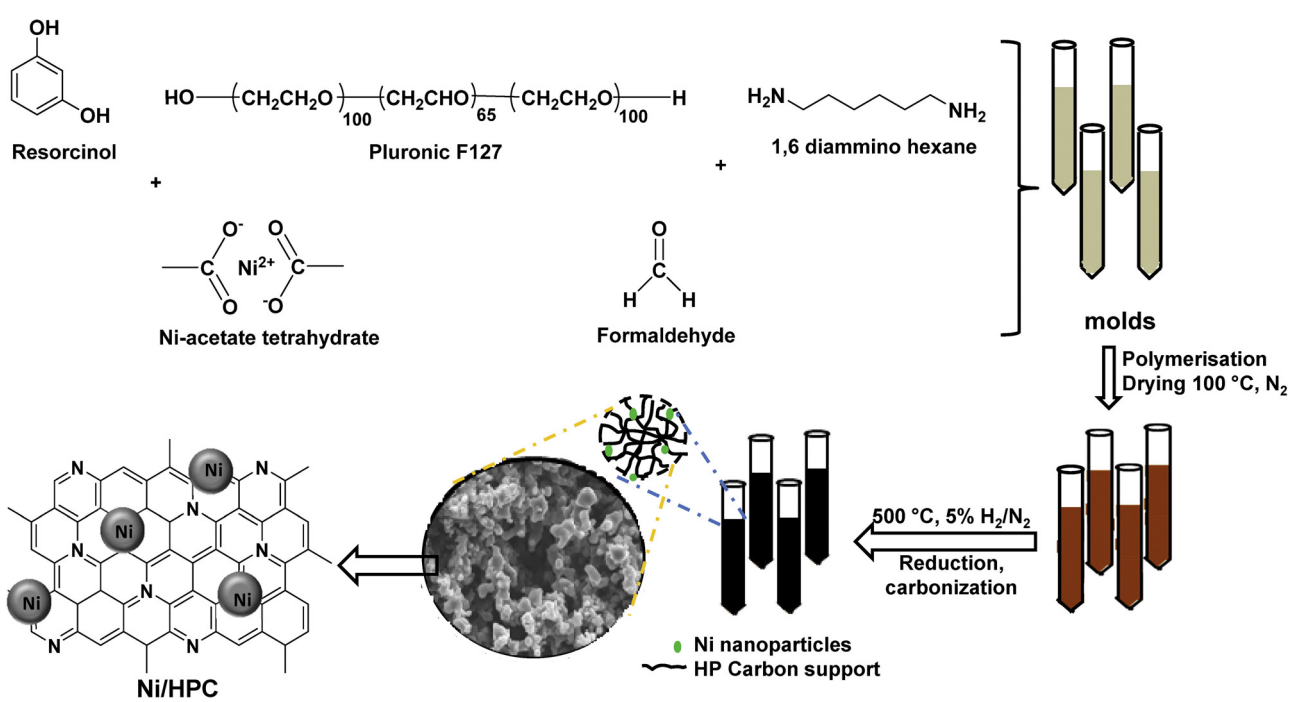

Fig. 1. Schematic representation of the synthesis of Ni/HPC monoliths.