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Short Communication

Magnetically recyclable Fe@Pd/C as a highly active catalyst for Suzuki coupling reaction in aqueous solution

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ABSTRACT

In this work, a novel catalyst Fe@Pd/C was synthesized by sequential reduction method. The core–shell catalyst exhibited efficient catalytic activity in Suzuki coupling reaction at mild condition in water. Moreover, the catalyst could be recycled by external magnetic field and the yields achieved above 86% after reused at least 5 times.

1. Introduction

Platinum-group metals, especially Pd, are excellent and versatile catalysts in various important reactions such as carbon–carbon coupling [1], alcohol oxidation [2], olefin hydrogenation [3] and electrochemical formic acid oxidation [4]. Pd nanoparticles (NPs) have been extensively applied in these reactions due to their high surface-to-volume ratio and ease of synthesis [5,6]. Unfortunately, catalytic reactions usually occur on the surface of a Pd NP catalyst and a large fraction of Pd atoms in the core are inactive [7]. Thus, it becomes a huge challenge that how to take full advantage of Pd atoms and to reduce Pd usage without sacrificing the catalytic performance. At present, the core–shell structure concept has been introduced to solve the difficulty and it has sparked increasing attention for the application of bi-metallic catalysts [8]. In this core–shell structure, the Pd is replaced by other non-noble metals such as Co, Fe, and Ni, which not only greatly reduces their cost but also can remarkably enhance their catalytic activities, as a result of the synergistic structural and electronic effects of the two metals (via the so-called strain and ligand effects) [9–11]. It is well-known that iron is an abundance and magnetism material. When it is successfully employed as the core, the obtained catalysts naturally combine the advantages of low cost and an easy recovery function derived from using of an external magnetic field [12–15].

It is representative that Palladium-catalyzed Suzuki and Heck coupling is a fascinating reaction for the construction of C–C bonds and plays an important role in pharmaceutical industry and organic synthesis [16–19]. Traditionally, the reactions are conducted with homogeneous catalysts, which are effective even with inactivated substrates and provide excellent turnover values [20]. In addition, most of the reaction medium is organic solvent. In this case, some obvious weaknesses appear. The employed organic solvents can be the source of environmental problems. Meanwhile, removing residual palladium and its ligands from the reaction medium is usually a labor-intensive process [21], which restricts the industrial reuse of these catalysts [22–27]. Therefore, we make a try to use heterogeneous catalyst, a kind of excellent catalyst that is usually inexpensive, readily obtained and easily removed from the reaction medium compared with homogeneous catalyst.

On the basis of these observations, we report a simple and efficient method for synthesizing carbon-supported Fe@Pd core–shell catalyst, which can be sufficiently applied for Suzuki reaction in aqueous solution. It could be expected to not only obviously decrease the usage of Pd but also improve yield and reusability compared with commercial Pd/C catalyst.

2. Experiment

2.1. Characterization methods

Pd content of the catalyst was measured by inductively coupled plasma (ICP) on an IRIS Advantage analyzer. The size and morphology of the magnetic nanoparticles were observed by a Hitachi-600 electron microscope, with an accelerating voltage of 100 kV. XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-K α radiation as the X-ray source in the 2θ range of 10–90°. Magnetic measurements of samples were investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied

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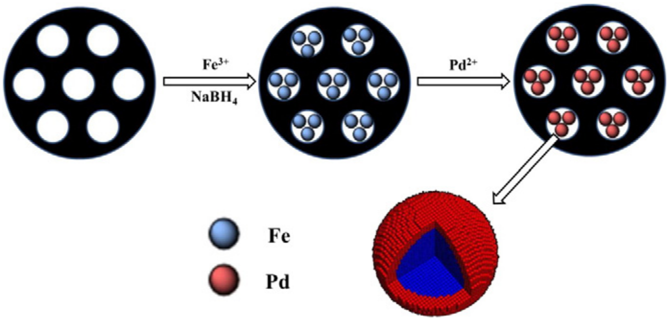

Scheme 1. The process for the preparation of the Fe@Pd/C catalyst.

magnetic field sweeping from − 15 to 15 kOe. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument.

2.2. Catalyst preparation

All chemicals were of analytical grade and used as received without further purification. The carbon supported Fe@Pd core–shell NPs were synthesized by a sequential reduction process [13] as shown in Scheme 1. Firstly, the active carbon (200 mg) was refluxed at 80 °C in nitric acid solution (2 M, 100 mL) for 3 h in order to remove impurities. For preparing Fe@Pd core–shell structured NPs with amorphous Fe core (molar ratio: Pd:Fe = 1:20), 100 mg handled active carbon and 289.6 mg $FeCl_3$ were dispersed in 30 mL water under sonication condition for 20 min. Then excess $NaBH_4$ (676.2 mg) was dissolved in 90 mL water and was added drop-wise into the mixture to reduce Fe^{3+} to Fe^0 (1). The mixture was violently shaken for 30 min till the hydrogen was released completely. Then the Fe/C NPs were collected using a magnet and washed with water and ethanol several times to remove excess sodium borohydride. Then 5 mL $PdCl_2$ solution (0.09 mmol) was added drop-wise in the Fe/C containing water (50 mL) and stirred for 1 h. The atoms in outer-layer of the Fe core were sacrificed to reduce Pd^{2+} to Pd^0 (2). Finally, the products were dried in a vacuum at 50 °C overnight.

$$2FeCl_3 + 6NaBH_4 + 18H_2O \rightarrow 2Fe(s) + 21H_2(gas) + 6B(OH)_3 + 6NaCl \quad (1)$$

$$Fe(s) + Pd^{2+} \rightarrow Fe^{2+} + Pd(s) \quad (2)$$

2.3. Catalytic Suzuki reactions

In a typical procedure, aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1.0 mmol), H_2O as solvent (3.0 mL) and the catalyst were taken in a 10 mL round bottom flask. The mixture was stirred for required time and temperature in an air atmosphere. After reaction completion, the catalyst was recovered magnetically by placing a magnet. The products were collected by extraction using ethyl acetate and analyzed by GC (P.E. AutoSystem XL) or GC–MS (Agilent 6890N/5973N). The separated catalyst washed with absolute ethanol could be reused by the addition of new portion substrate after drying at 50 °C under vacuum.

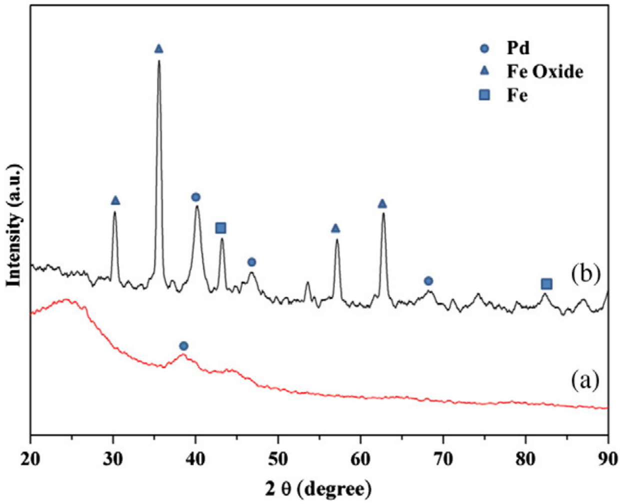

Fig. 2. XRD patterns of (a) commercial 10% Pd/C and (b) Fe@Pd/C.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1a shows the transmission electron microscopy (TEM) image of a representative sample. It is seen that the active carbon is of uniform pore shape and the NPs are isolated from each other with relatively homogeneous dispersion on the carbon substrate. Fig. 1b shows the HRTEM image of Fe@Pd/C. In addition, an annular dark-field scanning transmission electron microscopy (STEM) image, together with selected-area element analysis grayscale mapping of C, Fe and Pd (Fig. 1c), shows that Fe (yellow) is distributed on the carbon (red) substrate through the whole area, meanwhile, it reveals a partial covering of Pd atoms (green) on the outer layer of the iron core in the 3D core–shell nanostructures. Due to low content of Pd, the Pd^{2+} is reduced unhomogeneously on Fe core during the process of replacement reaction.

The XRD pattern of the samples Pd/C and Fe@Pd/C is shown in Fig. 2a and b, respectively. The reflection peaks of iron and iron oxide nanocrystals obviously indicate the existence of magnetic components in the

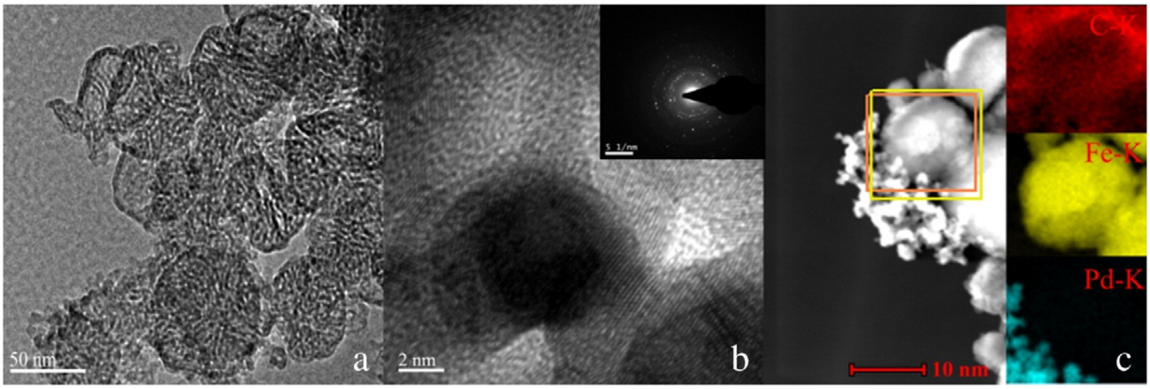

Fig. 1. TEM images of (a) Fe@Pd/C, (b) HR-TEM of Fe@Pd/C and (c) Fe and Pd EDX maps corresponding to the dark-field STEM image.