



A novel catalyst containing palladium nanoparticles supported on PVP composite nanofiber films: Synthesis, characterization and efficient catalysis



Liping Guo, Jie Bai*, Chunping Li*, Qingrun Meng, Haiou Liang, Weiyan Sun, Hongqiang Li, Huan Liu

Chemical Engineering College, Inner Mongolia University of Technology, Huhhot 010051, People's Republic of China

ARTICLE INFO

Article history:

Received 15 April 2013

Received in revised form 7 June 2013

Accepted 8 June 2013

Available online 26 June 2013

Keywords:

In situ reduction method

Electrospinning

Pd nanoparticles

Composite nanofibers

Catalytic

ABSTRACT

This paper studied the preparation of Pd nanoparticles/PVP composite nanofiber membranes catalyst. In the experiment, reductant was ethanol and PVP (polyvinyl pyrrolidone) served as the protecting agent as well as supporter of palladium nanoparticles. Pd nanoparticles/PVP sol was examined by UV–vis absorbance spectra (UV–vis); Pd NPs/PVP nanofibers were characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). The Pd NPs/PVP nanofibers films catalyst was applied to catalytic hydrogenation of aryl nitro compounds reduction and Heck reactions to test the catalytic activity, products were characterized by gas chromatograph (GC) and gas chromatograph mass spectrometer (GC–MS). Results showed that the diameters of Pd NPs were 3–10 nm and the Pd NPs/PVP nanofibers films catalyst possessed high-activity, improved the selectivity and yield, the conversion rate of paratoluidine was 74.36%, *N*-butyl cinnamate esters conversion rate still exceed 99% after catalyst be used three times. It overcomes the problems that palladium has leached badly and recovery difficultly in conventional homogeneous palladium catalyst field, and have a broad foreground of catalyst applications.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

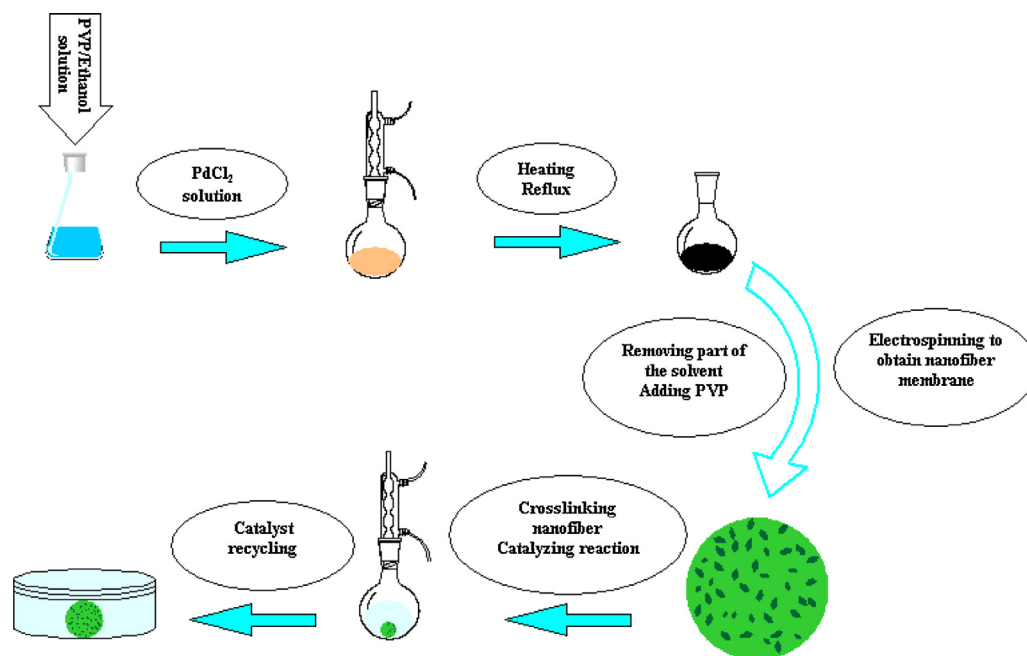
Aromatic amine compound as a kind of important organic intermediate has widely been used in dye, chemical fiber, medicine, pesticide, rubber additives, etc. At present, people prepare aromatic amine through the reduction of aromatic nitro derivatives mostly. Liquid phase catalytic hydrogenation technology possesses environmental friendly, product quality is stable, the craft is advanced, the catalysts of liquid phase catalytic hydrogenation usually include noble metal catalysts, such as Pd, Pt, Ru transition metal catalysts; porous metal catalysts; Nanoparticles catalysts and amorphous state catalysts [1,2]. Now, more and more people pay attention to it, for example, Wang et al. [3] prepared mesoporous Ni–P amorphous alloy nanospheres, in the liquid phase hydrogenation of nitrobenzene, the typical mesoporous Ni–P nanosphere catalyst exhibited much higher activity and better selectivity than the conventional nonporous Ni–P. Chary and Srikanth [4] introduced a series of Ru/SBA-15 catalysts (0.5–6.0 wt%), showed higher conversion/selectivities during hydrogenation of nitrobenzene.

Heck reaction was put forward by the Heck and Mizorok respectively at first, now it thoroughly becomes a general method for organic synthesis. It is a kind of key and powerful tool to build new carbon–carbon bond. In addition, Heck reaction possesses mildly reaction conditions; extensively adaptability to the different functional groups, substrate's selectivity is very broad, it has a wide range of applications in the preparation of compound dye, medicine, biology and other fields, becoming hot topic of the chemist [5–7].

Recently, more and more researchers have applied palladium catalysts to liquid phase hydrogenation of nitrobenzene reaction and Heck reaction and have made important progress, such as Osipov and Klyuev [8] studied the palladium-carboxylated carbon nanofibers (CNF) as a catalyst for the hydrogenation of nitrobenzene model reaction; Ma et al. [9] prepared Au@Pd bimetallic nanoparticles (NPs) catalysts by a seeding growth method using bayberry tannin grafted collagen fiber (BT-CF) as the matrix, catalyst exhibited high hydrogenation activity to various alkenes and nitro-compounds; Slamani et al. [10] introduced in situ formed catalytic system derived from the benzimidazolium salt and Pd(OAc)₂ was used in the Heck reaction between aryl halides and styrene in water. The corresponding Heck products were obtained in good yields; Nie et al. [11] introduced the catalytic activity of polyphenol microsphere-supported Pd catalyst as synthesized for the Heck

* Corresponding authors. Tel.: +86 471 6575722; fax: +86 471 6575722.

E-mail address: baijie@imut.edu.cn (J. Bai).



Scheme 1. The experimental flow graph of the preparation of Pd NPs/PVP catalyst in the paper.

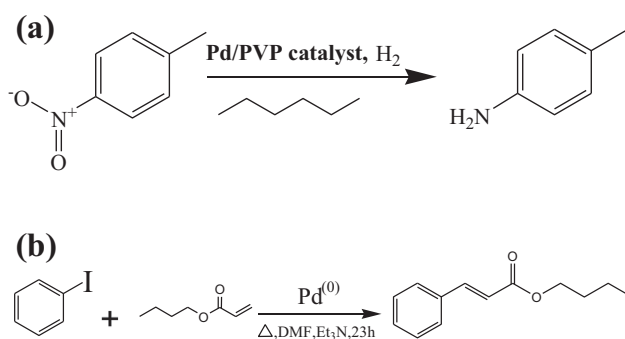
reactions of acrylic acid with aryl iodides was evaluated and preparation of Pd nanoparticles deposited on a polyaniline/multiwall carbon nanotubes nanocomposite and their application in the Heck reaction [12]; Kantam et al. [13] prepared N,N',N'',o -tetrafunctional Pd(II) complexes from the easily available amino acids which were shown to be highly efficient catalysts for the Heck reaction of deactivated aryl bromides and iodides.

Palladium as the activity center of catalyst has very high catalytic activity which plays a decisive role in organic synthesis. We know that it is great significant to synthesize high-activity and selectivity palladium catalyst in coupling reaction, with the advance of the technology and the development of society [14,15], more and more scientific and technical workers put the attention focus on how to improve the usage of the novel metal. The important solution is maximum to improve dispersion degree of the active center metal, to the greatest extent to decrease the size of the active center metal [16–18]. Traditional homogeneous palladium catalyst has a high response rate and conversions, but there are many defects when it is used, such as expensive and harsh reaction conditions, precious metals are difficult to recycle, the product difficult to purify and so on. The supported palladium catalysts which has been developed in the past several years possess more advantages [19–23], the catalysts can be recycled several times to reduce the waste of precious metals [24–26], this attracted researchers' attention deeply, for example Roy et al. [27] used a one-pot synthesis by the facile reduction of palladium chloride with citric acid in an aqueous solution of steric stabilizer polyvinyl alcohol (PVA) has been developed; Jabou et al. [28] published that nanostructured palladium particles were impregnated onto hydrogenotitanate anionates using two different impregnation procedures. This kind of catalyst has excellent promising applications.

Since the discovery of electrospinning technology in 1934, after development of decades, electrospinning technology has played a very important role in constructing one-dimensional nanostructure material field and scientists have successfully prepared a variety of nanofibers material. Electrospinning is the special form process that the electrostatic spray of high polymer fluid: not tiny droplets, but polymer tiny jet, can run a long distance, and ultimately curing into fiber. The electrospinning technique was applied

to prepare nanometer fiber materials in the field of materials science and technology nearly 10 years, because its manufacturing device is simple, low cost, spinning material variety, and process controllable, it is one of the most important activities in the academic and technical field [29,30]. In our team, several polymers (e.g. polyacrylonitrile, polystyrene and polylactic acid) have been applied in fabricating heterogeneous catalysts by electrospinning method successfully in corresponding systems.

This article introduces a new type of heterogeneous palladium catalysts through in situ reduction method and efficient electrospinning technology (Scheme 1), palladium nanoparticles/polymer composite catalyst. The preparation of nanosized palladium catalyst, ethanol as a reducing agent, PVP as a protective agent and carrier, palladium nanoparticles were prepared. We had prepared uniform morphology Pd NPs/PVP nanofiber by a kind of high efficiency and low consumption electrospinning technology. Macromolecule served as supporter, electrospinning complexes solution, with large specific surface area, solving the problem that ultrafine nanoparticles are difficult to participate to heterogeneous catalysis. Prepared palladium nanopolymer composite catalyst was applied in catalytic hydrogenation of aryl nitro compounds reduction (Scheme 2(a)) and the Heck reaction (Scheme 2(b)). The



Scheme 2. (a) The reaction equation of 4-methyl nitrobenzene catalytic hydrogenation reaction. (b) The reaction equation of the Heck reaction of iodine with benzene and *n*-butyl acrylate.

Download English Version:

<https://daneshyari.com/en/article/5353882>

Download Persian Version:

<https://daneshyari.com/article/5353882>

[Daneshyari.com](https://daneshyari.com)