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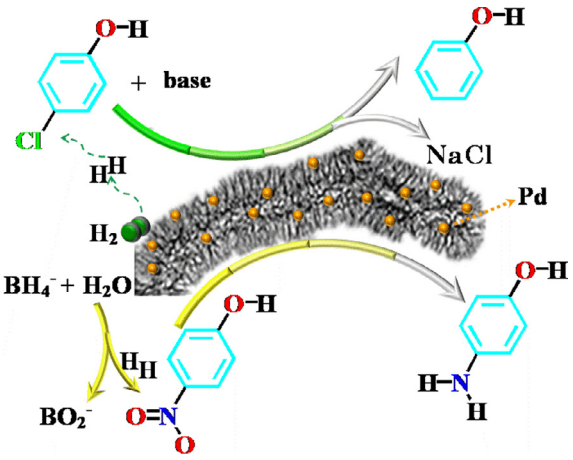
Hollow mesoporous silica nanotubes modified with palladium nanoparticles for environmental catalytic applications

Meng Tian [a], Yu Long [a], Dan Xu [a], Shuoyun Wei [b], Zhengping Dong [a,*]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Gansu Provincial Engineering Laboratory for Chemical Catalysis, Lanzhou University, Lanzhou 730000, PR China
[b] Key Laboratory of Evidence of Science and Technology Research and Application, Gansu Institute of Political Science and Law, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays, chemical catalytic methods for the treatment of organic wastes are attracting more and more research attention. In the current research, novel catalysts with palladium nanoparticles (Pd NPs) supported on the hollow mesoporous silica nanotubes (h-$mSiO_2$) were synthesized for the catalytic reduction of 4-nitrophenol (4-NP) and hydrodechlorination (HDC) of 4-chlorophenol (4-CP). The key point for the fabrication of the catalysts is that a certain thickness of the silica shell was wrapped on the multiwalled carbon nanotubes (MWNTs) or Pd/MWNTs through biphase stratification approach, and then the samples were calcined to remove the MWNTs. Thereby, h-$mSiO_2$ and Pd@h-$mSiO_2$ samples were obtained. The prepared materials have excellent pore structure and exhibit high specific surface areas. The reduction of 4-NP by the Pd/h-$mSiO_2$ and Pd@h-$mSiO_2$ catalysts showed higher TOF values than many other catalysts, and the yield of HDC of 4-CP to phenol reached 100% with a low loading of Pd in water solvent. The excellent catalytic activities of the Pd/h-$mSiO_2$ and Pd@h-$mSiO_2$ catalysts should attribute to the excellent connectivity of the h-$mSiO_2$ which not only can increase the accessibility of the Pd active sites but also enhance the mass transfer of the reactants. It is worth mention that, there is almost no Pd NPs aggregation or losing during the reaction process, and the prepared catalysts still showed good

* Corresponding author.
E-mail address: dongzhp@lzu.edu.cn (Z. Dong).

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catalytic activity and physical stability after recycling. Moreover, the catalyst shows potential for catalytic reduction of nitroarenes in a fixed bed reactor, thus could be used for continuously treat nitroarenes polluted water.

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1. Introduction

Ever since the concept of green chemistry has been proposed, the development of environmentally friendly chemical processes and the exploration of efficient methods of managing chemical pollutants have received extensive research attention [1,2]. Among most of the organic chemical pollutants, nitrophenols are carcinogenic and highly toxic and become a type of water pollutant that is not easily handled [2]. In particular, 4-nitrophenol (4-NP) has become a notorious industrial pollutant and an environmentally hazardous substance [3]. In addition to nitrophenols, chlorophenols (CPs) that widely used for synthesis of dyes, pesticides and preservatives etc., also have high toxicity, the antibiodegradable and accumulation of biological characteristics [4–6]. To protect the environment and ecological balance, various methods of dealing with these pollutants have been adopted and are under continuous research and development [7,8]. Among the commonly used methods, including chemical oxidation, physical adsorption, cohesion, catalytic degradation, and photocatalytic degradation [9], the catalytic degradation method is recognized and recommended because of its simple, safe and cost-effective features. Even more noteworthy is that their catalytic products, as useful chemicals, are often utilized in industrial applications. The product, 4-aminophenol (4-AP), reduced by 4-NP is a widely used organic compound in industrial production [5,10]. HDC of 4-CP also can obtain the product of phenol, which is a commonly used fine chemical. From the perspective of environmental protection and economic benefits, it is urgent to develop and fabricate an efficient and cheap catalyst for catalytic degradation of these organic toxicants. The literature reported that palladium nanoparticles (Pd NPs) have the best catalytic effect in the reductive degradation of nitrophenols and the HDC of CPs [11,12]. Therefore, to create an optimized Pd-based catalyst is urgently needed in the reductive degradation of nitrophenols and the HDC of CPs.

In recent years, supported catalysts are widely used in heterogeneous catalytic reaction system, because of their excellent physical and chemical properties [13]. The results showed that the composition, size and spatial structure of the support have a significant effect on the catalytic activity and selectivity of the catalyst [14]. In supported catalysts, when the noble metal NPs are highly homogeneously dispersed on the support and have a high proportion of active sites, the catalyst will show promising catalytic properties and physical properties accordingly. During the preparation of the catalyst and the chemical reaction, bare noble metal NPs tend to aggregate due to the existence of Vander Waals forces and high surface energy [15], thus subsequently reduces the catalytic activity and stability which in turn reduces production efficiency and increases economic costs. Therefore, the research of a new type of support material with large specific surface area, good flow-through diffusion structure and excellent physicochemical stability has attracted much attention. A variety of support materials have been reported in previous literatures, such as PPy nanocapsules [16], mesoporous carbon [17], graphene oxide [18]. However, these materials still have some drawbacks, such as poor stability and recyclability, and poor material transport diffusibility. An ideal catalyst support should have a stable pore structure, a larger specific surface area, a specific choice of mass transfer and lower costs. Therefore, to create a more perfect support material still needs further exploration.

Recently, mesoporous hollow materials that not only can support NMNPs on the mesopores but also can encapsulation NMNPs in their hollow core shows many excellent physicochemical properties [19]. These advantages are mainly due to the special structure that prevents the agglomeration of NPs but also the selective delivery of substances [19,20]. Moreover, these catalysts also can be easily separated from the heterogeneous reaction system by centrifugation or suction filtration, thereby recovering the catalyst for reuse. In this work, a hollow mesoporous silica nanotubes material (h-mSiO_2) was prepared through a biphase stratification approach, and the Pd NPs were encapsulated in the hollow core of h-mSiO_2 and supported on the mesoporous shell to form Pd@h-mSiO_2 and Pd/h-mSiO_2 catalysts, respectively. Pd@h-mSiO_2 and Pd/h-mSiO_2 catalysts showed good catalytic effect on the hydrogenation of 4-NP and the HDC of 4-CP. During the catalytic process, the reactants can fully contact the Pd active sites supported on the support, and the products can be easily transferred to the outside of the catalyst, which subsequently enhances the catalytic activity. Therefore, the Pd@h-mSiO_2 and Pd/h-mSiO_2 catalysts have a good prospect on the handling of toxic organic wastes and hazardous substances.

2. Experimental

2.1. Materials

Multiwalled carbon nanotubes (MWNTs, with diameters and lengths of 30–50 nm and 0.5–2 μm, respectively) were obtained from Chinese Academy of Sciences, Chengdu Organic Chemicals Co. Ltd.. Tetraethyl orthosilicate (TEOS), cetyltrimethyl ammonium chloride (CTAC), and triethanolamine (TEA) were purchased from Tianjin Heowns Biochemical Technology Co., Ltd.. $Pd(AcO)_2$, $NaBH_4$, 4-NP, 4-CP and other CPs were supplied by the Sinopharm Chemical Reagent Co. Ltd (China). Silica gel was received by Qingdao Ocean Chemical Co., Ltd.

2.2. Preparation of the h-mSiO_2

The dendritic mesoporous silica shell was prepared via biphasic stratification approach [21]. CTAC, TEA, TEOS and cyclohexane were used as template, catalyst, silica source and emulsion agent, respectively. In a typical method, 10 g CTAC and 0.36 g TEA were dissolved in 250 mL round bottomed flask with 100 mL deionized water, and then 300 mg MWNTs which was previously treated by HNO_3 was added to the above mixture solution and sonicated for about 30 min, followed by mechanical stirring for 1 h at 60 °C [22,23]. 4 mL TEOS solution (10 v/v% in cyclohexane) was carefully added to the above solution along the flask wall to form a two-phase delamination and maintain mechanical agitation at 60 °C for 24 h. Then, the upper oil phase layer was removed and the remaining liquid was collected by centrifugation, and washed for several times with water, finally washed with absolute ethanol and dried (in oven at 60 °C). Thus, a kind of MWNTs/mSiO_2 material was synthesized. Finally, the MWNTs/mSiO_2 sample was annealed in a tube furnace under air atmosphere, and the

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