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Palladium nanoparticles supported on SiO_2@Fe_3O_4@m-MnO_2 mesoporous microspheres as a highly efficient and recyclable catalyst for hydrodechlorination of 2,4-dichlorophenol and reduction of nitroaromatic compounds and organic dyes

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ABSTRACT

In this study, magnetic SiO_2@Fe_3O_4@m-MnO_2 microspheres with uniform morphology and mesoporous MnO_2 shell were successfully prepared. The MnO_2 sheets structured mesoporous shell could provide a large specific surface area, thereby increasing the catalytically active sites. Thus, magnetic SiO_2@Fe_3O_4@m-MnO_2 microspheres were used as a catalyst support. Palladium nanoparticles (Pd NPs) were successfully anchored with high dispersion on SiO_2@Fe_3O_4@m-MnO_2 surface, successfully obtained Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst with a Pd weight percentage of 6%. The obtained nanocatalyst was employed in the hydrodechlorination of highly toxic 2,4-dichlorophenol and catalytic reduction of the widely used nitroaromatics and organic dyes under ambient conditions. In these catalytic reactions, the Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst with large and accessible pore surface area exhibited excellent catalytic activity as compared to other noble metal supported catalysts. The Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst could also be easily and conveniently recovered from the reaction mixture by using an external magnet, attributed to its magnetism, thus preventing the catalyst loss. Moreover, it could also be reused for at least six times without significant decrease in the catalytic activity, indicating its excellent reusability and stability. This study provides a useful platform and a new perspective for fabricating mesoporous MnO_2 microspheres based noble metals modified catalysts for environmental catalysis.

1. Introduction

Over the last decades, with the continuous development of the chemical industry, significantly large amounts of organic hazardous substances have been discharged into the environment. One class of the organic hazardous substances includes the chlorophenols (CPs) [1–4], which are widely used in the synthesis of herbicides, dyes, and pesticides and as preservative agents for wood, paints, fibers, and leather. However, they have been identified as priority pollutants because of their acute toxicity, resistance to biodegradability, and strong bioaccumulation potential. Another type of hazardous organic pollutants includes the extensively used nitroaromatic compounds such as 4-nitrophenol (4-NP) and 2-nitroaniline (2-NA), which are also highly toxic compounds with potential carcinogenic and mutagenic effects [5–7]. The third class recognized pollutant includes the organic dyes (eg. Rhodamine B (RhB), methylene blue (MB), and methyl orange (MO)), although they are widely exploited in paper, textile, paints, printing, and plastics industries, their high toxicity and carcinogenic and mutagenic nature should not be ignored [8–10]. Therefore, with increasing consciousness for environment protection, proper disposal of the above mentioned organic hazardous pollutants becomes extremely necessary. Till date, several methods such as chemical oxidation, adsorption, flocculation, catalytic degradation, and electrooxidation have been developed to dispose these organic hazardous pollutants [11–16]. Among them, the catalytic degradation method is considered as the most effective, simple, and safe technique. Moreover, the catalytic method can lead to the effective conversion of the highly toxic organic compounds into

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harmless or significantly less toxic reaction byproducts [17,18]. Furthermore, these byproducts can always be efficiently utilized as potential candidates in several industrial applications. Therefore, design and fabrication of efficient catalysts for the catalytic conversion of highly toxic organic compounds into harmless and useful products is highly required.

Noble metal nanoparticles (NMNPs) based catalysts have been proved to be the most efficient catalysts for the organic molecule catalytic transformation [19]. However, attributed to the van der Waals forces and their high surface energy, the naked NMNPs are apt to irreversible aggregation in solution during the preparation and the catalytic process, which subsequently reduces the catalytic activity [20]. To overcome the above mentioned shortcomings, functional catalyst supports have attracted tremendous and increasing interest, thus paving the way for the fabrication of NMNPs supported catalysts. According to the recent literatures, several types of functional materials including mesoporous carbon [21,22], graphene oxide [23], mesoporous silica (SiO_2) [24], and metal–organic frameworks have been employed for the fabrication of NMNPs based catalysts [25–27]. In general, palladium (Pd) catalysts are initially synthesized as heterogeneous catalysts followed by loading onto active carbon, metal oxides, zeolites, polymers, or clay [28–34]. However, these catalysts still suffer from drawbacks such as comparatively complicated separation recycling process such as filtration and centrifugation. Therefore, fabrication of functional catalyst supports which exhibit easy recyclability, large surface area, tunable mesoporous structure, and high activity and stability is extremely meaningful for the preparation of NMNPs based catalysts. In these regards, mesoporous materials with magnetic component have attracted significant attention as promising candidates for catalysts supports [35–37]. In these years, magnetic catalysts have been reported to have the incomparable advantages over the traditional catalysts because of their high activity, magnetic recyclability, and reusability [38–42]. The magnetic mesoporous carbon and core–shell magnetic mesoporous SiO_2 have already been reported as catalysts supports for fabrication of recyclable catalysts [43–46]. However, the widely used, cost-effective transition metal oxides, for example manganese dioxide (MnO_2) and cerium(IV) oxide (CeO_2) have rarely been used for the fabrication of magnetic mesoporous transition metal oxides microsphere, probably due to the capability of these transition metal oxides always generate separate NPs, attributed to their high reactivity and low-solubility-product constants of the transition metal hydroxide. Thus, it is imperative to prepare magnetic mesoporous transition metal oxides microspheres with a mesoporous or hierarchical transition metal oxides shell and a magnetic core for the fabrication of supported catalysts exhibiting magnetic recyclable properties.

Based on the above mentioned considerations, herein we used the SiO_2 NPs as the core, ferrocene was employed as the precursor to fabricate the SiO_2@Fe_3O_4@C magnetic NPs, and then potassium permanganate ($KMnO_4$) was introduced to react with the surface carbon layers to form the mesoporous MnO_2 shell on the SiO_2@Fe_3O_4 NPs, thus the novel magnetic SiO_2@Fe_3O_4@m-MnO_2 catalyst support was successfully obtained. Finally, the Pd NPs were anchored on the mesoporous MnO_2 shell with high dispersion by impregnation-reduction method, which resulted in the formation of the Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst with a Pd weight percentage of 6%. The prepared nanocatalyst was empolyed for the environmental catalysis, hydrodechlorination (HDC) of highly toxic CPs, and catalytic reduction of the extensively used nitroaromatics and organic dyes under ambient conditions. The Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst exhibited excellent catalytic activities compared to other reported NMNPs based catalysts, attributed to the mesoporous structure of the MnO_2 shell and highly dispersed Pd NPs that led to the enhancement in the accessibility of the active sites and the mass transfer effect. Moreover, the Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst could be easily recovered and reused without any decrease in the catalytic activity and stability. This study may promote the research of fabricating magnetic mesoporous transition metal oxides microsphere support based catalysts for environmental catalysis.

2. Experimental

2.1. Reagents

Ferrocene, $KMnO_4$, and tetraethyl orthosilicate (TEOS), used for the fabrication of SiO_2@Fe_3O_4@C and SiO_2@Fe_3O_4@m-MnO_2, were purchased from Aladdin Reagents. CPs, 4-NP, 2-NA, RhB, MB, MO and other nitroaromatics used in the catalytic studies were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Other reagents and solvents were of analytical grade and used without further purification. Deionized H_2O was used for all the experiments.

2.2. Preparation of SiO_2@Fe_3O_4@C

SiO_2 NPs were synthesized by a modified Stöber protocol [47]. The SiO_2@Fe_3O_4@C microspheres were prepared by a modified hydrothermal process [48]. Briefly, SiO_2 NPs (100 mg) and ferrocene (200 mg) were dissolved in acetone (65 mL) by ultrasonication for 30 min to form monodisperse system. Next, H_2O_2 (2 mL) was added dropwise into the mixture by a syringe and the contents were magnetically stirred for 1 h, which resulted in the formation of a homogeneous suspension. Subsequently, this suspension was transferred to a Teflon autoclave and heated to 200 °C, and the temperature was maintained constant for 40 h. Further, the autoclave was cooled down to room temperature. The as-obtained products were washed with H_2O and acetone solution three times, respectively, and dried overnight at 40 °C in a vacuum oven.

2.3. Preparation of SiO_2@Fe_3O_4@m-MnO_2

Mesoporous MnO_2 layers were formed on SiO_2@Fe_3O_4@C spheres by the redox reaction between $KMnO_4$ and carbon layers. Briefly, SiO_2@Fe_3O_4@C spheres (200 mg) and $KMnO_4$ (140 mg) were added into H_2O (70 mL) by ultrasonication for 30 min and magnetic stirring for 10 min. Subsequently, the mixture was transferred to a Teflon autoclave and heated to 160 °C, and the temperature was maintained constant for 12 h. After cooling down to room temperature, the product was washed with deionized H_2O and ethanol three times, respectively, and dried overnight at 40 °C in a vacuum oven.

2.4. Preparation of Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst

Palladium acetate solution (1.2 mL, 10 mg mL^{-1}) was added dropwise into deionized H_2O (25 mL). Subsequently, SiO_2@Fe_3O_4@m-MnO_2 (94 mg) was added to the above mentioned solution and ultrasonically dispersed for 30 min and then magnetically stirred for 5 h. The dispersion was cooled down to 0 °C, and excess sodium borohydride ($NaBH_4$) solution was added dropwise. The solution was stirred for 12 h and the resulting Pd(6%)/SiO_2@Fe_3O_4@m-MnO_2 nanocatalyst was collected by using an external magnet, thoroughly washed with ethanol and deionized H_2O, and finally dried overnight at 40 °C in a vacuum oven.