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Pd@MIL-100(Fe) composite nanoparticles as efficient catalyst for reduction of 2/3/4-nitrophenol: Synergistic effect between Pd and MIL-100(Fe)

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ABSTRACT

Pd@MIL-100(Fe) composite nanoparticles were synthesized and characterized by high-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction analysis, nitrogen adsorption-desorption analysis, X-ray photoelectron spectroscopic (XPS) analysis, energy-dispersive X-ray spectroscopy (EDS) and element mapping. Due to the local restriction or confinement effect of the unique pore/surface structure within the MIL-100(Fe) nanospheres, small Pd nanoparticle (4–6 nm) were obtained with high stability without using any surfactant as stabilizer. The as-synthesized Pd@MIL-100(Fe) composite nanoparticles were then employed for the catalytic reduction of 2/3/4-nitrophenol, which exhibiting high catalytic activity and recyclability attributed to the synergistic effect between Pd nanoparticles and MIL-100(Fe) nanospheres.

1. Introduction

It is known that nitrophenol (NP) and its homologous series are highly hazardous organic contaminants which have gradually increased and widely existed in wastewater produced in the manufacture of industrial and agricultural products [1–4]. Most of them posed a serious threat to human beings and the environment and can remain in the environment for a long time with high toxicity and carcinogenicity, due to their stability and bioaccumulation. In the past few decades, several methods have been reported for removing of NP, including adsorption, ozonation, bioremediation, electrochemical degradation, and so on [5–10]. Among all these methods, catalytic reduction using $NaBH_4$ with precious metal nanoparticles (MNP, like Au, Pd and so on) as catalysts has been demonstrated to be an effective and eco-friendly approach, not only because of the feasibility of this method but also due to the practicability of the final products, that is aminophenol (AP), which is a notable chemical intermediate for synthesis of dyes, drugs, and additives [11–14]. However, metal nanoparticle catalysts often suffer from aggregation and activity decrease during the catalytic process due to their high surface energy [15]. Thus, it is of great significance to enhance the stability and prolong the service life of the catalyst.

Metal-organic frameworks (MOFs) represent an intriguing class of hybrid porous materials constructed from metal vertices linking by organic struts [16–18]. Owing to their fascinating features including high porosity, large surface areas, well defined pore architectures and tunable chemical compositions and physicochemical properties, MOFs are considered as excellent candidate for application in many fields as luminescent sensing, gas storage, molecular recognition and so on [19–23]. Particularly in the field of catalysis, MOFs can provide well-defined microenvironments for incorporating of metal nanoparticles due to their highly ordered uniform pore structure [24,25]. Great effort has been devoted to the design and fabrication of MNP/MOFs composite catalysts in recent years not only because of the enhanced stability with MOFs as host matrices for preventing MNP from migration and aggregation but also due to the host-guest synergistic effect to improve the catalytic activity [26–32]. Moreover, the porous structure of MOFs can not only guarantee the accessibility of the catalyst but also benefits the transportation and enrichment of substrates to the MNP active sites [33].

Bearing these facts in mind, we report here the preparation and characterization of Pd nanoparticles encapsulated in MIL-100(Fe)

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nanospheres, that is Pd@MIL-100(Fe) composite nanoparticles, and its application as efficient catalyst for the reduction of 2/3/4-nitrophenol. We chose MIL-100(Fe) as the MNP carrier because of the large pore size and surface area, high thermal and chemical stability as well as their adsorption ability over different organic molecules. Benefits from all these, the Pd@MIL-100(Fe) nanoparticles exhibit outstanding enhanced catalytic activity and prolonged recyclability toward the reduction of nitrophenols in the presence of $NaBH_4$.

2. Experimental details

2.1. Materials used

All reagents were purchased from commercial sources and were used without further purification. Specifically, Trimesic acid and anhydrous ferric chloride were provided by Aladdin Co. Potassium palladium chloride, nitrophenols, and sodium borohydride ($NaBH_4$, >99%) were purchased from Sigma-Aldrich.

2.2. Synthesis of MIL-100(Fe) nanospheres

MIL-100(Fe) nanospheres were synthesized *via* an assembly method according to previous literature with some modification [34]. Typically, ferric chloride (51.9 mg) and trimesic acid (76.6 mg) was dissolved in 8 mL EG and 6 mL DMF respectively, the mixture was stirred at ambient temperature for 5 min, and then stirred for another 2 h under 363 K. The resulting precipitate was extracted by centrifugation and washed with DMF and alcohol for several times. Finally, the product was dried and activated under vacuum at 373 K overnight.

2.3. Synthesis of Pd@MIL-100(Fe) nanoparticles

Pd@MIL-100(Fe) was prepared via a solution impregnation method combined with a hydrogen-reduction process. Typically, activated MIL-100(Fe) nanosphere (30 mg) was suspended in 20 mL H_2O and sonicated for 10 min until it became highly dispersed. Then 0.12 mL of aqueous K_2PdCl_4 solution (0.125 M) was added and stirred at room temperature for 12 h. After the impregnation, the suspension was centrifuged to separate the solid and washed with water. Finally, the solid was dried and followed by 1 h H_2 reduction at 473 K.

2.4. Material characterization

Transmission electron microscopy (TEM) images were collected on JEOL, JEM-1400. SEM images were recorded in a FEI QUANTA FEG250 SEM operating at 5 kV. Powder X-ray diffraction (XRPD) pattern of the sample was recorded by an X-ray diffractometer (Bruker D8 Focus 2000) using Cu Kα ($\lambda = 1.5406$ Å) radiation. The Brunauer-Emmett-Teller (BET) surface area was evaluated using N_2 adsorption data using a Micromeritics ASAP 2020 system. The samples were first degassed in a vacuum at 150 °C for 10 h. High-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL model JEM 2010 EX instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250XI XPS system. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700ce) was used to quantify Pd content.

2.5. Catalytic hydrogenation of nitrophenols

Catalytic hydrogenation reaction of nitrophenols was conducted at room temperature with Pd@MIL-100(Fe) as catalyst according to the following procedure. Typically, 54 mg $NaBH_4$ solution was first mixed with 40 mL aqueous solution of 4-NP (94 mg L^{-1}), 3-NP (470 mg L^{-1}), 2-NP (470 mg L^{-1}), separately, and stirred for 20 min. Then Pd@MIL-100(Fe) (0.525 mg, or commercial Pd/C catalyst with the same mole of Pd) was added to the reaction mixture. After that, the reaction mixture was taken out at specified time intervals and measured by UV-vis spectroscopy to monitor the reaction progress.

3. Results and discussion

3.1. Characterization

Morphology of the synthesized Pd@MIL-100(Fe) composite nanoparticles investigated by using the TEM is shown in Fig. 1 and Fig. S1. It can be seen that MIL-100(Fe) particles show monodisperse spherical shape with about 120 nm in diameter. These MIL-100(Fe) spheres are assembled by MIL-100(Fe) nanoparticles aggregating along certain lattice plane preferentially. Sizes of Pd nanoparticles were in the range of 4.0–6.0 nm with an average size of 5.1 ± 0.2 nm, which were highly dispersed on the surface and in the pore of MIL-100(Fe) nanosphere. No large Pd particle aggregations have been observed in the TEM images. The lattice fringe of 2.25 Å matches that of the (111) plane of face-centered cubic Pd according to the high resolution TEM analysis as shown in Fig. 1b [35,36].

Powder X-ray diffraction (XRD) patterns of the fresh and Pd-imbedded MIL-100(Fe) composites were shown in Fig. S2. The characteristic diffraction peaks of MOF particles are coincident with that of the simulated one, which confirms the formation of MIL-100(Fe). Moreover, XRD pattern of Pd@MIL-100(Fe) matched well with that of the parent MIL-100(Fe), indicating that MIL-100(Fe) keeps its structure unchanged after the incorporation of Pd particles. The absence of Pd diffraction peaks could probably be ascribed to the low Pd concentration and the small particle size.

Porosity and surface area of the two samples were confirmed from the nitrogen sorption-desorption isotherms at 77 K. As shown in Fig. 2, both the two materials display similar type-I adsorption isothermal curves. The adsorption amount of nitrogen increased sharply at a low relative pressure ($P/P_0 \leq 0.1$) indicated that the as-synthesized Pd@MIL-100(Fe) and MIL-100(Fe) particles exhibit the characteristics of a microporous structure.

The calculated Brunauer-Emmett-Teller (BET) surface area is 1232 $m^2\ g^{-1}$ for Pd@MIL-100(Fe) and 2041 $m^2\ g^{-1}$ for MIL-100(Fe). The appreciable decrease of surface area indicates that partial internal cavities of the host framework are occupied by Pd NPs formed within the pores of the MIL-100(Fe). The pore volume were found to be 0.89 $cm^3\ g^{-1}$ and 0.73 $cm^3\ g^{-1}$ for MIL-100(Fe) and Pd@MIL-100(Fe) respectively, which is similar to that of the

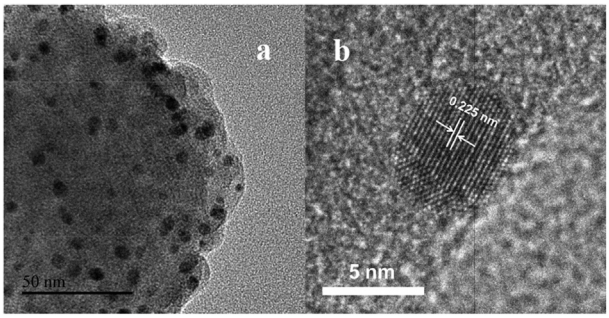

Fig. 1. HRTEM images of Pd@MIL-100(Fe).