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Ni@Pd core–shell nanoparticles modified fibrous silica nanospheres as highly efficient and recoverable catalyst for reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol

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ABSTRACT

In this study, a novel fibrous nano-silica (KCC-1) based nanocatalyst (Ni@Pd/KCC-1) was synthesized by modifying KCC-1 using Ni@Pd core–shell nanoparticles (NPs). The Ni@Pd/KCC-1 was used in the catalytic reduction of 4-nitrophenol (4-NP) and hydrodechlorination (HDC) of 4-chlorophenol (4-CP). KCC-1, prepared by hydrothermal method, exhibited a dandelion-like shape, high surface area, and easy accessibility of active sites. The Ni@Pd NPs possessed a magnetic nickel (Ni) core with palladium (Pd) shell structural composite. Thus, use of Ni led to the reduced consumption of Pd without sacrificing the overall catalytic performance, simultaneously making it reusable as it could be conveniently recovered from the reaction mixture by using an external magnetic field. Immobilization of the Ni@Pd NPs on KCC-1 nanospheres not only prevented their aggregation, but also significantly enhanced the accessibility of the catalytic active sites. The Ni@Pd/KCC-1 nanocatalyst displayed excellent catalytic activities for both the reduction of 4-NP and the HDC of 4-CP under green conditions. The above-mentioned approach based on fibrous KCC-1 and Ni@Pd NPs provided a useful platform for the fabrication of noble metal-based cost-effective nanocatalyst with easy accessibility, and acted as a promising candidate for numerous catalytic applications.

1. Introduction

Nitrophenols (NP) are among the most refractory water pollutants with carcinogenic character and high toxicity. In particular, 4-nitrophenol (4-NP) is a notorious industrial pollutant and environmentally hazardous material exhibiting high solubility and stability in water. 4-NP polluted water poses significant environmental and public health hazards [1–4]. Moreover, chlorophenols (CP), extensively employed in the manufacture of pesticides, disinfectants, and wood preservatives, are toxic, biorefractory, and bioaccumulative [5–8]. Therefore, the United States Environmental Protection Agency has listed most of the NP and CP as priority pollutants. Currently, many processes are developed for the disposal of these pollutants [9–12]. Among the processes contributing to the remediation of 4-NP, reduction of the nitro group is certainly the most characteristic one. Moreover, the reduction product 4-aminophenol (4-AP) is an extremely useful organic compound employed in various applications [13]. Hydrodechlorination (HDC) is considered as the most effective method for the disposal of CP, because the only product (phenol) can be subsequently recycled [14,15]. Till today, it is still necessary to develop low-cost, effective catalysts for the reduction of NP and HDC of CP from concentrated industrial effluents.

Recently, noble metal nanoparticles (NPs), in particular, palladium (Pd) NPs, have been extensively studied as catalysts due to their high catalytic activity for many organic catalytic reactions [16–20]. The catalytic activity of noble metal NPs is mainly dependent on their size, shape, crystallinity, and the surface state. Moreover, the development of nano-sized metal catalysts on catalyst supports has attracted considerable attention. Various supporting materials have been utilized to load Pd NPs as catalysts for organic catalytic reactions, including Pd/Al_2O_3 [21], Au@Pd@TiO_2 [22], Pd/SBA-15 [23] and Pd/C nanospheres [24]. All the above-mentioned materials have large specific surface areas and pores leading to the homogeneous dispersion of the catalytic sites, thus preventing the aggregation of NPs and improving the catalytic activity of the system. However, poor accessibility to these active sites inside the pores limits their applications for which

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significant mass transport is essential. Therefore, silica supports with easily accessible high surface areas, not due to the pores, are highly desirable.

Noticeably, most noble metal NPs catalytic reactions occur only on the surface of the NPs and a large fraction of atoms in the core are catalytically inactive. Therefore, to make a large percentage of noble metal atoms available for catalysis and to reduce their consumption, the inner noble metal atoms should be replaced by other non-noble metals. The presence of a different metal core usually provides control over the catalytic activity, selectivity, and stability owing to "synergistic effects" arising from core–shell metal interaction [25]. Among various non-noble metals, transition Fe-group metals such as Fe, Co, and Ni are often hybridized with noble metals to form magnetic NPs that can be conveniently recovered by using an external magnetic field [26–28]. However, cost-effective noble metal NPs catalysts with inactive cores, excellent catalytic activities, and efficient recoverable properties are extremely rare.

Therefore, in this study, we envisioned that the preparation of Ni@Pd magnetic core–shell NPs could reduce the consumption of Pd. And the immobilization of Ni@Pd NPs on the fibrous silica nanospheres (KCC-1) to fabricate the nanocatalyst Ni@Pd/KCC-1 would be promising for the purpose of preventing the aggregation of Ni@Pd NPs, increasing the accessibility of the active sites and conferring magnetic separation property to the nanocatalyst. KCC-1, first reported by Polshettiwar has the easily accessible high surface area attributed to its fibers and not pores [29,30]. In our previous work, we synthesized Ag/KCC-1 nanocatalyst with easy accessibility and excellent catalytic activity for the reduction of 4-NP and 2-nitroaniline (2-NA) using sodium borohydride ($NaBH_4$) in water at room temperature [31]. Here, the Ni@Pd/KCC-1 nanocatalyst was employed as highly efficient catalyst for the reduction of 4-NP and HDC of 4-chlorophenol (4-CP) under eco-friendly conditions. Importantly, the Ni cores of the Ni@Pd NPs reduced the consumption of Pd, simultaneously making the catalyst reusable due to its convenient recovery. Immobilization of the noble metal NPs with magnetic cores on the supports with high accessibility is a novel method to prepare catalysts with excellent catalytic activities and easily recovered properties; thus, exhibiting potential applications in numerous noble metals NPs based catalytic applications.

2. Experimental

2.1. Materials

Nickel(II) acetate tetrahydrate ($Ni(ac)_2 \cdot 4H_2O$), palladium(II) bromide ($PdBr_2$), oleyl amine (OAm), trioctylphosphine (TOP), chromatographically pure ethyl acetate ($CH_3COOC_2H_5$) and 3-mercaptopropyltriethoxysilane (MPTES) were purchased from Sigma–Aldrich and used as received. All other chemicals were of the reagent-grade purchased from Tianjing Guangfu Chemical Company and used as supplied. All solvents used for synthesis and measurements were redistilled before use.

2.2. Synthesis of Ni@Pd NPs

Ni@Pd core–shell NPs were synthesized via a one-pot high-temperature solution phase synthesis including the consecutive reduction of nickel (II) and palladium (II) in OAm as reported by Sun et al. [25]. Detailed synthetic procedures of the Ni@Pd NPs were shown in the supporting information.

2.3. Preparation of KCC-1

In this study, KCC-1 was successfully synthesized by a hydrothermal method instead of the reported microwave assisted technique [31]. The detailed experimental procedure was similar to the microwave assisted hydrothermal method and can be seen in the supporting information.

2.4. Fabrication of Ni@Pd/KCC-1

The schematic describing the preparation of Ni@Pd/KCC-1 is shown in Scheme 1. Firstly, 1 g of KCC-1 was added to 100 mL of anhydrous toluene under ultrasonic treatment for 10 min to disperse it homogeneously. Secondly, 0.3 g of MPTES was added dropwise, and the mixture was refluxed for 10 h in a N_2 atmosphere. Thirdly, the mixture was cooled to room temperature and the resulting mercaptopropyl functionalized KCC-1 (HS-KCC-1) was centrifuged; washed repeatedly with chloroform, dichloromethane, and ethanol; and finally dried in vacuum. Finally, 0.40 g of HS-KCC-1 was ultrasonically dispersed in 50 mL H_2O, and 0.08 g of Ni@Pd NPs was added. After being stirred and ultrasonically dispersed for 1 h, Ni@Pd/KCC-1 was obtained by centrifugation and dried in a vacuum.

2.5. Characterization

The size and morphology of the samples and the energy dispersive spectrometer (EDS) were observed by a Tecnai G^2 F^{30} transmission electron microscopy (TEM) and samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporating the solvent in air at room temperature. XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 10–80°. Magnetic measurements of Ni@Pd NPs and Ni@Pd/KCC-1 nanocatalyst were investigated with a quantum design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from -15 to 15 kOe. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702, and the C1S line at 291.4 eV was used as the binding energy reference. The nitrogen adsorption/desorption experiments were performed at 77 K in a micromeritics ASAP 2010 (USA). Elemental analysis (GmbH Vario El Elementar) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were employed to measure the N, C, H and Ni, Pd content of the samples. Thermal gravimetric analysis (TGA, Perkin Elmer Thermal Analyzer) and Fourier transform infrared spectrometer (FTIR, Bruker IFS66/S) were also used to characterize the samples KCC-1 and Ni@Pd/KCC-1. Ultraviolet–visible (UV–vis) absorption spectra were recorded with a TU-1901 UV-Vis spectrophotometer. The reaction conversion of the HDC reaction was estimated by using GC–MS (Shimazu QP2010S).

2.6. General procedure for the reduction of 4-nitrophenol

Firstly, 2.5 mL of aqueous 4-NP solution (0.12 mM) was mixed with 0.5 mL of freshly prepared aqueous $NaBH_4$ solution (0.5 M) and a deep yellow solution was formed. Then, 40 μL of catalyst (concentration 10 mg/mL) was added to the above yellow solution and the reaction was finished until the solution became colorless. The reaction progress was monitored by measuring the UV–vis absorption spectra of the reaction mixture.

The reduction reaction was amplified 20 times to study the reusability of the prepared catalyst. The catalyst was recovered by using a magnet and then washed with water and dried in vacuo at room temperature for the next catalytic run. This procedure was repeated six times.

2.7. General procedure for the HDC of 4-chlorophenol

The batch experiments for 4-CP HDC were performed in a 100 mL three-necked flask [14,32]. To evaluate the catalyst activity under green conditions, reaction conditions were established at