Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

Highly efficient and recyclable Ni MOF-derived N-doped magnetic mesoporous carbon-supported palladium catalysts for the hydrodechlorination of chlorophenols

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ABSTRACT

Ni MOF-derived N-doped magnetic mesoporous carbon-supported Pd nanoparticles (Pd/Ni-mCN) were prepared and used in the hydrodechlorination (HDC) of chlorophenols (CPs) water pollutants with H_2 at mild reaction conditions. The Pd/Ni-mCN catalyst was characterized in detail by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), N_2 adsorption/desorption, and vibrating sample magnetometry (VSM). The Pd/Ni-mCN nanocatalyst showed high activity and complete HDC conversion of a target pollutant such as 4-CP after 90 min at ambient conditions. Other CPs compounds such as 2-CP, 3-CP, 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) were also tested in the HDC reaction. 2-CP was the only intermediate product in the HDC of 2,4-DCP, with phenol being the final product. The HDC of 2,4,6-TCP proceeded with the intermediate formation of 2-CP and 2,4-DCP, this being potentially originated from the steric hindrance of the ortho-substituted Cl atom. Additionally, Pd/Ni-mCN exhibited high catalytic stability and recyclability. Thus, Pd/Ni-mCN was successfully recycled owing to its superparamagnetic properties and reused for at least five times showing stable conversions (above 99% at 90 min) the HDC of 4-CP.

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1. Introduction

Preventing water and soil pollution has attracted increasing interest in the scientific community since these issues represent a serious threat to people's daily life [1,2]. Stringent regulations have been enacted with the aim to control the emission of pollutants to the environment. Among the numerous environmental pollutants, commercially available organo–chlorinated chlorophenols (CPs) are frequently used as raw materials in the synthesis of pesticides and disinfectants [3–5]. When discharged to the environment, CPs can cause persistent pollution owing to its toxic, biorefractory, and bioaccumulative characteristics. Hence, CPs has been classified by the Environmental Protection Agency as potential groundwater pollutants and listed as one of the most important pollutants by the European Union [6,7]. Different CPs removal technologies have been investigated including Fenton [8], ozonization [9], hydrodechlorination (HDC) [10,11], heterogeneous photocatalysis [12,13], and adsorption processes [14]. Among the above-mentioned methods, catalytic HDC represents an effective, simple, and safe technology. Thus, HDC of chloro-compounds can be carried out under normal temperature and pressure conditions and within a wide range of concentrations [15,16]. Additionally, many highly toxic chlorinated compounds can be converted into harmless or considerably less toxic reaction byproducts by HDC [17]. For example, highly toxic CPs can be converted into low toxic phenols via HDC [18,19].

HDC of chloro-compounds is typically carried out over precious metal-catalysts. Thus, Pd, Pt, Au, Ru, and Rh have been supported on different commercially available inorganic supports (e.g., activated carbons, Al_2O_3, SiO_2, pillared clays) and thoroughly investigated in HDC processes [20–26]. However, precious metals have become increasingly rare in recent years. Additionally, the recovery of precious metal-catalysts from the liquid-phase reaction medium is very difficult, thereby leading to high costs for the entire catalytic process and seriously affecting the sustainability of this technology [27,28]. Thus, the development of high-efficiency precious metal-catalysts which can be efficiently recycled is highly required. The utilization of magnetic nanoparticles (NPs) as components of the catalyst supports may help overcome this recycling limitation [29–31]. Additionally, magnetic separation is a green process since

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it allows save energy, time, and solvent. In this sense, $Fe_3O_4@SiO_2$-based catalyst supports have been extensively studied [32–35]. However, silica-based magnetic supports cannot be used under alkaline conditions as they may suffer from aggregation during the catalytic process. In this sense, mesoporous carbon materials, showing anchored magnetic NPs, have a number of advantages over silica-based magnetic supports. Several magnetic mesoporous carbon materials have been prepared in recent years [36–40], although their preparation procedures are comparatively complicated. One pot carbonization of Ni-, Co-, and Fe-based MOF under inert atmosphere represents a facile method for the fabrication of magnetic mesoporous carbon materials [41–43]. In our previous work, a magnetic porous carbon material has been obtained from the carbonization of Fe-MOF, and was used to prepare Pd and Au supported recyclable catalysts [44]. In addition, as reported in the literatures that, the carbon materials doped with N should benefit for the noble metal precursor adsorption, enhancing nucleation and stabilizing the noble metal NPs and make them with high dispersion on the supports, and further enhance the catalytic acitivity [45–47].

Bearing all this in mind, we herein used a Ni-MOF precursor to fabricate a Ni NPs-based N-doped magnetic mesoporous carbon (Ni-mCN) by a simple carbonization method. Pd NPs were subsequently supported on the Ni-mCN support by incipient wetness impregnation and reduced by $NaBH_4$ to obtain the final Pd/Ni-mCN catalyst with high Pd NPs dispersion. Pd/Ni-mCN was used in the catalytic HDC of CPs showing superior catalytic efficiency and easy recovery and reusability.

2. Experimental

2.1. Chemicals

The reagents used for the preparation of the Ni-MOF ($Ni(NO_3)_2 \cdot 6H_2O$, 4,4′-bipyridine, and 1,3,5-benzenetricarboxylic acid) were purchased from Sigma-Aldrich. CPs were of analytical grade and supplied by Aladdin reagents. Some other frequently used reagents and solvents were used as supplied.

2.2. Preparation of Ni-mCN

The Ni-MOF were fabricated following the method reported by Jun Chen [48]. In a typical procedure, 3 mmol of 4,4′-bipyridine, 3 mmol of 1,3,5-benzenetricarboxylic acid, and 3 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 60 mL of dimethylformamide (DMF) at room temperature under vigorous stirring. The mixture was subsequently kept at 80 °C for 72 h in a teflon-lined autoclave. After cooling to room temperature, a green solid was obtained by filtration, washed thoroughly with DMF, and vacuum dried in an oven overnight. Finally, the dry Ni-MOF powder was calcined at 700 °C (5 °C min^{-1}) for 2 h under N_2 atmosphere in a tube furnace to obtain the Ni-mCN nanocomposite.

2.3. Preparation of Pd/Ni-mCN catalyst

A certain amount of $Pd(AcO)_2$ was dissolved in 20 mL of deionized water. 264 mg of Ni-mCN were subsequently added to the above solution and ultrasonically dispersed. The dispersion was cooled to 0 °C, and a $NaBH_4$ solution was added dropwise in excess. The solution was stirred overnight and the resulting solid was centrifugally separated to obtain the Pd/Ni-mCN nanocatalyst.

2.4. HDC of 4-CP

The HDC of 4-CP was carried out at 20 °C under atmospheric pressure. Typically, Pd/Ni-mCN (5 mg), 4-CP (192 mg, 1.5 mmol), and NaOH (60 mg, 1.5 mmol) were dissolved in 15 mL of deionized water. The flask was subsequently connected with a balloon filled with H_2, thereby allowing the air in the flask to be thoroughly replaced by H_2, and the reaction was immediately started under vigorous stirring. The reaction progress was monitored by collecting aliquots from the reaction mixture with a glass syringe at an interval of 10 min. The collected mixture was passed through a 0.45 μm membrane filter, and the filtrate was extracted by chromatographically pure $CH_3COOC_2H_5$. The HDC reaction conversion was then estimated by using gas chromatography coupled with mass spectrometry (GC–MS, Agilent 5977E). The spent Pd/Ni-mCN catalyst was recovered by using a magnet, washed with ethanol, and finally vacuum dried at room temperature in an oven for the next catalytic run. The catalytic procedure was repeated five times.

2.5. Characterization

The morphology of the Ni-MOF, Ni-mCN, and Pd/Ni-mCN materials was observed by scanning electron microscopy (SEM, JSM-6701F) and transmission electron microscopy (TEM, Tecnai G2F30) coupled with energy dispersive spectroscopy (EDS). Powder X-ray diffraction (XRD, Rigaku D/max-2400) measurements were performed in a diffractometer using the Cu-Kα radiation as the X-ray source within the 2θ range of 10–80°. X-ray photoelectron spectroscopy (XPS, PHI-5702) was recorded to analyze the electronic states of the surface components of Ni/m-CN using the C 1 s line at 284.6 eV as the binding energy reference. Magnetic measurements were carried out for Ni/m-CN by vibrating sample magnetometry (VSM) at room temperature with an applied magnetic field varying from −20 to 20 kOe. Nitrogen adsorption/desorption experiments were performed at 77 K in an ASAP 2010 device (Micromeritics, USA). Inductively coupled plasma atomic emission spectroscopy (ICP–AES) and elemental analysis (GmbHVario, El Elementar) were also used to measure the Ni, N, C, and H contents in Ni/m-CN.

3. Results and discussion

Herein, the Ni MOF-derived magnetic mesoporous carbon Ni-mCN, generated by carbonization of the Ni MOF under inert atmosphere, was used to prepare the Pd-based catalyst Pd/Ni-mCN. The morphology of the Ni MOF showed a shape with irregular plates (Fig. 1a). After carbonization under inert atmosphere, the Ni MOF was transformed into a mesoporous carbon framework with Ni NPs of ca. 8 nm diameter embedded in the C framework (Fig. 1b). The Ni NPs were generated during carbonization by reduction with carbon. The FTIR spectra also confirmed the Ni MOF to Ni-mCN transformation process (Fig. S1). Ni MOF showed a large number of —CH ($\nu_{2900\,cm^{-1}}$) and other organo-functional ($\nu_{500-1600\,cm^{-1}}$) groups before the carbonization process. The —CH group stretching vibration around 2900 cm^{-1} disappeared upon carbonization while other stretching vibrations at 1580, 1260, and 758 cm^{-1} (assigned to the stretching modes of CN heterocycles formed during the carbonization procedure) were generated [49,50]. The FTIR results revealed the presence of CN heterocycles in the mesoporous carbon framework. Fig. 1c shows a TEM image of Pd/Ni-mCN. It can be seen that the morphology and the structure of Ni-mCN was preserved after the impregnation/$NaBH_4$ reduction processes, while the Pd NPs were supported on the mesopores and on the surface of Ni-mCN. The EDS spectra showed the Pd/Ni-mCN catalyst to be mainly composed of C, N, O, Ni, and Pd elements (Fig. S2). With the aim to study the elemental distribution of Pd/Ni-mCN, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed (Fig. 1d). The framework of the Pd/Ni-mCN catalyst was mainly composed of C and N. The Ni NPs