



Nickel nanoparticles decorated on electrospun polycaprolactone/chitosan nanofibers as flexible, highly active and reusable nanocatalyst in the reduction of nitrophenols under mild conditions

Kadir Karakas^a, Asli Celebioglu^b, Metin Celebi^a, Tamer Uyar^{b,c,**,2}, Mehmet Zahmakiran^{a,*,1}

^a Nanomaterials and Catalysis (NanoMatCat) Research Laboratory, Department of Chemistry, Yüzüncü Yıl University, Van, 65080, Turkey

^b UNAM-National Nanotechnology Research Center, Bilkent University, Ankara, 06800, Turkey

^c Institute of Materials Science & Nanotechnology, Bilkent University, Ankara, 06800, Turkey

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ABSTRACT

Today, the reduction of nitro aromatics stands a major challenge because of the pollutant and detrimental nature of these compounds. In the present study, we show that nickel(0) nanoparticles (Ni-NP) decorated on electrospun polymeric (polycaprolactone(PCL)/chitosan) nanofibers (Ni-NP/ENF) effectively catalyze the reduction of various nitrophenols (2-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol) under mild conditions. Ni-NP/ENF nanocatalyst was reproducibly prepared by deposition-reduction technique. The detailed characterization of these Ni-NP/ENF based nanocatalyst have been performed by using various spectroscopic tools including ICP-OES, P-XRD, XPS, SEM, BFTEM, HRTEM and BFTEM-EDX techniques. The results revealed the formation of well-dispersed nickel(0) NP ($d_{\text{mean}} = 2.71\text{--}2.93\text{ nm}$) on the surface of electrospun polymeric nanofibers. The catalytic activity of the resulting Ni-NP/ENF was evaluated in the catalytic reduction of nitrophenols in aqueous solution in the presence of sodium borohydride (NaBH_4) as reducing agent, in which Ni-NP/ENF nanocatalyst has shown high activity (TOF = 46.2 mol 2-nitrophenol/mol Ni min; 48.2 mol 2,4-dinitrophenol/mol Ni min; 65.6 mol 2,4,6-trinitrophenol/mol Ni min). More importantly, due to the nanofibrous polymeric support, Ni-NP/ENF has shown a flexible characteristics along with reusability property. Testing the catalytic stability of Ni-NP/ENF revealed that this new catalytic material provides high reusability performance (at 3rd reuse 86% for 2-nitrophenol, 83% 2,4-dinitrophenol and 82% 2,4,6-trinitrophenol) for the reduction of nitrophenols even at room temperature and under air. The present study reported here also includes the compilation of wealthy kinetic data for Ni-NP/ENF catalyzed the reduction of nitrophenols in aqueous sodium borohydride solution depending on temperature and type of support material (Al_2O_3 , C, SiO_2) to understand the effect of the support material and determine the activation parameters.

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1. Introduction

Nitrophenols are a kind of the most widely used industrial nitro aromatic compounds (NAC's) and frequently employed as interme-

diates in the production of explosives, pharmaceuticals, pesticides, pigments, dye, wood preservatives and rubber chemicals [1,2]. Although, they are useful intermediates in the fabrication of various aforementioned materials, they also act as common environmental pollutants because of their toxicity and resistance to microbial degradation [3,4]. For these reasons, nitrophenols are considered as a priority pollutant by the Environmental Protection Agency (EPA) of USA, and its concentration in natural waters is restricted to less than 10 mg/L [5,6]. Up to date, various techniques such as membrane filtration [7,8], microbial degradation [9,10], photocatalytic degradation [11,12], electro-Fenton method [13,14], electrocoagulation [15,16], adsorption [17,18], electrochemical treatment

* Corresponding author.

** Corresponding author at: UNAM-National Nanotechnology Research Center, Bilkent University, Ankara, 06800, Turkey.

E-mail addresses: tamer@unam.bilkent.edu.tr (T. Uyar), zmehmet@yyu.edu.tr (M. Zahmakiran).

¹ Website: www.nanomatcat.com.

² Website: <http://unam.bilkent.edu.tr/~uyar>.

[19,20] and chemical reduction [21,22] have been reported for removing nitrophenols from contaminated water. Among these techniques, the chemical reduction of nitrophenols seems to be most efficient way to remove nitrophenols from waste contaminated water. Additionally, aminophenols formed via the reduction of nitrophenols usually find applications as a photographic developer of films, corrosion inhibitor, drying agent, precursor for the manufacture of analgesic and antipyretic drugs [23–25].

Over the last decade, nanotechnology, which deal primarily with the synthesis, characterization, and exploration of nanomaterials, has become a popular research area, where significant efforts have been made to use nanoscale systems [26]. The impact of these researches to both fundamental science and potential applications has been tremendous and is still growing [27]. Nanomaterials have already found many fascinating applications in a wide variety field of chemistry, physics, electronics, biology, medicine and catalysis. The latter application field of nanomaterials is of particular interest as it is the key for the development of starting chemicals, fine chemicals and pharmaceutical drugs from raw materials [28]. Compared to their bulk-counterparts, metal nanoparticles have much higher surface-to-volume ratio, thus, larger fraction of catalytically active atoms on the surface, and these surface atoms of nanoparticles do not order themselves in the same way as those in bulk metal [29]. Furthermore, the electrons in nanoparticles are confined to spaces that can be as small as a few atoms widths across giving rise to quantum size effects [30] and higher Fermi potential which leads to the lowering of reduction potential value, and hence metal nanoparticles can function as a catalyst for many electron-transfer reactions such as reduction of nitrophenols [31].

Hitherto, various types of ligands or surfactants stabilized Au [32], Ag [33], Pd [34], Pt [34,35] and Ni [36] nanoparticles have already been tested as active nanocatalyst in the reduction of nitrophenols in the presence of sodium borohydride as a reductant. However, the recovery of noble metal nanoparticles from such stabilizers-containing systems is not easy and also makes UV/vis spectroscopy monitoring of the reaction extremely difficult due to the presence of suspended nanoparticles in the reaction solution. In addition, there is another critical matter to obtain pure active metal surfaces by staying away from surface contamination resulting from surface protecting groups, which often lead to a decrease in the catalytic performance resulting from the blocking of active sites. Moreover, the low stability of these colloidal nanoparticles against agglomeration diminishes their reusability performances, which is one of the most important criterias in the heterogeneous catalysis. In this context, the generation of the metal nanoparticles on solid support materials has already been acknowledged for preventing aggregation of active metal nanoparticles and providing high reusability performances in the nitrophenols reduction [37–40]. Additionally, the use of supported metal nanoparticles as nanocatalyst in the reduction of nitrophenols may provide a kinetic control of the catalytic reaction, whereas it is almost impossible in the catalytic employment of colloidal metal nanoparticles. Despite all the advancement in supported metal nanocatalyst preparation [41], there is still great interest in developing catalyst supports with high stability and large surface area. At this concern, electrospinning has been considered as one of the powerful methods to generate nanofibrous support materials with a huge specific surface area [42–45]. Recent studies have already shown that electrospun polymeric nanofibers act as efficient support material in the stabilization of Fe(O) [46], Au(O) [47], Pd(O) [48], Pt(O) [49] and Ag(O) [50] nanoparticles for environmental remediation applications [46–51]. The catalytic stability results obtained in these studies prompted us to use electrospun polymeric nanofibers as catalyst support for guest catalytically active metal nanoparticles in the catalytic reduction of nitrophenols.

In this study, we report a facile synthesis of nickel nanoparticles (Ni-NP) decorated on electrospun polymeric (polycaprolactone(PCL)/chitosan) nanofibers, hereafter referred to as Ni-NP/ENF, and their excellent catalysis for the reduction of various nitrophenols including 2-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol in aqueous sodium borohydride (NaBH_4 ; as reducing agent) solution. Chitosan subunit has been selected in the preparation of electrospun polymeric nanofibers because of its $-\text{NH}_2$ groups, which may act as ligand stabilizer to surface bound Ni-NP. Some of us have already reported that the existence of surface grafted $-\text{NH}_2$ groups on solid support materials can act as stabilizing agents to supported PdAuCr [52], PdAg-MnO_x [53], PdAu-MnO_x [54] and Pd-MnO_x [55] nanoparticles. Ni-NP/ENF catalyst was simply and reproducibly prepared through surfactant-free deposition-*in-situ* reduction technique [56] at room temperature, and characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), powder X-ray diffraction (P-XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), bright field transmission electron microscopy (BFTEM) and high resolution transmission electron microscopy (HR-TEM). The sum of their results revealed that the formation of nickel(0) nanoparticles ($d_{\text{mean}} = 2.71\text{--}2.93$ nm) on the surface of electrospun PCL/chitosan nanofibers. These Ni-NP/ENF catalyst provide exceptional activities (TOF = 46.2 mol 2-nitrophenol/mol Ni min; 48.2 mol 2,4-dinitrophenol/mol Ni min; 65.6 mol 2,4,6-trinitrophenol/mol Ni min) in the reduction of nitrophenols even at room temperature and under air. Moreover, the excellent durability of Ni-NP/ENF and their flexible nature enable them reusable nanocatalyst for the nitrophenols reduction.

2. Experimental

2.1. Materials

Nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), methanol (CH_3OH), sodium borohydride (NaBH_4), 2-nitrophenol ($\text{O}_2\text{NC}_6\text{H}_4\text{OH}$), 2,4-dinitrophenol ($(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{OH}$), 2,4,6-trinitrophenol (picric acid; $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{OH}$), acetic acid (AA; $\text{CH}_3\text{CO}_2\text{H}$), formic acid (FA; HCOOH), polycaprolactone ($(\text{C}_6\text{H}_{10}\text{O}_2)_n$ PCL, Mw: 80,000 g/mol) and chitosan (Poly(D-glucosamine), low molecular weight) were purchased from Sigma-Aldrich® and used without any purification. Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware and Teflon-coated magnetic stir bars were washed with acetone and copiously rinsed with distilled water before drying in an oven at 323 K.

2.2. Characterization

Nickel contents of the Ni-NP/ENF, Ni/C, Ni/SiO₂ and Ni/Al₂O₃ samples were determined by ICP-OES (Leeman, Direct Reading Echelle) after each sample was completely dissolved in a mixture of HNO_3/HCl (1/3 ratio). The scanning electron microscope (SEM) (Quanta 200 FEG, FEI) was used for the morphological characterizations of nanofibers. Prior to imaging, samples were sputtered with 5 nm Au/Pd (PECS-682) and the average fiber diameter (AFD) was calculated from the SEM images by analyzing at least 100 fibers. During the SEM characterization, energy dispersive X-ray (EDX) measurements were also performed for the elemental analysis of the nanofibers. Bright field transmission electron microscopy (BFTEM) and high resolution transmission electron microscopy (HR-TEM) were performed on FEI-Tecna G2F30, operating at 300 kV. For imaging of TEM, electrospinning of nanofibers was performed directly onto the TEM grids. Then, the nanofibers collected onto TEM grids were exposed to treatment for the grow-

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