Polymer supported Nickel nanoparticles as recyclable catalyst for the reduction of nitroarenes to anilines in aqueous medium

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ABSTRACT

Polymer supported nickel nanoparticles, generated by calcination under nitrogen of a Ni(II) containing polyacrylamide, catalyzed the hydrogenation of nitroarenes to anilines in aqueous medium at room temperature in the presence of $NaBH_4$. The protocol generally favored the formation of the desired aniline as single product in high yields with short reaction times and proved to be highly selective in the hydrogenation of halonitrobenzene to haloaniline, avoiding the formation of hydro-dehalogenated side-products. The catalyst displayed excellent recyclability over at least five cycles (which is not trivial for nickel nanoparticle based catalysts used in water) and no leaching of metal into solution occurred, that made the overall system eco-friendly and economic. STEM analyses revealed that the thermally formed Ni nanoparticles turned into cubic nanotwins under reaction conditions, which remained almost unchanged with the re-cycles.

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1. Introduction

The last few years have witnessed an explosion in the use of new nanomaterials for catalytic application [1]. In this field, noble metal nanoparticles (NPs) have been widely employed in catalysis [2] and several studies have been devoted to the recyclability of these expensive materials [3]. Nevertheless, the high cost of noble metals has limited their practical use. The substitution of noble metals for abundantly available transition metals is an attractive strategy for lowering production costs and favoring noble-metal conservation in the planet [4]. In this context, recently, due to their low cost, Ni catalysts have been employed in several organic reactions (mainly hydrogenations) [5].

The hydrogenation of nitroarenes to give the corresponding aromatic amines is a basic chemical reaction used both for removing toxic nitro aromatics from aqueous medium and for synthetizing anilines. In fact, aromatic amines are important bulk chemicals and intermediates to produce fine chemicals, pharmaceuticals, polymers, herbicides, and more [6]. The industrial hydrogenation of nitrobenzene for the synthesis of aniline uses copper, palladium

or palladium-platinum supported on carbon or inorganic oxides, as catalysts, under high pressure (up to 3 MPa) and high temperature (up to 300 °C), and it is not able to avoid the formation of noxious azo- and azoxyderivatives, which lowers the yield into anilines [6]. Aiming at overcoming the above reported weaknesses, the scientific community tried to develop alternative protocols for the reduction of aromatic nitro compounds [7], including the use of different reducing agents, such as hydrazine [8], silane [9] and sodium borohydride [10] in the presence of Cu [11], Pd [12], Au [13], Ru [14], Ag [15], and, more recently, Co [16] and Ni [17] catalysts.

Nevertheless, the major problems remain still unsolved and designing new systems with different chemical and physical compositions and morphologies for catalytic reduction of nitroarenes under sustainable conditions is an urgent topic of current research.

In the search for innovative catalytic processes that enable chemical transformations under mild, cheap and sustainable conditions with high efficiency, we prepared an acryl amidic polymer supported nickel catalyst (in the following *Ni-pol*) and we evaluated its catalytic activity in the hydrogenation of nitroarenes in aqueous medium. The real active species were Ni nanoparticles with a peculiar nanostructure stabilized by the insoluble support, which were active, selective and recyclable in the reduction of various nitroarenes into anilines in water in the presence of sodium boro-

hydride, that is a cheap, easy-handling and ready available reducing agent with extensive applications in organic synthesis [18].

2. Experimental section

2.1. General considerations

Tap water was de-ionized by ionic exchange resins (Millipore) before use. All other chemicals were purchased from commercial sources and used as received. Nickel content in *Ni-pol* was assessed after sample mineralization by atomic absorption spectrometry using a Perkin–Elmer 3110 instrument. The experimental error on the nickel percentage was ± 0.3. Mineralization of N*i-pol* prior to Ni analyses was carried by microwave irradiation with an ETHOS E-TOUCH Milestone applicator, after addition of HCl/HNO$_3$ (3:1 v/v) solution (12 mL) to each weighted sample. Microwave irradiation up to 1000 W was used, the temperature being ramped from rt to 220 °C in 10 min and the sample being held at this temperature for 10 min. After cooling to room temperature, the digested *Ni-pol* was diluted to 1000 mL before submitting to Graphite Furnace Atomic Absorption Spectrometric nickel determination.

GC–MS data (EI, 70 eV) were acquired on a HP 6890 instrument using a HP-5MS cross-linked 5% pphenyl methyl siloxane (30.0 m × 0.25 mm × 0.25 μm) capillary column coupled with a mass spectrometer HP 5973. The products were identified by comparison of their GC–MS features with those of authentic samples. Reactions were monitored by GLC or by GC–MS analyses. GLC analysis of the products was performed using a HP 6890 instrument equipped with a FID detector and a HP-1 (Crosslinked Methyl Siloxane) capillary column (60.0 m × 0.25 mm × 1.0 μm). Conversions and yields were calculated by GLC analysis by using biphenyl as internal standard, or by column chromatography using silica gel and *n*-hexane/ethyl acetate as the eluent.

FT-IR spectra (in KBr pellets) were recorded on a Jasco FT/IR 4200 spectrophotometer. Elemental analyses were obtained on a EuroVector CHNS EA3000 elemental analyser using acetanilide as analytical standard material. The high-resolution mass spectrometry (HRMS) analysis was performed using a Bruker microTOF Q II mass spectrometer equipped with an electrospray ion source operated in positive ion mode. The sample solutions (CH$_3$OH) were introduced by continuous infusion with a syringe pump at a flow rate of 180 μL min^{-1}. The instrument was operated with end-plate offset and capillary voltages set to −500 V and −4500 V respectively. The nebulizer pressure was 0.4 bar (N$_2$), and the drying gas (N$_2$) flow rate was 4.0 L min^{-1}. Capillary exit and skimmer voltages were 90 V and 30 V, respectively. The drying gas temperature was set at 180 °C. The calibration was carried out with a sodium formate solution (10 mM NaOH in isopropanol/water 1:1 (+0.2% HCOOH)) and the software used for the simulations was Bruker Daltonics DataAnalysis (version 4.0). Thermogravimetric analyses (TGA) were performed in a nitrogen flow (40 mL min^{-1}) with a Perkin-Elmer Pyris 6 TGA in the range from 30 to 800 °C with a heating rate of 10 °C min^{-1}. Triplicate TGA runs have been performed to ensure reproducibility.

Surface morphology was investigated on a selected piece of Ni-supported catalyst considered to be representative of the material. Nova NanoSEM 450 manufactured by FEI Company, USA, was used to perform FESEM analysis on the selected samples. Tiny plate-like of the powdered catalyst were mounted on TEM copper grids, and gold-palladium sputtered (K550, Emitech Ltd, United Kingdom). Scanning Transmission Electron Microscopy (STEM) Detector allowed transmission images to be taken at 30 keV, lower energy level with respect to commonly used TEM, beam voltage 100–200 keV. Resolution limits of this microscope are remarkable: 1.4 nm @ 1 kV in high vacuum mode. The particle sizes were ana-

lyzed by STEM image analysis using the ImageJ software (freeware software: http://rsb.info.nih.gov/ij/).

2.2. Catalyst preparation

The supported catalyst (*Ni-pol*) was prepared by calcination under nitrogen of a polymer supported Ni(II) complex (*Ni(AAEMA)$_2$-pol*), which in turn was obtained by co-polymerization of the polymerizable complex Ni(AAEMA)$_2$.

2.2.1. Ni(AAEMA)$_2$
To a solution of KOH (579 mg, 10.3 mmol) in ethanol (10 mL), 2-(acetoacetoxy)ethyl methacrylate (HAAEMA) (2.211 g, 10.3 mmol) was added and left under stirring at room temperature for 5 min. The resulting solution was added to a solution of Ni(NO$_3$)$_2$· 6 H$_2$O (1.5 g, 5.16 mmol) in ethanol (15 mL), causing the sudden precipitation of Ni(AAEMA)$_2$ as a pale green solid. After 1 h stirring, the solid was filtrated and washed with water (3 × 5 mL), ethanol (3 × 5 mL) and pentane (3 × 5 mL), and dried overnight under vacuum. Anal. Calc. for NiC$_{20}$H$_{26}$O$_{10}$: C, 45.00; H, 4.92; Ni, 19.97. Found: C, 44.50; H, 4.99; Ni, 19.76. HRMS: (ESI, CH$_3$OH, positive ion mode) *m/z*: calcd. for NiC$_{20}$H$_{27}$O$_{10}$ [M + H]$^+$ 485.0952; found 485.0954. IR (cm^{-1}): 1720 (s), 1635 (s), 1623 (s), 1521 (s), 1385 (vs), 1259 (vs), 1161 (vs), 977 (m), 785 (m). UV–vis (CH$_2$Cl$_2$): 280 nm (ε = 10660 mol L^{-1} cm^{-1}), 227 nm (ε = 4800 mol L^{-1} cm^{-1}). m.p. = 120.3 ± 0.4 °C. Yield: 2.01 g, 80%.

2.2.2. Ni(AAEMA)$_2$-pol
Ni(AAEMA)$_2$ (4.0 mmol, 2.0 g) [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy) ethyl methacrylate] was dissolved in N,N−dimethylformamide (DMF, 5 mL) and the resulting solution was added of a mixture of N,N'-methylenebisacrylamide (1.2 mmol, 0.186 g) and N,N −dimethylacrylamide (43.2 mmol, 4.434 g) in DMF (6 mL) and heated at 120 °C under vigorous stirring. After 1 h from the addition of azaisobutyronitrile (5 mg), the green jelly solid which formed in the reaction vessel was filtered off, washed with acetone and diethyl ether, dried under vacuum, kept overnight in oven at 95 °C and grinded with a mortar to give a pale green powder. Yield: 4.04 g of polymer supported Ni(AAEMA)$_2$ [*Ni(AAEMA)$_2$-pol*]. Elemental Analysis (found): Ni 3.69; C 57.06; H 7.94; N 9.91%. IR (cm^{-1}): 3477 (bs), 2923 (bs), 1720 (s), 1622 (s), 1527 (s), 1256 (vs), 1144 (vs), 1355 (s), 780 (m).

2.2.3. Ni-pol
The as-obtained *Ni(AAEMA)$_2$-pol* was put in a tube furnace, ramped at 10 °C min^{-1} in flowing N$_2$ to 300 °C, and kept at the final temperature for 30 min, yielding a black powder referred to as *Ni-pol*. Yield: 3.83 g. Elemental Analysis (found): Ni 5.35; C 56.66; H 9.20; N 11.54%. IR (cm^{-1}): 3482 (bs), 2930 (bs), 1720 (s), 1631 (s), 1495 (m), 1402 (m), 1258 (m), 1144 (s), 1053 (m).

2.3. General experimental procedure for the reduction of nitroarenes catalyzed by Ni-pol

0.5 mmol of nitroarene, 10.2 mg of *Ni-pol* (Ni%$_w$ = 5.35, 9.3 10^{-3} mmol of Ni) and 10.0 mmol of sodium borohydride were stirred under nitrogen at room temperature in 2.5 mL of double deionized water and 2.5 mL of diethyl ether for the appropriate amount of time, using a three-necked flask equipped by a gas bubbler to discharge the hydrogen excess produced during reaction. The progress of the reaction was monitored by GLC. After completion of the reaction, the reaction mixture was centrifuged to separate the catalyst. The solid residue was first washed with deionized water and then with acetone and diethyl ether to remove any traces of organic material. The filtrate containing the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and then dried