



NiO nanoparticles prepared via thermal decomposition of the bis(dimethylglyoximato)nickel(II) complex: A novel reusable heterogeneous catalyst for fast and efficient microwave-assisted reduction of nitroarenes with ethanol

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ARTICLE INFO

Article history:

Received 28 September 2010

Accepted 25 November 2010

Available online 7 December 2010

Keywords:

Nanoparticles

NiO

Nitroarenes

Reduction

Microwave irradiation

Arylamines

ABSTRACT

NiO nanoparticles with an average size of 12 nm and a high specific surface area of 88.5 m²/g were easily prepared via the thermal decomposition of the complex Ni(dmgh)₂ and were characterized by TGA, XRD, FT-IR, TEM and BET surface area measurement. This nanosized transition metal oxide was used as a new heterogeneous catalyst for the reduction of nitroarenes under microwave irradiation. The efficient and selective reduction of aromatic nitro compounds into their corresponding amines was observed by using ethanol as a hydrogen donor (reducing agent) and KOH as a promoter under microwave irradiation. This highly regio- and chemoselective method is fast, simple, inexpensive, high yielding, clean and compatible with several sensitive functionalities, such as halogens, –OH, –OCH₃, –CHO, –COCH₃, –COOH, –COOEt, –CONH₂, –CN, –CH=CH₂ and –NHCOCH₃. This method is suitable for the large scale preparation of different substituted anilines as well as other arylamines. In addition, the catalytic activity of nanosized NiO is higher than that of the bulk sample.

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1. Introduction

The reduction of nitroarenes to arylamines is a synthetically important transformation both in the laboratory and in industry [1]. Arylamines are important starting materials and intermediates for the manufacture of numerous organic chemicals, such as dye-stuffs, pharmaceutical products, agricultural chemicals, surfactants and polymers [2,3]. This important transformation is traditionally performed using metals such as Fe, Zn and Sn in acidic or basic media, which generate a large amount of metal wastes [4–6]. In recent years, numerous reagents have been developed for the reduction of nitroarenes to their corresponding amines, including activated metals [7–10], Al/NH₄Cl/MeOH [11], Zn/CaCl₂/EtOH [12], Co₂(CO)₈/H₂O [13], Mo(CO)₆ [14], SnCl₂/H₂O [15], SnCl₂/ionic liquid [16], N₂H₄/FeCl₃ [17], N₂H₄/Zn [18], TiCl₃ [19], NaH₂PO₂/FeSO₄ [20], B₁₀H₁₄/Pd/C [21], FeCl₃/Zn/DMF/H₂O [22], HCOONH₄/Pd/C [23], HCOONH₄/Mg [24], HCOON₂H₅/Zn [25], N₂H₄/Ru(bpy)₂/hν [26], HCOOH/Raney nickel [27], N₂H₄/Raney nickel [28], HCOONa/K₃PO₄ [29], N₂H₄/AlH₃/AlCl₃ [30], HCOONH₄/Ni[P(OPh₃)₄] [31], N₂H₄-H₂O/Fe₂O₃/MgO [32], Na₂S/NEt₄Br [33], Sm/NH₄Cl/ultrasound irradiation [34], HCOON₂H₅/Raney Ni [35], HI [36],

S₈/NaHCO₃ [37], NaBH₄/Raney nickel [38], Fe(acac)₃/TMDS [39] and N₂H₄/A₂O₃/MWI [40]. Catalytic hydrogenation employing molecular hydrogen and catalysts such as Pd/C, Pd(II) complexes/Al₂O₃ or Raney nickel have also been reported for the reduction of nitroarenes [41–44]. However, each of these methods has its own advantages and limitations. From a practical viewpoint, the development of simpler, inexpensive, widely-applicable and environmentally-benign procedures is still an active area of research.

One of the most promising methods for the reduction of nitroarenes to their corresponding amines is catalytic transfer hydrogenation [45]. This method presents a special variation of catalytic hydrogenation in which the highly diffusible and flammable hydrogen gas is replaced with a safe, green and stable hydrogen donor, such as hydrazine hydrate, formic acid or alcohols. The use of hydrogen donors has some advantages over molecular hydrogen since it avoids the risks and the constraints associated with the highly flammable hydrogen gas as well as the necessity for pressure vessels and other expensive equipment. In comparison with homogeneous systems, heterogeneous catalytic transfer hydrogenation has potential advantages, including operational simplicity, high chemoselectivity and yield, no highly diffusible flammable hydrogen gas being used and no special equipment required. Pt, Pd, Ru and Raney Ni are classical heterogeneous catalysts employed in catalytic transfer hydrogenation [46]. These catalysts are expensive and require stringent precautions because

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of their flammable nature in the presence of air. Since this transformation requires catalysts with a high surface area and highly acidic active sites, it seems that nanosized materials which possess such characteristics could be very suitable for this purpose. In recent years, inorganic nanomaterials, such as silicate or aluminophosphate molecular sieve-supported transition metal ions [47–54], polymer-supported amorphous Ni–B nanoparticles [55], silica-supported gold nanoparticles (nano-Au/SiO₂) [56], Mg–Fe Hydrotalcite [57] and Faujasite NaY zeolite [58], have been employed as safe and green recyclable heterogeneous catalysts for the catalytic transfer hydrogenation of nitroarenes to arylamines. However, these reactions are usually conducted under conventional refluxing conditions, a process that requires several hours of time. Furthermore, the activity of most of the catalysts decreases with subsequent recycling.

Nanostructured transition metal oxides have attracted great interest in recent years due to their particular physical and chemical properties compared to bulk materials [59]. The properties of these materials mainly depend on their shape, size and structure, which are strongly determined by their synthetic processes. Among the various nanostructures of metal oxides, nanoparticles containing a high surface area and reactive morphologies have been considered as effective catalysts for organic reactions such as acetylation, hydrogenation, oxidation, and cross-coupling [60–69]. Nickel oxide (NiO) is one of the most common metal oxides used for catalytic purposes. It was reported that NiO nanoparticles are much more effective catalysts than commercial NiO powder for catalytic reduction of carbon dioxide to methanol [70]. There are many different methods reported for the synthesis of nanosized nickel oxide [71–74]. Among these methods, the solid-state thermal decomposition of Ni(II) complexes exhibits many advantages: no need for solvent, surfactant and complex apparatus, high yields, low energy consumption and simple reaction technology.

In continuation of our interest in exploring nanostructured catalysts for organic transformations [66–69], in this work NiO nanoparticles were easily prepared via the thermal decomposition of the bis(dimethylglyoximate)nickel(II) complex and their catalytic activities were evaluated in the reduction of nitroarenes to their corresponding amines with ethanol. The catalytic results indicate that the nanosized NiO oxide is a green, highly selective and efficient recyclable catalyst for the rapid reduction of nitroarenes to their corresponding amines by using ethanol as a hydrogen donor and potassium hydroxide as a promoter under microwave irradiation. To the best of our knowledge, this is the first report on the catalytic reduction of nitroarenes over a nanosized metal oxide in conjunction with microwave irradiation.

2. Experimental

All the nitroarenes were commercially available and were used without further purification. All the solvents were spectroscopic grade. A commercial bulk NiO sample with a surface area of 8.5 m²/g and an average particle size of 18 μm was purchased from Merck. Microwave irradiation was carried out using in a laboratory modified microwave oven (LG-30L, 900 W, MW frequency 2.45 GHz). All products of the reduction of nitroarenes are commercially available and were identified by comparing their physical and spectral data (m.p., TLC, FT-IR, GC–MS and ¹H NMR) with those of authentic samples or reported data.

2.1. Preparation of nanosized NiO catalyst

In order to prepare nanosized NiO particles, the bis(dimethylglyoximate)nickel(II) complex (Ni(dmgH)₂, 5 g) was placed in a porcelain crucible and was then heated in an electric furnace at

400 °C for 0.5 h in air. The temperature for the decomposition of the complex was selected from the results of thermogravimetric analysis (TGA). The decomposition product was cooled to room temperature and collected for characterization.

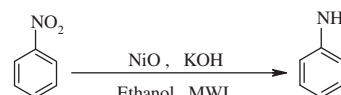
2.2. Catalyst characterization

The crystal structure and phase composition of the NiO nanoparticles were identified with a Bruker D4 Advance X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm). Infrared spectra were recorded on a Shimadzu system FT-IR 160 spectrophotometer using KBr pellets. Thermogravimetry analysis (TG) of the precursor was performed in a Netzsch STA 409 PC simultaneous thermal analyzer at a heating rate of 5 °C/min. The morphology of the catalyst was determined by a scanning electron microscope (SEM, Philips XL-30). The size of the catalyst particles was determined by a transmission electron microscope (TEM, LEO-906E) at an accelerating voltage of 80 kV. TEM samples were prepared by dropping the ethanol dispersion on a carbon-coated copper grid. The specific surface area was calculated by the BET method using N₂ adsorption–desorption experiments, carried out at –196 °C on a Micromeritics ASAP 2010. Before each measurement, the sample was outgassed at 150 °C for 1 h.

2.3. Catalytic tests

In a 100 mL Teflon-bottle was placed nitroarene (5 mmol), KOH (5 mmol), ethanol (10 mL) and NiO (50 mg) as the catalyst. The vessel was sealed and irradiated in a laboratory microwave oven at 180 W. The progress of the reaction was monitored by TLC and GC–MS. After completion of the reaction, the mixture was cooled to room temperature and the organic layer extracted with ethyl acetate (2 × 10 mL), dried over anhydrous Na₂SO₄ and concentrated under a reduced pressure. The residue was subjected to silica-gel plate or column chromatography using carbon tetrachloride–ethyl acetate to give the pure product. The reduction of nitroarenes was also carried out under the conventional heating in a similar manner except that the reaction mixture was refluxed for the appropriate time in an oil-bath. The results of initial experiments to obtain the optimized reaction conditions are summarized in Tables 1–3. The general results are presented in Table 4. The obtained results by using bulk NiO catalyst instead of nanosized NiO catalyst are compared in Table 5.

Table 1
Effect of the catalyst amount on the reduction of nitrobenzene with ethanol.^a



| Entry | NiO (mg) | Time (min) | Yield (%) ^b |
|-----------------|----------|------------|------------------------|
| 1 | 10 | 30 | 34 |
| 2 | 20 | 30 | 52 |
| 3 | 30 | 30 | 61 |
| 4 | 40 | 20 | 85 |
| 5 | 50 | 13 | 98 |
| 6 | 75 | 12 | 98 |
| 7 | 100 | 12 | 97 |
| 8 ^c | 0 | 25 | 0 |
| 9 ^d | 50 | 25 | 0 |
| 10 ^e | 50 | 20 | 0 |

^a Reaction conditions: nitrobenzene (5 mmol), KOH (5 mmol), ethanol (20 mL), under microwave heating.

^b Isolated yields. Selectivity was >99% in all cases.

^c Without catalyst.

^d Without KOH.

^e In the absence of MWI.

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