Magnetically separable core–shell iron oxide@nickel nanoparticles as high-performance recyclable catalysts for chemoselective reduction of nitroaromatics†

Puran Singh Rathore,a Rajesh Patidar,b T. Shripathic and Sonal Thakore*aa

A magnetically separable core–shell iron oxide@nickel (IO@Ni) nanocatalyst was synthesized by reduction of Ni2+ ions in the presence of iron oxide (Fe2+, Fe3+) by a simple one-pot synthetic route using NaBH4 as a reducing agent and starch as a capping agent. The synthesized nanoparticles (NPs) were characterized by several techniques such as X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDS). The core-shell iron oxide@nickel nanoparticles (IO@NiNPs) were found to have excellent activity for the hydrogenation reactions of aromatic nitro compounds under mild conditions using water as a green solvent. Excellent chemoselectivity and recyclability up to 30 cycles for the nitro group reduction was demonstrated.

Introduction

The concept of “Green Chemistry” has become one of the guiding principles of environmentally benign synthesis.1–3 Nanomaterial-catalyzed transformations in an aqueous reaction medium are one of the ideal solutions for the development of green and sustainable protocols. Nanocatalysis is a rapidly growing field which involves the use of metal nanoparticles as catalysts for a variety of organic reactions.4 The preparation and use of magnetic nanoparticles (MNPs) offers advantages in clean and sustainable chemistry as they are non-toxic, readily accessible, and retrievable.5 Additionally, the activity and selectivity of magnetic nano-catalysts can be manipulated by their surface modification.

The development and design of core–shell nanomaterials has emerged in recent years because of their multifaceted applications especially as catalysts for organic reactions.6,7 Magnetically separable nanocatalysts are an important class of core–shell nanocatalyst, which are robust, air stable, avoid traditional filtration processes and are recyclable.8 Various methods have been developed to synthesize specific application-based MNPs.9–13 Some of them are aimed at developing materials from waste such as iron tailings. Tailings refer to the waste material of beneficiation processes. Among several iron-based solid waste materials, iron ore tailings (IOTs) are one of the fastest accumulating wastes throughout the world due to the rapid expansion of iron and steel based industries and is becoming one of the serious environmental threats for the future generation. Presently, IOTs are mainly used with very little intervention of high technology and moreover, value addition is low. As a result, there is an increasing interest in the search for possible alternative uses of waste IOTs such as adsorption and catalysis or as precursors to value added products before their final discharge.14–17 Here we assess the potential of synthesizing magnetic iron oxide from IOTs and its use as a template for the synthesis of magnetically separable nickel nanoparticles (NiNPs).

The reduction of nitroarenes is an important process as the products, aromatic amines, are versatile intermediates and precursors in the preparation of dyes, pharmaceuticals, pigments, agrochemicals and polymers.28 The process is complicated as the reduction of a nitro group proceeds in stages and it often stops at an intermediate stage producing hydroxylamine and hydrazine as side products.21 A variety of procedures and reducing agents are available for this purpose.23 In the literature, a few procedures involving noble metal NPs such as Pd, Pt, Ag, Au, as well as Fe, Fe3O4@Ni and Ni@Ag NPs have been demonstrated for the reduction of nitro groups.7,22–24 The main limitations of earlier reported work were the necessity of high H2 pressures, prolonged reaction times, lower turnover numbers, organic solvents,
Nickel Nanoparticles as Efficient Catalyst for Electron Transfer Reactions

Puran Singh Rathore · Rajesh Patidar · Sonika Rathore · Sonal Thakore

Received: 7 October 2013 / Accepted: 17 November 2013 / Published online: 17 December 2013 © Springer Science+Business Media New York 2013

Abstract The catalytic efficiency of nickel nanoparticles was investigated in some electron transfer reactions. The nanoparticles brought about rapid room temperature reduction of a number of nitro aromatics in an aqueous medium with high chemoselectivity and also helped to speed up redox reaction of Fe(CN)₆³⁻ and S₂O₇²⁻. In addition, interesting results were obtained for microwave assisted decolourization of azo dye. The reactions were monitored through UV–Vis spectroscopy. The present study has additional advantages of reusability of catalysts and aqueous medium. The ultimate goal was to assess the suitability of low cost nanocatalyst for electron transfer reactions under aqueous conditions.

Keywords Ni nanoparticles · Ni catalyst · p-Nitroaniline · Azo dye · Reduction · Redox reaction

1 Introduction

Nanocatalysis is one of the rapidly developing areas in heterogeneous catalysis [1–5]. Strikingly novel catalytic properties including greatly enhanced reactivity [6] and selectivity [7] have been reported for metal nanoparticles (NPs) catalysts as compared to their bulk counterparts. In addition to noble metals, nanoparticles of nickel (NiNPs) also have proved as catalysts for various organic reactions [3] including the chemo selective oxidative coupling of thiols [7], reduction of carbon–carbon multiple bonds [8, 9], imine reduction [10], hydrodehalogenation of organic halides [11], reduction of sulfonates and aromatic compounds [12], homocoupling of aryl iodides [13], Wittig-type olefination [3], α-alkylation of methyl ketones with primary alcohols [14], reduction of aldehydes and ketones [15, 16], and supports for hydrogen adsorption [17, 18].

The reduction of aromatic nitro compounds to the corresponding amines is important in synthetic chemistry because aromatic amines are frequent intermediates in the production of pharmaceuticals, agrochemicals, polymers, dyes, and other fine chemicals [19]. A variety of procedures and reducing agents are available for this purpose [20]. In literature a few procedures involving noble metal NPs such as Pd, Pt, Ag, Au, as well as Cu, and Ni NPs have been demonstrated for the reduction of nitro group [20–22]. The main limitations of earlier reported work were the necessity of high H₂ pressures, organic solvents and high temperatures. Further, the selection of metal and its support, the hydrogen source and operational simplicity, which are the important parameters for effective conversions, are restricted. However, an alternative efficient, simple, chemoselective, green and cost-effective procedure is highly appreciated.

The role of metal nanoparticles is very important in redox reactions and can be explained in terms of electrochemical potentials [23]. The considerable catalytic activity for the NiNPs can be probably attributed to the following two factors: (1) larger surface than a bulk metal...
Novel Nanoparticle-Assisted Room-Temperature Synthesis of Methyl Esters from Aloe vera Seed Oil

Puran Singh Rathore,† Poonam Mangalorkar,‡ Padamanabhi S. Nagar,‡ M. Daniel,‡ and Sonal Thakore*†

†Department of Chemistry and ‡Department of Botany, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390002, Gujarat, India

ABSTRACT: Aloe vera has been used as a cosmetic and medical remedy since ancient times and has gained increasing popularity in recent years. Despite its widespread use, reports on biodiesel from Aloe vera seeds are lacking. The present investigation reports the fatty acid composition of Aloe vera seed oil (AVSO) and addresses the feasibility of using AVSO as a source of biodiesel. A novel ecofriendly catalyst was developed using triacetin as a model. Interestingly, the room-temperature conversion of AVSO and other nonedible oils to methyl esters could be achieved using this novel catalytic system consisting of ethylene diamine in the presence of nickel nanoparticles (NiNPs). The metal core, capping agent, and amine concomitantly contribute to make the system an effective catalyst.

1. INTRODUCTION

Biodiesel prepared by the transesterification of vegetable oil with methanol is an alternative fuel that can be used directly in any existing unmodified diesel engine. Because its properties are similar to those of diesel fuel, biodiesel can be blended at any ratio with diesel fuel. Among the various vegetable oil sources, nonedible oils are suitable for biodiesel production, as edible oils are already in demand for food and are much more expensive than diesel fuel. Among nonedible oil sources, Jatropha curcas1 and Derris indica are some of the species identified as potential biodiesel sources suitable for tropical and subtropical regions of the world.3 However, a species already having a high potential market can provide an extra edge to its selection. Aloe vera is one such species that has been exploited for medicinal, nutraceutical, and cosmetic purposes. Today, the aloe gel from the center of the leaves is processed. It primarily consists of polysaccharides to which many medicinal properties have also been attributed. However, the potential of Aloe vera seed oil (AVSO) from a biodiesel prospective has not yet been established. We have investigated the fatty acid composition of a number of oil species in the past.3,5 In the present study, we investigated the potential of AVSO for the production of biodiesel.

The use of a strong base such as KOH and mineral acids leads to the wastage of water and the large-scale generation of effluents.4 Hence, extensive research has been carried out for the development of suitable catalysts for biodiesel production. Solid catalysts such as ZnAl hydrotalcite,5 sulfated zirconia,6 KF/ZnO,7 hydrous zirconia-supported 12-tungstophosphoric acid,8 zinc dodecatungstophosphate (Zn12H16O26(P2O7)4O40),9 ZnPW) nanotubes,9 and acid catalyst10 have some shortcomings including high costs and easy deactivation. Solid organic bases have also been used as catalysts for the production of biodiesel.11 However, the recovery of the catalyst was tedious and expensive. In addition, it is advantageous to use low-boiling amines, which have also exhibited good catalytic activity and have a simpler recovery process.12,13 However, the vigorous conditions reported previously for such catalysts are not commercially and economically feasible. Because our group has been actively engaged in the synthesis and applications of metal nanoparticles,14d we decided to develop an easy method for the nanoparticle-assisted organic-amine-catalyzed synthesis of methyl esters.

Currently, metal nanoparticles (NPs) are used widely in many reactions,15 with advantages such as higher specific surface, lower mass-transfer resistance, easy separation, and less fouling than for other catalysts. The high efficiency of a nanoparticle system relies mainly on the approach to the metal core and the structure of the surface. Although a number of organic reactions have been catalyzed, the use of NPs in transesterification reactions has not been extensively reported. In an effort to identify catalyst characteristics that would be ideal for biodiesel synthesis, this study compared the catalytic activities of some organic amines in presence of nickel nanoparticles (NiNPs) with that of the conventional catalyst KOH. Initially, triacetin was used as the model system to simplify the analysis and to accelerate the screening for suitable amine–NP catalytic systems. Consequently, the optimized conditions were used for the synthesis of biodiesel from some recognized oils16a–e and finally applied to AVSO. The products of the new catalyst system were also compared against those obtained from conventional KOH-catalyzed reactions.

To our knowledge, this is the first report on the synthesis of biodiesel from AVSO using a novel catalytic system that works at room temperature.

2. EXPERIMENTAL SECTION

2.1. Materials. Nickel acetate [Ni(CH3COO)2·4H2O], soluble starch, sodium borohydride (NaBH4), liquid ammonia, triacetin, KOH, H2SO4, triethylamine (TEA), ethylenediamine (EDA), diethyl-
Metal nanoparticles assisted amine catalyzed transesterification under ambient conditions

Puran Singh Rathore a, Jacky Advani a, Sonika Rathore b, Sonal Thakore a,⁎

a Department of Chemistry, Faculty of Science, The M.S. University of Baroda, Vadodara 390 002, India
b Mangalam Drugs and Organics Ltd, Vapi 396 195, India

ARTICLE INFO

Article history:
Received 31 December 2012
Received in revised form 1 May 2013
Accepted 6 May 2013
Available online xxx

Keywords:
Transesterification
Nanoparticles
Catalysis
Ethylenediamine

ABSTRACT

Ethylenediamine provides excellent activity under ambient conditions when assisted by metal nanoparticles for the transesterification of higher to lower esters and vice versa. This is the first report on room temperature conversion of diethylnonate to dimethylnonate using this novel catalytic system. The nanoparticles were successfully recycled up to 24 cycles (although with an increase in reaction time) with no compromise in the yield. Various primary alcohols were used for transesterification. The scope was extended to aliphatic, heterocyclic and aromatic esters with various functional groups.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Catalytic transesterification of carboxylic esters with alcohols is an important organic synthesis [1] and an important tool in the synthesis of biologically active compounds and drugs [1a,2,3]. Esters play an important role in the multiple-step synthesis or as a protecting group of several natural products [4]. The large scale applications of transesterification are in polymerization processes [5], paint industry [6] and in conversion of fats (triglycerides) into biodiesel [7]. Carboxylic acids are sparingly soluble in organic solvents, whereas esters are normally soluble in most of organic solvents [8]. Transesterification being an equilibrium reaction, high conversions are difficult to attain. Hence, reactions are catalyzed by acids [6b,9] and bases [10] under homogeneous as well as heterogeneous conditions [11]. However, acid catalysts [12] exhibit low substrate selectivity and can cleave sensitive functional groups. They may also lead to formation of side products [13]. Strongly basic catalysts lead to high conversions, but fail for base-sensitive substrates [12]. Therefore, with either acidic or basic conditions, such transesterification reactions do not prove to proceed efficiently under mild reaction conditions [11c]. A number of organic amines have shown good catalytic activity for transesterification [14]. Although the recovery process is simpler the process has narrow range of applicability due to longer reaction time and low conversions.

On the other hand, nanoparticles (NPs) are core base materials for implementing nanotechnology and have promising applications in organic synthesis [15]. It has been proved that Ni and CuNPs as catalysts offer great opportunities for a wide range of applications in organic synthesis [16]. The high efficiency of NPs system relies mainly on the approach to the metal core, size, and surface modification. Various functional groups can be introduced on the surface of the NPs by using appropriate capping agent. In order to identify an ideal catalyst for transesterification, we decided to study the catalytic activity of some organic amines in presence of metal NPs. In the past, we have synthesized metal NPs with various capping agents which were used for biological applications [17]. In this paper, we report first protocol for metal NPs (nickel and copper) assisted amine catalyzed synthesis of higher to lower esters and vice versa under ambient conditions. Initially diethylnonate (DEM) was used as the model system to simplify the analysis and to accelerate the screening speed for suitable amine-NPs catalytic system. Consequently the optimized conditions were used for the synthesis of various esters.

2. Experimental

Details of synthesis and characterization of nanoparticles are mentioned in supporting information.

2.1. General procedure for room temperature transesterification

In a typical reaction methanol (20 mmol), amines (0.12 mmol) and starch capped nickel nanoparticles (NiNPs) (80 mg.) were
Nanoparticle-supported and magnetically recoverable organic–inorganic hybrid copper(II) nanocatalyst: a selective and sustainable oxidation protocol with a high turnover number†

Puran Singh Rathore, Rajesh Patidar and Sonal Thakore*

A magnetically recoverable copper-based nanocatalyst was prepared from inexpensive starting materials. With a particle size between 20 to 30 nm, it was shown to catalyze the oxidation of benzylic alcohols. The catalyst exhibited a high turnover number (TON) and excellent selectivity. The catalyst was characterized by several techniques, such as XRD, HR-TEM, SAED, EDS, FT-IR, VSM, and BET surface area. Factors affecting the reaction parameters, such as the substrate to oxidant molar ratio, weight of the catalyst, reaction time, etc., were investigated in detail. The reusability of the catalyst was examined by conducting repeat experiments with the same catalyst; it was observed that the catalyst displayed no significant changes in its activity even after seven cycles for the aerobic, as well as for the peroxide, oxidation of benzyl alcohol. Furthermore, the heterogeneous nature, easy recovery, and reusability, makes the present protocol highly beneficial for addressing environmental concerns and industrial requirements.

Introduction

The selective oxidation of alcohols to their corresponding carbonyl compounds is one of the most useful reactions in industrial processes.1 Oxidation reactions are usually difficult and typically require stoichiometric amounts of toxic heavy-metal salts or expensive catalysts involving noble metals, such as gold, ruthenium, rhodium, or palladium.2-4 Traditionally, non-catalytic methods with stoichiometric, toxic, corrosive, and expensive oxidants, such as permanganate, dichromate, and peroxo acids, under stringent conditions of high pressure and/or temperature have been widely used for alcohol oxidation.5-9 These reactions are also often carried out with high concentrations of bases and environmentally unfriendly organic solvents. Therefore, much attention has been paid to the development of heterogeneous catalytic systems that use clean and atom-efficient oxidants like molecular oxygen or \( \text{H}_2\text{O}_2 \) without organic solvents.10-13 Among these systems, the solvent-free aerobic oxidation of alcohols using molecular oxygen or air as the oxidant has become more attractive,14-16 due to positive effects in terms of cost, safety, and environmental impact. In this study, the objective was to develop an efficient catalytic system for the aerobic or \( \text{H}_2\text{O}_2 \) oxidation of various alcohols under solvent-free conditions.

The copper-catalyzed oxidation of organic compounds has attracted significant attention in recent years,17 owing to the high demand for mild and efficient oxidation catalysts.18 Copper is an abundant metal in the Earth’s crust and its redox properties make it ideally suited for catalytic oxidation processes, provided that the electron-transfer processes can be controlled by an appropriate ligand set. Therefore, a number of copper-catalyzed aerobic oxidation systems have been well-established.19 They employ copper salts in combination with 2,2,6,6-tetramethyl-piperidyl-1-oxide (TEMPO),20 and various N ligands such as 2,2’-bipyridine (Bpy),20a 1,4-diazabicyclo[2.2.2] octane (DABCO),20f and 4,4’-trimethylene-dipyridine (TMDP).20f However, they are homogeneous20 in nature and an additional base is often needed,20c,d,a which limits their application in the oxidation of the base sensitive alcohols.

Over the last few years, magnetic nanoparticles (e.g. \( \text{Fe}_3\text{O}_4 \)) have been extensively investigated as inorganic supports for the synthesis of organic–inorganic hybrid materials. They are potential alternatives to conventional materials, being robust, readily available, high-surface-area heterogeneous catalyst supports.21 They offer an added advantage of being magnetically separable, thereby, eliminating the requirement for catalyst filtration after completion of the reaction. Most importantly, when magnetic nanoparticles are used as supports, the size of the support materials decreases to the nanometer scale, and all

---

*Department of Chemistry, Faculty of Science, The M. S. University of Baroda, Vadodara, 390002, India. E-mail: chemistry2797@yahoo.com; Fax: +91-0265-2429814; Tel: +91-0265-2795552

*Analytical Discipline and CIF, Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), G. B. Marg, Bhavnagar, 364002, Gujarat, India

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra06599a