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Anatase supported nickel nanoparticles for catalytic hydrogenation of 4-nitrophenol

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ABSTRACT

Nickel nanoparticles supported on titania were prepared by a combined sol–gel and chemical reduction procedure. XRD reveals face centred cubic structure of nickel nanoparticles; while tetragonal anatase type structure for the supporting titania phase. The structural and morphological properties showed well dispersion of nickel nanoparticles on the supported titania lattice. From TEM images, the average crystallite size of nickel nanoparticles was found to be ~20 nm. HRTEM images identified lattice fringes with spacing around 0.203 nm, which matches with '*d*' value for the (1 1 1) plane of cubic nickel. The saturation magnetization, remanent magnetization, and coercivity values of supported nickel/bare nickel nanoparticles were higher than that of bulk nickel. This enhanced magnetization property was helpful for its separation from the reaction mixture by magnetic field. The influence of titania support on the performance of nickel catalysts for the hydrogenation of 4-nitrophenol was investigated. The catalytic performance was higher for supported nickel nanoparticles as compared to that of bare nickel nanoparticles. Supported nickel catalyst was found to be superior, cost effective, magnetically separable and recyclable in hydrogenation reactions.

1. Introduction

Nanoparticles (NPs) are promising candidates for catalytic chemical transformations because of their efficiency, selectivity, and yield of desired products. In particular, magnetic NPs are expected to be one of the key components in the nanotechnology revolution in the catalytic, and biological areas [1,2]. Excellent procedures such as photolytic reduction [3,4], sonochemical [5], Ionic liquids [6] or microemulsion mediated [7], chemical reduction [8], polyol process [9], etc. are available to synthesize colloidal nanomagnetic material with controlled sizes as well as shapes. However, about 90% of these procedures are carried out in organic media and at relatively high temperatures especially for single element magnetic materials like iron (Fe), copper (Cu), and nickel (Ni). In these metal NPs, the syntheses of Fe, Cu, and Ni in elemental form are relatively challenging task because of their ease oxidation to form oxides in the presence of atmospheric oxygen and quasi-homogenous mode in catalytic reactions [10]. Also, noble metals such as ruthenium, rhodium, iridium, palladium, platinium have played a dominant role in chemical transformations because of their high catalytic activity and efficiency. Thus the research on the first triad metals as catalysis remained in less explored for long time. Recently, the potential of these first triad elements realized after the successful demonstration of catalytic efficiency with several of such elements [11]. This class of materials has been gaining more attention due to cost effective compared to noble metal as well as ease separation from homogeneous media by magnetic field. In this investigation, the process development for preparation of Ni NPs and their use as a catalyst for hydrogenation reactions has been explored.

Among various forms of Ni, metallic form is quite commonly used compared to NPs in catalytic chemical transformations [12–16]. In the past few years, Ni NPs as catalysts have been investigated in a number of organic reactions such as chemo-selective oxidative coupling of thiols [14], reduction of aldehydes and ketones [15], hydrogenation of olefins [16], Wittig-type olefination for the stilbenes synthesis from alcohol [17], hydrothermal Heck reaction [18], hydrogenation and transfer hydrogenation reaction [19]. This is because of its heterogeneous and highly magnetic

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in nature for each separation as well as stability over the others. Du et al. [20] observed superior activity, selectivity and stability of nano-sized nickel in the hydrogenation of 4-nitrophenol to 4-aminophenol in comparison to conventional Raney nickel catalysts. The efficient hydrogenation of nitrobenzene was carried out using nickel nano-catalysts than Raney nickel [21]. Most of these literatures are concerned with synthesis of free Ni NPs in either aqueous or organic environments for catalytic reactions [22–28]. However, some major restrictions, like stability of suspensions, cost effective procedures and complexity, highlight the urgency of improved preparative routes. In fact, there are very few reports on supported Ni NPs systems; which were synthesized with their catalytic applications in view [29–31]. Ni NPs has ability to disperse into the supportive matrix homogeneously and provide higher surface to volume ratio while participating in the chemical reactions [31]. Higher selectivity of supportive Ni NPs towards reaction proceeds through less waste and ease separation, which could lead to safer technique and reduced environmental impact. Due to cheaper price and higher catalytic activity, supported Ni catalysts are widely used in various reactions [32–37]. Moreover, compared to unsupported nano-sized Ni catalysts; the supported Ni catalysts are easy to recover in a slurry reactor. A facile synthesis of metallic Ni NPs/metal oxide composites with controllable size and morphology of metal NPs is critical to the practical applications. A simple method to synthesize Ni/TiO_2 catalysts under a controllable manner via sol–gel at room temperature has been reported for the efficient hydrogenation of chloronitrobenzene to chloroaniline [38]. The effect of the interaction between Ni with different phases of Al_2O_3 on catalysis property for selective hydrogenation of isoprene in simulated gasoline has been demonstrated [39]. The Ni ions preferentially incorporate into the tetrahedral vacancies of γ-Al_2O_3 support to form strong metal–support interaction, while weak metal–support interaction was formed on κ-Al_2O_3 support with little tetrahedral vacancy [39]. The hydrogenation of benzaldehyde over Ni catalysts supported on Al_2O_3, SiO_2, TiO_2 and CeO_2 was studied at atmospheric pressure in the range temperature of 70–140 °C under H_2 flow [40].

In this paper, we report details of preparation of supported Ni NPs and their catalytic efficiency for catalytic hydrogenation of 4-nitrophenol at room temperature.

2. Experimental details

2.1. Materials

Analytical reagent grade of all the chemicals were used without any further purification. Nickel acetate, cetyl trimethyl ammonium bromide (CTAB) as capping agent as well as hydrazine hydrate as a reductant were used for synthesis of nickel NPs only. 4-Nitrophenol (4-NP) [Hi-Media Chemicals, India] was used for the catalytic reaction. In this catalytic reaction, sodium borohydride ($NaBH_4$) (Loba chem., India) was also used for conversion of 4-NP to 4-nitrophenolate ion. $NaBH_4$ solution was freshly prepared in distilled water for each use. Double-distilled water was used throughout the experiments. Earlier synthesized titania NPs [41] was used as the supportive material for Ni NPs. In synthesis of titania NPs, titanium (IV) isopropoxide (TTIP) was used as titanium precursor; while sodium dodecyl sulphate (SDS) (Sigma–Aldrich) was used as surfactant.

2.1.1. Synthesis of titania-supported nickel nanoparticles

Titania-supported nickel NPs were synthesized by a combination of sol–gel method followed by reduction method. Initially, anatase type nano-titania was synthesized by using a precursor containing TTIP with glacial acetic acid as well as SDS. The precursor solution was stirred for 2 h at room temperature. The pH of the resulting solution was adjusted to 10.00 using ammonia solution. The solution was stirred at 60 °C for 3 h and then cooled to room temperature. The precipitate was filtered, dried at 110 °C and calcinated at 300 °C for 5 h [41].

The Ni NPs were synthesized by using chemical reduction method. 5 mL (1×10^{-2} M) nickel acetate solution, 4 mL (1×10^{-2} M) cetyl trimethyl ammonium bromide and 3 mL (1.6×10^{-2} mM) hydrazine hydrate solutions were mixed together. This mixture was heated at 110 °C for 30 min with constant stirring in oil bath; which resulted in the black coloured Ni NPs. These Ni NPs were magnetically separated and washed with ethanol and calcinated at 300 °C for 2 h. For making composites, the formed Ni NPs were added into the 2 g anatase titania with 5 mL distilled water. The resulting mixture was stirred for 15 min at room temperature. The amount of nickel loading was in the range of 1.0 wt% to 5.0 wt%; which corresponds to nano-titania. Finally, this precursor solution was centrifuged for 1 h, and washed with deionized water and ethanol. The obtained catalyst powder was dried in an electric oven. The final catalyst was obtained after calcination at 300 °C for 4 h under static air.

3. Characterization techniques

X-ray diffraction (XRD) studies were carried out by using a Bruker D8-Advance diffractometer in the two theta range of 10–90° by using Cu Kα (1.5418 Å) radiation. UV–vis absorption spectra were recorded in the range of 250–700 nm by using Perkin–Elmer Lambda 750 model UV–VIS spectrophotometer. Fourier Transform Infra-Red (FTIR) spectra of samples were recorded in transmission mode by using Bruker Alpha FT-Infra-Red spectrometer with a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}. The morphology of the samples was observed using a Tecnai F30 field emission transmission electron microscope operating at 300 kV. Energy dispersive X-ray spectroscopy (EDAX) was recorded by using FEI Quanta 200 Environmental SEM. Magnetic measurements were carried out at room temperature by using B–H loop tracer. The compositional analysis of the samples (either catalysts or reaction filtrate) for nickel content only was carried out using Perkin Elmer atomic absorption spectroscopy (AAS, Analyst 300).

3.1. Heterogeneous catalytic activity

The hydrogenation reaction was performed in 1000 μl (1×10^{-4} M) 4-NP solution, 100 μl (0.2 M) $NaBH_4$ solution, 10 mg of supported or bare Ni NPs and 1 mL double distilled water in a 4 mL quartz cuvette at room temperature. This catalytic reaction was monitored using a UV–visible spectrophotometer by measuring absorption in the wavelength of 200–600 nm. To study the effect of Ni loading amount, 10 mg of 1.0, 3.0 and 5.0 wt% Ni@TiO_2 were tested while keeping other parameters constant. The catalyst was separated magnetically from the reaction mixture by using simple bar magnet followed by centrifugation. The recyclability of the catalyst was also performed for successive five cycles.

4. Results and discussion

4.1. XRD analysis

The XRD patterns of titania and a series of Ni@TiO_2 samples for the different Ni loadings are shown in Fig. 1. All the peaks were indexed with metallic Ni [JCPDS # 01-1258] and anatase titania [JCPDS # 84-1286]. The X-ray diffraction peaks at ~25.35°, 37.92°, 48.04°, 54.19°, 55.13°, 62.69°, 69.04°, 70.15°, 75.10° correspond to the characteristic planes such as (1 0 1), (0 0 4), (2 0 0), (1 0 5),

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