



REDUCTION OF p-NITROPHENOL TO p-AMINOPHENOL BY USING NiO CATALYSTS: A COMPARATIVE STUDY

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Keywords: nickel oxide; p-nitrophenol reduction; sodium dodecyl sulfate; p-aminophenol.

Different nickel oxide catalysts have been prepared by simple precipitation method using different nickel precursors and using surfactant sodium dodecyl sulfate (SDS) or without surfactant. The prepared catalysts have been characterized by using XRD and FT-IR. The particle sizes have been calculated by using the Scherrer equation. The nickel oxide catalyst prepared by using nickel acetate as precursor and surfactant SDS has shown less particle size as compared to other catalysts prepared by using other precursors. Also, nickel oxide catalyst prepared using nickel acetate precursor and surfactant SDS has shown higher catalytic activity for reduction of p-nitrophenol (PNP) to p-aminophenol (PAP) using sodium borohydride (NaBH₄). Also, for the said reaction effect of concentration of p-nitrophenol on catalytic efficiency has been studied.

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Introduction

Countless chemical protocols have been depended upon the catalysis, and the catalysts play a crucial role in the production and manufacture of chemicals and materials because catalytic reactions generally occur under milder conditions compared to the noncatalytic reactions.^{1,2,3} The use of heterogeneous catalysts is one of the best attractive alternatives for synthetic strategies and adopted by organic chemists for increasing the efficiency of a wide range of organic reactions.⁴

Recently, transition metal oxides as catalysts are to tailor and design according to their sizes, structure in nanodimensions and therefore their surface chemistry and catalytic properties.⁵⁻⁹ An increasing number of illustrations are accessible in the literature where nickel-based nanoparticles have been used as catalysts during organic transformations.^{10,11}

Nickel oxide (NiO) is a p-type semiconductor material with magnetic power and wide band-gap energy (3.6-4.0 eV). It has been exploited in many different areas such as gas sensing, biomedical, electrochemical, supercapacitors, photovoltaic devices, memory storage, fuel cells, conducting materials, and electrode materials.¹² Also, NiO nanoparticles have been used as heterogeneous catalysts for various organic transformations.¹³⁻¹⁶ The nanoparticulate NiO catalysts have shown an edge over the bulk NiO catalysts since they have a higher surface to volume ratios.¹⁷ NiO nanoparticles have been synthesized by various routes such as chemical precipitation method, microemulsion, electron spray synthesis, laser ablation, and hydrothermal method.^{18,19}

Arylamines are useful raw materials for several industries such as for the synthesizing rubbers, paints, plastics and

pharmaceutically significant value-added products. The wide commercial use of arylamines has led to the improvement of new and efficient protocols for the reduction of nitroarenes. The reduction of nitroarenes with sodium borohydride is one of the most simple, cleanest and most accepted methods, but the very slow hydrolysis of sodium borohydride makes this method unusable^{20,21} until some catalyst is used.

In this work, we have been prepared NiO nanomaterials by simple precipitation method (with and without surfactant) using two different precursors (nickel acetate and nickel nitrate). Prepared catalysts were characterized by XRD, FT-IR and applied for catalytic reduction of p-nitrophenol to p-aminophenol. **ES:**

Experimental

The main starting materials were nickel(II) acetate, nickel(II) nitrate hexahydrate, sodium hydroxide (NaOH), sodium dodecyl sulfate (SDS) and ethanol, all of them were analytical grade and purchased from Kemphasol and Sigma-Aldrich. These chemicals were used as received without further purification.

Synthesis of NiO nanoparticles

In this preparation, we have prepared two separate solutions; a solution of 16.65 g of nickel acetate in 83.25 mL of deionized water, and a solution of 10 g sodium hydroxide in 250 ml of deionized water. Amount of 6.34 g of surfactant sodium dodecyl sulfate has been added to above-mentioned nickel acetate solution with continuous stirring. Next, the prepared sodium hydroxide solution was added dropwise with constant stirring to the solution of nickel acetate and surfactant. The mixed solution was stirred by a magnetic stirrer at room temperature for 1 h. The resultant light-green solution was kept at room temperature for settle down. The formed precipitate was then filtered, washed with deionized water several times and dried at 50°C for 24 hours. Finally, the obtained powder has been calcined at 500°C for 4 hrs. The

catalyst is abbreviated as NiAC-SDS. By adopting a similar protocol, we have synthesized NiO nanoparticles by using nickel acetate as precursor without using surfactant and abbreviated as NiAC. Furthermore, we have prepared NiO nanoparticles by using nickel nitrate as a precursor, SDS as a surfactant and without surfactant. These catalysts are abbreviated as NiNT-SDS and NiNT respectively.

Characterization

X-ray diffraction analysis of prepared catalysts has been carried using X-ray diffractometer (Bruker) with CuK α irradiation at 40 kV and 40 mA. Phase identification of the nickel oxide was performed. Furthermore, FT-IR analysis has been conducted on Thermo Nicolet Nexus 670 spectrometer in the range 4000 to 400 cm $^{-1}$.

Conversion of *p*-nitrophenol to *p*-aminophenol

Firstly, *p*-nitrophenol (10 mg) was dissolved in 100 ml distilled water, the reaction mixture was kept for stirring for 1 h. The reducing agent sodium borohydride was added to the solution of *p*-nitrophenol in a round bottom flask and stirred for 30 min. After that 30 mg prepared NiO catalyst was added. The UV-visible spectra have been taken for samples collected after a different time interval from the reaction mixture. The various experiments of reduction of *p*-nitrophenol have been carried out by varying *p*-nitrophenol concentration.

Results and Discussions

X-Ray diffraction analysis

XRD was used for the identification of phase and size of NiO material and also gives information on unit cell dimensions. The Figure 1 shows the XRD pattern of NiO catalyst exhibited five XRD peaks at 2θ 37.1 $^\circ$, 43.3 $^\circ$, 62.9 $^\circ$, 75.2 $^\circ$ and 79.2 $^\circ$, corresponding to the (101), (012), (110), (113) and (202) planes, respectively of cubic NiO (JCPDS44-1159).²⁹

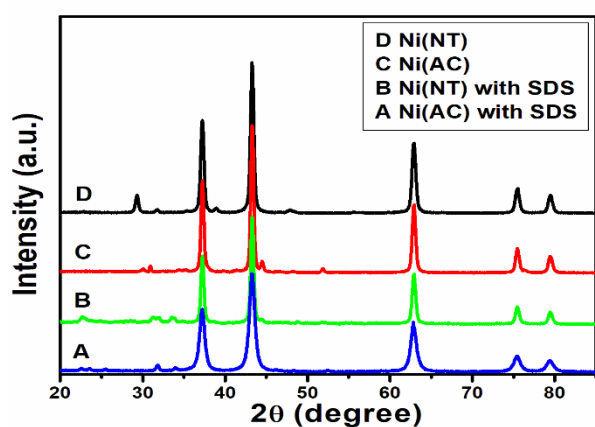


Figure 1. XRD pattern of NiO catalyst.

The particle size of the nanoparticles was calculated through the Scherrer's equation.³⁰

$$[D = k\lambda/\beta\cos\theta]$$

where D is the average crystallite domain size perpendicular to the reflecting planes, k is the constant, λ is the wavelength, β is the full width at half maximum and θ is the diffraction angle. The calculated average crystallite size of NiAC-SDS, NiAC, NiNT-SDS and NiNT are 11.76 nm, 19.23 nm, 20.08 nm and 21.55 nm, respectively.

FT-IR analysis

Figure 2 shows the FT-IR spectrum of the NiO catalyst (NiAC-SDS). The broad absorption band centered at 3319 cm $^{-1}$ is attributed due to the band O–H stretching vibrations, and the band at 1619 cm $^{-1}$ is attributed due to bending mode of H–O–H.

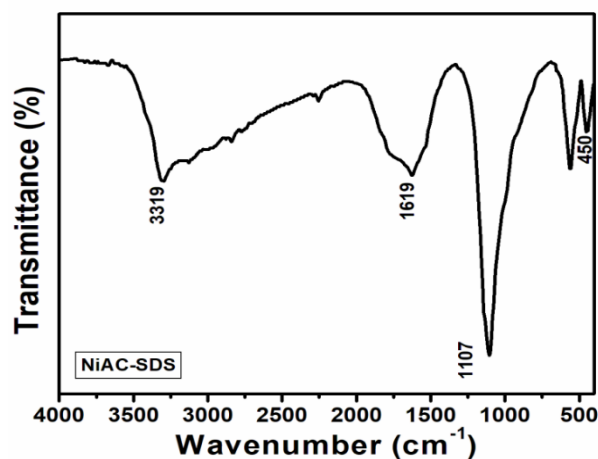


Figure 2. FT-IR spectrum of NiO catalyst (NiAC-SDS)

The band at 1107 cm $^{-1}$ is due to the fact that the calcined powder tends to absorb water and carbonate ion physically. The weak band at 450 cm $^{-1}$ corresponds to the bending vibration of metal oxide (Ni–O) bond.

Catalytic reduction of *p*-nitrophenol

Figure 3 shows the conversion of *p*-nitrophenol to *p*-aminophenol (Scheme 1) using sodium borohydride (10 mg) and the different catalysts. *p*-Nitrophenol having λ_{\max} at \sim 320 nm. After the addition of sodium borohydride, λ_{\max} was shifted from \sim 320 nm to 400 nm due to formation of *p*-nitrophenolate ion. After the addition of catalysts, the intensity of the band at 400 nm starts decreasing and new band will appear at 300 nm which is attributed to the formation of *p*-aminophenol. The initial color of *p*-nitrophenol is light yellow, becomes intense yellow on the addition of NaBH $_4$ (due to the formation of *p*-nitrophenolate ion) and after addition of a catalyst, the intensity of yellow color decreases.

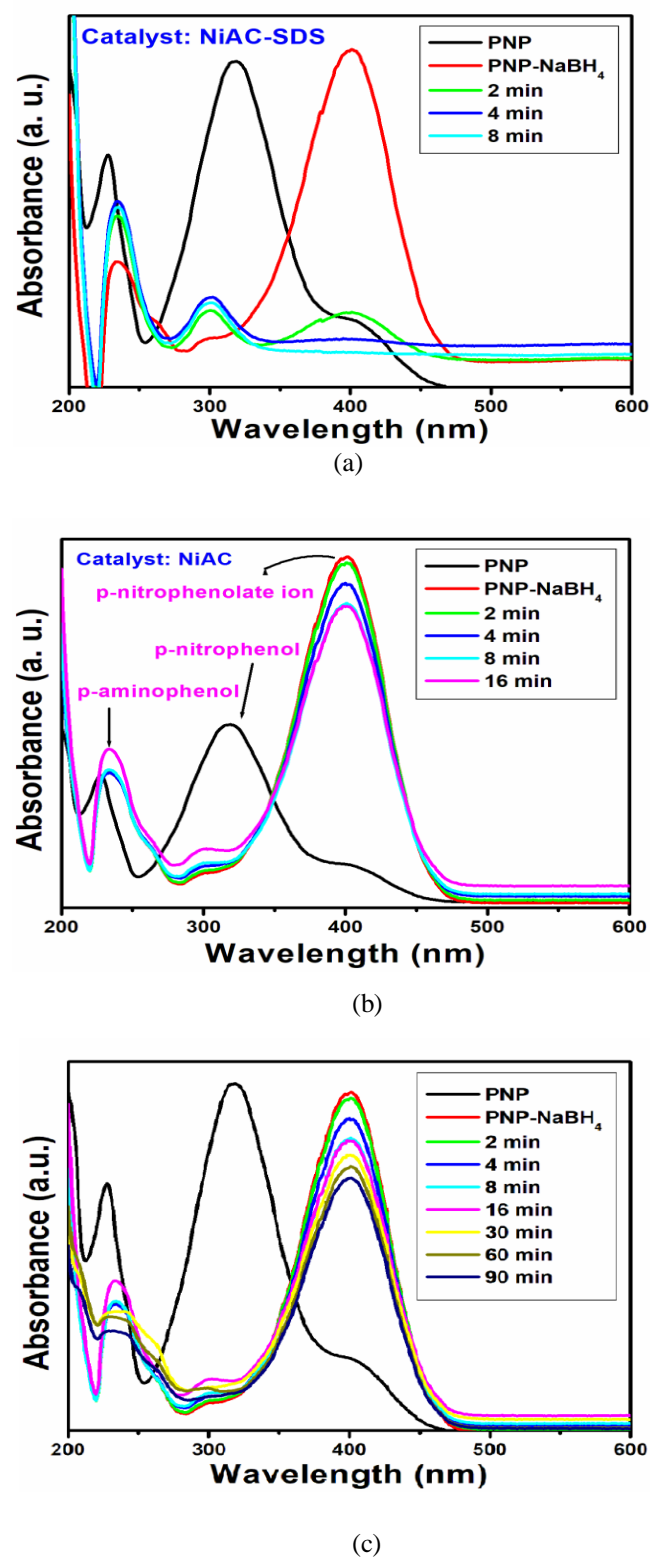
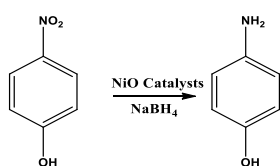


Figure 3. Conversion of PNP to PAP using catalysts a) NiAC-SDS, b) NiAC, c) NiNT-SDS.



Scheme 1. Conversion of *p*-nitrophenol to *p*-aminophenol

From Figure 3 among the four NiO catalysts prepared, the NiAC-SDS have considerably good activity for this reaction than other catalysts. We have carried out further study, by using NiAC-SDS catalyst.

Effect of concentration of *p*-nitrophenol

On increasing the concentration of *p*-nitrophenol, the rate of conversion to *p*-aminophenol decreases (Figure 4). It is due to a decrease in active sites of the catalysts as compared to a number of molecules of *p*-nitrophenol.

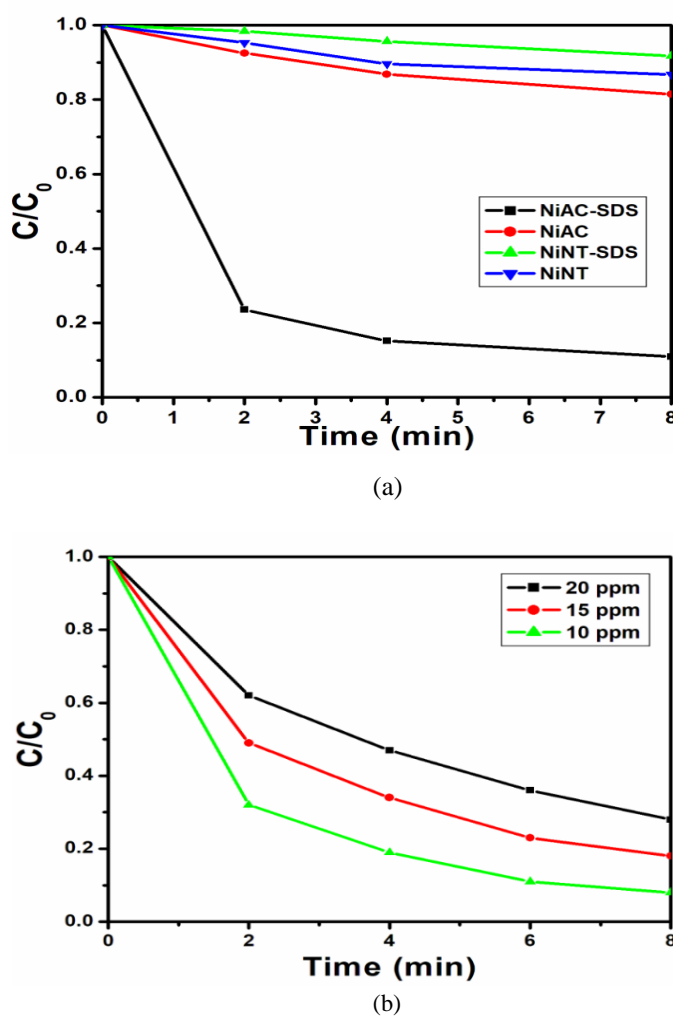


Figure 4. Kinetical parameters of PNP conversion into PAP using various catalysts (a) and the effect of *p*-nitrophenol concentration with using NiAC-SDS catalyst

Conclusions

We have successfully synthesized the NiO material by using a simple precipitation method and prepared catalysts having crystallite size on the nanometer scale. From the XRD analysis, NiO catalyst prepared by using acetate precursor and sodium dodecyl sulfate as surfactant have shown crystalline size 11.76 nm and formation of cubic phase. Furthermore, this catalyst has shown better catalytic activity for the conversion of *p*-nitrophenol to *p*-aminophenol.

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