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Chemical reduction technique for the synthesis of nickel nanoparticles

Ankur Pandey*, R. Manivannan**
*Department of Chemical Engineering National Institute of Technology Raipur, Chhattisgarh INDIA 492010
* * Department of Chemical Engineering National Institute of Technology Raipur, Chhattisgarh INDIA 492010

ABSTRACT
Chemical reduction technique was used to synthesize nickel powder using hydrazine hydrate as reducing agent, nickel chloride hexahydrate as precursor and polyvinylpyrrolidone (PVP) as capping agent in ethylene glycol medium. Experiments were carried out with mole ratios 13:1 and 20:1 of hydrazine to nickel chloride hexahydrate by keeping the amounts of ethylene glycol and NaOH as constant. Variation of capping agent concentration and temperature was also studied. X-ray diffraction (XRD) analysis was performed and the crystal size was calculated using Debye-Scherrer equation. XRD peaks where corresponds to that of the face-centered cubic nickel crystals, in accordance with the literature. Likewise, no oxygen peaks were found in XRD pattern, which confirm the absence of oxide formation in nickel. Morphological studies were performed using scanning electron microscopy (SEM) and the elemental composition was determined using energy dispersive X-ray analysis. The elemental composition was found to be nickel with small traces of oxygen.
KEYWORDS: Chemical reduction, ethylene glycol, hydrazine hydrate, nickel chloride hexahydrate, polyvinyl pyrrolidone.

I. INTRODUCTION

With the progression of chemical sciences, scientists have shown enormous interest towards the area of nanotechnology in the past few decades especially during the last 10 years. Nanoparticles refer to the particles in the size range between 1 and 100 nm for at least in one dimension. Nanotechnology, especially, works related to metal nanoparticles find a broad range of applications due their unique optical, electrical and magnetic properties [1-5]. Moreover, they are known to exhibit excellent catalytic activity. For example, the hydrogen transfer reduction of carbonyl compounds like 3-methoxyacetophenone using nickel nanoparticles as catalyst in the presence of iso-propanol at 76°C was reported by Alonso et al. with a good yield was obtained [6]. Gao et al. demonstrated that nickel nanoparticles can be successfully used for catalytic dehydrogenation of 2-butnanol to butanone at 103°C [3].

Literatures report the synthesis of nickel nanoparticles using microwave assisted synthesis [7,8], micro-emulsion synthesis [9,10], chemical reduction technique using suitable reducing agents like sodium borohydride [11], and hydrazine hydrate [12,13]. In the present work, hydrazine hydrate was used as reducing agent and ethylene glycol [13] was used as solvent.

The major problem associated with chemical reduction technique using hydrazine hydrate as reducing agent for the synthesis of nickel nanoparticles is agglomeration of particles synthesized owing to the fact that they have enormous surface energy. Also, formation of oxides of the nickel is also significantly affecting the properties in such a way that particles formed could not be utilized for several applications. To overcome this difficulty capping agents like polyvinyl pyrrolidone (PVP) [14, 15] and cetyl trimethyl ammonium bromide (CTAB) [16] are used.

II. EXPERIMENTAL SECTION

2.1. Chemicals and Materials

Nickel chloride hexahydrate (Loba chemie), hydrazine hydrate (Merck), sodium hydroxide (Merck), polyvinylpyrrolidone (Merck) and ethanol (Merck) used were of analytical grade and were used without any further purification. De-ionized water was used for all the synthesis experiments.

2.2. Synthesis of nickel nanoparticles using two different molar ratios of hydrazine hydrate to nickel chloride hexahydrate at three different concentrations of PVP

The experimental procedure includes the preparation of solution containing 0.436g of nickel chloride hexahydrate and 0.5g of polyvinyl pyrrolidone (PVP) in 99 ml ethylene glycol. The solution was green in colour, which turned to blue when 1.2 ml of hydrazine hydrate was added to the reaction mixture with a mild shaking. This corresponds to 13:1 molar ratio of hydrazine hydrate to nickel chloride hexahydrate. After addition of hydrazine hydrate, 1ml of 1M NaOH was added to the reaction mixture. The reaction was carried out in water bath shaker with a temperature maintained at 80°C for 1h and the final colour of the solution was found to be black indicating

the formation of the nickel nanoparticles. The pH was constantly monitored during the path of the reaction and it was found that initially it was acidic, which changes to basic when hydrazine hydrate was added and the alkalinity of the reaction mixture was maintained using sodium hydroxide solution. In the like manner, concentration of PVP was varied from 0.5g to 1g and 1.25g keeping other parameter as constant. A set of experiments with molar ratio 20:1 of hydrazine hydrate to nickel salt with these three concentrations of capping agent were also executed. The solution finally turns black, which was filtered and washed several times with ethyl alcohol and then held back for drying in hot air oven for 24 h. The product obtained was taken for characterization.

2.3. Synthesis of nickel nanoparticles at three different water bath temperature

The temperature variation study was conducted following the same sequence of addition of chemicals for hydrazine hydrate to nickel chloride hexahydrate with a molar ratio of 20:1 and PVP concentration of 1.25g at water bath temperatures of 60°C, 75°C and 90°C.

2.4 Characterization

The X-ray diffraction (XRD) analysis was made using PANalytical 3 kW X'pert Powder XRD – Multifunctional diffractometer with Cu Kα radiation source (λ= 0.15418 nm). The XRD pattern were recorded for 2θ values in the range of 20°-120° with step size of 0.0262°. The scanning electron microscopy (SEM) analysis was performed using Zeiss EVO 18 microscope at different magnifications. EDX analysis was performed to determine the elemental composition of the particles using Oxford - Energy Dispersive X-ray system (INCA 250 EDS with X-MAX 20mm Detector).

III. RESULTS AND DISCUSSIONS

The reaction mechanism involved here can be represented as [17, 18]

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni + N_2 + 4H_2O \quad (1)$$

As seen from the reaction above when hydrazine hydrate reacts with the nickel ions, nitrogen gas is liberated along with the formation of nickel nanoparticles. If the reaction is performed in closed container the nitrogen gas helps in the formation of inert atmosphere inside the reacting vessel. The capping mechanism of PVP is attributed to the fact that a PVP molecule contains a hydrophilic and a hydrophobic part. As soon as the nickel nucleus is formed the hydrophobic part of PVP molecule gets attached to nickel nucleus thereby reducing its surface energy and hence agglomeration can prevented [3].

3.1. X-Ray Diffraction analysis (XRD) analysis

The X-ray diffraction analysis was performed and results are reported here. Fig. 1 shows the XRD analysis of the particles synthesized using molar ratio of hydrazine hydrate to nickel chloride hexahydrate as 13:1 at three different concentrations of PVP (0.5g, 1g and 1.25g). Similarly, Fig. 2 shows the XRD patterns of the particles synthesized using molar ratio of 20:1 for different concentrations of PVP. The XRD patterns obtained here matches exactly with the literature [14] with 3 different peaks at 2θ values of 44.59°, 52° and 76.45°. These values corresponds to (1 1 1), (2 0 0) and (2 2 0) planes of the face centered cubic Nickel nanoparticles. These peaks exactly match with the JCPDS card number 04085 as given in literature[19]. XRD patterns for the particles synthesized at different temperatures were shown in Fig. 3. From the XRD results, it is clear that only Ni peaks were obtained for the above cases.

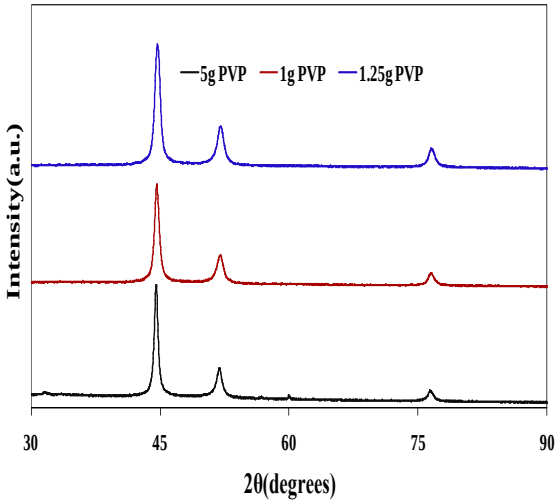

Figure 1.XRD analysis results for different concentrations of PVP, molar ratio 13:1.

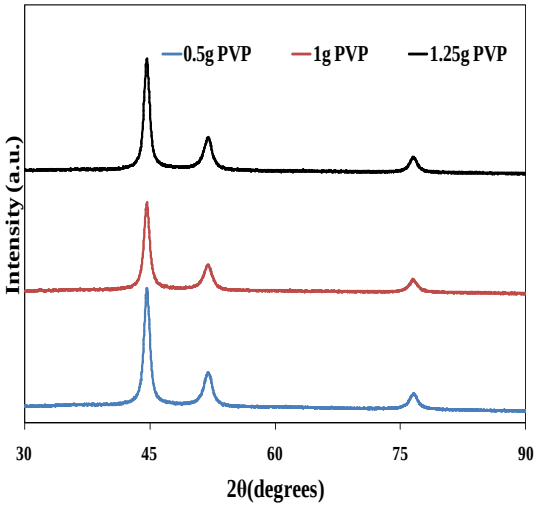

Figure 2.XRD analysis results for different concentrations of PVP, molar ratio 20:1.

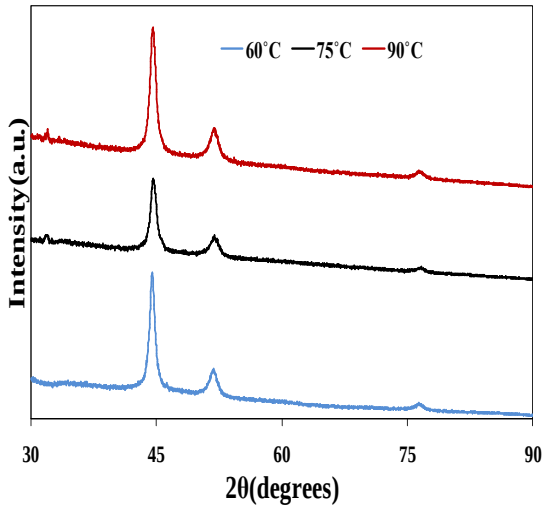

Figure 3. XRD analysis results for molar ratio 20:1 and PVP concentration of 1.25g at (a) 60°C (b) 75°C (c) 90°C.

3.2. Crystal size analysis

Crystal size of the particles synthesized at various conditions were calculated using Debye Scherrer equation [20],

$$d = \frac{K \times \lambda}{\beta \times \cos\theta} \qquad (2)$$

where, K is constant (K=0.89), λ is wavelength (0.15418 nm), β is full width at half maximum, measured for peak at 44.59° and θ is Bragg's angle.

The crystal sizes of the particles synthesized at various conditions were reported in Table 1. For molar ratio of 13:1, as the concentration of PVP was increased, the crystal size of the particles decreased from 13.03 to 10.87 nm. A similar trend was observed for the molar ratio of 20:1 and crystal size was found to be in the order of 2 nm. Crystal size of the particle was significantly decreased when the molar ratio was changed from 13:1 to 20:1. Decrease in the crystal size was achieved when temperature was increased from 60°C to 90°C. This trend was found to be in accordance with the literatures [20].

3.4. Energy Dispersive X-ray analysis

Elemental composition was determined using EDX analysis for molar ratio 13:1 and 20:1 at different concentrations of capping agent. It was found that nickel was present approximately 95% (by wt.) with trace amount of oxygen. For experiment with temperature of 60°C, molar ratio of 20:1 and PVP concentration of 1.25 g indicates the incomplete reaction with Ni(87%) Cl(3%), Na(5%) and trace amounts of nitrogen and oxygen.

TABLE 1. Crystal size calculations using Debye-Scherrer formula

Exp. No.	Molar Ratio*	Capping Agent Conc (g)	T(°C)	Crystal size(nm)
1	13:1	0.5	80	13.03
2	13:1	1	80	10.87
3	13:1	1.25	80	10.20
4	20:1	0.5	80	2.67
5	20:1	1	80	2.45
6	20:1	1.25	80	2.04
7	20:1	1.25	60	6.08
8	20:1	1.25	75	2.56
9	20:1	1.25	90	2.01

(* Hydrazine hydrate: Nickel chloride hexahydrate)

3.3. Scanning Electron Microscopy analysis

The surface morphology of the particles was analyzed using scanning electron microscopy technique. Fig. 4 shows the SEM images for molar ratio of 13:1 for three different concentrations of PVP. It can be seen that as the concentrations of PVP was increased the size of particles obtained was decreased. Similar trend was observed with further reduction of size when molar ratio was increased from 13:1 to 20:1, for three different concentrations of PVP as shown by Fig. 5. Fig. 6 shows the SEM images for three different water bath temperatures for molar ratio 20:1 and PVP concentration 1.25 g. As temperature was increased from 60 to 90°C there is decrease in the size of particles was observed. All the SEM images show that the particles were uniform and spherical in shape. They also show that particles were in agglomerated state and further optimization studies to prevent agglomeration are required.

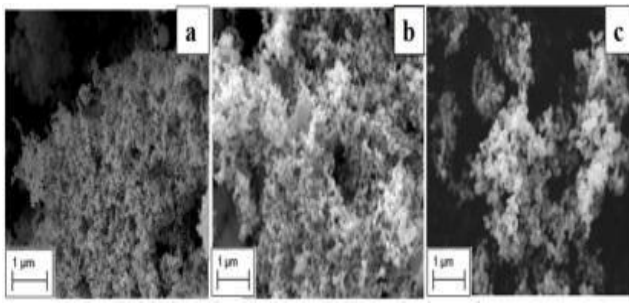

Figure 4. SEM images of nickel particles synthesized using different PVP concentrations for molar ratio of 13:1 (a) 0.5g (b) 1g (c) 1.25g.

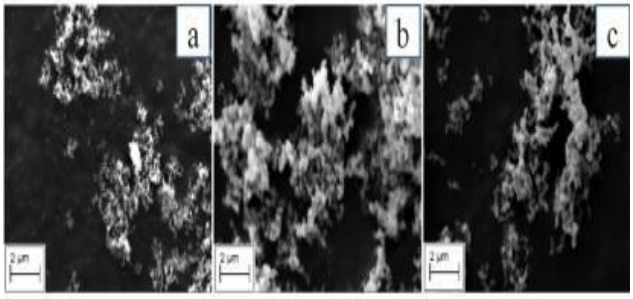

Figure 5. SEM images of nickel particles synthesized using different PVP concentrations for molar ratio of 20:1 (a) 0.5g (b) 1g (c) 1.25g.

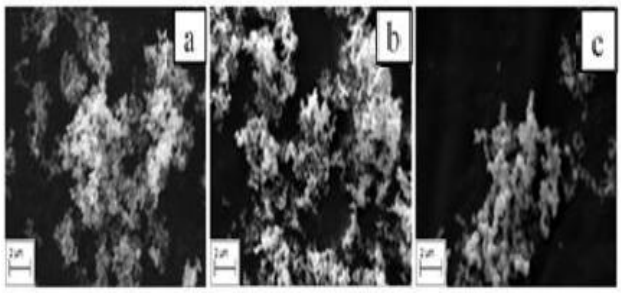

Figure 6. SEM images of particles synthesized using different temperatures for molar ratio of 20:1 and1.25g of PVP (a) 60°C (b) 75°C (c) 90°C.

IV. CONCLUSIONS

Synthesis of nickel nanoparticles using hydrazine hydrate as reducing agent, PVP as capping agent and ethylene glycol as solvent was reported. It was found that as PVP concentration was increased the crystal size was found to decrease. Also, with the use of PVP there was no sign of nickel oxide formation and the XRD peaks for nickel particles matches well with the literatures. SEM analysis showed that the particles formed were uniformly spherical and the EDX analysis shows only a little trace of oxygen.

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