Asian Journal of Chemistry; Vol. 23, No. 5 (2011), 1989-1992

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Effective Parameters in the Formation of Ni-Nanoparticles

A.J. NOVINROOZ*, N. SHAHBAHRAMI and A. REYHANI

School of Materials Research, Nuclear Science and Technology Institution, Karaj, Iran

*Corresponding author: E-mail: novinrooz@yahoo.com

(*Received*: 3 May 2010; *Accepted*: 12 January 2011) AJC-9470

The synthesis of nickel nanoparticles with various grain sizes has been achieved by spontaneous autocatalytic reduction in alcohol-water solution. It was found that, the concentration of NaOH and hydrazine catalysts play significant role in the formation of resultant nanoparticles. Investigations of different samples revealed that, a single phase nickel can be obtained at pH value 13.5 which was supported by XRD and FTIR analyses. The phase structures and morphologies of the Ni-nanoparticles have been carried out by using XRD and SEM. The crystallography studies of the samples indicate that resultant particles were crystalline fcc structure with average diameter sizes about 6.5 nm at room temperature. The nanoparticle sizes decreased by increasing of lattice constant and, increased by raising of the solution temperature from 25-175 ºC. Also, the AAS analyses indicated that the Ni concentration in mixed solution was high at higher catalyst concentration. The SEM images of the samples showed the particle sizes were narrow (*ca.* 50-80 nm) at pH value 13.5 and solution temperature 25 ºC.

Key Words: Nanoparticles, Nickel, Sodium hydroxide, Auto catalytic reduction method.

INTRODUCTION

In recent years lot of interest has been grown up in the synthesis of metal nano-particles such as Ni, Cu, Fe, Ag and SnO_2. This is substantially due to their unusual behaviour and potential applications in various industrial fields[1-4]. Although, massive metal nano-particles are being produced, but demand for high out put and low cost productions are being looked for different methods for preparation of these particles are documented, such as chemical method[5], radiolysis reduction[6], photolytic reduction[7] and alcohol reduction[8]. Among the various kinds of metal nano-particles, the synthesis of nickel, copper and iron are relatively difficult, because they are easily oxidized[9]. Moreover, nickel nano-particles have gained much attention due to their extensive prospects as conducting and magnetic materials. In literature survey, there are few reports on preparation of pure nickel particles. To avoid nickel oxide formation, their synthesis is usually carried out in organic medium[10]. In this work, we describe the synthesis and study of nickel nano-particles by spontaneous autocatalytic reduction in alcohol-water solution in presence of NaOH catalyst and the role of main components in controlling of Ni-nanoparticle. The particle sizes and structure of resultant particles are investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), FTIR and atomic absorption spectroscopy (AAS).

EXPERIMENTAL

The nickel nano-particles were obtained from a sol of nickel chloride hydrate ($NiCl_2 \cdot 6H_2O$) which is used as a precursor material and they were dissolved in a typical solution containing water- alcohol hydrazine. All of the materials were AR grade and supplied by Aldrich chemical. As the product was drastically pH depended, sodium hydroxide (20 µL mL^{-1}) was added to adjust pH of the solution accordingly from 9-14. Our observation on many samples revealed that the appropriate concentration of precursor was 0.2 M. The solution was then kept in ultrasonic for about 0.5 h at room temperature. At this stage spontaneous auto catalytic reduction takes place according to the following reaction:

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

The nano-particles of nickel were prepared under the experimental condition after 1 h. The XRD measurements were carried out by X-ray diffractometer using CuK_α radiation (λ = 0.154 nm). The average particle sizes of the samples were determined from the diffraction peak widths according to Scherrer's equation given as:

$$D = 0.9\lambda/\beta \cos(\theta) \quad (2)$$

where, β = full width half at maximum (rad.), λ = wave length of the X- ray, θ = angle between the incident and diffracted beam and D the particle size of the sample (nm). It should be

noted that, the formula very often was used to estimate the diameter of particles[11,12].

RESULTS AND DISCUSSION

The concentration effect of $NiCl_2 \cdot 6H_2O$ on the formation of Ni-nanoparticles is examined by XRD patterns and SEM images are shown in Figs. 1 and 2, respectively. As seen in Fig. 1(a-c) the dominant crystalline structure of resultant particles was only existed in Fig. 1(b) which is assigned to 0.2 M ($NiCl_2 \cdot 6H_2O$). Also, distinguished nickel particles were observed in SEM image shown in Fig. 2(b) corresponding to 0.2 M ($NiCl_2 \cdot 6H_2O$). Furthermore, no nickel particles could be traced by atomic absorption spectroscopy analysis in 0.1 and 0.3 M ($NiCl_2 \cdot 6H_2O$). This suggests that 0.2 M solution is necessary in the synthesis of Ni-nanoparticles.

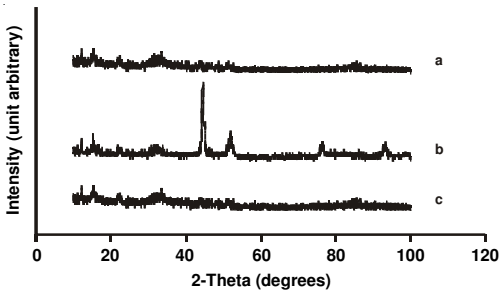


Fig. 1. X-Ray diffraction spectra of Ni-particles synthesized from typical solution of $NiCl_2 \cdot 6H_2O$ at (a) 0.1 M, (b) 0.2 M, (c) 0.3 M

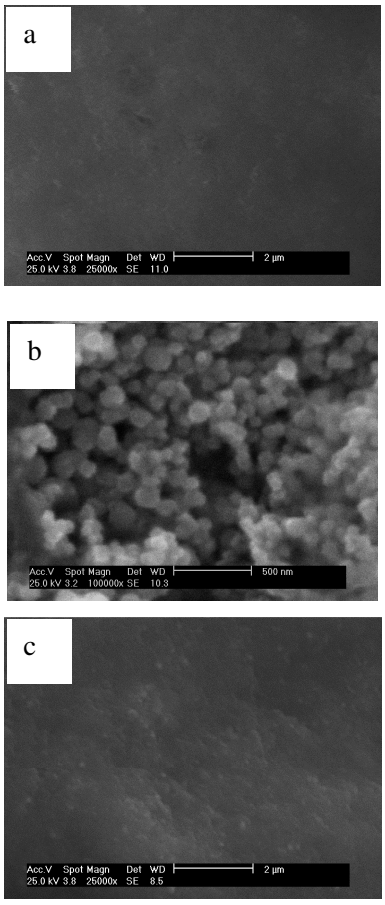


Fig. 2. SEM micrographs of Ni-nanoparticles synthesized from typical solution of $NiCl_2 \cdot 6H_2O$ at (a) 0.1 M, (b) 0.2 M, (c) 0.3 M

The nickel nanoparticles obtained under above mentioned condition were subjected to heat treatment. The XRD spectra of the samples corresponding to temperatures 25, 75 and 125 ºC is given in Fig. 3(a-c), respectively. Using relation No. (2) the nanoparticle sizes are found to be 8 nm (3a), 14.3 nm (3b) and 23.8 nm (3c). It was inferred from this figure that particle sizes were increased by increasing of solution temperature from 25-125 ºC. This event is quite clear from the SEM images of samples which are shown in Fig. 4(a-c) where, the smaller particles are seen in 4(a) which is assigned to 25 ºC. In addition, the AAS studies of the samples produced at different temperatures interpreted in terms of Ni-concentration and Ni-particles diameter. According to the plot in the Fig. 5 the more Ni-particles is assigned to smaller particle size, which is attributed to 25 ºC. It is observed that the agreement between this study and that of Figs. 3 and 4 is very good. For the formation of small nanoparticle size, the solution temperature 25 ºC was considered to be useful in this work.

In order to study the effect of NaOH catalyst on the nickel nano-particles size, various samples were prepared with different pH values at room temperature. The comparative X-ray diffraction spectra are shown in Fig. 6. Present studies on many samples revealed that, there was no peak related to Ni particles

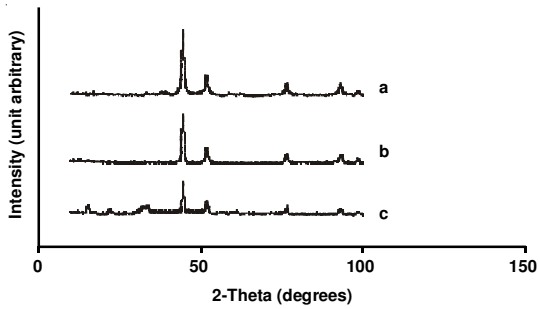
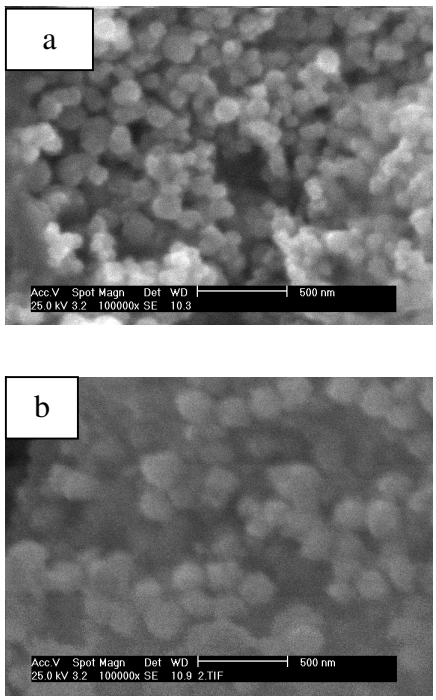


Fig. 3. X-Ray diffraction spectra of Ni-nanoparticles synthesized and at (a) 25 ºC, (b), 75 ºC, (c) 175 ºC



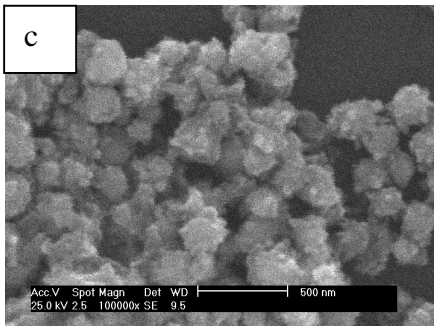


Fig. 4. SEM micrographs of nickel nanoparticles prepared and at (a) 25 ºC, (b) 75 ºC, (c) 175 ºC

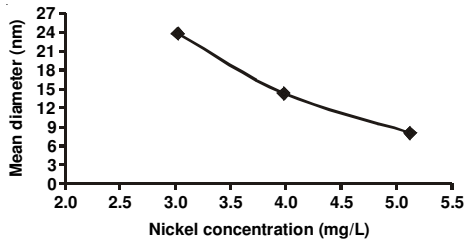


Fig. 5. Atomic spectroscopy of nickel particles at (a) 25 ºC, (b) 75 ºC, (c) 175 ºC

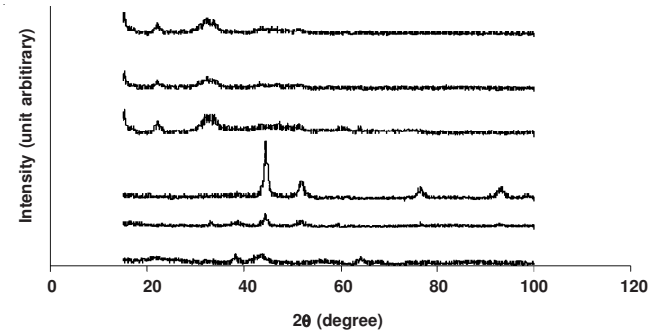


Fig. 6. X-Ray diffraction spectra of Ni-nanoparticles synthesised at room temperature and at (a) pH = 11.5, (b) pH = 12, (c) pH = 12.5, (d) pH = 13, (e) pH = 13.5

at pH value less than 11.5 whereas, in Figs. 6(a-f) there are characteristic peaks of resultant particles corresponding to pH values 11.5, 12, 12.5, 13, 13.5 and 14, respectively. The recorded peaks at $2\theta = 44.5, 51.8, 76.4$, could be assigned to miller indices (111), (200) and (222), respectively. As, there was no peak related to oxides or hydroxide such as NiO, Ni_2O_3 and $Ni(OH)_2$ were appeared except nickel particles, it can be said that the resultant particles crystallized in their single phase with fcc structure. Prevention of impurities in nickel matrix was inferred from the phenomenon that N_2 gas was produced and bubbled up during the reaction expressed in eqn. 1. The similar observation was also, reported by previous workers[3]. By increasing of pH value to 14 (Fig. 6f), although, sample was remained in single phase, but, the intensity of peaks were decreased. The variation of full-width at half maximum (FWHM) at different XRD peaks (Fig. 6) indicated a size distribution of the nanoparticles. The mean particle size of nickel nanoparticles calculated using Scherrer's relation were 20, 15.5, 8.0 and 6.5 nm with ± 1 % error corresponding to Figs. 6(c-e), respectively. On account of this investigation it could be said that synthesizes of nickel nanoparticles at pH value 13.5 is useful.

Fig. 7(a-f) illustrates the scanning electron microscopy of nickel nanoparticles synthesized from 0.2 M ($NiCl_2 \cdot 6H_2O$) under different pH values 11.5, 12, 12.5, 13, 13.5 and 14 at room temperature, respectively. As explained in forgoing section, pH of solution less than 11.5 and more than 13.5 are not in favour of Ni-nanoparticles formation. This event could be observed in Figs. 7(a) and 7(f). Moreover, the present investigations on many samples prepared with pH values higher than 13.5 showed poor crystallization and strong agglomeration without individual grain. According to Fig. 7(b-e), particle sizes are decreased by increasing of pH solution and reaches to lowest value (50 nm with ± 1 % error) corresponding to Fig. 7(e). There is good agreement between the observed SEM images and XRD patterns (Fig. 6). Furthermore, it can be realized from the Fig. 7 that in spite of micro structural differences between Fig. 7(b-e) all of the nanoparticles were spherical, no rod-like or fiber-like particles were observed. This could be attributed to the fact that the micelles were dynamic structures and the particle morphology was kinetically controlled[10]. It should also be noted that diameter of the nanoparticles calculated from X-ray analysis is different than the particle size obtained from SEM measurement. This may be due to picture taken by choosing a selected area in SEM and encapsulation of particles.

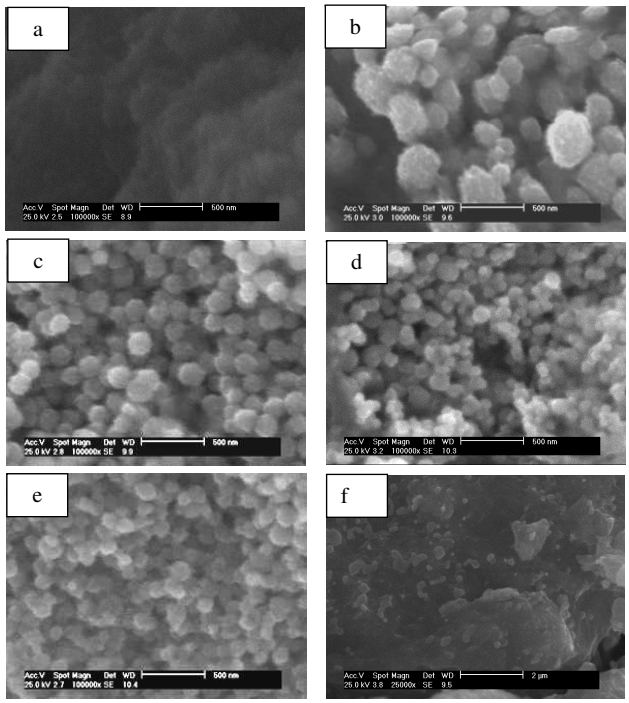


Fig. 7. SEM images of nickel nanoparticles at room temperature and at (a) pH = 11.5, (b) pH = 12, (c) pH = 12.5, (d) pH = 13, (e) pH = 13.5, (f) pH = 14

The variation of mean diameters of nanoparticles is plotted as a function of solution temperatures and lattice constant are shown in Figs. 8 and 9, respectively. It is obvious from Fig. 8 nickel nanoparticles size increased with increasing of temperature from 25-175 ºC. This is in good agreement with that was inferred from XRD pattern in Fig. 3 and also, SEM image analysis of Fig. 4. In addition, the plot in Fig. 9 indicates that the resultant particle sizes were decreased with increasing of lattice constant (Fig. 9).

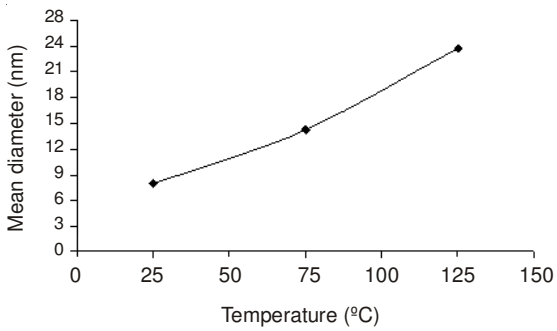


Fig. 8. Effect of solution temperature on mean diameter of nickel nanoparticles

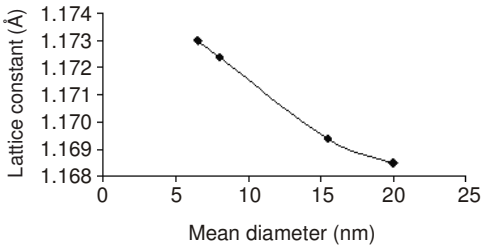
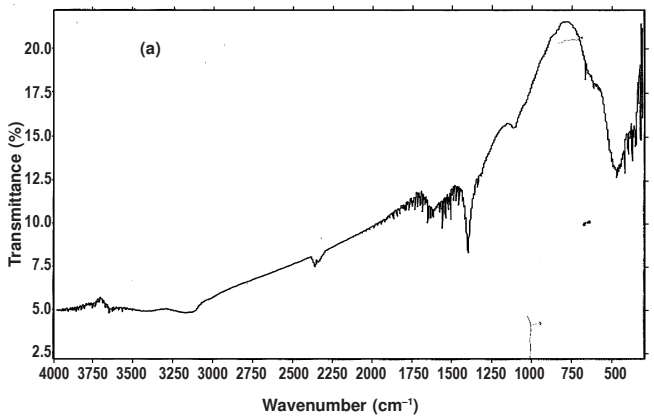


Fig. 9. Effect of lattice constant on mean diameter of nickel nanoparticles

In order to study the surface properties of nickel nanoparticles, the FTIR analysis was performed on the samples prepared with different pH values 12.5 and 13.5, represented by Fig. 10(a-b), respectively. The FTIR spectra are taken in the range of 4000-500 cm^{-1}. As shown in Fig. 10(b), the most intense peak at wave number 582 cm^{-1} is attributed to the stretching vibration of metal oxide. The similar peak is also observed in Fig. 10(a) but, with lower intensity. The characteristic peak recorded at 582 cm^{-1} in FTIR spectra confirms the presence of metal oxide Ni ferrite[13]. The absorbance band at 1463 cm^{-1} is assigned to the methylene scissoring[3]. The other peaks appeared in the spectra in Figs. 10(a-b) are 1620, 2358 and 3125 cm^{-1} seems to be related to adsorbed water on the surface of nickel particles[10]. A wave number 2358 cm^{-1} in Fig. 10 may be assigned to presence of atmospheric CO_2[14]. The absence of the peaks at 3460 and 3120 reveal the existence of C-H mode and C=H stretching mode, respectively. Finally, by comparison of spectra in Fis. 10(a-b), it can be realized that Ni particles synthesized at pH = 13.5 exhibits less contamination (impurities) and higher absorption rate.



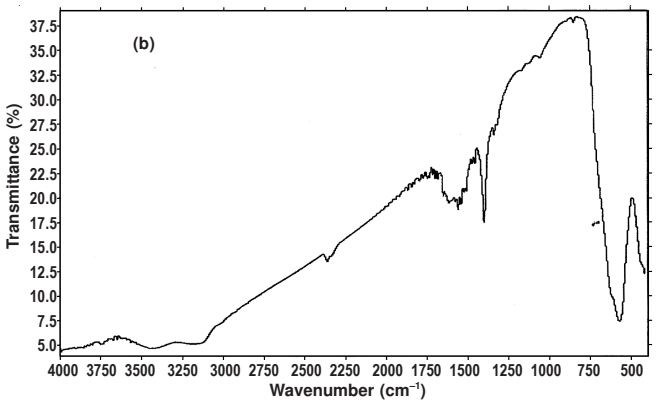


Fig. 10. Fourier transform spectroscopy of nickel nanoparticles at (a) pH = 12.5, (b) pH = 13.5

Conclusion

The nickel nanoparticles have been synthesized by reduction of 0.2 M nickel chloride hydrazine at different pH and temperature solution of water-alcohol containing appropriate amount of NaOH catalyst. The formation of resultant particles has been confirmed by XRD analysis as being pure nickel crystalline with fcc structure at 25 ºC solution temperature. Moreover, the particle size was sensitive to the pH of solution and this value was found suitable at 13.5. The studies about the FTIR spectra revealed that resultant particles can be obtained with less impurity at pH value 13.5. The mean diameter of Ni-nanoparticles was decreased with increasing of NaOH values and increased by decreasing of lattice constant. The Ni- concentration in mixed solution was high at higher catalyst concentration.

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