Cent. Eur. J. Chem. • 6(2) • 2008 • 253–257
DOI: 10.2478/s11532-008-0015-6

VERSITA

Central European Journal of **Chemistry**

Surfactant-assisted polyol preparation of nickel powders with different morphologies

Research Article

İlkay Şişman*, Çağla Tütünoğlu, Ali Osman Aydın

Department of Chemistry, Arts and Sciences Faculty,
Sakarya University,
54187, Sakarya, Turkey

Received 26 July 2007; Accepted 25 January 2008

Abstract: Sub-micrometer nickel powders of controlled size and morphology were produced by a surfactant-assisted polyol method, using ethylene glycol (EG) as solvent and reductant in the presence of sodium dodecyl sulfate (SDS) surfactant and NaOH. The resultant Ni powders were characterized by XRD, SEM, EDS, and FTIR. Spherical, hexagonal, and triangular fcc Ni powders from 0.30 to 0.60 μm were obtained in the presence of SDS; irregular spherical fcc Ni powders were obtained in its absence. The concentrations of SDS, NaOH and $Ni(CH_3COO)_2{\cdot}4H_2O$ greatly influence the product morphology and size.

Keywords: *Nickel powders • Surfactant-assisted polyol • SDS*

1. Introduction

Sub-micrometer or nanometer-sized nickel powders have shown potential in catalytic, magnetic materials, optical, rechargeable battery, electronic, *etc.* applications [1,2]. The application defines the required particle size, shape, crystallinity, and purity. For example, they have attracted attention as an inexpensive internal electrode in multilayer ceramic capacitors (MLCC) due to their good electrical conductivity, high melting temperature and low cost. To achieve ultra high capacitance, a Ni layer as well as an active layer must be competitively thinned to smaller non-agglomerated spherical powders with narrow size distribution [3].

Ni fine powders have been prepared by chemical vapor deposition, microwave-hydrothermal methods, and chemical reduction [4-6]. Chemical reduction methods give better control of size and shape and scale up more easily. Reduction in aqueous solution is rapid, but yields polydisperse particles [7]. Reduction in organic solvents is most extensively used not only owing to its rapidity and low cost but also to control size and shape.

The recently developed polyol process is a reducing agent - free method to prepare submicrometer metal particles using liquid polyols as both solvent and reductant [8]. In comparison with chemical reduction, the process takes place slowly - it requires high temperature and reflux for hours. In the presence of a suitable surfactant to prevent agglomeration, this method gives smaller stable metal particles [9]. The particles obtained by both the polyol process and chemical reduction are generally spherical [2,7,10].

SDS, a typical anionic surfactant, has been used only with cationic metal sources in making metal nanoparticles [11]. It simultaneously acts as both reductant and protective agent in making Pd and Ag nanoparticles; it is partially oxidized to dodecanol (4.41%) while the remaining SDS acts as protective agent under high-temperature reflux [12]. Thus, even when using a strong reducing agent SDS may contribute to reduction.

There have been more reports of chemical reduction syntheses of triangular and/or hexagonal Ag [13] and Pd [14] crystals than for Ni. The reason may be the strong reducing agents required to reduce Ni. The final product will have no choice but to take the thermodynamically favored spherical particles [15]. Recently, Zhang and co-workers [16] used the SDS-mediated polyol process to synthesize a mixture of triangular, dodecahedral,

---

* *E-mail: isisman@sakarya.edu.tr*

octahedral and snowflake-like Ni crystals. However, further studies are required to optimize conditions to control their morphology.

In the present work, we have made more detailed studies on the preparation of spherical, spherical-hexagonal and spherical-triangular Ni particles by the surfactant-assisted polyol method from $Ni(CH_3COO)_2 \cdot 4H_2O$/SDS/NaOH/ethylene glycol solutions. We examined the Ni particle shape and size dependence on concentrations of SDS, NaOH and $Ni(CH_3COO)_2 \cdot 4H_2O$.

2. Experimental Procedures

2.1. Powder synthesis

$Ni(CH_3COO)_2 \cdot 4H_2O$, SDS ($CH_3(CH_2)_{11}OSO_3Na$), NaOH, ethylene glycol (EG) and ethanol were all analytical grade and used as received. In a typical experiment, 0.002-0.006 mole of nickel acetate tetrahydrate was dissolved in 30 ml of EG in a 250 ml three-neck round bottom flask equipped with an oil-bath or heating mantle, a small magnetic stirring bar, a thermometer and a condenser. SDS (2.304-3.456 g) was introduced under stirring and 0.012-0.024 mole of NaOH dissolved in 10 ml EG was slowly injected under vigorous stirring. The reaction mixture was kept at 198°C for 60 min under vigorous stirring and reflux. After the reaction suspension was cooled to room temperature, the resultant Ni powder was centrifuged and washed with distilled water and ethanol several times, then dried at 40°C.

Different shaped Ni powders were obtained by changing the moles of SDS, precursor salt and/or NaOH. The reactant quantities and resulting product morphologies are listed in Table 1.

2.2. Characterization

Size and morphology of the nickel powders were examined on a scanning electron microscope (SEM, JEOL, JSM-6060LV, Japan). The crystalline phase was identified on an X-ray diffractometer (Rigaku, D-max 2200, Japan) using Cu*K*α radiation (λ=1.5405 Å). FTIR transmittance of S_4 in KBr pellets and FTIR spectra of liquid EG were recorded on a Mattson Infinity Series FTIR spectrometer from 4000 to 400 cm^{-1}.

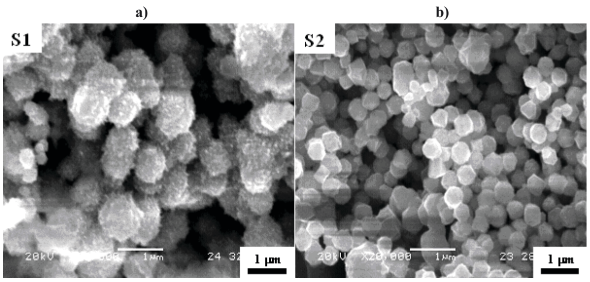

Figure 1. SEM images of Ni powders synthesized at ($Ni(CH_3COO)_2 \cdot 4H_2O$/SDS/NaOH) molar ratios: a) 1/0/5 (S_1); b) 1/2/5 (S_2).

3. Results and Discussion

3.1. Morphology

The general scheme for formation of metal particles by reduction of a metallic salt in a polyol is as follows: dissolution of the precursor, reduction of the dissolved species, nucleation, and growth [8]. The preparation of monodisperse particles requires control of the nucleation and growth steps. In such a process, metal particles have a tendency to coalesce during their formation. Surfactants, *e.g.* SDS, have been used by several groups as modifiers to avoid agglomeration [16,17]. The presence of a surfactant can change the surface energy of the newly produced metal particle, and thus can increase or decrease the reaction rate and the coalescence of small particles in solution [17].

The morphology and size of the product S_2–S_6 depended on the concentrations of SDS, NaOH and $Ni(CH_3COO)_2 \cdot 4H_2O$ (Table 1). Figures 1a and b show the SEM images when the molar ratios of $Ni(CH_3COO)_2 \cdot 4H_2O$: SDS : NaOH were 1 : 0 : 5 and 1 : 2 : 5, respectively. The average particle sizes of products S_1 and S_2 are about 0.85 μm in the absence of SDS and about 0.35 μm in its presence. Powders prepared without surfactant are agglomerated irregular spheres with rough surfaces, possibly composed of smaller particles. In the presence of SDS, the product is nearly

Table 1. Reactant quantities and nickel powder morphologies.

Product	$Ni(CH_3COO)_2 \cdot 4H_2O$ amount	EG amount	SDS amount	NaOH amount	Powder morphology
S_1	0.004 mole	40 ml	-	0.020 mole	irregular spherical
S_2	0.004 mole	40 ml	0.008 mole	0.020 mole	spherical
S_3	0.004 mole	40 ml	0.008 mole	0.012 mole	irregular spherical
S_4	0.004 mole	40 ml	0.008 mole	0.024 mole	spherical + hexagonal
S_5	0.006 mole	40 ml	0.012 mole	0.012 mole	spherical + triangular
S_6	0.002 mole	40 ml	0.012 mole	0.012 mole	spherical + triangular

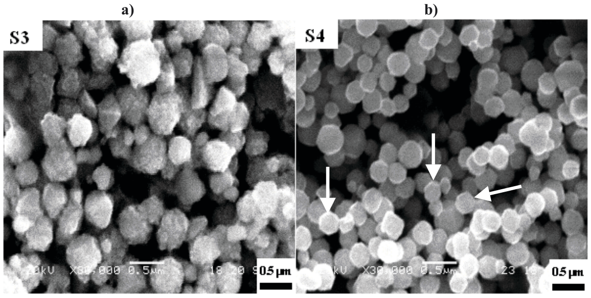

Figure 2. SEM images of Ni powders synthesized at ($Ni(CH_3COO)_2{\cdot}4H_2O$/SDS/NaOH) molar ratios: a) 1/2/3 (S_3); b) 1/2/6 (S_4).

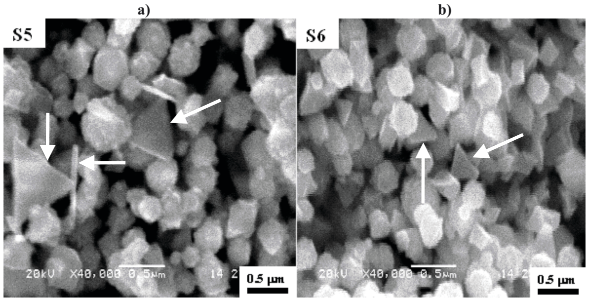

Figure 3. SEM images of Ni powders synthesized at ($Ni(CH_3COO)_2{\cdot}4H_2O$/SDS/NaOH) molar ratios: a) 3/6/6 (S_5); b) 1/6/6 (S_6).

spherical with clean surface morphology, demonstrating that the surfactant prevents agglomeration.

Another factor influencing the size and shape was the presence of hydroxyl ions. During the reaction, alkali plays an important role; it forms metallic hydroxide precipitates and accelerates the dehydration of ethylene glycol to aldehyde [18].

When [NaOH] increased the powder shapes and sizes changed. The average particle size decreased from 0.45 μm to 0.30 μm when the $Ni(CH_3COO)_2{\cdot}4H_2O$: SDS : NaOH ratio was increased from 1 : 2 : 3 to 1 : 2 : 6, (Fig. 2 a,b). As shown in Fig. 2a, powders with irregular spherical shape were obtained at low [NaOH] . When the amount of NaOH was increased from 0.012 to 0.024, the product consisted of both spherical and hexagonal (indicated by arrows) Ni particles (Fig. 2b). Powders prepared from high alkali concentration showed clean surface morphology although those obtained at a low alkali concentration showed a rough surface. Thus, fine, monodisperse, sphere- and hexagonal-like Ni powders can be obtained by adjusting [NaOH] to accelerate the reduction of $Ni(CH_3COO)_2{\cdot}4H_2O$ in EG with SDS. The decrease in particle size indicates enhanced reaction kinetics by NaOH. These results are in good agreement with the literature [19].

To examine the effect of precursor concentration, the reaction was performed using a range of molar ratios $Ni(CH_3COO)_2{\cdot}4H_2O$: SDS : NaOH (from 3 : 6 : 6 to 1 : 6 : 6). The particle sizes ranged from 0.40 to 0.60 μm at high $[Ni(CH_3COO)_2]$ concentration to 0.30 μm at low concentration (Fig. 3 a,b). The particles in both of the samples are triangular (indicated by arrows) and spherical. The results clearly show that decreasing $[Ni(CH_3COO)_2{\cdot}4H_2O]$ decreases the particle size, which can be explained by the promotion of Ni nucleation by the enhanced reduction rate [20]. A lower $Ni(CH_3COO)_2{\cdot}4H_2O$ concentration and a higher concentration of surfactant result in a smaller average particle size and both spherical and triangular shapes (Table 1).

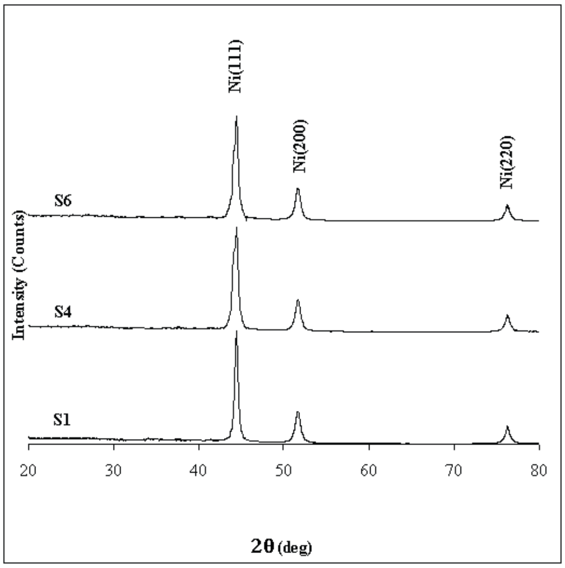

Figure 4. XRD patterns of S_1, S_4 and S_6 samples.

When the concentration of SDS is increased the coalescence of small particles is effectively prevented. The reaction is slow without the addition of alkali. These results indicate that the change of reaction rate obtained by adjusting the molar ratio of $Ni(CH_3CO_2)_2{\cdot}4H_2O$: SDS : NaOH leads to the different shape Ni powders.

3.2. Crystalline structure

Product crystallinity was confirmed by X-ray powder diffraction, shown in Fig. 4 (S_1, S_4, S_6). Three peaks at 2θ = 44.4°, 51.7°, and 76.3° can be indexed to the corresponding (111), (200) and (220) planes for face-centered cubic (fcc) nickel (JCPDS Card 04-0850). No peaks due to nickel hydroxides were detected, indicating their complete reduction. The strong and sharp peaks revealed that the nickel powders were well crystallized. The broader peaks for S_4 and S_6 indicate their smaller crystallite sizes than S_1.

Crystallite size can be estimated from the Debye-Scherrer equation using the full width half maximum (FWHM) values of the (111) diffraction peaks:

$$D = \frac{0.9\lambda}{\beta\cos\theta},$$

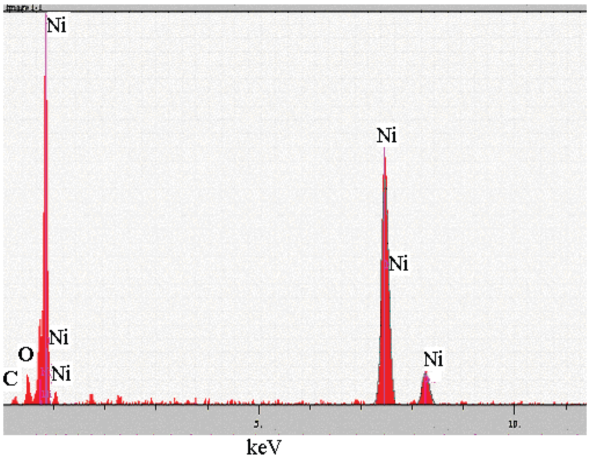

Figure 5. EDS spectrum of sample S_4.

where λ is the X-ray wavelength, θ the Bragg angle and β the FWHM of the diffraction peak. Crystallite sizes of S_1, S_4 and S_6 are found to be 25, 17 and 16 nm, respectively. Thus, the crystallite sizes are smaller than the SEM appearance. The particles observed by SEM are conglomerates of many crystals, in agreement with previous report [21].

The EDS spectrum (Fig. 5) shows strong peaks due to nickel. Weak peaks ascribed to carbon and oxygen are also observed. The presence of small amounts of C could be anticipated from the conducting resin present during measurements. Thus, EDS indicates that the powder is pure nickel.

3.3. FTIR analysis

According to Fievet *et al.* [8], EG dehydrates to acetaldehyde as follows:

$2CH_2OH\text{-}CH_2OH \rightarrow 2CH_3CHO + 2H_2O$

This can reduce metallic ions to elemental form.

Figure 6 a,b shows the FTIR spectra of pure EG and the Ni product S_4. Characteristic bands of EG are present in the Ni sample. The characteristic absorption band of sulphate at 1228 cm^{-1} (ν_s SO_3) corresponds to SDS in the sample. The other band of SDS at 1042 cm^{-1} (ν_s S=O) is overlapped by that of EG. The characteristic aldehyde absorption appeared at 1646 cm^{-1} in the FTIR spectra of S_4, showing that EG transformed partly to aldehyde.

When an anionic surfactant is used the interface is negatively charged. Metal cations will be preferentially located close to this interface, leading to the separation of reactants if the droplets are large [22]. When SDS was dispersed in EG, large numbers of micelles formed. The sulfate groups at the inner cells of the micelles could effectively coordinate the Ni^{2+} ions and Ni particles as confirmed by the FTIR analysis. The micelles are not static, of course – the chains and head groups are mobile [23]. Accordingly, Ni^{2+} ions that diffused into the inner cells of the micelles were reduced by EG.

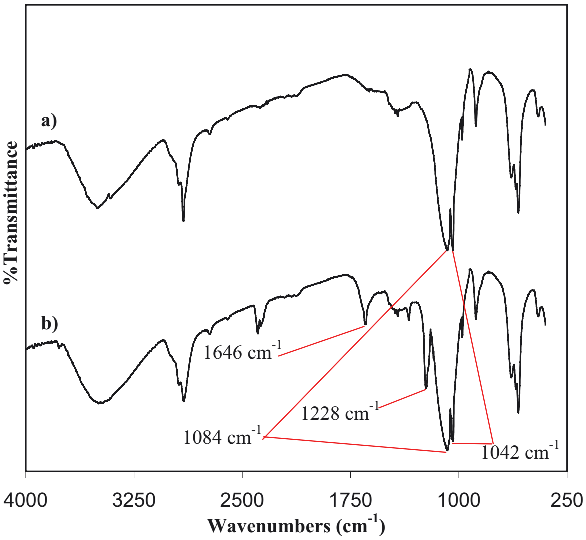

Figure 6. FTIR spectra of (a) pure EG, (b) sample S_4 with SDS.

4. Conclusion

We have optimized the preparation of shape-controlled Ni powders by a surfactant-assisted polyol method. Pure face-centered cubic Ni powders with different shape and particle size can be prepared from $Ni(CH_3COO)_2 \cdot 4H_2O$ with SDS as surfactant and EG as both solvent and reductant. The method allows synthesis of fine nickel powders 0.30–0.60 μm. Different shapes can be obtained by adjusting the molar ratio of $Ni(CH_3COO)_2 \cdot 4H_2O$: SDS : NaOH. SDS is beneficial in preparing both spherical-hexagonal and spherical-triangular powders. The presence of SDS and aldehyde in the product are confirmed by FTIR.

Acknowledgements

The financial support of the Sakarya University is gratefully acknowledged.

References

[1] J. Gao, F. Guan, Y. Zhao, W. Yang, Y. Ma, X. Lu, J. Hou, J. Kang, Mater. Chem. Phys. 71, 215 (2001)

[2] Z. Ying, J. Shengming, Q. Guanzhou, Y. Min, Mater. Sci. Eng. B 122, 222 (2005)

[3] J.-Y. Lee, J.-H. Lee, S.-H. Hong, Y.K. Lee, J.-Y. Choi, Adv. Mater. 15, 1655 (2003)

[4] Y.-W. Yen, S.-W. Chen, J. Mater. Sci. 35, 1439 (2000)

[5] K.H. Kim, H.C. Park, S.D. Lee, W.J. Hwa, S.-S. Hong, G.-D. Lee, S.S. Park, Mater. Chem. Phys. 92, 234 (2005)

[6] A. Degen, J. Macek, Nanostruct. Mater. 12, 225 (1999)

[7] J.-Y. Choi, Y.K. Lee, S.-M. Yoon, H.C. Lee, B.-K. Kim, J.M. Kim, K.-M. Kim, J.-H. Lee, J. Am. Ceram. Soc. 88, 3020 (2005)

[8] F. Fievet, J.P. Lagier, B. Blin, B. Beaudoin,M. Figlarz, Solid State Ionics 32, 198 (1989)

[9] M.S. Hedge, D. Larcher, L. Dupont, B. Beaudoin, K. Tekaia-Elhsissen, J.-M. Tarascon, Solid State Ionics 93, 33 (1996)

[10] K.-S. Chou, K.-C. Huang, J. Nanopart. Res. 3, 127 (2001)

[11] C.-L. Lee, C.-C. Wan, Y.-Y. Wang, Adv. Funct. Mater. 11, 344 (2001)

[12] C.-C. Yang, C.-C. Wan, Y.-Y. Wang, J. Colloid Interf. Sci. 279, 433 (2004)

[13] X. Tian, W. Wang, G. Cao, Mater. Lett. 61, 130 (2007)

[14] H. Choo, B. He, K.Y. Liew, H. Liu, J. Li, J. Mol. Catal., A-Chem. 244, 217 (2006)

[15] Y. Leng, Y. Li, X. Li, S. Takahashi, J. Phys. Chem. C 111, 6630 (2007)

[16] X. Zhang, H. Yin, X. Cheng, Z. Jiang, X. Zhao, A. Wang, App. Surf. Sci. 252, 8067 (2006)

[17] Y.D. Li, C.W. Li, H.R. Wang, L.Q. Li, Y.T. Qian, Mater. Chem. Phys. 59, 88 (1999)

[18] J. Sun, Y. Jing, Y. Jia, M. Tillard, C. Belin, Mater. Lett. 59, 3933 (2005)

[19] T. Hinotsu, B. Jeyadevan, C.N. Chinnasamy, K. Shinoda, K. Tohji, J. Appl. Phys. 95, 7477 (2004)

[20] B. Xia, I.W. Lenggoro, K. Okuyama, J. Mater. Res. 15, 2157 (2000)

[21] I. Capek, Adv. Colloid Interface Sci. 110, 49 (2004)

[22] I. Prakash, P. Muralidharan, N. Nallamuthu, M. Venkateswarlu, N. Satyanarayana, Mater. Res. Bull. 42, 1619 (2007)

[23] J.W. Goodwin, Colloids and Interfaces with Surfactants and Polymers–An Introduction (John Wiley & Sons Ltd, England, 2004)