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ORIGINAL CONTRIBUTION

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Nickel nanoparticles and solids using organic solvents

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Abstract Nickel colloids were prepared by codeposition of the metal with several organic solvents: acetone, ethanol, 2-propanol, 2-methoxyethanol and 1,2-dimethoxyethane at 77 K. The stabilities of the colloids and fine powders were measured. The metallic films and active solids were obtained by evaporation under vacuum at room temperature. The Ni-2-methoxyethanol colloids are stable over three months at room temperature, and the UV-VIS absorption spectra of the most stable colloids were obtained.

A chemical characterization of Ni solids was carried out by several techniques such as elemental analysis, FT-IR spectroscopy, differential scanning calorimetry (DSC), and thermogravimetry (TGA).

The IR studies show the presence of the solvent in the solids, which was confirmed by microanalysis. From TGA, DSC, and TGA-FTIR the metal-solvent was studied. From TGA, the kinetic parameters of decomposition reaction were calculated using the Freeman and Carroll equations.

Key words Colloids · Metal films · FT-IR · Thermal analysis · Nanostructures

Introduction

The bulk properties of metal nanoparticles are highly dependent on the size of the particles and the presence or not of interactions between their surfaces and solvent or supports. The size distribution of the particles must be controlled.

Cobalt nanoparticles between 1.6 nm and 2 nm showing a narrow size distribution have been reported [1]. In order to prevent the particles from coalescing, polymers have been commonly used to protect the particles [2]. The preparation of nickel particles stabilized with poly(vinylpyrrolidone) does not modify the electronic and magnetic properties [3].

Nickel clusters have been produced from Ni atom aggregation in cold pentane. They are very reactive with organic materials such as alkanes, alkenes, or esters, and always lead to the production of Ni_3C particles [4]. Ni atoms form clusters in the presence of cold pentane, and amorphous Ni clusters are formed. Ni particles of 30 nm were obtained by gas evaporation heated in H_2 in a fluidized bed [5].

A review of the advantages of the gas evaporation method including size controlled has been reported [6]. Nickel atoms codeposited with S_2N_2 allowed the synthesis of unusual material $Ni(S_2N_2H_2)_2$ [7].

Nickel atoms behave similarly to iron atoms; both $Ni{=}CH_2$ and $N_2Ni{=}CH_2$ were formed by co-condensation with diazomethane at 10 K. Then by photolysis of the matrix at 400 nm the product is enhanced [8]. Hydrogen reacted with $Ni{=}CH_2$ to yield CH_3NiH, which could also be obtained by photolysis of CH_4-Ni matrices [9]. The presence of Ni=Ni was observed in the IR. However, no studies on the formation of Ni atoms and/or small clusters stabilized in polar organic solvents have been reported.

Ni-acetone colloid is very unstable; however, Ni-2-propanol increases their stability, probably due to the

higher dielectric constant. The most stable colloid of nickel was obtained in 2-methoxyethanol, remaining in solution for several months [10]. The stability of 2-methoxyethanol is probably due to their reducing properties. Furthermore, in previous studies, acetone and 2-propanol were not able to stabilize the bimetal Ni-Cu colloids but they were able to stabilize other metal clusters under similar conditions [11–15].

In this paper, the main goal is to perform the synthesis of Ni colloids with 2-methoxyethanol, acetone, 2-propanol, and 1,2-dimethoxyethane without stabilizer or surfactant. A metal atom chemical liquid deposition method was employed [16].

Experimental

The metal atom reactor has been already described [17, 18]; as a typical example, a tungsten crucible coated with alumina was charged with 0.295 g Ni metal (pieces). Dry 2-methoxyethanol was placed in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 0.008 mbar while the crucible was warmed to red heat. A liquid nitrogen filled Dewar was placed around the vessel and Ni and acetone (100 ml) were deposited over 1 h using 40 A. The matrix was a blue color at the end of the deposition. The matrix was allowed to warm slowly under vacuum by removal of the liquid nitrogen Dewar for 1 h; upon meltdown a brown colloid was obtained. After addition of nitrogen up to 1 atm, the colloid was allowed to warm up for another 0.5 h to room temperature. The solution was siphoned out under nitrogen into a flask. Based on metal evaporated and acetone inlet the molarity in metal could be calculated. Several concentrations were prepared under the same conditions.

The film was obtained by stripping the solvent under vacuum. The solvent evaporation on a substrate can be speeded by a N_2 flow or by using a warm substrate.

Preparation of films

The films were prepared by slowly dripping the corresponding colloidal dispersions onto a substrate. To increase the speed of solvent evaporation a vacuum of 10^{-3} Torr was used over 4 h.

Thermogravimetric analysis

Thermogravimetric measurements were carried out using a Perkin-Elmer TGA-7 system. The weights of the samples were recorded accurately and were generally in the range of 5–10 mg. The sample pan was placed in the balance of the system and the temperature was raised from 25 °C to 550 °C at a heating rate of 10 °C/min. The weight of the sample pan was continuously recorded as a function of temperature.

Infrared spectra

IR spectra were obtained using a Nicolet Magna 5PC Fourier Transform Infrared Spectrometer. KBr pellets were prepared for all the films. One hundred and twenty-eight scans were accumulated for each spectrum.

UV measurements

The absorption spectra of two colloids were measured at room temperature in a Perkin-Elmer-UV-vis spectrometer (model Lambda 12).

Microanalysis

The samples were heated at 700 °C under an oxygen atmosphere and the oxides were determined by gravimetric analysis.

Results and discussion

The nickel colloids were obtained by co-condensation of the metal with organic solvents.

Scheme 1 Nickel colloids synthesis

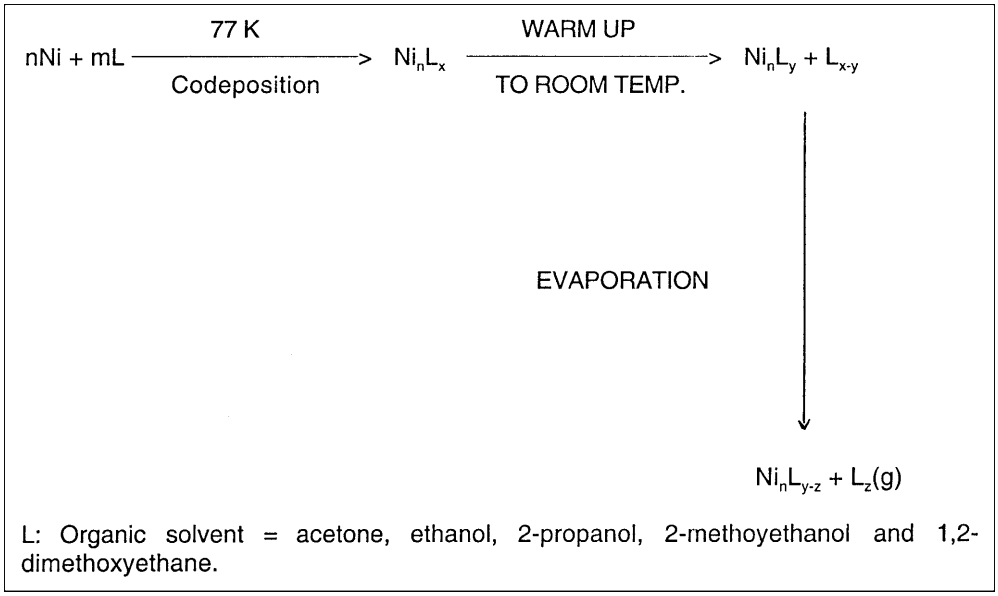
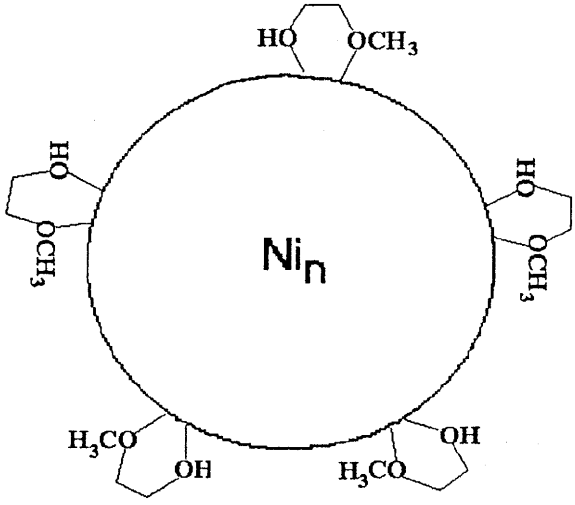


Table 1 Stability of Ni colloids with organic solvents

Colloid	Conc. ([M])	Stability (h)	Matrix color	Colloid color
Ni-2-methoxyethanol	0.005 0.040	>90[a]	Blue/purple	Brown
Ni-1,2-dimethoxyethane	0.051 0.072	24 h	Blue/purple	Brown
Ni-ethanol	0.019 0.064	72 h	Blue/purple	Brown
Ni-2-propanol	0.028 0.065	48 h	Blue/purple	Brown
Ni-acetone	0.026 0.032	1 h	Blue/purple	Brown

[a] Stable for over 4 months



Scheme 2 Ni-2-methoxyethanol colloid interaction

Scheme 1 shows the formation of the colloids and active solids under study. The solvents were added in excess to ensure the cluster solvation.

The colloids stability was studied at different metal concentrations and the results are summarized in Table 1. Several dispersions were prepared for each metal, most of them were unstable, 2-methoxyethanol being the most stable. The solvent molecules are solvating the metal clusters in solution. Metal clusters were formed in the reactor by 3–5 atoms [19]; smaller clusters can diffuse easier in the organic matrix.

The stability of these colloids depends on the efficiency of the solvation and the polarity of the solvent. The colloid stability increases in the alcohols, ethanol being more stable than 2-propanol. This is probably due to higher solvation capacity of the nickel in ethanol due to their smaller molecular size.

The 1,2-dimethoxyethane is less stable than alcohols due to their lower polarity. Ni-acetone represents the most unstable colloids, unlike the other systems studied such as Pd, Au, and Ag [11, 20, 21]. However, the Ni-2-methoxyethanol is stable for over 3 months at room temperature. This fact is in agreement with previous results on Ni-Cu and Au-Cu colloids [10, 22]. Figure 1 shows the micrograph and histogram of Ni-2-methoxyethanol colloid, the particles exhibiting average particles sizes of $\mu = 190.9$Å, $\sigma = 60.3$Å. This is the first report on nickel colloids particle size. Most probably the colloid is stabilized by five- or six-member rings in which the metal is linked to the oxygens of the solvent through a back bonding. There is no possibility of a good IR to confirm this statement.

Scheme 2 shows the model of the last system, in which the clusters are solvated by 2-methoxyethanol.

Several absorption spectra in the UV-VIS region were carried out. Figure 1 shows the spectrum with a maximum absorption at 255 nm for Ni-2-methoxyethanol. On the other hand, Ni-1,2-dimethoxyethanol shows

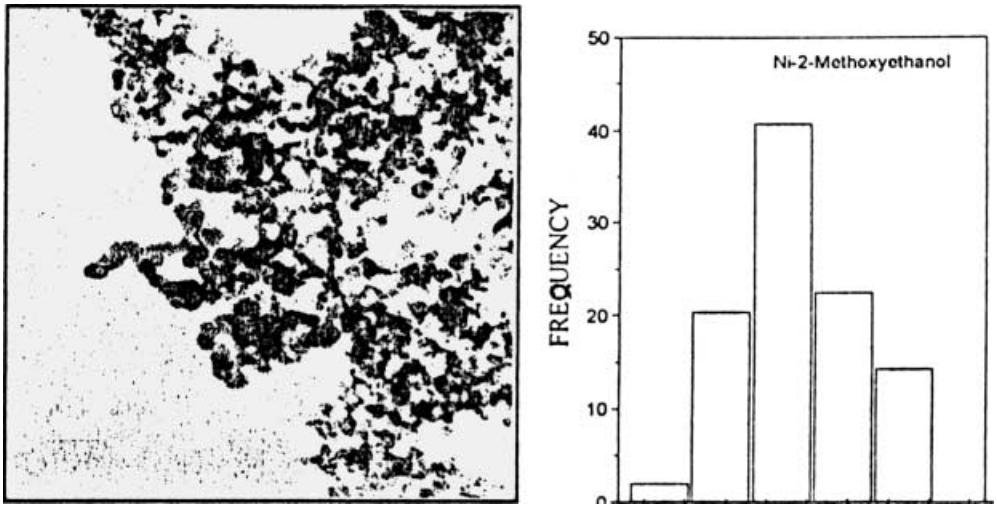


Fig. 1 TEM micrograph and histogram of Ni-2-methoxyethanol colloid. $\mu = 190.9$ Å, $\sigma = 60.3$ Å

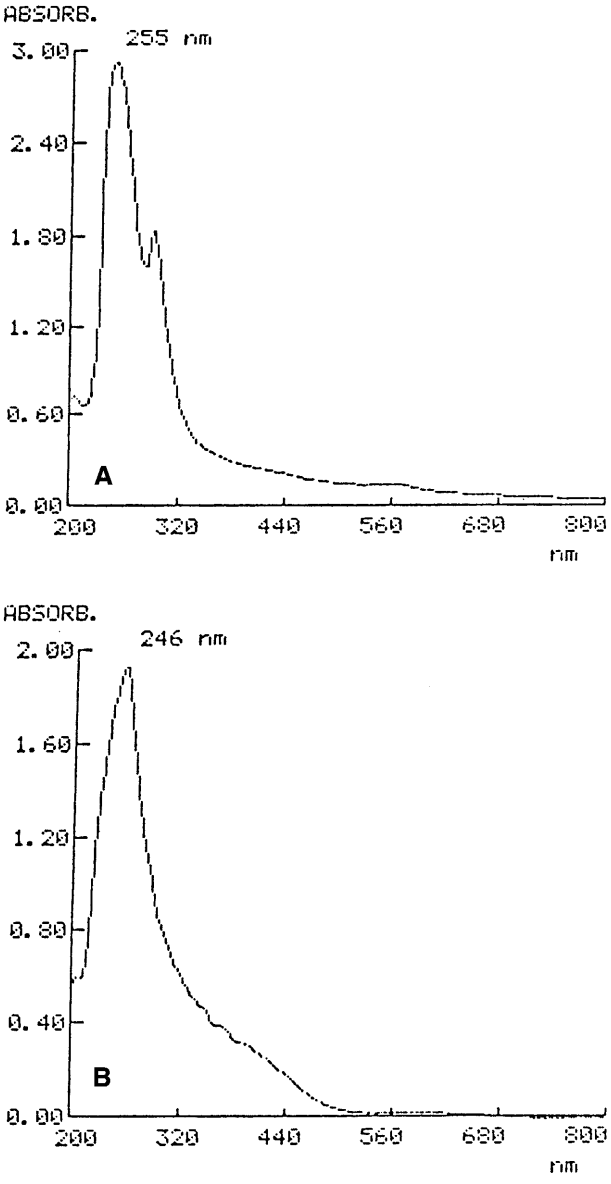


Fig. 2 **A** UV spectra of Ni-1,2-dimethoxyethane. **B** UV spectra of Ni-2-methoxyethanol

a λ_{max} at 255 nm (Fig. 2). This value is similar to that reported previously for Cd colloids in this solvent (253 nm) [23]. The results are in accordance with the theoretical calculations obtained from Creighton and Eadon [24], in which for spherical Ni particles of 10 nm diameter in aqueous media an absorption of 235 nm was reported. The differences in the UV absorption is due to the different sizes of the particles. In our case the colloids are almost twice as large as the size assumed by Creighton.

Table 2 summarizes the microanalysis of the powders produced by solvent evaporation from the colloids. All the solids contain similar amounts of nickel.

Table 2 Elemental analysis of nickel powders

Particles	Metal (%)	Carbon (%)	Hydrogen (%)
Ni-acetone	51.5	16.31	6.30
Ni-2-methoxyethanol	55.4	3.62	1.00
Ni-ethanol	58.3	7.45	1.83
Ni-1,2-dimethoxyethane	54.8	8.10	2.52
Ni-2-propanol	56.2	6.50	2.01

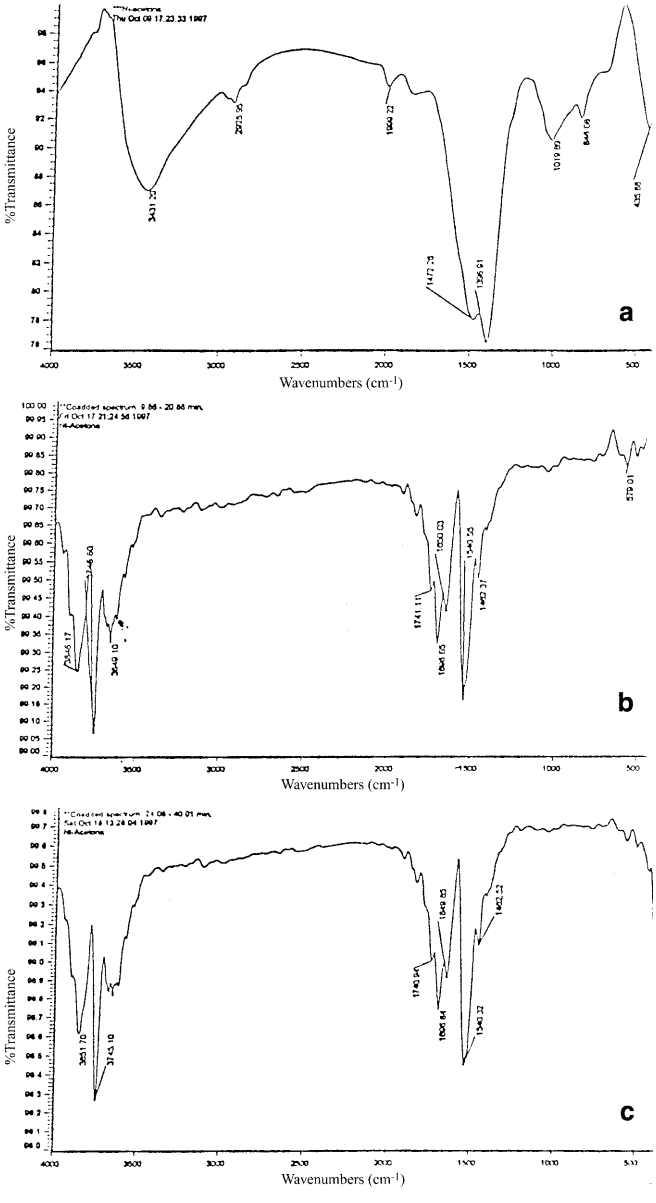


Fig. 3a–c FTIR of Ni-acetone films: **a** solvent; **b,c** gas phase acetone from the films

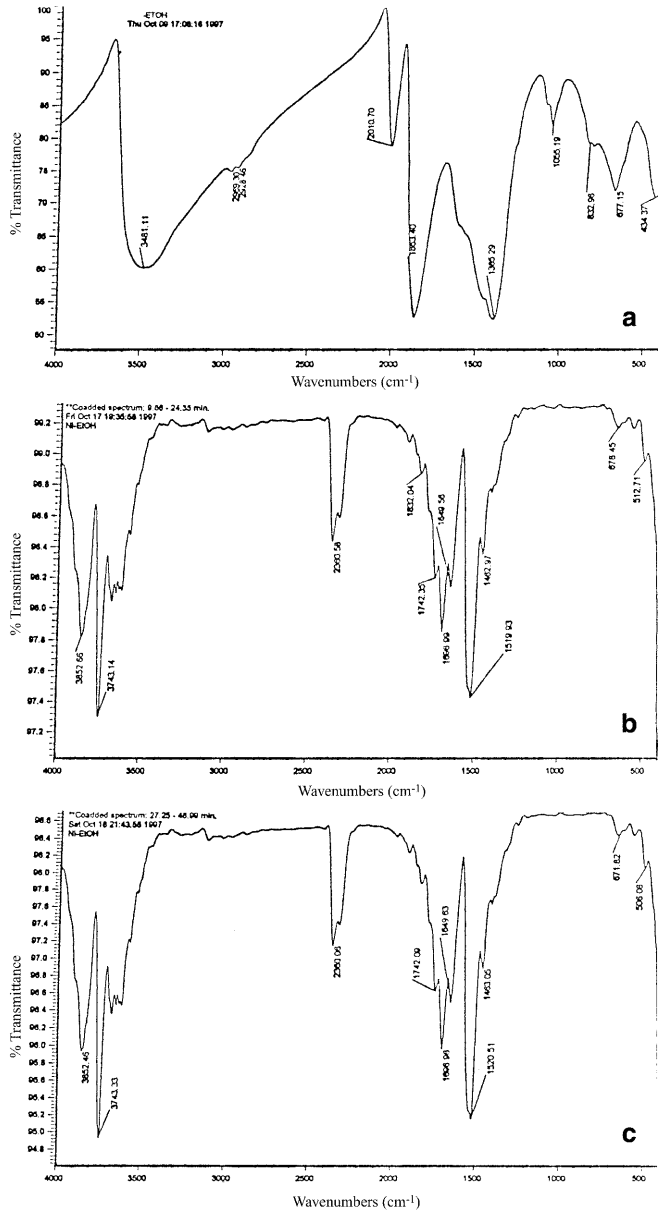


Fig. 4a–c FTIR of Ni-ethanol films: **a** solvent; **b,c** gas phase ethanol from the films

It is particularly interesting that the Ni-acetone solid exhibits a high content of C/H even though the powders were obtained after 2 h under vacuum at 50 °C. The high content of C/H is similar to that "slurry" obtained by Klabunde et al. [25] using pentane and hexane hydrocarbons. By simple molecular formula calculations, we can estimate the Ni_nL_x to give some structure in the amorphous films. The Ni films containing ethanol, 1,2-dimethoxyethane, and 2-propanol are approximately a formula $Ni_{10}L_{2-3}$ with some H_2O molecules on it. However, Ni-acetone shows a $Ni_8L_1(H_2O)_{14}$ and Ni-2-methoxyethanol a $Ni_{11}L_1(H_2O)$.

Table 3 FTIR bands for Ni-solids

Solvent	ν(cm^{-1})	Assignment	Observation
Acetone	3421	ν_s	O—H, humidity
	2926	ν_s	—CH_2—
	1740		C=O, acetone
	1472	δ_a	—CH_2—
	1019	ν_a	C—O
2-Propanol	3416	ν	O—H, humidity
	2960	ν_a	—CH_3
	1562		
	1371	δ	—CH_3
	1142	δ	C—O
	955		C—H
2-Methoxyethanol	3420	ν_s	O—H, humidity
	2965	ν_a	—CH_3
	1366	δ	—CH_3
	1055	ν_a	C—O (alcohol)
Ethanol	3481	ν	O—H, humidity
	2969	ν_a	—CH_3
	1385	ν	—CH_3
	1055	ν_a	C—O (primary saturated alcohol)
1,2-Dimethoxyethane	3426	ν_s	O—H, humidity
	2950	ν_a	—CH_3
	1580,11	δ_σ	H—O—H, humidity
	1384	δ_α	—CH_3
	1068		C—O

The IR spectra of the solids exhibit characteristic bands corresponding to the solvents incorporated in the films or powders. For Ni-acetone powders a decrease in the intensity of C=O bands is observed at 1740 cm^{-1}. Furthermore, a C—O band at 1019 cm^{-1} must be due to the interaction of the solvent with nickel clusters (see Fig. 3).

The Ni-ethanol solids show a band shifting to 1055 cm^{-1}; the normal region for C—O in secondary alcohol is around 1087 cm^{-1}. This is another example of the metal cluster interaction with the solvent. Due to the higher polarizability of Ni clusters they react with solvents. The host matrix is crucial in the metal atom growth process.

Another interesting point is the analysis of the gases evolved in the TGA-IR of the films. In the case of Ni-ethanol the presence of $\nu_{C=C}$ at 1696 cm^{-1} is due to the dehydroxylation of the solvent. However, it is not easy to explain the presence of $\nu_{C=O}$ at 1742 cm^{-1}, which should come from the oxidation of ethanol (see Fig. 4).

If we consider the Ni-acetone spectrum in TGA-IR the $\nu_{C=O}$ is at 1740 cm^{-1} which is the same for the film prepared at room temperature.

Also the $\nu_{C=C}$ at 1693 cm^{-1} is observed which can be explained due to a ceto-enol tautomerism produced by the Ni clusters (see Tables 3 and 4).

Table 4 TGA-FTIR spectrum of gas phase products from Ni-solvent powders

Films	ν_{O-H} (cm^{-1})	ν_{C-H} (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})	ν_{CH} (cm^{-1})	ν_{C-O} (cm^{-1})	$\nu_{C=C}$ (cm^{-1})
Ni-2-methoxyethanol							
(16–29 min)	3741		1745		1520		
(32–49 min)	3741		1744	1697	1517		1463
Ni-1,2-dimethoxyethane							
(6–24 min)	3748			1699	1527		1460
(9–20 min)	3602		1739		1533		
(26–39 min)	3741			1692	1533		
(32–49 min)	3741		1744	1692	1533		
Ni-ethanol							
(9–24 min)	3743		1742	1696	1519		
(37–46 min)	3743		1742	1696	1520		
Ni-acetone							
(9–20 min)		3745		1741	1696		1462
(24–40 min)				1740	1693		1462

Table 5 Kinetic parameters for thermal degradation of Ni films

Films	Temp. Range (K)	TD (K)	n	Ln A	Ea (kJ/mol K)
Ni-acetone	414–548	462	0	−2.63	21.86
Ni-2-methoxy-ethanol	552–600	585	0	−3.75	20.26
Ni-ethanol	479–525	508	0	0.20	32.87
Ni-1,2-dimethoxy-ethane	502–517	502	0	−2.63	20.28
	523–588	523	0	−5.75	8.48

Table 5 summarizes the data for the thermogravimetric studies. Ni-ethanol exhibits the highest activation energy of decomposition and similarities between 2-methoxyethanol, acetone, and 1,2-dimethoxyethane near 20 kcal/mol. The order is zero for all the systems in their first decomposition, indicating independence between solvent amount in the metal clusters.

Conclusions

Using polar organic solvents, it is possible to stabilize nickel clusters. The colloids following a decreasing pattern Ni-2-methoxyethanol < Ni-ethanol < Ni-2-propanol < Ni-1,2-dimethoxy ethane < Ni-acetone. No additives or surfactants were used.

The colloids of Ni-2-methoxyethanol and 1,2-dimethoxyethane exhibit UV absorption in the region of 250 nm. The Ni films prepared from solvent evaporation from the colloids contain substantial amount of solvents incorporated. This means that solvents are incorporated in the Ni films. All the Ni films decompose following a zero order kinetic, according to thermogravimetric data.

The TGA-FT proves that solvents are inside the metal clusters because the spectrum of the gases evolved showed the corresponding solvents.

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References

1. (a) Osuna J, de Caro D, Amiens C, Chaudret B, Snoeck E, Respaud M, Broto JM, Fert A (1966) J Phys Chem 100:14571; (b) Respaud M, Broto JM, Roboto H, Fert AR, Thomas L, Barbara B, Verelst M, Schnoeck E, Lecante P, Mosset A, Osuna J, Ely O, Amiens C, Chaudret B (1998) Phys Rev B 1:57
2. (a) Bradley JS (1994) In: Schmid G (ed) Clusters and colloids from theory to application. Weinheim, VCH, chap 6, p 459; (b) Bradley JS, Millar JM, Hill EQ, Klein C, Chaudret B, Dutiel A (1991) Faraday Discuss Chem Soc 92:255
3. Ely TO, Amiens C, Chaudret B (1999) Chem Mater 11:526
4. Hooker P, Ten BJ, Klabunde KJ, Snib S (1991) Chem Mater 3:947
5. Hayeshi T (1987) Hyomen Kagaku 8:358, CA 109(13):109,851y
6. Oda M (1987) Hyomen Kagaku 8:335, CA 108(18):153,014f
7. Woollins JD (1987) Polyhedron 939
8. Chang SC, Hange RH, Kafafi ZH, Margrave JL, Billups NE (1990) Inorg Chem 29:4373
9. Chang SC, Hange RH, Kafafi ZH, Margrave JL, Billups NE (1988) Inorg Chem 27:205
10. Cárdenas G, Oliva R (1998) Mater Res Bull 33:1599
11. Cárdenas G, Klabunde KJ, Dale EB (1987) Langmuir 3:986
12. Cárdenas G, Oliva R, Soto H, Pantoja O (1995) Bol Soc Chil Quím 40:83
13. Cárdenas G, Oliva R, Carbacho H (1995) Bol Soc Chil Quim 40:26
14. Cárdenas G, Alvial M, Klabunde KJ (1990) Bol Soc Chil Quim 35:277
15. Huang ZH, Mills G, Hajek B (1993) J Phys Chem 97:11,542
16. Cárdenas G, Shevlin PB (1987) Bol Soc Chil Quim 32:111

17. (a) Cárdenas G, Klabunde KJ, Dale EB (1987) Proc Opt Eng SPIE 821:206; (b) Cárdenas G, Klabunde KJ (1996) Polymeric materials encyclopedia, vol. 6. CRC Press, Boca Ratón, USA, p 4088
18. Cárdenas G, Oliva R, Klabunde KJ (1996) Eur J Solid State Inorg Chem 33:1135
19. Klabunde KJ, Cárdenas-Triviño G (1996) In: Furnster A (ed) Active metals: preparation, characterization and application. VCH, Weinheim, Germany, chap 6, pp 236–278
20. Lin ST, Franklin MT, Klabunde KJ (1986) Langmuir 2:259
21. Cárdenas-Triviño G, Vera V, Muñoz C (1998) Mater Res Bull 33:645
22. Cárdenas G, Gonzalez M, Salgado E, Morales J, Soto H (1999) Mater Res Bull 34:1911
23. Cárdenas G, Ponce A (1996) Colloid Polym Sci 274:788
24. Creighton JA, Eadon DG (1981) J Chem Soc Faraday Trans 87:3881
25. (a) Davis S, Severson SC, Klabunde KJ (1981) J Am Soc 103:3024; (b) Hooker P, Tan BJ, Klabunde KJ, Suib S (1991) Chem Mater 3:947