

# Chemical and Structural Properties of Nickel Hydroxide Xerogels Obtained by the Sol–Gel Procedure in the Presence of Acetic Acid

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The sol-gel route to glasses and ceramics has attracted an increasing amount of scientific and technological interest recently. In this process, sols with different concentrations are used as precursors for xerogels and to produce materials that consist of fine oxide particles. In the present work, nickel hydroxide gels have been obtained via the hydrolysis of a molecular precursor in the presence of acetic acid. The chemical aspects of the material transformation have been studied by using Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) for different acetic acid contents and several heat-treatment temperatures. The carboxylic acid acts as a ligand at a molecular level in the precursor, therefore modifying the entire hydrolysis and condensation process. Small-angle Xray scattering (SAXS) studies and density measurements have been performed for the structural characterization of the xerogels. A denser, final oxide material is obtained when a higher acetic acid concentration is used. The porosity of the dry gels coarsens when they are heat-treated up to a temperature of ~400°C and its density decreases. The material that has been heat-treated up to a temperature of 800°C densifies and exhibits a finer porosity. The chemical properties at a molecular level satisfactorily explain and are well correlated with the structural characteristics of the studied material.

## I. Introduction

**N**<sup>EW</sup> procedures for obtaining glasses and ceramics have been developed recently. These procedures lead to new materials that are able to meet the challenges of nonclassical applications.<sup>1</sup> Among them, the so-called "sol–gel" technique has a large domain of applicability. In this process, colloidal particles in liquid solution aggregate, gel, and transform into a disordered, branched, and continuous network, which is interpenetrated by the liquid solvent. Hydrolysis and polycondensation of organometallic precursors in the solution, followed by gelation and drying, are the main steps of the sol–gel route toward a highly porous material called xerogel. Subsequent heat treatment at high temperature leads to fine-grained oxide powders and, under particular conditions, monolithic and dense materials.

By varying the initial composition of the solution and other reaction parameters, wet gels and xerogels (dried gels) with a large variety of structural characteristics can be obtained. For example, the type of catalyst, acidic or basic, strongly affects the rate of hydrolysis and condensation. It has been demonstrated that acid catalysts control the hydrolysis rate in such a

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way that almost fully hydrolyzed precursors are formed and, after an adequate heat-treatment procedure, fine powdered products are obtained.

Several metal oxides—e.g., TiO<sub>2</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc. have already been synthesized via the sol–gel method, which leads to materials with a very fine porosity.<sup>2–5</sup> Despite the importance of nickel hydroxide/oxide materials for electrochemical reactions and electrochromic devices, only a few investigations that are related to their preparation procedures have been conducted.<sup>6,7</sup>

In this paper, we describe a new pathway for the preparation of nickel hydroxide/oxide materials in the presence of acetic acid using the sol–gel route. Acetic acid has been used as a catalyst to better control the rate and extent of the hydrolysis reaction of the nickel precursor.

Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) have been used to investigate the possibility of an additional role of the acetic acetate anion, namely its action as a ligand directly bound to the nickel ion. Small-angle X-ray scattering (SAXS) and density measurements have been performed to study the structural characteristics of the porous xerogels. We have investigated the transformations of different xerogels, which have been obtained from sols with different acetic acid contents, in samples that have been heat-treated at several temperatures, up to 800°C.

### **II. Experimental Procedure**

A precursor solution was prepared by dissolving a known amount of  $\text{NiCl}_2$  in butanol. The solution was stirred for 30 min and then 0.001–0.1 mol of acetic acid was added. The solution was refluxed at a temperature of 70°C for 30 min under continuous stirring to ensure a perfect homogeneity. Then, a controlled amount of water was added to the solution. The final solution was refluxed again for 3 h more and then cooled to room temperature. A schematic description of the sol–gel pathway that has been used in this work is shown in Fig. 1.

The FTIR and DSC chemical studies were performed on xerogels with different acetic acid concentrations ([*C*]). The heat-treatment temperatures range from 200°C to 450°C and from 60°C to 450°C for the FTIR and DSC studies, respectively. The DSC analysis was performed using a scan rate of  $10^{\circ}$ C/min.

The SAXS measurements were performed at the SAXS beamline of the National Synchrotron Light Laboratory (Campinas, Brazil). A monochromatic X-ray beam with an almost-pointlike cross section at the focusing plane and a wavelength  $\lambda$  of 1.608 Å was used. A one-dimensional X-ray position-sensitive detector was used to record the scattering intensity as a function of the modulus of the scattering vector q ( $q = (4\pi/\lambda) \sin \theta$ ,  $\theta$  being one-half of the scattering angle). The parasitic scattering from air and the beamline windows was subtracted from the total measured intensities. No mathematical desmearing of the experimental results was necessary, because of the almost-pinhole-like geometry of the X-ray beam. The bulk density of the sample was measured using a

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Fig. 1. Schematic diagram of the preparation of the studied xerogels.

standard densitometer for temperatures in the range of  $60^{\circ}$ –  $800^{\circ}$ C.

#### III. Results

An X-ray diffractometry (XRD) characterization of the studied materials indicated the presence of a crystalline Ni(OH)<sub>2</sub> phase up to a temperature of ~300°C. Above this temperature, a Ni<sub>2</sub>O<sub>3</sub> phase starts to appear. A single, crystalline NiO phase is obtained when the material is heated to temperatures of  $\geq$ 450°C. These phase transformations in materials that have been treated at increasing temperature involve the classical processes of nucleation and growth of the new phases. These processes and the crystallographic-related aspects have been intensively studied in the past.<sup>8</sup>

The morphology of the  $Ni(OH)_2$  particles was established by using scanning electron microscopy (SEM). A micrograph taken at a temperature of 250°C revealed approximately spherical particles, with sizes of 100–120 nm.

The FTIR spectra of a sample heat-treated up to a temperature of 200°C are plotted in Fig. 2 for different [*C*] values. The spectrum that corresponds to a powder with [*C*] = 0.1 mol exhibit a broad absorption peak at 3555 cm<sup>-1</sup> and sharper peaks in the wavenumber range of 1000–1600 cm<sup>-1</sup>. The absorption peak at 1570 cm<sup>-1</sup> shifts toward a higher wavenumber value (i.e., 1600 cm<sup>-1</sup>) as the [*C*] value increases from 0.001 mol to 0.1 mol. Similarly, the peak at 1440 cm<sup>-1</sup> shifts toward 1450 cm<sup>-1</sup>.

On the other hand, the absorption peaks in the wavenumber range of  $1000-1600 \text{ cm}^{-1}$  decrease in intensity as the temperature increases from  $200^{\circ}$ C up to  $300^{\circ}$ C and totally disappear when the sample is heated at  $450^{\circ}$ C, as shown in Fig. 3. The broadening of the peak at  $3550 \text{ cm}^{-1}$  decreases as the temperature increases.

The DSC results are plotted in Fig. 4. The curve that corresponds to the xerogel with an initial [*C*] value of 0.001 mol shows three endothermic peaks, at  $105^{\circ}$ ,  $202^{\circ}$ , and  $280^{\circ}$ C. The peaks at  $202^{\circ}$  and  $280^{\circ}$ C shift to higher temperatures (i.e.,  $225^{\circ}$  and  $310^{\circ}$ C, respectively) when the value of [*C*] increases from 0.001 mol to 0.1 mol. The peak at  $105^{\circ}$ C remains at the same



Fig. 2. FTIR spectra of xerogels synthesized in the presence of acetic acid with the indicated acetic acid concentrations ([C]) and heated up to 200°C. (The units "a.u." denote arbitrary units.)

temperature for all the [C] values. An extra endothermic peak at 168° is apparent in the DSC curve of the xerogel that corresponds to the highest [C] value (0.1 mol).

The spectra in Fig. 5 are the SAXS intensities (I(q)) that are produced by xerogels with different [C] values and a final heat-treatment temperature of 800°C. All the spectra exhibit an almost-linear behavior in a log I vs log q representation. The value of the modulus of the slope  $\alpha$  for [C] = 0.001 mol is 2.23 and decreases down to 1.97 as the value of [C] increases.



**Fig. 3.** FTIR spectra of xerogels corresponding to [C] = 0.001 mol and heated to the indicated heat-treatment temperatures. (The units "a.u." denote arbitrary units.)



**Fig. 4.** DSC curves of xerogels with [C] = 0.001 and 0.1 mol. Arrows indicate the temperature (in °C) of the main peaks.

The effect of temperature on the parameter  $\alpha$  in samples with [C] = 0.003 mol is shown in Fig. 6. This figure indicates that the value of  $\alpha$  increases from 2.28 to 3.07 for temperatures rising from 60°C to 450°C and then decreases down to 2.07 for the xerogel that has been heated to 800°C. A similar trend of  $\alpha$  with temperature, with a maximum at ~400°C, was observed for all the other [C] values, as shown in Fig. 7.

The effect of different acetic acid concentrations on the density of the xerogels that have been heat-treated up to 800°C for 1 h is shown in Table I. The density of the powders increases as [C] increases. The density of the xerogels with [C] = 0.001mol are shown in Table II as a function of the heat-treatment temperature. The density exhibits a minimum value at 450°C.



**Fig. 5.** Log–log data of SAXS intensity versus the modulus of the scattering vector (q) for the different indicated acetic acid concentration [C] (in mol) corresponding to samples heat-treated at 800°C. Statistical errors range from 1% at low q values up to 3% at high q values. (The units "a.u." denote arbitrary units.)



**Fig. 6.** Log–log data of SAXS results of xerogels heat-treated at the indicated temperatures with [C] = 0.003 mol. Statistical errors range from 1% at low q values up to 3% at high q values. (The units "a.u." denote arbitrary units.)

#### IV. Discussion

The broad absorption peak at 3555 cm<sup>-1</sup> in the spectra in Fig. 2, for different [*C*] values, was attributed to the OH<sup>-</sup> stretching mode.<sup>9</sup> The peaks in the range of 1000–1600 cm<sup>-1</sup> were attributed to organic-matter bonds and to OH<sup>-</sup> bonds of adsorbed water.<sup>10</sup> The peaks at 1450 and 1530 cm<sup>-1</sup> were assigned to C–C and C–O bonds, respectively. The spectra show a major contribution from organic matter that corresponds to the solvent and catalyst. The separation between the absorption peak of the  $\gamma_{sym}(COO)$  at 1570 cm<sup>-1</sup> and the shoulder of  $\gamma_{asym}(COO)$  at 1440 cm<sup>-1</sup> and 140–170 cm<sup>-1</sup> indicates that CH<sub>3</sub>COO acts as a bidentate ligand with the nickel atom as<sup>7,11–13</sup>





Fig. 7. Parameter  $\alpha$  versus temperature for the indicated acetic acid concentrations [C] (in mol). Error bars are smaller than the symbols.

 
 Table I.
 Effect of Acetic Acid Concentration on the Density and Average Pore Size of Xerogels Heat-Treated at 800°C

Acetic acid concentration (mol)	Density (g/cm <sup>3</sup> )	$\langle R \rangle / R_{\min}$ (a.u.)
0.001	6.35	1.36
0.005	6.42	1.34
0.1	6.55	1.33

 
 Table II.
 Effect of Temperature on the Density and Average Pore Size of Xerogels with an Acetic Acid Concentration of 0.001 mol

Temperature (°C)	Density (g/cm <sup>3</sup> )	$\langle R \rangle / R_{\min}$ (a.u.)
60	5.85	1.34
450	5.36	1.39
800	6.36	1.36

Moreover, the shifts of the  $\gamma_{sym}(COO)$  peak at 1570 cm<sup>-1</sup> toward a higher wavenumber (i.e., 1600 cm<sup>-1</sup>) as the value of [*C*] increases from 0.001 to 0.1 mol, and, similarly, the  $\gamma_{asym}(COO)$  shoulder shift toward 1450 cm<sup>-1</sup> are expected, because the increase in the value of [*C*] increases the number of strong metal–ligand bonds.<sup>14</sup> Therefore, the FTIR spectra that are presented in Fig. 2 clearly demonstrate that the acetate anions act as ligands that modify the precursor at a molecular level through a controlled hydrolysis and condensation during the evolution of the aggregation process.<sup>7</sup>

The decrease in the intensity of the absorption peaks in the wavenumber range of  $1000-1550 \text{ cm}^{-1}$  and the reduction of broadening of the OH<sup>-</sup> stretching peak at  $1600 \text{ cm}^{-1}$  with increasing treatment temperature (Fig. 3), are due to the removal of organic matter during heating.

The two endothermic peaks at  $105^{\circ}$  and  $202^{\circ}$ C in the DSC curves (Fig. 4) were attributed to adsorbed water on the surface and chemisorbed water, respectively. The endothermic peak at 280°C for low [C] values (0.001 mol) was associated with the transformation of nickel hydroxide to nickel oxide (still not stoichiometric). The shift of this peak toward a higher temperature (310°C) for a higher [C] value (0.1 mol) was attributed to a strengthening effect on the xerogel structure that was produced by the increasing number of chemical bonds between the ligand and nickel. This observation is in good agreement with the results of our FTIR study.

We considered the observed SAXS intensity, as produced by the interparticle and intraparticle nanopores and micropores that exist in xerogel samples. Because no clear linear behavior was observed in Guinier plots (log I vs  $q^2$ ),<sup>15</sup> we concluded that the pores have a rather wide size distribution. The linear behavior in log–log plots of the SAXS intensity (Figs. 5 and 6) implies that the q dependence of the SAXS intensity is given by

$$I(q) \propto q^{-\alpha}$$
 (1)

This behavior is expected for the intensity produced by a system that is composed of spheroidal particles (or pores) that are embedded in a homogeneous matrix, with a potential function for the radius distribution of  $g(R) \propto R^{-\gamma}$ .<sup>16</sup> It has been demonstrated that, under the above-mentioned specified condition,  $\gamma = 7 - \alpha$  for three-dimensional systems. In real porous materials, g(R) is generally defined in a range of  $R_{\min} < R < \infty$ , where  $R_{\min}$  is a minimum threshold value of the pore radius. Under these assumptions for the size-distribution function, the average pore radius size  $\langle R \rangle$  is given by

$$\langle R \rangle = \frac{\int_{R_{\min}}^{\infty} g(R) R \, \mathrm{d}R}{\int_{R_{\min}}^{\infty} g(R) \, \mathrm{d}R} = \frac{\int_{R_{\min}}^{\infty} R^{-\gamma+1} \, \mathrm{d}R}{\int_{R_{\min}}^{\infty} R^{-\gamma} \, \mathrm{d}R}$$
(2)

Consequently, the quotient  $\langle R \rangle / R_{\min}$  is

$$\frac{\langle R \rangle}{R_{\min}} = \frac{1 - \gamma}{2 - \gamma} = \frac{6 - \alpha}{5 - \alpha}$$
(3)

Equation (3) implies that the value of  $\langle R \rangle$  increases as the value of  $\alpha$ , which is the modulus of the slope in linear log–log plots of the SAXS intensity function, increases.

Our SAXS results that are presented in Fig. 5 indicate that  $\alpha$  decreases as [*C*] increases. Therefore, by applying Eq. (3), we concluded that samples with a higher [*C*] value promote a more-compact structure that contains smaller pores. The SAXS result is consistent with that obtained via FTIR spectroscopy: higher concentrations of ligand acetate ions would promote the formation of materials with a finer porosity.

The maxima of parameter  $\alpha$  (Figs. 6 and 7) imply, independent of the [C] value, that the material exhibits a coarser porosity (a larger  $\langle R \rangle$  value) when it is treated at an intermediate temperature (~400°C) than when treated to lower or higher temperatures. The increase in  $\langle R \rangle$  when the samples are heated from 60°C up to 250°C is due to the evaporation of physically and chemically absorbed water (as was also observed via DSC). The additional increase in pore size when the samples are heated to ~450°C is a consequence of the evaporation of organic compounds. This observation was also experimentally verified independently via FTIR spectroscopy on the sample with [C] = 0.001. The decreasing value of  $\langle R \rangle$  when the temperature is increased from ~400°C up to 800°C suggests a structural rearrangement, which leads to a densification of the inorganic matrix that is attributed to the startup of a sintering process.

The results that have been reported in Table I indicate an increase in the density of xerogels when the value of [C] is increased from 0.001 mol to 0.1 mol. This observation can be understood as a consequence of the formation of a more-compact structure that is composed of smaller particles and pores, for higher acetic acid contents. This result is in good qualitative agreement with our SAXS results (average pore size in Table I) and is consistent with the conclusion from FTIR and DSC measurements: the increase in density would be a direct consequence of the increase in the number of nickel–ligand bonds.

Table II reports a decrease in density when xerogels are heated from  $60^{\circ}$ C to  $450^{\circ}$ C. This observation can be attributed to the increase in pore size that is due to the evaporation of organic matter, as also suggested by our SAXS results (average pore size in Table II) and FTIR studies. Table II also indicates that, when the temperature increases from  $450^{\circ}$ C to  $800^{\circ}$ C, xerogels densify again, as a consequence of the correlated reduction in pore size.

## V. Conclusion

Acetic acid is used as a catalyst in the sol-gel route toward nickel hydroxide/oxide materials that provides acetate ions that act as strong bidentate ligands with nickel ions. Acetic acid modifies the metal precursor at a molecular level and is able to control the hydrolysis and condensation reaction to an appreciable extent during the sol preparation and sol-gel transition.

The increase in the temperature of transformation of nickel hydroxide to nickel oxide for increasing acetic acid contents is coherent with the existence of a larger number of strong nickel–ligand bonds. Xerogels that have been prepared with higher acetic acid concentrations are more dense and exhibit a finer porosity. These properties are also expected consequences of the increase in the number of nickel–ligand bonds.

The fine porosity that exists in the dried, non-heat-treated gels coarsens when the temperature is increased to  $\sim 400^{\circ}$ C, because of the removal of water and organic species, thus promoting a reduction in the density of the material. Heat treatment at higher temperature (800°C) leads to denser oxide materials with a finer porosity, which indicates the startup of sintering.

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#### References

<sup>1</sup>C. J. Brinker and G. W. Scherer, *Sol-Gel Science*. Academic Press, San Diego, CA, 1990.

<sup>2</sup>P. K. Sharma and A. Ramanan, "The Role of N,N-dimethylaniline in the

Formation of Titania Gel Monolith by Sol–Gel Method," J. Mater. Sci., 31 [3] 773–77 (1996).

<sup>3</sup>X. Orignac, H. C. Vasconcelos, and R. M. Almeida, "Structural Study of SiO<sub>2</sub>-TiO<sub>2</sub> Sol-Gel Films by X-ray Absorption and Photoemission Spectroscopies," *J. Non-Cryst. Solids*, **217** [2-3] 155–61 (1997).

<sup>4</sup>S. D. Ramamurthi, Z. K. Xu, and D. A. Payne, "Nanometer-Sized ZrO<sub>2</sub> Particles Prepared by a Sol–Emulsion–Gel Method," *J. Am. Ceram. Soc.*, **73** [9] 2760–63 (1990).

<sup>5</sup>M. Kumagai and G. L. Messing, "Enhanced Densification of Boehmite Sol– Gels by Alpha-Alumina Seeding," *J. Am. Ceram. Soc.*, **67** [11] C-230–C-231 (1984).

<sup>6</sup>M. C. A. Fantini, G. H. Bezerra, C. R. C. Carvalho, and A. Gorenstein, "Electrochromic Properties and Temperature Dependence of Chemically Deposited Ni(OH)<sub>x</sub> Thin Films," *SPIE Proc., Opt. Mater. Technol. Energy Efficiency Solar Energy Convers. X*, **1536**, 81–92 (1991).

<sup>7</sup>P. K. Sharma, M. C. A. Fantini, and A. Gorenstein, "Synthesis, Characterization and Electrochromic Properties of Ni(OH)<sub>2</sub> Thin Films Derived from Sol–Gel Method," *Solid State Ionics*, **115**, 457–63 (1998).

<sup>8</sup>M. Figlarz, B. Gérand, A. Delahaye-Vidal, B. Dumont, F. Harb, and A. Coucou, "Topotaxy, Nucleation and Growth," *Solid State Ionics*, **43**, 143–70 (1990).

<sup>9</sup>J. Livage, M. Henry, and C. Sanchez, "Sol-Gel Chemistry of Transition-Metal Oxides," *Prog. Solid State Chem.*, **18** [4] 259–341 (1988).

<sup>10</sup>C. Sanchez, J. Livage, M. Henry, and F. Babboneau, "Chemical Modification of Alkoxide Precursors," *J. Non-Cryst. Solids*, **100** [1–3] 65–76 (1988).

<sup>11</sup>S. Doeuff, M. Henry, C. Sanchez, and J. Livage, "Hydrolysis of Titanium Alkoxides—Modification of the Molecular Precursor by Acetic-Acid," *J. Non-Cryst. Solid.* **89** (1–2) 206–16 (1987).

*Cryst. Solids*, **89** [1–2] 206–16 (1987). <sup>12</sup>G. B. Deacon and R. J. Phillips, "Relationships Between the Carbon– Oxygen Stretching Frequencies of Carboxylate Complexes and the Type of Carboxylate Coordination," *Coord. Chem. Rev.*, **33** [3] 227–50 (1980).

<sup>13</sup>K. Nakamoto. Infrared and Raman Spectra of Inorganic Coordination Compounds, 3rd Ed. Wiley, New York, 1997.

<sup>14</sup>J. Chaibi, M. Henry, H. Zarrouk, N. Gharbi, and J. Livage, "Structural Characterization of Hybrid Materials Obtained from Zirconium *N*-proposide and 1,2-ethanediol," *J. Cryst. Solids*, **170** [1] 1–10 (1994).

<sup>15</sup>A. Guinier and G. Fournet. *Small-Angle Scattering of X-rays*. Wiley, New York, 1955.

<sup>16</sup>P. W. Schmidt, "Interpretation of Small-Angle Scattering Curves Proportional to a Negative Power of the Scattering Vector," *J. Appl. Crystallogr.*, **15**, 567–69 (1982).