Effect of Precipitating Agents on the Structural, Morphological, and Colorimetric Characteristics of Nickel Hydroxide Particles

Tamara M. Andrade, Marins Danczuk, Fauze J. Anaissi*

Universidade Estadual do Centro-Oeste, UNICENTRO, Departamento de Química, LabMat/CIMPE, R. Simeão Camargo Varela de Sá 03, Guarapuava, PR CEP 85040-080, Brazil

ARTICLE INFO

ABSTRACT

Nickel hydroxides are known for their characteristic green color, which when electrochemically modulated, may range from yellow to brown due to the electrochromic nature of these compounds. However, it was surprisingly found that the combination of nickel salts (acetate (Ac), chloride (Cl), and nitrate (Nit)) with hydroxides (sodium, potassium, and ammonium) generated solids of different colors and tones varying from green to yellow. The samples were characterized and identified as predominantly comprising the β-Ni(OH)$_2$ polymorph when combined with chloride and nitrate salts (degree of crystallinity between 68.2 and 76.2%), whereas nickel acetate generated a mixed phase of the α/β polymorphs (degree of crystallinity between 32.9 and 62.9%). Higher surface areas were obtained for the salts with NaOH: AcNa - 416.5 m^2 g^{-1}; ClNa - 114.30 m^2 g^{-1}; and NitNa - 103.7 m^2 g^{-1}, respectively. The α/β-Ni(OH)$_2$ materials presented low luminosity based on the CIELab method, unlike the other salts, whereas β-Ni(OH)$_2$ presented high luminosity.

Nickel occurs naturally in the form of mineral oxides and silicates, where the abundance of nickel in the earth's crust is approximately 0.01% [1]. Nickel compounds and nickel metal are used in batteries [2], supercapacitors [2], electrochemical sensors [3–4], for the adsorption of dyes [5], electrochromic devices [6], ceramic materials [7], or as catalysts and pigments [8].

Most studies on battery cathodes have focused on the α and β phases of nickel hydroxide and oxyhydroxide because these species present high charge efficiency and electrochemical stability [6]. These phases differ in terms of the interlamellar spacing and lamellar organization. In the β phase, the lamellae are arranged along the c-axis with an interlamellar distance of approximately 4.6 Å. In contrast, the α phase is disordered and with an interlamellar distance of approximately 8 Å. This difference in the interlamellar and organizational distance occurs due to the presence of significant amounts of water molecules and anions between the lamellae of the α phase, which has a smaller amount of hydroxyl ions (OH$^-$) than the β phase, leaving the lamellae positively charged and facilitating the intercalation of anions from the precursors used in the synthesis [2–6].

Due to these electrochemical characteristics, studies on the application of nickel hydroxide and oxyhydroxide as pigments are not widely reported in the literature. Most studies on nickel-based pigments have focused on the association of this metal with other elements such as iron [9] and titanium [10] to form double oxides.

Titanium is used to obtain pigments by generating titanium ilmenites (MTiO$_3$), where M represents Mg^{2+} or divalent transition metals such as Fe, Co, Mn, Ni, Zn, or Cu, which are used to obtain compounds with different colors and structures [11]. Moghtada and Shahruozianfar [12] synthesized cobalt titanate through a new wet chemical approach at a temperature lower than 50 °C and with ultrasonic treatment. The procedure yielded green nano-pigments with a mean particle size of 50 nm.

The association of nickel and titanium salts has received considerable attention for the synthesis of yellow pigments due to the high visible opacity of these composites and their good ability to reflect near-infrared (NIR) radiation from sunlight [11]. Several methods of synthesis have been used. The conventional solid-state reaction requires high temperatures (1000 °C) [13] as a disadvantage. Wet reactions such as the Pechini method [14], the polymer precursor method [15], and the precipitation method (as a sol-gel technique) [16] have also been utilized.

Mohammadi et al. [17] synthesized titanates based on perovskites in the form of nanocrystals by employing the umidic sleepychic methodology. XTiO$_3$ was obtained from XCl$_2$ and TiCl$_4$ (X = Ba, Sr, Ni, Ba$_x$Ti$_{1-x}$), and they evaluated the effects of the time and temperature of the ultrasound process. The materials were characterized by field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The characteristic

patterns, morphology of the clusters with a narrow size distribution, and the sonication time were found to be important parameters for controlling the morphology and shape of the powder products and elevated temperatures led to larger particle sizes as a function of diffusion and different precursors.

Moghtada et al. [18] synthesized $BaTiO_3$ by sonication of chloride solution in a strongly alkaline environment at a temperature of 50 °C. The results showed that the very thin nanocrystals, < 11 nm, were more effective for reducing the cost of ceramics as the sintering temperature was reduced in the new synthesis route. Ashiri et al. [19] clearly showed the influence of the Ba/Ti ratio ($BaCl_2$ and $TiCl_4$), the ultrasound time, and the concentration of the reagents used on the morphology and final phase of barium titanate ($BaTiO_3$) obtained.

It is known that the synthesis technique directly impacts the final structure and morphology of the products, which are crucial factors that define the applicability of the compound, such as in corrosion inhibitors [20], catalysts [15], electronic materials, energy storage devices [21,22], and pigments [16]. Considering that yellow [11] and green [12] pigments were obtained by the synthesis of nickel titanate [4,5] via different routes, most of which required high calcination temperatures, a study was proposed to evaluate the influence of different nickel precursors on the coloration of the final material. Although several studies related to the synthesis and characterization of colored nickel materials (obtained from the association of nickel with other elements for the preparation of new pigments) are documented, no attempt to compare the nature of the products obtained using nickel and different precipitating agents under the same conditions was found. The present study compares the structural, morphological, and colorimetric characteristics of samples prepared under the same conditions using different precursors.

The present work is based on combination of the direct precipitation of nickel salts [acetate ($Ni(CH_3COO)_2 \cdot 4H_2O$); chloride ($NiCl_2 \cdot 6H_2O$), and nitrate ($Ni(NO_3)_2 \cdot 6H_2O$)] with hydroxides [sodium (NaOH), potassium (KOH), and ammonium (NH_4OH)]. The combination generates nine samples with different optical properties, facilitating their application as synthetic inorganic pigments. The Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), and dynamic light scattering (DLS) methods are used to assign the color variation of the known polymorphs (Fig. 1).

The structural properties were probed by X-ray diffraction (XRD). Colorimetric measurements were used to differentiate the color tones (from green to yellow) obtained. Nickel hydroxides [$Ni(OH)_2$] were obtained from analytical grade reagents (P.A.) without prior purification or drying. The following were used: nickel acetate tetrahydrate [$Ni(CH_3COO)_2 \cdot 4H_2O$, Vetec], nickel chloride hexahydrate [$NiCl_2 \cdot 6H_2O$, Vetec], nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$, Vetec]; sodium hydroxide [NaOH, Vetec], potassium hydroxide [KOH, Synth], and ammonium hydroxide [NH_4OH, Synth]. The aqueous solutions were prepared with ultrapure water obtained from a Quimis reverse osmosis system, model Q842 10L.

The chemical precipitation of $Ni(OH)_2$ (Eq. (1)) is a one-step method in which a basic solution (NaOH, NH_4OH, KOH) is added, typically dropwise, to a nickel(II) salt solution $Ni(NO_3)_2$, $NiCl_2$, $Ni(CH_3COO)_2$, or vice versa. At sufficiently high pH, the hydroxide anion concentration exceeds the solubility limit and $Ni(OH)_2$ forms as a precipitate, as indicated in Eq. (1), where 'A' represents the anion (Cl^-, NO_3^-, CH_3COO^-) and 'C' represents the cation (K^+, Na^+, NH_4^+) [23,24].

$$Ni(A)_2 + 2COH \rightarrow Ni(OH)_2 + C^+ + A^- \tag{1}$$
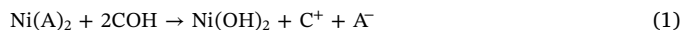
Distinct or mixed phases, such as the alpha/beta-$Ni(OH)_2$ phase, may be generated when anions or cations intercalate in the structure of $Ni(OH)_2$ (Eq. (2)). This is accompanied by a phase change as shown in Fig. 2 for AcK and $AcNH_4$, where mixed α/β-$Ni(OH)_2$ phases are formed [23,24].

$$Ni(A)_2 + 2COH \rightarrow Ni_{(1-x)}C_xA_y(OH)_{2-y} + C_x^+ + A_y^- \tag{2}$$
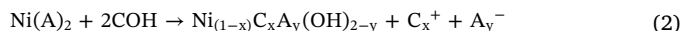
At room temperature, the aqueous solutions (2.0 mol L^{-1}) of the nickel salts (acetate, chloride, and nitrate) were combined with aqueous solutions (0.4 mol L^{-1}) of the precipitating agents (NaOH, KOH, and NH_4OH) in a 2:1 ratio (OH^-/Ni^{2+}). The precipitating agents were added under constant stirring until the nickel hydroxide particles formed and stirring was continued for ~90 min. After this period, the suspension was placed in an ultrasonic bath for 3 min to prevent the formation of large colloidal aggregates. The colloids were washed with distilled water to remove excess solubles and stabilize the pH (close to 7). For characterization purposes, a portion of each suspension was frozen and lyophilized; the finely powdered samples are denoted as shown in Table 1.

The $Ni(OH)_2$ samples in the aqueous suspension were frozen (by treatment at −7 °C for 12 h) and lyophilized using an LD series lyophilizer from Terroni Equipment Scientifics (BR). X-ray diffraction (XRD) analysis was performed on a Bruker D2 Phaser diffractometer with a copper cathode ($\lambda_{k\alpha}$ = 1.5418 Å) using a power of 30 kV, a current of 10 mA, and a scan rate of 0.05°min^{-1} in the 2θ range of 5–80°. The data were treated with the DIFFRAC.EVA, Bruker version, software for indexing of the integrated signals to the powder diffraction
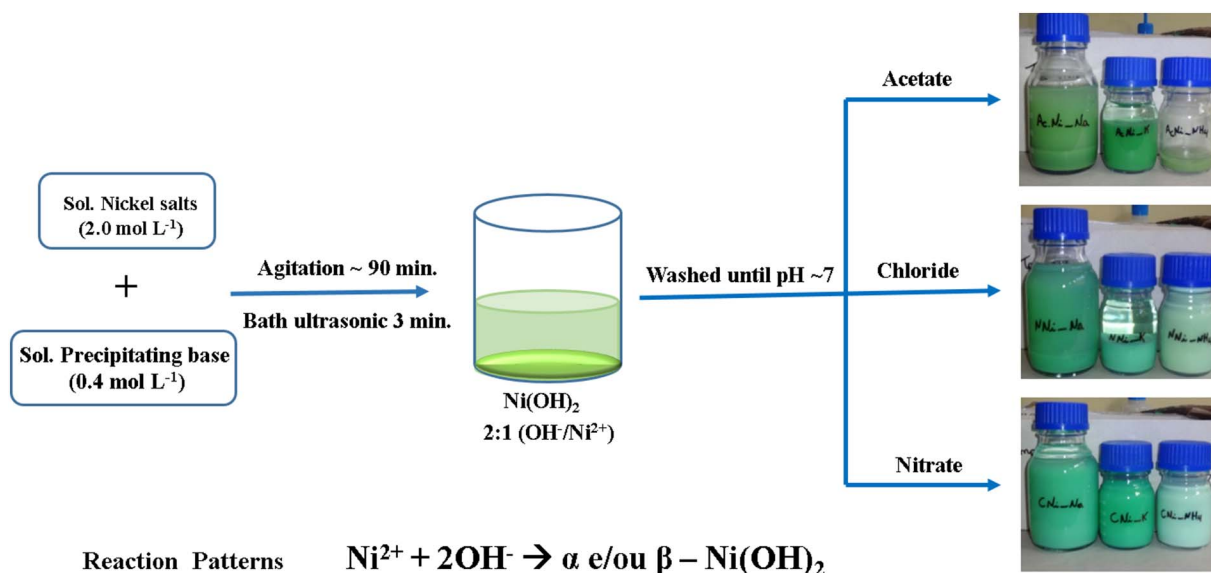

Fig. 1. Representation of the synthesis of $Ni(OH)_2$ samples.