Synthesis and Characterization of Cobalt and Nickel Orthophosphate Octahydtates

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ABSTRACT

$M_3(PO_4)_2 \cdot 8H_2O$ (M = Co and Ni), successfully were synthesized. The structure of the synthesized $M_3(PO_4)_2 \cdot 8H_2O$ and the calcined products were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The thermal property of synthesized samples were carried out by thermogravimetry/ differential thermogravimetric analysis/ differential thermal analysis (TG/DTG/DTA). The nickel and cobalt content of $M_3(PO_4)_2 \cdot 8H_2O$ were confirmed by atomic absorption spectrophotometry (AAS). The results from all techniques confirm the formula of the title compounds. The synthesized $Co_3(PO_4)_2 \cdot 8H_2O$ and $Ni_3(PO_4)_2 \cdot 8H_2O$ crystallize in the monoclinic crystal system. The thermal transformation product of $Co_3(PO_4)_2 \cdot 8H_2O$ in air at 700 ºC was found to be $Co_3(PO_4)_2$, while the calcined product at 900 ºC of $Ni_3(PO_4)_2 \cdot 8H_2O$ was found to be $Ni_3(PO_4)_2$.

บทคัดย่อ

ได้สังเคราะห์ $M_3(PO_4)_2 \cdot 8H_2O$ (M = Co และ Ni) อย่างเป็นผลสำเร็จ การพิสูจน์เอกลักษณ์ทางโครงสร้างของสารตัวอย่าง และผลผลิตที่ได้จากการเผาอาศัยเทคนิค XRD และ FTIR สมบัติเชิงความร้อนของสารตัวอย่าง วิเคราะห์ได้ด้วยเทคนิค TG/DTG/DTA ปริมาณนิกเกิลและโคบอลต์ใน $M_3(PO_4)_2 \cdot 8H_2O$ ยืนยันโดยใช้เทคนิค AAS ผลจากทุกเทคนิคยืนยันได้ว่าสารประกอบที่ได้มีสูตรโมเลกุลของสารประกอบตามชื่อเรื่อง สารสังเคราะห์ $Co_3(PO_4)_2 \cdot 8H_2O$ และ $Ni_3(PO_4)_2 \cdot 8H_2O$ ตกผลึกในระบบผลึกมอนอคลินิก ผลิตภัณฑ์เชิงความร้อนของ $Co_3(PO_4)_2 \cdot 8H_2O$ ที่อุณหภูมิ 700 ºซ ในอากาศคือ $Co_3(PO_4)_2$ ในขณะที่ผลิตภัณฑ์ที่ได้จากการเผา $Ni_3(PO_4)_2 \cdot 8H_2O$ ที่อุณหภูมิ 900 ºซ ในอากาศคือ $Ni_3(PO_4)_2$

Key Words: Cobalt and nickel orthophosphate octahydrates, simple synthesis, FTIR spectra

คำสำคัญ: โคบอลต์และนิกเกิลออร์โธฟอสเฟตออกตะไฮเดรต การสังเคราะห์อย่างง่าย เอฟทีไออาร์สเปกตรา

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Introduction

Orthophosphate of the type $M_3(PO_4)_2$ have various potential applications. They are used as selective catalysts, pigments, fertilizers, active substances of corrosion-protecting materials, components of medicinal formulations, and materials for phosphorous (Prokopchuk, Kopilevich, & Voitenko, 2007) such as $Co_3(PO_4)_2$ and $Mg_3(PO_4)_2$ have been used as catalysts for various organic processes (Aramendía et al., 1999; Aaddane et al., 2001) and $Zn_3(PO_4)_2$ either orthorhombic hopeite or triclinic parahopeite polymorphs was used in coating on steel for corrosive protection (Pawlig & Trettin, 1998).

Additional, cobalt and nickel phosphate are of considerable interest in a number of technological fields. They are the catalysts for organic synthesis reaction. For example, mesoporous nickel and cobalt phosphates are used as catalysts for styrene oxidation and a number of cobalt and nickel phosphates are used as pigments because of their properties such as color of pigment, insoluble in water and chemical stability (Meseguer et al., 2007)

Recently, Viter and Nagornyi (2009) reported the synthesis of $M_3(PO_4)_2{\cdot}8H_2O$ (M = Ni and Co) and $(Co_{1-x}Ni_x)_3(PO_4)_2{\cdot}8H_2O$ by reacting a mixture of $CoSO_4$ and $NiSO_4$ solution with a Na_2HPO_4 solution, at a P/(Co+Ni) molar ratio in the starting reagents of 0.67 (stoichiometric), at a temperature of 90 ºC, and reaction duration 1-5 days (Viter & Nagornyi, 2009). In this work, $M_3(PO_4)_2{\cdot}8H_2O$ (M = Co and Ni) were synthesized by wet chemical reaction between $Na_3PO_4{\cdot}12H_2O$ and $CoSO_4{\cdot}7H_2O$ or $NiSO_4{\cdot}6H_2O$, respectively, at lower temperature (70 ºC) and shorter time duration (24 h) compared to the literature.

Materials and methods

Materials

All chemicals and reagents used in this study are analytical grade and used without further purification.

Preparations

The cobalt and nickel phosphate octahydrate were synthesized by the simple wet chemical reaction between 0.5 M $Na_3PO_4{\cdot}12H_2O$ (Carlo Erba) and 0.5 M $CoSO_4{\cdot}7H_2O$ (Sigma-Aldrich) or $NiSO_4{\cdot}6H_2O$ (Univar), respectively, at Co/P or Ni/P ratio of 3:2. The mixture solution was heated for 24 hours at 70 ºC. The particular precipitates were obtained and isolated by filtration, washed with DI water several times and dried in a desiccator.

Characterizations

The nickel and cobalt contents of $M_3(PO_4)_2{\cdot}8H_2O$ compounds were determined by dissolving in 3% HNO_3 (70%, Carlo Erba) using atomic absorption spectrophotometry (AAS, Perki – Elmer Analyst 100). Thermal properties of the synthesized samples were investigated on a TG/DTG/DTA Pyris Diamond Perkin – Elmer Instrument. The experiment was performed at a heating rate of 10 ºC min^{-1} over the temperature range from 50 to 1000 ºC and N_2 atmosphere flow rate of 100 ml min^{-1}. The sample mass of about 5.9 mg (accurate) for $Ni_3(PO_4)_2{\cdot}8H_2O$ and about 5.2 mg (accurate) for $Co_3(PO_4)_2{\cdot}8H_2O$ were filled into an alumina pan. The thermograms of samples were recorded in an alumina pan using α-Al_2O_3 as the reference material. The synthesized $M_3(PO_4)_2{\cdot}8H_2O$ samples were calcined in a furnace (Lindberg/Blue) at 700 ºC and 900 ºC in air for 4 h and the thermal

transformation products were further characterized. The structure of the prepared samples and the calcined products were studied by X-ray powder diffraction (Phillips 3710) with Cu K_α radiation (λ = 0.15406 Å). The FTIR spectra of the synthesized compounds and the calcined products were recorded using KBr pellets on a Perkin–Elmer spectrum GX FTIR /FTRaman spectrophotometer with 32 scans in the range of 4000–370 cm^{-1} and the resolution of 4 cm^{-1}.

Results and Discussion

X-ray powder diffraction

The XRD patterns of the prepared $Co_3(PO_4)_2 \cdot 8H_2O$ and its calcined product at 700 ºC in air and $Ni_3(PO_4)_2 \cdot 8H_2O$ and its calcined product at 900 ºC in air are shown in Fig.1 and Fig. 2, respectively. All detectable peaks of the synthesized $M_3(PO_4)_2 \cdot 8H_2O$ and the calcined products are indexed as $Co_3(PO_4)_2 \cdot 8H_2O$, $Ni_3(PO_4)_2 \cdot 8H_2O$, $Co_3(PO_4)_2$ and $Ni_3(PO_4)_2$, which are identified using the standard data of PDF # 33-0432, PDF # 33-0951, PDF # 77-0225 and PDF # 38-1473, respectively. These results indicate that all crystal structures are in monoclinic system with space group $P2_1/a$, I2/m, $P2_1/n$ and $P2_1/a$, respectively. The average crystallite sizes and the lattice parameters of these compounds were calculated from XRD patterns (Noisong et al., 2008) and are tabulated in Table 1. The synthesized $Co_3(PO_4)_2 \cdot 8H_2O$ and $Ni_3(PO_4)_2 \cdot 8H_2O$ and the calcined products of these are isostructure. The lattice parameters of $Co_3(PO_4)_2 \cdot 8H_2O$, $Ni_3(PO_4)_2 \cdot 8H_2O$, $Co_3(PO_4)_2$ and $Ni_3(PO_4)_2$ are comparable to those reported in the standard data as demonstrated in Table 1.

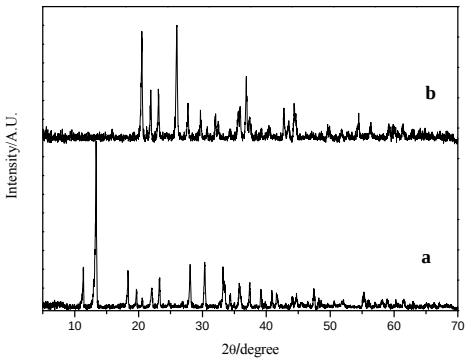

Fig. 1 The XRD patterns of the synthesized $Co_3(PO_4)_2 \cdot 8H_2O$ (a) and its calcined product at 700 ºC in air (b).

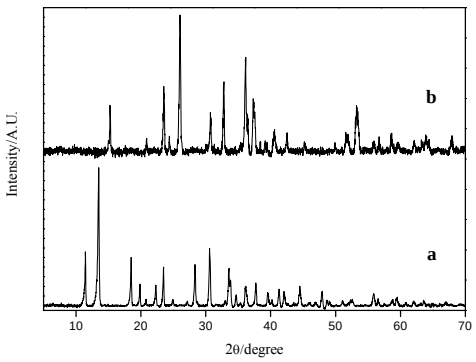

Fig. 2 The XRD patterns of the synthesized $Ni_3(PO_4)_2 \cdot 8H_2O$ (a) and its calcined product at 700 ºC in air (b).

TG/DTG/DTA results

The TG/DTG/DTA curves of cobalt and nickel orthophosphate octahydrate in N_2 at the heating rate 10 ºC min^{-1} are shown in Fig. 3 and 4, respectively. The TG curve of $Co_3(PO_4)_2 \cdot 8H_2O$ shows the weight losses between 50-1000 ºC (Fig. 3), which demonstrate 3 decomposition steps in the temperature range of 120–550 ºC. The corresponding observed total weight loss in this temperature range is 26.43 % (7.5 moles of water of crystallization) confirms

Table 1 Average particle sizes and lattice parameters of $M_3(PO_4)_2 \cdot 8H_2O$ (M = Co and Ni) and the calcined products in air calculated from XRD data.

Compound	Method	a (Å)	b (Å)	c (Å)	β (º)	Average particle sizes (nm)
$Co_3(PO_4)_2 \cdot 8H_2O$	PDF # 33-0432	9.926	13.33	4.678	102.31	-
	This work	9.916	13.33	4.679	102.30	78.5±1
	DIF.PDF-This work	0.010	0.00	-0.001	0.01	
$Ni_3(PO_4)_2 \cdot 8H_2O$	PDF # 33-0951	9.846	13.20	4.634	102.27	-
	This work	9.845	13.16	4.634	102.31	63.2±8
	DIF.PDF-This work	0.001	0.004	0.000	-0.04	
$Co_3(PO_4)_2$ ($Co_3(PO_4)_2 \cdot 8H_2O$ calcined 700 ^oC)	PDF # 77-0225	7.556	8.371	5.064	94.050	-
	This work	7.559	8.369	5.067	94.074	40.5±4
	DIF.PDF-This work	-0.003	0.002	-0.003	-0.024	
$Ni_3(PO_4)_2$ ($Ni_3(PO_4)_2 \cdot 8H_2O$ calcined 900 ^oC)	PDF # 38-1473	10.10	4.696	5.827	91.138	-
	This work	10.11	4.699	5.828	90.870	59.2±13
	DIF.PDF-This work	-0.01	-0.003	-0.001	0.268	

the formula $Co_3(PO_4)_2 \cdot 8H_2O$, which agrees well with the theoretical weight loss of 28.18%. The DTA curve of the synthetic $Co_3(PO_4)_2 \cdot 8H_2O$ at the heating rate of 10 ºC min^{-1} shows three maximum peaks at 152.1 ºC, 205.2 ºC and 213.5 ºC, with agree well with the DTG peaks at 150.1 ºC, 203.6 ºC and 211.7 ºC, respectively. One additional peak at 589.1 ºC of DTA curve was observed, which is suggested to be due to the phase transition from low crystallinity of $Co_3(PO_4)_2$ to higher crystallinity one. In the case of $Ni_3(PO_4)_2 \cdot 8H_2O$, the observed weight loss of 28.53% in TG curve (Fig. 4), corresponds to 8.1 moles of water in the crystalline hydrate (theoretical weight loss of 28.22%). The DTA curve of $Ni_3(PO_4)_2 \cdot 8H_2O$ illustrates one maximum peak at 202.0 ºC, which agrees with the DTG peak at 199.1 ºC. One more exothemic peak at 776.1 ºC is also suggested to be due to the phase transition from low crystallinity of $Ni_3(PO_4)_2$ to higher crystallinity one as in the case of $Co_3(PO_4)_2$.

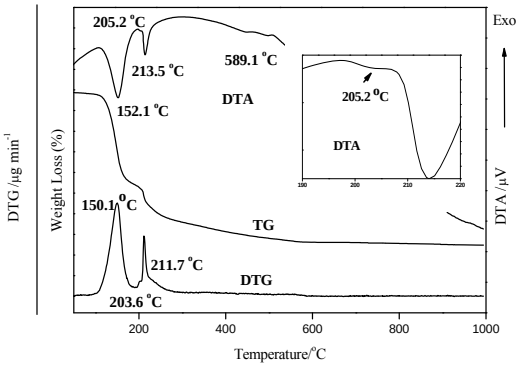

Fig. 3 The TG/DTG/DTA curve of the synthesized $Co_3(PO_4)_2 \cdot 8H_2O$ in N_2 at the heating rate 10 ºC min^{-1}.

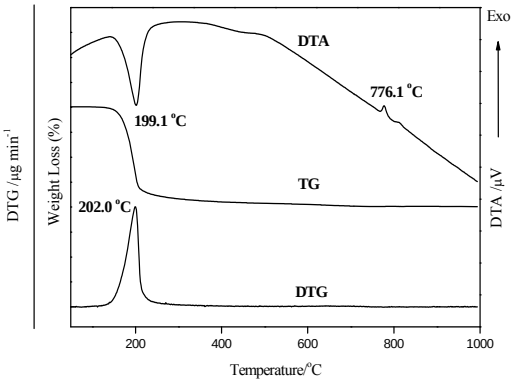

Fig. 4 The TG/DTG/DTA curve of the synthesized $Ni_3(PO_4)_2 \cdot 8H_2O$ in N_2 at the heating rate 10 ºC min^{-1}.

FTIR results

The FTIR spectra of the synthesized $Co_3(PO_4)_2 \cdot 8H_2O$, $Ni_3(PO_4)_2 \cdot 8H_2O$ show in Fig. 5 and the FTIR spectra of the calcined products at 700 ºC of $Co_3(PO_4)_2 \cdot 8H_2O$ and 900 ºC of $Ni_3(PO_4)_2 \cdot 8H_2O$ in air are illustrated in Fig. 6. The FTIR spectra of the synthesized $Co_3(PO_4)_2 \cdot 8H_2O$ and $Ni_3(PO_4)_2 \cdot 8H_2O$ are similar to those reported in the literature (Viter & Nagornyi, 2009). The vibrational bands in the region of 3200-3000 cm^{-1} are assigned to $\nu_1(A_1)H_2O$, whereas the bands at about 3400 cm^{-1} is attributed to $\nu_3(B_2)H_2O$. The bending mode of water, $\nu_2(A_1)H_2O$ was observed in the region of 1700-1600 cm^{-1}. The vibrational bands of water in $Co_3(PO_4)_2 \cdot 8H_2O$ occurred at higher wavenumber than $Ni_3(PO_4)_2 \cdot 8H_2O$. This can be interpreted to be due to the larger radius of Co^{2+} than Ni^{2+}. Therefore, the interaction between Ni-O in Ni-O-H-O should be stronger than Co-O in Co-O-H-O with the consequence of weakening of H-bond strength. The vibrational bands of PO_4^{3-} anion can be observed around 1080-1010 cm^{-1} as $\nu_3(F_2)PO_4^{3-}$, 990-840 cm^{-1} as $\nu_1(A_1)PO_4^{3-}$ and 600-540 cm^{-1} as $\nu_4(F_2)PO_4^{3-}$. Additional, the librational modes of water can be observed around 750 cm^{-1}, which disappear in the spectra of the calcined products. The bands in region of 1090-1010 cm^{-1} and 980-880 cm^{-1} of the calcined products are assigned to be $\nu_3(F_2)PO_4^{3-}$ and $\nu_1(A_1)PO_4^{3-}$, respectively. Moreover, $\nu_4(F_2)PO_4^{3-}$ and $\nu_2(E)PO_4^{3-}$ can be observed in the region of 640-530 cm^{-1} and around 450 cm^{-1}. The splitting of the $\nu_4(F_2)PO_4^{3-}$ and $\nu_2(E)PO_4^{3-}$ bands indicate that the T_d symmetry of phosphate group has been lowered.

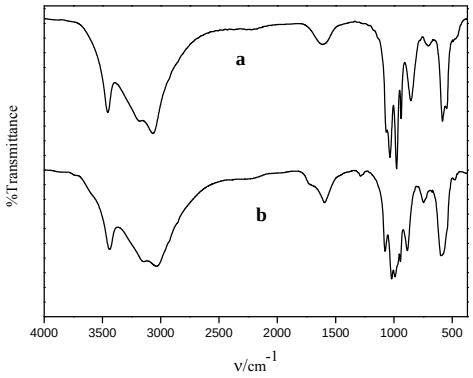

Fig. 5 The FTIR spectra of $Co_3(PO_4)_2 \cdot 8H_2O$ (a) and $Ni_3(PO_4)_2 \cdot 8H_2O$ (b).

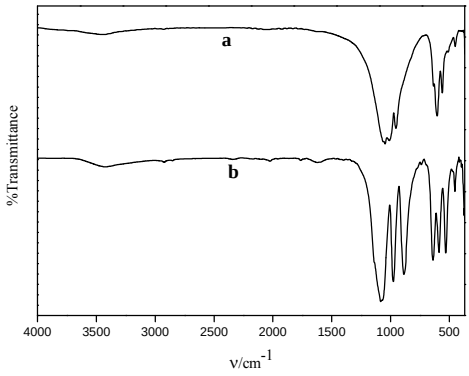

Fig. 6 The FTIR spectra of calcined product of $Co_3(PO_4)_2 \cdot 8H_2O$ at 700 ºC (a) and $Ni_3(PO_4)_2 \cdot 8H_2O$ at 900 ºC (b).

AAS Results

The metal contents of the synthetic $M_3(PO_4)_2 \cdot H_2O$ were found to be 3.06 mole of Co for $Co_3(PO_4)_2 \cdot 8H_2O$ and 2.75 mole of Ni in the case of $Ni_3(PO_4)_2 \cdot 8H_2O$, which agree well with theoretical value of 3 mole.

Conclusion

The $M_3(PO_4)_2 \cdot 8H_2O$ (M = Ni and Co) were successfully synthesized by using the rapid and the energy saving method compared with those reported in the literatures. The results from AAS, TG/DTG/DTA, FTIR, and XRD can confirm the formula of the synthesized compounds to be $Co_3(PO_4)_2 \cdot 8H_2O$ and $Ni_3(PO_4)_2 \cdot 8H_2O$ as well as the calcined products $Co_3(PO_4)_2$ (at 700 ºC) and $Ni_3(PO_4)_2$ (at 900 ºC), respectively.

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