ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 935–939. © Pleiades Publishing, Ltd., 2009.
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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis and Study of Solid Solutions between Cobalt and Nickel Phosphates with Varied Degree of Anion Protonation

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Received June 10, 2008

Abstract—Continuous substitutional solid solutions between cobalt and nickel phosphates with varied degree of anion protonation were obtained: $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$ and $(Co_{1-x}Ni_x)_3(PO_4)_2 \cdot 8H_2O$, where $0 \le x \le 1.00$. The thermolysis of the solid solutions was studied by the example of $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$. The phases synthesized were compared with the previously described continuous solid solution $Co_{1-x}Nix(H_2PO_4)_2 \cdot 2H_2O$.

DOI: 10.1134/S1070427209060019

Cobalt- and nickel-containing phosphates (individual compounds and solid solutions) are of considerable interest in a number of technological fields. In particular, they are catalysts for organic synthesis reactions. For example, a mesoporous nickel-cobalt phosphate has been used as a catalyst for styrene oxidation. The process efficiency strongly depended on the Co/(Co + Ni) in the material [1]. The solid solution of cobalt molybdate and chromium phosphate is a good catalyst for synthesis of *p*-aminophenol from *p*-nitrophenol [2]. Solid solutions of cobalt tertiary phosphate $Co_3(PO_4)_2$ and calcium or magnesium phosphate exhibit properties of acid or redox catalysts [3–5]. In addition, reduction of phosphates of metals belonging to the iron triad yields phosphides. These phosphides and related compounds are promising materials for hydropurification of oil products to remove compounds of sulfur, oxygen, and nitrogen [6–9]. A number of cobalt phosphates are used as pigments [10]. The nickel phosphates were suggested for the same purpose.

Thus, synthesis of new solid solutions of cobalt and nickel phosphates is of interest from both theoretical and practical standpoints.

Cobalt and nickel form hydrated phosphates of the same type, with varied degree of anion protonation: $M(H_2PO_4)_2 \cdot 2H_2O$, $MHPO_4 \cdot 1.5H_2O$, and $M_3(PO_4)_2 \cdot 8H_2O$, where M = Co, Ni. The corresponding cobalt and nickel compounds are isostructural and have close unit cell parameters [11, 12].

It has been found previously that interaction of 84.5% H_3PO_4 with a mixture of basic cobalt and nickel carbonates [P/(Co + Ni) molar ratio 4.99, temperature 20°C, interaction time 2–90 days] yields a continuous substitutional solid solution $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$ ($0 \le x \le 1.00$) (monoclinic crystal system, space group $P2_1/n$) [12]. Unit cell parameters of these hydrophosphates are close. As the content of Ni (cation with a smaller radius) in $Co_{1-x}Ni_x(H_2PO_4)_2 \cdot 2H_2O$ increases, the unit cell parameters decrease, but no linear dependence is observed. At the same time, the unit cell parameters and IR spectra of anhydrous cobalt and nickel tertiary phosphates $M_3(PO_4)_2$ are essentially different [13].

The above data enable a prognosis that $CoHPO_4 \cdot 1.5H_2O$ and $NiHPO_4 \cdot 1.5H_2O$, $Co_3(PO_4)_2 \cdot 8H_2O$ and $Ni_3(PO_4)_2 \cdot 8H_2O$ form continuous solid solutions (similarly to dihydrophosphates). However, this assumption can be verified only experimentally.

The aim of this study is to synthesize and study substitutional solid solutions between hydrated cobalt and nickel phosphates.

EXPERIMENTAL

The hydrophosphates were synthesized by reacting a mixture of basic cobalt and nickel carbonates with a 35% solution of H_3PO_4 at a P/(Co + Ni) molar ratio of 2.45 (a considerable excess of H_3PO_4), temperature 90°C, and interaction duration 1–30 days. The resulting hydrophosphate precipitates were filtered off, washed with water, and dried. In the course of the reaction, the possible admixture of Co(III) was reduced by introduction of H_2O_2 into the reaction mixture.

$(Co_{1-x}Ni_x)_3(PO_4)_2\cdot 8H_2O$ was synthesized by reacting a mixture of $CoSO_4$ and $NiSO_4$ solutions (total concentration in the reaction mixture 0.1 M) with a Na_2HPO_4 solution, at a P/(Co + Ni) molar ratio in the starting reagents of 0.67 (stoichiometric), temperature 90°C, and interaction duration 1–5 days. The resulting tertiary phosphates were filtered off, washed with water, and dried.

In both cases, the molar ratio between the metals in the starting reagents, W = Ni/(Co + Ni)×100, was varied from 0 to 100 mol % inclusive.

The chemical analysis of the starting and synthesized substances was performed as follows. The total content of cobalt and nickel was determined by back complexonometric titration in an urotropin buffer solution (pH 5.5). Xylenol orange served as indicator, and $ZnSO_4$, as titrant [14, 15]. Nickel was analyzed gravimetrically in the form of dimethylglyoximate [16]. The content of cobalt was calculated from the corresponding difference. Phosphorus was determined by the gravimetric quinoline-molybdenum method [17]. The content of water was found from the loss of mass by samples upon calcination.

An X-ray phase analysis was made with a DRON-4-07 diffractometer in the step-by-step mode (CoK_α radiation, SiO_2 and NaCl as standards). IR spectra were measured with a UR-20 instrument in the spectral range 400–4000 cm^{-1} in pellets with KBr. The thermolysis of the phosphates synthesized was studied with an MOM Q-1500 derivatograph (Hungary). The samples were heated in open platinum crucibles in the dynamic mode at a heating rate of 3.75 deg min^{-1}.

In synthesis of the hydrophosphates, an amorphous precipitate was originally formed and then transformed in the course of time to needle-like or prismatic crystals. As demonstrated by chemical analysis data (Table 1), the hydrophosphates synthesized at W of 0 to 100 mol % are characterized by molar ratios close to P/(Co + Ni) = 1.00 and H_2O/P = 2.00. These ratios are

Table 1. Characterization of substitutional solid solutions of cobalt and nickel phosphates (with varied degree of anion protonation)

Content of starting reagents, mol %		Chemical analysis data, wt %				Molar ratio		Compound
Ni	Co	P	Ni	Co	H_2O	P/(Co+Ni)	H_2O/P	
$Co_{1-x}Ni_xHPO_4\cdot 1.5H_2O$, $0 \le x \le 1.0$								
0	100	17.07	–	32.46	19.74	1.00	1.99	$CoHPO_4\cdot 1.5H_2O$
20	80	17.07	2.35	29.41	19.78	1.00	1.99	$Co_{0.91}Ni_{0.09}HPO_4\cdot 1.5H_2O$
40	60	17.13	6.82	25.51	19.75	1.01	1.98	$Co_{0.79}Ni_{0.21}HPO_4\cdot 1.5H_2O$
60	40	17.06	12.40	19.86	19.80	1.00	1.99	$Co_{0.61}Ni_{0.39}HPO_4\cdot 1.5H_2O$
80	20	17.11	20.36	11.93	19.83	1.01	1.99	$Co_{0.37}Ni_{0.63}HPO_4\cdot 1.5H_2O$
90	10	16.88	26.13	6.35	19.90	0.99	2.03	$Co_{0.19}Ni_{0.81}HPO_4\cdot 1.5H_2O$
100	0	17.11	32.19	—	19.85	1.01	1.99	$NiHPO_4\cdot 1.5H_2O$
$(Co_{1-x}Ni_x)_3(PO_4)_2\cdot 8H_2O$, $0 \le x \le 1.00$								
0	100	12.14	–	34.40	28.30	0.67	4.01	$Co_3(PO_4)_2\cdot 8H_2O$
20	80	12.22	5.05	29.40	28.34	0.67	3.99	$(Co_{0.85}Ni_{0.15})_3(PO_4)_2\cdot 8H_2O$
40	60	12.20	11.89	22.23	28.50	0.68	4.02	$(Co_{0.65}Ni_{0.35})_3(PO_4)_2\cdot 8H_2O$
60	40	12.19	15.32	18.91	28.60	0.68	4.03	$(Co_{0.55}Ni_{0.45})_3(PO_4)_2\cdot 8H_2O$
80	20	12.22	26.04	8.00	28.73	0.68	4.04	$(Co_{0.23}Ni_{0.77})_3(PO_4)_2\cdot 8H_2O$
100	0	12.13	34.02	–	28.82	0.68	4.08	$Ni_3(PO_4)_2\cdot 8H_2O$

Table 2. Unit cell parameters of the phosphates synthesized

Compound	*a*	*b*	*c*	β, deg	*V*, Å^3
	Å				
$CoHPO_4 \cdot 1.5H_2O$	8.417	15.515	13.090	–	1709.4
$Co_{0.91}Ni_{0.09}HPO_4 \cdot 1.5H_2O$	8.417	15.518	13.080	–	1708.4
$Co_{0.37}Ni_{0.63}HPO_4 \cdot 1.5H_2O$	8.400	15.520	12.935	–	1686.3
$Co_{0.19}Ni_{0.81}HPO_4 \cdot 1.5H_2O$	8.365	15.615	12.865	–	1680.4
$NiHPO_4 \cdot 1.5H_2O$	8.330	15.590	12.845	–	1668.1
$Co_3(PO_4)_2 \cdot 8H_2O$	10.055	13.355	4.692	104.80	609.2
$(Co_{0.65}Ni_{0.35})_3(PO_4)_2 \cdot 8H_2O$	10.015	13.320	4.675	104.80	603.0
$(Co_{0.23}Ni_{0.77})_3(PO_4)_2 \cdot 8H_2O$	9.980	13.280	4.650	104.65	596.3

stoichiometric for compounds of composition $MHPO_4 \cdot 1.5H_2O$, where M = Co, Ni. The X-ray diffraction patterns of all the hydrophosphates synthesized indicate that they are single-phase and similar to each other. The unit cell parameters of the hydrophosphates synthesized at *W* of 0 to 100 mol % are similar (Table 2). For individual cobalt and nickel hydrophosphates, these parameters are in good agreement with the JCPDS database [11]. Thus, a substitutional solid solution $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$ is formed in the system ($0 \le x \le 1.00$, rhombic crystal system, space group Pbca).

All the hydrophosphates obtained have alike IR spectra with respect both to the range of vibrations of the hydrophosphates anion {$\delta(O_3PO^-)$ = 350–580, γ(POH) = 700–900, ν[PO(H)] = 860–915, $\nu_s(PO_3)$ = 940–1010, $\nu_{as}(PO_3)$ = 1040–1170, δ(POH) = 1210–1400, ν(OH) = 2600–3250 cm^{-1}} and to δ(OH) and ν(OH) of water molecules (1600–1650 and 3000–3500 cm^{-1}, respectively). This fact indirectly confirms the close structural similarity of $CoHPO_4 \cdot 1.5H_2O$ and $NiHPO_4 \cdot 1.5H_2O$. As the nickel content in the solid solution increases, the positions of a number of absorption peaks in the IR spectra of the hydrophosphates steadily shift. The vibrations are assigned on the basis of generalized data [18]. Examples of IR spectra of the hydrophosphates are shown in Fig. 1a.

The reaction of Na_2HPO_4 with cobalt and nickel sulfates originally yielded bulk amorphous precipitates, which crystallized in time. The process was accompanied by a sharp decrease in their apparent volume. Also, the color of the precipitates changed as a result of transformation of a tetrahedrally coordinated cobalt to the octahedral state. A chemical analysis of tertiary phosphate octahydrates obtained at *W* of 0 to 100 mol % demonstrated (Table 1) that these samples were characterized by molar ratios close to P/(Co + Ni) = 0.67 and H_2O/P = 4.00. Thus, their composition corresponds to the stoichiometric formula $M_3(PO_4)_2 \cdot 8H_2O$, where M = Co, Ni. The X-ray diffraction patterns of these phosphates show that they are single-phase and similar to each other. The unit cell parameters and volume (Table 2) linearly depend on the nickel content of the samples. For $Co_3(PO_4)_2 \cdot 8H_2O$ and $Ni_3(PO_4)_2 \cdot 8H_2O$, the X-ray data are in good agreement with the JCPDS database [11]. The data presented above indicate that a substitutional solid solution $(Co_{1-x}Ni_x)_3(PO_4)_2 \cdot 8H_2O$ is formed by cobalt and nickel tertiary phosphates octahydrates ($0 \le x \le 1.00$, monoclinic crystal system, space group P2/*m*).

The IR spectra of the tertiary phosphates are similar with respect to an almost equal extent of the ranges in which appear bending [$\delta_s(PO_4)$ = 410–490, $\delta_{as}(PO_4)$ = 510–670 cm^{-1}] and stretching [$\nu_s(PO_4)$ = 930–990, $\nu_{as}(PO_4)$ = 975–1140 cm^{-1}] vibrations of the phosphate anion and also vibrations of water molecules. Examples of IR spectra of tertiary phos-phate octahydrates are shown in Fig. 1b.

It should be noted that cobalt and nickel tertiary arsenate octahydrates also form a continuous substitutional solid solution (these compounds are natural minerals) [19]. At the same time, anhydrous cobalt and nickel tertiary arsenates form limited solid solutions [20, 21].

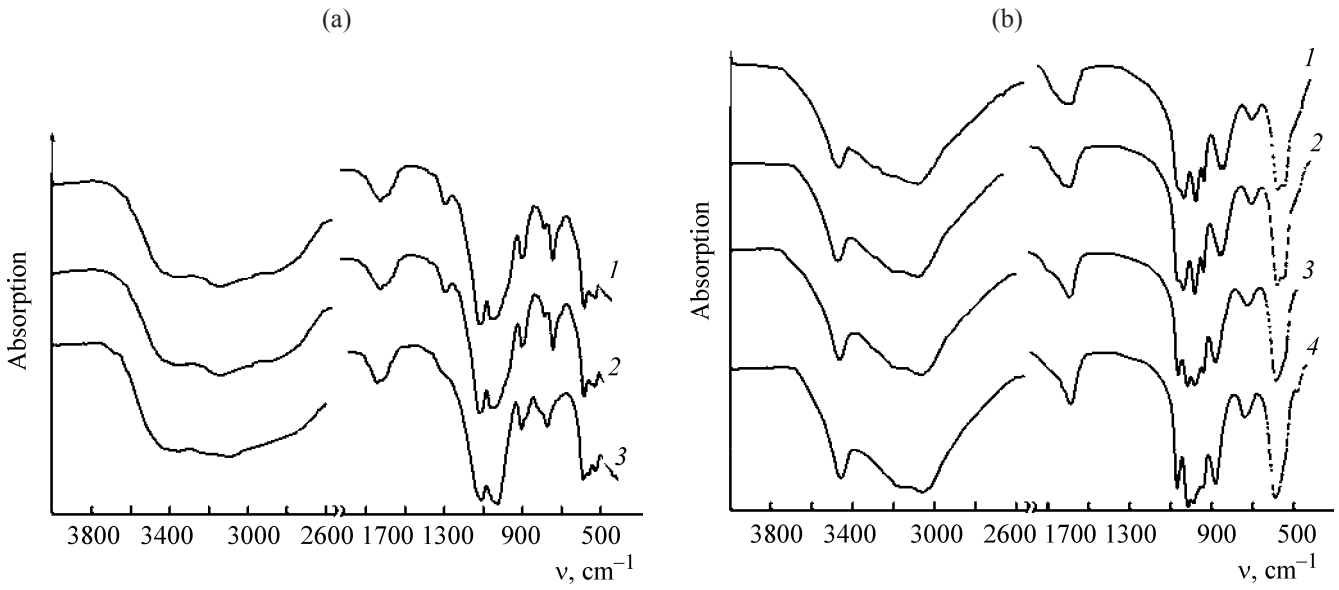

Fig. 1. IR spectra of the phosphates synthesized. (a) (*1*) $CoHPO_4 \cdot 1.5H_2O$, (*2*) $Co_{0.61}Ni_{0.39}HPO_4 \cdot 1.5H_2O$, and (*3*) $NiHPO_4 \cdot 1.5H_2O$. (b) (*1*) $Co_3(PO_4)_2 \cdot 8H_2O$, (*2*) $(Co_{0.85}Ni_{0.15})_3(PO_4)_2 \cdot 8H_2O$, (*3*) $(Co_{0.23}Ni_{0.77})_3(PO_4)_2 \cdot 8H_2O$, and (*4*) $Ni_3(PO_4)_2 \cdot 8H_2O$.

The thermolysis of the hydrophosphates synthesized was studied by the example of samples of the following compositions: $CoHPO_4 \cdot 1.5H_2O$, $Co_{0.61}Ni_{0.39} \cdot HPO_4 \cdot 1.5H_2O$, and $NiHPO_4 \cdot 1.5H_2O$.

The mass loss by cobalt hydrophosphates $CoHPO_4 \cdot 1.5H_2O$ begins at a temperature of about 120°C and ends at 350°C. The corresponding DTG curve shows three effects with minima at 150, 200, and 310°C. These effects correspond to loss of 0.4, 0.7, and 0.4 mol of water and are accompanied by endothermic effects in the DTA curve, with the first two endothermic effects superimposed. There are no other effects on the DTA curve. The DTA curve measured when cooling the sample has no effects at all.

The thermal decomposition of $Co_{0.61}Ni_{0.39}HPO_4 \cdot 1.5H_2O$ and $NiHPO_4 \cdot 1.5H_2O$ occurs in a single stage. The mass loss by these phosphates begins at 150 and 195°C, respectively. The DTG curves show a single effect associated with the mass loss (at 230 and 265°C), to which corresponds an endothermic effect in the DTA curves. In the case of $NiHPO_4 \cdot 1.5H_2O$, a minor exothermic effect peaked at around 680°C is also observed due to crystallization of $Ni_2P_2O_7$. For $CoHPO_4 \cdot 1.5H_2O$ and $Co_{0.61}Ni_{0.39}HPO_4 \cdot 1.5H_2O$, there is no effect of this kind. The dehydration of $Co_{0.61}Ni_{0.39}HPO_4 \cdot 1.5H_2O$ ends at 410°C, and that of $NiHPO_4 \cdot 1.5H_2O$, at 420°C.

CONCLUSIONS

(1) It was found that hydrated cobalt and nickel phosphates form continuous substitutional solid solutions $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$ (rhombic crystal system, space group Pbca) and $(Co_{1-x}Ni_x)_3(PO_4)_2 \cdot 8H_2O$ (monoclinic crystal system space group P2/*m*), where $0 \le x \le 1.00$.

(2) A comparison with a continuous solid solution $Co_{1-x}Ni_x(H_2PO_4)_2 \cdot 2H_2O$ demonstrated that, for these phases, the unit cell parameters of the phosphates are close and their IR spectra are similar.

(3) The thermolysis of the solid solutions obtained was studied by the example of $Co_{1-x}Ni_xHPO_4 \cdot 1.5H_2O$.

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