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# Synthesis and catalytic properties of Mg, Co(II), Zn phosphate solid solutions

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**Dihydrogenphosphates with the general formula $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ ($0 < x < 1$) and phosphates of composition $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ ($0 < x \leq 1$) were synthesized. The former crystallize in the monoclinic system, space group $P2_1/n$ (Z = 2), with the formation of a continuous substitutional solid solution. The latter form a limited solid solution. Their catalytic properties were investigated. The effectiveness of their action as catalysts for alcohol dehydration and methane oxidation was shown.**

**Phosphate / Solid solution / Synthesis / Catalyst**

## Introduction

Phosphates of polyvalent metals, due to their chemical properties and thermal stability, are widely used to produce active catalysts for organic synthesis [1-3]. It has been repeatedly stated that complex salts have greater catalytic effect than the individual ones [4,5].

In this regard, solid solutions of phosphates of divalent metals, particularly Mg, Co(II), and Zn, are of considerable interest. In their composition, there are two different cations, the content of which can be adjusted within a wide range. The crystal structure of the compound remains the same.

The purpose of this work was to synthesize solid solutions of hydrated Mg, Co(II), Zn phosphates and explore their effectiveness as catalysts in the reactions of tert-butanol dehydration and methane oxidation.

## Experimental

A solid solution of zinc and cobalt(II) dihydrogenphosphate was synthesized by crystallization at 25°C from phosphate solutions. The latter solutions were prepared by the interaction of concentrated phosphoric acid (64.13 wt.% $P_2O_5$), taken in an amount corresponding to 200% of the stoichiometric composition, with a mixture of zinc (77.25 wt.% ZnO) and cobalt (68.32 wt.% CoO) hydroxocarbonates. The atomic ratio $K = Zn^{2+}/Co^{2+}$ in this mixture ranged from 0 to 100 mol.%.

A solid solution of cobalt(II) and magnesium phosphates was obtained by interaction of aqueous solutions of $(NH_4)_2HPO_4$ and a mixture of cobalt(II) and magnesium chlorides, as described in [6]. The atomic ratio of the cations ($K = Co^{2+}/Mg^{2+}$) in the initial solutions was varied from 100 to 0.33. The ratio of phosphorus to the amount of precipitated cations was maintained equal to the value stoichiometrically required for the formation of a normal phosphate, $n = P/\Sigma Co^{2+},Mg^{2+} = 0.67$.

Identification of the synthesized phosphates was carried out using chemical analysis, X-ray diffraction (powder diffractometer DRON-4M, Fe *Kα* and Cu *Kα* radiation), and IR spectroscopy (infrared spectrophotometer Nexus-470 from the Nicolet Company, with Fourier transform and the software Omnic). Raman spectra were recorded on an upgraded DFS-24 device.

Tests of the catalytic activity of zinc-cobalt(II) dihydrogenphosphates in the reaction of tert-butanol dehydration were carried out in a flow type reactor. A set-up with a filtering layer of the catalyst while diluting alcohol vapor with argon was used. The samples were pre-activated in the temperature range 120-200°C. Analysis of the products was carried out by gas chromatography (chromatograph Tsvet-4). The degree of tert-butanol conversion was calculated from the yield of the final products – isobutylene and a liquid product.

The catalytic properties of solid solutions of cobalt(II)-magnesium phosphates were studied on the oxidation of methane in a set-up of the flow-circulation type at 600°C. The result of the oxidation was estimated based on the contents of formaldehyde, carbon(II) and carbon(IV) oxides.

The concentration of acid centers in the samples was determined by titration with n-butylamine in benzene in the presence of Hammett indicators in the range of p$K_a$ from 5.6 to 4.8; the specific surface was determined from the adsorption of benzene vapor [7].

## Results and discussion

The chemical analysis of the phosphates obtained by interaction of Zn and Co(II) hydroxocarbonates with phosphoric acid, confirmed the presence of two cations: zinc and cobalt. The contents of cations, phosphorus and water naturally vary depending on the composition of the initial hydroxocarbonates. The ratio P/∑Zn,Co (in atomic percent) was almost constant throughout the range of values of $K$ ($0.05 < K < 10.00$) and corresponds to that calculated for dihydrogenphosphate (Table 1).

The X-ray diffraction investigations established that the obtained dihydrogenphosphates were the only crystalline phase. The identification was made according to characteristics known for $Zn(H_2PO_4)_2\cdot 2H_2O$ and $Co(H_2PO_4)_2\cdot 2H_2O$. It showed that the synthesized dihydrogenphosphates belong to a series of compounds with similar structure $M^{II}(H_2PO_4)_2\cdot 2H_2O$, $M^{II}$ = Mg, Mn, Co, Zn, Cd [8]. The general formula can be presented as $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$. The chemical analysis revealed that the value of $x$ varies from 0 to 1.0, characterizing the formation of a continuous substitutional solid solution. The polycrystalline $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ samples, $0 < x < 1$, crystallize in the monoclinic system (space group $P2_1/n$, $Z = 2$). They are isostructural to $Zn(H_2PO_4)_2\cdot 2H_2O$ and $Co(H_2PO_4)_2\cdot 2H_2O$, which are the boundary representatives of the substitutional solid solution with $x = 0$ and 1, respectively.

Analysis of the IR and Raman spectra of $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ at different compositions showed that, retaining all types of vibration (both for the proton-containing groups and the skeletal vibrations of the anion sublattice), the total spectral pattern changes, reflecting the influence of the cation. The character of the absorption for $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ with $x \geq 0.5$ is similar to that for $Co(H_2PO_4)_2\cdot 2H_2O$ but differs largely by a shift of certain vibration frequencies [9]. The shape of the spectral envelope of $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ becomes more and more consistent with $Zn(H_2PO_4)_2\cdot 2H_2O$ with decreasing values of $x$ from 0.5 to 0.1, and for $Zn_{0.06}Co_{0.94}(H_2PO_4)_2\cdot 2H_2O$ the spectra coincide.

Table 2 presents the results of an analysis of the solid phase obtained by the interaction of aqueous solutions of the system $CoCl_2–MgCl_2–(NH_4)_2HPO_4$ for $n = P/(Co^{2+}+Mg^{2+}) = 0.67$ at 75°C for 7 days. Table 2 shows that, in the domain of composition with $K$ varying from 100 to 0.67, the ratio $n_1 = P/(Mg+Co)$ in the sediments amounts to 0.66-0.67, thus describing the precipitation of normal phosphates. In the absence of magnesium in the system (“$K$ = 100”) the precipitate was identified as $Co_3(PO_4)_2\cdot 8H_2O$, by comparing the X-ray diffraction pattern and IR spectroscopic characteristics with literature data [2,9].

The X-ray diffraction patterns of the phosphates obtained for $K$ = 5.00-0.67 showed that they represented the only crystalline phase in the samples, and had the structure of $Co_3(PO_4)_2\cdot 8H_2O$. The chemical analysis confirmed the presence of cobalt(II) and magnesium. This suggests isomorphic substitution of magnesium in the structure of $Co_3(PO_4)_2\cdot 8H_2O$. For decreasing values of $K$, 0.50-0.33, the diffraction patterns clearly indicated the presence of a second crystalline phase, identified as $MgHPO_4\cdot 3H_2O$.

**Table 1** Characteristics of zinc-cobalt(II) dihydrogenphosphate dihydrates.

| Composition of initial hydroxocarbonates, $K$ = Zn/Co, atomic | Composition of solid phase | | | | | |
|---|---|---|---|---|---|---|
| | Chemical composition, wt.% | | | | Formula from chemical analysis | Phase |
| | Zn | Co | P | $H_2O$ | | |
| – | 22.03 | – | 20.97 | 24.37 | $Zn(H_2PO_4)_2\cdot 2H_2O$ | $Zn(H_2PO_4)_2\cdot 2H_2O$ |
| 10.00 | 20.62 | 1.40 | 21.00 | 24.43 | $Zn_{0.93}Co_{0.07}(H_2PO_4)_2\cdot 2H_2O$ | Solid solution $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$, $0 < x < 1$<br>monoclinic system, $P2_1/n$, $Z = 2$ |
| 9.00 | 19.98 | 1.99 | 21.03 | 24.42 | $Zn_{0.90}Co_{0.10}(H_2PO_4)_2\cdot 2H_2O$ | |
| 2.00 | 17.95 | 3.82 | 21.01 | 24.45 | $Zn_{0.81}Co_{0.19}(H_2PO_4)_2\cdot 2H_2O$ | |
| 1.00 | 10.92 | 10.19 | 21.06 | 24.70 | $Zn_{0.49}Co_{0.51}(H_2PO_4)_2\cdot 2H_2O$ | |
| 0.25 | 5.85 | 15.01 | 21.12 | 24.80 | $Zn_{0.26}Co_{0.74}(H_2PO_4)_2\cdot 2H_2O$ | |
| 0.13 | 4.24 | 16.22 | 21.10 | 24.91 | $Zn_{0.19}Co_{0.81}(H_2PO_4)_2\cdot 2H_2O$ | |
| 0.10 | 2.82 | 18.35 | 21.16 | 24.93 | $Zn_{0.09}Co_{0.91}(H_2PO_4)_2\cdot 2H_2O$ | |
| 0.05 | 1.30 | 19.18 | 21.14 | 24.91 | $Zn_{0.06}Co_{0.94}(H_2PO_4)_2\cdot 2H_2O$ | |
| – | – | 20.00 | 21.45 | 24.93 | $Co(H_2PO_4)_2\cdot 2H_2O$ | $Co(H_2PO_4)_2\cdot 2H_2O$ |

**Table 2** Composition of the solid phase in the system $MgCl_2$–$CoCl_2$–$(NH_4)_2HPO_4$–$H_2O$.

| $K$ = Co/Mg, atomic | Chemical composition, wt.% | | | $n_1$ | Phase composition |
|---|---|---|---|---|---|
| | Co | Mg | P | | |
| 100.00 | 33.54 | 0 | 11.88 | 0.67 | $Co_3(PO_4)_2\cdot 8H_2O$ |
| 5.00 | 32.80 | 0.69 | 12.28 | 0.67 | $Co_{2.86}Mg_{0.15}(PO_4)_2\cdot 8H_2O$ |
| 3.00 | 32.74 | 0.70 | 12.16 | 0.67 | $Co_{2.85}Mg_{0.15}(PO_4)_2\cdot 8H_2O$ |
| 2.00 | 32.48 | 1.28 | 12.24 | 0.66 | $Co_{2.74}Mg_{0.26}(PO_4)_2\cdot 8H_2O$ |
| 1.50 | 31.82 | 2.18 | 12.24 | 0.66 | $Co_{2.47}Mg_{0.26}(PO_4)_2\cdot 8H_2O$ |
| 1.00 | 28.81 | 3.14 | 12.54 | 0.66 | $Co_{2.37}Mg_{0.63}(PO_4)_2\cdot 8H_2O$ |
| 0.67 | 25.82 | 5.12 | 12.95 | 0.66 | $Co_2Mg(PO_4)_2\cdot 8H_2O$ |
| 0.50 | 22.70 | 6.37 | 13.45 | 0.69 | Mixture of $Co_2Mg(PO_4)_2\cdot 8H_2O$ and $MgHPO_4\cdot 3H_2O$ |
| 0.33 | 13.34 | 9.68 | 14.97 | 0.77 | |

Comparison of the results of X-ray diffraction, infrared spectroscopy and chemical analysis indicated that, when $K$ = 5.00-0.67, a limited solid solution of phosphates with the general formula $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ is formed. Its homogeneity range is $0 < x \leq 1$, in agreement with the conclusions in [6]. The saturated solid solution is thus a phosphate of composition $Co_2Mg(PO_4)_2\cdot 8H_2O$.

To study the prospects of using the synthesized solid solutions $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ ($0 < x < 1$) and $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ ($0 < x \leq 1$) as catalysts, we evaluated their acid-base properties and catalytic activity. The research was conducted according to the procedure described in [10].

The values of the proton activity ($0.8\cdot 10^{-2}$-$1.08\cdot 10^{-3}$) and power characteristics of free phosphoric acid separated during the heat treatment of the dihydrogenphposphates $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ ($0 < x < 1$), calculated based on the experimental data, indicate catalytic activity in reactions catalyzed by hydrogen ions (the acid ionization constant for the first stage is $0.11\cdot 10^{-4}$-$0.59\cdot 10^{-4}$).

The activity of an acid catalyst depends on the migration processes of active protons. The mobility of active protons was assessed based on the results of a study of the products of the heat treatment of $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ by proton NMR. According to the results obtained at room temperature, when the protons are localized, the location and shape of the broad-lines of the spectrum of $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ with $x$ = 0.33, 0.5, 0.67 are due mainly to the length of the interproton distances and the presence of paramagnetic ions. In the spectra of samples heat-treated in the range 90-150ºC, narrowing of the line from acidic protons was observed. The minimum value of the width ($\Delta H = 0.6\cdot 10^{-4}$ T) was recorded at 120ºC. An analysis of the influence of the temperature on the width of this line showed that in the range of 120-200ºC the protons are in rapid diffusion mobility. This range has been found previously [11], and corresponds to the formation of a maximum amount of free phosphoric acid in the products of fired $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$. It was used to select the temperature of activation of the dihydrogenphosphates of the solid solution $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$, the catalytic properties of which were studied in the reactions of tert-butanol dehydration.

To clarify the nature of the narrow component that appears in the proton NMR spectra of the samples during heating, and confirm the correctness of its assignment to the formation of free phosphoric acid, the protons which have high mobility, phosphorous-31 NMR spectra of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2\cdot 2H_2O$ and the products of its thermal decomposition were studied. Based on these data, a relationship between the width of the line in the $^{31}$P NMR spectrum and the intensity of the line of the narrow component in the $^{1}$H NMR spectra of the thermolysis products was established (Fig. 1). A comparative analysis showed that the appearance of narrow lines in the proton NMR spectra (sample warmed up to 120ºC) correlates with a decrease of the width and second moment of the line in the $^{31}$P NMR spectra. The narrow intense band recorded in the $^{31}$P NMR spectrum, broadens with the fall of the intensity of the narrow component in the proton NMR spectrum when $Zn_{0.5}Co_{0.5}(H_2PO_4)_2\cdot 2H_2O$ is heated to 250 and 400ºC. Narrowing of the component in the $^{31}$P spectrum can be explained by the formation of a new phase containing more mobile phosphorus and the presence of mobile protons.

Test results of the catalytic activity of $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ (Table 3) showed that the free phosphoric acid, separated during the heat treatment, has higher thermal stability than industrial catalytic analogs used in processes of alcohol dehydration [12]. The dihydrogenphosphate solid solution retains catalytic activity with increasing temperature activation up to 300ºC. The degree of conversion of the alcohol and the selectivity of the catalyst was 100%. The temperature of operational conditions for $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ makes it possible to reduce the temperature of the tert-butanol dehydration process to 80ºC.

The effectiveness of the phosphate solid solution $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ ($0 < x \leq 1.00$) as a catalyst was studied in the reaction of methane conversion.

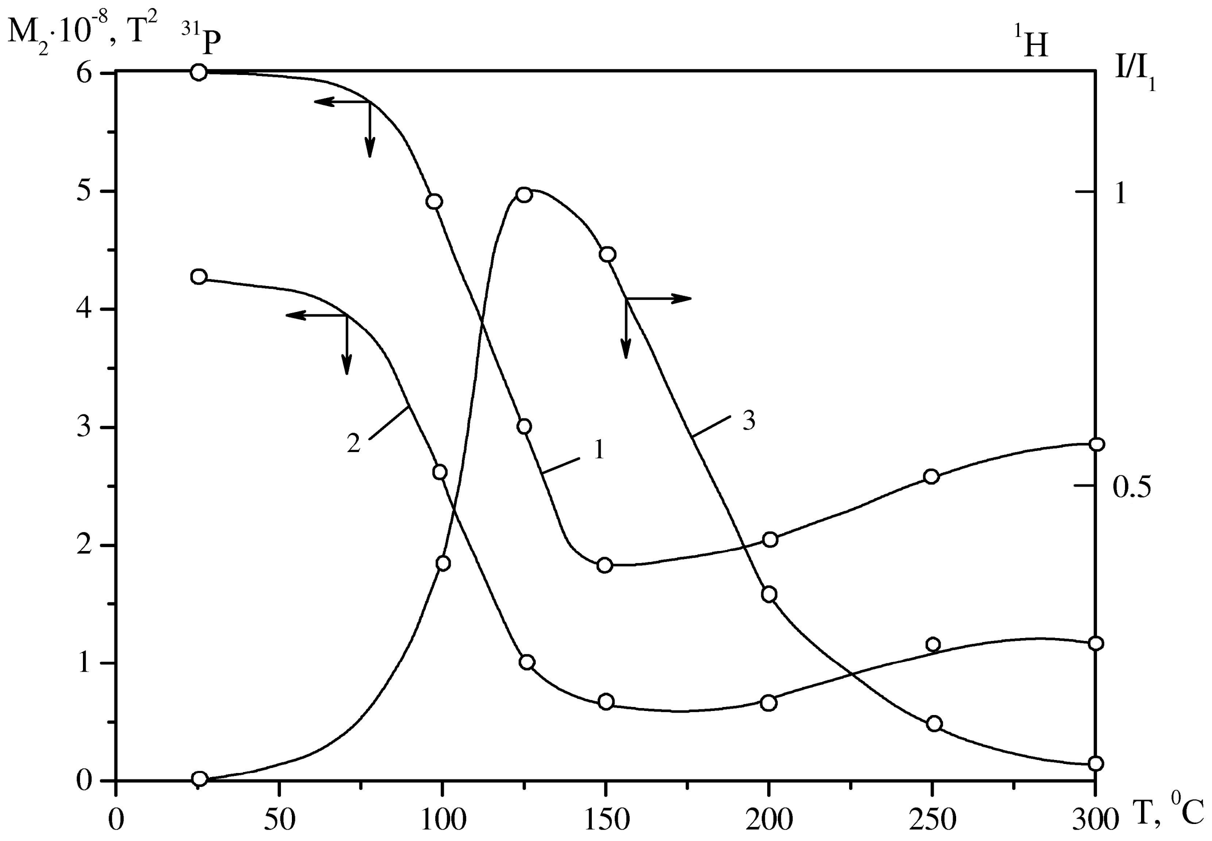

**Fig. 1** Interrelation of results of heat treatment of $Zn_{0.5}Co_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ at different temperatures as obtained by proton NMR and $^{31}P$ NMR (1 – width and 2 – second moment of lines in the $^{31}P$ NMR spectra; 3 – intensity of the narrow component in the $^{1}H$ NMR spectra).

**Table 3** Catalytic properties of $Zn_{1-x}Co_x(H_2PO_4)_2{\cdot}2H_2O$ on the dehydration of tert-butanol (feed rate of alcohol 0.6 h$^{-1}$, duration of the experiment 90 min).

| Catalyst [a] | Surface of the catalyst, $m^2/g$ | Temperature, °C | | Degree of conversion, % | |
|---|---|---|---|---|---|
| | | activation of the catalyst | experiment | liquid product | gaseous product |
| $Zn_{0.67}Co_{0.33}(H_2PO_4)_2{\cdot}2H_2O$ | 0.21 | 150 | 100 | 100.0 | 99.7 |
| | 0.21 | 150 | 90 | 99.3 | 98.6 |
| | 0.21 | 150 | 80 | 98.5 | 97.9 |
| | 0.29 | 300 | 100 | 100.0 | 98.3 |
| $Zn_{0.50}Co_{0.50}(H_2PO_4)_2{\cdot}2H_2O$ | 0.26 | 150 | 100 | 100.0 | 99.1 |
| | 0.26 | 150 | 90 | 97.7 | 96.8 |
| | 0.26 | 150 | 80 | 92.6 | 91.7 |
| | 0.28 | 300 | 100 | 100.0 | 99.4 |
| $Zn_{0.33}Co_{0.67}(H_2PO_4)_2{\cdot}2H_2O$ | 0.30 | 150 | 100 | 100.0 | 99.0 |
| | 0.30 | 150 | 90 | 100.0 | 99.7 |
| | 0.30 | 150 | 80 | 97.0 | 96.2 |
| | 0.32 | 300 | 100 | 100.0 | 100.0 |

[a] The selectivity of the catalyst was 100%.

The results showed that by varying the composition of the solid solution it is possible to obtain a product of methane conversion of an explicitly given composition. An increase of the magnesium content in $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ decreases the specific surface of the phosphate, from 9.1 $m^2/g$ for $Co_3(PO_4)_2\cdot 8H_2O$, to 6.0 $m^2/g$ for $Co_{2.0}Mg_{1.0}(PO_4)_2\cdot 8H_2O$. The concentration of acid centers also decreases. Changing these characteristics of the phosphate changes the catalytic action. The selectivity towards carbon(II) oxide increases by a factor 2.0-2.5 and amounts to 9% for $Co_3(PO_4)_2\cdot 8H_2O$, 17% for $Co_{2.5}Mg_{0.5}(PO_4)_2\cdot 8H_2O$, and 23% for the phosphate of composition $Co_{2.0}Mg_{1.0}(PO_4)_2\cdot 8H_2O$. The selectivity towards formaldehyde decreases and is, for the above-mentioned phosphates, 18, 11, and 8% respectively. The increase of the magnesium content in the solid solution produces a 6-8% increase of the degree of methane conversion.

## Conclusions

Dihydrogenphosphates of the general formula $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ $(0 < x < 1)$ and phosphates of composition $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ $(0 < x \leq 1)$ were synthesized. It was established that $Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ $(0 < x < 1)$ crystallizes in the monoclinic system (space group $P2_1/n$, $Z = 2$) with the formation of a continuous substitutional solid solution. $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ forms a limited solid solution. The catalytic properties were investigated. The effectiveness of the title compounds as catalysts for dehydration of alcohols ($Zn_{1-x}Co_x(H_2PO_4)_2\cdot 2H_2O$ $(0 < x < 1)$) and deep conversion of methane $Co_{3-x}Mg_x(PO_4)_2\cdot 8H_2O$ $(0 < x \leq 1)$ was established.

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