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Heterovalent doping of LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and temperature variation makes it possible to change the selectivity of catalysts

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# Conversion of aliphatic C1-C2 alcohols on In-, Nb-, Mo-doped complex lithium phosphates and HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> with NASICON-type structure

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#### Abstract

In-, Nb-, Mo-doped lithium complex phosphates and  $HZr_2(PO_4)_3$  with NASICON-type structure were synthesized in this paper. Particle size distribution lies between 50 and 300 nm. The obtained samples were characterized by X-ray diffraction analysis, scanning electron microscopy and X-ray microanalysis. Investigation of the catalytic properties of synthesized compounds in the C1-C2 alcohols conversions showed that heterovalent doping has a determining effect on the obtained catalysts' activity and selectivity.

It is shown that the thermodynamic factors and the dopant ability to change the degree of oxidation and acid function of the catalysts play a key role in methanol and ethanol conversion. A number of catalysts show the high activity and selectivity of the formation of dimethyl and diethyl ethers and ethylene. High selectivity for C4 hydrocarbons is achieved by  $\text{LiZr}_2(\text{PO}_4)_3$  and  $\text{Li}_{0.5}\text{Zr}_2\text{P}_{2.5}\text{Mo}_{0.5}\text{O}_{12}$  catalysts (64 and 49%, respectively) in the case of ethanol conversion.

Key words: Nasicon, heterogeneous catalysis, methanol conversion, ethanol conversion.

# ACCEPTED MANUSCRIPT Introduction

The main goal of green chemistry now is the search for environmentally friendly, renewable energy sources. Biomass is considered as a promising option and the bioalcohols appear while it's processing [1]. The main application of the obtained alcohols is reduced to their use as a fuel, or additives to it [2, 3]. But in the mass production of such alcohols, it will be expedient to use them also for the production of industrially important products, such as hydrocarbons, ethers, aldehydes, ketones, hydrogen, etc. In this regard, it is important to find suitable catalysts capable of effectively converting alcohols into these compounds.

According to the literature, plenty types of catalysts have been investigated in ethanol and methanol conversion processes, such as Zeolites [4], clays [5], mixed metal oxides [6, 7, 8], noble and non-noble metal catalysts on different supports [9, 10]. In the case of catalyst by metals the main process is steam reforming, hydrocarbons, olefin and ether formation is typical in the case of zeolite and ceramic catalysts. Bio-diesel production should be mentioned also in the case of the use of sulfonic acid and it`s derivatives [11].

The NASICON-type structure compounds (NA<sup>+</sup> Super Ionic CONductor) were chosen as catalysts in this work. Materials belonging to this structural type are compounds with the general formula  $A_xB_2(ZO_4)_3$ , where A is usually alkali or alkaline earth element, B is a polyvalent element (Zr, Ti, Sc etc.), Z is a phosphorus or silicon, or both immediately. Their structure consists of joined vertices of BO<sub>6</sub> octahedrons and ZO<sub>4</sub> tetrahedrons. A-cations are located in the cavities of this structure [12, 13].

NASICON-type compounds were first pointed be M. Sljukic and co. in 1967 [14]. The interest to these compounds has increased dramatically after Hong and other scientists' detection of high ionic conductivity in them [15-17]. This conductivity is achieved due to the presence of conduction channels in their structure, in which the A-ions move [13]. Among other advantages of NASICON-type structure compounds, it is worth to mention their high chemical and thermal stability, radiation resistance and structure variability, which makes it possible to

carry out both iso- and heterovalent doping without destroying the original cavity structure [18, 19]. These features determine a wide range of possible applications of these compounds as cathode materials in lithium current sources [20-23], ionic conductors in high-temperature fuel cells [24], in sensors [25-27], in radionuclide purification [28], in various types of heterogeneous catalysis [29-34], including membrane catalysis [35, 36] and photocatalysis [37].

The ability to heterovalent substitution is particularly important for their use as catalysts, since this allows to vary the number and strength of acidic (according to Lewis and Brønsted) and oxidation-reduction centers on the surface. Chemical and thermal resistance allow the use of catalysts based on these compounds under such conditions where metal-based catalysts are poisoned (SO<sub>2</sub> presence) or fused.

The aim of this work was to obtain heterovalently doped compounds with NASICON structure based on  $\text{LiZr}_2(\text{PO}_4)_3$  and to investigate their activity in the catalytic conversions of C1-C2 alcohols. It was assumed that the partial substitution of phosphorus by molybdenum may allow to improve their activity in redox reactions (dehydrogenation reactions) due to a change in the oxidation state of molybdenum ions. Partial substitution of zirconium for niobium or phosphorus for molybdenum can lead to a change in the Lewis acidity of these catalysts, as well as to a change their ability to form coordination bonds with oxygen atoms of alcohols. The increase in Brønsted acidity can be achieved due to the substitution of lithium by protons (HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>). Varying the composition can allow to change the catalytic activity in the dehydration and dehydrogenation of the alcohols.

# Material and Methods

In this work, we synthesized compounds of the composition  $LiZr_2(PO_4)_3$ ,  $Li_{1\pm0.5}Zr_{1.5}M_{0.5}(PO_4)_3$  (M = In or Nb),  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ , and  $HZr_2(PO_4)_3$ . The synthesis of  $LiZr_2(PO_4)_3$ ,  $Li_{1\pm0.5}Zr_{1.5}M_{0.5}(PO_4)_3$  (M = In or Nb) and  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  was carried out by the Pechini method [38, 39]. The stoichiometric sample weight of  $ZrOCl_{2*}8H_2O$ , citric acid (acid:M = 4:1, where M = Zr + In or Nb),  $Li_2CO_3$  and  $NH_4H_2PO_4$  were sequentially dissolved in an alumina crucible in a mixture of ethylene glycol (2 ml) and deionized water (10 ml). To obtain  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$ , the exact sample weight of  $In_2O_3$  calculated from the stoichiometry of the final product was dissolved in a minimum amount of hot concentrated nitric acid, ethylene glycol and water were added to the resulting solution, and then the remaining reagents in the above sequence. NbCl<sub>5</sub> dissolved in a minimal amount of concentrated hydrochloric acid was used for  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  syntheses. The resulting solution was mixed with ZrOCl<sub>2\*8</sub>H<sub>2</sub>O solution. A mixture of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> with (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> were used instead of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> for the Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub> synthesis. After addition of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, the pH of the solution was quickly adjusted to 5.5 by adding a concentrated ammonia solution to prevent precipitation of the zirconium phosphate. The resulting solution was kept for 24 hours, first at 95°C, 24 hours at 150°C, then 4 hours at 350°C and, after thorough grinding, subjected to final annealing at 750°C for 10 hours.

 $HZr_2(PO_4)_3$  was synthesized by the hydrothermal method. 1M solutions of  $ZrOCl_2*8H_2O$  and  $NH_4H_2PO_4$  in a ratio of 1:2 were mixed in an autoclave with Teflon insert. The autoclave was sealed and kept at 250°C for 24 hours. After that obtained precipitate was washed from the dissolved impurities and annealed at 500°C for 72 hours.

X-ray diffraction analysis (XRD) was carried out using a Rigaku D/Max-2200 X-ray diffractometer (CuK $\alpha_1$  – radiation) with thermal attachment. Heating speed for obtaining high temperature X-ray patterns was 10 K/min. Samples were held at a predetermined temperature for 5 minutes before measurement. Rigaku Application Data Processing software was used to process the diagrams and qualitative analysis. The Rietveld method refinement was provided by FullProf Suite software package.

The Scherrer equation was used to estimate the coherent scattering region (CSR) from the X-ray diffraction lines broadening:

$$d = \frac{k \cdot \lambda}{\sqrt{B^2 - b^2} \cdot \cos\theta}; \tag{1}$$

where k = 0.89 is the Scherrer constant,  $\lambda = 1.5406$  Å is the wavelength of the radiation used, B is the half-width at the half-height of the peak (in 2 $\theta$ ), b is the instrumental broadening (in 2 $\theta$ ), and  $\theta$  is the angle of the peak position. The lanthanum hexaboride powder LaB<sub>6</sub> (Standard Reference Material® 660a) was used as a standard for the determination of instrumental broadening.

The specific surface area was determined by the BET method using the Micromeritics ASAP 2020. The samples were heated to a temperature of 350°C and held for 1 hour for degassing. The analysis was carried out in the region of relative pressures  $0.01 \le p/p_0 \le 0.99$  in nitrogen atmosphere.

The micrographs of the samples were obtained by a scanning electron microscope (SEM) Carl Zeiss NVision 40 with an attachment for X-ray microanalysis. The accelerating voltage was 1 kV.

The FTIR spectra were recorded by Nicolet Protégé 380 FTIR spectrometer at 4 cm<sup>-1</sup> optical resolution. 20 mg of sample powder were pressed in a tablet and placed in a heating cell, attached to the spectrometer and vacuum line. Activation was performed in the vacuum at 400°C for 4 hours. The adsorption of pyridine was performed at room temperature, partial pressure of pyridine was 2 torr. Spectra were recorded after treatment of the pyridine exposed samples at 150°C in the vacuum to remove weakly sorbed pyridine. All spectra are presented after subtraction of the spectrum of activated sample. The subtraction of spectra was performed using OMNIC 7.3 software package.

The catalytic properties of the catalysts synthesized were studied in a conventional flow-type quartz reactor in a helium or argon streamline with an

admixture of alcohol vapors. The reaction products were analyzed qualitatively and quantitatively on a Crystallux 4000M chromatograph with a thermal conductivity detector on HayeSep T 60/80 mesh (3 m, 150°C, 30 ml/min, He), SKT-6 (3 m, 150°C, 30 ml/min, He), Mole Seive 5 A (3 m, 25°C, 10 ml/min, Ar) columns. All chromatograms were processed by using the NetChrom software package. The error of chromatographing method was  $\pm$  5%.

For the experiment, a 0.3 g catalyst was mixed with ground quartz (d = 250-500  $\mu$ m) and placed in a quartz reactor tube with a length of 25 cm with an internal diameter of 6 mm so that the length of the catalytic layer was 10 cm. Methyl and ethyl alcohols were used as reagents. The carrier gas was passed through a thermostatic bubbler with an alcohol at a flow rate of 20 ml/min to create the desired concentration of alcohol vapors in the feed gas mixture. The bubbler temperature was 0 and 11°C for methyl and ethyl alcohols, respectively.

The conversion was calculated using the following equation:

$$X = 100 \times \frac{\varphi_{ini} - \varphi_{curr}}{\varphi_{ini}};$$
<sup>(2)</sup>

where  $\varphi_{ini/curr}$  – the initial and current volume fraction of alcohol vapors in the feed mixture, respectively.

Selectivity was calculated as following:

$$S = 100 \times \frac{\varphi_{prod} \cdot n_{prod}}{(\varphi_{ini} - \varphi_{curr}) \cdot n_{alc}};$$
(3)

where  $\varphi_{\text{prod}}$  – product volume fraction;  $n_{\text{prod}}$  and  $n_{\text{alc}}$  – the number of carbon atoms in the product and alcohol molecule, respectively (in order to take in account the carbon balance).

To calculate the productivity (mmol/h\*g), the following equation was used:

$$A = \frac{X \cdot S \cdot \varphi_{ini} \cdot v}{10000 \cdot m \cdot V_m}; \tag{4}$$

where v – volumetric rate of the feeding alcohol-containing mixture (cm<sup>3</sup>/h); *m* is the sample weight of the catalyst (grams);  $V_m$  – molar volume (cm<sup>3</sup>/mmol); 10000 – is the coefficient that converts volume percentages into volume parts for X and S.

#### **Discussion of the results**

#### Characterization of the obtained samples

All obtained samples are single-phase. The samples  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{Li}_{1.5}\text{Zr}_{1.5}\text{In}_{0.5}(\text{PO}_4)_3$ ,  $\text{Li}_{0.5}\text{Zr}_{1.5}\text{Nb}_{0.5}(\text{PO}_4)_3$  and  $\text{Li}_{0.5}\text{Zr}_2\text{P}_{2.5}\text{Mo}_{0.5}\text{O}_{12}$  obtained by the Pechini method are monoclinic, the sample  $\text{HZr}_2(\text{PO}_4)_3$  obtained by hydrothermal synthesis is rhombohedral (Fig. 1). The X-Ray microanalysis data correspond to the expected composition within the error ranges. Refinement by Rietveld method gives satisfactory description of X-ray pattern of monoclinic lattice. The example of such description for  $\text{LiZr}_2(\text{PO}_4)_3$  with Bragg R-factor = 4.56 is given on Fig. 2.

Figure 1 is here

Figure 2 is here

X-ray pattern of  $\text{LiZr}_2(\text{PO}_4)_3$  obtained at high temperatures differ from those, obtained at room temperature. It's caused by phase transition from monoclinic structure into orthorhombic. This phase transition occurs in the temperature range 290 - 350°C (Fig. 3).

#### Figure 3 is here

According to the scanning electron microscopy all the obtained samples contain particles with the average size from 50 to 200 nm (Fig. 4).

The size of the CSR of all the samples obtained from XR-data, is somewhat smaller than the particle size estimated from the SEM data (Table 1), due to the agglomeration. All these samples have approximately the same specific surface area about 20 m<sup>2</sup>/g (Table 1).  $HZr_2(PO_4)_3$  obtained hydrothermally consists of particles whose shape is close to cubic with a clear facet (Fig. 4b).

Figure 4 is here

Table 1 is here

Infrared study of the prepared samples indicated vibration bands at ~ 1610, 1545 and 1450 cm<sup>-1</sup>, which are correspond to  $v_{8a} v(CC)$  Lewis,  $v_{19b} v(CN)$  Brønsted and  $v_{19b} v(CN)$  Lewis vibration bands [40] (Fig. 5). LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and Li<sub>1.5</sub>Zr<sub>1.5</sub>In<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> possess only Lewis acid sites, Li<sub>0.5</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>, Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub> and HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> showed both Lewis and Brønsted acid sites. In case of HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> the intensity of vibration bands is small, but this could be caused by lower specific surface area of this sample (10 m<sup>2</sup>/g vs 17-21 m<sup>2</sup>/g).

## Figure 5 is here

By measuring the shift of the 19b Lewis vibration band we can estimate the strength of the Lewis acid sites. It forms the following row:  $\text{LiZr}_2(\text{PO}_4)_3$  (1446 cm<sup>-1</sup>) <  $\text{Li}_{0.5}\text{Zr}_{1.5}\text{Nb}_{0.5}(\text{PO}_4)_3$  (1448 cm<sup>-1</sup>)  $\approx$   $\text{Li}_{0.5}\text{Zr}_2\text{P}_{2.5}\text{Mo}_{0.5}\text{O}_{12}$  (1448 cm<sup>-1</sup>)  $\approx$   $\text{HZr}_2(\text{PO}_4)_3$  (1448 cm<sup>-1</sup>) <  $\text{Li}_{1.5}\text{Zr}_{1.5}\text{In}_{0.5}(\text{PO}_4)_3$  (1451 cm<sup>-1</sup>). 19b Brønsted to 19b Lewis peak area ratio for  $\text{Li}_{0.5}\text{Zr}_{1.5}\text{Nb}_{0.5}(\text{PO}_4)_3$ ,  $\text{Li}_{0.5}\text{Zr}_2\text{P}_{2.5}\text{Mo}_{0.5}\text{O}_{12}$ ,  $\text{HZr}_2(\text{PO}_4)_3$  are following: 1:2.6, 1:6.7, 1:0.84 (In sample  $\text{HZr}_2(\text{PO}_4)_3$ , the  $v_{19b}$  v(CN) Brønsted line is very wide). The indium-doped sample has the stronger Lewis acid sites than the other samples and might be active in dehydrogenation processes.  $\text{HZr}_2(\text{PO}_4)_3$  has the lowest amount of acid sites but the Brønsted to Lewis peak area ratio for this sample is highest, so it might show activity in the dehydration processes.  $\text{Li}_{0.5}\text{Zr}_{1.5}\text{Nb}_{0.5}(\text{PO}_4)_3$  and  $\text{Li}_{0.5}\text{Zr}_2\text{P}_{2.5}\text{Mo}_{0.5}\text{O}_{12}$  might be active in both dehydrogenation and dehydration processes because of significant amount of Lewis and Brønsted acid sites, but for  $\text{Li}_{0.5}\text{Zr}_2\text{P}_{2.5}\text{Mo}_{0.5}\text{O}_{12}$  the Brønsted to Lewis

peak area ratio is the lowest, so the activity in dehydrogenation processes for this sample might be more pronounced.

#### **Catalytic properties**

All synthesized compounds showed activity in the alcohol's conversion (Fig. 6). In the case of ethanol conversion, the catalytic activities of all samples were really similar, only  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  has some advantages, the use of which allows to achieve the same conversion values at temperatures 30-50°C lower than for other catalysts. In methanol conversion the difference in activity is much distinctly.

 $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  catalyst has the highest activity in methanol conversion.  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  and  $HZr_2(PO_4)_3$  slightly inferior to  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ , whereas  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  and especially  $LiZr_2(PO_4)_3$  are significantly less active.

# Figure 6 is here

## Methanol conversion

Since the methanol molecule is fairly simple, its transformations can start with two main reactions:

$$2CH_{3}OH \leftrightarrow CH_{3}OCH_{3} + H_{2}O \qquad \Delta H^{0}_{298 \text{ K}} = -23.9 \text{ kJ/mole}$$
(5)  
$$CH_{3}OH \leftrightarrow CH_{2}O + H_{2} \qquad \Delta H^{0}298 \text{ }_{\text{K}} = 85.1 \text{ kJ/mole}$$
(6)

Comparing the thermodynamics of these processes, we can conclude that the most probable process at low temperatures is the dehydration of methanol with the formation of dimethyl ether. The dehydrogenation of methanol with the formation of formaldehyde also becomes possible at elevated temperatures (>500°C). Accordingly, the main product is dimethyl ether for all catalysts at low temperatures (Fig. 7). However, only in the case of  $HZr_2(PO_4)_3$ , the selectivity of dehydration process remains close to 100% in the entire temperature range (Fig. 7 e). The same high selectivity at lower temperatures is also characteristic for

Li<sub>0.5</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> and Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub> catalysts. Methanol conversion reaches values close to 82-85% (Fig. 6 a), which correspond to equilibrium yields and, therefore, are the highest for reaction (5). It should be noted that the same conversion values are also reached for  $HZr_2(PO_4)_3$ , for which this reaction dominates over the entire temperature range. However, above 420 and 350°C, significant amounts of methane and CO are formed on these catalysts (Fig. 7 c, d), and conversion reaches 100% for  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  and  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ . This corresponds to the fact that at high temperatures dehydrogenation processes take place, which become not thermodynamically banned.

#### Figure 7 is here

The most effective in dimethyl ether formation are catalysts with  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ ,  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  and  $HZr_2(PO_4)_3$  composition. The maximum productivity of this process was about 2.5 mmol/h\*g for  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  and  $HZr_2(PO_4)_3$  (Fig. 8).

## Figure 8 is here

The significant contribution is made by secondary reactions associated with the conversion of dimethyl ether for  $\text{LiZr}_2(\text{PO}_4)_3$  and  $\text{Li}_{1.5}\text{Zr}_{1.5}\text{In}_{0.5}(\text{PO}_4)_3$  even at low temperatures. These processes can proceed with the formation of formaldehyde, methane, hydrogen, carbon and carbon oxides (Fig. 7 a, b), for example, according to the following equations:

$$CH_3OCH_3 \leftrightarrow CH_4 + CO + H_2$$
  $\Delta H^0_{298 \text{ K}} = -1.3 \text{ kJ/mole}$  (7)

$$CH_3OCH_3 \leftrightarrow CH_4 + CH_2O$$
  $\Delta H^0_{298 \text{ K}} = -6,7 \text{ kJ/mole}$  (8)

$$CH_{3}OCH_{3} \leftrightarrow CH_{4} + C + H_{2}O \qquad \Delta H^{0}_{298 \text{ K}} = -132.6 \text{ kJ/mole}$$
(9)

The contribution of these processes is significant for such active catalysts as  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  and  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  at elevated temperatures. Methanol

conversion in these systems increases with temperature and approaches 100% (Fig. 7 c, d).

One could assume that the high activity of  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  and  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  is associated with the possibility of changing the degree of niobium and molybdenum oxidation. This effect should be less pronounced in the case of  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$ , what is actually observed in the experiment. In for  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ addition, reaction (5) is dominant even and  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  at low temperatures, which can occur, for example, due to proton binding by negatively charged lithium vacancies. These vacancies are formed by the intercalation of niobium and molybdenum cations having a higher charge in comparison with substituted zirconium and phosphorus. An alternative mechanism may be performed due to the adsorption of methanol molecules by these cations because of their lower coordination numbers in oxygen (6 and 4 respectively), which are far from limit [41]. In this case, the catalyst acts as a Lewis acid. In our opinion, this process is most probable.  $HZr_2(PO_4)_3$  is an essentially more active catalyst in comparison with  $LiZr_2(PO_4)_3$  (Fig. 6 a). The increased Brønsted acidity is the only difference (Fig. 5). At the same time, since the activity of  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  and  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  is even higher, it is precisely the Lewis acidity that is preferred for the dehydration reactions, the presence of which in samples doped with niobium is shown in [42]. Thus, it can be concluded that the main process in the first stage of dehydration is the adsorption of oxygen ions of methanol on polycharging cations having an unsaturated coordination.

It can also be noted that when methanol is converted on  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$ (Fig. 7 b) up to 34% of formaldehyde is formed according to the reaction (6). The activity of this catalyst in dehydration processes is significantly lower due to the Lewis acidity suppression when zirconium is replaced by an ion with a lower valence. Still lower activity in the dehydration of undoped  $\text{LiZr}_2(\text{PO}_4)_3$  (Fig. 6 a) seems to indicate that the reaction is possible, although less efficiently with basic catalysis.

The reactions of the alcohols conversion on these catalysts should not be considered as process for the hydrogen production. Its production is low and substantially inferior to those for the processes of steam reforming. The highest activity has  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  in the hydrogen formation by methanol conversion. But even for this catalyst the activity at such high temperature as 510°C reaches only 0.83 mmol/h\*g.

#### Ethanol conversion

More diverse products are characteristic for the ethyl alcohol conversion, during which the following reactions are possible:

$2C_{2}I_{15}OII - C_{2}I_{15}OC_{2}I_{15} + I_{12}O - \Delta I_{12}g_{8} - 24,4 \text{ KJ/IIIOIC} (1)$	$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$	$\Delta H^{0}_{298} = -24,4 \text{ kJ/mole}$	(10)
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$C_2H_5OH \rightarrow C_2H_4 + H_2O$	$\Delta H^{0}_{298} = +45,3 \text{ kJ/mole}$	(11)
$C_2H_5OH \rightarrow CH_3CHO + H_2$	$\Delta H^{0}_{298} = +68.8 \text{ kJ/mole}$	(12)

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \qquad \Delta H^0_{298} = +49.4 \text{ kJ/mole}$$
(13)

- $C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$   $\Delta H^0_{298} = +255,6 \text{ kJ/mole}$  (14)
- $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$   $\Delta H^0_{298} = +173,2 \text{ kJ/mole}$  (15)

It is noteworthy that, from the point of view of thermodynamics, all these processes can occur at relatively low temperatures, but the most possible process must be a dehydration which leads to the diethyl ether formation (10). Minor amounts of methane, carbon dioxide and carbon monoxide were also observed. In addition, the formation of heavier hydrocarbons is possible:

$$xC_2H_5OH \rightarrow yC_nH_m + xH_2O + H_2, n \ge 2$$
(16),

and products decomposition processes, accompanied by the catalyst coking, for example, according to the following reaction:

$$CH_3CHO \rightarrow 2C + H_2 + H_2O \quad \Delta H^0_{298} = -75.8 \text{ kJ/mole}$$
 (17)

The main products during the ethyl alcohol conversion were: diethyl ether, acetaldehyde, hydrogen, C<sub>2</sub>- and C<sub>4</sub>-hydrocarbons. The dehydration of ethanol with the formation of diethyl ether at low temperatures was the dominant process on  $LiZr_2(PO_4)_3$  and  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  catalysts (Fig. 9 a, c). The selectivity of this process reaches 90-91% at temperatures of about 300-330°C. The significant number of secondary processes take place on all catalysts at elevated temperatures.

#### Figure 9 is here

It is noteworthy that the heterovalent doping effect is most clearly manifested in the ethyl alcohol conversion. Thus, partial substitution of zirconium by indium or phosphorus for molybdenum significantly increases the dehydrogenating properties of the catalyst, and at low temperatures acetaldehyde formation predominates (Fig. 9 b, d). Obviously, in the case of  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ this is explained by the easier change of molybdenum degree of oxidation. Indium can also change its oxidation state on 1+, although this is less characteristic for it. The indium ion has a smaller positive charge compared to zirconium, so it will be negatively charged relative to the residual crystal structure. Therefore, such a defect will have tendency to adsorb of the alkyl side of the alcohol rather than it's hydroxyl group. This, in turn, should facilitate the processes, associated with abstraction of the proton and intensification of the dehydrogenation processes. At the same time, at elevated temperatures this process proceeds easily. In addition, in the case of indium, as noted above, the ability of the material to adsorb alcohols oxygen is suppressed, which complicates the dehydration processes course. It should be noted that in the case of  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  the deeper dehydration reaction becomes dominant at the temperatures above 390°C, which leads to the ethylene formation (reaction (11), Fig. 9 c). It is interesting that this process is also typical for  $HZr_2(PO_4)_3$ . In this case it is dominant for all temperatures (Fig. 9 d). Apparently, this is due to the high Brønsted acidity of this material.

Finally, it is worth noting that the possibility of obtaining  $C_4$ -hydrocarbons This attractive. process proceeds on  $LiZr_2(PO_4)_3$ seems very and  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ , and the selectivity in this case reaches 73% and 49%, respectively (Fig. 9 a, d). Even less selectivity - no more than 35% is typical for  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  (Fig. 9 b). Equation (16) shows that both dehydrogenation and dehydration should take place in the case of  $C_nH_m$  (n>2) formation. The relatively high activity of LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> suggests that zirconium itself can stimulate oxidationreduction transformations at elevated temperatures. The continuation of this transformations chain is the catalysts coking, which most actively occurs on  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  and  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$ , which leads to a decrease in the total selectivity (Fig. 9 b, d).

The  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  sample has the highest activity in hydrogen formation and this fact is in accordance with the assumption described above. It should be noted that the amount of hydrogen formed on it exceeds the amount of acetaldehyde formed by reaction (12) (Fig. 10). This may be explained by additional generation of hydrogen by secondary reactions, accompanied, as noted above, by catalyst coking.

#### Figure 10 is here

#### Conclusions

The synthesis of materials with the NASICON structure doped by heterovalent elements ((LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, Li<sub>1.5</sub>Zr<sub>1.5</sub>In<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>, Li<sub>0.5</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>, Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub>, HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>) were carried out by using Pechini and hydrothermal methods. The obtained samples were characterized by X-ray phase analysis, and transmission electron microscopy. The characteristic particle size of the obtained compounds was 50-300 nm. The specific surface area for Pechini samples (LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, Li<sub>1.5</sub>Zr<sub>1.5</sub>In<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>, Li<sub>0.5</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>, Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub>) was about 20 m<sup>2</sup>/g, and for the hydrothermal sample (HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>) was 10 m<sup>2</sup>/g.

All synthesized samples were catalytically active in the C1-C2 alcohols conversion. The main products in the methanol conversion were dimethyl ether, methane, formaldehyde, CO and hydrogen. For ethanol conversion were C2-C4 hydrocarbons, acetaldehyde, diethyl ether and hydrogen.

It should be noted the high activity and selectivity of a number of catalysts in the dimethyl and diethyl ethers formation, as well as the ethylene formation. The high selectivity for C4 hydrocarbons is achieved for  $\text{LiZr}_2(\text{PO}_4)_3$  and  $\text{Li}_{0.5}\text{Zr}_2\text{P}_{2.5}\text{Mo}_{0.5}\text{O}_{12}$  at elevated temperatures, reaching 64 and 49% respectively.

It is shown that the main directions of the process of methanol and ethanol conversion is determined by thermodynamic factors, as well as the heterovalent doping and ability of the doped polyvalent elements to change its degree of oxidation and their adsorption of alcohols through the oxygen atom with the Lewis acidity manifestation.

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Fig. 1. X-ray patterns of samples obtained by the hydrothermal (3) and Pechini (4-7) methods. Line-diagram for monoclinic  $\text{LiZr}_2(\text{PO}_4)_3$  Card No70-5819 (1), line-diagram for rhombohedral HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> Card No38-0004 (2), X-ray patterns for HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (3), LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (4), Li<sub>1.5</sub>Zr<sub>1.5</sub>In<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> (5), Li<sub>0.5</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> (6), Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub> (7).

Fig. 2. Rietveld method Refinement of the Pechini synthesized  $\text{LiZr}_2(\text{PO}_4)_3$  X-ray pattern.

Fig. 3. X-ray patterns obtained at different temperatures for  $\text{LiZr}_2(\text{PO}_4)_3$  sample.

Fig. 4. Typical micrographs of samples, obtained by Pechini (a) and hydrothermal (b) methods.

Fig. 5. FTIR spectra of pyridine on the LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (1), Li<sub>1.5</sub>Zr<sub>1.5</sub>In<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> (2), Li<sub>0.5</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> (3), Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub> (4), HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (5) samples. Positions of the  $v_{8a}$  v(CC) Lewis,  $v_{19b}$  v(CN) Brønsted and  $v_{19b}$  v(CN) Lewis vibration bands are presented (a). Enlarged spectra for 3-5 samples (b).

Fig. 6. The conversion temperature dependence of methanol (a) and ethanol (b) for  $LiZr_2(PO_4)_3$  (1),  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  (2),  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  (3),  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  (4),  $HZr_2(PO_4)_3$  (5).

Fig. 7. Temperature dependencies of methanol conversion selectivity for  $LiZr_2(PO_4)_3$  (a),  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  (b),  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  (c),  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  (d),  $HZr_2(PO_4)_3$  (e) with the formation of CH<sub>4</sub>, CO, CH<sub>2</sub>O and CH<sub>3</sub>OCH<sub>3</sub>.

Fig. 8. The temperature dependence of dimethyl ether productivity for  $LiZr_2(PO_4)_3(1)$ ,  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  (2),  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  (3),  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  (4),  $HZr_2(PO_4)_3$  (5).

Fig. 9. The selectivity temperature dependence during the ethanol conversion for  $LiZr_2(PO_4)_3$  (a),  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  (b),  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  (c),  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  (d),  $HZr_2(PO_4)_3$  (e) with the formation of C<sub>2</sub>- hydrocarbons, C<sub>3</sub>- hydrocarbons, C<sub>4</sub>- hydrocarbons, CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>.

Fig. 10. The temperature dependence of the hydrogen productivity for  $LiZr_2(PO_4)_3(1)$ ,  $Li_{1.5}Zr_{1.5}In_{0.5}(PO_4)_3$  (2),  $Li_{0.5}Zr_{1.5}Nb_{0.5}(PO_4)_3$  (3),  $Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$  (4),  $HZr_2(PO_4)_3$  (5).

Composition	Specific surface area,	Particle	e size
	m²/g	SEM, nm	CSR, nm
LiZr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	22 ± 1	138	56
Li <sub>1.5</sub> Zr <sub>1.5</sub> In <sub>0.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	20 ± 1	204	93
Li <sub>0.5</sub> Zr <sub>1.5</sub> Nb <sub>0.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	21 ± 1	149	67
$Li_{0.5}Zr_2P_{2.5}Mo_{0.5}O_{12}$	$17 \pm 1$	261	46
$HZr_2(PO_4)_3$	10 ± 1	215	>200













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Double zirconium phosphates with NASICON structure are catalysts of alcohols conversion. Zr substitution by In and P by Mo result in the increase in dehydrogenation activity. Zr substitution by Nb result in the increase in dehydration activity. HZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and Li<sub>0.5</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> have the highest activity in ethers formation. LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> and Li<sub>0.5</sub>Zr<sub>2</sub>P<sub>2.5</sub>Mo<sub>0.5</sub>O<sub>12</sub> are most active in C4-hydrocarbons formation.