Catalytic Activity of $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ -Based NASICON-Type Materials for Ethanol Conversion Reactions

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Abstract— $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ (x = 0, 0.05, 0.1) materials have been prepared by solid-state reactions and characterized by X-ray diffraction, low-temperature nitrogen adsorption measurements, and scanning electron microscopy. The materials consist of NASICON-type lithium hafnium double phosphates with a hexagonal structure. Milling in a planetary mill has been found to increase the specific surface area of the $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ materials by almost one order of magnitude (from 1.5 to 13 m²/g in the case of $\text{Li}\text{Hf}_2(\text{PO}_4)_3$). The materials with a larger surface area exhibit catalytic activity for ethanol dehydration reactions and are less active for ethanol dehydrogenation. Ethanol conversion predominantly yields diethyl ether at low temperatures and ethylene at higher temperatures. The diethyl ether selectivity for the catalytic processes reaches 85% at 350°C, with 60% conversion, and the ethylene selectivity from 4 to 8% and leads to the formation of C₄ hydrocarbons as reaction products. C₄ selectivity reaches 15 and 17% in the case of the $\text{Li}_{1.05}\text{Hf}_{1.95}\text{In}_{0.05}(\text{PO}_4)_3$ and $\text{Li}_{1.1}\text{Hf}_{1.9}\text{In}_{0.1}(\text{PO}_4)_3$ materials, respectively (420°C, 97 and 92% conversion, respectively).

Keywords: lithium hafnium double phosphate, NASICON, doping, indium, mechanochemical activation, catalysis, ethanol conversion

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INTRODUCTION

NASICON-type compounds constitute a large class of materials with the general formula $A_x B_2(PO_4)_3$, where A = H, Li, Na, K, H₃O, or NH₄ and B = In, Sc, Fe, Zr, Ti, Hf, Sn, Ge, etc. [1–4]. The alternating voids in their framework crystal structure ensure fast ion transport, which makes these materials potentially attractive solid electrolytes with considerable lithium-ion, sodium-ion, or proton conductivity [1-3, 5, 15]. The NASICON-type phosphates containing polyvalent cations capable of changing their oxidation state (Ti, Fe, and V) can be used as electrode materials [4, 16]. Other advantages of the NASICONtype materials are their high chemical and thermal stability, good ion-exchange properties [17], and catalytic activity for alcohol dehydrogenation and dehydration processes [18-35].

The catalytic conversion of alcohols is of great practical interest because it offers the possibility of obtaining important products, such as ethers, aldehydes, ketones, hydrocarbons, and hydrogen, by environmentally safe processes [18–42]. Catalysts for such processes typically have the form of metals on oxide

supports [39–45]. Another possible example of catalysts is NASICON-type mixed phosphates [18–35]. For example, it is well documented that $CuZr_2(PO_4)_3$, $Cu_{0.5}B_2(PO_4)_3$ (B = Ti, Zr, Sn), $AgB_2(PO_4)_3$ (B = Zr, Hf), $Na_{1-x}Cu_xZr_2(PO_4)_3$, and $Na_{1+x}Fe_xZr_{2-x}(PO_4)_3$ are active catalysts for the conversion of the butyl alcohols and isopropanol [31–34]. Note that ethanol is one of the most promising alcohols as a biomass decomposition product [2, 3]. Depending on the catalyst used and process conditions, ethanol conversion may follow different reaction paths, leading to the formation of ethylene, diethyl ether, acetaldehyde, hydrogen, water, carbon monoxide, ethyl acetate, or a mixture of products [29, 35–41].

In the NASICON-type phosphates, iso- or heterovalent substitutions on both the cation and anion sites are possible [1-3]. Such substitutions have a significant effect on both the ionic conductivity and composition of the products of alcohol conversion catalyzed by NASICON-type phosphates [27, 29, 36]. For example, indium- and molybdenum-doped LiZr₂(PO₄)₃-based materials offer high catalytic activity for dehydrogenation processes, whereas niobiumdoped materials exhibit higher activity for dehydration processes [29]. The NASICON-type materials with the general formula $(NH_4)_{1-x}H_xHf_2(PO_4)_3$ (x = 0-1) exhibit catalytic activity for ethanol dehydration reactions. Ethanol conversion predominantly yields diethyl ether at low temperatures and ethylene at higher temperatures. The composition of ethanol dehydrogenation and dehydration reaction products was shown to depend significantly on which singly

charged cation $(H^+ \text{ or } NH_4^+)$ enters into the composition of the hafnium double phosphate [36].

In this paper, we report the synthesis of $\text{Li}_{1+x}\text{Hf}_{2-x}$ -In_x(PO₄)₃ NASICON-type phosphates, their phase composition, and their catalytic activity for the ethanol conversion process. In addition, we examine the effect of mechanochemical processing on the particle size and catalytic activity of the materials.

EXPERIMENTAL

 $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_{x}(\text{PO}_{4})_{3}$ (x = 0, 0.05, 0.1) materials were prepared by solid-state reactions according to the following scheme:

$$6(NH_{4})_{2}HPO_{4} + (4 - 2x)HfO_{2} + xIn_{2}O_{3} + (1 + x)Li_{2}CO_{3}$$
(1)
$$\rightarrow 2Li_{1+x}Hf_{2-x}In_{x}(PO_{4})_{3}.$$

The starting chemicals used were $(NH_4)_2HPO_4$ (Roth, >97%), HfO₂ (Aldrich, 98%), In₂O₃ (analytical grade), and Li₂CO₃ (Merck, >99%). Stoichiometric ratios of the starting materials were mixed, thoroughly ground in a mortar, and fired at a temperature of 600°C for 6 h in platinum crucibles. Next, the resultant mixture was reground and pressed into pellets to improve chemical interaction between particles. The pellets were packed with powder of similar composition, containing 20% excess lithium carbonate, to prevent the volatilization of lithium compounds from the main material at high temperatures and annealed at 1000°C for 24 h.

The phase composition of the samples thus prepared was determined by X-ray diffraction on a Rigaku D/MAX 2200 diffractometer (Cu K_{α} radiation). For data processing and qualitative analysis of X-ray diffraction patterns, we used the Rigaku Application Data Processing and FullProf Suite software packages. The crystallite size was assessed from X-ray diffraction line broadening using the Scherrer formula:

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

where *d* is the crystallite size, λ is the X-ray wavelength used, θ is the diffraction angle, k = 0.9 is the Scherrer constant, *B* is the experimentally determined full width at half maximum (FWHM) of the line, and *b* is the FWHM of a line of a standard. As a standard for evaluating the instrumental broadening, we used LaB₆ powder (Standard Reference Material 660a).

INORGANIC MATERIALS Vol. 54 No. 7 2018

The mechanochemical activation of the samples was carried out in a Fritsch Pulverisette 7 planetary mill using agate bowls with an inner volume of 45 mL, each containing ten agate balls 10 mm in diameter. The powder load was 750 mg. To each vial, 8 mL of ethanol was added. The samples were milled for 24 h at a rotation speed of 400 rpm. Every 3 min, the milling process was interrupted for 2 min.

The specific surface area of the samples was determined by BET measurements with a Micromeritics ASAP 2020 analyzer. The samples were degassed at a temperature of 350°C for 1 h. Analyses were carried out at relative pressures (p/p_0) in the range from 0.01 to 0.99.

The samples were examined by scanning electron microscopy (SEM) on a Carl Zeiss NVision 40 equipped with an elemental analysis accessory. The accelerating voltage was 1 kV.

Catalytic properties were studied in a flow-type quartz reactor under flowing helium or argon with ethanol additions. The reaction products were analyzed on a Crystallux 4000 M chromatograph equipped with a thermal conductivity detector and HayeSep T 60/80 mesh (2 m, 150°C, 30 mL/min, He), SKT-6 (2 m, 150°C, 30 mL/min, He), and Mole Sieve 5 A (2 m, 25°C, 30 mL/min, Ar) columns. In our experiments, a weighed amount (0.3 g) of a catalyst was mixed with ground quartz ($d = 315-400 \,\mu\text{m}$) and placed in a reactor 6 mm in inner diameter so that the catalyst layer was 17 cm in thickness. To ensure an appropriate ethanol vapor concentration, the carrier gas was passed at a volumetric flow rate of 20 mL/min through a bubbler containing ethanol and thermostated at 11°C.

Conversion and selectivity were evaluated using the following relations:

$$X = \frac{\phi_0 - \phi_1}{\phi_0} \times 100\%,$$
 (3)

$$S = \frac{\varphi_i}{\varphi_0 - \varphi_1} \times 100\%,\tag{4}$$

where φ_0 and φ_1 are the initial and final volume fractions of the alcohol, respectively, and φ_i is the fraction of the alcohol consumed for the formation of product *i*.

RESULTS AND DISCUSSION

According to X-ray diffraction data, the synthesized lithium hafnium double phosphate LiHf₂(PO₄)₃ is single-phase and has a hexagonal NASICONrelated structure (PDF-2, card no. 53-0569). The X-ray diffraction patterns of the Li_{1+x}Hf_{2-x}In_x(PO₄)₃ (x = 0.05, 0.1) doped materials also contain only reflections from a hexagonal phase, which are slightly shifted (Fig. 1). In addition, near $2\theta \sim 27.3^{\circ}$, 45.3° , and 53.7° the X-ray diffraction patterns contain reflections from germanium, which was used as a standard (card no. 04-0545). The unit-cell parameters of



Fig. 1. X-ray diffraction patterns of the $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ samples with different degrees of indium substitution for hafnium.

the phosphates increase with an increase in the degree of indium substitution for hafnium (Table 1), which points to the formation of solid solutions. The observed increase in unit-cell volume can be accounted for by the larger ionic radius of In^{3+} in comparison with Hf^{4+} (0.80 and 0.71 Å, respectively [46]).

The mechanochemical processing of the samples in the planetary mill led to X-ray diffraction line broadening (Fig. 2). The crystallite sizes evaluated from linewidths are presented in Table 2. For example, the crystallite size of the as-prepared $\text{LiHf}_2(\text{PO}_4)_3$, Li_{1.05}Hf_{1.95}In_{0.05}(PO₄)₃, and Li_{1.1}Hf_{1.9}In_{0.1}(PO₄)₃ materials was 62, 41, and 42 nm, respectively. Mechanical processing reduced the crystallite size by a factor of 1.3–1.5, to 41, 32, and 33 nm, respectively (Table 2). X-ray diffraction line broadening can be due to both a small particle size and increased defect density in the structure [47, 48]. Electron microscopy data confirm that milling reduced the average particle size (Fig. 3). The as-prepared samples had the form of polydisperse crystalline materials ranging in particle size from 1 to 10 µm (Figs. 3a, 3b). After mechanical processing, the particles ranged in size from 30 nm to 1 μ m (Figs. 3c–3f). These values considerably exceed the crystallite size, suggesting that the samples consist of agglomerates of individual crystallites.

According to low-temperature nitrogen adsorption experiments, the unmilled $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ sam-



Fig. 2. Portions of the X-ray diffraction patterns of the $\text{LiHf}_2(\text{PO}_4)_3$ samples (1) before and (2) after milling.

ples had an extremely small surface area: $1-2 \text{ m}^2/\text{g}$. Milling increased the specific surface area S to $12-15 \text{ m}^2/\text{g}$ (Table 2).

Materials with a larger surface area are more active catalysts for ethanol conversion [21]. In view of this, we used ground materials in our catalytic ethanol conversion experiments. Those materials exhibited catalytic activity for ethanol dehydration and dehydrogenation reactions (Fig. 4). The main observed transformations can be represented by the following reaction schemes:

$$2C_{2}H_{5}OH \rightarrow C_{2}H_{5}OC_{2}H_{5} + H_{2}O,$$

$$\Delta H_{298}^{\circ} = -88.48 \text{ kJ/mol};$$

$$C_{2}H_{5}OH \rightarrow CH_{3}CHO + H_{2},$$

$$\Delta H_{298}^{\circ} = +17.36 \text{ kJ/mol};$$

$$C_{2}H_{5}OH \rightarrow C_{2}H_{4} + H_{2}O,$$

$$\Delta H_{298}^{\circ} = +28.99 \text{ kJ/mol}.$$
(5)
(7)

The major reaction products are ethylene, diethyl ether, C_4 hydrocarbons, acetaldehyde, and hydrogen. We also observed the formation of a small amount (<0.3%) of C_3 hydrocarbons.

The onset temperature for noticeable ethanol conversion (\geq 5%) and the composition of the product

Table 1. Unit-cell parameters of the samples with the general formula $Li_{1+x}Hf_{2-x}In_x(PO_4)_3$

Sample	<i>a</i> , Å	c, Å	$V_{\text{cell}}, \text{\AA}^3$
LiHf ₂ (PO ₄) ₃	8.825 (2)	22.007 (3)	1484.4(9)
Li _{1.05} Hf _{1.95} In _{0.05} (PO ₄) ₃	8.827(2)	22.014(1)	1485.4(7)
$Li_{1.1}Hf_{1.9}In_{0.1}(PO_4)_3$	8.829(1)	22.016(1)	1486.6(4)

INORGANIC MATERIALS Vol. 54 No. 7 2018

Sample	Crystallite size, nm	Particle size (SEM), µm	$S, m^2/g$
$LiHf_2(PO_4)_3$ (as-prepared)	62	1-10	1.5
LiHf ₂ (PO ₄) ₃	41	0.05-1	13
Li _{1.05} Hf _{1.95} In _{0.05} (PO ₄) ₃	32	0.03-1	12
$Li_{1.1}Hf_{1.9}In_{0.1}(PO_4)_3$	33	0.03-1	15

Table 2. Particle size and specific surface area of the $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ samples before and after milling



 $\textbf{Fig. 3. SEM} \text{ images of the as-prepared LiH} f_2(PO_4)_3 (a, b) \text{ and the milled samples: LiH} f_2(PO_4)_3 (c, d) \text{ and Li}_{1.1} H f_{1.9} In_{0.1} (PO_4)_3 (e, f).$

INORGANIC MATERIALS Vol. 54 No. 7 2018





Fig. 4. Temperature dependences of selectivity for the formation of ethylene, acetaldehyde, diethyl ether, and C₄ hydrocarbons in the presence of the (a) $\text{LiHf}_2(\text{PO}_4)_3$, (b) $Li_{1.05}Hf_{1.95}In_{0.05}(PO_4)_3$, and (c) $Li_{1.1}Hf_{1.9}In_{0.1}(PO_4)_3$ materials after milling and ethanol conversion as a function of temperature.

mixture at low temperatures (270–350°C) are similar for all of the materials studied (Fig. 4). At low temperatures, the most thermodynamically favorable process if dehydration to diethyl ether according to scheme (5). The selectivity for this reaction product is 80-85%, with 60% conversion at 350°C (Fig. 4).

On heating, the Gibbs energy of reactions (6) and (7)becomes negative and the reactions become feasible. With increasing temperature, dehydration to ethylene according to scheme (7) becomes the main ethanol conversion path on all catalysts, in spite of the poorer thermodynamics of this process. Ethylene selectivity reaches 96, 88, and 85% for the $\text{LiHf}_2(\text{PO}_4)_3$, Li_{1.05}Hf_{1.95}In_{0.05}(PO₄)₃, and Li_{1.1}Hf_{1.9}In_{0.1}(PO₄)₃ samples at 510, 450, and 450°C, respectively (at 100% conversion).

The dehydrogenation process (6) on these catalysts is less active and has a higher rate in the case of the indiumdoped materials. Acetaldehyde selectivity reaches 4% for LiHf₂(PO₄)₃ (510°C, 100% conversion) and 8% for $Li_{1.05}Hf_{1.95}In_{0.05}(PO_4)_3$ and $Li_{1.1}Hf_{1.9}In_{0.1}(PO_4)_3$ (420°C; 97 and 92% conversion, respectively).

in the addition, case In of the $Li_{1.05}Hf_{1.95}In_{0.05}(PO_4)_3$ and $Li_{1.1}Hf_{1.9}In_{0.1}(PO_4)_3$ samples we observed the release of C₄ hydrocarbons. The formation of C₄ hydrocarbons was found to pass through a maximum at 420°C. C_4 selectivity reaches 15 and 17% in the case of the $Li_{1.05}Hf_{1.95}In_{0.05}(PO_4)_3$ and $Li_{1,1}Hf_{1,9}In_{0,1}(PO_4)_3$ samples, respectively (420°C). Thus, the addition of a small amount of indium makes it possible to obtain C4 hydrocarbons, which were not detected in the case of $\text{LiHf}_2(\text{PO}_4)_3$ (Fig. 4).

Moreover, indium doping reduces the catalytic transformation temperature. Ethanol conversion reaches 100% at 510°C for LiHf₂(PO₄)₃ and at 450°C for $Li_{1+x}Hf_{2-x}In_x(PO_4)_3$. Comparison of the specific surface areas of the catalysts (Table 2), which differ very little, with catalysis results leads us to conclude that, in the indium-doped materials, the number and activity of centers responsible for the formation of C₄ hydrocarbons and acetaldehyde are higher. This changes the reaction path and the activity of the catalysts at high temperatures. The materials studied here were shown to be capable of stable operation for 24 h.

CONCLUSIONS

We have synthesized $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ (x = 0, 0.05, 0.1) NASICON-type materials, which crystallize in hexagonal symmetry. Milling in a planetary mill has been found to reduce the size of primary particles of $\text{Li}_{1+x}\text{Hf}_{2-x}\text{In}_x(\text{PO}_4)_3$ by a factor of 1.3–1.5 and increase the specific surface area of the materials by almost one order of magnitude (from 1.5 to $13 \text{ m}^2/\text{g}$ in the case of $LiHf_2(PO_4)_3$). Our results on the catalytic properties of the synthesized materials in ethanol conversion reactions demonstrate that they exhibit catalytic activity for ethanol dehydration reactions and are less active for ethanol dehydrogenation. Ethanol conversion predominantly yields diethyl ether at low temperatures (85% at 60% conversion at 350°C on $LiHf_2(PO_4)_3$) and ethylene at higher temperatures (96% at 100% conversion at 510°C on $\text{LiHf}_2(\text{PO}_4)_3$).

INORGANIC MATERIALS 2018 Vol. 54 No. 7

Indium doping reduces the 100% ethanol conversion temperature by 60°C and raises the yield of acetaldehyde and C₄ hydrocarbons at high temperatures. C₄ selectivity reaches 15 and 17% in the case of the $Li_{1.05}Hf_{1.95}In_{0.05}(PO_4)_3$ and $Li_{1.1}Hf_{1.9}In_{0.1}(PO_4)_3$ materials, respectively (420°C, 97 and 92% conversion, respectively).

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INORGANIC MATERIALS Vol. 54 No. 7 2018

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