

Solid electrolytes with anionic and cationic conductivity as catalysts for isobutanol conversion

I. I. Mikhalenko, A. I. Pylinina

Department of Physical and Colloidal Chemistry, Peoples Friendship University of Russia (RUDN University), Moscow, e-mail: mikhalenko_ii@pfur.ru

The perovskite's like complex oxides with electron-anionic conductivity (BIMEVOX family) and complex Na(Cs)-Zr-phosphates (NASICON like family solid solutions NZP or CZP) are of a special interest for catalytic application. The ternary bismuth vanadates with general formula $\text{Bi}_4\text{V}_{2-2x}\text{M}_{2x}\text{O}_{11-8x}$ with V^{+3} ions, replaced by $\text{M} = \text{Cu}^{+2}, \text{Fe}^{+3}, \text{Zr}^{+4}$, exist in several polymorphic modifications (α , or monoclinic; β , or orthorhombic and γ , or tetragonal). Ternary phosphates $\text{Cs}_{1-2x}\text{M}_x\text{Zr}_2(\text{PO}_4)_3$ with $\text{M} = \text{Ni}^{+2}, \text{Co}^{+2}$, partially replaced conducting Cs^+ ion, or double $\text{CsZr}_2(\text{PO}_4)_3$ and $\text{M}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ were studied in our work too. The general structures of solids solutions for two types of ionic conductors are shown in Fig. 1, a, b [1, 2].

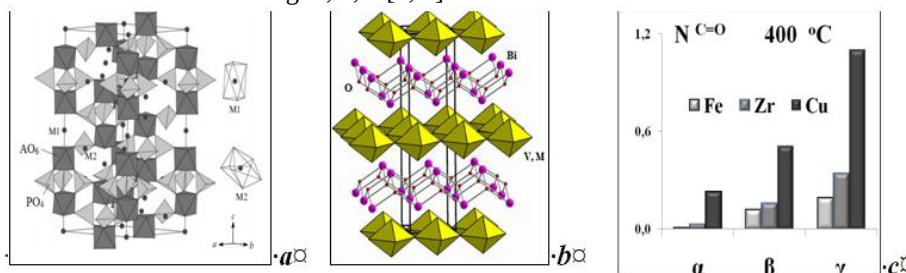


Fig. 1. The frameworks of NZP (a), BIMEVOX (b) and the yield of *i*-butanol ($N, \mu\text{M}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) at 400 °C for BICUXOX, BIFEVOX, BIZRVOX in α -, β - and γ -phase

Na-Zr-phosphates and BIMEVOX were studied earlier as catalysts for conversion of C3–C4 aliphatic alcohols in the temperature range 200–430 °C [3, 4]. With increasing M content in $\text{Bi}_4\text{V}_{2-2x}\text{M}_{2x}\text{O}_{11-8x}$, where $x = 0\div0.16$, the total degree of isobutanol's conversion changes negligibly for α -phase, reaching $\alpha_x \sim 10\%$, while it is in 5–6 times higher for the β - and γ -phases (more than 50 %). Only for γ -phase of most active BICUVOX catalysts the selectivity for olefin $S^{\text{C}=\text{C}}$ at high temperatures is about 20 % vs. $S^{\text{C}=\text{C}} \sim 10\%$ for $\text{Bi}_4\text{V}_2\text{O}_{11-8}$. Fig. 1, c demonstrates the rise in the dehydrogenation activity of BIMEVOX catalysts in the series of $\alpha \rightarrow \beta \rightarrow \gamma$ and $\text{Fe} \rightarrow \text{Zr} \rightarrow \text{Cu}$. Great differences in the catalytic activity of M in the BIMEVOX samples of α - and β , γ -phases are explained by the different states of oxygen ions in the ion pair $\text{M}^{\text{Z}+}-\text{O}^{2-}$ considered as catalytic active site of aldehyde formation. Highly conducting γ -phase corresponds the smallest values of apparent activation energy for dehydrogenation reaction $E_a^{\text{C}=\text{O}}$ and activation energy of

isobutanol formation correlates linearly with activation energy of conductivity. The phase changes do not affect the value of isobutene formation $E_a^{C=C}$.

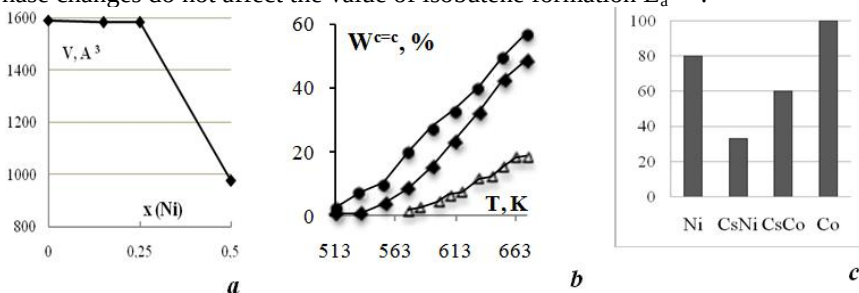


Fig. 2 The elementary cell volume of $\text{Cs}_{(1-2x)}\text{Ni}_x\text{Zr}_2(\text{PO}_4)_3$ framework – *a*; the temperature dependence of i -butanol conversion to i -butene for Cs-Ni-ZP with $x = 0.5$ (Δ), 0.25 ($\bullet$), 0.15 ($\blacklozenge$) – *b*; the comparison of apparent activation energy of i -butene formation over catalysts $\text{Cs}_{(1-2x)}\text{M}_x\text{Zr}_2(\text{PO}_4)_3$ – *c*

Cationic conductors with general formula $\text{Cs}_{(1-2x)}\text{M}_x\text{Zr}_2(\text{PO}_4)_3$ were obtained by sol-gel method and characterized by XRD, ESCA, SEM, BET. The ratio of P/Co and P/Ni in the surface layer indicates the lack of phosphate groups on the surface, but M/Zr and M/Cs have more twice elevated ratio comparing with stoichiometric ratio. The bond energy values for cobalt (+2), nickel (+2), cesium (+1) and zirconium (+4) remained the same in all zirconium orthophosphates.

The cell volume of double Zr-phosphates with Ni and Co was 2 times less than ternary ZP (Fig. 2, *a*). This is the major reason of olefin formation decrease (Fig. 2, *b*) that connects with the augmentation of apparent activation energy for dehydration reaction (Fig. 2, *c*). That's why we observed the synergism for pairs of conduction cations, such as CsCo and CsNi , in catalytic transformation of i -butanol on CZP.

So, catalytic activity of solid electrolytes with different type of conductivity depends on the nature of conducting material, its crystal structure, composition of the complex substance with active sites including the charge carrier in anion-deficient tetragonal phase of perovskites or Cs, Ni, Co in NASICON-like structure. The possible mechanisms of two paths for i -butanol conversions on complex active sites will be analyzed.

References

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