

# The effect of Co(II) cations and their position in $\text{NaZr}_2(\text{PO}_4)_3$ lattice on catalytic conversion of 2-propanol

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Complex phosphates are solid electrolytes of the Na-Super-Ionic CONductor (NASICON) [1]. The basic phosphate is sodium-zirconium phosphate  $\text{NaZr}_2(\text{PO}_4)_3$  (NZP). The composition of NZP can be varied by full or partial replacing of sodium (*a*) or zirconium (*b*) ions [2] without substantial changes in the crystal structure (Figure). The introduction of various ions into NZP offers promise for use it as active and selective catalysts with a micro porous structure formed by ionic conductivity channels. The purpose of this work is to study the role of  $\text{Co}^{+2}$  doping ion position in cationic (*a*) or in anionic (*b*) parts of complex phosphate on its catalytic activity in dehydrogenation reaction of 2-propanol. Note that in case *a*  $\text{Co}^{+2}$  ions can undergo the transfer from M1 to M2 at a temperature  $T^*$ , that influences the  $\text{Co}^{+2}$  surrounding.

Catalysts were prepared by the sol-gel method. The X-ray data substantiated the structure of NZP. The surface layer composition of NZP was characterized by X-ray photoelectron spectroscopy (XPS). The conversion of alcohol was performed in continuous-flow reactor at atmospheric pressure and 200–400 °C. The reaction mixture was analyzed chromatographically with a flame-ionization detector. In table  $N^{C=O}$  is the yield of aldehyde in  $\mu\text{mol}/(\text{g}\cdot\text{h})$ .

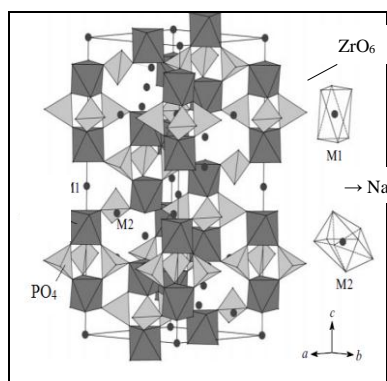


Fig.  $\text{NaZr}_2(\text{PO}_4)_3$  crystal structure

Table. The yield and selectivity of aldehyde			
		<i>a</i>	<i>b</i>
		$\text{Na}_{0.5}\text{Co}_{0.25}\text{Zr}_2(\text{PO}_4)_3$	$\text{Na}_3\text{ZrCo}(\text{PO}_4)_3$
Ratio Na : Co		2:1	3:1
Ratio Co : Zr		1:8	1:1
$N^{C=O}$	1) 300 °C	37	58
	2) 350 °C	181	135
$S^{C=O}\%$	350 °C	100	90
$E_a^{C=O}$ , kJ/mol		1) 93 ; 2) 60	11
$\ln N_0^{C=O}$		1) 16.2 ; 2) 9.7	2.0

We see that the content and the position *a* or *b* of the ion-dopant has little effect on the yield  $N^{C=O}$  when the selectivity does not change sufficiently  $S^{C=O}$  (Table). In a series of *a* cobalt cation transition is observed at  $T^* = 330^\circ\text{C}$ . The dehydrogenation reaction senses the change in the cobalt ions' position, due to the transition of some cobalt ions from the M1 to M2 position leading to a new catalytically active center (M1–M2) on which interaction with the OH group of alcohol occurs. These centers have higher bond energy with alcohol than the adsorption on the M1 center at low temperatures, so the value of apparent activation energy  $E_a^{C=O}$  is lowering in 1.5 times. The pre-factor  $\ln N_0$  is also decreasing.

## References

1. K. Ivanov-Shits, I. V. Murin, *Solid State Ionics* (2000), 1
2. E.I. Povarova, A.I. Pylinina, I.I. Mikhaleenko. *Russian Journal of Physical Chemistry A.* (2012) 86 (6): 935