Reactivity of $ZrOCl_2 \cdot 8H_2O$ and its application for the synthesis of NASICON framework phosphates

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This contribution is devoted to the reactivity of zirconium oxychloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, and its application for the synthesis of a series of framework NASICON phosphates $Li_{1+x}Cr_xZr_{2-x}(PO_4)_3$. In particular, thermal transformation of individual $ZrOCl_2 \cdot 8H_2O$ and its complex interaction with phosphate, carbonate and oxide mixtures will be discussed.

Experimental

Thermal transformation of the individual components and the reaction mixtures was investigated using TG-DTA analysis (20-1200 °C). Evolution of the phase composition during heating was analysed using powder XRD analysis. Combination of both techniques helped to understand the mechanism of the formation of the solid solutions and the chemical processes taking place in the mixtures during heating.

Results

Typically, decomposition of individual $ZrOCl_2 \cdot 8H_2O$ starts at 70 °C with elimination of eight molecules of its crystalline water, while above 230 °C it undergoes thermal hydrolysis leading to elimination of HCl and formation of ZrO_2. The temperature range and kinetics of the mentioned processes highly depends on the experimental conditions (i.e. atm. pressure, humidity).

Thermal behaviour of $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_2HPO_4$ mixture changes dramatically in comparison with the typical behaviour of the individual compounds. The typical features of thermal behaviour of this mixture are the following: dehydration of $ZrOCl_2 \cdot 8H_2O$ (endothermic effect at 160 °C, step-like mass loss between 70-230 °C) accompanied with interaction between $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_2HPO_4$ in molar ratio 1:2 leading to the formation of NH_4Cl, $NH_4H_2PO_4$ and ZrO_2; release of ammonia and dehydration of $NH_4H_2PO_4$ starts above 200 °C (gradual mass loss); sublimation and decomposition of NH_4Cl (endothermic effect at 350 °C, step-like mass loss between 310 and 410 °C).

When additional carbonate and oxide are included in the mixture composition, its thermal behaviour becomes even more complex and at the same time it still highly depends on the ratio between the $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_2HPO_4$ components. Accordingly, with increase of substitution degree x in the $(0.5+x/2)Li_2CO_3$-$(2-x)ZrOCl_2 \cdot 8H_2O$-$(x/2)Cr_2O_3$-$3(NH_4)_2HPO_4$ mixture from 0 to 2, the mechanism of the formation of the solid solutions changes dramatically. In particular, the mixtures with x < 2, undergo similar interaction as two-component $ZrOCl_2 \cdot 8H_2O$-$2(NH_4)_2HPO_4$ mixture leading to the formation of NH_4Cl, $NH_4H_2PO_4$ and ZrO_2 at low temperatures (< 160 °C), which involves lesser and lesser part of the mixture with increase of x and the corresponding decrease in $ZrOCl_2 \cdot 8H_2O$ content. However, with increase of x and the corresponding decrease of $ZrOCl_2 \cdot 8H_2O$ content in the mixture, the indicated process becomes less dominant. In other hand, unreacted amount of $(NH_4)_2HPO_4$ is increased and the corresponding effect of elimination of its ammonia becomes more and more prominent. The mixture with x = 2 can be characterised with typical behaviour of the mixtures of $(NH_4)_2HPO_4$ with oxides or carbonates. Thus, it can be concluded, when both $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_2HPO_4$ are present in the reaction mixture, the interaction between these two components became the dominant feature of the thermal transformation, while other processes play the minor role.

In most cases, calcination at 1200 °C during 6 h was sufficient for the formation of solid solutions; formation of $LiZr_2(PO_4)_3$ required calcination at 1300 °C, $Li_3Cr_2(PO_4)_3$ - 1150 °C.

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