Ammonium-exchanged phase of γ-titanium phosphate: Hydrothermal synthesis, crystal structure and thermal behavior

Jorge GARCIA-GLEZ[1], Zakariae AMGHOUZ[2], Sergei A. KHAINAKOV[2], Aranzazu ESPINA[2], Camino TROBAJO[1]

[1]Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo-CINN, 33006 Oviedo, Spain

[2]Servicios Científico-Técnicos, Universidad de Oviedo, 33006 Oviedo, Spain

Metal salts of phosphoric acid have been known for over a century. However, research into layered tetravalent metal phosphates and their derivatives only began in the late 1950's due to the recognition of the application of some of these salts as cation exchangers in radioactive waste streams. Because of their low solubility, tetravalent metal phosphates were only available as amorphous gels. The knowledge of the structure of the first layered crystalline compound, α-$Zr(HPO_4)_2 \cdot H_2O$, provided the possibility of relating the properties of these metal acid salts to their crystalline structure and the many potential applications in the fields of ion exchange, intercalation, catalysis and ionic conductivity prompted the comprehensive study of these class of compounds. Later, the existence of a new layered structure type, γ-$Zr(H_2PO_4)(PO_4) \cdot 2H_2O$ (γ-ZrP), was reported (although the formula was originally given as γ-$Zr(HPO_4)_2 \cdot 2H_2O$, ^{31}P MAS NMR studies showed that γ-ZrP contains tertiary phosphate groups and dihydrogen phosphate groups in equal amounts). Finally, the structure of γ-ZrP was solved from powder X-ray diffraction, and only three years ago novel structural features of its titanium based compound, γ-$Ti(H_2PO_4)(PO_4) \cdot 2H_2O$ (γ-TiP), was published [1].

In previous contributions [2] we have described the behavior of the γ-TiP as ion-exchanger. This material has very high affinity to both cesium [3] and ammonium cations [4], with the highest potential for use in the decontamination of radioactive metal wastes and renal dialysis treatment. Surprisingly, the crystal structure of γ-TiP ion-exchanged phases is unknown, and only the anhydrous monoammonium salt of γ-ZrP was solved up to now [5].

This contribution report the hydrothermal synthesis and crystal structure of the ammonium-exchanged γ-titanium phosphate phase, γ-$Ti(NH_4HPO_4)(PO_4)$, with highlight to its thermal data using a combination of scientific methods that have never been applied jointly to explore and clarify the thermal decomposition behaviour of this material.

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