COPRECIPITATION OF MIXED VANADIUM AND TITANIUM PHOSPHATES FROM ALKOXIDES

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Abstract Coprecipitation of mixed vanadium and titanium phosphates has been performed by adding anhydrous phosphoric acid solution (1M) to a solution mixture of vanadium n-propoxide ($\text{VO}(\text{OPr}^n)_3$) and titanium n-propoxide ($\text{Ti}(\text{OPr}^n)_4$). In protic solvents, such as parent alcohol, the coprecipitation is accompanied with a loss of vanadium species. So, tetrahydrofuran (THF) was used instead of alcohol. It allows obtaining stoichiometric precipitation and adjusting the kinetic precipitations of vanadium phosphate and titanium phosphate. Such synthesis leads to the preparation of metastable homogeneous materials which can not be obtained via classical methods (mixture of salts or powders). When $\text{V}_0.5\text{Ti}_0.5\text{P}_1$ composition is heat treated at 700°C , we obtain a V_2O_5 glass dispersed over TiP_2O_7 phase.

INTRODUCTION

The sol-gel synthesis of mixed oxide materials provides a new approach to the preparation of glasses and ceramics.¹ The first sol-gel synthesis of an inorganic compound has been performed by Ebelman,² when he observed that tetraethylorthosilicate (TEOS) slowly transformed into glassy silica in the presence of moisture. In the last decades, this process has been proved to be a very effective and very versatile method to prepare glasses and ceramics from molecular precursors (metal salts or alkoxides).

Concerning metal organic precursors (alkoxides), by far silicon alkoxides have been the most investigated ones. However, glasses and ceramics are not limited to silica derived materials ; other molecular precursors, such as transition metal alkoxides, are also of interest in ceramic and glassy preparation.

In our previous works^{3, 4}, we have developed an easy method to prepare crystalline $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with different morphologies and specific areas by reacting phosphoric acid with vanadium alkoxides ($\text{VO}(\text{OR})_3$; $\text{R} = \text{Pr}^n, \text{Pr}^i, \text{Am}^t$). In a similar way, we have tried to carry out coprecipitation of mixed vanadium and titanium alkoxides on the one hand and phosphoric acid on the other hand. This allows obtaining a mixture of vanadium and titanium at a molecular level, or, in the favourable case to obtain metastable phases. In protic solvents, such as alcohol, vanadium phosphates precipitation is slow.⁴ So, aprotic solvents, such as THF (tetrahydrofuran), have been used allowing us to adjust kinetic precipitations of vanadium phosphates and titanium phosphates.

EXPERIMENTAL PROCEDURE

Vanadium alkoxide ($\text{VO}(\text{OPr}^n)_3$) has been synthesized according to the method described by Cartan et al.⁵:

The alkoxide is then purified by vacuum distillation.

Titanium alkoxide ($\text{Ti}(\text{OPr}^n)_4$) and anhydrous phosphoric acid (H_3PO_4) are commercial (Fluca).

The alkoxides ($\text{VO}(\text{OR})_3$ and $\text{Ti}(\text{OR})_4$) and phosphoric acid are separately dissolved in the solvent to the concentration of 1M. Then, the phosphoric acid solution is added to the mixture of vanadium and titanium alkoxides solution. Reactions were studied on the line $\text{V}_x\text{Ti}_{1-x}\text{P1}$ of the phase diagram:

In alcohol, as solvent, precipitation is always accompanied with a loss of vanadium species. But in THF, precipitation is instantaneous and chemical analysis indicates that total precipitation of V, Ti and P occurred for all x.

RESULTS AND DISCUSSION

In preceding works,⁶ a ^{31}P MAS-NMR and X-ray studies have been carried out over the so prepared powders. Homogeneous materials are obtained when $x \geq 0.5$. When these samples are heat treated at 700°C , phase segregation occurs, except $\text{V}0.5\text{Ti}0.5\text{P}1$, which seems to be a pure TiP_2O_7 phase, even though chemical analysis indicates the presence of vanadium. In the following, we will try to determine the form in which vanadium is present in $\text{V}0.5\text{Ti}0.5\text{P}1$.

Thermal analysis

$\text{V}1\text{Ti}0\text{P}1$ composition

Two endothermic phenomena are observed around 120°C and 160°C (Fig. 1a) with a weight loss of 11%. They correspond to the departure of water molecules. An exothermic weight loss, due to combustion of residual organic groups, appears at 220°C . According to this diagram, x-ray and Infrared analysis this precipitate seems to be $\text{VOPO}_4 \cdot x\text{H}_2\text{O} \cdot y\text{ROH}$.

$\text{V}0.5\text{Ti}0.5\text{P}1$ composition

In this case, the departure of water molecules is observed at 130°C (Fig. 1b) followed by a slight exothermic loss corresponding to residual organic groups combustion. We note also an important exothermic transformation, centred on 650°C . This exothermic peak is accompanied with a very little weight loss which seems to correspond to a final condensation of hydroxyl groups.

$\text{V}0\text{Ti}1\text{P}1$ composition

The DT and TG curves (Fig. 1c) are similar to those of $\text{V}0.5\text{Ti}0.5\text{P}1$, nevertheless there is a large exothermic peak at about 500°C without weight

FIGURE 1 Thermogravimetry of powders coprecipitated from alkoxides :
a- V1Ti0P1, b- V0.5Ti0.5P1, c- V0Ti1P1.

loss assigned to the increase of phosphorus connectivity. By referring to X-ray analysis, the peak at 820°C is attributed to crystallisation and phase segregation into TiO_2 and TiP_2O_7 .

Powder diffraction analysis

According to thermogravimetry curves (Fig. 1), we have heat treated V0.5Ti0.5P1 sample at different temperatures under oxygen flow. As shown in Figure 2, when temperature calcination is below 500°C, amorphous materials are obtained. Crystallisation occurred between 500°C and 700°C with an acceleration between 650°C and 700°C associated to the large exothermic peak (Fig. 1b). At high temperature treatment, no significant modifications are obtained. Since no crystalline vanadium containing phase is observed, we suppose that it might be located as an amorphous phase (vanadium oxide or vanadium phosphate oxide).

FIGURE 2 X-ray diffraction patterns of V_{0.5}Ti_{0.5}P₁ heat treated at different temperatures during one hour under oxygen flow.

Indeed, such homogeneity can not be obtained from a mixture of powders precipitated and heat treated at different temperatures. In Figure 3, we have reported the X-ray diffraction pattern of V_{0.5}Ti_{0.5}P₁ heat treated at 700°C during two hours under oxygen flow ; precipitated from alkoxides (Fig. 3a) and from a mixture of V₁Ti₀P₁ and V₀Ti₁P₁ powders (Fig. 3b). It is obvious that from alkoxides an homogeneous sample is obtained while from precipitated powders a mixture of several phases is formed : TiO₂, α-VOPO₄, β-VOPO₄ and TiP₂O₇.

³¹P MAS-NMR analysis

Similarly, we have carried out some ³¹P Nuclear Magnetic Resonance experiments. At room temperature (Fig. 4a), the spectrum shows a very large signal, centred at -6 ppm, which can be assigned to an amorphous vanadium and titanium phosphate. Indeed, amorphous titanium phosphate exhibit a broad peak at -10 ppm (for the ratio P/Ti = 1) and a sharp peak at -21ppm (for

FIGURE 3 X-ray diffraction patterns of $V_{0.5}Ti_{0.5}P_1$ powders heat treated at $700^{\circ}C$ during two hours under oxygen flow : a- coprecipitation of alkoxides, b- mixture of precipitated powders.

the ratio $P/Ti = 2$).⁷ The signal at 6 ppm corresponds to $VOPO_4 \cdot 2H_2O$.³ Its intensity shows that it corresponds only to a minor phase. After heat treatment at $350^{\circ}C$ under oxygen flow, a single peak is observed at -25 ppm indicating an homogeneous material (Fig. 4b). At $550^{\circ}C$ (Fig. 4c), three peaks are present ; the first at -11.4 ppm ascribed to β - $VOPO_4$,⁴ the second at -29 ppm assigned to an amorphous vanadium and titanium phosphate, while the third at -45 ppm can be attributed, according to X-ray diffractogram (Fig. 2),⁶ to TiP_2O_7 phase. Thus the temperature around $500^{\circ}C$ is the temperature at which phase partitioning occurs. The thermal treatments at $600^{\circ}C$ and $850^{\circ}C$ lead to a series of peaks around -44 ppm due to TiP_2O_7 phase with a good crystallinity.

FIGURE 4 ^{31}P solid state MAS-NMR of $\text{V}_{0.5}\text{Ti}_{0.5}\text{P}_1$ heat treated at different temperatures for one hour under oxygen flow (chemical shift is given relative to 85% H_3PO_4 solution). Rotation bands caused by magic angle spinning are labelled with a *.

The ^{31}P MAS-NMR experiments corroborate the results obtained via thermogravimetry and X-ray studies. They indicate also that vanadium is located as an amorphous oxide or as a glass containing low quantity of

phosphorus. This has also been confirmed by ^{51}V MAS-NMR experiments. Indeed, it is well known that V_2O_5 gives glasses in the presence of P_2O_5 .⁸ Another confirmation is supplied by thermogravimetric analysis performed on the $\text{V}_0.5\text{Ti}_0.5\text{P}_1$ sample heat treated at 700°C under oxygen. It shows clearly an endothermic peak, without weight loss, at 600°C due to V_2O_5 melting point (Fig. 5).

FIGURE 5 Thermogravimetry of $\text{V}_0.5\text{Ti}_0.5\text{P}_1$ heat treated at 700°C for one hour under oxygen flow.

SUMMARY

In the present paper, we have shown that molecular precursors such as $\text{VO}(\text{OR})_3$ and $\text{Ti}(\text{OR})_4$ can be used to prepare homogeneous materials. Such synthesis can not be performed via classical reactions. These materials are metastable and segregate at 500°C . Nevertheless, $\text{V}_0.5\text{Ti}_0.5\text{P}_1$ material heat treated at $600\text{--}700^\circ\text{C}$ leads to TiP_2O_7 phase on which V_2O_5 is well dispersed as an amorphous compound. V_2O_5 is well known as a catalyst. So, catalytic properties of a such supported V_2O_5 will be undertaken. In recent works, interesting results have been obtained from VOPO_4 catalyst prepared via sol-gel method.⁹

Also, to prepare more homogeneous materials we think that using heterometal alkoxides, such as $V_nTi_mO_r(OR)_s$ will be a good alternate.

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