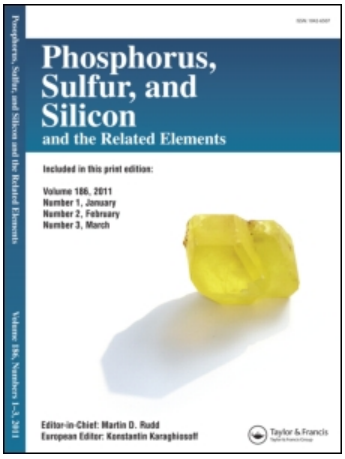

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ALUMINUM AND TITANIUM IMIDODIPHOSPHATES AS SINGLE PRECURSOR MOLECULES TO ALUMINUM AND TITANIUM PHOSPHATE MATERIALS

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ALUMINUM AND TITANIUM IMIDODIPHOSPHATES AS SINGLE PRECURSOR MOLECULES TO ALUMINUM AND TITANIUM PHOSPHATE MATERIALS

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The aluminum and titanium imidodiphosphates compounds respectively **1** and **2** are efficient single-source precursors to homogeneous aluminum and titanium phosphates materials. The conversion occurs pyrolytically at high temperature giving the corresponding compounds. Differential thermal and thermogravimetric analyses, ^{31}P and ^{27}Al MAS NMR, as well as vibrational spectroscopies were used to characterize the final materials. In the case of the aluminum compound **1** it was found that the ^{27}Al MAS NMR signal representative of the octahedral aluminum observed in the material obtained at 900 °C was transformed to a signal characteristic of a tetrahedrally aluminum by increasing the temperature to 1200 °C. This was confirmed by ^{31}P MAS NMR and XPS studies. The thermal evolution of **2** was studied by using Raman spectroscopy. The conversion of the phosphate material to TiO_2 in the rutile phase after a thermal treatment at 1400 °C during 3 hours was observed. The synthetic route to the phosphate materials described here could represent an alternative way to the sol-gel process and may offer certain advantages.

Keywords: Aluminum and Titanium imidodiphosphates; High-temperature phase transformations; ^{27}Al and ^{31}P MAS NMR; Raman; XPS

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INTRODUCTION

The chemistry connected with cyclic, acyclic and polymeric molecules containing the isoelectronic phosphazene -N= $P(R)_2$-[1] and siloxane -$OSi(R)_2$- groups is very extensive. The beginning of the phosphazene chemistry can be traced back to 1834 with the study by Liebig of the reaction of phosphorus pentachloride with gaseous ammonia, then modified by other authors by using ammonium chloride instead of NH_3[2–3]. This reaction which is still used on both academic and industrial laboratories, leads to cyclic and linear monomers or oligomers depending on the experimental conditions[4].

The linear chlorinated polymer $(NPCl_2)_n$ can be obtained – by bulk or solution thermal polymerization of the hexachlorocyclotriphosphazene $(NPCl_2)_3$ – by reaction of PCl_3 and NH_3 in the presence of gaseous hydrochloric acid[4] – and by bulk or solution polycondensation of the linear monomers Cl_3P=N-$POCl_2$[5] and Cl_3P=N-$SiMe_3$[6]. The substitution in these polymers of the chlorine atoms by alkoxy, phenoxy and especially by fluorine containing groups, leads to materials with a great deal of properties and potential applications as rigid plastics, elastomers, extruded fibers or thin films for examples[7].

Likewise a broad class of siloxane materials exists. They are generally obtained by hydrolysis of chlorosilanes synthesized according to the Rochow process that starts from elemental silicon and RCl. The controlled hydrolysis of dichlorosilanes R_2SiCl_2 can also yield cyclic derivatives $(R_2SiO)_{1-6}$. Polysiloxanes have a broad range of applications as fluids, greases, resins, elastomers or emulsions[8].

If numerous derivatives both of the phosphazenes and the siloxanes have been prepared over these past 50 years, on the other hand, scarce are the transition metal containing phosphazene and siloxane ring systems. Few years ago, Roesky and al. have found different methods to substitute one of the phosphorus atoms in hexachlorocyclotriphosphazene by a transition metal, and some of the obtained compounds were used as molecular precursors for polymeric materials[9]. Their studies have been extended to the synthesis of several cycloheterosiloxanes derivatives[10]. In the same field, Roesky and Don Tilley recently reported the synthesis of several molecular and soluble titanium silicates and titanium phosphates, which could be used as precursors to solid – state materials and as models to zeolites in terms of their structure, properties and catalytic activity[11–14]. We have

been also interested in: - the preparation and study of titanium halogen eight- membered ring precursors to homogeneous titanium-silica materials [15], -and according to the study carried out in our laboratory, connected with the preparation of polydichlorophosphazene by polycondensation of $Cl_3P{=}N\text{-}P(O)Cl_2$ with elimination of $P(O)Cl_3$[5], in the synthesis of metal containing systems susceptible to give rise to the same elimination[16].

Therefore, one of the objectives of this work was to study the thermal and chemical behavior of titanium and aluminum tetrachloroimidodiphosphate systems previously synthesized[16]. Indeed, these last could lead to materials similar to the titanium and aluminum phosphates which exhibit useful and interesting properties for applications in so far as ionic exchangers, ionic conductors, or materials with non linear optical properties[17- 20].

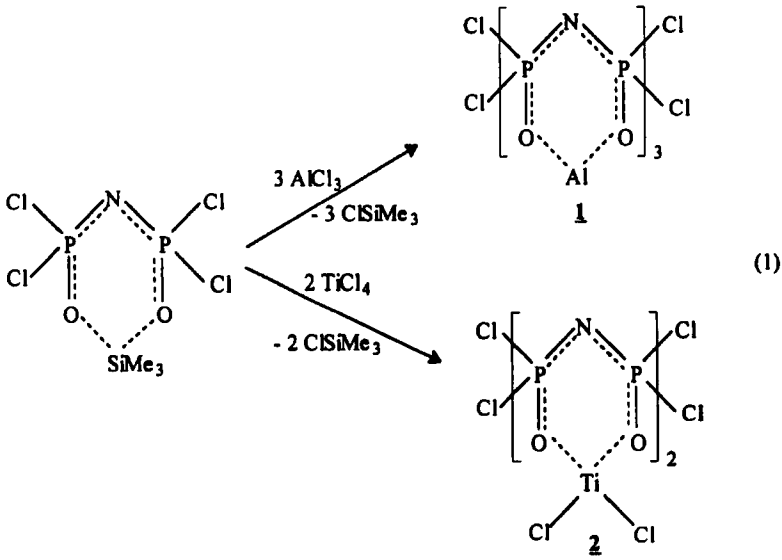
In this paper we give the results of differential thermal, thermogravimetric, NMR, Raman and XPS analyses carried out on these new compounds.

EXPERIMENTAL PROCEDURES

Materials

Aluminum **1** and titanium **2** imidodiphosphates were synthesized by reaction of N-trimethylsilyltetrachloroimidodiphosphate $Me_3SiN[P(O)Cl_2]_2$ with $AlCl_3$ and $TiCl_4$, respectively, in methylene chloride according to a procedure previously described[16]. The N-trimethylsilylated compound was first obtained from the reaction between the sodium salt of $HN[P(O)Cl_2]_2$ and Me_3SiCl[16]. By the use of this ligand, aluminum and titanium derivatives **1** and **2**respectively were obtained according to the reaction (1):

1 and **2** are colorless or light yellow solids whose solubility is only good in DMF. They are characterized in ^{31}P NMR spectroscopy by a singlet at $\delta = -18.4$ ppm indicating the equivalence of the two phosphorus atoms, and in IR spectroscopy by a broad intense band between 1340 and 1350 cm^{-1}attributed to the P=N stretching vibration modes. In the two cases the experimental and simulated molecular peaks in the mass spectrum are in good agreement.



(1)

Methods

The thermal behavior of the different compounds has been investigated by using several complementary techniques:

- Simultaneous TG – DTA experiments were performed in air in platinum crucibles with a Setaram TG 92/1600 Instrument using a 10 °C. min^{-1} heating-cooling rate.
- Raman spectra were recorded using a DILOR LABRAM multi-channel Raman microspectrometer. The 632.8 nm radiation from an helium neon laser was used for excitation. The spectral resolution was 8 cm^{-1} and the band positions were accurate to ± 1 cm^{-1}. The Raman microspectrometer used allowed us to analyse very small amounts of sample. More particularly, using a long working distance microscope objective, we were able to record directly through the glass wall the Raman spectra of micro-crystals stuck on the inner wall of the small sealed Pyrex tubes containing the samples.
- The NMR measurements were carried on a MSL-300 Bruker Spectrometer. The ^{27} Al NMR spectrum was recorded at 78.2 MHz and a magnetic field strength of 7.0 T in combination with a magnetic angle

spinning technique using a spinning rate of 3.5 kHz. In order to obtain an optimal signal-to-noise ratio, 5 μs delay time and 500 ms recycle times were used. Pulse length was 0.8 μs and pulse angle was 14.4°. Chemical shifts are expressed in ppm relative to solid $AlCl_3.6H_2O$. Peak areas are precise to ± 10% of each peak intensity.

The ^{31}P spectrum was collected at 121.4 MHz and a magnetic field strength of 7.0 T. Pulse of 4.0 μs with 5 s recycle times were sufficient to cause no changes in the relative peak intensities. The spinning speed used was 3.5 kHz. The ^{31}P chemical shifts are given with respect to 85% H_3PO_4 aqueous solution.

- XPS analysis allowed the determination of the elemental composition of the first surface atomic layers up to a depth < 10 nm and the identification of surface species. The analyses were performed using an ESCALAB 220X spectrometer (VG Scientific). The monochromatized Al source ($h\gamma$ = 1486.6 eV) was used for excitation at low power to give a 500 μm × ray spot diameter on the sample surface. The analyzer was operated with a constant pass energy (CAE = 30 eV) using the electromagnetic mode for the lens. Charge compensation was achieved by means of a low kinetic energy (10 eV) electrons flux. Binding energies shifts were compensated by reference to the C1s line at 285 eV for adventitious carbon. The powder samples were pressed on indium foil and covered with a 2 mm diameter metallic diaphragm grounded to the spectrometer. During analysis the vacuum level was about 5.10^{-8} Pa. The peak fitting and relative atomic concentrations were performed using the VG eclipse software.

RESULTS AND DISCUSSION

The thermal behavior of the synthesized precursors **1** and **2**, was investigated by thermogravimetric (TGA) and differential thermal (DTA) analyses in simultaneous mode. The corresponding curves are reported in figure 1.

In case of **1** (Fig. 1a), The TG curve shows that the loss of mass takes place in a continuous way and that it is impossible to detect temperature zones where a stable compound is obtained. Nevertheless, the DTA curve shows that the degradation process is not constant, two endothermic peaks

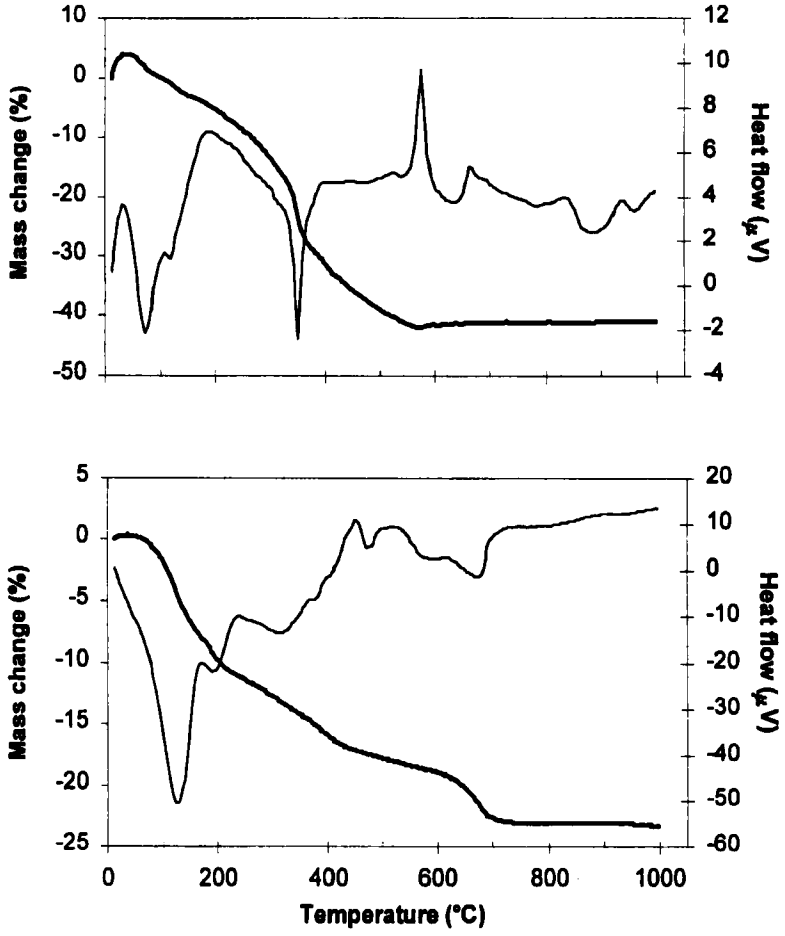


FIGURE 1 (a) TG/DTA curves for compound $Al[N(P(O)Cl_2)_2]_3$ **1**, (b) TG/DTA curves for compound $TiCl_2[N(P(O)Cl_2)_2]_2$ **2**

in the low temperature range (80- 400 °C) and an exothermic peak at higher temperature (590 °C) being observed. At 600 °C, the amount of residue, which is stable up to 1000 °C, is approximately 55 % of the original mass.

In the TG curve of the titanium derivative **2** (Fig. 1b) three degradation zones can be observed, between 50 and 200 °C, 200 and 400 °C, and

finally between 600 and 700 °C. A residue also stable up to 1000 °C is obtained at 700 °C. Its amount is higher (75 % of its original mass) than for **1**.

In the two cases, the first mass loss observed at a temperature lower than 200 °C, could be attributed to a partial hydrolysis of both compounds with elimination of HCl. The elimination of $POCl_3$ which generally begins around 300°C, was confirmed by the ^{31}P NMR spectrum of the volatile phase obtained by thermal degradation of **1** and **2** under vacuum. The DTA curve of compound **2** shows that the thermal decomposition process is more complicated at temperatures higher than 500 °C since several bands are observed in the sample, indicating the presence of at least the same number of steps of the decomposition process. The condensation is essentially complete at 700 °C for titanium and 600 °C for aluminum compounds.

The different thermal degradation stages and their domains of temperatures being known, we tried to isolate the intermediate phases. The purpose was to identify the phosphorus derivatives involved in the condensation process, and to see how the coordination of titanium and aluminum varied according to the temperature. Thus, masses of about 1 g of titanium and aluminum derivatives were treated at 300, 600, 900, 1200 °C during 3 hours in a tubular oven under air for both compounds.

^{31}P and ^{27}Al MAS NMR

On account of the insolubility and the amorphous character of the obtained residues, the number of techniques allowing their characterization was weak. Solid state nuclear magnetic resonance (NMR) which is one of these few techniques can give many informations. Particularly ^{31}P NMR spectroscopy is useful and permits the quantification of the relative amounts of Q^n phosphorus species, $PO_{4-n}(OP)_n$, since in favorable cases resonances due to each of these species can be resolved in the magic angle spinning (MAS) spectra. The ^{31}P MAS-NMR spectra obtained from the residues isolated at 300 and 600 °C, are characterized by the appearance of a multitude of signals in the wide range of chemical shifts between $\delta = 20$ and $\delta = 0$ ppm, with a relatively weak resolution. These signals can be attributed to a mixture of the phosphorus entities of type PO_4 (20 ppm), PO_3N (10 ppm) and PO_2N_2 (0 ppm)[21].

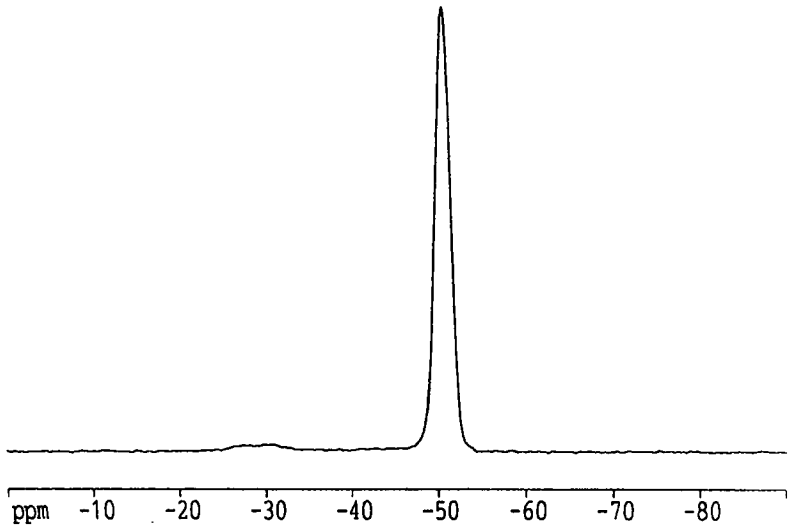


FIGURE 2 ^{31}P MAS- NMR spectrum of the residue of compound **1** after thermal treatment at 900 °C

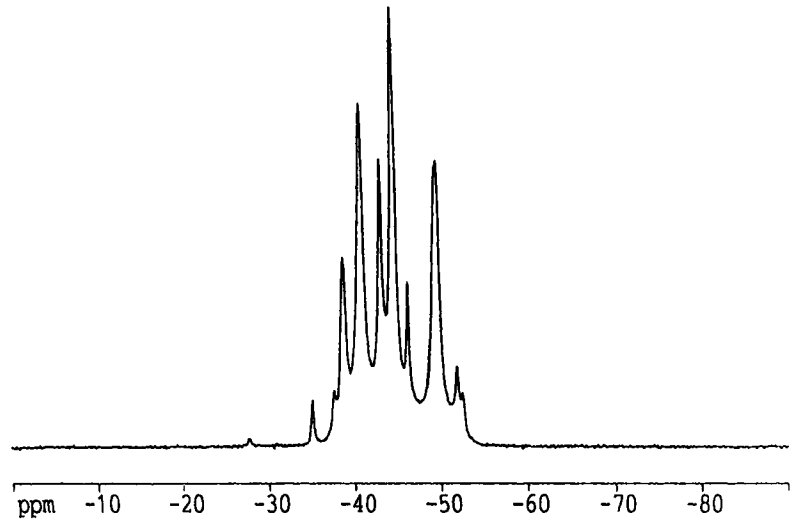


FIGURE 3 ^{31}P MAS- NMR spectrum of the residue of compound **2** after thermal treatment at 900 °C

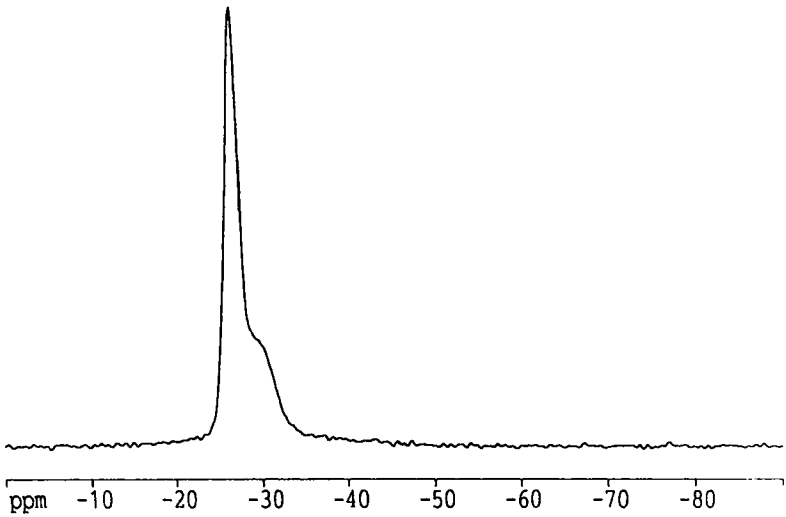


FIGURE 4 ^{31}P MAS- NMR spectrum of the residue of compound **1** after thermal treatment at 1200 °C

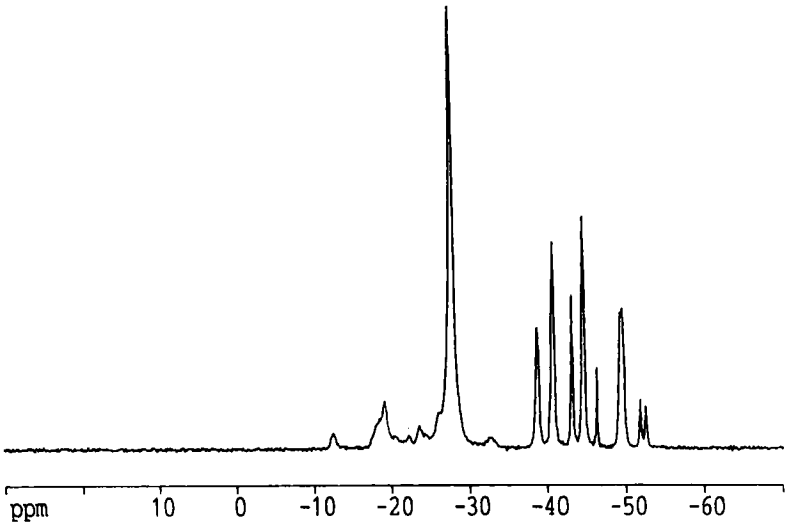


FIGURE 5 ^{31}P MAS- NMR spectrum of the residue of compound **2** after thermal treatment at 1200 °C

The spectrum obtained for the aluminum derivative **1** treated at 900 °C is more simple. It shows only a unique and sharp signal at $\delta = -50$ ppm indicating one type of phosphorus site in the residue (Fig. 2). According to the literature, this signal was assigned to condensed PO_4 groups connected to aluminum through one or more P-O-Al bonds. Indeed, previous studies have reported for these groups ^{31}P chemical shifts in the region from $\delta = -30$ to $\delta = -53$ ppm [22]. For example, a ^{31}P chemical shift of $\delta = -47{,}6$ ppm was given in the case of a P-Si gel heated at 700 °C and containing $P(OSi^{IV})(OSi^{VI})_3$ units[23]. On the other hand, the ^{31}P MAS-NMR spectrum of the titanium derivative residue isolated at the same temperature presents several signals in the same domain of chemical shifts probably due to the different environment of phosphorus nuclei in the residue (Fig. 3). In both cases the appearance of these signals, in the weak fields area is in good agreement with an homogeneous distribution of the phosphorus species essentially as phosphate entities and with the disappearance of the P-N bond in the material isolated at this temperature.

The most striking feature of the NMR spectra of the aluminum and titanium samples treated at 1200°C is the appearance of a new ^{31}P resonance line at δ around −27 ppm (Fig. 4) and (Fig 5) respectively. From consideration of the chemical shift alone this lowest frequency resonance could be due in the case of aluminum derivative to the condensed aluminum phosphate $AlPO_4$ in which the tetrahedral phosphorus is bonded to four aluminums via oxygen bridges $P(OAl)_4$, Q_4^0 sites[24].

These assignment are in good agreement with the ^{27}Al MAS-NMR study carried out on aluminum derivative **1**. Indeed the spectrum of the residue treated at 900 °C shows a sharp resonance line at $\delta = -21$ ppm which can be attributed to the octahedral aluminum that is AlO_6 units[25] (Fig. 6), and the one of the residue treated at 1200 °C, a peak at $\delta = 41$ ppm assigned to aluminum in a tetrahedral environment, in which aluminum is covalently bound to four phosphorus atoms via oxygen's bridges, in agreement with the presence of structural units AlO_4[26] (Fig 7). The assignment of these bands has recently been discussed by Hartman et al.[27].

Considering the phosphorus chemical shifts for the framework $NaTi_2(PO_4)_3$ titanium phosphate ($\delta = -27$ppm)[28]and for the anhydrous $Ti_2O(PO_4)_2$sample ($\delta = -19$ and -27 ppm) [29], the new NMR signal at $\delta = -27$ ppm in the titanium derivative treated at 1200 °C was also assigned to condensed PO_4 groups in titanium phosphates materials.

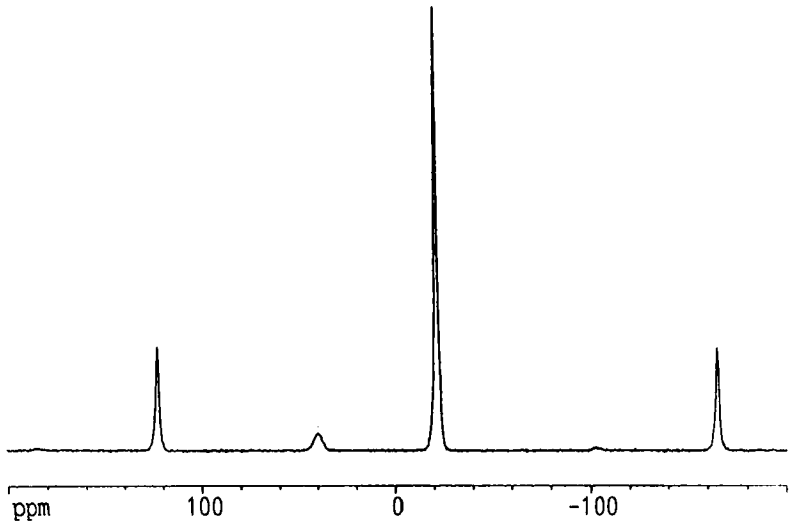


FIGURE 6 ^{27}Al MAS- NMR spectrum of the residue of compound **1** after thermal treatment at 900 °C

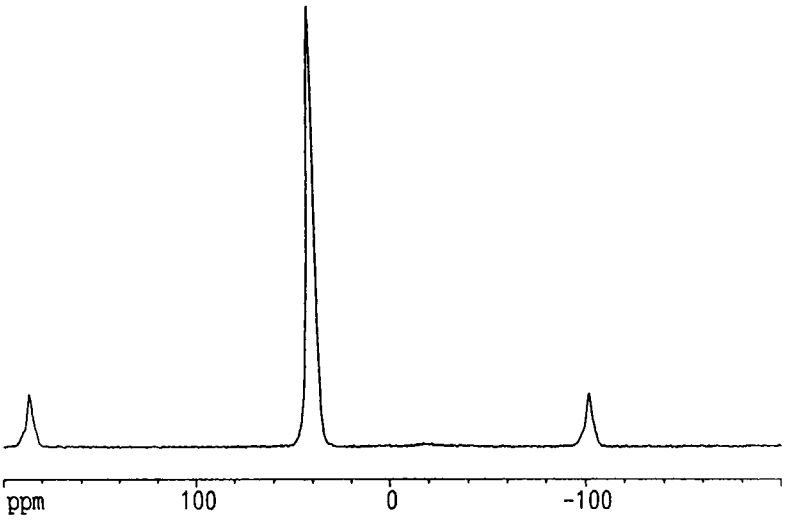


FIGURE 7 ^{27}Al MAS- NMR spectrum of the residue of compound **1** after thermal treatment at 1200°C

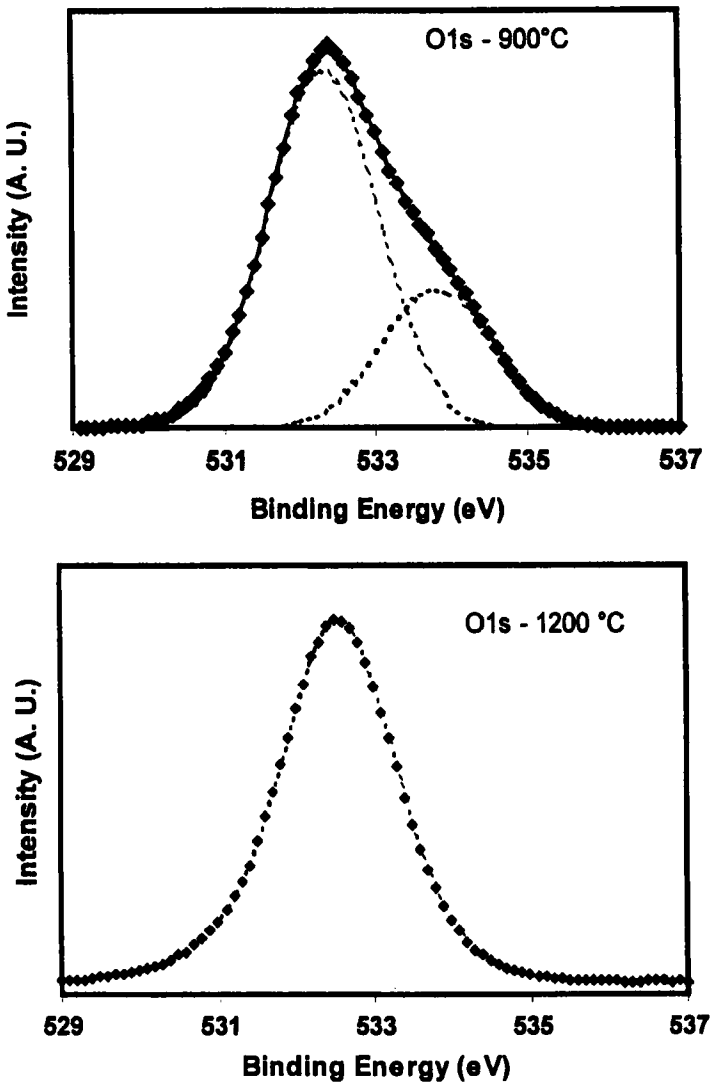


FIGURE 8 High-resolution O 1s spectra for compound **1** treated at 900 and 1200 °C

XPS analysis

Because of the complexity and the existence of different types of titanium phosphates in the samples obtained at higher temperatures (900–1200 °C),

we have restricted the XPS study in this work only on the aluminum derivatives treated at 900 and 1200 °C. Although, in addition to the peak due to aliphatic carbon contamination, Al_{2p}, P_{2p} and O_{1s} photopeaks were clearly observed on aluminum phosphate surfaces, no additional peak for N_{1s} has been detected. This result is in very good agreement with the absence of P-N bonds in the samples. Whereas, the Al_{2p} peak position (75.60 eV) did not vary during the thermal treatment, however, the 0.3 eV shift to higher binding energies of P_{2p} electrons when the materials were treated at 1200°C probably arise from a difference in the molecular environment surrounding the phosphorus atom as it has been mentioned earlier in ^{31}P NMR investigations.

Figure 8 shows the O_{1s} spectra of the aluminum phosphate treated at 900 and 1200°C. Narrow scans of the O_{1s}band were performed to obtain information on the chemical state of this element. Whereas, the O1s spectrum obtained from the sample treated at 1200 °C [E = 532.70 eV] is symmetrical with a full width at half-maximum of 1.7 eV revealing a lone oxygen species, the O 1s peak of the sample treated at 900 °C is dissymmetric and can be decomposed into two components with a ratio 72/28 [E = 532.3 and 533.8 eV]. The two peaks have been assigned to two different oxygen species: the lower binding energy peak O_{1s} at 532.3 eV being associated with the non-bridging oxygen and the higher energy peak O1s at 533.8 eV with the bridging oxygen (P-O-P-bonds) for the aluminum phosphate powder[30-32].

TABLE I XPS Data of Aluminum derivative **1** heated at 900 and 1200 °C

Temperature °C	*Binding Energy*			*Surface Atomic Stoichiometry*		
	Al2p	*P2p*	*O1s*	*Al/P*	*O/P*	*Al/O*
900	75.6 (1.48)	135.2 (1.89)	532 3 (72%) (1.7)	0.38	2.95	0.12
			533.8 (28%) (1.7)	*(0.33)*[a]	*(3)*[a]	*(0.11)*[a]
1200	75.6 (1.60)	134.9 (1.90)	532.7 (1.7)	0.86	3.82	023
				(1)[a]	*(4)*[a]	*(0.25)*[a]

(-) Full width at half-maximum (eV).

a. (-) theoretical atomic ratios for $Al(PO_3)_3$ (900 °C) and $AlPO_4$ (1200 °C) units.

XPS analyses gives also an evaluation of the atomic ratios Al/P, O/P, and Al/O (Table I). We can see that during the thermal process, the Al/O ratio increased from 0.12 for the residue obtained at 900 °C to 0.23 when the phosphate material was heated to 1200 °C. This increase of atomic ratio is consistent with the previous results and proves the transformation of the coordination of aluminum atom from octahedral to tetrahedral environment during the thermal process. It should be noted that the measured Al/O in these runs were quite similar to the theoretical Al/O values in $Al(PO_3)_3$and $AlPO_4$ units respectively.

Based on the data obtained from XPS, ^{31}P and ^{27}Al MAS NMR spectroscopies, then, we can so admit that the residues at 900 °C and 1200 °C are aluminum metaphosphate $Al(PO_3)_3$ and condensed aluminum phosphate $AlPO_4$ respectively.

Raman spectroscopy

Some additional informations concerning the thermal decomposition of the titanium compounds were obtained by Raman spectroscopy (Fig. 9). At first sight, the Raman spectrum of the sample obtained at 900 °C could be associated as the titanium orthophosphate type, whereas, the one obtained at 1200 °C as the condensed titanium phosphate materials. Characteristic vibrations of the PO_4 molecular units are observed around 1000 cm^{-1} (P-O symmetrical and asymmetrical stretchings), 532 cm^{-1} (O-P-O bending) and 319 cm^{-1} (O-P-O rocking)[33]. For a sample heated at 1400 °C, the most striking feature of the spectrum is the intense vibrations observed at 610, 440 and 248 cm^{-1}. This spectrum is exactly similar to the one obtained for the pure rutile form of TiO_2[34] (Fig. 9). As yet, the thermal conversion to the titanium oxide has not been elucidated. This mechanism is still under investigation.

The figure 10 gives an outline of the Raman spectra recorded from aluminum residues obtained at 900 and 1200 °C. Both spectra are completely different due to the structural change which occurs in the sample between these two temperatures, confirming the results previously mentioned. Indeed, the characteristic vibration bands of aluminum metaphosphate $Al(PO_3)_3$ are observed at 1250 and 680 cm^{-1} in the spectrum obtained for the residue treated at 900°C, whereas, the band at 1150 $cm^{-1}$is easily attributed to the condensed PO_4 tetrahedra in the residue obtained at 1200 °C.

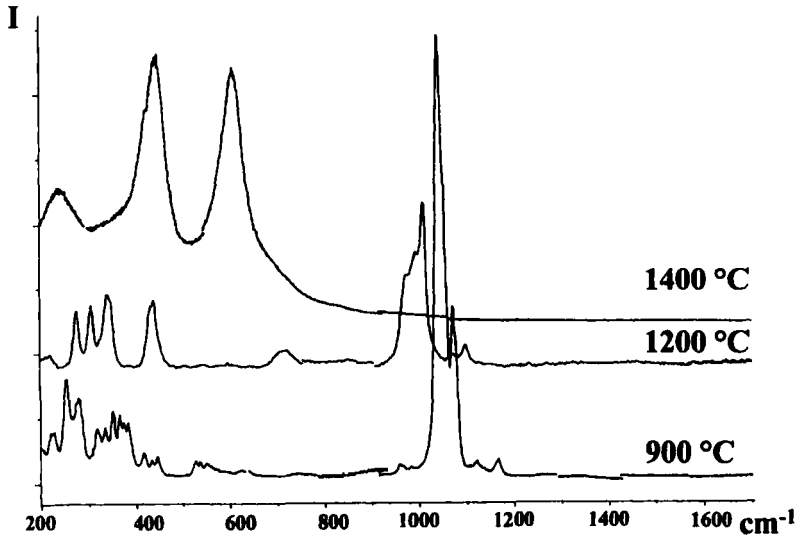


FIGURE 9 Raman spectra obtained after heating of compound 2 at 900, 1200 and 1400 °C

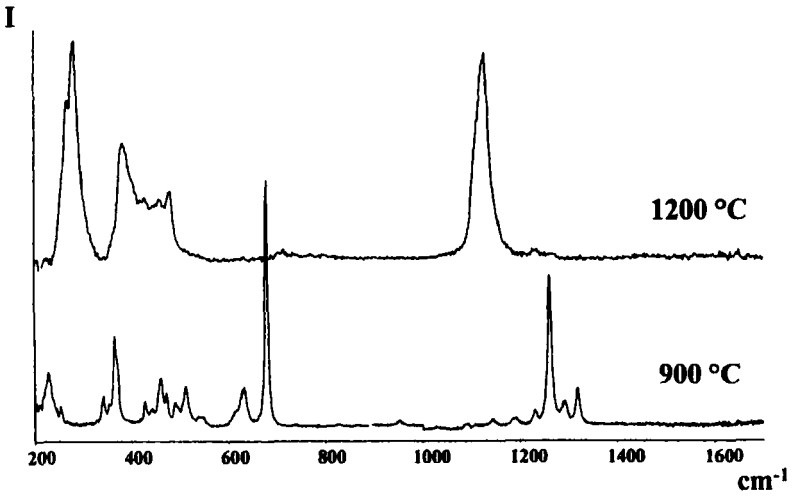


FIGURE 10 Raman spectra obtained after heating of compound 1 at 900 and 1200 °C

CONCLUSION

Aluminum or titanium imidodiphosphates **1** and **2** can be used as Al or Ti sources in the synthesis of AlPO or TiPO -based materials at high temperature. The thermal solid-state transformation of these compounds leads to relatively ordered structures. Even, if the mechanism of this transformation is not yet clarified, interesting effects of temperature have been observed in terms of product phase. The NMR and XPS results presented, confirm that the thermal transformation of the aluminum derivative **1** involves a number of structural changes. Finally the TiPO-based material is stable up to 1200 °C. At 1400 °C this material was converted to TiO_2 in the rutile phase.

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