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New insights into the thermal evolution of aluminophosphate solutions: A complementary XRD and solid state NMR study

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Abstract

The thermal evolution of aluminium phosphate solutions is investigated in this contribution. The study is based on complementary results obtained from standard X-ray diffraction (XRD) analyses accompanied by solid state nuclear magnetic resonance (NMR) investigations. Binders are prepared between 150 and 1400 °C from two aluminium phosphate solutions differing by their P/Al ratio (3 and 3.5). New insights about the presence of amorphous phases, minor compounds and residual phosphoric acid in the binders, not provided by previous XRD study, are afforded by XRD/NMR investigations, leading to a better understanding of the structure of the binders. At high temperature (>600 °C), both solutions (P/Al = 3 and 3.5) lead to the formation of binders composed of cubic aluminium metaphosphate, $Al(PO_3)_3$ [A]. However, the presence of residual phosphoric acid in the P/Al = 3.5 solution entails the formation of $Al(PO_3)_3$ [A] at lower temperature. Advanced solid state NMR sequences ($^{31}P\{^1H\}$ cross polarisation, 2D ^{31}P RFDR and 2D $^{31}P\{^{27}Al\}$ CP-HETCOR) allow for a complete ^{31}P and ^{27}Al NMR signals assignments.

Keywords: Aluminium phosphate; NMR Spectroscopy; Thermal properties; $Al(PO_3)_3$

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1. Introduction

Phosphate based materials have been used as binders in refractory material industry for more than 60 years due to their high strength, abrasion resistance and high temperature stability.[1,2] Most of these phosphate binders are based on industrial aluminium phosphate solutions whose formulations are characterised by the atomic P/Al ratio and the impurity content (boron, sodium). A large number of studies have been carried out to characterise the thermal evolution of solutions with P/Al ratio between 2 and 3.[3–9] It is now well established from all these studies that temperature induces a progressive polymerisation of the aluminophosphate species from $Al(H_2PO_4)_3$ to $AlH_2P_3O_{10},xH_2O$ and then to monoclinic and cubic $Al(PO_3)_3$ (denoted as $Al(PO_3)_3$ [B] and [A], respectively)[9] at 500–600 °C. $Al(PO_3)_3$ [A] is then stable until melting, which occurs at 1400 °C.

It is also important to be noted that an amorphous compound has been observed between 200 and 350 °C in some studies. It was thus reported that an efficient binder, mainly composed of aluminium metaphosphate, could be prepared from aluminium phosphate solutions at 500–600 °C. However, all the previous studies on aluminophosphate solutions were based on X-ray diffraction analyses (XRD) which are not capable of highlighting amorphous compounds, residual phosphoric acid or minor phases. Therefore, it appears that the structural characterisation of aluminium phosphate binders could be greatly improved by a complementary XRD and nuclear magnetic resonance (NMR) analyses, this latter technique being able to investigate amorphous compounds and detect phases present in minor proportion. It must be noted that a first attempt of studying thermal evolution of aluminium phosphate solution by solid state NMR was proposed by Han et al., but no supported assignment of the resonances was reported in this study.[3]

Solutions with P/Al ratios between 2 and 3 are widely involved in industrial applications, despite of a poor chemical stability at room temperature (they are affected by precipitation after few weeks)[7] which severely restricts the applications requiring long time storage or spray drying system, which can be damaged by precipitates. However, it is well known that the chemical stability is dramatically improved for solutions with

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P/Al ratio larger than 3, for which precipitation only occurs after years of storage. Despite of this better stability, only sparse information about the thermal evolution of these solutions is available in the literature.[9]

The thermal evolutions of two different aluminium phosphate solutions with P/Al of 3 and 3.5 are investigated in this contribution. These characterisations benefit from complementary results obtained from solid state NMR and XRD. The ^{31}P and ^{27}Al resonances assignments are supported by advanced NMR correlation sequences (^{31}P{^{1}H} cross polarisation, 2D ^{31}P RFDR and 2D ^{31}P{^{27}Al} CP-HETCOR). A scheme for the thermal evolution is then proposed for each solution.

2. Experimental procedures

The aluminium phosphate solution with a P/Al ratio of 3 was provided by Chemische Fabrik Budenheim (FFB 705, CFB, Germany). The solution with a P/Al ratio of 3.5 was prepared in our laboratory: 15.78 g of $Al(OH)_3$ were dissolved in 50 ml H_3PO_4 (85%) and 50 ml of distilled water. The solution was then heated at 80 °C under stirring during 4 h, until it became completely clear. Different thermal treatments (150–1400 °C) were applied to 4 g of each solution placed in a Pt-Au crucible. The temperature was reached with a heating rate of 1°/min, and a temperature dwell was then maintained during 1 h.

The XRD analyses were performed on a Bruker D8 Advance diffractometer equipped with an energy dispersion detector solX. The acquisition was recorded between 10 and 80°, with 0.02° scan step and 1 s, step time.

All the ^{31}P and ^{27}Al MAS NMR experiments were performed on a 400 MHz spectrometer (9.4 T) at 161.9 ($\nu_0(^{31}P)$) and 104.2 ($\nu_0(^{27}Al)$) MHz with a 4 mm triple channel probe operating at spinning frequency of 10 kHz. The acquisition parameters for the different experiments are reported in the figure captions. Nevertheless, it is important to mention that the relaxation delays used in the 1D MAS ^{31}P and ^{27}Al experiments allow for quantitative spectra.

The spatial proximity between the different phosphate sites was probed with the 2D ^{31}P Radio Frequency Driven Recoupling[10] (RFDR) sequence. The homonuclear dipolar interaction is reintroduced in this sequence through the application of rotor synchronised 180° pulses leading to off-diagonal correlation signal between spatially close phosphorous. The RFDR experiment reported here was set up with a short mixing time (delay during which the 180° pulses are applied to the sample) of 32 ms, allowing correlation only between spatially close phosphorous sites. Therefore, off-diagonal correlation signals indicate that the two correlated phosphorous belong to the same micro-crystallite (and thus to the same phase), whereas a lack of signal denotes the presence of different phases.[11,12]

The cross polarisation (CP) experiment is based on a through-space magnetisation transfer, ruled by the Hartmann–Hahn conditions[13] between two nuclei. The ^{31}P{^{1}H} CP experiment reported in this paper was used to probe the spatial proximity between proton and phosphorous sites. Since the magnetisation transfer from proton to phosphorous is strongly distance dependent ($1/r^3$), only the phosphorous sites spatially close to proton will benefit from the CP and thus will be observed in the recorded ^{31}P{^{1}H} CP spectrum.

A through space correlation map between aluminium and phosphorous sites is obtained with the 2D ^{31}P{^{27}Al} CP-HETCOR experiment,[14] which is the 2D version of the cross polarisation sequence previously described.

The 1D ^{31}P MAS NMR spectra are simulated with the DMFIT software.[15] The relative proportions between the different phosphorous sites are extracted from the simulations of the complete spectrum, including isotropic signals and spinning sidebands. When all the phosphorous resonances are assigned, the chemical composition of the binder (relative proportions between the different compounds present inside the sample) can be deduced from the relative proportions between the different phosphorus resonances. When a sample contains unidentified compounds, the chemical composition cannot be extracted and only the relative proportions between the different phosphorous sites are available.

3. Results and discussion

The crystalline phases identified with the XRD analyses are reported in Table 1. However, in addition to the observed phases, many diffraction peaks remain unassigned, indicating the presence of additional phases. Fig. 1a shows the ^{31}P spectra of the P/Al = 3 solution treated between 150 and 1400 °C. At low temperature (150 °C), the ^{31}P spectrum is composed of four main resonances centered at −4.5, −13.1, −15.8 and −18 ppm accompanied by three additional weak signals at −20.9, −22.9 and −32.5 ppm. The signals in the range of −13.1 to −32.5 ppm are still observed at 250 °C with different relative proportions. The disappearance of the signal at −4.5 ppm should be pointed out. In addition to the previously observed resonances at −20.9, −22.9 and −32.5 ppm, the spectrum of the sample obtained at 350 °C exhibits new signals centered at −0.5, −36.5, −37.6 and −43.3 ppm as well as a weak signal at −50.8 ppm. This latter becomes the main resonance in the spectrum of the sample treated at 500, 600 and 1000 °C. The spectrum obtained after treatment at 1400 °C exhibits broad resonances characteristic of an amorphous structure. ^{27}Al spectra (Fig. 1b) show the presence of different octahedral aluminium sites. A signal at −16.5 ppm is observed at 150 and 250 °C, whereas a group of three resonances (−13.2, −15.2 and −21.4 ppm) is noticed in the

Table 1
Crystalline compounds identified in the X-ray diffraction analyses of the binders produced from the two aluminium phosphate solutions

	P/Al = 3	P/Al = 3.5
150 °C	$Al(H_2PO_4)_3$	$Al(H_2PO_4)_3$
250 °C	$Al(H_2PO_4)_3$	–
350 °C	$AlH_2P_3O_{10},xH_2O + Al(PO_3)_3$ [B]	$Al(PO_3)_3$ [A]
500 °C	$Al(PO_3)_3$ [A]	$Al(PO_3)_3$ [A]
600 °C	$Al(PO_3)_3$ [A]	$Al(PO_3)_3$ [A]
850 °C	$Al(PO_3)_3$ [A]	$Al(PO_3)_3$ [A]
1000 °C	$Al(PO_3)_3$ [A]	$Al(PO_3)_3$ [A]
1200 °C	$Al(PO_3)_3$ [A]	$Al(PO_3)_3$ [A]
1400 °C	–	–

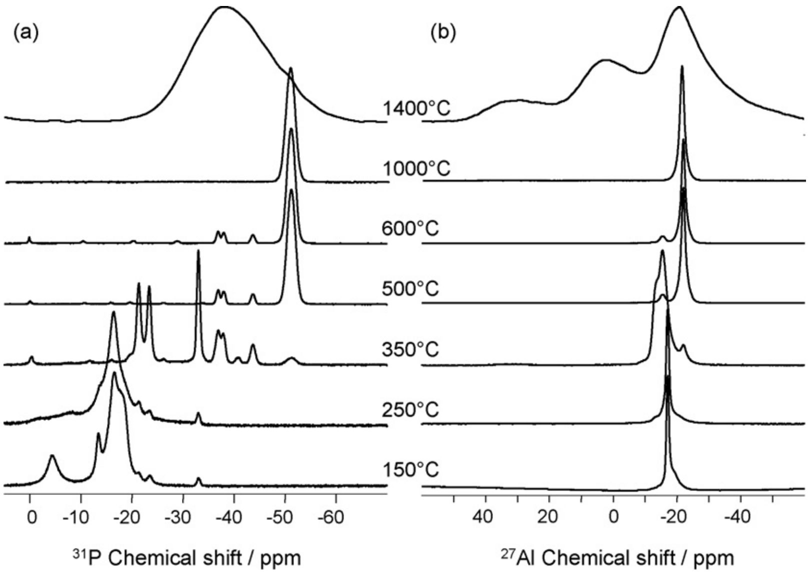

Fig. 1. (a) ^{31}P and (b) ^{27}Al MAS NMR spectra of the binders prepared at different temperatures from the P/Al = 3 aluminium phosphate solution. Quantitative 1D MAS ^{31}P spectra were recorded with a 1 μs pulse length (80 kHz radiofrequency (rf) field), 16 transients and a relaxation delay (r.d.) of 180 s. 1D MAS ^{27}Al spectra were acquired with a 1 μs pulse length (30 kHz rf field determined on a liquid), 1024 transients and a r.d. of 0.5 s.

spectrum obtained after the treatment at 350 °C. Then, the signal at −21.4 ppm becomes the main resonance above 500 °C. A typical spectrum of aluminium in glass can be observed at 1400 °C (three resonances at 30, 10 and −20 ppm, characteristic of tetra-, penta- and octahedral speciation, respectively).

In the 150–1000 °C temperature range, the higher the temperature, the more shielded the ^{31}P chemical shifts (shift towards negative values), which indicates a phosphate polymerisation with the temperature. This polymerisation from $Al(H_2PO_4)_3$ to $AlH_2P_3O_{10}$,xH_2O and to $Al(PO_3)_3$ [B] and [A] is supported by our XRD analyses and confirms the previous study.[3–9]

Nevertheless, it appears that the information deduced from the XRD analyses is not sufficient to fully explain the ^{31}P and ^{27}Al spectra and thus do not allow for a complete chemical characterisation of the binders. A complete assignment of the ^{31}P and ^{27}Al resonances is thus necessary to provide an improved understanding of the chemical composition of the binders. In a first step, the $^{31}P/^{27}Al$ signals at −15.8/−16.5 ppm, observed on the spectra of the samples prepared at 150 and 250 °C, are assigned to $Al(H_2PO_4)_3$ according to our XRD results. Then, literature data allow us assigning the $^{31}P/^{27}Al$ chemical shifts at −50.8/−21.4 ppm, obtained on samples prepared at 500–1000 °C, to the $Al(PO_3)_3$ [A] phase.[16] Finally, unambiguous assignments for the remaining signals are afforded by complementary results from 2D ^{31}P RFDR, $^{31}P\{^1H\}$ cross polarisation and 2D $^{31}P\{^{27}Al\}$ CP-HETCOR performed on the binder prepared at 350 °C. The 2D ^{31}P RFDR spectrum is displayed in Fig. 2. Three different groups of resonances can be distinguished through the off-diagonal correlation signals, indicating that the sample is constituted by three different phosphate phases. The first group is constituted by the three signals at −20.9, −22.9 and −32.5 ppm; the second one contains the signals at −36.5, −37.6 and −43.3 ppm, whereas the third group is constituted by a single resonance at −50.8 ppm.

Since the −50.8 ppm signal was previously assigned to $Al(PO_3)_3$ [A],[16] it appears, according to the XRD results, that the two remaining groups have to be assigned to $AlH_2P_3O_{10}$,xH_2O and $Al(PO_3)_3$ [B]. Unambiguous assignment finally comes from the $^{31}P\{^1H\}$ cross polarisation spectrum displayed in Fig. 3. Indeed, the spectrum recorded under cross polarisation conditions only exhibits the phosphorous sites spatially close to proton. There-

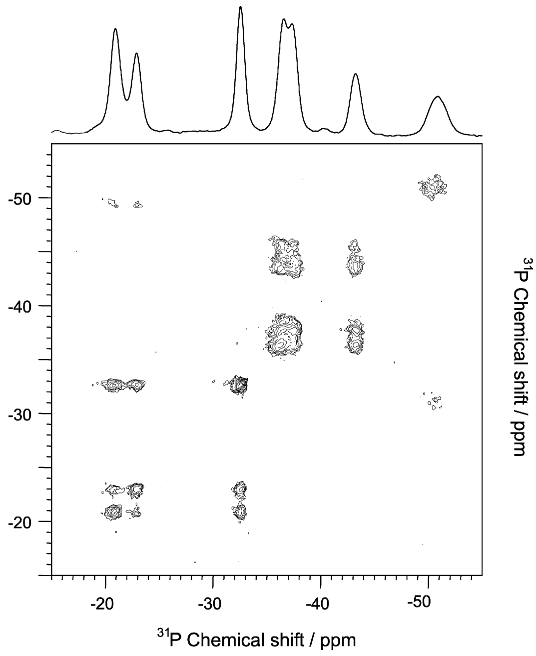

Fig. 2. ^{31}P RFDR spectrum recorded on the binder prepared at 350 °C from the P/Al = 3 aluminium phosphate solution. The acquisition is performed with a mixing time of 32 ms. The 4096 × 256 data points were collected employing a rotor synchronised t_1-increment of 100 μs and the TPPI method. Each transient is acquired with 64 accumulations and a r.d. of 20 s.

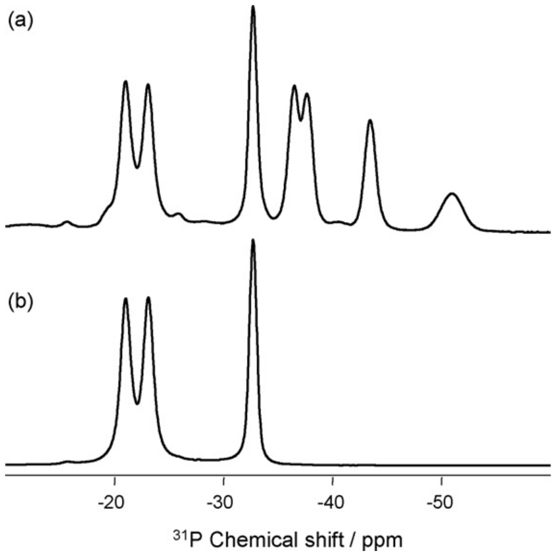

Fig. 3. (a) 1D ^{31}P MAS NMR spectra obtained on the binder prepared at 350 °C from the P/Al = 3 solution obtained with single scan (a) and $^{31}P\{^1H\}$ cross polarisation (b) sequences. The 3 ms cross polarisation step is obtained by applying rf fields of 60 kHz for ^{1}H and ^{31}P channels.

fore, signal is only expected for the phosphorus belonging to the $AlH_2P_3O_{10},xH_2O$ phase. Comparison between the single scan ^{31}P acquisition (3-a) and the $^{31}P\{^1H\}$ cross polarisation spectrum (3-b) allows us assigning the group of resonance at −20.9, −22.9 and −32.5 ppm to the $AlH_2P_3O_{10},xH_2O$ phase and thus the signals at −36.5, −37.6 and −43.3 ppm to the $Al(PO_3)_3$ [B] compound. The ^{27}Al signals were assigned on the base of the correlation spectrum between phosphorous and aluminium species, obtained with the $^{31}P\{^{27}Al\}$ 2D CP-HETCOR experiment (Fig. 4). The spectrum exhibits correlation signals between spatially close phosphorous and aluminium moieties belonging to the same structure. Correlation signals are observed between the ^{27}Al site at −15 ppm and the three ^{31}P resonances at −36.5, −37.6 and −43.3 ppm and between the ^{27}Al sites at −13.2 and −15.2 ppm and the ^{31}P signals at −20.9, −22.9 and −32.5 ppm. It can be inferred from this spectrum that the aluminium site at −15 ppm belongs to the $Al(PO_3)_3$ [B] compound, whereas two aluminium sites at −13.2 and −15.2 ppm have to be assigned to the $AlH_2P_3O_{10},xH_2O$ phase. Finally, the $^{31}P/^{27}Al$ resonances assignment, which improves the database of aluminophosphate compounds are reported in Table 2.

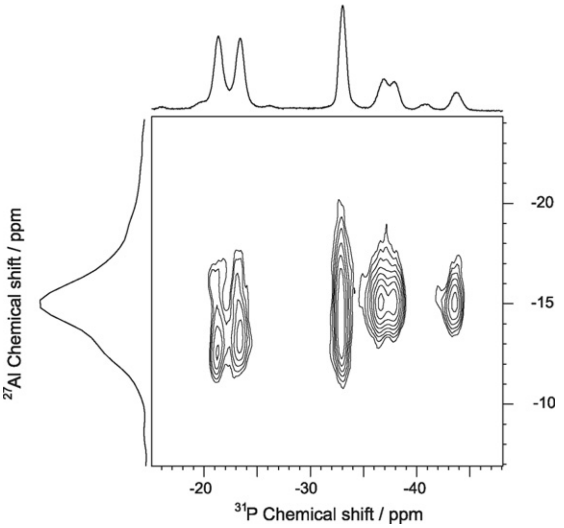

Fig. 4. 2D $^{31}P\{^{27}Al\}$ CP-HETCOR spectrum obtained on the binder prepared at 350 °C from the P/Al = 3 solution. The cross polarisation step of 5 ms between ^{27}Al and ^{31}P is achieved through the application of weak rf fields (6 and 6.5 kHz for ^{31}P and ^{27}Al, respectively) due to the quadrupolar character of the aluminium nucleus.[18] The 4096 × 80 data points were collected with the TPPI method, a rotor synchronised t_1-increment of 100 μs, 256 accumulations and a relaxation delay of 0.5 s.

Table 2
^{31}P and ^{27}Al chemical shifts determined for the aluminophosphate phases involved in the thermal evolution of the aluminium phosphate solutions

Phase	δ ^{31}P/ppm	δ ^{27}Al/ppm
$Al(H_2PO_4)_3$	−15.8	−16.5
$AlH_2P_3O_{10},xH_2O$	−20.9/−22.9/−32.5	−13.2/−15.2
$Al(PO_3)_3$ [B]	−36.5/−37.6/−43.3	−15
$Al(PO_3)_3$ [A]	−50.8	−21.4
H_3PO_4/HPO_3	0/−13	–

A condensation scheme can then be proposed for the P/Al = 3 solution (Fig. 5a) which confirms the established evolution from $Al(H_2PO_4)_3$ to $AlH_2P_3O_{10},xH_2O$, $Al(PO_3)_3$ [B] and [A];[3–9] the binder then melt at high temperature and a glass is produced by cooling the sample, as indicated by the broad resonances observed on the ^{31}P and ^{27}Al spectra. However, new information is afforded by our XRD/NMR investigations as compared to previous XRD studies:

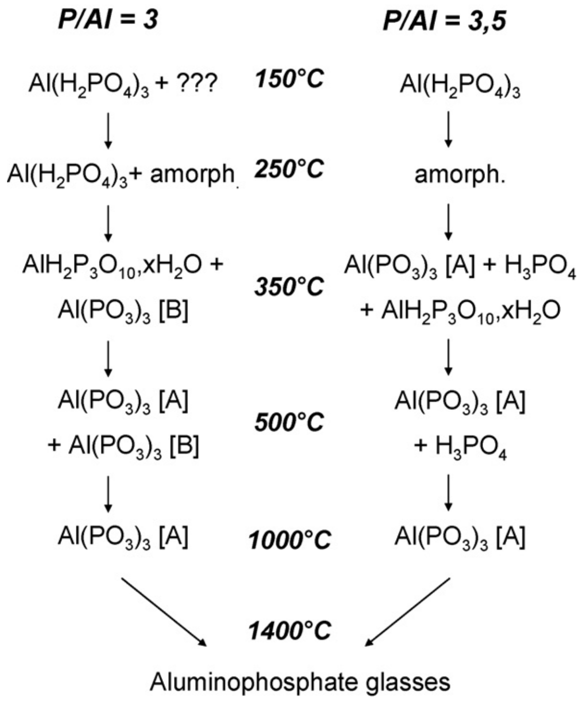

Fig. 5. Thermal evolution determined for the P/Al = 3 (a) and 3.5 (b) aluminium phosphate solutions. The schemes only exhibit major phases present in the binders (>5%).

Table 3
Chemical composition (given in molar percentage) of the aluminium phosphate binder prepared at different temperatures from the P/Al = 3 and P/Al = 3.5 solutions (+/− 1%)

P/Al = 3	$Al(PO_3)_3$ [A]/[B]	$AlH_2P_3O_{10}$	$Al(H_2PO_4)_3$	H_3PO_4/HPO_3	unk. (cryst/amor)
150 °C (*)	–	5.2	58.1	–	36.7/0
250 °C (*)	–	6.4	67.5	–	4.1/22
350 °C	4.7/23.1	71	–	1.2/–	–
500 °C	88.5/10.4	–	–	1.1/–	–
600 °C	88.1/9.9	–	–	1.1/0.9	–
1000 °C	100/–	–	–	–	–
P/Al = 3.5	$Al(PO_3)_3$ [A]/[B]	$AlH_2P_3O_{10}$	$Al(H_2PO_4)_3$	H_3PO_4/HPO_3	unk. (cryst/amor)
150 °C (*)	–	–	70.2	–	29.8/–
250 °C	–	–	–	–	–/100
350 °C	38.2/–	21.2	–	39.4/1.2	–
500 °C	66.4/–	–	–	32.3/1.3	–
600 °C	97.1	–	–	2/0.9	–
1000 °C	100	–	–	–	–

(*) Denotes samples for which the indicated percentages are related to the proportion of signal in regard to the global phosphorous content and not to relative proportions between the different phosphate compounds. unk.: unknown; cryst.: crystalline; amor.: amorphous.

(i) the complex ^{31}P spectrum recorded at 150 °C indicates that the mixture is not only composed of $Al(H_2PO_4)_3$ as indicated by the XRD results. The unassigned ^{31}P resonances at −4.5, −13 and −18 ppm highlight the presence of additional phases. These ^{31}P chemical shift values, close to the $Al(H_2PO_4)_3$ signal, surmise the presence of aluminium orthophosphate complexes, as suggested by van Wazer.[17]

(ii) $AlH_2P_3O_{10},xH_2O$ is detected at 150 °C ((−20.9/−22.9/−32.5 ppm in Fig. 1a), indicating that the $Al(H_2PO_4)_3$ condensation begins earlier than established.[5,9]

(iii) the binder prepared at 250 °C is constituted by crystalline compounds and by an amorphous part which represents 22% of the global phosphorous content, as indicated by the ^{31}P NMR spectrum simulation (Table 3).

(iv) the presence of aluminium metaphosphate $Al(PO_3)_3$ [A] in minor proportion (3.4%) is highlighted at 350 °C (−50.8 ppm).

When the phase identification is completed, the quantification of the different compounds in the binder can be easily achieved by fitting the ^{31}P spectra, leading to a better structural description of the samples. The detailed chemical compositions (given in molar percentage) of the different samples are reported in Table 3. In case of samples for which the identification is not completed, the indicated percentages express the relative proportions of phosphorous signal in regard to the global phosphorous content. Such samples are denoted by a (*) in Table 3.

Similar study is carried out for the first time on the chemically stable aluminium phosphate solution with a P/Al ratio

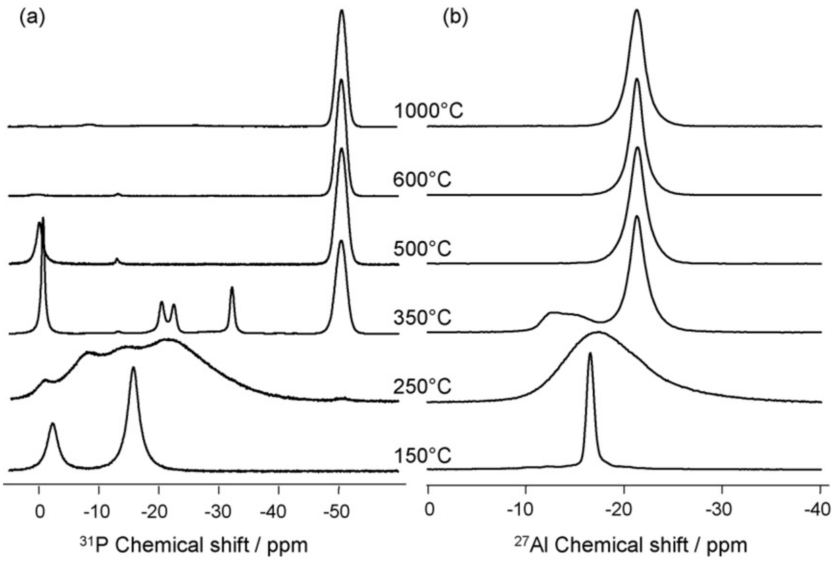

Fig. 6. (a) ^{31}P and (b) ^{27}Al MAS NMR spectra of the binders prepared at different temperatures from the P/Al = 3.5 aluminium phosphate solution.

of 3.5. The ^{31}P and ^{27}Al spectra are plotted in Fig. 6a and b, respectively and the XRD data are reported in Table 1. These results allow for a complete characterisation of the thermal evolution of the P/Al = 3.5 solution. The presence of $Al(H_2PO_4)_3$ is identified at 150 °C in the XRD analyses, and is confirmed by the ^{31}P and ^{27}Al NMR resonances at −15.8 and −16.5 ppm, respectively. An amorphous compound can then be observed at 250 °C as indicated by the broad resonances in the ^{31}P and ^{27}Al spectra. At higher temperature (350 °C), the amorphous part crystallises, giving rise to $AlH_2P_3O_{10}$,xH_2O and $Al(PO_3)_3$ [A]. New information is provided by the ^{31}P NMR analysis through the presence of a narrow peak centered near 0 ppm between 350 and 500 °C, indicating the presence of residual phosphoric acid in the binder. Treatment at higher temperature induces the polymerisation of $AlH_2P_3O_{10}$,xH_2O to $Al(PO_3)_3$ [A] and the evolution of residual H_3PO_4 to HPO_3 (small peak at −13 ppm) and P_2O_5 which is not observed in our spectra, due to a volatilisation between 500 and 600 °C. At 1400 °C, the binder melts, inducing the formation of a glass, as previously observed for the P/Al = 3 solution. The chemical compositions of the different binders, deduced from the ^{31}P NMR simulations are reported in Table 3.

In Fig. 6 are displayed the thermal evolution schemes for both solutions. Even if both solutions lead to the formation of binders, mainly composed of $Al(PO_3)_3$ [A] at 600 °C, some differences can be highlighted in the first steps of the thermal evolution:

(i) at low temperature (150 °C), the structure of the binder prepared from the P/Al = 3 solution is more complex than the binder obtained from the P/Al = 3.5 solution. The former contains small amount of $AlH_2P_3O_{10}$,xH_2O and additional peaks can be observed in the ^{31}P spectrum, which could be due to aluminium orthophosphate complexes.

(ii) an amorphous compound is observed at 250 °C for the P/Al = 3.5 solution whereas the binder prepared from the P/Al = 3 solution only exhibits a small amount of amorphous phases (22% of the global phosphorous content).

(iii) the chemical compositions of the binders prepared at 350 °C from both solutions are completely different (Tab. 3): the binder prepared from the P/Al = 3 solution is mainly constituted of $AlH_2P_3O_{10}$,xH_2O and small amounts of $Al(PO_3)_3$ [B] and [A], whereas the sample obtained with the P/Al = 3.5 is mainly composed of $Al(PO_3)_3$ [A] and H_3PO_4 in similar proportion (ca. 40%), accompanied by $AlH_2P_3O_{10}$,xH_2O (ca. 20%). No $Al(PO_3)_3$ [B] can be observed in this sample. Therefore, it seems that residual H_3PO_4 induces the formation of $Al(PO_3)_3$ [A] at lower temperature by allowing direct evolution from $AlH_2P_3O_{10}$,xH_2O to $Al(PO_3)_3$ [A] without the intermediate $Al(PO_3)_3$ [B] step.

(iv) higher temperatures (500–700 °C) induce the polymerisation of $AlH_2P_3O_{10}$,xH_2O to $Al(PO_3)_3$ [B] and $Al(PO_3)_3$ [A] in the case of the P/Al = 3 solution and the polymerisation of residual phosphoric acid to HPO_3 and P_2O_5 in the case of the P/Al = 3.5 solution.

Both solutions lead to binders composed of $Al(PO_3)_3$ [A]. The binders finally melt at 1400 °C and a glass can be obtained after quenching.

4. Conclusion

The thermal transformations of two aluminium phosphate solutions with P/Al ratios of 3 and 3.5 are investigated in this paper by complementary XRD/NMR analyses. This study leads to an improved characterisation of the binder chemical composition, including minor phases and phosphoric acid residues, which cannot be afforded by a standard XRD study. Advanced NMR techniques allow us for a complete ^{31}P and ^{27}Al signals assignment, thus improving the aluminophosphate chemical shifts database. The thermal evolution can be roughly described as a progressive polymerisation of $Al(H_2PO_4)_3$ species to $AlH_2P_3O_{10}$,xH_2O, $Al(PO_3)_3$ and finally to an aluminophosphate glass for both solutions. Nevertheless, even if the P/Al ratio does not change the chemical nature of the compounds formed during the thermal treatment, it appears that the formation of $Al(PO_3)_3$ [A] is induced at lower temperature by the excess of H_3PO_4 in the P/Al = 3.5 solution.

The P/Al = 3.5 solution exhibits a better chemical stability and leads to $Al(PO_3)_3$ [A] at lower temperature and could thus be considered as a better formulation than the usual P/Al = 3 solution. Unfortunately, the binder prepared at 350 °C with the P/Al = 3.5 solution contains a large amount of residual phosphoric acid (ca. 40%) which can be fatal for some industrial applications (corrosion of furnaces by volatilised P_2O_5). Nevertheless, we assume that this residual acid can be reduced by appropriate thermal treatments including longer dwells at low temperatures (150–250 °C). Moreover, the binding effect of aluminium phosphate solutions can be improved by the high reactivity of the residual phosphoric acid with fillers. Binders prepared with phosphate solutions (P/Al = 3 and 3.5) and different fillers (Al_2O_3, ZrO_2...) are currently investigated and results will be reported in forthcoming papers.

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