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Abstract

A study of the high temperature (up to 1200°C) degradation of aluminum metaphosphate $Al(PO_3)_3$ has been carried out to evaluate the stability of this compound used for many purposes. For the preparation of $Al(PO_3)_3$, an aluminum dihydrogen-phosphate $Al(H_2PO_4)_3$ solution has been heated at 700°C. Thermal degradation of $Al(PO_3)_3$ has been followed through the measurement of weight loss on isothermal mode at 1000 and 1200°C and by thermogravimetric analysis coupled with mass spectroscopy (TGA-MS). Structural data have been obtained by ^{27}Al, ^{31}P and ^{1}H MAS NMR spectroscopy. NMR analyses have shown that [A] and [B] allotropic forms of $Al(PO_3)_3$ are formed after the preparation procedure. In addition, NMR revealed that hydroxyls groups are also present in the sample, and they form P-OH groups. TGA-MS showed that they are decomposed at a temperature of 875°C, while the decomposition of $Al(PO_3)_3$ into $AlPO_4$ and P_2O_5 begins at 1000°C.

Keywords

1. Introduction

Aluminum metaphosphate materials have been used for years as binding agents in the refractory materials industry (Kingery, 1950; Vippola, 2000), as an acid compound for acid-base cements (Shubow, 1983; Tomic, 1983) and as precursors for protective coating against oxidation for Carbon/Carbon composite materials (Balhadere, 1994; Lu, 2002).

These materials are generally obtained by heating solutions of aluminum dihydrogen-phosphate $Al(H_2PO_4)_3$, which are characterized by their P/Al atomic ratio. It was shown that solutions with a P/Al atomic ratio above 3 are stable for long time, while solutions with a ratio between 2 and 3 are subjected to precipitation of $AlH_3(PO_4)_2.3H_2O$ after few weeks, thus limiting their use in industrial processes (D'Yvoire, 1961).

The heating of an aluminum dihydrogen-phosphate solution at a temperature between 600 and 700°C leads to the formation of an aluminum metaphosphate $Al(PO_3)_3$ binding agent. The different steps of formation of the aluminum metaphosphate from solutions of aluminum dihydrogen-phosphate with ratios between 2 and 3.5 have already been studied (Chen, 2003; Han, 2003; O'Hara, 1972; Tricot, 2008; Tsuhako, 1978; Vippola, 2002). The heating of the solutions induces a polymerization of $Al(H_2PO_4)_3$ into $AlH_2P_3O_{10},xH_2O$ and then into $Al(PO_3)_3$. A higher P/Al ratio of the initial solution increases the rate of the polymerization so the Al(PO3)3 is formed at lower temperatures. $Al(PO_3)_3$ was indeed already observed at 350°C after heating a solution with a ratio P/Al of 3.5. If the P/Al ratio is beyond 3, the excess of phosphorus leads to the presence of residual phosphoric acids after the heat treatment.

Since most applications of aluminophosphate materials are at high-temperatures, some authors studied the degradation of $Al(PO_3)_3$ with temperature (Kniep, 1986; Maier, 2005; Rickles, 1965). They showed that after heating the $Al(PO_3)_3$ phase above 1000°C, a weight loss is observed because $Al(PO_3)_3$ is degraded into $AlPO_4$ and P_2O_5, the latter being volatile for temperatures above 600°C (Haynes, 2016).

At 1400°C, $Al(PO_3)_3$ melts and forms an aluminophosphate glass after quenching (O'Hara, 1972; Tsuhako, 1978).

In this contribution, we report further insights in the thermal degradation of aluminum metaphosphate. A solution of aluminum dihydrogen-phosphate with a P/Al ratio of 3.2 was used. This specific P/Al ratio solution was selected for its better stability,. After a heat treatment of the solution at 700°C (which allows the formation of the aluminum metaphosphate according to the literature), we conducted a study of the evolution of the aluminum metaphosphate at temperatures between 700 and 1000°C. Indeed, this range of temperatures can be of interest in some applications of the aluminum metaphosphate (Balhadere, 1994; M. Mazany, 2007) and it has not been particularly investigated in the literature. Nowadays, the tendency is to decrease the elaboration temperature of the aluminophosphate materials at lower temperature such as 700°C, in order to decrease the associated energy cost. Thus, it is of importance to analyze the behavior of the aluminum metaphosphate between its temperature of elaboration and utilization. For instance, the presence of hydroxyl groups inside the aluminum metaphosphate after its elaboration can influence its properties when the material is used as a seal for electrical insulation (Berard, 2008; Norelli, 2016; Vetrivendan, 2017).

Thermogravimetric analyses coupled with mass spectroscopy were performed to study the degradation of the $Al(PO_3)_3$ until 1200°C. Structural data and new investigation on the presence and the localization of residual hydroxyls groups in the aluminum metaphosphate was performed by ^{31}P, ^{27}Al, ^{1}H and $^{31}P\{^{1}H\}$ cross polarization MAS NMR.

2. Experimental procedures

The aluminum metaphosphate ($Al(PO_3)_3$) sample has been prepared by the conventional procedure consisting in heating a solution of aluminum dihydrogen-phosphate ($Al(H_2PO_4)_3$), which has been purchased to Budenheim Gmbh (Mainz). Since some variability of the P/Al atomic ratio of the commercial solution has been observed, it was checked by inductively coupled plasma method (ICP)

on an ICP-OES Agilent 5100 machine. The measured P/Al ratio of the solution used was measured to be 3.2 ± 0.06. The heat treatment of the solution consisted in a first step of 2h at 220°C and a final step at 700°C for 1h. The heating rates between ambient temperature and 220°C is 1°C/min and the one between 200 and 700°C is 3°C/min.

Thermogravimetric analysis coupled with mass spectroscopy (TGA-MS) analyses have been performed on a TG 92 from Setaram coupled with an Omnistar MS from Pfeiffer. The sample was placed in a platinum crucible and was heated at 5°C/min until a temperature of 1200°C under air.

For the gravimetric analyses, the aluminum metaphosphate powder has been placed in a platinum crucible, which was introduced in an oven at 1000 or 1200°C for different durations. The crucible was then taken out of the oven, cooled at ambient air and weighted with a 0.1mg precision.

The Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) for ^{31}P, ^{1}H and cross polarization $^{31}P\{^{1}H\}$ experiments were performed at 9.4T on a Bruker spectrometer with a 3.2 mm triple channel probe operating at spinning frequency of 20 kHz. The relaxation delays/high power pulse for the $^{31}P$and ^{1}H were 300s/2µsand 120s/2.425µ,s respectively. The relaxation delay for the cross polarization $^{31}P\{^{1}H\}$ experiment, which permits the detection of the spatial proximity between the proton and the phosphorus nuclei, was 120s with a contact time of 2ms. . The ^{27}Al MAS NMR spectra were recorded at 18.8T on a Bruker spectrometer equipped with a 3.2 mm rotor spinning at 20 kHz. The relaxation delay/high power pulse was 2s/1 µs.

3. Results

The ^{27}Al and ^{31}P (Figure 1) MAS NMR results indicate the presence of the [B] form of $Al(PO_3)_3$ (-15 ppm resonance on the ^{27}Al spectrum and -36, -37, -43 ppm resonances on the ^{31}P spectrum [ref]) and also of the [A] form (-21.5 ppm resonance on the ^{27}Al and -50.6 ppm resonance on the ^{31}P spectrum [ref]). D'Yvoire (D'Yvoire, 1960) reported that 6 forms of $Al(PO_3)_3$ (denominated [A], [B], [C], [D], [E] and [F]) can be obtained. After a heat treatment of an aluminum dihydrogen-phosphate solution at 700°C, [A] and [B] forms have been observed, with ratios depending on the P/Al ratio [ref]. The higher

the ratio is, the higher the quantity of [A] formed is. $Al(PO_3)_3$ [A] is a tetrametaphosphate composed of cycles of 4 tetrahedral PO_4^{3-}, while $Al(PO_3)_3$ [B] is a hexametaphosphate composed of cycles of 6 PO_4^{3-}. The [B] form of $Al(PO_3)_3$ is metastable and is converted into the [A] form above 800°C (O'Hara, 1972).

The gravimetric analyses achieved at temperatures of 1000 and 1200°C are shown in Figure 2. A first weight loss of around 1% is observed after 5 min at 1000 and 1200°C. To make sure that this weight loss was not caused by adsorbed water on the surface of the sample, two samples were dried one night in an oven at 120°C, and the same weight loss of around 1% after 5 minutes at 1000 and 1200°C was found. This thus indicates that a specie is eliminated from the sample at a temperature bellow 1000°C. After the first 5 minutes, the weight loss increases linearly for both temperatures.

To investigate the first weight loss, thermogravimetric analysis coupled with mass spectroscopy of the aluminum metaphosphate was performed (Figure 3). Thermogravimetric analyses doesn't show any weight loss until 875°C. At this temperature, 1% of the mass is suddenly lost, which correlates with the 1% weight loss observed after the 5 first minutes in the previous gravimetric study. Mass spectroscopy analysis of H_2O shows a bump at 875°C, which corresponds to the first mass loss, and indicates the presence of –OH groups inside the sample. At 1000°C, a weight loss starts, which rate increases with temperature. As reported by Maier et al., this second weight loss corresponds to the decomposition of $Al(PO_3)_3$ into $AlPO_4$ and P_2O_5 (Maier, 2005).

The presence of –OH groups was investigated using ^1H (Figure 4) and $^{31}P\{^1H\}$ cross-polarization (Figure 5) MAS NMR. The ^1H spectrum (Figure 4) shows several resonances. The resonances at 1 and 7 ppm are attributed to the rotor signal and adsorbed water on the sample (Ratcliffe, 1985; Yesinowski, 1987), respectively. The resonances at 11 and 16 ppm are attributed to –OH groups (Mastikhin, 1987; Ratcliffe, 1985). On the $^{31}P\{^1H\}$ CP MAS-NMR spectrum (Figure 5), a resonance centered at -31 ppm and a shoulder centered at -45ppm are observed, which indicate the presence of P-OH groups. The small signal on noise ratio of this CP experiment indicates that only a small amount of P–OH groups is

present. It is worth noting that a HMQC $^{27}Al\{^{1}H\}$ MAS NMR experiment was also performed, but no signal was measured.

Further MAS NMR analyses were recorded to observe the evolution of the aluminum metaphosphate samples after the gravimetric analysis (2h at 1000 and 1200°C). ^{1}H MAS NMR spectra shows that there was less and no more –OH groups at 1000 and 1200°C, respectively (Figure 6). ^{27}Al and ^{31}P (Figure 7) MAS NMR spectra exhibit two resonances, at -21.5 and -50.6 ppm on the ^{27}Al and ^{31}P spectra, respectively, which show that only the [A] $Al(PO_3)_3$ form remains at these temperatures. In addition, resonances at 40 and -28 ppm on the ^{27}Al and ^{31}P spectra, respectively, are attributed to $AlPO_4$ [ref].

Discussion

The gravimetric analyses show a first sudden weight loss that occurs after 5 minutes at 1000°C or 1200°C and then a continuous weight loss is observed for the two temperatures. Since the latter weight loss increases linearly with time, it has a zero order kinetic and can thus be attributed to a decomposition reaction of the aluminum metaphosphate. The NMR analyses of the sample heated 2h at 1200°C shows the formation of $AlPO_4$, which confirms the decomposition of the $Al(PO_3)_3$ into P_2O_5 and $AlPO_4$ (Haynes, 2016). The formation of $AlPO_4$ is hardly detectable at 1000°C as the amount of $Al(PO_3)_3$ that has been decomposed is negligible.

The first weight loss was never detected nor investigated in the literature. TGA-MS indicates that, despite the preparation temperature at 700°C seems high enough to obtain a full dehydration of the initial solution, some hydroxyls groups (-OH) remain in the sample after the heat treatment since H_2O is detected for temperatures between 875 and 900°C. ^{1}H NMR confirms the presence of the –OH groups, and the CP MAS NMR indicates that the –OH groups are localized on the PO_4^{3-} cycles of the $Al(PO_3)_3$. Furthermore, the lack of HMQC $^{27}Al\{^{1}H\}$ MAS NMR indicates that these hydroxyl groups are not present as Al-OH groups. These hydroxyls groups are thus present only as P-OH bonds, and despite the weak CP intensity, the resonances are found at chemical shifts close to those of [A] and [B]

aluminum metaphosphate forms, thus indicating that P-OH groups are present on both forms. These P-OH groups are thus probably present as defects on the metaphosphate cycles. It is worth noting that the presence of such residual hydroxyl groups has also been detected in other phases like silica (Merle, 2012). When heated at a temperature above 875°C, these hydroxyl groups are decomposed and evaporate as H_2O, causing the weight loss on the TGA curve.

Conclusion

We conclude that the conventional heat treatment reported in the literature used to prepare aluminum metaphosphate from aluminum dihydrogen-phosphate solution is efficient, but some residual hydroxyls groups are still present in the product. TGA-MS and NMR analyses indeed show the presence of P–OH groups in the aluminum metaphosphate heated at 700°C. These hydroxyl groups are decomposed into H_2O at a temperature above 875°C. A heat treatment of 2h at 1200°C enables to prepare P–OH-free aluminum metaphosphate.

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Figures

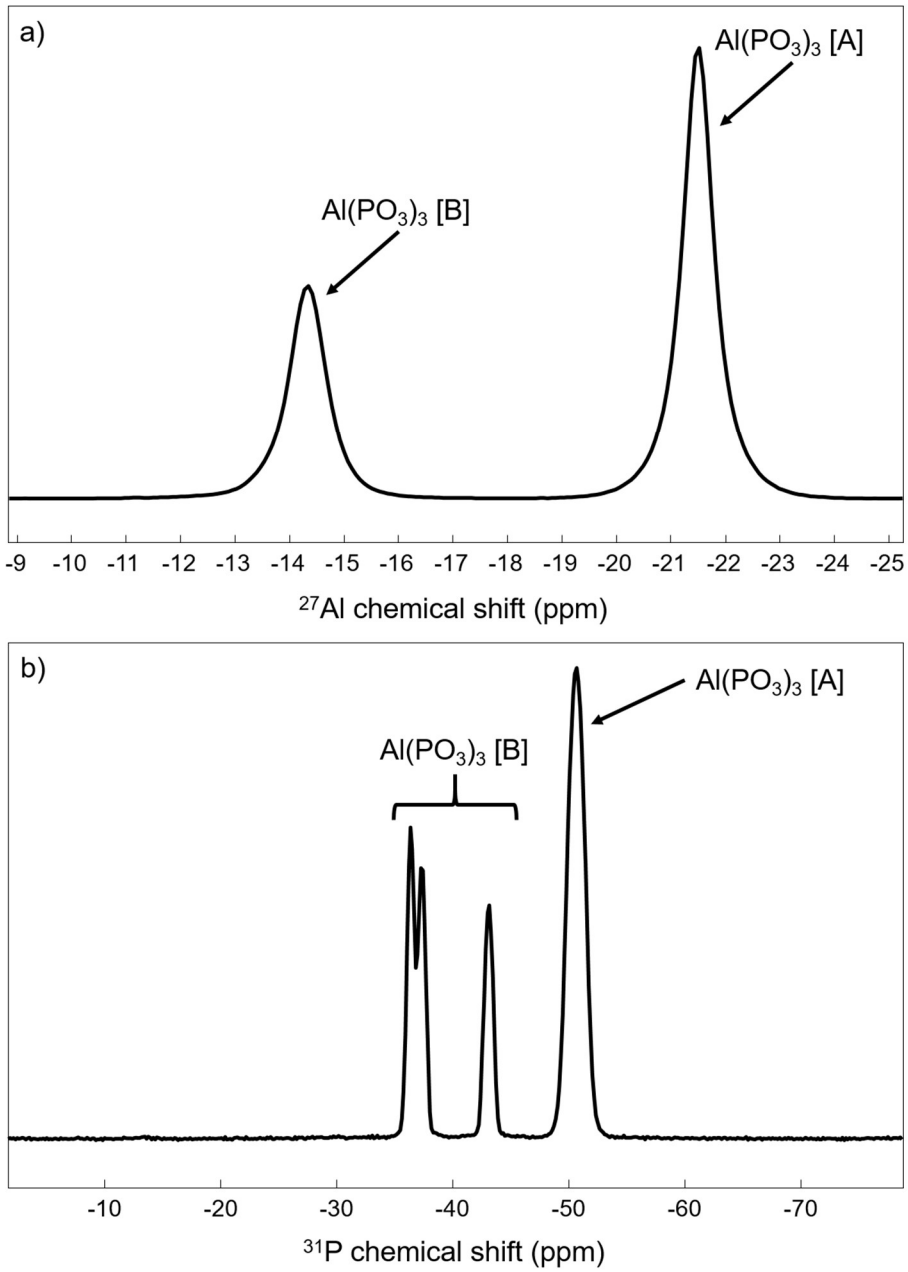

Figure 1 : ^{27}Al (a) and ^{31}P (b) MAS NMR spectra of aluminum metaphosphate.

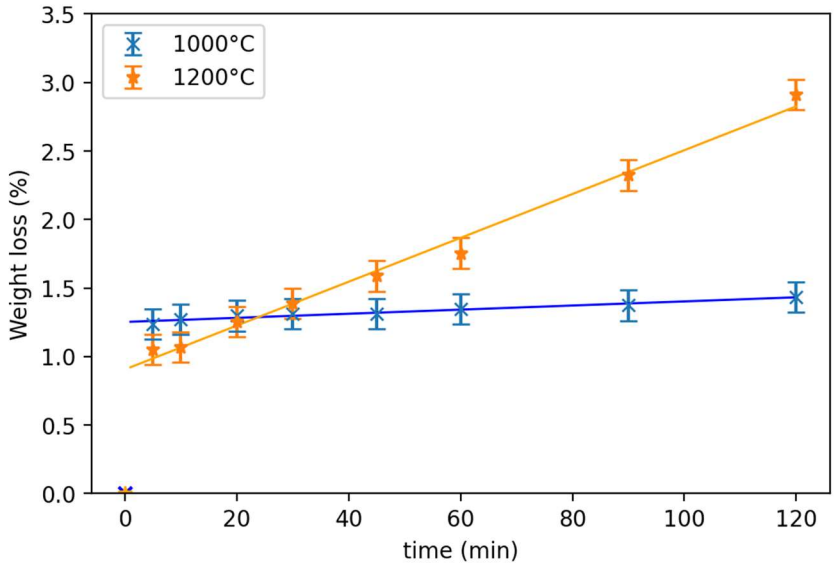

Figure 2 : Gravimetric analysis of aluminum metaphosphate.

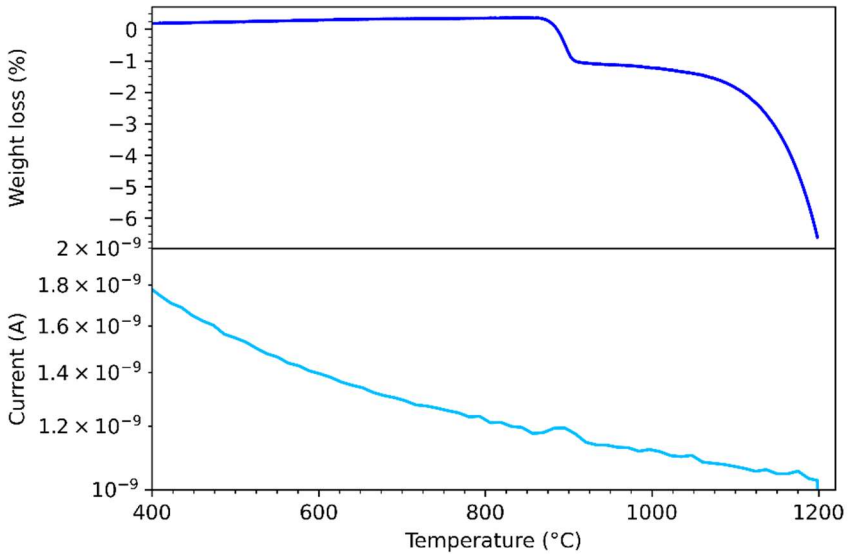

Figure 3 : Thermogravimetric analysis (top) and MS detection of H_2O (m=18) (bottom) of aluminum metaphosphate.

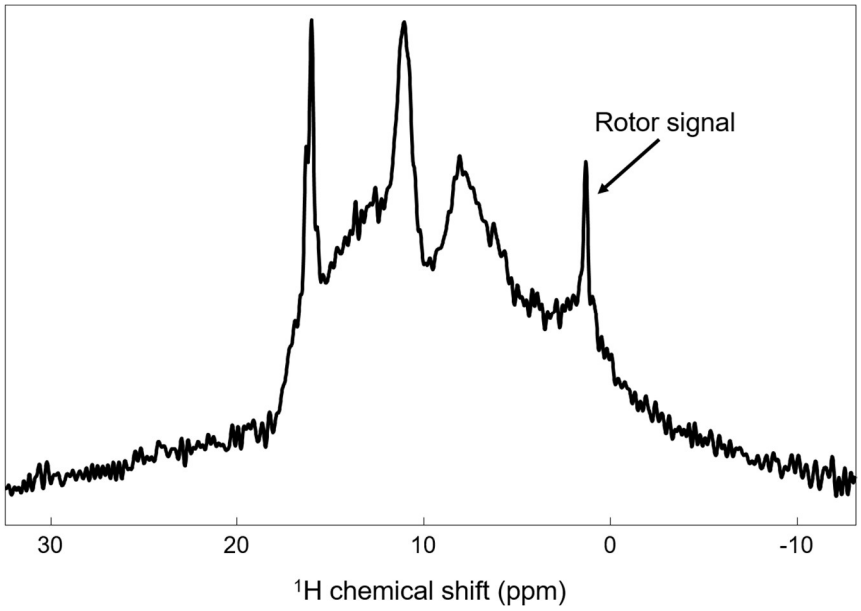

Figure 4 : ^{1}H MAS NMR spectrum of aluminum metaphosphate.

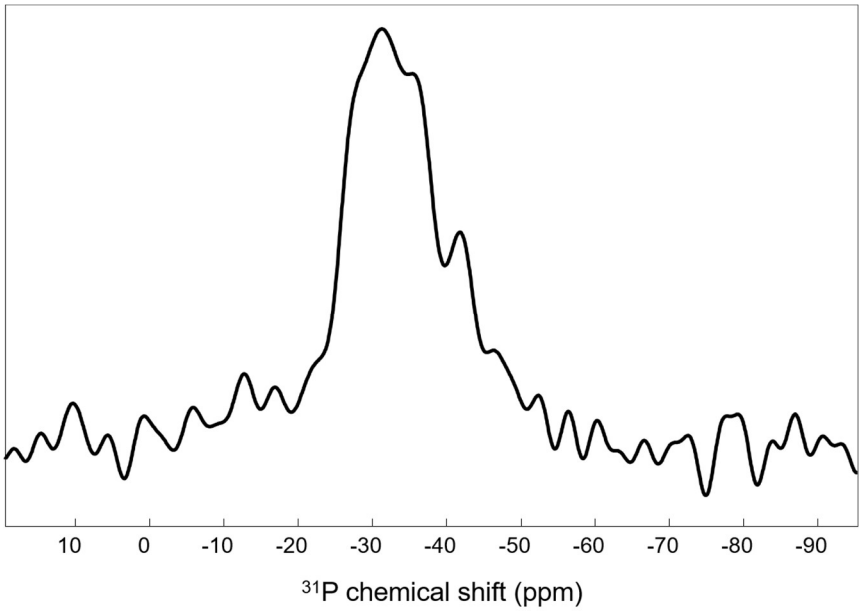

Figure 5 : ^{31}P{^{1}H} CP MAS NMR spectrum of aluminum metaphosphate

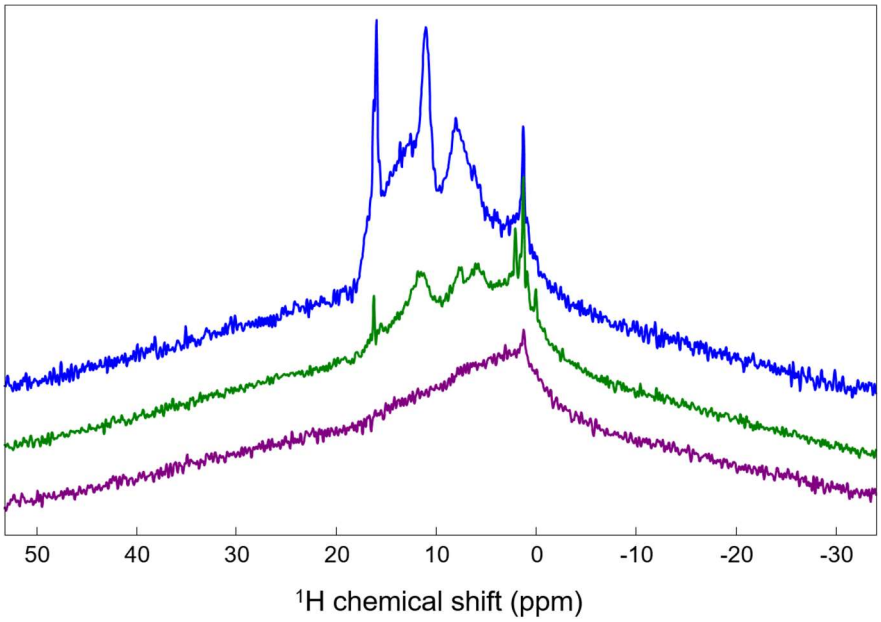

Figure 6 : ^{1}H MAS NMR spectra of aluminum metaphosphate, as prepared (blue), after 2h at 1000°C (green) and 2h and 1200°C (purple)

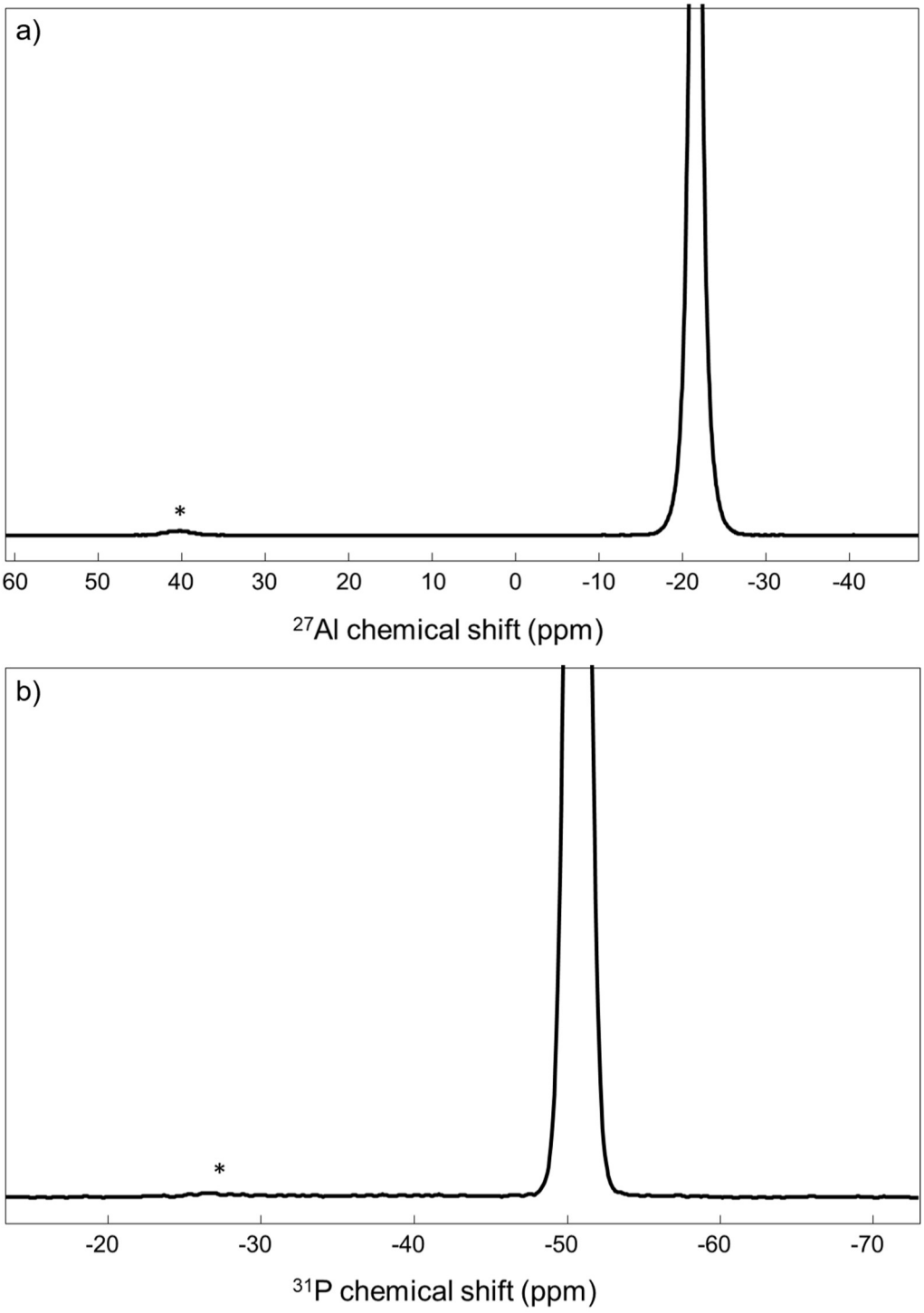

Figure 7 : ^{27}Al (a) and ^{31}P (b) MAS NMR spectra of aluminum metaphosphate after 2h at 1200°C.

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