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More insight in the structure of silicophosphate gels by ^{31}P – ^{29}Si CP MAS multidimensional experiments and ^1H – ^{31}P – ^{29}Si triple resonance experiments

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Abstract

Solid-state ^{29}Si , ^{31}P MAS and CP MAS NMR and X-ray powder diffraction have been used to study phosphosilicate gels of molar composition ($\text{TEOS}/\text{H}_3\text{PO}_4 = 1$) treated under various temperature conditions. It was found that the gel treated at 100 °C for 30 h had a structure consisting of a silica matrix including isolated molecules of phosphorous acid. In contrast, cross condensation (leading to the formation of Si–O–P bonds) was observed when the gel was treated at 136 °C for 6 days. Evidence for the formation of Si–O–P bonds was provided first by XRD, which showed the formation of the crystalline phosphosilicate phases $\text{Si}_5\text{O}(\text{PO}_4)_6$ and $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, and then by the use of two-dimensional (2D) NMR techniques: ^{31}P – ^{29}Si heteronuclear correlation (HETCOR) experiments, based on cross polarization transfer. Very few data concerning this type of experiments are available in the literature: therefore, CP dynamics was carefully studied under MAS. **To cite this article:** C. Coelho et al., C. R. Chimie 9 (2006).

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Résumé

Des analyses en RMN ^{29}Si , ^{31}P MAS à l'état solide ainsi qu'en diffraction des rayons X sur poudre ont été utilisées pour étudier des gels de phosphosilicates obtenus à partir de mélanges équimolaires de TEOS/ H_3PO_4 et traités sous différentes conditions de température. Dans le cas d'un gel séché à 100 °C pendant 30 h, le spectre RMN ^{31}P MAS montre un signal caractéristique de l'acide phosphorique piégé dans un réseau de silice amorphe. En revanche, le gel traité à 136 °C pendant six jours présente un réarrangement structural différent (phases cristallines $\text{Si}_5\text{O}(\text{PO}_4)_6$ et $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$). L'utilisation de techniques RMN 2D (expériences ^{31}P – ^{29}Si HECTOR) basées sur le transfert de polarisation croisée a permis de corréler les différents sites ^{31}P et ^{29}Si . **Pour citer cet article :** C. Coelho et al., C. R. Chimie 9 (2006).

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Mots clés : RMN solide ; Phosphosilicates ; Polarisation croisée $^{31}\text{P}/^{29}\text{Si}$; Expériences bidimensionnelles

1. Introduction

In the last few years, phosphosilicate gels have attracted much attention and many works have been carried out. Indeed, these materials present interesting technological and structural properties suitable for fast proton conductor [1–3] and for applications in biomaterials and catalysts [4].

A route to synthesize this class of materials is the use of the sol–gel process allowing the preparation of inorganic oxides through hydrolysis and condensation of the precursors in solution at room temperature [5].

More recently, D'Apuzzo et al. [3] have reported the synthesis by sol–gel process of phosphosilicate gels having the molar composition 10 P_2O_5 ·90 SiO_2 (10P) and 30 P_2O_5 ·70 SiO_2 (30P) using POCl_3 as phosphorous precursor and TEOS ($\text{Si}(\text{OCH}_2\text{CH}_3)_4$) as silica source. They have studied their structures by a detailed solid-state ^{29}Si , ^{31}P and ^1H SPE MAS NMR experiments for different heat treatments. It was found that the formation of Si–O–P bonds occurred for the (30P) gel and after heat treatment at 300 °C [6].

Moreover, the authors were interested in the spatial connectivities of ^{31}P Q_n resonances in the phosphosilicate gels. They established, by using two-dimensional NMR ^{31}P magnetization exchange experiments, that the (10P) gel contained distinct domains with different phosphorous connectivities [7].

In this paper, we report the synthesis and characterization of phosphosilicate gels obtained by a sol–gel method using TEOS and H_3PO_4 as precursors. The aim of this paper is to study the influence of the heat treatments in the structure of the material and above all, to show evidence for the formation of Si–O–P bonds within the matrix through a precise investigation by solid state NMR.

The emphasis will be made on heteronuclear experiments involving ^{29}Si and ^{31}P nuclei. CP cross polarization process between ^{31}P and ^{29}Si nuclei will be clearly demonstrated, leading to the set up of 2D ^{31}P – ^{29}Si CP experiments. Such experiments will be suitable for the direct evidence of spatial connectivities between nuclei.

2. Experimental

2.1. Sample preparation

The compounds were prepared by sol–gel process from tetraethoxysilane (TEOS, purchased from Fluka) and H_3PO_4 (orthophosphoric acid 85%, 33.0 mmol of H_3PO_4 purchased from Aldrich).

TEOS was diluted in ethanol, and then distilled water was added to the solution. The molar composition of TEOS/EtOH/ H_2O was 1:4:3 [8].

After a prehydrolyze stage (1 h) at room temperature, 1 equiv of H_3PO_4 was added to the mixture. The reaction is slightly exothermic.

The wet gels were obtained after 2 days at room temperature and after drying 2 weeks in air, the dry gels (pulverized into powders) were heated to 136 °C during 6 days (SiP-136) and to 100 °C for 30 h (SiP-100). High temperature phases heated at 500 °C (SiP-500) and at 800 °C (SiP-800) during 2 h were also investigated.

2.2. Characterization of phosphosilicate gels

XRD patterns were obtained with a Phillips diffractometer working with Cu $K\alpha$ radiation: $\lambda = 1.5418 \text{ \AA}$, in step mode between 5° and 75° of 2θ degrees and by using a step size of 0.04° and 4 s per step for the compounds heated at 136 °C.

Solid-state NMR experiments were carried out at $B_0 = 7 \text{ T}$, with $\nu_0(^{31}\text{P}) = 121.51 \text{ MHz}$ and $\nu_0(^{29}\text{Si}) = 59.63 \text{ MHz}$ (AVANCE 300 Bruker spectrometer). 7- and 4-mm Bruker probes were used for ^{29}Si single pulse experiment (SPE) spectra of SiP-136 and SiP-100, respectively. A 4 mm triple resonance Bruker probe was used for ^{31}P MAS, ^1H SPE MAS, the different experiments of cross polarization and for the 2D heteronuclear correlation (HETCOR) experiment.

Samples were spun at the magic angle using ZrO_2 rotors (5–15 kHz).

^{31}P NMR chemical shift are referenced to 85% H_3PO_4 and to TMS for ^{29}Si and ^1H .

Among the different NMR techniques used to characterize the phosphosilicate gels, we have in particular:

- the double cross polarization magic angle spinning (CP MAS) experiment, whose pulse sequence is shown in Fig. 1. As we can see, ^1H irradiation was used for relaxation purposes because of its shorter T_1 (when compared to ^{31}P), followed by a double $^1\text{H} \rightarrow ^{31}\text{P} \rightarrow ^{29}\text{Si}$ transfer using a ramp, namely, a variable amplitude cross polarization (VACP) [9] sequence during the contact time (t_{CP}), in order to broaden the Hartmann–Hahn profile. Then, proton CW decoupling was applied during the ^{29}Si acquisition;
- the 2D CP MAS HETCOR experiment, whose pulse sequence is depicted in Fig. 2. This technique consists of an extension of the basic 1D CP.

Because of the long $T_1(^{31}\text{P})$ a presaturation on the ^{31}P channel was applied, followed by a relaxation delay (RD) optimized to be the better compromise between the effective ^{31}P magnetization and the spectrometer time. After the time evolution in t_1 , a cross polarization $^{31}\text{P} \rightarrow ^{29}\text{Si}$ was performed using a VACP sequence dur-

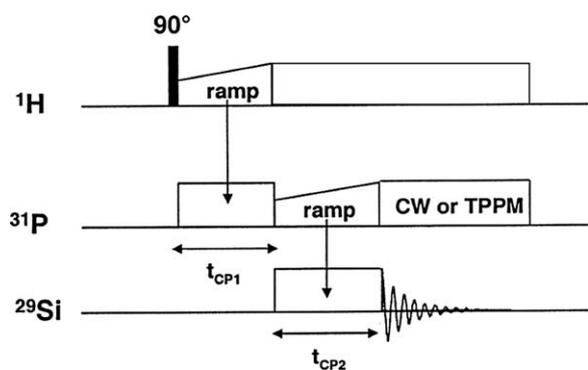


Fig. 1. CP $^1\text{H} \rightarrow ^{31}\text{P} \rightarrow ^{29}\text{Si}$ pulse sequence.

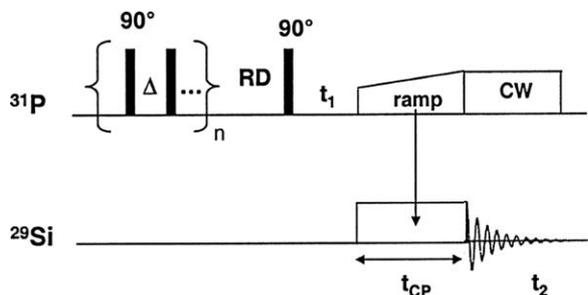


Fig. 2. $^{31}\text{P} \rightarrow ^{29}\text{Si}$ HETCOR pulse sequence.

ing the contact time. A CW ^{31}P decoupling was used then during the ^{29}Si acquisition.

3. Results and discussion

3.1. X-ray diffraction

Fig. 3A shows the XRD patterns of phosphosilicate gels heated at different temperatures, and Fig. 3B gives the attribution of the different peaks.

In the case of SiP-100, just a large peak corresponding to amorphous silica is observed.

However, after a heat treatment at 136 °C, several peaks appear clearly in the diagram, assigned to $\text{Si}_5\text{O}(\text{PO}_4)_6$ [10] [11] and $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ phases [12].

At higher temperature, a unique phase ($\text{Si}_5\text{O}(\text{PO}_4)_6$) is observed [11].

It seems from this X-ray powder diffraction study that the crystallization occurs between 100 and 136 °C.

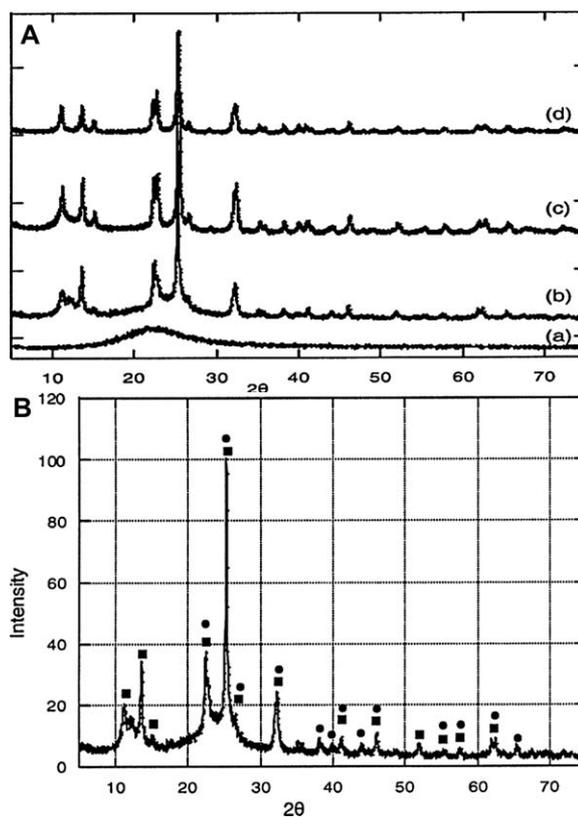


Fig. 3. (A) XRD patterns of the gels heated at different temperatures: (a) SiP-100, (b) SiP-136, (c) SiP-500, (d) SiP-800. (B) XRD patterns of SiP-136: ■ $\text{Si}_5\text{O}(\text{PO}_4)_6$ phase; ● $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ phase.

Such a low temperature was unexpected [6], showing the crucial role of the precursor used in the various synthesis.

All samples were further investigated by MAS, simple and double CP MAS experiments (^{29}Si , ^{31}P , ^1H).

3.2. Magic-angle spinning nuclear magnetic resonance spectroscopy

3.2.1. ^1H MAS NMR

As we can see in Fig. 4, the ^1H MAS NMR spectrum of the different gels are comparable. It shows a single resonance at 10.2 ppm assigned in majority to the POH groups, but we do not exclude the possible presence of SiOH groups and water molecules present notably in the $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ phase.

Moreover, it is important to note the absence of resonance between 1 and 4 ppm, suggesting that the hydrolysis and the condensation of ethoxy groups from TEOS have occurred totally.

3.2.2. ^{31}P dec $\{^1\text{H}\}$ and $^1\text{H} \rightarrow ^{31}\text{P}$ CP MAS NMR

For SiP-100 (Fig. 5a, b), we can observe the presence of three resonances at 0 ppm, ~ -10 ppm and ~ -25 ppm attributed, respectively, to Q_0 $\text{O}=\text{P}(\text{OH})_3$, Q_1 $\text{O}=\text{P}(\text{OP}/\text{OSi})(\text{OH})_2$ and Q_2 $\text{O}=\text{P}(\text{OP}/\text{OSi})_2(\text{OH})$ units (Q_1 and Q_2 components are very minor. Their relative intensities are strongly increased by the CP process. Q_0 units are underestimated under CP due to internal mobility) [13].

Now, concerning the SPE ^{31}P dec $\{^1\text{H}\}$ NMR spectra (Fig. 5c) of SiP-136, we can see the presence of several peaks. Besides the peak at 0 ppm corresponding to the orthophosphoric acid H_3PO_4 (Q_0), additional

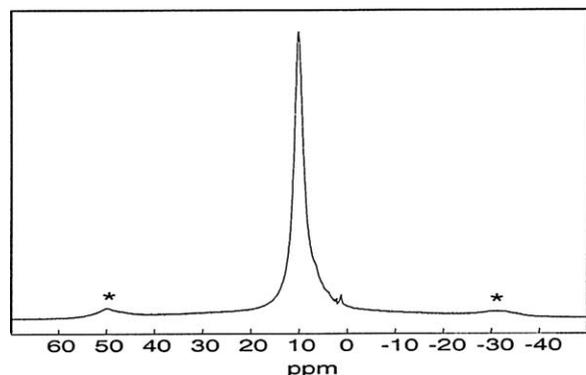


Fig. 4. ^1H MAS NMR spectrum of SiP-136. (\varnothing : 4 mm, RO: 12 kHz, NS: 4, RD = 10 s, 90° (^1H): 2.5 μs).

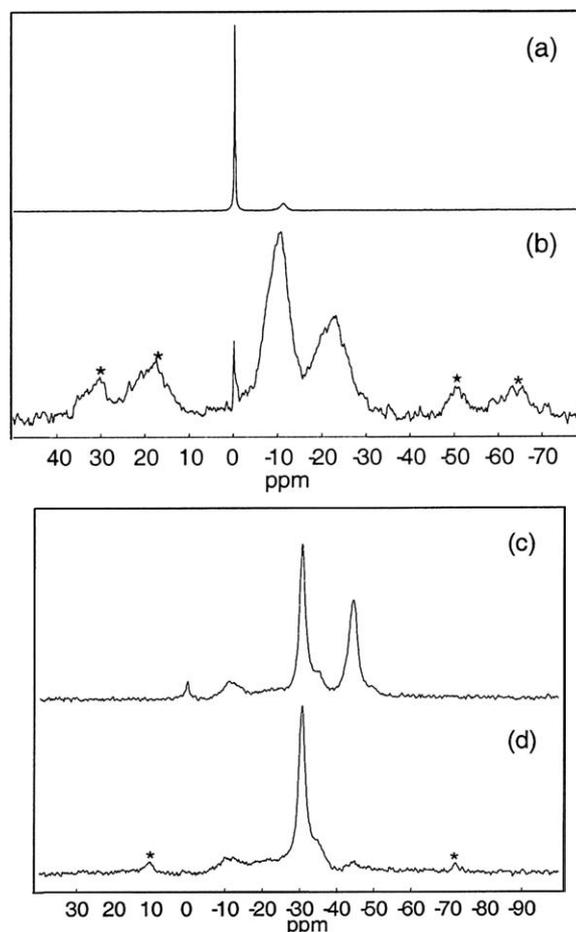


Fig. 5. (a) ^{31}P dec $\{^1\text{H}\}$ MAS NMR spectrum of SiP-100 (\varnothing : 4 mm, RO: 14 kHz, NS: 204, RD = 10 s, 90° (^{31}P): 9.0 μs , CW $\{^1\text{H}\}$ decoupling, LB = 10 Hz). (b) $^1\text{H} \rightarrow ^{31}\text{P}$ CP MAS NMR spectrum of SiP-100 (\varnothing : 4 mm, RO: 5 kHz, NS: 616, RD = 10 s, 90° (^1H): 2.6 μs , $t_{\text{CP}} = 2$ ms, tppm $\{^1\text{H}\}$ decoupling, LB = 50 Hz). (c) ^{31}P dec $\{^1\text{H}\}$ MAS NMR spectrum of SiP-136 (\varnothing : 4 mm, RO: 12 kHz, NS: 44, RD = 10 s, 90° (^{31}P): 9.0 μs , CW $\{^1\text{H}\}$ decoupling, LB = 30 Hz). (d) $^1\text{H} \rightarrow ^{31}\text{P}$ CP MAS NMR spectrum of SiP-136 (\varnothing : 4 mm, RO: 5 kHz, NS: 40, RD = 10 s, 90° (^1H): 3.7 μs , $t_{\text{CP}} = 3$ ms, CW $\{^1\text{H}\}$ decoupling, LB = 30 Hz).

★ Spinning side bands.

resonances are present at -12.0 , -30.9 and -35.0 ppm and assigned to Q_1 $\text{O}=\text{P}(\text{OP}/\text{OSi})(\text{OH})_2$ or Q_2 $\text{O}=\text{P}(\text{OP}/\text{OSi})_2(\text{OH})$ and Q_3 $\text{O}=\text{P}(\text{OP}/\text{OSi})_3$ units, respectively. Moreover, one resonance appears at -44.8 ppm assigned to Q_4 units.

In order to obtain information about the protonation of these phosphorous units, cross polarization $^1\text{H} \rightarrow ^{31}\text{P}$ experiments have been performed as reported in Fig. 5d.

The spectrum shows clearly the disappearance of the peak at 0 ppm suggesting again that the Q_0 species are strongly mobile in the silica matrix.

Concerning the resonance at -30.9 ppm, the intensity of lines permits to affirm that the associated Q_3 units come from a protonated phase, such as $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ [14].

However, the chemical shift of the last resonance (-44.8 ppm), and the corresponding decrease of its intensity under CP experiment, are consistent with the isotropic chemical shift of the $\text{Si}_5\text{O}(\text{PO}_4)_6$ phase [15].

At this stage of the analysis, it will be interesting to identify precisely the nature of the Q_1 and Q_2 units presents in the two samples (P–O–P and/or P–O–Si), by INADEQUATE ^{31}P – ^{31}P experiments or 2D heteronuclear ^{29}Si – ^{31}P experiments focused on these species.

3.2.3. ^{29}Si MAS, ^1H → ^{29}Si CP MAS, ^{31}P → ^{29}Si CP MAS, ^1H → ^{31}P → ^{29}Si CP MAS NMR

The Fig. 6 shows the ^1H → ^{29}Si CP MAS NMR spectrum of SiP-100. This spectrum shows the presence of Q_3 $\text{Si}(\text{OSi})_3(\text{OH})$ and Q_4 (SiO_4) units and is characteristic for condensed silica gels.

SiP-136 was investigated by ^1H → ^{29}Si , ^{31}P → ^{29}Si CP experiments, as well by ^1H → ^{31}P → ^{29}Si double CP experiments (Fig. 7) (the double CP pulse experiment is derived from the sequence depicted in Fig. 1, $\{^1\text{H}\}$ decoupling was suppressed and $\{^{31}\text{P}\}$ decoupling was applied).

According to the different spectra shown in Fig. 7 and to the literature, the resonances at -120.5 ,

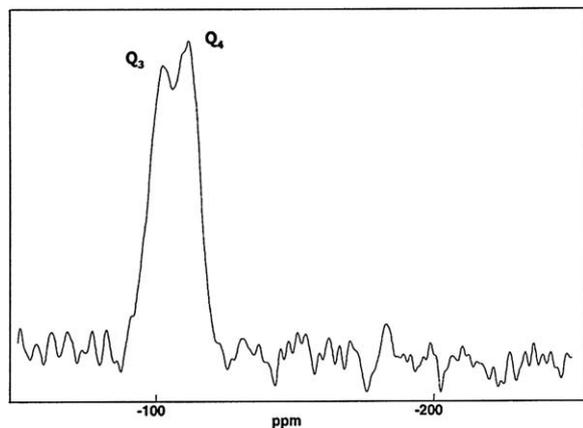


Fig. 6. ^1H → ^{29}Si CP MAS NMR spectrum of SiP-100 (\varnothing : 4 mm, RO: 5 kHz, NS: 5152, RD = 10 s, 90° (^1H): 2.3 μs , t_{CP} = 10 ms, tppm $\{^1\text{H}\}$ decoupling, LB = 100 Hz).

-214.5 ppm and the shoulder at -217.0 ppm are assigned to the four and sixfold coordinated silicon atoms present in the $\text{Si}_5\text{O}(\text{PO}_4)_6$ phase [15].

The narrow peak at -210.8 ppm is assigned to the sixfold coordinated silicons in the $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ phase [14].

Thanks to the ^{29}Si SPE MAS spectrum (Fig. 7a), we can note also the presence of a broad resonance at ~ -110 ppm attributed to amorphous silica (Q_4 units), not visible in the XRD patterns.

The ^1H → ^{29}Si CP MAS experiment (Fig. 7b) is able to discriminate the two phases $\text{Si}_5\text{O}(\text{PO}_4)_6$ and $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ by their protonation state. Besides, we have willfully used a long contact time (t_{CP} = 40 ms), that is why the resonance corresponding to the amorphous silica was not detected.

The ^{31}P → ^{29}Si CP MAS experiment (Fig. 7c) shows clearly the formation of Si–O–P bonds in the phosphosilicate gel SiP-136, by selecting the resonances of both crystalline phases $\text{Si}_5\text{O}(\text{PO}_4)_6$ and $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. In the Fig. 7d, the ^1H → ^{31}P → ^{29}Si CP MAS experiment overestimates the $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ resonance as expected.

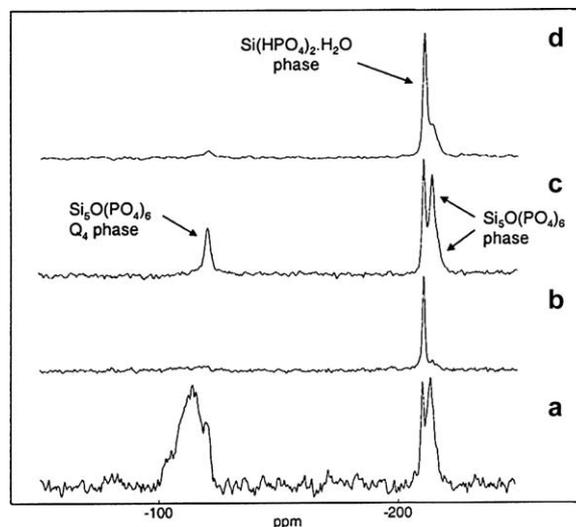


Fig. 7. NMR spectra of SiP-136. (a) ^{29}Si MAS (\varnothing : 7 mm, RO: 4 kHz, NS: 481, RD = 120 s, 90° (^{29}Si): 5.6 μs , LB = 41 Hz). (b) ^1H → ^{29}Si CP MAS (\varnothing : 4 mm, RO: 5 kHz, NS: 520, RD = 10 s, 90° (^1H): 5.4 μs , t_{CP} = 40 ms, CW $\{^1\text{H}\}$ decoupling, LB = 30 Hz). (c) ^{31}P → ^{29}Si CP MAS (\varnothing : 4 mm, RO: 5 kHz, NS: 1680, RD = 30 s, 90° (^{31}P): 5.8 μs , t_{CP} = 40 ms, LB = 40 Hz). (d) ^1H → ^{31}P → ^{29}Si CP MAS (\varnothing : 4 mm, RO: 5 kHz, NS: 2880, RD = 10 s, 90° (^1H): 3.7 μs , t_{CP1} = 3 ms, t_{CP2} = 40 ms, CW $\{^{31}\text{P}\}$ decoupling, LB = 60 Hz).

3.2.4. 2D ^{31}P – ^{29}Si HETCOR

In order to deepen this study, we have performed a two-dimensional ^{31}P – ^{29}Si HETCOR experiment, based on cross polarization, through dipolar coupling (as presented in Fig. 8). The pulse sequence is presented in Fig. 2.

^{29}Si resonances located at $\delta = -120.5$, -214.5 and -217.0 ppm are clearly related to a unique ^{31}P resonance located at $\delta = -44.8$ ppm. The three correlation correspond indeed to the $\text{Si}_5(\text{PO}_4)_6$ crystalline phase.

One more correlation is observed at $\delta(^{29}\text{Si}) = -210.8$ ppm and $\delta(^{31}\text{P}) = -30.9$ ppm: it is definitely assigned to the $\text{Si}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ phase.

These results show that 2D heteronuclear experiments can be safely used for the characterization of complex mixtures of phosphosilicates phases. It can be noticed that no correlation is observed at $\delta(^{31}\text{P}) = -12.0$ ppm not shown above. It tends to prove that this resonance can not be assigned to Si–O–P bonds.

However, the S/N ratio of the 2D experiment seems not sufficient for definite conclusions.

4. Conclusion

In this work, we have underlined the influence of the heat treatment in the structure of the silicophos-

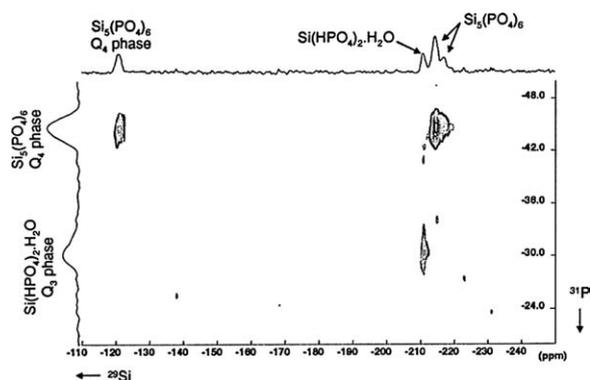


Fig. 8. 2D ^{31}P – ^{29}Si (HETCOR) NMR map of SiP-136 (\varnothing : 4 mm, RO: 5 kHz, NS: 64 for each t_1 increment, $\Delta = 30$ ms, $n = 20$, RD: 60 s, $90^\circ(^{31}\text{P})$: 5.8 μs , $t_{\text{CP}} = 40$ ms, CW $\{^{31}\text{P}\}$ decoupling, 64 h, LB = 40 Hz in F2 and F1).

phates gels. It was found by XRD and by a detailed analysis by solid-state ^{29}Si and ^{31}P NMR that the gel treated at 100°C for 30 h had a structure consisting of a silica matrix including isolated molecules of phosphorous acid. The heat treatment at 136°C permits the formation of Si–O–P bonds in the gel, evidenced by the 2D ^{31}P – ^{29}Si CP MAS NMR experiments.

At present, it will be interesting both to go further into the characterization of the Si–O–P bonds, by doing a solid-state NMR analysis through the J -coupling, to prove unambiguously the chemical bonding between Si and P atoms in the gel state and to perform ^{31}P – ^{31}P INADEQUATE experiments and 2D heteronuclear $^{29}\text{Si}/^{31}\text{P}$ experiments in order to identify the chemical nature of the Q_1 and Q_2 units. Works are in progress in both directions.

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