

Preparation and properties of silica hybrid gels containing phytic acid

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Silica-phosphate mixed gels have been prepared by the sol-gel process from tetramethoxysilane and phytic acid (IP₆H₁₂). They contain inositol phosphate ester units anchored by covalent P-O-X bonds (X=P or Si) as isolated polyphytate clusters either embedded or bound in the amorphous network. ³¹P NMR of the liquid phases at low temperature was used to monitor the initial steps of hydrolysis-condensation reactions at the sol stage. Dried gels have been characterized by ¹³C, ²⁹Si and ³¹P MAS NMR, powder X-ray diffraction and FTIR. The ability of these gels to sequester metallic ions, such as La³⁺ and Zn²⁺, on the open phosphate sites has been investigated. The resulting samples undergo structural modifications during the heat treatment which leads to the formation of silica-lanthanum phosphate and silica-zinc pyrophosphate mixtures. The specific influence of the inserted cation on the structure of the final silica-phosphate obtained at 600 and 900 °C is discussed.

1 Introduction

In recent years, the study of phosphate-containing silica, in some instances with inserted transition metals or rare-earth (lanthanide) cations, has attracted much attention. Physical properties of these solids (optical, conducting, luminescence) have led to many applications in the fields of optical fibres, surface coatings, ceramic filters and many more.¹⁻⁶

Among different preparation methods of phosphosilicate glasses, examples include high temperature procedures based on melting of different oxides⁷⁻⁹ or the use of sol-gel chemistry in which metallic alkoxides [M(OR)₄] are reacted with phosphoric acid (H₃PO₄) or alkylphosphates [PO(OH)_{3-x}(OR)_x, R=CH₃, C₂H₅,...].¹⁰⁻¹² More recently, phosphate ceramics have been synthesized using the sol-gel route by direct reaction of anhydrous P₂O₅ with metallic alkoxides.¹³

myo-Inositol hexakisphosphoric acid (IP₆H₁₂, phytic acid), with twelve axial protons on six phosphate ester groups, appears in aqueous solution in either of two conformations: axial or equatorial (Fig. 1) as a result of intramolecular hydrogen bonding between phosphate groups which leads to stabilisation of the equatorial form up to pH 10 and of the axial form at higher pH values.¹⁴ Ionisation constants reported by Brigando *et al.*¹⁴ span a remarkably large range (0 < pK_a < 12). The ability of this multifunctional ligand to complex metal

cations in acidic media^{15,16} is known to be stronger than that of phosphoric acid or of its alkyl derivatives. In the aim to produce a material for sequestering metallic cations and particularly heavy cations which are water polluting, we use phytic acid as the precursor of phosphate sites for the preparation of phosphosilicate gels by the sol-gel route. Because of its structure, phytic acid may be a good catalyst for the hydrolysis of alkoxy silanes and a condensation centre for the subsequent gel-growth. The low temperature maintained during the sol-gel process preserves the organic structure of the phytic acid. As opposed to the silica phosphate gels formed from phosphoric acid or P₂O₅, phosphate groups are organized in space in a specific network induced by the structure of the phytic acid. In this work, we first report on the sol-gel synthesis of a mixed silica-phosphate material using phytic acid as precursor and on the characterization of the obtained gel. Then, we describe its ability to sequester metallic cations (Zn²⁺ and La³⁺) on the phosphate anionic groups which are distributed in the silica network. Zn²⁺ and La³⁺ have been chosen as examples of diamagnetic and redox free cations suitable for NMR experiments in our experimental conditions and as good models for heavy polluting metals.

2 Experimental

2.1 Preparation of phosphosilicate gels

Reactants. Commercial grade tetramethoxysilane (TMOS) (Fluka), and hydrated sodium phytate (IP₆Na₁₂·30H₂O, Aldrich) were used without further purification. Phytic acid solutions were prepared from sodium phytate by ion exchange using a Dowex 50WX4 resin according to a reported method.¹⁴

Solution studies. In order to study the first stages of the condensation reaction between IP₆ and TMOS in solution, the evolution of the sol was followed by ³¹P NMR spectroscopy. Studied sols were prepared at 0 °C in order to slow down the reaction, initiated by mixing 1 ml IP₆ solution adjusted at 20 °C

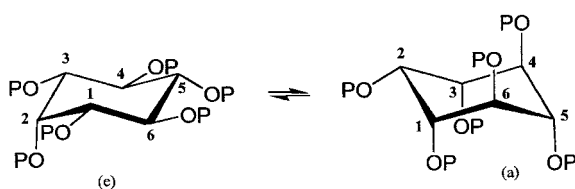


Fig. 1 Equatorial (e) and axial (a) conformations of phytic acid (IP₆). P = -PO₃H₂, -PO₃H⁻ or -PO₃²⁻ depending on pH. The numbering corresponds to cyclohexyl carbons bearing phosphate groups. Each phosphorus atom is labelled with the same number as the carbon to which it is linked.

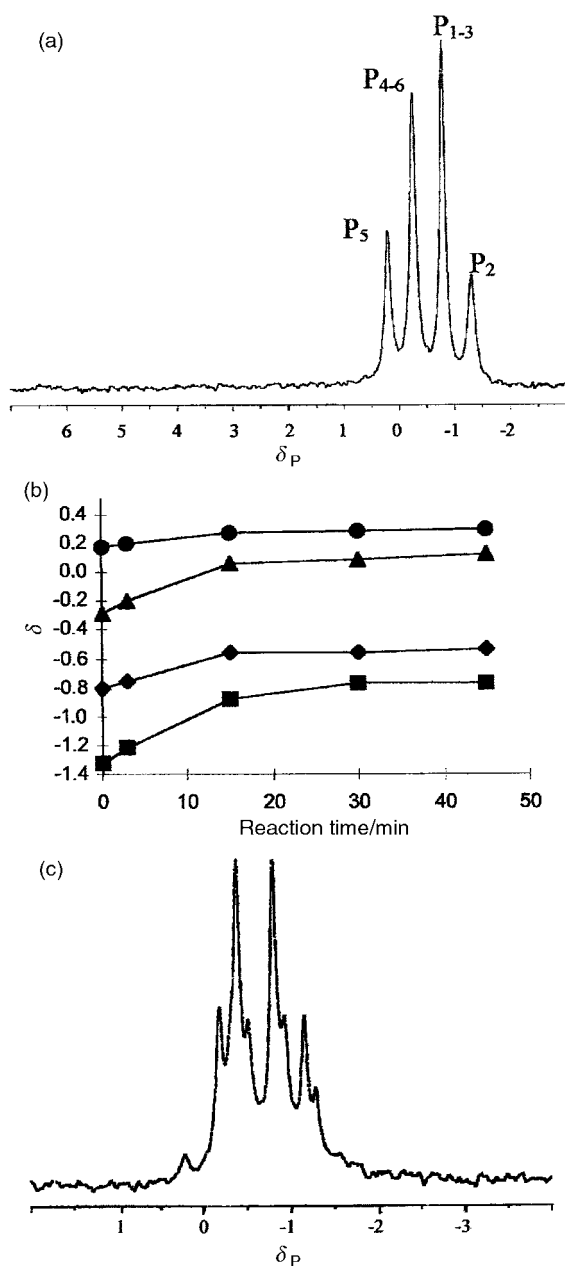


Fig. 2 ^{31}P solution NMR spectra of IP₆/TMOS showing evolution of the sol. (a) Starting IP₆ solution (pH=3), (b) variation of the chemical shifts of each type of phosphorus with the reaction time [P_{1,3} (◆), P₂ (■), P_{4,6} (▲), P₅ (●)] and (c) ^{31}P solution NMR spectra of IP₆ in the organic (TMOS) phase after a very short reaction time (1 min).

to pH=3 and 3 ml TMOS (P/Si=0.05; H₂O/TMOS=2.5). ^{31}P NMR spectra were recorded at 15 min intervals (Fig. 2). Aqueous IP₆ is not miscible with TMOS so that the reaction starts at the interface. As the reaction proceeds, enough methanol is released to homogenize the mixture. In spite of its low solubility, no precipitation of IP₆ was observed.

In order to study the distribution of IP₆ between the two phases, at the very beginning of the process, a separate sample was adjusted to pH=1 to further slow down the gelation process. Then TMOS was added in the same proportion as in the first experiment. After stirring for 1 min, the mixture was allowed to settle for 10 s at 0 °C. The aqueous and organic phases were then decanted off and ^{31}P NMR spectra were recorded at -5 °C. Under such conditions, the solution does not change, as revealed by the constancy of spectra recorded after a variety of times of reaction.

Study of the solid phases. The aqueous phytic acid solution was 0.8 M and the pH was adjusted to 0.3. 30 ml of this IP₆ solution was mixed at 0 °C with 10 ml of TMOS and vigorously stirred for 10 min at 0 °C, then left at room temperature under mild stirring. The gelation time was 40–50 min and the obtained gel was translucent, compact but crumbly. This sample, H₁₀₀, was dried in air at room temperature for 10 h, then at 100 °C for 10 h, and then powdered and dried again at 100 °C for 5 h (P/Si=0.21). After ageing for a week in a desiccator, sample H₁₀₀ was heated in a furnace in air at 600 °C and one sample was heated at 900 °C for 10 h. This gave samples H₆₀₀ (P/Si=0.21) and H₉₀₀ (P/Si=0.032) (P/Si ratios were determined by elemental analysis on the final samples).

Sequestration of metallic cations (Zn²⁺ and Ln³⁺). The sequestering capacity towards metallic ions was investigated in the following manner: 2 g of gel H₁₀₀, maintained in a desiccator for three months was suspended in 20 ml of 0.01 M zinc acetate or lanthanum acetate solution (the pH was adjusted to 2 to avoid precipitation of cations). The dispersion was sonicated for 14 min and allowed to equilibrate for 2 h at room temperature. After filtration the gels were dried at 100 °C. Samples with Zn²⁺ and La³⁺ cations are labelled Zn₁₀₀ (P/Zn=2.6, Si/Zn=85) and La₁₀₀ (P/La=3.4, Si/La=25), respectively. These gels were placed in a furnace maintained at 600 °C for 10 h to yield Zn₆₀₀ (P/Zn=1.5, Si/Zn=4.5) and La₆₀₀ (P/La=3.2, Si/La=6.7), respectively, while heating at 900 °C for 10 h gave samples Zn₉₀₀ (P/Zn=1.5, Si/Zn=4.7) and La₉₀₀ (P/La=2.5, Si/La=4.8), respectively.

2.2 Characterization techniques

A Metrohm E605 pH-meter coupled with a EA120 Metrohm combined glass microelectrode was used for pH measurements. The electrode was calibrated by means of standard buffers. The pH of the samples was adjusted to suitable values with ammonia or HCl.

The solution ^{13}C NMR spectra were recorded on a Bruker HX Fourier-transform NMR spectrometer operating at 400 MHz for ^1H . MeOH was used as an internal reference, with tetramethylsilane as the chemical shift reference (δ_0). The solution state ^{31}P NMR spectra were recorded on a Bruker ARX 200 Fourier-transform NMR spectrometer operating at 81.01 MHz. ^{31}P chemical shifts were measured relative to an external reference (85% H₃PO₄ in water).

MAS NMR spectra were recorded either on a Bruker MSL400 or a MSL300 spectrometer equipped with magic angle spinning. The ^{31}P NMR spectra were obtained at 162.0 MHz using a 5 mm Doty probe, with spinning rates ranging from 9 to 10 kHz. The acquisition parameters were the following: 1 μs pulse width, 3 s recycle delay. The ^{29}Si NMR spectra were recorded at 79.5 MHz using a 7 mm Bruker probe with a spinning rate of 4 kHz. The pulse width and recycle delays were 2 μs and 60 s, respectively. The ^{13}C NMR spectra (75.5 MHz) were recorded using the cross-polarisation sequence with a contact time of 3 ms. SiMe₄ (^{29}Si and ^{13}C) and H₃PO₄ (^{31}P) were used as chemical shift references. The Winfit program¹⁷ was used for the various simulations. FTIR spectra were recorded on a Nicolet 20 SXB spectrometer in the frequency range 400–4000 cm⁻¹ using 0.5–1% w/w of the compound in KBr pellets. XRD measurements were performed using a powder diffractometer (Philips PW1830) operating in the reflection mode with Cu-K α radiation and equipped with a graphite back monochromator. The patterns were analysed using the Philips PC APD 3.5 program package. The effective particle size was calculated applying the Scherrer formula to the line width at half maximum assuming Gaussian profiles for instrumental and experimental broadenings. Elemental analyses were performed at the Service Central d'Analyses du CNRS

(Vernaison, France) by inductive coupling plasma atomic emission spectroscopy.

3 Results and discussion

3.1 Synthesis of phosphosilicate gels

IP₆ as phosphate precursor, has gelation times similar to those of H₃PO₄⁷ which has been shown to be a more reactive precursor than phosphate triesters.¹⁸ For H₃PO₄, the short gelation times, compared to those obtained with triethylphosphate (TEP) are attributed to acid catalysis as well to the presence of phosphate ions which play a significant role in activating cleavage of Si–O–C bonds, through the nucleophilic attack of Si, whereas TEP does not interfere in the hydrolysis and condensation of TEOS.¹⁰ In a series of other experiments at variable P/Si ratios and at constant pH, shorter gelation times were obtained at higher P/Si ratios. With a constant starting P/Si ratio, the gelation time decreases when the pH is raised within the acidic range. From a series of experiments at higher pH, we can conclude that the effect of increasing P/Si is higher than that of decreasing the pH. As a phosphate precursor, IP₆ appears to be at least as reactive as H₃PO₄.

Study of the initial sol formation step in solution. Fig. 2(a) shows the ³¹P spectrum of the starting IP₆ solution at pH = 3. At 1 < pH < 4, IP₆ adopts an equatorial conformation.^{14,19,20} Up to pH = 3.6, the ¹H decoupled ³¹P NMR spectrum shows four peaks, which are very sensitive to pH, with intensity ratio 1 : 2 : 2 : 1 assigned to P5, P4 and P6 (P4,6), P1 and P3 (P1,3), and P2 (see Fig. 1). After mixing with TMOS, ³¹P NMR spectra are recorded at 15 min intervals. As the reaction proceeds, the peaks broaden and shift. P2 and P1,3 on one hand and P5 and P4,6 on the other become closer and fuse in a two-humped unresolved broad peak. The evolution with time of the chemical shifts of each signal is also shown in Fig. 2. All the ³¹P peaks are shifted downfield. It is seen that P2 (the only axial phosphate in the equatorial conformation) and P4,6 peaks undergo similar behavior and undergo larger variations than P1,3, whereas P5 shows only a very small shift. 15 min after the onset of the reaction, the chemical shifts of P5 and P1,3 remain nearly constant while those of P4,6 and particularly of P2 still move significantly downfield. Brigando *et al.*¹⁴ have shown that all the ³¹P chemical shifts of IP₆ move downfield when the pH is raised, as deprotonation of phosphate groups induces deshielding of the corresponding nuclei. One can relate the observed downshift to deprotonation of aqueous phosphate groups when TMOS approaches IP₆ in the sol during the first step of the reaction. As no signal at δ_p ca. –10 or –20, assignable to P–O–Si or P–O–P bonds⁸ is observed, we conclude that condensation takes place later. (Previous studies of ³¹P NMR in gels indicate that ³¹P isotropic chemical shifts become more negative as the degree of polymerization increases.^{15,18}) Atom P2 which is more exposed to the medium, undergoes the strongest interactions with surrounding TMOS molecules, more so than between P4 and P6 of IP₆ with TMOS. Atom P5 is not affected by the approach of siloxane side arms: either because it is already deprotonated at the start of the reaction or alternatively remains protonated during the process. Atoms P1 and P3 are more sheltered so that the observed variation in chemical shift is intermediate: this could be interpreted as an attenuated interaction with –Si–O–CH₃ groups attached to P2, P4 or P6, or from free TMOS reacting incompletely because of steric hindrance. The lower reactivity of the P5, P1 or P3 groups would leave pendent protonated phosphate groups.

The second experiment monitored by ³¹P NMR was performed in the slowest conditions compatible with the recording of spectra, in order to study the behaviour of IP₆ in the aqueous and organic phases during the initial reaction

steps. The spectrum of the starting IP₆ solution at pH = 1 before mixing is very similar to the spectrum shown in Fig. 2(a) with four peaks assigned to P5, P4,6, P1,3 and P2 with chemical shifts at δ –0.19, –0.39, –0.81 and –1.16, respectively. The slight modifications of the chemical shifts are due to the different pH used.

The spectrum of IP₆ in the aqueous phase after a very short reaction time with TMOS is also similar to the spectrum in Fig. 2(a). The chemical shifts vary slightly, moving downfield for P5, P4,6, P1,3, and P2 to δ –0.13, –0.34 –0.76, and –1.13, respectively. In aqueous medium, some TMOS has migrated and induces the beginning of deprotonation of IP₆.

The spectrum of the organic phase [Fig. 2(b)] exhibits two superimposed spectra, both typical of IP₆. The more intense spectrum is identical to the initial spectrum before mixing, with the same chemical shifts while the less intense spectrum is slightly shifted upfield. This establishes the immediate diffusion of IP₆ into the organic TMOS phase and its presence as early as the first minute, in two or several slightly altered forms of the free molecule. The upfield shift of the less intense spectrum in the TMOS phase confirms the set-up of the interaction between IP₆ and TMOS in the early stage of the condensation process.

3.2 Characterization of phosphosilicate gels

Elemental analysis of the H₁₀₀ gel gives a P/Si molar ratio of 0.21 showing the presence of phosphorus containing species within the silica network, which is X-ray amorphous. Spectroscopic techniques were thus used to obtain structural information.

MAS NMR study. The ¹³C MAS NMR spectra of crystalline IP₆Na₁₂·30H₂O as reference and of gel H₁₀₀ are shown in Fig. 3(a) and (b), respectively. In Fig. 3(a), a signal at δ ca. 73 with a shoulder at lower field is observed and a simulation gives two chemical shifts at δ 73.8 and 67.0, which correspond to the completely deprotonated form of IP₆, according to a ¹³C study¹⁴ in solution. The main signal at δ 73.8 is assigned to C1,3, C4,6 and C5 while the shoulder at δ 67.0 arises from C₂, the only carbon bearing an axial phosphate in the equatorial conformation of IP₆. The relative intensity of these two peaks is also in fairly good agreement with this assumption. In Fig. 3(b), the broad signal at δ 60–85 is assigned to phytic acid. The shoulder at δ 60–70 can be attributed to a modified C₂ carbon such as that found in the deprotonated molecule and confirms the results of the solution ³¹P NMR studies. The main peak at δ 70–85 is not informative about the state of the other five carbons by reference to free solvated IP₆ as their resonances only change from δ 72 to 78 upon titration with a strong base. The peak detected at δ ca. 20 is probably due to

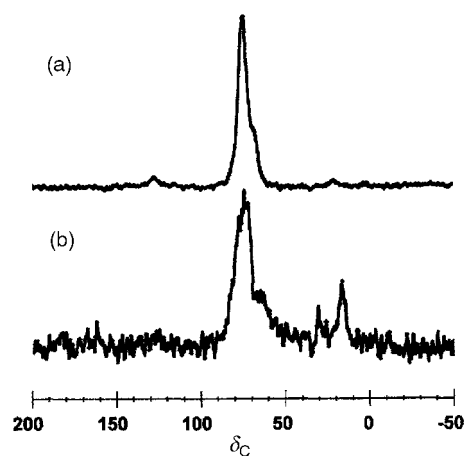


Fig. 3 ¹³C MAS NMR spectra of (a) crystalline IP₆Na₁₂·30H₂O and (b) of the gel H₁₀₀.

alkyl residues resulting from side products of the condensation reactions. In conclusion, gel H₁₀₀ is shown to be comprised of the cyclohexyl unit of IP₆ with the P2 site modified in a manner similar to the deprotonated state.

The ²⁹Si MAS NMR spectrum of the H₁₀₀ sample is quite similar to that of silica gel,¹⁸ with a main peak at δ ca. -110 assigned to a Q⁴ unit with a silicon-centred tetrahedron connected to four other silicon tetrahedra^{22,23} [Si(OSi)₄], and a minor component at δ ca. -102 assigned to a Q³ unit,^{24,25} [Si(OSi)₃(OZ) (Z=H or Me)]. The degree of condensation of the network, which gives the percentage of siloxy groups which have condensed, is close to 90%. The presence of Si(OSi)₂(OP)(OZ)¹⁸ units expected to lie in the range δ -102 to -112 is postulated as these two peaks are less resolved than in the spectrum of pure silica gels. It is remarkable that no peak at δ -120, assignable to Q⁴ units bonded to four phosphate groups, Si(-O-P)₄,¹⁸ is observed in these samples. The dimensions and geometry of IP₆ appear to prevent the approach of four bulky organic molecules around a single silicon atom.

Fig. 4 shows the ³¹P solid state MAS NMR spectra of the samples H₁₀₀ and H₆₀₀ together with the spectrum of crystalline IP₆Na₁₂·30H₂O. The spectrum for IP₆Na₁₂·30H₂O [Fig. 4(a)] shows a characteristic peak at δ 6.9 due to the phosphate side groups, PO₃²⁻ in unprotonated IP₆¹²⁻ molecules. The spectrum of sample H₁₀₀ [Fig. 4(b)] shows a broad signal with three peaks at δ -0.5, -10.6 and -21.0 with relative intensities 27:32:41. As ³¹P chemical shifts in glasses become more negative as the degree of condensation of the network increases,^{18,21} they are assigned as Q⁰, Q¹ and Q² phosphate sites,^{10,11,18,26} respectively, where Qⁿ refers to a phosphate group bound to *n* silicon atoms or to *n* phosphorus atoms through P-O-X bonds.¹⁰ The peak at δ -0.5 is in the range of pure phytic acid ³¹P resonances >CH-O-P=O(OH)₂, (Q⁰), as shown by the solution state study and assigned to free IP₆ molecules, simply adsorbed in the host silica or encapsulated in siloxane cages or to pendent protonated phosphate groups belonging to phytic acid molecules bound to the silica host network only by one or a few of their phosphate groups. It is unlikely that they correspond to free O=P(OH)₃ groups

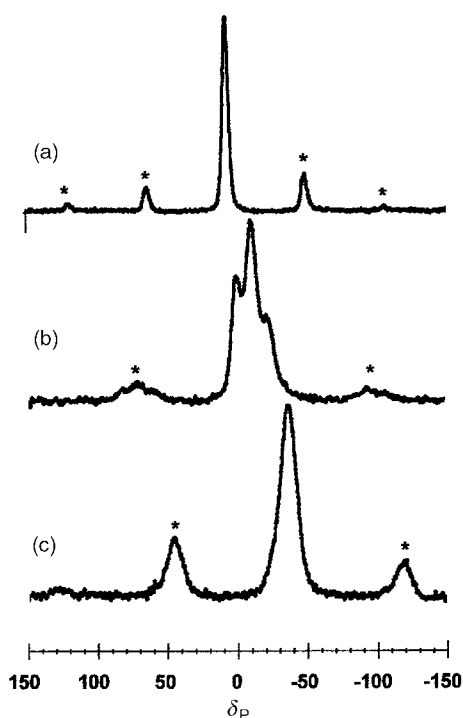


Fig. 4 ³¹P MAS NMR spectra of the prepared silica-IP₆ gels. (a) Crystalline IP₆Na₁₂·30H₂O, (b) sample H₁₀₀ and (c) sample H₆₀₀.

resulting from the partial hydrolysis of a fraction of IP₆.²⁷ Hydrolysis of IP₆ leading to a mixture of inositol and mono-, bis-, tris-, tetrakis- or penta-phosphates is difficult, incomplete and takes place at much higher temperatures under more drastic conditions. The second peak at δ -10.6 is assigned in the literature^{10,11,18} to singly bound Q¹ species: O=P(OH)₂(O-X-O-) or in our case to >CH-O-P=O(OH)(O-X-O-) (X=Si, P). These results show that many phytic acid molecules either are covalently bonded to the silica network or are polymerized, forming oligophytate clusters through P-O-P bonds. Sample H₆₀₀ [Fig. 4(c)] is characterized by a broad, slightly non-symmetric signal with two components at δ -26.7 and -37 with relative intensities of 7 and 93%. They are assigned to Q² and Q³ species, respectively, with a large majority of Q³ sites [O=P(O-X-O)₃]: this is in agreement with the decomposition of the inserted inositol species and a better cross-linking at the phosphorus sites at high temperature. Sample H₉₀₀ shows a very weak ³¹P signal which reveals the loss of phosphorus during heat treatment between 600 and 900 °C.

FTIR study. The spectrum of sample H₁₀₀ [Fig. 5(a)] is very similar to that of a pure silica gel with bands at 467 cm⁻¹ [δ (Si-O-Si)], 569 cm⁻¹ (as a shoulder of the band at 467 cm⁻¹), 799 cm⁻¹ (symmetric O-Si-O stretches), 966 cm⁻¹ (SiO₄ stretch perturbed by the presence of a neighbouring atom other than Si) and 1100 cm⁻¹ (O-Si-O asymmetric stretches). As already reported for phosphosilica gels⁷ these bands are intense and overlap the phosphate bands at ca. 500 cm⁻¹ for PO₄³⁻ and 780 cm⁻¹ for P-O-P bonds, from 900 to 1035 cm⁻¹ for P-O bond stretching and at 1260 cm⁻¹ for P=O double bond stretching.²⁸

In H₆₀₀, [Fig. 5(b)] some differences are of note upon comparison with H₁₀₀. The bands at 467 and 569 cm⁻¹ become a broad band at 486 cm⁻¹. A new double broad band appears between 642 and 678 cm⁻¹ which does not occur in SiO₂, but is described in the literature¹² as a phosphate O=P-O bending vibration, which is very sensitive to the size of bonded cations. The large peak around 1100 cm⁻¹ (Si-O-Si stretching) has a modified profile and covers the band at 966 cm⁻¹. This has been described elsewhere as the result of the transformation of low temperature (300 °C) amorphous phosphosilica coatings to more crystalline phosphosilicas at higher temperature (750 °C).⁵ Shoulders at 1325 and ca. 1200 cm⁻¹ appear on

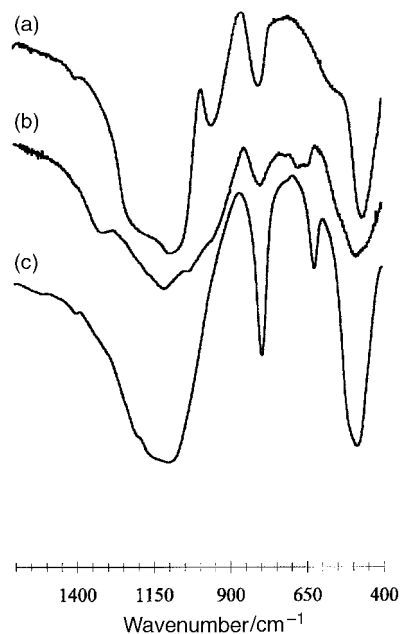


Fig. 5 IR spectra for samples H₁₀₀ (a), H₆₀₀ (b) and H₉₀₀ (c).

the broad Si–O, P–O peak and are likely due to the P=O stretching of phosphates.²⁶ In H₆₀₀ all the bands are broad and in H₉₀₀ [Fig. 5(c)], the same modifications are observed but the bands are sharper, particularly the double broad band, between 642 and 678 cm⁻¹, ascribed to a phosphate O=P–O bending vibration, which is now a single sharp medium band at 620 cm⁻¹.

Proposed structure for the phosphosilicate gel. The ¹³C MAS NMR spectrum confirms the insertion of IP₆ in the dried gel. The ²⁹Si MAS NMR spectrum shows a highly condensed network based on Q³ and Q⁴ sites. This important degree of crosslinking at the silicon atoms, and the large proportion of phosphorus atoms of Q¹ and Q² type show that condensation reactions have taken place on silicon and phosphorus atoms. The ²⁹Si and ³¹P MAS NMR spectra of the gels dried at 100 °C suggest homocondensation P–O–P and Si–O–Si with the formation of silicate and oligophytate species in a heterogeneous gel. However the ²⁹Si MAS NMR spectrum does not exclude the existence of some Si–O–P bonds between discrete silicate and clustered phytate regions. The existence of many Q⁰ phosphates in the gels preserves the sequestering properties of phytic acid in its inserted form. Fig. 6 shows an illustration of a possible structure of the gels formed in our experimental conditions.

3.3 Sequestration of metallic cations (Zn²⁺ and La³⁺)

X-Ray diffraction results. The XRD study shows that all the samples dried at 100 °C are amorphous. At 600 °C, Zn₆₀₀ shows an XRD pattern with peaks characteristic of zinc pyrophosphate, γ-Zn₂P₂O₇ (JCPDS file 43-0488) on top of a broad background typical of an amorphous phase. Sample La₆₀₀ shows a higher crystallinity, with peaks due to lanthanum phosphate, LaPO₄ (JCPDS file 32-0493). The diffraction pattern of La₉₀₀ shows a unique phase of lanthanum phosphate (Fig. 7) while that of Zn₉₀₀ is a superimposition of cristobalite and zinc pyrophosphate, β-Zn₂P₂O₇ (JCPDS file 8-0238). For comparison, the XRD pattern of H₉₀₀ is characteristic of a well crystallized phase of cristobalite: indeed the ³¹P NMR study has suggested that most of the phosphorus atoms have been lost during pyrolysis, being released as P₂O₅. Formation of LaPO₄ and Zn₂P₂O₇ phases shows the efficiency of the H₁₀₀ gel to trap both cations. From XRD data, the dimensions of the metal phosphate particles were estimated from which a size of 60 nm for LaPO₄ was obtained with good reliability as there

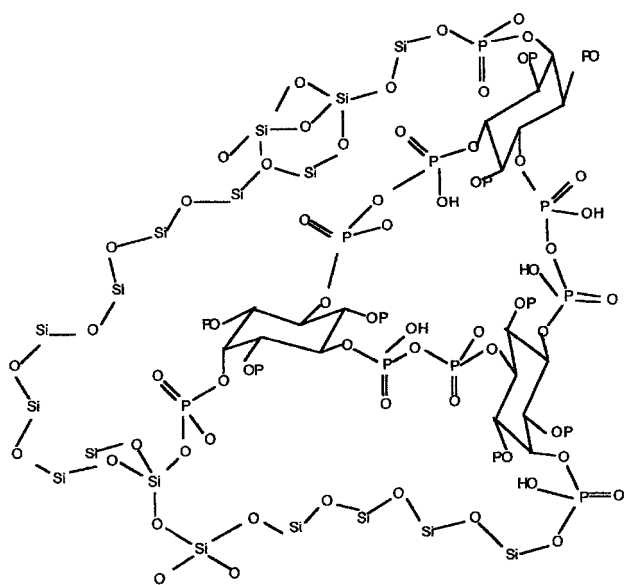


Fig. 6 Illustration of a possible structure of the gel H₁₀₀.

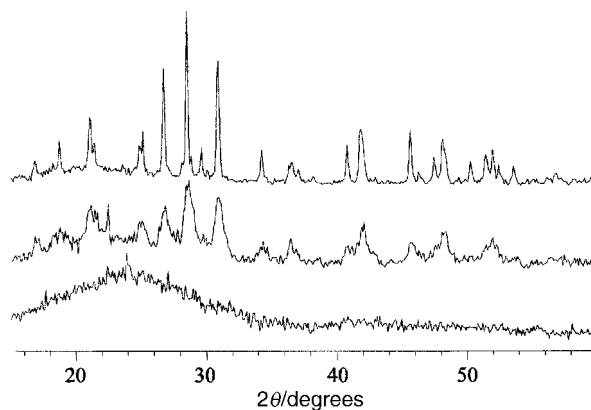


Fig. 7 X-Ray diffraction patterns of gels La₁₀₀ (a), La₆₀₀ (b) and La₉₀₀ (c).

are many lines. For Zn₂P₂O₇ the estimation is more difficult since there are few lines in superimposition with the diffraction pattern of cristobalite; an estimation indicated the dimensions of the particles to be ca. 100 nm.

FTIR spectra. Fig. 8 and 9 show the FTIR spectra of Zn₁₀₀, Zn₆₀₀, Zn₉₀₀ and La₁₀₀, La₆₀₀, La₉₀₀, respectively. Spectra for samples Zn₁₀₀ and La₁₀₀ are very similar to the spectrum of H₁₀₀. A sharp medium sized band around 620 cm⁻¹ undetected in the low temperature dried gels appears in all samples at 600 and 900 °C, even in H₉₀₀. We assign this band to a phosphate O=P–O bending vibration, modified by the presence of P–O–Si and/or P–O–P bonds. The influence of inserted metallic ions is more striking in the annealed samples, with the presence of some new small bands (at 589 cm⁻¹ for Zn₆₀₀; at 580 cm⁻¹ and a shoulder at 535 cm⁻¹ for La₆₀₀, and at 538, 564, 578 cm⁻¹ for La₉₀₀). These bands, which appear very strong in the same region in zinc phytate or phosphate, and lanthanum phytate or phosphate, are ascribed to metal bonded phosphate bending modes O=P–O or O–P–O.^{11,12,29} They are not present in spectra recorded on samples without phytic acid, such as pure SiO₂ gels reacted with a Zn acetate solution and heated to 600 °C (the sequestration of ions by the phosphate groups on IP₆ induces no evident changes in the 100 °C spectra). Metal–phosphate persists and induces important modifications in the bending modes of phosphate groups at 600 °C, when the inositol rings have been decomposed. The similarity of our La₆₀₀ spectrum with the IR spectrum of microcrystalline LaPO₄ gel synthesized by Guo *et al.*¹² in ethanol and dried

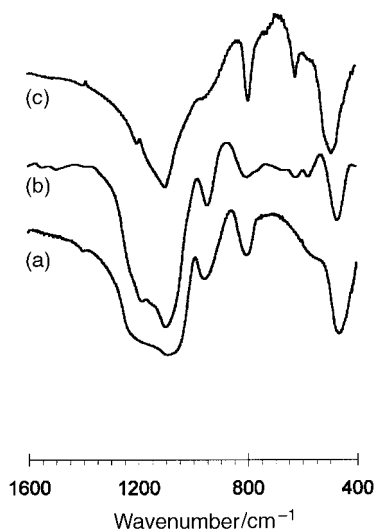


Fig. 8 IR spectra of Zn₁₀₀ (a), Zn₆₀₀ (b) and Zn₉₀₀ (c).

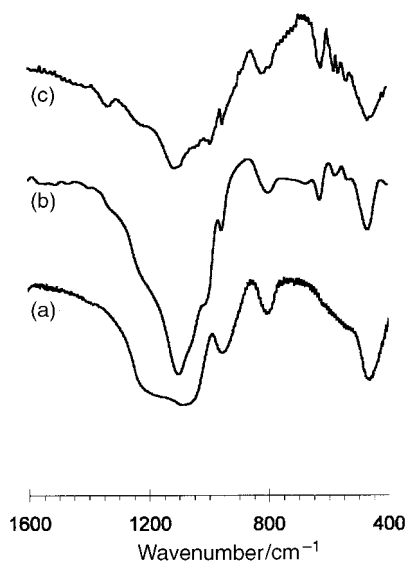


Fig. 9 IR spectra of La₁₀₀ (a), La₆₀₀ (b) and La₉₀₀ (c).

under vacuum is remarkable. By comparison to their published spectrum, only two additional absorptions are present (at 472 and 804 cm^{-1}) which are assigned to O–Si–O bending modes. Subsequent heating to 900 °C modifies the spectra in the region of the metal-dependent vibrations. The band at 589 cm^{-1} is almost absent for Zn₆₀₀ while for La₆₀₀, the bands at 580 and 535 cm^{-1} split into three bands at 538, 564 and 578 cm^{-1} .

MAS NMR study. The ³¹P MAS NMR spectra of Zn₁₀₀, Zn₆₀₀, Zn₉₀₀ and La₁₀₀, La₆₀₀, La₉₀₀ are shown in Fig. 10 and 11, respectively. For Zn₁₀₀ and La₁₀₀, the peaks are broader than those in the annealed compounds and confirm the transformation of amorphous phosphosilicate gels to crystalline phosphosilicates at higher temperature,⁷ as shown by the XRD study. The spectrum of Zn₁₀₀ [Fig. 10(a)] is similar to that of H₁₀₀ [Fig. 4(b)]. By contrast, Zn₆₀₀ presents a clearly different spectrum [Fig. 10(b)]. The Q⁰ peak is reduced and the Q² peak virtually disappears. Peaks ascribed to Q⁰ and Q¹ species become sharper and better resolved with a splitting of the Q¹ peak into two peaks at δ ca. -7 and -10. At 900 °C [Fig. 10(c)], the Q⁰ peak virtually disappears and the peak at δ

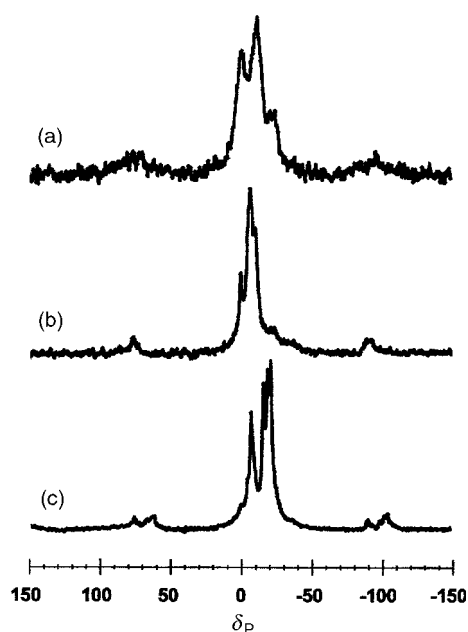


Fig. 10 ³¹P solid state MAS NMR spectra of compounds Zn₁₀₀ (a), Zn₆₀₀ (b) and Zn₉₀₀ (c).

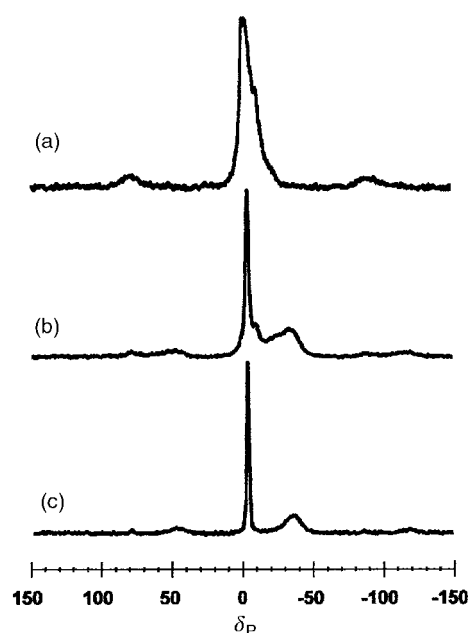


Fig. 11 ³¹P solid state MAS NMR spectra of compounds La₁₀₀ (a), La₆₀₀ (b) and La₉₀₀ (c).

-7 is reduced somewhat. There is no peak at δ ca. -10 but a new group of three peaks appears in the Q² region at δ -16, -19 and -21. It is remarkable that Q² species are present at 100 °C, and disappear at 600 °C probably as a consequence of decomposition of -CH-O-P bonds, as well as some P-O-P bonds. At 900 °C, new signals are observed owing to the formation of zinc pyrophosphate. No Q³ species are detected which suggests that all the P atoms are part of the pyrophosphate phase. The ²⁹Si MAS NMR spectrum of Zn₉₀₀ [Fig. 12(b)] shows a sharp peak at δ -110 similar to that found in H₉₀₀ [Fig. 12(a)] characteristic of crystalline cristobalite in accord with the XRD data.

The final product, Zn₉₀₀, can thus be described as a mixture of crystalline zinc pyrophosphate and cristobalite; the presence of an amorphous phase of phosphosilicate as a minor component can not be excluded, but is not clearly detected in the NMR spectra.

In contrast to the Zn system, the introduction of La³⁺ considerably changes the ³¹P MAS NMR spectrum of the gel [Fig. 11(a)] with the appearance of two broad signals at δ -0.8

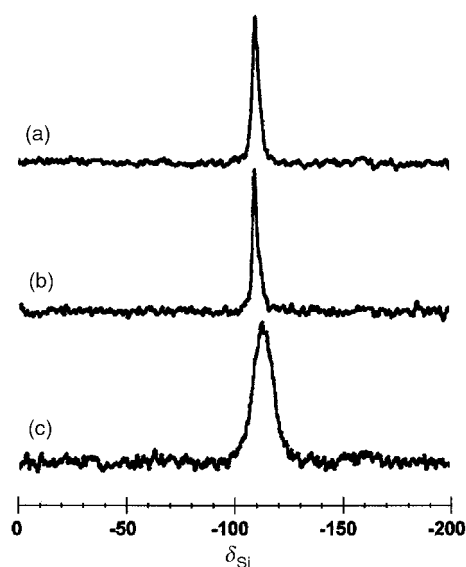


Fig. 12 ²⁹Si MAS NMR spectra of compounds H₉₀₀ (a), Zn₉₀₀ (b) and La₉₀₀ (c).

and -2.9 . At 600°C [Fig. 11(b)] the spectrum is very different from that observed for H_{600} with a sharp peak at $\delta -4.3$ and with a small shoulder at $\delta -10.0$. The peak at $\delta -4.3$ is similar to that observed by Guo *et al.* for LaPO_4 .¹² Additionally, a small asymmetric signal centred at $\delta -33.3$ is still present, similar to that observed for H_{600} and assigned to Q^2 and Q^3 sites. At 900°C , only two peaks remain, a sharp signal at $\delta -4.4$ due to LaPO_4 and a broad signal centred at $\delta -37.8$, due to Q^3 species (a peak at $\delta -38.3$ is reported as clearly characterising a P–O–Si linkage¹³). While the XRD results for La_{900} have revealed the presence of only one crystalline phase, LaPO_4 , the ^{29}Si MAS NMR spectrum [Fig. 12(c)] shows a broad signal centred at $\delta -113$ characteristic of the presence of an amorphous phase. This signal is shifted compared to that for silica suggesting the presence of a phosphosilicate phase in agreement with the ^{31}P NMR results. The final product, La_{900} can thus be described as a mixture of crystalline lanthanum phosphate and a residual amorphous phosphosilicate phase.

From the ^{31}P and ^{29}Si MAS NMR and FTIR spectra, we can conclude that in the starting gels, the La^{2+} cations influence the environment of the phosphate groups of the phytic acid molecules to a greater extent than the Zn^{2+} cations. However, at 600°C , both cations appear bonded to the phosphate groups after decomposition of the organic groups, and crystalline phosphate phases start to crystallize, as shown by XRD.

4 Conclusion

IP_6 appears to be at least as reactive as H_3PO_4 for the preparation of phosphosilicate gels *via* the sol–gel route. The study of the sol-to-gel transformation as monitored by ^{31}P NMR establishes the immediate diffusion of IP_6 into the organic TMOS phase and the early setup of the interaction between IP_6 and TMOS in condensation, this interaction occurring on P2, then on P4 and P6. Atom P5 is not affected by the approach of siloxane, thus leaving a number of free phosphate anions available for cation sequestration.

A solid state ^{13}C MAS NMR study establishes the insertion of the cyclohexyl moieties of IP_6 in the gel network. The absence of direct evidence for the presence of P–O–Si bonds in the gels is in favour of homocondensation reactions with the formation of a highly condensed silica network and oligophytate species in a heterogeneous gel. However, the ^{29}Si MAS NMR spectrum does not exclude the existence of some Si–O–P bonds between discrete silicate and clustered phytate regions. The existence of a large number of Q^0 phosphate species in the gel preserves the sequestering properties of phytic acid in its inserted form. X-Ray diffraction studies indicate the amorphous state of the dried gels and their transformation into cristobalite at 900°C , in accord with the FTIR spectra. A large loss of phosphorus occurs between 600 and 900°C as revealed by elemental analysis.

This gel, in contact with zinc acetate or lanthane acetate solution, can trap zinc or lanthanum cations. XRD, FTIR and MAS NMR (^{31}P and ^{29}Si) studies performed on samples heated to 600 and 900°C , clearly show the formation of zinc and lanthanum phosphate phases. The sequestering property of phytic acid in solution is thus retained in these hybrid gels and could be applied for the treatment of water polluted by heavy metals. This attempt to create hybrid solids able to fix metallic cations under mild conditions and to keep them trapped during drastic thermal treatment is thus successful. The range of temperature between 100 and 250°C under suitable conditions

to retain the organic component should be investigated to study cation rich materials quenched before total migration and condensation takes place. Such materials should display the properties of the cations in the dispersed state, which are not evident by strong interactions in tightly crystalline, high temperature phases: *e.g.* fluorescence, ionic or electronic conduction, magnetic properties. Such microparticulate well formed Zn and La phosphates imbedded in cristobalite (Zn) or in amorphous phosphosilica (La) described here open the way to many more examples of mixtures with other elements.

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