JOURNAL OF
Materials
CHEMISTRY

^{31}P and ^{29}Si NMR study of sol–gel-synthesized phosphate ceramics

Li-Qiong Wang,[*a] **William D. Samuels,**[a] **Gregory J. Exarhos,**[a] **Burtrand I. Lee**[b] **and Zhicheng Cao**[b]

[a] *Dept. of Materials Science, Pacific Northwest National Laboratory, Richland, WA 99352, USA*
[b] *Dept. of Ceramic & Materials Engineering, Clemson University, Clemson, SC 29634, USA*

^{31}P and ^{29}Si solid-state magic angle spinning (MAS) and liquid-state nuclear magnetic resonance (NMR) techniques have been applied to the study of sol–gel-synthesized phosphate ceramic composites. This study emphasizes the chemistry and structural properties for both sols and gels prepared by directly reacting P_2O_5 with tetraethoxysilane (TEOS). This new method of formation of both the sols and gels is a drastic improvement in the retention of phosphorus during the formation of the phosphosilicate gels, and it provides a lower temperature route to six-coordinate silicon. Both ^{31}P and ^{29}Si liquid-state NMR spectra for sols prepared without water showed the presence of P–O–Si bonds. The ^{31}P NMR spectra for sols prepared with water resembled those for the $PO(OH)_x(OR)_{3-x}$ precursors, while ^{29}Si NMR spectra indicated that TEOS had undergone partial hydrolysis and condensation. Hexacoordinated silicon was observed for the first time in gels prepared at low temperature (70 °C). P–Si gels prepared directly by using P_2O_5 were compared with those using other molecular precursors.

Sol–gel synthesis of phosphate ceramics has attracted much attention recently owing to its lower temperature of preparation and mixing of the starting materials on the molecular scale. Phosphate gels prepared *via* different molecular precursors have been studied by many research groups[1–14] for applications including optical fibers, host materials for fast ionic conductors, low thermal expansion materials and bioceramics.

Woignier *et al.*[1] synthesized monolithic aerogels of SiO_2–P_2O_5 and SiO_2–B_2O_3–P_2O_5 using trimethyl phosphate [$PO(OCH_3)_3$] as a precursor, while Livage *et al.*[2] obtained alkyl phosphate [$PO(OH)_x(OR)_{3-x}$] precursors by reacting P_2O_5 with an appropriate alcohol. Szu *et al.*[3] synthesized phosphosilicate gels using trimethyl phosphite, triethyl phosphate, and phosphoric acid. The ^{29}Si and ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of Szu's samples showed that the formation of Si—O—P and P—O—P networks was present for the gels fired at temperature above 200 °C. Kim and Tressler[4] examined the microstructural evolution in phosphosilicate gels prepared by hydrolyzing tetraethoxy silane with H_3PO_4. Both $Si_3(PO_4)_4$ and SiP_2O_7 crystalline phases were identified in the heat-treated phosphosilicate gel containing 56 mol% P_2O_5 at temperatures >300 °C. Tian *et al.*[5] have used ^1H, ^{13}C, and ^{31}P NMR to study the chemistry of the phosphosilicate sol and gel using $PO(OC_2H_5)_3$ as a precursor. They found no P—O—P or P—O—Si bonds in the sol nine hours after the reaction, but these bonds were observed in dried gels. Our previous work[6] reported on the synthesis of phosphate ceramics containing titanium using $PO(OH)_x(OR)_{3-x}$ (prepared from the anhydrous reaction of P_2O_5 with alcohol) and alkoxides of silicon and titanium. Hexacoordinated silicon was observed in the phosphate gels containing silicon and titanium upon firing at temperatures above 520 °C. Our most recent studies[7] have shown that phosphate ceramics could be synthesized using sol–gel techniques through direct reaction of P_2O_5 with tetraethoxysilane (TEOS) or titanium tetraethoxide [$Ti(OEt)_4$]. By using P_2O_5 directly, instead of other available phosphorus precursors, not only is the reaction simplified but also the problem of phosphorus loss upon firing is greatly improved.

NMR is a powerful tool in the structural characterization of reaction intermediates and final products. Although much work has been reported regarding the synthesis of phosphate gels using different precursors, few papers have reported a detailed and systematic study of sol–gel chemistry and structural properties for both sols and gels using NMR spectroscopy. Here both liquid- and solid-state ^{31}P and ^{29}Si NMR have been applied to a detailed study of chemistry and structural properties for both sols and gels prepared by directly mixing P_2O_5 with TEOS. Gels prepared using P_2O_5 directly were compared with those prepared using other molecular precursors. Since the interactions at the molecular level influence the physical and chemical properties of materials, understanding of the sol–gel chemistry at the molecular level is important for the design and synthesis of new materials.

Experimental

Synthesis

Appropriate amounts of P_2O_5 (14.2 g, 100 mmol) and TEOS (44.6 ml, 200 mmol) were mixed in an inert atmosphere glove box. The mixture was stirred and refluxed for 12 h under argon; the mixture appeared milky. A portion of the mixture was removed *via* a syringe for liquid-state NMR analysis. A second portion, approximately 10 ml, was removed and 1 ml of water added and the solution turned clear. The resulting sol was taken as a sample for liquid-state NMR analysis. The molar ratio of silicon to phosphorus was 1 : 1. The homogeneous sols were transferred into Teflon containers before being placed in a convection oven at 70 °C. The gels were aged for 5 d at 70 °C. Aged gels were then oven-dried in containers with loose-fitting covers. Selected dry gels were fired in air at temperatures of 100–900 °C for X-ray diffraction (XRD) and NMR measurements. More detailed procedures for the sample preparation have been reported previously.[6,7]

The appearance of the sols and gels covered in this work is presented in detail in our previous publications.[6,7] The sols initially became milky, which may or may not be due to nanosize particle formation. The spectroscopic evidence points to the formation of Si—O—P bonding. Complete gel formation is accelerated by the addition of predetermined amounts of water to give a clear sol which can be cast into clear thin films or monoliths. The syntheses were carried out at both Pacific Northwest National Laboratory (PNNL) and at the Department of Ceramic & Materials Engineering, Clemson University. The reproducibility of the results was acceptable when air-sensitive chemical manipulation techniques were

Table 1 P–Si sols and gels prepared under different conditions

sample	P : Si starting molar ratios	firing temperature/°C	crystallinity	P : Si molar ratios after firing
1P1S(sol)	1 : 1			
1P1S(H_2O-sol)	1 : 1			
1P1S-70	1 : 1	70	amorphous	1 : 1
1P1S-700	1 : 1	700	$Si_5O(PO_4)_6$ polycrystal and amorphous	1 : 0.99
1P1S-900	1 : 1	900	$Si_5O(PO_4)_6$ polycrystal and amorphous	1 : 0.98

observed. XRD data were taken to identify the phase and to calculate the amorphous content in phosphate gels. Table 1 identifies all samples for NMR measurements. In Table 1, the letters P and S with preceding numbers denote the molar ratio for phosphorus and silicon, respectively (1P1S means a molar ratio of 1 : 1 for P and Si). The firing temperatures are also included in sample names. For example, sample 1P1S-700 means a sample fired at 700 °C with a molar ratio of 1 : 1 for P and Si.

^{29}Si and ^{31}P (both liquid- and solid-state) NMR measurements were used to identify chemical species formed during the sol–gel process. NMR experiments were carried out with a Chemagnetic Spectrometer (300 MHz, 89 mm wide bore Oxford magnet) using a variable temperature double resonance MAS probe at frequencies of 120.77 and 59.29 MHz for ^{31}P and ^{29}Si, respectively. The solid powder samples were loaded into 7 mm zirconia PENCIL™ rotors and spun at 3–6 kHz, while the solution samples were put into the same rotors without spinning. Both ^{31}P and ^{29}Si spectra were collected using a single-pulse Bloch-decay method (with proton decoupling) with a 5 μs (90 °) pulse and a 30 s repetition delay. The repetition delay of 30 s was found to be long enough by checking several longer repetition delays. The number of repetitions was 20–100 for the ^{31}P spectra and 100–10 000 for the ^{29}Si spectra. The ^{29}Si chemical shift was referenced to tetramethylsilane (TMS), while ^{31}P solid-state NMR spectra were referenced to 85% H_3PO_4 ($\delta = 0$).

Results and Discussion

^{31}P and ^{29}Si NMR spectra for sols with composition of 1 : 1 molar ratio for P : Si are given in Fig. 1 and 2, respectively. For sol 1P1S(sol) prepared under anhydrous conditions, the ^{31}P liquid-state NMR spectrum [Fig. 1(a)] showed four distinguishable resonance regions centered at δ *ca.* −0.7, −11.2, −22.0 and −33.4, while two narrow resonances at *ca.* −82.4 and −91.4 are clearly shown in Fig. 2(a) in the ^{29}Si spectra. The resonance at $\delta - 0.7$ was attributed to a terminal PO_4 group. A previous study[3] has shown that resonances associated with P—O—P and P—O—Si^{IV} bonds could not be distinguished and the resonances in the region from $\delta - 9$ to −35 can be assigned to Q'*n* species (a phosphate bound to *n* phosphorus or silicon atoms through P—O—P or P—O—Si bonds). Thus, we assigned the resonances at $\delta - 11.2$, −22.0 and −33.4 to Q'1, Q'2, and Q'3 species, respectively. The formation of P—O—Si bonds is further evident in ^{29}Si NMR spectra. The resonance at $\delta - 82.4$ shown in the ^{29}Si spectrum [Fig. 2(a)] is attributed to the presence of TEOS, and the resonance at $\delta - 91.4$ to $Si(OEt)_3(OP)$ owing to the formation of a Si—O—P bond.[8]

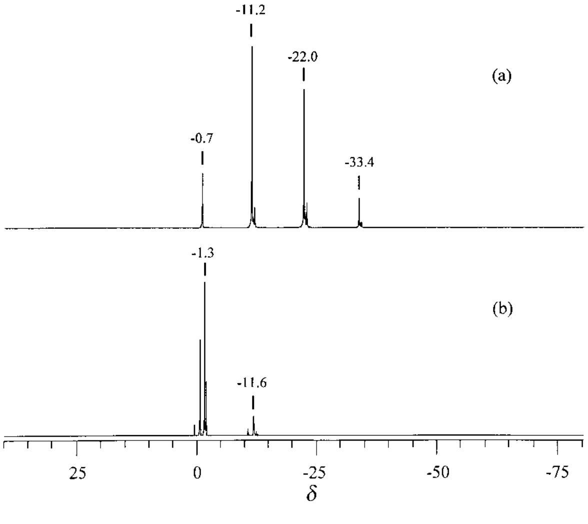

Fig. 1 Liquid-state ^{31}P NMR spectra for the sol 1P1S(sol) with a 1 : 1 molar ratio of P : Si (a) prepared under anhydrous conditions, and (b) prepared after adding water to the sol 1P1S(sol)

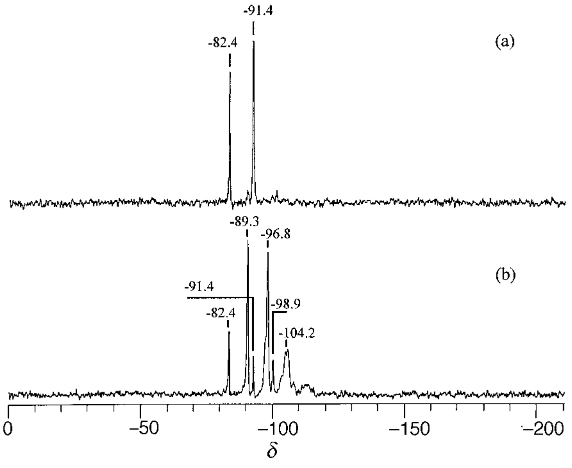

Fig. 2 Liquid-state ^{29}Si NMR spectra for the sol 1P1S(sol) with a 1 : 1 molar ratio of P : Si (a) prepared under anhydrous conditions, and (b) prepared after adding water to the sol 1P1S(sol)

From the area ratio of 1 : 1.9 for the resonances at $\delta - 82.4$ and at $\delta - 91.4$ in the ^{29}Si NMR spectrum [Fig. 2(a)], we estimated approximately 66% of total amount of TEOS reacted with P_2O_5 to form $Si(OEt)_3$—OP— units. Since the molar ratio of P : Si is 1 : 1 in the starting mixture, *ca.* 66% of the total amount of P sites should contain P—O—Si bonds. From the relative peak intensities in the ^{31}P NMR spectra [Fig. 1 (a)], the resonances at $\delta - 11.2$, −22.0 and −33.4 are associated with P sites containing one, two and three P—O—Si bonds, respectively, through $Si(OEt)_3$—OP— units. The formation of the Si—O—P bonds indicated that the Si—OEt bonds in TEOS were broken and replaced by P—O—Si bonding. In the study[8] of TEOS solutions with H_3PO_4 in ethanol by Fernandez-Lorenzo, resonances in the region $\delta - 9$ to −30 were assigned to Q'*n* species with only P—O—Si bonds. However, in our case the starting material P_2O_5 (more correctly P_4O_{10}) already contained phosphorus atoms with many P—O—P bonds. We do not expect the P—O—P bonds to completely disappear after mixing with TEOS. Thus, the resonances at $\delta - 11.0$ to −33.0 may also correspond to the P atoms with P—O—P bonds found in the starting material. As compared with the data taken for TEOS solutions with H_3PO_4 in ethanol,[8] the direct reaction of P_2O_5 with TEOS gives an additional resonance at $\delta -33.4$ and a larger relative peak intensity for the resonance at $\delta -22.0$, indicating a possible different mechanistic route for the reaction of P_2O_5 with TEOS. The formation of P—O—Si bonds under anhydrous conditions is likely to be due to the opening of the P_4O_{10} cluster by adding a —Si—OEt group onto a bridging oxygen and subsequent addition of —OEt to the P atom.

Adding a small amount of water to the mixture of P_2O_5 and TEOS changed both the ^{31}P and ^{29}Si spectra [Fig. 1(b) and 2(b)] significantly. The majority of the ^{31}P resonances for the sol designated 1P1S(H_2O-sol) is in the region from δ 0.8 to -1.7 with minor peaks around $\delta -11.6$ [Fig. 1(b)]. The ^{31}P spectra for the sol after the addition of water [Fig. 1(b)] resembled those for precursors $PO(OEt)_x(OH)_{3-x}$ ($x=0$–3) in the region δ 0.8 to -1.7.[2] Thus, we assigned those major peaks to the resonances associated with $PO(OEt)_x(OH)_{3-x}$ ($x=0$–3). During hydrolysis, P—O—P and P—O—Si bonds in chain or ring structures were broken, and a precursor solution was created similar to $PO(OEt)_x(OH)_{3-x}$ precursors prepared by adding P_2O_5 with EtOH. At the same time, partial condensation of TEOS was evident in the ^{29}Si spectra. In addition to the same two resonances at $\delta -82.3$ and -91.4, in the anhydrously prepared sample 1P1S(sol), the three major resonances at $\delta -89.3$, -96.8 and -104.2 shown in Fig. 2(b) correspond respectively to Q1, Q2, and Q3 for tetracoordinated silica.[15]

As indicated in the previous study of TEOS solutions with H_3PO_4 in ethanol,[8] the resonances associated with P—O—Si bonds disappear in the ^{31}P NMR spectra owing to the rapid hydrolysis of the Si—O—P bonds. Only a small number of P—O—P and P—O—Si bonds are retained in sols prepared after adding water to the mixture of P_2O_5 and TEOS. Furthermore, the fact that almost no P—O—Si bonds were observed for the sol after water addition suggests that homocondensation of the Si—O—Si bonds is favored over heterocondensation which would form P—O—Si bonds. This is possibly due to the higher rate of TEOS hydrolysis than that of heterocondensation. Direct reaction of P_2O_5 with TEOS opens the P_4O_{10} cluster by adding a —Si—OEt group onto a bridging oxygen and subsequent addition of —OEt groups to the P atom leads to species such as $(-O-)_{3-x}PO[OSi(OEt)_3]_x$ and $(-O-)_{3-x}PO(OEt)_x$ ($x=0$–3). The hydrolysis of these species gives $PO(OH)_x(OR)_{3-x}$ species. Therefore, it is understandable that when water was added to the sol containing P_2O_5 and TEOS, the sol appeared to mimic the $PO(OH)_x(OR)_{3-x}$ precursors. The gelation time for the direct reaction of P_2O_5 with TEOS was significantly shortened by addition of small amounts of water to the sol.[7] The faster gelation rate suggests a greater rate of condensation. The previous study[8] has also shown that the condensation reaction of SiOH+SiOP has a faster rate than that of SiOH+HOSi. Thus, the condensation reaction of SiOH+SiOP may predominate over the direct reaction of P_2O_5 with TEOS. Hydrolysis of $Si(OR)_4$ was also enhanced by H_3PO_4, formed from the reaction of P_2O_5 with water. The gelation rate for the direct reaction of P_2O_5 with TEOS is faster than that for the reaction using $PO(OR)_3$ as precursors owing to the slow hydrolysis of $PO(OR)_3$ species.

The structures of P–Si gels fired at different temperatures were studied using solid-state MAS NMR. Both ^{31}P and ^{29}Si solid-state NMR spectra are given in Fig. 3 for the sol 1P1S(sol) dried at 70 °C. The ^{31}P NMR spectrum exhibits two spectral regions, at $\delta -1.0$ and at *ca.* -30.0. Resonances at δ *ca.* -1.0 are attributed to terminal PO_4 groups, while the resonance at δ *ca.* -30.0 corresponds to Q'3 species with P—O—Si bonds (only a small amount of Q'1 and Q'2 species was observed in the region $\delta -10$ to -25). The ^{29}Si NMR spectrum [Fig. 3(b)] indicates the existence of hexacoordinated silicon ($\delta -212.0$) in addition to the normal tetracoordinated Q3 silicon ($\delta -104.1$).[15] This is the first time that hexacoordinated silicon was observed in gels prepared at such a low temperature (70 °C). In comparison of the spectra for sols (Fig. 1 and 2) with those for gels dried at 70 °C (Fig. 3), only spectra taken for gels show the existence of a significant number of P—O—Si bonds and hexacoordinated silicon in addition to the teracoordinated Q3 silicon. The different spectra for the sols and the gels suggest that gelation and drying processes substantially changed the structure of the sols.

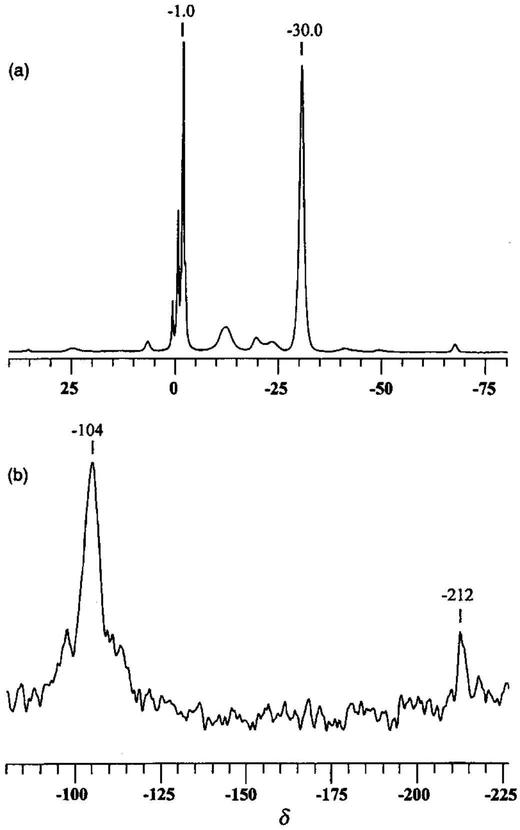

Fig. 3 (a) Solid-state ^{31}P NMR spectrum for the gel 1P1S-70 dried at 70 °C with a 1:1 molar ratio of P:Si; (b) solid-state ^{29}Si NMR spectrum for the gel 1P1S-70 dried at 70 °C with a 1:1 molar ratio of P:Si

^{31}P and ^{29}Si spectra are shown in Fig. 4 and 5, respectively,

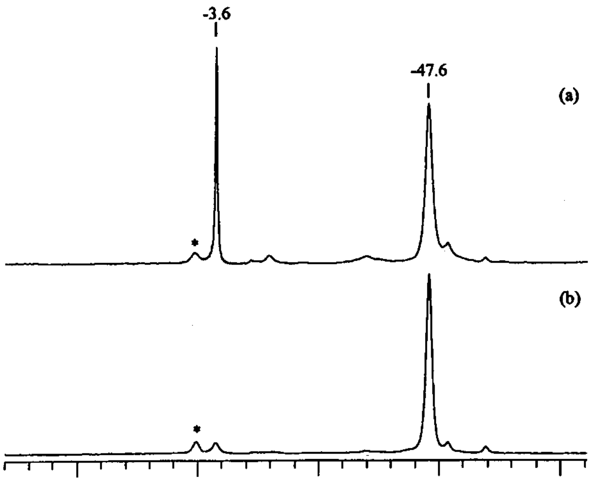

Fig. 4 (a) Solid-state ^{31}P NMR spectrum for the gel 1P1S-700 heated at 700 °C with a 1:1 molar ratio of P:Si. The peaks labelled by * are spinning sidebands; (b) solid-state ^{31}P NMR spectrum for the gel 1P1S-700 heated at 900 °C with a 1:1 molar ratio of P:Si.

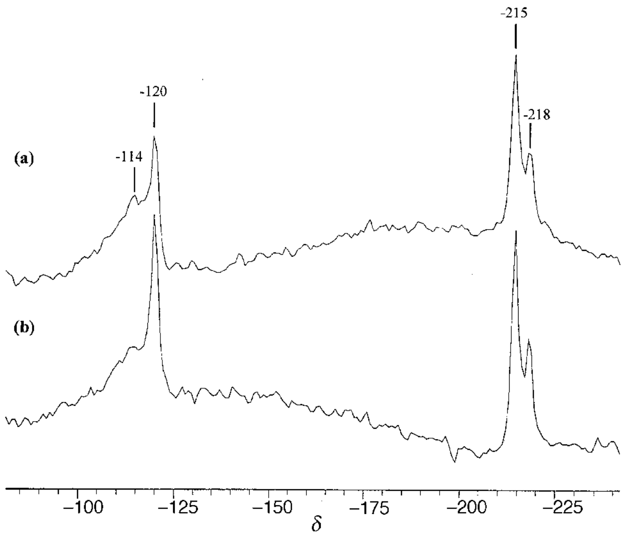

Fig. 5 (a) Solid-state ^{29}Si NMR spectrum for the gel 1P1S-700 heated at 700 °C with a 1 : 1 molar ratio of P : Si; (b) solid-state ^{29}Si NMR spectrum for the gel 1P1S-900 heated at 900 °C with a 1 : 1 molar ratio of P : Si

for 1P1S-700 and 1P1S-900 gels (prepared by $P_2O_5 + TMOS$ with P : Si molar ratio of 1 : 1) fired at temperatures of 700 and 900 °C. XRD measurements showed *ca.* 30 and 10% amorphous phases in samples treated at 700 and 900 °C, respectively. The major phase was identified as $Si_5O(PO_4)_6$, with SiP_2O_7 as the minor phase. Two narrow resonances at $\delta - 3.6$ and -47.6 are clearly shown in the ^{31}P spectra [Fig. 4(a)] for the P–Si gel fired at 700 °C. Several small peaks observed in the region $\delta - 10$ to -33 (Fig. 4) suggest almost no Q'*n* ($n = 1$–3) species in gels after firing. The only strong signal at $\delta - 47.6$ observed in the region $\delta - 40$ to -60 indicates one type of P site in $Si_5O(PO_4)_6$. As the firing temperature was increased to 900 °C, the resonance at $\delta - 3.6$ almost disappeared, whereas the resonance at $\delta - 47.6$ remained. The ^{29}Si NMR spectra exhibit four resonances at $\delta - 114$, -120, -215, and -218. The narrow resonance at $\delta - 3.6$ in the ^{31}P spectrum (Fig. 4) is attributed to isolated PO_4 units. The signal at $\delta - 47.6$ (Fig. 4) is assigned to condensed PO_4 groups connected to tetra- and hexa-coordinated silicon atoms through one or more P—O—Si bonds. Previous studies[16–18] have reported observations of octahedral silicon in the ^{29}Si chemical shift range $\delta - 200$ to -220 and the corresponding condensed PO_4 groups with ^{31}P chemical shifts in the region from $\delta - 30$ to -53. Comparison with previous results[17] shows that the ^{29}Si spectra for P–Si (1 : 1) gels fired at 700 and 900 °C are similar to the spectrum reported [Fig. 1(c) of ref. 17] for a glass prepared using a different method (devitrification at 1000 °C for 6 h employing hydrothermal methods). Similarly to the assignment given in the previous study,[3,17] resonances at $\delta - 215$ and -218 were attributed to $Si_5O(PO_4)_6$ and SiP_2O_7 phases, respectively. $Si_5O(PO_4)_6$ may also contribute to the intensity at $\delta - 218$.[17] Since the crystal structure of $Si_5O(PO_4)_6$ consists of isolated SiO_6 and Si_2O_7 units linked by PO_4 groups,[15] we assign the peaks at $\delta - 120$ and -215 in the ^{29}Si NMR spectra (Fig. 5) to tetra- and hexa-coordinated silicon in the $Si_5O(PO_4)_6$ phase, respectively, and the peak at $\delta - 48$ in the ^{31}P NMR spectrum (Fig. 4) to $P(OSi^{IV})(OSi^{VI})_3$ units. The resonance at $\delta - 114$ (Fig. 5) corresponds to Q4 units (the silicon tetrahedron connected to four other silicon tetrahedra) in amorphous silica. As the temperature was increased, the amount of amorphous silica ($\delta - 114$) decreased and both crystalline $Si_5O(PO_4)_6$ and SiP_2O_7 phases increased (see Fig. 5). This is in agreement with XRD measurements.

It is clear that the new method of formation of both the sols and gels by directly reacting P_2O_5 with tetraethoxysilane (TEOS) offers us a new insight into the chemistry and structural properties of both sols and gels. The direct synthesis route has not only simplified the preparation procedure but also greatly reduced the loss of phosphorus upon firing. The sample crystallinity and actual P : Si molar ratios after firing at higher temperatures are given in Table 1. Since the TG result[7] for our samples showed that there was <3 mass% loss from 300 to 1000 °C, the phosphorus retention was more than 97% of the initial content of P–Si gels. The mass conservation was greater in gels prepared from P_2O_5 than in those prepared from other available phosphorus precursors.[3,7] Chemical analysis indicated a large loss of phosphorus for the gels prepared using $PO(OEt)_3$ owing to the much slower hydrolysis rate of $PO(OEt)_3$ than that of TEOS. The high phosphorus loss upon heating most likely resulted from a large amount of unreacted $PO(OEt)_3$. Since both the hydrolysis and condensation in the direct reaction of P_2O_5 with TEOS are relatively fast, less phosphorus loss was observed. Previous studies[3,5] have found that $PO(OR)_3$ slowly hydrolyzed into $PO(OH)_x(OR)_{3-x}$ and the hydrolysis rate usually increases with acid catalysis. Since $PO(OH)_x(OR)_{3-x}$ precursors were hydrolyzed faster than $PO(OR)_3$ itself, the reaction rate is enhanced *via* the addition of acids, and the loss of phosphorus is decreased.

Conclusions

The chemistry and structural properties for both sols and gels prepared by directly reacting P_2O_5 with tetraethoxysilane (TEOS) have been studied using ^{31}P and ^{29}Si solid-state magic angle spinning (MAS) and liquid-state nuclear magnetic resonance (NMR) techniques. This new method of formation of both the sols and gels results in a drastic improvement in the retention of phosphorus during the formation of the phosphosilicate gels, and additionally, a lower temperature route to six-coordinate silicon. The formation of the P—O—Si bonds under anhydrous conditions is likely to be due to the opening of the P_4O_{10} cluster by addition of a Si—OEt group onto a bridging oxygen. The $PO(OH)_x(OR)_{3-x}$ species were observed in ^{31}P NMR spectra for sols after addition of water, while ^{29}Si NMR spectra indicated that TEOS had undergone partial hydrolysis and condensation. Hexacoordinated silicon has been observed for the first time in gels prepared at low temperature (70 °C). The hydrolysis and condensation for the reaction of P_2O_5 directly with TEOS are faster than those for the reaction using $PO(OR)_3$ as a molecular precursor. The heat-treated P–Si gels exhibit hexacoordinated silicon in both SiP_2O_7 and $Si_5O(PO_4)_6$ phases.

The authors would like to thank Mr. D. McCready for acquiring the XRD data. This work has been supported by the Division of Materials Sciences Office of Basic Energy Sciences US Department of Energy (US DOE). Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the US DOE by Battelle Memorial Institute under Contract DE-AC06–76RLO 1830.

References

1 T. Woignier, J. Phalippou and J. Zarzycki, *J. Non-Cryst. Solids*, 1990, **63**, 117.
2 J. Livage, P. Barboux and M. T. Vanderborre, *J. Non-Cryst. Solids*, 1992, **147**, 18.
3 S. P. Szu, L. C. Klein and M. Greenblatt, *J. Non-Cryst. Solids*, 1992, **143**, 21.
4 Y. S. Kim and R. E. Tressler, *J. Mater. Sci. 2*, 1994, **29**, 2531.
5 F. Tian, L. Pan, L, X. Wu and F. Wu, *J. Non-Cryst. Solids*, 1988, **104**, 129.
6 B. I. Lee, W. D. Samuels, L.-Q. Wang and G. J. Exarhos, *J. Mater. Res.*, 1996, **11**, 1.
7 (*a*) Z. Cao, B. I. Lee, W. D. Samuels, L.-Q. Wang and G. J. Exarhos, *J. Mater. Res.*, 1997, in press; (*b*) B. I. Lee, Z. Cao, W. N. Sisk,

J. Hudak, W. D. Samuels and G. J. Exarhos, *Mater. Res. Bull.*, 1997, **32**, 1285.

8 C. Fernandez-Lorenzo, L. Esquivias, P. Barboux, J. Maquet and F. Taulelle, *J. Non-Cryst. Solids*, 1994, **176** 189.

9 Y. Guo, P. Woznicki and A. Barkatt, *J. Mater. Res.*, 1996, **11**, 3.

10 S. Prabakar, K. J. Rao and C. N. R. Rao, *J. Mater. Res.*, 1991, **6**, 592.

11 E. A. Hayri and M. Greenblatt, *J. Non-Cryst. Solids*, 1987, **94**, 387.

12 J. P. Boilot and P. Colomban, *J. Mater. Sci. Lett.*, 1985, **4**, 22.

13 P. J. Dirken, M. E. Smith and H. J. Whitfield, *J. Phys. Chem.*, 1995, **99**, 395.

14 S. G. Kosinski, D. M. Krol, T. M. Duncan, D. C. Douglass, J. B. Machesney and J. R. Simpson, *J. Non-Cryst. Solids*, 1988, **105**, 45.

15 *Colloid Chemistry of Silica*, ed. H. E. Bergna, American Chemical Society, *Adv. Chem. Ser.* no. 234; Wijnen *et al.*, *Silica Gels from Aqueous Silicate Solutions*, 1994, p. 413.

16 M. W. G. Lockyer, D. Holland and R. Dupree, *Phys. Chem. Glasses*, 1995, **36**, 22.

17 T. L. Weeding, B. H. de Jong, W. S. Veeman and B. G. Aitken, *Nature*, 1985, **318**, 352.

18 I. L. Mudrakovskii, V. P. Mastikhin, V. P. Shmachkova and N. S. Kotsarenko, *Chem. Phys. Lett.*, 1985, **120**, 424.

Paper 7/05465C; *Received* 28*th July*, 1997