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# Identification of self- and cross-condensation products in organically modified silica sols by $^{29}\text{Si}$ and $^{17}\text{O}$ NMR spectroscopy<sup>1</sup>

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## Abstract

High resolution  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectroscopy has been used to identify self- and cross-condensation products in sols prepared from tetraethoxysilane (TEOS) and organically modified triethoxysilanes (RTES, where R is a methyl, ethyl or phenyl group). The sols were prepared by the acid catalyzed hydrolysis of TEOS and RTES with  $\text{H}_2\text{O}/\text{Si}$  mole ratios of 0.15, 0.3 or 0.5. Resonance assignments were made by comparing the positions and intensities of peaks in the spectra of single and multicomponent systems as a function of reaction time. Both  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectroscopy exhibit resonances which are uniquely attributed to species formed by cross-condensation reactions between TEOS and RTES. Approaches to improve the resolution of  $^{17}\text{O}$  NMR spectra were only moderately successful because the resonance envelopes have substantial contributions from inhomogeneous components.

## 1. Introduction

A powerful strategy for the design of improved materials has been the synthesis of multicomponent systems. The multicomponent approach has been used to prepare organic/organic copolymers, organic/inorganic hybrids and multicomponent inorganic materials. The effectiveness of the strategy often depends on the degree of mixing of the components. Mixing can be achieved on an intimate level when covalent bonds are formed between compo-

nents. In this study high resolution  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectroscopy were used to identify molecular products of self- and cross-condensation reactions in a series of organically modified silica sols.

Sol-gel synthesis of glasses and ceramics has become an effective method for preparing high-purity, homogenous materials [1–3]. Hybrid sol-gels are prepared by introducing an organic group into the inorganic matrix. Hybrid sol-gels are widely investigated materials due to their potential applications as optical devices and ceramic membranes for gas separation [4–6]. Tetraethoxysilane (TEOS) is a commonly used inorganic precursor. When TEOS is combined with an organically modified triethoxysilane (RTES, where R is a methyl (M), ethyl (E) or phenyl (P) group), both may undergo selfcondensa-

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tion, Eqs. (1) and (2) below, and cross-condensation, Eq. (3). The RTES silicon is represented by  $T_m^n$  and the TEOS silicon is represented by  $Q_m^n$  where  $n$  denotes the number of SiOSi bonds surrounding the silicon and  $m$ , the number of hydroxyl groups. These equations represent the simplest condensation reactions, the reaction of two singly hydrolyzed monomeric species to form a dimer:



The notation  $T^1 T^1$  represents the dimer formed by the self-condensation of two  $T_1^0$  species. The subscript zero for the dimeric species is omitted for convenience. Similarly  $Q^1 Q^1$  is the dimer formed by the self-condensation of two  $Q_1^0$  species and  $T^1 Q^1$  is the dimer formed by the cross-condensation of  $T_1^0$  and  $Q_1^0$ .

The reaction kinetics of organically modified silica sol-gels has been an area of active research because of the close relationship between kinetic pathways and the final structure and physical properties of the sol-gel prepared material. The effects of alkylsubstituted ethoxysilanes on the kinetics of TEOS were studied by van Bommel et al. [7] and the effects of TEOS on the kinetics of several alkyl chain substituted ethoxysilanes were studied by Delattre and Babonneau [8]. In these studies the overall condensation rates were measured but the distinction between self- and cross-condensation reactions was not observed.

Recently Sugahara et al. [9] used  $^{29}\text{Si}$  NMR spectroscopy to distinguish between self- and cross-condensed TEOS/MTES reaction products which were fully hydrolyzed and we [10] used a similar approach to observe self- and cross-condensed reaction products which were unhydrolyzed. Babonneau et al. [11] used  $^{17}\text{O}$  NMR to observe self- and cross-condensation bonds in several hybrid systems. In this paper we have used both  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectroscopy to identify self- and cross-condensed species in a series of organically modified silica sols.

$^{29}\text{Si}$  NMR spectroscopy was used to identify the self- and cross-condensed species in the TEOS/ETES and TEOS/PTES sols.  $^{29}\text{Si}$  NMR spectroscopy can identify the complete structure of

dimeric species and thus provides valuable input for the quantitative kinetic model which we are developing for these systems. The chemical shift trend of TEOS/ETES was similar to that previously reported for TEOS/MTES [10], however, the order of some

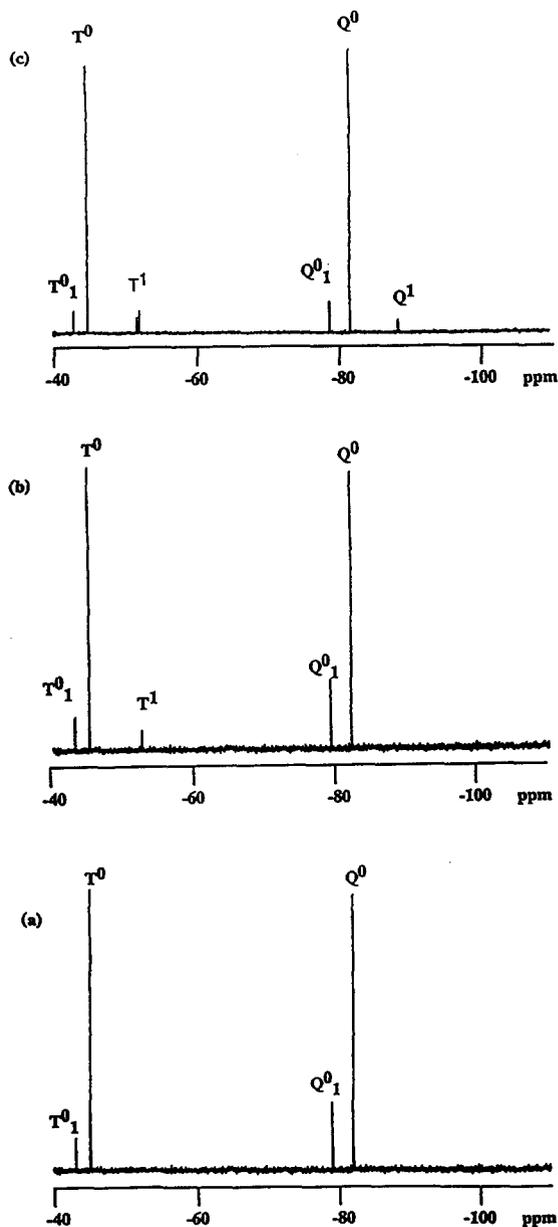


Fig. 1. The  $^{29}\text{Si}$  NMR spectra of the TEOS/ETES ( $r = 0.15$ ) sol-gel as a function of reaction time: (a) 6.5 min, (b) 12.5 min and (c) 16 min.

chemical shifts for the TEOS/PTES sol were inverted from those of TEOS/MTES. High resolution  $^{17}\text{O}$  NMR spectroscopy was used as a complimentary technique to study the methyl modified sol, TEOS/MTES, and methods to improve the resolution of these spectra were explored.

## 2. Experimental

Reagent grade TEOS, methyltriethoxysilane (MTES), ethyltriethoxysilane (ETES) and phenyltriethoxysilane (PTES) were used as received from Hüls America. The 20%  $^{17}\text{O}$ -enriched  $\text{H}_2\text{O}$  was purchased from Isotec Inc.

Sols of both single and multiple components for  $^{29}\text{Si}$  NMR spectroscopy were prepared by the acid-catalyzed hydrolysis of the respective alkoxides in ethanol. The silicon concentration was 2.2 M for all the sols, the TEOS/RTES mole ratio was 50:50 for the hybrid sols, the nominal pH was 2.8 and the  $\text{H}_2\text{O}/\text{Si}$  mole ratio was 0.15 or 0.3. Chromium acetylacetonate (CrAcAc), 5 mM, was added to reduce the  $^{29}\text{Si}$  spin-lattice relaxation time. Previous studies have reported no effect of the CrAcAc relaxation agent on the reaction rate or the product distribution of sol-gels [12–14].  $^{29}\text{Si}$  NMR spectra were taken within a few minutes after the samples were mixed and were recorded as a function of time. The reported reaction time occurs midway through the

spectrum accumulation period. The TEOS/MTES sols used for  $^{17}\text{O}$  NMR studies were prepared with  $^{17}\text{O}$ -enriched  $\text{H}_2\text{O}$  and a  $\text{H}_2\text{O}/\text{Si}$  mole ratio of 0.5.

The  $^{29}\text{Si}$  NMR spectra were acquired at 39.6 MHz (magnetic field 4.7 T) on a Chemagnetics console interfaced to a General Electric 1280 data station and pulse programmer. All the spectra were accumulated with a 10 mm probe at room temperature. Typical spectra were recorded with a pulse delay time of 10 s and the number of scans ranged from 4 during the early stages of the reaction to 256 after the sol had reacted for several hours. The 16 k free induction decay was zero filled to 32 k before Fourier transformation. The resonance linewidths were typically 0.3 Hz. Spectra were externally referenced to tetramethylsilane at 0 ppm.

$^{17}\text{O}$  NMR spectra were acquired on a Bruker AMX-400 spectrometer operating at 54.3 MHz using a 5 mm probe. A Hahn spin-echo pulse sequence was used in order to reduce baseline distortions. The spectra were recorded with a  $90^\circ$  pulse width of 20  $\mu\text{s}$ , a spin-echo time of 10  $\mu\text{s}$  and a 100 ms repetition delay. The number of scans was varied from 1 k to 4 k. All spectra were externally referenced to  $\text{H}_2\text{O}$  (0 ppm).

## 3. Results

The  $^{29}\text{Si}$  NMR spectra of the single and multiple component sols were recorded as quickly as possible

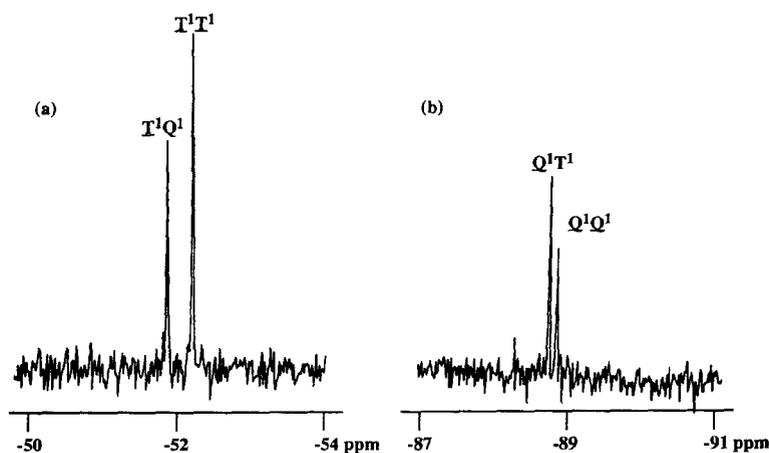


Fig. 2. The  $^{29}\text{Si}$  NMR spectrum of the TEOS/ETES ( $r = 0.15$ ) sol-gel reacted for 16 min showing (a) the  $T^1$  and (b) the  $Q^1$  region in expanded scale.

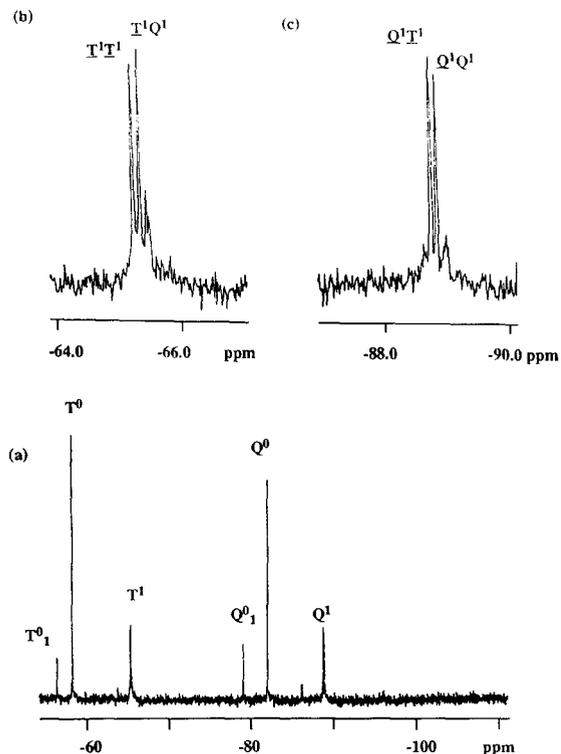


Fig. 3. The  $^{29}\text{Si}$  NMR spectrum of TEOS/PTEOS ( $r = 0.3$ ) sol-gel reacted for (a) 8 min and (b) the  $T^1$  and (c) the  $Q^1$  region in expanded scale.

after their preparation and were recorded at various intervals until the reactions were near completion. The spectra of the TEOS/ETES sol during the early stages of reaction are shown in Fig. 1. The spectrum at 6.5 min shows only hydrolysis species, the spectrum at 12.5 min shows the appearance of condensed  $T$  species, and the spectrum at 16 min shows both condensed  $T$  and  $Q$  species. The resonances labelled  $T^1$  and  $Q^1$  actually have fine structure as evidenced when they are expanded in Fig. 2. The fine structure corresponds to the functionalities of the adjacent silicon. Thus, these features are sensitive to the effects of self- versus cross-condensation. Their interpretation in a formalized manner will be discussed in the next section.

The  $^{29}\text{Si}$  NMR spectrum of TEOS/PTEOS 8 min after preparation is shown in Fig. 3(a). The  $T^1$  and  $Q^1$  resonances again have complex structure as shown in Fig. 3(b) and (c). The assignment of each compo-

nent to self- and cross-condensed reaction products will be discussed in the next section.

The  $^{17}\text{O}$  NMR spectra of the TEOS sol, the MTES sol and the TEOS/MTES sol are shown in Fig. 4(a), (b), and (c) respectively. The spectra were recorded several days after preparation and the reaction has gone essentially to completion. The TEOS resonance appears to consist of an individual line in both the single and multicomponent sol while the MTES resonance appears to be composed of several components. Fig. 5 shows the  $^{17}\text{O}$  NMR spectra of the TEOS/MTES hybrid as a function of temperature. The decreased viscosity of the sol at higher temperatures increases the molecular mobility of the species and results in some improvement in the spectral resolution. Similarly, a modest increase in spectral resolution is shown in Fig. 6 when the ethanol solvent is replaced by methanol.

#### 4. Discussion

The various resonance components in the  $T^1$  and  $Q^1$  regions of hybrid sols correspond to the functionalities of the silicon adjacent to the observed silicon. Since these peaks are dependent on the chemistries of two silicons bonded to each other, they enable us to identify self- and cross-condensed species. Be-

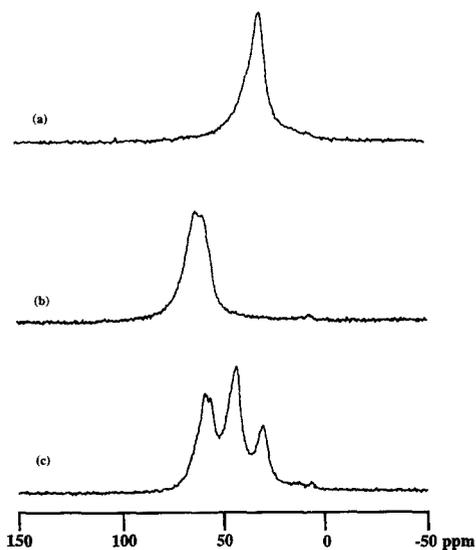


Fig. 4. The  $^{17}\text{O}$  NMR spectra of (a) TEOS, (b) MTES and (c) TEOS/MTES sol-gels.

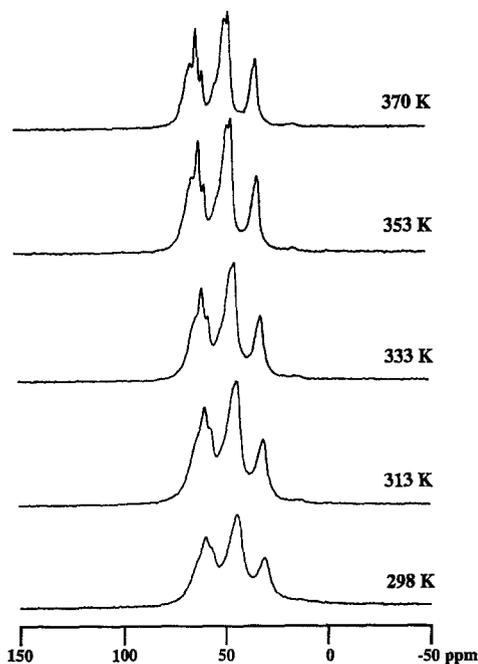


Fig. 5. Variable temperature  $^{17}\text{O}$  NMR spectra of TEOS/MTES sol-gels.

cause such a large number of species can be produced, and because many of the species are highly reactive, the use of model compounds to assign peaks in the  $^{29}\text{Si}$  NMR spectra is not practical.

We use a two-step approach for assignment of the resonance components. First, we record the spectra as a function of time for the individual components of a hybrid sol. The reaction is allowed to proceed

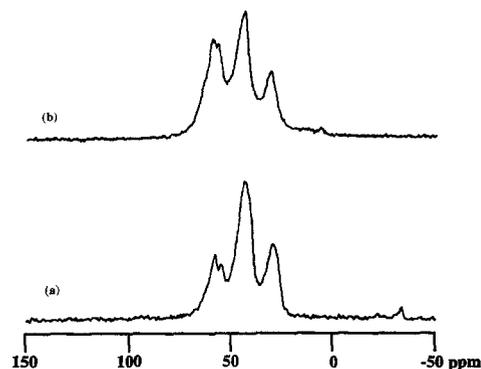


Fig. 6. The  $^{17}\text{O}$  NMR spectra of (a) TMOS/MTES in methanol and (b) TEOS/MTES in ethanol.

Observed Silicon	Adjacent Silicon	
	$T^1$	$T^2$
$T^1$	$T^1T^1$	$T^1T^2T^1$
$T^2$	$T^1T^2T^1$	—

Integral relationships:

$T^1T^1$ : Intensity Independent  
 $T^1T^2$ : Intensity of  $T^1 \sim$  Intensity of  $2T^2$

Fig. 7. Matrix showing the various species formed by condensation reactions between  $T$  species.

until the hydrolyzed species are very minor components. When limited amounts of water are used the primary products are then dimer and trimer units containing only unhydrolyzed  $Q^1$  and  $Q^2$  silicons for the TEOS sol and only unhydrolyzed  $T^1$  and  $T^2$  silicons for the organically modified triethoxysilane. Fig. 7 shows the various species present for an organically modified triethoxysilane. The list of species in the vertical column on the left represents the functionality of the observed silicons while the top horizontal row represents the functionality of the adjacent silicons bonded to the observed silicon. Each cell in the matrix corresponds to the detailed structure of both the observed silicon and the directly bonded silicons. From this matrix one can immediately recognize the complexity expected for each resonance region. For example, if only  $T^1$  silicons are present in the sol, the  $T^1$  region should consist of a single resonance corresponding to the  $T^1T^1$  species. If both  $T^1$  and  $T^2$  silicons are present, then the  $T^1$  region will have a resonance corresponding to the  $T^1T^1$  species and a resonance corresponding to the  $T^1T^2$  structure. The relationships between the integrals of the various resonances permit these two components to be assigned unambiguously to the appropriate structure. We have illustrated the analysis of a single component sol which does not contain hydrolyzed species. This approach can be extended to include hydrolyzed species [10].

Observed Silicon	Adjacent Silicon	
	$T^1$	$Q^1$
$T^1$	$T^1T^1$	$T^1Q^1$
$Q^1$	$Q^1T^1$	$Q^1Q^1$

Integral relationships:

$T^1$  region:

$T^1T^1$ : Intensity Independent

$T^1Q^1$ : Intensity of  $T^1$  = Intensity of  $Q^1$

$Q^1$  region:

$Q^1Q^1$ : Intensity Independent

$Q^1T^1$ : Intensity of  $Q^1$  = Intensity of  $T^1$

Fig. 8. Matrix showing the various species formed by condensation reactions between  $T$  and  $Q$  species.

When a hybrid sol is prepared, the matrix is drawn to include silicon types from both reactants. Fig. 8 shows the matrix for a TEOS/RTES hybrid for which dominant silicons are  $T^1$  and  $Q^1$  species. One expects the  $T^1$  region to consist of two components. One component,  $T^1T^1$ , will be independent of the intensity of any other resonance in the spectrum while the other component,  $T^1Q^1$ , will be always be equal to the  $Q^1T^1$  resonance in the  $Q^1$  region.

The two step approach provides a self-consistent check on the overall assignment process. The self-condensed species can be identified from the single-component sols and the cross-condensed species assigned by a process of elimination. The intensity relationships are then verified for each spectrum as a function of reaction time. For complex systems one can begin with limited amounts of water where predominately  $T^1$  species are produced and work up to higher water ratios and shorter reaction times where both fully condensed and hydrolyzed species are observed. One must recognize, however, that the complexity increases rather quickly. For example, if a hydrolyzed  $T^1$  silicon is observed early in the reaction, that silicon can be bonded to any other

silicon in the sol (except for monomeric silicons). Thus when an additional condensed silicon is observed, each resonance region has the potential of containing an additional component.

With this background we are now able to assign the various components in the hybrid sols. Fig. 2 shows that the  $T^1$  and  $Q^1$  regions of the TEOS/ETES hybrid each consist of two components. The assignments of specific dimeric species are indicated on the spectra. First, the positions of self-condensed resonances,  $T^1T^1$  and  $Q^1Q^1$ , were measured in the single component sols. The cross-condensed resonances in the hybrid,  $T^1Q^1$  and  $Q^1T^1$ , could then be assigned by a process of elimination. As a check, we expect that the resonances attributed to cross-condensed species would be equal in intensities throughout the reaction. This was established and is illustrated by the spectrum taken 16 minutes after preparation. As an additional confirmation we observe that after 12.5 min of reaction time, Fig. 1(b), the only condensed silicon present in significant quantities is  $T^1$ . This means that the  $T^1T^1$  dimer can be the only condensed species and confirms that the chemical shift of the self-condensed species in the hybrid sol is equal to its chemical shift in the single component sol. The chemical shifts for the monomeric and dimeric species present in the TEOS/ETES hybrid sol are summarized in Table 1.

The assignments for the self- and cross-condensed dimers in the TEOS/PTES sol were determined in the same manner and are illustrated in Fig. 3. Note that the chemical shift order of the resonances in the Q region are similar to those observed for the TEOS/ETES and the TEOS/MTES [10] hybrid sols. The chemical shift order of the  $T^1T^1$  and  $T^1Q^1$  resonances, however, are inverted from that observed for the alkyl modified hybrid sols. Since this inversion involves differences in shifts on the order of

Table 1  
 $^{29}\text{Si}$  NMR chemical shifts (ppm) for the TEOS/ETES system

Observed silicon	Monomer unit	Adjacent silicon	
		$T^1$	$Q^1$
$T^0$	-44.89	-	-
$T^1$	-	-52.28	-51.92
$Q^0$	-82.00	-	-
$Q^1$	-	-88.72	-88.82

Table 2  
<sup>29</sup>Si chemical shifts (ppm) for the TEOS/PTES system

Observed silicon	Monomer unit	Adjacent silicon	
		<i>T</i> <sup>1</sup>	<i>Q</i> <sup>1</sup>
<i>T</i> <sup>0</sup>	-58.11	-	-
<i>T</i> <sup>1</sup>	-	-65.26	-65.38
<i>Q</i> <sup>0</sup>	-82.00	-	-
<i>Q</i> <sup>1</sup>	-	-88.73	-88.83

only 0.1 ppm, we are unable to provide a chemical explanation for this effect. The inversion does show that the resonances for each sol must be rigorously assigned. The chemical shifts for the monomeric and dimeric species present in the TEOS/PTES hybrid sol are summarized in Table 2.

We observe a significant amount of cross-condensation in each of hybrid sols studied. The number of silicons incorporated into *T*<sup>1</sup>*T*<sup>1</sup> dimers in the TEOS/ETES and TEOS/MTES sols is much larger than the number of silicons incorporated into *Q*<sup>1</sup>*Q*<sup>1</sup> dimers. The number of each type silicon, *T* and *Q*, incorporated into cross-condensed *T*<sup>1</sup>*Q*<sup>1</sup> dimers is intermediate to the number of silicons incorporated into the self-condensed dimers. The number of each type silicon incorporated into self- and cross-condensed dimers is approximately equal for the TEOS/PTES sol. A quantitative model incorporating both self- and cross-condensation is being developed.

Although <sup>29</sup>Si NMR studies of silicate sols are quite extensive, there have been relatively few reports on <sup>17</sup>O NMR studies of such solutions [11,15,16]. This is due to the low natural abundance (0.04%) of <sup>17</sup>O and the rather broad line widths typically observed for quadrupolar nuclei such as <sup>17</sup>O. Since oxygen is a major component in many ceramics, <sup>17</sup>O NMR would be a promising spectroscopic tool for the analysis of metal–oxygen bond chemistry. In addition, suitable <sup>17</sup>O NMR spectra of <sup>17</sup>O-enriched sols can usually be obtained in a few minutes, whereas <sup>29</sup>Si NMR spectra of the same samples can take from several minutes to several hours to acquire.

Fig. 4 shows the <sup>17</sup>O NMR spectra of the fully reacted sols that were prepared using 20% <sup>17</sup>O-enriched H<sub>2</sub>O. The labeled oxygen is incorporated into the Si–O–Si bonds. Since SiOR and EtOH are not

enriched, they are not observed. Assignment of the observed resonances is similar to that reported by Babonneau et al. [11] except that we do not observe hydrolyzed species. The <sup>17</sup>O NMR spectrum of the TEOS sol shows a single peak at 30.4 ppm which is due to Q–O–Q siloxane bond. The <sup>17</sup>O NMR spectrum of the MTES sol also shows a single peak at 63.8 ppm, corresponding to a T–O–T siloxane bond. In the <sup>17</sup>O NMR spectrum of the MTES-TEOS sol, three resonances are observed at 58.9, 43.2, and 30.8 ppm, corresponding to T–O–T, T–O–Q, and Q–O–Q siloxane bonds, respectively. The <sup>17</sup>O NMR line widths are quite broad (ca. 400–700 Hz), resulting in considerable spectral overlap for the MTES-TEOS sol.

We have examined approaches for obtaining increased resolution for <sup>17</sup>O NMR spectra of multi-component sols. The broad lines of <sup>17</sup>O NMR spectra are usually attributed to the short relaxation times of the quadrupolar oxygen nuclei. The homogeneous component of the linewidth can be reduced by increasing the spin–spin relaxation time. An increase in the temperature of sample will increase the molecular mobility and thereby increase the spin–spin lattice relaxation time. Variable-temperature <sup>17</sup>O NMR spectra of the MTES-TEOS sol–gel are shown in Fig. 5. As the temperature is increased, the linewidths become narrower and a modest increase in resolution is obtained. We also observe some fine structure in the peaks at 58.9 and 43.2 ppm as the temperature is increased, although less pronounced for the 43.2 ppm peak. This fine structure could possibly be due to oxygen nuclei that are bonded to different trifunctional silicons (e.g. *T*<sup>1</sup>–O–*T*<sup>1</sup> versus *T*<sup>1</sup>–O–*T*<sup>2</sup>) in the case of the 58.9 ppm peak. A similar analogy might be used to explain the fine structure in the 43.2 ppm peak. Fine structure is not observed in the 30.8 ppm resonance. Unfortunately, higher temperatures have not appreciably decreased the width of the overall envelop of each set of resonances.

We also investigated the effect of a lower viscosity solvent on the spectral resolution of the hybrid sols. Fig. 6(a) shows the MTES-TMOS sol–gel prepared using methanol, while Fig. 6(b) shows the MTES-TEOS sol–gel prepared using ethanol. The viscosity of methanol at room temperature is only 50% of that of ethanol at room temperature. As

before, only a modest increase in resolution for the lower viscosity sol is observed. Evidently inhomogeneous contributions play a major role in the width of the spectra envelopes for the T–O–T and T–O–Q resonances. Straightforward approaches to increase the molecular mobility do not effect substantial improvements in the spectral resolution of these systems.

## 5. Conclusions

Formation of self- and cross-condensed reaction products in organically modified silica sol–gels was investigated by high resolution  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectroscopy. Significant amounts of both self- and cross-condensation products were formed in each hybrid sol studied.  $^{29}\text{Si}$  and  $^{17}\text{O}$  NMR spectroscopy are complimentary techniques.  $^{29}\text{Si}$  NMR is sensitive to the exact chemical structure of simple self- and cross-condensation reaction products. The method is time consuming, however, and is only practical for low water to silicon ratios.  $^{17}\text{O}$  NMR spectroscopy reflects the chemistry of the silicon on each side of the silicon–oxygen–silicon bond. Measurements are rapid when enriched  $^{17}\text{O}$  is incorporated into the sol and can be applied to more complex systems; including sols with higher water to silicon ratios.

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