

# Intermediates in the Sol-Gel Synthesis of Forsterite

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A precursor to the technologically important material forsterite, prepared by the reaction of 30%  $\text{H}_2\text{O}_2$  and water with  $\text{Si}(\text{OMe})_4$  (TMOS) and  $\text{Mg}(\text{OMe})_2$  in methanol, was analyzed by several methods to characterize intermediates. Headspace analysis showed that most of the TMOS was consumed after addition of an equimolar amount of water, in the presence of excess  $\text{Mg}(\text{OMe})_2$ . Iodimetric analysis revealed that peroxide was present in the sol and xerogel stages at  $\sim 56\%$  and  $25\%$  of its original concentration, respectively.  $^{29}\text{Si}$  NMR spectra of the initial stages in the synthesis displayed unprecedented peaks in the range  $-76.7$  to  $-81.3$  ppm. Although  $\text{H}_2\text{O}_2$  was needed for formation of several of these peaks,  $^{29}\text{Si}$  NMR spectra of triphenylsilyl hydroperoxide and related model compounds provided evidence against a silyl hydroperoxide in the sol. Raman spectroscopic analysis of the xerogel that formed upon removal of solvent, indicated that  $\text{MgO}_2$  had not formed.  $^{29}\text{Si}$  NMR analysis of mixtures of 30%  $\text{H}_2\text{O}_2$  with TMOS and  $\text{Mg}(\text{OMe})_2$  in low concentration showed products of condensation exclusively. The catalytic activity caused by  $\text{Mg}(\text{OMe})_2$  was comparable to that of common sol-gel catalysts  $\text{HCl}$  and  $\text{NH}_4\text{OH}$ , and other alkoxides ( $\text{LiOMe}$  and  $\text{NaOMe}$ ). The forsterite precursor synthesis occurred in two distinct mechanistic stages based on the concentration,  $M$ , of  $\text{Mg}(\text{OMe})_2$ : hydrolysis of TMOS, and possible formation of magnesium hydroperoxides occurred when  $M$  was high initially, followed by condensation of Si species (viz., base catalysis) when  $M$  was low.

## Introduction

Preparation of sol-gel precursors for synthetic forsterite,  $\text{Mg}_2\text{SiO}_4$ ,<sup>1</sup> and enstatite,  $\text{MgSiO}_3$ ,<sup>2</sup> was achieved recently by the  $\text{H}_2\text{O}_2$ -assisted hydrolysis of a solution of tetraethyl orthosilicate (TEOS) and magnesium methoxide in methanol. Previous solution methodologies used for the preparation of forsterite have entailed a mixing and heating of a mixture of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and TEOS in ethanol,<sup>3</sup> mixing of organomagnesium solutions with  $\text{Si}(\text{OR})_4$  solutions at gelation,<sup>4</sup> and adding  $\text{Mg}(\text{OC}_5\text{H}_{11}\text{OH})_2$  and TEOS to aqueous ammonia and heating.<sup>5</sup> The  $\text{H}_2\text{O}_2$ -assisted route to forsterite is unique in that (a) no strong acid or base catalyst was added to assist hydrolysis and (b) magnesium hydroxide did not precipitate during hydrolysis.

The reactions of tetramethyl orthosilicate (TMOS) and water have been widely studied. Typically acid or base catalysts have been used to promote hydrolysis and condensation.<sup>6</sup> Use of other types of catalyst is rare in the literature. These reactions have been examined using GC sampling,<sup>7</sup> and the intermediates have been probed with  $^{29}\text{Si}$  NMR spectroscopy.<sup>8</sup>

A few uses of hydrogen peroxide in sol-gel reactions have been reported. Titania gels have been prepared by the substitution of 30%  $\text{H}_2\text{O}_2$  for water.<sup>9</sup> Niobium pentachloride mixed with 30%  $\text{H}_2\text{O}_2$  has been used to make  $\text{NbO}_5$  gels.<sup>10</sup> Preparations of  $\text{SiO}_2$  raw materials, and high purity silica, have been accomplished in processes initially treating alkali metal silicates with hydrogen peroxide solutions.<sup>11,12</sup>

Sol-Gel methodology has been used in the manufacturing of materials in forms other than powders, such as thin films, fibers, and monoliths.<sup>13</sup> Forsterite has been proved useful in the area of advanced materials. In particular, Cr-doped forsterite has been applied as a solid-state lasing material.<sup>14</sup> Production of forsterite sols employing sol-gel methodology offers the potential for numerous novel applications such as coatings, fibers, and monoliths.<sup>1</sup>

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An understanding of the intermediates in the forsterite precursor synthesis is important to the applications of this new chemistry to materials problems. With fuller knowledge of the mechanistic details of the synthesis, effective use of the intermediates to introduce additives, modify structures, and control reactions should be possible. This approach has enabled us to tailor the sol-gel chemistry of the forsterite precursor synthesis to other applications, such as doping with Cr and other transition-metal ions.<sup>15</sup>

The reaction mechanisms in our solutions may be more complex than those in any of the previously mentioned studies on precursors for SiO<sub>2</sub> due to the combination of both H<sub>2</sub>O<sub>2</sub> and Mg(OMe)<sub>2</sub> with the silicon alkoxide. The discoveries of (a) magnesium methoxide catalyzed transesterification of TEOS to primarily TMOS, with a detailed study of the exchange reactions,<sup>16</sup> and (b) preliminary observations of catalyzed consumption of TMOS via the addition of 30% H<sub>2</sub>O<sub>2</sub>, caused by an unknown magnesium species in solution,<sup>17</sup> have been communicated.

Further knowledge of the catalytic ability of Mg(OMe)<sub>2</sub>-containing solutions was required in order to fully understand their potential. The fate of the starting materials (Mg(OMe)<sub>2</sub>, TMOS, and 30% H<sub>2</sub>O<sub>2</sub>) was probed by iodimetric titrations, <sup>29</sup>Si NMR, <sup>25</sup>Mg NMR, and Raman spectroscopy, and GC headspace analysis. Analysis of intermediates and reactions revealed two distinct stages in the forsterite precursor synthesis.

## Experimental Section

**General Techniques.** All operations were conducted under an atmosphere of dry Ar.<sup>18</sup> Silicon alkoxides were obtained from Aldrich. Aqueous solutions of H<sub>2</sub>O<sub>2</sub> were obtained from Fisher. Water was distilled and deionized. Degassed methanol, dried and distilled over Mg(OMe)<sub>2</sub>, was used as the solvent. Metal alkoxide catalysts were prepared by addition of the metal to the corresponding alcohol. All catalysts were used as prepared, with the exception of Mg(OMe)<sub>2</sub> solutions, which were filtered through a "medium"-porosity fritted funnel to remove oxide and machining residues. Solutions of aqueous H<sub>2</sub>O<sub>2</sub> were prepared by the addition of the commercial H<sub>2</sub>O<sub>2</sub> to dry methanol. The quantity of potentially reactive hydrogens was calculated assuming one from H<sub>2</sub>O and two from H<sub>2</sub>O<sub>2</sub>. The ratio of total equivalents of potentially reactive hydrogens to moles of silicon is called R<sub>3</sub>, analogous to the well-known R for water.<sup>6</sup> Water and 30% H<sub>2</sub>O<sub>2</sub> solutions were added with a syringe pump unless specifically stated that portions or aliquots of the solutions were added, in which case addition was conducted via a syringe directly. Magnesium acetate was prepared by addition of a stoichiometric quantity of glacial acetic acid to Mg(OMe)<sub>2</sub> in methanol. Magnesium turnings (99.99%) were obtained from Alfa. All other chemicals, including concentrated mineral acids and ammonium hydroxide, were reagent grade.

The methodology used to prepare the forsterite precursor solutions and powders has been reported previously.<sup>1</sup> Initial reaction mixtures were prepared by the addition of TEOS to a ~0.6 M solution of Mg(OMe)<sub>2</sub> in methanol, producing a final reactant ratio of 2 mol of magnesium/mol of silicon. Methanolic 30% H<sub>2</sub>O<sub>2</sub> was added over ~6 h until an R<sub>3</sub> of 3 was reached. Next a solution of water in methanol was added over ~12 h to give an R<sub>3</sub> of 6. Equal volumes of methanol were used to add both the water and 30% H<sub>2</sub>O<sub>2</sub>. The final volume of the reaction mixture doubled as a result of the additions, and the resulting mixture was a low-viscosity sol. To produce a high viscosity sol,

the solution was heated at 45 °C for 12 h. A finely powdered xerogel was produced as follows. An equal volume of toluene was added over 15 min, followed by water (total R<sub>3</sub> = 8), added over 1 h. The solution was heated for 12 h at 60 °C. The hazy mixture was centrifuged, and the sediment was washed sequentially with toluene and cyclohexane and then freeze-dried.

**Titration.** Titrations were conducted using a variation of the standard iodimetric method.<sup>19</sup> In place of the 4 N H<sub>2</sub>SO<sub>4</sub>, typically used, an acid solution composed of 3.5 N HF and 4 N H<sub>2</sub>SO<sub>4</sub> in a volume ratio of 1:2 was employed. Both the sample and the blank were run in polyethylene graduated cylinders to avoid attack of glassware. Polyethylene tubing was used to connect each cylinder through a septum attached to its top. Ar gas was continuously passed through both containers to exclude air, which would oxidize iodide. Samples to be analyzed were taken at three stages in the forsterite precursor synthesis. To facilitate digestion of the polymeric network, samples were heated at 60 °C. Samples from each stage were heated for 1, 3, and 5 h and titrated in the presence of the acid after each time period to ensure complete liberation of the peroxide by acid digestion. Actual titration methodologies remained unchanged.<sup>19</sup>

**Catalysis.** Reaction mixtures were prepared by addition of TMOS to methanol, ~0.5 M, in predried 250-mL three-necked round-bottom flasks equipped with three rubber septa and a Teflon-coated stirring bar. Catalysts were added to the reaction mixtures to induce the consumption of TMOS. Aliquots of solutions of aqueous H<sub>2</sub>O<sub>2</sub> in methanol that corresponded to R<sub>3</sub> of 0.05–0.25 were added instantaneously via syringe to the reaction mixtures. TMOS consumption was monitored using the headspace analysis technique described previously.<sup>16</sup>

Reaction mixtures in which Mg(OMe)<sub>2</sub> was compared to common sol-gel catalysts (HCl and NH<sub>4</sub>OH), other alkoxides (NaOMe and LiOMe), and Mg(OAc)<sub>2</sub> had ratios of 0.036, 0.020, and 0.020 mol of catalyst/mol of TMOS, respectively. The reaction mixtures in which Mg(OMe)<sub>2</sub> catalyzed reaction of TMOS with 30% H<sub>2</sub>O<sub>2</sub> or 50% H<sub>2</sub>O<sub>2</sub> contained 0.034 mol of catalyst/mol of TMOS. The comparison of catalytic Mg(OMe)<sub>2</sub> to a forsterite precursor used 0.020 and 2.0 mol of Mg(OMe)<sub>2</sub>/mol of TMOS, respectively. Unless otherwise stated, all catalyzed mixtures had aliquots of methanolic 30% H<sub>2</sub>O<sub>2</sub> added to them via syringe.

**NMR Spectroscopy.** (a) *General Techniques.* <sup>29</sup>Si NMR spectra were obtained on either a Varian VXR-400S 400-MHz instrument equipped with a Nalevac Cryogenics Corp. broadband probe (40–162 MHz) tuned to silicon or a Bruker AF-300 equipped with a probe modified by replacing all glass fittings with quartz inserts. Background signal from the NMR tubes and the probe were suppressed on the VXR-400S using the Carr-Purcell Meiboom-Gill sequence optimized to differentiate the silicon in the sample from the silicon in the glass using T<sub>2</sub><sup>20,21</sup> with a 90° pulse of 23.5 μs, relaxation delay of 10 s, and 60 ms to allow silicon relaxation in the glass. All NMR samples contained ~0.02 M Cr(acac)<sub>3</sub> as a relaxation agent. Phenyltrimethylsilane (PhTMS) was used as an internal shift standard set relative to TMS (0 ppm).

<sup>25</sup>Mg NMR spectra were obtained using parameters based on previous work conducted in methanol and aqueous media.<sup>22</sup> Samples were run on the Varian VXR-400S equipped with a broadband probe modified with extender rods to enable tuning to the magnesium nucleus. At 70° pulse of 30 μs, 15-kHz spectral width, and relaxation delay of 0.2 s were used. Samples typically required 4000 scans. A sealed capillary containing MgCl<sub>2</sub> in D<sub>2</sub>O was used as an internal shift and lock standard.

Reaction mixtures were prepared with silicon concentrations and apparatus analogous to those described above for the catalysis studies. In addition, each mixture contained ~0.1 M PhTMS as internal standard. An overview of the conditions used to prepare each reaction mixture and NMR sample is given in Table I.

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**Table I. Experimental Parameters Used To Prepare NMR Reaction Mixtures**

exp <sup>a</sup>	[TMOS] <sup>b</sup>	[Mg]/[Si] <sup>c</sup>	reagent	time (h)	R3 <sup>d</sup>
1.1	0.5	0.02	30% H <sub>2</sub> O <sub>2</sub>	9	0.8
1.2	0.5	0.2	30% H <sub>2</sub> O <sub>2</sub>	48	0.8
1.3	0.9	1.0	30% H <sub>2</sub> O <sub>2</sub>	48	0.8
1.4	0.5	2.0	30% H <sub>2</sub> O <sub>2</sub>	3	0.8
2.1	0.5	2.0	30% H <sub>2</sub> O <sub>2</sub>	3	0.8
2.2	0.5	2.0	30% H <sub>2</sub> O <sub>2</sub>	5	1.5
2.3	0.5	2.0	30% H <sub>2</sub> O <sub>2</sub>	5	2.2
2.4	0.4	2.0	30% H <sub>2</sub> O <sub>2</sub>	5	3.0
2.5	0.4	2.0	30% H <sub>2</sub> O <sub>2</sub>	7	3.0
			H <sub>2</sub> O	3	0.8
3.1	0.4	0.02	H <sub>2</sub> O	120	0.8
3.2	0.4	2.0	H <sub>2</sub> O	192	1.4
4.1	0.4	0.02	30% H <sub>2</sub> O <sub>2</sub>	6	0.8
4.2	0.4	0.02	H <sub>2</sub> O	5	0.8

<sup>a</sup> Trials sharing identical first digits are from related experiments (see text for details). <sup>b</sup> Initial concentration of TMSO (M). <sup>c</sup> Molar ratio of Mg to Si in the reaction mixtures. <sup>d</sup> See text for definition.

**Table II. <sup>29</sup>Si Chemical Shifts (ppm) of Model Compounds**

compound	solvent		
	CHCl <sub>3</sub>	ethyl ether	MeOH
Ph <sub>3</sub> SiCl	1.9	1.4	
TMS	0	0	0
PhTMS	-3.4	-4.3	-4.2
Ph <sub>3</sub> SiOOSiPh <sub>3</sub>	-3.9	<i>a</i>	<i>a</i>
Ph <sub>3</sub> SiOOH	-4.0	-7.6	-6.5
Ph <sub>3</sub> SiOAc	-9.6	-10.3	-10.0
Ph <sub>3</sub> SiOMe	-10.6	-11.9	-11.0
Ph <sub>3</sub> SiOH	-12.4	-16.7	-14.5
Ph <sub>3</sub> SiNH <sub>2</sub> <sup>b</sup>	-15.8	-16.8	
Ph <sub>3</sub> SiOSi(OPh)Ph <sub>2</sub>	-17.5		
Ph <sub>3</sub> SiOSiPh <sub>3</sub>	-17.8	<i>a</i>	<i>a</i>
Ph <sub>3</sub> SiOSi(OPh)Ph <sub>2</sub>	-40.5		
Ph <sub>2</sub> Si(OH) <sub>2</sub>		-34.0	

<sup>a</sup> Samples not soluble in the solvent employed. <sup>b</sup> Several attempts to produce the hydroperoxide from the amine failed, apparently due to base-catalyzed decomposition upon release of NH<sub>3</sub> into solution.

(b) <sup>29</sup>Si NMR Analysis of TMOS Reactions. The effect of Mg(OMe)<sub>2</sub> concentration on the silicon reaction mechanism was examined. The mixtures are presented by experiment numbers 1.1–1.4 in Table I. These reaction mixtures were prepared and mixed with Mg(OMe)<sub>2</sub> to give Mg:Si mol ratios of 0.02, 0.2, 1.0, and 2.0. Each solution had methanolic 30% H<sub>2</sub>O<sub>2</sub> added until R3 was 0.8.

The reactions of TMOS were monitored in the forsterite precursor synthesis. The five forsterite reaction mixtures prepared are shown by experiment numbers 2.1–2.5 in Table I. Methanolic 30% H<sub>2</sub>O<sub>2</sub> was added to the first four mixtures to produce R3 values of 0.8, 1.5, 2.2, and 3.0. The final mixture (no. 2.5) was treated with the solution of H<sub>2</sub>O until R3 was 3, and then with H<sub>2</sub>O in methanol until R3 was 3.8.

To determine the products formed with water in the forsterite precursor synthesis, two reaction mixtures were prepared that had Mg(OMe)<sub>2</sub>:TMOS mol ratios of 0.2 and 2.0 (3.1 and 3.2 in Table I). Solutions of water in methanol were added very slowly to the mixtures to give R values of 0.8 and 1.4, respectively.

To test the reactions of TMOS in the presence of catalytic amounts of Mg(OAc)<sub>2</sub>, two mixtures were prepared with Mg:Si mol ratios of 0.02 (4.1 and 4.2 in Table I). Water in methanol was added to one, and methanolic 30% H<sub>2</sub>O<sub>2</sub> to the other until R and R3 reached 0.8.

(c) Model Compounds. To aid in interpretation of the spectra of the forsterite precursor sols, several model compounds were prepared. Their <sup>29</sup>Si NMR chemical shifts in three solvents were examined (Table II).

Triphenylmethoxysilane (Ph<sub>3</sub>SiOMe),<sup>23</sup> hexaphenyldisiloxane (Ph<sub>3</sub>SiOSiPh<sub>3</sub>),<sup>24</sup> triphenylsilylamine (Ph<sub>3</sub>SiNH<sub>2</sub>),<sup>25</sup> diphenylsilylanediol (Ph<sub>2</sub>Si(OH)<sub>2</sub>),<sup>26</sup> pentaphenylphenoxydisiloxane (Ph<sub>3</sub>-SiOSi(OPh)Ph<sub>2</sub>),<sup>27</sup> and triphenylsilyl acetate (Ph<sub>3</sub>SiOAc)<sup>28</sup> were prepared by known methods.

The only reference that could be found for the preparations of bis(triphenylsilyl)peroxide (Ph<sub>3</sub>SiOOSiPh<sub>3</sub>) and triphenylsilyl hydroperoxide (Ph<sub>3</sub>SiOOH) used 98% H<sub>2</sub>O<sub>2</sub>,<sup>25</sup> which is commercially unavailable. A method analogous to that of Cookson et al. was employed for the preparation of Ph<sub>3</sub>SiOOSiPh<sub>3</sub>.<sup>29</sup>

A new method for the synthesis of Ph<sub>3</sub>SiOOH was developed, starting with triphenylsilyl acetate (Ph<sub>3</sub>SiOAc). Ph<sub>3</sub>SiCl was heated at reflux in an excess of glacial acetic acid (HOAc), which had been twice distilled from P<sub>2</sub>O<sub>5</sub>. The resulting product was isolated by trap-to-trap vacuum distillation at 50 °C into a trap at 0 °C. Residual HOAc was removed from the solid by adding dry toluene, forming an azeotrope with the acid, and removing the liquid mixture at 50 °C by trap-to-trap distillation into a LN<sub>2</sub> cooled trap. The crude Ph<sub>3</sub>SiOAc was dissolved in a minimum amount of hot acetone (50 °C) and recrystallized at -10 °C, mp 97.0–98.0 °C, lit.<sup>28</sup> mp 96.5–97.5 °C.

Triphenylsilyl hydroperoxide was produced by adding 3.0 g of 75% H<sub>2</sub>O<sub>2</sub> (66 mmol H<sub>2</sub>O<sub>2</sub>) to a solution of 1.7 g (5.3 mmol) of Ph<sub>3</sub>SiOAc in 20 mL of dry ethyl ether. The 75% H<sub>2</sub>O<sub>2</sub> was partly decomposed 98% H<sub>2</sub>O<sub>2</sub>, (FMC Corp.), as determined through iodometric titration. All of the starting acetate reacted to form Ph<sub>3</sub>SiOOH and Ph<sub>3</sub>SiOH within 24 h, as seen by the disappearance of the peak at -10.3 ppm and the formation of two new peaks in the <sup>29</sup>Si NMR spectra. This combination was isolated by removing the solvent by trap-to-trap distillation under vacuum. The mixture was characterized using IR (ν(SiOOH) 862 cm<sup>-1</sup>, lit.<sup>25</sup> 890 cm<sup>-1</sup>), <sup>29</sup>Si NMR spectroscopy (see Results), iodometric titrations, and formation of the characteristic decomposition product, Ph<sub>2</sub>Si(OH)<sub>2</sub>, on heating to 140 °C in anisole.<sup>26</sup> Ph<sub>2</sub>Si(OH)<sub>2</sub> was identified by comparison of its IR spectrum with that of an authentic sample. The Ph<sub>3</sub>SiOOH was produced and studied as a mixture with Ph<sub>3</sub>SiOH; no attempt was made to separate the two components.

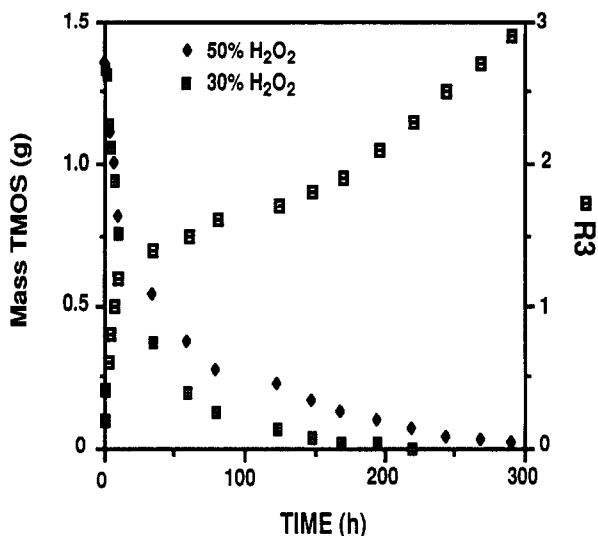
(d) <sup>25</sup>Mg NMR Analysis. The disappearance of Mg(OMe)<sub>2</sub> in a mixture with TMOS (2:1) was observed upon addition of a methanolic solution of 30% H<sub>2</sub>O<sub>2</sub> during 6 h (R3 of 3.0). An additional 1.8 mol of H<sub>2</sub>O/mol of TMOS was added over 3 h in the form of H<sub>2</sub>O in methanol. <sup>25</sup>Mg NMR spectra were recorded throughout both additions.

**Variations in the Forsterite Precursor Preparation.** The possibility of producing forsterite by utilizing Mg(OAc)<sub>2</sub> was examined by preparing a solution of TMOS in the presence of the acetate (2.0 mol of Mg/mol of Si). The low solubility of the acetate component limited the TMOS concentration to 0.09 M. A 0.5-mL portion of H<sub>2</sub>O was added instantaneously to the solution, resulting in a precipitation of a gel overnight. Headspace and <sup>29</sup>Si analyses were conducted before gelation. The gel was separated by centrifugation, dried under a heat lamp, and analyzed by microprobe (EDS). The supernatant liquid was evaporated to dryness under a heat lamp, and the resulting solid residue was examined with EDS.

The effect of H<sub>2</sub>O concentration on the consumption of TMOS in the forsterite precursor synthesis was examined. Two solutions of TMOS and Mg(OMe)<sub>2</sub> (1:2) were treated with identical aliquots of methanolic 30% and 50% H<sub>2</sub>O<sub>2</sub> with an R3 of 0.1–0.2. Headspace analysis was used to monitor the TMOS concentration.

**Raman Spectroscopy.** Raman spectra were collected on a computer-controlled Jarrell-Ash 25-300 spectrophotometer. Samples were contained in glass capillaries and were illuminated with 514.5-nm light from an argon ion laser in a 90° scattering geometry. Raman spectra were obtained from two xerogels prepared from forsterite precursor sols, to determine whether any magnesium peroxide could be isolated. The first sample was taken after addition of 30% H<sub>2</sub>O<sub>2</sub> (R3 of 3). A second sample was obtained at R3 of 6. Both were taken to dryness to trap-to-trap distillation, giving white xerogels.

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- (28) Takiguchi, T.; Abe, M. **1965**, *68*, 679.
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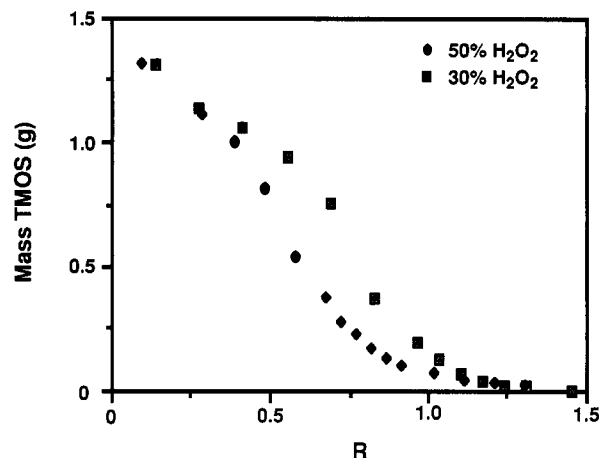
**Figure 1.** TMOS consumption with added 30% or 50%  $\text{H}_2\text{O}_2$  in the forsterite precursor synthesis. The solution of  $\text{H}_2\text{O}_2$  was added quickly for the first 10 h and then more slowly afterward.

### Results and Discussion

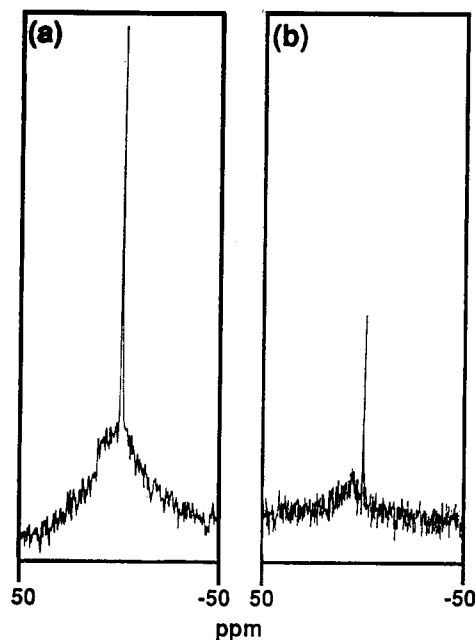
**Fate of Starting Materials. (a) TMOS Consumption in the Forsterite Synthesis.** In the forsterite precursor synthesis, TEOS underwent exchange with the methanol to produce primarily TMOS, with a small amount of  $\text{Si}(\text{OMe})_3(\text{OEt})$ .<sup>16,17</sup> The complexity introduced by the partially exchanged product led us to use pure TMOS in the following studies. To determine whether water or  $\text{H}_2\text{O}_2$  or both were reacting, two forsterite precursor solutions were treated with small portions of either 30% or 50%  $\text{H}_2\text{O}_2$  in methanol. Consumption of TMOS could be halted at any point by discontinuing the addition of the aqueous peroxide solution. The resulting consumption of TMOS, monitored by headspace analysis, is displayed in Figure 1. The 30%  $\text{H}_2\text{O}_2$  caused a greater consumption per mol of potentially reactive hydrogens added per mol of silicon. At the outset we assumed that one proton on  $\text{H}_2\text{O}$  and two on  $\text{H}_2\text{O}_2$  might react. The ratio of the moles of potentially reactive protons to the moles of silicon is expressed as  $R_3$ , by analogy with the well-known  $R$ .<sup>6</sup>

To determine whether water or  $\text{H}_2\text{O}_2$ , or both, was the main reactant initially, the data represented in Figure 1 were analyzed by examining the consumption of TMOS as a function of the moles of  $\text{H}_2\text{O}$  added. It became apparent (Figure 2) that the consumption of TMOS was directly proportional to neither the moles of water added nor the moles of potentially reactive hydrogens per mole silicon employed. Figure 2 shows 50%  $\text{H}_2\text{O}_2$  consumed more TMOS per mol of water added during the middle stages of the addition. Although both reactants required 1.4 mol of  $\text{H}_2\text{O}$ /mol silicon for total consumption of TMOS, 1 mol of  $\text{H}_2\text{O}$ /mol of silicon was all that was needed for reaction of 95% of it. This corresponded to an  $R_3$  of 2.1 in the 30%  $\text{H}_2\text{O}_2$  addition, the reactant used in the original forsterite synthesis. These results imply the existence of at least two reaction pathways in the initial steps. Since the consumption of TMOS was not directly proportional to the quantity of  $\text{H}_2\text{O}$  added,  $\text{H}_2\text{O}_2$ , or a magnesium species must be reacting as well. Water appears to be the dominant reactant, since both solutions required identical molar ratios of water to completely consume TMOS.

**(b)  $^{25}\text{Mg}$  NMR Spectroscopy.** Consumption of  $\text{Mg}(\text{OMe})_2$  was monitored by  $^{25}\text{Mg}$  NMR spectroscopy. A



**Figure 2.** Consumption of TMOS vs moles of  $\text{H}_2\text{O}$  added via 30% and 50%  $\text{H}_2\text{O}_2$  in the forsterite precursor synthesis.



**Figure 3.**  $^{25}\text{Mg}$  NMR spectra of  $\text{Mg}(\text{OMe})_2$  in the forsterite precursor synthesis;  $R_3$  values are (a) 0 and (b) 2.3. The sharp peak in the center of both spectra was produced by an internal capillary containing  $\text{MgCl}_2$  in  $\text{D}_2\text{O}$ .

forsterite precursor solution was prepared and treated sequentially with 30%  $\text{H}_2\text{O}_2$  and water. The spectrum of the precursor solution prior to any additions is shown in Figure 3a. The broad peak covering 40 to -40 ppm was identical to that of  $\text{Mg}(\text{OMe})_2$  in solution. This peak was still present, although slightly less intense, after all the  $\text{H}_2\text{O}_2$  was added. Due to the lack of shift sensitivity of the magnesium nucleus relative to its coordination,<sup>30</sup> it is possible that other  $\text{Mg}-\text{O}$  species were formed through the reaction with 30%  $\text{H}_2\text{O}_2$  and buried under the methoxide signal. Figure 3b shows the disappearance of the magnesium signal after the addition yielded and  $R_3$  of 2.3. A small hump covering  $\sim -20$  to 20 ppm was still present. At this point in the synthesis all the TMOS had been consumed, but  $\text{Mg}(\text{OMe})_2$  was still believed present based on the evidence from the spectrum. The methoxide was finally consumed, as witnessed by the disappearance of  $\text{Mg}$  signal, after  $R_3$  reached 4.8.

(30) Kraft, H. G.; Peringer, P.; Rode, B. M. *Inorg. Chim. Acta* 1981, 48, 135.

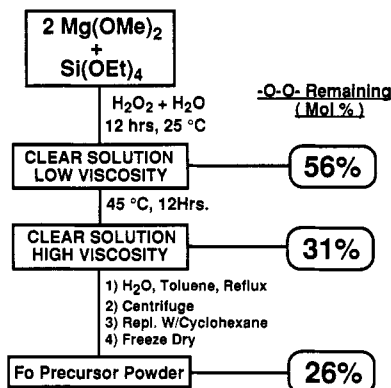


Figure 4. Peroxide content remaining at various points in the forsterite precursor synthesis, as determined by iodimetric titrimetry.

At the point in the forsterite precursor synthesis when TMOS has been totally consumed,  $^{25}\text{Mg}$  NMR spectra showed that  $\text{Mg}(\text{OMe})_2$  was probably still present. Signal from the methoxide did not vanish until all the  $\text{H}_2\text{O}_2$ , and an additional 1.8 mol of  $\text{H}_2\text{O}$ /mol of TMOS were added. This corresponded to total reactant ratios of 3.86 mol of  $\text{H}_2\text{O}$  and 0.468 mol of  $\text{H}_2\text{O}_2$ /mol of Si. No magnesium signal was detected past this point in the synthesis possibly due to the formation of unsymmetrical magnesium species, and consequent peak broadening.

(c) *Peroxide Analysis.* Samples from the forsterite precursor synthesis were taken from low- and high-viscosity sols, and from the xerogel. The results of the iodimetric titrations, and the corresponding reaction parameters used to prepare the samples, are given in Figure 4. Remaining peroxide (mol %) is based on the amount of  $\text{H}_2\text{O}_2$  initially added to the reaction mixture. Samples analyzed for peroxide content after 1-, 3-, and 5-h treatment with the mixture of acids ( $\text{HF}$  and  $\text{H}_2\text{SO}_4$ ) gave readings within  $\sim 1\%$ .

It has been well documented that  $\text{HF}$  in aqueous alcohol, and dilute or concentrated aqueous solutions of  $\text{HF}$ , react readily with silanols and siloxanes.<sup>31</sup> Even as low as 0.086 wt %  $\text{HF}$  in water has a fluoridating effect.<sup>31</sup> Enough  $\text{HF}$  was combined with the sol or xerogel to theoretically cleave all Si-O bonds present in the sample being analyzed. This should have destroyed any silicon networks formed and subsequently freed peroxide that might not readily have been available for reaction with the KI.

The survival of peroxide throughout the forsterite precursor synthesis indicated that a chance for further redox chemistry should exist. Incorporation of lowvalent iron or chromium into the sol in new low-temperature syntheses of olivine<sup>1</sup> and Cr-doped forsterite have been reported.<sup>15</sup> The nature of the peroxide functionality is discussed below. Its survival into the powder stage indicated a portion may be bound to one of the starting alkoxide metals.

**Analysis of the Early Stages of the Forsterite Precursor Synthesis.** The early stages in the forsterite precursor synthesis were examined with  $^{29}\text{Si}$  NMR spectroscopy. The spectrum in Figure 5a was taken at a point in the  $\text{H}_2\text{O}_2$  addition at an  $R3$  of 0.8. Unreacted TMOS ( $-78.4$  ppm) was still present to a large extent.<sup>8</sup> A peak developed at  $-76.8$  ppm, which could not be assigned to

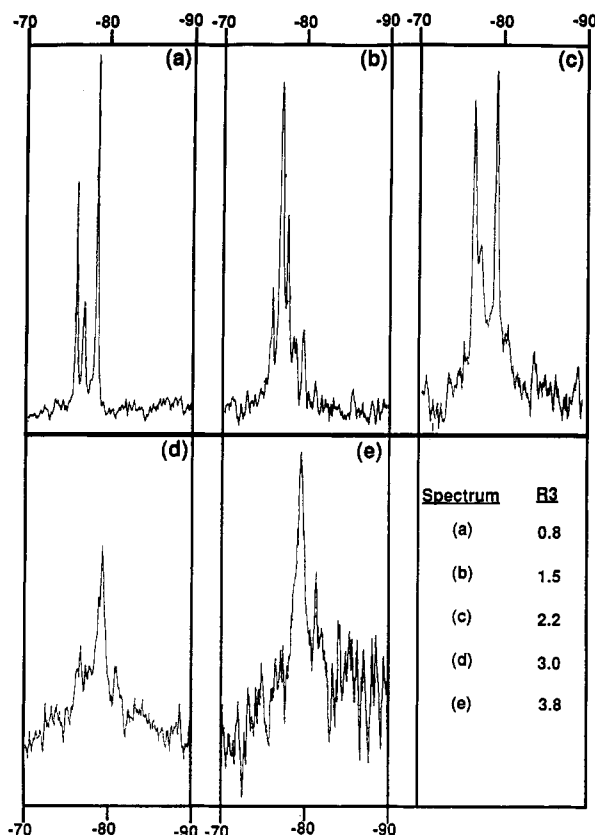


Figure 5.  $^{29}\text{Si}$  NMR spectra of TMOS treated with  $\text{H}_2\text{O}_2$  in the forsterite precursor synthesis.

any known compound. The peak at  $-75.7$  ppm is tentatively assigned to  $(\text{MeO})_3\text{SiOH}$ , the shift for which has been reported at  $-76.1$  ppm.<sup>8</sup> Complexation or reaction of this silanol with excess  $\text{Mg}(\text{OMe})_2$  may be responsible for the discrepancy.

After addition of half of the total  $\text{H}_2\text{O}_2$  ( $R3$  of 1.5), the spectrum of the resulting solution, Figure 5b, had developed three new peaks at  $-77.6$ ,  $-78.7$ , and  $-79.6$  ppm. The predominant peak in Figure 5b was located at  $-76.8$  ppm. None of these peaks have counterparts in the literature on TMOS reactions.

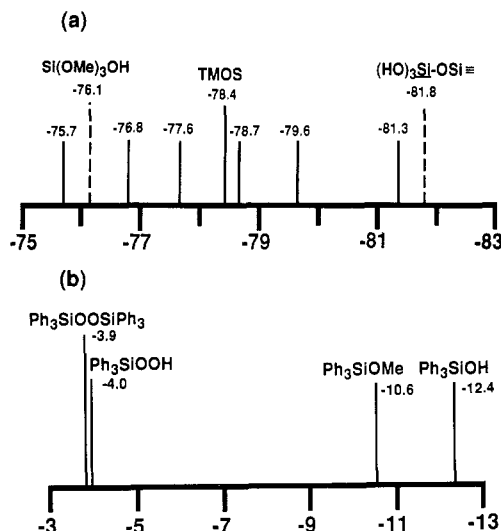
After addition of more  $\text{H}_2\text{O}_2$  solution, bringing  $R3$  to 2.2, the peak broadening had increased, and only two major peaks remained, Figure 5c. One was in the "hydrolysis" region (i.e., downfield from the TMOS signal) ( $-76.8$  ppm), and one was in the "condensation" region (i.e., upfield from the TMOS signal) ( $-79.6$  ppm). Peaks from known condensation products were absent.<sup>8</sup>

After  $\text{H}_2\text{O}_2$  addition was completed, all peaks were part of the same broad feature. The dominant peaks were at  $-76.8$ ,  $-79.6$ , and  $-80.9$  ppm, with the largest at  $-79.6$  ppm, Figure 5d. Products were starting to shift toward the "condensation" end of the spectrum.

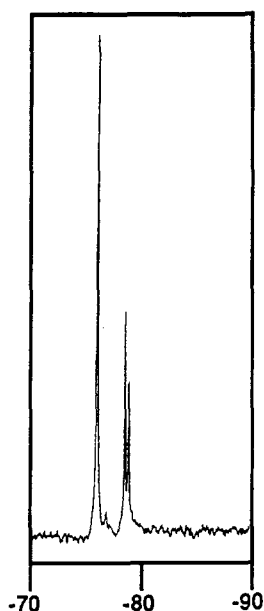
With the addition of 30%  $\text{H}_2\text{O}_2$  completed, water addition was initiated. Figure 5e shows the spectrum taken after 0.8 mol of  $\text{H}_2\text{O}$ /mol of silicon had been added. One predominant peak at  $-79.5$  ppm was present. A small peak at  $-81.3$  ppm was the only other discernible feature.

Assignment of most of the peaks in Figure 5 was problematic due to the lack of precedence. All the peaks were bracketed by known products of reactions between TMOS and water as illustrated by Figure 6a. Product peaks closest in shift to TMOS found in the literature were  $(\text{MeO})_3\text{SiOH}$  ( $-76.1$  ppm) and  $(\text{HO})_3\text{Si}-\text{OSi}$  ( $-81.8$

(31) Voorhoeve, R. J. H. *Organohalosilanes: Precursors to Silicones*; Elsevier Publishing Co.: New York, 1967; p 60.



**Figure 6.** Schematic representation of  $^{29}\text{Si}$  NMR chemical shifts in the (a) forsterite precursor preparation relative to those reported for some products from TMOS and (b) model compounds.



**Figure 7.**  $^{29}\text{Si}$  NMR spectrum ( $R3 = 1.4$ ) of TMOS treated with  $\text{H}_2\text{O}$  in the forsterite precursor synthesis.

ppm).<sup>8</sup> Comparison of Figure 6a with Figure 5 gave peaks at  $-75.7$  ppm, assigned to  $(\text{MeO})_3\text{SiOH}$ , and  $-81.3$  ppm as the closest matches.

In an attempt to simplify the reaction chemistry and subsequent spectral interpretations in the forsterite precursor synthesis, the initial hydrolysis was carried out with only water. Approximately 1.4 mol of  $\text{H}_2\text{O}$ /mol of silicon could be added to the forsterite precursor solution before any significant precipitation occurred, if the addition were made extremely slowly (192 h).  $^{29}\text{Si}$  NMR analysis of the resulting solution, Figure 7, showed two product peaks at  $-75.8$  and  $-78.7$  ppm; a small amount of residual TMOS ( $-78.4$  ppm) was still present.

Hydrogen peroxide was shown to be important for the formation of several of the peaks. Figure 7 indicated that the peaks at  $-78.7$  and  $-75.8$  ppm were produced by reactions that did not involve  $\text{H}_2\text{O}_2$ . Peaks at  $-76.8$ ,  $-77.6$ ,  $-79.6$ , and  $-80.9$  ppm in Figure 5 appeared to require the presence of  $\text{H}_2\text{O}_2$ .

A series of model compounds was prepared with functionalities analogous to species believed to be potential products in the early stages of the forsterite precursor synthesis. The chemical shifts of all model compounds prepared, starting materials ( $\text{Ph}_3\text{SiCl}$  and  $\text{Ph}_3\text{SiOH}$ ), decomposition products (Table II), remained basically unaffected by the solvent composition. The notable exceptions were the silanol, for which the shift dependence on solvent polarity has been noted,<sup>32</sup> and the hydroperoxide. No previous analysis of  $\text{Ph}_3\text{SiOOH}$  by NMR spectroscopy could be found in the literature. Its shift sensitivity was attributed to the presence of an acidic proton, analogous to that of the silanol. Dissociation of this proton would alter the electron density about the remaining oxygens, and subsequently, the shielding of the silicon nucleus.

Limitations were encountered in obtaining spectra for compounds in all three solvents; symmetrical hexaphenyl compounds showed solubility only in chloroform. Methanol proved to be a strong enough nucleophile to induce exchange, producing  $\text{Ph}_3\text{SiOMe}$  ( $-11.0$  ppm), with several of the compounds. The acetate exchanged over a few hours, while the silanol and chlorosilane exchanged completely overnight.

Model compounds were designed to aid in interpretation of Figure 5. Some plausible forsterite precursor products could contain Si-X functionalities, where  $\text{X} = \text{OOH}$  or  $\text{OOSiY}_3$ . The chemical shifts of the models are given in Table II. Using  $\text{Ph}_3\text{SiOMe}$  as a reference, the substitution of  $-\text{OSiPh}_3$  for the methoxy group created an upfield shift similar to that seen for silicon alkoxides.<sup>8</sup> Substitution of  $-\text{OH}$  for the methoxy ligand, however, did not produce the downfield shift expected.<sup>8</sup> The effect of solvent polarity on the shift of the silanol was judged to be too strong to use its peak shift in comparison to the methoxide. Substitution of both  $-\text{OOH}$  and  $-\text{OOSi}$  for the methoxy group in the model system created shifts downfield of both the hydroxy and methoxy analogues, as seen in Figure 6b. Spectra of forsterite precursors showed only peaks upfield of the hydrolyzed monomer,  $\text{Si}(\text{OMe})_3\text{OH}$ . From the model studies chemical shifts of  $(\text{MeO})_3\text{SiOOX}$  species ( $\text{X} = \text{H}$  or  $\text{Si}$ ) would be expected to be about  $-67$  ppm. Since no peaks were observed in this region, the peroxy analogues were ruled out as products in the forsterite precursor synthesis. Production of the magnesium analogues ( $\text{X} = \text{OMgY}$  or  $\text{OOMgY}$ ) has been hindered by lack of detailed synthetic procedures and data for characterization in the literature but are planned for the future.

**Search for  $\text{MgO}_2$  by Raman Spectroscopy.** The formation of  $\text{MgO}_2$  during the early stages of the forsterite precursor preparation could account for the continued solubility of magnesium-containing species throughout the synthesis. Raman spectroscopy was used in an attempt to detect peroxide ion. Due to the overlap of a large peak caused by methanol in the  $-\text{O}-\text{O}-$  stretching region, the samples had to be prepared as xerogels. The forsterite precursor solutions were sampled after  $R3$  values of 3.0 and 6.0 were reached. The absence of a peak near  $864\text{ cm}^{-1}$  for  $\text{MgO}_2$ <sup>33</sup> in the spectra of both samples suggested that  $\text{MgO}_2$  did not form (Figure 8).<sup>34</sup> Stable sols containing  $\text{MgO}_2$  have been formed by the addition of  $\text{Mg}(\text{OMe})_2$  to a solution of 30%  $\text{H}_2\text{O}_2$  in methanol;<sup>35</sup> xerogels from these

(32) Williams, E. A.; Carogiolli, J. D.; Larochelle, R. W. *J. Organomet. Chem.* 1976, 108, 153.

(33) Eysel, H. H.; Thym, S. Z. *Anorg. Allg. Chim.* 1975, 411, 97.

(34) Loehr, T., personal communication with J. M. Burlitch, 1992.

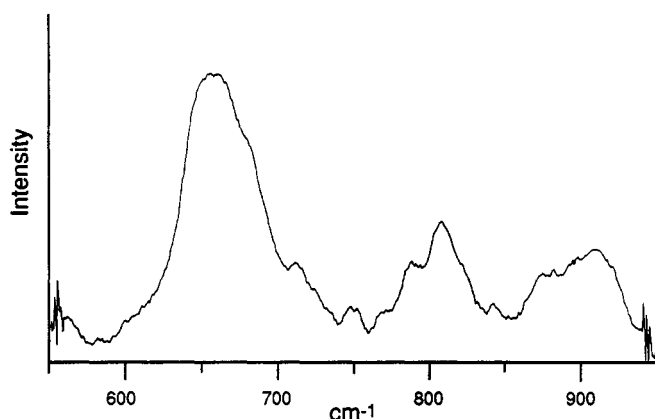
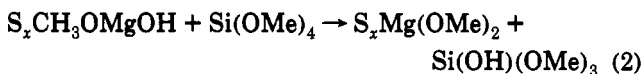
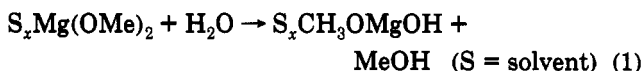


Figure 8. Raman spectrum ( $R3 = 6.0$ ) of a xerogel from the forsterite precursor synthesis.

sols show the characteristic peak for  $\text{MgO}_2$  at  $864\text{ cm}^{-1}$ . Although it is possible that  $\text{MgO}_2$  formed in the forsterite precursor sol then reacted while drying, its stability in MeOH makes it likely that it did not form in the first place. The possibility for the formation of a derivative of  $-\text{MgOOH}$  in the sol exists, but such a species would not have a well-defined Raman "signature". Strong peaks were seen at  $662$ ,  $804$ , and  $902\text{ cm}^{-1}$ . The first peak was in the region where the O-Si-O deformation would be expected ( $500\text{--}650\text{ cm}^{-1}$ ), and the latter two peaks in the region of Si-O stretching ( $800\text{--}1075\text{ cm}^{-1}$ ).<sup>36</sup> A small amount of unreacted  $\text{H}_2\text{O}_2$  may also be present in the xerogel; the weak peak at  $880\text{ cm}^{-1}$  may be due to the O-O stretch from trapped  $\text{H}_2\text{O}_2$ , which has been previously reported in the region  $878\text{--}882\text{ cm}^{-1}$ .<sup>37</sup>

A reaction scheme for the initial stage of the precursor synthesis can be postulated on the basis of the foregoing observations. The major product, a complexed silanol, can be viewed as the end result of the competition for water. Given the well-known voracity with which  $\text{Mg}(\text{OMe})_2$  consumes water to make  $\text{Mg}(\text{OH})_2$ , the observation that TMOS prevails in this competition is surprising. The initial reaction may proceed through a solvated, hydroxo-magnesium intermediate, which goes on to react with TMOS (eqs 1 and 2). The exchange of ligands, shown in



eq 2, may take place by way of a transient, hydroxide-bridged, double alkoxide after an initial nucleophilic attack on silicon. Formation of  $-\text{Mg-O-Si}$  linkages (eq 3),



X = halogen, H, OR, NHR, etc.

postulated to account for the binding of an organosilicon water-repelling agent to the surface of magnesia,<sup>38</sup> would explain the lack of peaks from condensation products in

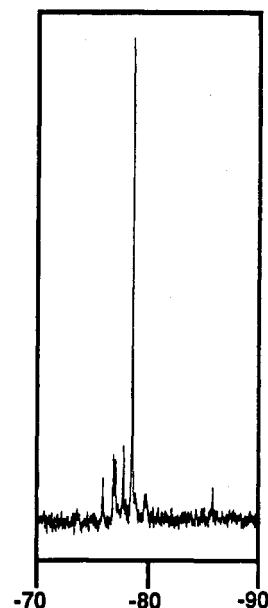
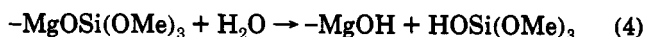


Figure 9.  $^{29}\text{Si}$  NMR spectrum of TMOS treated with 30%  $\text{H}_2\text{O}_2$  in the presence of 1 equiv of  $\text{Mg}(\text{OMe})_2$ ;  $R3 = 0.80$  and  $[\text{Mg}]/[\text{Si}] = 1.0$ .

the  $^{29}\text{Si}$  NMR spectra. In the present case, if  $\text{MeO-MgOSi}(\text{OMe})_3$  were an important intermediate, water would have to react with it more rapidly than with magnesium methoxide (eq 4) to form the silanol rather



than  $\text{Mg}(\text{OH})_2$ . In the presence of a relatively large amount of  $\text{Mg}(\text{OMe})_2$ , condensation was suppressed (as shown by the absence of peaks for condensation products in the  $^{29}\text{Si}$  NMR spectrum). As noted above, the primary hydrolysis product,  $\text{Si}(\text{OH})(\text{OMe})_3$ , may be complexed by or combined with  $\text{Mg}(\text{OMe})_2$ , and rendered less reactive toward condensation.

**Later Stages of the Forsterite Precursor Synthesis.** As  $\text{Mg}(\text{OMe})_2$  is consumed, first by 30%  $\text{H}_2\text{O}_2$  then by water,  $^{29}\text{Si}$  NMR analysis showed that the chemistry was altered drastically. Water has been used here<sup>1</sup> because experience has shown that excess  $\text{H}_2\text{O}_2$  caused unidentified precipitates to form, especially at lower Mg to Si ratios. A precursor for enstatite ( $\text{MgSiO}_3$ ), Figure 9, had peaks from the condensation product  $(\text{MeO})_3\text{SiOSi}(\text{OMe})_3$  at  $-85.7\text{ ppm}$ , and five peaks surrounding TMOS ( $-78.4\text{ ppm}$ ) analogous to those seen in Figure 5b. No condensation product peaks were seen in the spectrum previously shown in Figure 5a for the forsterite ratio of reactants. When the concentration of  $\text{Mg}(\text{OMe})_2$  was decreased an order of magnitude, the  $^{29}\text{Si}$  NMR spectrum showed only condensation products, (vide infra).

Thus two distinct stages were present in the synthesis of the precursor to forsterite: the early stage in which no condensation occurred, and the late stage in which condensation products evidently predominate. A comparison between the effects on TMOS consumption by a catalytic amount of  $\text{Mg}(\text{OMe})_2$  and by the amount employed in the forsterite precursor synthesis (Figure 10) showed some similarities and some differences. In both cases TMOS reaction ceased when addition of  $\text{H}_2\text{O}_2$  was stopped and resumed again when addition was restarted after  $\sim 200\text{ h}$ . An interesting region of Figure 10 starts at

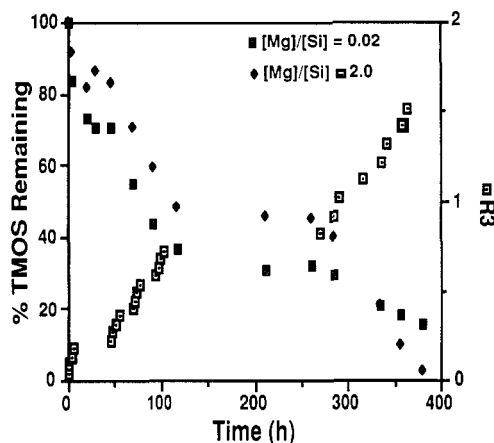
(35) Rywak, A. R.; Burlitch, J. M., unpublished observations, 1992.

(36) Nakamoto, K. *Infrared and Raman Spectra*; John Wiley and Sons: New York, 1986; p 474.

(37) Schumb, W. C.; Satterfield, C. N.; Wentworth, R. L. *Hydrogen Peroxide*; Reinhold Publishing Corp.: New York, 1954; p 330 and references therein.

(38) Voronkov, M. G.; Maletina, E. A.; Roman, V. K. *Heterosiloxanes*; Harwood Academic Publishers: London, 1988; p 96.





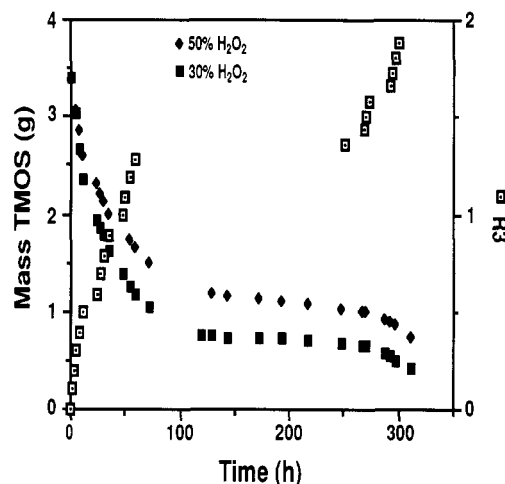
**Figure 10.** Comparison of TMOS reactivity with 30%  $\text{H}_2\text{O}_2$  for high and low concentrations of  $\text{Mg}(\text{OMe})_2$ . Addition of  $\text{H}_2\text{O}_2$  was stopped after 100 h and was resumed after 250 h.

~250 h and continues until the end; here the forsterite precursor curve crosses the catalytic curve, and TMOS consumption becomes more complete as the  $\text{Mg}(\text{OMe})_2$  catalyst is eventually deactivated.

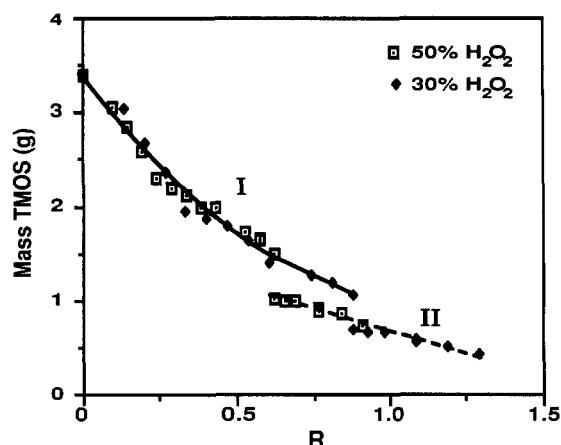
Consumption of TMOS was initially more rapid when a catalytic amount of the methoxide was present, with the initial slope  $\sim 2\times$  greater than the slope after the delay. This may be caused by the consumption of a portion of the catalyst over the period in which no  $\text{H}_2\text{O}_2$  was added. In the curve from the forsterite precursor the sections before and after the delay have similar slopes. The concentration of  $\text{Mg}(\text{OMe})_2$  remained high, and its effect on the reactivity of TMOS was largely unchanged. Thus, the crossover in the rates of TMOS consumption between the two solutions is a result of catalyst depletion. The greater amount of TMOS consumed in the early part of the catalyzed mixture might be accounted for by its reaction with water that is produced along with condensation products such as  $(\text{MeO})_3\text{SiOSi}(\text{OMe})_3$ .

**Catalysis.** The products from the reaction of TMOS with aqueous  $\text{H}_2\text{O}_2$  induced by catalytic portions of  $\text{Mg}(\text{OMe})_2$  were characterized by  $^{29}\text{Si}$  NMR spectroscopy. Peaks at  $-85.7$  ppm, corresponding to  $(\text{CH}_3\text{O})_3\text{Si}-\text{OSiR}_3$ , and at  $-93.8$  ppm, corresponding to  $\text{R}_3\text{SiO}-(\text{CH}_3\text{O})_2\text{Si}-\text{OSiR}_3$ ,<sup>8</sup> were observed. At low concentration,  $\text{Mg}(\text{OMe})_2$  preferentially caused condensation. No peaks corresponding to hydrolysis products, downfield of TMOS, were present. This analysis supports the hypothesis that clouding and precipitation observed in numerous solutions were a result of advanced condensation. The NMR spectrum of the methoxide-catalyzed solution resembled the reported spectrum for a base-catalyzed solution of TMOS and water.<sup>8</sup> It appears that the action of  $\text{Mg}(\text{OMe})_2$  was analogous to that of well-known base catalysts in both its induced consumption rate and reactions.

In an attempt to discern which component ( $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}_2$ ) was the preferred reactant for TMOS, a comparison between the effect of 30% and 50%  $\text{H}_2\text{O}_2$  was made (Figure 11). TMOS was consumed more extensively by 30%  $\text{H}_2\text{O}_2$  than it was by the 50%  $\text{H}_2\text{O}_2$ . Both solutions displayed the previously observed suspension of TMOS consumption when addition was discontinued. When  $\text{H}_2\text{O}_2$  addition was reinitiated after  $\sim 175$  h, TMOS reacted much more slowly than it did at the beginning of the experiment. After 290 h, additional  $\text{Mg}(\text{OMe})_2$  was added to both solutions and consumption of TMOS resumed. The loss of catalytic



**Figure 11.**  $\text{Mg}(\text{OMe})_2$  catalyzed reaction of TMOS with 30% and with 50%  $\text{H}_2\text{O}_2$ . Addition of  $\text{H}_2\text{O}_2$  was stopped after 72 h and was resumed after 250 h.



**Figure 12.** Consumption of TMOS vs moles of  $\text{H}_2\text{O}$  added via 30% and 50%  $\text{H}_2\text{O}_2$ . Region I (—) and region II (---) represent the areas in Figure 11 between 0–72 and 250–312 h, respectively.

activity over time indicated a slow consumption of the catalyst was occurring.

Since 30%  $\text{H}_2\text{O}_2$  has a proportionately greater amount of water than 50%  $\text{H}_2\text{O}_2$ , the increased extent of TMOS consumption could indicate that water is the primary reactant for TMOS. By plotting the data displayed in Figure 11 in a different format (Figure 12), the depletion of TMOS is seen to be proportional to the amount of water added. The consumption of TMOS for both 30% and 50%  $\text{H}_2\text{O}_2$  is expressed by a single curve when plotted against the moles of water added. In Figure 12, region I represents the early stages before the addition of  $\text{H}_2\text{O}_2$  is stopped at 175 h. TMOS is rapidly consumed for both of the solutions. When addition of  $\text{H}_2\text{O}_2$  was resumed, after 250 h (region II), the TMOS consumption of both solutions was linear with respect to the water added. This gives clear evidence that the magnesium species preferentially catalyzes reactions between TMOS and water. The role of  $\text{H}_2\text{O}_2$  is not yet fully understood.

Since water, not  $\text{H}_2\text{O}_2$ , reacts with TMOS, a mechanistic explanation for the process can be drawn from the well-known base-catalyzed reactions.<sup>39</sup> Initially, either an uncharacterized magnesium species, or  $\text{OH}^-$  from dissociation of such a species, could form and react to produce

(39) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: San Diego, 1990; pp 134, 145.



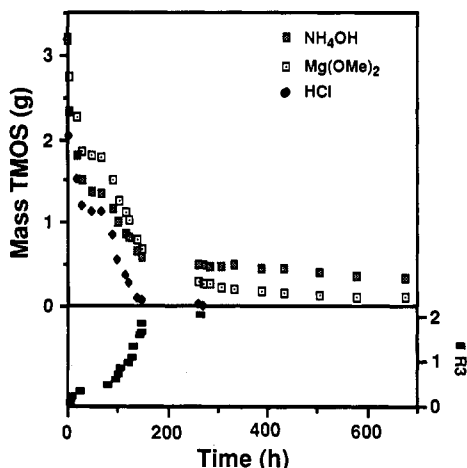


Figure 13. Comparison of  $\text{Mg}(\text{OMe})_2$  to common sol-gel catalysts in the reaction of TMOS with 30%  $\text{H}_2\text{O}_2$ .

the silanol. The newly formed silanol, in the presence of  $\text{OH}^-$  and excess TMOS, would undergo base catalyzed condensation. Eventually, as TMOS was depleted, the dimer would undergo further condensation.

Relating these findings back to the forsterite precursor synthesis allows us to break it down into two stages. The stage characterized by the presence of excess  $\text{Mg}(\text{OMe})_2$  was discussed above. After  $\text{Mg}(\text{OMe})_2$  is consumed (first by  $\text{H}_2\text{O}_2$ , then by water added separately), at an  $R_3$  of  $\sim 4.8$ , as indicated by  $^{25}\text{Mg}$  NMR spectroscopy (see above), the second stage (the base-catalyzed regime) begins. Since the first stage does not appear to affect more than one group on TMOS, i.e., it produces  $\text{Si}(\text{OMe})_3\text{OH}$ , the environment about silicon in the second stage should appear similar to that of the starting TMOS to the base catalyst and should undergo the typical base catalyzed condensation reactions. The final steps of the forsterite precursor preparation had many characteristics associated with condensation and network formation.<sup>1</sup>

**Other Catalysts.** To see if the catalytic abilities of  $\text{Mg}(\text{OMe})_2$  to promote TMOS consumption by aqueous  $\text{H}_2\text{O}_2$  were unique, several other catalysts for hydrolysis were examined. The ability of  $\text{Mg}(\text{OMe})_2$  containing reaction mixtures to catalyze consumption was compared with that of two conventional sol-gel catalysts (Figure 13); all catalysts were present in equal concentrations.  $\text{HCl}$  produced the quickest consumption of TMOS. Initially  $\text{NH}_4\text{OH}$  gave the second fastest TMOS consumption, but it was eventually passed by the  $\text{Mg}(\text{OMe})_2$  catalyzed solution. Both  $\text{Mg}(\text{OMe})_2$  and  $\text{NH}_4\text{OH}$  solutions turned cloudy and yielded a white precipitate when about 80% of the TMOS was consumed. This indicated that both probably catalyzed extensive condensation reactions of TMOS. The  $\text{HCl}$ -catalyzed mixture remained clear well after the disappearance of TMOS. All solutions displayed a lull in TMOS consumption when  $\text{H}_2\text{O}_2$  addition was temporarily halted at 19 h and resumed when addition was continued at 72 h. The temporary stoppage of TMOS consumption was a result of the limitation of the reactants, and not a unique characteristic of the  $\text{Mg}(\text{OMe})_2$  catalyst.

Alkoxides of the alkali metals also behaved as catalysts (Figure 14). The more basic Na and Li analogues, commonly used in sol-gel preparations,<sup>40</sup> produced a slightly greater extent of consumption. All three solutions

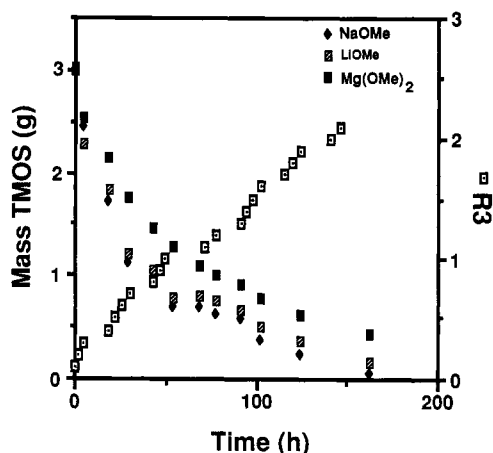


Figure 14. Comparison of  $\text{Mg}(\text{OMe})_2$  to other alkoxide catalysts for the reaction of TMOS with 30%  $\text{H}_2\text{O}_2$ .

turned cloudy at  $\sim 163$  h, at which point  $\sim 85\%$  of the TMOS initially added had been consumed. The catalytic activity of the alkali alkoxides probably derives from the hydroxide ion that is produced by their well-known reaction with water.

Since other salts of magnesium might be of use in the forsterite synthesis, the ability of  $\text{Mg}(\text{OAc})_2$  to catalyze TMOS consumption was examined.  $\text{Mg}(\text{OAc})_2$  was previously shown not to catalyze the alkoxy exchange.<sup>16</sup> It did, however, catalyze the reaction between TMOS and the  $\text{H}_2\text{O}_2$  solution. The extent of TMOS consumption was nearly identical for the acetate and methoxide solutions. Both turned cloudy during the final stages of reaction, which suggested extensive condensation reactions in both cases.

To determine whether the acetate was inducing behavior analogous to that of the methoxide, the reaction intermediates were analyzed. Samples of catalyzed reactions of TMOS with 30%  $\text{H}_2\text{O}_2$ , and with water, gave  $^{29}\text{Si}$  NMR spectra analogous to those obtained for the reactions catalyzed by  $\text{Mg}(\text{OMe})_2$ ; each had a peak from the  $(\text{MeO})_3\text{Si}-\text{OSi}\equiv$  species at  $-85.7$  ppm.

The foregoing observations indicated that  $\text{Mg}(\text{OAc})_2$  might be a potential substitute for the methoxide in the forsterite precursor synthesis. At magnesium to silicon ratios used to prepare forsterite, solution concentrations employing the acetate had to be reduced to 0.09 M in silicon to dissolve the salt. This dilution prohibited NMR analysis of these solutions.  $\text{Mg}(\text{OMe})_2$  reacts with water to form the sparingly soluble  $\text{Mg}(\text{OH})_2$ .<sup>41</sup> Because  $\text{Mg}(\text{OAc})_2$  is soluble in both water and methanol, direct addition of water was possible. The substitution of the acetate for the methoxide in the forsterite precursor caused precipitation to occur at an  $R$  value of 8. The physical behavior of these solutions matched those of solutions employing catalytic proportions of the methoxide species.  $\text{Mg}(\text{OAc})_2$  promoted consumption of TMOS about as well as the methoxide; both yielded condensation products. However, the silicon reaction products did not appear to change as the acetate concentration was altered. When the precipitate from such a reaction was isolated, EDS analysis showed it to consist primarily of silicon, with trace amounts of magnesium. When dried, the supernatant liquid yielded a white crystalline solid that contained mostly magnesium and only trace quantities of silicon.

(40) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: San Diego, 1990; p 217.

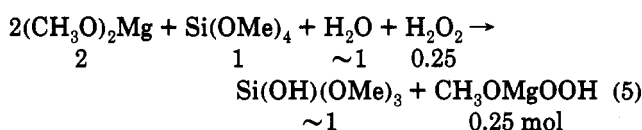
(41) Lund, H.; Bjerrum, J. *Chem. Ber.* 1931, 64, 210.

Thus magnesium was not incorporated into the precipitate formed during the attempted synthesis of a precursor for forsterite using the acetate.  $\text{Mg}(\text{OMe})_2$  appeared unique in its ability to induce distinctly different reactions in TMOS as a result of its concentration in solution.

### Conclusions

The forsterite precursor synthesis could be separated into two distinct stages. In the first stage, which had a high concentration of  $\text{Mg}(\text{OMe})_2$ , water in the aqueous  $\text{H}_2\text{O}_2$  reacted almost exclusively with TMOS and formed a hydrolysis product which, remarkably, showed little or no tendency to condense, possibly due to reaction with, or complexation by  $\text{Mg}(\text{OMe})_2$ . The  $^{29}\text{Si}$  NMR spectra of some of the products were unlike any previously reported. Interaction of the expected hydrolysis products with magnesium alkoxide may account for the unidentified peaks.

The circumstantial evidence to date suggests that the stoichiometry of the initial reaction (up to  $\sim 1$  mol of  $\text{H}_2\text{O}$ /mol of Si) is as follows:



Then, as the concentration of  $\text{Mg}(\text{OMe})_2$  was depleted, first by reaction with aqueous  $\text{H}_2\text{O}_2$  and then with  $\text{H}_2\text{O}$  added later, the second stage is reached. Here condensation reactions dominate and lead to the formation of a

sol. Since the dried ultrafine particulate xerogel contained  $\sim 25\%$  of the original peroxide and gave no Raman spectroscopic signal for  $\text{MgO}_2$ , a possible intermediate is the hydroperoxide of magnesium  $\text{LMg-OOH}$ , where  $\text{L} = \text{MeO}$  or  $\text{OOH}$ , which may exist in an oligomeric form. Current efforts are directed toward the characterization of this and some of the silicon-containing intermediates.

Small amounts of  $\text{Mg}(\text{OMe})_2$  catalyzed the reaction of TMOS with 30%  $\text{H}_2\text{O}_2$  in a manner ostensibly similar to the known base-catalyzed mechanism. The unidentified catalytic magnesium species is as efficient a catalyst as  $\text{NH}_4\text{OH}$ .

The role of  $\text{Mg}(\text{OMe})_2$  in the forsterite synthesis is multifaceted. First it catalyzes the alkoxy exchange of TEOS to TMOS<sup>16</sup> and then promotes reaction of the latter with water in the 30%  $\text{H}_2\text{O}_2$ . The course of the latter reaction depends on the *concentration* of the magnesium species. The ability to produce forsterite without addition of either traditional acid or base catalysts was made possible by the catalytic activity of the methoxide.

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