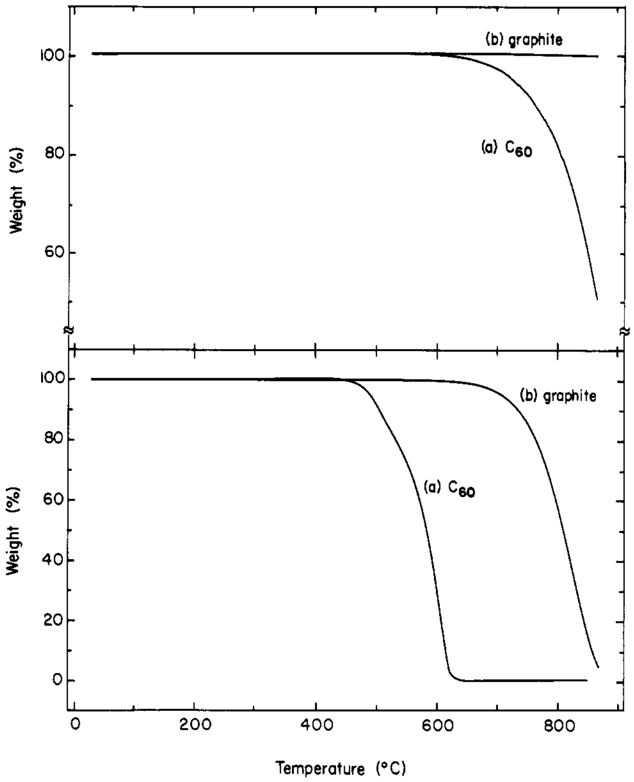

Figure 2. Top: TGA of (a) C_{60} and (b) graphite. Samples were heated at 10 °C/min to 860 °C under N_2 at a flow rate of 50 cm^3/min. C_{60} had been predried by heating at 210 °C for 16 h in a dynamic vacuum. Bottom: TGA of (a) C_{60} and (b) graphite. Samples were heated at 10 °C/min to 860 °C in air at a flow rate of 50 cm^3/min. C_{60} had been predried by heating at 210 °C for 16 h in a dynamic vacuum. A small effect from residual toluene can be observed.

in the TGA under nitrogen at 300 °C for 30 min was analyzed by using thermal desorption mass spectrometry. This analysis indicated the presence of appreciable amounts of toluene ($m/z = 92$ and 91, a prominent fragment ion) in the sample, suggesting that the volatile component observed in the TGA is toluene.

TGA studies were carried out to ascertain the heat treatment necessary for complete removal of toluene from the C_{60}. Surprisingly, the toluene was eliminated in a stepwise manner, as determined from heat treatments at various temperatures up to 600 °C. For example, when a sample of C_{60} was heated for 0.5 h at 350, 400, and 450 °C, the observed weight loss corresponded to approximately 1.0, 1.0, and 1.0%, respectively. Weight loss was rapid, occurring during the first 5 min at a particular temperature. To effectively remove all toluene, it was necessary to heat the sample at 600 °C for approximately 0.5 h. While attempting to prepare standard solutions of C_{60} that had been heated to 600 °C in the manner described above, we found that the material would no longer completely dissolve in toluene. This change in solubility suggested to us that some decomposition or transformation of C_{60} occurs when it is heated to 600 °C. To avoid this problem, toluene was removed by heating the C_{60} at 210 °C for 16 h in a dynamic vacuum. The C_{60} heated in this manner was completely soluble in toluene.

The thermal and oxidative properties of C_{60} predried to 210 °C in the manner described above were compared to those of graphite. Powdered samples of each were heated from 30 to 860 °C at 10 °C/min in nitrogen and air atmospheres at a flow rate of 50 cm^3/min. The upper panel of Figure 2 shows the thermal stability of C_{60} and graphite. When heated to 860 °C, graphite and C_{60} retain 100% and 40% of their weight, respectively. Moreover, C_{60} commenced to lose weight at ~600 °C. The lower panel of Figure 2 shows the comparative oxidative stability of C_{60} and graphite in air. When heated as described previously, a sample of C_{60} began to lose weight at ~480 °C with complete weight loss occurring at ~650 °C. Graphite commenced losing weight at ~700 °C and had lost 95% of its weight at 860 °C.

We presume that the weight loss observed when C_{60} is heated in nitrogen (Figure 2 upper panel) is due to sublimation. Krätschmer et al.[1] have reported that C_{60} sublimes in a vacuum at ~400 °C. Using Knudsen effusion mass spectrometric measurements, Pan et al.[9] have determined the heat of sublimation of C_{60} from a polycrystalline mixture of C_{60} and C_{70} to be 40.1 kcal/mol at the average temperature of 434 °C.

The TGA results presented in the lower panel of Figure 2 indicate that reaction of C_{60} with air does occur. If the weight loss of C_{60} in air were due to sublimation, the data should be identical with those observed in nitrogen. We conclude, therefore, that C_{60} is less stable than graphite powder when heated in air.

The tenacity of C_{60} for toluene was an unexpected observation. We expected complete degassing of toluene at 300 °C; however, TGA and mass spectral data suggest that toluene remains adsorbed at temperatures up to 600 °C. This behavior, however, is consistent with C_{60}–solvent interactions observed during crystal studies.[10] Two possible explanations for this solvent interaction come to mind: (1) toluene is a trapped impurity from the separation process and/or (2) some molecular interaction exists between C_{60} and toluene. In either case, the strong retention and stepwise elimination of toluene observed in the TGA suggests that different binding sites for toluene exist in C_{60}. We are continuing to investigate this phenomenon.

Acknowledgment. We thank the Office of Naval Research for support of this research.

Registry No. C_{60}, 99685-96-8; graphite, 7782-42-5; nitrogen, 7727-37-9; toluene, 108-88-3.

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Magnesium Methoxide Derived Catalysis of Transesterification, Hydrolysis, and Condensation of $Si(OMe)_4$ in the Sol–Gel Syntheses of Magnesium Silicates

Kirk E. Yeager and James M. Burlitch*

Department of Chemistry, Cornell University
Ithaca, New York 14853-1301

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In recent work in our laboratories, the preparation of sol–gel precursors for synthetic forsterite, Mg_2SiO_4,[1] and enstatite, $MgSiO_3$,[2] were achieved by the H_2O_2-assisted

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* Author to whom correspondence should be addressed.

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hydrolysis of a solution of tetraethyl orthosilicate (TEOS) and magnesium methoxide, in methanol. Although other solution chemical routes to forsterite have been reported,[3-6] our reactions are unusual in that (a) no strong acid or base catalyst was added to assist hydrolysis of TEOS and (b) magnesium hydroxide did not precipitate during the hydrolysis. These observations prompted us to analyze the reaction intermediates, and this report describes our preliminary findings of facile transesterification, hydrolysis, and condensation reactions that are brought about by catalysts generated in situ.

Gas chromatographic (GC) analysis of the vapors in the headspace above the Mg_2SiO_4 precursor reaction mixture prior to hydrolysis revealed that tetramethyl orthosilicate (TMOS) and $Si(OMe)_3(OEt)$ were present in place of the TEOS initially added.[7] The identities of the products were confirmed by retention time (for TMOS) and by GC-MS analysis; the peak due to $Si(OMe)_3(OEt)$ had a parent ion at *m/e* 166. The catalytic effect of $Mg(OMe)_2$ on the transesterification (alcohol interchange) reactions was revealed when the Mg:Si mole ratio was reduced to 0.03:1; headspace and GC-MS analysis showed that the entire series of intermediates, viz., $Si(OEt)_3(OMe)$, $Si(OEt)_2(OMe)_2$, $Si(OEt)(OMe)_3$, and TMOS, had formed from TEOS within 90 min. After 3.5 h, the starting TEOS (0.22 M) was completely converted to a mixture of TMOS and $Si(OMe)_3(OEt)$ in a ratio of 11.7 to 1. Without $Mg(OMe)_2$, this exchange did not reach completion even after 2 weeks. Since the exchange reaction is an equilibrium process,[8] the final ratio is dependent on the starting TEOS concentration. A higher TEOS concentration would produce more EtOH during exchange and would cause a greater tendency toward ethoxy substitution.

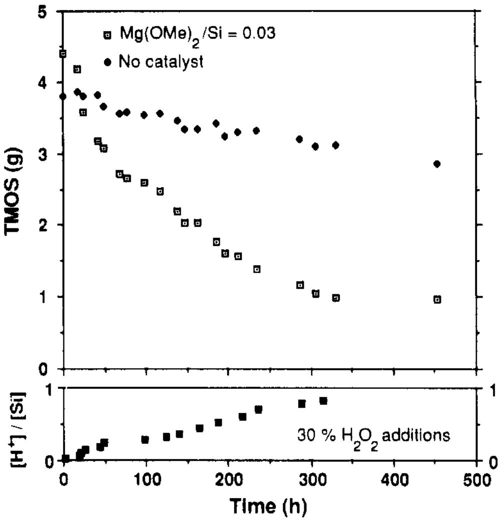

Figure 1. Consumption of TMOS in methanol with and without $Mg(OMe)_2$ after additions of 30% H_2O_2 in methanol; except for the last point, analysis was performed 3–12 h after each addition. The concentration of potentially reactive protons added is defined as $["H^+"] = [H_2O] + 2[H_2O_2]$.

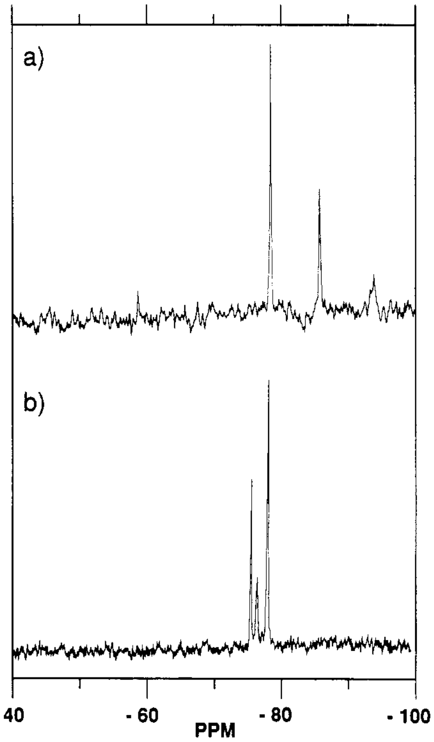

Figure 2. ^{29}Si NMR spectrum of solutions of TMOS and $Mg(OMe)_2$ in methanol treated with 30% H_2O_2 ($["H^+"]/[Si] = 0.8$): (a) catalytic mixture, $[Mg]/[Si] = 0.02$; (b) forsterite precursor, $[Mg]/[Si] = 2.0$.

To our knowledge, this is the first example of a catalytic effect of a transesterification reaction by a magnesium alkoxide. Solutions of TMOS in ethanol[9] and TEOS in methanol,[10] 2-propanol,[11] and 1-propanol[12] have been reported to undergo transesterification during hydrolysis; most studies utilized NMR spectroscopy for product characterization.[9-11,13] Various acids, bases, and sodium alcoholates have catalyzed alcohol exchange in organosilicon alkoxides.[14-17] Transesterification has been suggested to proceed through a type of bimolecular nucleophilic displacement reaction.[18] In view of the unusual catalytic properties of $Mg(OMe)_2$, other related compounds were examined by the convenient GC headspace analysis

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method[19] to see if they behaved similarly. The methoxides of lithium, sodium, and calcium also catalyzed the transesterification of TEOS in methanol, but no exchange was detected with magnesium acetate.

Transesterification is particularly important for sol–gel processing because of the large differences in reactivity that may exist as a function of the nature of the OR groups on $Si(OR)_4$, especially the ease with which they hydrolyze. Thus, the preparation of the forsterite precursor was facilitated by the in situ formation of the more readily hydrolyzed (but more toxic) alkoxide, TMOS.[9,10] This increased reactivity notwithstanding, without some catalyst for its hydrolysis, TMOS would not have hydrolyzed in the time frame of several hours needed for the synthesis. As determined by GC headspace analysis, the effect of $Mg(OMe)_2$ on the reactivity of TMOS with 30% H_2O_2 is shown in Figure 1. In the presence of a small amount (3 mol %) of $Mg(OMe)_2$, TMOS was consumed readily by aqueous, methanolic H_2O_2, added in small portions. In contrast, without $Mg(OMe)_2$, the reaction of TMOS proceeded to a very limited extent as hydrogen peroxide was added. The enhancement of reactivity brought about by the addition of $Mg(OMe)_2$ strongly indicates that some, as yet uncharacterized, magnesium-containing species, generated in situ, served as a catalyst for the reaction of TMOS.

^{29}Si NMR analysis of the catalyzed reaction mixture of TMOS and aqueous H_2O_2 revealed that the observed products derived from condensation. The peaks at −85.7 and −93.8 ppm in Figure 2a correspond to $(CH_3O)_3\mathit{Si}OSi{\equiv}$ and ${\equiv}SiO(CH_3O)_2\mathit{Si}OSi{\equiv}$ species, respectively;[20] the large peak at −78.4 ppm is from residual TMOS.[21] The spectrum resembles that from base-catalyzed reaction of TMOS and water for which peaks at −78.4 and −85.9 ppm were reported.[20] No peaks downfield of TMOS, expected for hydrolysis products, were present.[9,20,22]

In a similar experiment, in which water was substituted for the 30% H_2O_2 and was added very slowly by means of a syringe pump, condensation products were produced that had ^{29}Si NMR peaks identical with those seen in Figure 2a. The fact that water and 30% H_2O_2 produced identical products suggests that TMOS reacted primarily with water in both cases. Further support for this hypothesis comes from the observation that when ostensibly equivalent amounts of 30% H_2O_2 and 50% H_2O_2 were used in otherwise identical experiments, the former caused the greater consumption of TMOS. The foregoing observations point to a base, possibly one with a Mg–OH functional group, as the active catalyst. When a catalytic amount of anhydrous magnesium acetate[23] was used in place of $Mg(OMe)_2$, the same condensation products, described above, were detected by NMR analysis, irrespective of whether hydrogen peroxide or water was used. Hydrolysis of the active salt might account for a similar hydroxomagnesium-containing active catalyst.

Although numerous acids and bases have been added as catalysts for the hydrolysis of TMOS,[20,24] the reason none was required for the forsterite precursor synthesis became apparent in light of the newly found catalytic ability of the magnesium-containing species already present or generated in situ. The NMR spectra of the products from the early stages of the forsterite precursor synthesis differed significantly from those of the catalysis studies, in which the $Mg(OMe)_2$ concentration was 2 orders of magnitude less. A ^{29}Si NMR spectrum (Figure 2b), taken after the same extent of reaction as that shown in Figure 2a, had completely different product peaks. The peak at −75.6 ppm has a chemical shift close to that reported for $(MeO)_3SiOH$ (−76.1 ppm);[20] the small difference may be due to complexation by or reaction with magnesium methoxide. Unreacted TMOS appears at −78.4 ppm. The identity of the product(s) responsible for the peak at −76.8 ppm is not known, but one possibility is that it corresponds to a new product such as $(MeO)_3SiOOX$, where X may be MgOMe, MgOH, H, $Si(OR)_3$, etc. This peak was not observed when water was substituted for the hydrogen peroxide.[25]

From the foregoing observations, we conclude that, at the concentration used to prepare the forsterite precursor, a magnesium alkoxide derived catalyst, created in situ, facilitates hydrolysis and condensation reactions of TMOS in which the products differ markedly from those seen for a much lower concentration of $Mg(OMe)_2$. We know of only one previous report that claimed a metal alkoxide, viz., $Ti(OEt)_4$, acted as a catalyst for the hydrolysis and condensation of another alkoxide (TEOS).[26]

In summary, the role of $Mg(OMe)_2$ in the forsterite synthesis is multifaceted. Initially, it catalyzed the transesterification of TEOS with methanol to produce, in situ, the more reactive analogue, TMOS. Then again in situ, it produced a catalyst for the hydrolysis and condensation reactions of TMOS with 30% H_2O_2. Model studies are in progress to help characterize the new intermediates and to better define possible reaction mechanisms of $Mg(OR)_2$ and other metal alkoxides.

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(25) Precipitation was observed when the mole ratio of water to TMOS was >1, despite the very slow addition rate.

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