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Reaction of tetraethylorthosilicate and hexafluoroacetone trihydrate [☆]

Joseph P. Carpenter, C.M. Lukehart *, Brennan T. Price, James E. Wittig

Departments of Chemistry and of Applied and Engineering Sciences, Vanderbilt University, Nashville, TN 37235, USA

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Abstract

Neat tetraethylorthosilicate reacts with neat hexafluoroacetone trihydrate to give particulate silica xerogel precipitates. Particulates formed early in the reaction have spheroidal micromorphology, and control of the reaction conditions affords particle sizes approaching 25 nm in diameter. A mixture of tetraethylorthosilicate and $Ti(Oi\text{-}Pr)_4$ reacts with hexafluoroacetone trihydrate as neat liquids at 5 °C to give immediate precipitation of a Si/Ti mixed-metal oxide xerogel particulate having a Si:Ti molar ratio of approximately 9:6.

Keywords: Xerogel formation; Hexafluoroacetone trihydrate; Tetraethylorthosilicate

1. Introduction

We have reported recently that addition of varying relative amounts of the (trihydroxysilyl)-methylidynetricobalt carbonyl cluster complex (**1**) to a conventional sol–gel recipe for the formation of silica xerogels leads to apparent covalent incorporation of **1** into the resulting xerogel matrix through Si–OH condensation reactions, Eq. (1) [1]. Attempts to prepare similarly doped silica xerogels using aqueous HCl as a catalyst and prolonged gelation times leads to the decomposition of **1** to afford Co^{2+}. Successful incorporation of **1** into silica xerogels can be achieved using base catalysis and cosolvents as shown in Eq. (1). These conditions provide more rapid gelation times and minimize the amount of water present during gelation. However, subsequent reactivity and analysis of this molecularly doped xerogel indicate that a small amount of Co^{2+} ion might still have formed during its preparation. A more anhydrous method of xerogel formation is clearly needed for the preparation of doped xerogels in which water-sensitive dopants are used.

$$Si(OMe)_4 + \underset{\mathbf{1}}{(HO)_3SiCCo_3(CO)_9} \xrightarrow[NH_3(aq.)cat.]{H_2O/MeOH/DMF} SiO_2\ \text{xerogel}\cdot\mathbf{1} \qquad (1)$$

Xerogel formation under more anhydrous conditions than those used in conventional sol–gel recipes has been achieved by using non-aqueous solvents containing dilute concentrations of water, by generating water homogeneously in situ from a variety of chemical reactions, such as the dehydration of alcohols, or by the extrusion of water from inverse micelles [2–5]. We sought a means to effect a sol–gel conversion using tetraethylorthosilicate (TEOS) in which the presence of an alcohol cosolvent, water, or added aqueous catalyst would not be required. Hexafluoroacetone trihydrate (HFATH) seemed a likely reagent because (i) it is commercially available, (ii) it is a liquid at room temperature, (iii) the pK_a of the monohydrate, which exists as the geminal diol, $(CF_3)_2C(OH)_2$, is 6.58, so this species might itself serve as a catalyst for Si–OEt hydrolysis, and (iv) HFATH has apparently strong binding of the waters of hydration. Because HFATH and its lower hydrates might serve as both sources and 'getters' of water, the concentration of liquid water in HFATH should be very low. We now report that tetraethylorthosilicate and HFATH react as neat liquids to give silica xerogel formation. Results of an initial study of this reaction are presented below.

[☆] This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

* Corresponding author.

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2. Experimental

Tetraethylorthosilicate (TEOS), tetraisopropoxide titanium(IV) and hexafluoroacetone trihydrate (HFATH) were purchased from Aldrich Chemical Company, Inc. TEOS was further purified by distillation through a Vigreux column. Scanning electron microscopy (SEM) was performed on a Hitachi X-650 SEM equipped with an energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) was performed on a Philips CM20T TEM/STEM microscope operating at 200 kV. Microanalyses of bulk samples were performed by Galbraith Laboratories, Inc., Knoxville, TN.

2.1. Titration of commercial HFATH with Karl Fischer reagent

Fresh solutions of Karl Fischer reagent were prepared using standard procedures [6] and were standardized using sodium tartrate dihydrate. The standardized Karl Fischer reagent was stored under nitrogen and was transferred to a buret through a cannula using positive nitrogen pressure. All titrations were performed in dry methanol and during one time period. Aliquots of HFATH were added to 25 ml of methanol and were titrated with Karl Fischer reagent in triplicate analyses. Unlike acetone, trifluoroacetone does not react with Karl Fischer reagent, so the titration results gave directly the available water content of the commercial HFATH. This value was 3.04(4) mol of H_2O/mol of HFATH.

2.2 Reaction between HFATH and TEOS

Under a dry nitrogen atmosphere, aliquots of neat TEOS were mixed with neat HFATH in various relative molar amounts. Turbidity developed within 15 min of mixing. Reaction was continued at room temperature for ~20 h. The white xerogel precipitate was isolated by centrifugation and decantation and was washed with successive portions of ethanol, water, ether, and then a second washing with water. The wet xerogel was dried by heating for ~16 h at 130–160 °C in a vacuum oven to give an apparently dry powder. The reagent molar ratios of HFATH:TEOS used in this study were ~1:2, 3:4, 1:1, 4:3, 2:1 and 3:1. Xerogel yields were determined by analyzing the silicon content of each of the final xerogel powders. Microanalysis of a typical xerogel prepared by this method gave the following results: C, 2.72; H, 1.52; Si, 40.14; F, 0.088%. This reaction was also conducted at 64 or 5 °C in a similar fashion.

2.3. Preparation of a Si/Ti oxide mixed-metal xerogel

A homogeneous solution of 2.07 ml of neat TEOS and 0.55 ml of neat $Ti(Oi\text{-}Pr)_4$ under a nitrogen atmosphere was cooled to 5 °C. To this solution were added 2.07 ml of neat HFATH cooled to 5 °C to give immediate precipitation of a white solid. After 30 min of reaction, the reaction mixture was washed sequentially with ether, ethanol and ether to give a wet solid after decantation of the final liquid phase. The solid was dried in a vacuum oven to give 0.41 g (27% yield based on Si, 92% yield based on Ti) of apparently dry xerogel. *Anal.*: Found: C, 6.54; H, 2.47; Si, 16.87; Ti, 19.76%. The Si:Ti atom ratio thus determined was ~9:6.

3. Results and discussion

The overall conversion of a tetraalkylorthosilicate to SiO_2 and alcohol requires two moles of water as shown in Eq. (2). Usually excess water is used in such xerogel preparations because silica xerogels formed by this sol–gel method remain partially hydrated [7]. The appropriate alcohol is also usually present as a cosolvent to provide a homogeneous reaction solution. Qualitative reaction of neat TEOS with neat HFATH indicates that silica xerogels can be formed according to Eq. (3) without the addition of water or cosolvent. Use of HFATH as a source of water in sol–gel syntheses requires that the amount of water available per mol of HFATH be determined. This determination must include the total water content of HFATH and the fraction of that water chemically available for sol–gel reaction chemistry.

$$Si(OR)_4 + 2H_2O \longrightarrow SiO_2 + 4ROH \qquad (2)$$

$$\underset{\text{TEOS}}{Si(OEt)_4} + x\underset{\text{HFATH}}{(CF_3)_2C(OH)_2 \cdot 2H_2O} \xrightarrow{-x\text{HFA}} SiO_2 + 4EtOH \qquad (3)$$

The total water content of commercial HFATH, as measured by titration with freshly prepared Karl Fischer reagent, is found to be 3.04(4) mol of water per mol of HFATH. The fraction of this water available for sol–gel chemistry is determined by measuring the yield of silica xerogel as a function of HFATH:TEOS stoichiometry. These yield data are listed in Table 1 for reaction of TEOS with HFATH at several relative stoichiometries. The per cent yield of xerogel for each reaction is calculated knowing the amount of TEOS used and the Si content of each xerogel product (as determined by microanalysis). This yield corresponds to the ceramic yield of each reaction.

A plot of the ceramic yield versus HFATH/TEOS mole ratio is shown in Fig. 1. The ceramic yield increases with increasing HFATH/TEOS mole ratio until a nearly maximum yield is reached at a mole ratio of ~4:3. This value corresponds to a reaction stoichiometry in which all three water molecules of HFATH are used

Table 1
Yield of silica xerogel from reactions of TEOS with HFATH at various relative molar ratios

HFATH (mmol)	TEOS (mmol)	HFATH/TEOS	Xerogel yield (g)	Si (wt.%)	Ceramic yield (%)
1.90	2.60	0.73	0.0872	38.33	45.7
2.33	2.61	0.89	0.1061	38.18	55.3
2.89	2.54	1.14	0.1418	38.75	77.1
3.58	2.61	1.37	0.1597	37.61	81.8
5.04	2.54	1.99	0.1661	39.39	91.7
7.30	2.62	2.78	0.1741	37.86	89.4

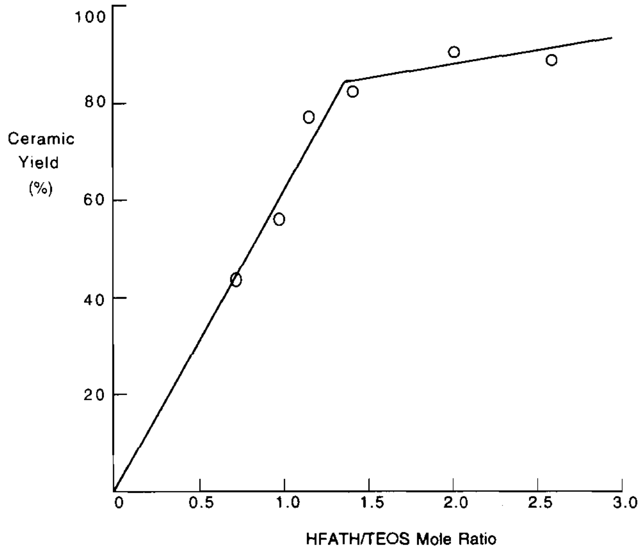

Fig. 1. A plot of the xerogel ceramic yield (in %) vs. the HFATH/TEOS mole ratio.

to hydrolyze each Si–OEt group to an Si–OH group. Although the fate of the hexafluoroacetone in this reaction has not been determined, it presumably exists as a mixture of hydrates as water is released during Si–OH condensations. Microanalysis of a typical xerogel product reveals only trace retention of fluorine (0.088 wt.%) in the xerogel.

The bulk density of xerogels prepared by this route, as measured by flotation in mixtures of CCl_4 and CH_2I_2, is found to be 1.99±0.03 g cm^{-3}. This value indicates that full densification of these xerogels has not occurred under these conditions, as expected for xerogel formation [7]. Silica xerogels prepared by single-step, acid-catalyzed hydrolysis of TEOS give increasing bulk densities with decreasing H_2O:TEOS mole ratios. At an H_2O:TEOS mole ratio of 4, silica xerogels prepared by this conventional method have bulk densities of ~1.65 g cm^{-3} [8]. Silica xerogels obtained from the HFATH route reported here have significantly higher bulk densities than those prepared by conventional acid-catalyzed hydrolysis under similar conditions.

A non-crystalline structure for these xerogels is confirmed by electron and X-ray diffraction. The micromorphology of these xerogel powders is evident from electron micrographs. Fig. 2(a) and (b) shows secondary electron SEM images of xerogel powder obtained from reaction of TEOS and HFATH at 64 °C for 30 min. The higher magnification image shown in Fig. 2(b) reveals a spheroidal particle shape with a typical particle diameter ranging from 0.1 to 1.5 μm. During the 30 min reaction time, the small spheroids have begun consolidation into a three-dimensional network.

Because the onset of opalescence is delayed by a decrease in reaction temperature, we examined in more detail the formation of xerogel particulates in the reaction of TEOS and HFATH at 5 °C. Fig. 3(a) shows an SEM image of a sample taken from a slightly turbid reaction solution after 1.5 h of reaction. Isolated spheres of ~750 nm to 2–3 μm diameter are observed; some

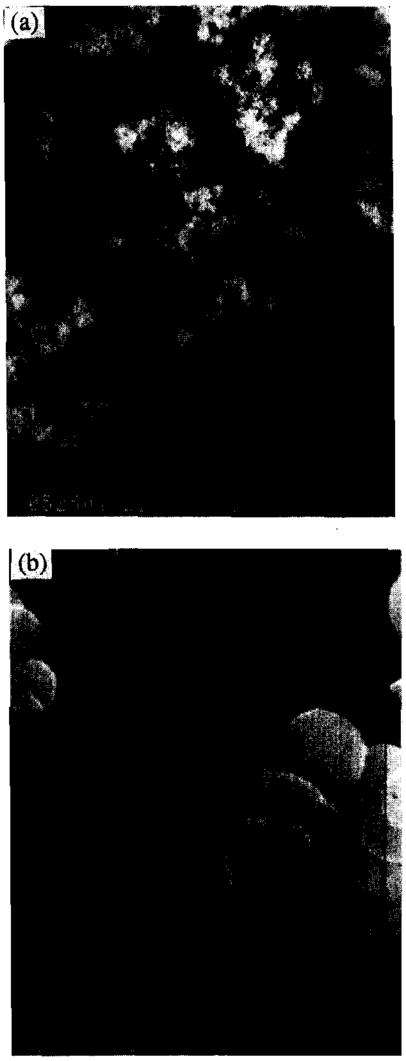

Fig. 2. SEM micrographs at lower (a) and higher (b) magnification of silica xerogel formed by reaction of TEOS and HFATH at 64 °C for 30 min.

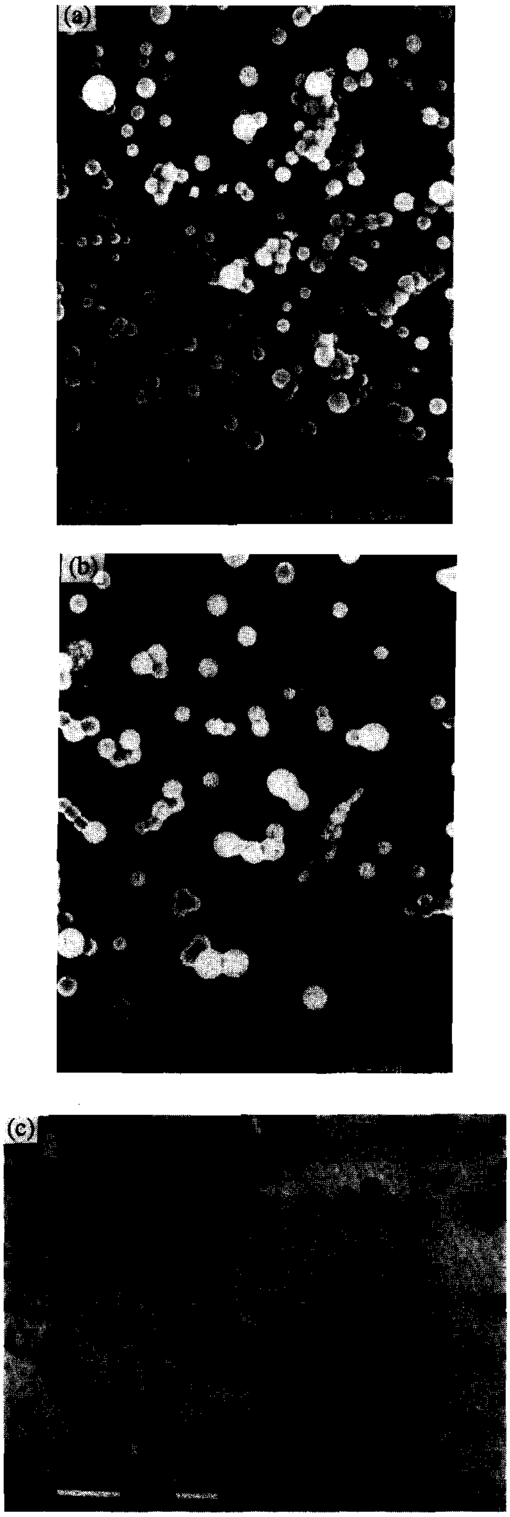

Fig. 3. Micrographs of silica xerogel formed by reaction of TEOS and HFATH at 5 °C for (a) 1.5 h, (b) 1.0 h, or (c) 0.5 h; STEM bright-field image.

single-sphere chains, small aggregates, and particle necking are also evident. EDS spectra confirm the presence of Si in these particulates. An SEM image of a sample taken from the homogeneous reaction solution after 1 h of reaction is shown in Fig. 3(b). Isolated spheres, single-sphere chains, and moderate aggregation are all clearly observable with sphere diameters ranging from ~300 nm to 1.7 μm. A STEM bright-field micrograph of a sample taken after only 30 min of reaction is shown in Fig. 3(c). Particle size is reduced still further to diameters ranging from ~25 to 200 nm. These data reveal a decrease in the apparent average particle size of xerogel particulates with a decrease in reaction time. This growth process is very similar to that reported for silica xerogels prepared by conventional routes using TEOS in aqueous ethanol solution [9].

Formation of a mixed-metal oxide xerogel by this synthetic method was also investigated. Addition of

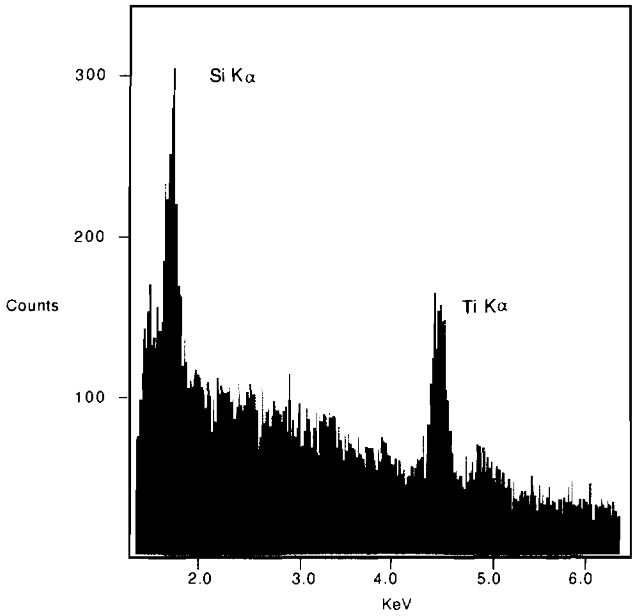

Fig. 4. Dispersive X-ray analysis of Si(Kα) and Ti(Kα) emission from the Si/Ti mixed-metal oxide xerogel obtained from reactions of TEOS, $Ti(Oi\text{-}Pr)_4$ and HFATH at 5 °C.

Fig. 5. SEM micrograph of the Si/Ti mixed-metal oxide xerogel obtained from reaction of TEOS, $Ti(Oi\text{-}Pr)_4$ and HFATH at 5 °C.

neat HFATH to a homogeneous mixture of TEOS and $Ti(Oi\text{-}Pr)_4$ in a 5:1 molar ratio of neat metal alkoxides at 5 °C gives immediate formation of a white precipitate. Microanalysis of the resulting xerogel powder reveals a Si:Ti ratio of ~9:6. Xerogel yields of 27% based on Si and 92% based on Ti indicate that the titanium alkoxide is the limiting reagent. An EDS spectrum of this xerogel, Fig. 4, confirms Ti and Si incorporation into the smallest xerogel particulates. An SEM image of a typical particulate is shown in Fig. 5. These results demonstrate the formation of mixed-metal oxide xerogels using HFATH to promote metal-alkoxide hydrolysis.

The successful preparation of silica or Si/Ti mixed-metal oxide xerogels using neat metal alkoxides and HFATH has been demonstrated. This alternative route to xerogel formation might be particularly useful for the preparation of molecularly doped xerogels in which the dopant species is reactive towards water or alcohol cosolvents.

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