A Two-Component, Non-Aqueous Route to Silica Gel

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Abstract. A new means for generating silica gel has been developed. Simple two component systems comprising tetraalkoxysilanes and strong carboxylic acids such as formic acid can react rapidly to give transparent monolithic gels. The acid serves as solvent, water source, and catalyst for both hydrolysis and condensation. Water need not be present as an initial reactant; it is generated in situ during the reaction. The gelation reaction is at least two orders of magnitude faster than those conducted in conventional acid-catalyzed aqueous systems at comparable pH*. Kinetic evidence indicates a lowering of the activation energy of condensation reactions, believed to be associated with reaction of silyl carboxylates and silanol groups. Physical properties of the dry gels such as bulk density more closely resemble conventional acid-catalyzed gels than those associated with other rapidly gelling systems. Dry gels often exhibit porosity so fine that nitrogen (at 77°K) is not absorbed at significant rates. Independent evidence of porosity arises from comparison of skeletal and bulk densities, sample immersion in water and adsorption isotherms of CO_2.

Keywords: carboxylic acids, mechanism, kinetics, ultrafine porosity, CO_2 adsorption

1. Introduction

The classic formulation for organometallic silica gel generation comprises four components: a polyalkoxysilane, water, an acidic or basis catalyst, and a solvent to provide compatibility between the normally immiscible alkoxysilane and water. The catalysts normally facilitate both hydrolysis and condensation reactions. For a given silane concentration, independent variation of the other components is well known to influence many sol and gel properties; one may accordingly contend with a complex compositional space in optimizing system behavior.

The alcohols customarily used as co-solvent become active participants in the sol-gel chemistry through reesterification and (where possible) transesterification reactions. Reesterification of silanol groups limits the participation of the most rapid condensation reaction— that between two silanols. There is also some evidence that alcohols can cleave disiloxane moieties in polysilicate structures.[1]

Acid-catalyzed gels generally show higher hardness, bulk density, clarity, surface area and finer pore size and narrower size distribution than their base-catalyzed counterparts.

However, the optimum conditions for generating such materials often corresponds to very slow rates of reaction.[2]

Several carboxylic acids have been investigated as catalysts in the usual aqueous-based silica sol-gel. Mackenzie [3] reported that acetic acid led to shorter gel times than other acids in dilute (5 mol% of the TEOS used) systems, and suggested a specific catalytic function for the acid. However, Coltrain [4] has shown that gelation rates correlate very well with measure pH* values for such systems, which included trifluoroacetic acid. Of particular relevance to the present work is Sakka's observation that gel times with a formic acid catalyst were twice those of acetic acid at the same concentration.[5]

A fairly broad range of behavior is described in the literature with respect to the reaction of glacial acetic acid and TEOS. In an equimolar mixture, no room temperature reaction is apparent, and the reaction to form silyl acetate groups is slow and incomplete even at reflux temperatures exceeding 100°.[6] A report of faster and more extensive reactions of TEOS and other
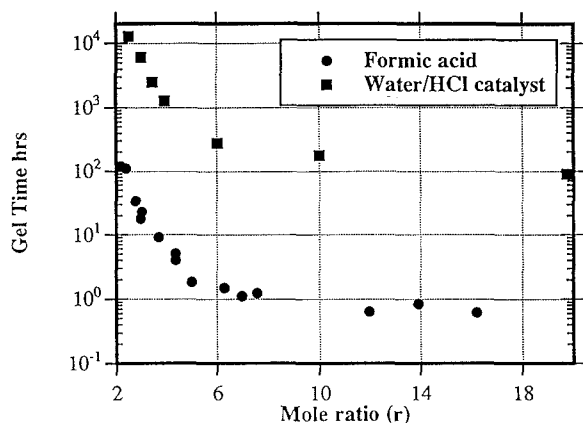
Fig. 1. Gelation times of TEOS in aqueous HCl-catalyzed and formic acid systems at pH* of about 1.5. r is the molar ratio of the hydrolytic agent—water or formic acid—to silane. Aqueous data from Ref. 12.

tetraalkoxysilanes with a molar excess of acetic acid to form esters at elevated temperatures exists.[7] The hydrolysis of TEOS in glacial acetic acid *as solvent* is "not particularly fast.[8]" Finally, there is a recent account [9] of the generation of precipitated silica microspheres from TEOS in the presence of equimolar water and acetic acid in the approximate molar ratios of 1:4:4 at room temperature.

2.   Results and Discussion

2.1.   *A New Non-Aqueous Route to Inorganic Networks*

We have found that simple two component systems of tetraalkoxysilanes and *strong* carboxylic acids such as formic or trifluoroacetic acid can be rapidly converted into transparent monolithic gels. The acid serves the multiple roles of solvent, water source and catalyst for both hydrolysis and condensation. The initial presence of water is not required; it is generated *in situ* during the reaction.

TMOS and TEOS are miscible with HCOOH and CF_3COOH [TFA]; $Si(OPr)_4$ [TPOS] becomes miscible with formic acid within minutes after mixing. The formation of gelled structures can occur in as little as 25 minutes at room temperature, at least two orders of magnitude faster than the corresponding aqueous-based sol-gel reactions at comparable values of pH* [10] (see Fig. 1). Only carboxylic acids whose pK_a is less than about 4.0 show the rapid gelation behavior; acids such as acetic and acrylic are ineffective on

comparable time scales. The resultant gels posses a very fine porosity and in general much more closely resemble acid-catalyzed aqueous gels rather the base- or fluoride ion-catalyzed systems also associated with high gelation rates. Reaction byproducts are water, alcohol and the ester resulting from reaction of the alcohol and acid. Gas chromatographic analysis of the volatile components of the pore fluid in r = 2.2 and 32 gels [11] shortly after gelation indicated that ethanol is almost entirely converted into ester in the presence of a large excess of formic acid. In the low r system, the acid is nearly consumed at the gel point and the pore fluid consists of ethyl formate (greater abundance) and ethanol, with a small amount of water.

2.2.   *Gelation Kinetics*

The HCOOH/TEOS systems shows a rapid exotherm with r values above about 4. For an r = 8.3 system, the maximum temperature rise was detected after 10 minutes (t_{gel} in a large container under nearly adiabatic conditions was 23 min.). In these high r systems, the hydrolytic, condensation and esterification reactions must be to some extent concurrent.

Figure 1 shows the dependence of gelation time on composition for gels generated by reaction of TEOS with 96% HCOOH in comparison to a .01 M HCl-catalyzed water/ethanol/TEOS system. The latter data [12] were acquired at 60° and have been converted to 25° values using an estimated activation energy of 14 kcal/mole. The rate of reaction ranges between two and three orders of magnitude faster in the formic acid. Despite the differential rates and the modes of condensation (see below), the dependence of the rate on composition is surprisingly similar for the two systems.

Gel formation in the HCOOH/TEOS system displays highly linear Arrhenius behavior. Figure 2 shows the relation of gel times vs. temperature for the systems containing r = 3 and 7 systems. The respective activation energies of 11.6 and 10.1 kcal/mole are about 3.5 and 7.5 kcal/mole less than those observed for aqueous systems of comparable molar compositions [13]. The present trend of lower activation energies with increasing hydrolytic agent is contrary to that observed in Ref. [13].

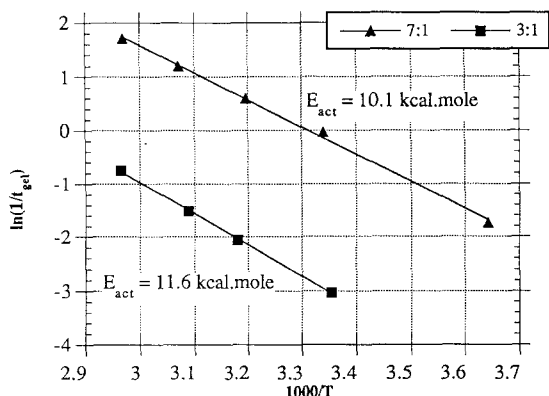The amount of water initially present has little influence on gelation rates. At r = 7.2 formic acid con-

Fig. 2. Arrhenius plots for gelation of formic acid:TEOS 3:1 and 7:1 systems.

taining 10 mole% water showed an identical gelation time (62 min. at 25°) to TFA containing 2 mole%, and "anhydrous TFA" (in the presence of 10 mol% of its anhydride) showed only slightly longer gelation times. In the latter system, scavenging of initially formed water and alcohol by unreacted anhydride would be expected to lead to an increase in gel time.

2.3. Behavior with TEOS and Various Carboxylic Acids

Formic (96% by weight) and trifluoroacetic (99 + % by weight) acids were the most commonly used gelation agents. Each was also used dried to the extent possible via anhydrides. A number of other carboxylic acids were explored, either as neat liquids or dissolved in co-solvents. As indicated in Table 1, acids whose pKa is < about 4.0 show the rapid gelling behavior, while weaker acids appear to react at least two orders of magnitude more slowly [14]. The pKa of acrylic acid (CH_2 = CHCOOH) (4.25) lies exactly between those of formic (3.75) and acetic (4.75). Despite the miscibility of the two reactants, the acid did not lead to the gelation of TEOS in one month at room temperature and a 26 hr. residence at 72°.

2.4. Behavior with Other [than TEOS] Alkoxysilanes

TMOS is completely miscible with 96% formic acid and, as expected, exhibits a shorter gel time than does

Table 1. Behavior of strong and weak carboxylic acids with TEOS.

Rapid Gelation Acids	pKa	Unreactive Acids	pKa
Trifluoroacetic	0.23	Acetic	4.75
Dichloroacetic	1.29	Acrylic	4.25
Formic	3.75		
Glycolic	3.81		

TEOS at comparable compositions. At r = 7.16, a HCOOH/TMOS mixture gelled in 40 minutes at 25°C; the comparable gel time for TEOS was 67 min. The gel was optically clear but was not investigated further.

(SiOn–Pr)$_4$ is not immediately miscible with 96% formic acid but partial reaction in high r systems does lead to clarification after about 15 minutes. A system with of a HCOOH:TPOS molar ratio of 7.2 gelled in 113 min. The gel was slightly hazy.

2.5. NMR Spectroscopy

^{1}H and ^{29}Si NMR were used to follow the sol-to-gel evolution of the reaction of TEOS with HCOOH. NMR solution studies were also used to examine behavior of simple model systems such as the reaction of Et_3SiOH with HCOOH. Fig. 3 shows the Si NMR spectrum of an r = 3 sol at $t = .7 t_{gel}$. The Q distribution and its evolution are fairly similar to those in aqueous-based gels. However, there are a much lower proportion of silanol groups, and Q^1 and Q^2 species formed from condensation appear at a much lower extent of TEOS conversion. Additional details will be provided elsewhere.

2.6. Mechanism

NMR evidence suggests that the observed rate enhancements arise from faster condensation reactions. This situation was established by removing most of the water and ethanol from a completely hydrolyzed aqueous/HCl TEOS sol, then combining either a six-fold molar excess of water or an equivalent amount of formic acid with two portions of the sol. The formic acid system gelled 42 times faster. Additional evidence for acid-induced condensation comes from the rapid shrinkage of wet gels containing little or no resid-
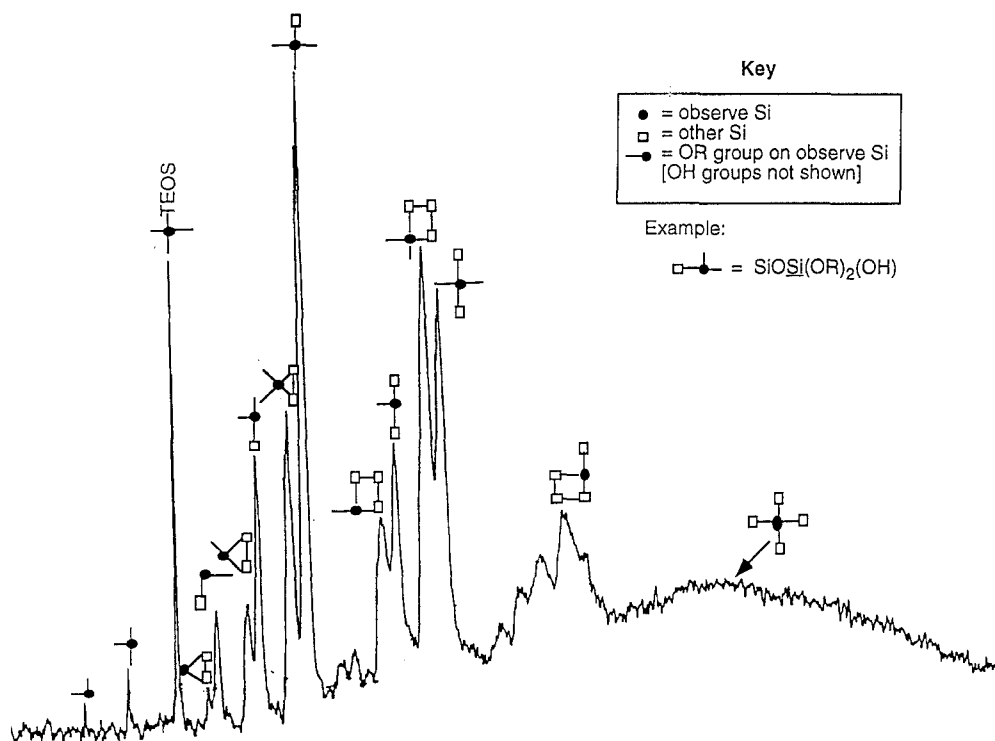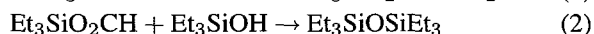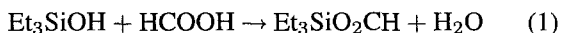
Fig. 3. ^{29}Si NMR spectrum of 3:1 formic acid:TEOS at $t = .7\, t_{gel}$. Tentative assignments as to molecular or structural species have been made with guidance from the literature.

ual acid when immersed in a large quantity of fresh acid [15].

The ineffectiveness of glacial acetic and other weak carboxylic acids under the same time scale and conditions may simply be due to their much slower rates of (uncatalyzed) esterification. Another factor could be the much faster reaction of formic than acetic acid with triethylsilanol, per reactions (1) and (2). The silyl formate and the disiloxane condensation product were readily observed under conditions where acetic acid was unreactive.

Silyl formates are difficult to assign in Si spectra, since chemical shifts have not been reported for molecules of the class $(RO)_x Si(O_2 CH)_{4-x}$. MeSi(OMe)$_3$ and MeSi(O$_2$CH)$_3$ have virtually identical chemical shifts [16]. ^{1}H NMR resonances just downfield of HCOOH are observed and tentatively identified as SiOOCH.
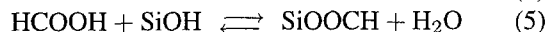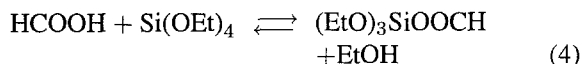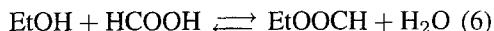
$$Et_3 SiOH + HCOOH \rightarrow Et_3 SiO_2 CH + H_2 O \qquad (1)$$
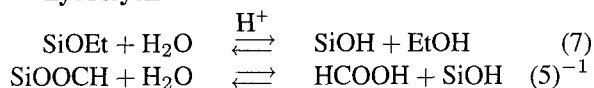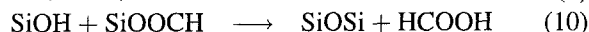$$Et_3 SiO_2 CH + Et_3 SiOH \rightarrow Et_3 SiOSiEt_3 \qquad (2)$$

Exchange reactions of the kind needed to generate alcohol in the absence of water are well known [17] for other systems

$$RCOOH + SiOEt \rightarrow SiOOCR + EtOH \qquad (3)$$
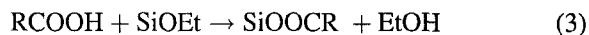
Taking the above observations into consideration, formic acid may be functioning in at least four important ways:

1. The acid can carboxylate silicon via reaction with silanols or alkoxysilanes, generating water or ethanol in the process.
2. The acid catalyzes the hydrolysis of Si–OR bonds by any water present.
3. The acid generates water and consumes alcohol via esterification of any alcohol present (the latter is generated by reactions (4), (7) and (9) below).
4. The acid greatly increases the rate of silicate condensation via formation of silyl formate groups, which can rapidly react with silanols to regenerate the acid.

The following scheme appears consistent with present knowledge of the system.

carboxylation

$$HCOOH + Si(OEt)_4 \rightleftharpoons (EtO)_3SiOOCH$$
$$+EtOH \qquad (4)$$
$$HCOOH + SiOH \rightleftharpoons SiOOCH + H_2O \qquad (5)$$

esterification

$$EtOH + HCOOH \rightleftharpoons EtOOCH + H_2O \qquad (6)$$

hydrolysis

$$SiOEt + H_2O \underset{\rightleftharpoons}{\overset{H^+}{}} SiOH + EtOH \qquad (7)$$
$$SiOOCH + H_2O \rightleftharpoons HCOOH + SiOH \qquad (5)^{-1}$$

condensation

$$2SiOH \longrightarrow SiOSi + H_2O \qquad (8)$$
$$SiOH + SiOEt \longrightarrow SiOSi + EtOH \qquad (9)$$
$$SiOH + SiOOCH \longrightarrow SiOSi + HCOOH \qquad (10)$$
$$SiOOCH + SiOEt \longrightarrow SiOSi + EtOOCH \qquad (11)$$
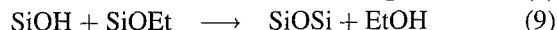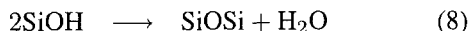
The alternative esterification reaction

$$SiOEt + HCOOH \rightarrow SiOH + EtOOCH \qquad (12)$$

has not been observed with other carboxylic acids at elevated temperatures. [16]

2.7. Gel Porosity

Attempts to measure porosity and surface area of dry gels with the standard BET analysis of nitrogen adsorption ($77°K$) gave very puzzling results. Some high r samples showed high surface areas (ca. $600 \, m^2/g$) and very fine pore structure, but most others led to virtually no nitrogen adsorption during a 4 hr experiment. Such a result could indicate lack of open porosity in the samples or extraordinarily fine pores which could not accommodate nitrogen in the duration of the experiment. Qualitative evidence for open porosity in several gels was obtained when the pieces of dry gel were immersed in water and rapidly fractured and generated gas bubbles. Quantitative indication of porosity arose from comparison of bulk (mercury porosimetry) and skeletal (He pycnometry) densities; the latter were consistently higher by at least 10%.

BET adsorption measurements were carried out for two samples with CO_2 at $195°K$. Both had showed essentially no surface area by N_2 adsorption. An r = 3 sample [18] showed ca. $200 \, m^2/g$. of surface area and a Type I adsorption isotherm. Pore volume and pore size distributions calculations were unsuccessful, apparently due to the extremely small pore sizes. An r = 1.5 sample [19] also showed a CO_2-based surface area of about $200 \, m^2/g$. This quadrupolar adsorbate molecule is known to adsorb preferentially on polar sites and is expected to underestimate the true surface area of a silica gel by a factor of roughly 3 to 4. [20] There are reports of ultrafine porosity carbonaceous materials which adsorb CO_2 at $195°K$ but not nitrogen at $77°$ K. [21] The differentiated behavior is believed due to a thermally activated adsorption process rather than the slightly smaller kinetic cross section of the CO_2 molecule. The author is now aware of a precedent for silica gel, and the origin of the behavior is not yet understood.

3. Experimental

3.1. Reagents

Formic acid is unstable as a strictly anhydrous material, [22] decomposing into CO and water, and is available commercially with 4 wt% water as a stabilizing agent. The 96% grade was purchased from Kodak and generally used as received.

Trifluoroacetic and dichloroacetic acids were analyzed by the Karl Fischer technique as containing 0.4 and 2.3 wt% water as received and were normally used without further purification, as were the other acids investigated. In some experiments, the water content of trifluoroacetic acid was further decreased via the reaction with excess trifluoroacetic anhydride at room temperature. The anhydride does not react directly with TEOS under conditions in which the acid reacts rapidly.

TEOS was purchased from Kodak. Any samples which showed impurities by either GC or ^{29}Si NMR were purified by distillation. Other alkoxysilanes were used as received from Petrarch or Aldrich.

3.2. Combining Reactants

Miscible alkoxysilanes such as TEOS and TMOS are simply added to the stirred acid. For relatively low r systems, the addition should be at fairly high rates, so as to avoid significant amounts of time in acid-rich composition. The reverse addition (i.e., of the acid to the silane) has been observed to lead to some turbidity or formation of particulates and was not normally used.

3.3.   Co-Solvents for Solid Acids

Solid carboxylic acids such as glycolic or chloroacetic are insufficiently soluble in alkoxysilanes as solids for convenient use. They were best used with a cosolvent such as THF rather than as neat molten materials. With high melting solids addition of the molten acid to TEOS often led to localized gelation before the reactants could be adequately mixed.

3.4.   Kinetic Analyses

For gel time determination, reactants were incubated in a constant temperature bath and re-admitted to the bath as soon as possible after mixing. Gelation was taken to correspond to the condition of no perceivable flow in the sample when containers were tilted.

The relative influence of formic acid and water on the condensation rates of silanols was explored as follows. TEOS, EtOH and water were combined in molar ratios of 1.00:5.00:16.00 and acidified to a pH of 2.00 with HCl. The solution was then refluxed at atmospheric pressure for two hours. Vega and Scherer [23] have determined that these conditions lead to a virtually completely hydrolyzed system. The solution was then cooled and water and ethanol removed in a rotary evaporator until the density [24] of the remaining solution reached 1.095 (it was 0.934 after the reflux procedure). The concentrated sol, which had lost about 63% of its mass, was then divided into two portions. Portion A was charged with a 6-fold molar excess of water. Portion B was charged with a comparable molar excess of formic acid. The gel time of Portion A was 61 min; that of portion B was 42 hours. In both systems, gelation times are quite insensitive to small variations in this region of **r**.

3.5.   NMR Spectrometry

^{29}Si NMR spectra samples were run at 59.6 MHz on a Bruker AM 300 as reacting liquid mixtures of HCOOH and TEOS and various trialkylsilyl model systems, as cited above. Use of the spin relaxation reagent (Cr(acac)$_3$) had no noticeable effect on system reactive behavior.

3.6.   Porosity

Qualitative indications of porosity on dried gels arose from immersion behavior under water. The gels rapidly fractured and liberated gas bubbles—clear indication of open porosity. [25] Bulk densities were determined from mercury porosimetry or from mass and dimensions of right cylinders grown in fluoropolymer tubes. Skeletal densities were determined from He pycnometry. Values will be reported elsewhere. BET measurements for both N$_2$ and CO$_2$ were run on Micromoretics instruments on samples which had been outgassed under high vacuum at a minimum of 150°C.

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10. That is, at comparable **r** and measured solution pH. a 3:1 molar mixture with TEOS shows an initial pH* of 1.3 evolving to a value of ca. 1.8 close to the gel point. 96% formic acid has a pH* of 0.7 ± 0.4.

11. **r** is taken to be the mole ratio of the carboxylic acid to silane; any water present is not included in the calculation.

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