

Sol-gel processing of spiro-silicates

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Abstract

The sol-gel transition of tetra-coordinated spiro-silicate via hydrolysis and condensation under acidic and basic conditions is examined to elucidate the effect of catalyst, reaction time and temperature on the properties of obtained gel. The main advantage of this process is the low temperature employed, producing a solid network with a high specific surface area. FTIR spectroscopy and TGA analysis were used to characterize the formation of siloxane bonds (Si–O–Si). It is found that spiro-silicate can be hydrolyzed under both acid and base catalyzed conditions. The condensation rate to silicates is shown to be at a minimum in 0.001M HCl, which is the iso-electric point of silica. The prepared xerogel has a low-density and is an amorphous material with a specific surface area of 596 m²/g. Besides the catalyst media, the type of precursor also has a strong influence on the gel formation. An aminospiro-silicate, six-membered ring, containing methyl and amino groups as substituents, was chosen for this study. The resulting xerogel is determined by the fact that to obtain the Si–O–Si bonds, a higher concentration of solvent and higher temperature are more favorable, due to the length and branching of alkyl portion. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Aminospiro-silicate; Siloxane; SiO₂; Sol-gel processing; Spiro-silicate; Xerogel

1. Introduction

The limited number of simple silicon containing starting materials restricts the potential role of inorganic and organometallic silicon compounds in the development of new polymeric glasses and ceramics. The main reason is that silicon-containing chemicals are almost exclusively prepared from element silicon, obtained from the carbothermal reduction of silica around 1200 °C, which is energy-intensive.¹ Organosilicate compounds are of interest for their potential as precursors in sol-gel processing to form complex preceramic shapes and structures, not readily accessible by melt processing.^{2,3}

Sol-gel chemistry of silicon alkoxides is rather simple, compared to that of complexes of transition metal alkoxides in which metal atoms may exhibit several coordination states.⁴ Molecular precursors of silicon alkoxides are always monomeric tetrahedral species Si(OR)₄. One

of the usual starting materials for silica glasses is tetraethylorthosilicate (TEOS).^{5,6} The size and shape of the primary sol particles and the rate of its gelation can be controlled by varying pH.^{7,8} The amount of water introduced into the reaction affects the hydrolysis rate and completeness as well as the porosity of the silica to be obtained.^{9–12}

Other alkoxide precursors can also be used to impart different properties to the gels.^{13–15} Recently, Wongkasemjit et al. have synthesized many types of metal alkoxides using an inexpensive and simple method, referred to as the “OOPS” process.^{16–18} The advantages of these species are hydrolytically stable, low cost, easy processability and environmental friendliness.¹⁹ Wongkasemjit et al. also studied the sol-gel processing of synthesized silatranes, and found that pyrolyzed ceramic products showed homogeneous microporous structure with high surface areas, 313–417 m²/g.¹⁹

The purpose of this work is to study the sol-gel processing of spiro-silicates under conditions of varying solvent content, acid versus base conditions, aging time and temperature and to investigate whether the resultant xerogels of spiro-silicate and aminospiro-silicate¹⁸ exhibit different product properties.

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2. Experimental

2.1. Materials

Fused silicon dioxide or HI-SIL 927 silica (SiO_2), with a surface area of $168 \text{ m}^2/\text{g}$, by BET, was donated by PPG Siam Silica Co., Ltd., and dried in oven at 100°C for 10 h. 2-Amino-2-methyl-1,3-propanediol [$\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2$] was purchased from Aldrich Chemical Company, used without purification and kept under nitrogen atmosphere. Ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$), purchased from Labscan, was used as reaction solvent. Triethylenetetramine [TETA, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_3$] was purchased from Facai Polytech Co., Ltd., and used as a catalytic base. Potassium hydroxide (KOH) was purchased from Baker Analyzed Reagent, and used as co-catalyst. Methanol (CH_3OH) and acetonitrile (CH_3CN) were purchased from Baker Analyzed Reagent and Lab-scan Analytical Science, respectively. Each was distilled using standard method to use as precipitating agents. UHP grade nitrogen gas with 99.99% purity was purchased from Thai Industrial Gases Public Company Limited (TIG). Hydrochloric acid (HCl) and ammonium hydroxide (NH_4OH) solu-

tions were purchased from Aldrich Chemical Company. They were diluted with deionized water at various concentrations to use as electrolytes.

2.2. Instrumental

FTIR spectra were obtained on a Vector 3.0 Bruker Spectrometer with 32 scans at a resolution of 4 cm^{-1} . The powder samples were pressed to form pellets by mixing with pure and dry crystalline potassium bromide, KBr. TGA measurement data were obtained on a Du Pont instrument, Du Pont TGA 2950, using a platinum pan, using samples of 12–15 weight. The temperature program was started from room temperature to 750°C , with a heating rate of $10^\circ\text{C}/\text{min}$ and a nitrogen flow rate of $25 \text{ ml}/\text{min}$. SEM digitized micrographs were obtained from a Jeol 5200-2AE (MP 15152001) scanning electron microscope with magnification range of $35\text{--}20,000\times$. Surface area of pyrolyzed product was determined by Autosorb-1 Gas sorption system (Quantachrome Corporation) with the Brunauer–Emmett–Teller method (BET). Each sample was degassed at 300°C for 3 h before measurement. The surface area of the samples was obtained from five-point adsorption.

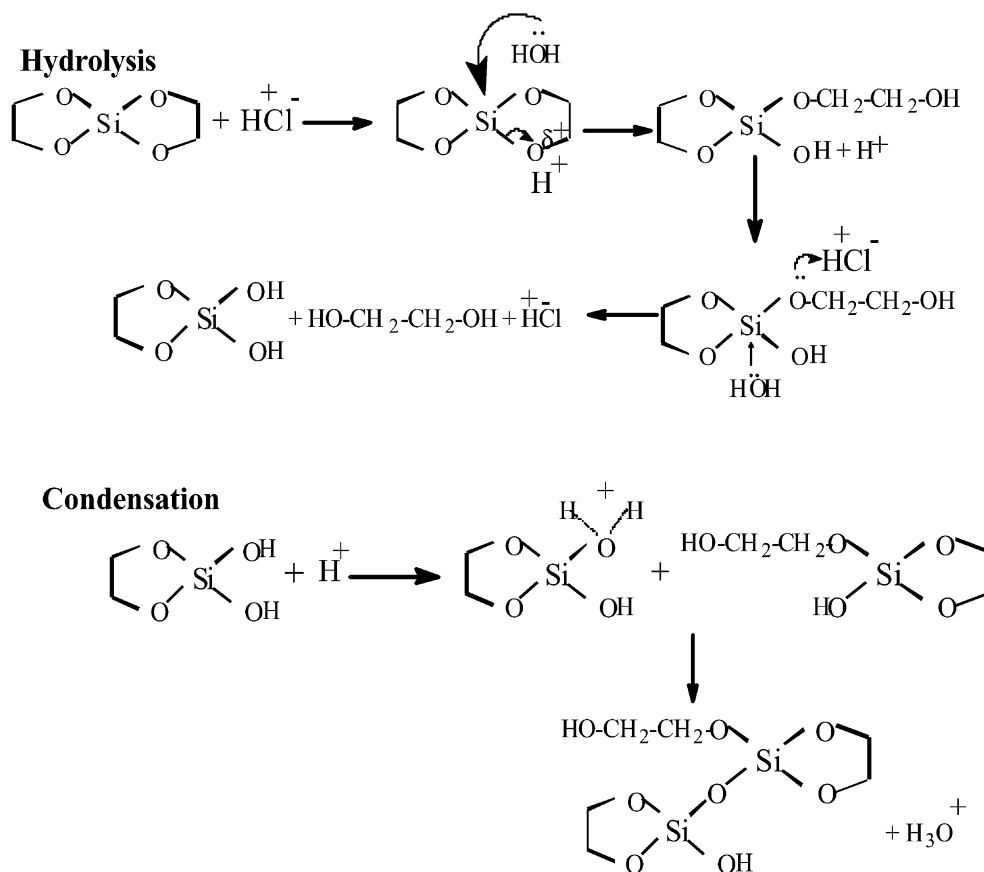
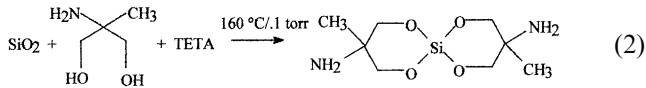
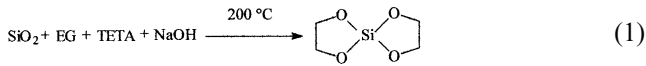


Fig. 1. Schematic of hydrolysis and condensation under hydrochloric acid solution.

2.3. Methodology

2.3.1. Synthesis method

Following the synthetic methods described by Wongkasemjit et al.,¹⁸ spiro-silicates were synthesized, as shown in Eqs. (1) and (2).



2.3.2. Sol-gel transition study

Hydrolysis of the spiro-silicate products was carried out by addition of either HCl or NH_4OH solution at various concentrations. The mixture was prepared directly in a crucible at room temperature, resulting in a formed-gel product. The gel was aged at room temperature. To study the sol-gel transition, at each hour the aliquots of mixture were deducted and dried using high vacuum (0.1 mm Hg) to remove solvent. The hydrolysis reaction also carried out was at 40 and 60 °C.

2.3.3. Pyrolysis of hydrolyzed products

The hydrolyzed gel was pyrolyzed in a furnace at a heating rate of 10 °C/min to 750 °C, and maintained at 750 °C for 7 h. The pyrolyzed products were then characterized by TGA, FTIR, BET, SEM and WXR. D.

2.3.4. Density measurement

The volumetric property of spiro-silicate, the stable hydrolyzed product, was determined using a 25 ml pycnometer (for powder form product) and distilled isooctane as media. The measurement was performed at 25 °C. The purified product in the bottle was weighed in the range of 0.5–1.0 g. The media was added until covering the product. Then the bottle was sonicated and incubated at 25 °C for 2 h before adding the media to the marked point. The same procedure was made with fused silica for comparison.

3. Results and discussion

It is well known that the catalyst used in a gelation reaction can have large effects on the microstructure of

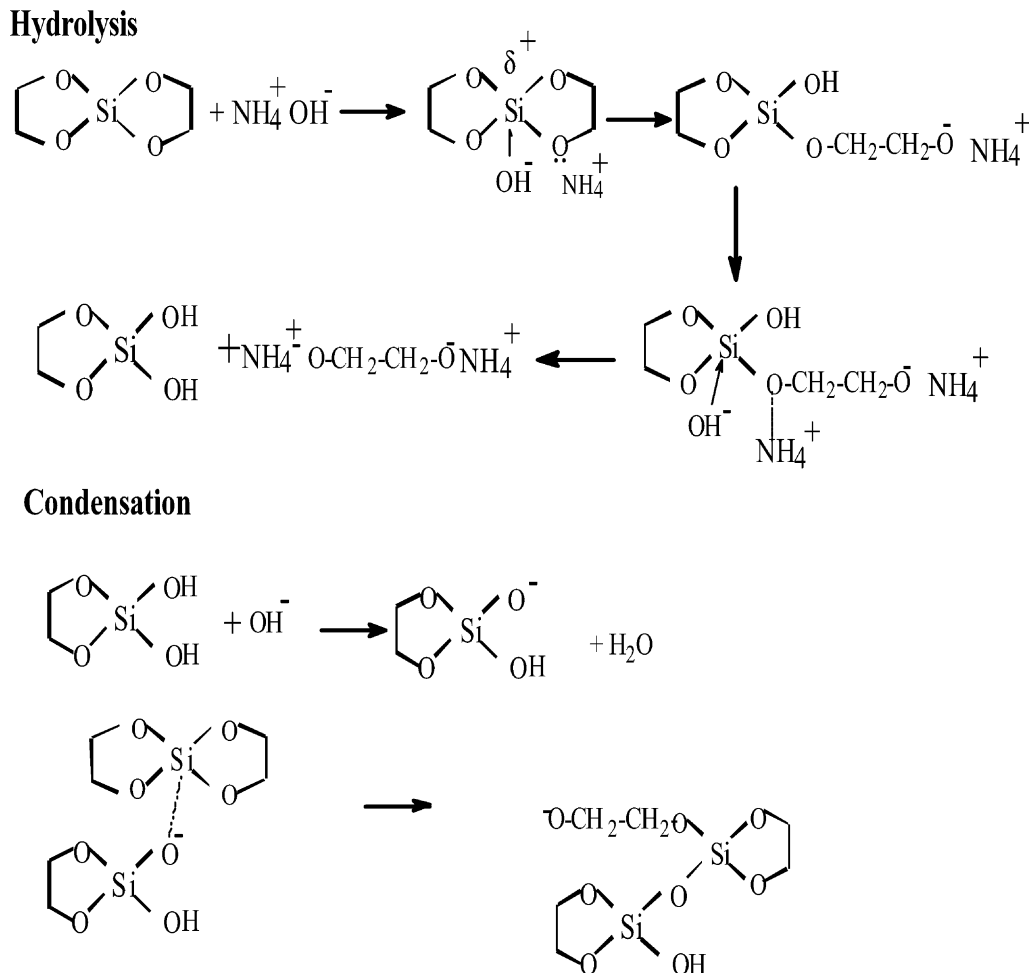


Fig. 2. Schematic of hydrolysis and condensation under ammonium hydroxide solution.

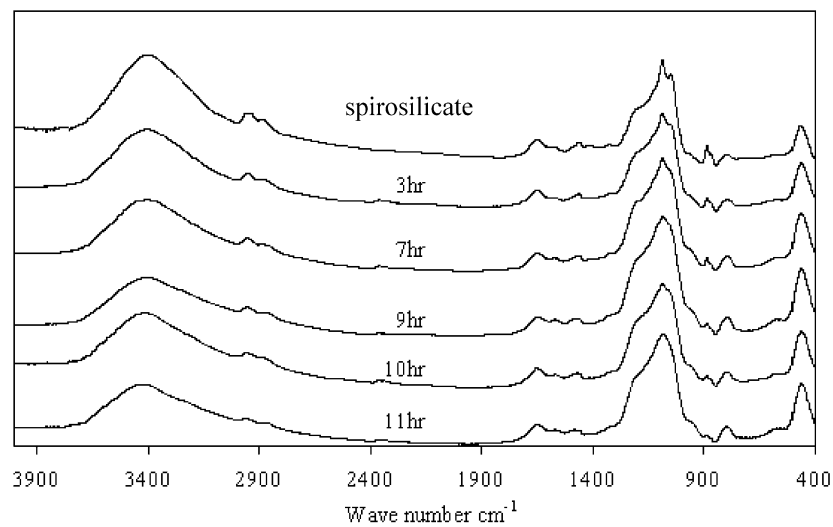
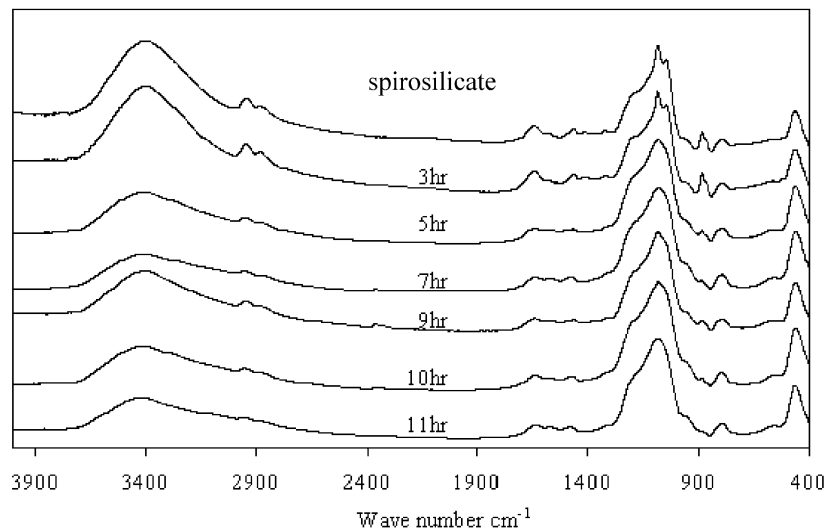


Fig. 3. FTIR spectra of hydrolyzed spirosilicate with (a) 0.001 and (b) 0.002 M HCl at room temperature.

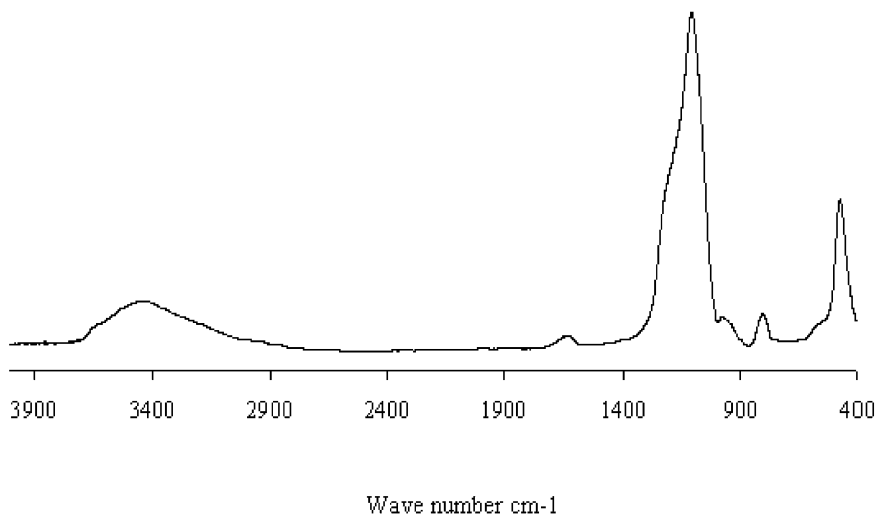


Fig. 4. FTIR spectrum of fused silica starting material.

the gels formed as well as on the rapidity of the gelation process.²⁰ During the sol to gel transition induced by applying solvent, the polymerization occurs via hydrolysis and polycondensation reaction. Figs. 1 and 2 show two proposed mechanisms of hydrolysis and condensation for tetracoordinated spiro-silicates under acidic and base conditions.

3.1. Spirosilicate

FTIR spectra of products obtained using 0.001 M HCl, see Fig. 3(a), showed that the characteristic peaks at 3405, 2951, 2883, 1086 cm^{-1} decreased as the time increased. The decrease in the absorption at 3405 cm^{-1} was attributed to the decrease in the amount of Si–OH

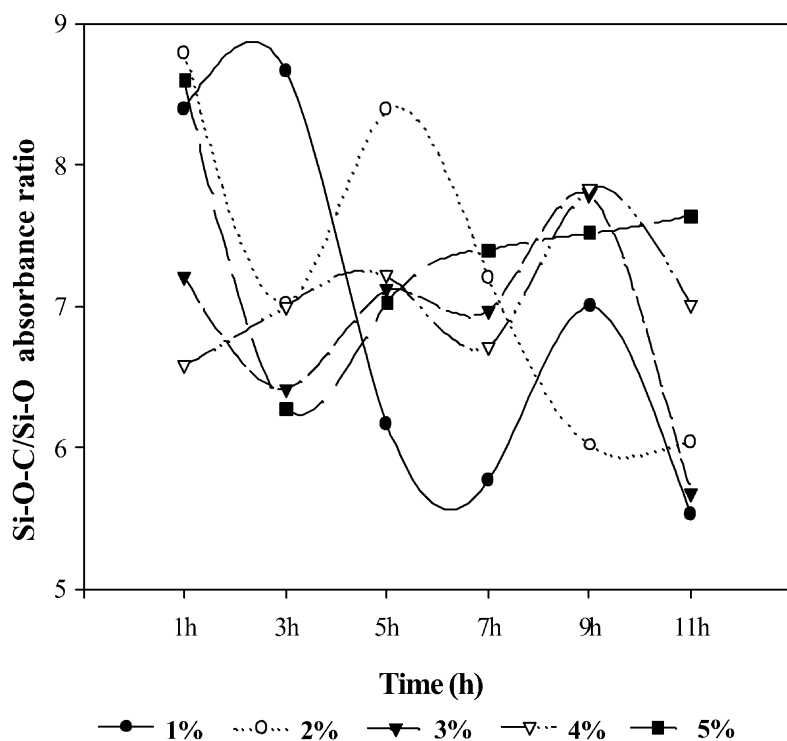


Fig. 5. The time-dependence of hydrolyzed spiro-silicate with 0.001–0.005 M HCl at room temperature.

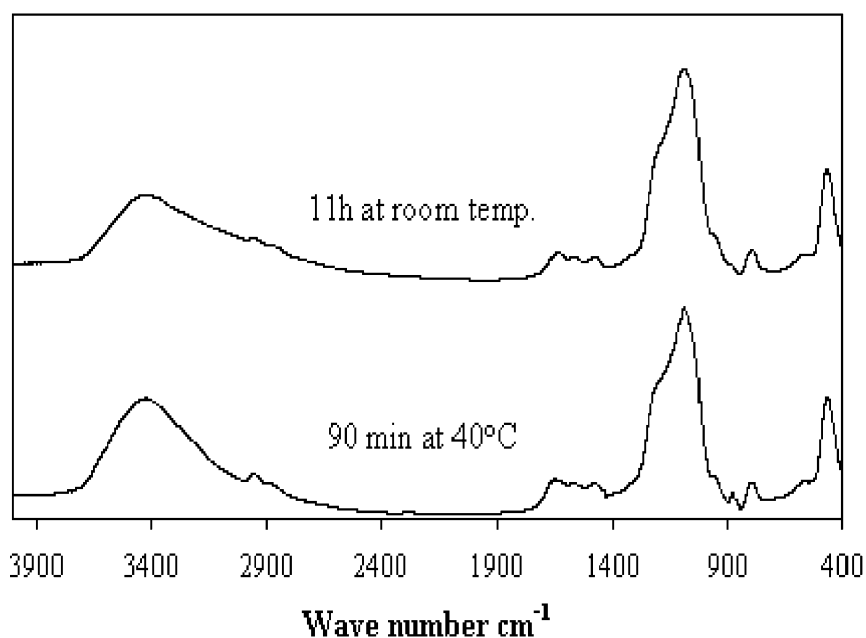


Fig. 6. FTIR spectra showing the effect of temperature on the hydrolyzed product.

due to the condensation of silanols.²¹ At the same time, the peak around 1648 cm^{-1} , which was assigned to the OH bending,²² also decreased in the same manner. The increase in the absorption peak at 1086 cm^{-1} suggested that crosslinking of Si–O–Si bonds occurred via hydrolysis and condensation. This was confirmed by comparison with the disappearance of absorption peaks at 3405 , 2951 and 2883 cm^{-1} , indicating a decrease of organic ligands. It should be noted that, at 9 h, the peaks at 3405 , 2951 , 2883 and 1086 cm^{-1} change in the reverse direction. This phenomenon was also detected by Brinker et al. that when hydroxyl groups on the surface of the particles condense to form siloxane bonds, the particles coalesce in an irreversible sol-gel transition, and when coalescence occurs without forming siloxane bonds, the sol-gel transition may be reversible.^{23,24} The structure obtained at 11 h of hydrolysis was very close to that of silica (Fig. 4). Using a higher concentration of catalyst, 0.002 M HCl , the obtained results were essentially identical [Fig. 3(b)]. However, the change of absorption peaks at 3405 , 2951 , 2883 and 1086 cm^{-1} decreased faster as compared to a lower concentration of HCl.

The overall results are summarized in Fig. 5, which displays the relationship between the ratio of Si–O–C/Si–O–Si (the peaks at 1086 and 463 cm^{-1}) plotted against time for hydrolysis of the spiro-silicate at various acid concentrations at room temperature. Fig. 5 indicates that the optimum condition, showing more effective

hydrolysis occurs when 0.001 M HCl is applied, as referred by Lippert for TEOS in 1988.²⁵ Thus, this condition was selected to further study the effect of temperature, as shown in Fig. 6. It was found that at $40\text{ }^\circ\text{C}$ the hydrolysis rate was much faster than that at room temperature. At $40\text{ }^\circ\text{C}$ it took less than 1 h for spiro-silicate to become silica while more than 10 h was needed to obtain silica at room temperature.

Changing the catalyst from acid to base using 1 M ammonium hydroxide solution gave different results, as shown in Fig. 7. $0.001\text{ M NH}_4\text{OH}$ gave little change in the structure of Si–O–C and Si–O–Si during the time period of 1–8 h. After 9 h, a substantial decrease of the peak ratio was observed. Subsequently, however, after 11 h, the ratio increased again.

Table 1
The pH results of different catalyst concentration

| Concentration of HCl (1M) (%) | pH result | Concentration of NH_4OH (1M) (%) | pH result |
|-------------------------------|-----------|--|-----------|
| 1 | 2.14 | 1 | 9.56 |
| 2 | 2.03 | 2 | 9.67 |
| 3 | 1.97 | 3 | 9.72 |
| 4 | 1.81 | 4 | 9.80 |
| 5 | 1.73 | 5 | 10.1 |
| 15 | 0.65 | 15 | 10.2 |

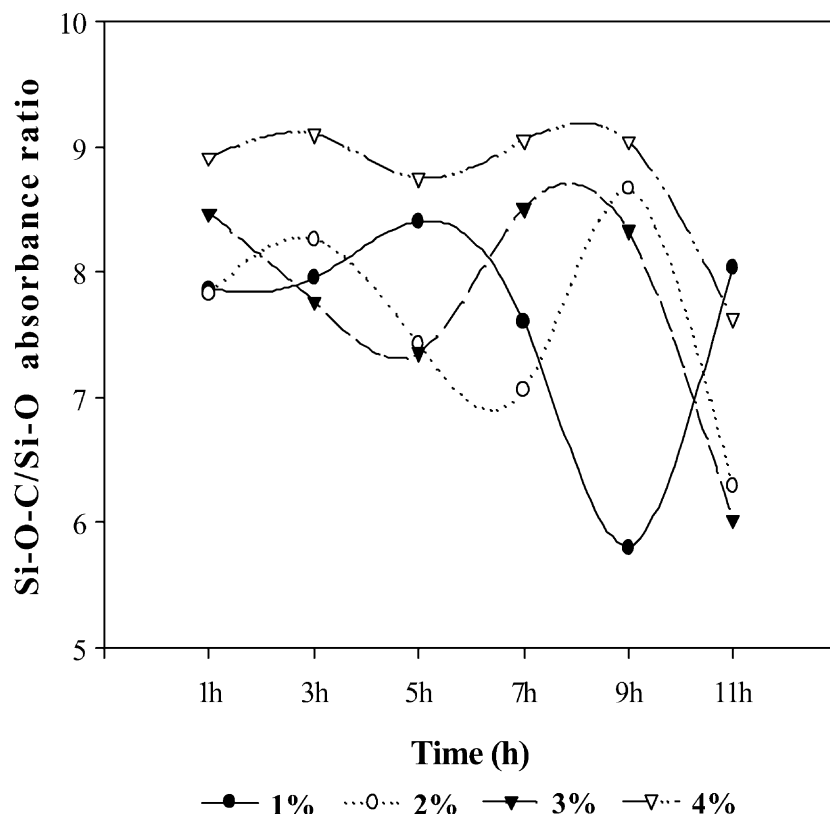


Fig. 7. The time-dependence of hydrolyzed products of spiro-silicate with $0.001\text{--}0.004\text{ M NH}_4\text{OH}$ at room temperature.

In summary, the kinetics of the sol-gel transition of spiro-silicate are slowest at 0.001 and 0.002 M HCl, for which $\text{pH} \approx 2$, due to the absence of ionized hydroxyl groups $[\text{Si}-\text{O}^- \text{ or } \text{Si}-(\text{OH}_2)^+]$,²⁶ see Table 1, as monitored by a decrease of the peaks at 3405, 2951, 2883 and 1086 cm^{-1} . This result is consistent with experimental studies of Brinker and coworkers,²⁴ who determined the optimal gel time of TEOS to be at pH near 2.

TGA analysis of spiro-silicate (Fig. 8) after hydrolysis with 0.001 and 0.002 M HCl were used to confirm the FTIR results shown in Figs. 3 and 5. Evidently, the kinetic data obtained from FTIR spectra and the ceramic yields obtained from TGA are in agreement. A

Table 2

The BET surface area measurement of spiro-silicate after hydrolysis with 0.001M HCl and NH_4OH at various time, followed by pyrolysis at 750 °C for 7 h, as compared to fused-silica starting material

| Time (h) | Surface area (m^2/g) | |
|--------------|--|---------------------------------|
| | 1% of 1M HCl | 1% of 1M NH_4OH |
| 3 | 307 | 296 |
| 5 | 354 | 278 |
| 7 | 369 | 307 |
| 9 | 339 | 347 |
| 11 | 596 | 280 |
| Fused silica | 167 | 168 |

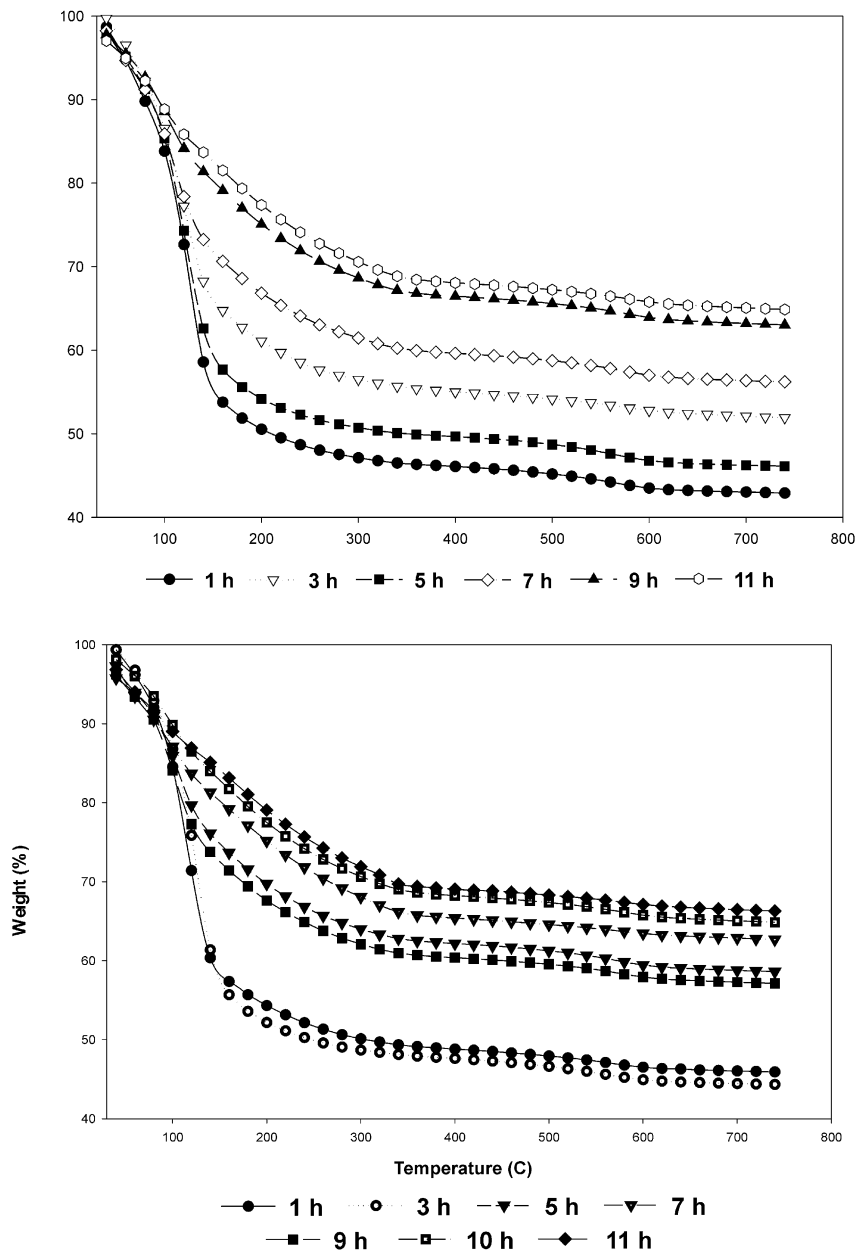


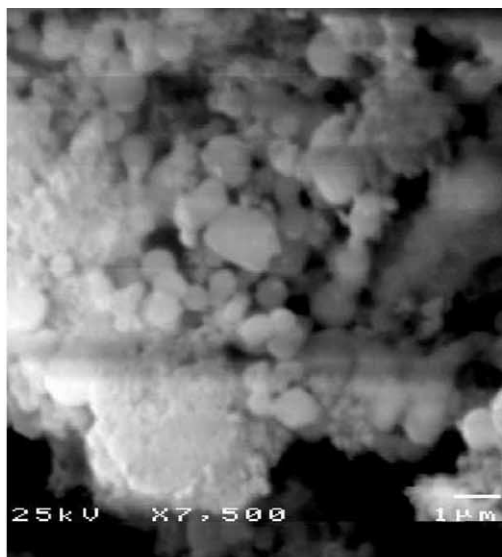
Fig. 8. TGA thermograms showing percent ceramic yields at various time after hydrolysis with HCl at (a) 0.001M and (b) 0.002M.

decrease in the Si–O–C peak long with an increase in Si–O–Si peak correlates to an increase in ceramic yield. Notably, the increase of Si–O–C peak at 9 h compared to 7 and 10 h using 0.001M HCl, correlates with a decrease of ceramic yield obtained from TGA.

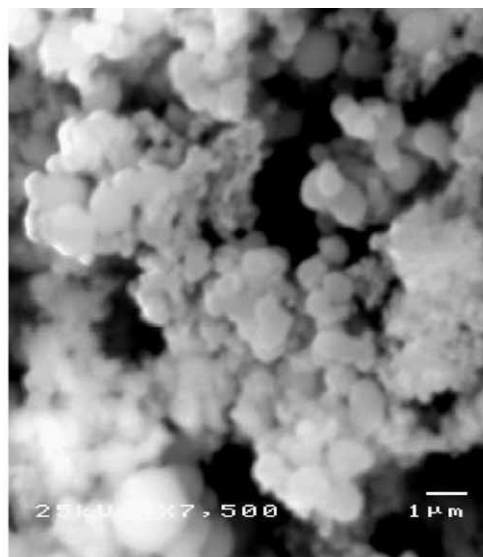
Thus, these surprisingly suggest that the reaction can proceed in the reverse direction, so called “reesterification”, in which an alcohol molecule displaces a hydroxyl group to produce an alkoxide ligand and water as a by product.²⁴

The BET surface area study of pyrolyzed product obtained from hydrolysis of spiro silicate at 750 °C for 7 h is shown in Table 2. The results from FTIR spectra, TGA and BET surface area measurement show that a decrease of –OH and Si–O–C peaks correlates to an increment of ceramic yield and surface area.

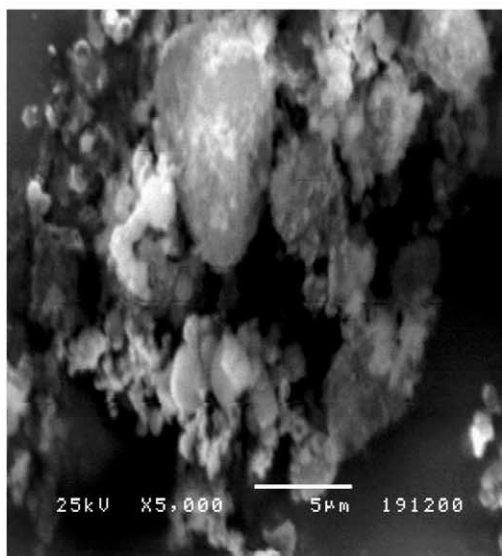
The morphology of the hydrolyzed aggregates was observed by scanning electron microscopy, as shown in Fig. 9. Fig. 9(a) and (b) show the characteristics of the dried gel, under acidic and basic conditions, respec-



(a) Hydrolyzed w/ 1% of 1M HCl

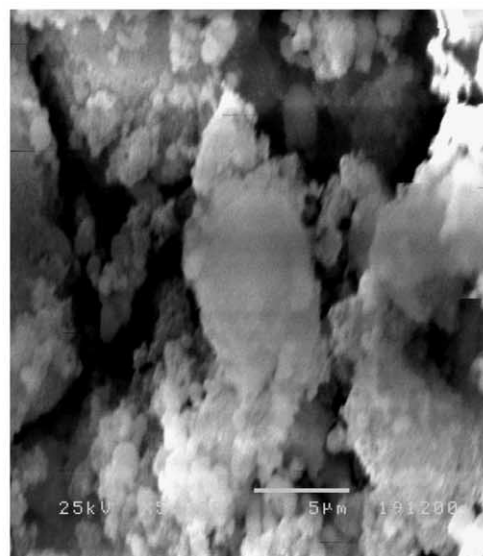


(b) Hydrolyzed w/ 1% of 1M NH₄OH



(c) Pyrolysis of material (a)

at 750°C, 7 h.



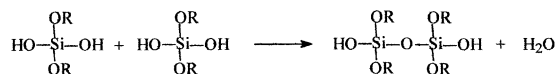
(d) Pyrolysis of material (b)

at 750°C, 7 h.

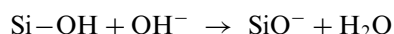
Fig. 9. SEM of hydrolyzed (a) and (b) and pyrolyzed (c) and (d) spiro silicate.

tively. Certain differences in morphology are evident, which can be traced to the effect of the different catalyst used.

Under acid catalysis, the hydroxylated monomer is formed via electrophilic (H^+) reaction. The condensation reaction continues via these hydroxylated monomers.



Using basic catalysis, (b) the sol particles formed tend to repel each other due to a high surface charge of SiO^- groups formed according to the following reaction.



Obviously, each condition has a distinct influence on the rate of condensation and porosity of the dried gel product. Thus, two variables were studied, namely, effect of catalysts on reaction time and gel properties.

As discussed previously, acid catalysis promotes the slowest reaction at 0.001M HCl corresponding to $\text{pH} = 2-2.5$. This is the pH near the iso-electric point, which gives no electrostatic particle repulsion.²⁶ By increasing the acid catalyst concentration, the reaction rate is increased whereas the gelling time is reduced. On the other hand, the base-catalyzed reaction takes place via nucleophilic attack,²¹ and the condensation reaction provides SiO^- , resulting in faster condensation before complete hydrolysis. Furthermore, with the base catalysis, repulsion of the sol structure gives more time for the particles to rearrange. Larger particles tend to form first. This

is different from using the acid catalyst, occurring via addition reaction in which many small molecules tend to grow slowly.²⁷ This phenomenon is confirmed by the SEM micrograph in Fig. 9(b), showing that the porosity of the sol structure is greater than that in Fig. 9(a).

It is known that, generally, the gel consists of two phases, the network solid phase and the connected pores filled with liquid phase.⁴ As the heat treatment is applied, the gel shrinks under capillary force as the liquid evaporates. It is evident in Fig. 9(a), that the HCl catalyzed gel contains small pores. If there was originally a large amount of water in the pore generated, upon heating the gel from the higher concentration of hydroxyl groups, this will result in a higher shrinkage of the gel, as shown in Fig. 9(c). On the other hand, the ammonia-catalyzed gel contains large pores and a small amount of water molecules, therefore smaller shrinkage occurs.

The density of product obtained from the gel hydrolyzed using 0.001M HCl was determined to be 0.54 g/cm^3 , a value much smaller than that of fused silica, 2.42 g/cm^3 . This results from the fact that the removal of alkoxy and hydroxyl groups by condensation reaction when the gel is heated, causes a large weight loss, producing new crosslinks and stiffening the structure.²⁸

3.2. Aminospinosilicate C4

In the case of the six-membered cyclic aminospinosilicate, ring is more stable than the five-membered spinosilicate ring. Moreover, the aminospinosilicate has bulkier substituents. As a result, hydrolysis of the

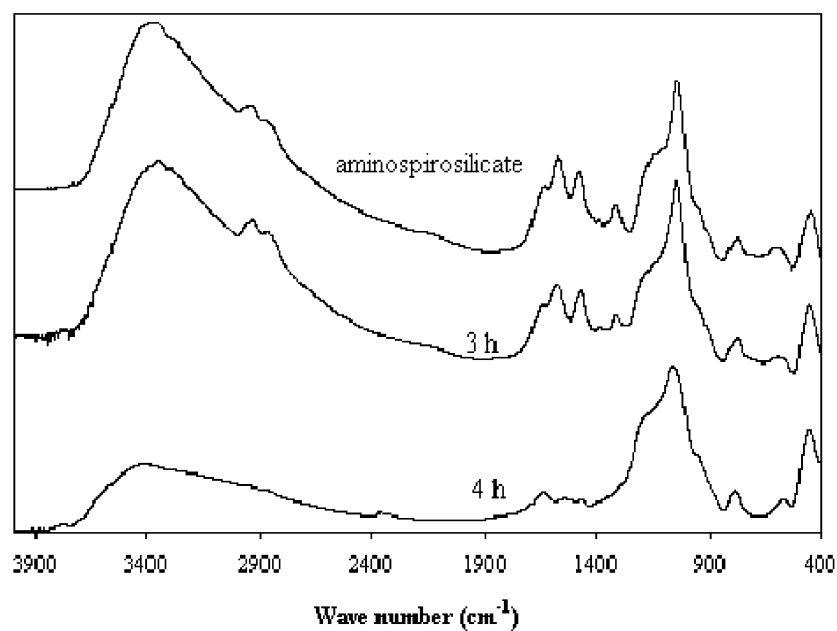


Fig. 10. FTIR spectra showing the effect of time on the hydrolyzed aminospinosilicate product at 60°C .

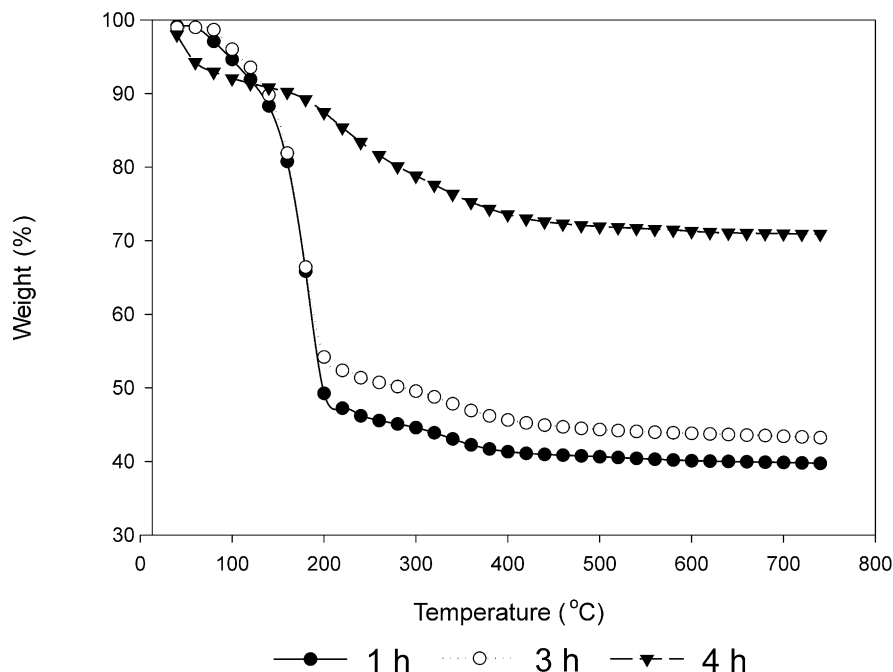


Fig. 11. TGA thermograms showing percent ceramic yields of hydrolyzed aminospirosilicate at 60 °C for 1, 3 and 4 h.

aminospirosilicate with either 1M HCl or 1M NH₄OH shows no significant reaction at room temperature and 40 °C. 1M HCl also shows no reaction on hydrolysis even at 60 °C. Thus, under acidic condition, protonation of alkoxy group is retarded due to the more stable ring structure, more steric hindrance, and the presence of amino group in the structure. This thus resulted in no structural change during hydrolysis of the products under acid condition.

Fig. 10 shows only the results of C4 hydrolyzed using 1M NH₄OH at 60 °C. Inspection of the decrease in the absorption peaks at 3405, 2951, 2883, 1086 cm⁻¹ indicates a slower hydrolysis rate. This is confirmed by the fact that the aminospirosilicate hydrolyzed at 60 °C for 4 h gives the highest ceramic yield, 70.89%, as shown in Fig. 11. The increased ceramic yield is due to a high concentration of reactive groups under base-catalysis and high temperature, allowing less time for the molecules to rearrange to form a crosslinked Si–O–Si network.

The BET analysis of aminospirosilicate sol-gel product pyrolyzed at 750 °C for 7 h indicated a surface area of 82.93 m²/g, reflecting the increase of reaction rate because of the increase in concentration of catalyst and temperature.²⁶

4. Conclusions

Spirosilicate can function as a reactive metal alkoxide group allowing sol-gel processing at room temperature or slightly elevated temperature. Near the IEP of silica

particle (pH ~ 2.0), the product gives high ceramic yield and high surface area, which is required in ceramic precursor processing. A low-density of product is reported to be an important result of the sol-gel method. The other factors that influence the structure of ceramic product from spirosilicate are temperature and aging time.

In addition, aminospirosilicate can serve as a model material for investigation of the sol-gel transition. Because of its higher stability and increased steric hindrance due to the extent of substitution, one needs a higher catalyst concentration and higher temperature for reaction to occur. It is possible to produce products with high ceramic yield and less shrinkage, which can be suitable for engineering industry applications.

Acknowledgements

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