



ELSEVIER

Journal of Non-Crystalline Solids 291 (2001) 206–210

JOURNAL OF
NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrsol

Amine catalyzed condensation of tetraethylorthosilicate

Steven M. Jones *

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, MailStop 125-109, Pasadena, CA 91109-8099, USA

Received 30 August 2000

Abstract

The catalysis of the condensation of hydrolyzed metal alkoxides by amines has been mentioned in the literature, but there has been no systematic study of their influence on the rate of the condensation reaction of the alkoxide and the microstructure of the resultant gel. The hydrolysis of tetraethylorthosilicate (TEOS) was catalyzed by a mineral acid and the condensation was catalyzed by various organic amines. The gelation times were found to vary widely with the different amines used as the catalyst and the microstructure of the resultant xerogels also differed significantly depending on the amine added. Gelation occurred in the shortest amount of time when 1,4-diazabicyclo{2.2.2}octane (DABCO) was used, whereas, systems catalyzed with imidazole (Im) and pyridine (Pyr) and their derivatives exhibited longer gel times and were composed of less coarse microstructures. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Mineral acids and bases are typically used to catalyze the hydrolysis and condensation of metal alkoxides in the sol–gel process. Acid catalysts cause the hydrolysis to rapidly approach completion, if there is sufficient water present. Acid catalyzed condensation tends to be directed toward the ends of the chains present and thus extended, highly branched linear polymers are formed [1]. Base catalysts are not as active in promoting hydrolysis, however, they tend to enhance the occurrence of condensation reactions in the middle of chains, creating more ramified structures [1].

The mechanisms of these reactions have been studied and well documented [1–7]. The variation of the pH of the precursor system and more specifically the base employed, has been shown to directly influence the reaction kinetics of sol–gel alkoxides [1,5,8,9]. However, the studies done on basic systems have employed primarily ammonium hydroxide and potassium hydroxide as the catalyst. There do exist a few references to the use of amines as catalysts in sol–gel reactions, but very little data have been reported [1,10]. Hurd et al. [11] described the use of potassium amide in the rearrangement of organopolysiloxanes and the effect of the strength of the electron donor group. However, no study has been done that compares the effect of different amines on the precursor system [12]. For this reason, a study was conducted employing several different amines and their derivatives to investigate their direct influence on the gelation and the resultant microstructure of the gels produced.

* Tel.: +1-818 345 7805.

E-mail address: smjones@pop.jpl.nasa.gov (S.M. Jones).

2. Experimental

2.1. Materials

Imidazole (Im), benzyl imidazole (BzIm), pyridine (Pyr), dimethylaminopyridine (DMAP), 1,4-diazabicyclo{2 2 2}octane (DABCO), tetraethyl-orthosilicate (TEOS), 200 proof ethanol and nitric acid were all used as received.

3. Sample preparation

Table 1 gives the compositions of the samples prepared for this study. The ethanol, TEOS and water (pH 1 with nitric acid) were combined and stirred for 1 min. A noticeable increase in temperature of the mixture indicated that extensive hydrolysis had occurred. The amine catalyst was then added, the sample was stirred briefly and allowed to stand undisturbed until gelation occurred. For each of the samples produced 10^{-3} mol of amine was added so that the concentration of the catalyst present was the same for each sample. Gelation was determined visually by the fact that the solution no longer exhibited bulk fluid behavior.

The samples were dried for several days by removing the cap from the sample tube so that xerogels were formed. Samples from each xerogel were adhered to a scanning electron microscopy stub with silver paint. The samples were sputtered with gold and observed with a scanning electron microscope.

4. Results

Table 2 gives the gelation time and a gross visual description of the gel produced by the different organic amines used as catalysts.

Table 1
Amine catalysis

Catalyst (g)	DABCO	Pyr	DMAP	Im	BzIm
Ethanol	1.006	1.007	1.011	1.023	1.004
TEOS	2.01	2.005	2.01	2.003	2.006
Water	0.511	0.529	0.517	0.513	0.513
Amine	0.112	0.086	0.16	0.068	0.154

Table 2
Amine catalysis

Catalyst	Gel time (s)	Appearance
DABCO	10	Opaque
Im	60	Translucent
BzIm	300	Translucent
Pyr	72 000	Translucent
DMAP	72 000	Translucent

Figs. 1(a)–(e) are SEM micrographs (magnification $10000\times$) of a cleaved surface of xerogels made with Im, BzIm, Pyr, N, N-DMAP and DABCO, respectively.

Figs. 3(a) and (b) are SEM micrographs (magnification $1000\times$) of gels made with Im and BzIm, respectively, showing distinctive colorations produced during the gelling process.

5. Discussion

Since previous studies have shown that the hydrolysis of TEOS in the presence of water and acid occurs very rapidly, the role of the amine catalysts must be in the condensation of the silanols present [13,14]. The gelation times given in Table 2 indicate the relative strengths of each amine in acting as a catalyst for the condensation of the hydrolyzed alkoxide. DABCO was observed to cause gelation in a matter of seconds, forming an opaque gel. In comparison, the Ims caused gelation to occur in a matter of minutes, while the Pyrs caused gelation to occur in a matter of hours.

Figs. 1(a)–(e) are SEM micrographs of the structures of the striations of cleaved surfaces of gels produced from different amine catalysts. Striations like these are typical of the cleaved surfaces of silicate sol–gel materials. Since the condensation of the alkoxide is directly influenced by the catalyst employed, the microstructure of the

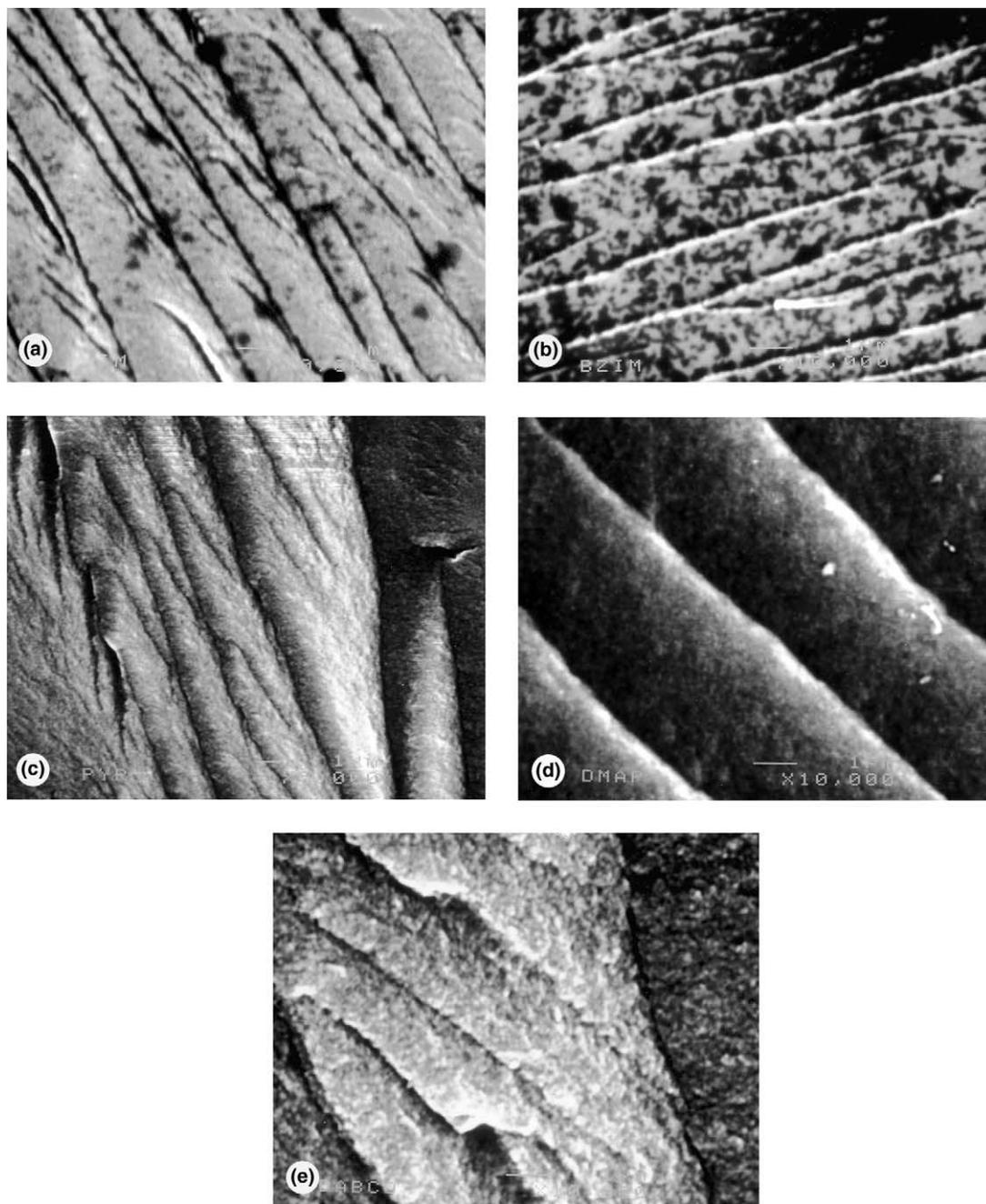


Fig. 1. (a) Scanning electron micrograph of a cleaved surface catalyzed with Im. (b) Scanning electron micrograph of a cleaved surface catalyzed with BzIm. (c) Scanning electron micrograph of a cleaved surface catalyzed with Pyr. (d) Scanning electron micrograph of a cleaved surface catalyzed with N, N-DMAP. (e) Scanning electron micrograph of a cleaved surface catalyzed with DABCO.

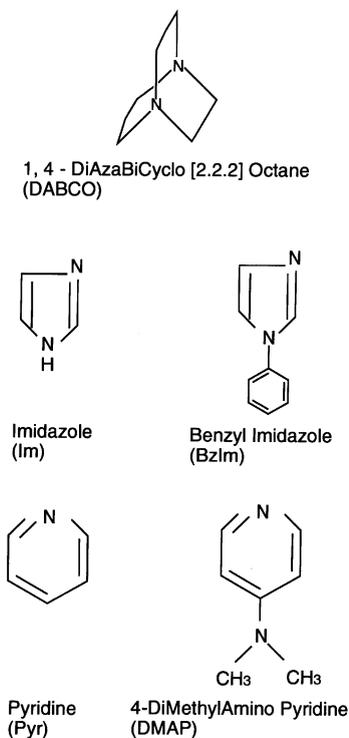


Fig. 2. Amine catalysts and their chemical derivatives.

resultant gel reflects the kinetics of the condensation reactions. The gels catalyzed by Im and BzIm display relatively fine surface features with dis-

tinctive discolorations. The striations observed on the Pyr and DMAP catalyzed gels are coarser than those of the Im and BzIm catalyzed gels, in that the distance between the striations is significantly greater. The DABCO catalyzed gel is the coarsest observed, with the distance between striations being ~ 20 mm. However, it is believed that these striations reveal something of the fundamental nature of the microstructure of the gel. The fact that the striations are relatively fine for some amine catalyzed samples and coarse for others is indicative of the primary particles which compose these structures. Therefore, the particles generated by Im catalysis are probably linear and relatively small, whereas, those catalyzed by DABCO are probably ramified and fairly large.

The differences in acid versus base catalyzed gels have been observed by electron microscopy [15,16]. These differences are clearly caused by the fact that in mineral acid catalyzed systems particle growth stops when the particles reach 2–4 nm, whereas in mineral base catalyzed systems it stops when the particles reach 5–10 nm [17]. Catalysis by amines continues this trend, in that, as weak bases they generate even larger particles, i.e., 100 nm. For precursor systems of pH 5–10 hydrolyzed silanes tend to react with an existing particle, rather than combining with other monomers to form new particles, thus generating fewer, larger particles which then condense to form the gel [18].

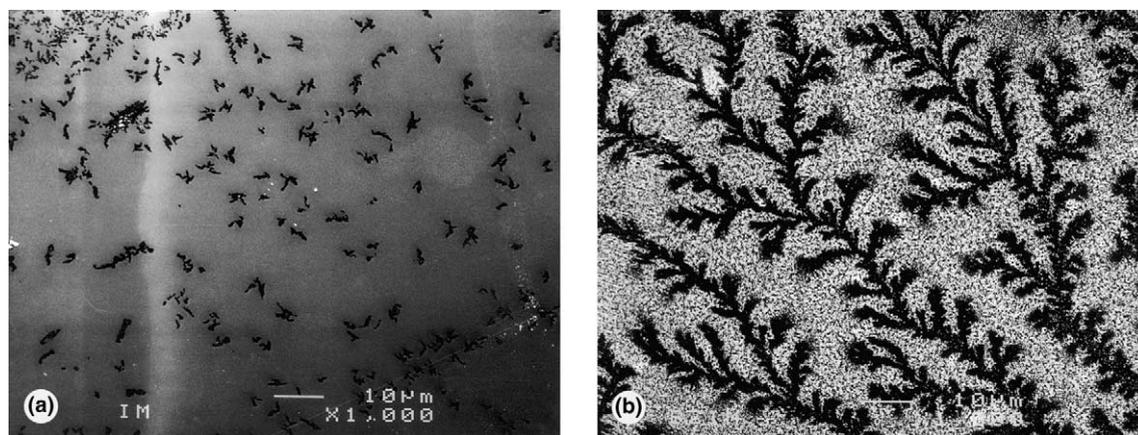


Fig. 3. (a) Scanning electron micrograph of surface of gel catalyzed with Im. (b) Scanning electron micrograph of surface of gel catalyzed with BzIm.

Hurd et al. [11] observed that compounds containing strong electron donor groups co-ordinate with and catalyze the condensation of siloxanes. In the amines used in this study, the nitrogen in the amine group acted as an electron donor in catalyzing the polymerization of siloxanes. The differences observed in the textures of the gels reflect the differences in the bases and their derivatives to act as catalysts (see Fig. 2). For example, the gel time was shorter and the texture was coarser of the gel catalyzed with DABCO than those by Im or Pyr since it acted as a stronger base.

Figs. 3(a) and (b) show curious dark areas which were ubiquitous for the Im and BzIm catalyzed samples. For the gel catalyzed with Im the darker areas were lesser in number and smaller in size, however, for the BzIm catalyzed gel the darker regions were extensive in size and dendritic in nature. These regions appear to be caused by a linear nucleation and may indicate a phase separation of two different polymerization reactions.

Since organic amines, e.g., have been shown to act as drying control agents for sol–gel materials, it is difficult to interpret what role the amines in this study may have played in the subsequent drying process [1,6]. However, since it has been demonstrated that amines do act as sol–gel catalysts and that their structure influences their catalytic activity, they can then be employed to further tailor the porous nature of the resultant sol–gel materials. Further studies investigating the effect of experimental parameters such as temperature and solvent, as well as, other amines and their derivatives, would further elucidate the role played by these molecular species in the sol–gel process.

Acknowledgements

The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

References

- [1] C.J. Brinker, G.W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, New York, 1990.
- [2] C.J. Brinker, *J. Non-Cryst. Solids* 100 (1988) 31.
- [3] E.J.A. Pope, J.D. MacKenzie, *J. Non-Cryst. Solids* 87 (1986) 185.
- [4] L.W. Burggraf, L.D. Davis, *Mater. Res. Soc. Symp. Proc.* 73 (1986) 529.
- [5] C.J. Garvey, B.E. Smith, *Mater. Res. Soc. Symp. Proc.* 180 (1990) 223.
- [6] L.L. Hench, J.K. West, *Chem. Rev.* 90 (1990) 33.
- [7] M.T. Harris, R.R. Brunson, C.H. Byers, *J. Non-Cryst. Solids* 121 (1990) 397.
- [8] K.D. Keefer, *Mater. Res. Soc. Symp. Proc.* 32 (1984) 15.
- [9] A.V. McCormick, A.T. Bell, C.J. Drake, *Mater. Res. Soc. Symp. Proc.* 121 (1988) 67.
- [10] T. Yamamoto, US Patent 4937208.
- [11] D.T. Hurd, R.C. Osthoff, M.L. Corrin, *J. Am. Chem. Soc.* 76 (1954) 249.
- [12] M.G. Voronkov, V.P. Mileshekevich, Y.A. Yuhelevskii, *The Siloxane Bond*, Consultants Bureau, New York, 1978.
- [13] S.M. Jones, S.E. Friberg, *J. Disp. Sci. Tech.* 13 (6) (1992) 669.
- [14] R.A. Assink, B.D. Kay, *J. Non-Cryst. Solids* 99 (1988) 359.
- [15] M. Nogami, Y. Moriya, *J. Non-Cryst. Solids* 37 (1980) 191.
- [16] C.J. Brinker, K.D. Keefer, D.W. Scherer, C.S. Ashley, *J. Non-Cryst. Solids* 48 (1982) 47.
- [17] J. Zarzycki, M. Prassas, J. Phalippou, *J. Mater. Sci.* 17 (1982) 3371.
- [18] K.D. Keefer, *Mater. Res. Soc. Symp. Proc.* 32 (1984) 295.