Sol–Gel Synthesis of Alumina in the Presence of Acetic Acid: Distinguishing Gels and Gelatinous Precipitates by NMR Spectroscopy

Saloua Rezgui† and Bruce C. Gates*

Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616

Received June 29, 1994. Revised Manuscript Received September 12, 1994®

^{1}H, ^{13}C, and ^{27}Al NMR spectroscopies were used to characterize the products of sol–gel synthesis with $Al(O\text{-}s\text{-}Bu)_3$ reactant used in the presence of acetic acid and *sec*-butyl alcohol. The molar ratio R of acetic acid to $Al(O\text{-}s\text{-}Bu)_3$ determined the nature of the product. When R was <2, the product was an opaque gelatinous precipitate, and when R was ≥ 2, the products were transparent gels. The gels were distinguished from the gelatinous precipitate by ^{1}H, ^{13}C, and ^{27}Al NMR spectroscopies. These techniques provide simple methods for determining the gel point.

Introduction

In the sol–gel process for preparation of metal oxides and other materials,[1–3] the reactants undergo chemical reactions that convert them from sols (dispersions of colloidal particles in a liquid) to solid particles with diameters of 1–100 nm.[4] As the colloids in a sol react with each other to form a continuous macromolecule gel,[1,2] the gel entraps solvent and reactants. The gel thus consists of a continuous framework enclosing a continuous liquid phase in spaces that ultimately may become pores of submicron dimensions as a result of drying.[1,2]

Several types of gels can be formed in sol–gel processes.[1,5] Polymeric gels consist of covalently linked atoms in a stable three-dimensional network.[1] Gelatin gels are entangled polymer chains. Particulate gels are colloidal gelular particles that are associated with each other through van der Waals forces; the interactions are so weak that a particulate gel may be dispersed by shaking.

The sol–gel transformation can in principle proceed until the last possible bonds in the polymeric product are formed. In practice, this limiting case is not observed because the viscosity of the mixture increases rapidly near the completion of the gel formation, and the transport restriction causes the rate to decrease sharply.[1,2] The approximate completion of the process is designated as the gel point, being observed when the material no longer flows readily. It is difficult to define the gel point precisely because the transformation from a viscous fluid to an elastic gel is gradual. Brinker and Scherer[1] pointed out that the sharp increase in viscosity that accompanies gelation essentially freezes in a particular polymer structure at the gel point. Thus gelation may be compared to a rapid solidification process. Because segments of the gel network still interact to allow further condensation or other bond-forming reactions, the nature of the material continues to change after the gel point is reached; this process is called aging.[1,2]

The goal of the research described here was to show how NMR spectroscopy can be used to provide evidence in addition to viscosity measurements[6–10] to characterize the sol–gel transformation more precisely. We report the preparation of Al_2O_3 gels from $Al(O\text{-}s\text{-}Bu)_3$ in the presence of acetic acid. Under the conditions of the process, the hydrolysis and condensation reactions proceed rather slowly, being controlled by the concentration of acetic acid, which is both a gelification agent and a catalyst.[11] The specific objective was to show how ^{1}H, ^{13}C, and ^{27}Al MAS NMR spectroscopies can be used to characterize the gel point.

Experimental Methods

Gel Preparations. Aluminum *s*-butoxide, $Al(O\text{-}s\text{-}Bu)_3$ (98%), *sec*-butyl alcohol, *s*-BuOH (99+%), and glacial acetic acid (99.99%) were supplied by Aldrich. With the reagents in a N_2-filled glovebag (or, alternatively, in air), $Al(O\text{-}s\text{-}Bu)_3$ was dissolved in stirred *s*-BuOH at room temperature to give a concentration of $Al(O\text{-}s\text{-}Bu)_3$ of 1 M. Various amounts of acetic acid were added to aliquots of this homogeneous solution, and different gels were obtained as products. The amount of acetic acid added is represented by $R = [CH_3COOH]/[Al(O\text{-}s\text{-}Bu)_3]$. R ranged from 0 to 4.

NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra of the gels were recorded with a 300-MHz General Electric QE 300 spectrometer. The samples were placed in 10-mm NMR tubes. The reference used in these experiments was TMS (tetramethylsilane). The number of scans recorded for each sample

---

† Current address: Département de Chimie, Faculté des Sciences de Bizerte, Zarzouna, Tunisia.

® Abstract published in *Advance ACS Abstracts*, October 15, 1994.

(1) Brinker, C. G.; Scherer, G. W. *Sol-Gel Science*; Academic Press: New York, 1989.

(2) Hench, L. L.; West, K. J. *Chem. Rev.* **1990**, *90*, 33.

(3) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259.

(4) Davis, J. T.; Rideal, E. K. In *Interfacial Phenomena*; Academic Press: New York, 1963.

(5) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter IX.

(6) Sakka, S.; Kamiya, K. *J. Non-Cryst. Solids* **1982**, *48*, 31.

(7) Sakka, S. In *Better Ceramics Through Chemistry*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Elsevier: New York, 1984; Vol. 32, p 91.

(8) Nogami, M.; Moriya, Y. *J. Non-Cryst. Solids* **1980**, *37*, 191.

(9) Ahktar, M. M. Ph.D. Dissertation, Alred University, New York, 1983.

(10) Mizuno, T.; Phalippou, J.; Zarzycki *J. Glass Technol.* **1985**, *26*, 39.

(11) Rezgui, S.; Gates, B. C.; Burkett, S.; Davis, M. E. *Chem. Mater.*, in press.

0897-4756/94/2806-2386$04.50/0

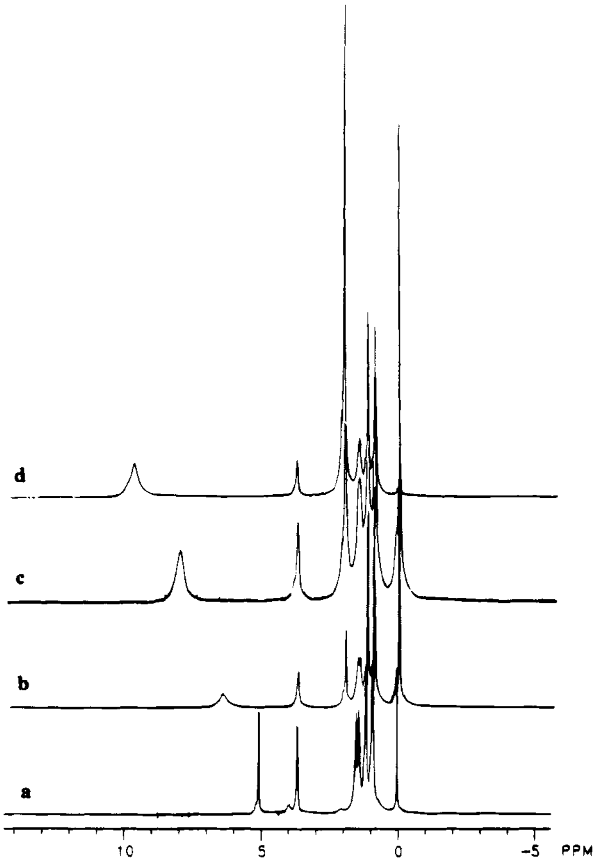

Figure 1. ^{1}H NMR spectra of freshly prepared materials: (a) $R = 1$ (gelatinous precipitate); (b) $R = 2$; (c) $R = 3$; (d) $R = 4$.

was 8 for ^{1}H and 240 for ^{13}C. ^{1}H and ^{13}C NMR spectra were recorded both for freshly prepared gels and for those that had been allowed to stand in the sealed tube. The ^{13}C NMR spectra were recorded with proton decoupling.

^{27}Al magic-angle spinning (MAS) NMR spectra were recorded at the California Institute of Technology with a Bruker AM 300 spectrometer operating at 78.21 MHz. A 4-μs pulse width with a delay time of 1 s was used. The gels were packed into 4-mm zirconia rotors and spun at 3 KHz; 1800 scans were recorded. Only freshly prepared samples were characterized with this instrument.

Results

Preparation of Al_2O_3 Gels and Gelatinous Precipitates from $Al(s\text{-}OBu)_3$ in the Presence of Acetic Acid. Acetic acid reacted with freshly prepared solutions of $Al(O\text{-}s\text{-}Bu)_3$ in alcohol, as evidenced by the formation, within minutes, of gels. The products included (1) gelatinous precipitates,[3] which were wet to the touch, opaque, and softer than the gels, and (2) gels, which were dry to the touch, transparent, and elastic.[3] The appearance of the gel products depended on the ratio R. When R was <2, the final product was a gelatinous precipitate. When R was ≥ 2, the products were gels.

^{1}H NMR Spectra. The ^{1}H NMR spectra of the freshly prepared and aged aluminas are shown in Figure 1. The resonance located at 5.1 ppm indicates the protons in the OH groups of the alcohol solvent $C(H_a)_3C(H_b)_2C(H_c)O(H_d)C(H_e)_3$. The resonances at 2.1 and 4 ppm are assigned to protons in positions b and c of the s-OBu ligand bonded to Al in aluminum alkoxide. The assignments are based on a comparison with the spectrum of $Al(O\text{-}s\text{-}Bu_3)$ (data not shown).

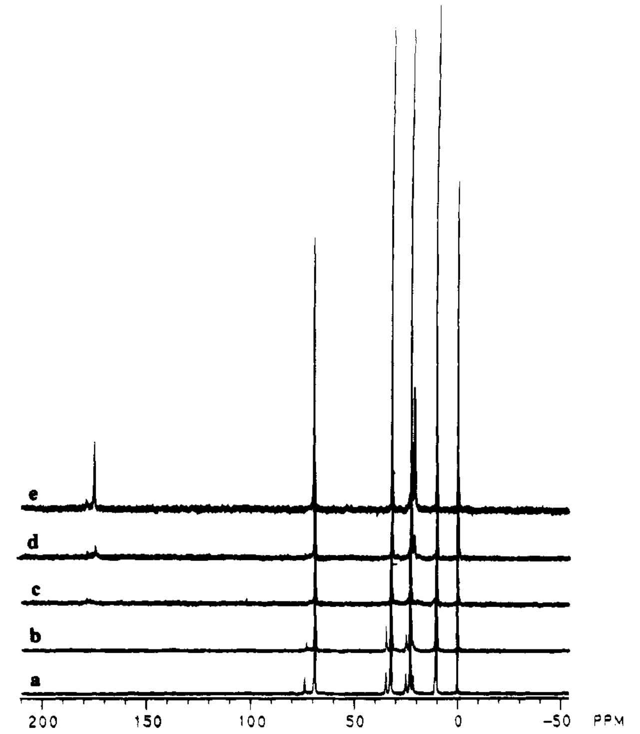

Figure 2. ^{13}C NMR spectra of freshly prepared materials: (a) $R = 0$; (b) $R = 1$; (c) $R = 2$; (d) $R = 3$; (e) $R = 4$.

When R increased beyond 1, the resonances at 2.1, 4, and 5.1 ppm disappeared, and new bands appeared between 6 and 10 ppm, which are attributed to protons in OH ligands. As R increased, the number of these resonances increased, and they shifted downfield.

^{13}C NMR Spectra. Each of the ^{13}C NMR spectra of Figure 2 includes, besides the TMS resonance at 0 ppm, four major resonances, at 10, 22, 32, and 69 ppm, attributed to the carbons a, d, b, and c, respectively, of the alcohol solvent $C_aH_3C_bH_2C_cHOHC_dH_3$, in a liquid-like state. There are four small bands in two of these spectra (Figure 2a,b) that are similar in location to the bands attributed to the alcohol. Thus these resonances (located at 10.5, 25, 35, and 73 ppm) are attributed to the carbons of alkoxide ligands, which could be bonded only to Al. (The band at 21 ppm is suggested to be indicative of an impurity, which was also present in the aluminum alkoxide, as indicated by its NMR spectrum. The impurity is probably an oligomer of the alkoxide.) As R increased, these bands decreased in intensity, still being present at $R = 1$ (Figure 2b) and disappearing at $R = 2$ as new bands appeared at 20, 175, and 179 ppm (Figure 2c). On the basis of a comparison with the spectrum of acetic acid (not shown), the first of these is attributed to CH_3 in acetate ligands. On the basis of a comparison with the spectrum of acetic acid, the bands at 175 and 179 ppm are attributed to two COO species in acetate ligands. The resonance at 175 ppm is in the same position as that of acetic acid itself. That observed at 179 ppm is thus attributed to COO in a different environment; it could be bonded to Al.

^{27}Al MAS NMR Spectra. The data characterizing a series of products including a gelatinous precipitate and gels are shown in Figure 3. When R was ≥ 2, resonances were present at -17 and -4.6 ppm. When R was 1, these two resonances were observed, in addi-

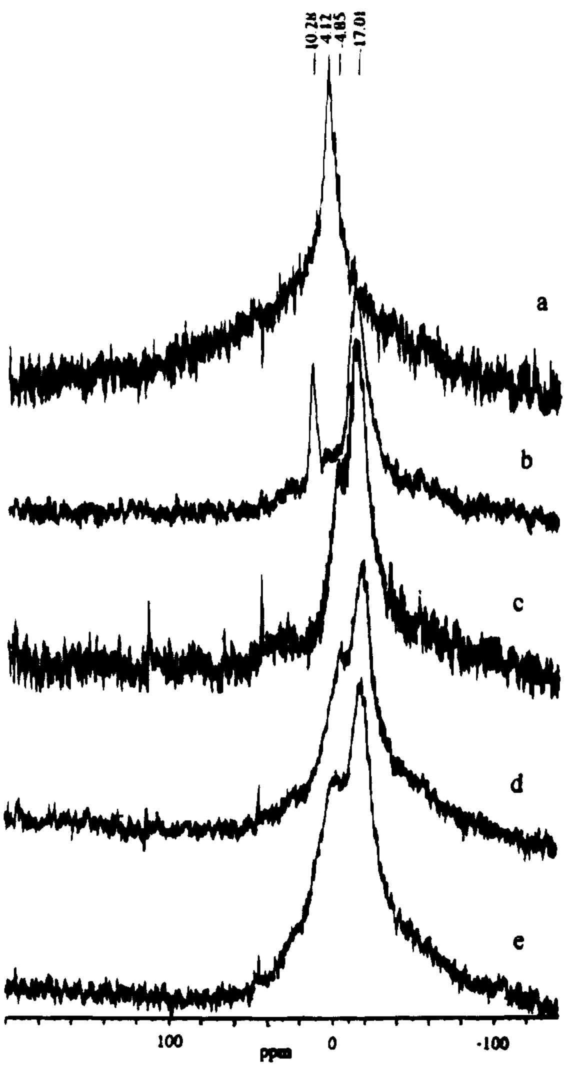

Figure 3. ^{27}Al MAS NMR spectra of freshly prepared materials: (a) $R = 0$; (b) $R = 1$; (c) $R = 2$; (d) $R = 3$; (e) $R = 4$.

tion to one at 10.2 ppm. All these resonances are attributed to six-coordinate aluminum species.[12-14] The resonances shifted to higher field as the density of the material increased.[15-18]

Discussion

^{1}H NMR Spectra. The ^{1}H NMR results provide a simple diagnostic to distinguish between these two kinds of sol–gel products, as follows: The spectrum of the gelatinous precipitate is characterized by a resonance at 5.1 ppm that is missing from the spectra of the gels. The spectra of the gels are characterized by resonances between 6 and 9 ppm that are missing from the spectrum of the gelatinous precipitate. Thus the presence or absence of these ^{1}H NMR resonances provides a determination of the gel point. The resonance at 5.1 ppm, characteristic of the gelatinous precipitate, is attributed to protons in OH groups of the alcohol solvent. The resonances between 6 and 9 ppm are attributed to OH species with rapidly exchanging protons donated by the acetic acid. The latter assignment was verified by measurement of the spectrum of a solution of acetic acid in *sec*-butyl alcohol.

^{13}C NMR Spectra. The resonances (observed at 10.5, 25, 35, and 73 ppm) attributed to the carbons of alkoxide ligands were still present in the spectrum of the gelatinous precipitate ($R = 1$, Figure 2b) but were absent from the spectrum of the gel ($R = 2$) whereas other resonances were present at 20, 175, and 179 ppm (Figure 2c). Thus the presence of the resonances of the aluminum alkoxide allows a distinction between the gel and the gelatinous precipitate.

^{27}Al NMR Spectra. The ^{27}Al MAS NMR spectra of the gelatinous precipitate are characterized by resonances at −4 and −17 ppm and by a resonance at 10.2 ppm. The ^{27}Al MAS NMR spectra of the gels are characterized by the same resonances at −4 and −17 ppm but not by the resonance at 10.2 ppm. Thus the presence or absence of the resonance at 10.2 ppm allows a distinction between the gelatinous precipitate and the gels.

Summary of the Sol–Gel Chemistry. In the sol–gel synthesis, several reactions occurred when acetic acid was added to the reaction solution, depending on the ratio *R*. The reaction that occurs first is the following:[11]

$$\mathrm{Al(O\text{-}\mathit{s}\text{-}Bu)_3 + CH_3COOH \rightarrow Al(O\text{-}\mathit{s}\text{-}Bu)_2(CH_3COO) + \mathit{s}\text{-}BuOH} \quad (1)$$

This reaction is exothermic. The acetic acid catalyzes the formation of water by dehydration of *sec*-butyl alcohol:

$$\mathrm{CH_3CH_2CHOHCH_3 \rightarrow CH_3CH{=}CHCH_3 + H_2O} \quad (2)$$

Water produced in the medium reacts with $\mathrm{Al(O\text{-}\mathit{s}\text{-}Bu)_2(CH_3COO)}$, as follows:

$$\mathrm{Al(O\text{-}\mathit{s}\text{-}Bu)_2(CH_3COO) + H_2O \rightarrow Al(O\text{-}\mathit{s}\text{-}Bu)(CH_3COO)(OH) + \mathit{s}\text{-}BuOH} \quad (3)$$

The products resulting from reactions 1 and 3 then undergo condensation catalyzed by acetic acid to give polymeric products, as follows:[11]

$$\mathrm{{-}Al{-}O{-}\mathit{s}{-}Bu + HO{-}Al{-} \rightarrow {\sim}{-}Al{-}O{-}Al{-}{\sim} + \mathit{s}\text{-}BuOH} \quad (4)$$

and/or

$$\mathrm{{-}Al{-}OH + HO{-}Al{-} \rightarrow {\sim}{-}Al{-}O{-}Al{-}{\sim} + H_2O} \quad (5)$$

All these reactions occur for all values of the ratio *R* but do not all proceed to completion for all values of *R*.[11] Acetic acid affects all these reactions; thus the rate of each depends on *R*. As *R* increases, the rate of water formation increases because acetic acid catalyzes the alcohol dehydration reaction. Likewise, the rate of condensation reactions increases because of the catalytic role of acetic acid. Therefore, more highly condensed products (gels) are formed for high values of *R*, whereas

---

(12) Muller, D.; Gessner, W.; Behrends, H. J.; Scheler, G. *Chem. Phys. Lett.* **1981**, *79*, 59.

(13) Fyfe, C. A.; Thomas, J. M.; Klinowski, J.; Gobbi, G. C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 259.

(14) Risbud, S. H.; Kirkpatrick, R. J.; Taglialavore, A. G.; Montez, B. *J. Am. Ceram. Soc.* **1987**, *70*, C10–C12.

(15) Alemany, L. B.; Timken, H. C.; Johnson, I. D. *J. Magn. Reson.* **1988**, *80*, 427.

(16) Komarneni, S.; Fyfe, C. A.; Kennedy, G. J.; Strobl, H. *J. Am. Ceram. Soc.* **1986**, *69*, C45–C47.

(17) Komarneni, S.; Roy, R.; Fyfe, C. A.; Kennedy, G. J.; Strobl, H. *J. Am. Ceram. Soc.* **1986**, *69*, C42–C44.

(18) Bonhomme-Coury, L.; Babonneau, F.; Livage, J. *Chem. Mater.* **1993**, *5*, 323.

less highly condensed products (gelatinous precipitates) are formed at low values of *R*.

When *R* was ≥ 2, unreacted acetic acid was present, as shown by the ^{13}C NMR spectra (Figure 2). The mobile species characterized by the ^1H NMR resonances in the range 6–9 ppm are suggested to be formed by exchange of protons between this unreacted acetic acid and basic oxygen atoms of alcohol molecules. When the exchange is rapid, the bands are broad, as shown in Figure 1 for the freshly prepared gels. As the gels aged, the resonances between 6 and 9 ppm changed in position and decreased in intensity (not shown), also becoming sharper, consistent with a decrease in mobility of the species. This decrease in mobility is explained by trapping of the mobile species within the confines of the gel. Thus the results are consistent with the inference that the gel point had already been reached when the spectra of Figure 1 were recorded for the sample for which $R = 2$. Further condensation occurred during the aging. Thus the resulting product was a polymeric gel, consisting of covalently linked atoms in a stable three-dimensional network.[1] In this case all the reactions described in eq 1–5 proceeded virtually to completion.

In contrast, when *R* was equal to 1, not all the reactions 1–5 proceeded to completion.[11] The evidence that $Al(O\text{-}s\text{-}Bu)_3$ was still present with $Al(OR)_2(CH_3COO)$ is shown (1) by ^1H NMR data indicating the presence of resonances at 2.1 and 4 ppm (Figure 1) attributed to protons of the *s*-OBu ligands in aluminum alkoxide[11] and (2) by ^{13}C NMR data (Figure 2b) indicating $Al(O\text{-}s\text{-}Bu)_3$. The remaining unreacted metal alkoxides are suggested to be characterized by the resonance at 10 ppm in the ^{27}Al MAS NMR spectrum (Figure 3b). This resonance is characteristic of less highly condensed species than the polymeric product.[11,12] These species remain to be identified; perhaps they are oligomeric.

The final product when *R* was equal to 1 is a mixture of (1) gelatin gels, i.e., entangled polymer chains resulting from reactions 1–5, which proceeded virtually to completion, and (2) particulate gels (colloidal gelular particles that are associated with each other through van der Waals forces) resulting from reactions 1–5 that did not proceed to completion. Thus we infer that the gel point was not reached in the gelatinous precipitate. What was missing was the acetic acid needed for reactions 1, 2, 4, and 5.

Acknowledgment. We thank Paul Bruins of the Department of Chemistry of the University of California at Davis for help with the ^1H NMR experiments. We thank S. Burkett and M. E. Davis of the California Institute of Technology for help with the ^{27}Al NMR experiments, which were done in their laboratory. S.R. was supported by a Fulbright Fellowship sponsored by AMIDEAST and was on leave from Faculté des Sciences de Bizerte, Tunisia.