# Spectroscopic characterization of sol-gel silica derived from 3-aminopropyl-triethoxysilane

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Aminofunctional silica gels were prepared from 3-aminopropyl-triethoxysilane (APTEOS). FTIR and <sup>13</sup>C and <sup>29</sup>Si CP/MAS NMR spectra suggested that aminopropyl and silanol groups mainly form an intramolecular hydrogen-bonded ring structure. The fluorescence of pyrene was used as an environmental probe. The intensity ratio of the third peak to the first peak  $(I_3I_1)$  decreased as the sol-gel process proceeded. The  $I_3I_1$  value in an APTEOS-derived xerogel was close to that in a tetraethoxy-derived xerogel, indicating that the environmental polarity in an APTEOS-derived xerogel is as high as TEOS-derived xerogel in spite of the presence of aminopropyl groups. Based on the cyclic structure model, the polar characteristics may be attributed to water molecules involved in the ring by hydrogen bonding interactions.

## 1. INTRODUCTION

Hybrid inorganic-organic materials have been widely studied because of their potential applications [1-4]. Hybrid sol-gels can be prepared by mixing organic components into inorganic matrices. As an alternative and elegant method, sol-gel precursors with an organic functional group can be applied. Si alkoxides with an organic functional group are often used. For example, organically modified tetramethoxy-silane (TMOS) and tetraethoxysilane (TEOS) are commercially available: RTMOS and RTEOS, where R is a hydrogen (H), methyl (M), ethyl (E), phenyl (Ph) or vinyl (V). Among them, 3-aminopropyl-trialkoxysilane has been extensively examined from various viewpoints [5-19].

A pyrene fluorescence probe has been used to characterize the polarity of gels [20-25]. The intensity ratio of the third band to that of the 0-0 band  $(I_3/I_1)$  decreases with an increase in the environmental polarity of pyrene. The environmental polarity of the probe molecules is quite high for sol-gel silica derived from TMOS and TEOS. When gels are prepared from RTMOS or RTEOS, the environmental polarity decreases due to organic substitution [23,25].

In this paper, we studied the gels derived from 3-aminopropyltriethoxysilane (APTEOS) by using spectroscopic methods, such as FTIR, <sup>13</sup>C and <sup>29</sup>Si CP/MAS NMR, and pyrene fluorescence.

## 2. EXPERIMENTAL

Chemicals: Pyrene (Aldrich) was recrystallized several times from ethanol. APTEOS and TEOS from Tokyo Kasei were used without additional purification. Ethanol was spectroscopic grade. Water was deionized and distilled. Sample preparation: The sol-gel solutions were prepared by the hydrolysis of APTEOS in ethanol at room temperature. Ethanol containing  $1\times10^{-5}$  M pyrene and APTEOS were mixed together, and then water was added. The solutions were stirred for 0.5 h and placed in plastic beakers sealed with a pinholed film. The molar ratio of APTEOS : water : ethanol was 1.0 : 6.4 : 4.0. Gels thus obtained were dried at room temperature over 3 months and designated as xerogels in this paper. TEOS derived xerogels were similarly prepared.

Measurements: The fluorescence spectra were taken with a spectrophotometer (Jasco FP-777) at room temperature with an excitation wavelength of 340 nm. Fourier transform IR (FTIR) transmission spectra were obtained using a spectrophotometer (Jasco FTIR-615). Samples for FTIR were prepared by pressing a mixture of KBr and powdered Solid-state CP/MAS NMR xerogels into discs. measurements were carried out with samples in double air bearing 6 mm rotor of zirconia on a Jeol-JNM-GSX-270 spectrometer operating at 67.8 MHz for <sup>13</sup>C and 53.5 MHz for <sup>29</sup>Si. Magic Angle Spinning was performed at a 5.6 kHz spinning rate. Chemical shifts are referred to adamantane in <sup>13</sup>C NMR and to external polydimethylsilane in <sup>29</sup>Si NMR. The TG measurement was taken by the Thermo plus TG 8120 (Rigaku).

## 3. RESULTS

The FTIR spectra of xerogels derived from TEOS (A) and APTEOS (B) are shown in Fig. 1. The spectrum of a TEOS-derived xerogel mainly consists of bands arising from siloxane bonds (1198, 1078, 796 and 463 cm<sup>-1</sup>), silanol groups at 953 cm<sup>-1</sup>, and water molecules at 3446 and 1643 cm<sup>-1</sup>

[26,27]. The spectrum of a xerogel derived from APTEOS exhibits characteristic bands due to aminopropyl groups in addition to the siloxane origins, such as 1034 and 469 cm<sup>-1</sup> and the silanol at 920 cm<sup>-1</sup>. For instance, peaks at 2933 and 2877 cm<sup>-1</sup> are attributed to the stretching modes of the C-H bond and that at 3358 cm<sup>-1</sup> to the stretching mode of the N-H bond [15]. Among them, noticeable peaks were at 1568 and 1491 cm<sup>-1</sup>, which are assigned to an internal hydrogen bonded six-membered ring (IV in Scheme 1). The water-related bands also appeared at 3427 and 1643 cm<sup>-1</sup>.

Fig. 2 shows the <sup>29</sup>Si CP/MAS NMR spectrum of an APTEOS xerogel. The peaks at -69.5 ppm and -61.5 ppm are assigned to the central Si atoms with three (Q<sup>3</sup>) and two siloxane bonds (Q<sup>2</sup>), respectively, as shown in Scheme 1 [16,17,19]. The relative integrated intensity of the peaks  $(I_{O3}/I_{O2})$  was  $\approx 2.5$ .

The <sup>13</sup>C CP/MAS NMR spectrum of neat APTEOS is shown in Fig. 3(A). The peaks at 58.0 ppm and 18.0 ppm are attributed to the carbon atoms in ethoxy groups [18,19]. The peaks at 7.5, 27.0, and 45.0 ppm are assigned to the carbons of the aminopropyl chains, respectively, as designated in Fig. 3(A). The peaks due to the ethoxy groups disappear in the spectrum of the xerogel derived from APTEOS, as shown in Fig. 3(B). These changes indicate that the ethoxy groups of APTEOS are almost completely hydrolyzed [18,19]. From the neat APTEOS to the xerogel, the C<sub>1</sub> peak shifts to a lower field, from 7.5 to 13.0 ppm, and the C<sub>2</sub> and C<sub>3</sub> peaks shift slightly to a higher field from 27.0 to 26.2 ppm and from 45.0 to 44.7 ppm, respectively. The broader resonance peaks are possibly related to a distribution of several oligomeric species. Fig. 4 shows the fluorescence spectra of pyrene at the various stages of the sol-gel processing of APTEOS. The intensity ratio of the third peak to the first peak,  $I_3I_1$ , changed at each stage. The  $I_3I_1$  values are plotted against time of the sol-gel process in Fig. 5.  $I_3I_1$  gradually decreased from 0.76 (just prepared) to 0.64 (after 10 days) and showed little change for 2 months. After curing at 100 °C under vacuum, the weight loss of the xerogel was 15.5 % and the  $I_3I_1$  ratio became 1.13. These results indicate that evaporation of solvent forms a polar environment around pyrene in the xerogel and further dehydration by vacuum evacuation brings about a less polar environment [21,28].

#### 4. DISCUSSION

The <sup>29</sup>Si NMR spectrum shows the silicon species with three and two siloxane bonds, Q<sup>3</sup> and Q<sup>2</sup>, respectively, as shown in Scheme 1. The relative intensity,  $I_{Q3}/I_{Q2}$ , is 2.5. The value is smaller than those of MTEOS-derived gel (5.0) and VTEOS-derived gel (3.5) [29], suggesting that there are more silanol groups in APTEOS gel than in MTEOS gel or VTEOS gel.

According to previous reports [15,18,19], the hydrolyzed APTEOS can have a variety of structures including extended chain structures and ring structures shown in Scheme 1. The FTIR bands at 1568 and 1491 cm<sup>-1</sup> in the APTEOS gels agree with those at 1575 and 1489 cm<sup>-1</sup> assigned to the ring structure [15], suggesting structures III, IV or V. Based on the result that the protonated amino groups show the chemical shift of the C<sub>2</sub> peak at 20 ppm [18,19], the present C<sub>2</sub> peak at 26.2 ppm indicates that the amino groups are not protonated in the xerogels. Structure III can be discarded.



Fig. 1. FTIR spectra of xerogels derived from TEOS (A) and APTEOS (B).



Scheme 1. Some possible structures for APTEOS-derived xerogels.



Fig. 2. <sup>29</sup>Si CP/MAS NMR spectrum of an APTEOS-derived xerogel.



 $(C_2H_5O)_3$  Si  $-CH_2$   $-CH_2$   $-CH_2$   $-NH_2$ 1 2 3



Therefore, both results of FTIR and <sup>13</sup>C NMR suggest that the alkyl chains have folded structures such as IV and V, where the amino groups have hydrogen bonding with the silanol group, as in SiOH----NH<sub>2</sub>. Namely, hydrolysis of APTEOS initially forms the intramolecular hydrogen bonded structure and further condensation proceeds while keeping the ring structure, resulting in folded chains. This intramolecular hydrogen bonded ring structure may suppress the intermolecular polymerization and consequently increase the residual  $Q^2$  silicon (silanol), compared with MTEOS and VTEOS.

The FTIR spectra also indicate that the APTEOS-derived water molecules than contains more other gel organic-functional gels such as HTEOS or PhTEOS-derived gels [23,24]. The weight loss % observed in TG from 25 to 200 °C was 19.0 % for the APTEOS gels, which is comparable to TEOS (17.0 %) and tetramethoxysilane gels (15.4 %) and is an order of magnitude larger than 1.6 % of HTEOS gels and 1.7 % of MTEOS gels [28]. The higher water content of the APTEOS gels in comparison with other modified gels can most likely be ascribed to the hydrophilic property of the amino groups. The amino groups can form hydrogen-bonded complexes with water molecules. Moreover, the intramolecular hydrogen-bonded ring structure can increase the residual silanol groups anchoring the water molecules. Based on the cyclic structure model, water molecules are considered to be involved in the ring like structure V shown in Scheme 1 by hydrogen bonding interactions. Structure V is more plausible than IV in the gels containing a considerable amount of water molecules.



Fig. 4. Fluorescence spectra of pyrene at the various sol-gel stages of APTEOS: (A) just prepared; (B) after 56 d; (C) cured at 100°C in a vacuum.



Fig. 5. Changes in  $I_{\mathcal{A}}I_{l}$  of pyrene fluorescence in the sol-gel system of APTEOS against aging time at room temperature and after curing.

The change in  $I_3/I_1$  over time is similar to that observed in the sol-gel system of TEOS [21]. The  $I_3 I_1$  value of 0.64 in the xerogel is very close to that of a TEOS-derived xerogel (0.63), indicating a polar environment. The value is smaller than those of modified xerogels derived from HTEOS (1.05), MTEOS (0.95), ETEOS (1.17) [23] and PhTEOS (0.85) [24]. These results are consistent with the findings that the APTEOS and TEOS xerogels contain more water molecules in comparison with other organic functional xerogels, as seen in the gravimetric and FTIR measurements. Dehydration of the APTEOS xerogel causes an increase in L/I1 from 0.64 to 1.13, supporting the explanation that the polar environment of the APTEOS xerogels is due to the residual water molecules. The  $I_3/I_1$  value of 1.13, which is close to that of an ETEOS xerogel (1.17), is attributed to the intrinsic polarity of the alkyl chains.

#### 5. CONCLUSION

The fluorescence of pyrene indicates that an APTEOS-derived xerogel is as polar as silica xerogels derived from tetraethoxysilane or tetramethoxysilane. The gravimetric and FTIR measurements also show that the quantity of residual water molecules in an APTEOS xerogel is essentially the same as that in silica xerogels and considerably larger than these for organically modified silica. Based on the cyclic structure model due to an intramolecular hydrogen bond between aminopropyl and silanol groups suggested by FTIR and NMR spectra, the water molecules are believed to be adsorbed in the ring by hydrogen bonding interactions.

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