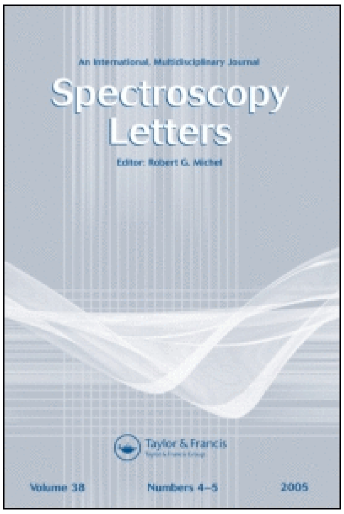

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Infrared Spectroscopy of Silica Sols-Effects of Water Concentration, Catalyst, and Aging

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INFRARED SPECTROSCOPY OF SILICA SOLS--EFFECTS OF WATER CONCENTRATION, CATALYST, AND AGING

Key Words: infrared spectroscopy, silica sols, aging

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ABSTRACT

Silica sols were investigated by Fourier transform infrared spectroscopy (FT-IR). The influences of water content, pH, and aging were studied. It was observed that the silica network gradually formed during aging and a more linear structure was present in the sol with low water content while high-water content sol possessed a more branched structure. The hydrolysis reaction was very fast in the sols with low pH compared with that in the high pH sols. Additionally, the sols with low pH had a greater concentration of silanol groups remaining after aging when compared with those with high pH. The IR spectra provide supplementary information about the sol to gel transformation and structure evolution.

INTRODUCTION

Sol-gel process has recently become an important method to prepare glass/ceramic thin films, fibers, and powders with high purity and novel properties. Generally, there are four steps involved in this method: (1) hydrolysis and polycondensation of a suitable precursor, (2) aging, (3) drying, and (4) heat treatment. By selecting suitable chemical compositions and acid or base catalysts, a wide range of samples can be prepared by this method.

Structural changes accompanying the silica sol-gel transformation have been studied extensively. An understanding of these changes is important, since sol structure plays a key role in the processing of specific products. The most important variables that affect the structure of sol-gel are water content and pH. Sakka found that sols with a low water content favor the formation of a linear structure which makes possible the drawing of glass fibers [1]. Most monolithic sol-gel glasses have been prepared using sols with high water content [2], while sols with high pH are required to produce pure silica powders [3]. The structure of the sols is especially important in the coating applications and has great influence on the properties of the coating.

Small angle x-ray scattering (SAXS) has been widely used to study sol structure in different chemical conditions [4]. From a plot of the scattering intensity versus the appropriate Fourier spatial frequency and the slope of the curve, one can deduce the shape of the polymer in the silica sol. Nuclear magnetic resonance (NMR) is also a useful tool in studying the sol structure. From the chemical shifts in the magnetic field, the sol structure can be characterized either qualitatively or semi-quantitatively [5-7].

Spectroscopy method (including Raman and Infrared) is a fast and easy method for studying a material's molecular structure [8-11]. However, the complexity of the spectra and the difficulty in their interpretations prevent its extensive use, especially in the sol system. This paper presents a study on the infrared spectroscopy of silica sols and the effects of varied water content, aging time and pH on the hydrolysis and polycondensation. Although more characterization techniques are required in order to understand completely the sol-gel system, the IR spectra does provide significant information about the structure and transformation of sols under various conditions.

TABLE 1

Chemical Compositions of Sols Used in This Work.

MR	TEOS (ml)	Alcohol (ml)	H_2O (ml)	pH
2	44.5	44.5	7.2	1.6
4	44.5	44.5	14.4	1.6-12
20	44.5	44.5	72.0	1.6

EXPERIMENTAL

Reagent grade (Fisher Scientific Company, Orlando, Fla) tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$), ethyl alcohol, and D.I. water were used to prepare the silica sols. Either hydrochloric acid (30 wt%) or ammonium hydroxide (28-30 wt%), depending on the required pH, was used as the catalyst.

Table 1 lists the sol compositions used in this work. Tetraethylorthosilicate and half of the required alcohol were mixed under rigorous stirring for 10 min. The rest of the alcohol was mixed with water while stirring and the pH was adjusted to the desired value. The pH measured in this ethanol plus water system only indicated the relative intensity of acidity or base from sol to sol. This solution was then quickly added to the first one (within 3 min). The as-prepared sol was sealed in a polypropylene bottle and then transferred to the liquid cell in the infrared spectrometer. Further aging of the sol was conducted in the same bottle at room temperature.

The instrument used for this study was a Nicolet 20 SXB FT-IR (Nicolet Analytical Instruments, Madison, Wis.) with a standard deuterated tri-glycerine sulfate (TGS) detector and a spectral range of 4000 to 400 cm^{-1}. For each spectrum there were 32 scans collected with a resolution of 2 cm^{-1}, which required about 1 min.

The liquid cell used was a Circle Cell^{TM} (Spectra Tech Inc., Stanford, Conn.) with a ZnSe crystal crystal and a useful transmission range from 20,000 to 454 cm^{-1}. The Circle Cell^{TM} is not a true transmission cell but rather a cylindrical internal reflection (CIR) cell with a fixed path length of 8 to 12 microns. A reproducible path length is mandatory if one is running an experiment over a long period of time which is the case for this investigation. For each spectrum, 6 ml of sample was used and the sample cell was covered to prevent evaporation during the analysis.

RESULTS AND DISCUSSION

Influence of Water Concentration and Aging

Figure 1 shows the absorption spectra of TEOS, ethyl alcohol, and a silica sol aged for 1 hr with H_2O/TEOS molar ratio=2 (MR=2). The assignments of all absorption band are listed in Table 2. The influences of the water concentration, aging, and pH on the IR spectra are observed in the range of 1400-700 cm^{-1}, which is the normal "finger-print" region for most organic materials.

Figure 2(A,B) shows the IR spectra of the sol with MR=2 during aging. The cross-linking and Si-O-Si network formation were observed in the range of 1200-1100 cm^{-1}. After 30 min, a broad shoulder began to appear and 24 hr later it was located at 1155-1122 cm^{-1}. A peak at 1156 cm^{-1} emerged from this shoulder after 2 wk and shifted to 1160 cm^{-1} with enhanced intensity after 4 wk. However, it was found that after 5 wk aging, the intensity of this peak started to decrease and continued to decrease even after 26 wk aging. Meanwhile, a new shoulder at about 1178 cm^{-1} appears after 3 wk aging. This shoulder became broad and intense during continued aging. The first peak at 1160 cm^{-1} was assigned to the more linear Si-O-Si stretching vibration while the shoulder at about 1178 cm^{-1} was attributed to the formation of a 3-dimensional Si-O-Si network [20]. These Si-O-Si peaks shifted to higher wavenumbers than reported in the literature, which are between 1100-1000 cm^{-1} [8-10,13,14,18]. This may be explained by considering the mass factor in the determination of oscillation frequency. The following equation, derived from Hooke's law, expresses the relationship between frequency of oscillation, atomic masses, and force constant of the bond [17] :

$$f = (1/2\pi C)\,[\,k(M_x + M_y)/(M_xM_y)\,]^{1/2} \qquad (1)$$

where f = the vibrational frequency (cm^{-1}), C = velocity of light (cm/sec)

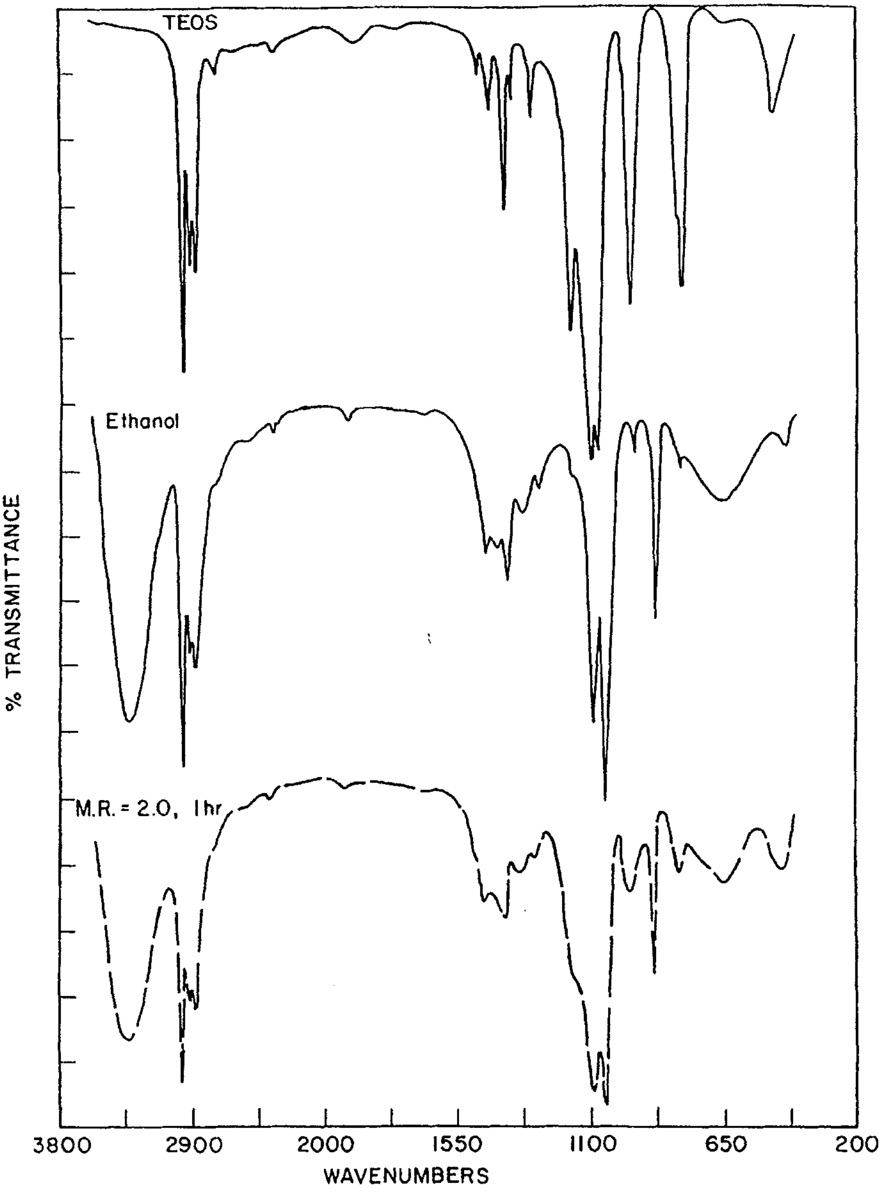


FIG. 1. IR spectra of TEOS, ethyl alcohol and sol 2/1.6, 1 hr after preparation. Sol 2/1.6 represents a MR=2 and pH at 1.6.

TABLE 2

Assignments of Peaks in the Spectra of MR=2 Sol Aged for 1 hr.

Frequency (cm^{-1})	Assignment	Reference
3500-3300	O-H stretching with inter-molecular H-bonding and strong H-bonded Si-OH (from ethanol,H_2O, and hydrolysis of TEOS)	9,10,12-15
2974	asymmetrical C-H stretching vibration in CH_3 (from TEOS and ethanol)	16, 17
2930	asymmetrical C-H stretching vibration in CH_2 (from TEOS and ethanol)	16, 17
2892	symmetrical C-H stretching (from TEOS and ethanol)	16, 17
1446	asymmetrical C-H bending vibration in CH_3 (from TEOS and ethanol)	16, 17
1381	symmetrical C-H bending vibration in CH_3 (from TEOS and ethanol)	13, 16, 17
1416, 1324	O-H in plane bending coupled with C-H wagging in CH_2 (from ethanol)	16
1275	C-H twisting/wagging in CH_2 (from ethanol and TEOS)	16, 17
1167	Si-O-C rocking (from TEOS)	
1082, 1043	C-O stretching vibration (from ethanol)	16
1111-1054	Si-O-C asymmetrical stretching vibration (from TEOS)	
970-950	Si-O-C symmetrical stretching vibration or Si-O stretching vibration in Si-OH or C-O (from TEOS, hydrolysis of TEOS, or IPA)	8-10,14,15 18
880	skeletal vibration (from ethanol)	19
788	? (from TEOS)	

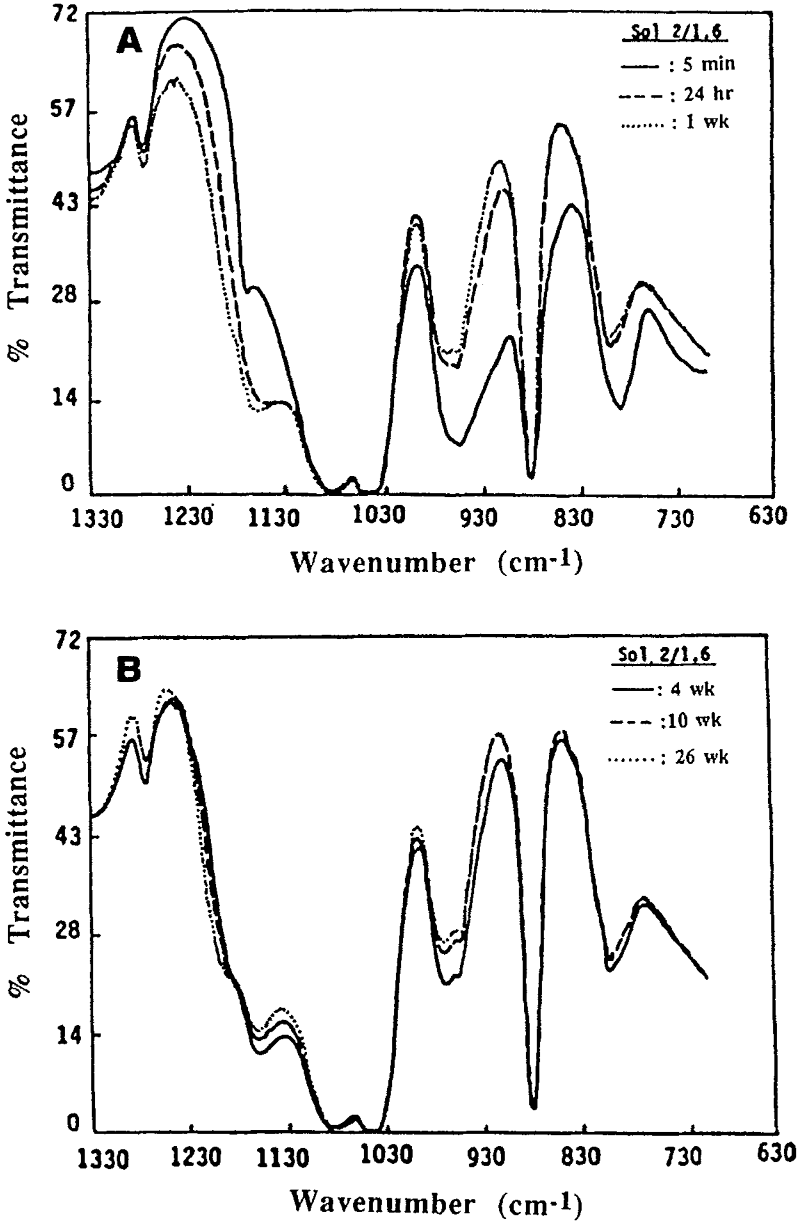


FIG.2. IR spectra of sol 2/1.6 during aging, (A) 5 min-1 wk (B) 4-26 wk.

k = force constant of bond (dyne/cm), M_x and M_y = mass (g) of atom x and atom y, respectively

In the case of sol and gel, the silica network which binds the atoms involved in the vibrations must be considered in the mass factor. Since the network in sol is not as completely formed as compared with gel and glass, the mass factor is smaller and results in a higher vibration frequency, although the force constant k in the former case may also be smaller.

The peak at 1160 cm^{-1} indicated that Si-O-Si bonds with a more linear structure were dominant in this sol during the early aging. These bonds were gradually formed due to the hydrolysis and polycondensation of TEOS and, therefore, the peak intensity at 1160 cm^{-1} increased. During aging, these linear chains entangled to form a 3-dimensional network and the intensity of this peak decreased but the shoulder at 1178 cm^{-1} became broader, indicating network formation. The peaks at 1052-1035 cm^{-1} and 1086-1082 cm^{-1} were primarily from the C-O stretching vibration. These peaks overlapped with TEOS bands and were difficult to identify.

The intensity of the peak at 880 cm^{-1}, which was due to the vibration of the ethanol skeleton, was relatively constant after the first hour of aging. This indicated that no appreciable hydrolysis reaction occurred during the rest of the aging ; otherwise this reaction would result in the intensification of the ethanol peak according to reaction (2).

$$\text{-Si-O-R} + H_2O \rightarrow \text{-Si-O-Si-} + \text{ROH} \qquad (2)$$

Fast hydrolysis was also observed in the study of the tetramethylorthosilicate (TMOS) system [2,15].

Ester exchange, which is the reaction between hydroxyl and alkoxyl groups [21], did not occur to any appreciable extent. If it had, it would have resulted in a reduction of ethanol and a corresponding decrease in its IR peaks.

The Si-OH stretching peak was initially within the 970-950 cm^{-1} region, where TEOS and iso-propyl alcohol (IPA) (from the reagent grade ethanol) both have intense peaks. The decrease of the peak intensity during aging was explained as the reduction of Si-OH groups due to the polycondensation reaction. After 26 wk, it was located at 969 cm^{-1} and overlapped with the IPA peak at 955 cm^{-1}. The Si-O-Si cross-linking due to reaction either between alkoxyl and hydroxyl groups

[14], or two hydroxyl groups [2], has been previously reported. In the present study, the latter reaction is preferred (equation (3)) since the ethanol peak at 880 cm^{-1} does not intensify accordingly during the network formation.

$$\text{-Si-OH} + \text{-Si-OH} \rightarrow \text{-Si-O-Si-} + H_2O \qquad (3)$$

The Si-OH peak is reported in the range of 960-940 cm^{-1} in the studies of silica gels [8-10,14,15,18], which is lower than the present work. This was attributed to the unhydrolyzed TEOS which had a broad band at 970-950 cm^{-1} or it might indicate that silanol groups were bonded to a smaller network structure than in the gel. This could account for the shifting of the peak to higher wavenumbers.

The intensity of the peak at 800-788 cm^{-1} continuously decreased within the first 5 wk. It is not appropriate to interpret this as the hydrolysis of TEOS, since the ethanol peaks were not intensified accordingly in the same time period. The ring structure of Si-O-Si network is reported in the literature in the same region [10,22] and therefore the decrease of the ring structure during aging may be a possible interpretation. However, further study is required to unambiguously identify the reactions responsible for this bond.

Figure 3(A,B) shows the spectra of the MR=20 sol during aging. The Si-O-Si cross-linking appeared again in the range of 1200-1100 cm^{-1} except that it was faster as compared with the sol with MR=2. After 15 min, the shoulder between 1126-1105 cm^{-1} was evident and gradually extended to 1160 cm^{-1} after only 24 hr. This shoulder began to shrink after 48 hr, while expanding in the higher wavenumber (above 1190 cm^{-1}) region. A wide shoulder located between 1160-1105 cm^{-1} indicated that a distribution of various bond configurations and strengths were present in the cross-linked structure of this sol. This behavior was in contrast to that for the MR=2 sol which had a well-defined peak and apparently a more linear structure. It also indicated that more complex network was formed in the sol with higher water concentration.

The ethanol peak at 880 cm^{-1} did not experience significant changes during the aging experiment. This indicated that the hydrolysis of TEOS was very fast and the reaction was essentially complete after 5 min.

Initially, a broad band appeared at 941 cm^{-1}, which included both Si-OH and IPA peaks. The band shifted to 969 cm^{-1} and its intensity decreased after 1 wk. This showed the reduction of the Si-OH groups due to the polycondensation reaction and the formation of a more extensive network.

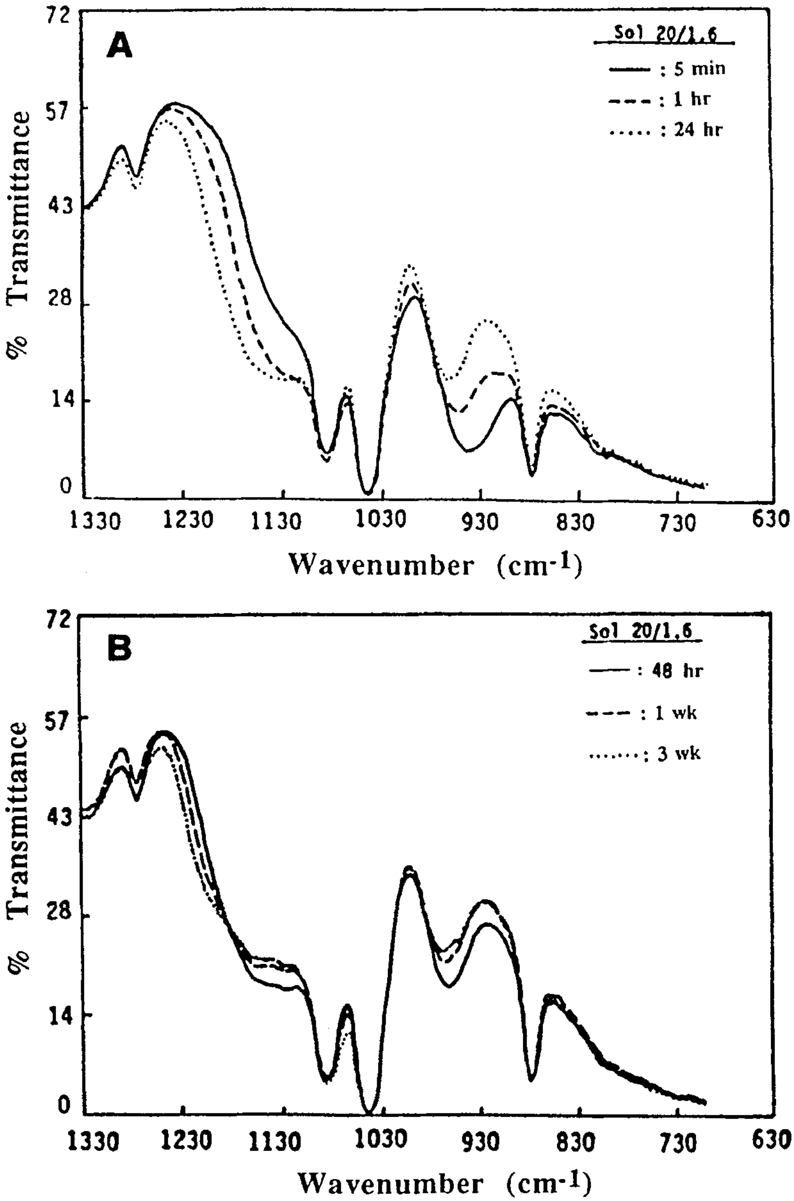


FIG. 3. IR spectra of sol 20/1.6 during aging, (A) 5 min-24 hr (B) 48 hr-3 wk.

The TEOS peak at 788 cm^{-1} was difficult to detect even in the first 5 min. This also suggested that most TEOS was hydrolyzed shortly after the water was introduced into the system.

The major differences in the IR spectra of sols with MR=2 and 20 are listed below :

(1) At 5 min after preparation, TEOS is mostly hydrolyzed in the MR=20 sol and Si-O-Si peak is present, while TEOS still remains in the MR=2 sol and no appreciable cross-linking is observed.

(2) After 4 wk aging, both sols show SiO_2 network formation except that there is a well-defined peak at 1160 cm^{-1} in the MR=2 sol while a broad band is observed in the MR=20 sol. More linear structure is present in the low-water content sol while the sol with high water content possesses a more branched structure.

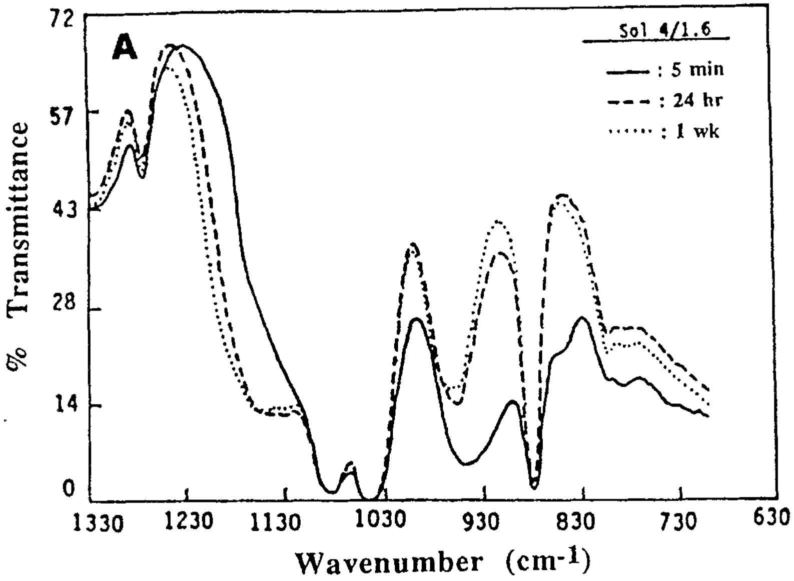
Influence of pH and Aging

Figure 4(A,B) shows the spectra of sol with MR=4 of pH=1.6 during aging. The IR spectra corresponding to the cross-linking of Si-O-Si was observed in the region of 1200-1100 cm^{-1}. After 15 min a shoulder appeared between 1160-1117 cm^{-1} and its intensity significantly increased after 24 hr. This band started to shift to higher wavenumbers (above 1180 cm^{-1}) after 1 wk. This trend persisted even as the sol approached gelation. After 9 wk, a broad shoulder was observed at 1163-1117 cm^{-1} and a hump at above 1180 cm^{-1} was also evident.

The hydrolysis of TEOS was again very fast, since no significant changes were observed in the ethanol peaks after 24 hr. The silanol peak was located at 970-950 cm^{-1} and its intensity decreased during aging due to the polymerization reaction. After 9 wk it was at 968 cm^{-1}, and overlapped with the IPA peak at 954 cm^{-1}.

Figure 5 shows the spectra of the sol with pH 4 and MR=4 during aging. It was found that there was almost no change present in the first hour of aging. The TEOS peaks at 1167, 960 and 788 cm^{-1} indicated that the hydrolysis reaction was very slow. The spectra were very complex in the region of 1100-1000 cm^{-1} due to the presence of TEOS and ethanol. Compared with Figure 4, it is clear that an increase in pH from 1.6 to 4 greatly decreases the hydrolysis reaction.

The intensity of the ethanol peak at 880 cm^{-1} increased during early aging due to the hydrolysis reaction. After 78 hr, most TEOS was hydrolyzed and therefore no significant change was observed.



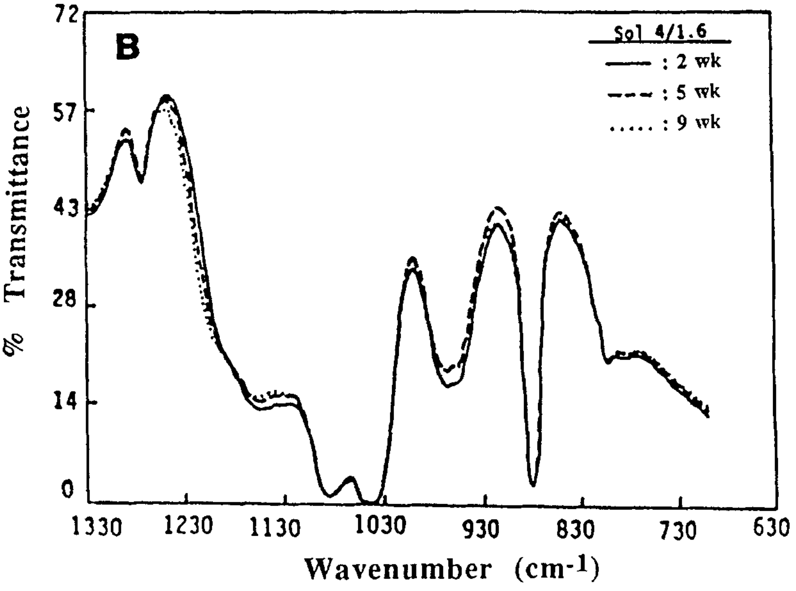


FIG. 4. IR spectra of sol 4/1.6 during aging, (A) 5 min-1 wk (B) 2-9 wk.

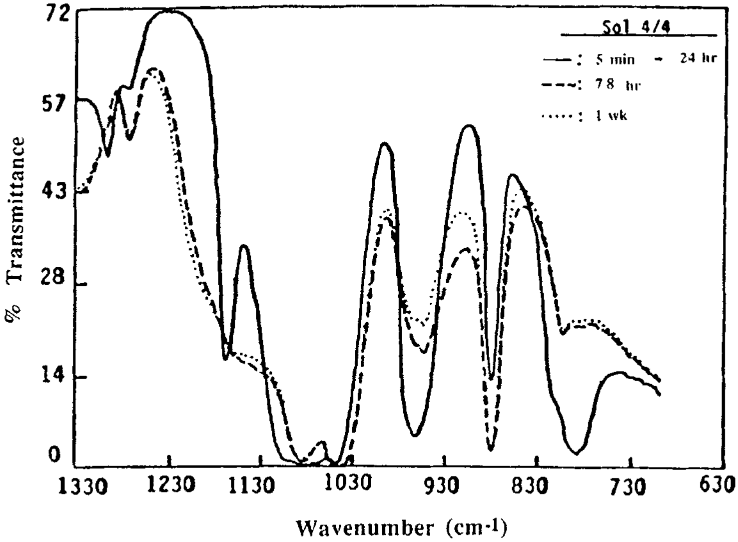


FIG.5. IR spectra of sol 4/4 during aging.

The peak at 960-954 cm^{-1} after 1 hr aging was due to both TEOS and IPA. After 24 hr a broad band at 951 cm^{-1} appeared and it was caused by the formation of silanol groups. The intensity of this peak continuously decreased and the peak was blue-shifted to 965 cm^{-1} after 1 wk, which was near the gelling point.

The shoulder at above 1117 cm^{-1} represented the Si-O-Si cross-linking, which was a relatively weak shoulder even near the gelling point as compared with the sol with pH 1.6. This might indicate that the degree of cross-linking was low and the number density of bridging oxygens was small.

The spectra of sol with pH 7 are shown in Figure 6. Further increases in pH resulted in a greater decrease in hydrolysis rate. Appreciable hydrolysis of TEOS was observed only after 78 hr aging. This was indicated by the decrease of peak intensity at 1167, 960, and 784 cm^{-1} (TEOS peaks) and the increase at 880 cm^{-1} (ethanol peak). A shoulder between 1200-1117 cm^{-1} appeared after 1 wk aging and this hump first formed at higher wavenumbers (> 1180 cm^{-1}) instead of lower wavenumbers (1160-1100 cm^{-1}) as in the case of sols with lower pHs. The degree of Si-O-Si cross-linking was lower than that of sol with pH 4, which was revealed

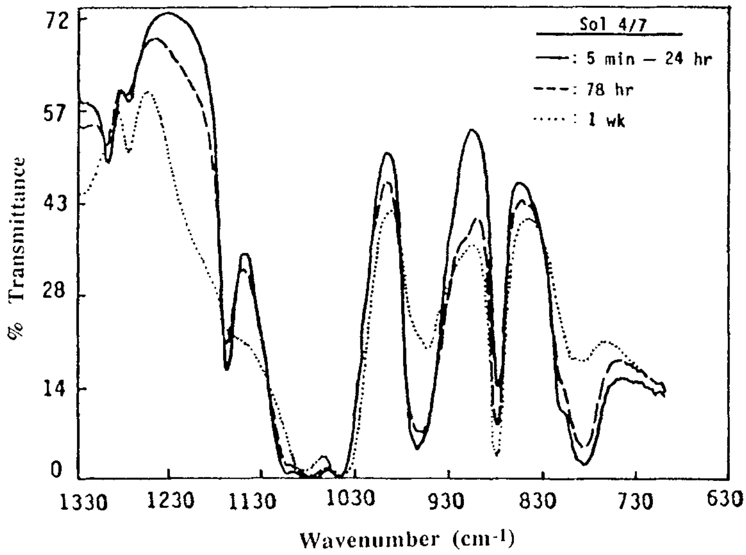


FIG.6. IR spectra of sol 4/7 during aging.

by the shoulder between 1200 to 1117 cm^{-1}. The TEOS peak at 784 cm^{-1} was present even after 186 hr, which was near the gelling point. It indicated that some TEOS was still left even near the gelation in this sol.

Figure 7 displays the spectra of sol with pH 9. Due to high pH, the hydrolysis reaction was extremely slow, as shown by the presence of the TEOS peaks at 1169 and 788 cm^{-1}, even after aging for 2 wk. The shoulder at high wavenumbers (above 1200 cm^{-1}) began to develop only after 2 wk aging.

The highest pH investigated (pH=12) resulted in sol precipitation within minutes. Since precipitates degraded the resolution, the spectra were taken from the sol which had been well stirred (Figure 8). After 78 hr aging, the TEOS peak was greatly diminished and the shoulder between 1220 and 1178 cm^{-1} was evident. As compared with sol with pH=9, an increase in hydrolysis and polymerization was observed. The intensity of the silanol peak at around 970-950 cm^{-1} was greatly decreased, and after 1 wk, only a very weak peak at 954 cm^{-1} was observed. Though a broad shoulder developed between 1220-1100 cm^{-1}, precipitation, instead of gelation occurred.

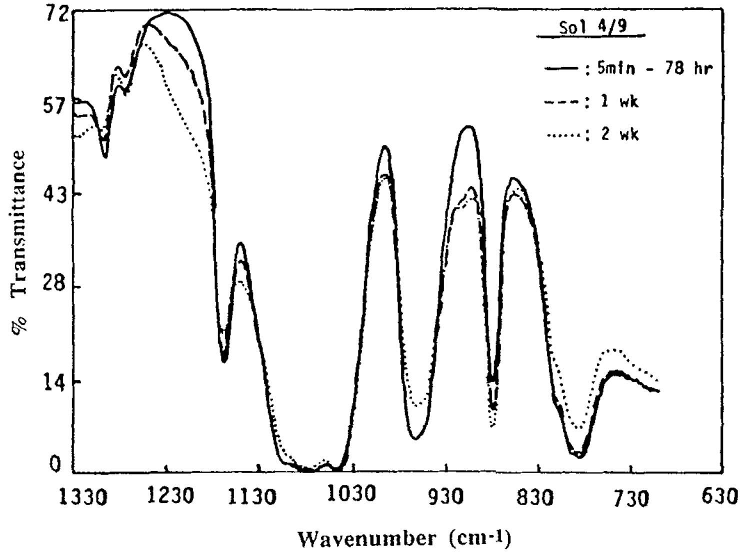


FIG.7. IR spectra of sol 4/9 during aging.

Figure 9 shows the IR spectra of sols with various pH after 1 wk aging. Though sols with low pH had broader bands in the 1200-1100 cm^{-1} region, their gelling rates were slower than those with medium pH. Another important result was the amount of remaining silanol groups in the sols with various pHs. More silanol groups were left in the sols with low pHs, which can be clearly seen from the IR spectra. This is consistent with the results found for the TMOS system in the literature [15].

SUMMARY

Infrared spectroscopy was used to study the silica sols with various water contents and pH during aging. Several results were obtained:

A. Influence of Water Content (pH=1.6)

(l) For the sol with pH 1.6, a more linear structure was present in the MR=2 sol, which resulted in the peak at 1160 cm^{-1}. During aging this linear structure progressively formed a 3-dimensional network with a peak above 1178 cm^{-1}.

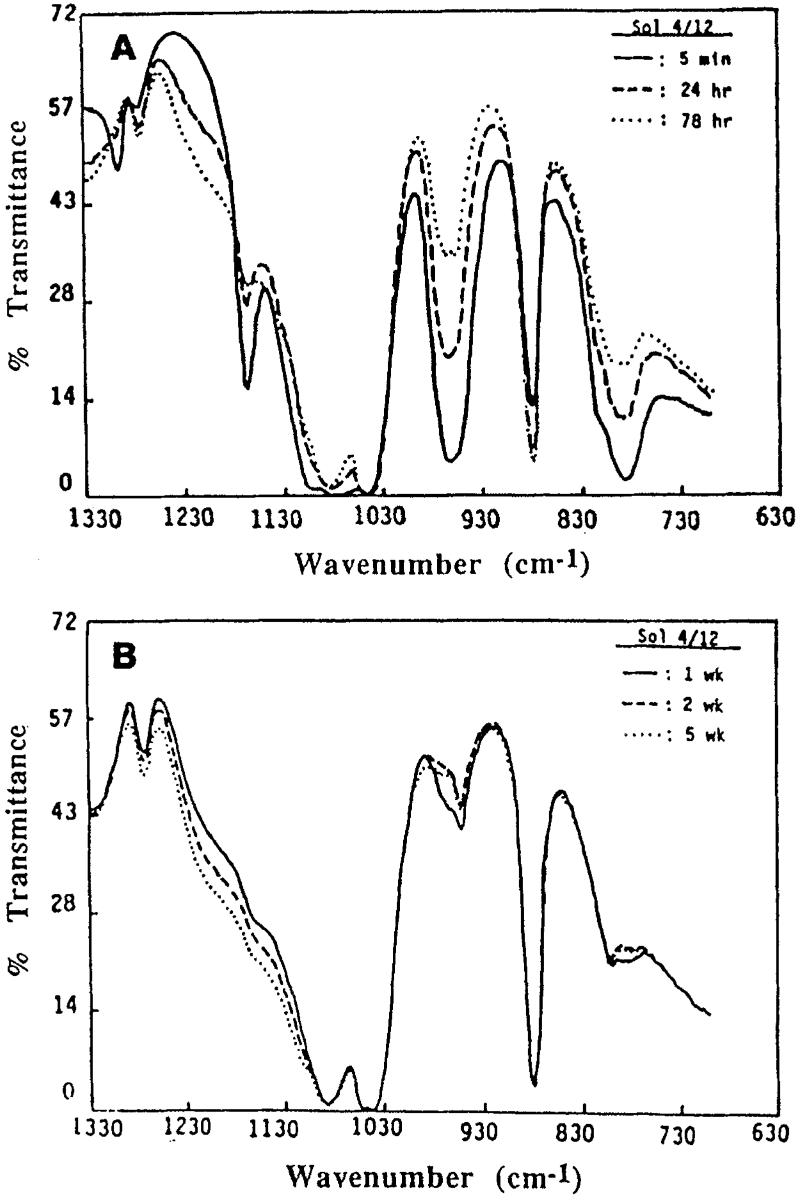


FIG.8. IR spectra of sol 4/12 during aging.

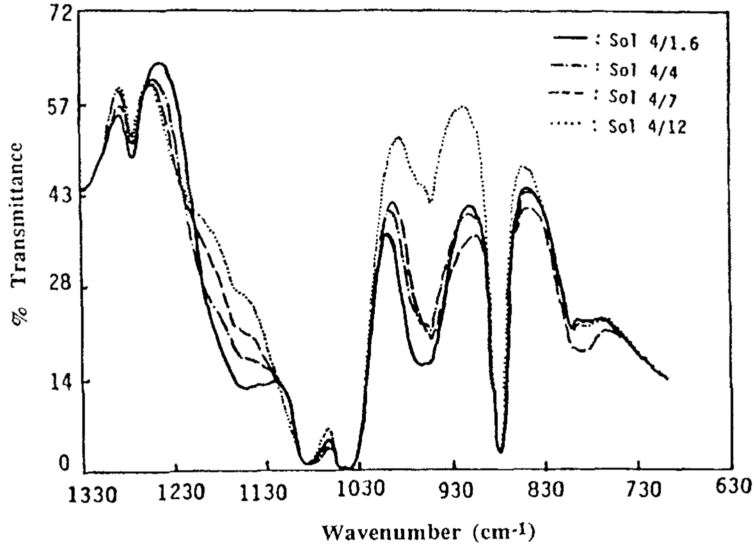


FIG.9. Comparison of IR spectra of sols with various pHs after 1 wk aging (MR=4).

In the MR=20 sol, faster SiO_2 cross-linking occurred with more variations in configuration and bond strength as compared with MR=2 sol. This was exhibited by the broader band between 1200-1100 cm^{-1}. The high frequency shoulder at above 1190 cm^{-1} developed at the expense of the band between 1160-1105 cm^{-1}, which was also observed in the MR=2 sol.

In both sols, a shift of the Si-O-Si stretching bands towards greater frequency was observed compared with those in the SiO_2 gel or glass. This was attributed to the incomplete network formation in the sol which reduced the mass factor and resulted in a higher vibration frequency.

(2) The hydrolysis reaction was very fast and there was no appreciable reaction after the first hour of aging in the sols with pH 1.6. This was indicated by the consistency of the ethanol peak at 880 cm^{-1} during aging. Some TEOS remained in the MR=2 sol due to the insufficient amount of H_2O while complete hydrolysis was observed in the MR=20 sol.

(3) Silanol groups (970-950 cm^{-1}) were formed due to the hydrolysis of TEOS. After 1 wk aging, the peak corresponding to unreacted silanol groups was located at 969 cm^{-1}.

B. Influence of pH (MR=4)

(l) Although an increase in pH from 1.6 to 9 significantly decreased the rate of hydrolysis, a further increase to 12 accelerated this reaction, where precipitation was observed.

(2) The cross-linking and network formation was exhibited in the region of 1200-1100 cm^{-1}. Sols with medium pHs (4-7) had faster gelling rates than those with low and high pHs. However, the gelling rate could not be determined from the IR spectra alone.

(3) More silanol groups were left in the sols with low pHs after aging compared those with high pHs.

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