

## A mechanistic study of the initial stage of the sintering of sol-gel derived silica nanoparticles

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**Abstract:** Dried silica gel powders were prepared by acid catalyzed controlled hydrolysis followed by polycondensation of tetraethyl orthosilicate (TEOS) in 1:1 by volume water-alcohol solution. The dried powders were pressed and isothermally heat treated over the temperature range of 200-600 °C. The mechanism of sintering of silica-gel particles during the initial stage of heating has been delineated and related to the formation of –Si-O-Si- siloxane bonds among the silica particles. This is experimentally substantiated by detailed diffuse reflectance infrared Fourier transformed spectroscopy (DRIFT) and thermo gravimetric/differential thermal (TG/DSC) analyses.

**Keywords:** Sol-gel, mechanism, sintering, DRIFT spectroscopy

### I. Introduction

Sol-gel derived silica glasses are branded for their wide applications in optics, electronic and other field of technology [1, 2]. Most of the cases in gel condition, especially for lakeside-derived silica gel, a water-alcohol solution remains in the space of the silica gel-network leaving high porosity upon drying. Preparation of monolithic gel is often very difficult because during drying a tremendously high stress is generated due to the presence of extremely fine capillary and the pressure gradient due to the differential shrinkage of the xerogel, frequently cause its cracking. This often leads to the formation of small granules of dried silica. Therefore to get the bulk sample one has to go through the sintering process of the powder sample at high temperatures. Sintering at high temperatures and the subsequent development of highly dense material is then the most important prerequisites of silica gel in achieving the desired applicability in this respect. A significant contribution has been made over a decade in understanding the physical background of the sintering process of the silica gel [3], particularly at a high temperature. However, there still remains plenty of space for research work. There is hardly any work reported in the literature on the structural changes that occur at the interface of the fine silica gel granules during the early period of heating. Thus the objective of this paper is to elucidate the bonding at the molecular level of the dried silica gel at the initial stage of heating, as it is extremely necessary in order to find ways to improving the quality of the prepared materials [4].

Fourier transformed Infrared spectroscopy (FTIR) is probably one of the best methods to investigate the structure of amorphous silica derived from sol-gel process [5-9] down to the molecular level. Among the various modes of techniques, associated with IR spectroscopy e.g., IR absorption (KBr technique), IR emission, IR reflectance (including both specular and diffuse reflectance), attenuated total reflection (ATR), photo acoustic Fourier transform infrared (PAS-FTIR) spectroscopy, the diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) is one of the most promising techniques for the qualitative analysis of the rough surface [10-12]. The positions of different O-H stretching vibrational bands are important in this respect: 3745 cm<sup>-1</sup> for O-H stretching vibrations of the isolated (or terminal) hydroxyl group that are not hydrogen bonded, 3660-3550 cm<sup>-1</sup> for O-H stretching vibration of H-bonded bridged hydroxyl groups that are in a chain, 3400-3300 cm<sup>-1</sup> for O-H stretching vibration of H-bonded water molecule, 960 cm<sup>-1</sup> for Si-OH stretching vibration of surface Si-OH group. In this paper we systematically make use of the DRIFT spectroscopy to better understand the mechanism of sintering of the silica gel during the early stage of heating. Thermo gravimetric (TG) and differential scanning calorimetric analysis (DSC) of silica gel further substantiate the observation delineated by the DRIFT spectroscopy.

### II. Experimental

The silica gels were prepared through the hydrolysis followed by poly-condensation of tetraethyl-orthosilicate (TEOS) in water/ethanol solution under acidic condition. In a typical process a homogeneous solution of 10 ml of absolute alcohol and 10 ml of double distilled water is added in drops to a solution of 10 ml of TEOS and 10 ml of absolute alcohol under constant stirring followed by the addition of a few drops of 8 (N) HCl as a catalyst to the solution. The solution is stirred for 15 min and left for gelling for 8–9 days at room temperature. The gel was air-dried at room temperature (310 K) for an extended period of time. To investigate the mechanism of the initial stage of the sintering, the air-dried gel was pressed uniaxially into a cylindrical disc of diameter 15.0 mm. The pellets of dried gels were isothermally heated over the temperature range of 200 °C to 600 °C in a horizontal tube furnace for 2 h. The heating rate employed to reach the desired temperature is 6 °C/min

**Thermal analysis:** Thermo gravimetric/Differential scanning calorimetry analysis (TG/DSC) of the gel was carried out from room temperature to 800 °C, using a Pyris diamond (PerkinElmer) thermal analyzer under nitrogen atmosphere with a flow rate of 150 ml/min.

**Diffuse reflectance Infrared Fourier Transform spectroscopy (DRIFT):** DRIFT spectra of the silica samples sintered at different temperature were collected using IR-prestige FTIR spectrometer equipped with a baseline diffuse reflectance kit over the wave number region of 400-4000  $\text{cm}^{-1}$ .

### III. 3. Result & Discussion

**3.1. TG-DSC analysis:** Figure 1 shows the thermal behavior of the silica gel sample prepared by sol-gel method. A two-step loss of the weight was found for the air dried-gel sample, of which, the first sharp drop of around 12% centered at ~ 90 °C in association with the endothermic trough at the same temperature is attributed to the removal of water and alcohol present in the pores of the gel [13]. The second slow weight loss of around 6% at 200 °C onwards upto 600 °C, is due to the elimination of water molecule generated from the condensation of silanol (-Si-OH) groups. Condensation predominately occurs at the surface of the silica particles and thus helps for the aggregation of the particles close to each other. The appearance of a broad exothermic hump in the same temperature range (200 °C-600 °C) is the signature of this densification process which results in the formation of new siloxane (-Si-O-Si-) bond at the interface by the condensation of the surface silanol groups [14]. Due to the formation of -Si-O-Si- bonds the product become more ordered which makes  $\Delta S$  negative This makes the enthalpy change ( $\Delta H = T\Delta S$ ) negative. Hence the exothermic peak appears in the DSC curve.

#### 3.2. DRIFT-spectroscopy analysis:

**Fingerprint region of water and hydroxyl group:** In order to unambiguously interpret the change in O-H vibration upon heat treatment, one thus necessarily needs to know the temperature limit within which dehydration and/or dehydroxylation has occur. Thus the TG and DSC analysis of the air dried gel was carried out in the present case to monitor the above fact and from the study (detail shown previously), the elimination of the adsorbed (or, molecularly associated) water molecule was found to occur in the temperature range of 100 °C to 200 °C. Figure 2 demonstrates the IR-spectra of all the silica samples for different OH stretching frequencies. It was observed that for initial heating conditions bands appeared at (1) 3260  $\text{cm}^{-1}$  and (2) 3635  $\text{cm}^{-1}$  which are due to the stretching modes of hydrogen-bonded bridged O-H group and for the stretching modes of hydrogen-bonded water molecule respectively [15]. While at relatively higher temperature, two bands appeared at (3) 3722  $\text{cm}^{-1}$  and (1) 3372  $\text{cm}^{-1}$  which are due to the free hydroxyl group and some H-bonded water molecule respectively [15]. Molecular arrangements of the different hydroxyl species are shown on the below of the figure 2. This means the removal of adsorbed water molecules followed by the removal of bridged hydroxyl groups leads to the formation of the free hydroxyl species. The appearance of the broad absorption in 3400-3300  $\text{cm}^{-1}$  for the 600 °C heated sample is also may be due to the progressive evolution and adsorption of the water molecule as the by-product of the condensation reaction at the surface.

Ideally, when silica samples are sintered, surface hydroxyl moiety (depending on the relative position, i.e. isolated, neighboring, external, internal, etc.) can be eliminated in the form of water molecule and new siloxane (-Si-O-Si-) linkages are formed. As shown in the figure 2, a strong band appeared at ~950  $\text{cm}^{-1}$  ascribed for the surface Si-OH stretching vibration [15], is present up to a temperature of 600 °C, but the sharpness of the appeared trough is progressively decreases. This is because there remain plenty of hydroxyl groups at the surface of the silica particles as the condensation does not eliminate all of them at the initial stages. However, the elimination of the surface bound -OH group at selective region of the silica surface can also be occur through the formation of the new -Si-O-Si- linkages between particles.

**Skeletal bonding structure of silica:** IR spectra of the dried and the heat treated silica samples were given in the figure 3. All the spectra exhibit three major absorption troughs for the fingerprints of silica, viz, at ~460, 785 and 1100  $\text{cm}^{-1}$ . These are the characteristics vibrations of Si-O-Si bridges cross linking the silica network. The band ~ 460  $\text{cm}^{-1}$  was attributed to the rocking (R) motion of the bridging oxygen (O) atom perpendicular to the Si-O-Si plane. The 785  $\text{cm}^{-1}$  band is due to the symmetric stretching (SS) of O atom along the bisector of the Si-O-Si bridge angle, and the high frequency band peaking at 1100  $\text{cm}^{-1}$  ascribed to the asymmetric stretching (AS) mode of O atom back and forth parallel to the Si-Si line [15]. However, in the present case the AS is accompanied by the presence of an intense shoulder at the high frequency site, whose nature will be discussed in the next section.

**Asymmetric stretching of silica:** While dealing with the IR-spectra of the silica samples, one important observation is the longitudinal-optic (LO) and transverse-optic (TO) splitting of the vibrational mode. This splitting, which was first observed by Galeener and Lucovsky [16] and later theoretically supported by other authors [17,18], was attributed to long range coupling of Columbic interactions arising due to the partial ionicity in the material. Though all the characteristic vibrational modes of silica shows the LO-TO splitting to different extents, the occurrence is more pronounced in the asymmetric stretching region of Si-O-Si bond constituting the  $\text{SiO}_4$  tetrahedral and is shown in the figure 4. The LO component for this part was found to appear typically at 1225  $\text{cm}^{-1}$ , while the TO component appear at 1065  $\text{cm}^{-1}$ . The deconvolution of the AS band (1300-1000  $\text{cm}^{-1}$ ) into two Gaussian curves gives the exact position of the respective LO and TO components. A typical deconvolution of the AS band in the absorption mode was shown in the figure 5 for the air dried gel and the detail information extracted from the deconvolution is listed in the table 1. From the table (as well as from the spectra Fig 3), it can

be observed that the frequency of LO mode appeared at higher wave number than that of the TO mode and the difference between the two modes ( $\nu_{LO}-\nu_{TO}$ ) increases with the increase in the heat treatment temperature. As pointed out by Kittel [19], for a given normal vibration the LO frequency,  $\nu_{LO}$ , is greater than the TO frequency,  $\nu_{TO}$ , because the local electric field causes polarization of the surrounding atoms in the opposite direction for the LO mode but in the same direction for the TO mode. Since the (LO-TO) splitting is originated from the long range Coulombic interaction, higher the splitting higher will be the long range Coulombic force. Kamitsos et al. [20] reported the increase in AS-(LO-TO) splitting width with annealing temperature, is associated with the formation of siloxane network. Thus the increase in the LO-TO splitting width from 200 °C to higher temperature as pointed in the table-1, is due to the increase in Si-O-Si crosslinkings which predominately occur at the surface of the silica particles during the heating of the sample. Thus the above IR spectroscopic data clearly establish that the increased cross linking of Si-O-Si bond at the surface with the elimination of the water molecule may allow the aggregation of the fine grained silica particles and be responsible for initial stage of the sintering process. This mechanism of initial sintering has been schematically shown in figure 6 starting with the initial air dried gel.

#### IV. Conclusion

From the details of DRIFT study of the sample in association with TG-DSC analysis it can be inferred that, dehydration followed by the condensation of surface OH groups of silica particles forms the siloxane bonds, which are responsible for initial sintering.

#### V. Acknowledgement

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#### Figure caption:

Figure 1: TG-DSC plot of the air dried silica gel

Figure 2: DRIFT spectra at the selective region for the stretching vibration of O-H group present in the air dried gel (a), and the silica gels heat treated at 200 °C (b), 400 °C (c), 600 °C (d).

Figure 3: DRIFT spectra at the fingerprint region of the silica for the air dried gel (a), and the silica gels heat treated 200 °C (b), 400 °C (c), 600 °C (d).

Figure 4: Asymmetric stretching vibration of the Si-O-Si bond for the air dried gel (a), and the silica gels heat treated 200 °C (b), 400 °C (c), 600 °C (d).

Figure 5: Typical deconvolution of the asymmetric stretching vibration of Si-O-Si bond for the air dried gel.

Figure 6: Pictorial representation of initial stage of sintering of sol-gel silica particle. Open circle and circular arcs represents the silica particles. (a) primary particles, (b) enhanced crosslinking at intermediate temperature, (c) agglomeration of silica particles.

**Table caption:**

Table 1: Analysis of the DRIFT spectra of the air dried and the heat treated silica samples

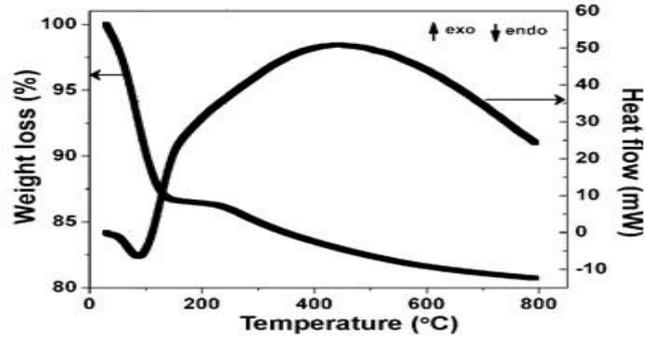


Figure 1: Pramanik et al.

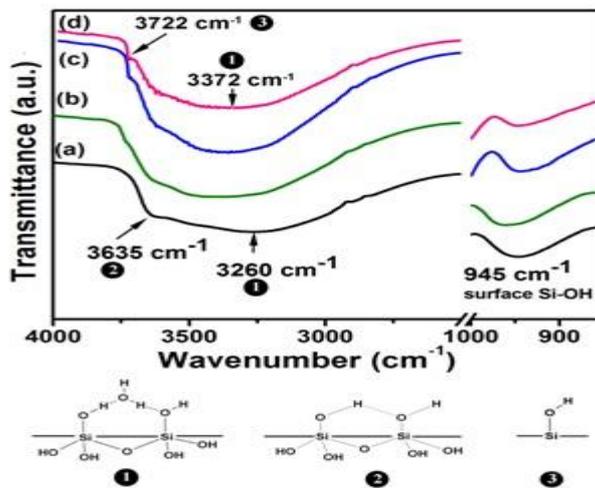


Figure 2: Pramanik et al.

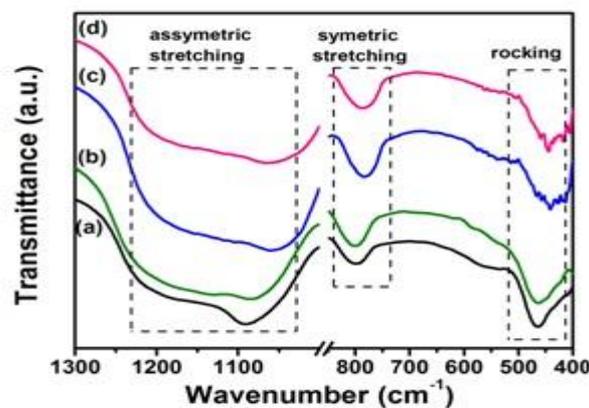


Figure 3: Pramanik et al.

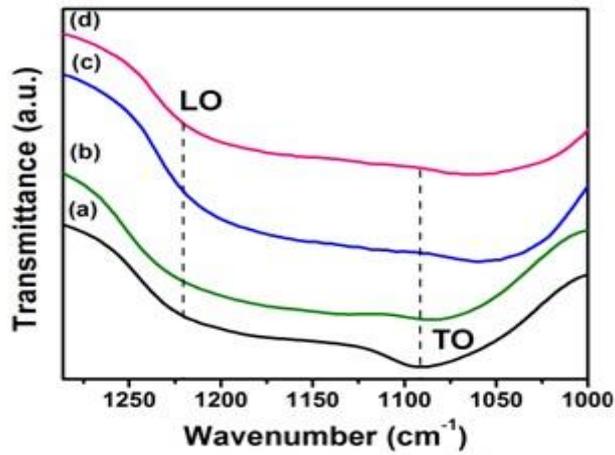


Figure 4: Pramanik et al.

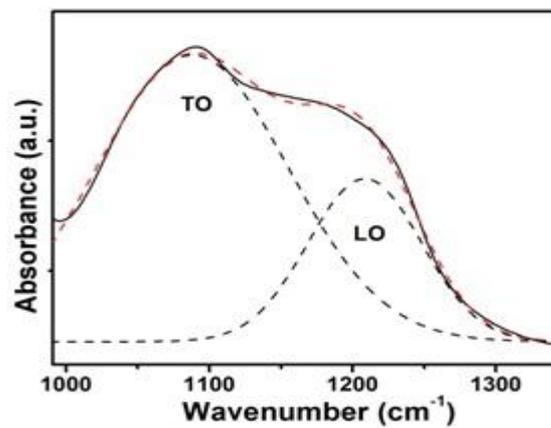


Figure 5: Pramanik et al.

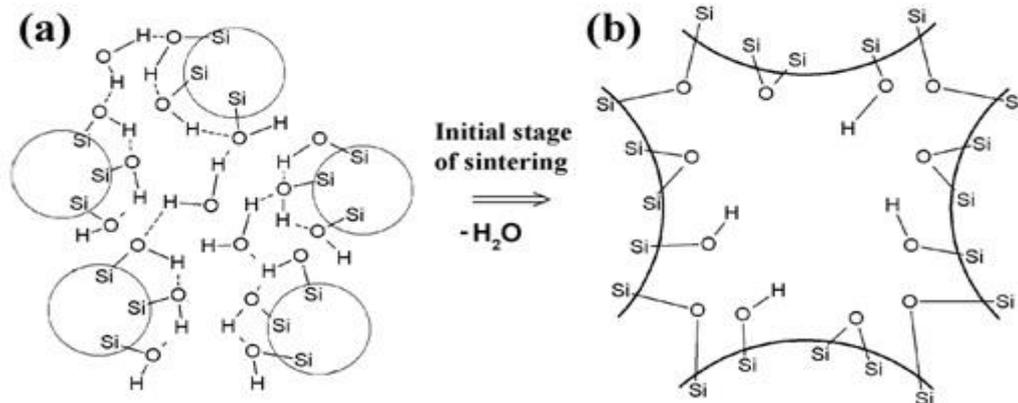


Figure 6: Pramanik et al.

Table 1: Pramanik et al.

Sample name	R (cm <sup>-1</sup> )	SS (cm <sup>-1</sup> )	AS-TO (cm <sup>-1</sup> )	AS-LO (cm <sup>-1</sup> )	LO-TO (cm <sup>-1</sup> )
Air dried gel	463	794	1085	1206	121
200 °C	463	800	1086	1211	125
400 °C	441	787	1052	1183	131
600 °C	443	781	1057	1192	135