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Infrared and thermogravimetric study of high pressure consolidation in alkoxide silica gel powders

T.M.H. Costa ^{a,b}, M.R. Gallas ^a, E.V. Benvenuti ^b, J.A.H. da Jornada ^{a,*}^a Instituto de Física, UFRGS, Caixa Postal 15051, 91501-970 Porto Alegre (RS), Brazil^b Instituto de Química, UFRGS, Caixa Postal 15003, 91501-970 Porto Alegre (RS), Brazil

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Abstract

High density, transparent, crack-free and hard compacts of silica gel were produced by compaction under nearly hydrostatic environment at 4.5 GPa, at room temperature. The starting material was used three days after synthesis by hydrolysis of alkoxides without additional treatment. Fourier transform infrared spectroscopy (FTIR), using the KBr technique and a high vacuum cell at temperatures up to 450°C, and thermogravimetric analysis (TGA) up to 900°C was conducted. A reduction up to 60% in the adsorbed water content of the compacted silica gel was observed. Changes in the 3000 to 3800 cm⁻¹ region indicate that the surface silanol groups became bridged, which promotes condensation reactions of dehydroxylation. Those results suggest that the mechanism for consolidation under high-pressure, is 'cold sintering' process, where silanol groups at the surface of the nanoparticles condense to form siloxane bonds between the particles and water, resulting in a stiff body with closed nanopores containing trapped water. © 1997 Elsevier Science B.V.

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1. Introduction

The attainment of highly dense and glassy silica compacts made of silica gel, synthesized by hydrolysis of alkoxides, has been widely studied due to its applications in many fields of technology [1–4]. Silica glasses produced from nanosize SiO₂ powders or gels derived from sol–gel process, show important advantages compared to those obtained by conventional methods. They have a high degree of homogeneity and can be sintered at about 800°C,

which is far below the crystallization temperature, approximately 1400°C, for conventional silica powders [1]. Successful fabrication of dense glassy SiO₂ by the sol–gel route mainly lies in removal of volatiles and gel densification. It is accomplished usually through slow drying at room temperature or in an oven at low temperatures, which can take several weeks [5,6]. After drying, the gels are heated at temperatures between 650 and 1000°C, depending on the desired properties [6]. Shrinkage and cracks occur in drying, which makes this procedure very critical.

Silica gel, prepared by hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS) in water and ethanol solution is a highly porous and amor-

* Corresponding author. Tel: +55-51 316 6492; fax: +55-51 319 1762; e-mail: jornada@if.ufrgs.br.

phous material. Incomplete polymerization of the silica sol produces a random distribution of two types of hydroxyl groups over the surface, free and hydrogen bonded ones. Progressive heat treatments dehydrate and dehydroxylate the silica gel surface. The dehydration takes place at about 200°C, whereas the dehydroxylation of the H bonded hydroxyl occurs in the range of 200 to 350°C, by reaction of two neighboring groups. For temperatures around 450°C, under vacuum, nearly all the H bonded silanols are removed from surface [7] and, according to Ying et al., 600°C is the highest temperature needed to eliminate the H bonded silanol groups [1,8]. At higher temperatures, dehydroxylation involves free hydroxyl groups, which are very difficult to remove and sometimes remain at 1150°C [1].

High-pressure is a potentially powerful technique to reduce porosity and produce high density compacts. Pressure can be considered a driving force for sintering [9,10] and hot-pressing attempts to densify silica gel are reported [4,11]. Green compacts with 74% of full density were obtained by cold isostatic pressing at pressures up to 1 GPa, with spray dried silica powders [2]. Recent works [12,13] report application of pressures to 5 GPa under nearly hydrostatic conditions to compact nanosize ceramics powders at room temperature, yielding well consolidated and hard bulk samples of high quality. Transparent silica gel and translucent γ -alumina, crackfree, with 86 and 92% of full density, respectively, were produced. These results make high-pressure a promising technique for processing nanosize powders synthesized by different methods, and also demand a clear understanding of the mechanisms involved.

Many different techniques, based on Fourier transform infrared spectroscopy (FTIR) have been widely used to characterize silica films and powders made by different methods [8,14,15]. FTIR techniques have been applied to characterization of hydroxyl groups in silica gel, studying their fundamental absorption region between 3200 and 3800 cm^{-1} . At low and moderate temperatures the infrared spectra reveal a broad band (3300–3650 cm^{-1}) due to absorption of bridged hydroxyl group, and near 3750 cm^{-1} a sharp band appears due to the free hydroxyl groups [7,16–18]. Study of these bands enables the obtainment of valuable information about the coverage of silica surface, specially if the hydroxyl groups

are bridged or free ones. The band due to the bending of molecular water (1640 cm^{-1}) is also present in the FTIR spectra of silica gel samples and can be used to study the adsorbed water.

In this work, the effect of high-pressure compaction at 4.5 GPa and room temperature, on hydrophilic properties of the surface adsorbed water content, and structure of silica gel were examined, in order to get information about mechanisms involved in a cold sintering process promoted by high-pressure.

2. Experimental procedure

Silica gel powders used were provided by NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) and some were produced in our laboratory. They were prepared by hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS) in water and ethanol solutions under acidic conditions [5,19]. Separate solutions of hydrofluoric acid (0.1 ml) in distilled water (1.6 ml) and TEOS (5 ml) in ethanol (5 ml) were prepared. The acid solution was dropped in the solution of TEOS in a continuous mixing with a magnetic stirrer for about 5 min. This mixture was then divided among three small plastic dishes, that were put in a large petri dish just covered, without sealing. Gelation was performed in air at room temperature, and after three days, small amounts of the gel could be removed and comminuted to use in the experiments. The average particle size estimated by TEM was about 15 nm.

For the high-pressure experiments the silica gel powder was initially precompacted in a piston-cylinder type die to approximately 0.1 GPa. The volume of a precompacted sample was about 102 mm^3 (diameter \sim 5 mm, height \sim 5 mm). Samples were then placed in a Pb container that acted as a pressure-transmitting medium in a toroidal-type high-pressure chamber. Compaction was accomplished at 4.5 GPa, at room temperature [12].

Powdered samples of silica gel were analyzed by transmission FTIR spectroscopy, using the KBr technique and a high-vacuum cell. For KBr analyses, samples were crushed in an agate mortar and sieved to 400 mesh, mixing thoroughly with powdered KBr to 1.5% by weight and pressed to form a transparent

pellet. The KBr was previously dried for 4 h at 150°C to eliminate water. The spectra were comprised of 64 scans.

For the vacuum cell, a self supporting disk of pure silica samples, with an area of $\sim 5 \text{ cm}^2$ and mass of $\sim 40 \text{ mg}$ was prepared. The cell, described elsewhere [20], was connected to a greaseless vacuum line and the sample heated for 1 h at 100, 200, 300, 400 and 450°C, under dynamic vacuum of 10^{-3} Pa. FTIR spectra were obtained at room temperature under vacuum, after each heat treatment, without exposing the sample to air. The equipment used was a Mattson FTIR spectrometer with a resolution of 4 cm^{-1} and a maximum of 400 scans were used in this series of measurements.

Thermogravimetric analysis was done on a Perkin Elmer thermogravimetric analyzer. The silica gel original powder was analyzed as-prepared, and compacts obtained by the high-pressure treatment were crushed in an agate mortar before analysis. The samples were heated from room temperature to 900°C at a rate of 20°C/min. in nitrogen atmosphere.

Surface areas were obtained with a Quantachrome Autosorb 1 system using a multipoint BET method.

3. Results

Silica samples obtained in the high-pressure experiments were crack-free, optically transparent and dense, with characteristics discussed in a previous work [12]. It was observed a great reduction in volume (about 64%) compared to precompacted samples. Their densities were $1.89 \pm 0.04 \text{ g/cm}^3$, corresponding to approximately 86% of full density. An average Vickers microhardness of $4.2 \pm 0.2 \text{ GPa}$ [3,12] was measured, indicating a very well consolidated body, if compared to silica quartz whose hardness is about 8–10 GPa. The measured surface area for the as-prepared samples was $317 \pm 16 \text{ m}^2/\text{g}$ and for the compacted samples was $3.8 \pm 0.2 \text{ m}^2/\text{g}$.

Typical FTIR transmission spectra for silica gel taken at room temperature using the KBr technique are shown in Fig. 1. The spectrum for as-prepared powder is shown in Fig. 1a. This is a representative spectrum of amorphous silica derived from an alkoxide gel [15]. Their characteristic absorption bands are: a large band at 1092 cm^{-1} that is attributed to

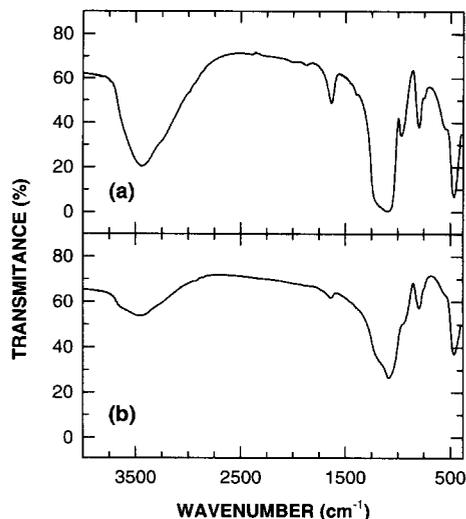


Fig. 1. Typical FTIR transmission spectra of silica gel samples. (a) As-prepared silica gel powder at ambient pressure. (b) Silica gel compacted at $P = 4.5 \text{ GPa}$ and room temperature.

stretching vibration of Si–O bond, the 803 cm^{-1} band corresponding to the ring structure of SiO_4 tetrahedra, and the 464 cm^{-1} band due to deformation vibration of Si–O–Si [6,15]. SiO_2 overtones are found at 1640, 1870 and 1960 cm^{-1} . In addition to silica bands, there are bands due to water: the very large band at 3440 cm^{-1} , that results from a superposition of vibration bands of hydroxyl groups and stretching vibrations of adsorbed water molecules, and the band at 1636 cm^{-1} due to bending of molecular water. Fig. 1b shows a spectrum for silica gel compacted at 4.5 GPa at room temperature. Clearly there are noticeable differences between Fig. 1a and b. There is a considerable area reduction for the very large band at 3440 cm^{-1} and for the 1636 cm^{-1} band, which was used to make a semiquantitative determination of water content of the samples. It can be seen in Fig. 1b that the area of this band decreases dramatically after high-pressure compaction. The area reduction has a value between 60 and 90% for several spectra, depending on the initial water content. There is also an area reduction for silica bands, although it does not exceed 30%. This change can be related to modifications in scattering properties of the samples, therefore we can estimate that the water content is reduced by a factor of 30–60%, after high-pressure compaction.

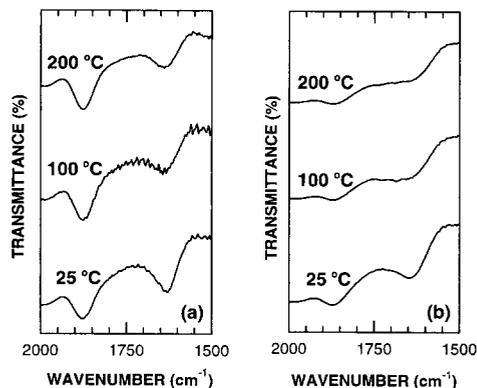


Fig. 2. FTIR transmission spectra of silica gel in vacuum cell after treatment at different temperatures. (a) As-prepared sample. (b) Compacted sample at 4.5 GPa and room temperature.

In Fig. 2 is FTIR transmission spectra obtained in the vacuum cell after treatment at different temperatures, in the range between 1500 and 2000 cm^{-1} for as-prepared powders and for compacted samples. The behaviors of the water band at 1636 cm^{-1} and the silica band at 1860 cm^{-1} were studied as a function of heat treatment temperature. The ratio of the areas of these two bands for each temperature was used to detect the remaining adsorbed water after high-pressure treatment. The uncertainty for all area calculations was not larger than 3%. These data

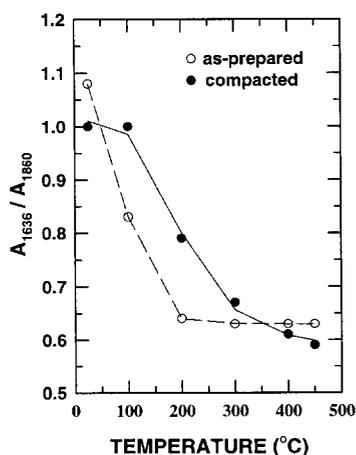


Fig. 3. The ratio between the areas of the 1636 and 1860 cm^{-1} bands, showed in Fig. 2, as a function of temperature: \circ for as-prepared samples, and \bullet for the compacted samples. The uncertainty for all area calculations was less than 3%. The lines are only a guide for the eye.

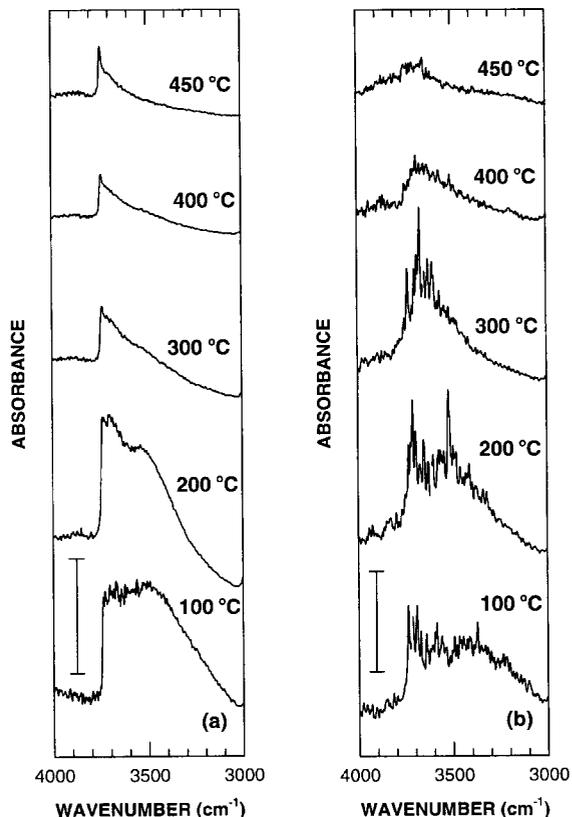


Fig. 4. FTIR absorption spectra of silica gel in vacuum cell after treatment at different temperatures, showing the OH stretching region. (a) As-prepared samples, where the bar value is 0.2 in absorbance units. (b) Compacted samples, where the bar value is 1 in absorbance units.

are presented in Fig. 3. For as-prepared powders subjected to vacuum, the area ratio of the two bands falls sharply, from 1.1 at 25°C to 0.64 at 200°C, indicating that the surface is cleaned of adsorbed water, as expected for the majority of inert powders. For temperatures higher than 200°C the area ratio becomes constant, and it does not reach a zero value, because the area of the 1636 cm^{-1} band includes a SiO_2 overtone near 1640 cm^{-1} . For compacted samples, the area ratio of the two bands is 1.0 at 25°C, remaining the same at 100°C. For higher temperatures it falls not so sharply as for as-prepared samples, and at temperatures as high as 400°C it seems not to reach a constant value.

The FTIR absorption spectra in the range from 3000 to 4000 cm^{-1} , after heat treatment in vacuum

at different temperatures, are shown in Fig. 4a and b. The broad band, from 3000 to 3800 cm^{-1} , is ascribed to OH stretching, i.e., bridges between adsorbed water and OH of silanol groups or stretching of OH from bridged silanol groups [1]. According to Fig. 4a, for as-prepared samples there is a band reduction with gradual heating up to 200°C, which is related to the elimination of adsorbed water. The continuous heating up to 450°C leads to a gradual decreasing of the band intensity corresponding to bridged SiOH groups. In this temperature range, the dehydroxylation of surface through the condensation reactions takes place [7]. During heat treatment between 200 and 450°C, a sharp peak at 3750 cm^{-1} becomes evident, indicating the presence of isolated silanol groups. As pointed out by many authors, these species can persist up to 1000°C or even more because they are very inert [7]. In Fig. 4b, it is observed that there is a large band between 3000 and 3800 cm^{-1} , despite the noise due to low transmittance in the spectra of compacted samples. This band begins to decrease as temperature increases with heat treatment, undergoing the same loss of adsorbed water and dehydroxylation that happens to as-prepared samples. However, it does not show evidence of the 3750 cm^{-1} band of free silanol groups to 450°C. This indicates that the SiOH groups became more close, establishing bridges between them.

Typical thermograms obtained for as-prepared powder (A) and for powders obtained by grinding

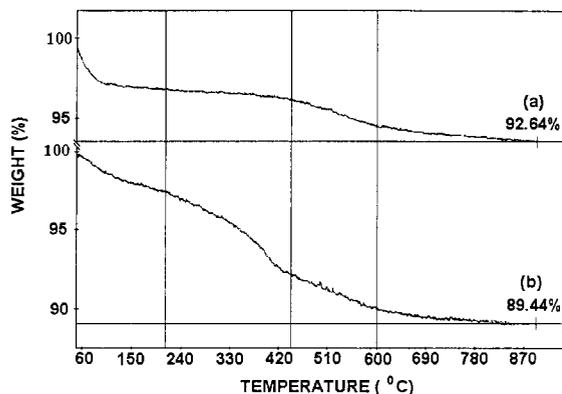


Fig. 5. Thermogravimetric curves for silica gel samples obtained in nitrogen atmosphere up to 900°C. (a) As-prepared samples and (b) crushed compacted samples, both at a heating rate of 20°C/min. The uncertainties in TGA measurements were 0.2% for temperature and 0.5% for weight.

Table 1

Thermogravimetric analysis of silica gel in nitrogen atmosphere, at a heating rate of 20°C/min. Sample A is as-prepared and sample B is powdered compacted

| Temperature interval | Weight loss % | |
|----------------------|---------------|------|
| | A | B |
| RT to 150°C | 3.8 | 1.4 |
| RT to 200°C | 3.8 | 1.9 |
| 200 to 350°C | 0.3 | 2.6 |
| 350 to 450°C | 1.0 | 3.0 |
| 200 to 450°C | 1.3 | 5.6 |
| 450 to 600°C | 1.8 | 1.8 |
| RT to final T | 7.4 | 10.6 |

compacted samples (B) are shown in Fig. 5. All powdered samples showed an initial weight loss from room temperature to 200°C. This weight loss stopped near 150°C for sample A, whereas for sample B we observe a continuous weight loss from 150°C to higher temperatures. Between 200 and 450°C, for sample A, it is observed a 'plateau' in the typical TG of Fig. 5a, where the weight loss is only 1.3% (Table 1). For sample B (Fig. 5b), there is a weight loss of 5.6% in this same range of temperature. The total weight loss in the whole temperature range is 7.4% for sample A and 10.6% for sample B (Table 1). Uncertainties in TGA measurements were 0.2% for temperature and 0.5% for weight.

4. Discussion

The observed decrease in surface area and the bulk density indicate densification and formation of non-connected pores. Measured densities were very high, considering that compaction was performed at room temperature. Our results are comparable to densification characteristics for silica gel achieved by heat treatment around 1000°C [1].

The data from Fig. 3 show a 'delay' to release water of compacted samples, indicating that free water is retained in closed pores. Total elimination of adsorbed water only will occur after a rupture of these closed pores, caused by internal pressure of water vapor, which becomes possible at higher temperatures. This indicates the existence of strong closed pore structure formed during the high-pres-

sure treatment. Of course, there will be a distribution of size and strength of these pores, therefore it is expected a temperature range to eliminate trapped water. Density and optical transparency of samples confirmed that there are a reduced number of pores and that their sizes are much smaller than the wavelength of light (nanopores). Densification can also be verified by surface area measurements, which for compacted samples was reduced by a factor of approximately 100, compared to as-prepared samples.

All FTIR results can be qualitatively explained by a sintering process promoted by high-pressure at room temperature, occurring through condensation reaction of surfaces silanol groups, which forms Si–O–Si bonds, described schematically in Fig. 6, as a three step process for ‘cold-sintering’ of SiO₂. Step 1 represents silanol groups present on the surface. In step 2 we have the interaction between silanol groups prompted by reduction of free space due to high-pressure compaction. In some cases, the particles would be so close enabling chemical forces to act, which prompts the formation of Si–O–Si bond and a water molecule, as depicted in step 3. This sequence

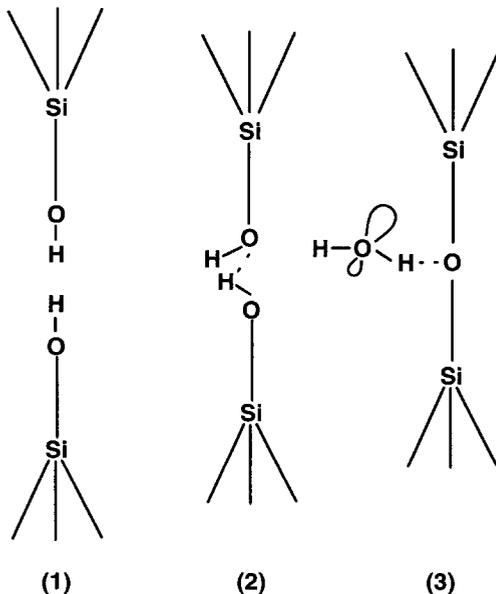


Fig. 6. Chemical reaction in a cold sintering process based on the slow fracture model [19]. (1) Silanol surface groups. (2) Interaction between them. (3) Siloxane bridge and water molecule formation.

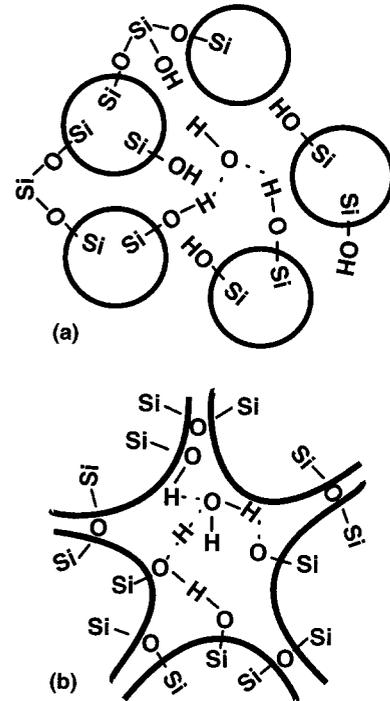


Fig. 7. Model for the structure of silica gel in a cold sintering process. (a) Primary particles linked by some siloxane bridges [17]. (b) Formation of closed porosity with trapped water by high-pressure compaction.

represents a condensation reaction, where surface is reduced and free water is produced. This is exactly the reverse of what occurs in the slow fracture model, proposed by Freiman and Michalske [21]. In this model, water molecule reacts with SiO bonds from silica glass, forming silanol groups and promoting crack propagation from the surface.

The mechanism of this cold sintering process at a microstructural level, and the formation of closed pores filled with water are shown schematically in Fig. 7. In Fig. 7a it is presented a picture of as-prepared silica gel with primary particles and some bridges between them. In Fig. 7b it is shown the condensation reaction between silanol surfaces forming closed pores. This could be explained through a kind of ‘zipper’ process forming the siloxane bonds. The infrared spectra of pressed samples confirm this fact, showing a clear reduction in the shoulder near 968 cm⁻¹, which is due to non-bridging oxygen

(Si–O stretching) and to the presence of silanol groups on the surface. The near absence of this band suggests that there are a few non-bridging oxygens and therefore the structure is nearly that of silica network [11]. This is an additional evidence of the ‘cold-sintering’ process.

TGA results are in agreement with FTIR and the mechanism discussed above. Regarding to initial weight loss, it was always lower for powders obtained from compacted samples and it is due to adsorbed water elimination. This could imply that the surface of these powders has less adsorbed water. This confirms FTIR results, where we observe a remarkable reduction of the molecular bending band of water (1640 cm^{-1}) after high-pressure treatment.

In the range between 200 and 450°C for sample A, the ‘plateau’ indicates that almost no weight loss is taking place, because adsorbed water was already eliminated up to 150°C and H bonded hydroxyl condensation process is not yet beginning. For sample B we observed a large weight loss in this temperature range, which can be explained by two processes already discussed in FTIR results: (1) at temperatures higher than 150°C, the nanopores start to break, releasing the trapped water and (2) condensation reaction of H bonded hydroxyl groups are greatly facilitated by high-pressure compaction if compared to as-prepared powders.

Results for total weight loss showed that dehydroxylation process occurs, in a greater extent, for samples submitted to high-pressure treatment. In this case, the existence of only bridged silanol groups and the absence of free silanol groups in compacted samples, as it is shown in FTIR spectra, could promote a complete condensation.

5. Conclusions

Irreversible transformations caused by high-pressure treatment in silica gel bulk samples were observed. High pressure treatment causes a reduction up to 60% in adsorbed water content, depending on its initial amount.

High density, relatively high hardness and transparency of these compacts, together with the ‘delay’ observed in the release of the water during heat treatment indicate a cold sintering process caused by a condensation reaction. An amorphous structure

with closed and very small pores is formed, containing trapped water.

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