



Near infrared spectroscopic characterisation of surface hydroxyl groups on hydrothermally treated silica gel

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Abstract

Surface hydroxyl groups on hydrothermally treated silica gel have been under discussion several decades back with contradictory conclusions. Some authors meant that the hydrothermally treated silica gel increases the concentration of hydrogen bonded silanol groups on the surface and some concluded that the hydrothermal treatment increases the concentration of internal hydrogen bonded silanol groups. The contradictory stand points arose because of the difficulty in finding a technique that could give evidence for the presence of surface hydrogen bonded silanol groups.

Recent investigation into the surface functionalities and adsorption evolution of water on silica gel surface by second derivative near infrared spectroscopy has provided spectroscopic evidence for the presence of surface hydrogen bonded silanol groups. The technique was employed to probe the surface of the hydrothermally treated silica gel samples. Two silica gel samples of varying surface characteristics have been used in this study. The samples were hydrothermally treated and their surface functionalities were probed using near infrared spectroscopy with second derivative approach.

The results clearly indicate that the hydrothermal treatment of silica gel primarily increases the concentration of hydrogen bonded silanol groups on the silica gel surface. This happens because of the chemical transformation of the siloxane groups into silanol groups. These new silanol groups increase the chance for hydrogen bondings with neighboring silanol groups. Therefore, the concentration of free silanol groups decreases with the hydrothermal treatment. The adsorption of water takes place at the vicinal OH groups first and spreads over the surface by forming hydrogen bondings and ends with bonding at free silanol OH groups.

A balanced concentration proportionality between free silanol groups and vicinal OH groups (arising from the hydrogen bondings between two or more of the neighboring silanol groups) is necessary for effective adsorption of water molecules on silica gel surface. A high proportion of the hydrogen bondings on the silica gel surface increase the concentration of vicinal OH and therefore the adsorption effectiveness of the sample decreases markedly.

Keywords: Near infrared spectroscopy, silica gel, hydrothermal treatment, second derivative

1. Introduction

The adsorption properties of silica gel are attributed to the surface silanol groups. These silanol groups are of different characteristics with varying degree of polarisation. The surface of the silica gel particles contain free silanol groups, silanol groups that are isolated and strongly hydrogen bonded [1-3] and some are far apart from each other and form weak hydrogen bondings [3]. Some silanol groups are hydrogen bonded in chain and they yield siloxane bondings when heated over 450°C.

Hydrothermal methods have been used in the past to prepare silica gel with various adsorption and structural properties [4-6]. The characteristic parameters such as pore size and particle size have been determined for the hydrothermally treated silica gel samples by using physical methods. However, the initial investigations [4, 7] into the characterisation of the chemistry of the surface have been unsatisfactory. This is because of the lack of proper instrumentation

and sampling accessories. The chemical nature of the surface had been characterised by wet chemical methods. Based on these, De Boer [7] suggested that the hydrothermal treatment of silica gel increased the surface OH groups by three fold. In contrast to this, Chertov [8] concluded that the hydrothermal treatment increased the concentration of internal hydroxyl groups and the concentration of surface hydroxyl groups remained the same.

Infrared spectroscopy both in the mid and near-infrared region has been used in the characterisation of surface functionalities of silica gel surface and the type of bondings take place when water molecules adsorb onto the silica gel surface. The infrared spectra of the hydrated silica gel samples are broader in the OH stretching and fingerprint regions. Because of this nature, it was difficult to characterise the type of functionalities present on the silica gel surface. There were also difficulties in the sampling for the

infrared spectroscopic measurements in the mid infrared region. Transmission techniques needed thin transparent discs containing the sample. Since the intensities of absorptions are smaller in the near infrared spectral region, thick samples could be used in measuring the near infrared spectra. However, measurements of dry samples of silica gel needed special setups [9].

Several different sampling techniques were made available during the past two decades that made spectral measurements easy in these spectral regions. Reflectance accessories are available to measure spectrum of a sample irrespective of its physical state. Transflectance accessory for near infrared spectrophotometers are useful in measuring near infrared spectra of powdered samples. Second derivative techniques in analysing the infrared spectra have also become useful in interpreting the absorption bands in the near infrared spectra [10-12]. Recently, Christy [13] used near infrared spectroscopy with the aid of second derivative techniques to follow the adsorption evolution of water on silica gel surface to characterise the surface hydroxyl groups. The approach provided a way to distinguish between adsorption of water by hydrogen bonded vicinal groups and free silanol groups on the surface.

During the adsorption of water molecules by a dry silica gel sample, one broad peak appears in the region 5600-5000 cm^{-1} indicating the combination absorption of the OH stretching and bending fundamentals of the water molecules. This peak composed of three bands having maximum at 5314, 5270 and 5119 cm^{-1} . By heating the sample at different temperatures and following the adsorption of water molecules on the surface, Christy was able to prove that the band at 5314 cm^{-1} was due to the OH groups of water molecules hydrogen bonded to free silanol groups and the band at 5270 cm^{-1} was due to the OH groups of water molecules hydrogen bonded to vicinal silanol groups on the surface. Christy [13] has also come up with a model for the adsorption of water molecules on the silica gel surface and concluded that the presence of vicinal groups on the surface of silica gel is a necessary condition for the effective adsorption of water molecules.

The question about whether hydrothermally treated silica gel increases the concentration of surface hydroxyl groups or internal hydroxyl groups could be answered by adopting a similar approach. The intention of this work is to subject silica gel samples to hydrothermal treatment and follow the adsorption evolution of water on the surface by using near infrared spectroscopy with the help of the transflectance accessory and use second derivative techniques to extract the underlying features in the

spectra and determine the nature of the hydroxyl groups on the silica gel surface and within the silica gel particles.

2. Material and Method

2.1 Materials, hydrothermal treatment and adsorption evolution of water on silica gel surface

Two different silica gel samples (Table. 1) with different surface areas, particle sizes and pore sizes were bought from Sigma-Aldrich. A steel bomb consisting of 25 cm steel pipe with 1cm internal diameter was used in the hydrothermal treatment experiments.

A ceramic heater (BA electric Bunsen from Electrothermal, UK) controlled by an external power supply was used in heating the samples. Samples were evacuated at 200°C two hours before using them in the water adsorption experiments.

Table 1. Silica gel samples used in the experiments

Silicagel samples	Surface area m^2/g	Particle Size μm	Pore size μm	Silanol number (OH-groups/ nm^2)
1	471	37-63	52	3.6
2	600	210-500	31	2.9

1g of dry silica gel sample was placed in the steel bomb and 1 cm^3 of distilled water was added to the bomb and sealed. The bomb was then placed in a chromatographic oven set at 160°C and left for two hours. The bomb was then removed and allowed to cool. The hydrothermally treated sample was removed and evacuated at 200°C to remove physically adsorbed water from the surface. The samples also were heated to 750°C and 1100°C to understand the effect of temperature on the silanol groups.

2.2. Near infrared (NIR) measurements

Each of the samples dried as mentioned above, cooled and transferred to a sample cup (around 0.3g) with an IR transparent window. The near infrared measurements were made using a PerkinElmer Spectrum One NTS FT-NIR spectrometer (Perkin Elmer Ltd, UK) equipped with a PerkinElmer transflectance accessory and deuterated triglycine sulphate detector. The sample cup containing the silica gel sample was placed directly on the crystal of the transflectance accessory and allowed to equilibrate with the surrounding air, and the near infrared spectrum of the sample was measured in the region 10,000–4000 cm^{-1} at a resolution of 16 cm^{-1} . A total of 30 scans were made each time.

The reflectance spectra showing the evolution of adsorption of water on silica gel were then converted to log (1/R) format and derivated twice and saved.

These spectra were used in the detailed analysis of the hydroxyl groups on silica gel sample.

3. Results and discussion

3.1. Chemical nature of silica gel surface

Most of the spectra acquired during the adsorption evolution of water are presented as second derivative profiles. Recognizing the features of a second derivative spectrum is important to understand the interpretations used in the data analysis. A detailed description of the applications of the second derivative can be found elsewhere [13].

Table 2. Near Infrared band assignments for a hydrothermally treated silica gel sample in the region 8000-4000 cm^{-1} [13].

Peak (cm^{-1})	Band assignment
7316	Overtone-OH stretchings free silanol groups
7225	vicinal silanol groups
7121, 6861	water molecules hydrogen bonded to silanol groups, water molecules hydrogen bonded to other water molecules
5311	Combination band OH stretching and bending water molecules hydrogen bonded to free silanol groups
5270	water molecules hydrogen bonded to vicinal silanol groups
5119	water molecules hydrogen bonded to silanol groups
4579	Combination band OH stretching free silanol and siloxane (Si-O-Si) bending
4518, 4422	Combination band silanol OH stretching (hydrogen bonded to water molecules) and siloxane (Si-O-Si) bending

Silica gel surface contains free silanol groups and silanol groups that are hydrogen bonded. There may be differences in the hydrogen bondings. Some of the silanol groups are isolated and strongly hydrogen bonded [1-3] and some are far apart from each other and form weak hydrogen bondings [1]. Some silanol groups are hydrogen bonded in chain. The silica gel surface undergoes changes when they are subjected to thermal treatment. First the physically adsorbed water is removed at lower temperatures. At elevated

temperatures the hydrogen bonded silanol groups start condensing to form siloxane bondings that are reversible.

Both of the hydrothermally treated silica gel samples behave in the same manner and therefore the following discussion will be focused on sample 2 from the table 2. The near infrared spectra of the silica gel (sample 2) directly from the shelf and after treating at 200 and 750 $^{\circ}\text{C}$ are shown in Fig.1. The spectra of the dry samples contain one asymmetric peak around 7300 cm^{-1} and another around 4500 cm^{-1} . The untreated and un-dried silica gel sample contains one peak around 5300 cm^{-1} in addition. This peak is due to the overtones of the hydroxyl groups of the water molecules hydrogen bonded to silanol groups on the surface. The asymmetric band around 7300 cm^{-1} contains the overtones of both free and hydrogen bonded silanol groups.

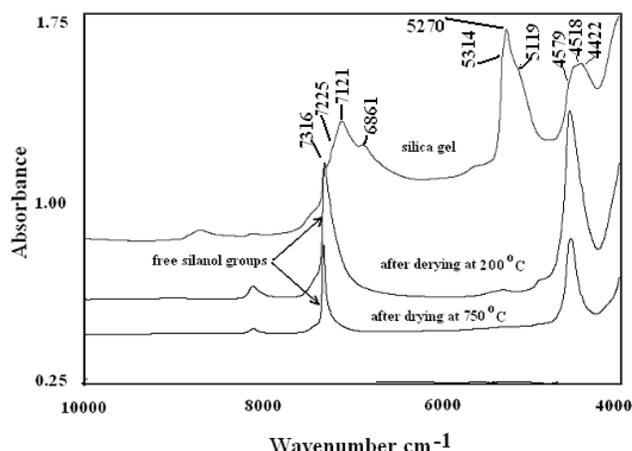


Fig. 1. Near infrared spectra of silica gel sample (sample 2) heated and evacuated at different temperatures

The near infrared spectrum of the hydrothermally treated, dried and evacuated (at 200 $^{\circ}\text{C}$) silica gel sample is shown in Fig. 2. The changes are obvious in the figures. The near infrared spectrum of the hydrothermally treated sample that was pre-treated at 200 $^{\circ}\text{C}$ shows a decrease in the concentration of free silanol groups and an increase in the concentration of hydrogen bonded hydroxyl groups.

In order to prove that the hydrothermal treatment increases the hydrogen bonded silanol groups on the surface, an approach that was used in a study by Christy [13] was used. By allowing the samples treated to adsorb water and follow the peak in the region around 5300 cm^{-1} and using second derivative technique, Christy [13] has shown that there are three bands at 5314, 5270 and 5119 cm^{-1} in this region of the spectrum for a silica gel sample adsorbing water molecules.

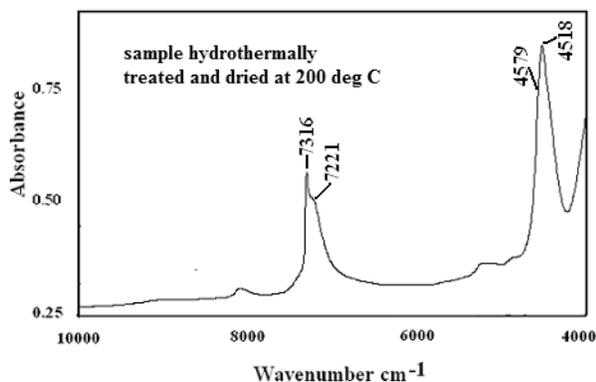


Fig. 2. Near infrared spectrum of hydrothermally treated silica gel sample

3.2 Adsorption evolution of water molecules on silica gel surface of the hydrothermally treated sample pre-treated at 200 °C

The near infrared spectral data of the hydrothermally treated and dried silica gel sample contain three sets of peaks like the untreated (dried) silica gel sample. The band assignments of the functional groups on a hydrothermally treated silica gel sample are given in Table 2. One set appears in the region 7600-6800 cm^{-1} indicating the overtone of the free and hydrogen bonded silanol OH groups,

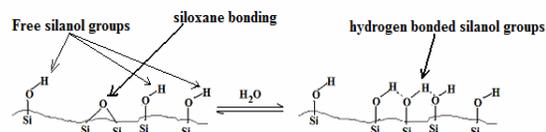


Fig. 4. A sketch showing the silica gel surface before and after hydrothermal treatment

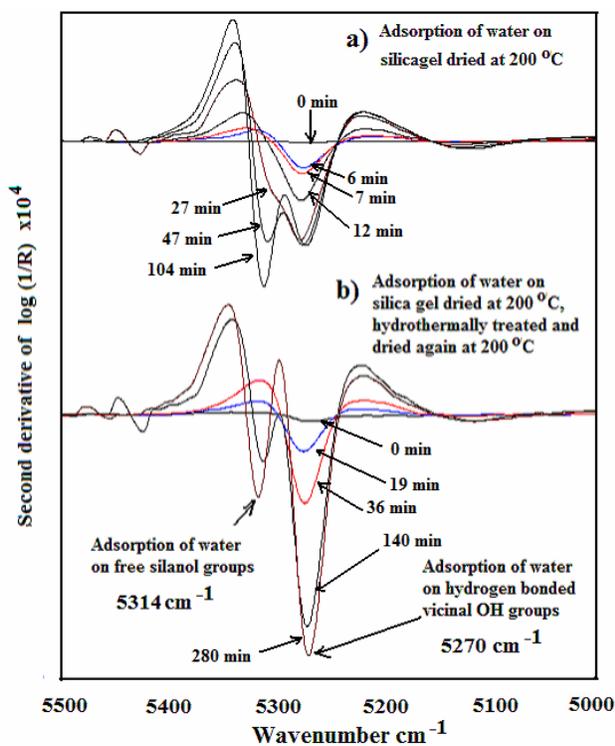


Fig. 3. Near infrared spectra acquired in the region 5500-5000 cm^{-1} during the adsorption evolution of water molecules

The NIR bands appearing at 5314 and 5270 indicate the presence of water molecules in two different environments, one with slightly stronger hydrogen bonding and one with weaker or no hydrogen bonding compared to hydrogen bonding of water molecules in liquid water [13]. The peaks appearing in the regions 7600-6800 and 4800-4200 cm^{-1} can also give some additional information regarding the changes taking place.

overtones of the symmetric and antisymmetric stretches of the OH groups of water adsorbed onto the silica gel surface. The second set appears in the region 5600-5000 cm^{-1} indicating the combination absorption of the OH stretching and bending fundamentals of the water molecules hydrogen bonded to silanol groups. The third set appears in the region 4800-4200 indicating the combination bands of the silanol OH stretching and siloxane (Si-O-Si) stretching vibrations.

3.3 Spectral region 5600-5000 cm^{-1}

Second derivative near infrared spectra of the dry silica gel sample (heated at 200°C) and the hydrothermally treated (and dried) sample equilibrated with surrounding air are shown in the region 5550-5000 cm^{-1} (Fig. 3). The band at the lower wave number (5270 cm^{-1}) appears and grows first and then the band at the higher wave number (5314 cm^{-1}) evolves and grows. The measurements were made until there is apparently no change in the bands. The near infrared spectra measured on untreated silica gel sample has intense peak at 5314 cm^{-1} . The peak at 5270 cm^{-1} is less intense compared to the peak at 5314 cm^{-1} . Christy [13] has proved that the peak at 5270 cm^{-1} was due to hydrogen bonded silanol groups. The near infrared spectra of the hydrothermally treated silica gel sample measured during the adsorption of water molecules results in the peaks at 5314 and 5270 cm^{-1} with completely different proportionalities than the peaks in the NIR spectrum of the untreated silica gel sample. The peak at 5270 cm^{-1} is more intense than the peak at 5314 cm^{-1} . When the hydrothermally treated silica gel sample was heated to 750 °C and the adsorption of water molecules followed by using near infrared measurements, no absorption peak appeared at 5270 cm^{-1} . This is an indication that the peak at 5270 cm^{-1} is purely from adsorption of water

molecules by the hydrogen bonded vicinal silanol groups.

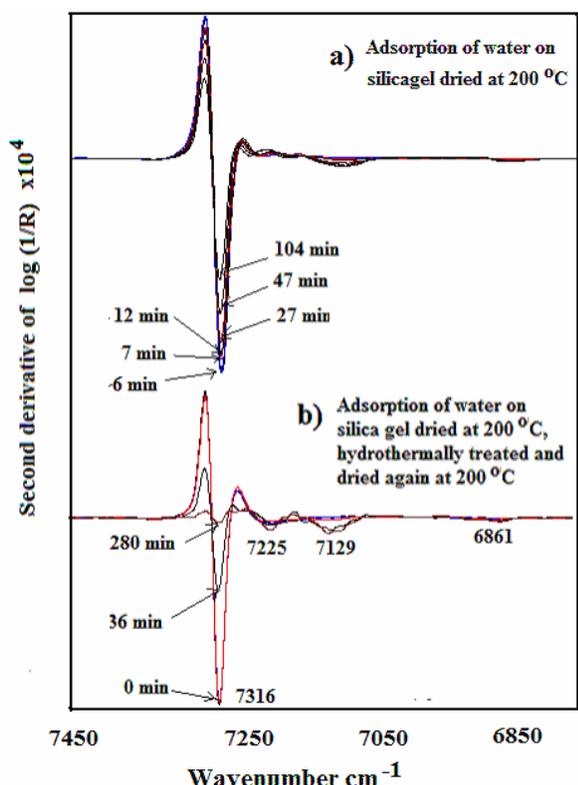


Fig. 5. Near infrared spectra acquired in the region 7450-67500 cm^{-1} during the adsorption evolution of water molecules

The heat treatment at 750 $^{\circ}\text{C}$ removes the hydrogen bonded silanol groups on the surface [1, 14]. This fact proves that the hydrothermal treatment of silica gel sample increases the concentration of hydrogen bonded surface silanol groups. The newly formed silanol groups engage into hydrogen bonding with neighbouring silanol groups (Fig. 4). This is the reason for the decrease in intensity of the peak at 5314 cm^{-1} .

The peak at 5270 cm^{-1} is slightly broader than the peak at 5314 cm^{-1} . However, the intensities of the peaks can be compared. The ratio of the peaks at 5270 cm^{-1} to 5314 cm^{-1} of the most intense peaks in Fig. 3. The ratio is 0.71 for the untreated silica gel sample and 3.00 for the hydrothermally treated sample. The results prove that the hydrogen bonded silanol groups on the surface increase several folds. The degree of formation of the hydrogen bonded silanol groups may vary depending on the way the hydrothermal treatment was carried out. The results are in support of De Boer's hypothesis [7].

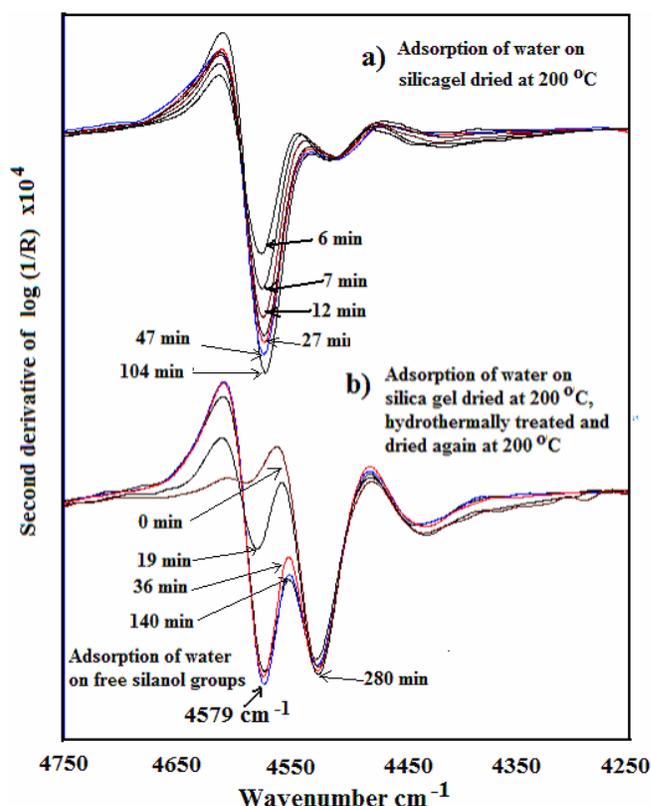


Fig. 6. Near infrared spectra acquired in the region 4750-4250 cm^{-1} during the adsorption evolution of water molecules

3.4. Spectral regions 7500-7000 cm^{-1} and 4800-4200 cm^{-1}

Near infrared spectra measured in these regions for the adsorption evolution of water molecules are shown in Figures 5 and 6 respectively. The Figures clearly show the differences in the adsorption of water molecules by untreated and hydrothermally treated samples. Second derivative spectra of the evolution of water adsorption on the surface of the dry shelf silica gel sample is shown in the region 7500-7000 cm^{-1} in Fig. 5. The progress of adsorption evolution of water on the surface is evidenced by the decrease in intensity of the absorption due to free silanol OH groups at 7316 cm^{-1} and appearance of the bands at 7121 and 6861 cm^{-1} due to the adsorption of water molecules on the silica gel surface. The band at 7225 cm^{-1} is due to the hydrogen bonded silanol groups on the surface.

The peak appearing in the region 4800-4200 cm^{-1} contains three bands (Fig. 6). The first band at 4579 cm^{-1} is arising due to the combination frequency of the OH fundamental and siloxane stretching vibrations. The intensity decreases with increasing water molecular adsorption. The decrease is evident in both untreated and hydrothermally treated samples.

4. Conclusion

Near infrared spectroscopic evidence has been presented in this paper to show that the hydrothermal treatment of silica gel samples increase the proportion of hydrogen bonded silanol groups on the silica gel surface. This increase takes place because of the reaction between siloxane groups and water. The siloxane bondings are strained in amorphous silica gel and they open up during the hydrothermal treatment and react with water. When new silanol groups are formed, they interact with the neighbouring silanol groups and engage in hydrogen bonding. This increases the hydrogen bonded silanol groups several folds.

The adsorption process is also slow on the hydrothermally treated silica gel sample compared to the untreated silica gel sample. This again gives a clue regarding the proportion of hydrogen bonded silanol and free silanol groups on the surface. The adsorption of water molecules starts from hydrogen bonded silanol groups. Then water molecules form a hydrogen bonded network with the first water molecule and spread until they reach a free silanol group. Equal proportion of these two types of silanol groups may increase the effectiveness of adsorption. In hydrothermally treated silica gel sample, there are fewer free silanol groups compared to the untreated silica gel sample. And the adsorption of water molecules on hydrogen bonded silanol groups will not be effective because the network of molecules need an ending at free silanol groups to remain adsorbed on to the surface.

Near infrared spectroscopy with second derivative technique has revealed some important aspects of silica gel surface of hydrothermally treated silica gel samples. Use of second derivative technique can reveal important information when applied to spectroscopic data.

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