New insights into the surface functionalities and adsorption evolution of water molecules on silica gel surface: A study by second derivative Near Infrared Spectroscopy

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Abstract

Surface functionalities and adsorption evolution of water molecules on silica gel samples were studied by second derivative Near Infrared Spectroscopy. Four different silica gel samples with varying surface area were used in this experiment. Each of the dry samples was allowed to equilibrate with surrounding air and the near infrared spectra were accumulated at different time intervals using reflectance technique. The evolved spectra were analysed by using second derivative technique to study the adsorption evolution of water molecules on the surface.

The second derivative spectral profiles have revealed some interesting features about the surface functionalities and some events of adsorption on silica gel surface that have never been reported in the literature. The near infrared spectroscopic evidence is provided for the first time to show the presence of hydrogen bonded silanol groups on silica gel surface. The results and the events show that the adsorption of water molecules readily takes take place on the hydrogen bonded vicinal silanol groups and spread over the space and ends with the hydrogen bonding at free silanol groups. Water molecules then build over these molecules to form a network of hydrogen bonded water molecules. There is clear evidence that the presence of hydrogen bonded silanol groups is a necessary condition for the effective adsorption activities on silica gel surface. Furthermore, the study reveals that while mono and multi-layer water molecular adsorption takes place at certain active sites of the surface, a large portion of the surface is free from any adsorption activities.

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1. Introduction

Silica gel produced by the condensation polymerisation of silicic acid is the amorphous form of silica. The bulk of the silica contains interlinked SiO groups with siloxane group or hydroxyl group at the surface. During the polymerisation colloidal particles containing silanol groups on the surface are formed. On drying, several of the colloidal particles are brought together and some of the surface OH groups will become buried in the bulk of silica gel particles. The surface hydroxyl groups are polarised due to hydrogen bondings and the silanol groups exhibit three different degrees of acidity. Furthermore, these silanol sites on the surface are sites for hydrogen bondings and water molecules are easily adsorbed on to the surface. The adsorbed water molecules can be removed by heating or subjecting the silica gel sample under vacuum. The process is reversible and dry silica gel samples adsorb water molecules when exposed to air.

The adsorption of water molecules and their interaction with silanol groups have been investigated by several authors during the past 70 years since the discovery of silanol groups on silica surface by Kiselev in 1936 [1]. Since the natures of the hydroxyl groups on the silica gel surface are different, the environments of the adsorbed water molecules on the surface are also different. The state of the water molecules on silica gel particles and related substances have been studied by using several different techniques including TGA [2], NMR [3,4], IR and NIR [5-19], AB initio calculations [20] and dielectric measurements [21]. Most of these studies were trying to give a picture of the water structure on silica surface based on the results from the respective analytical techniques. However, the interpretations and the models presented are not quite clear.

The use of infrared and near infrared spectroscopy has contributed to a certain extent in understanding the surface functionalities of silica gel surface and the type of bondings take place when water molecules adsorb onto the silica gel surface. When infrared spectroscopy in the mid-infrared region was used for measurements, the partially hydrated and fully hydrated silica gel samples gave rise to very broad peak in the OH stretching region for both silanol groups and OH groups from water. The fingerprint region gave even broader peaks. The nature of these broad peaks made it difficult to characterise the type of functionalities present on the silica surface.

This is due to the difficulties in the sampling for the infrared spectroscopic measurements in the mid infrared region. Measurements by transmission techniques needed thin transparent discs containing the sample. Furthermore, special cell arrangements were needed to measure dry silica gel samples. In this respect near infrared spectral region is useful because the intensities of absorptions of the overtones in the near infrared region are small compared to the intensities of absorptions in the mid-infrared fundamental region. Hence, thick samples can be used in the transmission measurements. However, measurements of dry samples of silica gel needed special setups [12].

There have been developments in the sampling techniques for both in mid and near infrared regions. Sampling technique such as transflectance has made near infrared measurements of solid samples in powder form very easy. The samples can be placed in a sample cup with an infrared transparent window and the measurements can be made on the samples (Fig. 1). Apart from the sampling techniques, there have also been improvements in the way the spectra were handled. The spectra measured both in the mid and near infrared regions contained overlapping bands. Some bands are completely buried under the peaks and their apparent shapes were misleading regarding the nature of the bands. Stone and Walrafen [10] used curve fitting to resolve infrared absorption peaks measured on fused optical silica fibres. None of the other research work used any other techniques to resolve peaks to give better understanding and interpretations of the absorptions in the infrared spectra of silica gel samples. Second derivative profiles of the infrared and near infrared spectra have revealed some important features in the spectra for interpretation purposes [22-24]. Use of second derivative techniques in qualitative and quantitative analysis in near infrared spectroscopy has become very common. A theoretical explanation and justification for the use of second derivative techniques in spectroscopy can be found elsewhere [25]. The same technique was used in this work to resolve the underlying bands in the near infrared absorption spectra.

The intention of this work is to carry out experiments on the adsorption of water on silica gel surfaces, measure their near infrared spectra with the help of the transflectance accessory and use second derivative techniques to extract the underlying features in the spectra. Furthermore, it is also the intention of this work to use the resolved features to get better understanding of the surface functionalities and water structure on silica gel samples.

2. Experimental

2.1. Materials and preparation of the samples

Four different silica gel samples (Table. 1) with different surface areas were bought from Sigma-Aldrich. A ceramic heater (BE electric bunsen from Electrothermal) controlled by an external power controller was used in heating the samples. The temperature of the sample was measured using a digital thermometer with a K type thermocouple. A powerful vacuum pump was used in the evacuation of the samples. All the samples were evacuated at 200ºC before using them in the experiments on adsorption studies. Samples were also heated to 500ºC and 750ºC for detailed study of the behaviour of the functional groups on the silica gel surface. The heating of the samples at 750ºC was carried out in porcelein crucibles. Undried silica gel samples are refered to as shelf silica gel samples in the text.

Each of the samples dried as mentioned above, cooled and transferred to a pre-weighed sample cup with an IR transparent window and weighed again to determine the quantity of silica gel in the sample cup. A cello tape was placed on the cup to prevent adsorption of moisture before start of the experiment.

2.2. Near infrared (NIR) measurements

The near infrared measurements were made using a PerkinElmer Spectrum One NTS FT-NIR spectrometer 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 (Fig. 1), the cellotape removed, 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. Near infrared spectra of the sample were then measured frequently in the beginning and the weight of the sample was recorded after each measurement. The reflectance spectra so obtained were converted to log $(1/R)$ format and saved. The measurements gave a series of spectra showing the evolution of water adsorption on silica gel surface. The weight difference and variations in the peaks appearing in the near infrared spectra should give information on structural features of water molecules on silica gel surface.

The spectra of the samples in log(1/R) format were derivated twice and saved. These spectra were used in the detailed analysis of the surface structure of silica gel samples.

2.3. Features of second derivative spectral profiles

Most of the spectra presented in this work are presented as second derivative profiles. Recognising the features of a second derivative spectrum is important to understand the interpretations used in the data analysis.

A first-order derivative spectrum gives the rate of change of absorbance with respect to wavelength. Therefore, the first derivative of a single peak in a spectrum starts at zero and finishes at zero. At the peak maximum the first derivative of the peak is zero and therefore the point where the first derivative crosses the wavenumber axis is the same as λ_{max} of the absorbance band. There are positive and negative bands either side of this crossing point. The maximum of the positive band and minimum of the negative band are at the same wavelengths as the deflection points in the absorbance band. The second-order derivative has a negative band with minimum at the same wavelength as the maximum in the absorption band. There are also two additional positive satellite bands either side of the negative main band.

In modern spectrometric instruments derivatives are calculated by an algorithm developed by Savitzky and Golay. The second derivative spectrum is presented as a plot containing two halves. There is a line marking zero line where the second derivatives of the spectrum with zero values cross. The remaining second derivative bands appear in the positive side and negative side of the line. A sharp band in the zeroeth order absorption spectrum will give three bands in the second derivative spectrum. Two satellite bands above the zero line and the main band with a minimum at the same wavenumber as the sharp band in the zeroeth order spectrum.

In quantitative analysis second derivative technique improves the accuracy of quantification by eliminating base line shift and scattering in the spectra. The derivative spectra (all the derivatives) follow Beer's law and therefore can be used in quantitative determination by calibration using intensities of the bands in the second derivative spectra. When a series of evolving spectra is collected, increase or decrease taking place in one of the absorption bands will be reflected in the second derivative as increase or decrease in the negative band.

When two bands one with narrow bandwidth and one with broad bandwith of equal intensities are present in a peak, second derivative using Savitzky and Golay algorithm would enhance the amplitude of the narrow band and suppress the amplitude of the broad band. This is useful

in improving the accuracy of quantification of a narrow band component in the presence of a broad band component. This characteristic is useful in this work because there are sharp absorption bands overlapping with broad absorption bands.

3. Results and discussion

3.1. Chemical nature of silica gel surface

It appears that the research work reported in the literature agrees to a silica gel surface with 1) free silanol groups 2) silanol groups that are hydrogen bonded. Some authors have indicated that there maybe differences in the hydrogen bondings. Some of the silanol groups are isolated and strongly hydrogen bonded [16-18] and some are far apart from each other and form weak hydrogen bondings [16]. Some silanol groups are hydrogen bonded in chain and they yield siloxane bondings when heated over 450ºC. The mid IR spectroscopic data presented in the literature were mostly focussed on the OH stretching region because of the strong absorptions in the OH bending region. A model of the silica gel surface and the absorptions arising from the surface functionalities in the OH stretching region are shown in Fig. 2. Since the absorption intensities of the overtones and combination frequencies are low, thick samples of silica gel could be used in measuring the spectra in the region 10000-4000 cm^{-1}. The near infrared spectral data reported in the literature agree on three sets of peaks for a shelf silica gel sample. One set appears in the region 7600-6800 cm^{-1} indicating the overtone of the free and hydrogen bonded silanol OH groups, overtones of the symmetric and antisymmetric stretches of the OH groups 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 OH bending fundamentals of the water molecules. 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.

Near infrared spectrum of a shelf silica gel sample{C}, spectrum of the same sample after drying and evacuating at 200ºC for 2 hours and the spectrum of the same sample after heating at 500ºC for 1 hour are shown in Fig. 3. Similar spectra were reported in most of the work published in the literature where near infrared spectroscopy was used to probe the silica gel sample surface. The spectrum of the dry sample contains one asymmetric peak around 7300 cm^{-1} and another around 4500 cm^{-1}. It contains only the absorptions from the functional groups in the silica gel sample. The asymmetric band

around 7300 cm^{-1} contains the overtones of both free and hydrogen bonded silanol groups. The spectrum of silica gel sample heated at 500ºC show a sharp peak around 7300 cm^{-1} and another peak around 4500 cm^{-1}. Several authors have shown that heating the sample in the temperature range 450- 700ºC forces hydrogen bonded silanol groups to form siloxane bondings leaving only free silanol groups on the surface [15-16]. A comparison of the spectra in Fig. 3 clearly shows that the asymmetry in the band at 7300 cm^{-1} arises because of the absorptions from the hydrogen bonded silanol groups lying under the absorptions arising from the free silanol groups. Furthermore, the absortption/s around 5300 cm^{-1} in Fig. 3a are purely from water molecules adsorbed on to the silica gel surface because these peaks disappear when the sample is heated and evacuated at low temperatures.

Second derivative spectra of the same spectra shown in Fig. 3 a, b and c are given in Fig. 4 a, b and c respectively. The asymmetry in the band at 7318 cm^{-1} is due to the buried absorptions due to silanol groups hydrogen bonded to each other. Apart from the asymmetry in the first peak, the profile shows three additional bands at 7225, 7122 and 6879 cm^{-1} respectively. There are three bands at 5311, 5270 and 5119 cm^{-1} in the middle region of the spectrum. The main peak is split into two showing that there are two bands lying under that main peak. This has never been reported in the literature. Since these bands are arising purely from the water molecules on the silica gel surface, their behaviour with temperature changes should give a clear picture of the surface structure and structure of water on silica gel surface. The third set show three bands at 4572, 4518 and 4420 cm^{-1}respectively. Here again, the first two bands at wavenumber 4572 cm^{-1} and 4518 cm^{-1} have never been reported as two bands in the literature.

Second derivative spectra of the shelf silica gel sample and of pure water are shown in Fig. 5. The spectra show that the OH stretchings of the water molecules adsorbed onto the silica gel surface are shifted to higher wavenumber compared to the same in pure water sample. This shift in the frequencies indicate that the water molecules on the silica gel surface are in less hydrogen bonded net work environment than in pure water. Furthermore, the NIR bands appearing in the 5300 cm^{-1} region suggests that the water molecules are in at least 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.

3.2. Adsorption evolution of water molecules on silica gel surface

3.2.1. Spectral region 7500-7000 cm^{-1}

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. 6. 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 7318 cm^{-1} and appearance of the bands at 7122 and 6879 cm^{-1} due to the adsorption of water molecules on the silica gel surface. The decrease in intensity of the free silanol groups is due to the hydrogen bonding with adsorbed water molecules. There is also evidence of a new band appearing at 7225 cm^{-1} after exposing the sample for some time. It is not clear about the origin of absorption for this band. This maybe due to the absorptions arising from the silanol groups hydrogen bonded to water molecules. The band at 7318 cm^{-1} indicates that the shelf silica gel sample still has some free silanol groups that are not hydrogen bonded to water molecules.

3.2.2. Spectral region 5400-5100 cm^{-1}

Second derivative spectra of the dry silica gel sample (heated at 250ºC) equilibrated with surrounding air are shown in the region 5600-5000 cm^{-1} (Fig. 7). The adsorption evolution of water as indicated by the bands appearing in the above region is relatively fast and provides some interesting details. The band at the lower wavenumber appears and grows first and after a while it remains relatively unchanged while the band at the higher wavenumber evolves and continues to grow until saturation reaches. Furthermore, the band width of the band at lower wavenumber is broader than the band at the higher wavenumber. The behaviour is the same with all the four samples of silica gel studied. The behaviour of these two bands is the same irrespective of the sample surface area. The split bands shift in the opposite directions. The band at the lower wavenumber experiences a red shift and the band at the higher wavenumber experiences a blue shift. This is the reason why there was no shift in this peak position observed in the near infrared spectra measured by the other research workers [10].

It appeared during the experiments that these had something to do with the environment of the silanol groups on silica gel surface. In order to clarify the behaviour, new heating experiments at 750ºC were carried out with all the samples. Each sample was heated first and allowed to equilibrate with the surrounding air and the adsorption of water was monitored on each sample by measuring their near infrared spectra. Second derivative

spectra of one of the silica gel samples (sample C) heated at 750ºC and equilibrated with surrounding air are shown in Fig. 8. The figure clearly indicates the appearance of the band at 5311 cm^{-1}. This band grows slowly and a small hump at the lower wavenumber appears after a while and remains unchanged for a long time. Even after several days there was not much change in the peaks. The humidity surrounding the sample was increased by placing a beaker with wet walls up side down covering the sample to facilitate the adsorption. The process of heating the sample to 750ºC would have removed all the hydrogen bonded silanol groups and only the free silanol groups will be remaining on the surface and the adsorption of water molecules proceeds at a very slow rate. The free silanol groups are involved in the adsorption of water molecules here because the hydrogen bonded silanol groups and silanol groups that are close to each other have condensed to form siloxane bondings and not immediately available for hydrogen bondings with water molecules.

The evolution of adsorption of water molecules by samples heated at 200ºC (Fig. 7) clearly shows that the band at the lower wavenumber appears first. This is an indication of silanol groups with strong polarisation and weak OH bonds involved in the adsorption of water molecules first and then the adsorption proceeds with the silanol groups that have a strong OH bond and weak polarisation. Obviously, these observations suggests that the OH groups that lead to the evolution of the band at lower wavenumber (5270 cm^{-1}) during the adsorption of water molecules are hydrogen bonded vicinal silanol groups, and the OH groups that lead to the evolution of the band at higher wavenumber are free silanol groups (Fig. 2). The greater band width of the band at 5270 compared to the higher wavenumber band also suggests that the absorption reflects a smaller network of hydrogen bonding.

The confirmation of the identity regarding the band at 5311 cm^{-1} as the band arising from the adsorption of water molecules by free silanol groups also comes from the linear correlation between the intensities of the bands at 7318 cm^{-1} and 5311 cm^{-1} (Fig. 9). The results from the experiments also suggest that the adsorption of water molecules on the surface starts readily with the vicinal OH groups that can form a network of water molecules spreading and leading to the formation of hydrogen bonds with free silanol groups (Fig.10).

The absence of hydrogen bonded silanol groups in the samples heated to 750ºC opens up the surface into large empty patches without any vicinal OH groupings. It means that the only available sites for the adsorption of water molecules are isolated free silanol

groups. The adsorption takes place at a very slow rate (Fig. 8). The slow process of water molecular adsorption by samples heated at 750ºC suggests that the presence of hydrogen bonded silanol groups (vicinal) on the surface is a necessary condition for an effective adsorption process of water molecules on the silica gel surface. These observations and conclusions are in agreement with the report of Hair [26].

Plot showing the relationship between the sum of the intensities of absorption at wavenumbers 5314 and 5270 cm^{-1} against the mass of the water molecules adsorbed on the silica gel surface is given in Fig.11. The intensities at these wavenumbers are also plotted against adsorption times (Fig. 12). Using the mass of adsorbed water, the surface area of the used silica gel sample in the experiment, the number of water molecules adsorbed was calculated. The numbers of water molecules adsorbed at different stages are given in all the figures showing the second derivative profiles of the adsorption evolution (Fig. 6, 7 and 13). The relationship is linear until the adsorption of 1.5 water molecules/nm^2 (Fig. 11 and 12) and it deviates from linearity when the number of water molecules adsorbed is more than 1.5 water molecules/nm^2. However, part of the surface area on the silica gel surface contains free silanol groups. The relative percentage of the free silanol groups not involved in the adsorption of water molecules can be calculated any time by comparing the intensity of the band at 7318 cm^{-1} of the sample under investigation with the intensity of the band of the silanol groups of the dry sample. For example, the Fig. 7 shows that the sample C contains around 68% of the silanol groups still remaining on the surface after adsorbing 1.5 water molecules/nm^2. The sample also has a silanol number 3 [27]. This means that the water molecules are bound to only 32% (around 1/3) of the silanol groups. In number of molecules this translates into 3 water molecules to 2 silanol groups. This result agrees with that of Yamauchi and Kondo [13]. However, the picture has to be looked in a different way. The water molecules are bound in patches to only around 33% of the surface containing free silanol groups and hydrogen bonded silanol groups. The second derivative spectra in Fig.7 show that the band arising from the adsorption of water molecules on to vicinal groups becomes apparently constant after the adsorption of 1 water molecule (0.94)/ nm^2. It means that out of 1.5 water molecules adsorbed 1 molecule is engaged in bonding with vicinal silanol groups. If 66% of the surface area is free on the surface then the number of water molecules adsorbed as monolayer should be 3x1.5 water molecules/nm^2. That is 4-5 water molecules are in the first layer covering the space of 1 nm^2 surface. Out of these

1.5 water molecules are bonded to free silanol groups and 3 water molecules are bonded to vicinal silanol groups.

The deviation of the adsorption curves from linearity is an indication that the intensity of absorption arising from the combined frequencies of the incoming additional water molecules is less. This again indicates that the hydrogen bondings are in a different environment and most of the active sites for water molecular adsorption are already occupied and further adsorption of water molecules can only take place by forming hydrogen bonds with already adsorbed water molecules. The short term adsorption of water molecules in this experiment results in a total of 3x2.35 water molecules adsorbed on the active sites. At this point 40% of the free silanol groups are not involved in any adsorption activities. Therefore, at the end of the experimental measurements, the second layer has acquired around 3 water molecules. However, the adsorption of water molecules will continue on the second layer. The build up of this hydrogen bonding network proceeds very slowly over long period of time. The adsorption of water molecules can be forced to continue by increasing the humidity around the sample.

The band at 5120 cm^{-1} is also increasing in intensity with water molecular adsorption on the surface. This band does not appear in the spectra of the samples analysed after heating to 750ºC. This observation suggests that this band is also arising from the combination frequencies involving OH groups on the surface other than free silanol groups.

3.2.3. Spectral region 4800-4200 cm^{-1}

The peak appearing in this region contains three bands [Fig. 13]. The first band at 4572 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. A linear correlation between the bands at 5314 and 4572 cm^{-1} (Fig. 14) is a proof that these two come from the same chemical functionality. The band at 4518 cm^{-1} remains unchanged but the intensity of the band at 4423 cm^{-1} increases during the water molecular adsorption. This band arises from the combination frequencies of the silanol groups hydrogen bonded with water molecules. A negative correlation between the intensities of the bands at 7318 and 4423 cm^{-1} indicates that the free silanol groups are converted to silanol groups hydrogen bonded to water molecules. This broad band did not appear during adsorption of water molecules in the sample heated at 750ºC. This is

another proof that the hydrogen bonded silanol groups are eliminated during high temperature treatment.

The adsorption of water molecules on the silica gel surface is a reversible process [26] at 200ºC. It also appears that the process is reversible even with samples heated at 500ºC. Similar changes take place in the bands throughout the spectral range during adsorption of water molecules by samples heated at 200ºC and 500ºC except the band at 4518 cm^{-1}. The intensity of the band decreases with adsorption of water molecules. It is not very clear why the band at 4518 decreases. It is possible that it has something to do with the changes in the siloxane concentration on the surface.

4. Conclusion

Near infrared spectroscopic evidence has been presented in this article to show that the adsorption of water molecules on silica gel sample takes place readily with hydrogen bonded silanol groups. The adsorption then continues by fabrication of hydrogen bonded network of water molecules that leads hydrogen bonding to the free silanol groups. The analysis shows that the first layer of adsorption consists of 4.5 molecules of water adsorbed to three silanol groups. When more water molecules are adsorbed, they form hydrogen bonding with already adsorbed water molecules. This happens even before the surface is covered by monolayer adsorption.

The bands present in the near infrared spectra of silica gel samples were easily identified by second derivative technique. This methodology has revealed some interesting features in the near infrared spectra of silica gel samples acquired during the adsorption of water molecules. Furthermore, the changes taking place on the silica gel surface in terms of functional groups during chemical reactions and physical treatment are again open for reinvestigation using second derivative spectroscopy. There are several unclear details regarding functionalities present in a silica gel sample subjected to hydrothermal treatment. It is believed that the application of second derivative technique can be employed to re-investigate changes taking place on the surface of silica gel sample subjected to hydrothermal treatment.

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Figure captions

Fig. 1. Photograph showing the placement of sample cup on the transflectance accessory for NIR measurements.

Fig. 2. A sketch showing the nature of the surface hydroxyl groups on silica gel surface.

Fig. 3. Near infrared spectra of a) Shelf silica gel (sample C) b) after heating and evacuating at 200ºC c) after heating and evacuating at 500ºC.

Fig. 4. Second derivative spectra of the spectra shown in Fig. 3 in the same order.

Fig. 5. Second derivative spectra of shelf silica gel sample and water. Scale adjusted for clarity.

Fig. 6. Second derivative spectra of the sample (dry) acquired in the region 7600-6600 cm^{-1} during adsorption of water molecules.

Fig. 7. Second derivative spectra of the sample (dry) acquired in the region 5600-5000 cm^{-1} during adsorption of water molecules.

Fig. 8. Second derivative spectra of the sample (after heating to 750ºC) acquired in the region during adsorption of water molecules. Second derivative spectrum of shelf silica gel sample C is also plotted for comparison.

Fig. 9. Plots showing the relationships between the band at wavenumber 7318 cm^{-1} and bands at 4572 and 5314 cm^{-1}.

Fig. 10. A sketch illustrating the adsorption of water molecules on silica gel surface.

Fig. 11. A plot showing the relationship between the total absorbance (intensity at 5314 and 5270 cm^{-1}) and mass of water adsorbed.

Fig. 12. A plot showing the relationship between the total absorbance (intensity at 5314 and 5270 cm^{-1}) and mass of water adsorbed.

Fig. 13. Second derivative spectra of the sample (dry) acquired in the region 4800-4200 cm^{-1} during adsorption of water molecules.

Fig. 14. Plot showing the relationship between the intensities of the bands at 5314 and 4572 cm^{-1}.

Table 1

Silica gel samples used in the experiments

Silicagel type	Surface area m^2/g	Silanol number (OH-groups/nm^2)
Sample A	402	3.1
Sample B	471	3.6
Sample C	600	2.9
Sample D	670	3.0