Near Infrared Spectroscopic study on the adsorption of methanol on silica gel

Alfred A. Christy

Department of Science, Faculty of Engineering and Science, University of Agder,
Serviceboks 422, N-4604 Kristiansand, Norway

email: alfred.christy@uia.no

Keywords: Silanol groups, methanol, Near infrared spectroscopy, second derivative profiles

Abstract. The silanol groups on Silica gel surface are sites for adsorption of polar molecules. Alcohols and other polar molecules are easily adsorbed by forming hydrogen bondings with OH groups on silica gel surface. A study on the adsorption of methanol on silica gel was carried out by using NIR spectroscopy in combination with ssecond derivative techniques.

Four of the well characterised silica gel samples were used in this study. Each of the silica gel (0.25g) samples with different surface areas and silanol number was pressed into a small disc, placed in a glass vial and the physically adsorbed water molecules from the surface of the silica gel particles were removed by heating the sample to 200 ^{o}C under vacuum. The near infrared spectra of the cooled sample was recorded by a Perkin Elmer spectrum one NIR spectrometer equipped with a transflectance accessory and a deuterated triglycine detector at a resolution of 16 cm^{-1}. The glass vial was then opened and a tiny tube filled with methanol was inserted in the glass vial. Then the near infrared spectra of the sample during the adsorption of methanol were recorded at regular time intervals until there is no apparent change in the spectra. The second derivative profiles of the spectra were obtained using the instruments' software. The mass of the silica gel pellet was determined by an analytical balance and the methanol adsorbed on the surface was calculated. The number of methanol layers on the silica gel surface was calculated using the silica gel particle characteristics of the samples.

The results show that the adsorption evolution of methanol progresses on the samples and the surface was covered by a mono layer within the first 60 minutes. Furthermore, it appears that the adsorption of multilayer on methanol starts after all the surface silanol groups are exhausted.

Introduction

The bulk of the amorphous form of silica contains interlinked SiO groups with siloxane group or hydroxyl group at the surface. During the formation of silica from silicic acid, colloidal silica particles cohere together and form particles with silanol groups on the surface. The silanol groups on the surface can be isolated silanol groups or hydrogen bonded silanol groups. The silanol groups that are closer form hydrogen bonding and lead to the formation of highly acidic hydrogen in the group.

The adsorption properties of the silanol groups are attributed to the acidic nature of the silanol groups. Polar molecules tend to adsorb on the silica gel surface by forming hydrogen bonding with the silanol groups. Adsorption of water on silica gel was the common topic on adsorption studies on silica gel surface. The characteristics of the silanol groups provide different environments on the surface for adsorption. Due to these differences the adsorbed molecules on silica gel also will have different characteristics. These differences have been studied with water molecular adsorption on silica gel [1].

Adsorption of methanol on silica gel has also been studied by several authors. Some of these involve the use of infrared spectroscopy both in mid and near infrared region [2-10]. Developments in sampling techniques have made the near infrared measurements easy and fast. Samples in powder form can easily be measured using transflectance accessory containing a single reflectance total reflectance crystal. The sample can be placed in glass vials directly on the crystal for near infrared measurements. Furthermore, developments in chemometric data handling softwares have made the resolution and analysis of the broad near infrared spectra easy and interpretation of the development in a series of evolving spectra [1] possible. Furthermore, the use of second derivative techniques in near-infrared spectroscopy to resolve underlying bands in broad peaks has become common in qualitative and quantitative analysis [1,11]. A theoretical explanation and justification for the use of second derivative techniques in spectroscopy can be found elsewhere [1]. A combination of second derivative techniques and Chemometrics was used in this work for the analysis of the evolving data during the adsorption of methanol on silica gel surface.

The intention of this work is to carry out experiments on the adsorption of methanol on silica gel surfaces, measure their near infrared spectra 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.

Experimental

Materials, preparation of pellet samples for adsorption studies and near infrared spectroscopic analysis. Two different silica gel samples with different surface areas, particle sizes and pore sizes were bought from Sigma-Aldrich (Table 1). The details and data on silanol number and surface area determination of these samples can be found elsewhere [1]

Table 1. Silica gel samples used in the experiments

Sample	**Surface area m^2/g**	**Silanolnumber**	**Number of methanol molecules adsorbed/nm^2**
Sample 1	471	3.5	6.7
Sample 2	600	3.0	6.6

A BA electric bunsen from Electrothermal, UK controlled by an external power supply was used in heating the sample under vacuum provided by a pump from Edwards, UK. A K type thermocouple connected to a digital thermometer was used in measuring the temperature of the sample. Each of the samples (around 0.25g) was placed in a mini pellet maker from Perkin Elmer and a disc form pellet was produced under a pressure of 10 tonnes. The pellet was then placed in a previously weighed glass vial with glass tube set up for evacuation and heated under vacuum at 200°C before using them in the experiments on adsorption studies. The mass of the evacuated dry pellet was recorded by difference after weighing the cooled glass vial with the pellet.

The near infrared spectrum of the pellet was made using a PerkinElmer Spectrum One NTS FT-NIR spectrometer equipped with a transflectance accessory and deuterated triglycine sulphate detector. The vial containing the sample was placed directly on the top crystal of the transflectance accessory and a total of 30 scans were made in the region 10,000–4000 cm^{-1} at a resolution of 16 cm^{-1}. Then the vial was open under a stream of nitrogen and a thin glass tube containing methanol was placed inside the glass vial. The Near infrared spectra of the pellet were then measured frequently using the same conditions of measurement as before. The reflectance spectra so obtained were converted to log (1/*R*) format and saved. The reflectance spectral profiles were then derivated twice and saved. The measurements gave a series of spectra showing the evolution of methanol adsorption on silica gel surface. The measurements continued until the scanned spectrum showed no difference in the profiles from the previous scan. These spectra were used in the detailed analysis of methanol adsorption on silica gel surface. The mass of the pellet after adsorption of methanol was determined by weighing the vial with the pellet after removing the glass tube containing methanol. The mass of the adsorbed methanol was then determined by difference in weight.

Determination of number of methanol molecules adsorbed on a silica gel surface. The mass of adsorbed methanol molecules, the mass and the surface area of the silica gel pellet were used in the determination of the number of methanol molecules (n_{CH3OH}) adsorbed per unit surface area (nm^2) at the end of an adsorption evolution experiment. The number of methanol molecules adsorbed can be calculated by the formulae.

$n_{CH3OH} = (m_{CH3OH} x N_A)/ (M_{CH3OH} x m_{s.gel} x A_{s.gel} x 10^{18})$ molecules of methanol/nm^2

(m_w= mass of methanol adsorbed in grams, m_s= mass of silica gel pellet in grams, N_A= Avogadro’s number, M_{CH3OH}=Molar mass of methanol (g/mol), A_S=surface area of the silica gel sample in m^2/g

Results and discussion

The near infrared spectra of a dry silica gel sample and methanol adsorbed silica gel sample are shown in Fig. 1. The spectra acquired from one of the samples (1) during the adsorption evolution of methanol on the surface and the second derivative profiles of the same spectra are shown (Fig. 2) in the regions 10,000-4000 cm^{-1} and 7600-6900 cm^{-1}

respectively. The spectra in Fig. 1 show that the infrared profile of the methanol adsorbed silica gel sample is very much different from the spectral profiles of the dry silica gel sample. The methanol adsorbed silica gel sample show clear evidence of the adsorbed methanol molecules on the surface. The near infrared band assignments for some of the absorptions are also given in Fig. 1.

The spectra in Fig. 2 show that the free silanol groups disappear during the first 54 minutes of methanol adsorption. The intensity of the free silanol groups plotted against the time of adsorption of methanol is shown for both samples in Fig. 3. It appears that the adsorption of methanol is slow during the first 20 minutes. Acceleration in the adsorption of methanol is clear in the next 30 minutes and then flattens after 54 minutes of adsorption. The intensity of absorption is proportional to the adsorption time.

A second derivative spectrum of silica containing adsorbed methanol together with pure methanol is shown in the region (5200-5000 cm^{-1}) Fig.4. The spectra clearly reveal that the intensities of the methanol OH stretching overtone and OH combination frequencies are weak compared to the intensities of water OH stretching overtone and combination frequencies.

This is due to the weak polarisation of the OH group in methanol. Furthermore, the combination frequencies of the methanol molecules on adsorbed on silica gel are 200 cm^{-1} red shifted. The intensity of the isolated OH overtone of the silanol groups shows greater variation during adsorption of methanol. Plots showing these variations are given in Fig 2b. The rate of decrease of the intensity of the OH overtone of silanol groups show that the adsorption rate is very slow in the beginning and follows a constant rate after a few minutes. Then it flattens out after an hour of adsorption. The combination bands of methanol OH show two different bands one around 5115 and the other around 4945 cm^{-1}. These two bands arise due to the OH combination frequencies of methanol molecules hydrogen bonded to isolated silanol groups and methanol molecules hydrogen bonded to vicinal silanol groups. Similar observations were made in the near infrared spectra of water adsorbed silica gel samples at 5314 and 5270 cm^{-1} for the respective absorptions. The band at 5270 cm^{-1} in Fig. 4 is due to the water molecules adsorbed onto the vicinal silanol groups. The observation is very interesting because the water molecules compete with the methanol molecules for the vicinal hydrogens to form hydrogen bonding. There is no evidence in the spectra that for hydrogen bonding of water molecules with isolated silanol groups. It has been shown in a previous paper [1] that the adsorption of water molecules start on the vicinal hydrogens in silica gel and then proceeds to the isolated silanol groups.

The number of methanol molecules adsorbed onto the silica gel surface until there is no apparent change in the NIR spectrum during adsorption is given in table 1. The values can be easily compared with the silanol number of the samples. The number of methanol molecules adsorbed onto silica gel samples is almost twice that of silanol number. These values well agree with the work of Yamauchi and Kondo [12]. The deviation from linearity in the intensity of the 7319 cm^{-1} peak clearly shows that there is a change in the adsorption characteristics of silica gel sample. The band due to isolated silanol groups disappear when the silanol groups on the silica gel surface are exhausted. The remaining adsorption takes place in the form discussed by Yamauchi and Kondo [12] (shown in Fig. 3).

Conclusion

It has been shown in this paper that the adsorption of methanol on silica gel can be studied by using Near infrared spectroscopy. The adsorption takes place in a similar fashion like water adsorption on silica gel. First the molecules hydrogen bonds to vicinal silanol groups and then adsorbs on to isolated silanol groups.

The intensity of adsorption is linear when methanol molecules are adsorbed as mono layer. The deviation from Linearity in absorption arises when molecules start binding on the same silanol groups. It appears that at the end of the experiments most of the silanol groups on the silica gel surface would contain more than one methanol molecule.

It is also clear from the adsorption of water molecules (trace amount in methanol) that the molecules compete for preferred hydrogen bonding with vicinal silanol groups. It appears that almost all the water molecules secure hydrogen bonding with the vicinal silanol groups on silica gel surface.

Acknowledgement

Tina Anita Engdal is thanked for infrared spectroscopic data used in this work. The experiments were conducted to confirm the previously tested experimental set up and evolutionary near infrared profiles of methanol adsorption on silica.

Corresponding Author

Alfred A. Christy; e-mail: Alfred.christy@uia.no, Tel: +47-38141502, +47-92292181

References

[1] A. A. Christy, New insights into the surface functionalities and adsorption evolution of water molecules on silica gel surface: A study by second derivative Near Infrared Spectroscopy, Vibrational Spectroscopy, Vib. Spectrosc. 54 (2010) 42-49.

[2] J.H. Anderson, K.A. Wickersheim, Near infrared characterization of water and hydroxyl groups on silica surfaces Surf. Sci. 2 (1964) 251-260.

[3] M.J.D. Low, N. Ramasubramanian, Infrared study of nature of hydroxyl groups on surface of porous glass, J. Phys. Chem. 70 (1966) 2740-2748.

[4] C. G. Armistead, A. J. Tyler, F. H. Hambleton, S. A. Mitchell and J. A.Hockey, The surface hydroxylation of silica, J. Phys. Chem., 73 (1969) 3947-3953.

[5] K. Klier, J. H. Shen, and A. C. Zettlemoyer, Silica and Silicate Surfaces. I. Partially Hydrophobic Silicas, J. Phys. Chem., 77 (1973) 1458-1465.

[6] R. P. W. Scott and S. Traiman, Solute –solvent interactions on the surface of silica-gel. 3. Multilayer adsorption of water on the surface of silica-gel, J. Chromatogr., 196 (1980) 193-205.

[7] J. Stone and G. E. Walrafen, Overtone vibrations of OH groups in fused silica optical fibers, J. Chem. Phys., 76 (1982) 1712-1722.

[8] H.P. Boehm, Chemical Identification of SurfaceGroups, Advances in Catalysis, 16 (1966) 179-274.

[9] P. Hoffman, E. Knozinger, Novel aspects of IR Fourier spectroscopy, Surf. Sci., 188 (1987) 181-198.

[10] B.A. Morrow, I.A. Cody, L.S.M. Lee, Infrared studies of reaction on oxide surfaces.7. Mechanism of the adsorption of water of dehydroxilated silica, J.Phys.

Chem., 80 (1976) 2761-2767.
[11] A. A. Christy, Effect of Hydrothermal Treatment on Adsorption Properties of Silica Gel, Ind. Eng. Chem. Res. 50 (2011) 5543-5554.
[12] H. Yamauchi and S. Kondo, The structure of water and methanol adsorbed on silica gel by FT-NIR spectroscopy, Colloid Polym. Sci., 266 (1988) 855-861.

Fig. 1

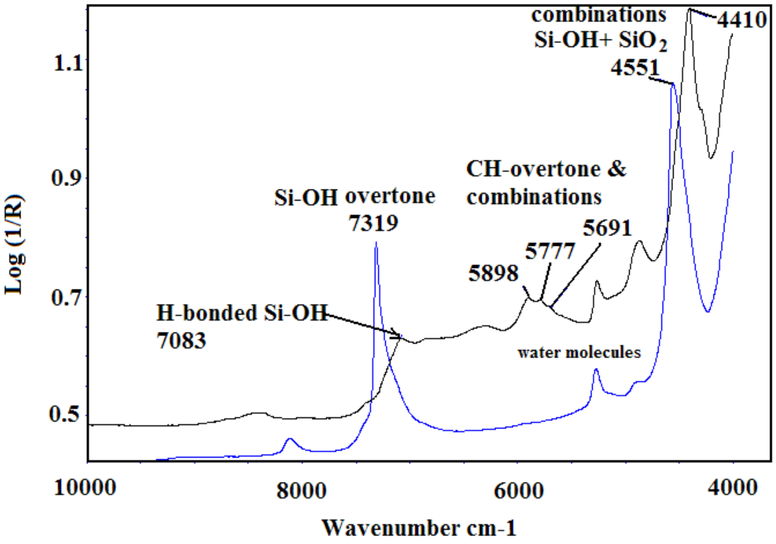

Fig. 1.The near infrared spectra of a dry silica gel sample and methanol adsorbed silica gel sample

Fig. 2

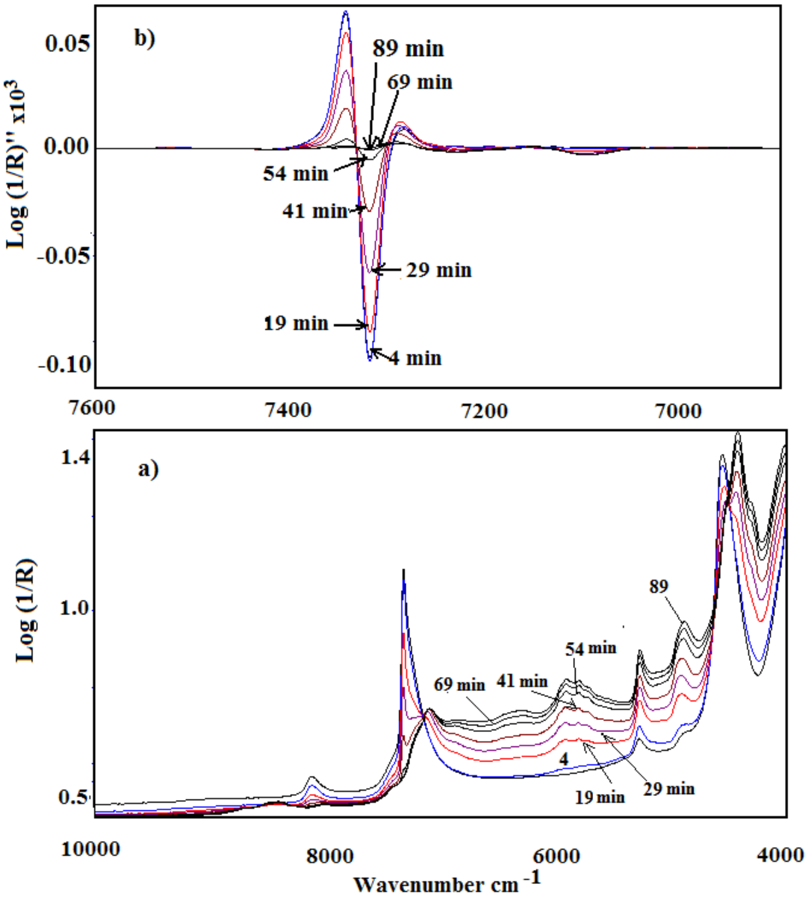

Fig.2. The spectra acquired from one of the sample 1 during the adsorption evolution of methanol on the surface (a) and the second derivative profiles of the same spectra (b)

Fig.3

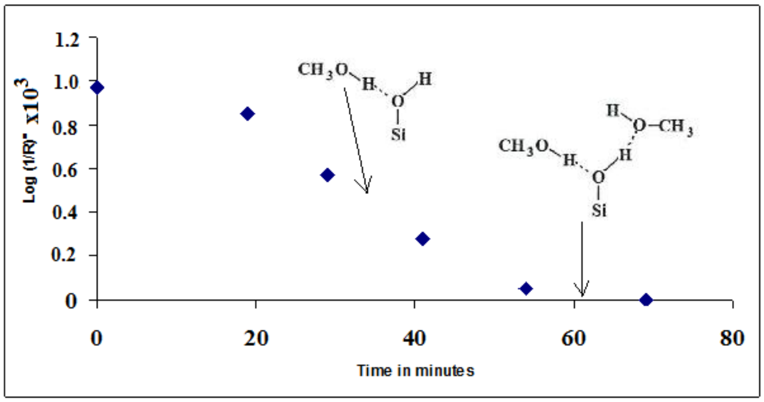

Fig. 3. The intensity of the free silanol groups plotted against the time of adsorption

Fig. 4

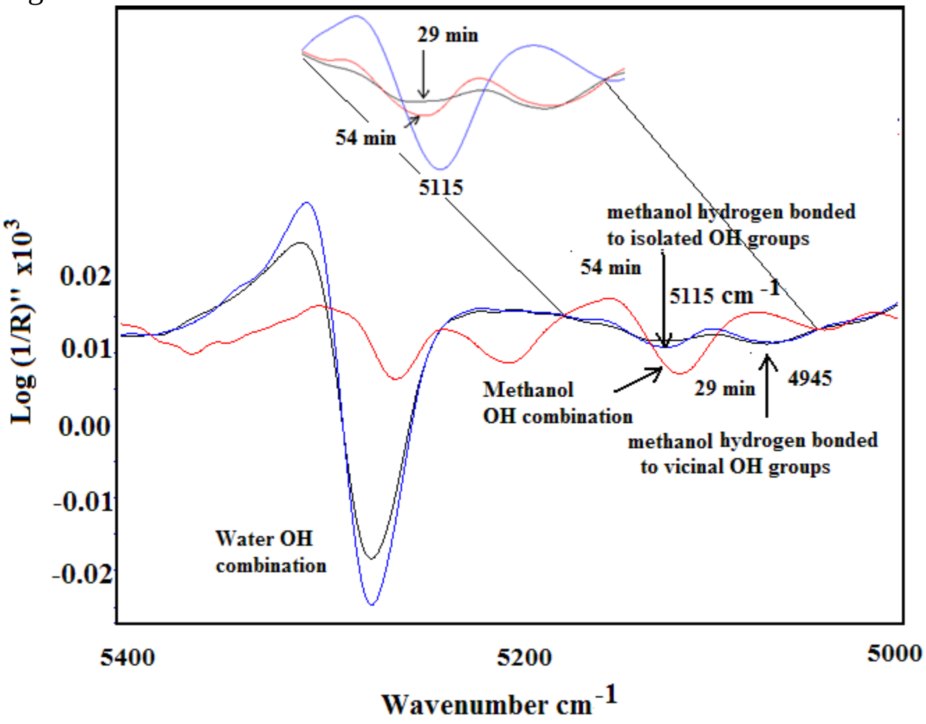

Fig. 4. Second derivative spectrum of silica containing adsorbed methanol together with pure methanol is shown in the region 5200-5000 cm^{-1}