

Surface Functionality and Water Adsorption Studies of α -Aluminium (III) Oxide Nanoparticles by Near Infrared Spectroscopy

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Abstract. The adsorption of water on aluminium (III) oxide nanoparticle surface was studied by near infrared (NIR) spectroscopy. The comparison of NIR spectra at 40% and 60% humidity were reported in this work and were analyzed using second derivative techniques. The second derivative spectra were used to understand the chemistry of adsorption of water molecules. Small amounts of samples were dried under vacuum at 230 °C before the analysis. The analysis of the spectra confirms the presence of three different hydroxyl groups on aluminium (III) oxide surface. The spectra acquired during the adsorption of water molecules show the characteristic peaks in the range of 5400-5100 cm^{-1} corresponding to the combination band of water molecules hydrogen bonded with hydroxyl groups. There is also evidence for the presence of free water in the bulk of aluminium oxide. Furthermore, the mass of water adsorption on Al_2O_3 nanoparticle surface have been determined by gravimetric analysis. The gravimetric analysis confirms the adsorption of water molecules by aluminium (III) oxide surface.

Introduction

Aluminium (III) oxide is the chemical compound that has been reported for a longtime as one of the important materials in several fields such as ceramics, pigments, cosmetics [1], and catalysis [2]. Nevertheless, it has also been used in the removal water in the gas purification process [2]. In all these applications, the hydroxyl groups on the aluminium oxide surface plays an important role. The study of aluminium (III) oxide surface was reported in previous researches that revealed the existence of hydroxyl groups on surface [3, 4, 5]. The Knözinger-Ratnasamy model explains the difference in the Al-OH groups and it is the most widely accepted model of the aluminium oxide surface [3]. This model mentions about the terminal hydroxyl groups on alumina surface. The hydroxyl polar surface of aluminium (III) oxide has a tendency to adsorb polar molecules such as water. Thus, the adsorption properties of aluminium (III) oxide lead to a large number of studies of its surface.

Adsorption of water molecules on aluminium (III) oxide has been reported by various authors [5, 6]. These authors reported hydrogen bonding between water molecules and hydroxyl groups on aluminium (III) oxide surface and showed hexagonal structure of water molecules on the surface. Christy [7] has studied the adsorption of water molecules by different surfaces using near infrared spectroscopy. His contribution and insight in this regard have provided ways to identify different species of hydroxyl groups on different surfaces of materials.

In this study, we investigated the surface functionality and water adsorption on α -aluminium (III) oxide nanoparticle surface by near infrared spectroscopy. The second derivative near infrared spectra were used to study the underlying features in the spectra and to reveal and resolve the types of hydroxyl groups on aluminium oxide surface. In addition, gravimetry was used in the determination of mass of water adsorbed on the surface.

Experimental

Materials and sample preparation. Al₂O₃ nanoparticle was purchased from Aldrich. A ceramic heater (BA electric Bunsen from Electrothermal, UK) was used to heat the samples. A powerful vacuum pump (Edwards, UK) was used in the evacuation process of the samples. The temperature of sample was recorded by a digital thermometer with K type thermocouple (Clasohlson, UK). All of samples were dried and evacuated at 230 °C before using them in the experiments. Undried Al₂O₃ samples are adverted to be shelf samples in the text. Each sample was dried as mentioned above and transferred to a sample cup with IR transparent ZnSe window.

Near infrared measurements. The spectra were measured by PerkinElmer Spectrum One NTS FT-NIR spectrometer (PerkinElmer Ltd., UK) equipped with a PerkinElmer transreflectance accessory and deuterated triglycine sulphate detector. The sample cup was directly placed on the transreflectance accessory and the NIR spectrum of the sample was measured in the region 10,000 to 4000 cm⁻¹ at a resolution of 16 cm⁻¹. A total of 20 scans were made each time. Then each sample was allowed to adsorb water molecules from humidity controlled atmosphere. The relative humidity was controlled by glycerol/water system [8]. The relative humidity of 40% and 60% were applied in the adsorption experiments and NIR measurements. The NIR spectra were derivated twice and saved [9]. The second derivative profiles of the NIR spectra were used in the identification of surface hydroxyl groups on the Al₂O₃ nanoparticles. The NIR spectral measurements were stopped when there was no apparent change in the intensity of absorption in the 5000-5400 cm⁻¹ region arising from the adsorption of water molecules. The humidity control chamber was removed and the NIR spectral measurements were continued until the adsorption of water molecules remained unchanged.

Mass of water adsorbed. The water adsorption was also carried out by using an analytical balance which was connected to a computer that recorded a mass change of every 0.0001 g with time. A portion of the dried sample (about 0.2 g) was quickly transferred to a pre-weighed sample cup and the cup was placed in the balance. The mass of each sample was continuously measured over a period of about 30 min. The sample was exposed to air that had a selected humidity. After 30 minutes of adsorption, the sample was exposed to room humidity and the mass recording continued until there was no change in the mass.

Results and Discussion

The near infrared spectra of alumina nanoparticle samples were measured in region 10,000-4,000 cm⁻¹. The NIR spectra of pure water, dried sample, shelf sample and wetted sample are shown in Fig.1. The spectrum of dried sample shows sharp peaks at 7296 and 7210 cm⁻¹ that are due to the first overtone of the OH stretching of Al-OH groups on the aluminium (III) oxide surface. This is in agreement with the literature reports [3-5]. The spectrum of shelf sample represents a sharp peak at 7225 cm⁻¹ of the first overtone of Al-OH hydrogen bonded to water molecules. This band shifts to higher wavenumber compared with the peak from the dried sample. Moreover, broad band next to 7210 cm⁻¹ is the overtone of water molecules hydrogen bonded to Al-OH groups, and water hydrogen bonded to other water molecules. The characteristic band of water adsorption on aluminium (III) oxide surface appears in the region 5400-5000 cm⁻¹ that represents the combination band of OH stretching and bending of water molecules. A sharp peak at 5312 cm⁻¹ is due to the combination frequencies of OH stretching of water molecules bonded to terminal Al-OH group. The neighboring broad band is the combination frequencies of OH stretching and bending vibrations of water molecules hydrogen bonded to other forms of Al-OH groups. This broad peak can also contain combination frequencies of the hydrogen bonded free water molecules. The last region (4900-4200 cm⁻¹) presents the combination band of Al-OH groups. The band assignments for aluminium (III) oxide with adsorbed water are shown in Table 1.

The second derivative spectra of dried and water adsorbed sample are shown in Fig. 2. There are five different absorptions but three are strong and significantly different absorptions (7362, 7294 and

7211) of the first overtone of the Al-OH groups in the dried sample. This is in agreement with the Mid-IR spectra of aluminium oxide published in references 4, 10, 11 and 12. This indicates that there are three significantly different OH groups on the aluminium oxide surface. These OH groups are terminal, bridged and tri-bridged with Al atom [12]. The shelf sample has three absorptions at 7214, 7240 and 7215 cm^{-1} . The shift in the frequency towards lower number is the effect of water adsorption by these OH groups [7]. Moreover, the spectrum of shelf sample clearly shows the combination band of the OH groups of water molecules hydrogen bonded to Al-OH groups (5316, 5230 and 5191 cm^{-1})

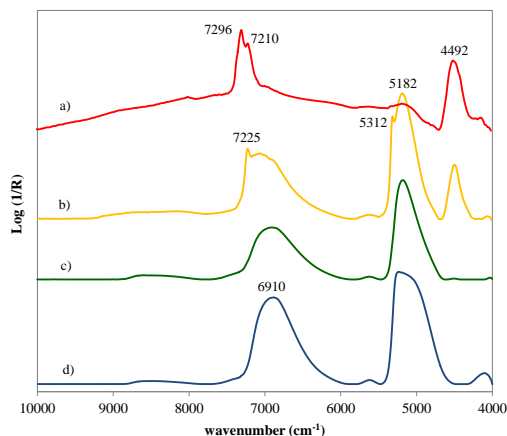


Fig.1 Near infrared spectra of aluminium (III) oxide; (a) dried sample, (b) shelf sample, (c) wetted sample and (d) pure water spectrum

Table 1 Near infrared band assignments of shelf aluminium (III) oxide

Wavenumbers (cm^{-1})	Band assignment
7362, 7294, 7211, 7210	Overtone -OH stretching of Al-OH groups
7200-6900	Broad band of overtone OH stretching of water H-bonded to Al-OH and water H-bonded to other water molecules
5500-4500	Combination band-OH stretching and bending of water molecules hydrogen bonded to Al-OH groups
5182	Combination band OH stretching and bending of free water molecules
4492	Combination band OH stretching and bending of Al-OH groups

The adsorption evolution of water molecules on aluminium (III) oxide surface provides information regarding the surface Al-OH groups. The NIR spectra acquired during the adsorption evolution of water on aluminium (III) surface at 40% and 60% relative humidity are shown in Fig. 3. The second derivative spectra in the region 7500-7100 cm^{-1} and in the region 5400-5100 cm^{-1} are shown Fig. 4a and 4b, respectively. The bands at 7362, 7294 and 7211 cm^{-1} decrease in intensity with the adsorption of water molecules. The adsorption evolution of water as shown by the absorption in the 5400-5100 cm^{-1} region is relatively fast and gives an interesting detail. Fig. 4b clearly shows the differences in water molecules adsorbed onto the surface. The water molecules are adsorbed by the Al-OH groups through hydrogen bondings. There is only one clear sharp peak for water adsorption (5316 cm^{-1}) and this is due to the terminal Al-OH groups on the surface and the water molecules are hydrogen bonded through oxygen atom. The broad band appears by the side of the band at 5316 cm^{-1} with peak maximum at 5230 and 5191 cm^{-1} . These arise from the adsorption of water molecules hydrogen bonded to bridged and tri bridged Al-OH groups.

The surface of aluminium (III) oxide was saturated with water molecules after 40 minutes of adsorption. The sharp band at 5316 cm^{-1} and the neighbouring broad band increase in intensity. These bands decreased in intensity when the samples were brought to the room humidity. This observation illustrates that the mass of water molecules adsorbed is humidity dependent. Furthermore, the

decrease in intensity of the broad band shows that there are water molecules weakly bonded to water molecules adsorbed on the aluminium oxide surface.

The mass of water adsorbed on aluminium oxide surface was determined by gravimetric analysis. The results are presented in Fig. 5 for relative humidities of 40 and 60%. The adsorption of water takes place at a higher rate at 60% relative humidity compared to 40% relative humidity. The figures also show the decrease in the mass of water adsorbed when the samples were brought to room humidity. The real mass of water adsorbed on aluminium (III) oxide surface at 40% and 60% relative humidity are 0.040 and 0.055 g/g, respectively.

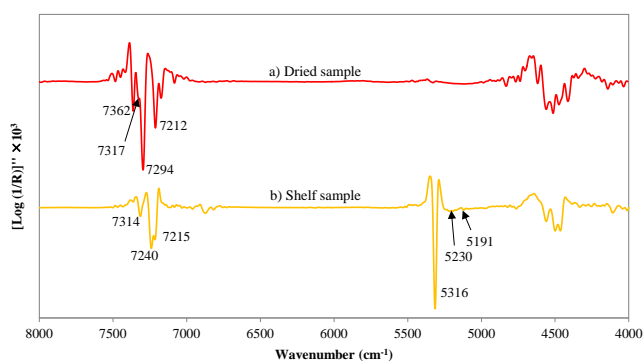


Fig. 2 Second derivative profiles of NIR spectra of aluminium (III) oxide; (a) dried sample, and (b) shelf sample

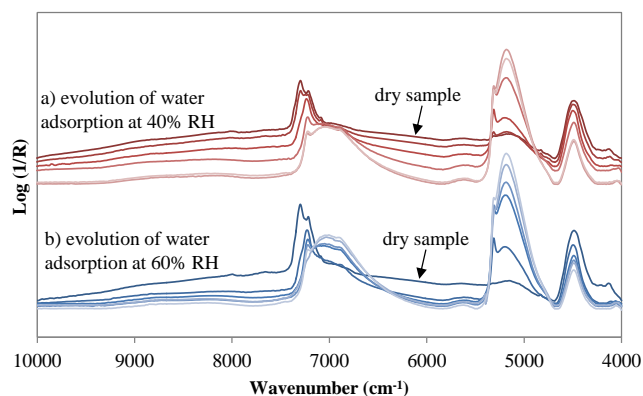


Fig. 3 Near infrared spectra of aluminium (III) oxide obtained during adsorption of water; (a) at 40% relative humidity and (b) at 60% relative humidity (0, 1, 2, 3, 5, 10 and 20 min)

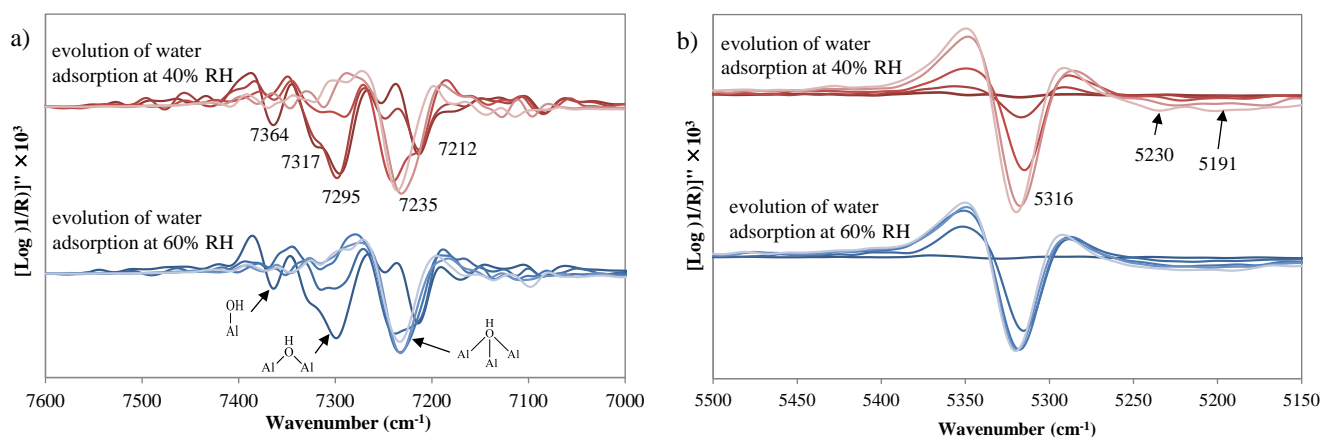


Fig. 4 Second derivative of Fig. 3 shown in the region; (a) 7500-7100 cm^{-1} and (b) 5400-5100 cm^{-1} (0, 1, 2, 3, 5, 10 and 20 min). Red line and Blue line represent the evolution of water at 40% and 60% RH, respectively

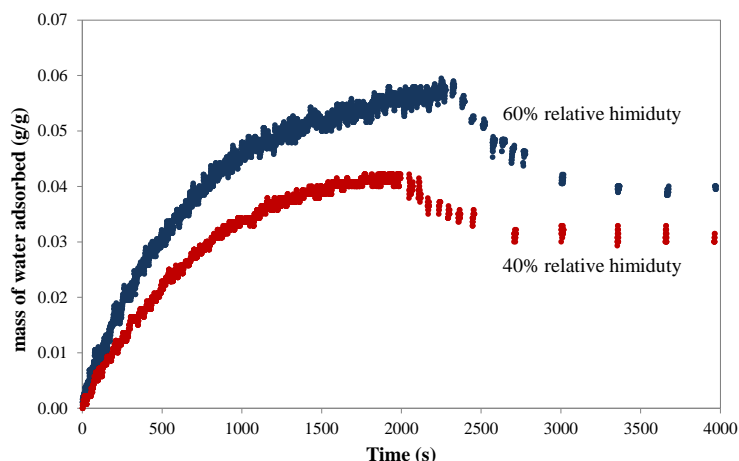


Fig. 5 Mass of water adsorbed on aluminium (III) oxide surface at 40% and 60% relative humidity

Conclusion

The functionality and adsorption evolution of water molecules on aluminium (III) oxide surface were studied using near infrared spectroscopy. The near infrared spectra and the second derivative profiles confirm that there are three significantly different Al-OH groups on the oxide surface. The sharp peak at 5316 cm^{-1} arising from the adsorption of water molecules confirms that one of the Al-OH groups behaves like a free Al-OH group. The bridged Al-OH and tri-bridged Al-OH groups do not provide single peaks in the combination frequency region. These involve in hydrogen bondings with more than one water molecule because of their higher acidities and results in the formation of broad bands that fall in the region $5250\text{-}4500\text{ cm}^{-1}$. The rate of adsorption of water by aluminium oxide at 60% relative humidity is 30% more than the mass adsorbed at 40% relative humidity.

The study clearly shows that the NIR spectroscopy with second derivative techniques provide an efficient and interesting methodology to study the water molecular adsorption by polar surfaces. Furthermore, the adsorption study carried out in this manner would provide understanding of the types and characteristics of the different OH groups (or polar groups) on the adsorbing surface.

References

- [1] L. C. Becker, I. Boyer, W. F. Bergfeld, D. V. Belsito, R. A. Hill, C. D. Klaassen, D. C. Liebler, J. G. Marks Jr, R. C. Shank, T. J. Slaga, P. W. Snyder, and F. A. Andersen, *International Journal of Toxicology* Vol. 35(Supplement 3). (2016), p. 16S-33S.
- [2] L. K. Hudson, C. Misra, A. J. Perrotta, K. Wefers, F. S. Willians, *Ullmann's Encyclopedia of Industrial Chemistry* Vol 2. (2000), p. 607-645.
- [3] D. B. Mawhinney, J. A. Rossin, K. Gerhart and J. T. Yates Jr, *Langmuir* Vol 16. (2000), p.2237-2241.
- [4] C. Morterra and G. Magnacca, *Catalysis Today* Vol. 27. (1996), p. 497-532.
- [5] N. G. Petrik, P. L. Huestis, J. A. LaVerne, A. B. Alexandrov, T. M. Orlando and G. A. Kimmel, *The Journal of Physical Chemistry C* Vol. 122 (17). (2018), p. 9540–9551.
- [6] P. Thissen, G. Grundmeier, S. Wippermann and W. G. Schmidt, *Physics review B* Vol. 80 (2009), p. 245403: 1-6.
- [7] A. A. Christy, *Advances in Natural and Applied Sciences* Vol. 14 (2015), p. 14-19.
- [8] C. F. Forney and D. G. Brandl, *HortTechnology* Vol. 2(1). (1992), p. 52-54.
- [9] A. A. Christy, *Vibrational Spectroscopy* Vol. 54. (2010), p. 42-49.
- [10] www.innovaltec.com/aluminium-oxide-surfaces-blog/, accessed on 3rd Nov.2018.
- [11] J. B. Peri, and R. B. Hannan *J. Phys. Chem.* Vol. 64 (1960), pp 1526–1530.
- [12] A. A. Tsyganenko and V. N. Filimonov *J. Mole. Str.* 19 (1973) 579-589.