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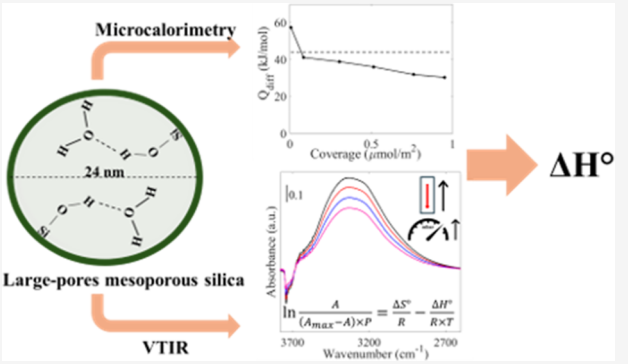
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ABSTRACT: The heat of water adsorption on large-pores mesoporous silica suitable for hemostatic applications has been assessed. The values were determined by means of microcalorimetry (as differential heat of adsorption, Q_{diff}, at 318 K) and variable temperature IR (VTIR) spectroscopy through the thermodynamic analysis of spectroscopic data based on the van't Hoff equation (as standard enthalpy of adsorption, ΔH^0, in the temperature range 318−360 K). The results obtained by the two different techniques are in satisfactory agreement, leading to a value of the water heat of adsorption between 30 and 37 kJ/mol, ascribed to the interaction of water molecules with terminal silanols via one H-bond. The heat of water adsorption (below 44 kJ/mol) reveals that the surface of the large-pores mesoporous silica herein investigated may be considered mainly hydrophobic. For the first time, VTIR spectroscopy of water adsorption has been applied for the characterization of the surface hydrophilicity/hydrophobicity of a silica material.



INTRODUCTION

Mesoporous silicas are still considered interesting and very promising materials due to their tunable physicochemical properties that can be employed in a wide range of applications such as catalysis, adsorption, and chemical separation.[1] In particular, in the last two decades, various biomedical applications of mesoporous silica particles have been explored including diagnosis, drug delivery, antitumor therapy, bone disorders, and hemostasis.[2,3] In this contest, large-pores mesoporous silicas have been shown to have excellent hemostatic properties,[3] achieving rapid hemostasis also due to their ability to adsorb a large amount of water.

Water adsorption represents a crucial factor in the mechanism of hemostasis, and indeed other inorganic silica-based materials characterized by high water adsorption capacity, such as zeolites, have been proposed and used as hemostats. Unfortunately, the adsorption of water on zeolitic materials can be highly exothermic, due to the strong interactions between the water molecules and the adsorption sites, which may cause severe undesired side-effects such as thermal injury of the surrounding tissue at the bleeding site.[3]

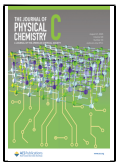
The heat of water adsorption is therefore a fundamental parameter for a feasible use of large-pores mesoporous silicas as hemostats and, in general, for biomedical applications of these materials, where the interaction of the surface with the water molecules of a biological medium occurs.

The heat of water adsorption on materials in the powder form can be directly assessed by means of microcalorimetry.[4,5] Microcalorimetry has been used to measure the molar heat of adsorption, as differential heat of adsorption, of water on several amorphous and crystalline silicas and zeolitic materials.[6−8] Usually, a molar heat of adsorption of 44 kJ/mol (i.e., the enthalpy of liquefaction of water) is considered as a threshold value to distinguish between hydrophilic (>44 kJ/mol) and hydrophobic (<44 kJ/mol) materials.[4,9]

An alternative route to evaluate the heat of adsorption of molecules is represented by spectroscopic analysis of the adsorption at variable temperatures. In particular, variable temperature infrared (VTIR) spectroscopy of adsorbed species, through the thermodynamic analysis of spectroscopic data based on the van't Hoff equation, can yield accurate values of both the standard enthalpy of adsorption, ΔH^0, and the corresponding change in entropy, ΔS^0.[10] This approach was used to investigate the adsorption thermodynamics of small molecules, such as carbon monoxide, dinitrogen, and dihydrogen, on zeolites and MOFs.[10,11] VTIR was also used to study the adsorption of ammonia molecules from the vapor phase on the surface of amorphous silica.[12]

Moreover, water adsorption on MgO was investigated by infrared spectroscopy in the temperature range 313−363 K by Foster et al.[13] and the thermodynamic analysis of data allowed

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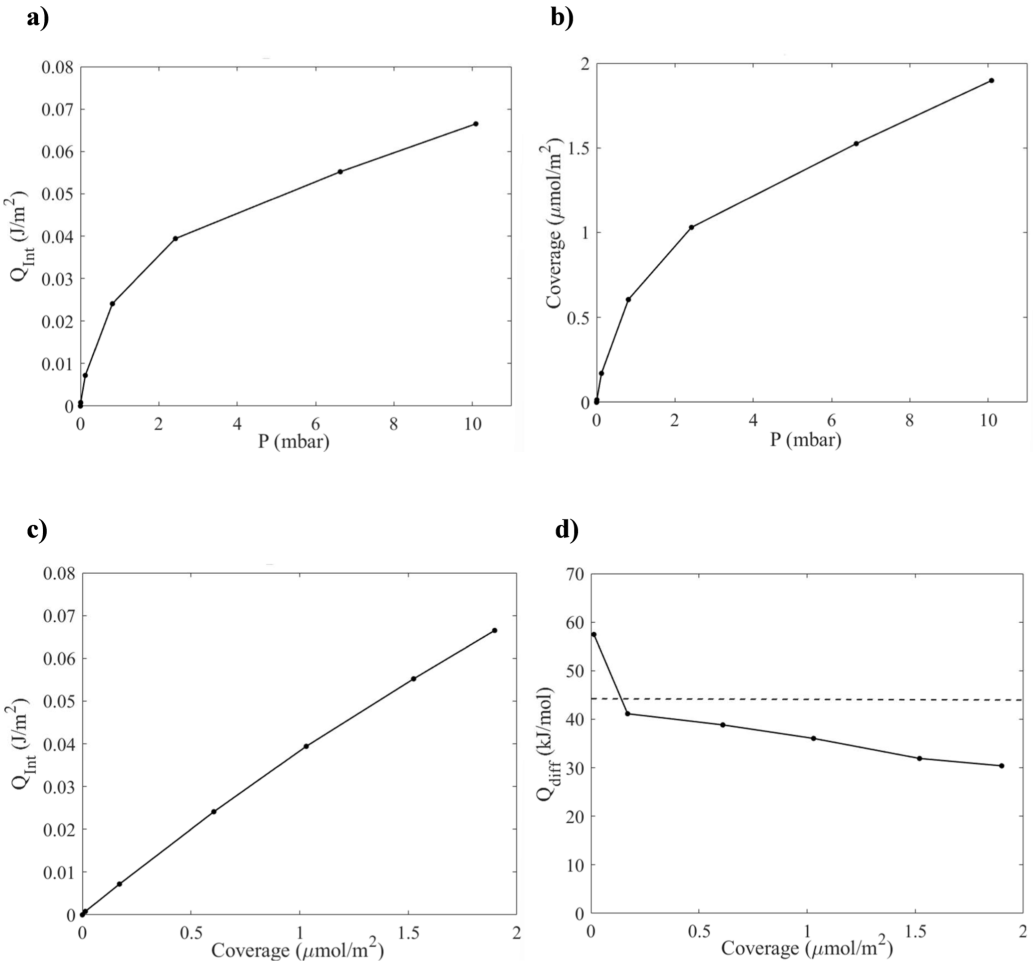


Figure 1. Adsorption microcalorimetry of water at 318 K on large-pores mesoporous silica previously outgassed at 423 K. (a) Calorimetric isotherm; (b) volumetric isotherm; (c) integral heat of adsorption as a function of coverage; (d) differential heat of adsorption as a function of coverage.

evaluating the enthalpy of adsorption. This previous study suggests the feasibility of using VTIR to estimate the water adsorption heat.

To the best of the present authors' knowledge, VTIR was never used before to characterize the adsorption of water molecules on the silica surface. The present work reports for the first time the characterization of water molecules adsorption on a large-pores mesoporous silica, which was previously shown to possess valuable hemostatic properties,[14] by means of a joint microcalorimetry and VTIR spectroscopy study.

The relevance of the results herein presented concerns not only the measure of the heat of water adsorption, enriching the knowledge about this class of materials in view of their use as novel hemostats, but it is also the first example of the evaluation of the heat of adsorption of water on a silica surface by VTIR. It is shown that the IR spectroscopic investigation of the interaction of surface silanols with water molecules at variable temperature is a powerful tool to determine the thermodynamic features of the adsorption process.

EXPERIMENTAL SECTION

Materials. Pluronic P123, tetraethyl orthosilicate (TEOS, 99.999% trace metals basis), hydrochloric acid (ACS reagent, 37%), potassium chloride (purity ≥99,0%), and mesitylene (98%) were provided by Sigma-Aldrich (St. Louis, MO, USA). Water (LC−MS grade) was purchased from Merck (Billerica, MA, USA).

Synthesis and Characterization of Large-Pores Mesoporous Silica. The large-pores mesoporous silica was prepared as previously reported by Mohamed et al.[14] except for the amount of reactants, which was doubled. Briefly, 240 g of H_2O (LC−MS grade) were mixed with 47.2 g of HCl (37% w/w), followed by the addition of 8.0 g of Pluronic P123 and 12.2 g of KCl. After that, 6.0 g of mesitylene was added and the solution was stirred for 2 h. Then, 17 g of TEOS was added dropwise and the mixture was stirred vigorously for 10 min. The final molar ratios of TEOS/P123:mesitylene/KCl/HCl/H_2O were equal to 1:0.017:0.6:2:5.85:165. The mixture was kept under static condition at 308 K for 24 h, it was then transferred into a sealed PTFE bottle and maintained at 373 K for 24 h. The resulting solid precipitate was recovered by filtration, washed with distilled water, and dried at 333 K in an oven overnight. The dried material was calcined in a muffle furnace at 773 K for 6 h (heating rate of 15 K/min) to remove the template.

Textural properties were evaluated through the nitrogen adsorption−desorption isotherm at 77 K, using a Micromeritics ASAP 2020 Plus Physisorption analyzer (Micromeritics, Norcross, GA, USA). Before the adsorption measurement, the sample was outgassed at 423 K for 2 h. The specific

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surface area (SSA) was calculated using the Barret-Emmett-Teller (BET) method in the relative pressure range of 0.10−0.20. The total pore volume was determined at a relative pressure of about 0.99. The pore size distribution curve was achieved through the density functional theory model, and the average pore size was determined. The values of the BET SSA, pore volume, and average pore diameter were 539 m^2/g, 1.01 cm^3/g, and 24 nm, respectively.

Adsorption Microcalorimetry of Water. Adsorption microcalorimetric analyses were performed by using a Tian-Calvet heat flow calorimeter (C80D, Setaram) equipped with a volumetric vacuum line. Each sample (0.1 g, 40−60 mesh) was first evacuated under dynamic vacuum at 423 K for 12 h (residual pressure ca. 2×10^{-5} mbar), then the analysis was performed at 318 K introducing successive doses of water previously degassed. After each dose, the thermal effect of the adsorption was recorded and the corresponding equilibrium pressure was measured by means of a capacitance pressure gauge (CERAVAC, Lybold). The analysis was carried out until an equilibrium pressure of about 10 mbar was reached. From the experimental data, plots of the volumetric isotherm (relating the amount of water adsorbed to the corresponding equilibrium pressure) and the calorimetric isotherm (relating the integral heat of adsorption to the corresponding equilibrium pressure) were obtained.

IR and VTIR Spectroscopy of Water Adsorption. VTIR spectroscopy was performed using a commercial IR cell (AABSPEC) equipped with a capacitance pressure gauge (CTR100, Oerlikon-Leybold) and an electronically controlled heating element. The temperature inside the cell was measured by means of a K-thermocouple, placed directly in contact with the sample, connected to a digital thermometer (CHY 502 A, Tersid). For VTIR measurements, a thin autosupported pellet of the large-pores mesoporous silica sample, prepared by pressing the powder with a hydraulic press, was inserted inside the IR cell. The sample was outgassed in dynamic vacuum (residual pressure $<10^{-3}$ mbar) for 30 min at 423 K; then the cell was cooled down to 318 K and a blank spectrum of the pellet was recorded. After that, the IR cell was dosed with an increasing amount of H_2O (equilibrium pressure varying from 1 to 12 mbar), and a series of IR spectra were recorded at constant temperature (318 K). Then, the IR cell was closed and the IR spectra were acquired at different fixed temperatures, in the range 318−360 K, simultaneously recording the temperature and the water equilibrium pressure. All IR spectra were acquired from 4000 cm^{-1} to 600 cm^{-1}, with a resolution of 2 cm^{-1}, using an Equinox 55 spectrometer (Bruker, Billerica, MA, USA), equipped with a MCT cryo-detector.

The FT-IR spectrum was fittedwith a log−normal function in the wavenumber range 3760−3690 cm^{-1} after subtracting the baseline,using FityK 1.3.1 software.

RESULTS AND DISCUSSION

Adsorption Microcalorimetry of Water. Adsorption microcalorimetry is one of the classical techniques for experimental determination of the heat of water adsorption. The adsorption of water on silicas and silica-based materials is mainly governed by H-bonding with surface silanols.[9] Heats of adsorption in the range 60−90 kJ/mol were usually associated with the strong interaction of molecular water on pairs of silanols, with water acting as both an H-bond acceptor and donor. Heats of adsorption lower than 44 kJ/mol, i.e., the enthalpy of water liquefaction, were ascribed to the very weak interaction of water molecules with silanols through a single H-bond.[9,15,16]

Figure 1 reports the microcalorimetric data of water adsorbed at 318 K on the large-pores mesoporous silica, previously outgassed at 423 K. Combining the calorimetric (Figure 1a) and the volumetric (Figure 1b) isotherms, a plot of the integral heat of adsorption (Q_{int}) as a function of coverage (Figure 1c) can be drawn. A description of the influence of the surface coverage on the energetics of the adsorption can then be obtained by calculating the differential heat of adsorption (Q_{diff}), which represents the molar heat of adsorption, and reporting it as a function of coverage (Figure 1d).

Only at the initial coverage of 0.014 $\mu mol/m^2$, corresponding to 0.0084 molecules/nm^2, the differential heat of adsorption, Q_{diff}, approaches the value of 60 kJ/mol (Figure 1d), which may be ascribed to the presence of sites able to adsorb a water molecule through two H-bonds.[6]

For coverages between ca. 0.17 $\mu mol/m^2$ and 1.9 $\mu mol/m^2$ (corresponding to 0.10 and 1.14 molecules/nm^2, respectively), Q_{diff} remains constantly below 44 kJ/mol (dashed line in Figure 1d), reaching a value of about 30 kJ/mol at the highest coverage of 1.9 $\mu mol/m^2$, which corresponds to an equilibrium pressure of ca. 10 mbar.

Considering that 44 kJ/mol for the heat of water adsorption is the threshold value that allows solid adsorbents to be classified as hydrophilic (>44 kJ/mol) or hydrophobic (<44 kJ/mol),[9] the observed trend of Q_{diff} as a function of coverage indicates that the surface of the large-pores mesoporous silica is predominantly hydrophobic.

Moreover, the values of the differential heat of adsorption suggest that the interaction of the water molecules with the surface silanols occurs to a much greater extent via one H-bond.[9] In fact, experimental values of the heat ascribed to the interaction of water molecules with terminal silanols via one H-bond have been observed in the range 25−35 kJ/mol,[17] and ab initio calculations gave a value of ca. 32 kJ/mol for the binding energy.[18] The slightly decreasing trend observed for Q_{diff} (Figure 1d) may be ascribed to differences in the H-bonding strength for the surface silanols. For instance, it is known that H-bond acceptor silanols in H-bonded silanols pairs or chains are slightly more acidic than isolated silanols[19] and computational results revealed that this affects the heat of water adsorption.[20]

It is worthy to note that the heat of water adsorption on the large-pores mesoporous silica presented here, characterized by an average pore size of 24 nm, is definitely lower than that reported for the MCM-41 mesostructured silica (50−70 kJ/mol) at similar coverages (between 0.1 and 2 $\mu mol/m^2$).[19,21] This may be at least partially ascribed to the effect of the curvature of the surface inside the pores, according to the finding that the heat of adsorption increases as the pore size decreases.[22] Indeed, the MCM-41 samples investigated in the previous studies[19,21] were characterized by pores with a significantly smaller size (3.5−4.5 nm) compared to the present silica sample.

Eventually, a final comment may be devoted to the absence of water capillary condensation inside the mesopores. Capillary condensation of water in mesopores with dimensions between 5 and 7 nm was observed to occur at relative humidity higher than 50%.[23] Assuming a value of saturation pressure of water at 318 K equal to about 95.9 mbar,[24] capillary condensation is not expected to occur at pressures lower than 47−48 mbar. Moreover, considering that the mesopores of the silica herein

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investigated are significantly larger than 7 nm, capillary condensation of water in mesopores is expected to occur at pressures that are higher than those used in the present study.

IR Spectroscopy of Water Adsorption at Constant Temperature. Figure 2 reports the IR spectrum, in the silanol stretching region, of the large-pore mesoporous silica previously outgassed at 423 K.

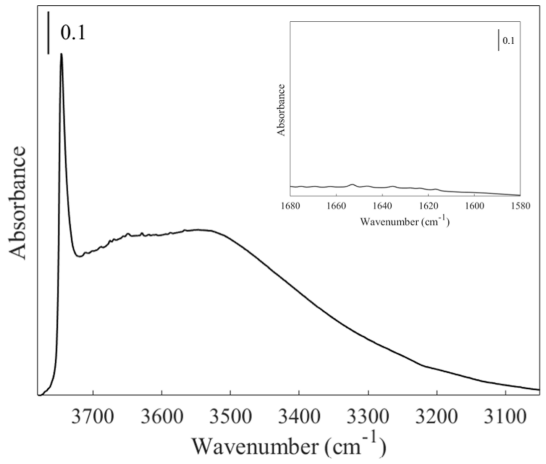


Figure 2. FT-IR spectrum of the large-pores mesoporous silica outgassed at 423 K in the hydroxyls stretching region (the inset refers to the range 1680−1580 cm^{-1}).

The spectrum is typical of amorphous silica,[25,26] where two regions can be observed: the region of the free OH silanols, with a narrow band showing the maximum at 3746 cm^{-1}, and the region at lower wavenumbers, in the 3700−3100 cm^{-1} range, with a broad and complex absorption band due to proton donor, hydrogen-bonded silanols. A fundamental characteristic of H-bonds is that silanols acting as proton donors suffer a bathochromic shift compared to free OH groups, with the magnitude of this shift depending on the strength of the interaction, which is correlated to the hydrogen-bond distance.[27]

The region above 3700 cm^{-1} includes also the stretching mode of H-bond acceptor silanols (which are only proton acceptors, with their own proton not involved in H-bonding). They are known to absorb at lower wavenumbers than free silanols, approximately in the 3730−3700 cm^{-1} range[28,29] and to be slightly more acidic than free silanols.[25] We will refer to all of the silanols responsible for absorptions above 3700 cm^{-1} as "terminal silanols".

For the sake of completeness, the range where the band due to the water bending mode may be observed (1680−1580 cm^{-1}) is reported in the inset of Figure 2. No significant absorption is observed, revealing that the thermal treatment under vacuum was effective in removing adsorbed molecular water.

Prior to the recording of IR spectra of adsorbed water at variable temperatures, water vapor adsorption has been monitored at constant temperature, collecting spectra at increasing equilibrium pressures. The values of the intensity of the absorption band and the corresponding equilibrium pressure can be used to draw a Langmuir plot. This allows the validity of the Langmuir model to be verified in the analysis of the spectroscopic data, at least in the ranges of temperature and pressures used for the VTIR study. The reason for this preliminary measurement is that the fundamental of the thermodynamic analysis of spectroscopic data at variable temperature based on the van't Hoff equation is that the intensity of a characteristic IR absorption band (assumed to be proportional to the coverage) and the corresponding equilibrium pressure may be used to determine or to express the equilibrium constant of the adsorption. This is reliable and straightforward if the adsorption process may be described by the Langmuir model.[10]

Figure 3 reports the difference IR spectra of adsorbed water in the 3780−2600 cm^{-1} range, obtained after subtracting the

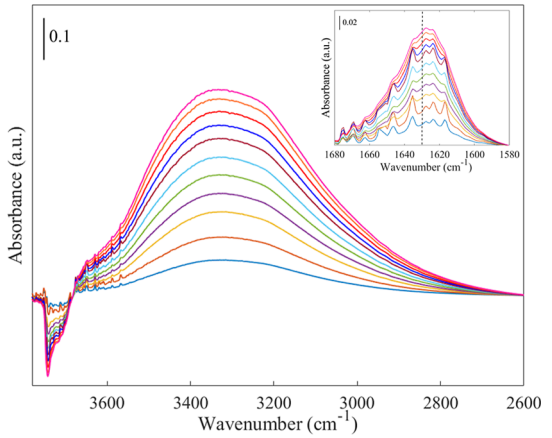


Figure 3. Difference IR spectra at increasing coverage at 318 K (equilibrium pressure between 1 and 12 mbar). The inset reports the spectra in the range 1680−1580 cm^{-1} (the vertical broken line corresponds to 1630 cm^{-1}).

blank spectrum of Figure 2, recorded at increasing equilibrium pressures in the range 1−12 mbar at 318 K. In each spectrum, the negative band refers to species that are consumed by the interaction with water molecules (which are the adsorbing sites, i.e., the silanols), whereas the positive contribution can be ascribed to the stretching modes of species formed during adsorption, i.e., silanols engaged in H-bonding with water molecules[29] and water molecules themselves.[13,21,30] An isosbestic point is observed at 3681 cm^{-1}.

The inset in Figure 3 reports the spectra in the range 1680−1580 cm^{-1}, where the bending mode of the adsorbed water molecules is observed. The maximum of the band definitely appears below 1630 cm^{-1}, as made evident by the vertical broken line. This frequency is largely lower than the value typical of liquid water (~1650 cm^{-1}),[31] and it is lower than the value reported for multilayers of adsorbed water (1636 cm^{-1}).[32]

This evidence confirms that adsorption occurs through specific interactions between the water molecules and the surface adsorbing sites.

The negative band above the isosbestic point at 3681 cm^{-1} appears to be made up of two components at 3742 cm^{-1} and 3720−3710 cm^{-1} due to terminal silanols. The former appears to grow at a higher equilibrium pressure than the latter, indicating that it is related to silanols that give rise to a weaker interaction with water molecules. This evidence confirms that the component at 3742 cm^{-1} is due to free silanols and that the component at 3720−3710 cm^{-1} is due to the terminal H-bond acceptor silanols, which are slightly more acidic and interact more strongly with the water molecules.

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The intensity values, obtained as band area by the integration of the entire negative band, have been used to draw a Langmuir plot corresponding to the linear form of the Langmuir equation, as follows

$$\frac{1}{A} = \frac{1}{\mathrm{K} \times A_{\max} \times \mathrm{P}} + \frac{1}{A_{\max}}$$

where K is the Langmuir constant, P is the water equilibrium pressure, and $A_{\max}$ corresponds to the maximum intensity, i.e., the full coverage.

Figure 4 reports the obtained plot, which indeed results to be linear, confirming the validity of the Langmuir model to

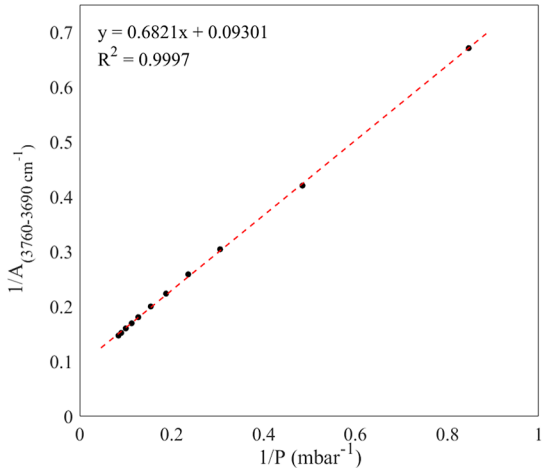


Figure 4. Langmuir plot applied to intensity values in the region of the stretching mode of terminal silanols (3760−3690 cm^{-1}).

describe the adsorption based on the intensity of the terminal silanol stretching modes.

The validity of the Langmuir model suggests that the adsorbing sites may be considered equivalent, despite the presence of at least two types of silanols (i.e., almost-free and H-bond acceptor silanols) involved in the interaction with water molecules. This means that tiny differences in the strength of interaction with water, as revealed by the decreasing trend of Q_{diff} in the same range of equilibrium pressures (Figure 1d), may be somehow neglected, giving rise to an almost-ideal adsorption behavior.

The value of $A_{\max}$ obtained by the Langmuir plot is 10.8 and deserves a comment. This value is proportional to the total amount of adsorbing sites and corresponds to the intensity of the silanol stretching mode at zero coverage (Figure 2). Therefore, it may be compared with the value obtained from the experimental spectrum. To this purpose, a fitting of the spectrum in the range of 3760−3690 cm^{-1} with a Log−normal function was carried out (using FityK 1.3.1 software). The result is reported in Figure S1, and the value obtained for the band area of the simulation is 13.8, which is not so distant from the value obtained by the Langmuir equation (10.8), thus confirming the validity of the Langmuir model in the thermodynamics analysis of the data.

The analysis of the intensity values, i.e., band areas, of the positive broad band below the isosbestic point is more complicated. In fact, several signals overlap in this region due to H-bonded water molecules and silanols; moreover, this band may also be affected by Fermi resonance contributions.[32] For these reasons, this spectral region is not considered reliable for the calculation of the standard enthalpy of water adsorption by means of the application of the van't Hoff equation in the VTIR study. Nevertheless, an attempt has been made to draw the Langmuir plot using the intensity values obtained by the integration of the spectra in the range of 3680−2600 cm^{-1}. The result (Figure S2) shows a linear correlation, which further supports the use of the Langmuir model for the thermodynamic analysis of the spectroscopic data of water adsorption herein presented.

VTIR Spectroscopy of Water Adsorption. A necessary condition for the VTIR method to be applied is that the adsorption process brings about a characteristic IR absorption band of the adsorbed molecule or a specific change in a characteristic IR absorption band of the adsorbing site.[10] In the present case, the characteristic IR absorption band of the adsorbing site is due to the stretching of terminal silanols.

Figure 5 reports the VTIR spectra in the region of the stretching mode of the terminal silanols.

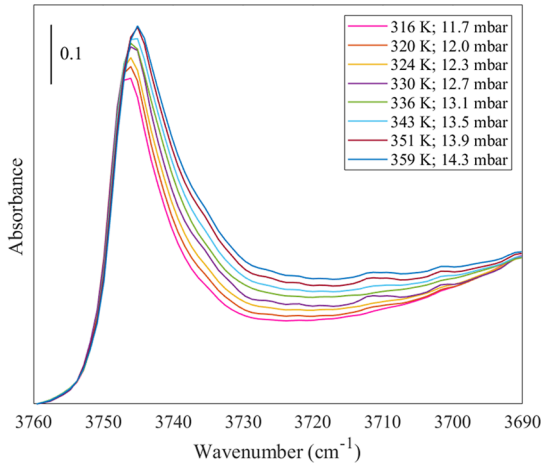


Figure 5. VTIR spectra in the region of the stretching mode of terminal silanols. Temperature in the range 316−359 K; equilibrium pressure in the range 11.7−14.3 mbar.

Based on the Langmuir model, the van't Hoff equation can be written as

$$\ln \frac{\theta}{(1-\theta) \times P} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{R \times T}$$

where θ is the coverage calculated from the intensity of the characteristic IR absorption band, which is proportional to the amount adsorbed, and P is the equilibrium pressure.[10] In this case, the coverage is calculated as $A/A_{\max}$, where A is the intensity calculated by the difference between the blank spectrum (Figure 2) and the spectrum at a given T and P (Figure 5), in the range of the stretching mode of terminal silanols. $A_{\max}$ is the maximum intensity that represents the full coverage, and its value (13.8) was obtained by the simulation of the band, as previously described.

The previous equation can be therefore rewritten as

$$\ln \frac{A}{(A_{\max} - \mathrm{A}) \times \mathrm{P}} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{\mathrm{R} \times \mathrm{T}}$$

which gives direct access to both ΔS^0 and ΔH^0, under the usual assumption of their constancy with respect to temperature.[10]

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Figure 6 shows the plot of the left-hand side of the equation against the reciprocal of the temperature obtained from the

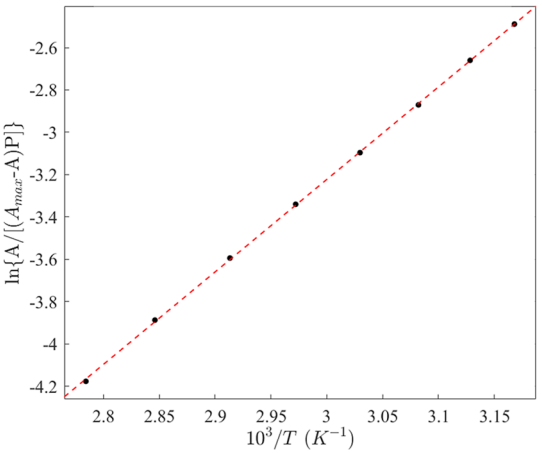


Figure 6. Plot of left side of van't Hoff equation vs reciprocal temperature for intensity of the terminal silanols stretching mode. A_{max} from simulated peak.

whole set of spectra recorded in the temperature range of 316−359 K.

The plot results in a straight line (R^2 = 0.9998), which first confirms the validity of the thermodynamic analysis of data by means of the used equation. The obtained straight line allows calculating the corresponding values of the standard adsorption enthalpy and entropy, which result in ΔH^0 = −36 kJ/mol and ΔS^0 = −136 J/mol, respectively.

The calculated standard adsorption enthalpy is in agreement with the molar heat of adsorption values obtained by microcalorimetric analysis (Figure 1d).

This result confirms that the interaction of water molecules with the surface of the large-pores mesoporous silica occurs mainly via one H-bond with terminal silanols, which behave as an energetically homogeneous family of adsorbing sites.

Usually, when A_{max} is not available, a refined value of A_{max} can be obtained by an iteration procedure, which involves discrete changes of the starting (approximate) value of A_{max} at each stage[10] and the starting value of A_{max} can be obtained by the Langmuir equation (10.8 in the present case). This approach was also used for the sake of completeness, and the result is represented in Figure 7. A straight line was again obtained (R^2 = 0.9999), and the values of standard adsorption enthalpy and entropy resulted to be ΔH^0 = −37 kJ/mol and ΔS^0 = −137 J/mol, respectively, confirming the results previously discussed.

A final comment has to be devoted to the mutual interacting silanols, which are responsible for the broad band below 3700 cm^{-1} in the spectrum of the large-pores mesoporous silica (Figure 2). These species may be considered as the adsorbing sites that give rise to a Q_{diff} value close to 60 kJ/mol observed at the initial coverage in the microcalorimetric measurement (Figure 1). In fact, the silanols pairs able to give strong interactions, where water molecules act as both acceptor and donor of H-bond, are usually considered the interacting silanols.[6] Unfortunately, the variation of the intensity of their stretching mode band upon water adsorption cannot be monitored, because it falls in the range of the stretching modes of adsorbed water molecules (below the isosbestic point in Figure 3). Moreover, the change of the absorption due to the

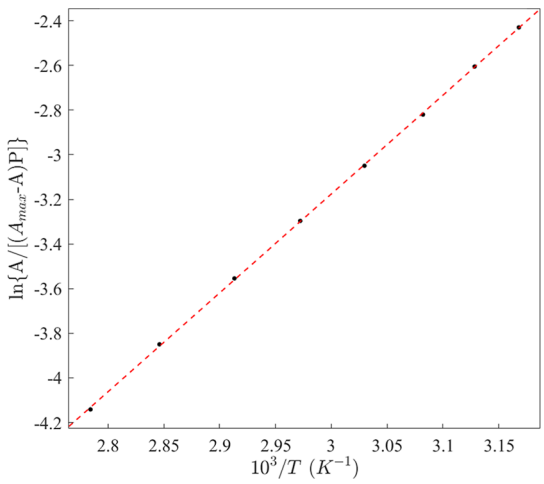


Figure 7. Plot of left side of van't Hoff equation vs reciprocal temperature for intensity of the terminal silanols stretching mode. A_{max} obtained by refining left side of van't Hoff equation vs reciprocal temperature.

stretching of interacting silanols represents a further contribution, besides those previously discussed, that affects the analysis of the intensity values of the positive broad band below the isosbestic point, so that this spectral region is not considered reliable for the calculation of the standard enthalpy of water adsorption by means of the application of the van't Hoff equation.

Nevertheless, based on the evidence that the analysis of the intensities in this spectral region also satisfies the Langmuir equation (Figure S2), the application of the van't Hoff equation has been attempted and the result is shown in Figure 8.

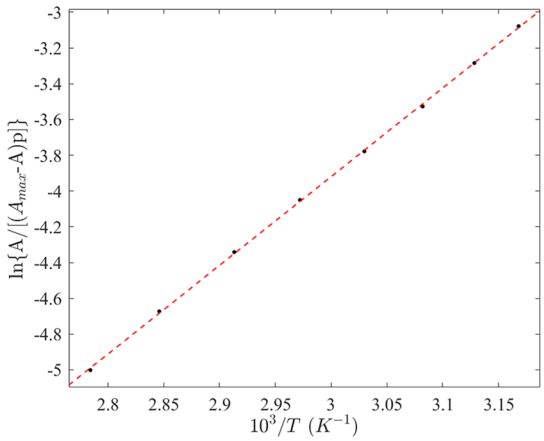


Figure 8. Plot of left side of van't Hoff equation vs reciprocal temperature for intensities in the range 3680−2600 cm^{-1}.

Values of A are calculated in the range 3680−2600 cm^{-1} from spectra obtained at given T and P (Figure S3a), by subtracting the blank spectrum of Figure 2 so that difference spectra are obtained (Figure S3b). In this case, A_{max} was not available and the refined value of A_{max} obtained by the iteration procedure[10] was used in the equation. Despite the complexity of contributions affecting the intensity, as previously described, a straight line was obtained (R^2 = 0.9997), allowing to obtain values of standard adsorption enthalpy and entropy equal to −41 kJ/mol and −156 J/mol, respectively. The value of ΔH^0

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results higher than that obtained previously but, however, lower than 44 kJ/mol. This is in agreement with the data obtained by adsorption microcalorimetry and confirms that the surface of the large-pores mesoporous silica may be considered mainly hydrophobic.

A detailed analysis of spectra in Figure S3b reveals a preferential erosion at higher frequency of the broad band due to H-bonded hydroxyls with increasing the temperature from 316 to 359 K. This may be ascribed to the breaking of the weaker hydrogen bonds upon increasing temperature.

The whole set of data presented herein reveals, for the first time, the possibility of using the VTIR spectroscopy for the characterization of the surface hydrophilicity/hydrophobicity of materials.

Eventually, considering the potential application of the large-pores mesoporous silica as hemostatic materials, the results obtained by the microcalorimetric and VTIR investigations of water adsorption clearly show that the heat of adsorption is significantly lower than that of other classes of materials previously used as hemostats, such as zeolites, for which heats of adsorption in the range 80−60 kJ/mol were reported.[7] This feature indeed strengthens the interest for the development of novel hemostats based on the large-pores mesoporous silica.

CONCLUSIONS

The joint study of water adsorption by means of microcalorimetry and variable temperature IR spectroscopy has been carried out for the first time on a large-pores mesoporous silica, which was previously shown to possess valuable hemostatic properties.

The results have shown that adsorption of water at 318 K occurs at the largest extent through one H-bond, giving rise to a differential heat of adsorption which remains constantly below 44 kJ/mol for coverages between 0.17 μmol/m^2 and 1.9 μmol/m^2 (corresponding to 0.10 and 1.14 molecules/nm,[2] respectively), reaching a value of about 30 kJ/mol at the highest coverage of 1.9 μmol/m^2. Considering the threshold of 44 kJ/mol between hydrophilic (>44 kJ/mol) and hydrophobic (<44 kJ/mol) surfaces, the measured heat of adsorption indicates that the surface of the large-pores mesoporous silica is predominantly hydrophobic.

For the first time, variable-temperature IR spectroscopy was applied for the assessment of the water heat of adsorption (as standard enthalpy of adsorption, ΔH^0, in the temperature range 318−360 K). The heat of water adsorption resulted to be 37−36 kJ/mol, in satisfactory agreement with the value obtained by microcalorimetry. The IR spectroscopy study confirmed that the interaction of water molecules occurs mainly with terminal silanols. They act as a single family of adsorbing sites, giving rise to an almost-ideal adsorption behavior, which may be well described by the Langmuir model.

Concerning the potential application of the large-pores mesoporous silica as hemostatic material, the whole set of results shows that its heat of water adsorption is significantly lower than that of other classes of materials previously used as hemostats, such as zeolites. This feature indeed strengthens the interest for the development of novel hemostats based on the large-pores mesoporous silica.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.5c02528.

IR band of terminal silanols: band simulated by fitting and experimental data points; Langmuir plot applied to intensity values in the range 3680−2600 cm^{-1} of spectra; VTIR spectra in the range 3780−2600 cm^{-1}; and difference in the VTIR spectra in the range 3680−2600 cm^{-1} (PDF)

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Notes

The authors declare no competing financial interest.

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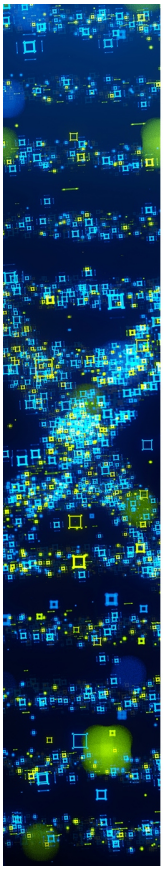
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