

Dielectric Study of Hydration Water in Silica Nanoparticles

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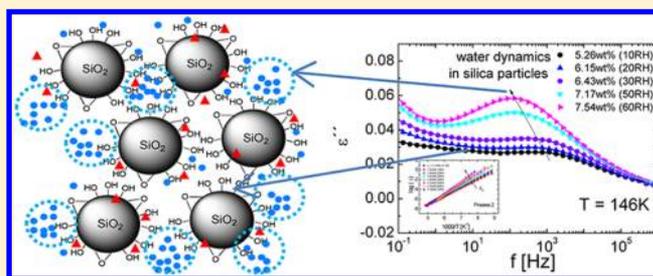
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Supporting Information

ABSTRACT: The effect of water content on silica nanoparticles was examined by thermogravimetry analysis (TGA), broadband dielectric spectroscopy (from 10^{-2} to 10^7 Hz), and differential scanning calorimetry for a wide temperature range (110–250 K). Silica nanoparticles were dried and rehydrated at different water levels to determine the critical factors affecting the dielectric response. The dynamics of both hydration water and hydrated silanol groups were addressed. Whereas hydration water dynamics depend on the water content, the dynamics corresponding to hydrated silanol groups are almost water independent once the maximum hydroxylation level is reached. In addition, we determined that during hydration water molecules prefer to form clusters instead of filling a complete layer around the particles. Finally, we observed that contrary to other water containing systems, the corresponding relaxation times of water molecules do not show any crossover (from high-T super-Arrhenius to low-T Arrhenius behavior).



INTRODUCTION

The introduction of nanoparticles with an extremely large specific surface into polymeric materials improves several characteristics of the compound such as electrical, optical, or mechanical properties. In particular, amorphous silica plays a significant role in many different disciplines of chemistry, and it has become widely used as an integral component of several industrial products. Silica nanoparticles can easily be prepared; they possess a high chemical stability and environmentally friendly nature,¹ and therefore they are used in many products (such as plastics, adhesives, paints and coatings, insulation materials, elastomers, or concrete). The optical, chemical, and mechanical properties of the final products strongly depend on the chemistry of the particles' surfaces; in particular on the concentration and distribution of both hydroxyl groups and water molecules on its surface.

Silica (silicon dioxide, SiO_2) is the major constituent of rock-forming minerals in magmatic and metamorphic rocks.² Precipitated silica particles are the synthetic, white, amorphous form of silicon dioxide, and they consist of silicon and oxygen atoms arranged in a tetrahedral structure of a three-dimensional lattice. The surface of precipitated silicas is covered by silanol groups ($-\text{Si}-\text{OH}$) which can be divided into three kinds: isolated or free silanol ($\text{O}=\text{Si}-\text{OH}$), the geminal silanol or silanediol group [two $-\text{OH}$ hydroxyl groups on the same silicon atom, $\text{O}=\text{Si}(\text{OH})_2$], and vicinal silanol (hydrogen bonded silanol groups) as illustrated in Figure 1. The number

of free, vicinal or geminal silanol groups on the silica surface depends on the calcination temperature. In addition, hydrophobic (and nonpolar) siloxane groups ($\text{Si}-\text{O}-\text{Si}$) are also present. Free silanols can develop hydrogen bonds, and therefore they promote interparticle hydrogen bonding. In addition, the terminal hydroxyl groups promote the adsorption of water and other polar molecules, and the amount of water adsorption is directly related to the number of surface hydroxyl groups.³

Precipitated silica particles are used in numerous applications but the oldest and most important is the reinforcement of elastomeric products such as tire compounds, cables, or shoe soles.¹ The addition of 20–100 parts by weight of precipitated silica to 100 parts by weight of synthetic rubbers improves the tensile strength, hardness, and abrasion of the vulcanized material.² When silica particles are used as reinforcement, water molecules as well as hydroxyl groups remain on its surface, and they play an important role in compounding which is not yet well understood.⁴ For this reason, it is crucial to understand at first how water interacts with silica particles in order to control its properties and optimize the surface of the particles for different applications.

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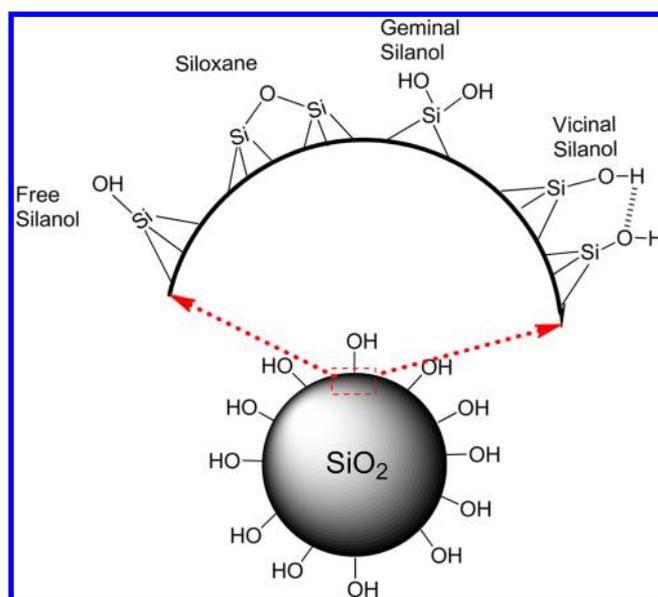


Figure 1. Classification of silanol groups on the surface of silica particles.

The molecular properties of silica particles and other siliceous materials such as mesoporous molecular sieves (MCM-41) or zeolites were mainly studied in the literature by using a combination of different techniques: thermogravimetry, vibrational spectroscopy (i.e., Fourier transform infrared spectroscopy (IR), Raman, diffuse or total reflectance IR, and photoacoustic IR), and solid-state NMR spectroscopy^{5–11}). These studies were focused on the surface structure, surface chemistry, and water adsorption on silica particles. Dielectric studies of water confined in MCM-41 and similar materials have also been published.^{12–16} These studies were mainly focused on the dynamics of water in deeply supercooled states, itself, more than in the matrix. Finally, in addition to these experimental studies, Zuravlev,^{17,18} based on results of different

experimental techniques, develops a model for the dehydration, dehydroxylation, and rehydroxylation states of the surface of amorphous silica. Although dielectric studies could provide some insight of the water dynamics on the silica surface, studies regarding the dynamical response of silica particles are missing in the literature.

In this article, we report a systematic study by means of broadband dielectric spectroscopy (BDS) of the dynamics of both the hydration water molecules and hydroxyl groups of the silica particles surface considering a broad water concentration range. We will focus on the effects of both drying temperature and hydration level on the dielectric response. In addition, calorimetric and thermogravimetric experiments were also performed to complete the characterization of the materials. We will show that two main relaxation processes are observed at low temperatures (110–250 K), and they are interpreted as fluctuations of clusters of water molecules and hydrated silanol groups on the surface of silica particles, respectively.

EXPERIMENTAL SECTION

Materials and Silica Hydration. Precipitated silica particles (Z1165 MP-Rhodia) with a specific surface, $S_{\text{specific}} = 165.8 \text{ m}^2/\text{g}$ (mean diameter of the primary particles is $\sim 25 \text{ nm}$) and pore volume = $1.74 \text{ cm}^3/\text{g}$ were used in this work. First, silica particles were extensively dried at 393 K in a vacuum oven for 3 days. At this temperature most of the water was evaporated, although some water molecules could remain extremely trapped on the silica structure (inner water). In addition, silanol groups on the silica surface also remain. After this drying, silica was immediately weighed and transferred to a hydration chamber where both the relative humidity (RH) and the temperature can be controlled. Silica particles were hydrated by exposing them at different relative humidities (from 10 RH to 80 RH) at a temperature of 295 K. The samples were maintained at a constant relative humidity for 4 days in order to achieve the equilibrium for each hydration level. Once the silica particles were hydrated to the desired

Table 1. Samples Used in This Work^a

Silica Particles Dried at Different Temperatures									
sample identification	drying temperature (K)	$c_{w,\text{total}}$ (wt %)	$c_{w,\text{outer}}$ (wt %)	process 2		process 3		Θ	
				E_a (eV)	$\log(\tau_0)$	E_a (eV)	$\log(\tau_0)$		
S-923K	923	0.02	–	–	–	–	–	–	
S-393K	393	2.76	0	–	–	0.59	–21.40	–	
S-373K	373	4.88	2.12	0.34	–15.73	0.62	–21.55	0.38	
Silica Particles Exposed at Different Humidity Levels									
sample identification	relative humidity (RH)	$c_{w,\text{total}}$ (wt %)	$c_{w,\text{outer}}$ (wt %)	process 2		process 3		Θ	
				E_a (eV)	$\log(\tau_0)$	E_a (eV)	$\log(\tau_0)$		
S-10RH	10	5.26	2.50	0.34	–15.56	0.57	–19.93	0.45	
S-20RH	20	6.15	3.39	0.37	–16.61	0.58	–20.14	0.60	
S-30RH	30	6.43	3.67	0.39	–16.99	0.58	–20.32	0.66	
S-40RH	40	6.71	3.95	0.43	–18.43	0.57	–19.64	0.71	
S-50RH	50	7.17	4.41	0.46	–18.92	0.59	–20.35	0.79	
S-60RH	60	7.54	4.78	0.49	–20.02	0.74	–24.88	0.85	
S-70RH	70	8.55	5.79	0.48	–19.52	–	–	1.03	
S-80RH	80	11.23	8.47	0.52	–20.66	–	–	1.51	

^aThe total water content ($c_{w,\text{total}}$) was calculated as the loss weight at 433 K from thermogravimetry analysis (TGA) measurements. The total water content is calculated with respect to dry silica. $c_{w,\text{outer}}$ is defined as the water in the external surface, and it was calculated as $c_{w,\text{outer}} = c_{w,\text{total}} - 2.76$. E_a is the activation energy, and $\log(\tau_0)$ is the pre-exponential factor corresponding to processes 2 and 3 in Figure 6. Θ is the number of water layers at the surface of the silica particles estimated as $c_{w,\text{outer}}/5.88$.

level, samples were weighed and immediately measured. Additionally, one sample was dried under vacuum for 3 days at 373 K, and one more was dried for 1 day at 923 K under a nitrogen atmosphere. Table 1 shows both the relative humidity and the water content reached at each humidity level calculated from thermogravimetric measurements.

Alternatively, following the work of Spanoudaki et al.¹³ and Meier et al.,¹⁹ it is possible to estimate the water content necessary to obtain a monolayer of water on the silica surface by assuming a hexagonal arrangement of the water molecules on the surface. Assuming a lattice constant $d = 3.2 \text{ \AA}$, which corresponds to the size of a water molecule, the water content necessary to form a monolayer ($c_{w,mono}$) around a particle can be estimated as

$$h_{mono} = S_{specific} \frac{2}{\sqrt{3} d^2} \frac{M_{H_2O}}{N_A} \quad (1)$$

where M_{H_2O} is the molar mass of water, and N_A is Avogadro's number. For our silica particles, the water content corresponding to a monolayer is $c_{w,mono} = 5.6 \text{ wt } \%$, in agreement with Meier et al.¹⁹ Table 1 shows the number of water layers found with each water content calculated as $\Theta = c_{w,outer}/c_{w,mono}$.

Thermal Characterization. Standard calorimetric measurements were performed by means of a differential scanning calorimeter (DSC) Q2000 (TA Instrument) using cooling and heating rates of 10 K/min. Hermetic aluminum pans were used for all of the samples. The sample weight was about 10 mg. Thermogravimetric analyses were done using a TGA-Q500 (TA Instruments). All the measurements were conducted under a high-purity nitrogen flow over a temperature range of 303–1273 K with a ramp rate of 5 K/min.

Broadband Dielectric Spectroscopy. Broadband dielectric spectroscopy (BDS) is a technique based on the interaction of an external field with the electric dipole moment of the molecules of the sample.²⁰ With this technique, it is possible to study the molecular dynamics over a broad frequency (from 10^{-6} to 10^{11} Hz) and temperature (100–350 K) range. To perform a dielectric measurement, the sample is placed between two metallic electrodes which form a capacitor. For the parallel-plate configuration, the capacitance is expressed as $C = \epsilon d/A$, where ϵ is the dielectric permittivity of the sample, A is the sample surface area, and d its thickness. The material properties are characterized by the complex dielectric permittivity, ϵ^* , which is defined as $\epsilon^*(\omega) = C^*(\omega)/C_0 = \epsilon'(\omega) - i\epsilon''(\omega)$, where C_0 is the capacitance of the free space and $\omega = 2\pi f$.

A broadband dielectric spectrometer, Novocontrol Alpha analyzer, was used to measure the complex dielectric function, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, in the frequency range from 10^{-2} to 10^7 Hz. The samples were prepared by placing the silica particles between two parallel gold-plated electrodes (30 mm in diameter) with the thickness of about 0.5 mm. Isothermal frequency scans were performed every three degrees over the temperature range 110–200 K, and every five degrees from 255 to 300 K. Sample temperature was controlled by a nitrogen gas flow with stability better than ± 0.1 K.

RESULTS

Thermal characterization. Figure 2 shows the results of the thermogravimetric analysis for some dried and hydrated silica particles. Three typical steps on the thermograms are observed (seen as peaks in the derivative plot in the inset of Figure 2). The first rapid initial drop of the mass (from room

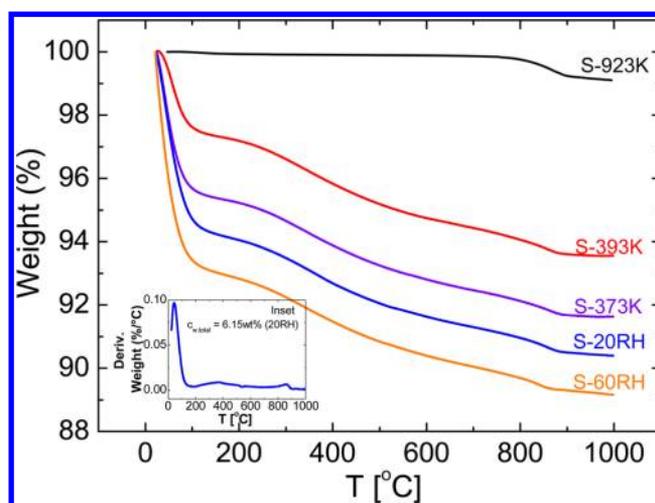


Figure 2. Thermogravimetric measurements (TGA) of the loss mass up to 1273 K for different silica particles as indicated in the figure. The inset shows the weight derivative plot for silica particles hydrated at 20 RH.

temperature up to ~ 473 K) corresponds with the loss of both adsorbed water on the silica surface and structurally bound water within the silica skeleton.¹⁷ Above 473 K, vicinal and geminal silanol groups on silica particles are condensed to siloxanes, and this is seen as a weight drop in a broad temperature range from 473 to 873 K. In this broad temperature range, free silanols are still stable. Finally, the last drop (from 873 to 1273 K) corresponds with the release of free siloxanes and other thermal decompositions.^{17,18} The total moisture content (c_w , expressed as grams of water per grams of dry particles) for hydrated- and vacuum-dried silica particles was calculated as the loss of mass at 433 K divided by the sample weight at the same temperature. The results are shown in Table 1.

Thermal behavior of silica particles was characterized by DSC and the results are shown in Figure 3. No calorimetric features (on cooling or heating) were observed for samples with water content lower than 8 wt % (~ 65 RH), and therefore water remains amorphous in the whole temperature range analyzed (see dashed line). In addition, for the sample with $c_{w,total} = 8.55 \text{ wt } \%$, a small exothermic peak on cooling was observed in the calorimetric response, indicating water crystallization (see solid line). The inset in Figure 3 reports the calorimetric response of the sample S-80RH at a cooling and heating rate of 1 K/min. At this slow cooling rate, two clear peaks observed (at 232 K and 223 K, respectively) are indicative of two water populations in the samples at high hydration levels. The behavior of this crystalline sample will not be further discussed in this paper.

Dielectric Response of Silica Particles. Figure 4 (panels a and b) shows the isothermal dielectric loss spectra for silica particles dried at 373 K and 393 K, respectively. The dielectric loss spectra $\epsilon''(\omega)$ for the least dried sample (S-373K) exhibit three relaxation processes labeled 1, 2, and 3 from the fastest one to the slowest one (see Figure 5, panels a and b). As it will be discussed in the next section, process 2 is due to the relaxation of water molecules in the outer shell, whereas process 3 is mainly due to the reorientation of hydrated vicinal/geminal silanol groups. Process 1 appears only at very low temperatures (between 100 and 125 K), and it is required to appropriately fit the dielectric response at high frequencies/low temperatures.

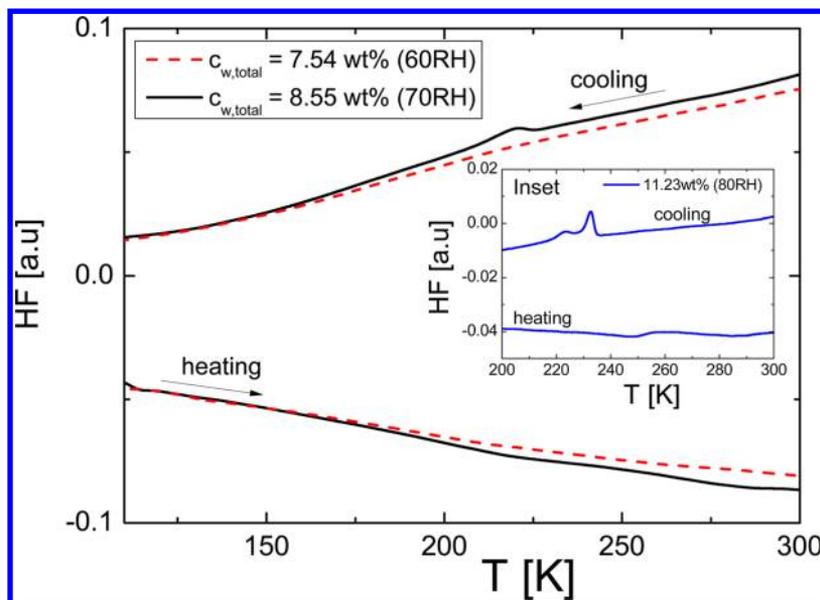


Figure 3. Heat flow measured by DSC during cooling and heating at a rate of 10 K/min for silica particles with two water contents. No calorimetric features are observed in silica hydrated up to a $c_{w,\text{total}}$ of 7.54 wt %. However, crystallization and melting peaks due to water crystallization are observed in the sample with $c_{w,\text{total}} = 8.55$ wt %. The inset shows the calorimetric response, for a narrower temperature range, at a rate of 1 K/min for hydrated silica at $c_{w,\text{total}} = 11.23$ wt %.

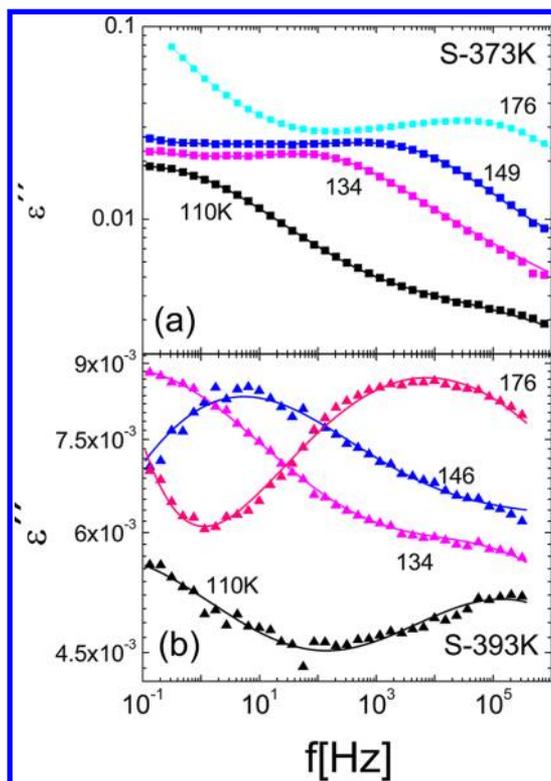


Figure 4. Dielectric loss spectra of (a) S-373K and (b) S-393K measured at different temperatures (110, 134, 149, and 176 K). The solid line through the data points represents the fits to the experimental data.

By increasing the drying temperature at 393 K (sample S-393K), the dielectric spectra of silica particles reveal only two relaxation processes (1 and 3 in correspondence with that in sample S-373K, see Figure 5b). In addition, for the sample S-923K, no processes were detected in the dielectric response in the broad frequency/temperature range analyzed.

Figure 6a shows the isothermal dielectric loss spectra at $T = 146$ K for dried samples together with one of the hydrated samples. By increasing the drying temperature from 373 to 923 K, the dielectric signal progressively becomes broader and weaker until it almost disappears at the highest drying temperature. Note that the behavior of the least hydrated sample (S-10RH, $c_{w,\text{total}} = 5.26$ wt %) is similar to that of the sample S-373K as they have a similar water content.

Figure 6b shows the dielectric response for hydrated samples at different water concentrations at $T = 146$ K. Two processes, a well-resolved peak at high frequencies (process 2) and a shoulder at low frequencies (process 3) can be observed. By increasing the water content, two effects on the dielectric signal can be observed: the total dielectric signal increases and the main relaxation peak (process 2) moves to lower frequencies. Due to this, process 2 masks process 3 at a high water content. In order to appropriately describe the data of the hydrated samples (as previously discussed for dried samples), an extra process at low temperatures/high frequency (process 1) is necessary to describe the dielectric data. Therefore, the dielectric response of hydrated samples can also be described with three dielectric relaxation processes, similar to those used for sample S-373K.

Fitting Procedure and Shape Parameters. Each of the relaxation processes above-mentioned have been analyzed in terms of the Cole–Cole (CC) function since all the processes are symmetric. The Cole–Cole function is defined by²¹

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau)^\alpha]} \quad (2)$$

where α is the shape parameter that determines the symmetric broadening of the relaxation peak ($0 < \alpha \leq 1$); $\Delta\epsilon = \epsilon_s - \epsilon_\infty$, is the relaxation strength, and ϵ_∞ and ϵ_s are the unrelaxed and relaxed values of the dielectric constant. τ is a characteristic relaxation time, and ω is the angular frequency.

At low temperatures (lower than 140 K), two processes are visible in our frequency window (see Figure 5a). In this case,

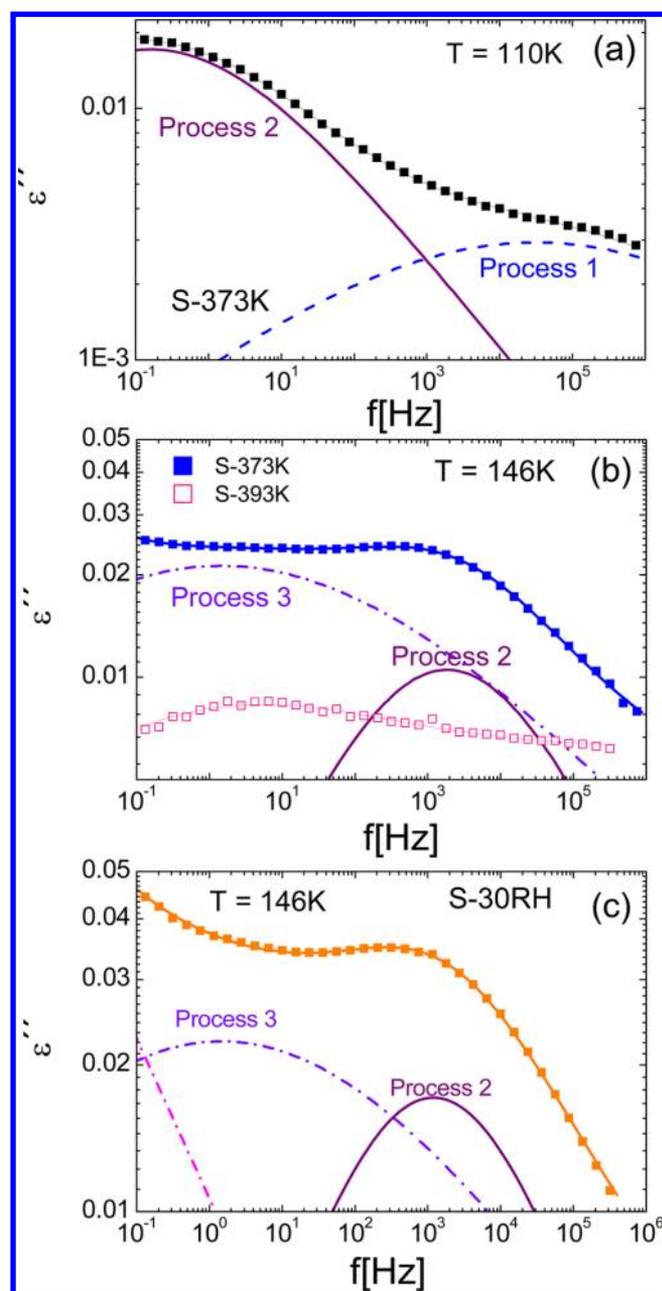


Figure 5. (a) Dielectric loss spectrum at a fixed temperature (110 K) of S-373K. Processes 1 (dashed line) and 2 (solid line) denote the two dielectric processes observed at this temperature. (b) Dielectric loss spectra at $T = 146$ K of S-373K and S-393K. At this temperature, processes 2 (solid line) and 3 (dashed dotted line) are observed. (c) Dielectric loss spectra at $T = 146$ K of S-30RH. At this temperature, processes 2 (solid line) and 3 (dashed dotted line) are observed. For all of the figures, the solid line through the data points represents the fits to the experimental data.

two CC functions were used to describe the whole spectrum at each temperature. At higher temperatures, between 140 K and 220 K, two processes are also observed in our frequency window (processes 2 and 3), and therefore two CC functions were used to describe the spectrum at each temperature. In addition, at low frequencies, conductivity effects become dominant (from approximately 160 K), and a power law term was added to the sum of CC functions. All the parameters were left free during the fitting procedure. Solid lines through the

data points in both Figures (5 and 6) show the best fit to the experimental data.

The relaxation strength obtained from the fitting procedure corresponding to process 2 ($\Delta\epsilon_2$) is temperature independent in the T-range here analyzed (see Figure S1 of the Supporting Information) but depends on the amount of water. In Figure 7, average values of $\Delta\epsilon_2$ were plotted as a function of c_w . The dielectric strength increases almost linearly up to a water content of 3.5 wt %. At a higher water content, $\Delta\epsilon_2$ deviates from this behavior increasing much faster. Finally, when water crystallization starts, the dielectric strength decreases because less water molecules are involved in this relaxation process because some of them become part of the ice network (see the arrow in Figure 7). With regards to α_2 (see Figure S2 of the Supporting Information), it slightly increases with temperature and becomes systematically smaller by increasing the water content, indicating a more heterogeneous environment. Regarding process 3, the relaxation strength ($\Delta\epsilon_3$) is also temperature independent, and the average value increases from 0.07 to 0.19 from samples S-393K to S-373K. Besides that, $\Delta\epsilon_3$ is more or less constant for the rest of the water content, and this indicates that the intensity of this relaxation is not related to the level of hydration in the samples.

Relaxation Map. Figure 8a shows the relaxation map for sample S-373K where the three above-mentioned processes (1, 2, and 3) can be observed. In addition, Figure 8b shows how process 2 becomes slower with an increasing water content. Contrarily, the relaxation time corresponding to process 3 (Figure 8c) slightly changes with water content. This behavior reflects the fact that it is possible to distinguish between different types of dipoles relaxing on the sample. The relaxation time for all of these processes follows an Arrhenius behavior [$\tau = \tau_0 \exp(E_a/kT)$] in the whole temperature range here analyzed. The activation energies, E_a , and $\log(\tau_0)$, were calculated, and both values are shown in Table 1 for the processes 2 and 3. For process 1, the activation energy is $E_a = 0.11$ eV and $\log(\tau_0) = -10.70$ s.

DISCUSSION

As mentioned in the introduction, the surface of silica particles is covered by polar silanol groups (isolated, vicinal, or geminal) as well as apolar siloxanes ($-\text{Si}-\text{O}-\text{Si}-$). These silanols have a strong dipole moment comparable with that of water molecules (1.85D). As dielectric spectroscopy is sensitive to fluctuations of dipole moments, it is not surprising to observe two different dynamics related to the two dipolar species in hydrated silica (water molecules and silanol groups). In addition, modeling of physical and chemical properties of the amorphous silica–water interface has been reported in the literature.²² Hassanal and Singer²² pointed out the evidence for the affinity of water molecules for silanol groups. Also the existence of “hydrophobic regions” (regions with high density of siloxanes) on the silica surface was observed. The existence of these regions leads to water clustering. In this work, we study silica particles with an increasing water content. This methodology allows for the distinguishing of two different dielectric relaxations: the slower one (process 3), which is almost independent of the hydration level, and the other one (process 2), faster and clearly dependent on the hydration level. With all these ideas in mind, we are going to discuss the dielectric behavior of both dried and hydrated silica particles.

Dielectric Response of Dried Silica Particles. We start the discussion with the most dried sample (S-923K). The silica

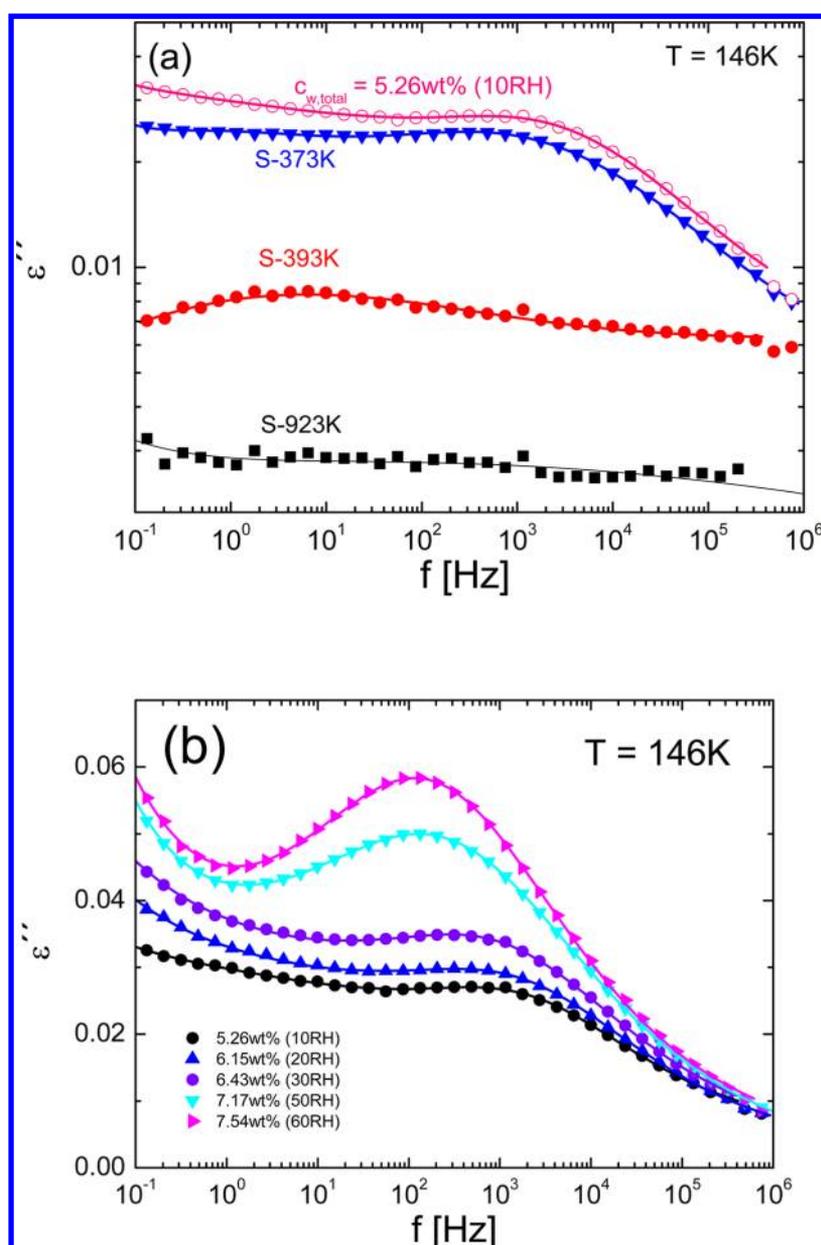


Figure 6. (a) Comparison of the dielectric loss spectra at a fixed temperature (146 K) of silica particles dried under vacuum. (b) Dielectric loss spectra at a fixed temperature (146 K) of hydrated silica particles. The solid line through the data points represents the fits to the experimental data.

particles lost most of the silanol groups (only a few free silanol groups remain), and its surface is mainly covered by siloxane groups. We have confirmed the absence of vicinal or geminal silanol groups by means of thermogravimetric measurements, since there is no weight loss in the temperature region between 473 and 873 K (see Figure 2). Taking into account that no dielectric processes were observed for this sample (where only siloxanes and a small quantity of free silanol groups remain on the surface), we can conclude that both siloxane groups and free silanols do not substantially contribute to the dielectric response.

For the sample dried at 393 K (S-393K), most of the water molecules on the surface are removed. However, a water content of 2.76 wt % remains (as detected by TGA). These water molecules are mostly located on the inner surface of the particles. We define this fraction of water as the internal water content or “inner water content” in the silica particles ($c_{w,inner} =$

2.76 wt %) in the sense that these water molecules are hardly removed by standard drying. As shown in Figure 5b and 6a, the dielectric response of sample S-393K shows a single relaxation peak (process 3). We also note that by drying at 393 K, the particle surface remains in a state of maximum hydroxylation,¹⁷ and therefore the reorientation of silanols on the surface (which have a large dipolar moment, comparable with that of water molecules) can be attributed as the origin of this relaxation. This assignment includes only the hydroxyl groups in the vicinal or geminal silanol groups, since previously we have shown (for sample S-923K) that free silanols do not appreciably contribute to the dielectric response. Note, at first view, that we cannot discard the “inner water” as the origin of this relaxation. However, the temperature dependence of the relaxation times do not show the typical crossover from super-Arrhenius to Arrhenius behavior by decreasing the temperature, typical of confined water in nanometric cavities.^{23–25} The

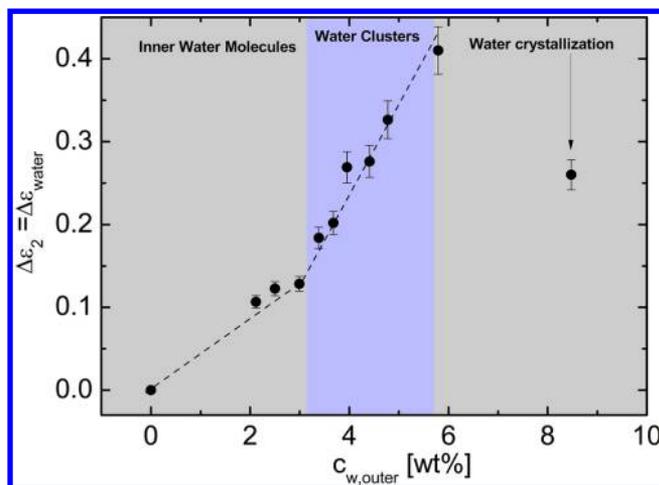


Figure 7. Relaxation strength ($\Delta\epsilon_2$) as a function of water content for process 2. Error bars are indicated in the plot. “Inner water molecules” indicate water molecules in the internal surface of the silica particles (no rotational water). The label “Water clusters” refers to the ability of water molecules to join together instead of being uniformly distributed; “water crystallization” refers to the ability of water to crystallize at a high c_w , as seen by DSC.

assignment of this relaxation as due to the reorientation of the hydrated hydroxyl groups in the silanol groups is consistent with the small variation of the dielectric strength ($\Delta\epsilon_3$) observed with increasing hydration (see next section) and similar with dry xerogel and dry MCM41.^{13,16}

Finally, we also studied a sample dried at 373 K (S-373K). The total water content for this sample is 4.88 wt %. If we considered that the 2.76 wt % corresponds with the “inner water” then we can define a water content, $c_{w,outer} = c_{w,total} - 2.76$ wt %, which represents the fraction of water mainly located on the outer surface of the silica particles. Table 1 shows $c_{w,outer}$ for all of the samples analyzed in this work. For sample S-373K, a new relaxation process emerges (process 2). The strength of this process increases rapidly with water content (as we will see in the next section), and therefore, it is assigned to the reorientation of water molecules located at the outer surface of the silica particles. In addition, process 3 is still visible at lower frequencies, and its intensity is 3 times higher than that of sample S-393K. When annealing at 373 K (instead of 393K), a more hydroxylated surface is obtained, and it is likely that the intensity of process 3 increases. In addition, as more water molecules are present in the samples, its relaxation strength also increases.

The relaxation time corresponding to process 3 for S-373K is slower than that of S-393K. This is likely because water molecules bonded to hydroxyl groups prevent its reorientation, and therefore the relaxation becomes slightly slower. In addition, the activation energy is 0.62 eV. This energy value is similar to that found in reference 26, studying adsorption of water on silica surfaces. In that case, the heat of adsorption was found in the interval from 0.62 to 0.93 eV, and it was associated with the strong interaction of molecular water on pairs of interacting silanols in agreement with our interpretation. Figure 9 (panels a and b) shows a schematic drawing of our model for dried silica nanoparticles as deduced from the analysis of the dielectric response.

Dielectric Response of Hydrated Silica Particles. Now we focus the attention on the hydrated silica particles. Figure 6b shows the rapid increment of process 2 by adding water. This

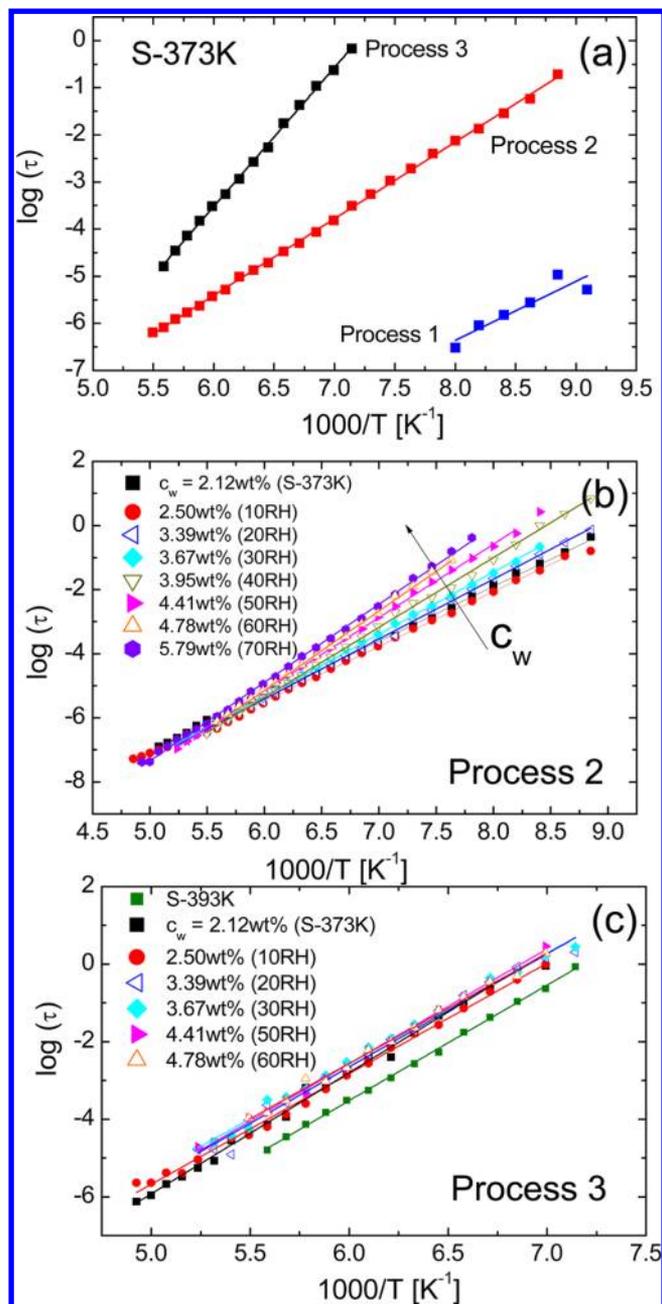


Figure 8. Plot of the characteristic relaxation times (τ) for all of the samples analyzed in this work. (a) Temperature dependence of τ for sample S-373K. The three relaxation processes (1, 2, and 3) can be observed. (b) Temperature dependence of τ corresponding to process 2 with a different water content. The relaxation time becomes slower by increasing the water content. (c) Temperature dependence of τ corresponding to process 3 with a different water content. The solid lines are fits of the Arrhenius equation to the data.

fact leads to infer that this relaxation is related with the reorientation of water molecules. In fact, this process has already been observed in a variety of water containing systems by several different experimental techniques^{12,13,16,25–31} and also in hydrated silica-filled rubbers.¹⁹ Figure 7 shows the variation of the average relaxation strength ($\Delta\epsilon_2$) with the water content. $\Delta\epsilon_2$ increases moderately with increasing concentration until $c_{w,outer} = 2.5$ wt %. After that, a much stronger increment is observed which indicates a larger dipole moment reorientation in the high water concentration range.

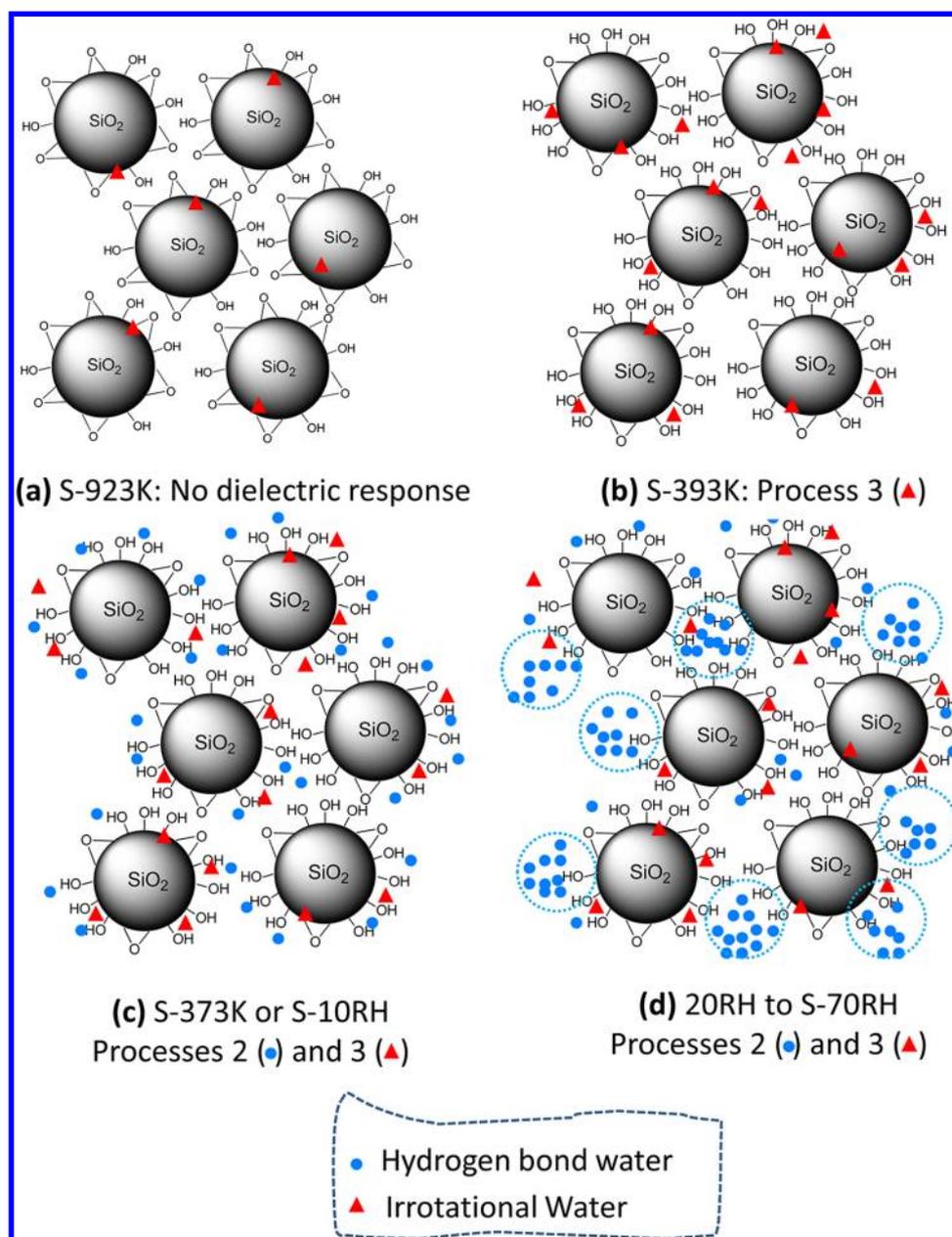


Figure 9. Schematic drawing of the water adsorbed at the surface of the silica particle at different hydration levels. (a) For S-923K only siloxanes, free silanols, and a few water molecules (which are bound in the inner surface) are present. No dielectric processes are observed, and therefore all of these groups (irrotational water and siloxanes) do not contribute to the dielectric response. (b) For S-393K, silanol groups are present at the surface of silica particles as well as water molecules. These water molecules cannot lead to a dielectric process and therefore are still irrotational. Process 3 appears in the dielectric response originating from the hydrated silanol groups. (c) S-373 and S-10RH: A new dielectric process appears in the dielectric spectra (process 2). At these low hydration levels, extra water molecules (located in the external surface of the silica particles) have more mobility than the previous ones. (d) S-20RH up to S70RH: Further water molecules prefer to join other water molecules (forming clusters) instead of distributing homogeneously. Circles indicate clustering of water.

Finally when water crystallizes, the dielectric signal falls because less water molecules are involved in the relaxation as some of them become part of the water crystals. The dependence of $\Delta\epsilon_2$ with concentration is typically observed in other water solutions^{29,30} and also in hard confinements.^{22,23}

In addition, the temperature dependence of the relaxation times follows the Arrhenius behavior for all the water concentrations, characteristic of a local or secondary relaxation as pointed out by some of us³² and by other authors.^{12,31,33} The activation energy increases with water content from 0.34 eV for 2.12 wt % to 0.52 eV for 8.47 wt %. This last energy value is

compatible with that associated with the dielectric reorientation of water molecules having a large mean number of hydrogen bonds (0.54 ± 0.4 eV).²⁵ At the same time, the value of τ_0 (obtained from the Arrhenius fit) is lower than 10^{-14} (the reciprocal of typical vibrational frequencies) for all c_w , until it reaches the unphysical value of $\log(\tau_0) = -20.66$ for sample S-80RH. Moreover, even for low water content, $\log(\tau_0)$ is less than 10^{-14} . This indicates that the local water relaxations do not fit Starkweather's definition^{34,35} of a simple relaxation, showing cooperative effects. This suggests that water molecules do not distribute uniformly, but likely they go first to the more

favorable sites, as also suggested by the behavior of the relaxation strength (Figure 7). Consequently, our picture is consistent with the fact that water molecules prefer to form clusters from the initial stages of hydration instead of forming uniform layers of adsorbed water around the particles. This explanation is compatible with simulations of water in the amorphous silica surface²², and that behavior was due to the presence of hydrophobic patches formed by siloxane groups. Figure 9 (panels c and d) shows a schematic drawing of our model for hydrated silica nanoparticles.

Now we focus on the temperature dependence of the water relaxation time corresponding with process 2. On the basis of previous results of water dynamics in mixtures of glasses and proteins (soft confinement)^{25,31,36,37} or hard confinements,^{12,16,23,24} the temperature dependence of the relaxation time of the water dynamics was found to show a crossover from low temperature Arrhenius behavior to another Arrhenius or Vogel–Fulcher–Tamman (VFT) behavior at higher temperatures. The origin of this crossover is still controversial in the literature, and it was related with (a) the existence of a fragile to strong transition related with that predicted for bulk water,³⁸ (b) the splitting of α - and β -relaxation,³⁹ and (c) as due to the intrinsic property of a Johari–Goldstein (JG) relaxation (water was identified as a JG relaxation),^{40,41} or (d) the onset of finite size effects due to soft- or hard-confinement.^{23,24,27}

For water around silica particles, we do not observe such crossover. Instead, the temperature dependence of the relaxation time is Arrhenius type on the whole temperature range analyzed. The absence of this crossover was also reported by Mamontov et al.⁴² in studies of water on rutile (TiO₂ nanoparticles) from quasielastic neutron scattering (QENS) experiments for water content below one monolayer. However, a crossover was reported at higher hydration levels. Contrarily, water in silica particles retains the Arrhenius behavior even for high water content. For water confined in MCM-41 such crossover was observed at $T \sim 180$ K¹² or at $T \sim 190$ K.¹⁶ Note that in both cases (MCM-41 and silica particles), the surface contains similar silanol groups. The main difference between these two systems is the fact that in MCM-41, water is confined in nanopores (~ 10 Å), whereas in the surface of the silica particles this restriction does not emerge since water molecules are located on the external surface. Therefore, from our point of view, it is likely that the presence of a crossover in the temperature dependence of the relaxation time (around 160–200 K) is related with finite size effects, and it cannot be observed for water in silica particles because there is no spatial restriction for water molecules.

Finally, focusing on the slower process 3, we note that the activation energy does not show a large variation with increasing hydration having an average value of about 0.60 eV for the different water content. As this process was attributed to the dynamics of hydrated silanol groups and for all the hydrated samples, the number of reactive silanol groups per unit area should be the same, it is reasonable that both the activation energy and the relaxation strength do not increase with the water content.

CONCLUSIONS

We have systematically explored the effect of hydration on the dielectric properties of silica nanoparticles. On the basis of our results, two relaxation processes are evident, and they were related with hydrated silanol groups (process 3) and hydration water (process 2). By increasing the degree of hydration, it is

possible to observe that water molecules prefer to form clusters. The results also show that the water relaxation depends on water content, whereas the relaxation corresponding to hydrated silanol groups is almost independent of the hydration level. Contrary to the observed behavior of water molecules in hard confinement, the temperature dependence of the relaxation time corresponding to process 2 is Arrhenius-like in the whole concentration and temperature range (i.e., the relaxation time does not exhibit any fragile-to-strong transition).

ASSOCIATED CONTENT

Supporting Information

Figure S1 shows the temperature dependence of the relaxation strength, and Figure S2 shows the temperature dependence of the broadening parameter. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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