Properties of water adsorbed in porous silica aerogels

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Silica aerogels have been prepared by hydrolysis and condensation of sols of composition TMOS–methanol–H₂O with molar ratio TMOS: H₂O = 4:1 and volume ratio TMOS: methanol = 0.2:0.3; 0.4 and 0.6. Their true and apparent densities, BET surface area, total pore volume and pore size distribution have been systematically investigated as a function of densification heat treatment. The relaxation properties of water adsorbed on the highly reactive surface have been studied by dielectric and nuclear magnetic resonance techniques as a function of the H₂O coverage (0 < θ_{H₂O} < 6) and temperature.

1. Introduction

When a wet gel is dried under supercritical conditions, the product is called an aerogel. During this process the network does not experience capillary pressure and consequently suffers little shrinkage. Aerogels have a low bulk density, a high pore volume and a large surface area.

According to Ilver [1], the properties of large surface area amorphous silicates are dominated by the surface chemistry of the solid phase, which is generally terminated by hydroxyl groups. The average OH surface coverage of 100 samples of amorphous silicates, determined by Zhuravlev [2], was 4.9 OH/nm² and appeared to be independent of the form or synthesis conditions. Thermal, vacuum and chemical treatments allow dehydroxylation of the surfaces with OH groups being removed through OH condensation or chemical reaction. The dehydroxylation alters drastically the physical and chemical properties of the surface which becomes more hydrophobic and presents different ring statistics. The rehydration of a dehydroxylated surface involves adsorption followed by dissociative chemisorption. This phenomenon seems to be nucleated by strained surface acidic sites (two- or three-membered rings), and then extends to adjacent areas. Subsequent water absorption occurs preferentially on silanols formed by hydrolysis of these rings and then extends at a much lower rate to the remaining patches of the rehydrated surface. The surface hydroxyl groups are therefore the sites where the physical adsorption of polar molecules such H₂O occurs. On a completely hydroxylated surface, H₂O molecules start to cover all the accessible isolated and H-bonded silanols. However, before the completion of a monolayer, the formation of clusters of H-bonded H₂O molecules has been observed [3], followed by multilayer condensation. Differential scanning calorimetry (DSC), dielectric relaxation spectroscopy (DRS) and nuclear magnetic resonance (NMR) have also shown that a portion of the H₂O adsorbed directly adjacent to the surface ('bound water') does not show a freezing or melting transition but remains diffusively mobile and the remaining fraction exhibits a suppressed melting point (T_m < 0°C). Since the shape of the pores is not well characterized, the definition of the true thickness of the bound water layer is meaningless. Therefore, the values determined for the monolayer coverage of H₂O differ greatly amongst authors. This reflects the difficulty of characterization of the hydroxylated state of the surfaces and the determination of the correct cross-sectional area of H₂O molecules. A detailed review of these phenomena is given in ref. [4].

To our knowledge, the properties of water adsorbed on the surface of silica aerogels have...
not been studied. In this paper, we report on the structural properties of silica aerogels measured during their densification and the relaxation properties of adsorbed $\text{H}_2\text{O}$ measured by DRS and NMR techniques.

2. Experimental procedure

Silica gels were prepared by hydrolysis and condensation of sols of composition TMOS—methanol—water with molar ratio $[\text{TMOS}]:[\text{H}_2\text{O}]=4:1$ and volume ratio $X=\text{TMOS}:\text{methanol}=0.2; 0.3; 0.4$ and 0.6 under neutral condition. The gels are labelled M100X-N. Aerogels in form of cylinders (diameter 15 mm, length 16 cm) were obtained by hypercritical drying at $T_{\text{max}}=310^\circ\text{C}$, $P_{\text{max}}=190$ bar. Samples, cut with a diamond saw, were heat treated in air under the following conditions: heating rate $2^\circ\text{C}/\text{min}, T=600^\circ\text{C}, 700^\circ\text{C}, 800^\circ\text{C}, 912^\circ\text{C}, 1000^\circ\text{C}, 1052^\circ\text{C}$ and $1100^\circ\text{C}$ for different time periods. Their $\text{N}_2$ BET surface area, total pore volume, pore size distribution, average pore radius, and true and apparent densities have been determined using a Hg pycnometer and Micromeritics equipments Accusorb 2100E and Multivolume Pycnometer 1305.

3. Results

The nitrogen BET areas, $S$, are shown in fig. 1 as a function of the sintering temperatures, $T_s$. For unsintered samples, $S$ is larger for lower TMOS:methanol ratios; however the temperature dependence is practically identical.

The apparent (bulk) density, $\rho_b$ (g/cm$^3$), of unsintered aerogels shows an opposite behavior: it remains almost constant up to $T_s=700^\circ\text{C}$ and then increases steadily up to $\rho_b=2.2$ g/cm$^3$ at full densification (fig. 2(a)). The temperature variation of the structural (true) density, $\rho_s$ (g/cm$^3$), measured by the pycnometer shows a complex behavior (fig. 2(a)). Similar, but less strongly marked variations have been reported for xerogels and various interrelated mechanisms have been suggested [5]. In our case the structural density of all samples starts around $\rho_s=2.0$ g/cm$^3$; in agreement with previous results on xerogels [6,7], it increases drastically to a maximum value at $T_s=800^\circ\text{C}$ (for a heat treatment of 2 h) and then equilibrates at $=2.2$ g/cm$^3$ when full densification is achieved. We also found that the $\rho_s$ values depends of the time of the sintering treatment. Figure 2(b) shows a typical example for the M40-N aerogel. The $\rho_s$ values obtained at intermediate sintering temperatures (500—900°C) seem unrealistic; the pycnometry may not be an adequate technique for these types of materials. Considerable additional research is necessary to fully explain these behaviors.

A typical temperature evolution of the pore radius distribution and the average pore radius are shown in figs. 3 and 1 respectively for the aerogel M60-N. At low $T_s$, the aerogels have a broad, continuous and slowly increasing distribution of pores, peaking at a well defined radii. This sharp cut-off as well as the mean radius value depend on the sintering temperature. At higher $T_s$, the distribution becomes smoother.

When left in a humid atmosphere, the porous gels adsorb water. The adsorption kinetics were studied for the M60-N aerogel series, previously dried at 200°C, and placed in a 95% RH atmosphere. The time evolution of the relative ratio...
Fig. 2. (a) Evolution of the structural (true) density, $\rho_s$ (g/cm$^3$), and apparent density, $\rho_a$ (g/cm$^3$), for various aerogels as a function of sintering temperature (heat treatment of 2 h). (b) Time evolution of the structural (true) density, $\rho_s$ (g/cm$^3$), for aerogels M40-N heat treated at 600 and 800°C.

\[ K = [M(t) - M(0)]/[M(\infty) - M(0)] \]

where $M$ is the mass of the gel + water at the indicated times, was found identical for all gels, independent of the sintering temperature, $T_s$. The kinetics initially follow a $t^{1/2}$ law characteristic of a diffusion mechanism and 260 h were necessary to obtain full saturation ($K = 1$). The relative H$_2$O content, $W_s$ (gH$_2$O/gSiO$_2$ dry), at saturation, diminishes with $T_s$ but the relative ratio, $W_s/V_p$, where $V_p$ is the total pore volume, increases with $T_s$, a value of 1 being only obtained for $T_s > 912$°C. This variation, also observed for aerogels [8], is probably related to the rough, fractal structure of the gel surface observed at low $T_s$, indicating that the adsorption behavior of H$_2$O is largely governed by pore geometry rather than surface chemistry as was thought by Iler [1].

Fig. 3. Evolution of the pore size distribution for aerogels M60-N heat treated in air at: $\circ$, 400°C; $\square$, 600°C; $\triangle$, 912°C; $\circ$, 1052°C; and $\ast$, 1100°C.

4. Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance relaxation techniques are well suited to study water molecules absorbed in the vicinity of an interface. Various studies have been reported for silicate gels [9–17]. The older works [9,11] dealt with commercial products and the results were strongly affected by impurity effects. In pure silica gels, a marked decrease of the proton longitudinal and transversal relaxation time $T_1$ and $T_2$ is observed compared with the values in pure water. All the models proposed suggest that the pore fluid contains at least two separate phases: a surface phase (bound water) which has a short relaxation time and a bulk phase with a long relaxation time. These two phases are in rapid exchange. The
observed relaxation times and population fractions have been calculated as a function of the lifetime of the nuclei in these two phases [11–14].

The temperature dependence of the longitudinal and transverse relaxation times $T_1$ and $T_2$ of the aerogel M60-N, heat treated at 600°C for 2 h and rehydrated to different H$_2$O coverages, $0 \leq \theta_{H_2O} < 6$, has been measured using a pulse NMR spectrometer working at 24.04 MHz. $T_1$ was determined by the progressive saturation method [18]; the $T_2$ values, longer than 100 μs, were determined by spin–echo technique (excitation pulse $\pi/2 = 2$ μs, dead time of detector = 12 μs) and the faster values have been obtained directly from the free induction decay of the magnetization following a $\pi/2$ pulse. Contrary to Woessner [14], the relaxation curves exhibited only a single component whatever the temperature and water coverage.

The room temperature $T_1$ data are in excellent agreement with those of Hanus and Gillis [16] obtained for a silica powder used for catalysis support (Alfa Division). Using the indices ‘a’ to describe the bulk H$_2$O phase and ‘b’ for the bound H$_2$O phase, the normalized relaxation rate $R_1 = T_1^{-1}$ obs/$T_1$ increases linearly with the silica–water ratio $C$ (fig. 4). The slope of the straight line is

$$\alpha = 2.99 \times 10^{-5} \sigma S \left( \frac{R_{1b}}{R_{1a}} - 1 \right) = 1.43,$$

where $\sigma = 9.25$ (nm$^{-2}$) [10–15] is the bound water molecular surface density and $S = 787$ m$^2$/g is the aerogel specific surface. The lower limit for the relaxation ratio $T_{1b}^{-1}/T_{1a}^{-1}$ being 7.6, $T_{1b}$ (bound water) is therefore $\leq 0.25$ s, indicating the existence of cross-relaxation between the protons in the bound phase and the surface nuclei (protons of the hydroxyl groups).

The room temperature variation of $T_2$ is shown in fig. 5 and clearly indicates a drastic change for water coverage around $\theta = 2.2$ which is believed to delimit the transition between bound and bulk water.

Three typical temperature dependences of $T_1$ and $T_2$ are shown in fig. 6 for water coverage $\theta = 3.7$, 2.8 and 0.6, respectively. When the temperature decreases, the $T_1$ values diminish and pass through a minimum. The data obtained with

![Fig. 4. Normalized relaxation rate, $R_1 = T_1^{-1}$ obs/$T_1$, measured at room temperature versus silica–water ratio $C$ (gSiO$_2$/mH$_2$O) for the aerogel M60-N heat treated at 600°C for 2 h. The value $T_{1a} = 0.5$ s was used to scale down the straight line to $R_1 = 1$ for $C = 0$ and corresponds to the value of pure water containing $5 \times 10^{18}$ O$_2$ molecules/g H$_2$O [19]. The water coverage, $\theta$, shown by the arrows were calculated assuming a H$_2$O molecule area of 0.108 nm$^2$ [10–15] ($\theta = 1$ corresponds to one monolayer).]

\[\theta = 3.7\] indicate a change of state (depressed freezing point) occurring at $-20°C$. This transition is not as pronounced for $\theta = 2.8$ and does not occur for $\theta = 0.6$. Moreover, the shift of the

![Fig. 5. Room temperature variation of the transverse relaxation time, $T_2$, of the aerogel M60-N versus the silica–water ratio, $C$ (gSiO$_2$/mH$_2$O). The arrows indicate the water coverage, $\theta$, calculated with $A_{H_2O} = 0.108$ nm$^2$ [10–15].]
tence, for $\theta = 2.8$, of a bulk water phase which freezes at $T < 0^\circ$C, the temperature shift being larger for decreasing values of $\theta$. The low water coverage data are similar to those obtained by Woessner [13] and Michel [15]. The maximum of $T_2$ at $-25^\circ$C and the subsequent decrease of $T_2$ at higher temperature (also observed in the two other samples) result from nuclear transfer which occurs more rapidly with increase of temperature. In all samples, the low temperature increase of $T_2$ with temperature has the same apparent activation energy of $\approx 7.2$ kcal/mol as found by Woessner [13].

The ‘freezing’ process observed at low temperature does not necessarily indicate ice formation but only a reduction in molecular mobility due to the formation of a more rigid and structured layer, since the $T_2$ value for ice is still one order of magnitude lower.

5. Dielectric relaxation

The dielectric constant of fused silica measured at 20°C at audio frequencies is $\varepsilon \approx 3.8$ and decreases slightly ($\Delta \varepsilon'/\varepsilon' = 0.008$) down to 4 K [21]. Dielectric losses are observed only at low temperature. A peak at $T = 27$ K was attributed to deformational losses (oscillation of bridging oxygen in nearly collinear Si–O–Si bonds) and another peak at $T < 1.3$ K was attributed to the presence of hydroxyl groups [22].

The dielectric relaxation of silica gels has been studied by various authors [8,23–28] and has been reviewed by Hench and West [5,29]. At room temperature, pure, dehydroxylated materials do not exhibit dielectric relaxation. When only surface silanol groups are present ($\theta_{\text{H}_1\text{O}} = 0$), a loss peak is observed at GHz frequencies, which is attributed to SiOH dipolar orientation [25,27].

Liquid water molecules have only one dipolar relaxation peak at 23.4 GHz. However, when they are adsorbed on surfaces, other relaxation frequencies appear. The bonding to the silanols causes modification in the GHz region [27]; the relaxation has been attributed both to the relative lifetimes of H-bonds formed by clusters of adsorbed water and to the rate of transfer of pro-
tons between the adjacent H-bonded water molecules adsorbed on surface SiOH groups. For \( \theta_{\text{H}_2\text{O}} > 1 \) [27], a second relaxation peak was observed at 14 GHz at 0°C; it is related to the formation of a free water phase.

Dielectric relaxation is also observed at audio frequencies, the frequency position of the maximum of \( \tan \theta \) depending strongly on water coverage and temperature [8,23,24,26,30]. The relaxation has been attributed to interfacial polarization (charge build up at the electrodes) resulting from proton conduction in the adsorbed water layer via a hopping mechanism which depends on the structure of the adsorbed water and its thickness. Direct current conductance across the terminals also causes dielectric absorption but at lower frequencies.

Adsorbed water in aerogels presents similar relaxation. Figure 7 shows the frequency variation of \( \varepsilon' \) and \( \tan \delta \) measured at 25°C with the aerogel M60-N for different water coverage. For \( \theta = 0 \), \( \varepsilon' \) is frequency-independent and its value is smaller than that of fused silica, reflecting the porous nature of the material [28]. For \( \theta > 0 \), the dielectric constant, \( \varepsilon' \), presents a typical dispersion behavior and its value, measured at 10^6 Hz, increases more than linearly with the \( \text{H}_2\text{O} \) content up to \( W_{\text{a}} = 0.30 \) g\( \text{H}_2\text{O}/\)g\( \text{SiO}_2 \) corresponding to \( \theta_{\text{H}_2\text{O}} = 1.5 \) (maximum value which was possible to adsorb without breaking the aerogel). By contrast with xerogels [26] the loss peaks are only observed for \( \theta > 1 \); at lower coverage, they are located at low frequencies and are masked by dc effects even if very low applied ac signals are applied. The frequency variation versus \( \text{H}_2\text{O} \) content is shown in fig. 8 together with results

![Figure 7](image1)

![Figure 8](image2)
obtained for SiO$_2$ xerogels [26]. The faster variation and the large shift of the peaks frequency may result from different water structure caused by the fractal nature of the aerogel surface.

6. Conclusion

A systematic study of the structural properties of silica aerogels prepared from TMOS : methanol : water sols has been presented. The main original finding is related to the drastic variation of the structural density observed during the sintering procedure. The relaxation properties of water adsorbed on the aerogel surface has been studied by dielectric relaxation spectroscopy and nuclear magnetic resonance techniques as a function of the temperature and water coverage. The overall behavior corroborates that found for silica gels or xerogels. The adsorbed water molecules belong to two different phases: H$_2$O molecules bonded to silanol groups and adjacent to the surface which do not show a freezing behavior and bulk H$_2$O molecules observed for $\theta = 2$ showing a depressed freezing temperature.

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References