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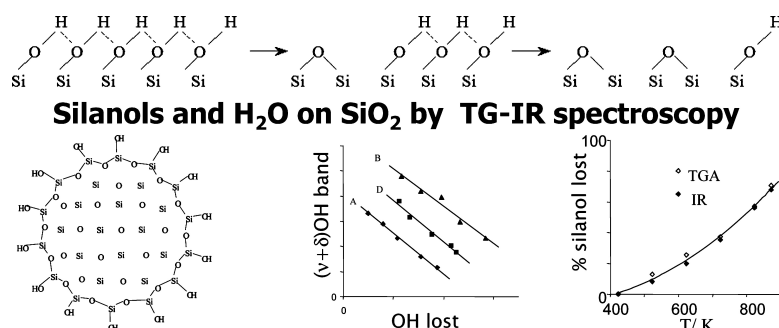
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## Quantification of Water and Silanol Species on Various Silicas by Coupling IR Spectroscopy and in-Situ Thermogravimetry

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Five silica samples (four precipitated silicas provided by commercial suppliers and one with the MCM-41 structure) have been studied by infrared spectroscopy and by a homemade thermogravimetry–infrared spectrum (TG-IR) setup. The silanol amount, accessibility to water, and different alcohols, and the affinity to water of these various silicas were compared and quantified. TG-IR measurements allowed the precise determination of the integrated molar absorption coefficient of the  $(\nu + \delta)\text{OH}$  band,  $\epsilon_{(\nu + \delta)\text{OH}} = (0.16 \pm 0.01) \text{ cm } \mu\text{mol}^{-1}$ . It is independent of the sample origin and the concentration of silanol groups on silicas. For the precipitated dried samples evacuated at room temperature, the silanol concentration  $C_{\text{OH}}$  varies between 3.6 and 7.0  $\text{mmol g}^{-1}$ . It is 5.3  $\text{mmol g}^{-1}$  in the case of the MCM-41 sample. Exchange experiments with  $\text{D}_2\text{O}$ , followed by back-exchanges with different alcohols (methanol, propan-2-ol, 2-methyl-propan-2-ol, and 3-ethyl-pentan-3-ol) have been followed by infrared spectroscopy. All of the silanols of the MCM-41 sample are accessible to water and alcohol molecules. By contrast, about 20% of the silanols in precipitated samples are not exchanged by  $\text{D}_2\text{O}$  (internal silanols). Accessibility decreases with alcohol size; the main effect is relative to methanol. Taking into account the sample specific surface areas and the silanol accessibility to  $\text{D}_2\text{O}$ , the surface silanol density of precipitated silicas is close to 8 OH per  $\text{nm}^2$ , at maximum coverage. At variance, the silanol surface density of the MCM silica is much lower, 4 OH per  $\text{nm}^2$ . The TG-IR setup has also been used to determine the amount of water adsorbed on silicas through the intensity of the  $\delta\text{H}_2\text{O}$  band. It varies linearly with the concentration of adsorbed water, whatever the silica sample. The integrated molar absorption coefficient of two bands,  $\epsilon_{\delta\text{H}_2\text{O}} = (1.53 \pm 0.03) \text{ cm } \mu\text{mol}^{-1}$  and  $\epsilon_{(\nu + \delta)\text{H}_2\text{O}} = (0.22 \pm 0.01) \text{ cm } \mu\text{mol}^{-1}$ , have been determined. The number of  $\text{H}_2\text{O}$  molecules adsorbed per  $\text{nm}^2$  has been compared on the five samples under an equilibrium pressure of 13 hPa at room temperature. Taking into account the number of silanols accessible to  $\text{D}_2\text{O}$  for each sample, the silica–water affinity has been defined by the  $\text{H}_2\text{O}/(\text{SiOH}_{\text{surf}})$  ratio. It is close to 0.8–0.9 for the precipitated samples but lower (0.7) in the case of the MCM one. This result is explained by the more important amount of isolated silanol groups presented by this sample.

### 1. Introduction

Silica ( $\text{SiO}_2$ ) is widely used in industry, for instance, as an absorbent, a catalyst support, a reinforcing agent, a component of chemical sensors, or in many pharmaceutical applications. Its efficiency and usefulness depend strongly on its surface composition, i.e., silanol and water contents.<sup>1</sup> Water content is a key parameter when  $\text{SiO}_2$  is used for applications involving functionalization of the material: the reactant used for grafting any organic molecule being generally very reactive to moisture, the presence of adsorbed water is often not desired.<sup>2</sup> However, the hydrophilic properties of silica are required for its use in applications as a desiccant.

One industrially important application of some silica is as support for olefin polymerization catalysts.<sup>3</sup> Highly active and selective single site metallocene-based catalysts with their promoters (alumoxanes for instance) are built on such supports.

Both the active moiety and its promotor are relatively bulky and water sensitive molecules.

The silanol groups are the main surface reactive sites and their properties (nature, concentration, distribution, accessibility, etc.) will determine the chemical activity of the silica. While their concentration can be measured by infra-red (IR) or nuclear magnetic resonance (NMR) spectroscopies or thermogravimetry (TG), their accessibility to reactants is very dependent upon the pore size distribution, which, in turn, can be tuned during synthesis.<sup>4</sup> All of the silanol groups are not equally accessible to bulky molecules,<sup>5,6</sup> and therefore, the silanol content becomes a meaningful parameter only when the accessibility to each reactant is reported.

IR spectroscopy is a powerful and proven technique to study the surface species present on silica surfaces<sup>7</sup> and allows one to quantify water content, silanol density, and accessibility. Water can be easily distinguished from the silanol groups in the near-infrared range, in particular, the combination band  $\nu_2 + \nu_3$  of

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**Table 1. Textural Properties and Nature of the Five Studied Silica<sup>a</sup>**

silica	supplier	type	specific surface area (m <sup>2</sup> g <sup>-1</sup> )		pore volume (cm <sup>3</sup> g <sup>-1</sup> )	pore diameter (nm)
			BET <sup>b</sup>	$\alpha$ plot		ads. branch
A	INEOS	ES-70X	220	215	0.90	20
B	FUJI SILYSIA	P-10	255	260	0.92	17
C	PQ corporation	MS-3030	270	265	0.79	14
D	GRACE	SP9-446	415	415	0.81	9
E	laboratory-made	MCM-41	765	730	1.10	60

<sup>a</sup> Because of its MCM type, silica E is characterized by  $S_{\text{MCM}} = 530 \text{ m}^2 \text{ g}^{-1}$ ,  $S_{\text{ext}} = 200 \text{ m}^2 \text{ g}^{-1}$ ,  $V_{\text{MCM}} = 0.52 \text{ cm}^3 \text{ g}^{-1}$ , and  $V_{\text{ext}} = 0.58 \text{ cm}^3 \text{ g}^{-1}$ . Using the KJS algorithm, the pore size of the regular mesopores is 3.8 nm, and the mean pore size of the textural mesopores is about 60 nm. <sup>b</sup> In the estimation of  $S_{\text{BET}}$ ,  $a_{\text{m}}(\text{N}_2) = 0.135 \text{ nm}^2$  is assumed.

molecular water, called  $(\nu + \delta)\text{H}_2\text{O}$  hereafter, and the  $(\nu + \delta)\text{OH}$  of hydroxyl groups enable one to discriminate both species.<sup>8</sup> Moreover, it has been demonstrated that quantitative IR transmission data are obtained by coupling IR and TG in a single measurement cell (TG-IR).<sup>9</sup> The aim of this article is to determine the molar absorption coefficients of the characteristic water and silanol bands to use them for a quantitative measurement of silanol and water content on various commercially available silica. The accessibility of the various hydroxyl groups are then derived by isotopic H/D exchange from probe molecules of increasing molecular size.

## 2. Experimental Section

Five silica samples, named A to E, were used in this work. They originated from different suppliers and were proposed as supports of single-site catalysts for ethylene polymerization. Samples A to D are silica-gels, while sample E is a MCM-41 mesoporous silica provided by Total. This mesostructured material was obtained after a pseudomorphic transformation of a preformed porous silica by dissolution/recrystallization of a commercial silica from Rhodia (ZEOSIL 175MP), a method introduced by Martin et al. in 2002.<sup>10</sup> The synthesis procedure, well described in ref 11, is detailed in the Supporting Information. The nature and the textural properties of the five samples used are reported in Table 1.

TG and IR measurements were carried out simultaneously in the homemade setup described elsewhere.<sup>9</sup> This setup allows one to maintain the sample (self-supporting pellet, 4.91 cm<sup>2</sup>, ca. 15 mg cm<sup>-2</sup>) at a fixed position in the infrared beam of the spectrometer (Nicolet, Avatar System 360, resolution 4 cm<sup>-1</sup>, one-level zero-filling, MCT detector) while its mass is recorded. Prior to each experiment, the silica sample was dehydrated under vacuum ( $10^{-5}$  hPa) at room temperature until the mass loss rate was negligible, and the  $(\nu + \delta)\text{H}_2\text{O}$  band vanished, i.e., about 1 h under degassing. During the measurement of the molar absorption coefficient of adsorbed water, the relative water partial pressure inside the cell was then increased gradually to 13 hPa. At each pressure, an IR spectrum was recorded after reaching equilibrium, marked by a constant mass of the pellet.

Gradual dehydroxylation of the silica allows the determination of the molar absorption coefficient of silanol. The dry sample was heated progressively (ramp 5 K min<sup>-1</sup>) and kept at each temperature until the recorded mass loss was insignificant. All of the spectra, except the initial one (no dehydroxylation) were recorded at the same temperature, 423 K, since no difference had been observed previously between spectra recorded after evacuation at 298 and 423 K.<sup>7</sup>

The accessibility measurements were performed at room temperature on self-supporting discs (2 cm<sup>2</sup>, ca. 10 mg cm<sup>-2</sup>) of silica evacuated overnight under vacuum ( $10^{-5}$  hPa). All spectra were recorded on a Nicolet Magna System 550 spectrometer (resolution 4 cm<sup>-1</sup>, one-level zero-filling, DTGS detector). Liquid reagents (methanol, propan-2-ol, 2-methyl-propan-2-ol, and 3-ethyl-pentan-3-ol) of analytical grade were used after drying over 3A molecular sieves. Nitrogen adsorption isotherms were measured with an ASAP 2000 apparatus, after drying the silica under vacuum ( $10^{-3}$  hPa) at 375 K for 3 h.

## 3. Results and Discussion

**3.1. Textural Properties of Silicas.** Physisorption results from both specific and nonspecific interactions, depending on the nature of the adsorbate (N<sub>2</sub>, Ar, or Kr).<sup>12</sup> In the case of porous hydroxylated silica, values of specific surface area<sup>13</sup> (extracted as BET surface area) differ appreciably because the spherical noble gas molecule, not prone to polarization, investigates only the texture of the solid, whereas interaction of the silanol proton electrical field with the quadrupole moment of dinitrogen could take place. For adsorption on silica having considerable amount of hydroxyls, the dinitrogen molecule adsorbs perpendicular to the surface. Its molecular surface area decreases to 0.135 nm<sup>2</sup>, which obviously changes the BET area.<sup>14</sup>

Textural parameters of the five silicas under study were extracted from nitrogen sorption isotherms at 77 K and are reported in Table 1. Isotherms are plotted in Figure 1A. Total pore volume was read at relative pressure  $P/P^0 = 0.99$ . Specific surface area was determined through BET modeling in the  $[0.03-0.25] P/P^0$  range but also by  $\alpha$ -plot method<sup>15</sup> using Silica-1000 (22.1 m<sup>2</sup> g<sup>-1</sup> assumed) as a reference.<sup>16</sup> Pore size distributions, plotted in Figure 1B, were extracted from the adsorption branch using the BJH method<sup>17</sup> including the KJS correction<sup>18</sup> when necessary. Amorphous samples A to D have similar pore volumes about 0.8–0.9 cm<sup>3</sup> g<sup>-1</sup> with unimodal pore size distribution in the mesoporous range. But, due to narrower average pore size, the surface area of sample D (415 m<sup>2</sup> g<sup>-1</sup>) is markedly higher than those of samples A to C (210–270 m<sup>2</sup> g<sup>-1</sup>). In contrast, sample E shows a typical isotherm of tubular (KJS estimated  $D = 3.8$  nm) mesoporous material. The hysteresis loop at the high pressure part of the isotherm has been considered as revealing an incompleting transformation of the amorphous parent silica<sup>10</sup> with an additional textural porosity

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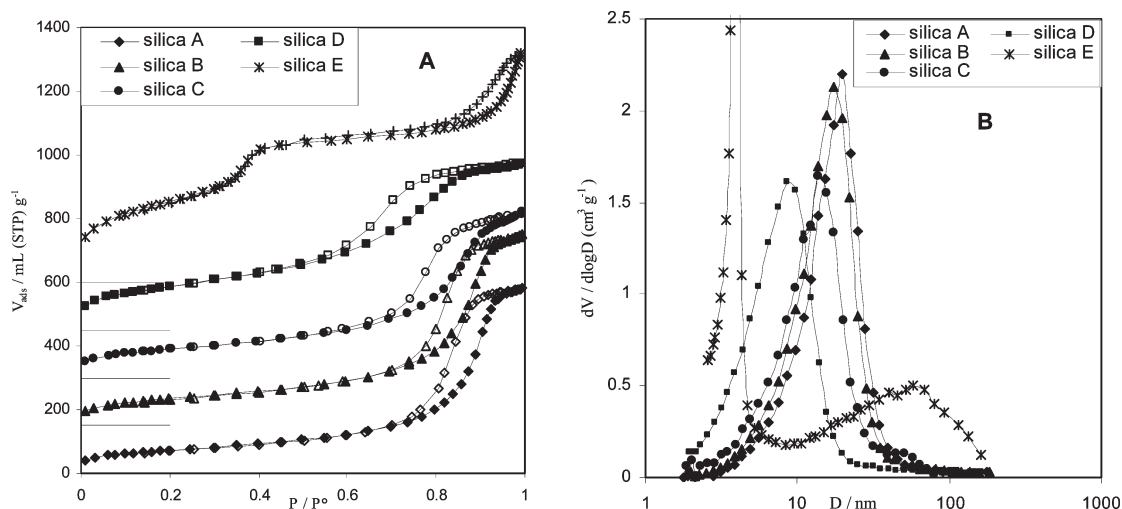
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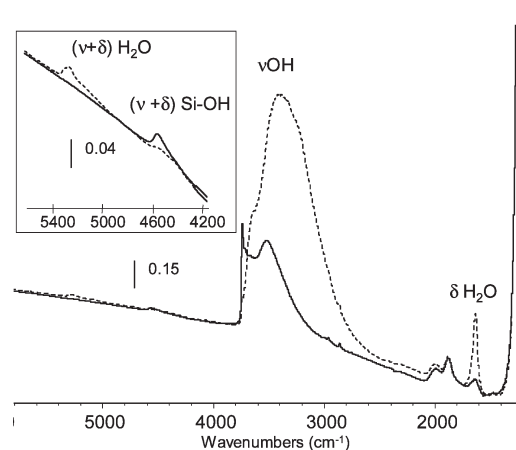


**Figure 1.** (A) N<sub>2</sub> adsorption isotherms of the five silicas. Closed symbols correspond to the adsorption branch and open symbols to the desorption branch. For the sake of readability, the isotherms are shifted upward for  $n \times 150 \text{ mL g}^{-1}$ . (B) Pore size distribution.

characterized by a broad pore size distribution centered at about 60 nm as given from the adsorption branch analysis. For this sample, surface and volume are divided into contributions for the regular and textural porosities (see the footnote at the bottom of Table 1).

**3.2. Qualitative Description of IR Spectra.** *3.2.1. Various Silanol Types Presented by Dehydrated Silicas.* Extended literature results report that adsorbed water species are characterized by a  $\delta\text{H}_2\text{O}$  band near  $1630 \text{ cm}^{-1}$  and a  $(\nu + \delta)\text{H}_2\text{O}$  combination band at about  $5260 \text{ cm}^{-1}$ .<sup>2</sup> As shown in Figure 2 (solid line), water was not detected at the silica surface after outgassing under  $10^{-5} \text{ hPa}$  for 1 h at room temperature (RT) since the  $5260 \text{ cm}^{-1}$  had completely vanished. The persistence of a weak band near  $1620 \text{ cm}^{-1}$  is explained by the occurrence in this range of a combination or an overtone band involving the framework silica vibration.<sup>19</sup> The silanol groups are characterized by their  $\nu\text{OH}$  and  $(\nu + \delta)\text{OH}$  absorption bands in the  $3800\text{--}3000 \text{ cm}^{-1}$  and  $4800\text{--}4200 \text{ cm}^{-1}$  regions, in agreement with ref 2.

Figure 3 collects the spectra of silica B at various stages of dehydroxylation. In spectrum a,  $\nu\text{OH}$  bands appear at about  $3520, 3670, 3710$  (sh), and  $3745 \text{ cm}^{-1}$ . They are assigned to H-bonded, internal, terminal, and isolated silanol groups, respectively.<sup>20</sup> When the dehydroxylation process occurs by heating under vacuum at increasing temperature, the relative proportions of these species vary as shown by the change in the relative band intensities. According to Scheme 1, the first step would be the elimination of two H-bonded hydroxyls, while the number of terminal silanols remains constant. In the second step, the complete elimination of the remaining H-bonded hydroxyls would lead to the formation of isolated silanols. Such a scheme explains well the intensity decrease of the  $\nu\text{OH}$  band related to the H-bonded species ( $3520 \text{ cm}^{-1}$ ), which almost disappears at  $723 \text{ K}$ , and the increase of the isolated hydroxyl band ( $3745 \text{ cm}^{-1}$ ) with the temperature increase (Figure 3, b–f). The wavenumber of this band depends on the pretreatment temperature, the shift being correlated to the concentration of H-bonded silanols relative to that of isolated silanols.<sup>21</sup>



**Figure 2.** Infrared spectra of silica C in the  $1200\text{--}5800 \text{ cm}^{-1}$  range. Dotted line: spectrum recorded under room atmosphere. Solid line: spectrum recorded after outgassing the sample under vacuum ( $10^{-5} \text{ hPa}$ ) during 1 h.

The band intensity of internal silanols ( $3670 \text{ cm}^{-1}$ ) decreases more slowly when the temperature of evacuation increases while a weak shoulder remains at  $873 \text{ K}$ . By contrast, the  $(\nu + \delta)\text{OH}$  combination band intensity regularly decreases with the increase of temperature. After dehydroxylation at high temperature [ $823\text{--}873 \text{ K}$ ], the maximum of this broad composite band is shifted from  $4560$  to  $4520 \text{ cm}^{-1}$ .<sup>22</sup> This shift is explained by the occurrence of two bands resulting from a coupling between the  $\delta\text{OH}$  mode and a vibration of the  $\text{O}_3\text{SiOH}$  group as evidenced by the two components at  $4590$  and  $4515 \text{ cm}^{-1}$  arising in the spectrum recorded at  $77 \text{ K}$ .<sup>23</sup> The perturbation of silanols rationalizes well the variations of intensity of the two components with temperature variation.<sup>22</sup>

In Figure 4, the spectra of the five silicas are shown for comparison, the spectra being normalized to the same mass. Intensity of the  $(\nu + \delta)\text{OH}$  band provides a ranking of the  $C_{\text{OH}}$  specific concentration (in  $\text{mmol g}^{-1}$ ) of all the hydroxyl groups. The decreasing order  $D > E > C \sim B \sim A$  is obtained.

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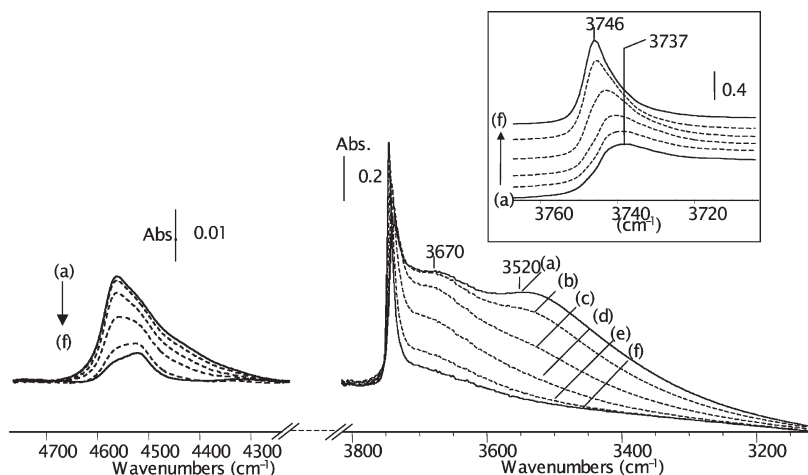
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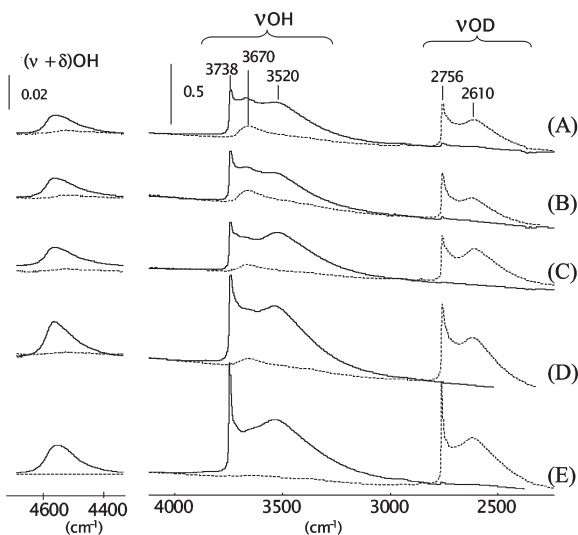
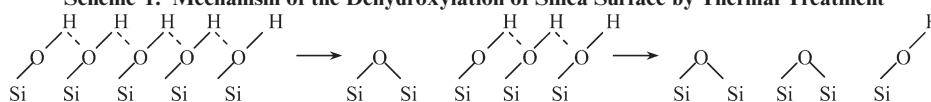
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**Figure 3.** Spectra of silica B recorded after outgassing at 423 K (a), 523 K (b), 623 K (c), 723 K (d), 823 K (e), and 873 K (f).

**Scheme 1. Mechanism of the Dehydroxylation of Silica Surface by Thermal Treatment**



**Figure 4.** IR spectra of the dehydrated silicas A, B, C, D, and E before (solid line) and after  $D_2O$  treatment (dotted line). Spectra are normalized to a mass of 10 mg.

However, the  $\nu OH$  band profile gives insight into the distribution between the different silanol groups: the distribution varies from one silica to another one. Since absorption coefficients of silanols strongly depend on H-bonding interactions, only qualitative conclusions can be derived. Sample E has the greatest population of isolated silanols and very few internal ones. By contrast, the four other silicas present internal silanols. Silica A and B are quite similar; silica C presents more associated silanols (band at  $3520\text{ cm}^{-1}$ ) and less internal ones (band at  $3670\text{ cm}^{-1}$ ). The most important  $C_{OH}$  concentration for silica D can be related to its high surface area. The  $3670\text{ cm}^{-1}$  band intensity is weak relative to those of the other bands, indicating the presence of a smaller number of internal silanols.

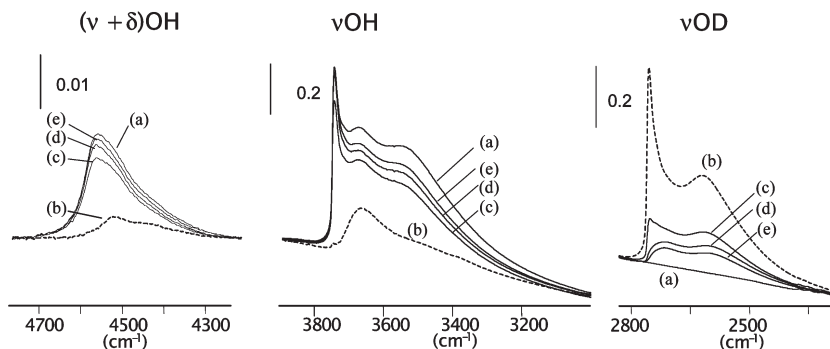
**3.2.2. Silanol Accessibility.** The silanol groups are the major sites for adsorption and reactions on silica. They undergo various interactions, some of which can drastically alter the surface chemistry of  $SiO_2$ , such as its hydrophilic property.

It was proposed that the extent to which silanols react with hydrogen sequestering agents or deuterated alcohols depends not only on the silanol density but also on the size of reactants and steric factors such as silanol accessibility.<sup>5</sup> H-D exchange using reactants of various sizes has proved to be an excellent method to determine the OH accessibility at the molecular level and therefore could assess the potential of a particular surface for the grafting of functionalized molecules.<sup>5,6</sup> H-D exchanges have been performed on the five silica samples. They have been followed by IR spectroscopy since this technique is very sensitive to the isotopic substitution: upon OH/OD exchange, there is a downward shift of the stretching vibration, from  $3750\text{ cm}^{-1}$  ( $\nu OH$ ) to  $2760\text{--}2600\text{ cm}^{-1}$  ( $\nu OD$ ).

The procedure used in this study is as follows: all accessible silanols have been exchanged by repeated exposure at RT of the dried silica to deuterated water vapor (each exposure was followed by evacuation). After each exchange, an IR spectrum was recorded, and the process repeated until no measurable difference was observed. Then a large excess of alcohol probe molecules was successively introduced at RT on the deuterated silica sample in the order of decreasing size (3-ethyl-pentan-3-ol, 2-methyl-propan-2-ol, propan-2-ol, and methanol) and then evacuated at room temperature to evaluate silanol accessibility to reactants bulkier than water.

The IR spectra of all of the dried silicas before and after the final  $D_2O$  treatment are collected in Figure 4. A strong decrease of intensity in the  $\nu OH$  range parallels the formation of the  $\nu OD$  bands. A broad signal centered at  $3670\text{ cm}^{-1}$  remains, its intensity varying from one sample to the other. This band characterizes the Si-OH groups inaccessible to water molecules and is therefore assigned to perturbed OH groups, located on the interparticle surfaces or/and inner surfaces. They have been called internal structural water but are in fact internal hydroxyl groups.<sup>24</sup> It is clear that their number is about the same for silicas A and B and lower for silicas C and D, whereas it is quite negligible for silica E.

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**Figure 5.** IR spectra of silica B recorded after dehydration (a), then after H/D exchange by D<sub>2</sub>O treatment (b-dotted line), and then after back-exchange successively by 3-ethyl-pentan-3-ol (c), 2-methyl-propan-2-ol (d), and methanol (e). The spectrum after back-exchange with propan-2-ol is not shown for the sake of clarity.

As an example, Figure 5 displays the spectra of silica B before and after exchange with D<sub>2</sub>O (spectra a and b) and after successive back-exchanges with the different alcohols (spectra c–e). The intensity increase in the  $\nu$ OH range and the simultaneous decrease in the  $\nu$ OD range are due to the back-exchange of SiOD groups accessible to the alcohol introduced into the cell. The  $\nu$ OD band remaining after the adsorption of a given alcohol is assigned to the silanol groups exchangeable with D<sub>2</sub>O but inaccessible to the OH group of this alcohol.

In the case of silica B, methanol, propan-2-ol (not shown), and 2-methyl-propan-2-ol (Figure 5, spectra d and e) almost regenerate isolated silanols. Unchanged silanol groups are characterized by  $\nu$ OD bands at 2710 and 2600 cm<sup>−1</sup> corresponding to  $\nu$ (OH) at 3670 cm<sup>−1</sup> (internally accessible to D<sub>2</sub>O but not to alcohols) and 3530 cm<sup>−1</sup> (H-bonded silanols). After back-exchange with the bulkiest alcohol, 3-ethyl-pentan-3-ol, in addition to these two bands, a  $\nu$ OD band is noted at 2754 cm<sup>−1</sup>, characterizing isolated silanols inaccessible to this alcohol. They are similar to the silanol groups localized in the small channel (~0.55 nm) of low aluminum MFI zeolites.<sup>25</sup>

These back-exchange experiments show that silica E is unique since, at variance with the four mesoporous silica samples, all of the silanols are back-exchanged whatever the alcohol used. Use of bulkier molecules such as silazane is more discriminant.<sup>26</sup> The fraction of the silanol groups accessible to water and the different alcohol molecules will be determined in the quantitative part of this work.

**3.2.3. Hydrated Silica.** As reported before, the spectrum of hydrated silica (Figure 2, dotted line) displays a  $\delta$ H<sub>2</sub>O band around 1630 cm<sup>−1</sup>. The fundamental O–H stretching vibrations ( $\nu_1$  and  $\nu_3$  modes) of adsorbed water give rise to bands in the 2800–3750 cm<sup>−1</sup> range. They overlap the  $\nu$ (Si–OH) bands, which are red-shifted from their position in the spectra of dehydrated silica, due to H-bonding interaction between silanol groups and water molecules. This explains the occurrence of the broadband at about 3300 cm<sup>−1</sup> (Figure 2, dotted line). Since it occurs from both silanol and water vibrations, it cannot be used to quantify adsorbed water molecules. By contrast, the  $\delta$ H<sub>2</sub>O band at 1630 cm<sup>−1</sup> and the  $(\nu + \delta)$ H<sub>2</sub>O combination band at 5260 cm<sup>−1</sup> are specific to water molecules,<sup>2,27</sup> and therefore their intensities are tools to quantify the amount of water adsorbed on silica.

**3.3. Quantitative Aspect.** **3.3.1. Silanol Population.** As reported before (Scheme 1), the thermal treatment of silica

results in dehydroxylation due to the elimination of water molecules by condensation of two vicinal OH groups. Consequently, it is possible to evaluate the total amount of hydroxyl groups from classical thermogravimetric measurements (TG): the number of OH groups is estimated from the mass loss between the dry, fully hydroxylated sample and the completely dehydroxylated one.<sup>28</sup>

The area of an IR band specific to a species allows its quantification through the application of the Beer–Lambert law (see Supporting Information). Since in the case of hydroxyl groups, the molar integrated absorption coefficient of the fundamental  $\nu$ OH band,  $\epsilon_{\nu\text{OH}}$ , strongly depends on H-bonding interactions,<sup>29,30</sup> the area of the whole  $\nu$ OH massif is not proportional to the OH concentration; the relative proportions of its different components vary from one sample to the other and with temperature. By contrast, it is shown here that the molar integrated absorption coefficient  $\epsilon_{(\nu + \delta)\text{OH}}$  of the  $(\nu + \delta)$  OH combination band does not vary with the nature and the concentration of silanol groups present on a given silica sample. Absorbance at maximum of this band has been already used by Dodd and Fraser<sup>31</sup> to determine the OH content of silica glasses. More recently, different authors such as Davis et al.<sup>32</sup> or Carteret<sup>33</sup> have determined  $\epsilon_{(\nu + \delta)\text{OH}}$  by separated IR and TG experiments, but their results are quite different. Our (TG-IR) setup allows the simultaneous measurements by infrared and gravimetry; we can therefore unambiguously determine the  $\epsilon_{(\nu + \delta)\text{OH}}$  coefficient.

Only three (A, B, and D) of the five silicas have been reported because the thermogravimetric measurements of the other two were perturbed by electrostatic interferences. The silica treated at 423 K, i.e., totally dehydrated but not dehydroxylated, was chosen as the reference state for calculation of the percent loss.<sup>7,34</sup> The TG-IR results simultaneously obtained allow one to plot (Figure 6A) the  $(\nu + \delta)$ OH band area, [4200–4800 cm<sup>−1</sup>], versus the quantity of OH lost reported as  $\mu\text{mole per unit area of pellet}$  ( $\mu\text{mol cm}^{-2}$ ) simply by considering that the loss of one H<sub>2</sub>O molecule results from the condensation of two Si–OH groups. Temperature was increased from 423 to 873 K. The data obtained for each of the three measured silicas are well fit with

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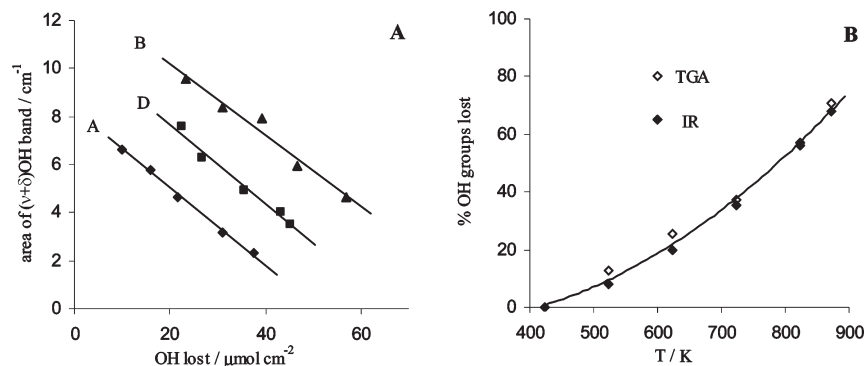
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**Figure 6.** (A) Evolution in the 423–873 K range of the  $(\nu + \delta)\text{OH}$  area (from 4200 to 4800  $\text{cm}^{-1}$ ) of silicas A, B, and D wafer versus the number of OH lost per unit surface of pellet in  $\mu\text{mol per cm}^2$  deduced from TG measurements. (B) Percentage of OH lost versus the temperature of outgassing for silica A determined by IR or TG measurement.

straight lines. Therefore, the dehydroxylation degree of the silica surface does not significantly influence the  $(\nu + \delta)\text{OH}$  integrated molar absorption coefficient. The slope of each straight line leads directly to the integrated molar absorption coefficient. The averaged value,  $\epsilon_{(\nu + \delta)\text{OH}} = (0.16 \pm 0.01) \text{ cm } \mu\text{mol}^{-1}$ , is in good agreement with that obtained by Carteret ( $0.17 \pm 0.01) \text{ cm } \mu\text{mol}^{-1}$ .<sup>33</sup> As illustrated in Figure 6B for silica A, the degree of dehydroxylation calculated from the mass loss (open symbols) is in good agreement with that calculated from the IR spectra (closed symbols). The area of the  $(\nu + \delta)\text{OH}$  band is then a good tool for measurement of the total silanol concentration whatever the outgassing temperature.

The concentration  $C_{\text{OH}}$  ( $\text{mmol g}^{-1}$ ) was calculated at each temperature for all of the samples (Table 2), using this molar integrated absorption coefficient. The  $C_{\text{OH}}$  concentration at RT specifies the order reported above obtained from qualitative observations. As the degassing temperature increases, the ranking  $\text{D} > \text{E} > \text{C} \sim \text{B} \sim \text{A}$  is roughly maintained, whereas the amounts of silanol significantly decrease. Note that the methodology used in the present study leads to the determination of the total number of silanols, including the internal ones. Their relative amount has been measured by FTIR using exchange with  $\text{D}_2\text{O}$ . In the next paragraph, we report all of the quantitative data relative to silanol accessibility.

**3.3.2. Silanol Accessibility.** Silanol accessibility (Table 3) is determined from the residual intensity of the combination band  $(\nu + \delta)\text{OH}$ , at around 4550  $\text{cm}^{-1}$  after each exchange experiment. The fraction of accessible OH to a given alcohol is calculated from the area of this band after back-exchange, the area of the band due to silanols nonexchanged by  $\text{D}_2\text{O}$ , and the area recorded for the dried sample (see Supporting Information). Almost all of the silanols (99%) of silica E, even those present in the small tubular pores, are accessible whatever the alcohol used for the back-exchange. For the other samples, a similar trend is observed: the bigger the reactant molecule, the lower the accessibility; only around 80% of the silanols are accessible to  $\text{D}_2\text{O}$ . A large decrease of the accessible silanol number takes place when methanol is the probe in the case of silica A, C, and D, whereas a more regular effect of the alcohol size is observed in the case of silica B.

No relationship is found between the accessibility and the texture or the silanol amount of the silicas (Tables 1 and 2). However, it has been demonstrated that the roughness of the silica surface plays a pre-eminent role in the sorption properties.<sup>35</sup> The fractal dimension of a silicic acid surface has been

**Table 2. Quantification of Silanol Population  $C_{\text{OH}}$  ( $\text{mmol g}^{-1}$ ) Using the  $(\nu + \delta)\text{OH}$  Vibration Band at Various Evacuation Temperatures**

silica	T/K						
	298	423	523	623	723	823	873
A	3.6	3.5	3.4	3.0	2.5	1.8	1.5
B	4.2	4.1	3.8	3.4	2.7	2.0	1.6
C	4.4	4.3	4.1	3.7	3.1	2.5	2.2
D	7.0	6.9	6.5	5.6	4.3	3.1	2.5
E	5.3	5.1	4.5	3.9	3.3	2.5	2.0

**Table 3. Silanol Accessibility to Probe Molecules: Fraction of Silanol Groups Accessible to  $\text{D}_2\text{O}$  and Alcohol Molecules, According to Their Size**

probe molecule	size <sup>a</sup> ( $\text{nm}^2$ )	silica				
		A	B	C	D	E
$\text{D}_2\text{O}$	0.106	0.80	0.77	0.81	0.86	0.99
methanol	0.180	0.45	0.69	0.51	0.61	0.98
propan-2-ol	0.276	0.42	0.66	0.50	0.55	0.98
2-methyl-propan-2-ol	0.316	0.40	0.63	0.48	0.51	0.98
3-ethyl-pentan-3-ol	0.410	0.37	0.52	0.40	0.51	0.97

<sup>a</sup>Sizes of the molecules are determined from the liquid density at room temperature.

estimated to be 2.94 from the adsorption of alcohols.<sup>36</sup> Other studies estimate a fractal dimension between 2 to 3.<sup>37</sup> In the present study, quantitative data on the sorption capacity of the silica under study are not available because IR data quantify reactive sorption at specific silanol sites. However, it is clear that all of the sorbed alcohols have a molecular section far below the width of the pores, and it is remarkable that the silica with the less open pores, the E material, does not discriminate the sorption of the alcohols. In fact, alcohols probe the accessibility of the silanol sorption sites at the molecular level, investigating steric effects near the surroundings of the OH group. This limited set of data indicates that the MCM silica E exhibits a smooth surface (not hindering reaction with the silanols), while the others samples display rougher surfaces, leading to limitations for reactivity and grafting capacity.

**3.3.3. Determination of the Surface Silanol Density: Comparison with Zhuravlev Results.** The  $C_{\text{OH}}$  values reported in Table 2 are relative to the total amount of silanols per gram of silica. Taking into account the fraction  $f$  of silanols accessible to  $\text{D}_2\text{O}$  (Table 3), considered as surface silanols, it is possible to evaluate the silanol surface densities  $\alpha_{\text{OH}}$  per  $\text{nm}^2$ . The results

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are reported in Table 4 at 298 K (maximum hydroxyl coverage). Whereas the silanol densities for the samples A, B, C, and D are similar (about 8 OH per nm<sup>2</sup>), that relative to sample E (4.4 OH per nm<sup>2</sup>) is much lower. The silanol densities determined for samples A to D are greater than the value quoted by Zhuravlev ( $\alpha_{\text{OH}} = 4.9$  OH per nm<sup>2</sup>) for over 100 various silica samples. However, recent studies report lower values for mesoporous silicas.<sup>38</sup>

Zhuravlev followed by mass spectrometry the deuterium–hydrogen exchange between D<sub>2</sub>O and the silanol groups to determine the number of hydroxyl groups at the surface of the samples. In the present study, the same exchange is quantified by IR spectroscopy. Therefore, the discrepancy between the  $\alpha_{\text{OH}}$  values reported by the two groups cannot be due to the definition of the surface silanols (i.e., silanols exchangeable by D<sub>2</sub>O). However, the determination of  $\alpha_{\text{OH}} = 602 \text{ f } C_{\text{OH}}/S$  from  $C_{\text{OH}}$  involves the specific surface area  $S$  of the sample. Zhuravlev determined  $S$  by the BET method from the low temperature adsorption of Kr, considering that the molecular surface area  $a_{\text{m}}(\text{Kr})$  is equal to 0.215 nm<sup>2</sup>.<sup>24</sup> Such a value seems overestimated. Gregg and Sing, in their reference book,<sup>15</sup> emphasized the large uncertainty of the Kr method (at least  $\pm 20\%$ ) and concluded on a more useful value  $a_{\text{m}}(\text{Kr}) = 0.195 \text{ nm}^2$ .

By the way, Zhuravlev used, in his first published paper,<sup>39</sup> N<sub>2</sub> adsorption with an  $a_{\text{m}}(\text{N}_2)$  value of 0.162 nm<sup>2</sup>. Aristov and Kiselev<sup>40</sup> comparing Ar and N<sub>2</sub> adsorption on silica gels reported that equivalent surface area values are obtained if  $a_{\text{m}}(\text{N}_2) = 0.136 \text{ nm}^2$ . This is the value we have adopted in the present study since it has been recently confirmed.<sup>14</sup>

Therefore, the discrepancy between the  $\alpha_{\text{OH}}$  values reported by Zhuravlev and those presented in this study mainly originates from the specific area determination. In our opinion, the  $a_{\text{m}}$  values used by Zhuravlev are too high, which underestimate the  $\alpha_{\text{OH}}$  values reported in his review.

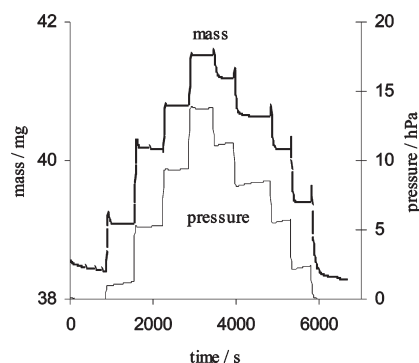
**3.3.4. Quantification of Water Content.** IR spectroscopy usually estimates the water content of the material from the characteristic bands of the H<sub>2</sub>O molecule, i.e., the fundamental  $\delta\text{H}_2\text{O}$  and the combination  $(\nu + \delta)\text{H}_2\text{O}$  bands. In this work, the TG-IR setup coupling infrared and microgravimetric measurements allows the measurement of the molar absorption coefficients of the  $\delta\text{H}_2\text{O}$  band, without an assumption of the reproducibility of the H<sub>2</sub>O content in separated IR and TG, NMR, or analytic experiments necessary to process the data obtained in previous studies.<sup>33,41</sup> The course of a typical combined TG-IR experiment is shown in Figure 7.

Both water adsorption and desorption experiments were carried out in order to eliminate any possible influence of specific adsorption on heterogeneous sites. It is known that desorption differentiates between sites of different affinity toward the adsorbate, in contrast to adsorption, the latter being a faster process. For the silicas used in this study, no difference was found between those two procedures.

**3.3.5. Quantification Using the  $\delta\text{H}_2\text{O}$  Vibration.** For illustration, IR spectra of adsorbed water on silica D recorded for various equilibrium pressures of water in the IR cell are presented in Figure 8A. For quantification of water through

**Table 4. Surface Silanol Densities for the Five Silicas at Maximum Hydroxyl Coverage (at 298 K)**

A	B	C	D	E
Specific Surface Area (m <sup>2</sup> g <sup>-1</sup> ) (from Table 1)				
215	260	265	415	730
$C_{\text{OH}}$ (mmol g <sup>-1</sup> ) (from Table 2)				
3.6	4.2	4.4	7.0	5.3
Fraction of Surface Silanols (from Table 3)				
0.80	0.77	0.81	0.86	0.99
$\alpha_{\text{OH}}$ per nm <sup>2</sup> at 298 K				
8.1 $\pm$ 0.8	7.6 $\pm$ 0.8	8.0 $\pm$ 0.8	8.8 $\pm$ 0.9	4.4 $\pm$ 0.5



**Figure 7.** Variations of the mass of the pellet and of the pressure of water into the cell recorded with the TG-IR apparatus during a hydration–dehydration cycle for silica D.

the  $\delta\text{H}_2\text{O}$  band, a linear baseline was drawn tangent to the difference spectrum, i.e., the spectrum recorded at RT of the wet sample minus the one of the completely dried sample, allowing measurement of the absorbance at the maximum of the band and integration over the 1450–1785 cm<sup>-1</sup> range. The areas of the  $\delta\text{H}_2\text{O}$  band versus the concentration of adsorbed water (in  $\mu\text{mol cm}^{-2}$ ) measured by gravimetry are plotted in Figure 8B. Clearly, a single molar absorption coefficient for the  $\delta\text{H}_2\text{O}$  bending vibration band can be used for the five different silica samples. The slope of the straight line obtained with the full set of data leads to the value of the integrated molar absorption coefficient,  $(1.53 \pm 0.03) \text{ cm } \mu\text{mol}^{-1}$ . This value is in agreement with the previous work of Carteret<sup>33</sup> ( $1.5 \text{ cm } \mu\text{mol}^{-1}$ ), who worked with two silica in separate experiments.

We note that the fwhm (full-width half-maximum) and the position of the maximum of the  $\delta\text{H}_2\text{O}$  band are sensitive to the concentration of adsorbed water. The spectra recorded at low and high water content (Figure 9, spectra A-a and A-b, respectively) indeed show the appearance of a high wavenumber tail with a shift of the position of the maximum from 1627 to 1632 cm<sup>-1</sup> and an increase of the fwhm from 40 to 50 cm<sup>-1</sup>. This explains the nonlinear relationship between area and the absorbance at the maximum (Figure 9B). Moreover the variation of the  $\delta\text{H}_2\text{O}$  band area with the water concentration remains linear for high concentrations of water, whereas this is not the case of the absorbance at the maximum; a parabolic curve is more appropriate to fit the data. The  $\delta\text{H}_2\text{O}$  band area is therefore more suitable than the absorbance at the maximum for quantitative water analysis.

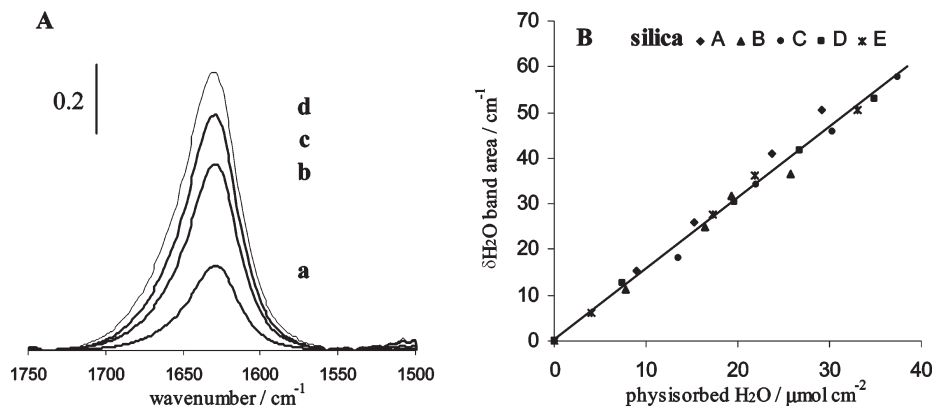
The amount of molecular water adsorbed by silica under room atmosphere depends on the relative humidity of the air. In order to compare the five silicas, common conditions (room

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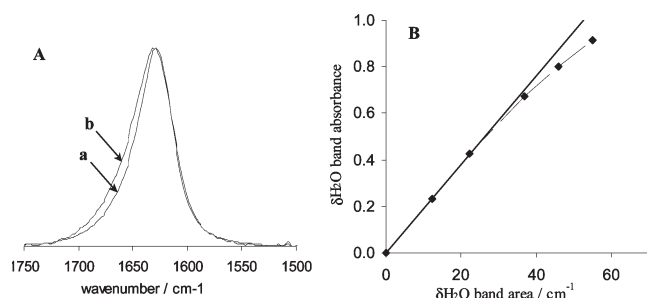
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**Figure 8.** (A)  $\delta\text{H}_2\text{O}$  band of water adsorbed on silica D during the hydration experiment (spectra of silica with adsorbed water minus the spectrum of dry silica). Spectra a, b, c, and d correspond to 7.5, 19.7, 26.8, and 34.8  $\mu\text{mol cm}^{-2}$  of adsorbed water, respectively. (B) Area of the  $\delta\text{H}_2\text{O}$  band versus the concentration of adsorbed water.



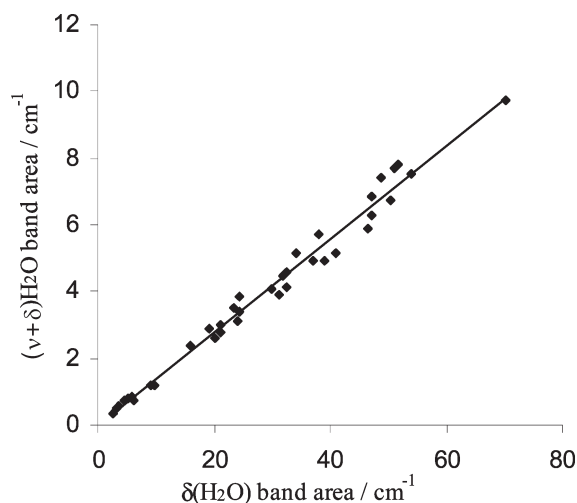
**Figure 9.** (A) Spectra of the  $\delta\text{H}_2\text{O}$  band (full scale) corresponding to concentrations of adsorbed water onto silica A equal to 9  $\mu\text{mol cm}^{-2}$  (spectrum a) and 29  $\mu\text{mol cm}^{-2}$  (spectrum b). (B) Absorbance of the  $\delta\text{H}_2\text{O}$  band at the maximum versus the  $\delta\text{H}_2\text{O}$  band area.

**Table 5. Quantification of Adsorbed Water Content under an Equilibrium Water Pressure of 13 hPa**

silica	$\text{H}_2\text{O}$ wt %			$N_{\text{H}_2\text{O}}$ per $\text{nm}^2$			$N_{\text{H}_2\text{O}}/N_{\text{OHsurface}}$
	IR	TG	average	IR	TG	average	
A	5.2	4.7	4.95	8.0	7.2	7.6	$0.9 \pm 0.1$
B	4.6	4.9	4.75	6.0	6.3	6.15	$0.8 \pm 0.1$
C	5.0	5.1	5.05	6.3	6.5	6.4	$0.8 \pm 0.1$
D	10.0	10.4	10.2	8.1	8.3	8.2	$0.9 \pm 0.1$
E	6.8	6.7	6.75	3.1	3.1	3.1	$0.7 \pm 0.1$

temperature and equilibrium water pressure of 13 hPa) have been chosen. The TG data are simultaneously measured. Table 5 summarizes the amount of water calculated from the  $\delta\text{H}_2\text{O}$  band area using the determined molar integrated absorption coefficient  $\epsilon_{\delta\text{H}_2\text{O}}$  of the band and from the mass loss. The values obtained by both methods are close, highlighting the usefulness of infrared spectroscopy for quantitative applications.

**3.3.6. Quantification Using the  $(\nu + \delta)\text{H}_2\text{O}$  Combination Band.** The spectrometer used for the TG-IR experiments does not allow one to monitor the  $(\nu + \delta)\text{H}_2\text{O}$  combination band due to a low signal-to-noise ratio. To determine the integrated molar absorption coefficient of the  $(\nu + \delta)\text{H}_2\text{O}$  combination band, the areas of the  $\delta\text{H}_2\text{O}$  and the  $(\nu + \delta)\text{H}_2\text{O}$  bands, over the 5500–4800  $\text{cm}^{-1}$  range, of numerous silicas from various origins were measured with a spectrometer more appropriate for simultaneously NIR and MIR measurements. In Figure 10, the  $(\nu + \delta)\text{H}_2\text{O}$  area is plotted versus the  $\delta\text{H}_2\text{O}$  area. The linear relationship obtained for all of the hydrated silicas leads to an integrated molar absorption coefficient  $(\nu + \delta)\text{H}_2\text{O}$  value of  $(0.22 \pm 0.01) \text{ cm } \mu\text{mol}^{-1}$ .



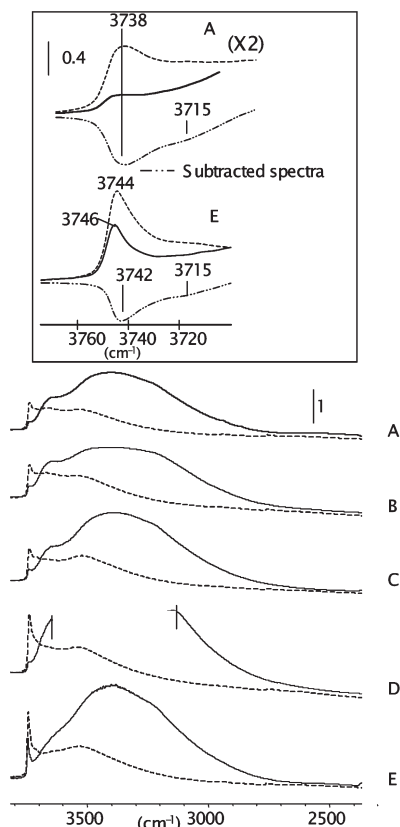
**Figure 10.** Area of the  $(\nu + \delta)\text{H}_2\text{O}$  band versus the area of the  $\delta\text{H}_2\text{O}$  band. Data are deduced from spectra recorded for all of the hydrated silicas.

This value is close to that reported in the literature:  $(0.23 \pm 0.01)$  for Vycor and Geltech silicas<sup>33</sup> and  $(0.23 \pm 0.02)$  for four aluminosilicates.<sup>41</sup> The  $(\nu + \delta)\text{H}_2\text{O}$  band therefore allows one to quantify the adsorbed water content of silicas in various hydration states even though the  $(\nu + \delta)\text{H}_2\text{O}$  band seems to be more complex than that associated with the  $\delta\text{H}_2\text{O}$  mode.

For practical applications, the band at 1630  $\text{cm}^{-1}$  can be used for light pellets and/or low water contents, while the 5260  $\text{cm}^{-1}$  band is preferably used for heavy pellets and/or high water contents since its absorption coefficient is one-seventh that of the fundamental  $\delta\text{H}_2\text{O}$  one. However, it is worthwhile noticing that in the case of a heavy pellet, the light scattering could be important in the NIR range and would give rise to an increase of the intensity of the  $(\nu + \delta)\text{H}_2\text{O}$  band<sup>42</sup> and therefore would lead to overestimated values of the water content. Results reported in Table 5 are relative to measurements of the 1630  $\text{cm}^{-1}$  band intensity.

**3.4. Relationship between Water and Silanol Contents.** Hydrophilic properties could be scaled as the water content (weight %) of the silica sample: sample D has the highest water content (10.2 wt%), silica A, B, and C the lowest ones (4.7–5.0 wt%), and silica E an intermediate value (6.8 wt%). These contents correspond to macroscopic data. At the molecular

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**Figure 11.** IR spectra of the five silicas: dried samples (dotted line); hydrated samples under  $P(\text{H}_2\text{O}) = 13$  hPa (solid line). Inset:  $\nu\text{OH}$  band of silicas A and E sensitive to water adsorption.

level, water density calculated using specific surface areas has to be considered. From the values in Table 5, a different order is obtained:  $\text{NH}_2\text{O}$  per  $\text{nm}^2$  decreases from silica D,  $A > B, C > E$ . Such an order could be explained taking into account the density of silanol groups of each silica sample since a  $\text{H}_2\text{O}/\text{SiOH}$  ratio close to 1 has been reported in the literature.<sup>43</sup> However, this ratio depends on the partial pressure of water. Clearly, the  $\text{N}_{\text{H}_2\text{O}}/\text{N}_{\text{OH}_{\text{surface}}}$  ratio is more appropriate to specify the silica water affinity because only silanols accessible to  $\text{D}_2\text{O}$  (surface silanols) can interact with water.

This ratio is reported in Table 5 taking into account the number of silanols only accessible to water as reported in Table 4. This ratio is close to 0.8–0.9 for silicas A to D and slightly lower in the case of silica E.

It is worthwhile noticing that the  $\text{N}_{\text{H}_2\text{O}}/\text{N}_{\text{OH}_{\text{surface}}}$  ratio is obtained by dividing two experimental values with an error of about 5%. Such an uncertainty does not allow one to conclude that the values obtained are significantly different. To check the results, spectra of the different silicas under a similar water pressure (13 hPa) have been compared. Figure 11 shows that under such a condition, only  $\nu\text{OH}$  silanol bands of wavenumbers higher than  $3700\text{ cm}^{-1}$  can be studied unambiguously since the others are overlapped by  $\nu\text{H}_2\text{O}$  bands. Only a very weak silanol band persists in the case of samples A to D, which does not allow one to differentiate the behavior toward  $\text{H}_2\text{O}$  adsorption. By contrast, the spectrum of silica E under the same water pressure displays a noticeable  $\nu\text{OH}$  silanol band at  $3746\text{ cm}^{-1}$ , showing that a part of the silanol groups is not affected. This confirms the

lower value of the  $\text{N}_{\text{H}_2\text{O}}/\text{N}_{\text{OH}_{\text{surface}}}$  ratio reported in Table 5 for silica E. This could be related to the larger amount of isolated silanol groups presented by this sample relative to that by the others (Figure 4).

It has been shown in the case of precipitated silicas that the most reactive silanol groups toward water molecules are the terminal ones.<sup>44</sup> Their perturbation is evidenced by the shoulder at  $3715\text{ cm}^{-1}$  in the subtracted spectra relative to silicas A and E (insert of Figure 11). As for isolated silanols, they have been differentiated according to their water affinity.<sup>44</sup> Those with a low wavenumber ( $3730\text{--}3740\text{ cm}^{-1}$ ) named as type II (neighboring silanols or geminal silanols on which water adsorption involves two OH groups) are preferentially affected than those with a high wavenumber ( $3746\text{--}3748\text{ cm}^{-1}$ ) considered as truly isolated. In agreement, the spectra from silica E presented in the insert of Figure 11 show that the silanols remaining under water atmosphere absorb at  $3746\text{ cm}^{-1}$ , whereas those interacting with water absorb at  $3742\text{ cm}^{-1}$ .

#### 4. Conclusions

Although the relative number of different silanol groups (H-bonded, internal, terminal species, and isolated silanols) varies from one silica to another in the case of precipitated silicas, the fraction of silanols accessible to  $\text{D}_2\text{O}$  (about 0.8) and the surface silanol density, about 8 OH per  $\text{nm}^2$ , are very close. The similarity at the molecular level is also evidenced by the silanol affinity toward water: taking into account the number of internal silanols, a  $\text{N}_{\text{H}_2\text{O}}/\text{N}_{\text{OH}_{\text{surface}}}$  ratio close to 0.8–0.9 has been determined under a water pressure of 13 hPa at room temperature. Silanol accessibility toward alcohol molecules decreases when the alcohol size increases, but the main effect arises from methanol back-exchange. It is therefore concluded that the main parameter differentiating the four precipitating silica samples studied is their specific surface area.

By contrast, the MCM-41 results are quite different: (i) all of the silanol groups are accessible whatever the alcohol size, and (ii) their water affinity is lower than that of precipitated silica. This is explained by the greater amount of isolated silanol groups in the MCM-41 sample. Such a difference between precipitated silicas and a MCM-41 silica illustrates that the reactivity of the silica surface cannot be predicted from the total silanol amount measured by the classical methods (TG,  $^1\text{H}$  NMR, etc.). Instead, it stresses that a very detailed characterization is required where accessibility is monitored by methods such as the one described in this contribution. The insights gained in such a study are, for instance, important to the rational design of supported metallocene polymerization catalyst. Such a methodology could also be used with NMR spectroscopy, albeit without the sensibility obtained by the simultaneous measurement of IR spectra and mass evolution of the samples.

This information has been obtained with a homemade TG-IR setup, enabling simultaneous gravimetric measurements and IR characterization on the same pellet in the same experimental conditions (pressure and temperature). These are difficult to reproduce using separate thermogravimetric and infrared equipment. The linear variation between the area of the  $(\nu + \delta)\text{OH}$  band and the OH lost (Figure 6a) validates the use of the Beer–Lambert law for quantitative measurements by infrared spectroscopy. Morterra et al. checked the validity of such a law for methanol adsorption on silica<sup>45</sup> in a systematic study where

(43) Morimoto, T.; Nagao, M.; Imai, J. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1282–1288.

(44) Burneau, A.; Barrès, O.; Gallas, J.-P.; Lavalley, J.-C. *Langmuir* **1990**, *6*, 1364–1372.

(45) Morterra, C.; Magnacca, G.; Bolis, V. *Catal. Today* **2001**, *70*, 43–58.

the influence of parameters such as specific surface area, sample thickness, and scattering properties of the absorbent on the value of the molar absorption coefficients has been investigated. They concluded that “the use and comparison between absorption coefficients seemed to work reasonably well ... if samples of comparable scattering features, comparable surface area and comparable sample weight were actually used.” The silicas studied in the present article obey these conditions.

The TG-IR setup and all of the data relative to the different silicas reported in this article will be applied for further studies relative to the grafting of organic molecules on silica samples.

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**Supporting Information Available:** Method used for the calculation of the quantity of water and hydroxyl groups and silanol accessibility including the measurement accuracy, and synthesis procedure of the mesoporous silica, N<sub>2</sub> isotherms, and pore size distribution of the mesoporous material and the parent silica. This material is available free of charge via the Internet at <http://pubs.acs.org>.