Study of the Acidic Sites and Their Modifications in Mesoporous Silica Synthesized in Acidic Medium under Quiescent Conditions

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The number and nature of silanol groups could be estimated in mesoporous silica prepared with cetyltrimethylammonium bromide (CTMBr) in acidic medium to obtain a material appropriate as a stationary chromatographic phase, using thermogravimetric analysis (TGA) and diffuse reflectance infrared spectroscopy (DRIFT). The temperature-programmed desorption of pyridine in the DRIFT cell was quantitatively correlated to the change in intensity of the two IR bands, 1595 and 1446 cm^{-1}, assigned to pyridine interacting respectively with hydrogen-bonded and free silanol groups, after the determination of the absorptivities for the two bands. For calcined or solvent extracted samples, the silanol density (3−4 groups/nm^2), is represented mainly by hydrogen-bonded silanol groups. A significant increase is obtained by rehydroxylation. Activation by heating above 200 °C promotes the condensation of the vicinal silanol groups.

1. Introduction

With their high surface area and organized pore structure, the mesoporous silica is interesting material in catalysis, adsorption, or analytical processes such as high-resolution liquid chromatography (HPLC).[1−4] The synthesis of mesoporous silica can be addressed to produce materials with certain porous structure, particle morphology, and surface properties according to its applications. For instance, its use as a stationary phase for HPLC requires a material with isometric particles with size larger than 3 μm. Mesoporous silica with spherical particles ~4−10 μm has been synthesized in acidic medium by using the cationic surfactant cetyl trimethylammonium chloride (CT-MACl)[5] as well as nonionic surfactants.[6] The synthesis of mesoporous silica in acidic medium using CTMACl or CT-MABr produces materials with two-dimensional hexagonal structure, designed by Stucky et al. as SBA-3 type.[7,8] For the synthesis in acidic medium using the nonionic surfactant Triton X100 the mesoporous material exhibits mesoporous channels with wormlike forms designed as the MSU X type.[9] The surfactant used as a template for the pores during the synthesis is removed by calcination or solvent extraction to obtain the material with the porosity available for adsorption processes. Their adsorption properties are related to the density of silanol groups (SiOH), which has been determined by ^{29}Si MAS NMR, transmittance IR spectroscopy, and TG/DTA in several studies.[10−12] For mesoporous silica MCM41, prepared in basic medium, the silanol density varies between 2.5 and 3.0 silanol groups/nm^2.[11] This value is smaller than the average value of 4.9 groups/nm^2 found for amorphous silicas[13] and has a contribution from three types of silanol groups: Single or isolated (SiO)$_3$.Si−OH, hydrogen-bonded (SiO)$_3$•Si−OH−OH and geminal (SiO)$_2$•Si−(OH)$_2$, among which only the single and geminal have a weak acidic character.[11,12] On aluminum-containing MCM-41 samples additionally Bronsted and Lewis acid sites have been observed.[12] The silanol group content depends on the mesoporous synthetic procedure but also can be modified by changing the temperature of calcination or by effecting a postcalcination thermal activation or chemical modification. Depending on their application, the mesoporous materials, after calcination, can undergo thermal activation or chemical modification, to change their surface properties. If organic molecules, like chlorosilanes, are grafted on the silanol groups, the hydrophilic character of the silica decreases through the formation of Si−O−R groups and the materials become more stable under hydrolytic conditions.[14] It is known that hydrogen-bonded SiOH groups have a low tendency to react with the silylating reagents, due to their nonacid character, and therefore only free silanol groups, which can be geminal or isolated, react during the modification process.[11] For this reason, before the silylation of mesoporous silica, it is very important to have not only an appropriate amount of silanol groups but also a high proportion of the free ones. The determination of these values, based on the acid properties of the different SiOH groups, is made with a basic probe molecule whose characteristics depend on the chemical and physical nature of the solid under study. Pyridine is appropriate for the determination of weak to strong acidic sites,[15] in materials with pores larger than 5 Å.

In this study we attempted to modify the density of silanol groups of a mesoporous silica SBA-3 type, prepared with CTAMBr under acidic quiescent conditions: (a) in as-synthesized materials by the removal of the surfactant under different conditions; (b) in calcined materials by rehydroxylation in the presence of NH$_4$OH and thermal activation at different temperatures. When silica is heated at constant heating rate, physisorbed and chemisorbed water is eliminated between 100 and 200 °C whereas dehydroxylation occurs at a higher temperature. During dehydroxylation by condensation of vicinal silanol groups, which can be geminal or hydrogen-bonded, a slight increment of isolated silanol groups is expected.

The nature and the concentration of SiOH groups, which are present in the modified silica, were determined by DRIFT and TGA analyses on these materials after exposition to pyridine vapors.

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2. Experimental Section

Reagents: pyridine (Merck, H_2O < 0.01%); cetyltrimethylammonium bromide (CTMABr, Fluka, purity 99%); tetraethyl orthosilicate (TEOS, Aldrich, purity 98%); hydrochloric acid (Merck, reactive grade); ammonium hydroxide (NH_4OH, EM Science, reactive grade).

Synthesis of the Material. A 31.25 g sample of TEOS is added under strong agitation to a solution containing 9.3 g of the surfactant (CTMABr), 1900 mL of H_2O, and 82 mL of 12 M HCl at 25 °C. After 10 min of agitation, the solution is transferred to a polypropylene bottle and heated 2 days at 80 °C. The solid is recovered by filtration.[6]

Surfactant Removal. The surfactant is removed by (a) calcination in air, increasing the temperature from 25 °C up to 500, 580, and 680 °C at 1.5 °C/min (samples C500, C580, and C680), or (b) solvent extraction under refluxing by 4 h, twice, with a solution of 1 M HCl in ethanol (solid/liquid: 1 g/15 mL, sample E). The solid is recovered by filtration and is dried at 80 °C for 12 h. The surfactant removal is guaranteed in all cases because the infrared spectrum for the calcined materials do not show absorption bands corresponding to CH groups of it.

Rehydroxylation. The calcined material at 680 °C is left in contact with a solution of 0.05 M NH_4OH (silica/solution: 1 g/200 mL), under mild stirring at room temperature for different times: 2, 6, 12, and 24 h (samples C680R2h, C680R6h, C680R12h, and C680R24h, respectively). The solid is recovered by filtration and dried at 80 °C for 12 h.

Thermal Activation. To determine the effect of heating on the nature and content of silanol groups, sample C680R12h was heated under vacuum for 1 h at 100, 200, 300, and 400 °C.

Porosity and Superficial Area. The samples were analyzed by nitrogen adsorption in an ASAP 2010 Micromeritics equipment, with a degassing temperature of 250 °C under vacuum for 6 h. The specific surface was evaluated with the BET method; the pore volume and pore size distribution (BJH method) were performed with the software of the apparatus. The most frequent pore size was estimated from the pore size distribution graph.

X-ray Diffraction. The XRD patterns were recorded in the 2θ range 1−10° with a Philips PW1130 diffractometer (Cu Kα radiation).

Pyridine Adsorption. All the materials were activated at 200 °C under vacuum for 1 h and then left in contact with pyridine vapors for 24 h at room temperature.

Thermogravimetric Analysis. The pyridine desorption was observed in a TGA (Dupont 2000 Hi-head 2995) as the sample was heated, in air, using the following temperature program: (1) Heating at 5 °C/min from 25 to 50 °C and holding this temperature for 5 min. (2) Heating at 2 °C/min from 50 to 100 °C and holding this temperature for 10 min. (3) Heating at 10 °C/min from 100 to 250 °C. A graph of weight loss as function of temperature was obtained.

DRIFT Analysis. The silica was packed in a sample cell, which is inside of the diffuse reflectance accessory of the FTIR (Perkin-Elmer, model Spectrum 1) and allows evacuation and controlled heating. The spectra were obtained using 32 scans with a resolution of 4 cm^{-1}. The infrared analyses were used (a) to monitor, in a qualitative way, the effect that the thermal activation before the pyridine adsorption has on the hydroxyl groups, and (b) to quantify the silanol groups for the different samples, after the pyridine adsorption.

For the quantification of silanol groups, the 1600−1400 cm^{-1} infrared region was used because in this region characteristic

TABLE 1: N_2 Adsorption Characteristics and TGA Pyridine Desorption Results

sample	T_{cal} (°C)	% PL[a] T_1	T_2	T_3	P[b] (mg)	A_{BET}[c] (m²/g)	d[c] (nm)	V[c] (cm³)
C500	500	21.0	5.4	4.5	10.5280	1222	2.13	0.49
C580	580	14.2	4.9	4.2	15.0270	1046	2.09	0.40
C680	680	13.7	6.7	4.8	16.7110	1013	2.07	0.52
E	n.c.[d]	18.7	7.4	6.2	18.0220	1201	2.21	0.67
C680R$_{2H}$	680	18.7	4.2	3.0	8.8290	985	2.75	0.68
C680R$_{6H}$	680	22.0	3.8	2.6	6.1270	913	2.94	0.68
C680R$_{12H}$	680	19.6	6.1	4.9	15.8257	840	2.77	0.56
C680R$_{24H}$	680	18.7	6.2	4.2	10.5150	750	3.21	0.61

[a] Pyridine loss weight % for the desorption peaks at T_1 = 48 °C, T_2 = 100 °C and T_3 = 140−150 °C. [b] Weight in mg of the sample used in the controlled desorption. [c] Specific surface Area (BET), the most frequent pore diameter and pore volume determined by the BJH method. [d] n.c: not calcined.

vibrations of adsorbed pyridine appear. The region of OH extension vibrations was used to follow the evolution of the SiOH groups by thermal activation.

Quantification of the Silanol Groups. To correlate the absorbance values of the vibration bands of the SiOH−pyridine interactions, with the superficial concentration of the hydroxyl groups, it is necessary to determine the molar absorptivities of pyridine interacting with the different SiOH groups of the silica.

These values were obtained for the sample C680 by the following procedure: after the pyridine absorption, in a first step, the reaction cell temperature is increased at 6 °C/min from 25 to 50 °C, remaining at this temperature for 90 min. The desorbed pyridine was carried by a small N_2 flow to be collected in water. Its quantification was made by UV absorption at 250 nm, using a calibration curve built with standard mixtures of pyridine/water of known composition. The previous procedure was repeated using the same temperature rate and starting at 70, 90, 100, 120, 140, 160, 180, 200, and 250 °C.

3. Results and Discussion

3.1. Characterization of the Materials. The results obtained from the N_2 isotherms and the pyridine desorption TGA graphs for the extracted, calcined, and rehyroxylated samples are summarized in Table 1.

The porous characteristics determined by the adsorption N_2 isotherms: Area BET and pore diameter and volume indicate that all materials have mesoporous properties, which change depending on the conditions of calcination and posttreatment. Rehydroxylation produces a material with large pore diameter and volume whereas the increase in calcination temperature does not produce significant change in these parameters. By doing different analyses of the nitrogen isotherms such as observation of the points at the limits on the BET curve and comparison of the mesoporous volume with the volume corresponding to the highest point used to determine the specific surface, the microporous volume can be neglected.

The power X-ray diffraction patterns (not shown) exhibit broad reflection at low angle with a d spacing around 42−45 Å, which corresponds to a mesoporous disordered hexagonal form SBA-3 type. It seems that the aggregation process to grow up the spherical particles produces mesoporous silica poorly organized.

3.2. Quantification of Silanol Groups Using TGA Analysis. According to the literature, amorphous silica[16] or mesoporous silica MCM41-type[11] shows two pyridine desorption peaks in the range 50−170 °C, with maxima at temperature values depending on the heating rate. The first peak (50−100 °C range)
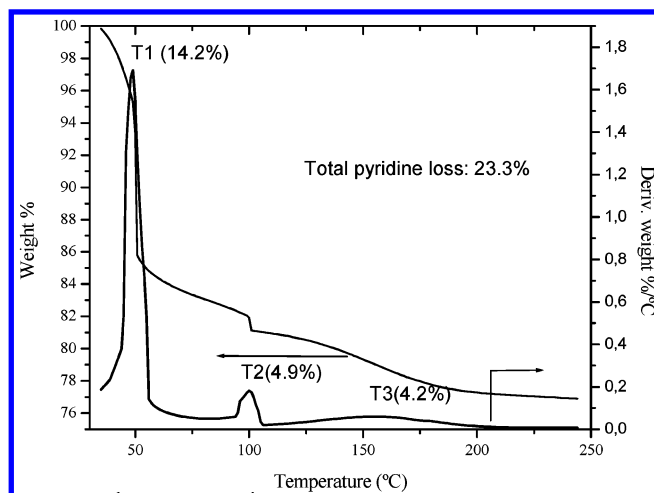
Acidic Sites in Mesoporous Silica

J. Phys. Chem. B, Vol. 107, No. 35, 2003 **9277**

Figure 1. TGA/DTGA graph for the C580 material after pyridine absorption.

TABLE 2: Silanol Groupsin Each Adsorption Site Calculated from TGA Pyridine Desorption[a]

	C500	C580	C680	E	C680R$_{2h}$	C680R$_{6h}$	C680R$_{12h}$	C680R$_{24h}$
				silica sample				
				Number of Silanol Group per nm^2				
N$_1$	2.62	2.06	1.76	2.40	2.87	3.65	3.55	3.80
N$_2$	0.34	0.35	0.49	0.47	0.32	0.31	0.55	0.63
N$_3$	0.27	0.31	0.42	0.40	0.23	0.22	0.44	0.42
N$_t$	3.23	2.72	2.61	3.27	3.42	4.18	4.54	4.85

[a] N$_1$ = bonded silanol groups, N$_2$ = free silanol groups, N$_3$ = silanol groups corresponding to the third desorption peak, N$_t$ = total silanol groups.

is associated with pyridine interacting with hydrogen-bonded SiOH groups; the second peak (120−170 °C, range) corresponds to pyridine desorbed from free SiOH groups. In this work three desorption peaks were observed (Figure 1) with maximum temperatures at 50 °C (T$_1$), 100 °C (T$_2$), and 140−150 °C (T$_3$). If the first two peaks are assigned as before, the third broad peak can be assigned to pyridine desorption from bonded and free silanol groups in small cavities, which are formed by aggregation of particles during the synthesis growing process and that offer a more restricted access to pyridine. Their diversity in sizes is probably responsible for the heterogeneity in energy of desorption. This behavior seems to be inherent to this material.

If we assume that for each pair of hydrogen-bonded silanol groups (peak T$_1$) one pyridine molecule reacts, it is possible to calculate the number of hydroxyl groups (Table 2).

The number of silanol groups determined by ^{29}Si MAS NMR[6] in the same silica calcined at 540 °C, was 3.31/nm^2, which is similar to the values found here, by TGA. We can observe that when the calcination temperature increases, the total content of silanol groups decreases and their relative distribution changes with the decrease of the number of bonded silanol groups. Removal of the surfactant by extraction increases the content of SiOH groups.

3.3. Quantification of Silanol Groups Using the DRIFT Technique. The DRIFT spectrum of sample C680 at 25 °C (Figure 2), after pyridine adsorption, shows two new bands, one at 1595 cm^{-1}, which is assigned in this work to pyridine hydrogen-bonded with hydrogen-bonded silanol groups and another at 1446 cm^{-1} due to the interaction of pyridine with free weakly acidic silanol groups.[12] The wide band centered at ∼3050 cm^{-1} corresponds to vibration of free and hydrogen-bonded silanol groups in interaction with pyridine. Because the

absorptions that are seen (at 25 °C) for the vibration bands associated with physisorbed pyridine (1580, 1572, 1482, and 1479 cm^{-1}) are very low, the presence of liquid pyridine can be considered as negligible. Figure 2 (left) shows that a temperature increase from 25 to 90 °C, produces a decrease in the area of the 1597 cm^{-1} band, the appearance of a wide absorption at 3640 cm^{-1}, due to the OH vibration of bonded silanol groups,[10,17] and almost no change in the band at 1446 cm^{-1}.

The pyridine loss associated with free silanol groups begins to be appreciable at temperatures higher than 90 °C, producing a decrease in the intensity of the band at 1446 cm^{-1} and the regeneration of the band at 3740 cm^{-1}, which belongs to these groups. The pyridine that remains in interaction with bonded SiOH above 90 °C (in micropores or small cavities) desorbs simultaneously with the pyridine interacting with free silanol groups (Figure 2, right). It was proved that the total quantity of pyridine, which remains adsorbed on the solid, diminishes linearly with the temperature increase above 90 °C (Figure 3a).

To quantify the SiOH groups by infrared, it is necessary to estimate the molar absorptivities for pyridine at 1597 and 1446 cm^{-1} for each kind of material. It has even been proved in the case of zeolites that the molar absorptivities depend on the experimental conditions.[18] These values can be obtained using the Lambert−Beer law: $A = Py*\epsilon$, where A, Py, ϵ, are respectively the area, the quantity of adsorbed pyridine, and the molar absorptivity coefficient for the vibration band at 1595 or 1446 cm^{-1}.

The total amount of pyridine on the silica surface (Py$_T$ (μmol)) can be expressed as Py$_T$ = $(A_{1595}/\epsilon_{1595}) + (A_{1446}/\epsilon_{1446})$. For temperatures higher than 90 °C, a temperature increment (ΔT) produces a (ΔPy$_T$) decrease in the amount of the remaining pyridine on the silica surface and a decrease in the areas of the 1596 and 1446 cm^{-1} bands (ΔA_{1596} and ΔA_{1446} taken in Kubelka Munk units/cm). The last equation can be written in terms of these increments as

$$\left(\frac{\Delta A_{1595}}{\Delta T}\right) = \epsilon_{1595}\left(\frac{\Delta Py T}{\Delta T}\right) - \frac{\epsilon 1595}{\epsilon 1446}\left(\frac{\Delta A_{1446}}{\Delta T}\right) \quad (1)$$

(ΔPy$_T$/ΔT) can be obtained from the slope of the Py$_T$ vs T plot (Figure 3a). The remaining pyridine (μmol), at each heating temperature, is figured out by subtracting from the total desorbed pyridine (collected during heating from 25 to 250 °C) the amount desorbed at the corresponding temperature. From the slope and the intercept of the plot ($\Delta A_{1595}/\Delta T$) vs ($\Delta A_{1446}/\Delta T$) in Figure 3b, the values of ϵ_{1595} and ϵ_{1446} can be figured out.

Four analyses were carried out for the sample C680, giving the following average ϵ values: $\epsilon_{1446} = 0.62 \pm 0.06$ cm^{-1} μmol^{-1}, $\epsilon_{1595} = 0.25 \pm 0.04$ cm^{-1} μmol^{-1}. These values were estimated by measuring peak areas in the infrared spectrum at different temperatures between 90 and 200 °C. Even though the infrared absorptivities theoretically change with temperature, when the experiment is repeated, cooling until 30 °C after each desorption step and measuring the peak area at 30 °C, the values for the absorptivities were $\epsilon_{1446} = 0.62$ cm^{-1} μmol^{-1}, $\epsilon_{1595} = 0.20$ cm^{-1} μmol^{-1}, which are inside of the range defined by the precision given by the method.

The number of free silanol groups or weakly acidic sites (SiOH$_{wa}$) per nm^2 is determined from the total area of the 1446 cm^{-1} band at 25 °C, after the pyridine adsorption, using eq 2. It is also possible to find from eq 3 the number of hydrogen-bonded silanol groups (SiOH$_{bp}$) per nm^2, if it is assumed again an equivalence of two silanol groups per pyridine. In these equations: S is the specific surface area in m^2/g, $W = W_p -$
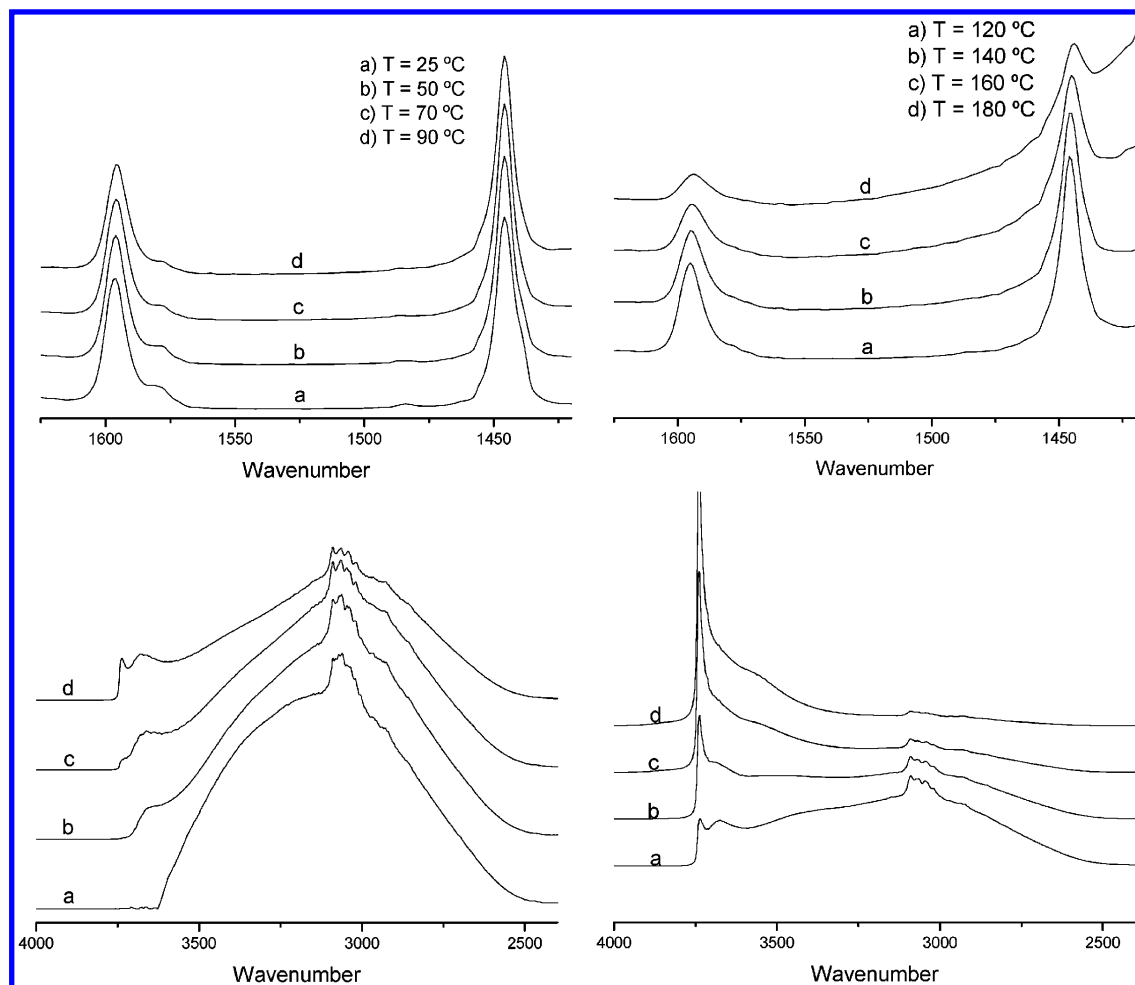
Figure 2. Evolution of the IR spectra (in Kubelka−Munk units versus wavenumber) for the C680 sample during pyridine desorption. Left: heating from 25 to 90 °C. Up: intensity changes of the 1595 cm^{-1} band. Down: regeneration of the 3640 cm^{-1} band, due to bonded silanol groups. Right: heating from 120 to 180 °C. Up: intensity changes of the pyridine bands at 1595 and 1446 cm^{-1}. Down: regeneration of the 3740 cm^{-1} band of free silanol groups.

(% PL$_T$/100W_p); W_p is the weight of sample used for the pyridine desorption analyzed by infrared, and % PL$_T$ is the total amount of pyridine desorbed (in grams, estimated from the TGA weight losses at the different steps T$_1$, T$_2$, T$_3$)

$$SiOH_{wa} = 0.602\left(\frac{A_{1446}}{\epsilon_{1446}SW}\right) \qquad (2)$$

$$SiOH_{bp} = 1.204\left(\frac{A_{1595}}{\epsilon_{1595}SW}\right) \qquad (3)$$

Table 3 shows the results of SiOH$_{wa}$ and SiOH$_{bp}$ contents for all the analyzed materials. The total number of silanol groups/nm^2 obtained by infrared analysis is higher than those obtained by TGA analysis, as can be observed in Tables 2 and 3. This difference can be due to the fact that TGA analysis cannot distinguish between free SiOH groups and bonded SiOH groups that are in the small cavities or micropores. Because the pyridine loss at T$_3$ was considered due only to free silanol groups, only one silanol group was taken into account for each pyridine molecule desorbed.

3.4. Changes in the Content of SiOH Groups by Rehydroxylation and Thermal Activation. From the infrared absorption of the bonded and free silanol groups of the rehydroxylated sample C680R$_{12h}$ (Figure 4a), it can be concluded that both types of silanol groups increase as the contact

time, with the solution of NH$_4$OH, increases (the spectra were taken after 1 h of activation at 100 °C in a vacuum, in which the water is almost completely removed). When the sample C680R12h was then heated from 100 to 400 °C in the DRIFT reaction cell, the condensation of vicinal silanol groups occurred (Figure 4b).

Even though the condensation of vicinal hydrogen-bonded silanol groups must increase the content of isolated groups, the band at 3740 cm^{-1}, corresponding to the OH stretching frequency of geminal and isolated silanol groups, does not change significantly. The area of this peak, measured after deconvolution, remains practically constant until 200 °C and decreases slightly at higher temperatures. Two possible explanations for this behavior can be proposed: (1) In the condensation of vicinal geminal groups, for each pair of these groups four geminal silanol groups disappear and only two free silanol groups are generated, producing a decrease in the concentration of free groups, which depending on the temperature can be equivalent or higher than the increase resulting from condensation of vicinal silanol groups. (2) The area of the peak is proportional to the factor (no. of SiOH/nm^2)SW, where S and W correspond to the specific surface and weight of the sample, respectively. Because the weight of the sample decreases during condensation of silanol groups, where water is liberated and removed by evacuation, the resulting area can decrease even though the number of SiOH per nm^2 must increase.
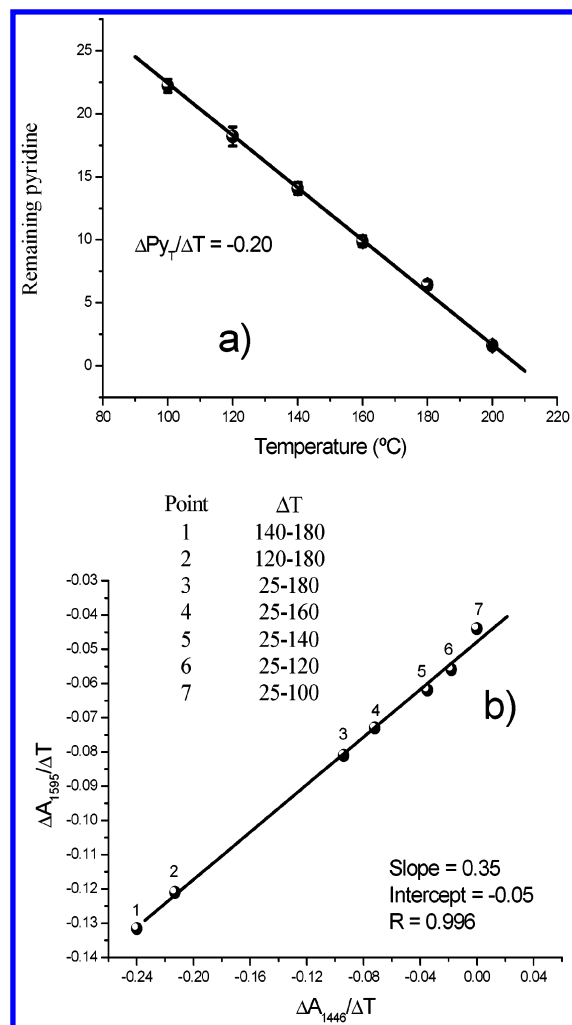
Acidic Sites in Mesoporous Silica

J. Phys. Chem. B, Vol. 107, No. 35, 2003 **9279**

Figure 3. (a) Changes in the amount (μmol) of remaining pyridine with desorption temperature for the C680 sample. Vertical bars show the standard deviations. (b) ($\Delta A_{1595}/\Delta T$) vs ($\Delta A_{1446}/\Delta T$). The slope and the intercept of one analysis is shown.

TABLE 3: Determination of the Weak Acidic, Bonded and Total Silanol Groups

				groups/nm^2		
sample	W^a	$A_{1446}{}^b$	$A_{1595}{}^b$	$SiOH_{wa}{}^c$ ± 0.1	$SiOH_{bp}{}^d$ ± 0.07	$SiOH_T$ ± 0.1
C580	0.0274	11.01	17.85	0.4	3.01	3.4
C680	0.0247	15.39	13.28	0.6	3.23	3.8
E	0.0199	16.29	14.32	0.7	2.88	3.6
C680R$_{2h}$	0.0208	13.00	13.73	0.6	3.23	3.8
C680R$_{6h}$	0.0158	12.98	11.56	0.9	3.86	4.8
C680R$_{12h}$	0.0230	20.54	15.52	1.0	3.87	4.9
C680R$_{24h}$	0.0200	23.40	15.50	1.5	4.97	6.5

^{a} Weight in grams of the sample used in each analysis. ^{b} Total area of the 1446 and 1597 cm^{-1} bands at 25 °C, before the heating steps. ^{c} Free silanol groups. ^{d} Bonded silanol groups.

4. Conclusions

We compared two methods, based on TGA and DRIFT measurements, to characterize the silanol group content in mesoporous silica prepared in acidic medium ($S^+X^-I^+$ mechanism). The DRIFT method using pyridine as a probe molecule gave more specific information about their nature. We concluded that the silanol group content is smaller than the one of precipitated silica, used as stationary phases for high performance liquid chromatography (HPLC) or as adsorbents, which have values around 4.9 OH/nm^2. Therefore, if these mesoporous
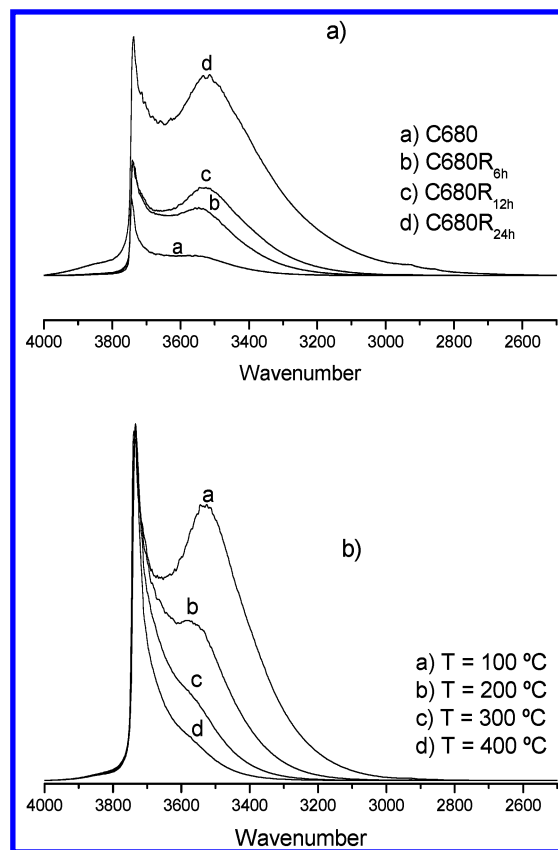

Figure 4. (a) Evolution of the silanol groups by rehydroxylation for the C680 sample. (b) Evolution of the silanol groups by thermal treatment for the C680R12h sample.

silica are used in normal phase HPLC, the low concentration of silanol groups will give poor specific analyte−stationary phase interactions. Moreover, the silanol groups are necessary to functionalize the silica for reverse phase HPLC or other applications such as catalysis. Because the yield of this reaction is generally not very high, the materials will have low bonded phase density. The rehydroxylation process used in this work increases significantly the number of silanol groups.

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