Mesoporous Benzene−Silica Hybrid Materials with a Different Degree of Order in the Wall Structure: An IR Comparative Study

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Recent joint IR and computational work (Onida et al. *J. Phys. Chem B* **2005**) has allowed a detailed characterization of the isolated silanols at the surface of highly ordered benzene−silica hybrid material. In the present paper, a similar characterization is provided for a less ordered sample. The comparison permits the assignment of IR features to the interaction of silanols either with one another or with benzene rings of the structure. The extent of structural imperfections appears to be limited, for example, no more than pairs of interacting silanols are found, readily healed by thermal treatment. Evidence is also provided that probe molecules with simultaneous H-acceptor and H-donor properties (benzene, methylacetylene) may interact with both the acidic proton in silanols and the electronic cloud in the framework aromatic rings.

Introduction

Periodic mesoporous organosilica (PMO) are hybrid materials synthesized from organosilane precursors and surfactant templates, capable of being further processed so as to acquire properties as functional materials, adsorbents, and catalysts.[1−12] In 2002, Inagaki and co-workers reported the first preparation of an ordered benzene−silica hybrid mesoporous material (Ph-HMM) with a crystal-like wall structure,[13] where the surface of the inner pores alternate periodically hydrophilic and hydrophobic layers, composed of silica and benzene, respectively. Very recently, Morell et al. reported an in situ synchrotron SAXS/XRD study on the synthesis of this system, showing that periodicity onsets simultaneously at the mesoscopic scale and within the pore walls.[14]

Figure 1a shows an idealized model of this system, showing the presence of alternating silica−benzene layers: silanols pave the internal surface as they would in ideal ordered mesoporous silica. Section b reports a magnified portion of the structure, showing two stacked benzene rings and isolated silanols, all equivalent, involving a Si atom linked to two O atoms and one C atom of a benzene ring.[13] To characterize this hybrid surface and its adsorptive properties, we have recently carried out a joint FTIR spectroscopy and ab initio molecular modeling study.[15]

Experimental evidence and computational results show a remarkable agreement. The presence of the aryl group in the coordination sphere of the Si atom brings about isolated surface silanols exhibiting both O−H and Si−O stretching modes at lower frequencies than in silica. This is also the reason for a lesser acidity of silanol, as shown by H-bonding interactions with several probes (N₂, CO, NH₃, acetone, etc.), where the
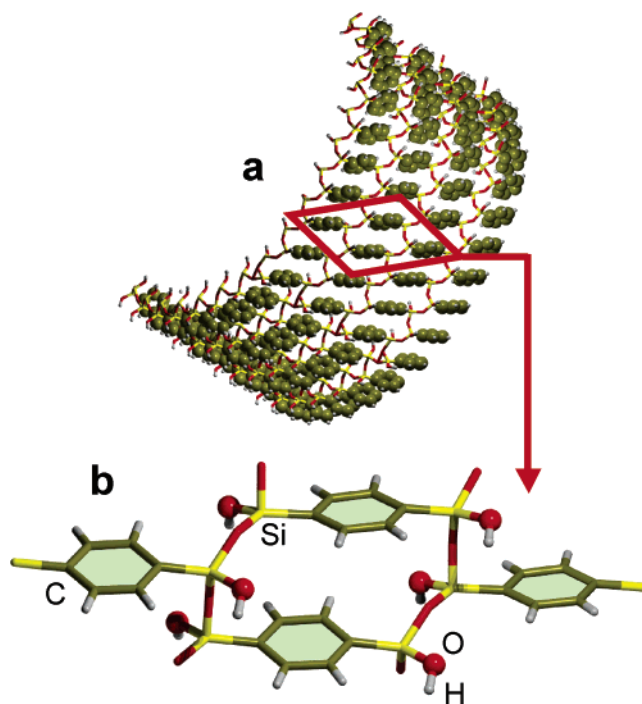

Figure 1. (a) Cartoon of a portion of the wall of Ph-HMM: benzene rings shown as hexagons of C atoms, represented by van der Waals spheres. (b) Magnification of a significant portion, showing silanol groups and the occurrence of pairs of stacked benzene hexagons.

bathocromic O−H frequency shift is systematically smaller with Ph-HMM than with silica by a factor of 0.93 ± 0.005.[15]

Some features in the IR spectra remained unexplained, which are addressed in the present paper, devoted to the comparison between a sample with a high degree of structural order and another sample owing defects.

A second point investigated is the possibility of the simultaneous interaction of adsorbates with both silanols and benzene rings. To this purpose, two molecules have been chosen in

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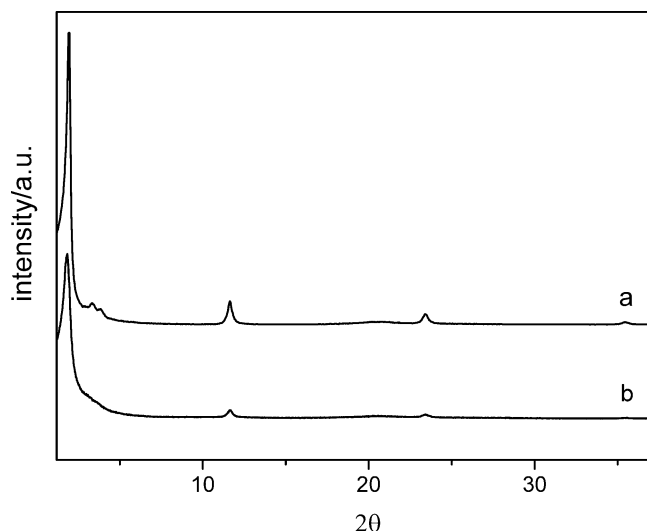Mesoporous Benzene−Silica Hybrid Materials

J. Phys. Chem. B, Vol. 109, No. 46, 2005 **21733**

Figure 2. XRD patterns of samples Ph-HMM-A (curve a) and Ph-HMM-B (curve b).

Figure 3. IR spectra of Ph-HMM-A outgassed at different temperatures.

Figure 4. IR spectra of Ph-HMM-B outgassed at different temperatures.

particular, having both H-acceptor and H-donor properties in H-bonding: benzene itself (one of the ingredients of the system) and methylacetylene.

Experimental Section

Synthesis. The ordered benzene−silica hybrid mesoporous material (sample Ph-HMM-A) was prepared and characterized as in ref 13, and a remarkable degree of wall crystallinity was obtained with an aging temperature of 368 K. The use of a lower temperature (343 K) has led to a sample with a lower degree of order (sample Ph-HMM-B). Figure 2 compares the XRD spectra of the two samples, and that of sample Ph-HMM-B (curve b) shows weaker and less defined peaks.

FTIR Study. For FTIR measurements, samples were pressed (2 t/cm^2) into thin self-supporting wafers, then placed into a quartz cell allowing thermal treatments in a controlled atmosphere. Before adsorption, samples were outgassed at regular intervals between 373 and 723 K. Spectra were recorded using a Bruker FTIR Equinox 55 spectrometer, equipped with a MCT cryodetector, at a resolution of 2 cm^{-1}.

Dosage of benzene and methylacetylene (Sigma Aldrich) was carried out by connecting the IR cell to a vacuum frame (residual pressure <10^{-3} mbar).

Results and Discussion

Vibrational Properties of the Samples. According to the ideal structure in Figure 1, only one type of silanol is present in Ph-HMM, not interacting with one another, so that only one O−H stretching mode is expected. Note that, as it concerns adsorption on them, silanols in Ph-HMM would constitute an ideal ensemble in the thermodynamic sense.

Figure 3 reports the IR spectrum in the range 3800−2500 cm^{-1} of sample Ph-HMM-A outgassed successively at 373, 573, 673, and 723 K. Absorptions between 3100 and 2700 cm^{-1}, due to C−H stretching of organic moieties, do not change with thermal treatment. This suggest that the organic part of the structure is not significantly affected by the thermal treatment. In contrast, changes are observed in the 3800−3100 cm^{-1} range. Instead of the single OH band expected in principle with a perfect sample, the sample outgassed at 373 K shows three bands: (i) a prominent one at 3730 cm^{-1}, (ii) a component at 3705 cm^{-1}, and (iii) a broad band centered at 3510 cm^{-1}. A weak shoulder around 3640 cm^{-1} is also present, though hardly
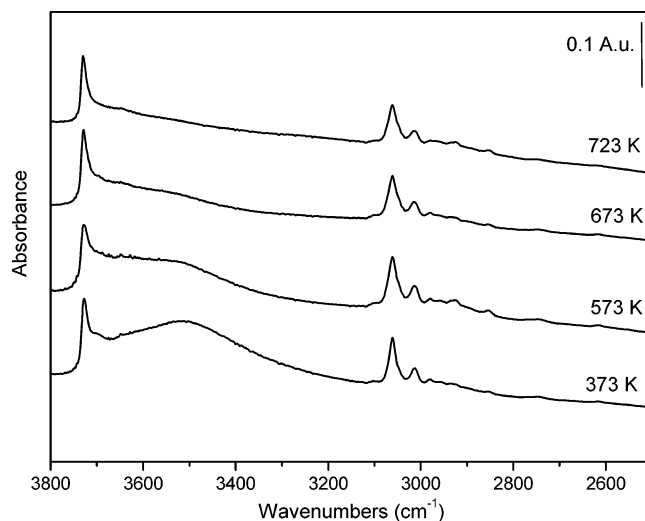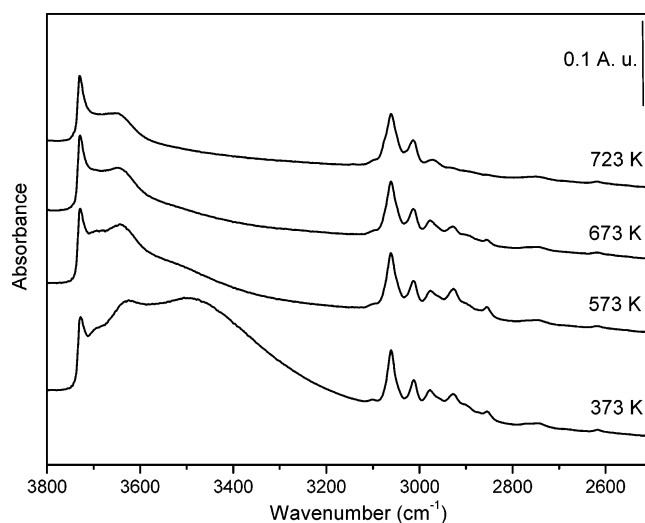
discernible in this spectrum, and best seen after treatment at 723 K, because of the decrease of the other bands.

The band at 3730 cm^{-1} is readily related to the isolated silanol, those at 3705 and 3510 cm^{-1} to other features (defects) in the structure. The main peak at 3730 cm^{-1} is not affected, both in frequency and in intensity, by thermal treatment at increasing temperatures, whereas the components at 3705 and 3510 cm^{-1} do decrease: thermal treatments apparently heal the structural defects without giving rise to new isolated species.

Figure 4 reports a similar set of spectra, concerning the more defective sample Ph-HMM-B. Basically the same features are observed, yet to a larger extent, so supporting the assignment of the bands at 3705, 3640, and 3510 cm^{-1} to defects. Again, heating at increasing temperatures decreases bands at 3705 and 3510 cm^{-1}, which disappear together at 723 K, so suggesting that they constitute a couple. Instead, the 3730 cm^{-1} band remains unaffected. In the present case, the last spectrum still shows a definite band at 3640 cm^{-1}; the intensity of which did not significantly change upon thermal treatment.

The O−H spectrum of defective Ph-HMM may be usefully compared with similar bands observed with amorphous silica samples of various nature.[16,17] In particular, the three bands at 3730, 3705, and 3510 cm^{-1} resemble the bands of hydrated silica at 3747, 3720, and 3520 cm^{-1}. These are, respectively,

SCHEME 1. Possible Configurations of a Pair of Silanols

Figure 5. Cartoon showing a pair of interacting silanols in Ph-HMM.
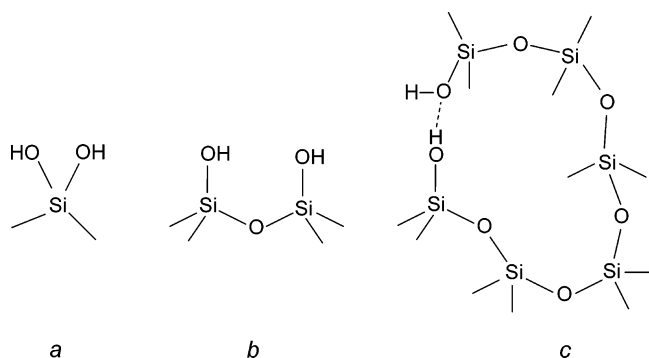
assigned to the O—H stretching mode of isolated silanols and to a pair of H-bonded silanols, the 3720 cm^{-1} band being due to the H-acceptor SiO—H species and the 3520 cm^{-1} band to the H-donor group. Frequencies are close to each other, though not identical. Also, their behavior with thermal treatments is similar (the bands at 3720 and 3520 cm^{-1} disappear together for thermal treatments below 773 K), though again not identical. In particular, the constant location and intensity of the 3730 cm^{-1} band in Ph-HMM is remarkable, because the isolated silanol in silica is known to increase its frequency (though moderately) with thermal treatments and also increase its intensity in the range of temperatures under investigation.

Silanol condensation in amorphous silica is a complex process, implying inter alia the reaction between pairs of adjacent geminal species, involving the release of water and the formation of rather strained siloxane rings. This process cannot occur for all silanol groups due to their rather low number: the strained ring structures, however, slightly perturb the frequency of the residual OH groups.

Also, groups of interacting silanols larger than a pair are present, as documented by the presence in the O—H stretching region of absorption well below 3520 cm^{-1}. Silanol condensation in Ph-HMM appears definitely to be a simpler phenomenon: only pairs of interacting silanols are present, the condensation of which does not lead to new SiOH species (hence the constancy in intensity of the 3730 cm^{-1} band), nor imply any evident strain (hence the constancy in frequency).

As to the nature of the two interacting silanols in silica, it has to be noted that both geminal species (structure a, Scheme 1) and vicinal species (structure b, Scheme 1) are not able to interact with each other, as shown either by ab initio molecular dynamics on periodic amorphous silica models[18a,b] or from experimental studies of tetramethyldisiloxane-1,3-diol diluted in CCl$_4$.[19] Hydroxyls sitting on Si atoms further apart (i.e., hydroxyl species sitting on Si atoms in a six-membered Si—O ring, structure c in Scheme 1) are able to interact nearly freely, giving rise to the 3720–3520 cm^{-1} pair as shown for instance for the hexamethyltrisiloxane-1,5-diol in CCl$_4$[19] and by theoretical calculations.[18a,b] We are led to assume that the pair at 3705 and 3510 cm^{-1} has to be related to a pair with a comparable freedom of orientation. A scheme is proposed in Figure 5, which describes the presence of the two interacting silanols as due to a failed condensation.

As already reported, and discussed in detail in the previous paper,[15] the isolated silanols in silica are more acidic than those in Ph-HMM.

Let us examine the implications of this different acidity as it concerns the mutual interaction of a couple.

The shift suffered by the H-acceptor silanol in Ph-HMM is 3730–3705 = 25 cm^{-1}, while the corresponding shift with silica
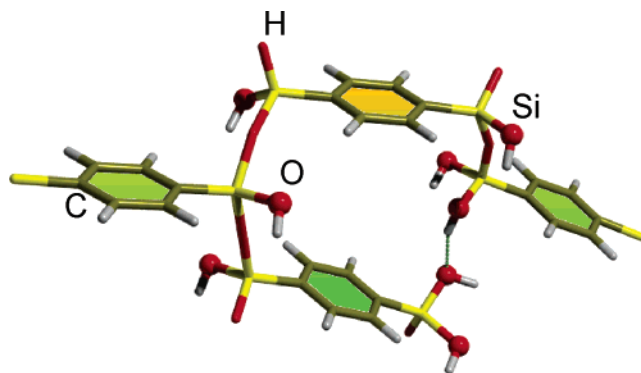
is 3747–3720 = 27 cm^{-1}. The shift suffered by the H-donor silanol is for Ph-HMM 3730–3510 = 220 cm^{-1}, whereas that for silica is 3747–3520 = 227 cm^{-1}. The two pairs of values are very close to each other. With the former couple of values affected by an uncertainty of at least ±2 cm^{-1}, and the latter couple of at least ±5 cm^{-1}, the two sets may even be assumed to coincide. The reason probably is as follows: when the SiOH group is considered, the proton is less acidic in Ph-HMM than that in silica, because it carries a lower positive charge; in contrast, the oxygen atom has a larger electronic charge and results therefore as more basic. As a consequence, when two SiOH species interact, a compensation is likely to take place, giving a similar H-bonding strength.

Interaction with Probe Molecules. The absorption at 3640 cm^{-1} has no definite counterpart in silica systems. Since the absorption is related to structural imperfections, it possibly arises from the interaction of silanols with the structural benzene rings. To check this hypothesis, adsorption of benzene was studied in the IR. Figure 6 reports a set of spectra obtained at increasing equilibrium pressure. The band at 3730 cm^{-1} decreases to the increase of a new band initially at 3640 cm^{-1} (then shifts to lower frequencies at high coverages), due to isolated silanols interacting via a H-bond with the π-cloud of the benzene molecule. A clear isosbestic point is seen.

With the frequency of the new OH band being identical to that under investigation, we propose that the 3640 cm^{-1} absorption, observed as a tail for Ph-HMM-A (Figure 3) and as a definite band for Ph-HMM-B (Figure 4), is due to the interaction of silanols with the π-cloud of the benzene rings in the structure: this defect, obviously not present in silica, is not significantly healed by thermal treatments, even at 723 K.

Since the interaction with benzene is weak and reversible, it is possible to draw an adsorption isotherm entirely through optical means.[20,21] Consider a spectrum at the equilibrium pressure p, with intensity A of the silanol stretching band. The fraction θ of silanol engaged in H-bonding is readily calculated as $(A° - A)/A°$, with $A°$ being the intensity of the silanol peak of the sample before interaction.

As suggested by the model structure in Figure 1a, all adsorption sites (isolated silanols in Ph-HMM) are expected to be equal and noninteracting. As it concerns the adsorption isotherm, a Langmuir behavior is expected, with $\theta = Kp/(1 + Kp)$ and K being the related equilibrium constant. The interaction of ammonia with the isolated silanol in Ph-HMM was reported in ref 15, and indeed, a Langmuir isotherm was observed over the entire range of pressure. A straightforward check of the model is the plot of the quantity $\theta/(1 - \theta)$ against the pressure, which results as linear, the proportionality factor being the equilibrium constant of the H-bonding process.
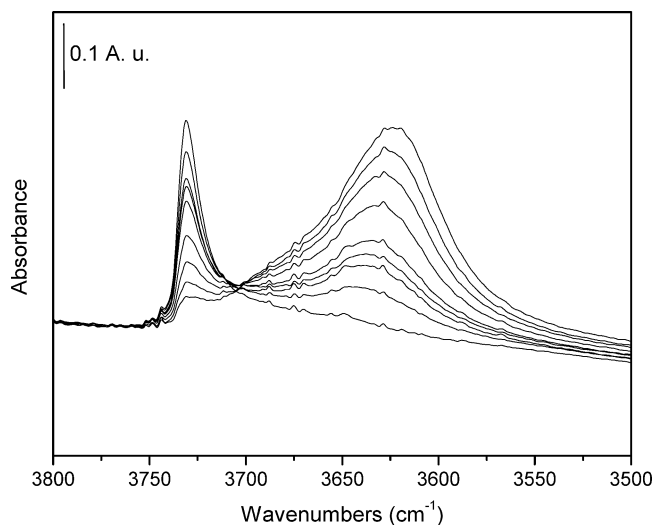
Mesoporous Benzene−Silica Hybrid Materials

J. Phys. Chem. B, Vol. 109, No. 46, 2005 **21735**

Figure 6. IR spectra concerning the interaction of benzene at increasing equilibrium pressure with Ph-HMM-A. Benzene pressures in the range of 0.1−12 mbar.
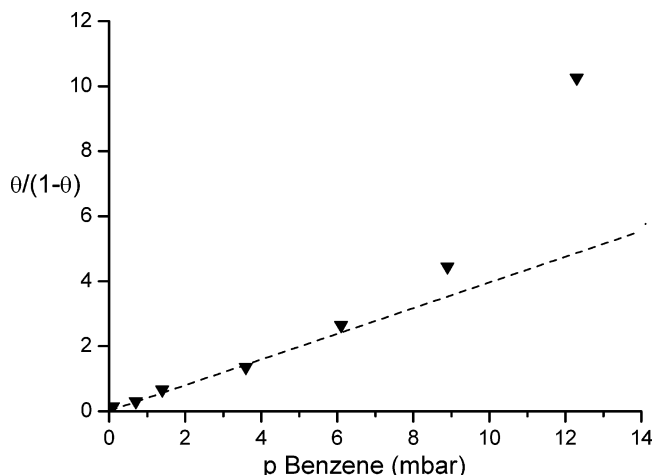

Figure 7. Linearized form of the Langmuir isotherm for benzene adsorption on Ph-HMM-A.

Figure 7 reports this type of plot for the benzene experiment. Linearity, that is, the Langmuir behavior, is not observed over the entire range of pressure. A deviation from the ideal behavior occurs at high coverage because the SiOH/benzene adducts begin to be solvated by other incoming benzene molecules.[20] This behavior is expected, because benzene is a liquid at ambient temperature, whereas ammonia is a gas. This phenomenon is also the cause of the shift observed in the 3640 cm^{-1} band at relatively high coverages. The linear portion of the $\theta/(1 - \theta)$ vs p plot in Figure 6 allows, however, the calculation of the equilibrium constant. That for Ph-HMM results in 0.4 mbar^{-1}.

The evaluation of the adsorption isotherm through IR measurements and successive interpretation of data with the Langmuir model is also possible with strongly dehydrated silica, because of the low surface density of silanols.[20] The equilibrium constant measured for NH$_3$ is rather close in the two cases (silica and Ph-HMM), and a marginally lower value is observed with Ph-HMM, which we ascribe to the lesser acidity of the related silanols. The situation with benzene is quite different: for dehydrated silica, a value larger than 0.4 mbar^{-1} is expected, whereas the value of 0.06 mbar^{-1} was measured.[20] This sevenfold difference in K is evidence of an additional stabilization of the H-bonded adduct of benzene with Ph-HMM and corresponds to a difference in $\Delta G° = -RT \ln K$ of 4.7 kJ,
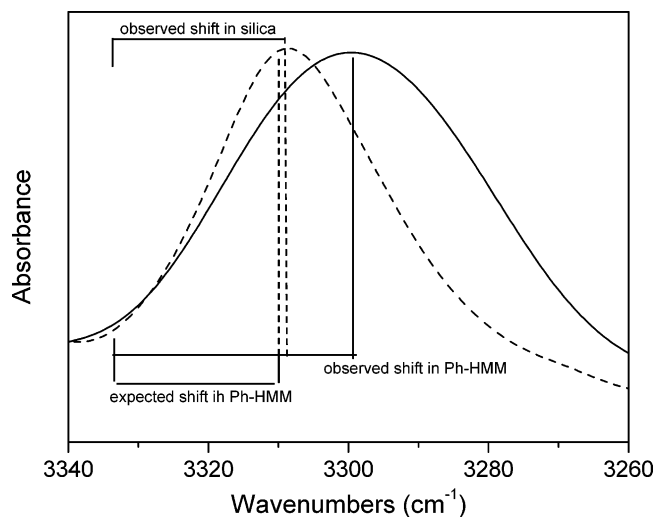

Figure 8. IR spectra comparing the ≡C−H stretching mode of methylacetylene interacting with Ph-HMM-A (solid curve) and dehydrated HMS silica (broken curve) (normalized at the same intensity).

probably ascribable entirely to a difference in the enthalpy of adsorption. As it concerns the nature of the extra stabilization, we consider that other van der Waals interactions can take place: dispersive interactions (expected to play a role with highly polarizable objects such as benzene electronic clouds) or H-bonding-like interactions involving the slightly acidic C−H groups of benzene and aromatic rings belonging to the framework, similar to those observed in benzene molecular clusters.[22]

To magnify the role of additional interactions, a molecule with simultaneous H-acceptor and H-donor properties was chosen, methylacetylene. This molecule features both the electronic cloud, which provides the basic counterpart for interaction with the acidic proton in SiOH and the partially acidic H atom of the ≡C−H moiety. To monitor the H-acceptor interaction at the triple bond of methylacetylene, the ≡C−H stretch may be used, which decreases in frequency, and becomes even more sensitive than the C≡C mode. Direct interaction of the ≡C−H moiety with basic centers also decreases the frequency.

Figure 8 reports two spectra concerning the adsorption of methylacetylene on amorphous silica (broken curve), the other (solid curve) on the sample Ph-HMM-A. The corresponding mode in the free molecule is at 3334 cm^{-1},[23] which undergoes bathochromic shifts to 3308 cm^{-1} with silica and to 3299 cm^{-1} with Ph-HMM. Since the H-bond interaction between the silanol and the triple bond is weaker in Ph-HMM than that in silica, a smaller shift for the ≡C−H stretching mode is also expected, as depicted in Figure 8. Instead, a definitely larger shift is measured. We ascribe this larger C−H shift observed for Ph-HMM to an additional C−H···π-cloud interaction with the framework aromatic rings. In this case, the contribution of interactions other than H-bonding between silanols and the adsorbate molecule is remarkable and it accounts for about 25% of the CH shift. Evidence of a direct C−H···π-cloud interaction is also provided by the large width of the C−H band with Ph-HMM (Figure 8).

Conclusions

The results in the present paper add to those recently reported[15] that, in Ph-HMM outgassed at 723 K, hydroxyl species mainly consist in isolated silanols, with the O−H stretching mode at lower frequency than that well-known for isolated SiOH species in silica, because of the aryl group.

In the present paper, the characterization of a sample with a lower degree of crystallinity in the walls has allowed the assignment of other features, concerning silanols interacting with one another or with the framework benzene rings. Structural imperfections appear limited, in that no more than pairs of interacting silanols are found, which are readily healed by thermal treatments. A structural imperfection resisting thermal healing consists of silanols interacting with benzene rings.

Evidence is also provided that adsorbates may have interactions with the surface functionalities besides H-bonding with silanols. On one hand, Ph-HMM is more polarizable than silica, so that the contribution of dispersion to the overall energy of interaction may be important. On the other hand, molecules with both H-acceptor and H-donor properties (benzene, methylacetylene) may interact with both silanols and the electronic cloud in the framework aromatic rings.

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