Spectroscopic Evidence for a Persistent Benzenium Cation in Zeolite H-Beta

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Abstract: Experimental evidence of protonation of an aromatic ring by a zeolite is hereby presented for the first time. The changes in vibrational properties and electronic transitions of the highest polymethylbenzene homologue, that is, hexamethylbenzene, were investigated after introducing the compound directly into a H-beta zeolite. Protonation of the aromatic ring, and thus the loss of symmetry, activated a vibrational ring mode at 1600 cm^{-1}. Furthermore, an electronic transition around 26 000 cm^{-1}, which was totally absent for the neutral species, was an obvious consequence of protonation. A parallel study of hexamethylbenzene adsorbed on a beta zeolite virtually free from protons did not show those distinctive spectral features. On the basis of the gas-phase proton affinity of hexamethylbenzene, a complete proton transfer from the zeolite framework to the molecule is, according to conventional considerations, not expected. The hexamethylbenzenium ion is stable in the zeolite cavities at least up to 200 °C. The remarkable persistence of this carbenium ion may be attributed to spatial constraints imposed by the tight fit of the cation inside the zeolite channels. Hexamethylbenzene is a relevant reaction intermediate in the methanol-to-hydrocarbons reaction and also plays a central role as a coke precursor in zeolite-catalyzed reactions that involve polymethylbenzenes.

1. Introduction

During the past 40 years, protonated zeolites have grown in importance as acidic catalysts in hydrocarbon conversion processes, and they are now widely used in, for example, the refinery industry. As late as one decade ago, it was believed that zeolites possessed superacidity and that the reacting molecules were fully protonated to carbenium ions inside the zeolite cages. However, early attempts to verify the existence of simple alkyl carbocations in zeolites by solid-state NMR failed.[1−7] The results unexpectedly indicated that the alkyl groups were bound to the zeolite framework rather than present as carbenium ions. This result inspired Haw and co-workers to perform a systematic study of carbenium ion formation from various hydrocarbons in zeolites.[7−9] As a result of this effort,

zeolites were reclassified as conventional strong acids with acidity slightly lower than 100% sulfuric acid. This view is now generally recognized. In a recent work, Haw reviews the investigations that led to the reclassification of zeolite acidity and the consequences this had for the theory of carbenium ion chemistry in zeolites.[10]

Surprisingly, few carbenium ions have thus far been found to persist in zeolites. In 1989, Haw et al. proved, by solid-state NMR, the formation of alkyl substituted cyclopentenyl carbenium ions such as **1** (proton affinity (PA) = 902.1 kJ/mol)[10] when propene was reacted over HY.[2] (The carbons on which protonation or hydride abstraction have been reported to occur in molecules **1−6** are marked with asterisks.) Very recently, Chua et al. obtained the vibrational spectrum of the same cation in H-ZSM-5 by UV Raman spectroscopy.[11] In 1994, Xu and Haw reported 1-methylindene **2** (PA = 877.8 kJ/mol)[10] to persist as a carbenium ion in H-ZSM-5.[8] UV−vis and IR spectroscopy were employed to detect the cation of the diphenylpentadiene **3**, assumably generated by abstraction of a hydride, in H-ZSM-5 and H-mordenite.[12]
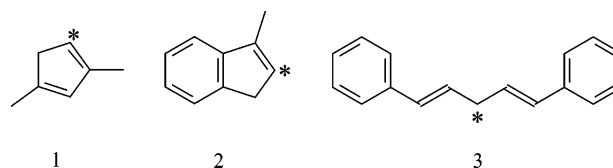

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1   2   3

The *gem*-dimethyl benzenium cation 1,2,2,3,5-pentamethyl-benzenium, that is, the protonated form of 1,5,6,6-tetramethyl-3-methylenecyclohexa-1,3-diene **4** (PA = 951.4 kJ/mol),[10] was the first benzenium related cationic species that was observed in a zeolite.[13] Very recently, the protonated form of 1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene **5** (PA not available, but is expected to be higher than that of **4**) was observed in the H-beta zeolite by NMR spectroscopy.[14] It must be emphasized that **4** and **5** are not aromatic systems, but cyclohexadienes with an exocyclic double bond that easily accepts a proton. A protonation of these species does not disrupt an aromatic system, and, conversely, a deprotonation of their cations does not restore an aromatic system. The carbenium ions of **4** and **5** were both generated by benzene methylation reactions, not by protonations. An attempt to protonate benzene (PA = 750.2 kJ/mol)[10] in zeolite HY was unsuccessful.[15] It has been reported that it takes several orders of magnitude of acidity above 100% sulfuric acid to fully protonate benzene.[16] Very recently, a benzenium-type carbenium ion, based on 3-meth-ylphenyl-2,4-dimethylphenylmethane **6** (PA 821 kJ/mol),[17] was found to be stable in a zeolite framework by computational techniques.[17]
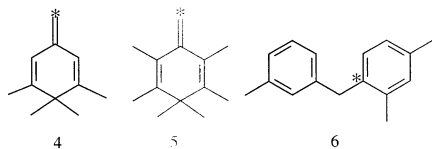
Until now, carbenium ions formed inside a zeolite by protonation of a benzene ring have not been reported from experimental data.

Characterization of persistent carbenium ions confined in zeolite frameworks is still rarely reported, and the majority of the species observed thus far are cyclic, resonance stabilized tertiary cations. To predict the persistence of carbenium ions in zeolites, Haw and Nicholas correlated gas-phase basicities (experimental and theoretical determined proton affinities) of a series of olefinic and aromatic hydrocarbons to their interactions with zeolite protons.[9,10] In this way, 874 kJ/mol was established as the lower proton affinity limit of compounds that can be expected to be fully protonated by a zeolite. Hexamethylbenzene (HMB) **7** (PA = 860.6 kJ/mol)[10] is, according to this lower basicity limit, on the borderline or slightly too weakly basic to persist as a carbenium ion in zeolites. However, when proto-nation reactions are considered, not only the PA of the base but also the acid strength of the proton donor (i.e., the zeolite) should be accounted for. In addition, as the zeolite framework may contribute to stabilize a confined cation, spatial conditions

may in some cases play a crucial role. Thus, when parameters such as zeolite topology, acid site density (i.e., the aluminum content of the zeolite), and copresence of Lewis and Brönsted sites are altered, different results should be expected.

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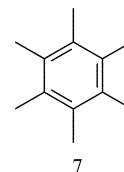
In this work, we have studied the interaction of HMB with the acidic zeolite H-beta by FT-IR and UV–vis spectroscopy. This study has been performed on H-beta zeolite because its acidic properties are well known and it has channels large enough for the guest HMB (see Supporting Information). We have been able to demonstrate, from experimental results, that the hexamethylbenzenium ion is persistent in H-beta, at least up to 200 °C, and that a zeolite may protonate species with a proton affinity slightly below 874 kJ/mol.

Apart from giving a deeper basic understanding of zeolite acidity and carbenium ion chemistry, this study is of immediate interest to the methanol-to-hydrocarbons reaction (MTH) and aromatic-based petrochemical processes, such as alkylations, transalkylations, and disproportionations over protonated zeo-lites. Dahl and Kolboe proposed some 10 years ago that the MTH reaction proceeds in an indirect manner, via a "hydro-carbon pool" mechanism.[18–20] Later, strong evidence has been found that polymethylbenzenes, particularly HMB, play a crucial role as reaction centers in the catalytic cycle.[21–25] It is believed that protonation or methylation of methylbenzenes is followed by dealkylation, yielding the olefin products. Two mechanisms have been proposed to explain the role of polymethylbenzenes as "hydrocarbon pools": The first is the paring reaction, initially proposed by Sullivan et al.[27] In this reaction, a stabilized methylbenzenium ion rearranges monomolecularly and splits off an alkene. The second mechanism, initially proposed by Mole and co-workers[28,29] and further elaborated by Haw and co-workers,[25,26] is based on the formation of an exocyclic double bond. The exocyclic double bond may be methylated by methanol, and the resulting alkyl group is split off as an alkene. The relative importance of these two alkene formation reactions is undoubtedly linked to the persistence of polymethylbenzenium ions inside the zeolite. The observation of persistent hexam-ethylbenzenium ions in a beta zeolite, reported here for the first time, represents a step ahead on the details of the hydrocarbon pool mechanism.

2. Experimental Section

A commercially available H-beta (Si/Al = 12) from P.Q. Zeolites B.V. has been used as starting material for this study. Dealumination

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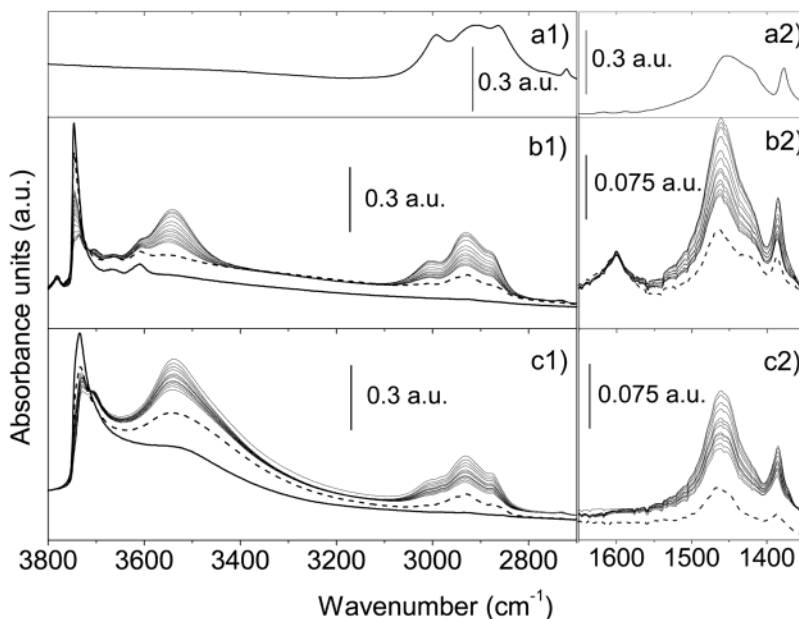(29) Mole, T.; Bett, G.; Seddon, D. *J. Catal.* **1983**, *84*, 435–445.

Figure 1. FT-IR spectra of HMB. (a) HMB in a wafer diluted with KBr; (b) HMB adsorbed on a wafer of H-beta (Si/Al = 12, bold solid-drawn plot represents the activated zeolite prior to HMB adsorption) which subsequently was outgassed, first at room temperature (solid-drawn plots), and finally at 100 °C for 30 min (dashed plot); (c) same as (b) for the dealuminated H-beta (Si/Al = 210). Parts b2 and c2 are shown at a higher magnification and are reported as difference spectra.

was carried out by treating the sample with oxalic acid for 3 h at 70 °C. The dealumination resulted in an Si/Al = 210 without lowering the crystallinity of the sample significantly. Details on the dealumination procedure and the zeolite characterization have been described previously.[30]

For the IR measurements, the zeolite samples were compressed into self-supporting wafers, while powdered samples were used for the UV–vis measurements. Before adsorption of HMB, the samples were outgassed in situ, under high vacuum, for 1 h at 400 °C to remove water and other adsorbed impurities.

The IR cell was directly attached to a reservoir containing solid HMB (Fluka > 99%). Special care was taken to avoid water contamination. After the pretreatment, the connection to the HMB reservoir was opened, and the entire accessory was treated at 65 °C for 2 h to increase the vapor pressure of HMB. To remove physisorbed HMB, the sample was subsequently outgassed, first at room temperature with the cell connected to a 77 K cold trap and finally at 100 °C for 30 min.

Because of the larger quantity of zeolite powder required for UV–vis experiments, HMB was introduced to the pretreated zeolite directly by mixing the two powders in a glovebox. The cell was thereafter closed, and the spectrum was recorded. To obtain a further increase in the internal HMB coverage, the cell was heated for 6 h at 65 °C. After the spectrum of the highest loading was collected, the sample was outgassed at 200 °C for 1 h. Finally, 40 Torr NH_3 was dosed twice to the cell to probe the response of the system on addition of an excess of a relatively strong base.

The IR spectra were obtained in transmission mode on a Bruker IFS 66 FTIR spectrometer, equipped with a cryogenic MCT detector, at 2 cm^{-1} resolution. The diffuse reflectance UV–vis spectra were obtained on a Perkin-Elmer spectrophotometer.

3. Results and Discussion

The beta zeolite has a three-dimensional channel system with 12-membered ring apertures with cross sections of 5.6 × 7.3 Å[31] and thus allows a direct introduction of HMB. As mentioned introductorily, according to the gas-phase proton affinity limit of 874 kJ/mol, HMB is slightly too less basic to be expected to persist as a carbenium ion in a zeolite. However, evaluation of

the stability of a cation being confined within a zeolite framework solely on gas-phase basicities appears incomplete, at least in cases where the cation experiences severe steric constraints. In such instances, spatial considerations have to be taken into account. The contribution to cation stabilization by the zeolite framework will accordingly depend on the steric properties of the embedded carbenium ion and on the geometry of the zeolite cavities. Thus, we found it worthwhile to investigate a sterically demanding base with a proton affinity slightly below the established limit. The spatial relationship between the host and the probe molecule should in this case lead to a quite optimal stabilizing contribution from the zeolite framework. In addition to these fundamental aspects on carbenium ion stability, HMB is highly relevant as a reaction intermediate in the methanol-to-hydrocarbons reaction, that is, in the so-called hydrocarbon pool mechanism.[21–25] HMB is evidently an essential constituent of the catalytic cycle of this reaction, and the characteristics of this species within the zeolite pores are not yet fully understood.

3.1. IR Spectroscopy. A protonation of the aromatic ring of HMB will lower the symmetry of the system and activate silent vibrational modes as observed for, for example, benzene in superacidic media.[32] Accordingly, IR spectroscopy appeared to be an appropriate technique for studying a possible protonation of HMB in zeolite H-beta.

The IR spectra of HMB in different media are presented in Figure 1. Parts a represent the vibrational properties of HMB in a wafer diluted with KBr. The remaining spectra of Figure 1 were collected for a series of decreasing HMB coverages on the parent sample of the beta zeolite (Si/Al = 12, Figure b1 and b2), and on the severely dealuminated beta zeolite virtually

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free from protons (Figure c1 and c2). The dashed curves in Figure 1b and 1c, representing the lowest HMB coverages, were collected after outgassing the sample at 100 °C for 30 min. The low-frequency segments of Figure 1, parts b2 and c2, are shown at a higher magnification (×4) and are reported as difference spectra.

The bands between 3020 and 2830 cm^{-1} in the reference spectrum, Figure a1, represent a fingerprint pattern for HMB. This complex of bands arises from CH$_3$ vibrations complicated by a Fermi resonance effect between symmetric CH$_3$ stretching and a CH$_3$ deformation overtone.[33] In the low-frequency segment, part a2, the spectrum is characterized by two distinct bands at 1453 and 1377 cm^{-1} and a shoulder at 1417 cm^{-1}. The former band is assigned to the stretching vibrations of the aromatic ring,[34] and the two bands located at lower frequencies are both ascribed to C−H bendings of the methyl groups.

The IR spectra of the parent sample of zeolite H-beta with different HMB coverages are presented in Figure 1b. The spectrum of the activated zeolite (bold solid-drawn curve) shows four bands in the O−H stretching region, that is, between 3800 and 3600 cm^{-1}. The sharp peak at 3746 cm^{-1} is attributed to the O−H stretching vibrations of free silanols (i.e., isolated or terminal situated hydroxyls not interacting through hydrogen bonds),[35,36] and the band at 3610 cm^{-1} arises from O−H stretching of strongly acidic bridging hydroxyls mainly located inside the pores. Two additional components, observed at 3782 and 3667 cm^{-1}, are ascribed to less acidic groups associated with partially extra lattice aluminum or extra lattice aluminum.[37−39] CO adsorption at low temperature (data are reported as Supporting Information for the sake of brevity) has shown the presence of strong Lewis sites and has confirmed the existence of at least three families of Brönsted sites with acidic strength decreasing in the following order: bridged hydroxyls, Al−OH species, and Si−OH groups.[37−41]

Upon HMB dosage, spectral perturbations take place, and formation of hydrogen-bonded adducts is particularly evident. At the highest HMB loading of Figure 1b1, the silanol band at 3746 cm^{-1} is severely eroded with a parallel growth of a prominent absorption centered at 3542 cm^{-1} ($\Delta \nu = 204$ cm^{-1}) and a minor component at 3704 cm^{-1} ($\Delta \nu = 42$ cm^{-1}). The minor component, representing weakly perturbed silanols, is most likely associated with sites barely accessible for the HMB

molecules. Thus, when considering interactions involving such a sterically demanding probe molecule, not only the acid strength of the sites but also their accessibility must be taken into account.

The remaining unperturbed silanols, mainly located on the low-frequency side of the band, are probably associated with internal sites. Also, this behavior can be rationalized for by the steric properties of HMB. The band at 3782 cm^{-1} remains unchanged, confirming the modest acidic character of the O−H groups represented by this band.

The interaction between HMB and Brönsted sites, originally absorbing at 3667 and at 3610 cm^{-1}, is testified by a particularly broad absorption in the range 3500−3000 cm^{-1} ($\Delta \nu$ about 400 cm^{-1}). A similar behavior has been observed for benzene.[37] A quantitative evaluation of the site consumption in this case is complicated by the partially overlapping absorption of hydrogen-bonded silanols.

In the C−H stretching region (3080−2810 cm^{-1}), the spectra of adsorbed HMB are very similar in shape and components to that of the pure solid, except that all of the maxima are blue shifted about 10 cm^{-1}. Successive reduction of HMB loadings was obtained by progressive pumping at room temperature, using a line equipped with a 77 K cold trap (giving the decreasing intensity series of solid-drawn plots), and by outgassing at 100 °C for 30 min (giving the dashed plot). This procedure resulted in partial erosion of the absorption associated with vibrational modes of HMB, a decrease of the component with maximum at 3542 cm^{-1} (H-bonded silanols), and the disappearance of the component at 3704 cm^{-1} (very weakly perturbed silanols). Only a partial parallel restoration of the silanol band is observed, revealing that physisorbed HMB not has been completely removed. This is also evidenced by the presence of the C−H-stretching bands. Finally, the dashed curve suggests that a rather modest fraction of the strong Brönsted sites have been consumed irreversibly upon interaction with HMB. The reason that the entire set of Brönsted sites is not involved might be that only a fraction of the HMB molecules leave the external surfaces and penetrate the pores. A blank experiment, carried out with H-ZSM-5 (Si/Al = 15), documented that HMB interacts weakly with the acidic sites located on the external surface. As the channels of ZSM-5 are delimited by 10-membered rings, HMB cannot enter the internal structure, and protonation was hence not observed. ^{27}Al NMR has documented the presence of amorphous octahedral extraframe-work aluminum in our sample. The presence of such species will contribute to a slow or restricted diffusion of HMB in the channels of the zeolite. However, as the absorption representing H-bonded species (broad absorption in the 3500−3000 cm^{-1} range) remains unchanged, it is evident that a noteworthy part of the sites are involved in a strong interaction. A quantitative estimate of this part was made possible by UV−vis spectroscopy (vide infra).

Figure 1b2 covers the region of the ring stretching modes and C−H bending vibrations of adsorbed HMB. Also in this region, the components are shifted to higher frequencies as compared to free HMB (part a2). A striking feature is the appearance of a band at 1600 cm^{-1}. This band, completely absent in the reference spectrum (part a2), is made IR active due to the asymmetry induced by the interaction between the probe molecule and the Brönsted sites. The irreversible character of this adsorption, even upon evacuation at 100 °C, indicates

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that this component is associated with a species involved in a strong interaction with the zeolite framework. It is plausible to assign this band to protonated HMB, that is, to the hexamethylbenzenium cation.

To shed further light on the role of the protons in the beta zeolite on the perturbations of HMB, a parallel experiment was carried out on a sample virtually free from protons. The IR spectra of the dealuminated sample with different HMB coverages are presented in Figure 1c. As can be seen from the figure, the IR spectrum of this zeolite sample recorded after activation (bold solid-drawn plot) is characterized by broader and less resolved components which all can be ascribed to silanol groups. This picture has been confirmed by low-temperature CO measurements, which show the presence of very weak Brönsted sites and absence of Lewis sites. Parallel ^{27}Al NMR measurements support this thesis.

As a result of dealumination, the silanol band has broadened and the maximum is now located at 3735 cm^{-1}. This shift to a lower frequency is most likely ascribed to an increase in the number of weakly perturbed internal silanols in defective positions (end of hydrogen-bonded silanols chains)[35,36] when aluminum is extracted from lattice positions. Furthermore, a broad band, extending until 3200 cm^{-1}, has been associated with medium strength hydrogen-bonded species due to hydroxyls present in internal defects, that is, so-called "silanol-nests".[42,43]

When HMB is adsorbed on the dealuminated beta zeolite, the silanols are perturbed in a manner similar to that observed for the parent sample. The high-frequency tail of the band centered at 3735 cm^{-1} is eroded, while an absorption centered around 3540 cm^{-1} ($\Delta\nu = 204$ cm^{-1}) grows in a parallel way. Also for this sample, a minor component at 3704 cm^{-1} ($\Delta\nu = 31$ cm^{-1}) can be observed. The broad absorption between 3600 and 3200 cm^{-1}, that was assigned to the strongly perturbed Brönsted sites of the parent sample, is, as expected, absent for this proton free material. In this case, outgassing at 100 °C (dashed curve) did not restore the original spectrum completely, confirming the difficulty in removing the physisorbed phase. The spectra in part c2 show the same features as those presented for the parent sample with the exception of the band at 1600 cm^{-1}, previously suggested to arise from the hexamethylbenzenium cation.

In the same manner as the lower polymethylbenzenes, HMB is known to undergo disproportionation/transmethylation when reacted over a protonated zeolite at elevated temperatures.[24] The products of such a reaction are pentamethylbenzene (PMB) and the heptamethylbenzenium cation (heptaMB$^+$). Thus, from Figure 1b2 we cannot rule out the possibility that the 1600 cm^{-1} band actually has arisen from a transmethylation, forming heptaMB$^+$, rather than a protonation. To clarify this point, parallel experiments with PMB were conducted. In Figure 2, comparisons are made between the vibrational properties of PMB (dashed plots) and HMB (solid-drawn plots) in a wafer diluted with KBr (upper part) and adsorbed on the parent sample of the beta zeolite (lower part, difference spectra). The bands in the 1580–1540 cm^{-1} region shown by PMB are completely absent for HMB and are the most evident differences in the vibrational properties of the two compounds. If HMB reacts
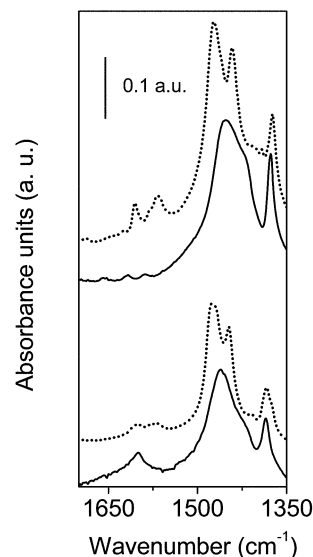

Figure 2. FT-IR spectra of PMB (dashed plots) and HMB (solid-drawn plots) in wafers diluted with KBr (upper part of the figure) and adsorbed on a wafer of H-beta (Si/Al = 12, lower part of the figure). Spectra have been vertically shifted for clarity.

according to a disproportionation path and forms heptaMB$^+$, equivalent amounts of PMB will necessarily be formed. According to Figure 2, this is not the case, and a disproportionation reaction has not been of significance under the employed conditions.

3.2. UV−Vis Spectroscopy. The final proof of the formation of the hexamethylbenzenium cation in the beta zeolite as well as a quantitative estimate was provided by UV−vis spectroscopy. This technique is well known to be highly sensitive to conversions of aromatic compounds into carbenium ions. In fact, the pronounced interference of the aromatic system associated with the proton transfer gives rise to numerous striking properties of charged complexes, that is, their intense electronic absorption in the visible range. Many examples are available for carbocations obtained from aromatic hydrocarbons with Lewis acids in the presence of hydrogen halides or in strong acids,[44,45] while data on similar charged systems, stabilized in solid acids, such as zeolites, are missing completely.

The results obtained after introducing HMB to the beta zeolite are presented in Figure 3 for the visible and the first UV spectral range (20 000−45 000 cm^{-1}). The spectra of HMB in 96% sulfuric acid (solid-drawn plot) and in cyclohexane (dashed plot) are compared in Figure 3a. HMB in cyclohexane shows a band at 37 000 cm^{-1} (commonly designated as the α-band), related to the π-electron system of the aromatic ring.[46,47]

In 96% sulfuric acid, the HMB spectrum changes dramatically by showing a new broad absorption centered around 26 000 cm^{-1}, with a shoulder around 31 000 cm^{-1}. Furthermore, a shift in the 37 000 cm^{-1} band to a slightly higher frequency (maximum at 37 600 cm^{-1}) can be observed. The spectrum corresponds well with that of protonated benzene in a superacidic solution.[44] Removal of the degeneracy of the energy levels

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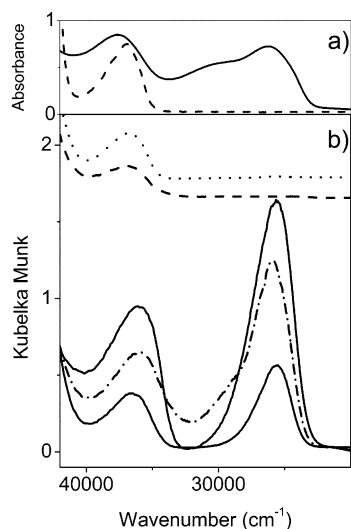
Figure 3. Diffuse reflectance UV−vis spectra of HMB: (a) in 96% sulfuric acid (solid-drawn plot) and cyclohexane (dashed plot); (b) increasing coverages on H-beta (Si/Al = 12) (solid-drawn plots, lower part) followed by outgassing at 200 °C for 2 h (dash−dotted plot), and finally exposure of 2 × 40 Torr ammonia (dashed plot, upper part). The dotted-drawn plot in the upper part of (b) represents HMB adsorbed on the dealuminated H-beta (Si/Al = 210).

upon protonation gives new electronic transitions and thus new spectral components, one of which is in the visible region. Another important element useful for differentiating between neutral and carbocationic species is that the intensity of the band located around 37 000 cm^{-1} (corresponding to the neutral compound) is approximately 50 times smaller[45,46] than the carbocationic fingerprint located at about 26 000 cm^{-1}.

The solid-drawn plots in Figure 3b represent increasing HMB coverages, obtained according to the procedure described in the Experimental Section. The sample changed from white to pale yellow when brought in contact with HMB. In particular, two bands, centered around 25 600 and 36 100 cm^{-1}, can be seen. The first is completely new, and the second is shifted to a lower frequency as compared to the spectral features of HMB in cyclohexane or HMB adsorbed on the proton free zeolite (dotted curve reported in the upper part of Figure 3b). After the highest HMB loading was obtained, the sample was outgassed at 200 °C for 2 h, giving the dash−dotted plot in Figure 3b. As the reduction of the 25 600 cm^{-1} band upon this treatment is fairly low, the hexamethylbenzenium cation is apparently rather stable in the beta zeolite. The dashed plot in the upper part of Figure 3b shows how the system responded when ammonia was added. The disappearance of the 25 600 cm^{-1} band and the intensity decrease of the component at higher frequency (now centered at 36 800 cm^{-1}) are consistent with the conversion of carbocationic species to neutral moieties: A proton transfer between ammonia and the hexamethylbenzenium cation has formed the ammonium ion and neutral HMB.

The spectral changes obtained upon NH$_3$ dosing can provide an estimate of the HMB fraction which has been protonated by the zeolite. As compared to the band of the neutral moiety observed in the near UV range, the extinction coefficient of the component in the visible region is about 50 times higher. The dashed curve is about 7 times less intense than the curve obtained prior to NH$_3$ contact. Thus, we can estimate that about 15% of the HMB measured in the presence of NH$_3$ was previously present as the hexamethylbenzenium ion in the beta zeolite. Reflectance spectroscopy cannot, however, be considered to be a quantitative tool, and 15% is most likely only correct as far as the order of magnitude is concerned.

4. Conclusion

This is the first time protonation of an aromatic ring by a zeolite has been demonstrated experimentally. On the basis of gas-phase proton affinity considerations, hexamethylbenzene was not expected to form a persistent carbenium ion within the cavities of a zeolite. IR and UV−vis spectroscopy did, however, provide clear evidence that a proton was transferred from the zeolite framework to the aromatic ring.

The embedded hexamethylbenzenium ion was stable in the cavities of H-beta at least up to 200 °C. From the UV−vis data, it can be inferred that protonation involves a significant fraction of the adsorbed phase, suggesting that the less extensive protonation observed by IR measurements can be ascribed to the diffusion constraints hexamethylbenzene experiences in the zeolite pores. External surface does not play a role in the formation of the hexamethylbenzenium cation. The amorphous octahedral aluminum present in the sample may restrict the diffusion of hexamethylbenzene in the zeolite channels.

To rationalize the observed protonation of hexamethylbenzene in zeolite H-beta, our results suggest that, in addition to the gas-phase proton affinity of the base, also the acid strength, the pore geometry, and size of the base have to be considered. Properties such as zeolite topology, acid site density, copresence of Lewis and Brönsted acid sites, and the size of the base may rationalize the observed protonation of hexamethylbenzene.

Supporting Information Available: Data concerning: (i) molecular mechanics study of HMB adsorption in beta framework; (ii) IR spectroscopy of CO in interaction with the parent sample of H-beta; and (iii) HMB adsorbed on H-ZSM-5 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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