Surface Modification of H-Ferrierite by Reaction with Triethoxysilane

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The interaction of triethoxysilane (TES) with H-ferrierite (H-FER) and its effects on acidity have been investigated by infrared spectroscopy. TES adsorbs only on the external surface of H-FER and allows the almost complete disappearance of the external silanol groups. New SiH groups are formed which appear to be inactive in acid−base interactions. The adsorption of propionitrile, which diffuses into the zeolitic channels, provides evidence for the lack of substantial perturbation of the strongly acidic internal bridging OH groups. On the contrary, the adsorption of the hindered basic probe molecule *o*-toluonitrile, which cannot penetrate the FER channels, shows that not only terminal silanols but also Al³⁺ Lewis acid sites present on the external surface of H-FER almost totally disappear after TES treatment. Treatment with TES seems to allow virtually the total deactivation of the H-FER external surface.

Introduction

Protonic ferrierite (H-FER) is an acidic catalyst applied in industry for the skeletal isomerization of *n*-butenes to isobutenes.[1,2] It is a typical medium-pore protonic zeolite. Its structure presents two families of perpendicular channels with diameters [001] 4.2 Å × 5.4 Å and [010] 3.5 Å × 4.8 Å interconnected with a larger cage (6−7 Å diameter). Although discussion is still open on the mechanism of olefin isomerization reaction, it is ascertained that selectivity to isobutenes is favored by shape selectivity effects typical of zeolitic catalysis. According to Mériaudeau and Naccache,[2] who reported an extensive review on *n*-butene isomerization, the selective reaction occurs through a monomolecular mechanism and the main factor governing the isobutene selectivity is restricted transition-state shape selectivity, in agreement with previous experimental studies.[4] Also, it has been remarked that the acidic sites on the external zeolite surface are not shape selective and have to be removed or poisoned[2] to improve selectivity. The nature of the acid sites at the external surface of H-FER has been the object of previous investigations from our group:[5−7] medium-strength Brønsted acid sites constituted by acidity-enhanced silanol groups and Lewis acid sites have been found outside the channels of H-FER. On the contrary, it has been confirmed that strongly acidic bridging OH groups are only confined in the internal cavities.

To limit the possible effect of nonselective external sites of zeolites, treatments aimed at covering the external surface with inactive layers can be performed. Alkoxysilanes such as tetraethoxysilane (TEOS) are applied for this purpose.[8] In this way silica-type layers could be grown on the external surface of zeolite crystals. However, the formation of silanol groups similar to those of silica on the newly formed external surface likely occurs. These groups still retain some acidity although very weak. In a recent paper we reported on the surface coverage of silica with triethoxysilane (TES).[9] We report here on the attempt we made to poison the active sites of the external H-FER surface with this molecule, and on the characterization of the catalytic material resulting from this treatment. Propionitrile and *o*-toluonitrile have been used here as basic probes. In fact, the dimensions of the FER cavities suggest that propionitrile can enter them without substantial hindrance while access of *o*-toluonitrile is expected to be impossible, like that of any other bisubstituted aromatic compound.[10]

Experimental Section

The starting material used in the present study was an NH₄-FER (SiO₂/Al₂O₃ = 55, S_{BET} = 480 m²g⁻¹) supplied by Zeolyst.

FT-IR spectra were recorded on a Nicolet Nexus Fourier transform instrument provided with a DTGS KBr detector: for each spectrum 100 scans in the range 4000−400 cm⁻¹ were recorded, resolution 4 cm⁻¹. The spectra are shown on the absorbance scale; in the figures that present more than one spectrum the absorbance scale refers only to the first one from the bottom, the others being shifted without any scale modification.

The surface characterization was carried out on a H-FER sample and on the TES-treated H-FER. The experiments were performed using pressed disks (2.5 cm diameter) of pure NH₄-FER powder. The disk weight was calibrated to have, in all cases, the best spectral conditions. The disks were prepared in air and then located inside an IR cell connected to a conventional manipulation/outgassing ramp that allows the disk to stay, alternatively, in the IR beam path or inside an oven. The samples were treated by outgassing at 773 K in the IR cell. Spectra were collected after the pretreatment and after adsorption of TES, which was distilled under vacuum and then contacted with the sample surface through the ramp. Both pure H-FER and TES-modified H-FER acidic sites were successively characterized through in situ adsorption of differently hindered organic nitriles

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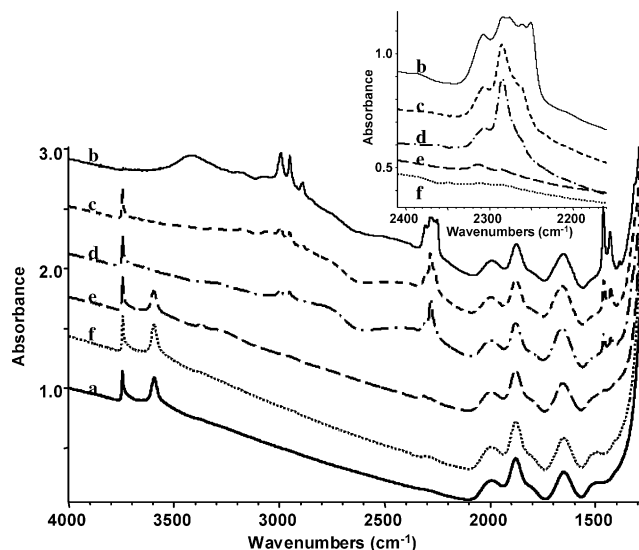 † Università di Genova.
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Figure 1. Adsorption of PrN onto H-FER. FTIR spectra: a, thermally treated sample; b, after adsorption of PrN; c, after evacuation at room temperature; d, after evacuation at 373 K; e, after evacuation at 473 K; f, after evacuation at 573 K. Inset: zoom on the ν(CN) region.
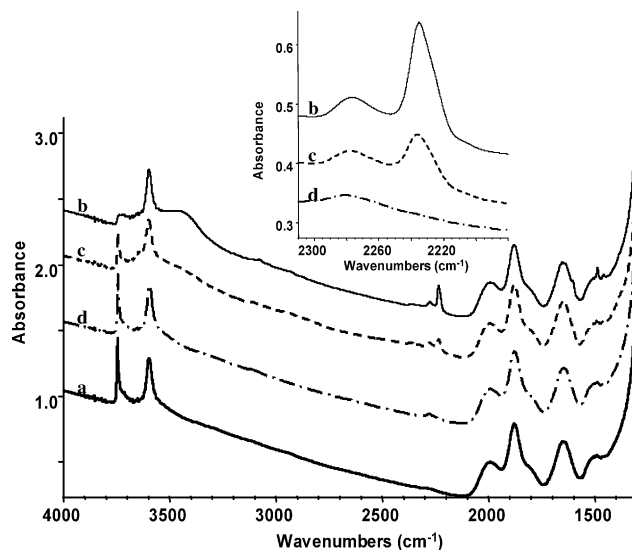

Figure 2. Adsorption of *o*-TN onto H-FER. FTIR spectra: a, thermally treated sample; b, after adsorption of *o*-TN; c, after evacuation at room temperature; d, after evacuation at 373 K. Inset: zoom on the ν(CN) region.

(provided by Aldrich) that act as basic probe molecules. The adsorption procedure for all adsorbates including TES involves contact of the pretreated sample disk with vapors at room temperature and at a pressure of 15 Torr for 20 min, and outgassing in steps from room temperature to higher temperatures (up to 773 K).

Results and Discussion

Adsorption of Propionitrile (PrN) and *o*-Toluonitrile (*o*-TN) on H-FER. After the thermal treatment under vacuum at 773 K (Figure 1, spectrum a), H-FER is characterized by a spectrum with two ν(OH) bands: a very sharp band at 3747 cm^{-1} due to external terminal silanol groups and a slightly broader band at 3597 cm^{-1} due to bridging Si−OH−Al groups. The latter have been proven to be placed exclusively inside the zeolitic cavities.[5−7] After the surface is contacted with PrN vapors (Figure 1, spectrum b), both ν(OH) bands disappear (except a very tiny component at 3743 cm^{-1}) and new bands are formed. We can observe the formation of a very broad band centered at ca. 3420 cm^{-1} together with the typical ABC pattern already described and discussed in detail for the adsorption of acetonitrile onto different zeolites.[11] The adsorbate interacts with the bridging OH groups through strong H-bonding, and this causes the OH stretching to shift down significantly, while the in-plane and out-of-plane OH bendings shift up significantly, up to their first overtones interacting with the stretching through a Fermi resonance. The minima between A and B and between B and C broad components correspond to the positions of the first overtones of the in-plane and out-of-plane modes.

Two band systems are present due to CH stretching (peaks at 2994, 2951, 2919, 2891, and 2846 cm^{-1}) and deformation (1464, 1432, and 1388 cm^{-1}) modes. A quite complex absorption system is evidenced also in the ν(CN) region with five main components at 2308, 2286, 2278, 2262, and 2252 cm^{-1}. These data suggest that practically all OH groups (external and internal) can interact with PrN, whose molecular dimensions allow its diffusion inside the zeolitic channels. In parallel with what has already been reported for acetonitrile (AN) interaction, the H-bonding of the external silanol groups with the nitrile results in a broadening and a shift of the corresponding ν(OH) band from 3747 to around 3420 cm^{-1}. The strong H-bonding

of the ν(OH) band of the internal bridging OH groups gives rise to the ABC pattern.

After evacuation at room temperature (Figure 1, spectrum c), the silanol stretching at 3747 cm^{-1} is restored and the broad band at 3420 cm^{-1} is no longer detected. The CN stretching band system now has only two main components at 2308 and 2286 cm^{-1} (and a shoulder at 2262 cm^{-1}). Evacuation at 473 K (Figure 1, spectrum e) causes the disappearance of the ABC pattern and the parallel restoration of the bridging OH band at 3599 cm^{-1}. The CH absorptions are almost completely eroded, and in the ν(CN) region the component at 2314 cm^{-1} is now predominant, although weak.

The ν(CN) band system (Figure 1, inset) and the positions of single components give an indication of the number and strength of the acidic sites located on the inner and outer zeolitic surfaces. The components at 2252 and 2280 cm^{-1} that immediately disappear upon evacuation at room temperature are probably due to some very weak interaction (liquidlike or van der Waals interacting species). The component at 2262 cm^{-1} that after evacuation at room temperature is weakened and almost completely disappears at 373 K (when the band at 3747 cm^{-1} has roughly recovered the original intensity) is due to the PrN H-bonded complex with terminal silanols that are quite weakly acidic. The band at 2286 cm^{-1} is certainly due to CN groups interacting with internal bridging OH groups as it resists evacuation up to 373 K and drops at 473 K when the band at 3597 cm^{-1} reappears. The very tiny difference in the bridging ν(OH) band position before contact with PrN and after evacuation could be an indication of the multiplicity of such a band that has already been discussed by other authors.[12] The lower the acidic strength of OH groups, the earlier the break of the complex with the nitrile and the lower the frequency of the band.

The highest frequency ν(CN) component, 2308 cm^{-1}, is not associated with perturbation of OH stretching bands. The very high position of this band allows its assignment to a Lewis acid−base complex with Al^{3+} coordinatively unsaturated sites. This component is still evident after evacuation at 573 K (Figure 1, spectrum f), indicating that this site family is quite strongly Lewis acidic.

After H-FER is contacted with *o*-TN, the bridging OH stretching band is unperturbed (Figure 2, spectrum b). A

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previous study from our group has shown that FER cavities are not penetrated (at least after short contact times at room temperature) by benzonitrile. This has quite obviously been interpreted as the effect of steric hindrance.[7] It is in fact well-known that the access of the H-FER cavities to aromatic compounds is normally not possible at room temperature,[10] although it can occur very slowly at higher temperatures.[6] In agreement with this, the internal bridging OH groups of H-FER do not interact with *o*-TN molecules either.

The silanol stretching band (Figure 2, spectrum b), on the contrary, is almost completely eroded, and a new broad band at 3440 cm^{-1} appears. At the same time, several bands typical of *o*-TN are evident: very weak bands around 3000 cm^{-1} are due to aromatic ν(CH) (above 3000 cm^{-1}) and to aliphatic ν-(CH) (below 3000 cm^{-1}), and the bands at 1606, 1509, 1484, and 1464 cm^{-1} are associated with aromatic ν(CC) and aromatic and aliphatic CH deformations. In the ν(CN) region (Figure 2, inset, spectrum b), only two components are well evident at 2278 and 2236 cm^{-1}. In the liquid *o*-TN spectrum the ν(CN) band frequency is 2225 cm^{-1}. The most intense band of adsorbed *o*-TN at 2236 cm^{-1} quickly decreases after evacuation at room temperature (Figure 2, inset, spectrum c) when the silanol group's band is partially restored and the band at 3440 cm^{-1} is significantly weakened. Such a ν(CN) band is clearly associated with the formation of a H-bonding complex between silanol groups and the probe molecule. The fact that the silanol stretching band is a little less shifted with respect to the case of adsorption of PrN indicates that the complex between silanol groups and the *o*-TN molecules is more labile than the complex formed with PrN. It is worth noting that, notwithstanding the longer exposure of the surface to the nitrile vapors, the silanol stretching band is not completely perturbed. This fact could indicate that a part of the silanol groups are allocated inside the zeolitic cavities instead of on the outer surface.

The CN stretching component at 2278 cm^{-1} resists evacuation at 523 K (Figure 2, spectrum e) and is attributed to the Lewis acid−base complex formed between *o*-TN and Al^{3+} Lewis acid sites, in parallel with what we found upon adsorption of benzonitrile onto the same zeolite.[7] Almost the same position has been found for *o*-TN adsorbed onto the Lewis sites at the external surface of H-MFI zeolite.[7]

In this case, again, we can note a shift to lower frequency of the band associated with the formation of the Lewis acidic sites with the probe molecule, with respect to the case of the complex formed with PrN.

Interaction of TES with H-FER. To study the effect of the silanization of the zeolite on the acidic properties of its surface, we used a treatment with TES, allowing it to adsorb onto the surface from the gas phase (Figure 3). The characteristic ν-(SiH) band in the gaseous TES spectrum is at 2200 cm^{-1}. After adsorption (Figure 3, spectrum b), in the spectrum of H-FER the silanol stretching band at 3747 cm^{-1} almost completely disappears and a new broad band grows at 3330 cm^{-1}. The band at 3597 cm^{-1} is significantly weakened as well even though a broad component is still evident. New bands due to adsorbed TES are evident: 2980, 2938, 2903, 1449, and 1395 cm^{-1} assigned to CH stretching and deformation modes. In the ν-(SiH) region a multiple band is present with two main maxima at 2225 and 2196 cm^{-1}. Outgassing from room temperature to 773 K (Figure 3, spectra c−h) causes a progressive disappearance of the CH stretching and deformation bands of the ethoxy groups that are no longer present at all after evacuation at 773 K (Figure 3, spectrum h); this phenomenon is associated with a progressive shift toward higher frequencies of the ν(SiH) band
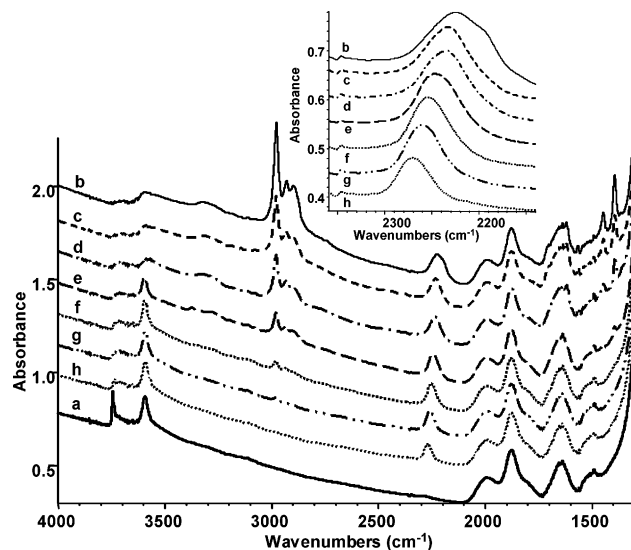

Figure 3. Adsorption of TES onto H-FER. FTIR spectra: a, thermally treated sample; b, after adsorption of TES; c, after evacuation at room temperature; d, after evacuation at 373 K; e, after evacuation at 473 K; f, after evacuation at 573 K; g, after evacuation at 673 K; h, after evacuation at 773 K. Inset: zoom on the ν(SiH) region.

system. After evacuation at room temperature (Figure 3, spectrum c), the component at 2196 cm^{-1} disappears and the main maximum is at 2234 cm^{-1}. Evacuation at 373 K (Figure 3, spectrum d) does not cause any important changes, whereas at 473 K (Figure 3, spectrum e) the main maximum shifts to 2255 cm^{-1}, even though the component at 2234 cm^{-1} is still quite strong. A further rise of the evacuation temperature produces a new shift to 2262 cm^{-1} (at 673 K, Figure 3, spectrum g) and finally to 2273 cm^{-1} (at 773 K, Figure 3, spectrum h). At this stage the bands attributed to the ethoxy groups cannot be seen anymore. As far as the ν(OH) bands are concerned, evacuation at increasing temperatures causes, starting from 473 K (Figure 3, spectrum e), the restoration of the bridging OH stretching band and a small increase of the intensity of the residual silanol band; at the same time the band at 3330 cm^{-1} decreases. After evacuation at 773 K (Figure 3, spectrum h) the 3599 cm^{-1} band is completely restored; a residual very weak 3747 cm^{-1} band is still present and has slightly increased, whereas the 3330 cm^{-1} band has disappeared.

In a recent publication, the interaction between TES and silica has been described,[9] and we found that the initially physisorbed TES gives rise to the condensation of TES with the isolated free silanol groups. The chemisorbed species initially retain two of the ethoxy groups. Increasing the evacuation temperature results in a progressive grafting of the silane molecule to the surface via the reaction with further nearby silanol groups or siloxane bridges, evolving ethanol or ethylene. This chemistry has been previously investigated.[9] As the silane becomes more and more linked to the surface losing its ethoxy groups, the corresponding SiH stretching band shifts toward higher frequency values. After evacuation at 773 K no ethoxy groups are detectable and the silane is necessarily linked to the surface via three Si−O−Si bonds.

On the basis of this study, we can interpret the present data. The multiple band with a main component at 2225 cm^{-1} and a shoulder at 2196 cm^{-1} that we see after TES adsorption can be assigned to physisorbed TES (2196 cm^{-1}) and to chemisorbed species grafted through one Si−O−Si bond. The evolution followed by the 2196 cm^{-1} band is parallel with that of the band at 3330 cm^{-1} due to silanols perturbed by physisorbed TES: both features completely disappear after the first stages
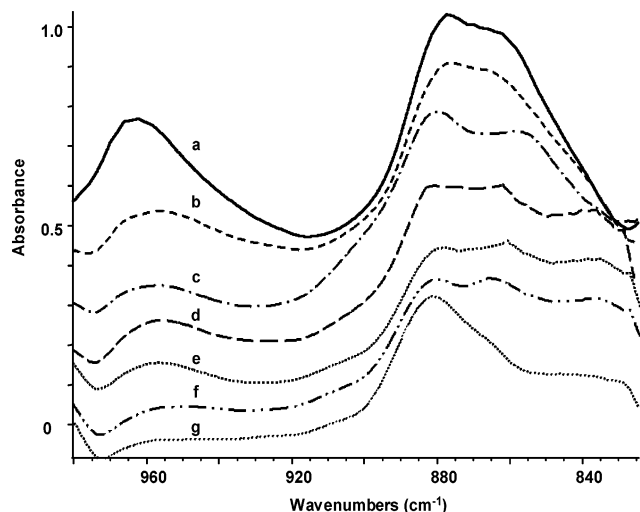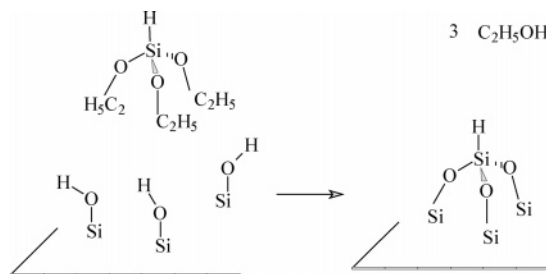
Figure 4. FTIR subtraction spectra: a, H-FER after contact with TES; b, after evacuation at room temperature; c, after evacuation at 373 K; d, after evacuation at 473 K; e, after evacuation at 573 K; f, after evacuation at 673 K; g, after evacuation at 773 K. The thermally treated H-FER sample spectrum was subtracted.

SCHEME 1: Structure of the Surface Silanization Product with TES

of evacuation. After outgassing at 773 K the full disappearance of ethoxy groups together with the shift of the ν(SiH) band at 2273 cm^{-1} indicates that the silane grafting process is complete (Scheme 1).

At the end of our treatment the inner bridging OH groups seem unperturbed. The initial perturbation of the band is likely not due to an irreversible chemisorption of the silane whose dimensions are probably too large to allow the diffusion inside FER cavities at room temperature. It is more likely due to an interaction with species deriving from the silane grafting reaction, such as ethanol.

In any case, the picture after evacuation at 773 K clearly shows that almost all the silanol groups have interacted with the silane. The silane is grafted onto the surface and has lost all the ethoxy groups. The inner bridging OH groups are unperturbed.

In the spectral range 1000−800 cm^{-1} (Figure 4), we can observe a window in the cutoff region due to the SiO$_2$ bulk vibrations. In Figure 4 we show the spectra obtained by subtracting the spectrum of thermally treated H-FER from all the spectra reported in Figure 3 and focusing on the 1000−800 cm^{-1} range. After contact of TES with the H-FER surface (Figure 4, spectrum a), new bands appear in this region at 860, 875, and 960 cm^{-1}. The 960 cm^{-1} band can be assigned to ν(CC) of the ethoxy groups,[13] and as expected, it quickly weakens till disappearance after evacuation at 773 K (Figure 4, spectrum g). The multicomponent band centered around 870 cm^{-1} (Figure 4, spectrum a) evolves during evacuation at increasing temperature (Figure 4, spectra b−g), till becoming
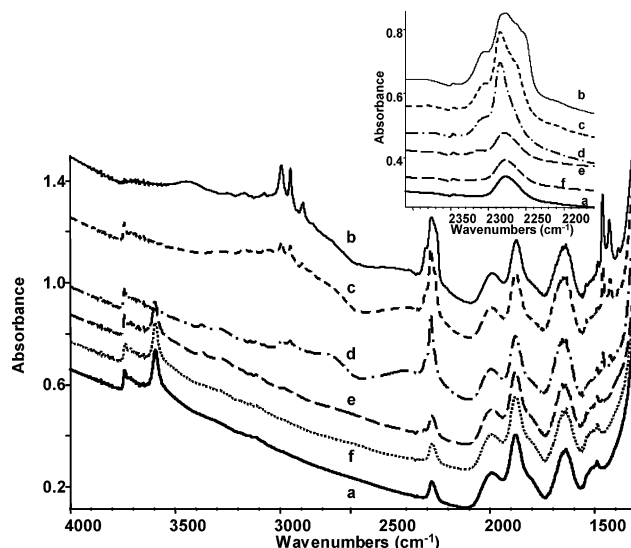

Figure 5. Adsorption of PrN onto TES-treated H-FER. FTIR spectra: a, thermally treated sample; b, after adsorption of PrN; c, after evacuation at room temperature; d, after evacuation at 373 K; e, after evacuation at 473 K; f, after evacuation at 573 K. Inset: zoom on the ν(SiH) and ν(CN) region.

a single band centered at 880 cm^{-1}, with very weak components toward lower frequency values. The 880 cm^{-1} band is assignable to the δ(SiH) mode.[14] As already observed for the ν(SiH) band, the position of this absorption is related to the presence of ethoxy groups bound to the surface silane species, although to a lower extent. The lower the number of ethoxy groups, the higher the frequency of the band. The shift to the final value of 880 cm^{-1} is linked to the disappearance of the 960 cm^{-1} band.

Adsorption of Nitriles on TES-Treated H-FER. To study the silanization effect occurring on the acidic properties of the zeolite, we have repeated the adsorption of nitrile probe molecules on the TES-treated FER sample (TES−FER, evacuated at 773 K).

After adsorption of PrN (Figure 5, spectrum b), the spectrum shows the same groups of bands as seen in the experiment involving PrN adsorption onto H-FER. If we focus on the ν-(CN) region (Figure 5, inset), we can see again a quite complex band system with the same components but with slightly different relative intensities. We can note, however, that these bands are superimposed on the SiH stretching band. The subtraction spectra (Figure 6, spectra a and b, both recorded after outgassing at 373 K) here show that the low frequency components at 2255 and 2262 cm^{-1} are less intense, whereas those at 2280 and 2308 cm^{-1} have more or less the same intensities as without TES treatment. This behavior agrees with the much lower number of silanol groups after TES treatment, whereas, apparently, the amount of PrN adsorbed on Al^{3+} Lewis sites is not significantly decreased.

The adsorption of o-TN onto the TES−FER surface (Figure 7) gives rise to a much weaker spectrum of the adsorbed nitrile. In the ν(CN) region (Figure 7, inset), a shoulder around 2240 cm^{-1} grows on the ν(SiH) band centered at 2273 cm^{-1}. Comparing the subtraction spectra obtained by subtracting the spectrum of thermally treated H-FER and TES−FER from the spectra recorded after o-TN adsorption onto both materials (Figure 6, spectra c and d) is quite interesting: in the case of H-FER two bands are well evident at 2236 and 2276 cm^{-1} assigned to CN interacting with SiOH and Al^{3+} sites, respectively; in the case of TES−FER only a weak band at 2236 cm^{-1}

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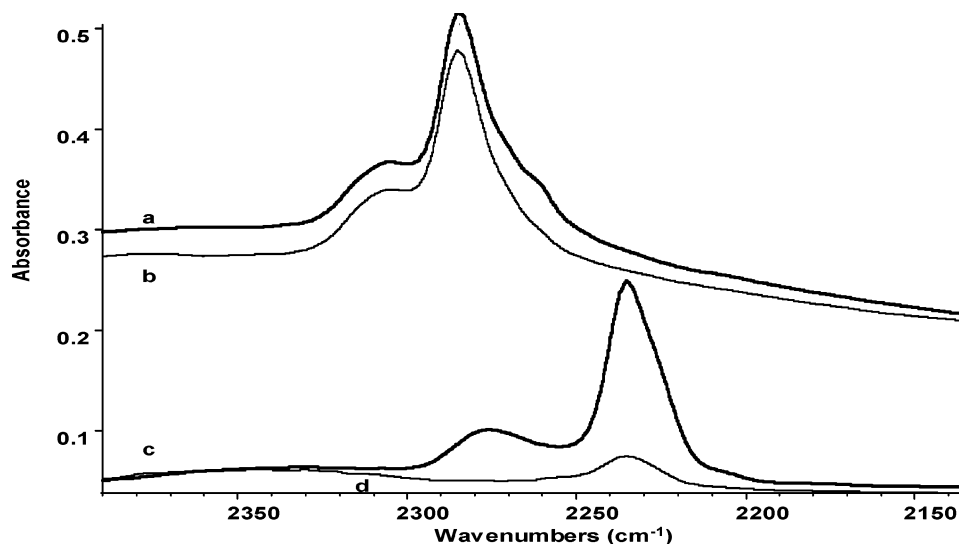*J. Phys. Chem. B, Vol. 109, No. 2, 2005* **883**

Figure 6. FTIR subtraction spectra. Surface spectra arising from the adsorption of probe molecules: a, adsorption of PrN onto H-FER; b, adsorption of PrN onto TES-treated H-FER; c, adsorption of *o*-TN onto H-FER; d, adsorption of *o*-TN onto TES-treated H-FER. The spectra of thermally treated samples were subtracted.
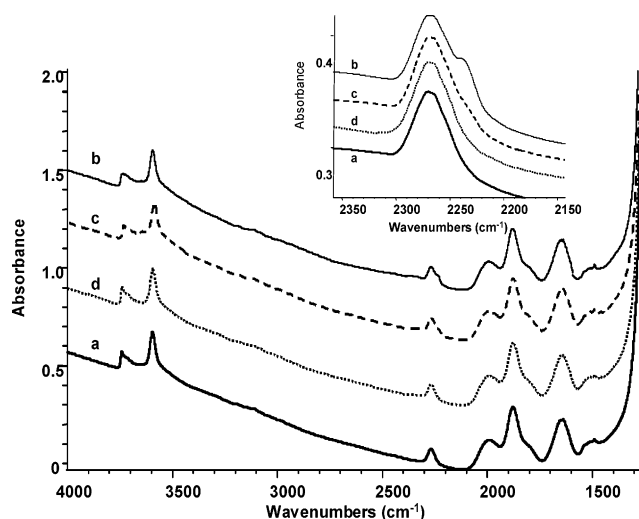

Figure 7. Adsorption of *o*-TN onto TES-treated H-FER. FTIR spectra: a, thermally treated sample; b, after adsorption of *o*-TN; c, after evacuation at room temperature; d, after evacuation at 373 K. Inset: zoom on the ν(SiH) and ν(CN) region.

is present. This means that only a few external silanol groups and practically no external Al^{3+} Lewis sites are available for interaction with *o*-TN. Thus, adsorption of *o*-TN is strongly inhibited.

Conclusions

H-FER acidic properties have been studied before and after a silanization process.

The silanization process involves contact between the zeolitic surface and TES vapors followed by evacuation steps at increasing temperature up to 773 K. At the end of the treatment, the inner bridging OH stretching band appears unaltered whereas the silanol stretching band is almost completely eroded. A ν-(SiH) band at 2273 cm^{-1} indicates that the silane has lost all of its ethoxy groups and is grafted onto the surface through three Si−O−Si bonds.

The silanization does not seem to influence the acidic strength of inner bridging OH sites that are of great importance in the catalytic processes where H-FER is used as a solid acidic catalyst.

The external sites, on the other hand, whose presence is negative for those processes that depend on the zeolitic shape selectivity effect, seem to be poisoned by the interaction with TES. Such a poisoning effect involves both external silanol groups and external Al^{3+} Lewis sites.

The use of TES, instead of TEOS, allows no new silica-type silanol groups to be produced, so having virtually a totally inactive external surface.

The comparison of the results reported here shows that on untreated H-FER a significant part of the Lewis sites are actually located at the internal cavity surface. These sites too are not poisoned by TES and are available to PrN and unavailable to *o*-TN. The H-FER studied here does not seem to have significant extraframework material. Despite this, internal Lewis acidic Al ions are found. The possible behavior of framework Al ions as Lewis acid sites is still not ascertained.

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