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Heterogeneity of Framework Ti(IV) in Ti−Silicalite as Revealed by the Adsorption of NH₃. Combined Calorimetric and Spectroscopic Study[†]

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The room-temperature adsorption of NH₃ on Ti−silicalite (TS-1) was studied by means of IR and XANES−EXAFS spectroscopies and by microcalorimetry. The propensity of framework tetrahedral Ti(IV) heteroatoms to expand their coordination shell upon adsorption of NH₃ was monitored by the perturbation induced on the Ti-sensitive framework stretching band (960 cm⁻¹) and on the preedge peak at 4967 eV in XANES spectra. In both cases a modification of the local geometry of titanium sites upon adsorption of NH₃ as an additional ligand was deduced. The amount of NH₃ specifically adsorbed on the Ti(IV) sites was estimated by comparing volumetric data obtained for TS-1 with those obtained for a Ti-free silicalite taken as reference material. At p_{NH_3} = 50 Torr, the number of NH₃ molecules adsorbed per Ti atom was found to be close to 2, indicating that virtually all Ti atoms are involved in the interaction and have completed their 6-fold coordination shell. The molar heats of adsorption on the Ti(IV) sites were estimated following the same procedure. It was found that the molar heat of NH₃ adsorption on titanium is higher (q_m = 95−83 kJ/mol) than that measured for the silicalite matrix (q_m = 66−58 kJ/mol). The interaction with ammonia was found to be essentially reversible at room temperature but for a significant amount of adsorbed species irreversibly held on titanium sites. The zero-coverage heat of adsorption was quite high ($q \approx$ 200 kJ/mol) not only for the first run of adsorption involving both irreversible and reversible interaction but also for the second run involving only the reversible component ($q \approx$ 130 kJ/mol). The evolution of the heat of adsorption with coverage was typical of heterogeneous surfaces; this is due not only to the presence of sites active toward ammonia on the silica matrix but also to the heterogeneous distribution of Ti(IV) sites, suggesting that a considerable number of framework sites (among the 12 available in the orthorhombic MFI framework) are occupied in a nearly equidistributed way. EXAFS measurements allowed the elongation of the Ti−O bond upon interaction with NH₃ (0.05 ± 0.03 Å), the Ti−N distance (1.93 ± 0.03 Å), and the average number of adsorbed NH₃ molecules per Ti site (1.9 ± 0.3) to be estimated. The results were in good agreement with the volumetric−calorimetric data. The effect of the pretreatment of TS-1 samples with ammonium acetate aqueous solution was also investigated by comparing the spectroscopic and the quantitative calorimetric results for both untreated and treated TS-1 samples.

Introduction

Titanium silicalite (TS-1)[1] is very active in selective oxidation of organic compounds by employing hydrogen peroxide under mild conditions.[2] Among its applications

ammoxidations can be cited, requiring both H₂O₂ and NH₃.[3]

This catalyst was proposed in the early 1980s, and since then, many attempts have been made to understand the role of titanium centers in the catalytic process, as has been recently reviewed.[4] The structure of TS-1 has been

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extensively studied, in particular in order to confirm or discard the hypothesis that titanium atoms are isomorphically replacing silicon atoms in the framework. XRD studies, on the original TS-1 samples, confirmed that the presence of titanium atoms in lattice positions is an essential feature for the catalysts to be active.[5]

The experimental evidence for titanium incorporation in the zeolite structure as the tetrahedral Ti(IV) species is well assessed by XRD, IR, Raman, UV−vis, XANES, and EXAFS;[5−16] in fact, these techniques can allow assessment of whether titanium species are inserted as 4-fold coordination heteroatoms in the MFI structure or whether they are present as extraframework species, i.e., as a segregated TiO_2 phase or TiO_2 nanoclusters inside the channels (in which case Ti(IV) should exhibit a 6-fold coordination). In detail, this can be explained as follows.

(i) XRD data show that the unit cell volume of silicalite increases linearly with Ti content when Ti(IV) atoms are inserted in the framework but not when Ti(IV) are present as extraframework hexacoordinated titanium species.[5,6]

(ii) The IR spectra of TS-1 in the framework stretching region shows an absorption band located at 960 cm^{-1}, virtually absent in perfect silicalite and in other Al-containing zeolites or in anatase; this band is generally taken as a proof that Ti(IV) heteroatoms are inserted in the zeolite structure. In fact, it corresponds to the ν_{asym} (SiOSi) or to the asymmetric stretching of the $[SiO_4]$ unit, strongly perturbed by the presence of the partially positive Ti(IV) ions in the near vicinity. It has been shown that the two descriptions are essentially equivalent.[10] It has been also proved that the intensity of the 960 cm^{-1} band is linearly correlated with the framework Ti content.[1]

(iii) The UV−vis spectra of TS-1 in vacuo gives a simple and clear proof of the presence of tetrahedral Ti(IV) in the zeolite framework; in fact, a band located at ∼48.000 cm^{-1} can be unambiguously assigned to the charge transfer transition from the oxygen ligand to an unoccupied orbital of a Ti(IV) ion tetrahedrally coordinated in isolated $[TiO_4]$ or $[TiO_3OH]$ units (vide infra Schemes 2 and 3). In the case of Ti(IV) octahedrally coordinated, as in anatase or in a segregated TiO_2 phase, the band is located at ∼32.000 cm^{-1}.[9,12,13]

(iv) XANES spectroscopy shows that a narrow and intense preedge peak at 4967 eV due to the 1s → 3d electronic transition involving Ti atoms in tetrahedral coordination is present in well manufactured Ti−silicalite. This peak is virtually absent in the case of Ti(IV) octahedrally coordinated. Indeed, the transitions $A_{1g} \rightarrow T_{2g}$ are symmetrically forbidden in the case of octahedral coordination of Ti(IV), but the transition $A_1 \rightarrow T_2$ is allowed in the case of tetrahedral coordination of Ti(IV), as in the case of $[TiO_4]$ or $[TiO_3OH]$ units.[11−15]

In conclusion, it is now relatively well assessed how to determine whether a TS-1 sample is containing only four-coordinated Ti(IV) or whether extraframework species containing six-coordinated Ti(IV) species are also segregated in the channels of the zeolite with a consequent loss of catalytic efficiency. In fact, the turnover number in oxidation reactions employing hydrogen peroxide as an oxidant is correlated with the concentration of framework titanium.[17]

However, since the tetrahedral coordination is somewhat unusual for Ti(IV), the four-coordinated framework Ti species are expected to have a pronounced tendency to expand their coordination. It is a matter of fact that a pure tetrahedral coordination is present only in outgassed TS-1, completely deprived of the adsorbed water acting as an additional ligand, while on highly hydrated samples, an increase of the coordination from four (tetrahedral) up to six (octahedral) passing through a coordination of five (trigonal bipyramidal), according to the extent of hydration, is observed. The progressive increase of the coordination of Ti heteroatoms upon an increasing amount of adsorbed water is witnessed by a gradual transition of the spectroscopic properties toward those of octahedral Ti(IV).[7−10,12−15,18−20]

The aim of the present work is to investigate the stoichiometry and the energetic effects related to the propensity of titanium species to expand their coordination sphere upon the adsorption of controlled amounts of a basic probe. This is a key point because the capacity of titanium heteroatoms to bind one or two additional ligands following Scheme 1 may be important in defining the path of the catalytic reaction and the role played by titanium heteroatoms.

Ammonia, being a relatively strong basic ligand and being also one of the reactant molecules in some processes catalyzed by TS-1,[2−4] was chosen to probe the ability of titanium species to increase their coordination number. The adsorption at room temperature of the probe was studied by combining infrared spectroscopy and adsorption microcalorimetry to assess (i) the stoichiometry of the complexes, (ii) their reversible or irreversible character, and (iii) the degree of heterogeneity of the Ti centers. XANES data allowed the changes in the symmetry of the titanium local environment caused by the contact with ammonia to be described, whereas EXAFS results allowed evaluation of the coordination number of titanium sites both in vacuo and in the presence of ammonia.

For all measurements, a TS-1 sample containing a very high fraction (∼100%) of framework titanium has been studied, and the results will be compared with those

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Scheme 1
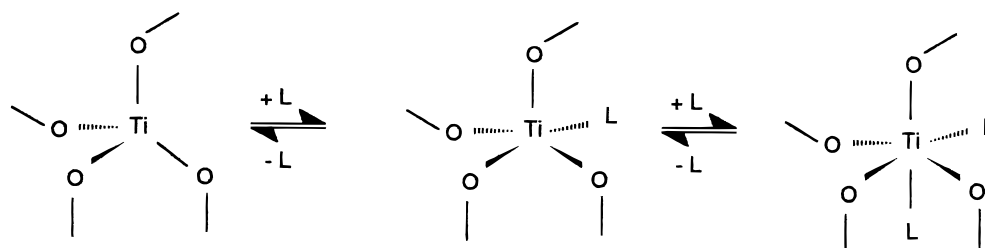
obtained on a Ti-free silicalite sample, taken as a reference material. The effect of sample pretreatment with an ammonium acetate aqueous solution was also studied. The ammonium acetate pretreatment is routinely made on TS-1 samples before the XRD measurements as recommended by Perego et al.[5] In fact, it is known that structural data from XRD of pretreated samples allow a better correlation between the cell volume increase and the titanium content, making the determination of the amount of framework titanium more accurate.[5,6]

Recent EXAFS and photoluminescence studies[16] evidenced the presence (in vacuo conditions) of (at least) two framework Ti(IV) species characterized by different "local" environments, i.e., $[TiO_4]$ and $[TiO_3OH]$ (vide infra Figures 2 and 3, respectively). As far as the long-range environment is concerned, some theoretical studies have suggested that titanium heteroatoms in the zeolite framework are randomly distributed.[21−23] On the contrary, other authors[24,25] suggest the presence of preferential substitution sites, among the 12 available for an orthorhombic MFI cell. Recently, some of us tried to localize preferential substitution sites by performing Rietveld analysis on several high-quality XRD patterns collected at the BM16 beamline of the ESRF.[6] No clear evidence for a preferential distribution of Ti heteroatoms in one or in a few particular site(s) was found, in agreement with theoretical results reported in refs 21−23.

Adsorption microcalorimetry results reported in the present work were thus also aimed to check whether the adsorption enthalpy at the Ti(IV) sites is typical of heterogeneous or homogeneous distributions. In fact, owing to the high dilution of the titanium centers in the system, we expect a homogeneous distribution of the Ti active sites only in the case of preferential location of the heteroatoms. On the other hand, in the case of nonpreferential location of titanium atoms, a heterogeneous distribution of the energy of the sites is expected.

Experimental Section

Materials. TS-1 sample (2.99wt % TiO_2) was synthesized in EniTecnologie laboratories following the procedure described in the original patent.[1] The presence of ~100% of framework titanium species was confirmed by XRD data, not reported for the sake of brevity.

Silicalite was also prepared following the same procedure used for the synthesis of TS-1 but without introducing the titanium precursor. Crystallinity and structure of the sample were confirmed by XRD measurements.

Methods. The heats of adsorption of NH_3 (q_{ads}) were measured at 303 K by means of a heat-flow microcalorimeter (standard Tian−Calvet type, Setaram-France) following a well-established stepwise procedure, previously described.[26,27] The calorimeter was connected to a high-vacuum gas-volumetric glass apparatus that enabled the adsorbed amounts (n_a) and the heats evolved (Q^{int}) to be determined simultaneously for small increments of the adsorbate. The adsorbed amounts, reported per unit mass as a function of the equilibrium pressure of the adsorbate (n_a vs p), are taken as a measure of the population of the sites active in the ammonia adsorption. The differential heats of adsorption, reported as a function of coverage (q_{ads} vs n_a), are taken as a measure of the energy of interaction between NH_3 and the surface sites. The initial heat value (q_0), estimated from the extrapolation of the heat of adsorption curves to zero coverage, gives an estimate of the energy of the strongest sites. The calorimetric measurements were performed in two runs. The *first run* (I) of adsorption was performed on the samples previously outgassed at ambient temperature (20 h, 10^{-5} Torr; 1 Torr = 133.322 Pa) in order to reach the desired degree of dehydration of the surface and then transferred into the calorimeter without further exposure to the atmosphere. The reversible component of the adsorbate was then evacuated at the calorimeter temperature. A *second run* (II) was then performed to evaluate the contribution of the reversible component to the total adsorption. The pressure was monitored by means of a transducer gauge (Barocell 0-100 Torr, Edwards) enabling accurate measurements up to ca. 90 Torr (±0.01 Torr).

XANES and EXAFS spectra have been performed in the transmission mode, at the EXAFS3 beam line of the DCI storage ring of LURE laboratories in Orsay (Paris, France), using airfilled ionization chambers for both incident and transmitted beams. The incident beam was monochromatized using a double crystal Si (311) for XANES and Si (111) for EXAFS detuned up to 1/2 of the rocking curve to avoid harmonics (integration time, 2.0 s/point; sampling step, 0.5 eV for XANES and 2.0 eV for EXAFS). A specifically designed stainless steel cell allowing measurements under carefully controlled atmosphere[16] was used. This cell, equipped with two Mylar windows, was connected to: (i) a vacuum line for sample pretreatment (activation for 1 h at room temperature under a dynamic vacuum of ca. 10^{-6} Torr); (ii) a gas line where the desired amount of high purity NH_3 can be dosed in situ. A more detailed description of the X-ray absorption experimental setup can be found in ref 16. EXAFS data analysis has been performed following a standard procedure[28] as described in detail elsewhere[16] using Michalowicz programs.[29]

IR measurements were performed at nominally room temperature. Thin self-supporting wafers of TS-1 were prepared and outgassed at room temperature (20 h, 10^{-5} Torr) inside an IR cell which allowed in situ measurements to be made. The IR spectra were recorded in transmission mode on a BRUKER FTIR88 spectrometer equipped with an MCT cryo-detector.

Results

Infrared Spectra. In Figure 1, the IR spectra in the $\nu(OH)$ stretching region (4000−3000 cm^{-1}) of outgassed

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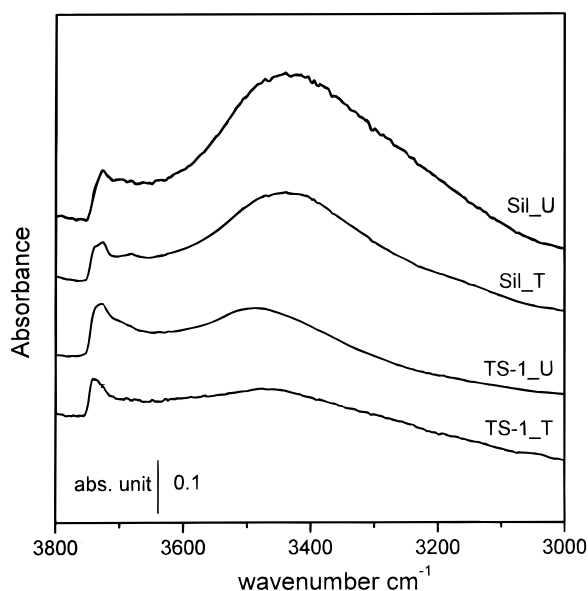
Figure 1. From top to bottom IR spectra in the OH stretching region of silicalite untreated (U) and treated (T) and of TS-1 untreated (U) and treated (T)

TS-1 and silicalite, both as such and treated with ammonium acetate, are reported. Both TS-1 and silicalites are defective materials containing internal hydroxyl nests. The spectra in the ν(OH) stretching region are intense and very complex and, as far as TS-1 is concerned, the spectroscopy of hydroxyls is also complicated by the possible copresence of silanols and titanols which are characterized by very similar O−H stretching frequencies and are not distinguishable.[8] The reported spectra can be divided into two main regions: 3800−3650 cm^{-1} (stretching modes of unperturbed or weakly perturbed OH groups) and 3650−3200 cm^{-1} (stretching modes of medium intensity hydrogen bonded OH groups). [8,30−33]

The high-frequency absorptions are mainly associated with unperturbed or very weakly perturbed silanols for silicalite and silanols and titanols for TS-1. The adsorption is clearly composite due to the presence of a few unresolved components whose assignments are, for the time being, not completely understood. It is worth noticing that the treatment with ammonium acetate reduces the intensity and complexity of this composite absorption, resulting in an apparent narrowing of the absorption and in a blue shift of the maximum, from 3732 to 3740 cm^{-1} for TS-1 and from 3725 to 3730 cm^{-1} for silicalite (where a high-frequency component at 3742 cm^{-1} emerges in the treated samples). Moving to lower frequencies (3700−3650 cm^{-1}), a band probably due to internal OH groups weakly interacting with the walls of the nests is also observed (particularly evident in silicalite).[8,30−33]

The broad absorption observed in the 3650−3200 cm^{-1} region is connected with the presence of silanols (titanols) perturbed by hydrogen bonding.[8,30−33] This band is much more important for silicalite than for TS-1 and, in both cases, is more pronounced on the untreated sample. Moving from silicalite to TS-1, a blue shift of the maximum

is observed (from 3430 to 3470 cm^{-1}). The spectroscopic effects caused by the ammonium acetate pretreatment can be interpreted as being due to a reduction of internal defects (i.e. nests of hydroxyls). As the effect of titanium insertion in the framework is also similar, because it is associated with a decrease of the concentration of OH groups, this means that the heteroatoms are fixed preferentially at T vacancies (internal nests), being T ≡ Si.

The interaction with ammonia strongly influences the ν(O−H) peaks of TS-1, as shown in Figure 2, part a untreated and part b treated samples. In both sections, the upper part reports the adsorption experiment and the lower one the desorption process performed by outgassing at room temperature. In the insets, the first spectrum of the adsorption experiment (sample in vacuo) and the last spectrum of the desorption experiment (sample outgassed at 1 h at room temperature) are compared. The erosion of the previously discussed bands together with the parallel growth of a broad band in the 3400−2600 cm^{-1} interval upon increasing ammonia pressure is evidenced by the presence of an isosbestic point (see arrows in Figure 2). This indicates that all silanol (titanol) groups are involved in the interaction with the probe and that the SiOH···NH$_3$ (TiOH···NH$_3$) hydrogen bonds are stronger than the SiOH···OHSi (SiOH···OHTi) hydrogen bonds responsible for the band at 3200 cm^{-1}. The prominent peak at 3396 cm^{-1} is due to the asymmetrical stretching modes of NH$_3$ perturbed by interaction with the adsorbing silanols, titanols, and Ti(IV) sites (the ν_{asym} NH$_3$ frequency of the free molecule being at 3444 cm^{-1}). The exact location of the less intense band due to the symmetrical stretching modes of NH$_3$ is not so straightforward due to the presence of Fermi resonances with bending modes;[34] however, it is reasonably assigned to the weak peak observed at 3298 cm^{-1} (the ν_{sym} NH$_3$ frequency of the free molecule being at 3336 cm^{-1}).

As can be seen by comparing the curves reported in the two insets the desorption process at nominally room temperature (actually at the beam temperature) is not complete, revealing the presence of an irreversible fraction of interacting ammonia. This phenomenon is more relevant in the untreated sample (Figure 2a). Evidence that adsorption and desorption processes do not follow the same path comes also from the location of the isosbestic points, moving from 3430 to 3415 cm^{-1} in the untreated TS-1 and from 3444 to 3439 cm^{-1} in the treated sample. On the contrary, the same experiments performed on silicalite reveal that desorption of ammonia on both treated and untreated samples nearly totally restores the initial conditions (spectra not reported for brevity). These qualitative findings will be quantified by microcalorimetry measurements (vide infra). As a final comment to the experiments reported in Figure 2, it is not possible from the present IR data to assess whether a chemical reaction of NH$_3$ with Ti−O−Si bridges and subsequent formation of Ti(NH$_2$)···HOSi has occurred or not. In fact no band attributable to the σ(NH$_2$) mode (at ∼1600 cm^{-1}) could be evidenced.

The adsorption of ammonia affects also the intensity and the spectral position of the 960 cm^{-1} band; in fact, a clear upward shift of the maximum of the band is observed upon NH$_3$ dosage, as shown in parts a and b of Figure 3, where data for TS-1 untreated (a) and treated (b) samples are reported. It must be noticed that, while the perturbations of the OH bands reported in Figure 2 give information

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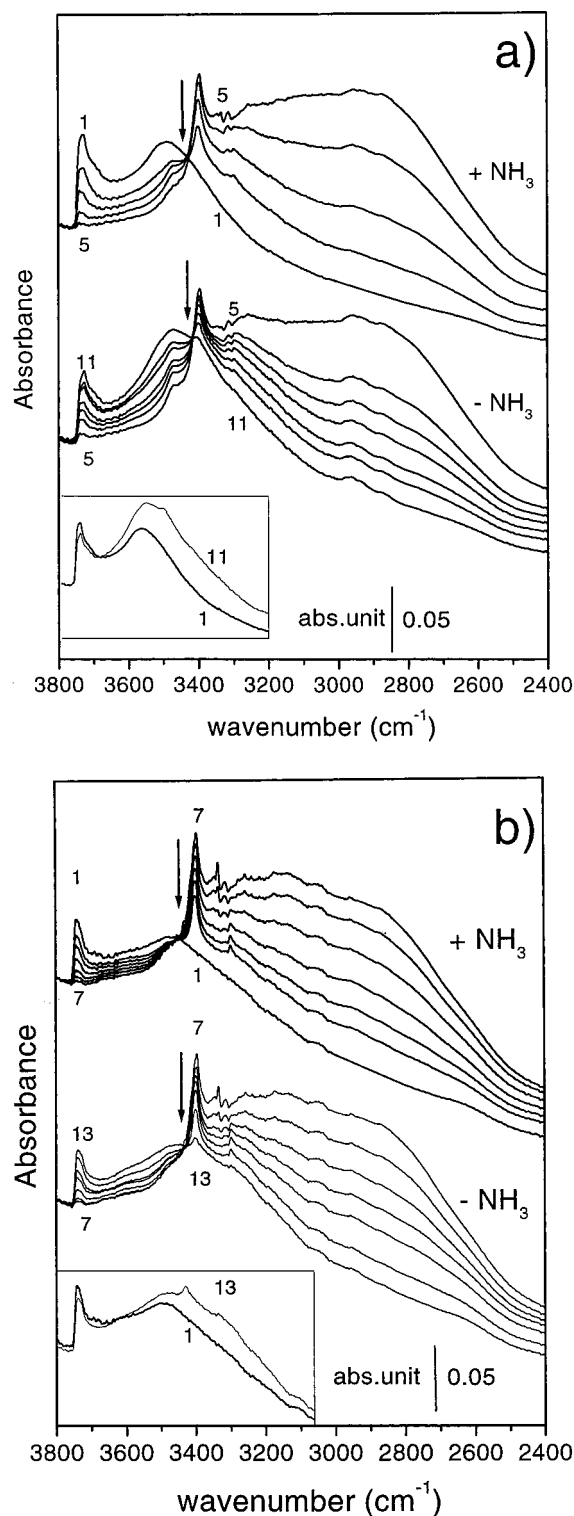
Figure 2. (a) IR spectra, in the O–H and N–H stretching region, of untreated TS-1 in interaction with NH_3. Upper part, spectra 1–5, describe the absorption experiment from vacuo up to 60 Torr equilibrium pressure; the lower part reports the desorption experiment, spectra 5–11 (obtained after 1 h of pumping at room temperature). Vertical arrows indicate the isosbestic points. The inset reports the direct comparison between the spectrum in vacuo (curve 1) and that obtained after prolonged outgassing (curve 11). (b) Same as (a) but for the treated sample; spectra 1–7 and 7–13 correspond to adsorption and desorption experiments, respectively.

on the interaction of NH_3 with titanols and with the much more abundant silanols, the perturbation of the 960 cm^{-1} band is specifically related to the perturbation of Ti sites,
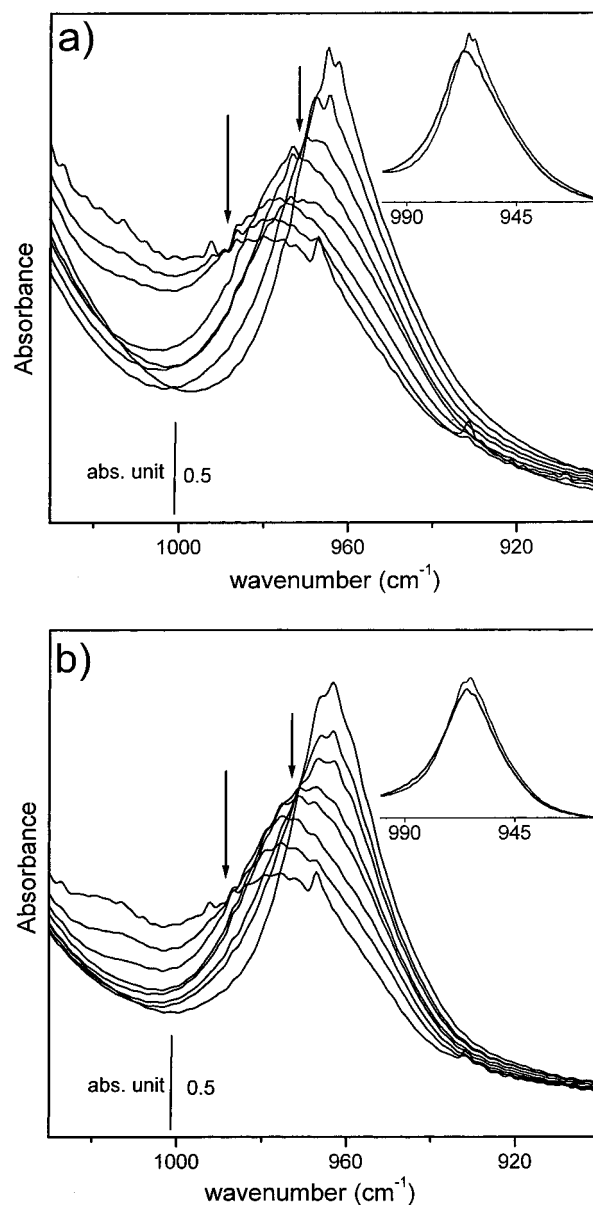
Figure 3. (a) IR spectra, in the framework stretching region, of untreated TS-1 interacting with NH_3 at increasing equilibrium pressures. The inset reports the comparison of the sample in vacuo (upper curve) and the sample after prolonged outgassing (lower curve). Vertical arrows indicate the isosbestic points. (b) Same as (a), but for the treated sample.

caused by direct insertion of NH_3 in the first coordination sphere of Ti.[7,10,13] EXAFS data will give direct proof of this phenomenon. Also, from the data reported in Figure 3 (see insets) we can deduce that the interaction with ammonia is not fully reversible; in fact, while the spectral position is mostly recovered upon outgassing, the same does not occur for the intensity. Again, the effect was found to be more pronounced for untreated TS-1. The evolution of the 960 cm^{-1} band suggests a two-step mechanism of adsorption. Indeed, on both treated and untreated samples, two isosbestic points at 972 cm^{-1} (first step) and at 988 cm^{-1} (second step) are observed (see arrows in Figure 3).

XANES. In Figure 4, the XANES spectra of outgassed TS-1 and TS-1 contacted with ammonia at increasing equilibrium pressure and after evacuation at room temperature (see inset) are reported. Part a refers to untreated TS-1 while part b correspond to treated TS-1. The intensity of the preedge peak at 4967 eV, typical of 4-fold coordinated titanium, is significantly depressed upon adsorption of
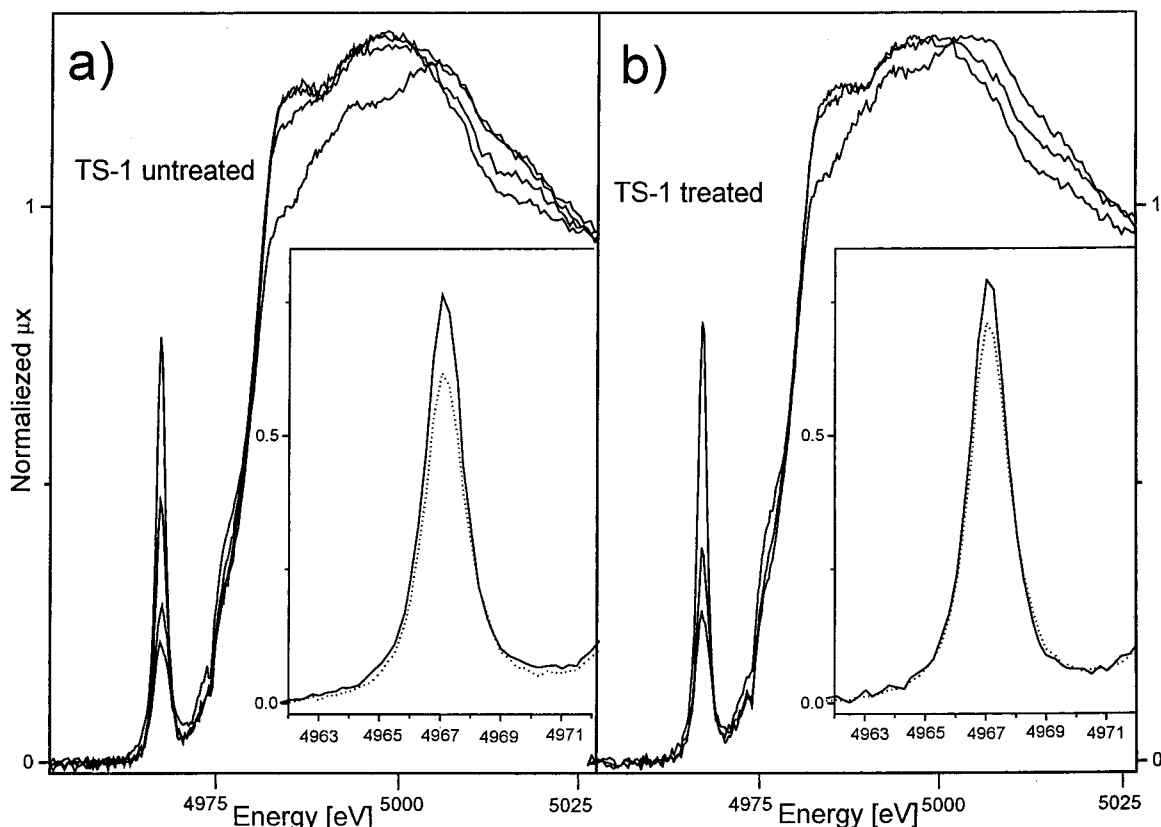
Figure 4. (a) Effect of interaction with increasing NH_3 equilibrium pressures (from vacuo up to 60 Torr) on the XANES spectra of untreated TS-1. In the inset the comparison on the preedge peak between the spectrum in vacuo (solid line) and that obtained after prolonged outgassing at room temperature (dotted line) is reported. (b) Same as (a), but for treated TS-1.

Table 1. Adsorbed Amounts, Evolved Integral Heats, and Molar Heats at p_{NH_3} = 10 and 50 Torr[a]

untreated (U) samples	n_{ads} (mmol/g) p = 10 Torr	n_{ads} (mmol/g) p = 50 Torr	Q^{int} (J/g) p = 10 Torr	Q^{int} (J/g) p = 50 Torr	$q_m = [Q^{int}/n_{ads}]$ p = 10 Torr	$q_m = [Q^{int}/n_{ads}]$ p = 50 Torr
TS-1 (I) total	1.67	2.47	126	163	75	66
TS-1 (II) reversible	1.55	2.19	107	136	69	62
Sil (I ≡ II)	1.12	1.71	74	100	66	58
TS-1 (I)−Sil total on Ti(IV)	0.55	0.76	52	63	95	83
TS-1 (II)−Sil reversible on Ti(IV)	0.43	0.48	33	36	77	75
TS-1 (I-II) irreversible on Ti(IV)	0.12	0.28	19	27	158	96

[a] Untreated (U) Ti−silicalite (TS-1), and silicalite (Sil), outgassed at 303 K. Symbols (I) and (II) are referred to first and second run of adsorption, respectively.
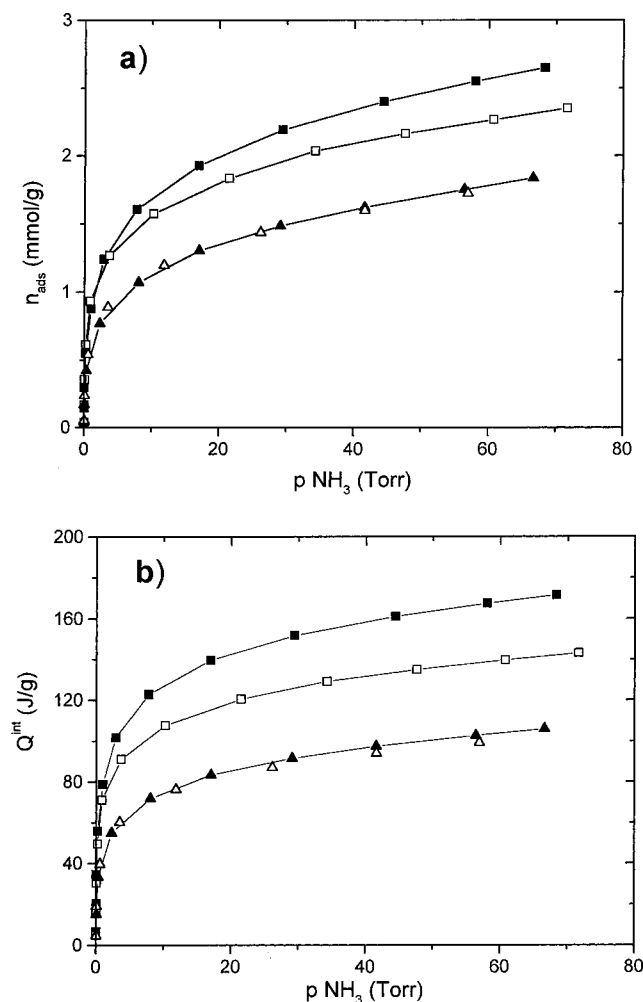
ammonia indicating a modification in the local geometry of Ti from a nearly tetrahedral situation through a 5-fold up to a 6-fold (nearly octahedral geometry) coordination (see point (iv) of the Introduction). With the intensity of the band not being fully recovered by outgassing the samples at room temperature (see insets), the qualitative results obtained by IR spectroscopy concerning the residual of an irreversible fraction are confirmed. We were not able to detect any significant blue shift of the 4967 eV peak upon interaction with NH_3. Finally, it is worth noticing that the reduction of the pre-edge peak is accompanied by a significant increase of the white line peak.

Adsorption Microcalorimetry. In Figure 5a, the volumetric adsorption isotherm of NH_3 on the untreated TS-1 sample is compared with that obtained in the same conditions for the silicalite sample. In part b of the figure, the relevant calorimetric isotherms of ammonia adsorbed on untreated TS-1 and silicalite are compared. For both samples, the first and second runs of the adsorption isotherms are reported per unit mass of the sample.

From the reported data, it is clearly emerging that a specific interaction occurs between ammonia and Ti(IV);

in fact, a significant amount of NH_3 is adsorbed on TS-1 which exceeds that observed on pure silicalite. It is not straightforward to distinguish the different species of ammonia (i.e., those adsorbed on titanium and those on silica matrix). To isolate the contribution of ammonia adsorbed on the sole titanium species, the silicalite isotherms were subtracted from the TS-1 ones. This was made on the basis of a quite rough but reasonable assumption that the silica matrix is behaving in a similar manner in the two cases. This is certainly not completely true because it has been observed that silicalite exhibits a higher amount of defects than TS-1 (see Figure 1 and related discussion). However, the error we are introducing by following this assumption is an underestimation of the contribution of the adsorption on Ti(IV) sites more than an overestimation. This procedure was followed at two different equilibrium pressures, 10 and 50 Torr, and it was found that the amounts of ammonia adsorbed only on titanium sites increase with the increase of equilibrium pressure.
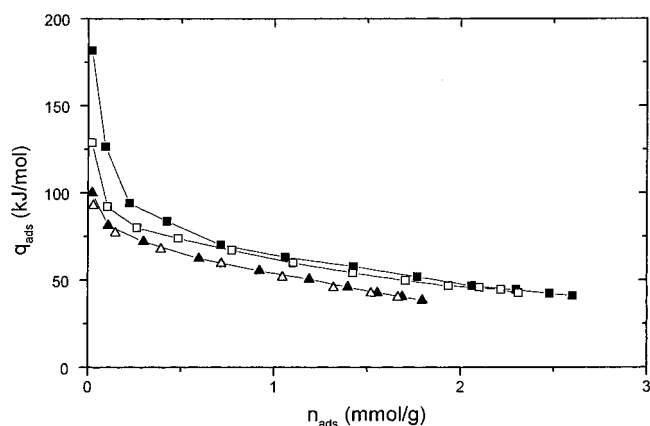
In Table 1, the adsorbed amounts and the integral heats evolved during the adsorption process are reported. The molar heats of adsorption, i.e., the $q_m = Q^{int}/n_{ads}$ ratio, are

Figure 6. Heat of adsorption as a function of coverage of NH_3 for untreated (U) TS-1 ($\square$) and silicalite ($\triangle$) samples. Solid and open symbols correspond to first run and second run adsorption isotherms, respectively.

Figure 5. (a) Volumetric isotherms of NH_3 adsorbed on untreated (U) TS-1 ($\square$) and silicalite ($\triangle$). (b) Calorimetric isotherms of the samples of (a). Solid and open symbols correspond to first run and second run adsorption isotherms, respectively.

also reported. Such values allow for an estimate of the energy of the interaction of the probe with the surface at the given equilibrium pressure. The molar heats of adsorption at both pressures are significantly higher on TS-1 ($q_m = 75-66$ kJ/mol) than on pure silicalite ($q_m = 66-58$ kJ/mol). The molar heat of adsorption on TS-1 is comprehensive of both the molar heat of the NH_3/Ti(IV) and of the NH_3/silicalite interactions. Thus, following the assumption outlined before, the molar heat value associated with the sole adsorption on titanium sites can be evaluated from the $q_m = Q^{int}/n_{ads}$ ratio of the integral heat and adsorbed amount values obtained by subtracting the silicalite contribution. From this, it is more clearly emerging that the interaction of ammonia with titanium sites is much more energetic than the interaction of ammonia with the silica matrix. For instance, at $p = 10$ Torr, q_m is 95 kJ/mol for the Ti(IV)/NH_3 interaction, against $q_m = 66$ kJ/mol for the SiO_2/NH_3 interaction. At $p = 50$ Torr, q_m is 83 kJ/mol for Ti(IV)/NH_3 against $q_m = 58$ kJ/mol for SiO_2/NH_3 interaction.

In full agreement with IR and XANES results, it is confirmed that the adsorption of ammonia on TS-1 is only partially reversible as indicated by the noncoincidence of the first and second run adsorption isotherms. This is opposite to what was found for silicalite, for which the virtual coincidence of the isotherms of the first and second adsorption runs indicates that, in absence of titanium

species, the process is completely reversible (in agreement with IR results). The difference between the first and second *run* isotherms allows estimation of the amount of the irreversible component of the adsorption, entirely ascribable to the interaction of the probe with Ti(IV) sites. The volumetric and calorimetric data for the first and second runs of ammonia adsorbed on untreated TS-1, as well as the estimated values of the irreversible component, are reported in Table 1. It is noteworthy that the irreversibly adsorbed amounts, as well as the heat evolved during the adsorption, increase with increasing equilibrium pressure. The molar heat of the irreversible adsorption ($q_m = 158-96$ kJ/mol) is significantly higher than the total ($q_m = 75-66$ kJ/mol) and reversible values ($q_m = 69-62$ kJ/mol) for the adsorption on both Ti(IV) sites and silica matrix, and much higher also than the total ($q_m = 95-83$ kJ/mol) and reversible values ($q_m = 77-75$ kJ/mol) for the adsorption on the sole Ti(IV) sites. From the difference between the second run adsorption isotherms of untreated TS-1 and of silicalite, the amounts reversibly adsorbed on titanium centers were estimated, as reported in Table 1.

To have a more detailed description of the evolution with coverage of the adsorption energy of the different kinds of sites, in Figure 6 the heat of adsorption on untreated TS-1 and on silicalite is reported as a function of the adsorbed amounts of the probe. Both first and second run isotherms of adsorption isotherms are reported for the two samples. It can be noticed that for both pure and titanium-containing silicalite the heat of adsorption decreases with coverage, which is a behavior typically shown by heterogeneous surfaces. However, in the whole examined coverage interval, the heat values for untreated TS-1 are higher than those for untreated silicalite; this means that the interaction of ammonia with Ti(IV) is stronger than the interaction with the silicalite matrix. The zero-coverage heat of adsorption is also quite high ($q_0 \approx 200$ kJ/mol) in the case of TS-1. (The zero-coverage heat of adsorption for NH_3 adsorbed on silicalite is only ~100 kJ/mol). This result indicates that among the different kinds of Ti(IV) sites, a small fraction is very reactive. At coverages higher than 0.5 mmol/g, the decrease of the heat of adsorption with coverage becomes linear for both TS-1 and pure silicalite and reaches ~ 50 and ~40 kJ/mol, respectively, values that are much higher than the latent heat of liquefaction of ammonia, i.e., 23 kJ/mol.
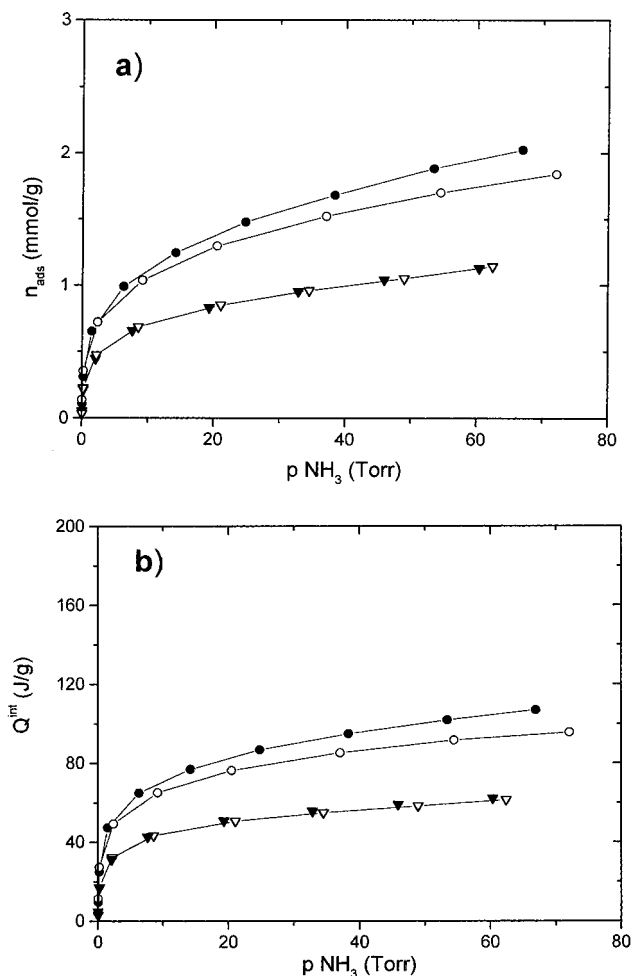
The initial heat of the reversible adsorption on untreated TS-1 is also still larger ($q_0 \approx 130$ kJ/mol) with respect that measured for untreated silicalite ($q_0 \approx 100$ kJ/mol); this

Table 2. Adsorbed Amounts, Evolved Integral Heats, and Molar Heats at p_{NH_3} = 10 and 50 Torr[a]

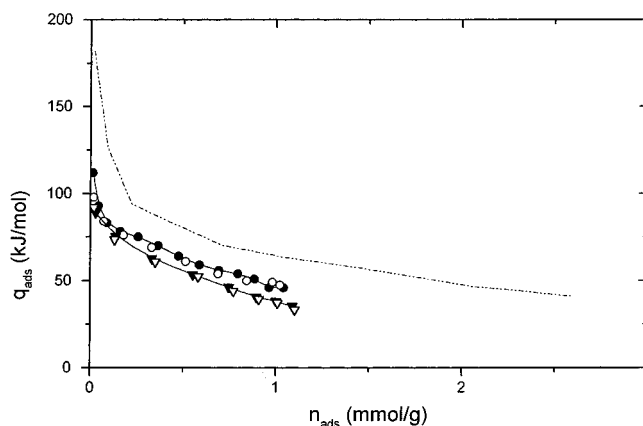| treated (T) samples	n_{ads} (mmol/g) $p = 10$ Torr	n_{ads} (mmol/g) $p = 50$ Torr	Q^{int} (J/g) $p = 10$ Torr	Q^{int} (J/g) $p = 50$ Torr	$q_m = [Q^{int}/n_{ads}]$ $p = 10$ Torr	$q_m = [Q^{int}/n_{ads}]$ $p = 50$ Torr
TS-1 (I) total	1.10	1.84	71	100	65	55
TS-1 (II) reversible	1.04	1.65	65	89	63	54
Sil (I ≡ II)	0.69	1.10	44	59	64	54
TS-1 (I)−Sil total on Ti(IV)	0.41	0.74	27	41	66	55
TS-1 (II)−Sil reversible on Ti(IV)	0.35	0.55	21	30	60	55
TS-1 (I−II) irreversible on Ti(IV)	0.06	0.19	6	11	100	58

[a] Treated (T) Ti−silicalite (TS-1) and silicalite (Sil), outgassed at 303 K. Symbols (I) and (II) are referred to first and second run of adsorption, respectively.

Figure 8. Heat of adsorption as a function of coverage of NH_3 for treated (T) TS-1 (○) and silicalite (▽). Solid and open symbols correspond to first run and second run adsorption isotherms, respectively. Dot-dashed curve: untreated (U) TS-1 (see Figure 6).

Figure 7. (a) Volumetric isotherms of NH_3 adsorbed on treated (T) TS-1 (○) and silicalite (▽). (b) Calorimetric isotherms of the samples in (a). Solid and open symbols correspond to first run and second run adsorption isotherms, respectively.

is indicating that, even if the most reactive sites are saturated irreversibly during the initial stage of the first run, part of the titanium centers interact reversibly but very strongly with ammonia. In fact, in the whole examined coverage interval, the heat of the reversible adsorption on TS-1 is always larger than the heat of adsorption on silicalite. First and second run curves are virtually overlapped in the case of silicalite, whereas for TS-1 the two adsorption heat curves, quite different in the early stages of the adsorption process, merge together and then decrease linearly at increasing coverage. A linear decrease of the heat of adsorption with coverage was previously observed for the interaction of ammonia with different SiO_2 polymorphs (crystalline and amorphous).[26,27]

In Figure 7, the volumetric (part a) and calorimetric (part b) isotherms of NH_3 on TS-1 and silicalite treated

in ammonium acetate aqueous solution are shown. Also in this case it is clearly evident that a specific interaction of NH_3 with titanium is occurring, because the isotherms (reported per unit mass of sample) are higher for Ti-containing silicalite than for pure silicalite. It is worth noticing that isotherms of both TS-1 and silicalite-treated samples are lower (by ca. 25% for TS-1 and ca. 35% for silicalite at $p = 50$ Torr) than those of the untreated samples (compare Figures 5 and 7 or Tables 1 and 2). Furthermore, while the NH_3 adsorption isotherms on silicalite are still overlapped (so indicating a virtually complete reversibility of the adsorption), on TS-1 the first and second run isotherms do not coincide; this shows that the adsorption of NH_3 on Ti(IV) sites is not completely reversible. However, the amount of the irreversible adsorption on Ti(IV), on the treated TS-1, is lower than that on untreated TS-1 at all examined coverages (but mostly at lowest pressure). For instance, at $p = 10$ Torr, the irreversible adsorption is ~7% of the total adsorption for the untreated sample and only ~5% for the treated one. At $p = 50$ Torr, it is ~12% of the total adsorption for the untreated sample and ~10% for the treated one. By subtracting the contribution of silicalite, as already done for the untreated sample, the amount adsorbed on the sole titanium sites was estimated. Moreover, by making the difference between the first and second run isotherms for TS-1, the amounts irreversibly held by titanium centers were evaluated as well as the related energetics. In Table 2, all quantitative and energetic data for the treated samples are reported as previously done for the untreated ones.

In Figure 8, the evolution of the heat of adsorption of ammonia (first and second runs) with coverage for treated TS-1 and silicalite are compared. Also, in this case, the curves are typical of heterogeneous surfaces but the heterogeneity is much less pronounced than in the case

Table 3. Quantitative and Energetic Features of NH_3 Adsorbed on the Sole Ti(IV) Sites[a]

TS-1	NH_3 molecules per Ti atom total	NH_3 molecules per Ti atom reversible	NH_3 molecules per Ti atom irreversible	$q = [Q^{int}/n_{ads}]_{tot}$ NH_3 on Ti(IV) total	$q = [Q^{int}/n_{ads}]_{rev}$ NH_3 on Ti(IV) reversible	$q = [Q^{int}/n_{ads}]_{irrev}$ NH_3 on Ti(IV) irreversible
U (10 Torr)	1.5	1.2	0.3	95	77	158
U (50 Torr)	2.0	1.3	0.7	83	75	96
T (10 Torr)	1.1	0.9	0.2	66	60	100
T (50 Torr)	2.0	1.5	0.5	55	55	58

[a] Untreated (U) and Treated (T) Ti−silicalite outgassed at 303 K.
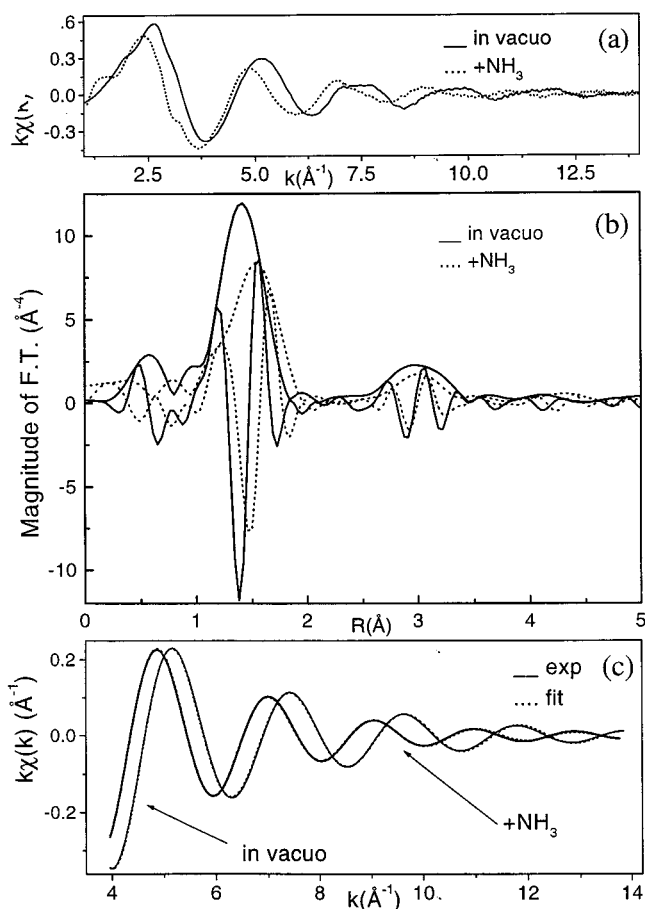
Figure 9. EXAFS data obtained for treated TS-1 in vacuo and after interaction with 60 Torr of NH_3. (a) Averaged $k\chi(k)$. (b) k^3-weighted FT of the EXAFS data reported in section (a). (c) First shell filtered EXAFS signals (full lines) and corresponding fits (dotted lines).

of untreated samples (compare Figures 6 and 8). In particular the zero-coverage heat of adsorption on TS-1 (first run) is not as high as in the case of untreated TS-1 ($q_0 \approx 120$ kJ/mol against ~ 200 kJ/mol), whereas for silicalite the zero-coverage heat of adsorption is very close to that measured for the untreated sample ($q_0 \approx 100$ kJ/mol). The heat of the reversible adsorption (second run) on TS-1 treated in ammonium acetate ($q_0 \approx 110$ kJ/mol) is not far from that obtained for silicalite. However, in the whole examined coverage interval, the heat of adsorption of ammonia on TS-1 is still significantly higher than that on silicalite, owing to the specific interaction of ammonia with titanium sites.

In Table 3, the quantitative and energetic data concerning NH_3 adsorption on the sole Ti(IV) sites on both untreated and treated TS-1 are summarized.

EXAFS. In Figure 9, the EXAFS spectra of treated TS-1 (outgassed at room temperature) and after in situ dosage of NH_3 (60 Torr equilibrium pressure) are shown. Each EXAFS spectrum was repeated several times (five times

for the sample in vacuo and four for the sample in the presence of NH_3) under the same experimental conditions. The extracted $\chi(k)$ functions were averaged before the EXAFS data analysis. Standard deviation calculated from the averaged spectra was used as an estimate of the statistical noise for the evaluation of the error associated with each structural parameter.[28] Part a of the figure shows the averaged $k\chi(k)$ function obtained estimating the atomic contribution by a polynomial fit (fifth degree) and then subtracted from experimental data following the procedure proposed by Lengeler and Eisenberger[35] (the preedge being modeled with a line). From a simple inspection of Figure 9a, the higher frequency of oscillation in the $\chi(k)$ function obtained after interaction with ammonia is evident, indicating qualitatively an average elongation of the Ti first coordination shell bond distance. Figure 9b reports the k^3-weighted Fourier transform (moduli and imaginary parts) of the EXAFS functions reported in part a. From this phase uncorrected radial distribution, we can qualitatively observe a displacement toward higher R of the first coordination shell peak upon interaction with NH_3. The first-shell peak of both radial distribution is then Fourier back-transformed into k-space in order to isolate the first-shell contribution to the EXAFS signal (see full line curves in Figure 9c). EXAFS data analysis was then performed, following standard procedures,[28] in the frame of a single scattering curved wave approximation using Michalowicz programs[29] as extensively described elsewhere.[16] Experimental phase shift and amplitude functions have been extracted from an anatase model compound by arbitrarily setting the Debye−Waller factor σ to 0.07 Å.

The fit of the sample in vacuo was a single-shell fit, the optimized parameters being R, N, ΔE, and σ; see Table 4. The most relevant data obtained from this study are (i) the number of atoms in the first coordination shell of titanium, $N = 4.30 \pm 0.25$ and (ii) the lengths of the Ti−O bond $R = 1.79$ Å ± 0.01. As already discussed,[16] a coordination number greater than 4 has been interpreted in terms of the copresence of both closed [TiO_4] and open [TiO_3OH] sites (vide infra Schemes 2 and 3, respectively). Please note that in an ideal EXAFS experiment performed on a TS-1 sample containing only [TiO_3OH] sites, the expected first shell coordination number is $N = 5$ (vide infra).

After interaction with ammonia, a two-shell fit must be imperatively performed, since R, ΔE, and σ are supposed to be different for the T−O and the Ti−N subshells. Due to the fact that oxygen and nitrogen differ only by a single electron, the use of the same phases and amplitude functions for both subshells is a good approximation. To limit the number of fitted parameters, the number of framework oxygen atoms linked to Ti (N_O) has been fixed to 4.3 (i.e., the value obtained for the sample in vacuo) in a first set of minimization processes or to 4.0 in a parallel one. The later fit has been found to better reproduce the experimental first-shell filtered $\chi(k)$ function; see Figure

(35) Lengeler, B.; Eisenberger, P. *Phys. Rev. B* **1980**, *21*, 4507.

Table 4. Filtering Ranges and EXAFS Results for First Coordination Sphere of the TS-1 Sample in Vacuo (One Shell Fit) and After Interaction with 60 Torr of NH$_3$ (Two Shells Fit)^a

sample conditions	Δk (Å^{-1})	ΔR (Å)	shell	R (Å)	N	σ (10^{-2} Å)	ΔE (eV)
in vacuo	3.34–14.31	1.07–1.84	Ti–O	1.79 ± 0.01	4.30 ± 0.25	5.5 ± 0.6	−2 ± 1
+ NH$_3$	2.93–14.09	0.96–1.96	Ti–O	1.84 ± 0.03	4	9 ± 2	−4 ± 4
			Ti–N	1.93 ± 0.03	1.9 ± 0.3	6 ± 2	+5 ± 4

^{a} Δk interval of k-space to R-space FT; ΔR R-space interval selected to perform the first shell-filtered back FT into K-space; R, bond distance; N, coordination number; σ, relative Debye−Waller Factor; ΔE, energy shifts.

9c. The most relevant structural parameters obtained from this two-shell fit are (i) $R_O = 1.84$ Å ± 0.03 ($N_O = 4$), (ii) $R_N = 1.93$ Å ± 0.03, (iii) $N_N = 1.9$ Å ± 0.3 (for all remaining data see Table 4).
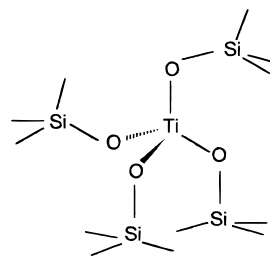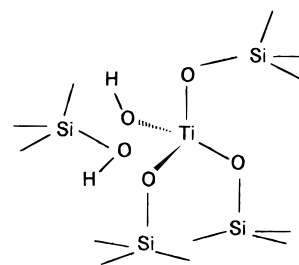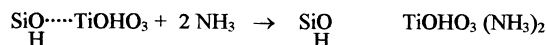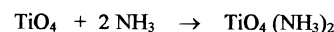
Discussion

Specific Interaction of NH$_3$ on Untreated TS-1. All data obtained by using quite different but complementary techniques have shown that on silicalite different kinds of sites active in reversible ammonia adsorption are present. The adsorption of NH$_3$ was found to involve different processes. The dominant surface sites (mainly silanols on external surfaces and on the walls of internal nests) were found to be heterogeneous. A small fraction of strong sites (preferentially strained siloxane bridges or other defects) were also evidenced. These sites are associated with a larger heat of adsorption. In TS-1 an additional element of heterogeneity is present because of the presence of titanium in the framework. Tetrahedral coordination is indeed unusual for titanium and thus Ti centers show a relatively high propensity to expand their coordination shell by adsorbing basic ligands. This propensity is clearly illustrated by the experiments described in the present work. A specific interaction of NH$_3$ with Ti(IV) sites is specifically monitored by the perturbation of the 960 cm^{-1} band. A stepwise shift of the spectral position of the band is in fact observed as a consequence of the contact with ammonia (see Figure 3). This has been interpreted as due to the coordinative adsorption of NH$_3$ on Ti(IV), with a subsequent change from 4-fold to 6-fold coordination. The insertion of additional NH$_3$ ligands into the coordination sphere of Ti(IV) is associated with an outward movement of the Ti(IV) with respect to the framework. Consequently, the asymmetric Si−O−Ti stretching mode at 960 cm^{-1} acquires progressively more ν(SiO) character and moves toward higher frequencies.[7,10,13] On this ground, the two isosbestic points observed both during the adsorption and the desorption runs can be interpreted as the indication of the stepwise formation of pentacoordinated and hexacoordinated species. The fact that, unlike that observed on silicalite, the interaction is not fully reversible, testifies that Ti(IV) sites have a strong affinity toward NH$_3$. XANES results (see Figure 4) seem to confirm this data, because they are also indicating a not completely reversible modification in the local geometry of the titanium sites upon adsorption of ammonia.

Two types of titanium sites have been hypothesized on TS-1, the "regular" site [TiO$_4$] (Scheme 2) and the "open" site [TiO$_3$OH] (Scheme 3).[10,12−14,16,36] The open site can be considered as deriving from the regular one by hydrolysis of one Si−O−Ti bridge or deriving from incomplete reaction of Ti(IV) with the hydroxyls of a nest. It has been suggested that Ti(IV) species in an open structure are able to interact also with the oxygen atom of a nearby silanol, which can thus be considered as part of the first coordination sphere of Ti(IV).[10,12−14,16]

Upon interaction with an high equilibrium pressure of NH$_3$ (50−60 Torr) both EXAFS and microcalorimetry have evidenced an average number of adsorbed NH$_3$ molecules

Scheme 2

Scheme 3

Scheme 4

$$\text{TiO}_4 + 2\,\text{NH}_3 \rightarrow \text{TiO}_4\,(\text{NH}_3)_2$$

$$\underset{\text{H}}{\text{SiO}}\cdots\text{TiOHO}_3 + 2\,\text{NH}_3 \rightarrow \underset{\text{H}}{\text{SiO}} \quad \text{TiOHO}_3\,(\text{NH}_3)_2$$

per Ti site close to 2. This implies that both regular and open sites are able to coordinate two ammonia molecules, leading a final local environment characterized by 6-fold symmetry, as already documented by IR, UV−vis, and XANES spectroscopies (see Introduction). As far as the [TiO$_3$OH] sites are concerned, the only way to justify the insertion of two NH$_3$ ligand molecules into the Ti(IV) coordination sphere is to suppose that NH$_3$, being a strong base, can displace the oxygen of the adjacent silanol (not chemically bonded to Ti) from the coordination sphere of Ti(IV). This hypothesis is supported by the EXAFS data analysis, where the fit obtained by fixing $N_O = 4.0$ was more satisfactory than that obtained by fixing $N_O = 4.3$ (value obtained for the sample in vacuo). In conclusion, an adsorption scheme for "regular" and "open" sites can be hypothesized (Scheme 4).

As far as the first coordination shell is concerned, it is evident that, after the interaction with two NH$_3$ molecules, the open and closed site are nearly undistinguishable. It must be added that it is not possible to completely exclude that, at low coverage, ammonia is also capable of reacting with a few surface Si−O−Ti bridges giving rise to open structures. The initial heat of adsorption can be invoked to support the occurrence of both kinds of processes at low coverage. However, the zero-coverage heat of adsorption measured for the second run adsorption is also quite high ($q_0 \approx 130$ kJ/mol); this indicates that the reversible interaction occurring on a small fraction of Ti(IV) sites is also relatively strong. These data do not allow a certain conclusion to be drawn about the processes occurring for coverages near zero. The IR results seem to be able to

<div style="text-align:center">

Scheme 5

Si-OH + NH$_3$ →   Si-OH···NH$_3$

Ti-OH + NH$_3$ →   Ti-OH···NH$_3$

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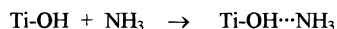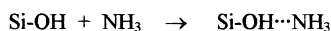
shed some light on this point. In fact, it can be seen (Figure 2) that after desorption at room temperature, small traces of molecularly adsorbed NH$_3$ remain on the surface (see the vestiges of ν_{asym}(NH$_3$) and ν_{sym}(NH$_3$) accompanied by a broad absorption band in the 3600−3200 cm^{-1} interval). We hypothesize that this broad absorption is due to hydrogen bonding interaction between coordinated NH$_3$ and adjacent hydroxyl groups in the "open structures".

In addition to the coordinative interaction with Ti(IV), NH$_3$ is adsorbed on silanols and titanols of the open sites of TS-1 as well as on the silanols of the silica matrix. This is clearly shown by the IR spectra in the O−H vibration region, where all original OH bands are eroded upon NH$_3$ adsorption giving a strong and broad absorption at lower frequencies (see Figure 2). In this interaction, hydrogen bonded complexes between OH groups and ammonia, as reported in Scheme 5, are formed. The location of the ν_{asym}(NH$_3$) and ν_{sym}(NH$_3$) bands of hydrogen bonded NH$_3$ indicates that the perturbation bond due to this interaction is not very large.

Very few quantitative and energetic data are available in the literature regarding the adsorption of probes on TS-1. The adsorption of ammonia was studied calorimetrically.[37,38] The authors of the reported papers refer that sites not particularly acidic are mainly present on TS-1, being the heat of adsorption comprised in the 60−100 kJ/mol interval, but for a few sites relatively strong associated to a heat of adsorption of ∼160−200 kJ/mol.[37]

In the present work we describe in detail from both a quantitative and energetic point of view the interaction of NH$_3$ with Ti(IV) sites present on TS-1. Owing to the simultaneous adsorption of ammonia on Ti(IV) and on the silicalite host, the volumetric and the calorimetric isotherms obtained were subtracted by the silicalite contribution. It resulted that the adsorption of ammonia on titanium sites is pressure dependent and that at ca. 50 Torr the number of ammonia molecules adsorbed per titanium atom is close to 2. The results, reported in Table 1, imply that all titanium species are involved in the interaction with ammonia and that, at p_{NH_3} = 50 Torr, all have completed their coordination shell. The amount of ammonia irreversibly adsorbed at room temperature on titanium sites increases with increasing equilibrium pressure, whereas the amount of ammonia reversibly adsorbed does not change appreciably (1.2 NH$_3$ molecules per Ti atom at p = 10 Torr and 1.3 molecules per atom at p = 50 Torr). The molar heat of the irreversible interaction is quite high (q_m = 158 kJ/mol) at low pressure (p = 10 Torr) and progressively decreases with pressure, so indicating that the irreversible process involves first the most energetic sites, as expected. However, at p = 50 Torr, the molar heat of adsorption is still quite high (q_m = 96 kJ/mol). Also, the molar heat of the reversible adsorption on Ti(IV) sites is higher than that measured on silicalite, (q_m = 77−75 kJ/mol for NH$_3$ on Ti(IV) sites against 66−58 kJ/mol for NH$_3$ on SiOH groups).

The significant amount of irreversibly adsorbed species has to be ascribed to the particular affinity of NH$_3$ toward

titanium. NH$_3$ is indeed a hard base and Ti(IV) a hard cation (acid) in the Pearson classification,[39,40] and so, the interaction between these two species is expected to be quite strong. Thus, the relatively large amount of ammonia irreversibly bound to the titanium sites has to be interpreted as an indicator of the high propensity of titanium heteroatoms to expand their coordination shell more than to the presence of highly defective Ti(IV) sites.

Effect of Pretreatment with Ammonium Acetate Aqueous Solutions. It is well-known that the routinely made treatment of TS-1 with aqueous solutions of ammonium acetate and subsequent calcination, allows samples of better defined crystallinity to be obtained which can be fruitfully used to obtain a very accurate determination of the structural parameters (and thus to estimate very carefully the amount of framework titanium from the linear increase of the structural parameters).[5,6] To obtain further information on the effect caused by the pretreatment with ammonium acetate, the behavior of this sample with respect to the adsorption of ammonia was studied in comparison with the untreated TS-1 parent sample. A similarly pretreated silicalite sample was taken as a reference material.

The first significant information comes from vibrational spectroscopy; in fact, from the inspection of the OH group vibration region in the IR spectra (Figure 1) it is noticed that the amount of interacting silanols is significantly depressed in both the TS-1 and silicalite sample, suggesting that in treated samples structural defects are less abundant. The interaction with ammonia is apparently very similar to what is observed for the untreated samples, as shown by the IR spectra reported in Figure 2. The adsorbed amounts on both treated TS-1 and silicalite are lower than those obtained for untreated samples: however, if we consider only the amount adsorbed on Ti(IV) sites, the difference between treated and untreated samples is not very large. Indeed, while at p = 10 Torr the ammonia on Ti(IV) sites is 1.1 NH$_3$ molecules per Ti atom (against 1.5 NH$_3$ molecules obtained for the untreated sample), at p = 50 Torr the number of NH$_3$ molecules per titanium atom is 2.0 for both untreated and treated samples. This means that also, in treated TS-1, all titanium sites can completely expand their coordination shell up to 6 by adding two additional ligands (see Scheme 5). On treated TS-1, however, the amount of ammonia irreversibly held is lower than in the case of the untreated sample (0.5 against 0.7 NH$_3$ molecules per Ti atom). The most striking difference between untreated and treated samples is connected with the energy of interaction of ammonia with the titanium sites. In fact, the zero-coverage heat of adsorption for the first run on treated TS-1 is only ∼120 kJ/mol, i.e., a value, much lower than on untreated TS-1 (∼200 kJ/mol) and very close to that obtained for the second run (reversible) adsorption. This means that the treatment in ammonium acetate caused the few most energetic sites responsible for the very strong, likely dissociative interaction with NH$_3$ to be suppressed. The same treatment, however, left the sites responsible for the strong reversible adsorption of ammonia virtually unmodified. This result is in agreement with the suggestion that structural defects, strains, and imperfections of the structure are smoothed off by the chemical treatment without affecting the unique features of the catalyst.

Finally, EXAFS measurements allowed estimation of the number of atoms in the first coordination shell of Ti(IV) as well as of the bond lengths between titanium

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and oxygen atoms in outgassed samples and between titanium and oxygen and titanium and nitrogen atoms in TS-1 in the presence of NH_3. For all these parameters, the method gives values averaged over all types of Ti coordination in the sample. The coordination number of 4.30 ± 0.25 in the case of outgassed TS-1 reflects the presence of a fraction of titanium atoms having a fifth oxygen in the first coordination sphere owing to the interaction of tetracoordinated Ti in an "open site" with the oxygen atom of a silanol in the nearness (see Scheme 3). In the data processing of TS-1 in the presence of adsorbed ammonia, the best results were obtained when the number of oxygen atoms surrounding Ti heteroatoms was fixed to 4.0, which is the number of oxygen atoms chemically bonded to a central titanium heteroatom in both "open" and "regular" sites. This means that for Ti in "open" sites the insertion of a strong ligand such as ammonia implies the removal of the fifth oxygen ligand (adjacent silanol, not chemically bonded to Ti) from the first coordination shell of titanium. The average number of ammonia molecules bound to the central site was estimated to be 1.9 ± 0.3, in quite nice agreement with the volumetric–calorimetric data. In the presence of ammonia, the Ti–O distance was found to increase significantly (1.84 ± 0.03 Å against 1.79 ± 0.01 Å) with respect to outgassed TS-1 as expected when an increase of coordination shell of the central titanium from tetrahedral (4-fold coordinated) to octahedral (6-fold coordinated) occurs. This result is in full agreement with the IR results concerning the Ti-sensitive band at 960 cm^{-1}. The elongation of the Ti–O bond is partially inhibited by the fact that Ti atoms are embedded as highly diluted heteroatoms in a crystalline siliceous matrix with well-defined lattice parameters. The distance of the Ti–N bond (1.93 ± 0.03 Å) was found to be significantly higher than the Ti–O one (1.84 ± 0.03 Å), in agreement with the coordinative character of the interaction. A parallel set of experiments recently performed on a TS-1 sample with lower Ti content (Ti = 1.0 wt %) confirms the here-described picture.[41]

Conclusions

The propensity of framework Ti(IV) centers to expand their coordination number from 4 up to 6 is revealed by IR and XANES–EXAFS spectroscopies and quantitatively and energetically described by adsorption microcalorimetry, using NH_3 as a probe. Ammonia is indeed able to interact with Ti(IV) centers causing the local coordination of the site to change from 4 to 5 and 6. Variation in the local geometry of the Ti(IV) sites was monitored by the changes of the Ti-sensitive band at 960 cm^{-1} in the IR framework stretching region as well as by the 4967 eV preedge peak in XANES spectra, both bands being a fingerprint of tetrahedral Ti(IV) in isolated [TiO$_4$] or [TiO$_3$OH] units. By adsorption microcalorimetry, the number of NH_3 molecules adsorbed for 50 Torr of equilibrium pressure was estimated to be close to 2, suggesting that a complete expansion of the coordination shell of all Ti(IV) inserted in the framework occurs under the adopted conditions. The evolution of the heat of adsorption with coverage was found to be typical of heterogeneous surfaces, not only because sites active toward ammonia on the silicalite matrix are heterogeneous but also because the distribution of Ti(IV) sites in the different structural positions is random. This important findings discard the presence of a strongly preferential substitutional site among the 12 sites of the orthorhombic MFI cell. On silicalite, where only reversibly adsorbed species are involved, the heats of adsorption are comprised in the 100–40 kJ/mol interval, whereas on TS-1 they are comprised in the 200–50 kJ/mol interval for the first run, involving both irreversibly and reversibly adsorbed species. The interaction of NH_3 with TS-1 is in fact only partially reversible ($q_0 \approx 130$ kJ/mol). However, it is likely the pronounced and reversible tendency of Ti(IV) sites to increase their coordination shell to be connected with the unique properties of the TS-1 catalyst. Routinely made treatment in ammonium acetate aqueous solutions was found not to affect this tendency, neither qualitatively nor quantitatively, with only the most defective sites being eliminated. Finally, EXAFS measurements allowed estimation of the local parameters of Ti(IV) centers in outgassed TS-1 and in the presence of NH_3. The lengths of the Ti–O and Ti–N bonds were compared, and the average number of atoms surrounding a central titanium heteroatom in the presence of ammonia was estimated. All data obtained were found to be in good agreement with the volumetric–calorimetric data of adsorption and with IR results.

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