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Probing the Brønsted and Lewis acidity of Fe-silicalite by FTIR spectroscopy of H_2 adsorbed at 20 K: Evidences for the formation of Fe^{3+}/H_2 and Fe^{2+}/H_2 molecular adducts

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Abstract

We report on the spectroscopic characterisation of a Fe-silicalite sample in terms of Brønsted and Lewis acidity using H_2 as a probe molecule at low temperature (20 K). At 20 K, H_2 is able to form adducts with surface sites present in the internal (and external) surface of zeolites: Brønsted, silanols, and metal ions. The spectroscopic manifestations of the different H_2 adducts are found in distinct spectral regions depending on the nature and strength of the adducts: $\bar{\nu}_{HH}$ modes of $OH\cdots H_2$ adducts are found in the 4170–4100 cm^{-1} region, and those of $Fe^{x+}\cdots H_2$ adducts are found in the 4100–3900 cm^{-1} region. Four distinct $Fe^{x+}\cdots H_2$ adducts (at 4050, 4028, 3990, and 3960 cm^{-1}) were formed on extra-framework Fe sites, created by controlled migration of Fe from the framework as a consequence of thermal treatments. The dependence on red–ox treatments of the relative concentration of these sites allowed identification of two Fe^{2+} and two Fe^{3+} distinct sites, interacting with H_2 mainly by electrostatic forces. The importance of these sites as active species for the selective oxidation of hydrocarbons with N_2O is discussed.

Keywords: H_2 adducts; Fe-zeolite; α-Oxygen; IR spectroscopy; N_2O decomposition

1. Introduction

Adsorption of H_2 at temperature as low as 20 K has been successfully used to probe the Brønsted and Lewis acidity in the confined spaces of microporous materials by vibrational spectroscopy [1]. In the case of zeolites, Brønsted acidity is related mainly to structural ≡Si(OH)Al≡ [or ≡Si(OH)Fe≡] groups, whereas Lewis acidity is produced by exchange of the protons with metal (usually alkaline or alkaline earth) ions. Additional sources of acidity can be represented by structural defects, such as ≡Al–OH and ≡Si–OH (Brønsted sites) or extra-framework M^{3+} or ($M = Al$, Fe, etc., Lewis sites), which are present on the external surface and/or formed on the internal surface during thermal treatments for zeolite purification or activation.

All the aforementioned species are able to adsorb molecular hydrogen at temperatures of 77–20 K to give $O{-}H\cdots H_2$ (Brønsted sites) and $M^{n+}\cdots H_2$ (Lewis sites) adducts, which can be detected and investigated by infrared vibrational spectroscopy. The interaction is mainly electrostatic in nature and results in the IR activation of the H–H stretching mode and in its displacement to lower frequency, with the shift $\Delta\bar{\nu}_{HH}$ with respect to the free H_2 molecule being roughly proportional to the adsorption energy [1]. Typical $\Delta\bar{\nu}_{HH}$ values for the $O{-}H\cdots H_2$ interaction are in the range from ≈ -70 (strongly acidic ≡Si(OH)Al≡ groups in H-SSZ-13 zeolite) to ≈ -30 cm^{-1} (weakly acidic ≡Si–OH species in silicalite) [2], whereas for H_2 adsorption on extra-framework Lewis sites, the shifts lie in the ~160 (extra-framework Al^{3+}) to ~60 (alkaline cations) cm^{-1} range [1,3]. It is noteworthy that, compared with the spectroscopic data about adsorption on the same sites of the popular CO probe, shifts of the $\bar{\nu}_{CO}$ and $\bar{\nu}_{HH}$ frequencies are linearly correlated and $\Delta\bar{\nu}_{HH} \approx 2\Delta\bar{\nu}_{CO}$. This is due to the fact that the $\bar{\nu}_{HH}$ of the single H–H bond is more sensitive than the $\bar{\nu}_{CO}$ of the triple C–O bond to local effects (e.g., structure, num-

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ber of ligands in the coordination sphere) possibly influencing the physicochemical properties of the adsorbing centres [1].

When Fe-based zeolites are involved, a very complex situation is usually present. Whereas in the as-synthesized zeolite, iron is present in framework tetrahedral positions as Fe^{3+} [giving rise to Brønsted acidity associated to the presence of ≡Si(OH)Fe≡ bridged sites], thermal treatments, which are required to induce catalytic activity, result in breaking of the Si–O–Fe framework bonds [4] and in migration and partial reduction of iron. As a result, a heterogeneous distribution of Fe^{2+} and Fe^{3+} sites with varying nuclearity (from isolated ions to oligomers and large clusters) and local environments is usually present in thermally treated Fe-zeolites [5–7]. The relationship between the structure of the Fe sites and the activity and selectivity of the Fe-zeolite catalysts (in selective oxidation of benzene to phenol with N_2O and selective reduction of NO_x with hydrocarbons or ammonia) has been the subject of a lively debate over the last 10 years [8–13]. One of the most widely accepted hypotheses is that the active sites for selective oxidation are isolated Fe^{2+} sites in close vicinity to framework Al^{3+} (or Fe^{3+} ions) [14–16].

The coexistence of at least two Fe^{2+} sites (isolated and clustered), both able to decompose the oxidizing agent N_2O but forming adsorbed oxygen atoms with different selectivity, has been proposed independently by many authors [17–19]. Similar results, in terms of two distinct Fe^{2+} sites with different selectivities, were obtained in relation to the activity of Fe-zeolites in the selective reduction of NO_x [20]. A weak probe molecule like H_2, sensitive to the local structure of the adsorbing site and thus able to detect small differences, could be a useful tool for characterising complex catalysts such as Fe-zeolites, providing additional information on the nature and structure of active sites in selective catalytic oxidation. In this paper the adsorption of hydrogen on Fe-silicalite was studied by Fourier transform infrared (FTIR) spectroscopy at low temperature (20 K), with the primary aim of adding further insight into the nature of the extra-framework Fe^{2+} and Fe^{3+} species in relation to their activity in selective red–ox catalysis.

2. Experimental

Fe-silicalite ($Si/Fe = 50$) was synthesized following the method of Szostak et al. [21], and subsequently washed, dried, and calcined at 823 K. H_2 adsorption was investigated on three different types of samples: (i) protonic Fe-Sil (activated at 573 K in vacuum), containing mainly iron, as Fe^{3+}, in tetrahedral framework positions; (ii) standard (catalytically active) Fe-Sil (activated by outgassing in high vacuum at 973 K), in which iron is present mainly as a mixture of Fe^{2+} and Fe^{3+} species in extra-framework positions [6]; and (iii) oxidized Fe-Sil, prepared by further treating standard samples in oxygen (13 kPa) at 773 K and outgassing at 573 K. Silicalite and high-surface area amorphous SiO_2 (Aereosil) samples, used here as a reference, were outgassed at 1073 K before H_2 dosage. The thermal treatments were performed in the same cryogenic apparatus, capable of operating in the entire 20–300 K temperature range in vacuum or in controlled atmosphere [22], used for recording the IR spectra.

The spectra were recorded on a Bruker Equinox 55 FTIR spectrometer (operating at 1 cm^{-1} resolution), properly modified to host the cryogenic cell [22]. The zeolite samples were in the form of self-supporting pellets suitable for transmission IR experiments.

3. Results and discussion

The spectra obtained on dosage of H_2 [equilibrium gas pressure $p(H_2) \approx 8$ kPa] at 20 K on an acidic (activated at 573 K), standard (activated at 973 K) and oxidized (treated in O_2 at 773 K and evacuated at 573 K) Fe-Sil are compared in Fig. 1. In the same figure the spectra of H_2 adsorbed, in the same experimental conditions, on silica and pure silicalite (previously outgassed at 1073 K) are also reported for comparison.

We can immediately distinguish two different spectral regions. In the first (4170–4100 cm^{-1}), all of the samples show medium-strong absorptions; in the second (4100–3900 cm^{-1}), bands are present only on the Fe-containing systems activated at sufficiently high temperature (973 K) to give rise to iron migration from framework to extra-framework positions (standard and oxidized Fe-Sil). Based on this observation, the assignment of the peaks at 4050, 3990, and 3960 cm^{-1} (on standard) and at 4040 (broad) and 3978 cm^{-1} (on oxidized) Fe-Sil to interaction products of H_2 with extra-framework Fe^{2+} and Fe^{3+} species is straightforward. The absence of similar manifestations in Fe-Sil activated at low temperature (Fig. 1) is in agreement with the fact that tetrahedral Fe^{3+} in framework positions has no adsorptive capability [4]. The assignment of the bands in the 4100–3900 cm^{-1} interval to H_2/Fe^{2+} and H_2/Fe^{3+} interaction products is further supported by the evidence that (unlike those in the 4170–4100 cm^{-1} region) they are highly sensitive to thermal treatment in oxygen: it can be in fact observed in Fig. 1 that on passing from standard to oxidized Fe-Sil, the band at 4050 cm^{-1} disappears (leaving a very weak and broad absorption centred at 4040 cm^{-1}), whereas the spectrum gains intensity in the 4000–3900 interval, where a medium-strong broad band is formed at 3978 cm^{-1}. It is noteworthy that the spectrum typical of the H_2/standard system can be nearly completely restored if oxidized Fe-Sil is treated in vacuo at 773 K and contacted again with H_2 at 20 K (results not shown for brevity). Based on the ascertained capability of extra-framework Fe^{2+} and Fe^{3+} to be mutually interconverted by effect of oxidizing agents like O_2 or N_2O ($Fe^{2+} \rightarrow Fe^{3+}$) and by spontaneous self-reduction on heating in vacuo ($Fe^{3+} \rightarrow Fe^{2+}$) [6,10], we can definitely conclude that the manifestations appearing in the 4100–4000 cm^{-1} interval are due to interaction of H_2 with reduced Fe^{2+} sites, whereas those in the 4000–3900 cm^{-1} region involve Fe^{3+}. The detailed assignment of the spectra of these H_2/Fe^{n+} adducts is given later in the paper, when the effect of the H_2 equilibrium pressure is taken into account.

As far as the spectra in the 4170–4100 cm^{-1} region are concerned (Fig. 1), the following comments can be made.

(i) The spectrum of H_2 adsorbed at 20 K on amorphous silica is dominated by a single, nearly symmetrical band at

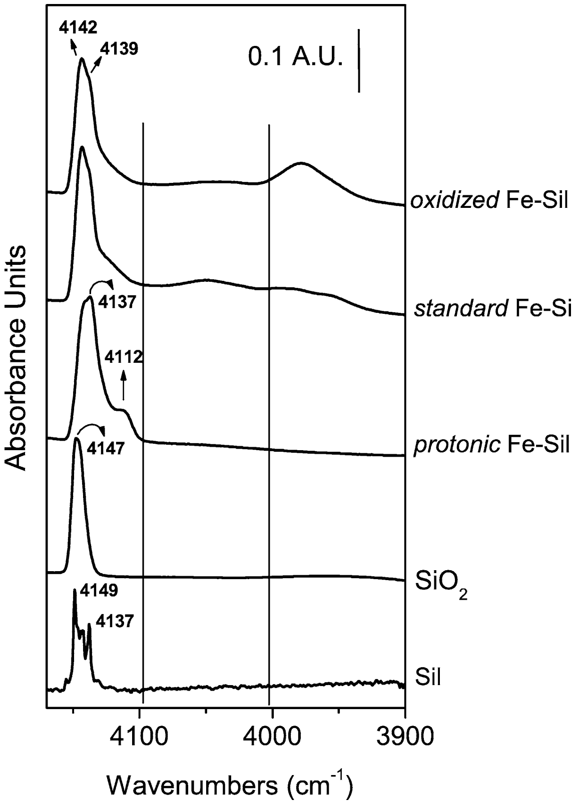

Fig. 1. IR spectra in the $\bar{\nu}_{HH}$ region of H_2 adsorbed at 20 K and $p(H_2)\approx$ 8 kPa on: (i) Fe-silicalite activated at 573 K (protonic Fe-Sil); (ii) Fe-silicalite activated at 973 K (standard Fe-Sil); (iii) Fe-silicalite activated at 973 K, oxidized at 773 K and degassed at 573 K (oxidized Fe-Sil); (iv) amorphous silica outgassed at 1073 K (SiO_2); and (v) pure Silicalite outgassed at 1073 K (Sil). The vertical lines delimitate the spectral regions where the $\bar{\nu}_{HH}$ modes of H_2 adsorbed on Brønsted (4170–4100 cm^{-1}) and Lewis (4100–ca. 4000 cm^{-1} – Fe^{2+}; ca. 4000–3900 cm^{-1} – Fe^{3+}) acid sites are falling.

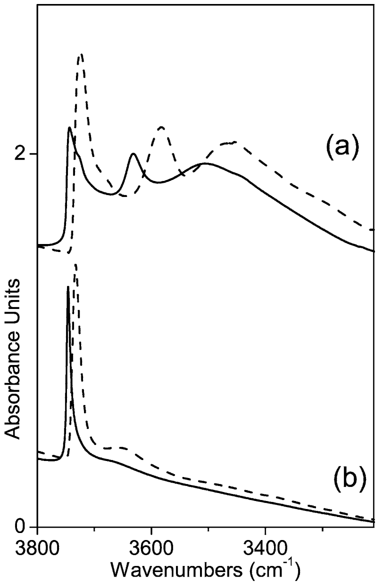

Fig. 2. IR spectra in the $\bar{\nu}_{OH}$ region of (a) protonic Fe-Sil (activated at 573 K) and (b) standard Fe-Sil (activated at 973 K) before and after H_2 dosage at 20 K ($p\approx$ 8 kPa), full and dashed lines, respectively.

4147 cm^{-1}. Without getting into detail beyond the scope of this paper, we mention that this absorption is due to the $\bar{\nu}_{HH}$ mode of $\equiv SiOH\cdots H_2$ adducts involving the isolated silanol groups located on the (external) surface of SiO_2 [1,23].

(ii) The band at 4149 cm^{-1} on silicalite has the same origin; the involved silanol-like groups are actually mainly those located on the external terminations of the zeolite microcrystals. The reduced width of the $\bar{\nu}_{HH}$ band on silicalite (<5 cm^{-1} at half maximum) compared with SiO_2 (10 cm^{-1}) is noteworthy. This difference is the consequence of the crystalline nature of the zeolitic material, which makes the local structure of the surface silanol groups less disordered. A second narrow component at 4137 cm^{-1}, not observed on SiO_2, is associated with H_2 molecules adsorbed at the surface of the internal channels typical of the silicalite MFI framework [24]. Thus this band represents a sort of fingerprint for the presence of regular nanoporosity.

(iii) The spectrum of H_2 adsorbed on protonic Fe-Sil shows an intense absorption that is the clear superposition of two components, one located at 4137 cm^{-1} and a second, weaker and appearing as a shoulder, located at 4146–4140 cm^{-1}. Compared with the spectra obtained on SiO_2 and silicalite (and by the transformation observed in the $\bar{\nu}_{OH}$ region; see below and Fig. 2), these are assigned to hydrogen adsorbed in the internal voids of the zeolite and on the external $\equiv$Si–OH groups, respectively. A third band at 4112 cm^{-1} is due to the $\bar{\nu}_{HH}$ mode of $OH\cdots H_2$ adducts formed on the structural $\equiv$Fe(OH)Si$\equiv$ Brønsted acid sites. This assignment is supported by literature data concerning H_2 adsorption on [Fe]HZSM-5 [25] and HZSM-5 [1] acid zeolites, where bands of the same origin are observed at 4106 and 4109 cm^{-1}, respectively, and by the observation of the $\bar{\nu}_{OH}$ region (Fig. 2). This band is greatly reduced in intensity on the standard and oxidized specimens (vide infra).

(iv) The bands due to H_2 adsorbed on external (4142 cm^{-1}) and internal surfaces (4139 cm^{-1}) are still present in spectra of the standard and oxidized Fe-Sil/H_2 systems; however, it is noteworthy that their relative intensity is now inverted with respect to protonic Fe-Sil. Moreover, the absorption due to the $OH\cdots H_2$ adducts formed on the structural $\equiv$Fe(OH)Si$\equiv$ sites is reduced in intensity and broadened and appears now as tail, covering the 4130–4100 cm^{-1} interval, of the previous bands. We can then conclude that all of the manifestations related to H_2 adsorption in the inner parts of the zeolite (including the structural Brønsted sites) have become less significant with respect to those related to the outer surface; this is a clear symptom of iron dislodgment from the framework and partial amorphization of the Fe-silicalite structure.

The migration of Fe sites from framework to extra-framework positions can be followed by the analysis of the $\bar{\nu}_{OH}$ modes of the $\equiv$Fe(OH)Si$\equiv$ Brønsted sites. Fig. 2 shows the spectra of protonic and standard Fe-Sil in the $\bar{\nu}_{OH}$ region before (full lines) and after interaction with H_2 (dashed lines). The spectrum of protonic Fe-Sil before H_2 interaction is characterised by a band at 3744 cm^{-1} (with a shoulder at lower frequency) assigned to isolated (free) $\equiv$Si–OH groups present mainly on the external surface of the zeolitic microparticles, and by one peak at 3630 cm^{-1} due to the $\bar{\nu}_{OH}$ modes of the

≡Fe(OH)Si≡ Brønsted sites. The broad band centred around 3500 cm^{-1} is due to hydrogen-bonded ≡Si–OH species in fully hydroxylated nanovoids (hydroxil nests) [4]. Moving to standard Fe-sil (bottom curves), only the peak due to ≡Si–OH groups at 3744 cm^{-1} (with a tail at lower frequency) is present, whereas the band at 3630 cm^{-1} due to ≡Fe(OH)Si≡Brønsted sites has practically disappeared. This indicates the massive migration of Fe sites from framework to extra-framework positions. The disappearance of the broad band centred around 3500 cm^{-1} and the narrowing of the band at 3744 cm^{-1} due to the increased activation temperature indicates a deep rearrangement of the zeolitic structure with thermal treatments, with a decrease in local defects [4]. On H_2 adsorption at 20 K, all the above bands are perturbed and shifted to lower frequency, indicating the formation of $–OH\cdots H_2$ adducts. A detailed discussion of these bands is outside the scope of this paper; detailed discussions are provided elsewhere [1,2].

Having assigned the manifestations associated to the interaction of H_2 with the Brønsted (in the 4170–4100 cm^{-1} region) and the Lewis (4100–3900 cm^{-1}) acid sites and, among the latter, those due to Fe^{2+} (4100–4000 cm^{-1}) and Fe^{3+} (4000–3900 cm^{-1}) extra-framework species, we now illustrate and discuss in more detail the manifestations of the Fe^{2+}/H_2 and Fe^{3+}/H_2 interaction products. Our aim is to better clarify the nature of the involved Lewis sites and the interaction mechanisms. We focus the discussion on standard Fe-Sil, where the precursors of the sites active in selective oxidation reactions should be present, and finally we comment briefly on the H_2/oxidized Fe-Sil case. The spectral series (optical isotherms) obtained on standard and oxidized Fe-Sil on reducing the pressure from ca. 8 (most intense spectrum) to 10^{-5} kPa (less intense spectrum) are reported in Fig. 3. For the sake of clarity, these sequences are discussed as obtained in the reverse order, that is, on progressively increasing $p(H_2)$; this does not represent a limitation, because the hydrogen adsorption process is fully reversible at 20 K.

It is evident from Fig. 3a (H_2/standard Fe-Sil) that the bands discussed earlier at 3990 and 3960 cm^{-1} are formed already at very low equilibrium pressure; moreover, all of the responsible sites are immediately saturated, as demonstrated by the fact that the doublet is not affected (or little affected) on further increasing $p(H_2)$ except for a small downward shift of ca. 1–2 cm^{-1}. We assign these bands, falling in the region typical of the hydrogen interaction with ferric species, to two different H_2/Fe^{3+} adducts, hereafter denoted as A (giving rise to the 3990 cm^{-1} component) and A′ (3960 cm^{-1}). In the 4100–4000 cm^{-1} region (typical of the Fe^{2+}/H_2 interaction products), no bands are observed at low pressure. Absorption first appears at 4028 cm^{-1} at medium $p(H_2)$; subsequently, this is rapidly subsumed on increasing pressure by the more intense 4050 cm^{-1} component discussed earlier. Hence for Fe^{2+} we are dealing with two families of sites giving rise to Fe^{2+}/H_2 adducts, denoted as B (4050 cm^{-1}) and B′ (4028 cm^{-1}), of slightly different stability.

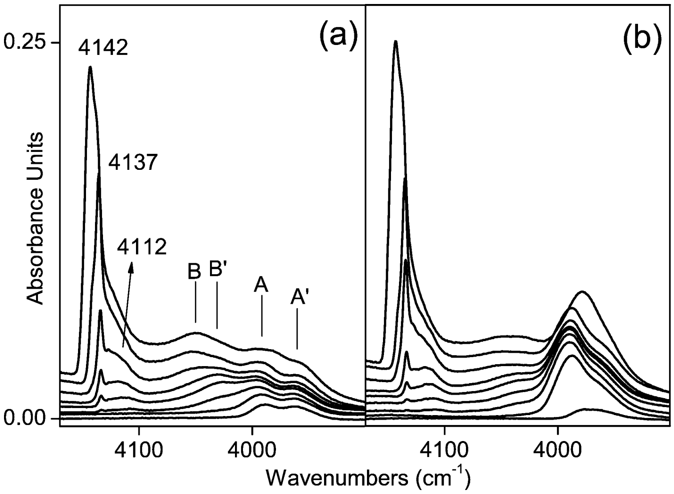

Fig. 3. Effect of changing the $p(H_2)$ equilibrium pressure (from 8, more intense curve, to $<10^{-5}$ kPa, less intense curve) at constant temperature (20 K) on the spectrum of H_2 adsorbed on standard (a) and oxidized Fe-Sil (b). Assignment of the bands: (A) $L_3N_mFe^{3+}\cdots H_2$ adducts; (A′) $L_3N_{m'}Fe^{3+}\cdots H_2$ adducts ($m' < m$); (B) $L_2N_2Fe^{2+}\cdots H_2$ adducts; and (B′) $L_2NFe^{2+}\cdots H_2$ adducts.

The existence in Fe-silicalite activated at high temperature of various extra-framework Fe^{3+} and Fe^{2+} centres in concentrations depending on iron content and activation procedure, has been hypothesized and demonstrated in previous works based on various experimental techniques [6,7], including the results obtained using IR spectroscopic probes such as NO and CO. In particular, the NO probe turned out to be very sensitive to structural effects and revealed three families of Fe^{2+} sites with remarkably different adsorptive properties: (i) highly coordinatively unsaturated, isolated centres able to coordinate up to 3NO molecules to give $Fe^{2+}(NO)_3$ adducts; (ii) species of medium unsaturation, giving rise to $Fe^{3+}(NO)_2$ di-nitrosyls; and (iii) poorly unsaturated clustered species capable of forming $Fe^{2+}NO$ mono-nitrosylic complexes only [6]. The structures of these sites can be schematically represented as (i) L_2NFe^{2+}, (ii) $L_2N_2Fe^{2+}$, and (iii) $L_2N_3Fe^{2+}$, that is, Fe^{2+} ions grafted to the zeolite surface through two strong oxygen ligands (L), belonging to framework $≡SiO^-$ groups, and one (i), two (ii), or three (iii) weaker oxygen ligands (N) belonging to vicinal ≡SiOSi≡ siloxane bridges [6]. The L_2NFe^{2+} species have been proposed as precursors of the active species in selective oxidation reactions [13,19]. CO, acting as a weaker base, was found to be able to interact only with the more unsaturated centres [(i) and (ii)], forming monocarbonylic $Fe^{2+}CO$ adducts characterized by $\bar{\nu}_{CO}$ frequencies at 2162 ($L_2N_2Fe^{2+}CO$) and 2173 cm^{-1} ($L_2NFe^{2+}CO$) [6].

In the extra-framework Fe^{3+}, the NO probe revealed the presence of two different families of sites, both capable of forming exclusively mono-nytrosil complexes. The limited NO uptake is a consequence of the low unsaturation degree of the metal centres, the local structure of which can be schematised as $L_3N_mFe^{3+}$ [the two families differing in the number (m) of weak siloxane oxygen ligands (N) in the Fe^{3+} coordination sphere] [6]. CO was not sensitive to structural heterogeneity and gave rise to a single monocarbonylic band at 2215 cm^{-1} ($\Delta\bar{\nu}_{CO} = +72\ cm^{-1}$) [6]. It is then evident that H_2, revealing the presence of two Fe^{2+} and two Fe^{3+} families of sites, behaves like the CO probe in the ferrous species and like NO with the ferric species. These findings indicate that the H_2 molecule has great potential for the characterisation of complex systems, where mixtures of Fe^{2+} and Fe^{3+} sites with slightly different environments are present. Moreover, the interaction of H_2 with Fe sites is totally reversible, whereas the interaction of NO with Fe sites causes permanent modification of the Fe species [26].

In an attempt to find a correlation between the spectra of the Fe^{2+}/H_2 and Fe^{3+}/H_2 adducts with the structures of the Fe^{n+} Lewis sites proposed in the literature and cited earlier, it is useful to first summarize some basic characteristics of homogeneous $[Fe(\eta^2\text{-}H_2)L_n]$ complexes (where usually iron is present as Fe^{2+}, and L are cyclopentadienyl ligands or chelating agents containing nitrogen and/or phosphine groups) [27–29]. Although direct observation of the $\bar{\nu}_{HH}$ stretching vibration of the H_2 ligand in these complexes is often difficult (because of its low intensity and superposition to the strong manifestations of the other ligands [30–32]), it is commonly located at about 3000 cm^{-1} [31], more than 1000 cm^{-1} below the Raman frequency of the free molecule (4162 cm^{-1}). As in the Cu^+/H_2 interaction [33], here such a large shift is the result of overlapping between the H_2 σ and π orbitals and the d metal orbitals, resulting in a σ-donation, π-backdonation bonding mechanism that causes significant weakening of the H–H bond [34,35]. The $\Delta\bar{\nu}_{HH}$ shifts observed for the Fe^{2+}/H_2 and Fe^{3+}/H_2 interaction in Fe-silicalite are one order of magnitude smaller (ca. 100–200 cm^{-1}) and are comparable with those reported for H_2 adsorbed on metal centres without d orbitals, such as highly coordinatively unsaturated Mg^{2+} at the MgO surface [36] or extra-framework Al^{3+} species in zeolites [1]. This finding allows to reasonably rule out the occurrence of overlap forces and favours the view of an interaction involving mainly electrostatic forces (i.e., polarization of the H_2 molecule by the electric field exerted by the Fe^{n+} centres). This hypothesis is in full agreement with experimental data of Figs. 1 and 3, from which the larger perturbation of the $\bar{\nu}_{HH}$ mode for the interaction of H_2 and Fe^{3+} species with respect to (less polarizing) Fe^{2+} is emerging from the $\Delta\bar{\nu}_{HH}$ (−172 and −202 cm^{-1} for Fe^{3+} sites and −112 and −134 cm^{-1} for Fe^{2+} sites). Taking onto account the possible role of the ligands surrounding the adsorbing centre in the evaluation of the polarizing power of the structure revealed by CO and NO, the following Lewis acidity scale can be reasonably hypothesized:

$$L_2N_3Fe^{2+} < L_2N_2Fe^{2+} < L_2NFe^{2+} < L_3N_mFe^{3+} < L_3N_{m'}Fe^{3+},$$

where $m' < m$. On this basis, the assignment that we propose for the $\bar{\nu}_{HH}$ bands of H_2 adsorbed on the Fe^{n+} extra-framework centres of standard Fe-Sil (Fig. 1a) is given in Table 1, where, in analogy with the data on CO adsorption [6], we assumed that H_2 is not perturbed by the highly coordinated $L_2N_3Fe^{2+}$ sites. On the basis of literature data [37–39], we hypothesize that most likely the geometry of the $Fe^{n+}H_2$ adducts is of the side-on type. We believe that the possibility of H_2 bridging between the metal centre and the surrounding oxygen atoms [40] can be ruled out because of the negligible basicity of the oxygen atoms in the silicalite framework.

As discussed briefly in the Introduction, for electrostatic-type interactions, the shifts $\Delta\bar{\nu}_{HH}$ and $\Delta\bar{\nu}_{CO}$ of the $\bar{\nu}_{HH}$ and $\bar{\nu}_{CO}$ modes of H_2 and CO adsorbed on the same Lewis or Brønsted sites are roughly linearly correlated, and $\Delta\bar{\nu}_{HH} \approx 2\Delta\bar{\nu}_{CO}$. The data reported in Fig. 4 clearly show that the relationship is verified for a number of systems, including SiO_2, acidic and exchanged zeolites, oxides, and others [1]. Note the scattering of the points corresponding to Cr^{2+} species grafted on silica, a system in which covalent contributions play a specific role in both the Cr^{2+}/CO interaction and the Cr^{2+}/H_2 interaction [41].

Adding the data on H_2 and CO adsorption on the extra-framework Fe^{3+} (A and A′ species) and Fe^{2+} (B and B′ species) sites of standard Fe-Sil to Fig. 4 results in these sites being located in an intermediate position. This suggests that overlap contributions, although weak, are not negligible. For reasons discussed earlier, the Fe^{n+}/H_2 interaction is expected to be dominated by electrostatic forces, and hence overlap contribution should operate mainly in the case of the CO ligand. This further supports the previously advanced hypothesis of a certain degree of covalence in the Fe^{n+}/CO interaction [6].

Considering now the effect of $p(H_2)$ on the spectra of hydrogen adsorbed on the oxidized Fe-Sil (Fig. 3b), it becomes clear that oxidation has little effect on the A′ species, the band of which at 3960 cm^{-1} remains visible with nearly unchanged intensity in the first spectrum of Fig. 3b while it causes the preferential transformation of $L_2N_2Fe^{2+}$ (B) and L_2NFe^{2+} (B′) sites into $L_3N_mFe^{3+}$ (A) sites. The band due to $L_3N_mFe^{3+}/H_2$ interaction at 3990 cm^{-1}, visible at intermediate $p(H_2)$, gained significant intensity on the oxidized samples. The selective oxidation of Fe^{2+} to Fe^{3+} is in agreement with the recent reports of the presence of two Fe sites with different activities toward oxidation [17–19]. This finding could be an indication that H_2 may be used as a probe to better characterise the active sites in selective oxidations [6,12,13,15]. Finally, at the highest $p(H_2)$, the 3990 cm^{-1} band shifts to lower frequency to give the 3978 cm^{-1} component (see also Fig. 1). This phenomenon occurs in correspondence of pore filling by a liquid like H_2 phase [2], and is in our opinion associated with the changes of the overall dielectrical properties in the zeolitic voids (vide infra).

The evolution with $p(H_2)$ of the spectra in the region due to H_2 adducts with the Brønsted acid sites (4170–4000 cm^{-1}) merits some final comments:

(i) The spectral sequences of standard (Fig. 3a) and oxidized (Fig. 3b) Fe-Sil are very similar. This means that the oxidative treatment does not substantially affect the number, the type, or the distribution of the Brønsted sites.

(ii) The absorption (tail) covering the 4130–4110 cm^{-1} interval in the spectrum at maximum coverage (Fig. 1) assigned above to the $\equiv Fe(OH)Si\equiv/H_2$ interaction appears as a distinct broad band (which suggest structural heterogeneity) centred at ca. 4112 cm^{-1} in the spectra at low $p(H_2)$ (Fig. 3).

(iii) The band at 4133 cm^{-1} appears in the very early stages of the adsorption process, almost simultaneously with the previous band. This further supports the hypothesis that it is due to the interaction of H_2 and the zeolite internal surfaces.

Table 1
Frequency ($\bar{\nu}_{HH}$), shift ($\Delta\bar{\nu}_{HH}$) and assignment of the IR bands observed upon adsorption of H_2 at 20 K on Lewis and Brønsted sites of standard Fe-Sil. The literature values of the shifts $\Delta\bar{\nu}_{CO}$ observed by formation of monocarbonylic adducts on the same sites are reported in the last column for sake of comparison. The shifts were calculated with respect to the 4162 cm^{-1} ($\bar{\nu}_{HH}$; Raman active) and 2143 cm^{-1} ($\bar{\nu}_{CO}$) frequencies of the gaseous molecules

Band label	$\bar{\nu}_{HH}$ (cm^{-1})	$\Delta\bar{\nu}_{HH}$ (cm^{-1})	Assignment	$\Delta\bar{\nu}_{CO}$ (cm^{-1})
B	4050	−112	$L_2N_2Fe^{2+}/H_2$	19[a]
B′	4028	−134	L_2NFe^{2+}/H_2	30[a]
A	3990	−172	$L_3N_mFe^{3+}/H_2$	72[a]
A′	3960	−202	$L_3N_{m'}Fe^{3+}/H_2$	72[a]
Silanol	4142	−20	External OH/H_2	−5[b]
Cavities	4133	−29	Internal surf./H_2	17[b]
Brønsted	4130–4110	−32– − 52	Si(OH)Fe/H_2	29[b]

[a] From Ref. [6].
[b] From Ref. [42].

(iv) The 4142 cm^{-1} component, assigned to the H_2 interaction with surface silanols, appears in the highest pressures only, in agreement with the very weak acidity of the ≡SiOH groups. It is conceivable to assume that when this band is formed (adsorption on the external surfaces), the internal channels of the zeolite are filled by a dense H_2 phase [2] that influences the overall dielectrical properties in the zeolitic voids.

(v) The experimental data well fit the portion of Fig. 4 relative to electrostatic perturbations.

4. Conclusions

We report about the spectroscopic characterisation of a Fe-silicalite sample in terms of Brønsted and Lewis acidity by using H_2 as a probe molecule at low temperature (20 K). At 20 K, H_2 can form adducts with surface sites present in the internal (and external) surface of zeolites: Brønsted, silanols, and metal ions. The spectroscopic manifestations of the different H_2 adducts are found in distinct spectral regions depending on the nature and strength of the adducts: $\bar{\nu}_{HH}$ modes of $OH\cdots H_2$ adducts are found in the 4170–4100 cm^{-1} region, whereas those of $Fe^{x+}\cdots H_2$ adducts are found in the 4100–3900 cm^{-1} region.

In the first spectral region (4170–4100 cm^{-1}), manifestations due to the formation of H_2 adducts with ≡Fe(OH)Si≡ Brønsted sites and ≡Si–OH groups are observed on the sample activated at low temperature (573 K, protonic Fe-Sil). Increasing the temperature activation (973 K, standard Fe-Sil) results in the disappearance of the modes due to ≡Fe(OH)Si≡ Brønsted sites, in agreement with the migration of Fe framework sites to extra-framework positions. A partial amorphization of the zeolite structure after thermal treatment at 973 K is indi-

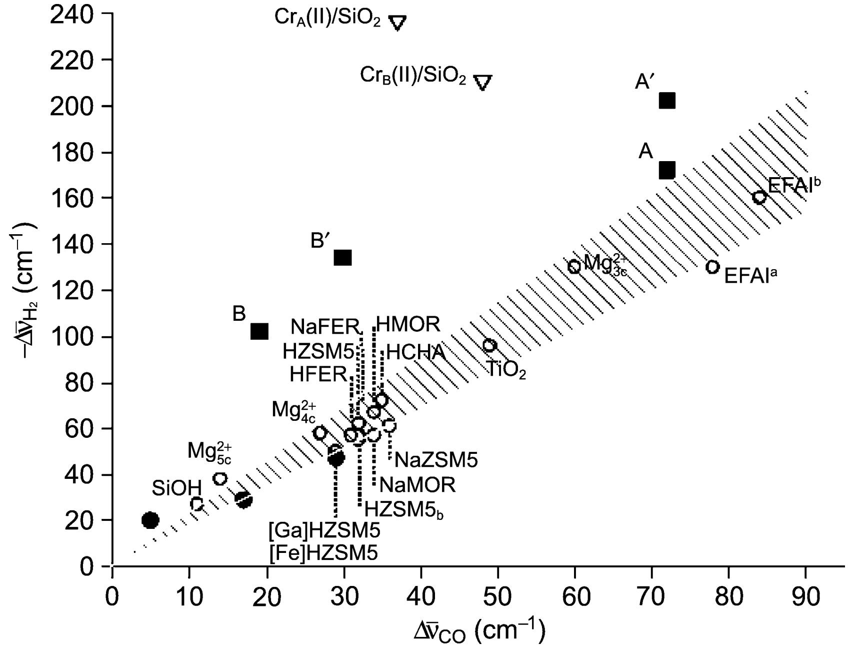

Fig. 4. Plot of the shifts $\Delta\bar{\nu}_{HH}$ for H_2 adsorbed on the Lewis or Brønsted acid sites of zeolitic and oxidic materials vs. the corresponding shifts observed for CO ($\Delta\bar{\nu}_{CO}$). Open circled data are taken from Zecchina et al. [1]. Triangles refer to the Cr^{2+}/SiO_2 system (Phillips catalyst) [41]. The data concerning the Fe-Sil Lewis acid sites are represented by filled squares ($\Delta\bar{\nu}_{CO}$ values taken from Berlier et al. [6]: A and A′ refer to Fe^{3+} centres, B and B′ to Fe^{2+}); those concerning the Brønsted sites by filled circles. The region delimited by the greyed region corresponds to H_2 and CO interaction mechanisms prevalently dominated by electrostatic forces.

cated by the disappearance of the typical modes of H_2 adsorbed at the surface of the internal zeolite channels [24].

In the second spectral region (4100–3900 cm^{-1}), bands are formed only after migration of Fe from framework to extra-framework positions (standard and oxidized Fe-Sil). Four distinct $Fe^{x+} \cdots H_2$ adducts (at 4050, 4028, 3990, and 3960 cm^{-1}) were formed on extra-framework Fe sites. The dependence on red–ox treatments of the relative concentration of these sites allowed identification of two distinct Fe^{2+} and two Fe^{3+} sites interacting with H_2 mainly by electrostatic forces. Fe^{2+} is transformed into Fe^{3+} on oxidation, and back-reduced to Fe^{2+} by thermal treatments in vacuo. This red–ox behaviour is in agreement with the catalytic activity of extra-framework Fe^{2+} sites in the selective oxidation of hydrocarbons with N_2O. Moreover, the presence of two different Fe^{2+} sites with various activities and selectivities in the decomposition of N_2O has been reported by others [17,18]. Notably, similar results, in terms of two distinct Fe^{2+} sites with different selectivities, were obtained in relation to the activity of Fe-zeolites in the selective reduction of NO_x [20]. A highly sensitive probe molecule such as H_2, sensitive to the local structure of the adsorbing site and thus able to detect small differences, could be a useful tool for characterising complex catalysts such as Fe-zeolites.

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