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Are the active sites of protonic zeolites generated by the cavities?

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Abstract

The surface hydroxyl groups and the surface acidity of silica, silicalite, silica–aluminas, silicated aluminas, aluminated silicas and silicalite, and of H-MFI and H-FER zeolites have been investigated by IR spectroscopy. CO, pyridine and lutidine have been used as molecular basic probes. The data suggest that bridging hydroxyl groups Si–OH–Al are fully stable structures only in the cavities of zeolites; they are associated to strong IR absorption bands at 3630–3500 cm^{-1} well correlated with the framework Al content. These species do not exist at the external surface of zeolites and on silicated aluminas. Extremely small bands near 3610 cm^{-1} may be found on some silica–alumina samples (mostly prepared in organic media) and on aluminated silicas. These bands certainly correspond to very few OH groups and impurities (such as bicarbonates) might contribute to their formation. On the other hand, in disordered mesoporous or microporous amorphous materials, zeolite-like pores may accidentally form and host bridging sites. Acidity-enhanced terminal silanols seem to represent the predominant Brønsted acid sites in non-zeolitic materials based on combinations of silica and alumina.

Keywords: Zeolites; Silica–alumina; Aluminated silica; Surface acidity; IR spectroscopy; CO adsorption

1. Introduction

Protonic zeolites, such as H-FER, H-MFI, H-BEA, H-MOR and H-FAU, find industrial application as acid catalysts in several hydrocarbon conversion reactions [1]. They represent environmentally friendly solid acids [2] and their use does not give rise to the environmental problems produced by the usual liquid acid catalysts such as sulphuric or fluoridric acids.

It is unanimously recognized that the bridging hydroxyl groups Al–(OH)–Si which are located at the walls of the zeolitic cavities constitute the strong acidic sites of protonic zeolites. The proton balances the charge defect due to the Al for Si substitution in the framework. The location of these sites in the interior of the cavities causes shape selectivity and molecular sieving effects. The existence of these sites is well documented through IR spectroscopy due to their strong OH stretching bands in the region 3650–3500 cm^{-1}.

Amorphous silica–aluminas have been applied for many years as cracking catalysts and find today relevant application in acid catalysis [3]. Protonic zeolites are stronger Brønsted acids than amorphous or mesoporous silica–aluminas, which have the same or very similar composition, but no zeolite-like ordered cavities. On the other hand, it is ascertained that silica–aluminas, both amorphous and mesoporous, are stronger Brønsted acids than silica and alumina.

Several studies reported that in the case of silica–aluminas no bands in the region 3650–3500 cm^{-1} of the IR spectrum are present [4–7]. The question has been discussed in a recent publication [8], where, based on our own experimental data [9,10] and on a literature review, it has been concluded that the bridging hydroxyl group could not be a stable structure on non-zeolitic surfaces. However, other investigations reported very small bands in the region of the bridging OH stretching for mesoporous silica–aluminas [11–13] and this allowed some authors to conclude that the active sites of these materials are the same as those of zeolites. New results have been reported in a very recent paper where the existence of bridging OHs on mesoporous silica–alumina has been proposed [14].

Thus the question arises on what are the requirements to form Si–(OH)–Al bridging hydroxyl groups and to have strong Brønsted acidity on silica and alumina based materials. We report here some new data on the acidity characterization of materials based on combinations of silica and alumina. The IR spectroscopy of low temperature adsorption of CO has been chosen because it is today a very popular technique for the characterization of solid surfaces [15,16], including protonic

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zeolites [17]. Experiments using also pyridine and 2,6-dimethyl-pyridine (lutidine) as molecular probes will also be discussed.

2. Experimental

2.1. Preparation procedures

Amorphous silicas were purchased from Carlo Erba (silica gel 297 $m^2\ g^{-1}$) and from Degussa (aerosil 200, ca. 200 $m^2\ g^{-1}$), commercial silica alumina (13% Al_2O_3) cracking catalyst was purchased from STREM Chemicals (330 $m^2\ g^{-1}$), 1.5 mol.% SiO_2-containing Alumina Siralox 1.5 from SASOL Germany. Silicalite was supplied by Enitecnologie.

MFI zeolite samples ($SiO_2/Al_2O_3 = 50$ and 30) were supplied by Zeolyst. FER zeolite was from Tosoh. Silica–alumina aerogels and mesoporous materials were prepared according to Refs. [18,19], respectively.

Silica, silicalite and silica–aluminas were impregnated with Al nitrate and later calcined at 723 K for 3 h to produce aluminated surfaces. 6.5% (w/w) Al_2O_3 was added.

2.2. FT-IR spectroscopic experiments

The FT-IR spectra were recorded with a Nicolet instrument with a resolution of 4 cm^{-1} using pressed disks of pure catalyst powders, activated by outgassing (generally at 773 K) into the IR cell. A conventional gas manipulation/outgassing ramp connected to the IR cell was used. The adsorption procedure involves contact of the activated sample disk with gases and vapors at increasing pressures and outgassing in steps at r.t. or increasing temperatures. Pyridine and lutidine adsorbants were purchased from Aldrich, CO cylinders were supplied by Siad.

3. Results

3.1. Characterization of the surface OHs of amorphous silicas

In Fig. 1 the spectra of two different silicas, one microporous (silica gel) and the other almost non-porous (fumed), after different activation treatments are reported. In both cases the very sharp band of the free surface silanol groups is already present near 3740 cm^{-1} after outgassing in mild conditions. It sharpens by increasing outgassing temperature, the maximum being, at the highest treatment temperature, located at 3747 cm^{-1}. Two main broad features are present in the spectra recorded after outgassing at mild temperature, at 3530–3520 and at 3660–3650 cm^{-1}. In the case of the microporous silica gel sample these absorptions are stronger (relative to the band of the free silanols) than in the case of the fumed silica. They have been assigned to clusters of H-bonded silanols [20] which at least in part condense at high temperature giving rise to siloxane bonds. In fact, their condensations do not contribute significantly to the increase of the band of free silanols [21].

The band of the residual free silanols after outgassing at 873 K is similar in both cases for position and breadth. However, in the case of the porous sample the band has a little more pronounced tail towards lower frequency, as evident in the inset of Fig. 1. In practice, it seems quite evident that the band of free silanols may actually be composed of different very sharp components, one of them being located, more or less, at 3747 cm^{-1}. This feature, according to previous studies [22,23], could be due to the geminal silanols, which are hardly distinguished from isolated silanols in the IR spectra.

The comparison of the spectra of the two silica samples show that porosity may affect the distribution between different

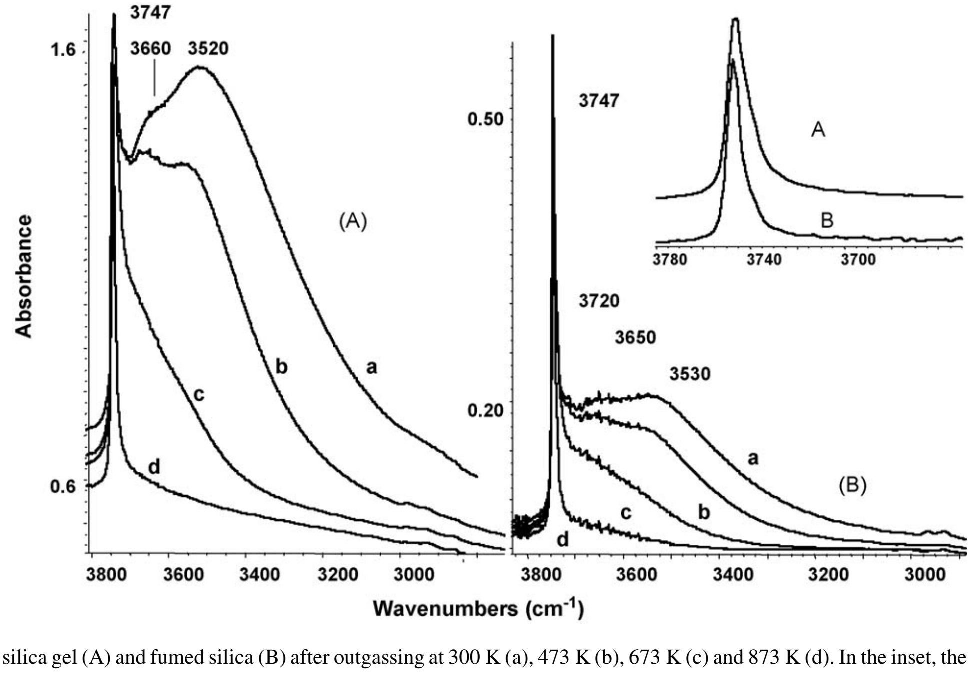

Fig. 1. FT-IR spectra of silica gel (A) and fumed silica (B) after outgassing at 300 K (a), 473 K (b), 673 K (c) and 873 K (d). In the inset, the two samples outgassed at 873 K, enlarged.

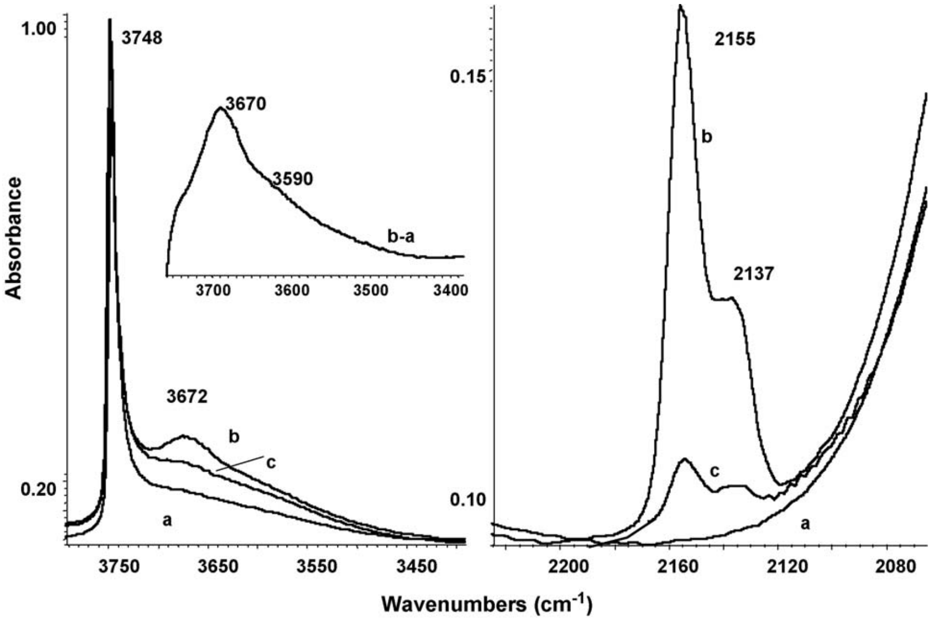

Fig. 2. FT-IR spectra of fumed silica activated at 773 K and cooled at 130 K (a), after saturation with CO at 130 K (b) and further outgassing at 130 K (c). In the inset subtraction spectrum (b)-(a).

surface structures such as isolated, geminal and vicinal H-bonded silanol groups.

In Fig. 2 the spectra relative to the experiments of CO adsorption on the fumed silica sample are reported. The spectra observed for the other silica samples are very similar. The adsorption of CO over the sample outgassed at medium-high temperature causes the partial shift of the band of the free silanols to lower frequencies. The new component, assigned to silanols interacting with CO through the lone pair at the carbon atom, is centered at 3670 cm^{-1}, but a component at 3590 cm^{-1} is also evident in the subtraction spectrum. This suggests that in the case of pure silica, in spite of the sharpness of the band of the terminal silanols, some heterogeneity of these sites occurs, part of them being more acidic than others ($\Delta\nu \sim 75$ cm^{-1}; $\Delta\nu \sim 155$ cm^{-1}).

In the CO stretching region two bands due to adsorbed carbon monoxide appear. The lower frequency one is observed at 2137 cm^{-1}, i.e. almost at the same position of the band of liquid CO. This band is observed very frequently upon adsorption of CO at low temperature on solids and is assigned to liquid-like CO. The band at 2155 cm^{-1} is well shifted above, and this indicates that an electron withdrawing center interacts with the carbon atom. This band is usually assigned to CO H-bonded to the silanol groups [20].

3.2. Characterization of the surface OHs of defective silicalite

The spectrum of defective silicalite (Fig. 3) is by far more complex, in the OH stretching region, than that of amorphous silicas. In particular, peaks are observed at 3744 (shoulder), 3726 and 3692 cm^{-1}, due to three different OH groups whose hydrogen is free from H-bonding. Additionally, a broad absorption is observed in the region 3500–3200 cm^{-1}, due to H-bonded silanols. This is due to the presence of silanol nests associated to defects in the crystal lattice [24–26]. According to Flego and Dalloro [26] the bands at 3744 and 3726 cm^{-1} are due to isolated silanols on the external and internal surfaces, respectively. The band at 3692 cm^{-1} should be due to OH in terminal positions of H-bonded chains. CO adsorbs on both internal and external silanol groups whose hydrogen atom is not involved in H-bonding (as studied in detail by Zecchina et al. [24]). The spectrum of adsorbed CO is very similar to that observed for amorphous silica, although in the case of silicalite two rotational components may be found at the higher and lower frequency sides of the main bands, located again at 2157 cm^{-1} (CO adsorbed on silanols) and at 2137 cm^{-1} (liquid-like CO). Interestingly, it seems that the CO stretching of H-bonded carbon monoxide is essentially non-sensitive to its position, either in the cavity of silicalite or in the open surface of amorphous silica and of silicalite.

3.3. Characterization of the channel OHs of H-MFI zeolite preparations

In Fig. 4 the spectrum of a typical low Al content protonic zeolite, H-MFI, is reported. As usual, it shows two bands. The band at 3748 cm^{-1} is assigned to terminal silanol groups while that observed at 3615 cm^{-1} is assigned to bridging Al–(OH)–Si groups that constitute the strong acidic sites of protonic zeolites. The very weak feature observed for this sample at 3675 cm^{-1} is assigned to OHs on extraframework material.

By adsorbing CO the most evident interaction is associated to the shift of the bridging OHs stretching band from 3615 to 3304 cm^{-1} ($\Delta\nu_{OH} \sim 310$ cm^{-1}), and to the formation of the CO stretching band at 2175 cm^{-1}. Additional OH stretching shoulders near 3480 and 3415 cm^{-1} are likely due to

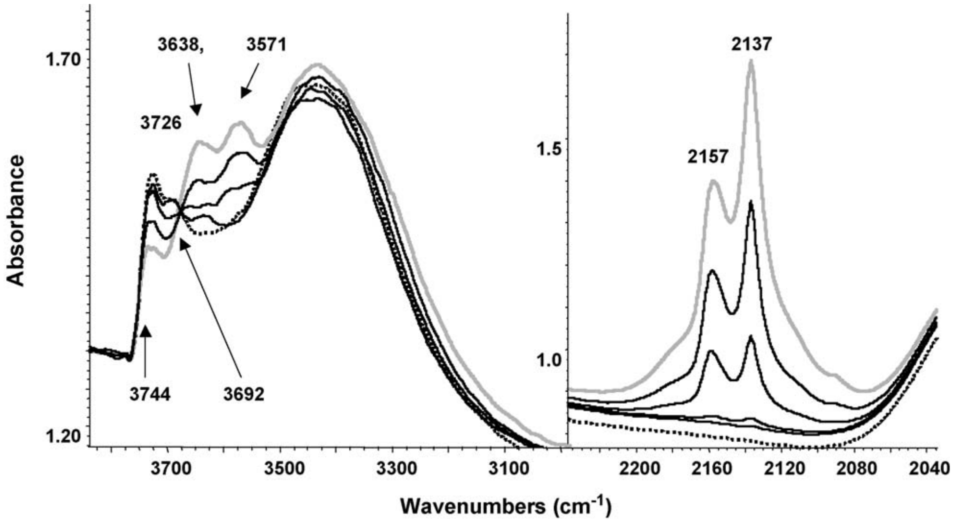

Fig. 3. FT-IR spectra of silicalite: activated at 573 K and cooled at 130 K (dotted line), after saturation with CO at 130 K (gray line) and outgassing at increasing temperatures (from top) in the range 130–180 K.

perturbation by adsorbed CO of the weak band near 3675 cm^{-1}. The further band at 2138 cm^{-1} is again assigned to liquid-like CO. Very weak features at 2230 and 2200 cm^{-1} are due to CO adsorbed on Al^{3+} Lewis sites, possibly mostly located at the external surface of the zeolite [27].

These assignments are further confirmed by the study of larger Al-content H-MFI sample (Fig. 5). The presence of extraframework material gives rise to additional bands in the OH stretching spectrum, i.e. at 3780 and 3670 cm^{-1} (Fig. 5a). The low-temperature CO adsorption experiment confirms the strong acidity of the bridging OHs of this zeolite, absorbing at 3622 cm^{-1} and shifted upon interaction with CO to 3290 cm^{-1} ($\Delta\nu_{OH} \sim 330$ cm^{-1}). Additionally, significant acidity of the OHs on extraframework material is evident (see the shift from 3670 to 3470 cm^{-1}, $\Delta\nu_{OH} \sim 200$ cm^{-1}). The shift of at least part of the terminal silanol band from 3747 to 3600 cm^{-1} ($\Delta\nu_{OH} \sim 150$ cm^{-1}) is similar to that of part of silanols of pure silica (see above), confirming their quite low acidity. Looking at the CO stretching region, CO H-bonded to the bridging OHs is essentially responsible for the strong and complex band centered at 2170 cm^{-1} but shifting, by decreasing CO coverage, to 2180 cm^{-1}. Additionally, the ν_{CO} components at 2230 and 2194 cm^{-1} are certainly due to Al^{3+} ions acting as strong Lewis sites.

As a summary, we conclude, in agreement with the previous literatures [15,17], that the interaction of CO with the very strong Brønsted acidic bridging OHs of the zeolites causes a shift down of their OH stretching of around 310–330 cm^{-1} and the shift up of the CO stretching of more than 30 cm^{-1}, to 2170–2180 cm^{-1}. These OHs are, in all zeolites, responsible for a band observed in the region 3650–3500 cm^{-1}, generally well evident and quite sharp. The weaker interaction of CO with terminal silanols gives rise to a shift down of the OH stretching of no more than 160 cm^{-1} with a shift up of the CO

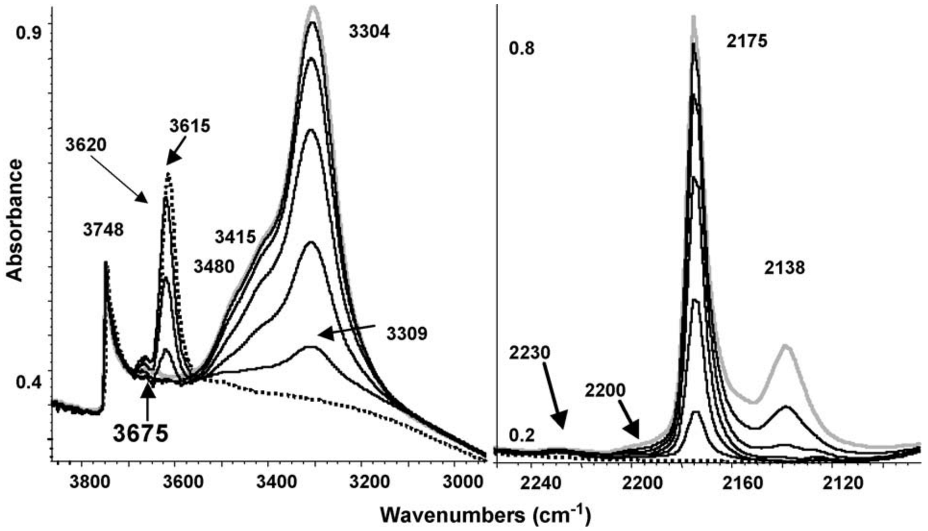

Fig. 4. FT-IR spectra of H-MFI (SiO_2/Al_2O_3 = 50): activated at 773 K and cooled at 130 K (dotted line), after saturation with CO at 130 K (gray line) and outgassing at increasing temperatures (from top) in the range 130–180 K.

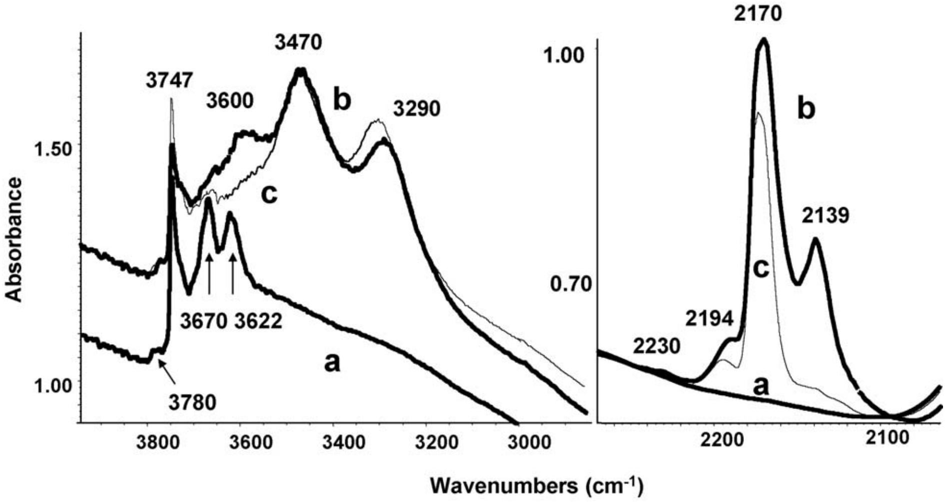

Fig. 5. FT-IR spectra of H-MFI ($SiO_2/Al_2O_3 = 30$) activated at 773 K, recorded at 130 K (a), after saturation with CO at 130 K (b) and outgassing at 170 K (c).

stretching of less than 20 cm^{-1} up to 2160–2155 cm^{-1}. OHs of extraframework material have intermediate acidity ($\Delta\nu_{OH} \sim 200$ cm^{-1}).

3.4. Characterization of the external acid sites of protonic zeolites

To test the external surface of zeolites, bulky molecular probes are needed that are not able to access the cavities. A similar experiment has been carried out with ferrierite zeolite using 2,6-dimethyl-pyridine as a molecular probe (Fig. 6). This molecule has been proposed for testing the external surface of zeolites by volumetric titration [28]. In this case the OH stretching band of internal bridging OHs at 3600 cm^{-1} is fully unperturbed, showing that 2,6-lutidine does not enter at all the cavities of H-FER. This is expected because the cavity size of ferrierite does not allow the entrance of aromatics at r.t. The total absence of any perturbation of the band of bridging OHs, conversely, demonstrates that they are not located at the external surface onto which lutidine is allowed to adsorb. On the contrary this probe causes the full disappearance of the band of terminal silanols (3745 cm^{-1}) which is, at least in part, shifted to lower frequencies. The adsorption of 2,6-lutidine, certainly occurring on the external surface, is both molecular (bands at 1600 and 1570 cm^{-1}) and reactive (bands of lutidinium cations at 1650–1625 cm^{-1}). However outgassing at 373 K causes the almost complete disappearance of the molecular forms, the protonated form being retained. This shows, in agreement with our previous data [27], that at least part of the silanols at the external surface of H-FER carry significant Brønsted acidity. Lewis acidity, due to

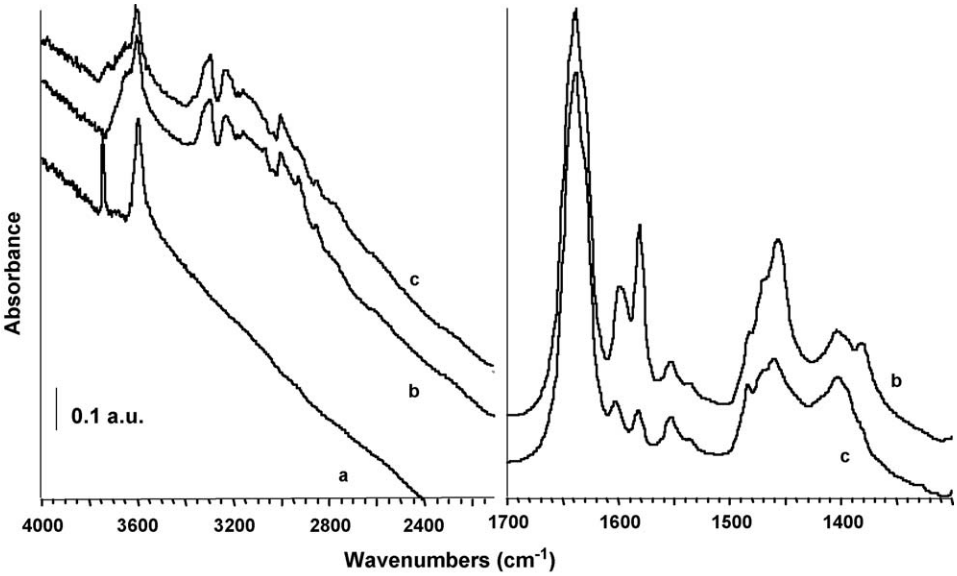

Fig. 6. FT-IR spectra of H-FER activated at 773 K (a), put into contact with lutidine vapor at r.t. (b) and outgassed at 373 K (c). In the right section the spectrum of H-FER has been subtracted.

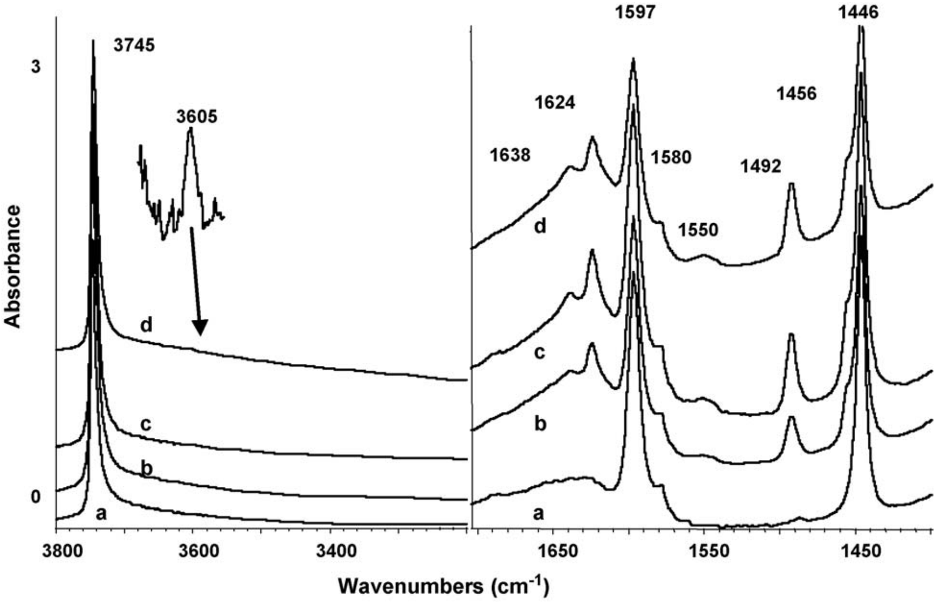

Fig. 7. FT-IR spectra of pure silica (a) and of silica containing 2% (b), 4% (c) and 8% (w/w) alumina (d) aerogels after activation at 773 K (left) and after adsorption of pyridine at r.t. (right).

incompletely coordinated Al cations, is present as well at the external surface of H-FER.

Similar studies from this laboratory have been devoted to the differentiation between internal cavity sites and external surface sites in protonic zeolites. This has been done using differently hindered nitriles that are able to enter the cavities or, on the contrary, only to interact with the external surface of the zeolites. In particular it has been shown that 2,2-dimethyl-propionitrile (pivalonitrile) does not enter, at room temperature and low partial pressures, the cavities of H-FER and H-MFI. To make a similar experiment for H-MOR the use of a more bulky compound, 2,2-diphenyl-propionitrile has been necessary. These studies showed that in the cases of H-FER [27], H-MFI [27] and H-MOR [8,29] the bridging OHs are only located at the internal surface while terminal silanols are essentially located at the external surface although they may also be observed in defects of the internal structure of defective protonic zeolites.

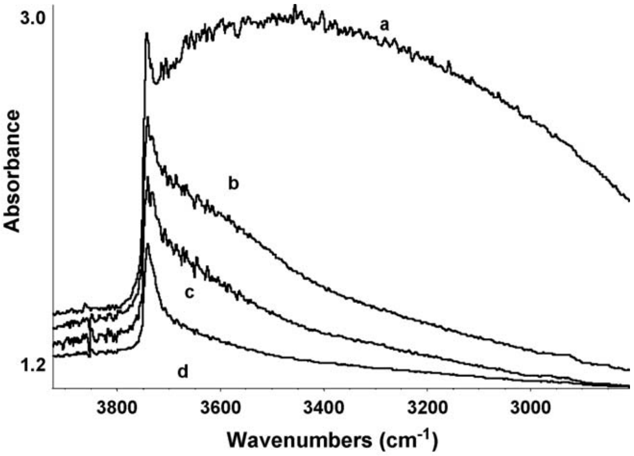

Fig. 8. FT-IR spectra of mesoporous silica–alumina (Si/Al = 15) outgassed at 300 K (a), 573 K (b), 673 K (c) and 773 K (d).

3.5. Characterization of the surface OHs of amorphous and mesoporous silica–alumina

The spectra of silica–aluminas (either mesoporous or microporous) always present, like for pure silica, a very prominent sharp band at 3746 cm^{-1}. In Fig. 7 the spectra of aerogel materials constituted by pure silica and by silica containing 2, 4 and 8% (w/w) alumina are reported after activation. In all cases the spectrum shows the band of terminal silanols a little asymmetric. Only in the case of the sample containing 8% alumina (Si/Al ratio 9.2) an extremely weak additional feature just at 3605 cm^{-1} is observed. The area of this peak corresponds to 0.5% of the area of the main OH stretching band at 3745 cm^{-1}.

In the right part of Fig. 7 the spectra of pyridine adsorbed on the four samples are shown. On pure silica only H-bonded pyridine is observed (vibrations denoted as 8a and 19b, bands at 1597 and 1446 cm^{-1}). On the Al-containing sample also Lewis bonded pyridine is observed (vibrations denoted as 8a and 19b, bands at 1624 and 1456 cm^{-1}). Additionally, also the features of pyridinium ions are observable weak though, only in the case of the Al-containing samples, mostly characterized by the 8a, 19b and 19a vibrations with bands at 1638, 1550 and 1492 cm^{-1}. This shows that the presence of Al in amorphous silica produces some Brønsted acidity, in agreement with the previous literature.

In Fig. 8 the spectra of a silica–alumina MCM41-type mesoporous material (Si/Al = 15) are shown after different activation treatments. Again, a tail at the lower frequency side of the band of silanol groups is evident but, for all mesoporous samples we investigated, never a definite band in this region has been found [5].

In Fig. 9, the spectrum of a commercial cracking catalyst, a silica–alumina with 13% (w/w) alumina, is shown. It also shows the strong band of terminal silanols at 3746 cm^{-1}

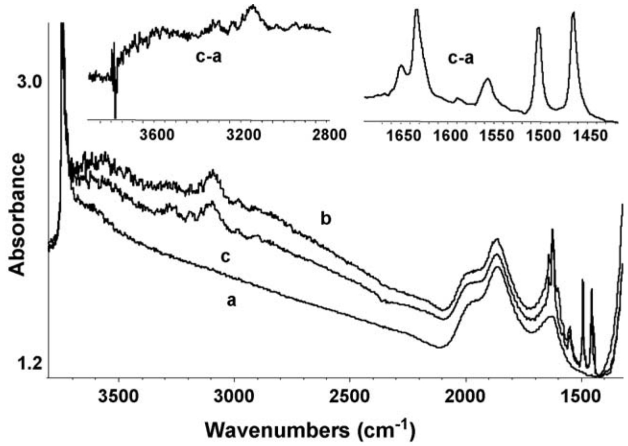

Fig. 9. FT-IR spectra of a 13% silica–alumina after outgassing at 773 K (a) after contact with pyridine vapor (b) and after outgassing at 373 K (c). In the insets, the subtraction spectrum c − a.

together with a broad absorption in the region 3700–3500 cm^{-1}. However, this absorption does not show any well evident maximum. After adsorption of pyridine, H-bonded and Lewis bonded pyridine together with pyridinium ions are observed. After outgassing at 373 K all H-bonded pyridine disappears, leaving only Lewis bonded pyridine and pyridinium ions. In the subtraction spectrum a negative sharp band is observed in these conditions near 3740 cm^{-1}. No trace is found of any evident peak near 3600 cm^{-1} in the subtraction spectrum nor in the original ones.

In the left part of Fig. 10 we show the spectrum of the same microporous commercial silica–alumina catalyst recorded at 130 K after activation at 873 K. The main band is again at 3748 cm^{-1}, with a tail towards lower frequencies. The inspection of the spectrum could allow to envisage an extremely small component at 3610 cm^{-1} (the asterisk in Fig. 10(left)). However this feature is so small that it cannot be really distinguished from the noise. Additionally, automatic smoothing procedures cancel it. As we discussed elsewhere [30], instead, components in the main band can be distinguished although the difference of their maxima is also so small that the resolutions is doubtful.

Over amorphous silica–alumina (Fig. 10, right) the spectra of adsorbed CO show a band at very high frequencies (2231 cm^{-1}) and a broad component near 2200 cm^{-1}, which can be attributed to CO on Lewis acidic Al^{3+} ions. The bands at 2173 and 2156 cm^{-1} may be attributed to CO interacting with two different kinds of hydroxyl groups, one of them being strongly acidic zeolite-like (2173 cm^{-1}) the other one weakly acidic silica-like (2156 cm^{-1}). On the other hand, after adsorption of CO at least three weak components are observed in the OH stretching region, at 3667, 3580 and 3415 cm^{-1}, due to three different H-bonded complexes with CO.

Because of the absence of other evident features, it is straightforward to attribute the three observed absorptions at 3667, 3580 and 3415 cm^{-1}, to three different types of terminal silanol groups that when unperturbed give place to an unresolved band near 3748 cm^{-1}. The first two components are very similar to those observed on pure silica (see Fig. 2) but the third one is only evident in silica–aluminas.

This means that the presence of Al ions gives rise to few silanol groups whose acidity is strongly enhanced: the shift undergone by the band of these OHs upon CO adsorption is $\sim$330 cm^{-1}, just as that undergone by the zeolitic bridging OHs. This agrees with the position of the CO stretching band, observed at 2173 cm^{-1}.

3.6. Characterization of the surface OHs of aluminated silica and aluminated silicalite

In order to have further information, we investigated silica and silicalite samples where Al species have been added by impregnation. In Fig. 11 the spectra relative to the adsorption of CO over an ‘‘aluminated silica’’ sample are reported. The

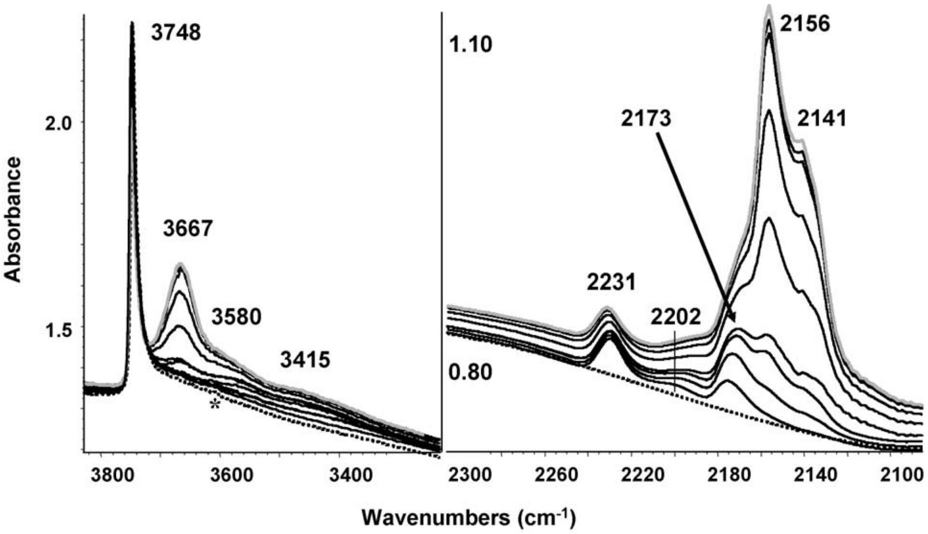

Fig. 10. FT-IR spectra of a 13% silica–alumina: activated at 773 K and cooled at 130 K (dotted line), after saturation with CO at 130 K (grey line) and outgassing at increasing temperatures (from top) in the range 130–180 K.

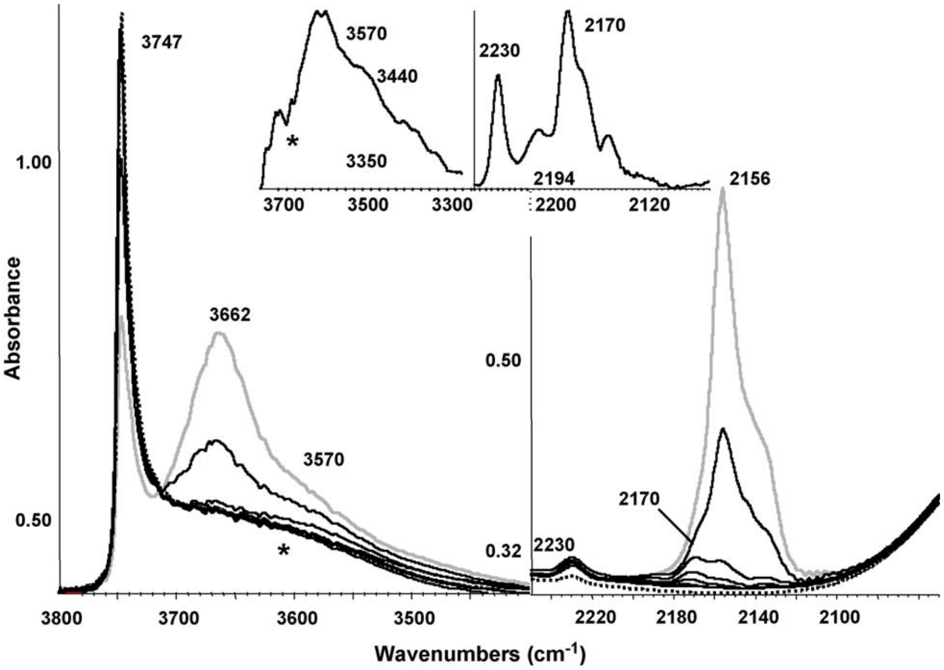

Fig. 11. FT-IR spectra of aluminated silica: activated at 773 K and cooled at 130 K (dotted line), after saturation with CO at 130 K (grey line) and outgassing at increasing temperatures (from top) in the range 130–180 K. In the insets, subtraction spectrum, (grey line spectrum)-(dotted line spectrum).

addition of Al ions causes a small decrease of the OH stretching band intensity at 3747 cm^{-1}, with the apparent growth of the broad tail at its lower frequency side. The presence of an extremely small peak near 3610 cm^{-1}, shown in the spectrum with an asterisk, is very doubtful indeed. However, upon adsorption of CO a negative very weak peak can be found in the subtraction spectrum recorded upon outgassing, near this frequency (the asterisk in the inset), together with a new weak positive component near 3440 cm^{-1} and those, found also for pure silica, at 3662 and 3570 cm^{-1}. An additional weak component is also possibly observed near 3350 cm^{-1}. In the CO stretching region a well evident component appears at 2170 cm^{-1} together with the bands at 2156 and 2137 cm^{-1} observed also in the case of pure silica. Additionally, peaks at 2230 and 2194 cm^{-1} are observed (see the subtraction spectrum in the inset), due to CO adsorbed on Lewis acidic Al^{3+} ions. The peak at 2170 cm^{-1}, together with the components near 3440 cm^{-1} and 3350 cm^{-1} (the last extremely weak) suggests that CO also adsorbs on Brønsted acidic OHs. It seem very likely that the extremely weak component at 3350 cm^{-1} is due to the shift of the extremely weak peak found at 3610 cm^{-1}. The corresponding shift is $\Delta\nu \sim 260$ cm^{-1}. On the contrary the more evident component at 3440 cm^{-1} is most likely due to the shift of one of the unresolved components in the main peak at 3747 cm^{-1}. This should confirm that strongly acidic terminal silanols actually exist ($\Delta\nu \sim 300$ cm^{-1}).

The formation of a weak but well evident peak at 3615 cm^{-1} has been found in the case of aluminated silicalite, as evident in the spectra in Fig. 12 and in the subtraction spectrum found in

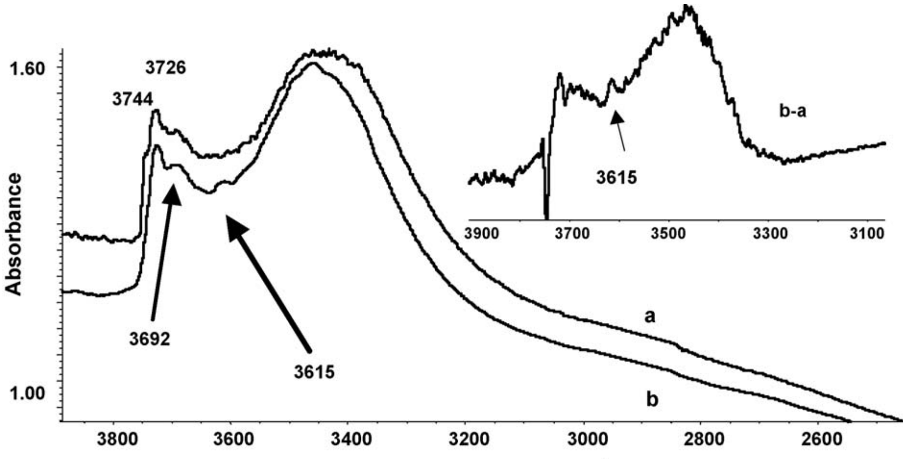

Fig. 12. FT-IR spectra of silicalite (a) and aluminated silicalite (b) after activation at 573 K. Inset: subtraction spectrum (b)-(a).

the inset. The addition of aluminum clearly causes a decrease in intensity of the band at 3744 cm^{-1} and this indicates that Al species exchange the external surface silanols. However, also the absorption near 3300 cm^{-1} decreases in intensity while that near 3400 cm^{-1} increases in intensity. These features suggest that part of Al ions are located near the silanol nests of defective silicalite and perturb them. Part of Al ions possibly go to occupy the vacant Si positions of defective silicalite [24] and build up bridging hydroxyl sites.

The CO adsorption experiments on aluminated silicalite do not allow to show definite differences with respect to that on pure silicalite, shown in Fig. 3 except for a very little band at 2170 cm^{-1}, showing that strong Brønsted sites, similar to those of H-MFI zeolite, may be present.

3.7. Characterization of the surface OHs of silicated alumina

Studies of the surface acidity of silicated alumina [9] and of aluminas containing small amounts of silica [31] have been reported some years ago. Here we report data on a commercial sample of silica-containing alumina (Fig. 13). The IR spectrum of the activated sample shows sharp bands at 3728 and 1071 cm^{-1} which have been attributed to OH stretching and Si–O stretching, respectively, of a surface hydrogen-silicate ion. In Fig. 13 the spectra relative to the adsorption of pyridine on this sample is reported. It is shown that protonation of pyridine does not occur at all on this sample, as usually observed for alumina samples containing small amounts of silica [9,31]. Lewis bonded pyridine, characterized by the bands at 1614 cm^{-1} (vibration 8a) and 1456 cm^{-1} (vibration 19b) is well evident and in parallel the Si–O stretching band of the hydrogen-silicate group shifts to 1030 cm^{-1}. Hydrogen-bonded pyridine is also formed (vibration 8a, band at 1595 cm^{-1}) and a broad OH stretching band in the region 3600–3200 cm^{-1}. This suggests that pyridine Lewis bonds on Al ions and H-bonds on terminal hydrogen-silicate species. One can suppose that silanol groups and aluminum ions can work as a ‘‘drawbridge’’: on the surface of silicated alumina the drawbridge is open while in the zeolites is closed.

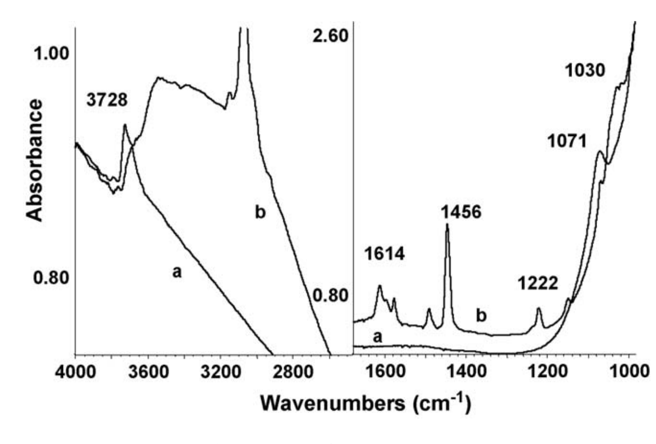

Fig. 13. FT-IR spectra of activated 1.5% SiO_2-containing alumina activated at 773 K (a) and after adsorption of pyridine (b).

4. Discussion

The IR spectra here described show that all silica-containing materials are characterized by a sharp band in the 3750–3720 cm^{-1} region due to the OH stretching of terminal silanol groups. On the materials where silica is predominant this band is mostly located in the range 3750–3740 cm^{-1}, while when silicate ions are deposed on ionic oxides (like on alumina, see above and [9,31], but also on titania [32]) the position is at slightly lower frequencies (3740–3730 cm^{-1}). For terminal silanols in internal defects of zeolites, like in silicalite (see above and Refs. [24,26]), H-MFI [27], H-BEA [33] and H-MOR [34] the position is mostly near 3725 cm^{-1}. On the other hand, the silanol band, although generally sharp, may contain unresolved or poorly resolved components. According to some authors the position of the band of geminal silanols is at slightly lower frequency than that of the isolated ones [22,23]. The spectra above show that at least two different families of silanol groups exist on silicas, whose OH stretching bands are unresolved when they are free: they can be distinguished by their different shift upon adsorption of molecules like CO. It is also evident that the porosity of the sample may significantly affect the distribution of isolated, geminal and vicinal silanols.

Our data also confirm, in agreement with all the literature, that the band of bridging Si–OH–Al groups is well evident in the region 3630–3550 cm^{-1} in the case of protonic zeolites like H-MFI and H-FER. When the bridging OHs interact with a weak basic probe molecule like CO, this band shifts very much according to the strong acidity of the hydroxyl groups and its perturbed position is well evident.

The bridging hydroxyls of zeolites, instead, do not interact with bulky bases that do not enter cavities. Thus, apparently they exist only in the zeolite cavities. At the zeolites external surface bridging OHs do not exist. Also in the case of all samples where silica and alumina mix but that lack of structural porosity, a band at the same position cannot be seen at all, or is extremely weak, in a few cases.

The addition of silicate species to alumina (at the surface or in the bulk) does not produce bands in the region of bridging OHs, nor significant Brønsted acidity is observed. This is explained supposing that the silicate species tend to maximize the interaction with the bulk of alumina by orienting three oxygen atoms towards the bulk, while the fourth necessarily stands up, with respect to the surface. To limit the free energy, the fourth oxygen standing up binds with a proton. It seems obvious that it cannot bend to bridge surface aluminum cations. Thus only terminal silanols exist on silicated aluminas. The resulting Brønsted acidity is consequently that of isolated silanols, and it is weak.

The addition of Lewis acidic Al ions to open surfaces containing terminal silanols, like that of silica, does not cause a significant decrease of the sharp band of terminal silanols, nor the formation of new OH stretching bands having significant intensity. Only an extremely weak band in the position typical for bridging OHs is observed, if at all. Evidence for the formation of quite strong and abundant Brønsted acid centers is, however, provided by the detection of a well evident CO band at

2170 cm^{-1}. The position of this peak is at slightly lower frequency with respect to the typical position of CO interacting with the Brønsted acid sites of zeolites (2174–2180 cm^{-1}), but at definitely higher frequency than CO adsorbing on "normal" silanols (2155–2157 cm^{-1}). As above discussed, the most abundant Brønsted acidic sites in aluminated silica are apparently part of terminal silanols that shift from near 3740 to 3440 cm^{-1} ($\Delta\nu \sim 300$ cm^{-1}) by H-bonding CO, although a very small amount of bridging OHs may exist and shift, upon interaction with CO, from near 3610 to 3350 cm^{-1} ($\Delta\nu \sim 260$ cm^{-1}).

On some silica–alumina samples and after some activation procedures, extremely weak bands near 3610 cm^{-1} can be seen, in full agreement with Góra-Marek et al. [14] and some previous literature data [11,12]. These small bands are usually present in samples produced in the presence of organic precursors. It is not excluded that they might arise from impurities, like bicarbonate ions which have typically the OH stretching just near 3610 cm^{-1}. Alternatively, the presence of this band may suggest that very few bridging hydroxyl groups may exist in some silica alumina samples. Parallel ^{1}H NMR and IR studies show that the IR extinction coefficient of the bridging OHs is far higher than for silanol groups [35]. Consequently, the bridging OHs in silica–aluminas are, if any, extremely few even when the weak feature at 3610 cm^{-1} is observed.

Accordingly, in contrast with Ref. [14], we believe that these sites, if actually exist, are not responsible for the Brønsted acidity of silica–aluminas. Brønsted acidity is, in fact, evident also for samples in whose spectrum this band is not present at all. All data we have indicate that there is no relation between the ability of the surface to protonate pyridines or to give rise to the band of H-bonded CO at ~2170 cm^{-1} and the presence of the band at 3610 cm^{-1}, always very weak when present. In our opinion the data show that the enhanced acidity of part of terminal silanols contributes in a predominant way to the Brønsted acidity of silica–aluminas. This conclusion seems to be in agreement with the results of ^{1}H MAS NMR studies [36–38] and ^{27}Al MAS NMR techniques [39,40] which provide evidence for a structurally different active site in silica aluminas with respect to zeolites.

The data reported here suggest that bridging hydroxyl group are fully stable structures only in the cavities of zeolites, where they produce strong bands well correlated with the framework Al content, and a well evident sharp ^{1}H NMR resonance near 4.6–4.2 ppm [36–38]. Advanced NMR techniques indicate that the most acidic protons in different silica–aluminas preparations resonate at 3.8 ppm [37], 3.5 ppm [41] or at 2.6 ppm [42], i.e. at a well distinct position. The presence of very weak features at 3610 cm^{-1} in some silica–alumina preparations, if not due to impurities, may indicate that in these disordered mesoporous or microporous amorphous materials, zeolite-like pores may accidentally form and host these bridging sites.

The lack of substantial formation of these sites by reacting silica surfaces with Al ions or alumina surfaces with silicate ions, and also on mixed oxides, such as silica–alumina, provides evidence for a substantial instability of the Si–OH–Al bridge which is likely stabilised by the rigidity of the zeolite framework and/or by some interaction of the proton with the opposite wall of the cavity. In agreement with this, it is quite evident that the position of the OH stretching is somehow sensitive to the size of the cavity, as discussed elsewhere [29,8].

Finally, we would like to mention that clusters containing bridging Si–OH–Al groups, utilized in the past to model the active sites of silica–aluminas and zeolites, are possibly not good models for both. We believe that these bridges are not the active sites of most silica–aluminas. Additionally, they do not exist without the opposite wall of the zeolitic cavities, which likely contributes to their stabilization. Thus, the model of protonic zeolites, in order to be reliable, should include the cavity.

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