The origin of the band at 1462 cm^{-1} generally appearing upon desorption of pyridine from acidic solids. Steps towards a more comprehensive understanding

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The pyridine adsorption–desorption method, followed by IR spectroscopy, is generally applied for acidity determination of solid catalysts. A peculiar band at 1462 cm^{-1} was observed by several authors upon pyridine desorption at higher temperatures and was interpreted in various ways. A new complex between Lewis framework acid sites and pyridine is proposed and several evidences are reported.

Keywords: acidity; pyridine adsorption–desorption; IR spectroscopy; zeolites; silica–aluminas

1. Introduction

Pyridine adsorption monitored by IR spectroscopy has been a generally accepted and applied method for determining the acidity of solids for a long time [1]. Generally two bands are observed, which are attributed to pyridine–acid sites interaction [2]: the absorption of pyridinium ions (generated by interaction of pyridine with Brønsted acid sites) at 1540 cm^{-1}, and that of the coordinatively bonded pyridine complexes (formed in the interaction between pyridine and Lewis acid sites) at 1455 cm^{-1}. Measuring the desorbed amount of pyridine bonded on Brønsted and Lewis sites, using the decrease of intensities of IR bands at 1540 and 1455 cm^{-1} as measure, valuable information is obtained about the strength of these acid sites [2–4]. Upon desorption of pyridine at higher temperatures, a peculiar band appears very often at about 1460 cm^{-1} [1,5]. The position of this band is at higher frequencies than that usually assigned as Lewis site bonded pyridine at 1450–1455 cm^{-1}. This new adsorbed pyridine band has been interpreted in various ways.

Some authors suggested that it is a signal of pyridine adsorbed on strong Lewis acid centres, as this band appears at higher frequency than the usual Lewis–pyridine band [3,4,6]. These Lewis acid sites are assumed to be formed upon heat treatment as a result of dehydroxylation and/or dealumination of zeolite [7].

The band at 1462 cm^{-1} is generally observed upon desorption of pyridine at higher temperatures, but not adsorption. This finding led to the second explanation, which is simply as follows: there are acid sites inaccessible for pyridine at about room temperature [8].

The third probability is the formation of these surface species at high temperature from pyridine already bonded to the solid, since conjugated iminium ions (dihydropyridinium ions) were detected by UV–Vis spectroscopy as surface intermediates in dealuminated mazzite [9].

According to the fourth assumption, modification and decomposition of adsorbed pyridine were also suggested as source of splitting the Lewis–pyridine band at 1455 cm^{-1} [10].

As the appearance of the band at 1462 cm^{-1} upon pyridine desorption is common for acidic solids, the understanding of its chemistry is of utmost importance. The points to be cleared up are the following: (i) the link between the presence of extraframework aluminium and the appearance of the band at 1462 cm^{-1}, (ii) the generation of tricoordinated aluminium ions as intermediate sites on pyridine ad- and desorption, (iii) the connection of this new absorption with Brønsted acidic centres of zeolite.

In this paper, we report on results concerning the assignment of the band discussed previously.

2. Experimental

Zeolite β after different treatments, H-ZSM-5 zeolite and amorphous silica–aluminas were tested. The two silica–aluminas were commercial samples from Solvay Catalysts (PK 200) and from AKZO Chemie (HA-1.5E) having different Si/Al ratios but similar BET areas. Zeolite H-ZSM-5 and β were prepared in our laboratories. The main characteristics of samples are summarized in table 1.

Table 1
Characteristics of samples used in the experiments

Sample	Si/Al	Al/Na	Acidity (mmol/g)	
			Brønsted	Lewis
AS-β	14	1.9	0.28	0.26
BO-β	14	1.9	0.15	0.49
NH-β	14.5	>100	0.26	0.15
H-β	14.5	>100	0.26	0.18
D-β	16.5	>100	0.28	0.09
HZSM-5	46.4	>40	0.19	0.04
HA-1.5E	12.5	–	0.03	0.06
PK-200	7.6	–	0.04	0.18

AS-β is an "as-synthesized" material containing template and sodium ions. After burning the template off at 823 K a sample designated as BO-β was obtained which contained sodium ions as charge compensating cations. Exchanging this sample in ammonium-acetate solution sodium ions were replaced for ammonium ions (after repeated ion-exchange three times only traces of sodium were detected), this sample is marked as NH-β, H-β sample was prepared from NH-β by heat treatment at 823 K in air. Dealuminated zeolite β (D-β) was obtained after acid leaching of the H-β sample in 0.1 mol/ℓ HCl solution.

H-ZSM-5 zeolite was prepared from its sodium form by ion-exchange in ammonium-acetate solution followed by heat treatment at 823 K in air.

Commercial silica–alumina samples were used without any modification.

From specimens self-supported wafers (with a thickness of 10 mg/cm^2) were pressed, placed into the sample holder of the IR cell and outgassed at 773 K in vacuum for 1 h before the pyridine adsorption experiments were performed.

The method we used for pyridine ad- and desorption was as follows. After pretreatment at 773 K in vacuum, the wafers were loaded to 10 Torr of pyridine at room temperature, treated in the presence of pyridine at 473 K for 1 h followed by evacuation at 473, 573, 673 and 773 K for an additional hour. From the integral absorbances of the corresponding bands and the thickness of wafer, the concentrations of acid sites were calculated using published extinction coefficients of pyridine bonded to Brønsted or Lewis acid sites [11].

Spectra were recorded with a Perkin-Elmer 1730 FT-IR spectrometer and processed using IR DM II software.

3. Results

Fig. 1 shows the spectra of adsorbed pyridine for AS-β (A), BO-β (B), NH-β (C) and H-β (D) zeolites. Each sample has Brønsted and Lewis acidity. Bands at 1446, 1456, 1490 and 1544 cm^{-1} are attributed to pyridine on sodium ions, Lewis acid sites, combination band of pyridine on Lewis and Brønsted sites and Brønsted sites, respectively. For samples without sodium ions, the corresponding absorption is absent. With increasing desorption temperature the intensities of both Brønsted and Lewis bonded pyridine bands at 1544 and 1456 cm^{-1} decreased. Simultaneously, partial restoration of OH vibrations took place as can be seen in the spectra of pyridine perturbed OH vibration of OH groups for AS-β (a) and D-β (b) zeolites in fig. 2. The OH vibrations associated with extraframework aluminium (~3660 cm^{-1}) appeared first, followed by those of bridged hydroxyls at 3618 cm^{-1}. The latter wavenumber was somewhat higher than those measured before pyridine adsorption for the activated samples (3605 cm^{-1}). When desorption was performed at 673 K a new Lewis–pyridine band appeared at 1462 cm^{-1}, and became clearly observable for AS-β, less pronounced for NH-β and hardly visible for BO-β and H-β samples after evacuation at 773 K.

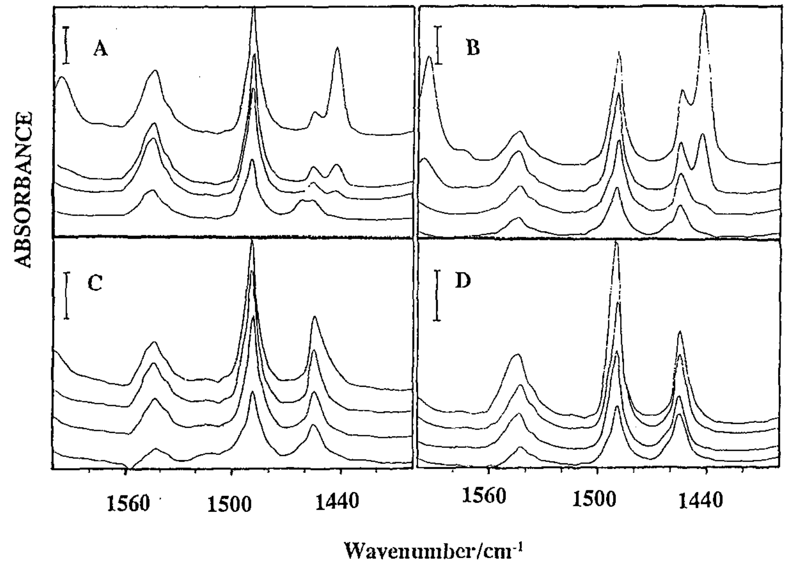


Fig. 1. Spectra of pyridine desorbed at 473, 573, 673 and 773 K (from top to bottom) in vacuum from AS-β (A), BO-β (B), NH-β (C) and H-β (D) zeolite samples. (|——|) corresponding to 0.2 of absorbance.

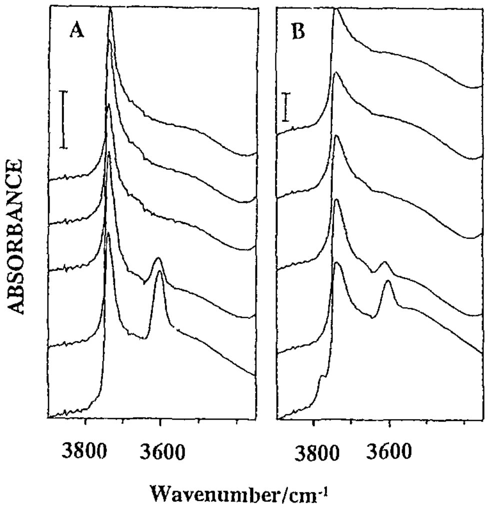


Fig. 2. Spectra of OH groups perturbed by adsorbed pyridine for AS-β (A) and D-β (B) samples. Spectrum of unperturbed sample and after desorption of pyridine at 773, 673, 573 and 473 K (from top to bottom). (|——|) corresponding to 0.1 of absorbance.

In fig. 3 spectra of pyridine adsorbed on zeolites D-β and H-ZSM-5 are depicted. After evacuation of pyridine loaded samples at increasing temperature, the new Lewis–pyridine band developed. Here again, the appearance of this new band occurred parallel to the partial reappearance of OH bands. It is to be noted, that the position of the new Lewis bonded pyridine band is identical for each sample.

The feature of pyridine desorption was also similar for amorphous silica–aluminas (fig. 4). Here, for these samples the new band is not as developed as for zeolites, nevertheless, they are well detectable.

4. Discussion

As far as the origin of the pyridine band at 1462 cm^{-1} is concerned, our results do not prove strict correlation between the presence of extraframework aluminium in the sample and the appearance of this band. The arguments to this point are as follows: (i) The AS-β sample, not treated under conditions leading to dealumination, does not contain extraframework aluminium, however shows the new bands at 1462 cm^{-1}, the intensity of which is very close to that of the dealuminated D-β sample (figs. 1 and 3), containing 14% octahedral aluminium as been proven by ^{27}Al-NMR spectroscopy [12]. (ii) Further, for amorphous silica–alumina samples, where heat treatment does not result in essential structural modification, the new

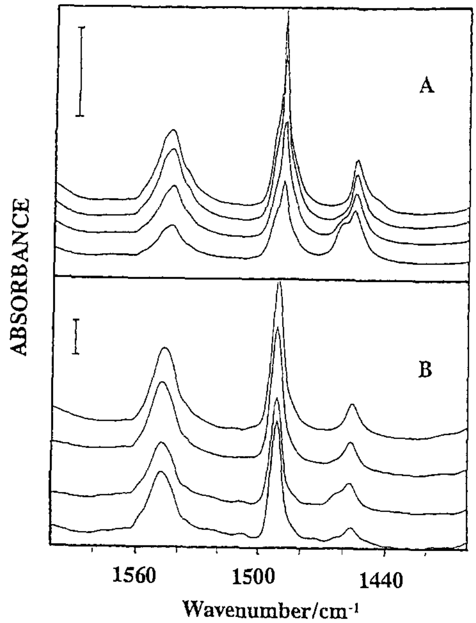


Fig. 3. Spectra of pyridine after desorption at increasing (473, 573, 673 and 773 K, from top to bottom) temperatures for D-β (A) and HZSM-5 (B) zeolites. (├──┤) corresponding to 0.2 of absorbance.

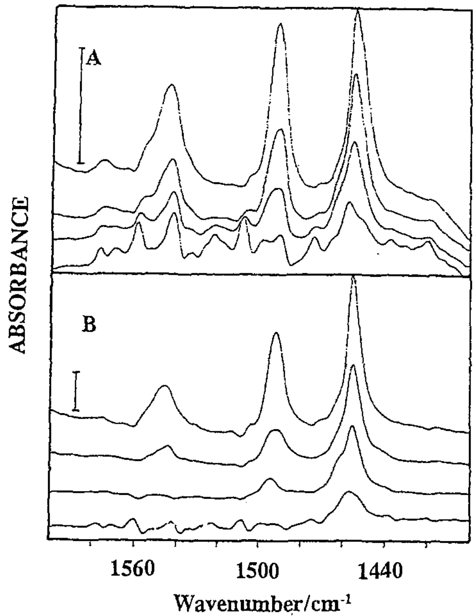


Fig. 4. Spectra of pyridine desorbed at different temperatures from HA-1.5E (A) and PK 200 (B) amorphous silica–alumina samples. (Desorption temperatures were 473, 573, 673 and 773 K, from top to bottom.) (|——|) corresponding to 0.15 of absorbance.

Lewis–pyridine band can still be detected (fig. 4). (iii) On the other hand, on the H-β sample, which had 71% tetrahedral and 29% octahedral aluminium, the new Lewis–pyridine band is hardly detectable (fig. 1).

Our results did not give evidence for occurrence of irreversible change in the structure of zeolites or amorphous materials upon pyridine desorption. Therefore

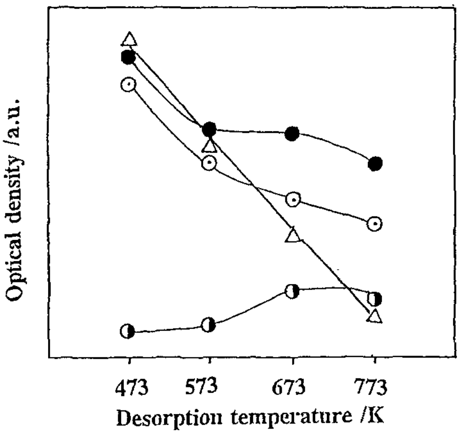


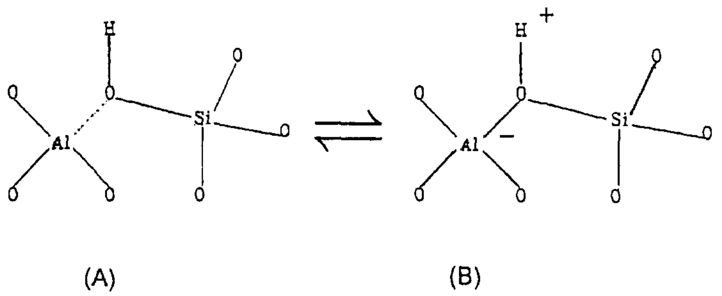
Fig. 5. Change of optical density of bands due to different pyridine complexes. (⊙) 1445 cm^{-1}, (◑) 1462 cm^{-1}, (●) the sum of (⊙) and (◑), (△) 1546 cm^{-1} due to Brønsted–pyridine.

the origin of this adsorbed pyridine band at 1462 cm^{-1} should be sought in the adsorption–desorption process.

The role of water in generation of surface species absorbing at 1462 cm^{-1} is also excluded since we have not detected water formation during pyridine desorption. Fajula et al. came to the same conclusion from their rehydration experiment [7].

We found that the Lewis- and Brønsted–pyridine bands at 1455 and 1545 cm^{-1} decrease, whereas that at 1462 cm^{-1} increases above 573 K desorption temperature (fig. 5). It follows that the source of pyridine required for generation of new Lewis–pyridine complex, which gives the band at 1462 cm^{-1} should be those pyridine molecules released from Brønsted and Lewis acid sites and still present in the pores.

Acid sites are associated with the aluminium being either framework constituent or in extraframework position. A Brønsted acid site can be represented as follows:



The ionic or acidic character of the hydrogen is strongly influenced by the interaction of aluminium and oxygen of the Si–OH group. Particularly, the bond lengths and bond angles, determined by the crystallographic position of aluminium affect the extent of charge partition, thereby the acidity of these centres. Recent quantum chemical studies on the acidity of H-ZSM-5 zeolite revealed that a Brønsted acid site can be desorbed rather by a tricoordinated Al–$(OSi)_3$ species forming a dative bond with the HO–Si$(OSi)_3$ adjacent unit than by an ionic interaction like an $(SiO)_3$–Al^- stabilized with $(SiO)_3$–Si–OH^+ unit [13].

The heterogeneity of the strength of the Brønsted acid site is theoretically related to the number of aluminium atoms sitting in crystallographically non-equivalent positions in the solid and to the partial neutralization of the sites [14].

As spectra show, parallel with the appearance of the band at 1462 cm^{-1} OH bands partially reappear (fig. 2 and refs. [9,15]). At low desorption temperatures the band at 3660 cm^{-1} (associated with extraframework aluminium) becomes visible followed by partial recovering of a band (3618 cm^{-1}) near the frequency characteristic for bridged OH-s (3605 cm^{-1}). The appearance of this OH band is accompanied by the development of the band at 1462 cm^{-1} or vice versa, therefore a correlation between them seems to be probable. While pyridine is being released from a certain acid site, the acid strength of the remaining sites should also be influenced. The frequency shift of the reappeared OH band to higher wavenumbers can be explained as follows: taking two adjacent OH groups, the acidity of the free OH group should decrease, when the other is occupied by a pyridine molecule.

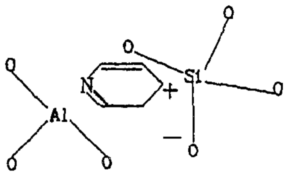
Pyridine is hydrogen bonded to the Brønsted acid sites at around room temperature and forms pyridinium ion at higher temperatures [16]. Pyridine molecules and pyridinium ions are mobile at elevated temperature; they jump from site to site [17]. After a mean lifetime of 5×10^{-7} s at 313 K pyridinium ion desorbs as pyridine molecule and jumps to another Brønsted site and transfers again into pyridinium ion. Less frequently (after average lifetime of 10^{-5} s) a jump as pyridinium ion carrying the proton from the hydroxyl group to another oxygen of the zeolitic framework. If pyridine finds a Lewis acid site along a series of jumps it may adsorb on it. The probability of such an adsorption increases with decreasing the distance between the acid sites.

During this pyridine desorption–diffusion process Brønsted sites of type A can be generated when pyridine is desorbed as a molecule. The partial appearance of the bridging OH band after desorption of pyridine at higher temperatures strongly supports this interpretation. If a desorbed pyridine molecule finds this tricoordinated aluminium ion it may adsorb on it, forming a new Lewis acid site bonded pyridine molecule. It absorbs at higher frequency since the bond formed must be stronger than that between pyridine and Brønsted site (the pyridine already desorbed from this site) or between pyridine and a Lewis site present after activation of the zeolite. We must also take into consideration the presence of a SiOH group adjacent to the new Lewis site, which can increase the strength of pyridine bonding. When the zeolite is loaded or overloaded with pyridine this situation does not exist, since the acid sites are covered with pyridine. A partial desorption of pyridine must occur before generation of this new Lewis site.

5. Conclusion

Upon pyridine desorption from acidic catalysts a new IR absorption band was observed at 1462 cm^{-1}, and assigned as a complex between pyridine and Lewis acid sites. In this complex pyridine interacts simultaneously with a tricoordinated aluminium operating as Lewis acid site and an OH group present in the same framework position, or formed during the desorption–diffusion process by jumping of pyridine as pyridinium ion. The structure on the atomic level in the pores is the following:

The bonding of pyridine on this complex adsorption centrum is stronger because



of the presence of the adjacent SiOH group. This explanation may interpret the experimental observations on the appearance of the new pyridine band for amorphous silica–aluminas and zeolites.

References

[1] R.L. Richardson and S.W. Benson, J. Phys. Chem. 61 (1957) 405;
M.R. Basila, T.R. Kantner and K.H. Rhee, J. Phys. Chem. 68 (1964) 3197;
K.H. Bourne, F.R. Cannings and R.C. Pitkethly, J. Phys. Chem. 74 (1970) 2197;
F.R. Cannings, J. Phys. Chem. 72 (1968) 4691.

[2] E.R. Parry, J. Catal. 2 (1963) 371.

[3] J. Take, T. Veda and Y. Yoneda, Bull. Chem. Soc. Japan 51 (1978) 1581.

[4] A.K. Ghosh and G. Curthoys, J. Chem. Soc. Faraday Trans I 74 (1983) 805.

[5] H.G. Karge, Z. Phys. Chem. NF 122 (1980) 103;
B. Borade and R. Clearfield, J. Phys. Chem. 96 (1992) 6729;
L. Kubelkova, S. Beran, A. Malecka and V.M. Mastikhin, Zeolites 9 (1989) 12.

[6] R. Beaumont, P. Pichat, D. Barthomeuf and Y. Trambouze, in: *Proc. 5th Int. Congr. on Catalysis*, Vol. 1, ed. J.W. Hightower (Elsevier, Amsterdam, 1973) p. 343.

[7] N.-Y. Topsøe, K. Pedersen and E. Derouane, J. Catal. 70 (1981) 41;
M. Maache, A. Janin, J.C. Lavelley, J.F. Joly and E. Benazzi, Zeolites 13 (1993) 419.

[8] D. Ballivet, D. Barthomeuf and P. Pichat, J. Chem. Soc. Faraday Trans. I 68 (1972) 1712.

[9] B.H. Chiche, F. Fajula and E. Garrone, J. Catal. 146 (1994) 460.

[10] C. Mirodatos, B.H. Ha, K. Otsuka and D. Barthomeuf, in: *Proc. 5th Int. Congr. on Zeolites*, Naples 1980, ed. L.V.C. Rees (Heyden, London) p. 382.

[11] J. Take, T. Yamaguchi, K. Miyamoto, H. Ohyama and M. Misono, in: *Proc. 7th Int. Zeolite Conf.*, Tokyo 1986, eds. Y. Murakami et al. (Kodansha/Elsevier, Amsterdam/Tokyo) p. 495.

[12] I. Kiricsi, C. Flego, G. Pazzuconi, O.W. Parker, R. Millini, C. Perego and G. Bellussi, J. Phys. Chem. 98 (1994) 4627.

[13] A. Redondo and P.J. Hay, J. Phys. Chem. 97 (1993) 11754.

[14] V.I. Zholobenko, M.A. Makarova and J. Dwyer, J. Phys. Chem. 97 (1993) 5962, and references therein.

[15] C. Jia, D. Barthomeuf and P. Massiani, J. Chem. Soc. Faraday Trans. I 89 (1993) 3659.

[16] E.A. Paukhstis, L.G. Karakchiev and N.S. Kotsarenko, React. Kinet. Catal. Lett. 6 (1977) 147.

[17] D. Freude and H. Pfeifer, in: *Proc. 5th Int. Congr. Zeolites*, Naples 1980, ed. L.C.V. Rees (Heyden, London) p. 732;
H.-J. Rauscher, D. Michel, H. Pfeifer, J. Mol. Catal. 12 (1981)1, 159.