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Monitoring the Brönsted acidity of zeolites by means of in situ FT-IR and catalytic testing using chloromethane as probe molecule

Denis Jaumain, Bao-Lian Su*

Laboratoire de Chimie des Matériaux Inorganiques, The University of Namur (FUNDP), 61 rue de Bruxelles, B-5000 Namur, Belgium

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Abstract

The Brönsted acidity of a series of protonated zeolites with different structures and Si/Al ratios such as HY (Si/Al $= 2.4$), H(Na)EMT (3.6), HMOR (9.5), HZSM-5 (21.7) and HBeta (12.5) have been studied at room temperature and at various temperatures by means of in situ FT-IR spectroscopy using chloromethane as probe molecule. CH_3Cl was found to interact by its negatively charged chlorine atom with the polarised hydrogen atoms of hydroxyls of zeolites through hydrogen bonding, causing the red-shift of the hydroxyls vibration. The extent of the red-shift supplies important information on the strength of Brönsted acidity of zeolites which ranks in the order: HBeta $>$ HMOR $\approx$ HZSM-5 $>$ H(Na)EMT $\geq$ HY. The study made at various temperatures revealed that the interaction of chloromethane with hydroxyls of zeolites was dependent on the temperature, reflecting the strength and the heterogeneity of acidic hydroxyls of zeolites. This temperature-dependent study confirms also the acid strength ranking obtained on the basis of the extent of the red-shift. The direct conversion of CH_3Cl was carried out in the temperature range of 200–500 °C. The intrinsic activity of the five investigated zeolites has been compared with and was found to vary in the sense as acid strength. The selectivity of products of chloromethane conversion was also correlated with the Brönsted acid strength of the zeolites. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chloromethane; Probe molecule; Brönsted acidity; Zeolite; Conversion; FT-IR

1. Introduction

Because of its importance in catalytic applications, the Brönsted acidity of zeolites, which is related to the framework hydroxyl groups Si–OH–Al, has been widely investigated with experimental and quantum methods [1–9]. The spectroscopic study using probe molecules has been shown to be an important way to determine the nature and the number of acid sites in solid catalysts. The different probe molecules have greatly enlarged the amount of available information on the zeolite acidity. Two main types of probes have been developed [9]. First the probe molecules such as NH_3, pyridine and amines form a chemical bond with the protons of hydroxyls, this gives access to the concentration of acid sites of zeolites. On the other hand, aromatics, olefins, CO and H_2S can be used to acquire informations on the strength of protonic sites and on the accessibility of the Brönsted acid sites to the probe molecules. However, the role, the nature and the strength of acid sites in solid catalysts have been the object of a dispute which is far from being settled and searching a judicious molecular probe is still of important interest. The criteria for the selection of probe molecules has been summarised in an excellent review by Knözinger [9].

Recently, different small halogenated hydrocarbon molecules have been studied (mostly ethane and ethene derivatives) employing IR and NMR

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* Corresponding author. Fax: +32-81-725414.
E-mail address: bao-lian.su@fundp.ac.be (B.-L. Su).

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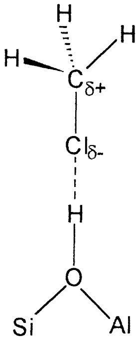

Fig. 1. Schematic representation of the interaction of CH_3Cl with hydroxyls of zeolites.

as analytical tools for the measurement of shift in wavenumbers and chemical shifts of the signals originating from the interaction of these molecules with acidic bridging OH groups of zeolites [10,11]. Monitoring chloromethane adsorption can be also used as a measure of acidity of zeolites [12] since the high electronegative chlorine atom is negatively charged and can thus interact with the hydroxyls through hydrogen bonding (Fig. 1). The extent of the shift in IR wavenumber of hydroxyls due to their interaction with CH_3Cl and the temperature dependence of such interaction can provide information not only on the strength of the accessible acidic sites but also on the number of these sites. Here, we report the first results of our study on the acid strength of zeolites using chloromethane as probe molecule. The studied zeolites have been used as catalysts in direct conversion of chloromethane to establish the correlation between the acidity and intrinsic activity of zeolites. A comparison with the results obtained using other molecular probes has been made.

2. Experimental

2.1. Materials

A series of protonated zeolites with different structures and Si/Al ratios such as HY (Si/Al = 2.4), H(Na)EMT (Si/Al = 3.6), HZSM-5 (Si/Al = 21.7), HMOR (Si/Al = 9.5) and HBeta (Si/Al = 12.5) were used. HY, H(Na)EMT, HBeta and HZSM-5 were prepared by ion exchange with 1 M ammonium chloride from their Na form [5–7]. HMOR is a commercial product provided by Toyosoda Company.

2.2. Infrared study

Self-supported zeolite wafer ($15\,mg\,cm^{-2}$) was first calcined in a Pyrex IR cell at 723 K in a flow of dry oxygen overnight and followed by evacuation for 6–8 h at same temperature in a vacuum line. After cooling the cell to room temperature, the spectrum of zeolite wafer alone was recorded as reference using a Perkin-Elmer Fourier Transform Infrared Spectrometer Spectrum 2000. The adsorption of known and increasing amount of CH_3Cl was performed on wafer. After each introduction of CH_3Cl, 1 h equilibration was made and the IR spectrum of zeolite adsorbed CH_3Cl was then recorded. The adsorption, the equilibration and recording the spectra were conducted at room temperature. The interaction of CH_3Cl with the studied zeolites was also studied at various temperatures. A large amount of CH_3Cl was contacted with zeolite wafer at room temperature (zeolites were saturated by CH_3Cl). The sample was then cooled to liquid nitrogen temperature. The spectra were recorded at various temperatures from −140 to 100 °C. All the peak values were obtained by deconvolution of the IR spectra using Winspec program.

2.3. Catalytic testing

The conversion of chloromethane was studied in a plug flow microreactor operating at atmospheric pressure. Hundred milligrams of catalyst powders were first calcined in a flow of dry air at 450 °C for 10 h and the dry air was then replaced by He. The temperature was adjusted to the desired reaction temperature. The CH_3Cl flow diluted by He in a molar ratio of 1/4 ($WHSV = 0.76\,h^{-1}$) was introduced. The reaction products were analysed using a gas phase chromatograph with a FID detector and a HP PLOT Q column.

3. Results and discussion

3.1. At room temperature

3.1.1. Adsorption of chloromethane in HY

Fig. 2A reports the changes in the IR absorbance spectra of hydroxyls of HY zeolite in the range of

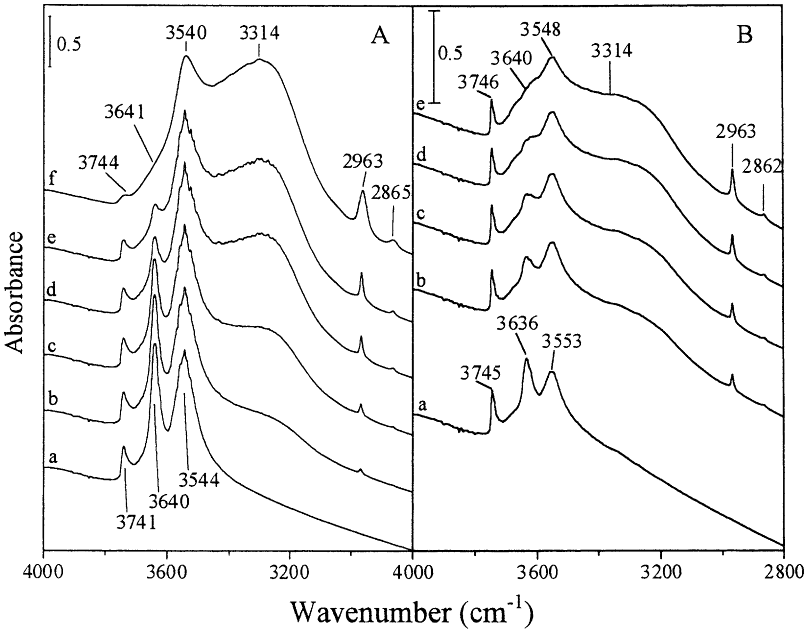

Fig. 2. FT-IR spectra of hydroxyls region of HY (A) and H(Na)EMT (B) zeolites after pretreatment (a) and upon adsorption of chloromethane (m/u.c.): (A) b, 4.0; c, 10.0; d, 30.0; e, 60.0; f, a high pressure of chloromethane in the IR cell; (B) b, 4.0; c, 10.0; d, 20.0; e, 40.0.

2800–4000 cm^{-1} upon adsorption of increasing and known amounts of chloromethane. Three peaks at 3741, 3640 and 3544 cm^{-1} were observed on HY zeolites after pretreatment (spectrum a of Fig. 2A). The hydroxyls which give rise to the band at 3741 cm^{-1} have previously been attributed to the external silanols. Two other peaks at 3640 and 3544 cm^{-1} arise from the bridging framework Si–OH–Al groups located in the large cages and those in the sodalite cages and hexagonal prisms, respectively. Adsorption of CH_3Cl on the zeolites induces an important modification of the IR spectra in the hydroxyls region. When first molecules of chloromethane (four molecules per unit cell) were introduced into the cell (spectrum b of Fig. 2A), two bands at 2963 and 2865 cm^{-1}, corresponding respectively to the CH_3 asymmetric and symmetric stretching vibrations, appeared immediately, indicating the adsorption of chloromethane on HY zeolite. It was also observed that the intensity of the peak at 3640 cm^{-1}, assigned to the bridging framework Si–OH–Al located in the large cages, decreased and a new broad band in the range of 3100–3400 cm^{-1} appeared simultaneously. The bridged Si–OH–Al groups interacting with CH_3Cl were shifted to a lower value in wavenumber and generated a broad band which progressively moved to higher wavenumber with increasing CH_3Cl loading. This is in accordance with the observations previously reported [5–7]. With increasing the amount of chloromethane introduced, the intensity of the broad band increased while that of the peak at 3640 cm^{-1} decreased. When a high pressure of chloromethane was introduced into the cell, the peak at 3640 cm^{-1} disappeared completely and the broad band centred at 3314 cm^{-1} became the most intense. The silanol peak decreased also in intensity and a new shoulder at 3641 cm^{-1} was generated, indicating that part of silanols can also interact with CH_3Cl. It should be worth to note that the peak at 3544 cm^{-1} was not affected upon adsorption of chloromethane, even in the presence of a high pressure of CH_3Cl, indicating the inaccessibility of these OH groups to chloromethane molecules. Indeed, the vibration band at 3544 cm^{-1} corresponds to the bridged Si–OH–Al located in the sodalite cages and the hexagonal prisms. No interaction between these OH groups and chloromethane shows that chloromethane cannot penetrate into these small cages.

3.1.2. Adsorption of chloromethane in H(Na)EMT

Same experiments have been made on H(Na)EMT and the spectra of hydroxyls of this zeolite in the range of 2800–4000 cm^{-1} upon adsorption of increasing and known amounts of CH_3Cl are depicted in Fig. 2B. Three peaks at 3745, 3636 and 3553 cm^{-1} were observed after pretreatment of H(Na)EMT (spectrum a of Fig. 2B). The hydroxyls at 3745 cm^{-1} are attributed to external silanols. The two other peaks at 3636 and 3553 cm^{-1} arise from the bridging framework Si–OH–Al groups located in the large cages and in the sodalite cages and hexagonal prisms, respectively. EMT is the hexagonal analogue of faujasite. Two large cages (hypo- and hypercages) are present in EMT which are different from the supercages in faujasite. Furthermore, the sodalite cages and hexagonal prisms in EMT structure are not equivalent to those occurring in faujasites. The wavenumber of Si–OH–Al groups located in the large cages (3636 cm^{-1}) and in the small cavities (3553 cm^{-1}) in EMT structure are therefore slightly different from those of faujasite (3640 and 3544 cm^{-1}, respectively). Similar changes upon adsorption of increasing and known amounts of CH_3Cl as in the case of HY zeolite were observed. The bridged Si–OH–Al groups located in the large cages were shifted to low wavenumber and generated a broad band centred at 3314 cm^{-1} due to their interaction with CH_3Cl. The OH groups located in the small cavities remained unaffected, only the wavenumbers changed slightly upon adsorption of CH_3Cl, implying their inaccessibility for chloromethane molecules. The intensity of the peak belonging to silanols decreased slightly, indicating interaction of part of silanols with CH_3Cl.

3.1.3. Adsorption of chloromethane in HMOR, HZSM-5 and HBeta zeolites

In HMOR, three peaks at 3746, 3658 and 3608 cm^{-1} were detected after pretreatment and assigned to the silanols, the hydroxyls attached to the extra-framework Al species and the bridging framework Si–OH–Al groups, respectively (spectrum a of Fig. 3A). Upon adsorption of CH_3Cl, a broad band centred at 3194 cm^{-1} and a shoulder at 3417 cm^{-1} appeared at the expense of the peaks at 3608 and 3658 cm^{-1}, respectively. At higher chloromethane loadings, the peak of silanol decreased also in intensity, generating a new band at 3615 cm^{-1}. This indicated that all three OH groups present in H-mordenite can interact with CH_3Cl.

In HZSM-5, besides the silanols at 3745 cm^{-1}, a small peak at 3724 cm^{-1}, a sharp peak at 3611 cm^{-1} and a broad band in the range 2900–3745 cm^{-1} were recorded after pretreatment (spectrum a of Fig. 3B) and attributed respectively to two kinds of the isolated silanols (3745 and 3724 cm^{-1}), the bridging framework Si–OH–Al groups and the hydrogen bonds formed by the internal silanols. Upon adsorption of CH_3Cl, the peak at 3611 cm^{-1} decreased progressively in intensity and a broad band centred at 3201 cm^{-1}, steming from the interaction of the bridging OH groups with CH_3Cl, grew in intensity (spectra b–f of Fig. 3B). In the presence of a high pressure of chloromethane in the cell, the peak at 3611 cm^{-1} disappeared completely. The silanols decreased in intensity, generating a broad band centred at 3610 cm^{-1}, originating from the interaction of silanols with CH_3Cl. This part of results indicates that both silanols and bridging framework OH groups of HZSM-5 can interact with chloromethane. The changes of the peak at 3724 cm^{-1}, upon adsorption of CH_3Cl, cannot be closely followed due to its low intensity.

In HBeta, other than the external silanols at 3745 cm^{-1}, a small peak at 3781 cm^{-1} and a sharp peak at 3610 cm^{-1}, corresponding respectively to the Al–OH species near to one or more Si–OH generated when Al leaves the framework and to the bridging OH groups were observed. Upon adsorption of CH_3Cl, the complete disappearance of the bridging framework hydroxyls was accompanied by the generation of a broad band at low wavenumber, 3183 cm^{-1} (Fig. 3C). The peak at 3745 cm^{-1} disappeared completely in the presence of a high pressure of CH_3Cl, giving an intense broad band at 3614 cm^{-1}. This means that all the silanols in HBeta can interact with CH_3Cl. This was not observed in the other studied zeolites. The high intensity of the band at 3614 cm^{-1} was due to the large number of silanols present in HBeta zeolite.

It was well known that OH groups interacting with adsorbed bases generate a new band shifted to lower wavenumber, the extent of the red-shift being characteristic of the strength of the Brönsted acidic sites. The extent of the red-shift observed for the hydroxyls in different zeolites was measured and is listed in Table 1. The hydroxyls in HBeta zeolite gives the highest red-shift value upon adsorption of

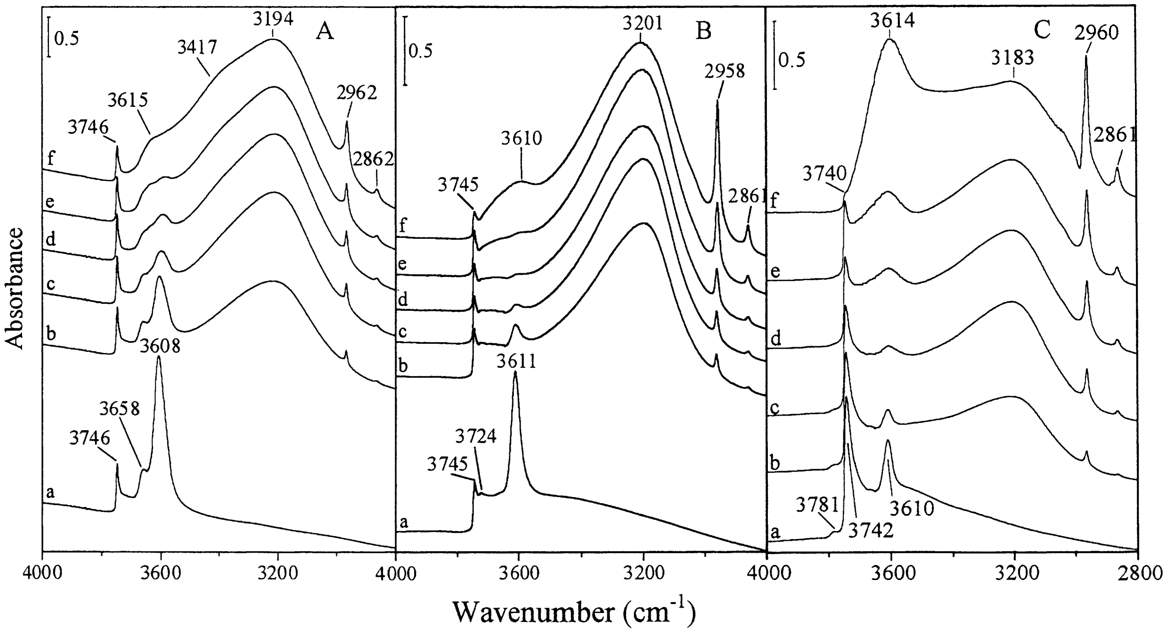

Fig. 3. FT-IR spectra of hydroxyls region of HMOR (A), HZSM-5 (B) and HBeta (C) zeolites after pretreatment (a) and upon adsorption of chloromethane (m/u.c.): (A) b, 2.0; c, 5.0; d, 10.0; e, 20.0; f, a high pressure of chloromethane in the IR cell; (B) b, 2.0; c, 3.0; d, 6.0; e, 20.0; f, a high pressure of chloromethane in the IR cell; (C) b, 2.0; c, 10.0; d, 30.0; e, 60.0; f, a high pressure of chloromethane in the IR cell.

chloromethane and those in large cages of HY zeolite give the lowest red-shift value. The acid strength of bridged framework hydroxyls ranks therefore in the order: HBeta > HMOR ≈ HZSM-5 > H(Na)EMT ≥ HY. This order is quite similar to what observed using benzene as probe molecule [6]. The hydroxyls attached to extra-framework Al gives a shift value of 241 cm^{-1} upon adsorption of chloromethane, indicating a medium acidity while only a very low shift extent was observed for silanols in all the five studied zeolites, showing their low acid strength.

Table 1
Chemical composition and characteristics of the studied zeolites and extent of the shift, $\Delta\nu_{\mathrm{OH}}$ (cm^{-1}), of different hydroxyls in all the studied zeolites upon interaction with CH_3Cl

Zeolite	Chemical composition	Si/Al ratio	Characteristics	$\Delta\nu_{\mathrm{OH}}$ (cm^{-1})			Si–OH–Al/192T[a]
				Si–OH–Al	Extra-framework	Terminal silanols	
HY	$H_{58}Al_{58}Si_{134}O_{384}$	2.4	Large pore	325[b]	–	100	58
H(Na)EMT	$Na_{3.5}H_{17.5}Al_{21}Si_{75}O_{192}$	3.6	Large pore	330	–	106	35
HMOR	$H_4Al_4Si_{44}O_{96}$	9.5	Large pore	415	241	132	16
HBeta	$H_{4.7}Al_{4.7}Si_{59}O_{128}$	12.5	Large pore	427	–	128	14.1
HZSM-5	$Na_{0.4}H_{3.6}Al_4Si_{92}O_{192}$	21.7	Medium pore	412	–	132	7.2

[a] The comparison of bridged framework hydroxyls was made at the same number of tetrahedra since the unit cell contains 192 tetrahedra for faujasite, 96 for EMT, 48 for MOR, 64 for Beta and 96 for ZSM-5and by taking also into account of sodium content in zeolites since in HEMT and HZSM-5, some sodium cations remain.

[b] Only the hydroxyls located in the large cages interact with CH_3Cl and the hydroxyls at 3544 cm^{-1} for HY and at 3553 cm^{-1} for H(Na)EMT are inaccessible for CH_3Cl and unaffected.

3.2. Temperature-dependent study

A high pressure of chloromethane was introduced into the IR cell containing zeolite wafer which was cooled in liquid nitrogen. The temperature of the IR cell was progressively increased and then the spectrum was recorded at various temperatures. As a general tendency, one can observe that the rate of coverage of the hydroxyls of the five studied zeolites by CH_3Cl molecules was closely dependent on temperature and acid strength of the hydroxyls.

HY (Fig. 4A) and H(Na)EMT (Fig. 4B) gave the very similar behaviour. It was found that only part of bridged framework hydroxyls located in the large cages of HY and H(Na)EMT can interact with CH_3Cl at very low temperatures (below −95 °C). All these hydroxyls were consumed at around −85 °C. Indeed, from −130 to −85 °C a progressive decrease in intensity of the peak of the bridging framework Si–OH–Al located in the large cages can be observed, while a new broad band increased in intensity and the wavenumber of this broad band was shifted toward lower values as temperature was increased. From −85 to 15 °C for HY (spectra d–h of Fig. 4A) and from −85 to 35 °C for H(Na)EMT (spectra d–h of Fig. 4B), no significant changes were observed. Above 15 °C for HY (spectrum i of Fig. 4A) but 35 °C for H(Na)EMT (spectrum i of Fig. 4B), the hydroxyls located in the large cages increased in intensity and the broad band was blue-shifted toward higher wavenumbers, indicating the regeneration of hydroxyls and the desorption of chloromethane from zeolite wafer. The results that the liberation of chloromethane adsorbed from hydroxyls of H(Na)EMT is at higher temperature indicate clearly the stronger acidity of hydroxyls located in the large cages of H(Na)EMT than those of HY. In the studied temperature range, no modification of the peak related to the hydroxyls located in the small cages was

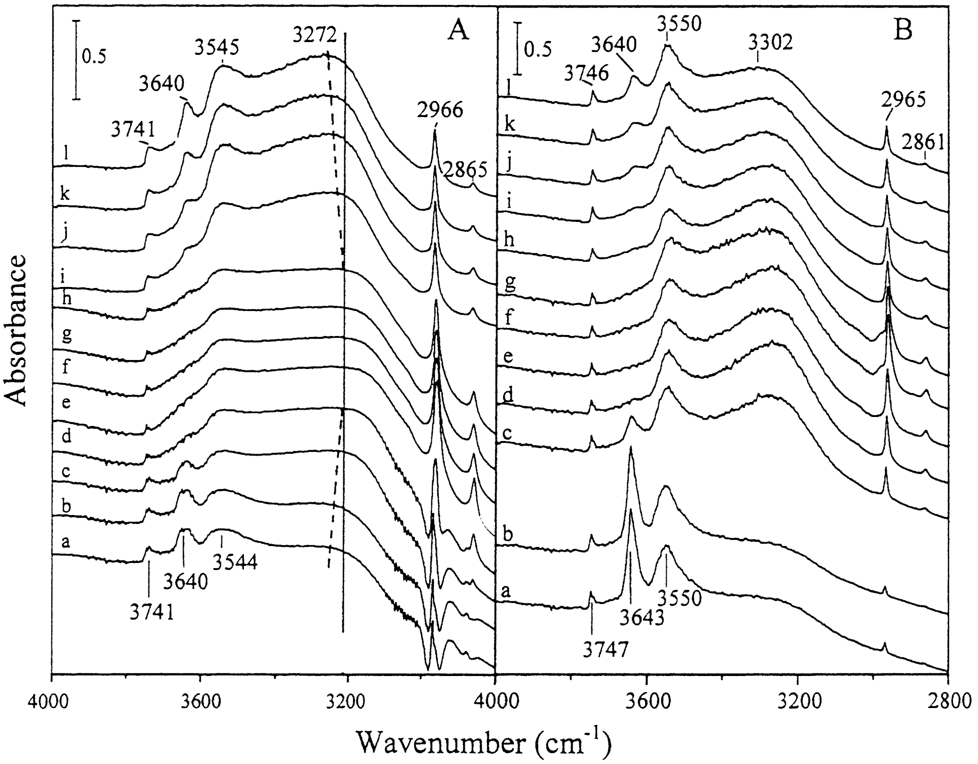

Fig. 4. FT-IR spectra in absorbance of hydroxyls in HY (A) and H(Na)EMT (B) as a function of temperature (°C) (zeolites were in contact with a high pressure of chloromethane): (A) a, −120; b, −103; c, −95; d, −85; e, −38; f, −10; g, 0; h, 15; i, 25; j, 35; k, 46; l, 54; (B) a, −133; b, −103; c, −93; d, −84; e, −74; f, −17; g, 0; h, 25; i, 46; j, 68; k, 80; l, 95.

detected. This suggests that these hydroxyls are not accessible for chloromethane in a large temperature range. The regeneration of hydroxyls at higher temperature is due to the increase in kinetic energy of chloromethane with increasing temperature. The interaction between hydroxyls and CH_3Cl is weakened. This temperature-dependent study shows clearly that the heterogeneity on acid strength of hydroxyls in zeolites. Only part of very strong acid sites can interact with chloromethane and can retain these molecules at higher temperatures.

For HMOR (Fig. 5A), HZSM-5 (Fig. 5B) and HBeta (Fig. 5C) zeolites, at −130 °C, all the bridged framework hydroxyls were already consumed upon interaction with CH_3Cl and no regeneration of these groups was observed even over 70 °C, indicating stronger interaction of the framework hydroxyls with CH_3Cl in these zeolites than that in HY and H(Na)EMT. This evident temperature dependence is quite important to rank the Brönsted acidity of zeolites. With increasing temperature, only a slight shift toward higher wavenumber was observed for broad band indicating the progressive weakening of the hydrogen bonds between hydroxyls and chloromethane molecules.

Over the five zeolites, the variation in the intensity of the silanol vibration band at around 3745 cm^{-1} can also be observed. Indeed, a progressive decrease of this band occurred because of the interaction of the silanols with CH_3Cl molecules. For HY and H(Na)EMT, this decrease was very slight, while over HMOR, HZSM-5 and HBeta, the variation in intensity of this vibration band with temperature is quite significant. Furthermore, a new broad band was generated at lower wavenumber, around 3610 cm^{-1} for HMOR, HZSM-5 and HBeta. This broad band was the most intense in the case of HBeta because of its greater number of silanols. The lowest intensity of the silanol peak was observed at −18 °C for HZSM-5 and HMOR and −36 °C for HBeta. At higher temperatures, the silanol band was progressively restored, indicating the weak interaction strength between silanols and CH_3Cl molecules.

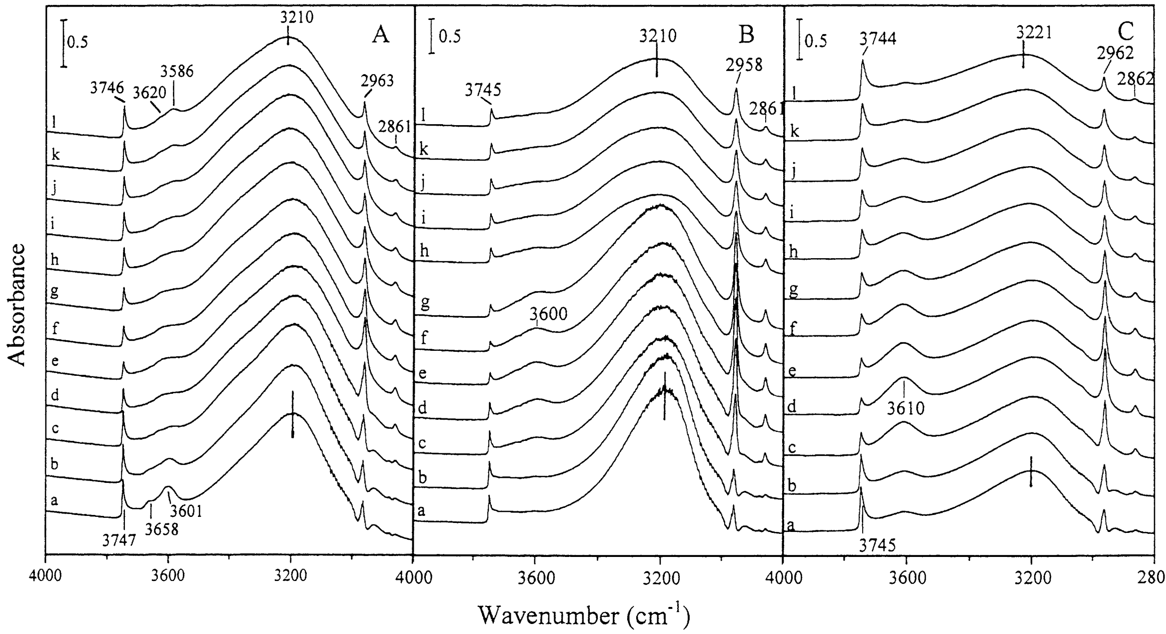

Fig. 5. FT-IR spectra in absorbance of hydroxyls in HMOR (A), HZSM-5 (B) and HBeta (C) as a function of temperature (°C) (zeolites were in contact with a high pressure of chloromethane): (A) a, −120; b, −106; c, −92; d, −78; e, −38; f, −18; g, 1; h, 25; i, 35; j, 45; k, 62; l, 71; (B) a, −122; b, −100; c, −86; d, −60; e, −34; f, −17; g, 0; h, 25; i, 46; j, 54; k, 69; l, 76; (C) a, −91; b, −86; c, −68; d, −38; e, −17; f, 2; g, 25; h, 48; i, 59; j, 71; k, 86; l, 100.

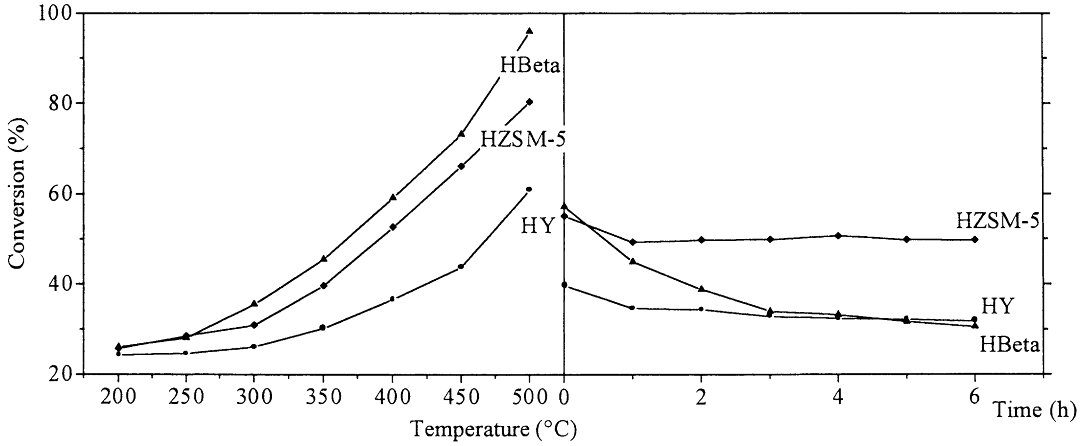

Fig. 6. Initial catalytic activity of chloromethane conversion on HY, HZSM-5 and HBeta zeolites as a function of temperature (A) and ageing test on these zeolites at 400 °C (B).

3.3. Chloromethane conversion on HY, HBeta and HZSM-5 zeolites

The conversion of chloromethane was studied over three zeolites with very different acid strength of hydroxyls, HBeta, HZSM-5 and HY, by catalytic testing to establish the correlation between the acidity probed by chloromethane and intrinsic activity of these zeolites. Under reaction conditions used, almost no activity was observed below 200 °C (Fig. 6A). The conversion was found to increase with reaction temperature. The order of initial conversion ranks in the order of HBeta > HZSM-5 > HY in the studied reaction temperature range. The selectivity of products obtained over these three zeolites was quite different due to their difference in structure and acidity. It is not the aim of the present paper to discuss in detail the catalytic results which will anyway be published elsewhere [16]. What we want to show is the very interesting observation that the order obtained in the conversion of chloromethane varies in the same sense as acid strength of these zeolites probed with chloromethane by means of FT-IR. The same order in catalytic activity was also found by Ghosh and Kydd [17] in propene conversion reaction. From selectivity analysis (Table 2), it seems that the selectivity was also linked with the acid strength of zeolites since at 200 °C (only the selectivity obtained at this temperature was analysed because at higher temperatures, the cracking of products and coke deposition will occur and affect the analysis), it was observed that more acid zeolites (HBeta and HZSM-5), more C_3H_8 and i-C_4H_{10} products. While over less acid zeolites, for example, HY, more C_2H_4, n-C_4H_8, $C_5 + C_6$ products and aromatics were obtained. It is quite worth to note from ageing tests (Fig. 6B) that HZSM-5 due to its medium pore systems deactivated much slowly than large pore HBeta and HY zeolites which favour the accumulation of cokes. Our thermal analysis study [16] on the coke formation during chloromethane

Table 2
Products distribution (mol.%) of chloromethane conversion over HY, HZSM-5 and HBeta zeolites at 200 °C

Zeolites	Products distribution (mol.%)						
	CH_4	C_2H_4	C_3H_8	n-C_4H_8	i-C_4H_{10}	$C_5 + C_6$	A_6
HBeta	–	4.5	10	–	70	12	–
HZSM-5	–	2.5	13	10	41	28	5
HY	–	35	–	12	–	42	5

conversion has shown clearly that coke formation was the main deactivation cause of the catalysts. On the basis of the activity, selectivity and ageing results, ZSM-5 zeolite seems to be the best candidate for chloromethane conversion to higher hydrocarbons.

4. General discussion

From Table 1, it is clear that OH groups associated to the framework Al are more acid than other hydroxyls, and the bridging framework hydroxyls of HBeta gives the highest shift value, being suggestive of the highest acid strength of framework hydroxyls of this zeolite in all the accessible hydroxyls of studied zeolites. The acid strength ranks in the following order for the studied zeolites: HBeta ($\mathrm{Si/Al} = 12.5$) $>$ HMOR (9.5) $\approx$ HZSM-5 (21.7) $>$ H(Na)EMT (3.6) $\geq$ HY (2.4). This is not in the same order as that of Si/Al ratio, indicating the strong effect of zeolite structure on the acid strength although Eichler et al. [13] evidenced on the basis of quantum chemical results that the effect of composition (Si/Al ratio) is much more important on acidity of zeolites. Previous works using benzene and ammonia as probes reported that a highly exchanged HEMT is more acid than HY [5–7], and that HBeta ($\mathrm{Si/Al} = 14$ and 22) is less acid than a HZSM-5 ($\mathrm{Si/Al} = 35$) [2]. The presence of some $\mathrm{Na^+}$ ions in H(Na)EMT zeolite and the low Si/Al ratio of our present HZSM-5 ($\mathrm{Si/Al} = 21$) zeolite can reduce the acid strength and using different molecular probes can probably result in the difference in the order of acid strength as very recently reported by Kotrel et al. [18]. Nevertheless, the higher acid strength of the present HBeta zeolite compared to our present HZSM-5 is confirmed by the present catalytic results of $\mathrm{CH_3Cl}$ conversion. The same order was also observed in propene conversion using these zeolites as catalysts [14–16]. The higher acidity of HMOR compared to HZSM-5 was previously demonstrated by Ghosh and Kydd [17]. Not only the reaction conversion varies in the same sense as acid strength, but also the products distribution seems to be linked also with acid strength of zeolites. The catalytic results confirm strongly the FT-IR observation. Neither catalytic results of chloromethane conversion nor the extent of shift value of hydroxyls upon adsorption of chloromethane seem to be dominated by the total number of Brönsted acid sites (Table 1). In a very recent paper dealing with the characterisation of zeolite acidity by spectroscopic and catalytic means, Knözinger et al. pointed out that spectroscopic and catalytic observations for different zeolites do not match perfectly since the additional effects can influence the course of an acid-catalysed reaction. However, our present catalytic results are consistent quite well with spectroscopic observation. This is because the characterisation of acid strength by spectroscopic method and by catalytic means uses the same molecule probe. That is not the case in the study of Knözinger et al. since they used $\mathrm{N_2}$, $\mathrm{H_2}$ and CO to determine the acid strength of acidic hydroxyls of zeolites by means of IR, and then they tried to correlate these results with acid-catalysed reaction, *n*-hexane cracking. Two different approaches using different probe molecules can unavoidably produce different ranks since different molecules will probe different acidity. These results indicate that chloromethane could be an efficient molecule probe for study of Brönsted acidity of zeolites. We will go further to determine quantitatively using this probe molecule the number of accessible Brönsted acid sites in zeolites.

5. Conclusions

The present work evidences that the Brönsted acidity of zeolites can be monitored by using chloromethane as molecular probe. Both the extent of the shift in wavenumber of different groups of hydroxyls due to their interaction with $\mathrm{CH_3Cl}$ and the temperature dependence of such interaction can provide information not only on the strength of the accessible acidic sites but also possibly on the number of these sites. Both experiments give the same rank in acid strength. The application of chloromethane as a probe for IR studies correlates to the earlier work on the adsorption of trichloro- and trifluoromethane in Y-zeolites as studied by IR spectroscopy and multinuclear solid-state NMR by Bosch et al. [19]. The obtained information are very useful not only for quantum calculation, for a better understanding of the role and the nature of acid sites in zeolites, but also in the classification of acid strength of protonated zeolites to choose the adequate acidity for a given catalytic reaction. The catalytic conversion results of chloromethane confirm strongly the acid strength rank. Hence, the obtained acid strength order using chloromethane as probe is convincing and reflects the real acidity of zeolites. However, the verification of the present results via application of independent techniques such as microcalorimetry, TPD, ^{1}H MAS NMR, suitable test reaction and adsorption heat measurements should be made.

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