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Acidic and catalytic properties of aluminated mordenite zeolite: Effect of extraframework aluminium

Peng Wu, Takayuki Komatsu and Tatsuaki Yashima*
Department of Chemistry, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

The nature of the extraframework aluminium generated in dealuminated mordenite by alumination with $AlCl_3$ and its effect on acidity and catalytic activity have been studied. A series of mordenites with framework Si/Al atomic ratios between 11 and 220 was obtained by alumination of dealuminated mordenite and was characterized using atomic absorption spectrophotometry, IR spectroscopy, MAS NMR and reaction studies.

Alumination below 873 K preferentially introduced Al atoms into the extraframework sites instead of into the framework sites, while alumination at 873 K and higher temperatures led to the incorporation of more Al into the framework. In all cases a significant portion of the extraframework Al species was not ion-exchangeable with an aqueous solution of NH_4NO_3 and was unobservable by ^{27}Al MAS NMR, suggesting its lack of symmetry. IR studies with NH_3 and pyridine probes demonstrated that the extraframework Al species acted as Lewis acid sites. The mordenite aluminated at 873 K showed a comparable specific activity to the parent and dealuminated mordenite for toluene disproportionation and *o*-xylene coversion as measured by turnover frequency based on the number of Brønsted acid sites. Those aluminated below 873 K, however, exhibited enhanced specific activity for both reactions. The enhancement is explained by the Lewis acidic extraframework Al exhibiting electron-withdrawing properties and thus intensifying the Brønsted acidity of the framework Al.

The acidity of zeolite including the concentration and the strength of acid sites has been, and continues to be, an important subject in the field of zeolite catalysis. Acid site concentration, or the so-called extensive factor, is conceptually well defined for proton-type zeolites. Brønsted acid sites are composed of labile protons in the neighbourhood of tetrahedrally coordinated aluminium atoms in the framework. Therefore, the amount of Brønsted acid sites is equal to that of the framework aluminium (FAL). For some special zeolites, the FAL concentration can be varied over a wide range by controlling the aluminium content in the hydrothermal synthesis gel. For example, the FAL content in ZSM-5 zeolites is continuously variable over several orders of magnitude.[1] More practically, it can be varied by means of postsynthetic methods, dealumination[2–6] and alumination.[7–11] Lewis acidity is generally believed to be due to the extraframework aluminum (EFAL) species, which are present in steam-dealuminated zeolites.[2] The amount of EFAL can be varied by controlling the dealumination conditions. However, the concentration of Lewis acid sites subsequently generated is not so easy to determine owing to the fact that Lewis acidity depends on the nature of the EFAL and that a part of the EFAL species may exist in ^{27}Al MAS NMR-invisible states.

The concept of acid strength, or so-called intensive factor, however, is relatively complicated. In the case of Y zeolite, Beaumont and Barthomeuf observed that mild dealumination over the range 56 to 37 Al [unit cell (uc)]$^{-1}$ resulted in the removal of inactive and weak acid sites, while extensive dealumination caused a loss of activity.[12] They concluded that the acid strength in Y zeolites should be constant for Si/Al $\geqslant$ 6. These phenomena were first interpreted by Dempsey, Mikorsky and Marshall in the (DMM) model, in which acid strength is related to the environment and the distribution of FAL, and only FAL with no Al atoms in its second-nearest neighbour shell, *i.e.* isolated FAL, exhibits strong acidity. The acid strength of such FAL is nearly the same.[13,14] This model has been supported by experimental evidence involving hexane cracking, isobutane conversion and pentane cracking over dealuminated Y zeolites.[2–4] In all these reaction studies, acid strength was shown to be essentially constant when the aluminium content was lower than an optimum value. Thus, increasing the concentration of FAL induces an increase in the concentration of acid sites, but the acid strength is reduced by the extensive increase in FAL, probably due to delocalization of the negative charge density on the framework.

According to these discussions, acid sites in high-silica zeolites are expected to have equal strength as FAL atoms have nearly the same environment when they are far apart from each other. Haag *et al.* found that the activity for hexane cracking increased linearly with aluminium content in a range of 20 $\leqslant$ Si/Al $\leqslant$ 20 000, suggesting that Al atoms in 'clean framework' ZSM-5 show the same intrinsic activity and the same acid strength.[1] Similar observations have also been reported recently on the dealuminated mordenites.[15]

Beside the concentration of FAL, dislodged or extraframework Al species formed during dealumination treatments also play an important role in affecting acid strength. Mirodatos and Barthemouf observed that the NH_3-TPD spectrum of steamed mordenite showed an additional peak at a higher temperature than that obtained with the parent mordenite, and postulated a scheme in which Lewis acid sites bridge to the structural hydroxy groups to form super acid sites.[16] The proposal of Lewis–Brønsted acid interaction enhancing the acid strength of the FAL atoms was confirmed by the investigations on H-Y and H-ZSM-5. Mild steaming of Y zeolites dealuminated with ammonium hexafluorosilicate resulted in an increase in activity for isobutane conversion[2] and for pentane cracking[4] compared with the dealuminated parents with 'clean framework'. This was attributed to a synergism between FAL atoms and EFAL atoms generated during the steaming. Alternative explanations suggested for the enhancement of acid strength were that more acidic Brønsted sites are associated with the presence of amorphous silica–alumina inside the pores of dealuminated Y zeolites,[17] and that extraframework polyvalent aluminium oxide species located in the sodalite cages of H-Y zeolites withdraw electrons from the framework hydroxy groups.[18] The presence of super acid sites has also been observed for mildly steamed

ZSM-5 zeolites. Lago *et al.* reported that the mild steaming resulted in a fourfold increase in hexane cracking activity of ZSM-5 and attributed this phenomenon to partial hydrolysis of one of the Al atoms in a framework Al pair, which acted as a strong electron-withdrawing site to enhance the acid strength of the remaining tetrahedral Al atom.[6] On the other hand, the enhanced catalytic activity has also been explained by the idea that a reactant molecule interacts simultaneously with a bridging OH group and with an EFAL atom, where an optimum activity needs a balance of FAL and EFAL.[19]

So far, super acid sites showing enhanced activity for hydrocarbon conversion are reported mainly on dealuminated Y and ZSM-5 zeolites prepared by mild steaming, but little has been reported on aluminated zeolites. Treatment with $AlCl_3$ vapour at elevated temperatures on highly siliceous ZSM-5 zeolites can incorporate aluminium into the framework as tetracoordinated species.[7–11] The nature of acid sites generated by this alumination treatment was shown to be quite similar to those in synthesized ZSM-5 for hexane cracking[7] and for methanol conversion to hydrocarbons.[8] Recently, Yamagishi *et al.* observed that alumination generated Brønsted acid sites having comparable cumene cracking activity to those in conventionally synthesized ZSM-5, while the aluminated ZSM-5 exhibited the enhanced activity for octane cracking: the reason for this has not yet been addressed clearly.[10]

We have carried out an alumination treatment on dealuminated mordenites with $AlCl_3$ at elevated temperatures and demonstrated the incorporation of Al atoms into the framework of mordenite as FAL.[20,21] We investigated the reaction mechanism for the generation of FAL in the mordenite framework by means of IR and MAS NMR spectroscopy, and proposed that the alumination proceeded not through an isomorphous substitution of aluminium for the framework silicon but through an insertion of Al atoms into the defect sites formed by hydroxy nests. In these studies, we have concentrated on the phenomena occurring on FAL and have not dealt with the issue of introducing Al atoms as EFAL. In general, the acidic and catalytic properties of aluminated mordenites especially with respect to the EFAL species from an external (non-zeolitic) source have never been studied. The present study was undertaken to clarify the acidic and catalytic properties of the aluminium sites incorporated into the mordenite by alumination with $AlCl_3$. The most fundamental issues are to discuss the mechanism for the generation of EFAL and to identify the effect of EFAL on the acidity as well as on the catalytic activity.

Experimental

Materials

H-mordenite, denoted as M(11) (Tosoh Co. Ltd., framework Si/Al atomic ratio of 11) was used as a starting material for dealumination. A reference mordenite, M(13) with a framework Si/Al ratio of 13 was obtained by extracting M(11) with 2 mol l^{-1} HNO_3 at room temperature for 8 h. Highly siliceous mordenites, M(151), M(195) and M(220) listed in Table 1 were prepared by the dealumination of M(11) as described elsewhere.[21] Dealuminated H-mordenite M(71) (framework Si/Al ratio of 71) was also obtained from Tosoh, and used for alumination without any further dealumination.

Alumination procedures

For a typical alumination, 2 g of dealuminated mordenite was placed in a vertical quartz reactor, and dried at 773 K for 4 h under a dry helium stream at a flow rate of 50 cm^3 min^{-1}. The reactor was then brought to reaction temperature (573–973 K). The helium stream was diverted through a bed of anhydrous $AlCl_3$ powder in another quartz container placed over the reactor. The $AlCl_3$ container was heated to achieve a desired vapour pressure 11 kPa. The helium carrier containing $AlCl_3$ vapour was passed through the zeolite bed at the reaction temperature to bring about the alumination. The contact of zeolite with $AlCl_3$ vapour was maintained for 1 h, followed by purging with a pure helium stream at 673 K for 1 h to remove any residual, unreacted $AlCl_3$ from the zeolite. After cooling to room temperature, the aluminated zeolite was washed with a large amount of deionized water, ion-exchanged with 0.1 mol l^{-1} NH_4NO_3 at 343 K for 48 h, and then dried in air at 383 K for 24 h. The aluminated mordenite was designated as Al-M(*n*)-*T*, where *n* and *T* were the Si/Al atomic ratio of the parent and the alumination temperature, respectively.

Analytical methods

Relative crystallinity of both dealuminated and aluminated mordenites was checked by X-ray diffraction (XRD) and BET surface area to be uniformly good with a decrease within 10% compared with that of the parent M(11).[21] Atomic absorption spectrophotometry was used to determine the amount of bulk aluminium.

IR spectra were recorded on a Shimadzu FTIR-8100 spectrometer with a spectral resolution of 2 cm^{-1}. 20 mg of

Table 1 Characterization results and catalytic activity of mordenites

sample[a]	framework[b] Si/Al	aluminium content /mmol g^{-1} bulk[d]	FAL[e]	EFAL[f]	Acid sites[c] /abs. g^{-1} Brønsted	Lewis
M(11)	11	1.17	0.98	0.19	13.2	9.0
M(71)	71	0.23	0.21	0.02	3.3	1.7
M(151)	151	0.09	0.09	0	1.0	0.9
M(195)	195	0.07	0.07	0	0.8	0.7
M(220)	220	0.06	0.06	0	0.5	0.3
Al-M(71)-873	30	0.86	0.48	0.38	5.8	9.9
Al-M(151)-573	63	0.84	0.30	0.56	4.0	12.4
Al-M(151)-673	53	0.81	0.32	0.49	4.5	11.2
Al-M(151)-773	45	0.79	0.39	0.40	5.0	10.8
Al-M(151)-873	44	0.71	0.43	0.28	5.5	7.9
Al-M(195)-673	68	0.65	0.26	0.39	3.6	9.7
Al-M(195)-873	50	0.62	0.36	0.26	4.4	6.7
Al-M(220)-673	65	0.56	0.22	0.34	3.2	8.2
Al-M(220)-873	60	0.52	0.29	0.23	3.7	5.6

[a] Alumination was carried out at 11 kPa of $AlCl_3$ vapour for 1 h. [b] Determined by ^{29}Si MAS NMR. [c] From IR spectra of adsorbed pyridine after desorption at 423 K. [d] Determined by atomic absorption spectrophotometer. [e] Determined by ^{27}Al MAS NMR. [f] The difference between the amount of bulk Al and that of FAL.

sample was pressed into a self-supported wafer with a diameter of 20 mm. The wafer was set in a quartz IR cell which was sealed with CaF_2 windows and connected to a vacuum system. After the wafer was evacuated at 773 K for 1.5 h, a spectrum was measured in absorbance mode at room temperature. In the pyridine adsorption experiment, the wafer pretreated at 773 K for 1 h was exposed to pyridine vapour (1.3 kPa) which had been purified by freeze–pump–thaw cycles. After equilibrating at 423 K for 1 h, the desorption was carried out stepwise at 423, 523, 623, 723 and 823 K for 1 h at each temperature. The adsorption of ammonia was carried out at 323 K by introducing 13.3 kPa of ammonia into the cell for 0.5 h, followed by stepwise evacuation at 323, 423, 523, 623 and 723 K for 1 h, respectively. All the spectra after pyridine or ammonia desorption were also collected at room temperature. Between different mordenites, the IR spectra were normalized on the absorbance of the 1882 cm^{-1} band corresponding to the Si—O overtone of the zeolite framework.[7,8]

The framework Si/Al atomic ratio and the amount of FAL were determined by ^{29}Si and ^{27}Al MAS NMR, respectively. The spectra were recorded on a Bruker AM-400 FT-NMR spectrometer equipped with a magic-angle probe. ^{29}Si NMR spectra were obtained at 79.50 MHz using a spinning rate of 3 kHz, a 30° pulse length of 2.3 μs and a pulse interval of 5 s; 5000 scans were accumulated to obtain a satisfactory signal-to-noise ratio. ^{27}Al NMR spectra were recorded at 104.26 MHz using a pulse width of 4 μs and a pulse interval of 2 s. Chemical shift references were TMS and $[Al(H_2O)_6]^{3+}$ for ^{29}Si and ^{27}Al NMR, respectively.

Catalytic reactions

Toluene disproportionation and *o*-xylene conversion were performed using a fixed-bed reactor with a continuous flow system at atmospheric pressure. A typical catalyst loading was 0.2 g, and W/F values were 2.6 and 2.5 g h mol^{-1} for the toluene and *o*-xylene reactions, respectively. The catalyst powder was placed in a quartz reactor and dehydrated in a dry helium stream at 773 K for 1.5 h. The reactor was then brought to a reaction temperature (573 K for the toluene disproportionation and 473 K for the *o*-xylene conversion). The reaction was started by feeding the reactant into the reactor with a microfeeder under a helium carrier gas. The reaction products were collected periodically with a cold trap and analysed by gas chromatography (GC) with an flame ionization detector.

Results and Discussion

Effect of temperature on alumination

In our previous paper,[21] we examined the effect of the alumination temperature, partial pressure of $AlCl_3$ vapour and process time on the incorporation of Al atoms, and found that an alumination treatment at 873 K and 11 kPa of $AlCl_3$ for 1 h effectively incorporated Al atoms into the mordenite framework as FAL. In the present study, the effect of reaction temperature on the amount of EFAL as well as that of FAL was investigated on the same dealuminated mordenite, M(151), which had an aluminium content of 0.09 mmol g^{-1} with no appreciable EFAL. The amount of EFAL was obtained by subtracting the amount of FAL determined by ^{27}Al MAS NMR from that of bulk Al. The results of ^{27}Al MAS NMR spectra will be discussed in detail later. As shown in Fig. 1, the FAL amount first increased with increasing temperature, reached a maximum around 873 K and then decreased. This is very similar to the dependence of the absorbance of the 3610 cm^{-1} IR band on the alumination temperature.[21] Thus, both MAS NMR and IR demonstrate that the alumination temperature of 873 K is optimum for the incorporation of the maximum amount of FAL. It is obvious from Fig. 1 that an alumination temperature lower than the optimum temperature of 873 K is favourable to introduce Al atoms as EFAL. Similar results were also obtained on the alumination of other dealuminated mordenites, M(195) and M(220), as shown in Table 1. It is clear from Fig. 1 and Table 1 that in the mordenites aluminated at 873 K and higher, the amount of FAL was larger than that of EFAL, while in the mordenites aluminated at temperatures lower than 873 K (denoted as Al-M(n) < 873), the EFAL amount was larger than the FAL amount. These differences in the aluminium species among the aluminated mordenites may potentially alter the nature of acid sites, which could lead to significant changes in their catalytic performance.

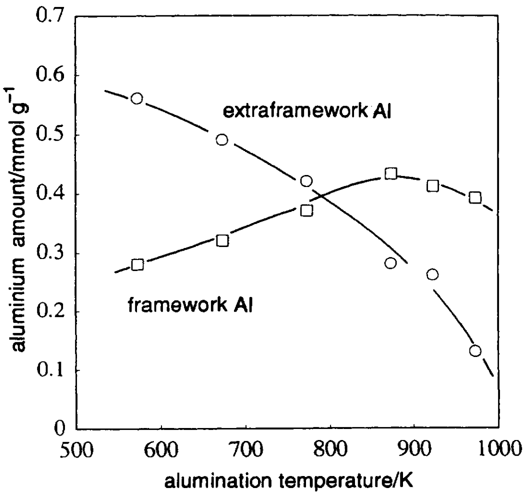


Fig. 1 Effect of reaction temperature of the alumination of M(151) at 11 kPa of $AlCl_3$ vapour for 1 h

Zeolite acidity

The absorbance of the 3610 cm^{-1} band has been shown to be proportional to the amount of FAL for both aluminated and dealuminated mordenites.[21] In the present study, IR spectroscopy using ammonia and pyridine as probes was adopted to characterize their acidity. Fig. 2 shows the spectra of M(151) together with those of Al-M(151)-573 and Al-M(151)-873, which were aluminated from M(151) at 573 and 873 K, respectively. In the hydroxy stretching region of IR spectra before ammonia adsorption (Fig. 2A), M(151) showed a very strong band at 3745 cm^{-1} due to terminal SiOH groups, a weak band at 3610 cm^{-1} due to structural Si(OH)Al groups characteristic of Brønsted acid sites, and two strong bands around 3700 and 3500 cm^{-1} related to internal SiOH groups forming hydroxy nests.[20–23] As the alumination is proved to proceed through the reaction between $AlCl_3$ with internal SiOH groups,[11,21] the 3700 and 3500 cm^{-1} bands were no longer

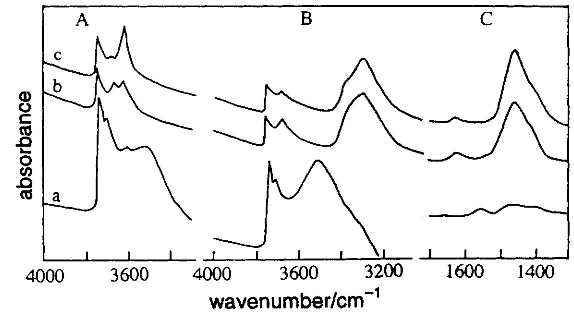


Fig. 2 IR spectra: A, before ammonia adsorption; B and C, after ammonia adsorption and desorption at 423 K. (a) M(151); (b) Al-M(151)-573; (c) Al-M(151)-873

visible for Al-M(151)-573 and Al-M(151)-873, while a noticeably stronger 3610 cm^{-1} band was observed as a result of increase in FAL [Fig. 2(b) and (c)]. A new band at 3660 cm^{-1} was also observed for the aluminated mordenites. This band has been assigned to the hydroxy groups associated with EFAL species.[24] Therefore, the 3660 cm^{-1} band is another indication of the EFAL species existing in the aluminated mordenites. Al-M(151)-573 exhibited a stronger 3660 cm^{-1} band than Al-M(151)-873, which is consistent with Fig. 1, to indicate that the former contains larger amounts of EFAL.

After ammonia adsorption and desorption at 423 K for 1 h (Fig. 2B), the 3610 cm^{-1} band disappeared completely, indicating that the 3610 cm^{-1} hydroxy group is strongly acidic and ammonia molecules can reach all the Brønsted acid sites without steric hindrance.[22] However, the intensities of the 3745, 3700, 3500 and 3660 cm^{-1} bands decreased slightly or remained with ammonia adsorption, suggesting that these hydroxy groups are only weakly acidic or non-acidic. Upon ammonia adsorption, a broad band appeared at 1460 cm^{-1} (Fig. 2C). This band is characteristic of Brønsted acid sites in zeolite.[25–27] The spectra also showed a weak band at 1620 cm^{-1} due to NH_3 deformation vibration and a broad band at 3400–3000 cm^{-1} due to the NH_3 stretching vibration.[27] Martin *et al.*[27] used the former band to characterize Lewis acidity, while Kiovsky *et al.*[25] adopted the latter one to quantify the amount of Lewis acid sites. Because of these inconsistent assignments for Lewis acid site, we did not use NH_3-IR to discuss the Lewis acidity. After a removal of physisorbed ammonia at 423 K, the area of the 1460 cm^{-1} band was integrated to evaluate the concentration of Brønsted acid sites. Fig. 3A shows the relationship between the absorbance of the 1460 cm^{-1} band and the FAL content. The absorbance increased proportionally with the FAL content for the parent, dealuminated and aluminated mordenites. We have reported the proportional relationship between the absorbance of the 3610 cm^{-1} band and the FAL content for the same series of mordenites to demonstrate that FAL incorporated by alumination can form structural Si(OH)Al groups just like the ordinary framework Al atoms in the dealuminated mordenites.[21] Fig. 3A shows that these structural Si(OH)Al groups can react with ammonia as Brønsted acid sites in a similar manner to those in dealuminated mordenites.

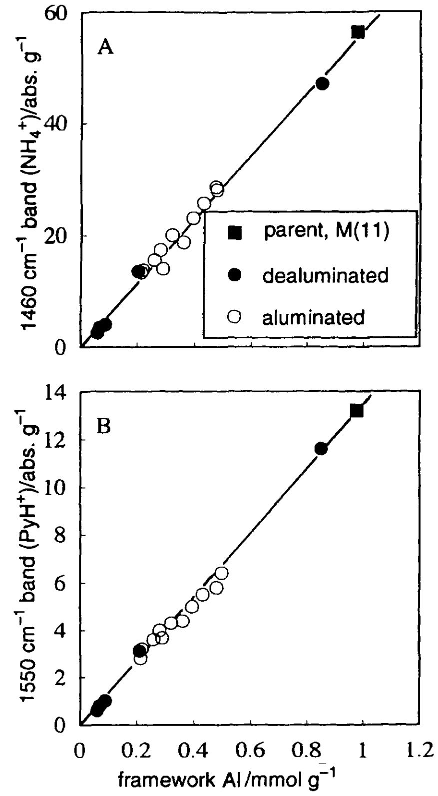


Fig. 3 Relationship between the amount of Brønsted acid sites and the framework Al content in mordenites: A, from NH_3-IR; B, from pyridine-IR. The desorption temperature for adsorbed ammonia and pyridine was 423 K.

As NH_3-IR spectra provided only the information on the Brønsted acidity, we used pyridine as a probe to study the zeolite acidity of both Brønsted and Lewis acid sites. After an adsorption of pyridine at 423 K, the 3610 cm^{-1} band was no longer observed, while the 3745, 3700, 3660 and 3500 cm^{-1} bands were almost unchanged. This is consistent with the result of NH_3-IR indicating that the former is a strongly acidic site and that the latter are non-acidic. We observed the adsorption bands of pyridinium ion (PyH^+) at 1635 and 1550 cm^{-1}, the bands of pyridine coordinated with Lewis acid sites (PyL) at 1620 and 1450 cm^{-1}, and that of both PyH^+ and PyL at 1490 cm^{-1}.[28] The bands at 1550 and 1450 cm^{-1}, free from overlap of other absorption bands, were used to characterize the Brønsted and Lewis acid sites, respectively. After desorption of physisorbed pyridine at 423 K for 1 h, the concentrations of Brønsted and Lewis acid sites were obtained as in Table 1. By comparing the acidity of M(151), M(195) and M(220) with that of the aluminated mordenites, it is apparent that alumination with $AlCl_3$ generated not only Brønsted acid sites but also a large amount of Lewis acid sites. This is consistent with the IR results reported on the aluminated ZSM-5 zeolites.[10] The development of Lewis acid sites may be related to Al atoms inserted into the extraframework sites, which will be discussed in detail later. Fig. 3B shows the relationship between the absorbance of the 1550 cm^{-1} band and the FAL content. Similar to the result of NH_3-IR (Fig. 3A), the absorbance was proportional to the FAL content for the parent, dealuminated and aluminated mordenites.

Sawa *et al.* reported that for mordenites with FAL content of higher than 1.65 mmol g^{-1} (corresponding to a framework Si/Al ratio lower than 7.5), the amount of acid sites decreased with increasing aluminium content, and assumed the generation of non-acidic FAL atoms owing to the strong interaction between the paired Al atoms.[22] Niekerk *et al.*, however, found a good 1 : 1 relationship between the acid amount determined by NH_3-TPD and the tetrahedral aluminum content in a wider range (0–2.5 mmol g^{-1}) of Al content, and suggested that all the FAL atoms in mordenites were acidic.[29] In this study, the highest FAL content of 0.98 mmol g^{-1} is lower than that in mordenites containing non-acidic Al atoms assumed by Sawa *et al.*[22] Thus, in accord with the results of both Sawa *et al.* and Niekerk *et al.*, Fig. 3 indicates that all FAL atoms can form Brønsted acid sites attached by pyridine.

In summary, the alumination incorporates Al atoms into the framework and the extraframework sites simultaneously. The increased FAL atoms react with ammonia and pyridine to act as Brønsted acid sites in a similar manner to the FAL atoms in conventionally dealuminated mordenites, indicating that the constriction of the pore aperture is not important even for pyridine with a relatively larger molecular dimension. On the other hand, the EFAL species generated by the alumination are not Brønsted acid sites.

Catalytic activity

Toluene disproportionation. The catalytic activity of the dealuminated and aluminated mordenites was measured for toluene disproportionation, which is believed to be catalysed by strong Brønsted acid sites. The reaction was carried out at 573 K to control the conversion of toluene within 20%. The products were mainly benzene and xylene isomers (>98 mol%), with a small amount of trimethylbenzenes as by-products especially at higher conversions. The ratio of the rate

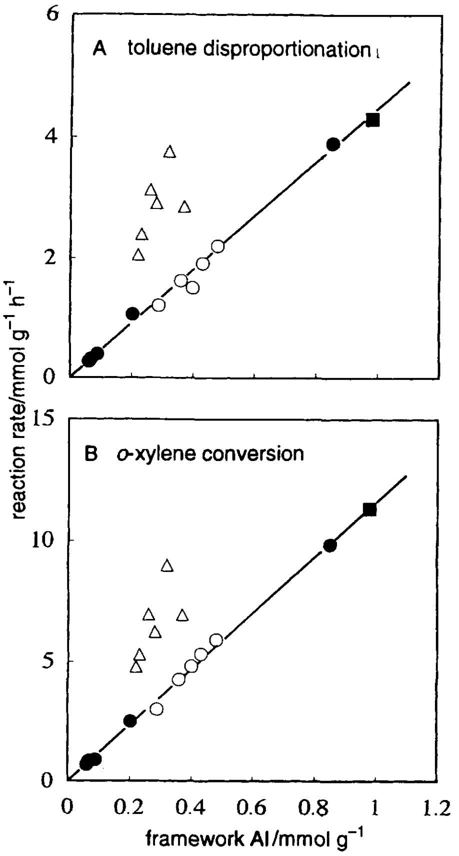


Fig. 4 Dependence of A, toluene disproportionation activity and B, *o*-xylene conversion activity on the FAL content: (■) parent, M(11); (●) dealuminated mordenites; (○) Al-M(*n*)-873; (△) Al-M(*n*)<873. Toluene disproportionation, $T = 573$ K and $W/F = 2.6$ g h mol^{-1}; *o*-xylene conversion, $T = 473$ K and $W/F = 2.5$ g h mol^{-1}.

of formation of benzene to that of xylenes was approximately unity throughout the reaction, indicating a so-called 'clean disproportionation'.[30] The selectivity for *p*-xylene was *ca.* 60% for both dealuminated and aluminated mordenites, indicating that the EFAL species play no significant role in altering the shape-selective properties. At the initial stage of the reaction the dealuminated mordenites and Al-M(*n*)-873 mordenites exhibited a progressive increase in activity with time on stream. The activity was found to reach a maximum at between 0.5 and 1.5 h on stream, and then decrease gradually with time on stream. Al-M(*n*) < 873 mordenites, however, exhibited no activation period observed for the dealuminated mordenites and Al-M(*n*)-873 at the initial stage but showed continuous deactivation with time on stream.

For the determination of the activity of Brønsted acid sites, the reaction rate measured at 1 h on stream was plotted against the FAL content as shown in Fig. 4A. The catalysts fell into two groups. The first group consisted of the parent, the dealuminated mordenites and Al-M(*n*)-873. A good linear relationship was observed for these mordenites. The second group consisted of Al-M(*n*) < 873 mordenites which exhibited remarkably enhanced activity compared with the catalysts in the first group.

***o*-Xylene conversion.** *o*-Xylene conversion was also examined. This reaction is believed to require Brønsted acid sites of at least medium strength. Both isomerization to *p*- and *m*-xylene isomers and disproportionation into toluene and trimethylbenzenes were observed at 473 K. As in the case of toluene disproportionation, two groups of the mordenites were discerned with respect to the effect of time on stream. The first group consisting of the parent, the dealuminated mordenites and Al-M(*n*)-873 showed no deactivation and the ratio of isomerization to disproportionation of *ca.* 3.0–5.0 did not change with 1 h on stream, where the activity was determined. The second group consisting of Al-M(*n*) < 873 mordenites always deactivated through the reaction, and showed a ratio of isomerization to disproportionation of *ca.* 1.3–2.0 at 1 h on stream where the activity was measured as their total activity. As disproportionation needs stronger acid sites than isomerization, the lower ratio of isomerization to disproportionation shown by the mordenites in the second group suggests that they contain stronger acid sites. The dependence of the activity of *o*-xylene conversion on the FAL content is depicted in Fig. 4B. The catalytic activity varied linearly with the FAL content in a composition range of *ca.* 0.0–0.98 mmol g^{-1} for the parent, the dealuminated mordenites and Al-M(*n*)-873 K. Al-M(*n*) < 873 mordenites, however, showed enhanced activity. Moreover, no obvious changes in the selectivity for the isomerization product of *p*-xylene was observed for all of the mordenites. The above results are very similar to those observed for toluene disproportionation.

The linear dependence of catalytic activity on the FAL content in Fig. 4 indicates that every FAL atom in the dealuminated mordenites and Al-M(*n*)-873 has the same activity, *i.e.* a constant turnover frequency (TOF) for toluene disproportionation and *o*-xylene conversion over a wide range of aluminium concentration. The intensive factor of FAL in so-called 'clean framework' zeolites is considered to be related to the distribution of FAL.[13,14] Our ^{29}Si MAS NMR spectra showed that all the mordenites except M(11) and M(13) had only Si(1Al) sites due to isolated Al atoms and Si(0Al) sites, but no Si(2Al) sites due to paired Al atoms. The number of paired Al atoms even in M(11) and M(13) was less than 10% of the total FAL content. This is quite in agreement with the aluminium distribution calculated for mordenites by Ding *et al.* who, by means of a Monte Carlo method, showed that the number of FAL in Si(1Al) increased linearly with respect to the FAL content, while the number of FAL in Si(2Al) was almost zero over the FAL content range studied in the present work.[31] Furthermore, as mentioned above, IR measurements have demonstrated that all structural hydroxy groups can react with ammonia or the even bigger pyridine molecule without steric hindrance for their diffusion to show Brønsted acidity. Toluene and *o*-xylene are also suggested to reach all these Brønsted acid sites during the reactions. Therefore, it is reasonable that the catalytic activity increases linearly with increasing the FAL content as depicted in Fig. 4. In fact, Barthomeuf predicted, in terms of structural parameters, that the maximum activity occurs at Si/Al = 10 for mordenite when the activity is plotted against the aluminium content.[32] On the other hand, Lombardo *et al.* verified this prediction recently and gave an actual Si/Al of 8 corresponding to the maximum activity for the conversion of neopentane, isobutane or *n*-hexane on mordenites.[15]

Al-M(*n*) < 873 K catalysis, however, showed higher activity than the mordenites on the straight line by a factor of 1.6–2.7 with respect to TOF. Table 1 and Fig. 1 show that these low-temperature aluminated mordenites contained a larger amount of EFAL than of FAL. These EFAL species may be responsible for the generation of the enhanced active sites in the aluminated mordenites.

Extraframework aluminium

Generation of EFAL. Here we consider the generation of EFAL species by the alumination and their role in the zeolite acidity and catalytic performance. Fig. 5 shows IR and MAS NMR spectra of the parent M(151) and $AlCl_3$-treated mordenite followed by various treatments. M(151) showed IR vibration bands at 3745 cm^{-1} (strong) due to terminal SiOH, at 3700 and 3500 cm^{-1} (strong) due to internal SiOH and at 3160 cm^{-1} (weak) due to structural Si(OH)Al groups, Fig.

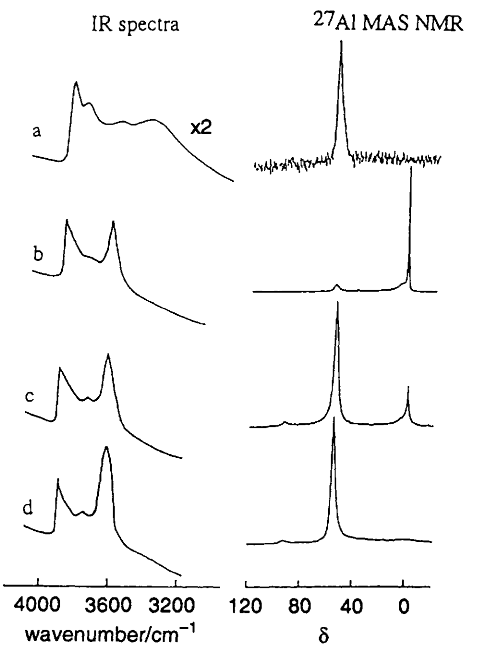
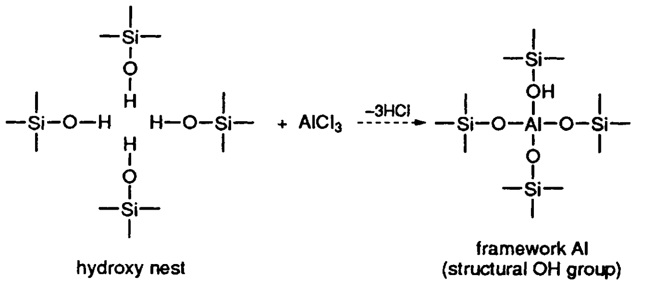


Fig. 5 IR and MAS NMR spectra: (a) parent M(151); (b) M(151) aluminated at 873 K without any treatment (as-prepared); (c) as (b) washed with water, (d) as (c) ion-exchanged with NH_4NO_3

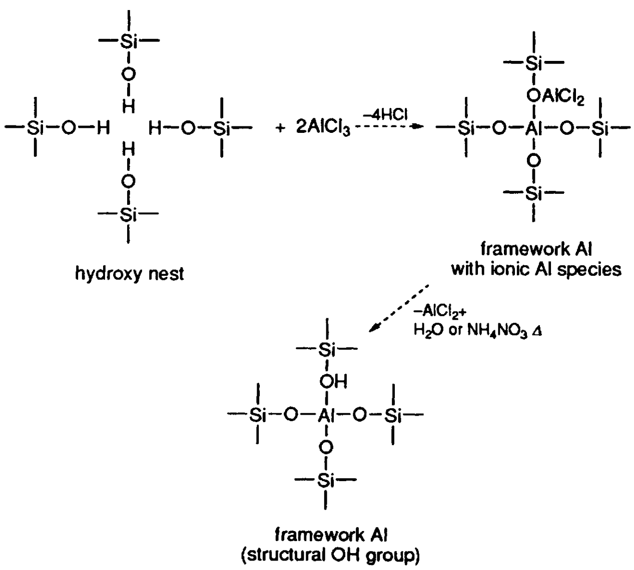
5(a). Upon alumination with $AlCl_3$ at 873 K, a strong and distinct band at 3610 cm^{-1} appeared with the disappearance of the 3700 and 3500 cm^{-1} bands. This is explained by the alumination mechanism proposed before,[11,21] where Al atoms are incorporated into the framework through the reaction of $AlCl_3$ with internal SiOH groups clustering as hydroxy nests as shown in Scheme 1.

The 3610 cm^{-1} band increased on washing with water and further increased with iron-exchange by NH_4NO_3 followed by calcination [Fig. 5(c) and (d)]. This could be explained by the removal of an ion-exchangeable Al species introduced into the cation sites during the alumination, as proposed for the alumination of highly siliceous ZSM-5.[8] This process can be shown as in Scheme 2.

This observation was confirmed by MAS NMR. The MAS NMR spectra were plotted on a fixed-peak-height basis in Fig. 5 and, therefore, are not intended for quantitative comparison. The ^{27}Al MAS NMR spectrum of the parent M(151) showed a very poor signal-to-noise ratio, indicating it is highly siliceous. M(151) exhibited only a resonance at 55 ppm due to structural tetrahedral aluminium in the framework sites and no resonance at 0 ppm due to octahedral aluminium in the extra-framework sites,[5] indicating that M(151) is lacking in EFAL. In fact, the amount of bulk Al in M(151) was the same as that of FAL (Table 1). As-prepared $AlCl_3$-treated mordenite showed an ^{27}Al MAS NMR spectrum with a good signal-to-noise ratio as a result of the increase in FAL, and exhibited a new resonance at 0 ppm. The ionic aluminium species, $AlCl_2^+$ illustrated in Scheme 2, may be responsible for this resonance. The 0 ppm resonance decreased in intensity with water washing and disappeared completely on ion-exchange with NH_4NO_3. These results are in agreement with Scheme 2 and demonstrate clearly that the ionic EFAL species can be generated by the alumination, however, they are partially removed by washing with water and are ion-exchanged readily by NH_4NO_3.



Scheme 1



Scheme 2

As shown in Table 1, the bulk Al content is always higher than the FAL content for all the ion-exchanged aluminated mordenites. This indicates the presence of EFAL in these aluminated mordenites even after ion-exchange. As ^{27}Al MAS NMR spectrum [Fig. 5(d)] showed only one resonance of 55 ppm, those EFAL species in the ion-exchanged mordenites should exist in 'NMR-invisible' states.[4,5]

As depicted in the IR spectra (Fig. 5), the 3745 cm^{-1} band of M(151) [Fig. 5(a)] decreased significantly through the $AlCl_3$-treatment [Fig. 5(b)]. Reaction of $AlCl_3$ with silica[33] or with highly siliceous ZSM-5 zeolite[10] has been demonstrated to involve the surface silanol groups. Similarly, the dramatic decrease of the 3745 cm^{-1} band is a consequent of the reaction of $AlCl_3$ with terminal SiOH groups on the external surface of the zeolite crystals according to Scheme 3.

The aluminium species in Scheme 3 are not tetra-coordinated. Therefore, they are responsible for a kind of EFAL. In the case of the alumination of ZSM-5, a portion of these species have been shown to be removed by hydrolysis with HCl.[10] However, when the aluminated mordenite was washed with water and ion-exchanged with NH_4NO_3, the intensity of the 3745 cm^{-1} band was not affected, as evidenced in Fig. 5. This result indicates that this kind of EFAL resist the hydrolysis with water and is not ion-exchangeable. Residual chloride was analysed using Volhard's titration method[34] and was not detected in the water washed or ion-exchanged aluminated mordenites. This observation suggests that the hydrolysis of the EFAL species formed in Scheme 3 occurs during these treatments as shown in Scheme 4.

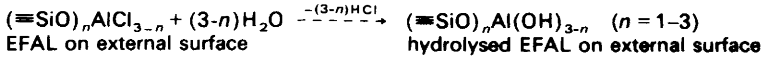
Fig. 5 shows that the aluminated mordenite after water washing and ion-exchange exhibited a weak band at 3660 cm^{-1} which is attributed to EFAL species.[24] The aluminium species of the hydrolysed form in Scheme 4 may be responsible for this weak band.

The aluminated mordenites prepared from the same parent, M(151), at temperatures lower than 873 K, for example Al-M(151)-573, exhibited the 3745 cm^{-1} band with an intensity

$$n\equiv SiOH + AlCl_3 \xrightarrow{-nHCl} (\equiv SiO)_nAlCl_{3-n} \quad (n = 1\text{–}3)$$

terminal silanol **EFAL on external surface**

Scheme 3



$$\underset{\text{EFAL on external surface}}{(\equiv SiO)_nAlCl_{3-n} + (3-n)H_2O} \xrightarrow{-(3-n)HCl} \underset{\text{hydrolysed EFAL on external surface}}{(\equiv SiO)_nAl(OH)_{3-n}} \quad (n = 1\text{–}3)$$

Scheme 4

comparable to that of Al-M(151)-873 [Fig. 2(b) and (c)]. The comparable decrease in the 3745 cm^{-1} band on alumination implies that the amount of EFAL species generated by the reaction of $AlCl_3$ with terminal SiOH (Scheme 3 and 4) is nearly the same for both catalysts. However, it is apparent from Fig. 1 that a lower alumination temperature preferentially introduces Al atoms as EFAL instead of FAL. There must be another route for the generation of EFAL during the low-temperature alumination. Fig. 2(b) and (c) show that the 3700 and 3500 cm^{-1} bands were not visible for Al-M(151)-573 just like for Al-M(151)-873. This indicates that $AlCl_3$ reacted with all the internal SiOH groups really even at 573 K. The FAL content of Al-M(151)-573, however, was lower than that of Al-M(151)-873. We have demonstrated that alumination at 873 K causes the FAL content to reach a maximum (Fig. 1), where the number of generated FAL atoms is nearly equal to that of consumed hydroxy nest estimated by ^{29}Si MAS NMR.[21] It is concluded that EFAL species in Al-M(151)-873 K mainly result from the reaction of $AlCl_3$ with terminal SiOH (Schemes 3 and 4), while in the case of Al-M(151)-573, a portion of the reaction between $AlCl_3$ and internal SiOH generates EFAL instead of FAL. Considering that Al-M(151)-573 contained almost two times the amount of EFAL species in Al-M(151)-873 (Table 1), the reaction of one hydroxy nest with two $AlCl_3$ molecules is assumed to generate such EFAL species, although it is still not easy to determine the exact number of $AlCl_3$ molecules owing to the difficulty in determination of the EFAL amount generated in Scheme 3 and 4. This process can be described as shown in Scheme 5.

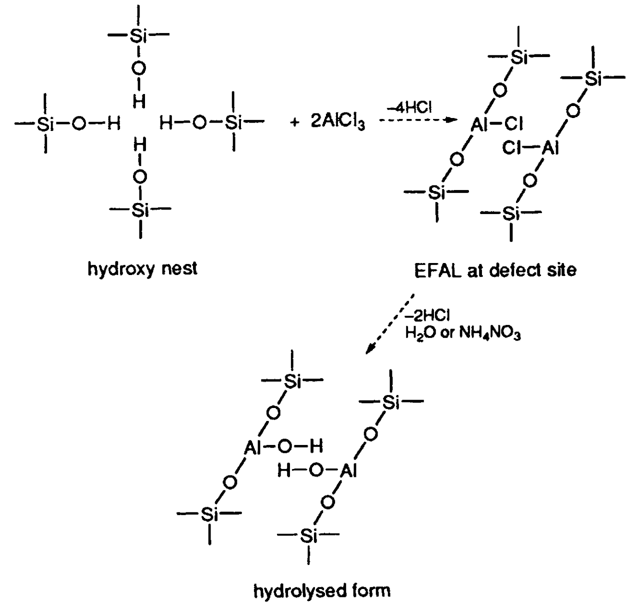
These aluminium species in Scheme 5 are expected to exist in a dislodged state of coordination. Therefore, they are invisible by the conventional ^{27}Al MAS NMR measurements due to the loss of symmetry. As depicted in Scheme 5, the hydrolysis produces two hydroxy groups related to Al atoms. These hydroxy groups may show similar IR vibration to that in Scheme 4. In fact, Al-M(151)-573 showed a stronger 3660 cm^{-1} band than Al-M(151)-873 [Fig. 2(B) and (C)].

In spite of the significant amount of EFAL detected, it is surprising that all the aluminated mordenites showed no crystalline peaks other than those of mordenite in XRD patterns and had surface area close to the parent mordenites.[21] These facts also suggest that EFAL are not present as large particles of oxide, but exist in a finely dispersed form either outside the crystal surface (Scheme 3 and 4), or within the crystals (Scheme 5), so as not to affect the surface area.

Lewis acidity. Those EFAL species generated through Schemes 3–5 may respond to the Lewis acidity in the aluminated mordenites as determined by the earlier pyridine-IR measurements (Table 1). Adsorption of water on the zeolites preabsorbed with pyridine was carried out to investigate the nature of Lewis acid sites. Fig. 6 shows the IR spectra in the pyridine region of Al-M(151)-873 together with a dealuminated mordenite, M(13) which was free of EFAL. Lewis acid sites existed in these two zeolites as evidenced by a band at 1450 cm^{-1} (PyL) in Fig. 6(a). After the addition of water to the zeolites preabsorbed with pyridine, M(13) showed no 1450 cm^{-1} band, but an increase in the 1550 cm^{-1} band (PyH$^+$) and a strong band around 1620 cm^{-1} due to water.[35] The complete removal of Lewis acid sites by water addition is consistent with the previous observation that Lewis acid sites in conventional proton-type zeolite are a result of partial dehydroxylation of the structural Si(OH)Al groups at temperatures higher than 473 K, and that they are reversibly returned to Brønsted acid sites by the adsorption of water.[35,36] On the other hand, the introduction of water to Al-M(151)-873 resulted in no change in the 1550 cm^{-1} band, but a shift of the 1450 cm^{-1} band to the lower frequency region by 10 cm^{-1} as shown in Fig. 6(b). A similar band at 1445 cm^{-1} has been assigned to H-bonded pyridine.[29] It is obvious that the Lewis acid sites in the aluminated mordenites are so-called 'true' Lewis acid sites which arise from the EFAL species.

Fig. 7 depicts the relationship between the absorbance of the 1450 cm^{-1} band and the EFAL content for both mordenites aluminated at 873 K and at lower temperatures. A proportional relationship exists in all the aluminated mordenites. This implies that all Al atoms introduced into the extra-framework sites coordinate with pyridine to act as Lewis acid sites, although they may exist in different environments, that is, on the external surface (Scheme 3 and 4) or within the crystals (Scheme 5).

Acid strength. As shown earlier, Al-M(*n*)-873 series exhibited comparable catalytic properties to those of the dealuminated mordenites, while the Al-M(*n*) < 873 series behaved quite dif-



Scheme 5

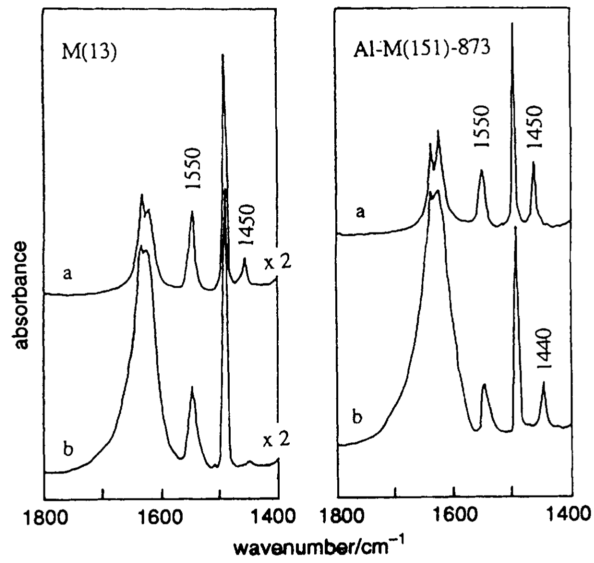


Fig. 6 IR spectra (pyridine vibration region): (a) after pyridine desorption of 523 K for 1 h; (b) as (a) followed by addition of water vapour at 523 K for 1 h

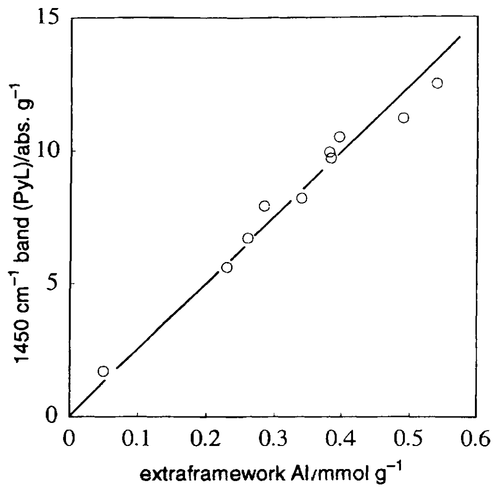


Fig. 7 Relationship between the amount of Lewis acid sites and the extraframework Al content in the aluminated mordenites. The desorption temperature for adsorbed pyridine was 423 K.

ferently. This may be due to the presence of Brønsted acid sites with different strength in these two series of catalysts. The distribution of the acid strength was measured from the thermodesorption of pyridine by IR measurements according to a method in ref. 10. The acid strength was compared between the Al-M(*n*)-873 series and the Al-M(*n*)-673 series. Fig. 8 shows the result measured by pyridine-IR for the two series of aluminated mordenites obtained from the parents M(151), M(195) and M(220). The changes in the absorbance of the 1550 cm^{-1} band with desorption temperature indicate that both weak Brønsted acid sites corresponding to low desorption temperature and strong Brønsted acid sites corresponding to high desorption temperature have been generated by the alumination. The Al-M(*n*)-873 series showed higher absorbance values for the 1550 cm^{-1} band than their partners in the Al-M(*n*)-673 series at desorption temperatures lower than 723 K. The absorbances became nearly the same at 723 K, indicating that the amount of Brønsted acid sites with medium strength are comparable in these two series of aluminated mordenites. When the desorption temperature is higher than 723 K, reverse variations of the absorbance value occurred. As only pyridine adsorbed on stronger acid sites remains when the desorption temperature increases, this result implies that the Al-M(*n*)-673 series contain a larger amount of strong Brønsted acid sites than the Al-M(*n*)-873 series. On the other hand, no significant difference was observed for the Lewis acid site distribution between Al-M(*n*)-873 and Al-M(*n*)-673.

The acid strength was also characterized with NH_3-IR which gives information only on the Brønsted acidity (Fig. 9). In agreement with the observation given by pyridine-IR, NH_3-IR also demonstrated that the alumination generated a larger amount of strong Brønsted acid sites in Al-M(*n*)-673 than in Al-M(*n*)-873, although it developed more of the total amount of Brønsted acid sites in the latter. Comparing Fig. 8 and Fig. 9, the desorption temperature corresponding to a turn point where the amount of Brønsted acid sites reversed for the two series of aluminated mordenites was observed to be 200 K higher by pyridine-IR than by NH_3-IR. It seems that the basic probe of ammonia characterizes the strength distribution of Brønsted acid sites more effectively.

The higher proportion of strong Brønsted acid sites present in Al-M(*n*) < 873 K is suggested to be responsible for the enhanced activity for toluene disproportionation and *o*-xylene conversion as shown in Fig. 4. Mirodatos and Barthomeuf found that super acid sites showing enhanced activity for toluene disproportionation arose in mordenite upon steaming treatment, and proposed that this was due to an interaction of structural OH groups with Lewis acid sites formed from polymeric oxoaluminum species in the zeolites channel.[16] Beyerlein *et al.* reported that hydrothermally dealuminated Y zeolites containing a low fraction of dislodged aluminium exhibited markedly higher activities for isobutane conversion, and suggested that very strong acid sites arose depending on a balance between FAL and FAL entrained in the lattice during steaming.[2] Lago *et al.* studied the steam-dealumination on ZSM-5 zeolite and found that mild steaming resulted in a fourfold increase in hexane cracking activity. They proposed a

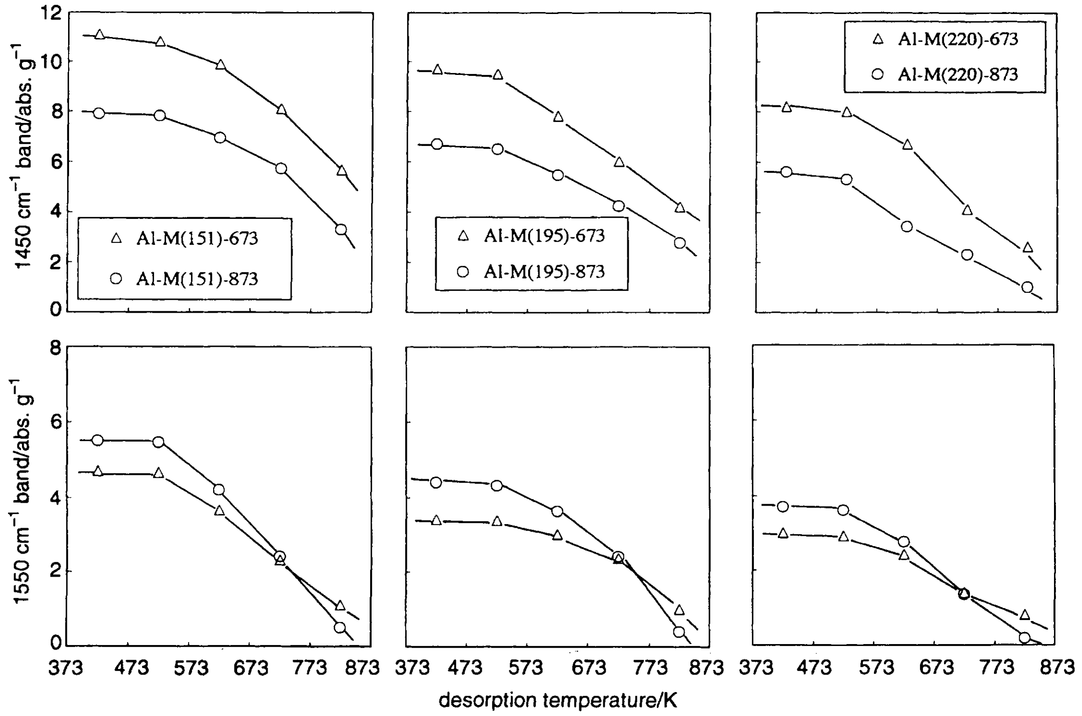


Fig. 8 Comparison of Brønsted and Lewis acid site distribution between Al-M(*n*)-673 and Al-M(*n*)-873. The amount of acid sites was determined from pyridine-IR spectra.

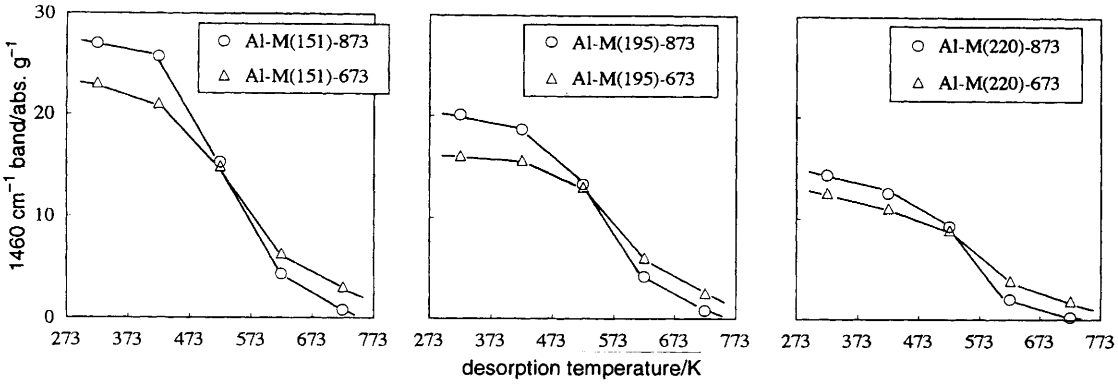


Fig. 9 Comparison of Brønsted acid site distribution between Al-M(*n*)-673 and Al-M(*n*)-873. The amount of acid sites was determined from NH_3-IR spectra.

kinetic model of paired FAL atoms to show that the enhanced active sites were formed by partial hydrolysis of the Al pair.[6] In agreement with these suggestions, we assume a synergism between FAL and EFAL species, *i.e.* between Brønsted and Lewis acid sites, is responsible for the generation of stronger Brønsted acid sites which enhance the catalytic activity of Al-M(n) < 873. As shown in Fig. 6 and 7, those Al atoms introduced into the extraframework sites could coordinate with pyridine to act as 'true' Lewis acid sites. Therefore, these electron acceptors would withdraw a portion of electrons from the structural OH groups to lower the strength of the OH bonds and consequently to enhance their Brønsted acidity.

The enhancement of Lewis acid sites on the strength of Brønsted acid sites has been considered to be related with the balance between the amount of EFAL and that of FAL. In agreement with the model of paired Al atoms generating stronger acid sites by Lago *et al.*,[6] Sendoda and Ono assumed that a dislodged aluminium preferentially interacted with one acidic hydroxy group to form a stronger acid site.[37] Beyerlein *et al.* have concluded that stronger acid sites arose at an optimum EFAl to FAl ratio of *ca.* 0.4.[2] Shertukde *et al.*, however, suggested that the enhanced activity was independent of the lattice Al atoms but just associated with the EFAL content.[4] Thus, it is still a matter of debate whether the EFAL content effectively creates strong acid sites. In the present study, the EFAL to FAL ratio calculated using the data in Table 1 was 0.6–0.8 for Al-M(n)-873. Although this ratio is slightly lower than the value obtained for Al-M(n) < 873, it is near to or higher than the value in the above references,[2,4,37] where the enhancement of acid strength was observed. The series of Al-M(n)-873 catalysts, however, did not exhibit catalytic enhancement properties, but showed the same activity to those dealuminated mordenites with respect to TOF (Fig. 4). Therefore, other factors than the absolute amount of EFAL and the EFAL to FAL ratio may be responsible for the enhancement of Brønsted acidity.

As mentioned above, EFAL species in Al-M(n)-873 were generated mainly through the reaction of $AlCl_3$ with terminal SiOH groups and were located on the external surface (Schemes 3 and 4), while a portion of EFAL species in Al-M(n) < 873 was also created by the reactions of $AlCl_3$ with internal SiOH groups and was present inside the channels (Scheme 5). It is reasonable to conclude that the former EFAL species does not interact with the Brønsted acid sites inside the channels and that the latter EFAL species interact with the structural OH groups in close vicinity to them to enhance the Brønsted acidity, that is, the local environment and the siting of EFAL species may play a significant role in the enhancement of zeolite acidity.

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