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Catalytic Properties of the Aluminium Form of Zeolite Y modified with Trifluoromethane

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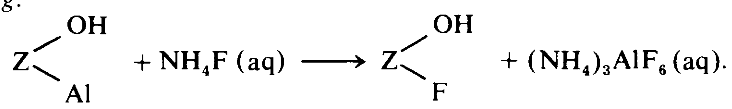
Trifluoromethane has been used in a gaseous fluorination of the aluminium form of zeolite Y in order to avoid removal of aluminium during fluorine modification, which was observed previously for the procedure with NH_4F aqueous solution. The samples modified with CHF_3 showed an increase in catalytic activity for reactions involving acid sites; however, the maximum activity was reached for much lower fluorine content and it was slightly lower than that for samples fluorinated with NH_4F.

We have previously used two different methods for the fluorination of zeolites.[1–4] In one case [fig. 1(*a*)] the hydrogen forms of zeolites were directly treated with fluorination agents and we believe that some hydroxyl groups in the zeolite were replaced by fluoride anions. The strength of the remaining hydroxyls was enhanced owing to the inductive effect of the adjacent fluorine atoms. This procedure was successfully applied to the high-silica zeolites (mordenites, ZSM-5), where superacid centres[5] were found after fluorination. However, this procedure could not be employed for the modificaiton of faujasite-type zeolites, since their crystalline structure was substantially affected by the fluorination agents, even under very mild fluorination conditions.[2,6]

For low-silicon content zeolites we applied another method [fig. 1(*b*)], involving the introduction of Al cations into the zeolite before fluorination, hoping that Al cations would react with the fluorination agent in the inner spaces of zeolite to produce AlF_3 or another Al–F species. These Lewis-acid-type compounds could interact with acidic OH groups to enhance the acid strength of the modified zeolite. Our recent study[1] showed a considerable increase in the catalytic activity of the Al form of zeolite Y modified with an aqueous solution of NH_4F. We found, however, that some aluminium was removed from the zeolite during fluorination, the amount of which was proportional to the amount of fluorine introduced into the zeolite. Some dealumination of the zeolite framework was also noticed. This above suggested that reaction (*b*) in fig. 1 cannot be the only process taking part in fluorination and other reactions have to be taken into account, *e.g.*



$$\mathrm{Z}{<}^{\mathrm{OH}}_{\mathrm{Al}} + \mathrm{NH_4F\,(aq)} \longrightarrow \mathrm{Z}{<}^{\mathrm{OH}}_{\mathrm{F}} + \mathrm{(NH_4)_3AlF_6\,(aq)}.$$

According to the above scheme, some of the fluorine introduced is attached to the zeolite lattice, similarly as in case of direct fluorination and enhanced activity results from the inductive effect of fluorine on the structural OH groups.

The interaction between the structural OH groups and the Lewis acids (*e.g.* AlF_3) is more easily achieved if the fluorination procedure of the Al modification is performed with a gaseous fluorinating agent. The low volatility of Al–F compounds and the lack of solvent can provide appropriate conditions for retaining aluminium in the zeolite. We have chosen trifluoromethane, which was used in our previous study[3,6] as an effective fluorination agent.

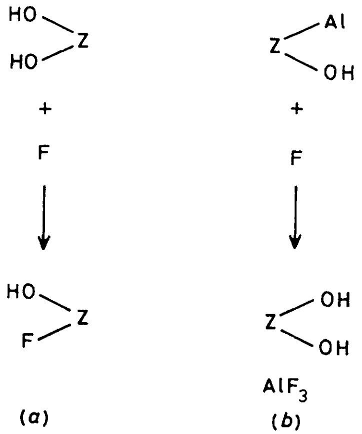


Fig. 1. Simplified reactions illustrating two ways of fluorination.

Table 1. Conditions of fluorination and amount of fluorine introduced

sample	activation temp./°C	fluorination time/h	fluorine (wt %)	F content[a]
G-1	200	1	0.3	2.0
G-2	200	3	0.7	4.6
GA-2	450	3	1.3	8.5
G-3	200	5	0.9	5.0
G-4	200	20	1.5	9.9
HAl-Y-F-1	samples modified with aqueous NH_4F[1]		0.64	4.2
HAl-Y-F-3			0.71	4.6
HAl-Y-F-5			0.76	5.0
HAl-Y-F-10			1.00	6.6
HAl-Y-F-20			1.35	8.8
HAl-Y-F-5			2.47	16.2

[a] Approximate number of F atoms per faujasite unit cell.

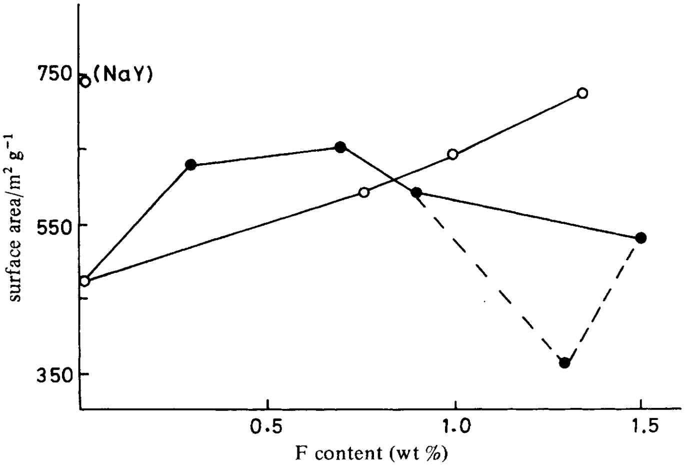


Fig. 2. Formal specific surface area *versus* fluorine content: ●, samples fluorinated with CHF_3; ○, samples fluorinated with NH_4F; (---) sample calcined before fluorination.

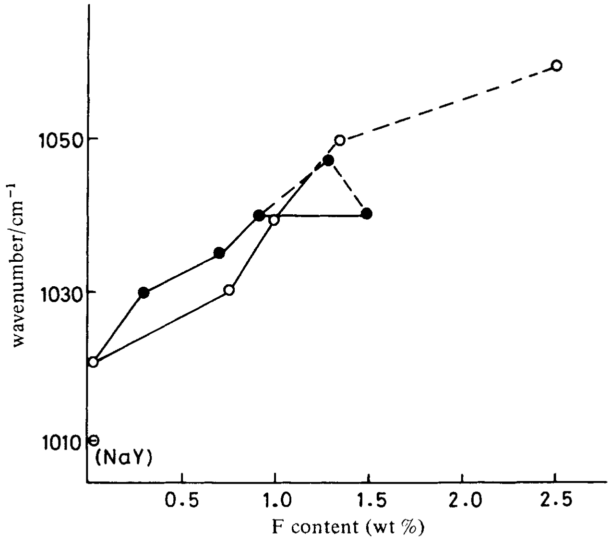


Fig. 3. Frequency of the main asymmetric stretching band as a function of fluorine content, samples marked as in fig. 2.

The aim of the following investigation is to study the catalytic properties of zeolite HAl-Y fluorinated with CHF_3 and to compare them with those of the same zeolite modified with NH_4F.

Experimental

The initial sample of zeolite NAl-Y was the same as that described in our previous paper.[1] The sample was washed and dried after ion exchange with $Al(NO_3)_3$ without further calcination. The composition of the sample was

$$H_xNa_{22}Al_{12}(OH)_y(AlO_2)_{53}(SiO_2)_{139}.$$

The proton number and the number of OH groups combined with Al cations were not estimated; however, the presence of both components has been considered. The samples fluorinated with NH_4F, used for comparison, were the same as described before.[1]

Fluorination was carried out under static conditions, using a glass tube reactor connected to two vessels containing 400 cm^3 of trifluoromethane. The powder samples (6 g) were activated in the reactor in a helium stream for 4 h before fluorination. Activation was carried out at temperatures as low as 200 °C (except for sample GA-2, which was heated at 450 °C) in order to avoid dehydroxylation and subsequent migration of Al cations from large cavities. For the same reason fluorination was performed also at 200 °C. The amount of fluorine introduced was regulated by the treatment time. After fluorination samples were purged in a helium stream at 450 °C for 4 h. The fluorine content was analysed using an ion-selective electrode.[6] The preparative conditions are listed in table 1, which also lists data for samples modified with NH_4F[1] in respect to their fluorine content.

The crystallinity of the samples was examined by X-ray diffraction, and all the samples (including GA-2) showed well preserved crystallinity. The formal specific surface area of the samples was estimated by means of low-temperature adsorption of nitrogen after the samples had been purged with helium at 300 °C for 6 h (fig. 2).

The infrared spectra of the samples were recorded using a Perkin-Elmer 180 spectrometer. For the range 1300–400 cm^{-1} the KBr pellet technique was applied (1 mg of the sample was mixed with 200 mg of KBr). Dealumination of the zeolite framework

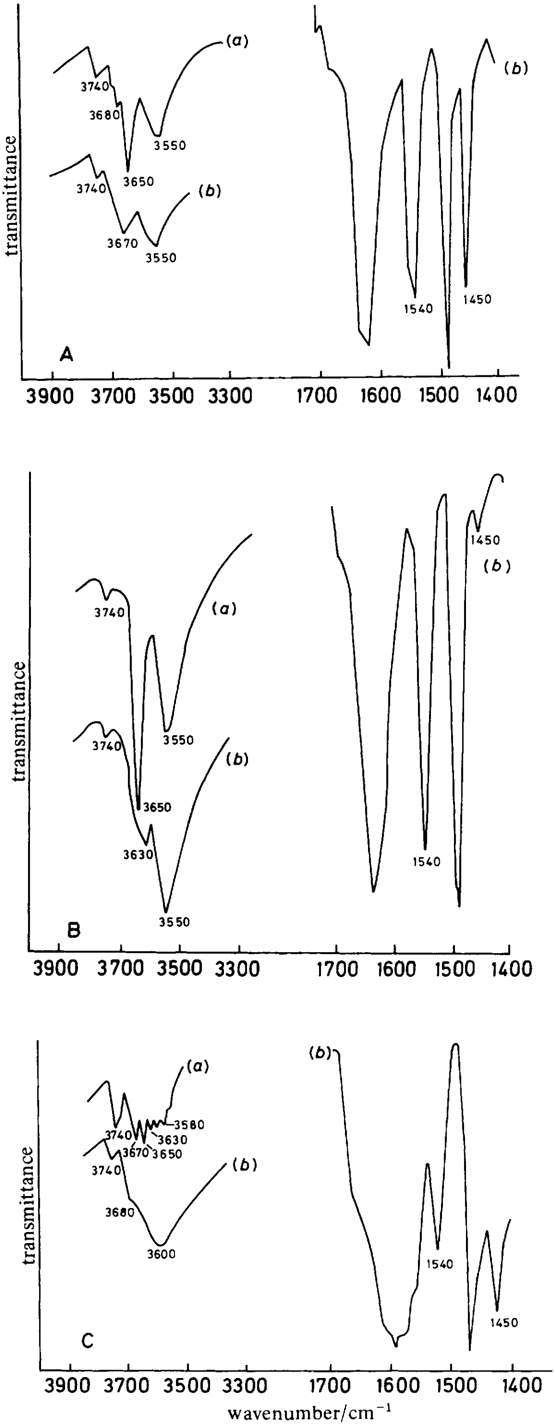


Fig. 4. Infrared spectra of the most characteristic samples: (A) HAl-Y; (B) G-4; (C) HAl-YF-20; (*a*) samples evacuated at 450 °C; (*b*) samples after pyridine adsorption.

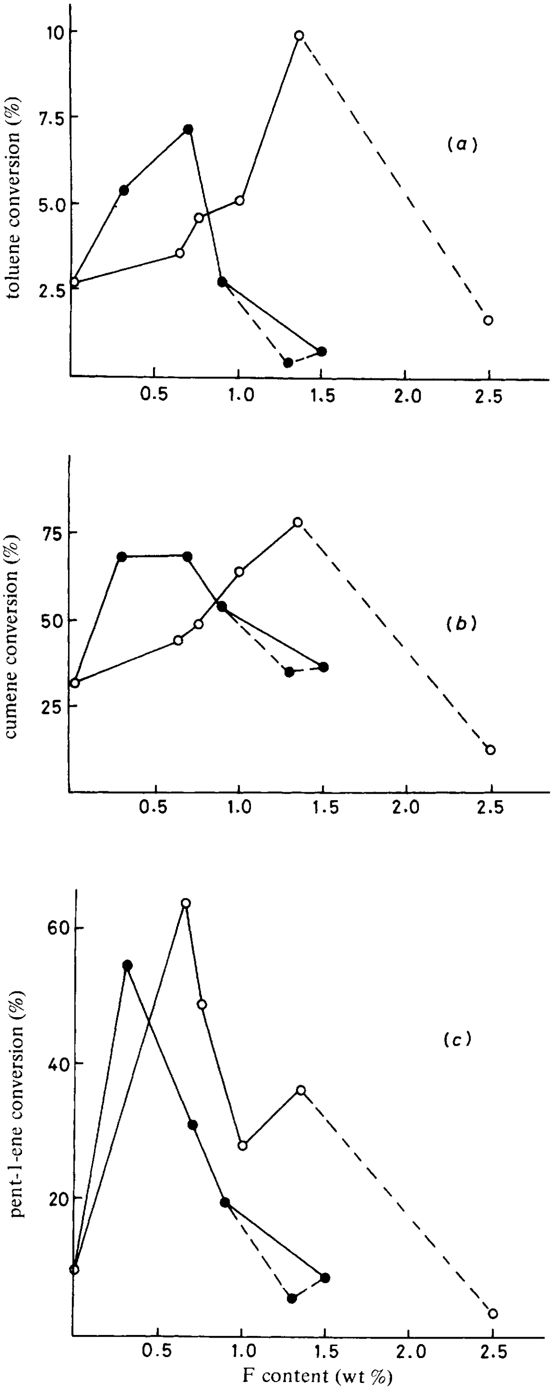


Fig. 5. Activity for reactions as a function of fluorine content: (*a*) conversion of toluene at 450 °C; (*b*) conversion of cumene at 400 °C; (*c*) conversion of pent-1-ene; samples marked as in fig. 2.

Table 2. Parameters of the catalytic tests

reaction	catalyst wt/g	reaction temp./°C	carrier He flow-rate /$cm^3\ min^{-1}$	pulse dose /$10^{-3}\ cm^3$
toluene disproportionation	0.05	490–370	50	0.5
cumene cracking	0.01	450–300	100	1.0
pent-1-ene isomerization	0.01	150	150	10

occurring during fluorination was observed as a shift of the main asymmetric stretching bands at *ca.* 1000 cm^{-1} (fig. 3). The hydroxyl region (4000–3000 cm^{-1}) was measured using self-supported wafers and a vacuum cell. Samples were activated at 450 °C under vacuum (10^{-5} mmHg†) for 6 h. After recording the bands of OH groups, pyridine was adsorbed for 2 h at room temperature and then samples were evacuated again at 150 °C for 3 h. After this procedure spectra were recorded again in the range of 4000–3000 cm^{-1} and in the range 1800–1400 cm^{-1}. The latter range contained the bands of chemisorbed pyridine. The most characteristic spectra are given in fig. 4. The ratio of Brønsted to Lewis acid sites was estimated as a quotient of the heights of the bands 1550 and 1450 cm^{-1}, which are assigned, respectively, to protonated and coordinatively bonded pyridine.

The catalytic activity of the samples under study was tested for reactions requiring acid sites of different strengths. Toluene disproportionation and cumene dealkylation are catalysed by very strong protic acid sites,[7] while isomerization of alkenes requires weak Brønsted or Lewis acid sites. These reactions were carried out in a pulse micro-reactor under the conditions listed in table 2. The powder catalyst samples were activated before the reactions in a helium stream for 1 h at 450 °C. Toluene underwent disproportionation towards xylenes with a high selectivity, nevertheless small amounts (*ca.* 2%) of other alkylbenzenes (especially ethylbenzene) were also detected. For cumene cracking only negligible amounts of products other than benzene and propylene were found.

The reaction of pentene was also carried out at temperatures higher than 150 °C, but the selectivity of the isomerization process decreased with temperature and the cracking products became predominant. Even at 150 °C some contribution of processes other than isomerization was noticeable. A correlation between the fluorine content and the catalytic activity for the reactions investigated is shown in fig. 5.

Discussion

The results listed in table 1 show that gaseous fluorination with CHF_3 is an effective way of modification, even at temperatures as low as 200 °C. McVicker *et al.*[8] suggested that cleavage of the C—F bond occurred above 400 °C, thus it is likely that decomposition of trifluoromethane at lower temperatures takes place due to the catalytic action of zeolite HAl-Y.

The amount of fluorine introduced into the zeolite can be regulated by the time of treatment. The correlation between the fluorine content and time of fluorination (fig. 6) fits a parabola described by the equation: $y^2 = cx$. The amount of fluorine introduced, calculated per faujasite unit cell, is lower than the number of Al cations, even for the samples richest in fluorine. Therefore, the transformation of all Al cations to AlF_3 is

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† 1 mmHg = 1.33322×10^2 Pa.

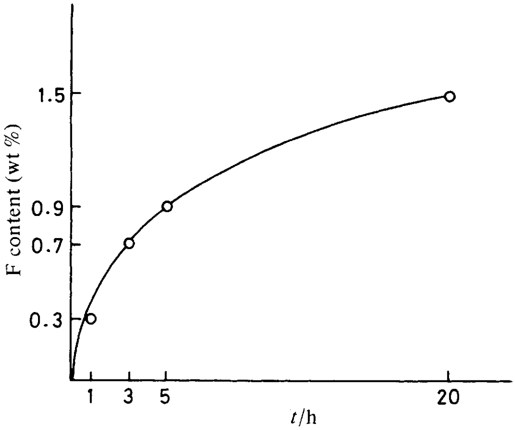

Fig. 6. Correlation between the time of fluorination and amount of fluorine introduced.

impossible. Besides, some additional Al cations are released from the lattice during the fluorination process. Thus, the formation of species 'unsaturated' in fluorine (*e.g.* $AlOHF^+$, AlF_2^+ *etc.*) seems to be more likely.

The thermal activation of the initial sample before gaseous fluorination plays a decisive role in determining the properties of the resulting modification. As for fluorination with NH_4F, the sample calcined at 450 °C (sample GA-2) differs significantly from the other fluorinated zeolites. Sample GA-2 contains almost twice as much fluorine as sample G-2, prepared under the same conditions (except for the activation temperature).

Calcination of zeolite HAl-Y results in dehydration and dehydroxylation of Al cations and subsequently in their migration from the supercages. Therefore, the fluorination agent can react with the zeolite framework and affect the structure of the zeolite.

Although X.r.d. does not indicate a distinctive decrease in crystallinity of sample GA-2, its specific surface area is considerably lower than that for the other samples (*ca.* 360 $m^2\ g^{-1}$). Such a substantial reduction of surface area (that for G-2 is *ca.* 650 $m^2\ g^{-1}$) reflects a structure deformation in sample GA-2. The surface area of the initial sample HAl-Y is relatively low (470 $m^2\ g^{-1}$) compared with zeolite Na-Y (*ca.* 750 $m^2\ g^{-1}$). Probably a substantial part of the supercage is filled with the ligands surrounding aluminium cations, *i.e.* H_2O molecules and OH groups. Fluorination with NH_4F brings about an almost linear increase in surface area with fluorine content. The above correlation results most likely from a removal of aluminium from the zeolite during fluorination. The large cavities become more accessible to the adsorbate molecules after replacing bulky Al cations combined coordinatively with the ligands by the small protons. The surface area of the samples fluorinated with CHF_3 increases up to the level of 0.7% F and then decreases for the extensively fluorinated samples. This relationship is not very clear. Perhaps a small amount of fluorine is substituted for the ligands or even changes the coordination number of the Al cations, which is reflected in higher surface area. The decrease in surface area for the samples richest in fluorine is possibly caused by the formation of larger species (*e.g.* Al_2F_6) which block the entrances to the cavities.

Although gaseous fluorination cannot cause removal of aluminium from the zeolite, the mid-infrared spectra of the samples show noticeable shifts in the bands due to dealumination of the zeolite framework. The samples calcined before fluorination show the highest dealumination. Considering the correlation between the framework composition (Al/Al + Si) and the frequency of the main stretching band[9] we can estimate the degree of dealumination of the samples under study. The initial value of Al/Al + Si (0.27) for the sample HAl-Y is altered to 0.22 for G-4 and 0.20 for HAl-YF-20. In the

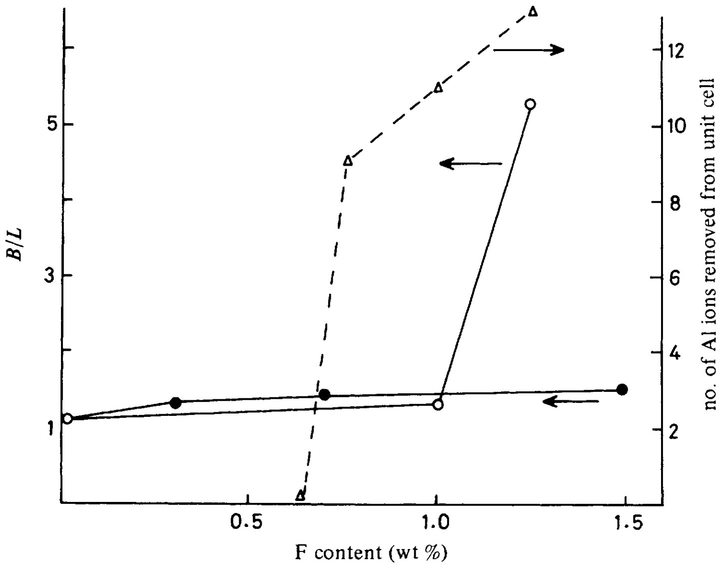

Fig. 7. The Brønsted to Lewis acid sites ratio estimated from intensities of pyridine bands (1450 and 1540 cm^{-1}). Numbers of Al ions removed from ref. (1).

case of the calcined samples the respective values are 0.20 for GA-2 and 0.18 for HAl-AF-5. The above estimate suggests that almost one third of the lattice aluminium can be removed into extra-framework positions during fluorination. These results are, however, only very preliminary, since the presence of fluorine in zeolites can affect the correlation[9] between the framework composition and the band frequency.

The infrared spectra of the samples, recorded in the range 4000–3000 cm^{-1}, and those of adsorbed pyridine indicate considerable differences, reflecting different types of fluorination. The spectrum of the initial sample HAl-Y [fig. 4(A)] consists of the bands at 3550, 3650 and 3740 cm^{-1}, which are usually observed for the hydrogen forms of faujasite.[7,10] In addition, a distinctive shoulder at 3680 cm^{-1} is also seen. The latter is assigned to OH groups combined with Al cations. Another band at 3800 cm^{-1} of the same origin was observed in our earlier study[11] for the sample activated at 180 °C. The band disappeared after heating at 450 °C. Adsorption of pyridine reduces the intensity of the band at 3650 cm^{-1}. Both pyridine bands at *ca.* 1450 cm^{-1} and 1540 cm^{-1} are very intense for sample HAl-Y, indicating a high concentration of protic and aprotic acid sites. The relatively high contribution from the Lewis-acid sites ($B/L = 1.1$) issues from the presence of the Al cations introduced. The Al cations are considered as the true Lewis-acid sites in zeolites.[10] The introduction of a limited amount of fluorine by means of NH_4F results in the appearance of several additional low-intensity bands in the range 3700–3550 cm^{-1}. After further fluorination these small bands disappear and only three intense bands (3545, 3650 and 3740 cm^{-1}) remain. The adsorption of pyridine affects mostly the band at 3650 cm^{-1}. The increase in fluorine content brings about a higher contribution from the Brønsted-acid sites. This effect is particularly pronounced for the samples richest in fluorine (HAl-YF-20), where the band at 1540 cm^{-1} is predominant. The high intensity of the bands at 3650 and 3550 cm^{-1} as well as the very high Brønsted/Lewis acid ratio most likely results from the removal of a substantial part of the aluminium from the zeolite during fluorination (fig. 7). The hydroxyl groups recorded in infrared spectra of fluorine-rich samples are not combined with Al cations, since many of them are removed, but rather with the framework of the zeolite. After the removal of aluminium, a substantial part of the fluorine is bonded to the zeolite lattice. The

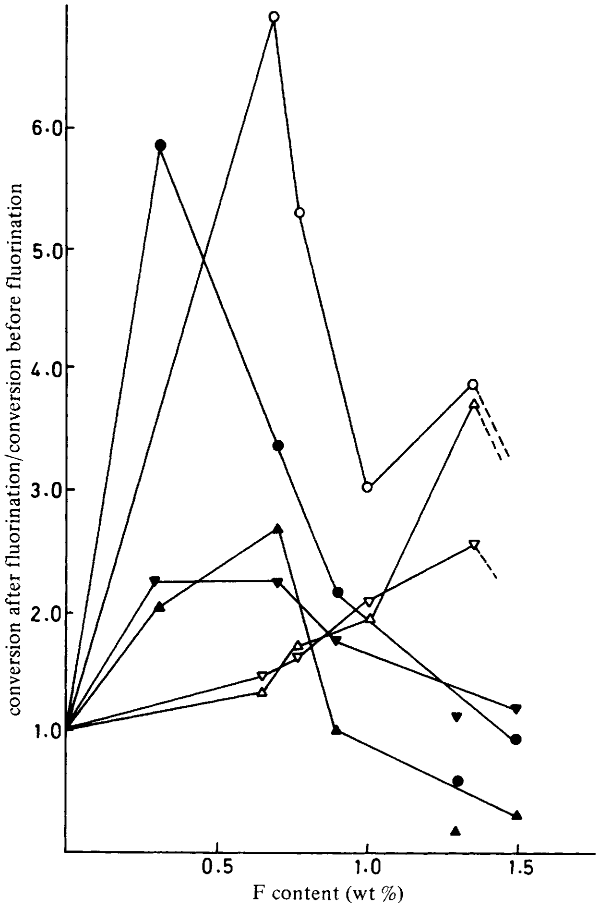

Fig. 8. Correlation between fluorine content and changes in activity after fluorination for the reactions: ●, ○, pent-1-ene isomerization; ▲, △, toluene disproportionation; ▼, ▽, cumene cracking; the filled symbols represent series treated with CHF_3.

increased strength of the acidic OH groups results from interaction with adjacent fluorine atoms. In case of the samples fluorinated with CHF_3 the small bands in the region 3700–3550 cm^{-1} are predominant, even for the samples richest in fluorine. These bands can be attributed to OH groups combined with Al cations and fluorine (*e.g.* $AlFOH^+$, AlF_2OH *etc.*). The thermal stability of these hydroxyls is high, since the purging after fluorination and the pretreatment before recording spectra were carried out at 450 °C. It is interesting that the band at 3740 cm^{-1}, assigned to silanol OH groups, is not noticeably affected either with CHF_3 or with NH_4F, suggesting that silicon is not so involved in the reaction with fluorine as is aluminium. The adsorption of pyridine reduces most the intensity of the bands at higher wavenumber (3700–3650 cm^{-1}). The Brønsted/Lewis acid ratio increases with fluorine content (fig. 7).

The results of the catalytic tests show a considerable increase in activity of the catalyst after treatment with CHF_3. The maximum activities, however, are always slightly lower than those for the samples fluorinated with NH_4F. The correlation between fluorine content and catalytic activity differs remarkably for both series of catalysts. In both cases the introduction of fluorine brings about an increase in activity, but the maximum catalytic activity is reached for much lower fluorine content after gaseous fluorination.

In the series of catalysts treated with NH_4F the sample HAl-YF-20 (1.38 % F) shows the highest activity for the reactions of toluene and cumene, whereas the sample HAl-YF-1 (containing 0.64% F) appears to be the most active for pentene isomerization. Further increase in the fluorine content reduces the activity for the latter reaction; however, another smaller maximum of activity is seen for the sample HAl-YF-20.

In the case of the samples fluorinated with CHF_3 the highest activity for the toluene reaction was found for sample of G-2, containing 0.7% F (*i.e.* almost half as much fluorine as for sample HAl-YF-20). The activity of samples G-2 and G-1 is similar for cumene cracking. At lower reaction temperatures the activity of sample G-1 (0.3% F) is noticeably higher. Sample G-1 is the most active among the catalysts of the series for the pent-1-ene isomerization.

It is worthwhile mentioning that during pentene isomerization the catalysts undergo very rapid deactivation and the catalyst usually becomes completely inactive after several injections. Further activation at 450 °C in helium does not restore the initial activity, because a substantial amount of coke is formed in side-reactions.

The relative changes in activity caused by fluorination of the initial samples are illustrated in fig. 8. The introduction of a small amount of fluorine results in a very drastic increase in the activity for pentene isomerization (*ca.* six times higher than for the starting zeolite), while further fluorination causes a reduction in the activity for pentene reaction (except for sample HAl-YF-20). This suggests that under mild fluorination a large number of relatively weak acid sites is generated. The number of acid sites is reduced after further fluorination, whereas their strength is enhanced. Sample G-1 certainly also contains a fraction of stronger protic acid sites, since it is active for cumene cracking. The latter catalyst is one of the most active for this reaction. The mildly fluorinated zeolites exhibit activity higher than that of the starting sample HAl-Y for toluene disproportionation, reflecting the presence of very strong acid centres in these samples. The contribution of very strong sites is more pronounced for the samples richer in fluorine. Samples G-2 (0.7% F) and HAl-YF-20 (1.35% F) are the most active for the toluene reaction. The details concerning transformation of the acid sites are not very clear so far.

The nature of acid sites in the series of fluorinated samples under comparison is different. The maximum activity for the reactions involving strong sites is attained in the case of samples in which a considerable amount of Al was removed by means of treatment with NH_4F. The acid strength of structural OH groups is probably enhanced mostly by the inductive effect of adjacent fluorine. The highest activity in the case of zeolites fluorinated with CHF_3 is observed for almost half the concentration of F. The Al–F–OH species generated during fluorination contribute to the catalytic activity. The decrease in activity after passing a value of 0.7% F possibly results from the creation of large species (*e.g.* Al_2F_6), which can block the entrances to the supercages.

Conclusions

Fluorination of the Al form of zeolite with trifluoromethane is an effective method of modification. The fluorine content can easily be regulated by changing the treatment time.

The thermal pretreatment before flurorination affects remarkably the properties of the resulting modification.

The properties of the samples fluorinated with CHF_3 differ noticeably from those treated with NH_4F. The formal specific surface area increases almost linearly with fluorine content for zeolites treated with NH_4F, but for samples modified with CHF_3 it decreases after passing a level of 0.7% F. The reduced surface area for the samples richest in fluorine possibly results from generation larger Al–F species.

Despite the gentle treatment, the samples undergo dealumination of the zeolite framework during fluorination.

Infrared spectra of the samples treated with CHF_3 show several OH groups in the range 3700–3550 cm^{-1}, which can be attributed to the Al–F–OH species. In the other series two bands of OH groups at 3650 and 3550 cm^{-1} are seen (particularly for the fluorine-rich samples), suggesting that fluorine combines preferentially with the zeolite framework than with Al cations. The contribution of the protic acid sites (B/L ratio) increases with fluorine content.

The introduction of fluorine into zeolite HAl-Y enhances its catalytic activity significantly for reactions involving acid centres. The maximum activities, however, are approached for much lower fluorine contents in the case of zeolites modified with CHF_3. On the other hand, the maximum conversions over the catalysts modified with NH_4F are slightly higher.

Introduction of a small amount of fluorine results in the generation of high population of relatively weak acid sites, which brings about the maximum activity for pentene isomerization. Further increases in the fluorine content reduces the number of the latter sites, but the stronger protic centres, active for transformation of aromatic compounds, are created instead.

It is likely that the high catalytic activity of samples modified with NH_4F results mostly from an inductive interaction between fluorine and the framework and the adjacent structural OH groups. In the case of gaseous fluorination, the contribution of Al–F–OH species in the catalytic effect has to be considered. The contribution of the above species is much more distinctive than that resulting from an interaction of AlF_3 and structural OH groups.

A more detailed explanation of the role of introduced fluorine in the catalytic properties of modified zeolites requires further investigation into the nature of fluorine-bearing species generated in zeolites.

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References

1 K. A. Becker and S. Kowalak, *J. Chem. Soc., Faraday Trans. 1,* 1987, **83**, 535.
2 S. Kowalak, *React. Kinet. Catal. Lett.*, 1985, **27**, 441.
3 K. A. Becker and S. Kowalak, *J. Chem. Soc., Faraday Trans. 1,* 1985, **81**, 1161.
4 K. A. Becker, K. Fabianska and S. Kowalak, *Acta Phys. Chem.*, 1985, **31**, 63.
5 K. A. Becker and S. Kowalak, *J. Chem. Soc., Faraday Trans. 1,* 1986, **82**, 2151.
6 K. A. Becker, S. Kowalak and M. Kozłowski, *React. Kinet. Catal. Lett.*, 1985, **29**, 1.
7 P. A. Jacobs, *Carboniogenic Activity of Zeolites* (Elsevier, Amsterdam, 1977) and references therein.
8 G. B. McVicker, C. J. Kim and J. J. Egert, *J. Catal.*, 1983, **80**, 315.
9 E. M. Flanigen, *ACS Monograph 171, Zeolite Chemistry and Catalysis* (Am. Chem. Soc., Washington D.C., 1976) p. 80, and references therein.
10 W. J. Mortier and R. A. Schoonheydt, *Prog. Solid State Chem.*, 1985, **16**, 1.
11 S. Kowalak and M. Ziółek, *Zeolites*, in press.

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