Catalysis Letters 39 (1996) 173–178

Gas phase synthesis of MTBE on fluoride-modified zeolites

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Received 2 October 1995; accepted 4 March 1996

The gas phase synthesis of MTBE was studied using three series of zeolites modified by ion-exchange with ammonium fluoride, the parent materials being HY, H-mordenite, and HZSM-5. Modification of zeolites by fluoride-exchange was found to enhance the MTBE synthesis activity for all three types of zeolites without impairing their excellent selectivity to MTBE. The mechanism of activity enhancement by fluoride-modification appears to be related to the formation of extra-lattice Al rather than the presence of fluoride-ions.

Keywords: etherification; H-mordenite; HY; HZSM-5; MTBE; fluoride; zeolites

1. Introduction

Tertiary alkyl ethers have been the main focus of industrial research for octane enhancement in the last decade [1–4], as a result of the increasing environmental concerns about fuel quality [5,6]. MTBE (methyl tert-butyl ether) is currently extensively utilized as a gasoline additive due to its favorable physicochemical properties, superior antiknocking behavior, and an observed reduction in the emission of toxic and polluting compounds such as CO and hydrocarbons from internal combustion engines [7–10].

The current commercial MTBE synthesis process, liquid phase reaction of methanol and isobutene, is typically catalyzed by a sulfonated ion-exchange resin whose corrosive properties and lack of thermal stability and regeneration are major drawbacks [3,11]. Zeolites have been examined as potential alternative catalysts for MTBE formation due to their superior selectivity to MTBE even at less favorable reactant ratios and excellent thermal stability [3,12]; however, their activities have been found to be significantly lower than that of the resin catalyst [3,13].

A moderate improvement in zeolite activity for etherification has been observed by modification of their acidity with strong electron-withdrawing compounds like triflic acid [14] and ammonium sulfate [15]. In addition, a significant activity increase by modification of zeolite acidity resulting from ion-exchange with fluoride-ions (ammonium fluoride) has been reported for other acid-catalyzed reactions, such as cumene and *n*-hexane cracking [16–20]. It is thus conceivable that ion-exchange with ammonium fluoride could result in a strong increase in zeolite activity for ether synthesis, making fluoride-exchanged zeolites more attractive for commercial etherification processes.

This study reports on an investigation of the ion-exchange of zeolites with ammonium fluoride and the resulting variation in zeolite activity for the formation of MTBE.

2. Experimental

Three series of post-synthesis modified zeolites were studied, the three parent zeolites being HY (LZ210-12, from UOP), H-mordenite (H-Zeolon, Norton) and HZSM-5 (Mobil). These materials were obtained as fine powders (crystallite size of ca. 1 μm). Their different structural morphology could be utilized for a comparative evaluation of these ion-exchanged zeolites in terms of activity for the synthesis of MTBE.

Modification of the parent zeolites was performed by ion-exchange with ammonium fluoride (NH_4F). Portions of ca. 0.5 g of each of the parent zeolites was slurried in a series of dilute aqueous solutions of ammonium fluoride at 50°C under stirring, the ammonium fluoride being in various concentrations (0.01–0.1 M) in order to achieve different levels of ion-exchange. The slurries were then filtered and dried without washing at 110°C in air for 12 h. This modification process is similar to that reported in the literature [16,17].

Various techniques were used to characterize the catalysts studied. The chemical composition of the zeolite catalysts, in terms of Si, Al, residual cation (such as Na^+) content, as well as the extent of ion-exchange (fluorine content), was identified by atomic absorption spectroscopy (performed by Galbraith Laboratories). The Si/Al ratio and lattice Al content of the zeolite catalysts were also determined by ^{29}Si and ^{27}Al magic-

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angle-spinning (MAS) NMR. ^{27}Al NMR was also used to check on the possible formation of extra-lattice Al as a result of the ion-exchange process. These measurements were performed at ambient temperature and pressure using a Bruker MSL-300 NMR spectrometer. Samples of ca. 200 mg of the non-dehydrated, non-pretreated parent and fluoride-exchanged zeolites were typically placed in a zirconia rotor which was in turn placed in the solid-state probe. For ^{29}Si NMR the parameters used were: spectral frequency (SF) of 59.627 MHz, spectral width (SW) of 62.5 kHz, a spinning rate of ca. 4 kHz, and a repetition time of 10 s [21]. A dilute tetramethylsilane (TMS) solution was used for determining the Si chemical shifts (Si was quantified directly by elemental analysis). The parameters used for ^{27}Al NMR were: SF = 78.205 MHz, SW = 62.5 kHz, a spinning rate of 3–3.5 kHz (in order to avoid possible interference of spinning side-bands with the signal corresponding to octahedrally-coordinated Al), and a repetition time of 1 s [21]. A sample of an aluminium (Al^{3+}) solution in dilute HCl (Certified AAS, Fisher Scientific) was used as a standard for determining the Al chemical shifts.

The number of active sites for the synthesis of MTBE was estimated by assuming one Brønsted acid site per lattice Al free of residual cations (like Na^+). The agreement of this estimation with the proton content of various zeolites, as measured by ^{1}H MAS NMR of thoroughly dried samples, has been shown in previous studies [21].

The degree of crystallinity of the zeolites, both prior to and after modification was determined by X-ray diffraction (XRD) and the patterns obtained were compared to those in the literature [22].

Reaction experiments were performed using a quartz glass fixed-bed microreactor with on-line GC-FID analysis. The flow system was equipped with mass flow controllers and a back pressure regulator, thus offering accurate control of the flows and partial pressures of the reactants. Methanol (Aldrich, ACS HPLC grade) was vaporized by flowing helium (UHP grade) through a glass saturator maintained at 28 ± 0.2°C. Isobutene was fed as a 10% mixture in He (Liquid Carbonic). The reaction temperature was continuously monitored by a thermocouple inserted in the catalyst bed. The oven and heated transfer line temperatures were controlled to within ±0.5°C. Products were identified using an off-line mass spectrometer (GC-MS). Prior to reaction, all catalysts were activated at 400°C for 2 h after heating with a rate of 2°C/min under helium flow.

The reaction conditions used were: temperatures of 40–90°C, reaction pressure of 156 ± 7 kPa, MeOH/IB molar feed ratio of 1.0, MeOH partial pressure of 6.9 kPa, He as the inert diluent, catalyst weight of 10–20 mg, and total flow of 52 ± 0.5 cm^3/min. These conditions were chosen to obtain differential conversions and to minimize the influence of possible external heat/mass transport limitations. Initial activity data were obtained after 5 min of reaction in order to establish constant reactant concentration in the zeolite pores and to minimize inaccuracies induced by temperature gradients resulting from the strong exothermicity of the reaction. At each reaction temperature the reaction was monitored until a pseudo-steady-state was established (typically in ca. 1 h). The reactant flow was then substituted by helium flow and the system was cooled to the next reaction temperature.

A series of experiments performed with variable reactant gas flow rates (5–55 cm^3/min) indicated the absence of significant mass transfer limitations for flows above 25 cm^3/min.

3. Results

3.1. Catalyst characteristics

The characterization results for the modified zeolites before any activation are reported in table 1. The extent of fluoride-modification is reported in wt% and in mmol of fluoride-ions per gram of zeolite. The modified zeolites are identified by the parent name (M for mordenite, Y for Y, and Z for ZSM-5) followed by the amount of exchanged fluoride in wt%. Thus, the zeolite Y(F-0.43) is HY containing 0.43 wt% fluoride-ions.

^{27}Al MAS NMR experiments on the fluoride-exchanged samples (subjected to no activation or other treatment after the ion-exchange process) showed no indication of formation of extra-lattice Al as a possible outcome of the exchange process. ^{27}Al NMR spectra for the parent HY as well as two fluoride-exchanged HY zeolites are presented in fig. 1. The only peak observed (at 54 ppm) corresponds to lattice Al (Al_L). Similar spectra were obtained for all the other fluoride-exchanged samples. Modification of zeolites with fluoride ions probably positioned in the vicinity of lattice Al could be expected to cause some heterogeneity in the magnetic moments of Al nuclei and thus a broadening of the observed Al peaks. However, any broadening seen was well within the uncertainty resulting from the tuning of the instrument. It is interesting to note that although some extra-lattice Al was measured for the parent mordenite (probably as residue from its synthesis process), none was detected for the fluoride-exchanged mordenite samples, apparently resulting from its solvation and removal in the acidic aqueous solution during the exchange process.

X-ray diffraction was used for an evaluation of the crystallinity of the modified zeolites. No detectable loss of crystallinity was observed for the fluoride-exchanged zeolites as compared to the parent ones. The diffraction parent zeolites were in very good agreement with those in the literature [22].

Table 1
Characteristics of NH_4F-modified zeolites before activation

Zeolite	Modif. extent[a]		Al_L[b] (mmol/g)	Al_E[c] (mmol/g)	Lattice Si/Al[d]	Mod./Al_L[e] (%)
	(wt%)	(mmol/g)				
H-mordenite[f]	0	0	1.35	0.25	9.5	0
M(F-0.12)	0.12	0.06	1.35	0	9.5	4.4
M(F-0.37)	0.37	0.20	1.35	0	9.5	14.8
M(F-1.53)	1.53	0.81	1.35	0	9.5	60.0
HY[f]	0	0	2.20	0	6.0	0
Y(F-0.12)	0.12	0.06	2.20	0	6.0	2.7
Y(F-0.43)	0.43	0.23	2.20	0	6.0	10.5
Y(F-0.85)	0.85	0.45	2.20	0	6.0	20.5
HZSM-5[f]	0	0	1.20	0	12.0	0
Z(F-0.08)	0.08	0.04	1.20	0	12.0	3.3
Z(F-0.13)	0.13	0.07	1.20	0	12.0	5.8
Z(F-0.54)	0.54	0.28	1.20	0	12.0	23.3

[a] From atomic absorption spectroscopy (AAS).
[b] From ^{27}Al MAS NMR and Al elemental analysis (AAS); accuracy: ±0.2 mmol/g for all zeolites.
[c] From ^{27}Al MAS NMR of the non-activated samples.
[d] From ^{29}Si and ^{27}Al MAS NMR and Si, Al elemental analysis (AAS).
[e] Ratio of extent of fluoride-modification to lattice Al content of zeolites.
[f] Unit cell compositions: $H_{4.6}(AlO_2)_{4.6}(SiO_2)_{43.4}$ for H-mordenite, $H_{24.1}Na_{3.3}(AlO_2)_{27.4}(SiO_2)_{164.6}$ for HY, and $H_{8.0}(AlO_2)_{8.0}(SiO_2)_{88.0}$ for HZSM-5.

3.2. Effect of fluoride-exchange on MTBE synthesis

The activity of the fluoride-exchanged zeolites for the synthesis of MTBE, expressed in terms of steady-state rates of MTBE formation at 90°C, is plotted in fig. 2 as a function of the ratio of the extent of fluoride-exchange to the lattice Al content of the zeolite samples (F^-/Al_L). The reason for choosing this ratio as the independent variable for the graph of fig. 2 was to facilitate a comparison of the activity performance of the three types of modified zeolites by normalizing the level of modification on a per active site basis, since they were formed from materials with different concentrations of active sites. If the extent of fluoride-exchange were chosen instead, only a minor concentration or expansion of the curves along the x-axis would be produced, but the observed trends would essentially remain the same.

The activity curves presented in fig. 2 clearly indicate that for all three types of zeolites studied an increase in the extent of fluoride-exchange resulted in a substantial

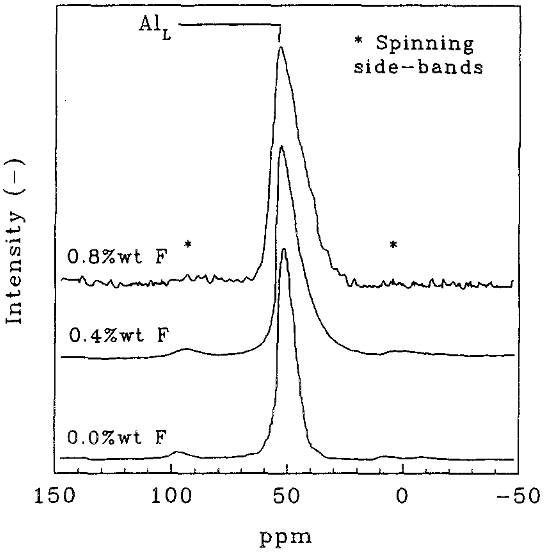

Fig. 1. ^{27}Al MAS NMR of non-activated fluoride-exchanged HY zeolites.

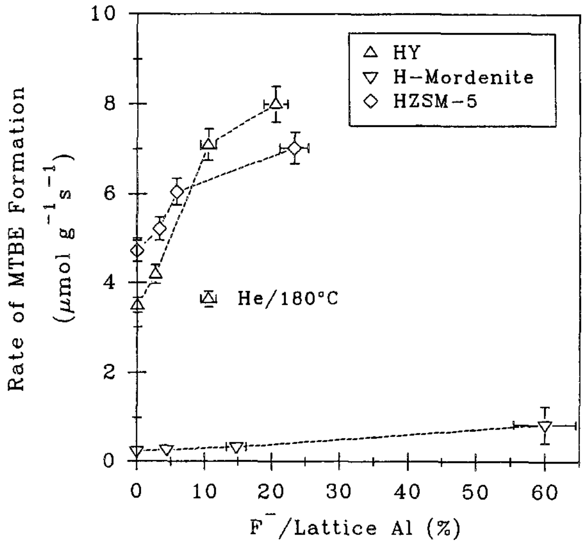

Fig. 2. Comparison of steady-state MTBE synthesis activities of fluoride-exchanged zeolites at 90°C.

increase in MTBE synthesis activity. In particular, for the Y zeolite an exchange of ca. 20% of its site concentration with fluoride-ions was found to result in a more than 100% increase in its activity for MTBE formation. A 50% activity increase with a similar modification level was obtained for ZSM-5. The activities of all the mordenite samples were significantly lower than those of the other zeolites; however, on a percent-basis a similar activity increase as for the other two zeolite-types was obtained.

Similar trends to those presented in fig. 2 were observed by plotting the initial activity data for MTBE formation (obtained after 5 min on stream) instead of the steady-state data, thus suggesting that these trends are not significantly influenced by deactivation. A deactivation level of ca. 10–25% was measured for the Y zeolites at the given conditions. The ZSM-5 zeolites exhibited lower deactivation compared to the Y ones, probably due to an enhanced resistance to coke formation, known to be a characteristic of ZSM-5 [23]. The mordenite zeolites also showed lower deactivation, apparently due to their low activity for MTBE synthesis. In all cases, deactivation was higher for the samples exhibiting higher activities. Since all the catalysts studied deactivated slowly, there were no detectable byproducts at the reactor outlet, thus, the reaction was essentially 100% selective to MTBE. In addition, the catalyst properties reported in table 1 (extent of modification, extent of extra-lattice Al formed) would not be expected to change due to catalyst deactivation as a result of coke deposition.

It is interesting to note that zeolite Y(F-0.43), after being activated only at 180°C in He flow for 2 h (as opposed to at 400°C), exhibited significantly lower MTBE synthesis activity compared to the sample activated at 400°C, as shown in fig. 2. This rather unexpected observation seems to indicate that the activation of the fluoride-modified zeolites at elevated temperatures (400°C) could be at least partially responsible for the observed enhancement in MTBE synthesis activity, ruling out the presence of fluoride-ions alone as the cause of the increased activity.

In order to evaluate the possible influence of mass transfer limitations on the activity data and thus on the effect of fluoride-modification presented in fig. 2, Arrhenius-type experiments were performed on all the zeolite catalysts in the temperature range of interest. Similar experiments were also performed for this reason on other series of zeolites examined for MTBE formation [24,25]. The experimental methodology for these experiments has been described in detail elsewhere [25]. An Arrhenius-type behavior was observed for all the parent and fluoride-modified catalysts between 60 and 90°C, and the measured apparent energies of activation in this range were 75 ± 10 kJ/mol. On the other hand, the apparent activation energy values obtained at lower temperatures (40–60°C) were ca. 135 kJ/mol (i.e., about 2 times the average value measured at 60–90°C), suggesting that the kinetic data obtained above 60°C were at least partially influenced by internal diffusion. However, in agreement with observations discussed in our previous studies [24,25], the activity trends presented in fig. 2 cannot be an artifact of diffusion, since diffusion has a greater effect on the more active catalysts, and thus the observed activity enhancement for the modified zeolites would have been even more pronounced in the absence of diffusion limitations.

4. Discussion

As mentioned above, post-synthesis modification of zeolites with fluoride-ions has been found to result in a zeolite activity enhancement for various acid-catalyzed reactions, like cumene and *n*-hexane cracking [16–20]. A model that has been proposed in order to explain these observations involves the ion-exchange of fluoride-ions with hydroxyl-ions in the zeolite lattice. Such an exchange apparently causes a decrease in the concentration of Brønsted acid sites, along with a more substantial increase in the acid strength of these sites, due to the strong electron-withdrawing character of the fluoride-ions, thus enhancing the overall acidity of the zeolite catalyst [16–19].

On first inspection, the activity results on the synthesis of MTBE presented in fig. 2 appear to be in agreement with this model of acidity enhancement by fluoride-ions. Indeed, an increase in the extent of fluoride-exchange was found to be accompanied by enhanced zeolite activity for MTBE formation. However, the observation that fluoride-modification did not result in an MTBE synthesis activity enhancement unless it was coupled with a high temperature activation process appears to indicate that the combination of these two processes may produce a variation in the acidity function of zeolites and thus in their catalytic performance. Therefore, this suggests that the previously proposed model of activity enhancement by fluoride-exchange needs to be reevaluated.

In a study of the synthesis of MTBE on a series of dealuminated Y zeolites, a major finding was that an enhancement in zeolite acidity by dealumination (formation of extra-lattice Al) resulted in a significant increase in MTBE synthesis activity [24]. Furthermore, in a study of MTBE formation on HY zeolites modified by impregnation with triflic acid, another strong electron-withdrawing compound, the observed increase in activity for MTBE synthesis was related to an acidity increase which was attributed to the formation of extra-lattice Al during the modification process rather than to direct involvement of the modifying species [25]. Based on these observations, it could be hypothesized that (a) the high-temperature activation of the fluoride-modified zeolites may have resulted in the formation of extra-lattice Al, and (b) it is this extra-lattice Al formation which causes the observed increase in zeolite activity.

In order to examine the possible formation of extra-lattice Al during activation, ^{27}Al NMR was performed for the activated samples, the activation process being identical to that used prior to reaction (i.e., heating to 400°C at 2°C/min under He flow and holding at that temperature for 2 h). ^{27}Al NMR spectra of the HY zeolites whose spectra were presented in fig. 1 are shown in fig. 3 for comparison purposes. Besides the lattice Al (Al_L) peak, a peak corresponding to extra-lattice Al (Al_E) was also observed, clearly indicating the formation of extra-lattice Al during activation of the fluoride-exchanged samples. In addition, higher amounts of extra-lattice Al were measured for increasing fluoride-levels for all types of zeolites, in agreement with similar results from other modification processes [25].

It is evident that zeolite modification with fluoride-ions in combination with the high temperature activation process resulted in the formation of extra-lattice Al as well as an increased activity for MTBE formation. The combined effect of modification and activation is highly unlikely to be determined solely by the activation temperature; other parameters (such as the acidity of the system during the modification process) could also be expected to play important roles.

The question that logically follows is whether the source for the observed superior performance of the fluoride-modified zeolites is an acidity enhancement related to the formation of extra-lattice Al, rather than to the direct presence of the strong electron-withdrawing fluoride-ions, as previously proposed [16–19].

In order to examine the new hypothesis, the steady-state activities of the fluoride-modified HY zeolites, expressed in terms of turnover frequency (TOF), defined as rate (mol per g of zeolite per second) divided by the concentration of Brønsted sites (lattice Al), are plotted in fig. 4 as a function of the ratio of extra-lattice to lattice Al, Al_E/Al_L. The Al_E/Al_L ratio was chosen as the independent variable in this graph since it was previously found to be correlated with the TOF of dealuminated HY zeolites for MTBE synthesis [24]. Also shown in fig. 4 are the TOFs of two series of modified HY zeolites which had been produced from the same HY zeolite used for the fluoride-exchange (LZ210-12 with a Si/Al ratio of 6.0), the modifications being dealumination by mild steam treatment [24] and impregnation with triflic acid [25]. The activities of these HY zeolites for MTBE formation have been previously reported [25] and are shown here for comparison purposes. Not all active sites in microporous zeolites are accessible to diffusing reactant species. There is, however, no absolute technique for measuring the accessible active sites for a given reaction. The TOFs in fig. 4 were determined based on total lattice Al for catalysts produced from the same parent zeolite with only limited degrees of modification, where only minor differences in site accessibility would be expected. Such differences would not significantly influence the correlation shown in fig. 4.

The results presented in fig. 4 clearly indicate that the specific activities (TOFs) of the fluoride-exchanged HY zeolites follow the same correlation with the Al_E/Al_L ratio (and not the amount of Al_E) as that obtained for the TFA-modified and steam-dealuminated HY zeolites. No other correlation was observed for these three modified zeolite series. This common correlation suggests that the source for the improved catalytic performance of the fluoride-modified zeolites for MTBE formation is an enhancement in acidity related to the presence of extra-lattice Al, discussed extensively in the studies on the effect of steam-dealumination [24] and

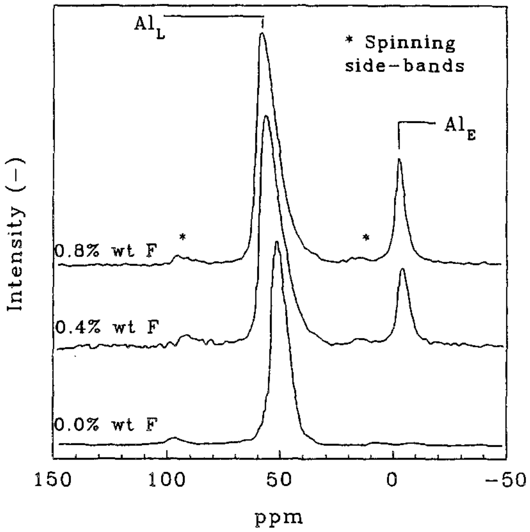

Fig. 3. ^{27}Al MAS NMR of fluoride-exchanged HY zeolites activated at 400°C under inert flow.

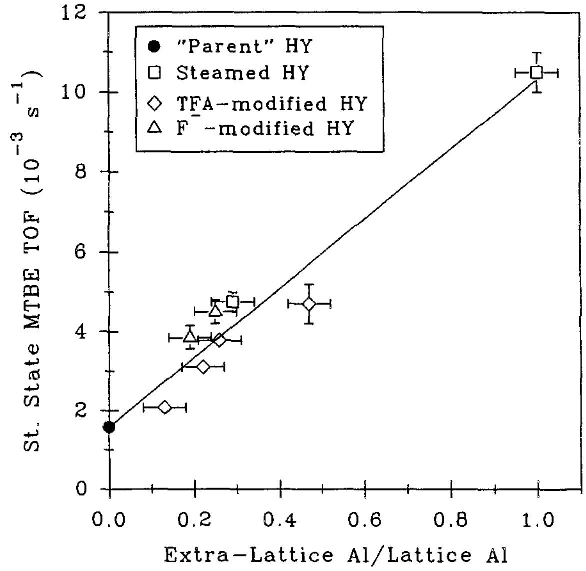

Fig. 4. Influence of extra-lattice Al/lattice Al on MTBE synthesis turnover frequency at 90°C.

TFA-modification [25] on zeolite activity for the synthesis of MTBE. The physical significance of the Al_E/Al_L ratio as a major parameter for determining the activity of modified zeolites may be speculated as an enhancement in the acid strength of the sites (associated with lattice Al) possibly by coupling with neighboring strong Lewis-type sites associated with extra-lattice Al [24]. It should be noted that the straight line shown in fig. 4 was not drawn in order to imply a direct proportionality between the MTBE synthesis TOF and the Al_E/Al_L ratio, but simply to indicate a common monotonic increase of the measured TOF with this ratio for all three sites of modified HY zeolites. It should also be noted that similar activity trends were also observed for the other two types of fluoride-exchanged zeolites. The reason for focusing on the HY series in fig. 4 was simply the fact that no directly comparable data on the other modified zeolite series were available.

5. Conclusions

Three series of zeolites modified by ion-exchange with ammonium fluoride were studied for the gas phase synthesis of MTBE in an attempt to investigate the influence of fluoride-exchange on catalytic activity for MTBE formation. This post-synthesis modification was found to result in an increase in their activity for MTBE synthesis without impairing their selectivity. The observed increase in MTBE synthesis activity is attributed to an enhancement in zeolite acidity resulting from the formation of extra-lattice Al species rather than the direct presence of fluoride-ions. The formation of this extra-lattice Al appears to be the result of a high temperature (400°C) activation process following the fluoride ion-exchange process.

Acknowledgement

Funding for this study from the Materials Research Center of the University of Pittsburgh, through AFOSR Grant 91-0441, is gratefully acknowledged.

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