JOURNAL OF CATALYSIS **158,** 76–82 (1996)
ARTICLE NO. 0007

Gas Phase Synthesis of MTBE on Triflic-Acid-Modified Zeolites

A. A. Nikolopoulos,* A. Kogelbauer,* J. G. Goodwin, Jr.,*,[1] and G. Marcelin†

Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, and †Altamira Instruments, Inc., 149 Delta Drive, Suite 200, Pittsburgh, Pennsylvania 15238

Received December 19, 1994; revised August 30, 1995; accepted August 31, 1995

The gas phase synthesis of MTBE (methyl *tert*-butyl ether) was studied using three series of triflic acid (TFA)-modified zeolites, the parent materials being HY, H–mordenite, and HZSM-5. Impregnation with TFA was found to enhance MTBE synthesis activity only for the large-pore zeolite Y and only up to a certain extent of modification. A high level of TFA modification caused a reduction in activity, apparently due to blockage of the active sites by TFA molecules and extra-lattice Al formed during the modification process. The mechanism of activity enhancement by TFA modification appears to be related to the formation of extra-lattice Al rather than the direct presence of TFA. © 1996 Academic Press, Inc.

INTRODUCTION

The increasing environmental restrictions concerning the quality of gasoline (1, 2) have recently resulted in the extensive use of oxygenates (alcohols and ethers) for gasoline improvement (3–5). MTBE (methyl *tert*-butyl ether) is currently accepted as the most suitable gasoline additive because of its favorable physicochemical properties compared to alcohols and its excellent performance in terms of antiknocking behavior and control of the emissions from the internal combustion engine (4, 6). The worldwide production of MTBE has increased more than tenfold in the past decade (7–9).

The commercial process currently in application, liquid phase reaction of methanol (MeOH) and isobutene (2-methyl propene, IB) at temperatures below 100°C and moderate pressures, uses a sulfonated ion-exchange resin catalyst whose lack of thermal stability and corrosive properties are major disadvantages (10). Zeolites have been considered as promising alternative catalysts for MTBE synthesis because of their excellent thermal stability and high selectivity toward MTBE even at less favorable reactant ratios (8, 11).

Being an acid-catalyzed reaction, the formation of MTBE would be expected to be influenced by the acidic character of the catalyst used. Thus, another outstanding advantage of zeolites is their alterable acidity, which could be optimized for maximizing the formation of MTBE under a given set of reaction conditions. Although the synthesis of MTBE on zeolites has been examined (8, 11–16), only a few studies on the effect of acidity have been reported. In a study of the effect of acid strength variation on MTBE formation using a series of partially alkali-exchanged HY zeolites, no influence in initial MTBE synthesis activity was observed, apparently due to a strong mediating effect of adsorbed methanol on the strength of the acid sites (14). On the other hand, an enhancement in zeolite acidity by dealumination was found to result in increased activity for MTBE synthesis (16).

This paper reports on an investigation of the variation of zeolite acidity by addition of a strong electron-withdrawing compound, namely triflic acid, and its impact on zeolite performance for MTBE synthesis. Modification of the acidity of solid acids by incorporation of strong electron-withdrawing compounds like triflic acid (12) or ammonium sulfate (17) has been found to result in enhanced activity for etherification. However, no systematic investigation of the manner in which such acidity modification methods influence the zeolite activity has been reported.

EXPERIMENTAL

Three series of postsynthesis modified zeolites were used, the three parent zeolites being HY (LZ210-12, from UOP), H–mordenite (H-Zeolon, Norton) and HZSM-5 (Mobil), obtained as fine powders (crystalline size of ca. 1 μm). These zeolites have different structural characteristics, thus allowing a determination of the influence of zeolite morphology on catalytic performance for the formation of MTBE.

Modification of the parent zeolites was performed by impregnation with triflic acid (trifluoromethane sulfonic acid, CF_3SO_3H, TFA). TFA in various concentrations was dissolved in 5 ml of acetone. Each of these solutions was used to impregnate ca. 0.5 g of zeolite that had been precalcined at 400°C in air under shallow bed conditions. The

---

[1] To whom correspondence should be addressed.

0021-9517/96 $12.00

impregnation was performed at ambient temperature in excess liquid and was followed by evaporation of the acetone. The catalyst was then washed with ca. 1 ml of acetone and was dried at 110°C in air for 12 h. This procedure is similar to the one reported in the literature (12).

Various techniques were used to characterize the catalysts studied. The Si/Al ratio and the lattice Al content of the zeolites were evaluated by ^{29}Si and ^{27}Al magic-angle-spinning (MAS) NMR and atomic absorption spectroscopy (AAS). ^{27}Al NMR was also used to check on the possible formation of extra-lattice Al as a consequence of TFA adsorption. The crystallinity of the zeolites was determined by X-ray diffraction (XRD). The extent of TFA modification was measured by thermogravimetric analysis (TGA) and verified by elemental analysis of fluorine (AAS).

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 reaction gases. Methanol (Aldrich, A.C.S. 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).

Literature reports (12) as well as TPD experiments on TFA-modified zeolites indicated that TFA readily desorbs from zeolites at $T > 220$°C. For this reason, all zeolite catalysts were pretreated *in situ* prior to reaction by heating to 180°C at a rate of 2°C/min under helium flow and holding for 2 h. No desorption was observed after this activation process (no weight loss was detected by TGA).

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, catalyst weight of 10–20 mg, and total flow of 52 cc/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 a 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 cc/min) indicated the absence of significant mass transfer limitations for flow rates above 25 cc/min.

RESULTS

Catalyst Characteristics

A summary of the characterization results of the zeolite catalysts is given in Table 1. The extent of modification with TFA (i.e., TFA loading) is reported in wt% and in mmol of TFA 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 TFA incorporated in wt%. Thus, the zeolite Y(T-2.8) is HY containing 2.8 wt% TFA.

^{27}Al MAS NMR experiments indicated the formation of extra-lattice Al (Al_E) in the TFA-modified zeolites. The amount of extra-lattice Al formed increased for the zeolites modified with higher levels of TFA. The concentration of acid sites of the zeolites was calculated by assuming one Brønsted site per lattice Al (Al_L).

X-ray diffraction was used to evaluate the crystallinity of the zeolites. No detectable loss of crystallinity was observed for the TFA-modified zeolites as compared to the parent zeolites. The diffraction patterns of the parent zeolites were in very good agreement with those in the literature (18).

Effect of Temperature on MTBE Synthesis Activity

Steady-state activities for MTBE formation of the zeolite catalysts were obtained in the temperature range 40–90°C. All the zeolite catalysts, both unmodified and modified, were found to exhibit similar behavior, and the activity data for two representative zeolites, the unmodified HY and zeolite Y(T-2.8), are presented in the Arrhenius plots shown in Figs. 1 and 2. The Arrhenius results were plotted in two separate figures (Figs. 1 and 2) due to the fact that they constitute two sets of experiments. Because some deactivation occurs at each temperature during the attainment of steady state, the Arrhenius rate data were obtained first at the highest temperature shown followed by the data at subsequently lower temperatures. At each temperature the reaction was allowed to reach steady state. At the end of the experiment the rate was measured at the initial highest temperature, thus allowing the determination of the total deactivation for the temperature cycle of interest (for example: 90, 80, 70, 60, and back to 90°C). Typically, the amount of total deactivation determined was ca. 30%. Consequently, the rate shown in Fig. 1 at 60°C (last data point measured, therefore affected by deactivation at 60°C and all previous temperatures) is lower than that shown in Fig. 2 (first data point measured, therefore affected by deactivation only at 60°C).

As demonstrated in Fig. 1 the activities of all the zeolites were found to obey Arrhenius-type kinetics and thus it could be concluded that these activity data were not influenced by thermodynamic equilibrium limitations (16). The

TABLE 1

Characteristics of TFA-Modified Zeolites

Zeolite	Modif. Extent[a]		$\mathrm{Al_L}$[b]	$\mathrm{Al_E}$[c]	Lattice	Mod./Al[e]
	(wt%)	(mmol/g)	(mmol/g)	(mmol/g)	Si/Al[d]	(%)
H-mordenite[f]	0	0	1.35	0.25	9.5	0
M(T-1.2)	1.2	0.08	1.30	0.30	9.9	5.9
M(T-1.7)	1.7	0.11	1.25	0.35	10.3	8.1
HY[f]	0	0	2.20	0	6.0	0
Y(T-1.4)	1.4	0.09	1.95	0.25	6.4	4.1
Y(T-2.0)	2.0	0.13	1.80	0.40	7.3	5.9
Y(T-2.8)	2.8	0.19	1.75	0.45	7.5	8.6
Y(T-3.6)	3.6	0.24	1.70	0.50	7.8	10.9
Y(T-11.5)	11.5	0.77	1.50	0.70	8.8	35.0
Y(T-16.4)	16.4	1.09	1.30	0.90	10.2	49.5
HZSM-5[f]	0	0	1.20	0	12.0	0
Z(T-1.3)	1.3	0.09	1.10	0.10	13.1	7.5
Z(T-2.3)	2.3	0.15	1.00	0.20	14.4	12.5

[a] From TPD of TFA modified zeolites (by TGA); accuracy, ±0.2 wt% or ±0.015 mmol/g.

[b] From ^{29}Si and ^{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 nonactivated samples; accuracy, ±0.2 mmol/g for all nonzero values.

[d] From ^{29}Si and ^{27}Al MAS NMR and Al elemental analysis (AAS).

[e] Ratio of extent of TFA modification to *initial* 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.

measured apparent energies of activation in the temperature range 60–90°C were 75 ± 10 kJ/mol, in good agreement with values calculated from data reported in the literature (12). However, the values of the apparent energy of activation in the temperature range 40–60°C were found to be ca. 135 kJ/mol (twice the average value measured in the high-temperature range 60–90°C), indicating that the kinetic results obtained above 60°C were influenced by internal diffusion. The observed difference in the apparent energies of activation cannot be attributed to catalyst deactivation during the measurements since, if anything, deactivation would have led to higher rather than

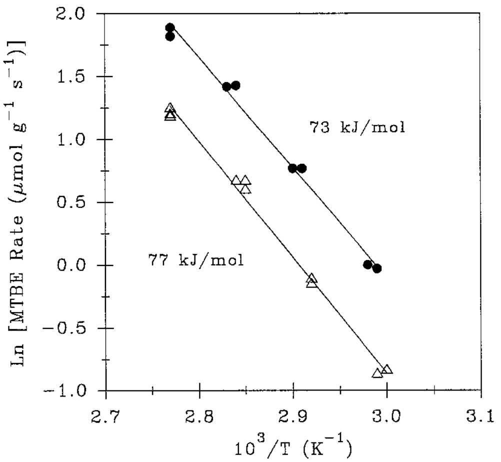

FIG. 1. Arrhenius plot of steady-state MTBE synthesis activities of TFA-modified HY zeolites (T = 60–90°C, MeOH/IB = 1.0): (△) unmodified HY, (●) Y(T-2.8).

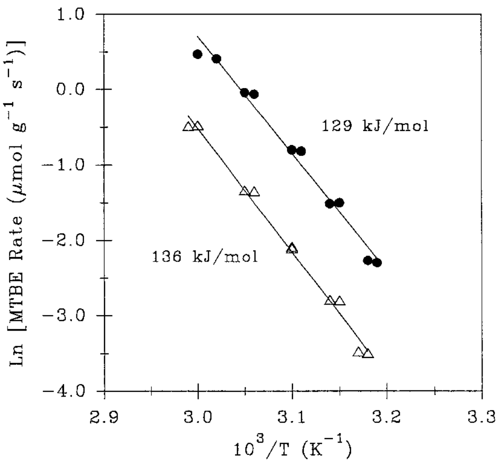

FIG. 2. Arrhenius plot of steady-state MTBE synthesis activities of TFA-modified HY zeolites (T = 40–60°C, MeOH/IB = 1.0): (△) unmodified HY, (●) Y(T-2.8).

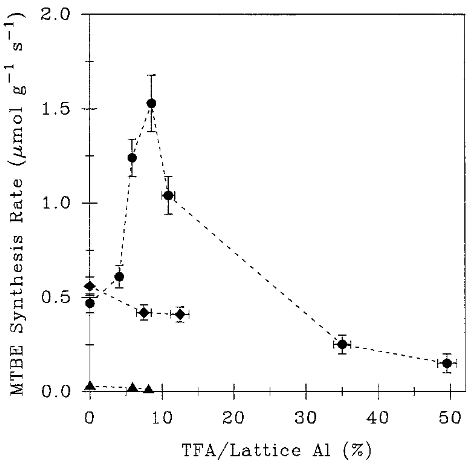

FIG. 3. Comparison of steady-state MTBE synthesis activities of TFA-modified zeolites at 60°C (MeOH/IB = 1.0): (●) HY, (▲) H-mordenite, (◆) HZSM-5.

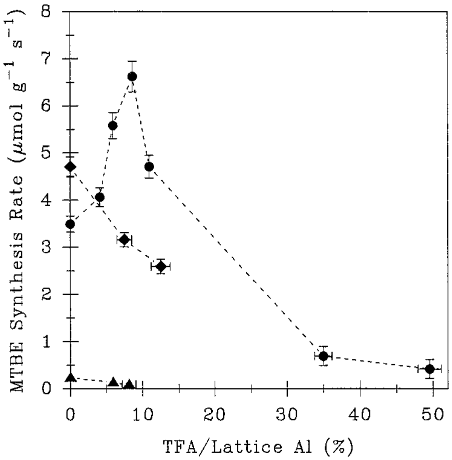

FIG. 4. Comparison of steady-state MTBE synthesis activities of TFA-modified zeolites at 90°C (MeOH/IB = 1.0): (●) HY, (▲) H-mordenite, (◆) HZSM-5.

lower activation energy values, especially for the higher temperature range where deactivation can be more significant.

Effect of TFA Modification on MTBE Synthesis Activity

The effect of TFA modification on zeolite activity, expressed as steady-state rates of MTBE formation at 60°C (where no influence of diffusion was observed), is shown in Fig. 3. The ratio of the extent of TFA modification to the initial lattice Al content (prior to the modification process) is used as the independent variable for this graph. The reason for this choice was to facilitate a comparison of performance of the three types of modified zeolites, since they were produced from zeolites with different concentrations of active sites. If simply the extent of TFA modification were chosen, a minor expansion or contraction of the curves along the x-axis would be seen, but the observed trends would remain the same.

As shown in Fig. 3, an increase in the extent of TFA modification up to ca. 3 wt% TFA resulted in an increase in the activity of the modified Y zeolites for MTBE synthesis. However, a rapid decrease in activity with further increase in TFA loading was observed. On the other hand, the activities of both the modified ZSM-5 and mordenite zeolites were found to decrease with increasing levels of TFA. These results are in qualitative agreement with the literature (12) for TFA-modified HY and HZSM-5 zeolites.

It should be noted that the same trends can be observed by using the initial MTBE synthesis activity data (obtained after 5 min on stream), suggesting that these trends are not significantly influenced by deactivation. Under the conditions used, the deactivation of the Y zeolites was ca. 10–30% and was higher for the samples exhibiting higher activities. The ZSM-5 zeolites exhibited lower deactivation, probably due to an enhanced resistance against coke formation, as is known to be the case for ZSM-5. The mordenite zeolites also showed lower deactivation, apparently due to their low activity for MTBE synthesis. All the catalysts studied showed no by-product formation and thus 100% selectivity to MTBE.

In order to determine any influence of mass transfer limitations on the effect of TFA modification on MTBE synthesis activity, the steady-state activities of zeolites for MTBE synthesis at 90°C are plotted in Fig. 4. Based on the similarities between the activity results at 60°C (Fig. 3) and at 90°C (Fig. 4), it appears that the presence of diffusion limitations on the activities measured at high temperatures (90°C) did not have a significant impact on the observed trends concerning the effect of TFA modification on MTBE synthesis activity.

DISCUSSION

The existence of a maximum in the MTBE synthesis activity of modified HY zeolites with respect to the extent of TFA modification seems to indicate that there are two main parameters which determine the kinetic behavior of these catalysts. One parameter, which is apparently related to the modification by TFA, seems to be responsible for the observed increase in activity at low TFA loadings, whereas the other parameter, which is negatively correlated with TFA loading, appears to result in a substantial activity decrease. An obvious hypothesis for this second parameter is simply the blockage of the available active sites by the relatively bulky TFA molecules (compared to zeolite pore openings of ca. 5.5 to ca. 7.5 Å) and possibly by extra-lattice Al species formed by the modification process, making some of the active sites inaccessible to the reactant molecules. The hypothesis of activity loss due to site blockage by TFA molecules had been previously suggested in the literature for TFA-modified HY and HZSM-5 zeolites (12).

The activity curves of the modified ZSM-5 and mordenite zeolites, where no increase was observed, can be quite well explained by the site blockage hypothesis. A more dramatic activity loss, e.g., at lower levels of TFA, would be expected for medium-pore zeolites such as ZSM-5 (as opposed to large-pore Y) and for large-pore zeolites having a unidimensional channel system such as mordenite. It is conceivable that the activity maximum would shift to lower levels of TFA for zeolites where a more severe site blockage can be expected. It is thus quite possible that the activity curves for the modified ZSM-5 and mordenite zeolites also have maxima, possibly corresponding to very low levels of TFA (close to the *y*-axis in Figs. 3 and 4); however, our results can neither prove nor disprove this possibility.

The observed increase in MTBE synthesis activity of the modified HY zeolites with low TFA loadings (up to ca. 3 wt% TFA) can be suggested to be due to an enhancement of acidity of these zeolites, which appears to be related to the modification by TFA. In order to explain this activity increase two possible models of zeolite acidity enhancement by direct involvement of TFA have been proposed (19). These models involve the formation of (i) Lewis sites by reactive adsorption of TFA (accompanied by release of water) and (ii) new Brønsted sites possibly of high acid strength by dissociative adsorption of TFA. These models were based on characterization studies (19, 20) in which zeolite dealumination during modification with TFA was not reported. However, the ^{27}Al and ^{29}Si NMR data presented in these studies (19, 20) suggest the formation of extra-lattice Al during the modification with TFA. Our experiments also provide evidence for the presence of extra-lattice Al as a result of the modification process.

The extent of TFA modification and the amount of extra-lattice Al formation, both given in Table 1, were plotted with respect to one another in Fig. 5 in order to examine the possibility of a correlation between these properties. An increasing level of TFA was found to result in increasing amounts of extra-lattice Al for all three types of zeolites. Although the data range for the modified ZSM-5 and mordenite zeolites is rather limited, it appears that the slopes of the lines produced by each of these sets of data are close to unity, suggesting that for each TFA molecule that is adsorbed one Al atom is removed from the lattice. On the other hand, the curve for the modified HY zeolites showed a slope of ca. 2 at low levels (<0.2 mmol/g) of TFA and a slope of less than unity at high levels of TFA.

It is quite conceivable that, due to a relatively high density of acid sites (and thus of lattice Al atoms associated with them) in an HY zeolite, a TFA molecule could adsorb on two neighboring sites, resulting in the extraction of two Al atoms from the lattice. However, for the cases of ZSM-5 and mordenite, with almost half the site density of the HY zeolite studied, adsorption of TFA on two sites would seem rather unlikely. In addition, site blockage by TFA could make some of the acid sites inaccessible for TFA adsorption. This could possibly be the case for the HY zeolites with high levels of TFA, where a less than one-to-one TFA to extra-lattice Al correlation was observed.

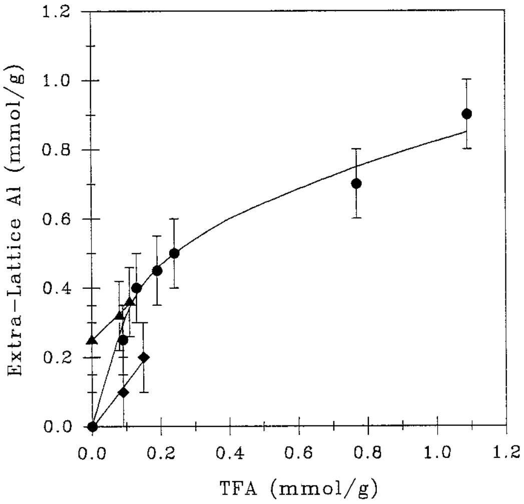

FIG. 5. Correlation between extent of TFA modification and extra-lattice Al formation: (●) HY, (▲) H-mordenite, (◆) HZSM-5.

Considering the correlation between the adsorption of TFA and the formation of extra-lattice Al in all the zeolite catalysts studied, it seems conceivable that the presence of extra-lattice Al could be responsible for the observed MTBE synthesis activity increase rather than the presence of adsorbed TFA directly. In a previous study of MTBE synthesis on a series of dealuminated HY zeolites (16), the observed activity increase was attributed to an enhancement in acidity due to the formation of extra-lattice Al.

In order to examine this hypothesis, the steady-state activities of the TFA-modified HY zeolites, expressed in terms of turnover frequency (TOF), defined as rate (mol per gram of zeolite per second) divided by the concentration of Brønsted sites (lattice Al), were plotted as a function of the ratio of extra-lattice to lattice Al, Al_E/Al_L (Fig. 6). The Al_E/Al_L ratio was chosen as the independent variable in this graph because it was previously found to be correlated with the TOF of dealuminated HY zeolites for MTBE synthesis (16). Also shown in Fig. 6 are the TOFs of two HY zeolites which had been produced from the same HY zeolite used for the TFA impregnation (LZ210-12 with an initial Si/Al ratio of 6.0) using dealumination by mild steam treatment, as described elsewhere (16).

It can be seen from Fig. 6 that the increase in TOF for the TFA-modified HY zeolites with low levels of TFA

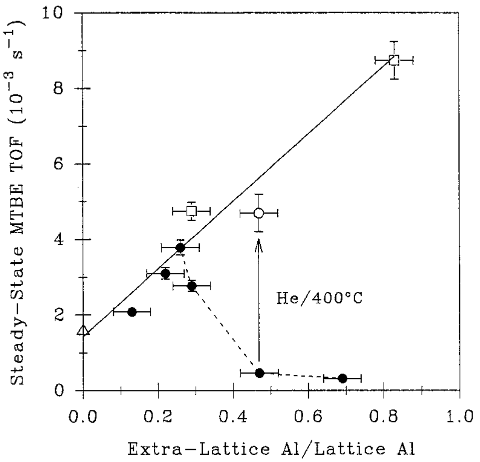

FIG. 6. Influence of extra-lattice Al/lattice Al on MTBE synthesis turnover frequency at 90°C (MeOH/IB = 1.0): (△) unmodified HY, (●) TFA-modified HY, (□) steam-dealuminated HY, (○) heat-treated TFA-modified HY [Y(T-11.5)].

(resulting in low levels of extra-lattice Al) appears to be in excellent agreement with the corresponding increase in TOF of the steam-dealuminated HY zeolites. At high levels of TFA (resulting in high levels of extra-lattice Al) an increasing deviation from the expected activity performance can be observed, something that has been attributed to the blockage of the sites as discussed previously. It should be noted that the straight line shown in Fig. 6 was not drawn in order to imply a proportionality between the MTBE synthesis TOF and the extra-lattice to lattice Al ratio, but simply to indicate a common monotonic increase of TOF with this ratio for both sets of zeolites.

This common correlation of the activities of the two sets of HY zeolites with the ratio of extra-lattice to lattice Al seems to support the hypothesis that the main factor for the observed activity increase is an enhancement in acidity caused by the formation of extra-lattice Al rather than the dissociative or reactive adsorption of TFA, as has been suggested elsewhere (12). In order to further verify this hypothesis, a separation of the phenomena of TFA adsorption and extra-lattice Al formation would be desirable. This can be achieved by (i) producing a TFA-modified HY zeolite without the formation of extra-lattice Al, or (ii) reversibly desorbing the TFA from a TFA-modified HY zeolite, thus leaving the extra-lattice Al as the only possible source of enhancement in catalytic activity.

The second experiment was performed by *in situ* mild heat treatment of a TFA-modified HY zeolite, namely zeolite Y(T-11.5), under helium flow. The heat treatment included heating to 180°C at 2°C/min (similar to the activation process prior to reaction) followed by heating to 400°C at 0.5°C/min (the lowest reproducible heating rate attainable by our system) and maintaining this temperature for 2 h. An almost complete removal of adsorbed TFA from the zeolite by this treatment was demonstrated by independent TPD experiments. The zeolite was then cooled to the reaction temperature (90°C) under helium flow. Such a treatment was not expected to influence the amount of extra-lattice Al present in the zeolite.

The activity of this treated zeolite for the formation of MTBE, expressed as steady-state TOF, is also shown in Fig. 6. A decrease in TFA concentration in zeolite Y(T-11.5) by the above method resulted in an increase in MTBE synthesis activity to the level expected by the correlation with the extra-lattice to lattice Al ratio. The slight deviation observed can be attributed to a possible nonideal and incomplete removal of TFA from the zeolite. This experimental evidence seems to clearly support the hypothesis that TFA by itself is not responsible for the increase in MTBE synthesis activity for the TFA-modified HY zeolites but rather the formation of extra-lattice Al is.

CONCLUSIONS

Three series of zeolites modified by impregnation with triflic acid were studied for the gas phase synthesis of MTBE in an attempt to investigate the influence of TFA on catalytic activity for MTBE formation. Modification of the acidity of an HY zeolite by TFA adsorption was found to result in an increase in activity for MTBE formation only for low levels of TFA (up to ca. 3 wt% TFA). Further incorporation of TFA resulted in an activity decrease, which could be attributed to blockage of the active sites by TFA molecules and extra-lattice Al formed during the modification process. A more severe case of site blockage was observed for the TFA-modified medium-pore zeolite, HZSM-5, and the large pore zeolite, H–mordenite, having a unidimensional channel system. In the latter two cases our experimental evidence showed no increase in catalytic activity.

There appears to be a correlation between the extent of TFA modification and the amount of extra-lattice Al formed in the zeolites. Contrary to literature suggestions that the activity increase observed for TFA-modified zeolites is related to an acidity increase caused directly by the adsorption of TFA, our results seem to indicate that it is rather the formation of extra-lattice Al that is responsible for the observed increase in MTBE synthesis activity. It has been suggested previously (16), based on the correlation of results, that it is most likely the combination of extra-lattice Al with the acid sites (associated with the lattice Al) which results in increased MTBE synthesis activity. The extra-lattice Al by itself does not seem to be the source of the activity increase (16).

In an attempt to evaluate the modification of zeolites with TFA in terms of their catalytic performance for the synthesis of MTBE, it appears that this method is beneficial only under serious limitations in terms of zeolite characteristics and level of modification. In addition, similar if not better results can in general be obtained from other simpler and less costly methods, such as dealumination using mild steam treatment.

ACKNOWLEDGMENTS

Funding for this study from the Materials Research Center of the University of Pittsburgh, through AFOSR Grant 91-0441, is gratefully acknowledged. The authors also thank Professor Dan Fărcaşiu for helpful discussions.

REFERENCES

1. Potter, F. L., *Fuel Reformulation* **1**(1), 22 (1991).
2. Peeples, J. E., *Fuel Reformulation* **1**(1), 27 (1991).
3. Mills, G. A., and Ecklund, E. E., *CHEMTECH* **19**(10), 627 (1989).
4. Piel, W. J., and Thomas, R. X., *Hydrocarbon Process.* **69**(7), 68 (1990).
5. Chang, E. J., and Leiby, S. M., *Hydrocarbon Process.* **71**(2), 41 (1992).
6. Unzelman, G. H., *Fuel Reformulation* **1**(2), 50 (1991).
7. Reisch, M. S., *Chem. Eng. News,* April 13, 16 (1992).
8. Hutchings, G. J., Nicolaides, C. P., and Scurrell, M. S., *Catal. Today* **15,** 23 (1992).
9. Haigwood, M. B., *Fuel Reformulation* **1**(1), 52 (1991).
10. Takesono, T., and Fujiwara, Y., U.S. Patent 4, 182,913, 1980.
11. Chu, P., and Kühl, G. H., *Ind. Eng. Chem. Res.* **26,** 365 (1987).
12. Le Van Mao, R., Carli, R., Ahlafi, H., and Ragaini, V., *Catal. Lett.* **6,** 321 (1990).
13. Chang, K. H., Kim, G. J., and Ahn, W. S., *Ind. Eng. Chem. Res.* **31,** 125 (1992).
14. Kogelbauer, A., Öcal, M., Nikolopoulos, A. A., Goodwin, J. G., Jr., and Marcelin, G., *J. Catal.* **148,** 157 (1994).
15. Nikolopoulos, A. A., Oukaci, R., Goodwin, J. G., Jr., and Marcelin, G., *Catal. Lett.* **27,** 149 (1994).
16. Nikolopoulos, A. A., Kogelbauer, A., Goodwin, J. G., Jr., and Marcelin, G., *Appl. Catal. A* **119,** 69 (1994).
17. Rodriguez-Ramos, I., Guerrero-Ruiz, A., and Fierro, J. L. C., *Prepr. Div. Pet. Chem. Am. Chem. Soc.* **36**(4), 804 (1990).
18. Von Ballmoos, R., and Higgins, J. B., *Zeolites* **10,** 313S (1990).
19. Le Van Mao, R., Nguyen, T. M., and McLaughlin, G. P., *Appl. Catal.* **48,** 265 (1989).
20. Le Van Mao, R., and Huang, L., *in* "Novel Production Methods for Ethylene, Light Hydrocarbons, and Aromatics" (L. F. Albright, B. L. Crynes and S. Nowak, Eds.), p. 425. Dekker, New York, 1990.