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MTBE Synthesis on Partially Alkali-Exchanged HY Zeolites

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The influence of the acid strength of zeolites upon gas-phase formation of MTBE from methanol and isobutene was studied detached from other parameters such as structure, framework composition, and site density. A series of partially ion-exchanged HY zeolites which had been ion-exchanged to the same extent by Li, Na, and Rb was used, yielding materials with similar concentrations of protons but different acid strengths. All zeolites exhibited similar initial activities for the formation of MTBE at temperatures below 100°C, although for other acid-catalyzed reactions such as 1-butene isomerization an increase in the activities with increasing acid strength of the zeolites had been previously observed. Steady-state activities, however, were found to be strongly influenced by the different deactivation behavior of the investigated samples. For the partially Rb-exchanged sample, blockage of pores (probably by isobutene oligomers) caused an expressed decrease in rate of reaction during the first 30 min on stream. The presence of excess methanol in the pores is regarded as a possible cause for the similarity of the initial reaction rates. © 1994 Academic Press, Inc.

INTRODUCTION

One of the major concerns regarding the industrial application of zeolites as catalysts for the synthesis of methyl *tert*-butyl ether (MTBE) is their considerably lower activity compared to ion-exchange resins such as Amberlyst-15. Nevertheless, zeolites exhibit several properties such as shape selectivity and excellent stability at elevated temperatures which offer interesting possibilities for their use in MTBE synthesis. In order to compensate for the lower activity one could conceive either of performing the reaction at higher temperatures, which is not very useful due to thermodynamic equilibrium limitations (1–3), or of increasing the acid strength of the catalytically active sites, thus achieving enhanced reaction rates at lower temperature. Since there are several parameters which can affect zeolite acidity and subsequently catalytic activity, it would be desirable to study these effects separately.

This paper describes an investigation of the influence of the acid strength of a zeolite upon MTBE synthesis while keeping the crystalline structure, Si/Al ratio, number of acid sites, and charge of balancing cation constant. A series of HY zeolites that were partially cation-exchanged (cation: Li^+, Na^+, Rb^+) to the same level was used. It is well known that the exchange of alkali cations leads to a variation in acid site strength in the order Li > Na > Rb due to the higher electrostatic potential of the smaller cations (4–8). The catalysts used in this study have been shown previously to vary in their reaction rates for typical acid-catalyzed reactions; this was concluded to be due to an increase in the acid strength of the protons (9).

EXPERIMENTAL

In order to eliminate any influence of the concentration of acid sites upon the acid strength, the parent HY zeolite (80% NH_4^+-exchanged NaY obtained from Strem Chemicals) was repeatedly exchanged with alkali nitrate (Li, Na, Rb) and analyzed in order to produce partially ion-exchanged zeolites with the same amount of Brønsted acid sites but different alkali cations. The detailed preparation procedure is described elsewhere (9). The compositions of the zeolites as determined by atomic absorption spectroscopy (AAS) and solid-state NMR are shown in Table 1.

TPD experiments were carried out in an automated Altamira AMI-1 system. Typically, a 50-mg sample of a catalyst was activated in helium flow by heating to 400°C at a rate of 2°C/min and maintaining that temperature for 2 h. Subsequently, ammonia (pyridine) was adsorbed at 50°C (100°C). The samples were then flushed with helium at 100°C for 1 h to remove physisorbed molecules. TPD was performed at a heating rate of 10°C/min from 100 to 600°C. The reactor effluent was analyzed using a TCD.

The reaction experiments were carried out in a flow microreaction system using a 6-mm quartz glass U-tube as reactor. Typically this reaction is carried out commercially in the liquid phase, and the catalyst used, a copolymer ion-exchange resin, needs to be swollen before its use. However, since our interest was in doing a kinetic study, our experimental setup was designed for reaction from the gas phase in order to minimize mass transport

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TABLE 1

Composition of the Alkali–HY Zeolites (9)

Catalyst	Si/Al[a]	Na/Al[b]	M/Al[c]	H^+/Al[d]
HY	2.48	0.20	—	0.80
LiHY	2.45	0.16	0.24	0.60
NaHY	2.44	0.43	0.23	0.57
RbHY	2.48	0.16	0.22	0.62

[a] From MAS-NMR.

[b] From AAS.

[c] M = Li, excess Na above HY level, or Rb.

[d] Calculated number of Brønsted acid sites per lattice Al.

effects. The reaction system was equipped with mass flow meters and a back pressure regulator, allowing precise control of the flow and the partial pressure of all reactants. Methanol (Aldrich, A.C.S. HPLC Grade) was fed by bubbling helium (99.999%) through a jacketed saturator. Isobutene was obtained from Liquid Carbonic as a 10% mixture in helium. No constituents other than isobutene were observed in a GC analysis of this gas mixture. The temperatures of the saturator (28°C), the reactor furnace (60–100°C), and the heated transfer lines (100°C) were kept constant to within ±0.2°C. Samples of the reactor effluent were injected into a GC by means of a sampling valve and analyzed using a Porapak-Q column and an FID.

For a reaction run a catalyst sample of approximately 40 mg was activated by heating at a rate of 2°C/min under flowing helium to 400°C and maintaining this temperature for 2 h. The catalyst was then allowed to cool to 90°C before reaction was started. The catalyst was contacted with the reactants at 1 atm pressure using a WHSV between 19.2 and 20.7 h^{-1}. The feed consisted of a 1 : 1 mixture of methanol and isobutene (6.8 mol% each), the balance being helium. The reaction was monitored until steady state was reached (typically in 2 h). Then the reactants were replaced by a helium flow and the system was cooled to the next reaction temperature. Apparent energies of activation were determined between 90 and 70°C. After the lowest reaction temperature, the reaction was again carried out at 90°C in order to determine the amount of deactivation. In some experiments the deactivated catalyst was also cautiously regenerated in air at 400°C to determine the amount of irreversible deactivation. The conversion was kept below 5% in all experiments in order to maintain a differential reaction regime.

For determination of the coke content, the zeolite samples after one reaction cycle as described above were used. Approximately 10 mg of zeolite was heated to 400°C under air in a TGA system (TA Instruments 2950) and the weight loss during this treatment was determined. Complete combustion was assumed when the weight did not change further with time.

The reproducibility of all the measurements was within ±5%. However, the errors for the initial reaction rates and the apparent energies of activation were somewhat higher, ca. 10%.

RESULTS AND DISCUSSION

As can be seen in Table 2, the concentration of acid sites as calculated from the results in Table 1 was practically the same for all the partially alkali-exchanged samples. Since this number is based on the calculation of the difference between alkali cations and aluminum atoms, it was also desired to have a direct measurement of the amount of acid sites. In order to account for differences in the accessibility of sites due to the size of the reactants and products [kinetic diameters: σ_k(methanol) = 0.39 nm, σ_k(isobutene) = 0.49 nm, σ_k(MTBE) = 0.62 nm], TPD of ammonia and of pyridine [kinetic diameters: σ_k(ammonia) = 0.26 nm, σ_k(pyridine) = 0.59 nm] was carried out. The concentration of acid sites as determined by TPD of ammonia corresponds well with the calculated number of acid sites (see Table 2). Except for RbHY, all the zeolites showed a slightly higher value of ammonia desorbing than predicted. This can be related to the desorption of a small amount of ammonia associated with the alkali cations (8, 10, 11). TPD of pyridine, on the other hand, measured only approximately 50% of the number of acid sites determined by ammonia, indicating a significantly lower number of accessible sites to the larger molecule. It has been reported before that, even with pyridine, a complete coverage of all acid sites can be achieved on HY zeolites (12, 13). Since pyridine is too bulky to penetrate into the sodalite cages, the protons have to be readily mobile or the base molecule has to attract the protons located in these cages. The acid sites located in the sodalite cages have been claimed to interact only weakly with pyridine, not yielding a protonated complex (12). In our case, the results suggest that such sites readily desorb pyridine at 100°C during the flush procedure before TPD. It is assumed that in the case of MTBE synthesis only those

TABLE 2

Characteristics of the Acid Sites in the Alkali–HY Zeolites

Catalyst	Concentration of acid sites (mmol/g)			Partial charge of the proton[b]
	Calculated[a]	NH_3 TPD	Pyridine TPD	
HY	3.5	3.6	1.6	0.112
LiHY	2.7	2.9	1.3	0.083
NaHY	2.5	3.0	1.7	0.077
RbHY	2.6	2.4	1.3	0.073

[a] Using Table 1.

[b] Calculated by method given in Ref. (16).

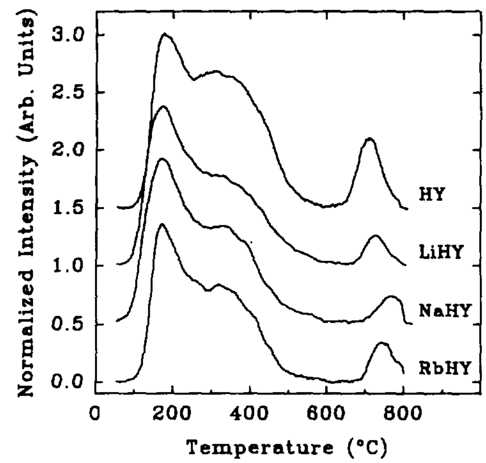

FIG. 1. TPD of ammonia from the alkali–HY zeolites.

sites retaining pyridine adsorbed at temperatures above 100°C are capable of proton transfer and may, thus, be considered catalytically active for the reaction. The specific reaction rates expressed as turnover frequencies (TOFs) will consequently be based on the concentration of acid sites determined by TPD of pyridine.

A somewhat surprising result found for TPD of NH_3 from all the catalysts was the similar locations of the maxima in the rate of desorption (see Fig. 1). An increase in acid strength of the sites should be reflected in a higher temperature of the desorption maxima (8, 11). It is well known that the effects of readsorption and diffusion can render the interpretation of TPD spectra for zeolites somewhat difficult (14, 15). For relatively small differences in acid strength, the expected shift of the maxima thus might not be clearly discernible. Nevertheless, an effect of the different alkali ions on the acid strength has been reported by O'Donoghue and Barthomeuf (4), who related the shift of the OH stretching vibration of the Brønsted acid sites to lower wavenumbers for partially alkali-exchanged zeolites in the order Li > Na > Rb to an increase in acidity of the proton. For a quantitative estimate of the variation in acid strength in the alkali–HY series, we calculated the partial charge of the protons according to Sanderson's electronegativity model (16) (see Table 2). The plausibility of this approach has been demonstrated before (17, 18).

TABLE 3

MTBE Synthesis on the Alkali–HY Zeolites

Catalyst	Initial rate at 90°C (μmol g^{-1} s^{-1})	Steady-state rate at 90°C (μmol g^{-1} s^{-1})	Initial TOF (10^{-3} s^{-1})	Steady-state TOF (10^{-3} s^{-1})	E_a (kJ/mol)
HY	1.72	1.21	1.07	0.75	122
LiHY	1.72	1.51	1.29	1.14	107
NaHY	1.82	1.45	1.10	0.87	103
RbHY	1.63	0.70	1.28	0.55	111

The results for MTBE synthesis on the alkali–HY series of zeolites are compiled in Table 3. Under our reaction conditions, MTBE was the only reaction product detected for all catalysts. Since MTBE synthesis can be severely suppressed by thermodynamic equilibrium at temperatures above 100°C (1–3), one has to be extremely careful in interpreting reaction results. In order to obtain genuine kinetic data, it is mandatory to verify the absence of equilibrium limitations under the reaction conditions applied. For this purpose we calculated the expected equilibrium conversion from literature data (19, 20) for the temperature range from 60 to 120°C, a total pressure of 101.3 kPa, and reactant partial pressures of 6.9 kPa. Figure 2 shows the results of this calculation together with the experimentally obtained conversions for the alkali–HY series. For the highest reaction temperature of 90°C, the maximum conversion predicted by thermodynamic equilibrium lies around 10%, which is approximately twice the value determined for the initial stages of reaction on the alkali–HY zeolites. For comparison purposes we have included in Fig. 2 the values for an identical experiment using Amberlyst-15 as catalyst. The decrease in the conversion at constant flow rates with increasing temperature indicates that this catalyst is at least partially subjected to equilibrium limitations. The fact that the measured conversions for Amberlyst-15 are lower than the ones predicted by our calculations may be related to the characteristics of the flow reactor, i.e., incomplete contact of the reactants and a finite length of the catalyst bed. Neverthe-

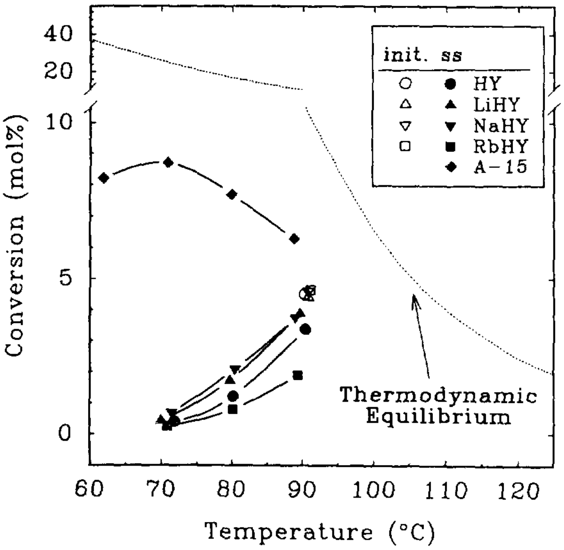

FIG. 2. Comparison of equilibrium limitation for MTBE synthesis to reactant conversion on the alkali–HY zeolites as a function of temperature.

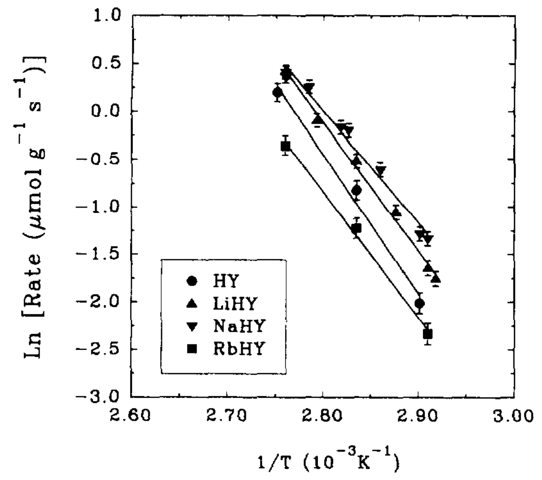

FIG. 3. Arrhenius plots for the formation of MTBE on the alkali–HY zeolites.

less, the conversions obtained with the alkali–HY series are substantially lower. In earlier experiments, using various HY zeolites and different reactant ratios (21), we observed a strong curvature in the Arrhenius plots and an expressed decrease in the rate at reaction temperatures above 100°C which was concluded to be caused by equilibrium limitations. Figure 3 shows the temperature dependence of the rates of MTBE formation in the form of an Arrhenius plot for the stabilized alkali–HY zeolites. Other than a minimal curvature which was caused by continuing deactivation with time-on-stream, almost perfectly straight lines were obtained for all zeolites. The values for the apparent energies of activation, as compiled in Table 3, lie on the upper end of the range reported in the literature (22). Thus, it can be concluded that the results reported here for the alkali series of zeolites are not limited by thermodynamic equilibrium or mass transfer but reflect inherent catalytic activities.

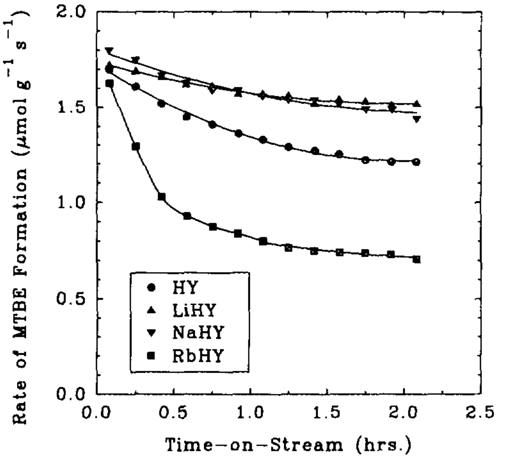

FIG. 4. Catalytic activity of the alkali–HY zeolites for MTBE synthesis at 90°C as a function of time-on-stream.

If one compares the steady-state rates (or steady-state TOF's) at 90°C (see Table 3), they increase in the order Rb < Na < Li, as does the partial charge on the protons. This initially suggests a straightforward relation between acid strength and catalytic activity. The fact that the parent HY zeolite shows significantly lower activity might be considered somewhat surprising at first. In an earlier study looking at the double bond isomerization of 1-butene on this catalyst series, a similar behavior was observed (9). It was concluded that the acid sites of the parent HY zeolite were less acidic than those of the partially Li-exchanged HY zeolite due to mutual interaction and the weakening of the hydroxyl groups present in abundance on the zeolite surface and that the lower activity of the parent HY zeolite was not due to deactivation. However, Fig. 4, showing the deactivation behavior of the partially alkali-exchanged HY zeolites during MTBE synthesis at 90°C, allows two important observations which reveal a substantially different behavior of the alkali–HY series in the case of MTBE synthesis.

First, based on the time-on-stream behavior, it is quite evident that deactivation is the main cause for the differences in the steady-state activities. The results of the determination of the coke content of the zeolites after the same cycle of MTBE synthesis reaction are compiled in Table 4. The amount of coke after one reaction cycle increases in the series Rb < Na < Li < H, which reflects the expected increase in acid strength of the zeolites. Considering the very strong deactivation of the RbHY zeolite during the first 30 min on stream, it is obvious that lesser amounts of coke result in greater deactivation in the case of RbHY. Magnoux and Guisnet (23) have shown that, for narrow-pore zeolites such as erionites, very small amounts of coke result in a dramatic loss of activity. They related this effect to the partial blocking of the channel system. Rb, having an ionic radius of 1.48 Å, might when present decrease the pore openings enough so that the pores become completely blocked as soon as coke precursors (mainly isobutene dimer and oligomers) are formed.

TABLE 4

Coke Content of the Alkali–HY Zeolites after MTBE Reaction

Catalyst	Coke content (wt%)
HY	6.1
LiHY	5.2
NaHY	4.4
RbHY	3.2

Thus, parts of the zeolite framework may become inaccessible for reactants.

Additional support for this supposition can be found by comparing the Arrhenius plots in Fig. 3 of the temperature dependence of steady-state reaction rates and the apparent energies of activation as listed in Table 3. The calculated apparent energies of activation range from 103 to 111 kJ/mol for the partially alkali-exchanged HY zeolites. The slightly higher value of 122 kJ/mol for the parent HY zeolite is attributed to the effect of continuing deactivation even at lower reaction temperatures. This result suggests that for all samples the same kinetic step is rate limiting. For RbHY this means in particular that transport limitations due to possible pore narrowing as a consequence of coke deposition cannot be the cause for the drop in the catalytic activity. Rather, the loss in activity is due to a total blockage of numerous active sites, either by direct coking or by indirect coke blockage of access to the pores.

The more expressed deactivation of the parent HY zeolite in comparison to the Li- and Na-exchanged samples cannot be explained in a similar way since protons are much smaller than Li^+ and Na^+ cations. In contrast to the partially alkali-exchanged zeolites, the initial activity could not be restored completely after controlled burning of the coke. This seems to indicate that a strong poisoning of the acid sites is responsible for the deactivation of the parent HY sample. Since no impact of the acid strength upon the initial rates of reaction was seen, it is suggested that the higher density of acid sites is a possible cause for the stronger deactivation, perhaps by increasing the concentration and subsequently the probability for reaction of reactant molecules in the zeolite cavities.

Under our reaction conditions, no isobutene dimer was detected as a product in the gas phase. It is, however, well known that hydrocarbons which form very stable carbenium ions (a tertiary carbenium ion in the case of isobutene) undergo rapid oligomerization in contact with acids even at room temperature (24). The reaction products of such a dimerization or oligomerization process may be strongly bound to the zeolite surface, resulting in some sort of desorption control of these products at lower temperatures. Another study carried out in our laboratories (25) makes us very confident that this mechanism is responsible for the deactivation of the zeolite catalysts used in our study.

The second notable observation made from Fig. 4 pertains to the initial activities of the zeolites. Although there is a relatively large error in the determination of initial activities due to the exothermicity of the reaction, the data shown in Fig. 4 and given in Table 3 suggest that all the samples have more or less similar initial activities (see also Fig. 5). Since the number of acid sites as determined by pyridine TPD (considered to be the active sites for MTBE formation) is also practically the same on all the HY zeolites, the initial TOFs of the catalysts turn out to be the same also. In order to verify that approach to thermodynamic equilibrium at the reaction temperature of 90°C was not limiting the conversions and hence producing similar measured rates of reaction, initial and steady-state rates were also determined at significantly lower temperatures. The results for reaction at 60°C on LiHY and RbHY as a function of time-on-stream are given in Fig. 6. Again, equal initial rates were observed for LiHY and RbHY, and RbHY showed a pronounced loss of activity during the first 30 min of reaction. These observations indicate that the equal initial rates are a genuine kinetic phenomenon.

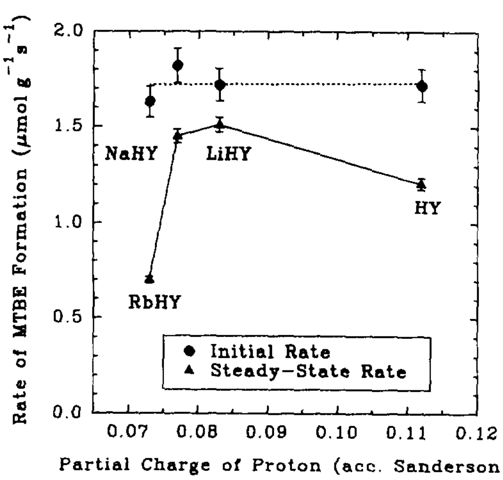

FIG. 5. Comparison of catalytic activities of the alkali–HY zeolites at 90°C.

Generally, for an acid-catalyzed reaction an increase in TOF is expected as the strength of the acid sites increases, and this has been reported for alcohol dehydra-

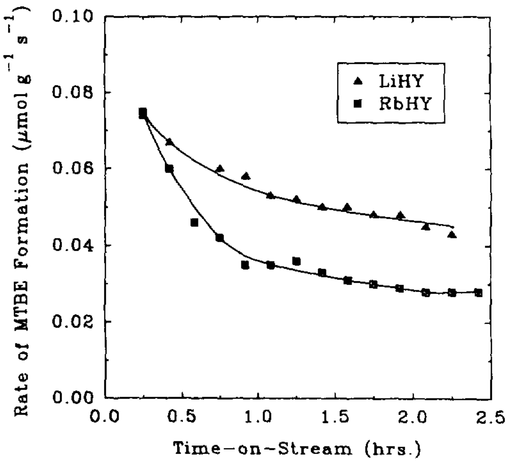

FIG. 6. Catalytic activity of LiHY and RbHY for MTBE synthesis at 60°C as a function of time-on-stream.

tion (4, 18, 26, 27), 1-butene isomerization, and propene oligomerization (9). The fact that this increase in TOF was not observed for MTBE synthesis but was for other acid-catalyzed reactions (9) would seem to suggest that the acid strength of zeolites apparently does not play as significant a role in MTBE synthesis. However, we have observed a strong enhancement in the activity for MTBE synthesis by a mild steaming of zeolites similar to that found for cracking reactions (21), indicating a favorable effect of acid strength upon catalytic activities. There are several possible explanations that could account for this seemingly inconsistent behavior.

First, an increase in acid strength would cause an increase in rates of MTBE formation only if the surface reaction represents the rate-limiting step. We consider our values for the apparent energies of activation ranging from 103 to 122 kJ/mol to be a good indication of this. The apparent energies of activation determined for partially dealuminated HY zeolites and silica–alumina are around 70 and 90 kJ/mol, respectively (21). These values correspond well with those reported in the literature for ion-exchange resins (22), where the surface reaction has been claimed to be the controlling kinetic step. Hence, we conclude that the surface reaction is rate limiting in our case also and that we should observe an effect of acidity change upon initial reaction rates.

If the increase in acid strength is relatively small, a reaction requiring highly acidic sites will not be enhanced substantially. This would mean that the variation in neutralizing alkali cations may not be sufficient to generate enough differences in acid strength to have an impact upon MTBE synthesis. However, Chang *et al.* (28) reported that mainly sites of weak-to-medium acid strength were active for MTBE synthesis over Ti-silicalite. Propene oligomerization, on the other hand, has been reported to require strong acid sites (9). The fact that increasing rates of reaction together with an increase in the concentration of branched oligomerization products were determined on the present alkali–HY series for propene and 1-butene oligomerization (9) makes the picture of insufficient acidity enhancement by cation exchange rather improbable.

Since the major difference between olefin oligomerization and MTBE synthesis is the participation of the alcohol molecule in the latter, it is reasonable to assume that the cause for the different behaviors of the alkali–HY series for these two reactions may be the presence of methanol during MTBE synthesis. Such a particular role of methanol has been reported for the liquid-phase synthesis of MTBE on Amberlyst-15 (29). Based upon the observations of Gates and Rodriguez (30), who concluded the SO_3H group in the ion-exchange resin to be more acidic than the solvated proton, Ancillotti *et al.* (29) have suggested that two different mechanisms predominate in MTBE synthesis on ion-exchanged resins. The first is a concerted mechanism at low methanol concentrations, where a surface acid group (SO_3H) acts as a protonating agent. The second is an ionic mechanism at high methanol concentrations, where methanol solvates the proton of an acid site and the resulting methoxonium ion acts as a protonating agent. As a consequence of the dissipation of the positive charge on the methoxonium ion, the ability for proton transfer decreases and reaction rates tend to level off. As will be shown, we consider a somehow comparable effect to occur in zeolites.

The presence of protonated methanol clusters in zeolites at partial pressures above 10^{-3} mbar and at temperatures up to 200°C has been reported earlier (31, 32). The number of methanol molecules determined in such a cluster corresponds surprisingly well with the "magic number" of 3 (representing the most stable complex) reported for gas-phase clusters (33–35). However, spatial constraints due to smaller dimensions of the zeolite pores could confine the size of such clusters (32). Although gas-phase ion chemistry can be applied to zeolites only in a limited manner due to the high electrostatic field gradients in the lattice, the presence of unperturbed OH groups in adsorbate clusters on HZSM-5 zeolites (31, 36) indicates that the interaction with the zeolite lattice can be rather small where geometric factors like large cavities and high Si/Al ratios allow it. On the other hand, when this is not the case, additional interaction of adsorbate clusters with the zeolite lattice should further stabilize them and, consequently, make them less susceptible to further interactions or reactions. From adsorption experiments under reaction conditions (25) we have determined that on the average two methanol molecules are adsorbed per Brønsted acid site in the zeolite pores. Consequently, it seems quite conceivable that, under our reaction conditions, adsorbed methanol or clusters of methanol once formed act as protonating agents. If the arguments presented above hold true, the intrinsic increase in the acid strength of the Brønsted acid sites may be masked by the formation of an adsorption complex of methanol and the Brønsted acid sites. In this context, Mirth *et al.* (37) have found that all protons in methanol clusters formed on HZSM-5 are equivalent. Furthermore, they concluded that the average strength of the hydrogen bonds in such clusters decreases as the cluster size increases.

The disagreement of this conclusion with the results found for dealuminated HY zeolites, where we observed an increase in TOF's of MTBE formation as the acid strength of the zeolites increased (21), may be attributed to a less effective leveling effect of methanol in the earlier results. For the dealuminated zeolites, the acid strength was much greater than that for the series of alkali exchanged zeolites. Also, in the case of the dealuminated zeolites, extralattice alumina appeared to play an indirect role in enhancing the activity. At this stage in our investigations, however, we cannot say whether a single explanation should apply to all the results for MTBE synthesis on zeolites or whether multiple phenomena may be extant. What may be occurring are two different effects. In the case of partially dealuminated zeolites, the higher charge of the practically isolated protons may induce a much higher charge on the adsorbate cluster, thus giving rise to enhanced reaction rates. On the other hand, in an environment where acid sites are present in abundance, as is the case for the alkali–HY zeolites, the formation of a quasi-condensed liquid due to extended hydrogen bonding of methanol may reduce the effective acid strength of the protons due to charge dissipation. The latter case would be similar to what has been found for ion-exchange resins, where a duality of mechanisms has been proposed. We emphasize that the presence of excess amounts of methanol in the zeolite pores under reaction conditions could also explain the previously described excellent selectivity of large pore zeolites toward MTBE at low methanol to isobutene ratios (38, 39).

CONCLUSION

Some unexpected behavior of a series of partially alkali-exchanged HY zeolites in the synthesis of MTBE at low temperatures was observed. Although the zeolites had a variation in their acid strengths as determined by the double bond isomerization of 1-butene, no significant effect upon initial rates for the formation of MTBE was observed. Deactivation due to the formation of olefin oligomers had a strong impact on the steady-state activities. For the zeolite containing bulky Rb cations, a pore blocking mechanism seems to be responsible for the expressed loss of activity. The similar initial activities may be related to a leveling effect of adsorbed methanol upon acid strength.

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