

EXECUTIVE SUMMARY

Objectives

The objectives of this work were to investigate the formation of ethers, in particular methyl tert-butyl ether (MTBE), during Fischer-Tropsch (FT) reaction. Three reaction schemes were investigated: (1) addition of i-butylene during the formation of methanol and/or higher alcohols directly from CO and H₂; (2) addition of i-butylene to FT liquid products including alcohols; and (3) addition of methanol to an FT synthesis making iso-olefins. These processes were to be evaluated in both gas-phase and slurry-phase. In order to accomplish the latter, a laboratory-scale slurry bubble column reactor (SBCR) was designed and built.

Experimental Approach

The experimental approach involved a study of two types of catalysts: acid catalysts capable of performing MTBE synthesis from isobutylene and methanol at elevated temperatures (ca. 200°C), and supported metal catalysts capable of performing methanol or higher alcohol synthesis at the same temperature. Zeolites and supported palladium catalysts were studied for these two purposes, respectively.

Results and Conclusions

Addition of isobutylene during CO hydrogenation showed that MTBE formation cannot be carried out on metal sites and likely always requires the presence of acid sites. However, MTBE was formed when acid sites, provided by a zeolite, were present in the vicinity of the methanol synthesis sites. Addition of isobutylene during CO hydrogenation over a composite catalyst consisting of Li-Pd/SiO₂ and a hydrogen-zeolite resulted in the formation of measurable, but small, amounts of MTBE. The major byproducts of the reaction scheme were isobutane, the dimer of isobutylene, and other hydrocarbons.

Because of the strong influence of thermodynamics, the catalytic behavior for MTBE synthesis of various acid catalysts was found to be very similar at elevated temperatures. At low temperatures, however, significant variations on MTBE production were observed. These results suggest that the catalytic activity for MTBE synthesis is

enhanced with increasing acid strength up to a threshold value, above which no significant activity enhancement is observed. Very high acid strength was detrimental to selectivity since it enhanced the formation of byproducts.

The processes did not perform well in a slurry medium, primarily due to the very rapid deactivation of the catalysts. This deactivation is suspected to be due to coke or oligomers coating the catalytic sites. It is suggested that the relative solubilities of the MTBE-forming components, i.e., methanol and isobutylene, are widely different in the liquid hydrocarbon medium used, and that it favors the solubility of the non-polar isobutylene. This, in turn, leads to a high isobutylene/methanol ratio which favors the formation of oligomers rather than MTBE.

Recommendations

The formation of ethers via this route does not appear possible using simply metal catalysts and is severely limited by thermodynamic considerations at the temperatures commonly used to synthesize alcohols. It is recommended that any further work in etherification during FT or alcohol synthesis be limited to processes operating at low temperature, i.e., below 150°C. Since few low temperature alcohol synthesis processes have been reported, some research effort should also be directed to that area.

OBJECTIVES

The objective of this project was to investigate three possible routes to the formation of ethers, in particular methyl tert-butyl ether (MTBE), during slurry phase Fischer-Tropsch reaction. Three reaction schemes were investigated, viz.:

- Addition of i-butylene during the formation of methanol and/or higher alcohols directly from CO and H₂ during slurry-phase Fischer-Tropsch.
- Addition of i-butylene to FT liquid products including alcohols in a slurry-phase reactor containing an MTBE or other acid catalyst.
- Addition of methanol to slurry phase FT synthesis making iso-olefins.

TECHNICAL REPORT

1. MTBE SYNTHESIS OVER ACID CATALYSTS

1.1 INTRODUCTION

Methyl tert-butyl ether (MTBE) is made commercially by the acid-catalyzed reaction of methanol and iso-butylene using a commercial sulfonic acid ion-exchange resin, viz.:



This reaction is typically carried out in the liquid phase at relatively low temperatures ($T < 100^\circ\text{C}$). This low temperature limit is partly imposed by the increasingly unfavorable thermodynamics of the reaction and partly by the instability of the resin at elevated temperatures. Although the reaction proceeds via an acid catalyzed reaction pathway, little is known about the requirements of the catalyst to form the MTBE product selectively, particularly at the higher temperatures required to form the ether from one of the proposed syngas routes.

This portion of the project examined the use of catalysts stable to high temperature, namely zeolites, on the selective gas phase MTBE synthesis. Zeolites are ideal materials for this reaction since they possess high acidity and can be prepared with a wide range of acid characteristics. Although some previous studies have addressed the use of zeolites for MTBE synthesis (1), no systematic investigation dealing with the effect of temperature or acid characteristics was reported.

1.2 EXPERIMENTAL

1.2.1 Catalysts

Eight acid catalysts were tested for the gas phase MTBE synthesis reaction. Five of these were HY zeolites with different acid characteristics. Zeolites Y62, Y82 and LZ210-12 were obtained commercially from UOP. Two other HY zeolites, referred to as D(Y62)7 and S(LZ12)8, were prepared by ammonium hexafluorosilicate (AHS) dealumination of Y62 at 75°C and mild steam dealumination of LZ210-12 at 500°C , respectively, as described elsewhere.(2,3)

A sixth zeolite examined was a ZSM-5 (Mobil), with a silicon to aluminum ratio of 15. It was obtained in the Na^+ form and it was ion-exchanged to the ammonium form by addition to a 3.5 M ammonium acetate solution in distilled water, with the ammonium ion being in excess, heating up to 100°C under stirring and holding for 2 hours. The mixture was then cooled to room temperature, filtered, and the zeolite powder was dried at 50°C for 12 hours.

Two other catalysts were also studied. An amorphous silica-alumina catalyst (Si-Al-O), obtained from American Cyanamid and having a silicon to aluminum ratio of 1.5 and the commercial MTBE synthesis catalyst, Amberlyst-15 resin (Rohm & Haas). The latter is a macroporous sulfonated copolymer of polystyrene and 20 wt% divinylbenzene, with a surface area of $40\text{-}100\text{ m}^2/\text{g}$, an average pore diameter of $240\text{-}320\text{ \AA}$, and an ion exchange capacity of 4.8 mequiv./g (4,5).

1.2.2 Catalyst Characterization

Comprehensive characterization of the HY zeolites used in this study has been already reported (2,3,6). ^{29}Si and ^{27}Al magic-angle-spinning (MAS) NMR were used for determining lattice aluminum content and atomic absorption analysis for total aluminum and sodium content.

The acid site concentration for ZSM-5 was similarly determined by ^{27}Al MAS-NMR, using a Bruker MSL-300 Spectrometer. The parameters used were: spectral frequency (SF) of 78.205 MHz, spectral width (SW) of 62.5 kHz, spinning rate of 3.5 kHz and a repetition time of 1.0 seconds. The number of scans taken was 4000. A sample of an aluminum solution in dilute hydrochloric acid (Certified A.A.S., Fisher Scientific), was used as a standard for determining the chemical shifts. A zeolite sample of known aluminum content was used as a basis for calculating the acid site concentration. The silicon and aluminum content of the silica-alumina material was determined by atomic absorption analysis.

Temperature programmed desorption (TPD) of pyridine was used to characterize the surface acidity. Catalyst samples were heated under helium flow from ambient temperature to 150°C at a rate of $3^\circ\text{C}/\text{min}$ and were held at that temperature for 3 hours. Pyridine was adsorbed at 100°C for 2 hours, followed by a helium flush at the

same temperature. The pyridine TPD spectrum was recorded up to 700°C at a heating rate of 10°C/min, using a thermal conductivity detector. The signal was integrated against a standard volumetric pulse in order to obtain the total amount of pyridine adsorbed. The site densities were determined by assuming that each pyridine molecule is adsorbed on one acid site. The site density for Amberlyst-15 resin was not measured because of its thermal instability. It was taken as equal to its ion exchange capacity of 4.8 mequiv./g.

The average acid strength of each zeolite was estimated based on the turnover frequency (TOF) for n-pentane cracking at 400°C over these catalysts, as reported previously (2,3,7). Silica-alumina is known to be weakly acidic and thus it was considered to have lower acid strength than the zeolites. Amberlyst-15 is unstable at the temperatures necessary for direct comparison. Its acid strength was considered to be of at least the same order as that of the highly acidic zeolites.

1.2.3 Reaction System and Procedure

A schematic representation of the reaction system used in this study is given in Figure 1.1. The reaction was carried out using a 7 mm i.d. lab scale U-shaped glass tube fixed bed reactor with on-line GC-FID analysis. The reactor was placed in an oven equipped with a temperature controller. A thermocouple was inserted in the reactor in such a way that there was continuous monitoring of the bed temperature.

The feed was composed of helium (UHP grade), methanol (Certified A.C.S) and isobutene (liquefied gas, CP grade). A glass saturator was used for vaporizing methanol by flowing helium. The saturator temperature was held constant at 30°C by a circulating water bath.

Product analysis was performed with a gas chromatograph equipped with a Porapak Q column (80/100 mesh, 1.8 m length), using a ramp from 90 to 200°C at a rate of 4°C/min. Calibration was based on relative sensitivities reported in the literature (8) and experimentally verified. Product identification was performed using a mass spectrometer and the resulting fragmentation pattern was compared to patterns from the literature (9).

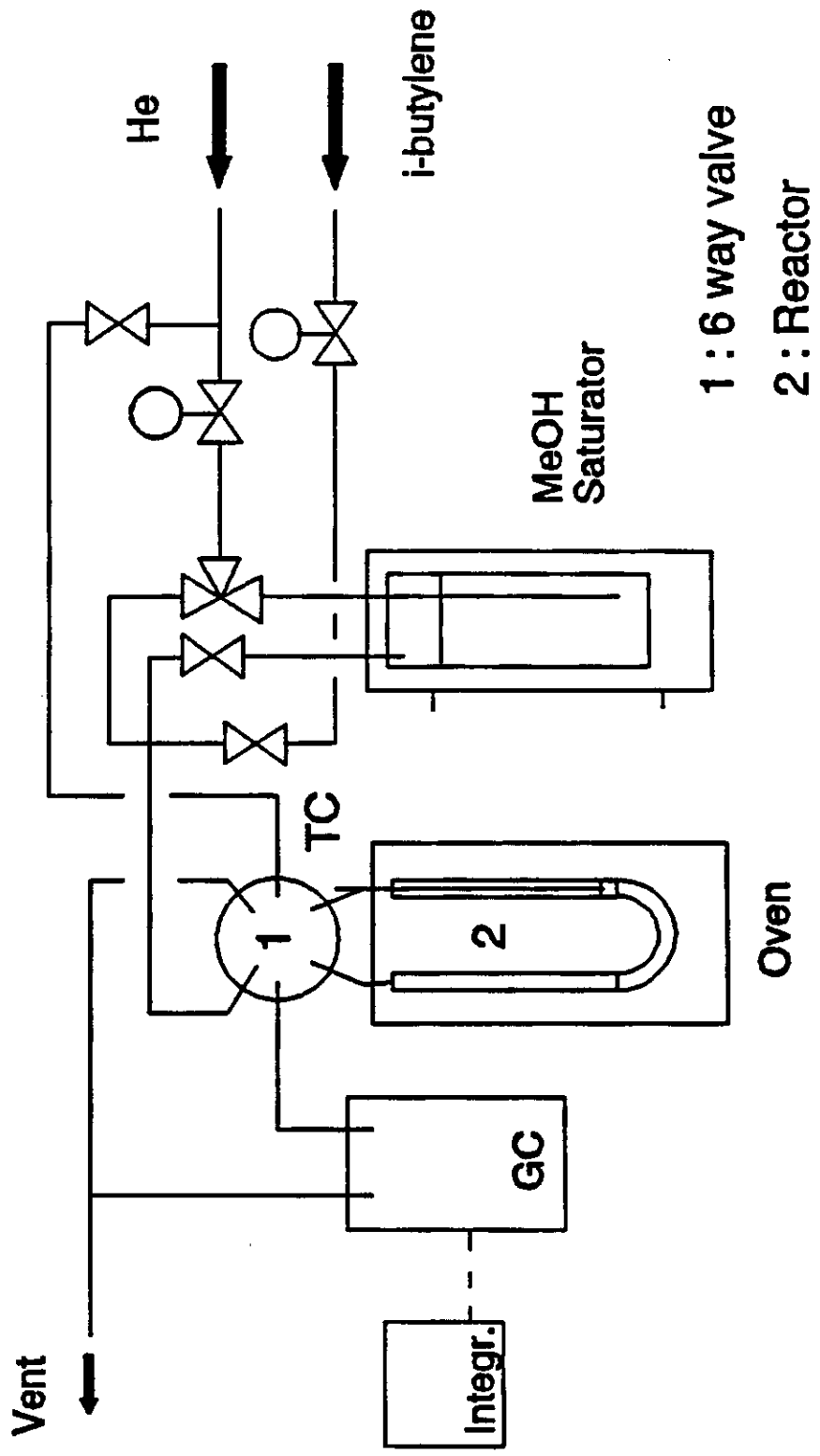


Figure 1.1 Schematic diagram of reaction system used for MTBE synthesis studies.

Prior to reaction, all catalysts were pretreated in-situ by heating to 400°C, or 100°C for Amberlyst-15, under helium flow of 30 cc/min, at a rate of 2°C/min and holding at that temperature for 12 hours. By this procedure, the catalysts in the ammonium form were deaminated to proton form.

The reaction conditions used were: 1 bar pressure, helium to methanol feed ratio of 4, methanol to isobutene feed ratio of 0.55, catalyst weight of 40-50 mg and weight hourly space velocity (WHSV) of 17-20 h⁻¹. Each experiment consisted of a cycle of 4 isothermal steps, at 100, 175, 230 and back to 100°C. At each step, steady-state was reached prior to changing to a new temperature under helium flow.

Because of pressure drop effects across the catalyst bed, the reactant inlet pressure was slightly higher than atmospheric. Since the methanol partial pressure was determined only by the saturator temperature, a variation in the actual reactant ratio above the catalyst compared to the nominal ratio of 0.55 was observed. The actual reactant ratio values were measured from the effluent analysis .

1.3 RESULTS

1.3.1 Catalyst Characteristics

The structural and acid properties of the catalysts studied are summarized in Table 1.1. The acid site densities were calculated by assuming that each lattice aluminum, as determined by NMR, and after subtracting the Na⁺ content, corresponds to one Brønsted acid site. The concentration of acid sites was also evaluated from pyridine TPD data. For the HY zeolites, pyridine adsorption gave about 30% lower acid site concentration. This is probably due to the weak basicity of pyridine and significant geometric inhibition resulting in restricted adsorption (10-12) For the amorphous silica-alumina, the pyridine TPD value obtained indicated that not all aluminum atoms correspond to acid sites, so a range of acid densities is reported.

Table 1.1 Summary of Structural and Acid Properties of Catalysts

Catalyst	Source	Lattice Si/Al Ratio	Extra-lattice Al ($10^{20}/g$)	Brønsted Site Density ($10^{20}/g$)	Pyridine Uptake (mmol/g)	Relative Acid Strength ^a
Y62	Commercial (Linde)	2.5 ^b	3 ^c	25 ^d	2.2	1.0
Y82	Commercial (Linde)	5.1 ^b	10 ^c	16 ^d	1.85	6.5
LZ210-12	Commercial (Linde)	6.0 ^b	0 ^c	13 ^d	1.7	4.1
S(LZ12)8	Steam Dealuminated LZ210-12	8.3 ^b	3 ^c	10 ^d	1.2	10.3
D(Y62)7	Ammon. Hexafluorosil. Dealuminated Y62	7.0 ^b	2 ^c	9 ^d	—	3.4
ZSM-5	Commercial (Air Products)	15 ^e	7.3 ^c	6.3 ^e	—	6.0
Si-Al-O	Commercial (American Cyanamid)	1.5 ^f	—	10-40 ^g	1.65	<<1 ^h
Amberlyst-15	Commercial (Rohm & Haas)	—	—	29 ^f	—	>>1 ^h

a. Defined as the ratio of turnover frequency (TOF) of each material over the TOF of Y62 for n-pentane cracking at 400°C [20,21,25]; b. From ²⁹Si and ²⁷Al NMR [20,21,24]; c. From ²⁷Al NMR and Al atomic absorption analysis [20,21,24]; d. Lattice aluminum free of Na⁺ [20,21,24]; e. From ²⁷Al NMR; f. Commercial analysis; g. Based on pyridine TPD measurements - Si and Al atomic absorption analysis; h. Estimate.

1.3.2 Reaction Measurements and Analysis

A series of experiments performed in the fixed-bed reactor using variable total gas flow rates indicated the absence of significant external mass transfer limitations. The effect of the variable flow rate on the reaction rate at 100°C over zeolite LZ210-12, is shown in Figure 1.2.

1.3.3 Kinetic Behavior at Various Temperatures

Figure 1.3 summarizes the results for the reaction over zeolite LZ210-12, as a function of time, including total methanol conversion, methanol conversion to MTBE, and equilibrium conversion to MTBE at the given conditions. The first data point at each temperature corresponds to 5 minutes reaction time. Steady state was typically achieved after about 2 hours on stream.

At high temperatures significant deactivation was observed and the overall MTBE formation was severely limited by its thermodynamic equilibrium, whereas the formation of 2 byproducts, dimethyl ether and isobutene dimer, was favored. Similar results were obtained for all catalysts except for Amberlyst-15, for which they were obtained only at 100°C.

1.3.3.1 Catalyst Comparison at Low Temperatures (100°C)

The steady-state kinetic results for MTBE synthesis at 100°C over all catalysts studied, are shown in Table 1.2. In general the zeolites were found to be superior to the resin in terms of both activity and selectivity to MTBE, under the experimental conditions used.

The HY zeolites showed comparable or even better activities than the resin, while ZSM-5 gave the best results overall. Silica-alumina exhibited low activity, probably in relation to its low acid strength. All zeolites gave excellent selectivities to MTBE, showing byproduct formation of less than 5%. Amberlyst-15, on the other hand, showed poorer selectivity to MTBE and significant isobutene dimer formation, in agreement with the literature (13).

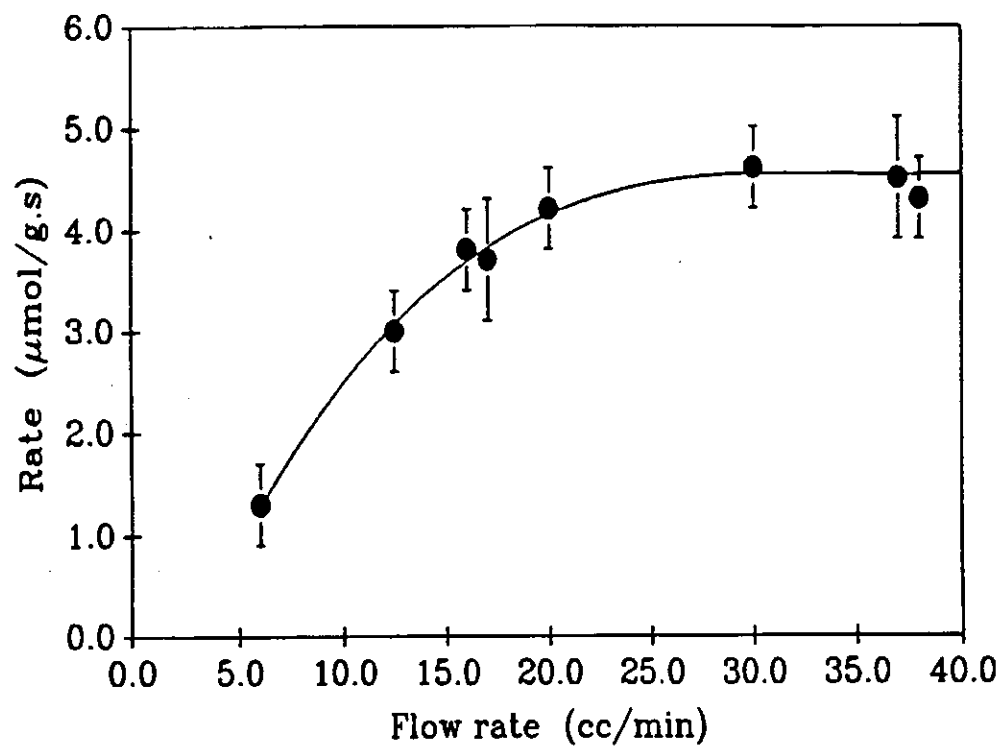


Figure 1.2 Effect of flow rate on MTBE synthesis reaction rate over LZ210-12 zeolite.

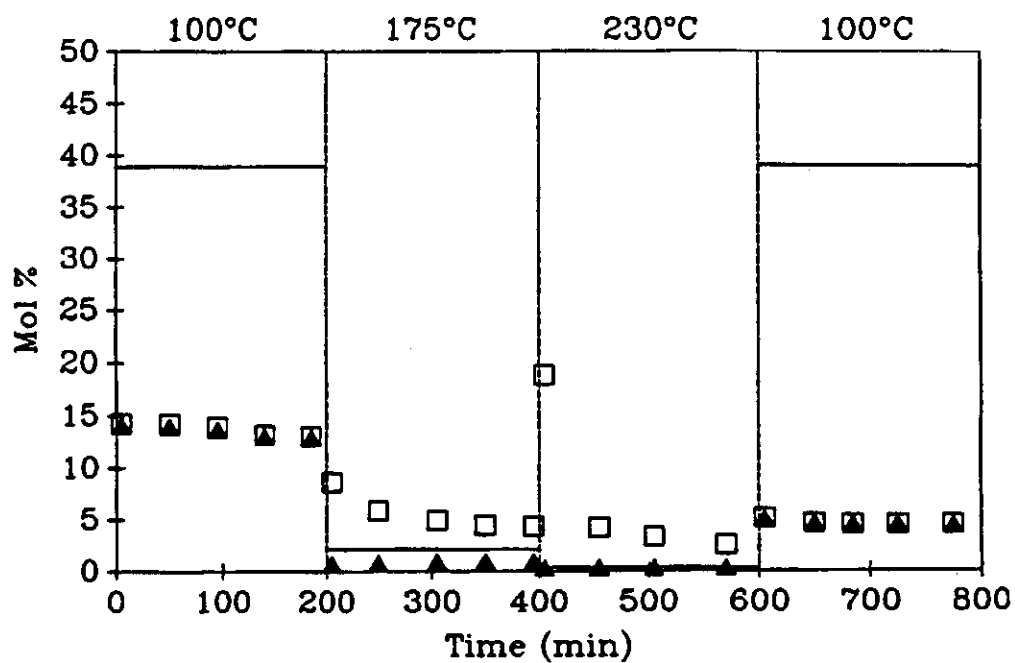


Figure 1.3 Methanol conversion (□) and methanol conversion to MTBE (▲) as a function of time for LZ210-12. Horizontal lines depict the calculated equilibrium conversion. Vertical lines denote change in reaction temperature.

Table 1.2 Steady State Results for MTBE Synthesis
Over Acid Catalysts at 100°C.

	Amberlyst	Y62	Y82	LZ210-12	S(LZ12)8	D(Y62)7	ZSM-5	Si-Al-O
Cat. Weight (mg)	50.4	50.0	40.0	50.0	40.0	50.0	40.0	50.0
WHSV (h ⁻¹)	20	20	18	19	17	17	19	20
MeOH / IB ratio	2.3	2.0	2.1	2.0	2.1	2.4	2.0	2.0
MeOH conv. (mol%)	15.2	12.4	11.9	13.0	10.6	12.8	8.2	5.5
MTBE yield (mol%)	14.7	12.3	11.8	12.9	10.5	12.8	8.1	5.5
Rate ($\mu\text{mol g}^{-1} \text{s}^{-1}$)	5.0	4.3	3.9	4.2	3.1	3.1	2.6	2.0
TOF* 10 ⁴ (s ⁻¹)	10	10	16	19	19	20	25	3 ^a -12 ^b
ANALYSIS (mol%)								
<u>Hydrocarbons:</u>								
C1-C7	0	0	0	0	0	0	0	0
DIB	49	4	2	3	3	4	1	1
<u>Oxygenates:</u>								
DME	0	0	0	0	0	0	0	0
n-PrOH	1	0	0	0	0	0	0	0
t-BuOH	0	1	1	1	0	0	1	0
MTBE	50	95	97	96	97	96	98	99

- a. Based on total Al content (atomic absorption).
b. Based on Pyridine TPD acid site measurements.

1.3.3.2 Catalyst Comparison at High Temperatures (175, 230°C)

Steady-state kinetic results for MTBE synthesis at 175 and 230°C over the zeolites and silica-alumina are presented in Table 1.3. The observed MTBE production was lower than that observed at 100°C. Likewise, the formation of dimethyl ether and isobutene dimer was significantly favored at the higher temperatures. These changes could not be attributed to deactivation, since separate experiments performed at 175°C and under the same conditions gave similar results. A comparison of the results for the one (at 175°C) and two (at 100°C and then at 175°C) step experiments, over zeolites LZ210-12 and ZSM-5, are presented in Tables 1.4 and 1.5, respectively.

The changes previously mentioned are likely due to thermodynamic equilibrium limitations. The error in the selectivities measured is estimated to be ca. 12%, due to differences in the flow pattern and reactant feed ratio over the catalysts, which could affect the deactivation behavior and the selectivity to the various products.

The deactivation behavior of the zeolites for the whole cycle of MTBE synthesis was expressed in terms of a deactivation coefficient, defined as the difference between first and final 100°C steady-state methanol conversion to MTBE, normalized to the first value. Thus, the closer to unity, the higher the deactivation. This coefficient is also shown in Table 1.3.

It was observed that all the HY zeolites deactivated significantly, with LZ210-12 and D(Y62)7 showing the least deactivation among the H-Y types. Silica-alumina showed good resistance to deactivation, something probably due to its low acid strength. Overall, ZSM-5 showed the best behavior, probably because of its small pore size, which inhibits the formation of bulky oligomers and coke precursors (14,15)

1.3.3.3 Product Yield Variation with Reaction Time

The variation of product selectivity for MTBE synthesis over zeolite LZ210-12 at 175°C, as a function of reaction time, is presented in Figure 1.4a. A small decrease in isobutene dimer selectivity, along with an increase in dimethyl ether and MTBE selectivity with time was noted. This behavior was typical and observed for all zeolites.

In order to take into account the reduction in total yield with time, due to catalyst deactivation, the relative product yield, i.e. the yield at a given time normalized to the

Table 1.3 Steady State Results for MTBE Synthesis
Over Acid Catalysts at 175 - 230 °C.

	Y62	Y82	LZ210-12	S(LZ12)8	D(Y62)7	ZSM-5	Si-Al-O
Cat.Weight (mg)	50.0	40.0	50.0	40.0	50.0	40.0	50.0
WHSV (h ⁻¹)	20	18	19	17	17	19	20
MeOH / IB ratio	2.0	2.1	2.0	2.1	2.4	2.0	2.0
Temperature (°C)	175 230	175 230	175 230	175 230	175 230	175 230	175 230
MeOH conv.(mol%)	2.0 2.3	5.0 6.0	4.3 2.5	3.2 6.1	3.4 3.9	3.5 4.3	1.8 13.4
MTBE yield (mol%)	0.7 0.1	0.7 0.1	0.9 0.3	0.6 0.1	0.8 0.1	0.6 0.1	0.7 0.1
Rate (μmol g ⁻¹ s ⁻¹)	0.2 0.03	0.2 0.03	0.3 0.08	0.2 0.03	0.2 0.03	0.2 0.03	0.2 0.03
ANALYSIS (mol%)							
Hydrocarbons:							
C1-C7	1	1	1	0	1	1	0
DIB	50	39	45	55	66	56	76
Oxygenates:							
DME	22	37	39	45	27	23	28
n-PrOH	1	5	1	6	1	3	2
t-BuOH	0	0	0	0	0	0	0
MTBE	26	6	20	2	16	5	14
Deactivation Coefficient	0.93	0.96	0.66	0.87	0.57	0.38	0.72

Table 1.4 MTBE Synthesis over Zeolite LZ210-12
Comparison between 1 and 2 step experiments at 175°C

W = 30.0-50.0 mg ; p = 1 atm ; T = 175°C.
He / MeOH = 4 ; MeOH / IB = 0.50
WHSV : 17-19 h⁻¹

	1-step		2-step	
	Init.	St.State	Init.	St.State
MeOH conversion (%)	8.2	4.3	8.3	4.3
MeOH selectivity to MTBE (%)	6.3	14.2	7.1	21.8
MTBE yield (%)	0.5	0.6	0.6	0.9

Product Analysis (mol%) :

Hydrocarbons :

C ₁ -C ₇	8	0	5	1
C ₈	57	37	69	55

Oxygenates :

DME	30	46	22	27
n-propanol	0	1	0	1
t-butanol	0	0	0	0
n-butanol	1	0	0	0
MTBE	4	16	4	16

Accuracy for major components (>2%) : ± 12%
Accuracy for minor components (≤2%) : ± 20%

Table 1.5 MTBE Synthesis over Zeolite ZSM-5
Comparison between 1 and 2 step experiments at 175 °C

W = 40.0 mg ; p = 1 atm ; T = 175 °C.
He / MeOH = 4 ; MeOH / IB = 0.50
WHSV : 17-19 h⁻¹

	1-step		2-step	
	Init.	St.State	Init.	St.State
MeOH conversion (%)	14.1	2.7	18.7	3.5
MeOH selectivity to MTBE (%)	3.4	21.3	2.7	17.2
MTBE yield (%)	0.5	0.6	0.5	0.6

Product Analysis (mol%) :

Hydrocarbons :

C ₁ -C ₇	3	1	2	1
C ₈	52	61	42	45

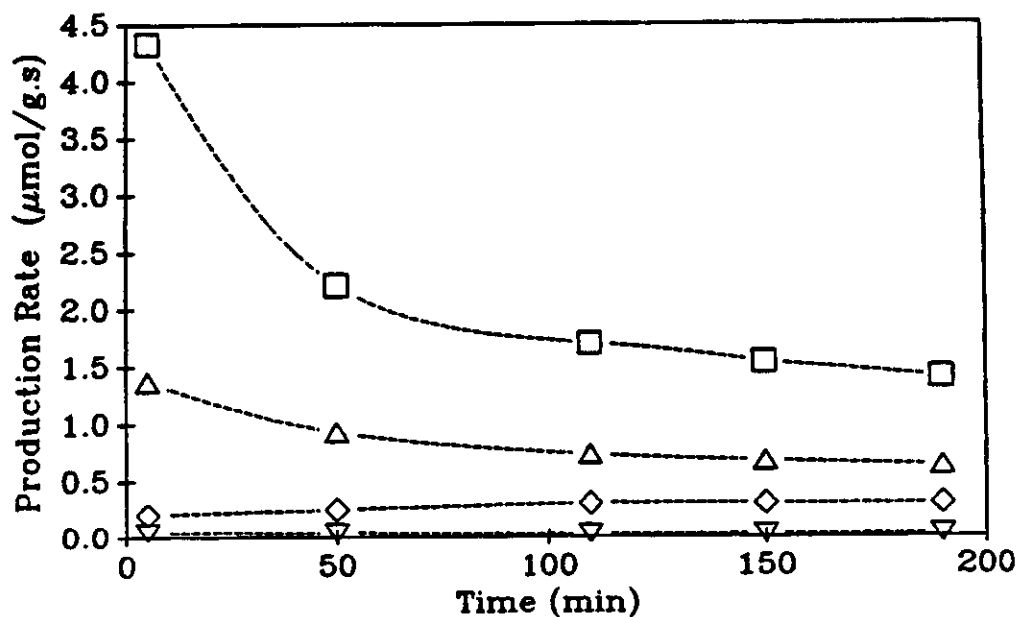
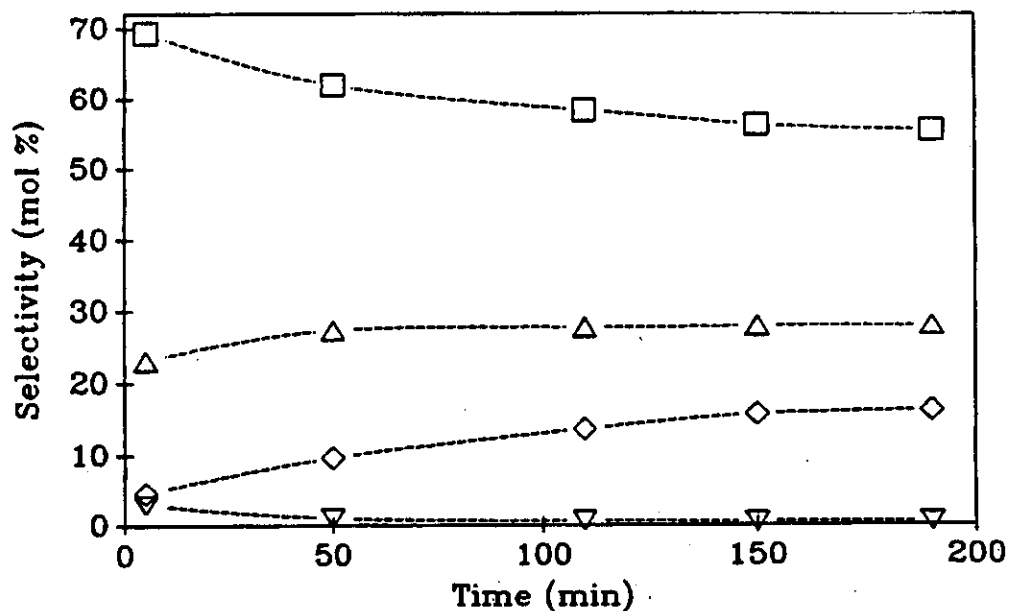
Oxygenates :

DME	41	23	51	35
n-propanol	1	2	2	3
t-butanol	0	0	0	0
n-butanol	0	0	0	0
MTBE	3	13	3	16

Accuracy for major components (>2%) : ± 12%

Accuracy for minor components (≤2%) : ± 20%

Figure 1.4 Effect of time-on-stream on: A -- selectivities; and B -- Production rates of various products. \square : C8 dimer; \triangle dimethyl ether; \diamond : MTBE; and ∇ : t-Butanol.



5 minutes reaction time value, as a function of reaction time, is shown in Figure 1.4b. The observed relative yield of isobutene dimer and dimethyl ether decreased significantly and moderately with time, respectively, whereas the MTBE yield remained nearly constant. A similar and even more expressed behavior was observed at 230°C. At 100°C, almost no deactivation was observed and the variation of product selectivity with reaction time was negligible.

Since the highly acidic sites should be expected to show faster deactivation, this behavior could indicate that the formation of isobutene dimer (and perhaps dimethyl ether) occurs at higher acidity sites than MTBE formation.

1.4 DISCUSSION

Because of the strong influence of thermodynamics, the catalytic behavior for MTBE synthesis of the various catalysts studied, was found to be very similar at elevated temperatures. However, at 100°C, significant variations on MTBE production were observed. The catalytic activity for MTBE synthesis at 100°C, expressed both as initial (5 minutes reaction time) and steady-state turnover frequency, as function of relative acid strength, is represented in Figure 1.5.

For the HY zeolites, an almost constant activity was observed for a 4-fold increase in acid strength. Only zeolite Y62, which has a lower acid strength than the other zeolites, exhibited significantly lower activity, similar to the weakly acidic silica-alumina. The activity change between initial and steady-state conditions, which can be considered as an indication of the extent of deactivation, was found to be a slightly increasing function of acid strength. ZSM-5 did not follow the behavior of the other zeolites, suggesting that parameters other than simply acid character could be of importance for MTBE synthesis.

The same steady-state activities, given as a function of acid site concentration, are presented in Figure 1.6. Activities for n-pentane cracking over the same zeolites are also shown for comparison (2,6). At low acid site concentrations, MTBE synthesis activity remained constant, implying uniform acid strength of the sites, and decreased only for zeolites with high acid site concentrations, such as Y62. This is similar to the behavior

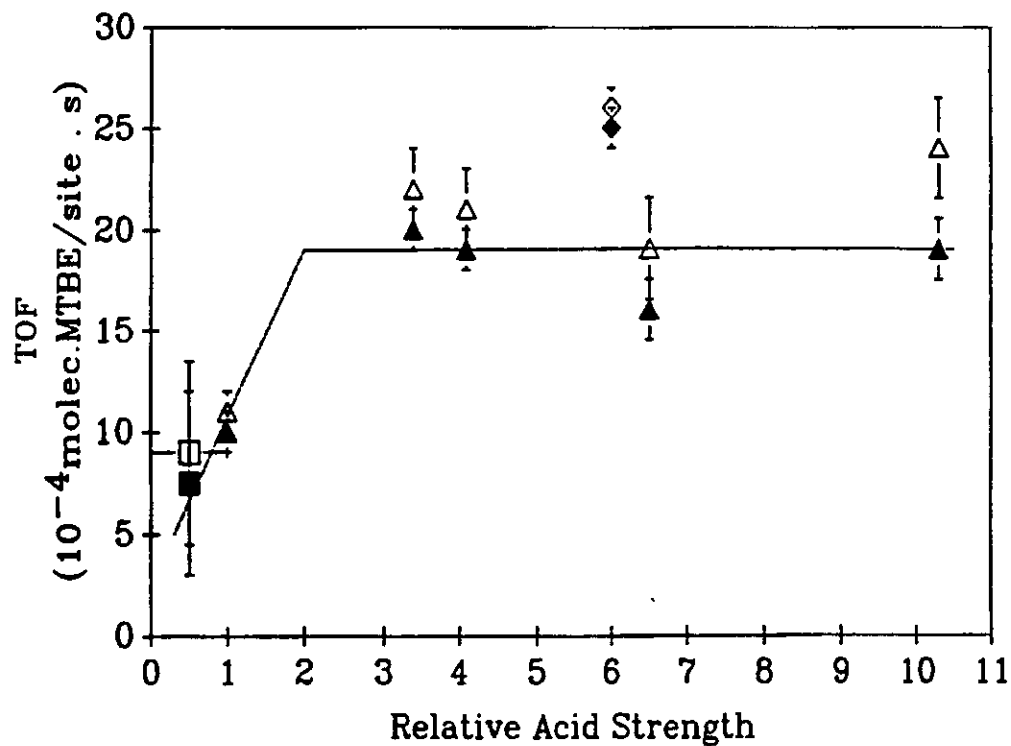


Figure 1.5 Turnover frequency for MTBE synthesis for the various materials studied at 100°C. Open symbols represent initial activities; closed symbols represent steady-state activity. \blacktriangle , \triangle : HY zeolites; \blacklozenge , \lozenge : H-ZSM-5; \blacksquare , \square : Si-Al-O.

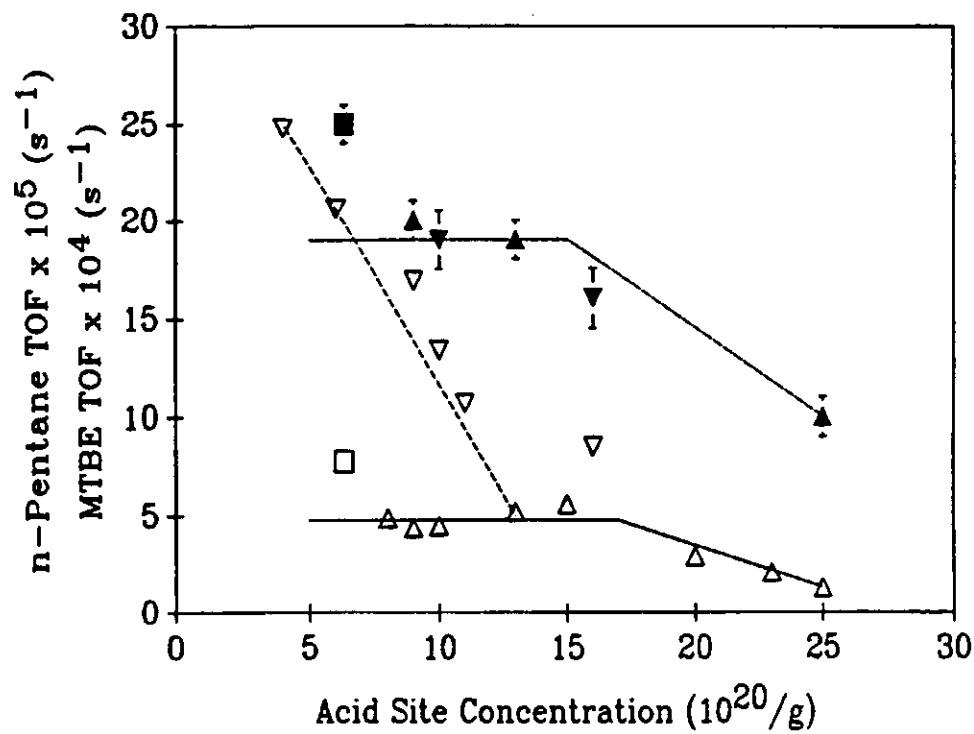


Figure 1.6 Steady-state activity as a function of acid site concentration for MTBE synthesis (solid symbols) and n-pentane cracking (open symbols). \blacktriangle , \triangle : Commercial and AHS-treated zeolites; ∇ , ∇ : steam-treated zeolites; \blacksquare , \square : H-ZSM-5.

observed for n-pentane cracking (7) and for other acid catalyzed reactions, like methanol dehydration, cumene dealkylation and hexane cracking (16,17).

Interestingly, the strongly dealuminated zeolites Y82 and S(LZ12)8 did not show higher activities than the other zeolites, as in n-pentane cracking. This indicates that the acid strength enhancement due to dealumination did not significantly contribute to the activity for MTBE synthesis.

The almost uniform activity of the HY zeolites observed, seems to imply that acid strength does not have a significant effect on activity for MTBE synthesis. On the other hand, the activity of Y62, which has a lower acid strength due to its high acid site density, was significantly lower, like that of silica-alumina.

These results seem to suggest that the catalytic activity for MTBE synthesis is enhanced with increasing acid strength, up to a threshold value, above which, no significant activity enhancement is observed. Lower acid strength causes a reduction in MTBE formation, as evidenced for Y62 and silica-alumina. However, high acid strength does not enhance the activity for MTBE, but the formation of byproducts, such as isobutene dimer and dimethyl ether, and also catalyst deactivation.

It is interesting to note that this threshold or breakpoint of acid strength was found to occur at an acid site concentration of ca. 15×10^{20} sites/g, or ca. 30 lattice Al/unit cell. This value is in agreement with the breakpoint values reported in the literature for the other acid catalyzed reactions mentioned previously (7,16,17).

It should also be noted that, for almost the same site density increase, a 2-fold decrease in TOF was observed for MTBE synthesis, in contrast to a 4-fold decrease for n-pentane cracking, as can be seen in Figure 1.6. This behavior could suggest that the former is less strongly acid demanding than the latter, thus an enhancement in acid strength should influence the cracking reaction more than the MTBE synthesis, in agreement with the hypothesis stated previously.

It is also possible that methanol solvates the protons via an ionic mechanism, as it has been suggested in the literature for MTBE synthesis over the resin (18,19) Such solvation might result in the formation of an activated, partially or fully protonated, intermediate, by charge transfer from the proton site to adsorbed methanol.

The activity of an acid site would thus depend upon the extent of formation and stabilization of such an intermediate. A certain level of acid strength should be adequate and required for this intermediate formation. However, high acid strength should have no further contribution to activity, whereas lower acid strength could possibly inhibit the formation of a sufficiently reactive intermediate and thus result in lower activity. This mechanism seems to be in agreement with the almost negligible increase in initial activity with increased acid strength observed and with the reduced activity of Y62, as shown in Figure 1.5.

It appears that the concentration of methanol at the sites should determine which of the two hypothesized mechanisms described above would impact the catalytic behavior for MTBE synthesis. At similar reactant ratios and at low temperatures (60°C), proton solvation seems to be dominant for the resin (19). By fitting kinetic data, methanol was found to be preferentially adsorbed on the resin sites, even at elevated temperatures, due to a presumably similar value of heat of adsorption with isobutene (20).

Since the zeolites seem to enhance the adsorption of methanol compared to the resin, it is probable that the methanol concentration at the zeolite sites is significantly higher than that implied by the reactant feed ratio. Consequently, the proton solvation mechanism seems to dominate the catalytic behavior of the zeolites for MTBE synthesis, under the experimental conditions used.

The excellent selectivity behavior of the zeolites over the resin has been attributed to shape selectivity (13), but the role of acidity has not been investigated. The selectivity to MTBE of the HY zeolites, was comparable to that of ZSM-5, although a poorer performance might be expected based on pore dimensions.

Acidic HY zeolites with relatively high aluminum density have been shown to be "hydrophilic", thus having a strong tendency to adsorb polar compounds such as methanol (21). The adsorbed molecules become protonated and tend to form clusters which could be stabilized by the lattice oxygen. The enhanced adsorption of methanol and possible cluster formation could significantly restrict isobutene diffusion to the sites and thus further reduce the isobutene dimer formation.

The suggestion that isobutene dimer formation occurs over higher acidity sites than MTBE formation and that these sites are mainly responsible for catalyst