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QUARTERLY TECHNICAL PROGRESS REPORT No. 5

Covering the Period October 1, 1991 to December 31, 1991

SYNTHESIS OF OCTANE ENHANCERS DURING SLURRY-PHASE FISCHER-TROPSCH

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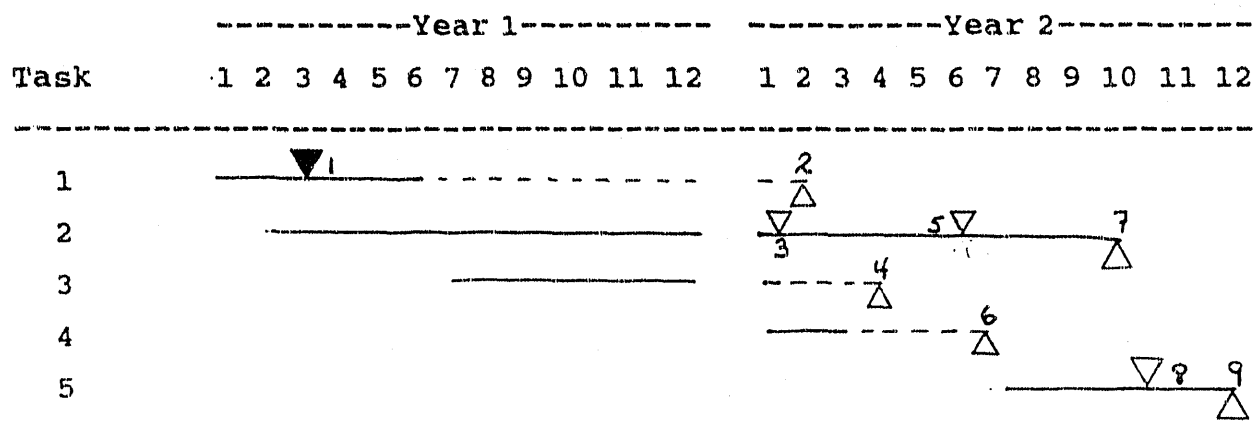
PLANNED TASK AND MILESTONE SCHEDULE



M = denotes milestone

List of Milestones

Number	Description
M1	Finalize design of slurry bubble column reactor (SBCR).
M2	Finalize construction and testing of SBCR. Topical report prepared.
M3	Completion of catalyst screenings for study of isobutylene addition during formation of alcohols. Decision made on catalysts to be studied in SBCR.
M4	Completion of slurry reaction of isobutylene addition during formation of alcohols.
M5	Completion of catalyst screenings for study of isobutylene addition to FT liquid products using acid catalysts. Decision made on catalysts to be studied in SBCR.
M6	Completion of slurry reaction of isobutylene addition to FT liquid products using acid catalysts.
M7	Completion of catalyst screenings.
M8	Completion of slurry reaction of alcohol addition during iso-olefin synthesis.
M9	Final report issued.

OBJECTIVES

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

* Addition of isobutylene during the formation of methanol and/or higher alcohols directly from CO and H_2 during slurry-phase Fischer-Tropsch.

* Addition of isobutylene 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.

WORK ACCOMPLISHED THIS QUARTER

Work during the fifth quarter continued to concentrate in the completion of the SBCR construction and in the screening of acid catalysts for the conversion of syngas-produced alcohols and isobutylene to MTBE (scheme 2). Both of these tasks are nearly complete. Other tasks have been delayed due to equipment problem. We expect to be testing the SBCR during the first month of the next quarter.

Tasks 3, 4, and 5 are awaiting implementation of the SBCR system.

FIFTH QUARTER'S TECHNICAL REPORT

1. Construction of Slurry Bubble-Column Reactor

The construction of the slurry bubble-column reactor has made significant progress during this quarter. The system, which had been previously fully pressure tested, developed a small leak in one of the gaskets. This required a partial disassembly and consumed a significant amount of time to resolve. All electrical components are now in place except for some heat-trace lines.

We expect completion of the BCSR in the first month of next quarter. Shake-down runs will follow shortly thereafter.

2. Gas-Phase Synthesis of MTBE Using Acid Catalysts

INTRODUCTION

In the fourth quarter's technical report, the kinetic results for the gas phase MTBE synthesis reaction on various catalysts were presented, along with some preliminary conclusions about the effect of their acid properties and a study of the effect of certain system parameters, i.e., space velocity, on the results obtained.

This report continues these experiments and includes a presentation of results of replicate runs on some of the same catalysts as well as a ZSM-5 zeolite catalyst. Some of these experiments were repeated because they had been performed under slightly different conditions and were thus not allowing a direct comparison with our other results. With the addition of these new experiments a more detailed and complete study of the effect of the catalysts' acid properties on the reaction is presented.

EXPERIMENTAL

A Na-ZSM-5 catalyst with a Si/Al ratio of 15 was obtained from Air Products. It was ion-exchanged to the ammonium form by slurrying about 0.5 g of the zeolite into 60 mL of a 3.5 M solution of ammonium acetate. The mixture was heated to 100°C

and stirred for two hours. The solid was then filtered, washed, and dried in air at 50°C overnight.

The experimental set-up for the gas phase MTBE synthesis reaction and the procedure were presented in the previous report. Some small changes were made to the experimental system during this quarter in order to improve its performance and reliability. The recurring problem of unstable flow of isobutylene was successfully solved by placing a needle valve for flow control immediately after the line pressure regulator and by minimizing the line length before the main reaction stream line. A new type of reactor was designed having a constriction, in place of a glass frit, for holding the catalyst bed. This resulted in a significant reduction in the pressure drop across the bed. A number of problems were encountered with the operation of the gas chromatograph but these have been solved.

Temperature programmed desorption (TPD) of pyridine was used to characterize the acid strength of the catalysts. The catalysts were ramped in helium from ambient temperature to 150°C at 3°C/minute and held at the upper temperature for two hours. Pyridine was adsorbed at 100°C for two hours followed by a helium flush at the same temperature. The TPD spectrum of pyridine was recorded between 100 and 600°C at 10°C/minute using a TCD detector. The signal was integrated against a standard volumetric pulse in order to obtain the total amount of pyridine adsorbed. The acid site density of the catalysts was determined by assuming that one pyridine molecule will occupy one acid site.

RESULTS AND DISCUSSION

Two of the previously reported catalysts were evaluated again, namely the Amberlyst-15 resin and zeolite Y82. The previous experiment with the Amberlyst had been performed using an isobutylene-to-methanol ratio (R) of one, while all other experiments used R = 1.8. The repeated resin experiment not only allowed direct comparison with the results from the other

catalysts, but also allowed some preliminary conclusions about the effect of reactant ratio on the results.

The steady-state kinetic results for MTBE synthesis over Amberlyst-15 resin for both ratios of R = 1.8 and R = 1.0 are presented in Table 1. The time-on-stream behavior for the two cases is shown in Figure 1. A comparison of the results shows that both MeOH conversion and MTBE selectivity are larger for R = 1.8 than for R = 1.0. Conversely, the selectivity for dimethyl ether (DME) is lower at the higher R. The lower DME formation noted at the higher R is likely due to the decrease in MeOH concentration. The increase in MTBE formation with R must be due to the increase in isobutylene concentration and resulted in the overall net increase in MeOH conversion.

Interestingly, the hydrocarbon selectivity, mainly to the isobutylene dimer, did not increase as it would be expected. This might be due to the large isobutylene concentration which could lead to a zeroth order kinetics of dimer formation. It should be noted, however, that no literature data under these conditions were found in order to support this assumption.

A replicate run of the Y82 zeolite experiment was carried out because previous results showed a significant deviation from all other ones. Additionally, we were suspicious of the results due to the much greater pressure drop that was noted across the catalyst bed. The steady-state kinetic results for MTBE synthesis over zeolite Y82 at 100, 175, 230 and again 100°C are shown in Table 2. The MeOH conversion and MTBE yield as functions of the reaction time for the four parts of the experiment are presented in Figure 2.

The 100°C data show an increase of about 30% in MeOH conversion and MTBE yield compared to the previous experiment. At higher temperatures, the MeOH conversion is high but the MTBE

Table 1. MTBE Synthesis over AMBERLYST-15 Resin. Effect of reactant ratio.

T = 100 °C. p = 1 atm.
WHSV : 15 (gr/gr cat. *h)

IB / MeOH Ratio	1.8	1.0
MeOH conv.%	10.7	8.1
MTBE prod.% of MeOH	75.5	54.5
MTBE yield%	8.1	4.4
Equil. MTBE yield %	38.9	31.0
Product Analysis (mol%) :		
Hydrocarbons :		
C1	0.	0.2
C2	0.	0.1
C3	0.	0.
C5	0.6	0.7
C6	0.3	0.5
C7	0.	0.
C8	2.9	4.7
DIB	36.1	34.7
Oxygenates :		
DME	8.2	17.1
t-BuOH	0.2	0.3
MTBE	51.7	41.3
2-Pentanol	0.	0.4

Figure 1.

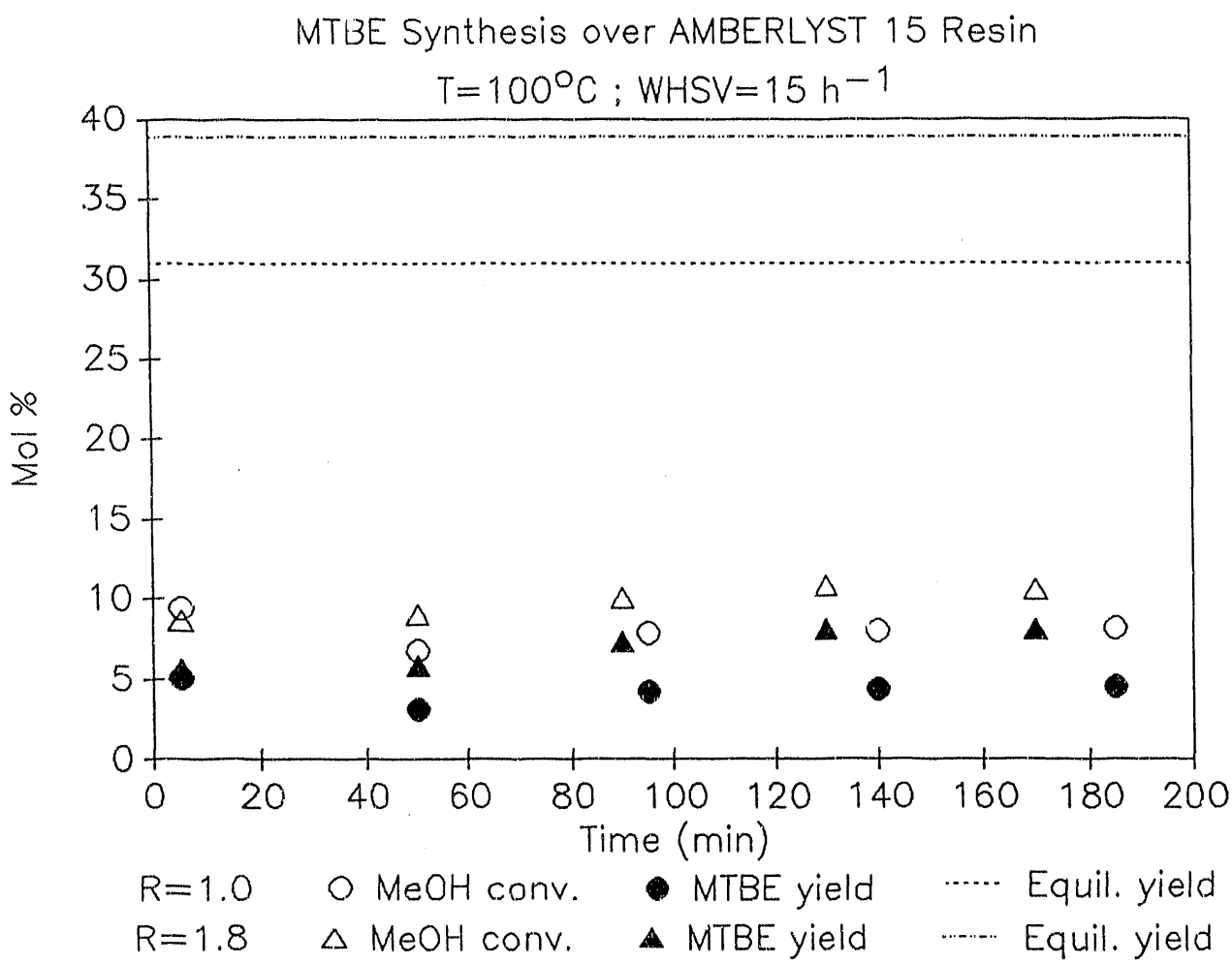
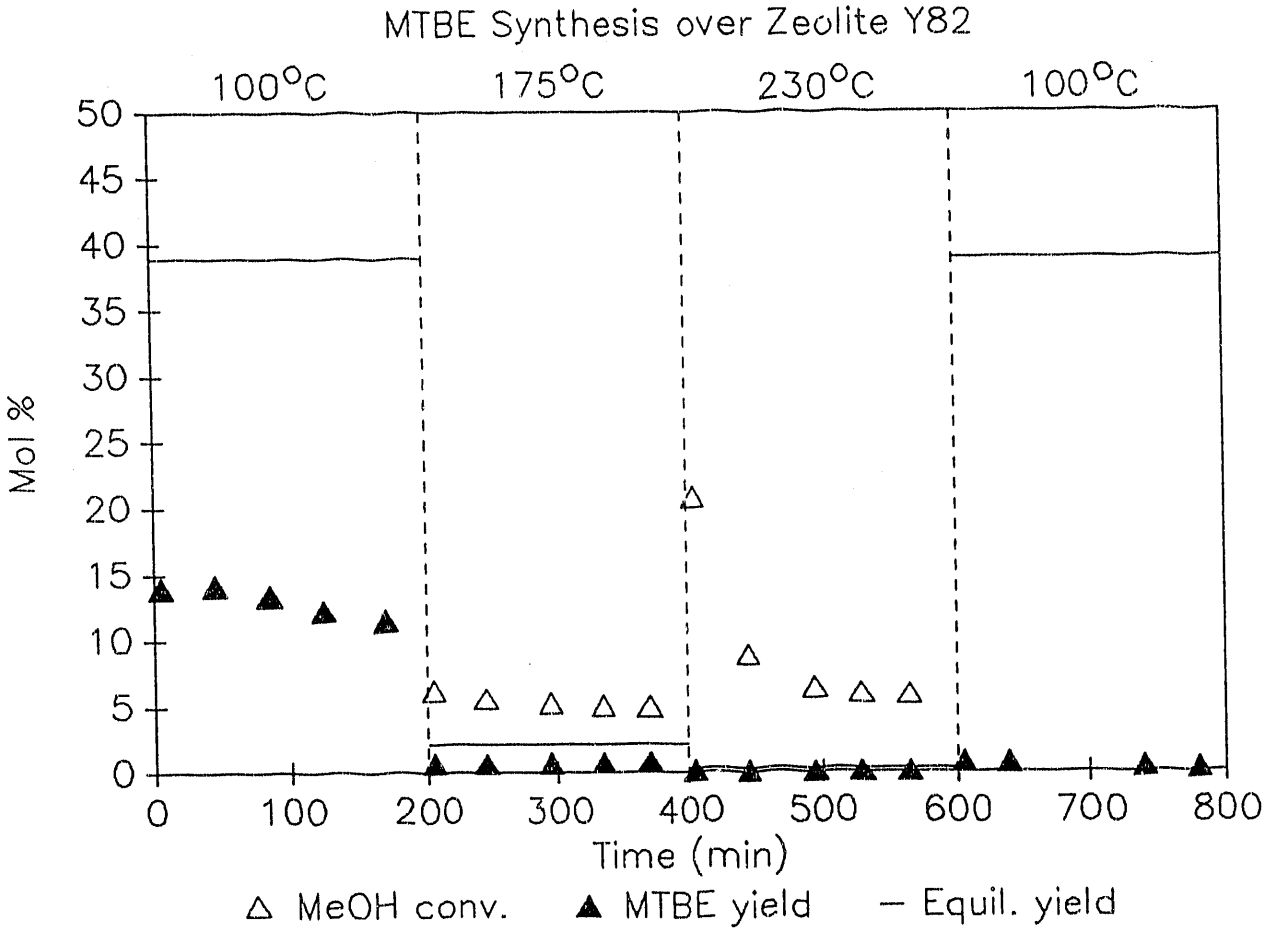

MTBE Synthesis over AMBERLYST 15 Resin
T=100°C ; WHSV=15 h⁻¹
Mol %
40
35
30
25
20
15
10
5
0
0
20
40
60
80
100
120
140
160
180
200
Time (min)
R=1.0 ○ MeOH conv. ● MTBE yield ····· Equil. yield
R=1.8 △ MeOH conv. ▲ MTBE yield ····· Equil. yield

Table 2. MTBE Synthesis over Zeolite Y82.

m = 40 mg. p = 1 atm. T = 100,175,230,100 °C.
He Flow Rate : 6 cc/min.
IB Flow Rate : 3 cc/min.
IB : MeOH Ratio : 1.8
WHSV : 15 (gr/gr cat. *h)

Temp. (°C)	100	175	230	100
MeOH conv.%	11.9	5.0	6.0	0.4
MTBE prod.% of MeOH	99.2	14.5	1.3	100.0
MTBE yield%	11.8	0.7	0.1	0.4
Equil. MTBE yield %	38.9	2.15	0.36	38.9
Product Analysis (mol%) :				
Hydrocarbons :				
C1	0.	0.	0.6	0.
C2	0.	0.2	0.6	0.
C3	0.	0.2	0.6	0.
C5	0.1	0.2	0.	0.
C6	0.	0.	0.	0.
C7	0.	0.	0.	0.
C8	0.	2.3	3.3	0.
DIB	1.8	36.6	41.3	2.9
Oxygenates :				
DME	0.	39.1	45.5	0.
n-PrOH	0.	1.5	6.2	0.
t-BuOH	0.8	0.3	0.	0.
MTBE	97.3	19.6	1.9	97.1

Figure 2.


MTBE Synthesis over Zeolite Y82
100°C
175°C
230°C
100°C
Mol %
50
45
40
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
Time (min)
△ MeOH conv.
▲ MTBE yield
— Equil. yield

yield is approximately the same as previously reported. The constancy in MTBE yield is not unexpected since thermodynamic limitations largely control the reaction at high temperatures. Accordingly, the MTBE selectivity is lower than previously reported. This in turn results in a significant increase in the selectivity to both DME and n-propanol.

It is possible that the difference between the two experiments may be due to the difference in pressure drops across the catalyst beds. In the earlier experiment a high pressure drop was noted. This would result in an increase in the reactor's inlet pressure and thus a decrease in the methanol concentration (recall that we are controlling the partial pressure of the methanol via a constant temperature saturator). Such a decrease will affect the reaction mixture entering the catalyst bed.

A summary of the results for the gas-phase synthesis of MTBE over ZSM-5 at the various temperatures is presented in Table 3. The time-on-stream behavior is shown in Figure 3.

Table 4 summarizes the structural and acid properties of the catalysts studied. Temperature programmed desorption (TPD) of pyridine was carried out in all the H-Y zeolite catalysts and the silica-alumina in order to give another estimate of acid site density. It was not possible to conduct TPD experiments in the Amberlyst resin due to its high temperature instability. Similar TPD experiments for the ZSM-5 catalyst will be forthcoming.

Because of its large size, the pyridine molecule can only access the acid sites found within the supercage structure of the zeolites. Thus, the TPD data give an underestimate of the site density, i.e., the acid site density calculated from these data is lower than that determined based on lattice aluminum site density. The underestimation is in the order of about 50%. In

Table 3.

MTBE Synthesis over Zeolite ZSM-5

m = 40 mg. p = 1 atm. T = 100,175,230,100 °C.
He Flow Rate : 7.5 cc/min.
IB Flow Rate : 3.2 cc/min.
IB : MeOH Ratio : 1.8
WHSV : 16 h^{-1}

Temp. (°C)	100	175	230	100
MeOH conv.%	8.2	3.5	4.3	5.1
MeOH selectivity to MTBE (%)	99.5	17.2	2.2	99.3
MTBE yield%	8.1	0.6	0.1	5.0
Equil. MTBE yield %	38.9	2.2	0.4	38.9
Product Analysis (mol%) :				
Hydrocarbons :				
C1	0.	0.5	0.1	0.
C2	0.	0.	0.1	0.
C3	0.	0.	0.9	0.
C4	0.	0.6	9.5	0.
C5	0.	0.	1.4	0.
C6	0.	0.	0.3	0.
C7	0.	0.	0.	0.
C8	0.	5.7	8.0	0.
DIB	0.6	45.8	47.8	0.6
Oxygenates :				
DME	0.	31.2	22.2	0.
n-PrOH	0.	2.6	8.4	0.
t-BuOH	0.5	0.	0.	0.7
MTBE	98.9	13.6	1.3	98.7

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

Figure 3.

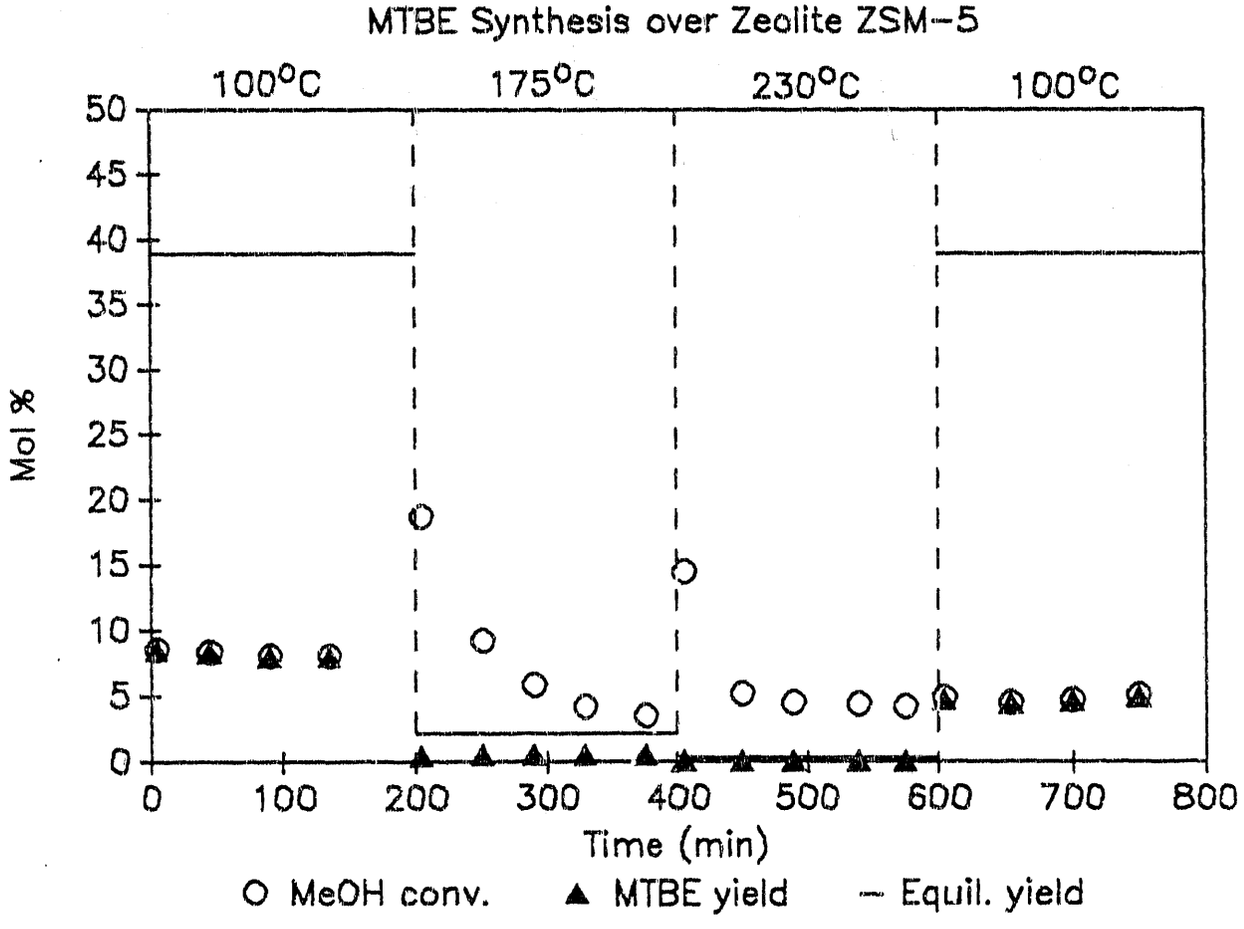

MTBE Synthesis over Zeolite ZSM-5
100°C
175°C
230°C
100°C
Mol %
50
45
40
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
Time (min)
O MeOH conv.
▲ MTBE yield
— Equil. yield

Table 4.

Summary of Structural and Acid Properties of Catalysts.

Catalyst	Source	Si/Al Ratio	Brönsted Site Density (10^{20}/g)	Relative Acid Strength[d]	Pyridine TPD (μmol/g)
Y62	Commercial (Linde)	2.5[a]	27[a]	1.0	2200
Y82	Commercial (Linde)	5.1[a]	16[a]	5.8	1850
LZ210-12	Commercial (Linde)	6.0[a]	15[a]	4.0	1700
S(LZ12)8	Steam Dealum. LZ210-12	8.3[a]	10[a]	8.8	1200
ZSM-5	Commercial (Air Products)	15	6.3	6.0	—
Si-Al-O	Commercial (Am.Cyanamid)	1.5	10-40[b]	$<<1$[e]	1650
Amberlyst-15	Commercial (Rohm & Haas)	—	30[c]	$>>1$[e]	—

a. From ^{29}Si NMR.
b. Based on pyridine TPD - Aluminum Content.
c. M. Iborra, J. Tejero, J. F. Izquiedro, F. Cunill, Br. Pol. J., 23 (1990).
d. Defined as ratio of TOF's over TOF for Y62 for n-pentane cracking at 400°C.
e. Estimate.

the case of Si-Al-O, it was not possible to unambiguously determine the acid site density. Thus, a working range was used having the lower limit calculated from the pyridine molecules adsorbed per gram of catalyst and the upper limit from the aluminum site density.

A detailed comparison of the activity and selectivities, at 100°C, of all the zeolites tested for MTBE synthesis is presented in Table 5. These tables include some data presented in a previous report but is shown again for the sake of completeness. This Table reveals some interesting differences between the various catalysts. It can be seen that the zeolites are in general superior to the resin in terms of MTBE selectivity (about 50% for the resin, about 95% for all others). The resin favors formation of DME (about 8%) and of the iso-butylene dimer (about 40%). This reduced MTBE and greatly enhanced dimer selectivity may be due to the very strong acid character of the resin which favors many secondary reactions. Shape selectivity can also be important. The resin structure is quite open, having an average pore radius of about 160 Å (Marcelin et al.). In contrast, the small zeolite pores can inhibit isobutylene diffusion and thus dimer formation, resulting in enhanced MTBE selectivity.

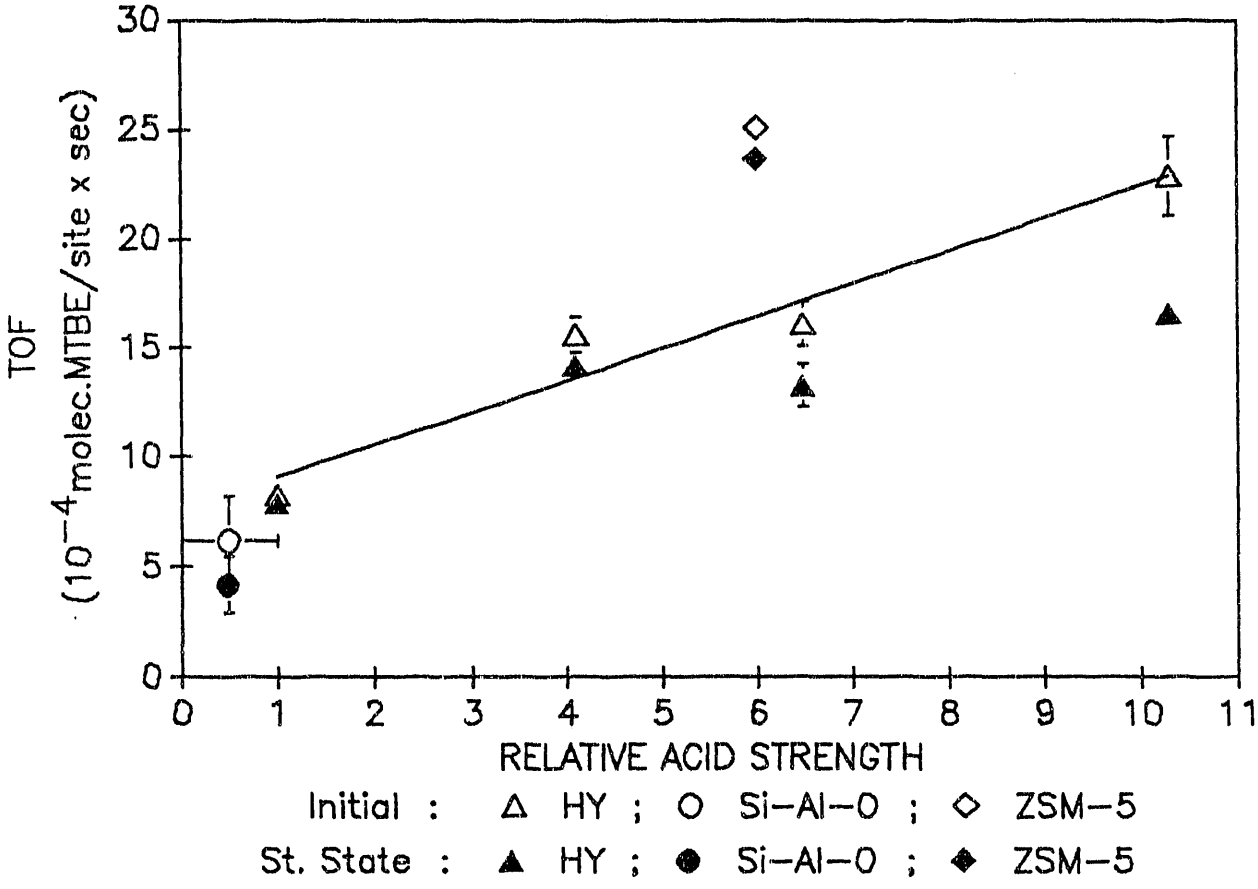
The effect of acid strength on the reaction can be seen in Figure 4, where the turnover frequency, TOF, for MTBE production is plotted as a function of relative acid strength. It can be seen that the initial intrinsic rates lie in an approximate straight line, while steady-state rates are lower due to deactivation. For the family of H-Y zeolites, it can be noted that the difference between initial rate and steady-state rate appears to be an increasing function of acid strength. These correlations do not carry exactly for the ZSM-5 zeolite.

Table 5.

MTBE Synthesis Over Acid Catalysts at 100°C.
Comparison of Ion Exchange Resin and Zeolites at Steady-State.

	Amberlyst	Y62	Y82	LZ21012	S(LZ12)8	ZSM-5	Si-Al-O
Cat.Weight (g)	0.05	0.05	0.04	0.05	0.04	0.04	0.05
i-Butylene/MeOH	1.8	1.8	1.8	1.8	1.8	1.8	1.8
WHSV (hr^{-1})	15	17	15	15	15	16	18
MeOH conv. (%)	10.7	12.4	11.6	13.0	10.6	8.1	5.6
MeOH selectivity to MTBE (%)	75.5	99.0	99.2	98.6	99.9	99.5	99.5
TOF*10^4 (sec^{-1})	4.0	7.5	13.5	14.5	16.5	24.0	4.5
ANALYSIS MOL%							
Hydrocarbons:							
C1-C7	0.9	0.0	0.1	0.0	0.0	0.0	0.0
C8	39.0	3.7	1.8	2.5	3.3	0.7	0.9
Oxygenates:							
DME	8.2	0.0	0.0	0.0	0.0	0.0	0.0
t-BuOH	0.2	0.9	0.8	1.4	0.2	0.4	0.4
MTBE	51.7	95.4	97.3	96.1	96.5	98.9	98.7

Figure 4.
Relationship between TOF for MTBE Synthesis and Acid Strength at 100°C



A summary of the high temperature (175 and 230°C) results is given in Table 6. These data indicate that the behavior of all catalysts is strongly restricted by thermodynamic limitations at high temperatures. Also presented in this table is a measure of the deactivation experienced by the various catalysts in terms of a "deactivation coefficient" which is defined as the difference in steady-state conversion at initial and final reaction at 100°C divided by the steady-state conversion at the initial 100°C. The deactivation coefficient appears to be somewhat related to the acid strength of the zeolites, with strongly acidic zeolites, such as Y-82 deactivating more that the weaker LZ210-12. The lowest deactivations were noted for the ZSM-5 and the LZ210-12. In the case of the LZ210-12 it is speculated that the absence of extralattice aluminum and the intermediate acid strength are optimized in such a way as to reduce coking in the initial stages of the reaction. For the ZSM-5 zeolite, it is believed that its small pores restricts the formation of intermediates leading to coke deposits, thus limiting the rate of deactivation.

CONCLUSIONS

From the data presented it appears that the catalytic behavior for MTBE synthesis is strongly dependent on acid strength. Low acid strength is apparently not adequate for sufficient MTBE formation. In contrast, high acid strength favors the formation of MTBE but it also leads to rapid deactivation. Consequently, there seems to be an optimum acid strength which results in an optimum catalytic behavior for MTBE synthesis. Of the catalysts studied two catalysts appear to present good activity and low deactivation characteristics. These are the zeolite LZ210-12 and the ZSM-5. We propose to use these two materials in further studies in the BCSR.

Table 6.
Summary of High Temperature (175,230°C) Reaction at Steady State and Overall Deactivation.

	Y62	Y82	LZ210-12	S(LZ12)8	ZSM-5	Si-Al-O
175°C						
MeOH conv. %	2.0	5.0	4.3	3.1	3.5	1.8
MTBE yield %	0.7	0.7	1.0	0.65	0.6	0.65
230°C						
MeOH conv. %	2.3	6.0	2.5	6.1	4.2	13.4
MTBE yield %	0.15	0.1	0.1	0.1	0.1	0.1
Deact. Coeff.*	0.93	0.95	0.66	0.88	0.38	0.72

WHSV = 15-18 hr^{-1} ; i-butylene/methanol = 1.8

* Deactivation coefficient : Steady-state conversion difference between initial and final reaction at 100°C, divided by the initial 100°C value.

REFERENCES

G. Marcelin, D.C. Cronauer, R.F. Vogel, M.E. Prudich, and J. Solash, Ind. Eng. Chem., Process Des. Dev., 25 (1986) 747.

3. Work Planned for Next Quarter

During the sixth quarter of this work we plan to evaluate some additional acid catalysts and start the bubble column studies of the catalysts selected.

END

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