Catalysis Letters 27 (1994) 149–157

Selectivity behavior during the equilibrium-limited high temperature formation of MTBE on acid zeolites

A.A. Nikolopoulos [a], R. Oukaci [a], J.G. Goodwin Jr. [a,1] and G. Marcelin [a,b]

[a] *Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA*
[b] *Altamira Instruments, Inc., 2090 William Pitt Way, Pittsburgh, PA 15238, USA*

Received 8 February 1994; accepted 3 May 1994

The synthesis of MTBE was studied in the gas phase at elevated temperatures (up to 175°C) and low pressures (150 kPa) where the MTBE formation rate is limited by thermodynamic equilibrium, using various solid acid catalysts (Amberlyst-15 resin, silica–alumina, HY and H-ZSM-5 zeolites). All the zeolites studied were found to exhibit better selectivities to MTBE than the commercially used Amberlyst-15 resin catalyst. The formation of byproducts increased with increasing temperature and appeared to have a strong enhancing effect on catalyst deactivation. H-ZSM-5 seems to be more suitable for high temperature formation of MTBE because of its excellent selectivity towards MTBE and low deactivation behavior.

Keywords: Amberlyst-15; etherification; HY; H-ZSM-5; MTBE; zeolites

1. Introduction

The high quality standards imposed upon gasoline by the Clean Air Act Amendments [1,2] have made MTBE (methyl tert-butyl ether) the additive of choice for gasoline improvement. This is due to its good antiknocking performance, excellent physicochemical properties compared to alcohols, and better control of the production of environmentally hazardous emissions from the combustion process [3,4]. During the last few years the commercial production of MTBE has substantially increased [5–7].

The commercial process currently used for MTBE synthesis involves the liquid phase reaction of methanol and isobutene (2-methylpropene) at temperatures below 100°C and pressures up to 2 MPa, using a sulfonated ion-exchange resin as catalyst. However, the thermal instability of this organic resin and high possibility of corrosive behavior are considered to be significant drawbacks [8,9]. Inorganic solid acid catalysts, especially zeolites, have received attention for the synthesis of

---

[1] To whom correspondence should be addressed.

MTBE, due to their excellent thermal stability and high selectivity towards MTBE even at reactant ratios favoring undesirable byproduct formation with the resin catalyst [9,10]. Being an exothermic reaction, the extent of MTBE formation is limited by thermodynamic equilibrium at elevated temperatures. However, it could be economically desirable to combine this reaction with other processes, such as direct synthesis of alcohols from syngas. In such cases, the requirement for operation at elevated temperatures (> 100°C) could result in producing MTBE under equilibrium conditions. Thus, the crucial factors for determining MTBE yield would be the selectivity and the deactivation resistance of the catalyst utilized.

The main objective of this study was to examine the MTBE synthesis reaction in the gas phase at elevated temperatures using various zeolite catalysts and to investigate their selectivity and deactivation behavior.

2. Experimental

Four HY zeolites were examined for MTBE synthesis; three of which are identified by their commercial names as Y62, Y82, and LZ210-12 (UOP). Zeolite S(LZ12)8 was prepared by mild steam dealumination of LZ210-12 at 500°C, as described elsewhere [11]. An H-ZSM-5 zeolite (Mobil), an amorphous silica–alumina catalyst (American Cyanamid), and a commercially used MTBE synthesis catalyst, Amberlyst-15 ion-exchange resin (Rohm & Haas) were also examined for comparison. All the zeolites used were in the form of fine powders (crystal size of ca. 1 μm [11]). Amberlyst-15 was obtained in the form of beads and was ground to a fine powder prior to use. Characterization of the inorganic catalysts was done using ^{29}Si and ^{27}Al MAS NMR, atomic absorption spectroscopy (AAS), and TPD of pyridine. The characterization results have been presented elsewhere [11,12].

The catalyst evaluation for the formation of MTBE was performed in a fixed-bed glass micro-reactor with on-line GC-FID analysis. The reaction feed was composed of helium (UHP grade), methanol (Certified ACS), and isobutene (liquefied gas, CP grade). A glass saturator was used for vaporizing methanol into flowing helium. Products were identified using a mass spectrometer.

Prior to reaction, all catalysts were pretreated in situ by slow heating (2°C/min) to 400°C (100°C for Amberlyst-15) under helium and holding at temperature for 12 h. This activation process ensured transformation of the acid sites into the active proton form by complete desorption of ammonia (for zeolites in the NH_4^+ form) and other adsorbed molecules and avoided dealumination of the zeolites by steaming [11]. The thermal instability of Amberlyst-15 for $T > 120$°C mandated an activation only up to 100°C.

The reaction conditions used were: reaction pressure of 150 ± 10 kPa, reaction temperature of 70–175°C, methanol-to-isobutene feed ratio of 0.5, isobutene partial pressure of 27.6 kPa, and weight hourly space velocity (WHSV) of 20 ± 2 h^{-1}. These conditions were chosen so as to minimize the influence of possible heat/mass transport limitations. At each temperature, a pseudo-steady-state was reached, typically in ca. 2 h, prior to changing to a new temperature. A feed ratio of 0.5 was selected in order to enhance the formation of byproducts and thus to allow a better comparative evaluation of the acid catalysts investigated in terms of their selectivity behavior.

3. Results and discussion

A summary of the acidic properties of the catalysts examined is presented in table 1. Some of these results have been previously presented [11,12] and are shown here for the sake of completeness. The acid site concentration of the zeolites was estimated by assuming one Brønsted acid site per lattice aluminum. The available acid site density was also estimated from the extent of pyridine adsorption as measured by TPD, by assuming that each pyridine molecule is adsorbed on one acid site. A difference of ca. 30% was observed for these two estimates for the HY zeolites due to the fact that the bulky pyridine molecules cannot approach acid sites that are located in the sodalite cages [13,14].

A comparison of the steady-state conversion to MTBE for zeolites LZ210-12 and H-ZSM-5 and for Amberlyst-15 resin in the temperature range of 70–175°C is presented in fig. 1. Also shown in fig. 1 is the calculated equilibrium conversion to MTBE under the given reaction conditions, evaluated based on thermodynamic data from the literature [15]. The expression for the obtained equilibrium constant K is in good agreement with the one reported by Tejero et al. [16] and with computer simulations (PRO/II, Simulation Sciences Inc.). It is clear that the extent of MTBE formation is equilibrium limited for temperatures greater than 100°C for

Table 1

Summary of structural and acid properties of catalysts [11,12]

Catalyst	Source	Lattice Si/Al ratio	Extra-lattice Al (mmol/g)	Brønsted site density (mmol/g)	Pyridine uptake (mmol/g)
Y62	commercial (Linde)	2.5 [a]	0.5 [b]	4.2 [c]	2.5
Y82	commercial (Linde)	5.1 [a]	1.7 [b]	2.7 [c]	1.9
LZ210-12	commercial (Linde)	6.0 [a]	0 [b]	2.2 [c]	1.7
S(LZ12)8	steam dealuminated LZ210-12	8.3 [a]	0.5 [b]	1.7 [c]	1.2
H-ZSM-5	commercial (Mobil)	12.0 [a]	0 [b]	1.2 [c]	–
Si-Al-O	commercial (American Cyanamid)	1.5 [d]	–	6.6 [d]	1.7
Amberlyst-15	commercial (Rohm & Haas)	–	–	4.8 [e]	–

[a] From ^{29}Si and ^{27}Al NMR.

[b] From ^{27}Al NMR and Al atomic absorption analysis.

[c] Lattice aluminum free of Na^+.

[d] Commercial analysis.

[e] Estimate.

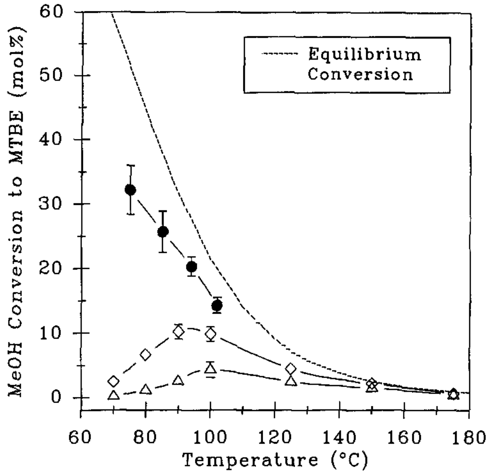

Fig. 1. Effect of temperature on the conversion of methanol to MTBE. MeOH/IB = 0.5; p(IB) = 27.6 kPa; WHSV = 20 h^{-1}. (●) Amberlyst-15; (◇) H-ZSM-5; (△) LZ210-12.

the zeolites and 75°C for the resin at the given pressure. The activity profiles of all the HY zeolites were similar to that of LZ210-12 shown in fig. 1. Thus, the catalytic activity for MTBE synthesis at elevated temperatures is determined simply by chemical equilibrium and not by any specific characteristic of the catalyst used. This is in contrast to the activity behavior observed on the same catalysts at lower temperatures [12]. It should be noted that the "apparent activation energy" for MTBE synthesis under equilibrium conditions was found to be ca. −40 kJ/mol, which corresponds well with the value for the heat of reaction under these conditions, as would be expected.

The catalyst selectivity towards MTBE in the same temperature range (70–175°C) is shown in fig. 2. MTBE selectivity was found to decrease with increasing temperature, due to equilibrium limitations on its formation as well as to increasing byproduct formation. The formation of byproducts was not limited by thermodynamic equilibrium under the conditions applied and may have been determined by either intrinsic reaction kinetics or diffusion. The apparent energy of activation for the dimerization of isobutene, which was the main side reaction to MTBE synthesis at elevated temperatures, was found to be 60–70 kJ/mol, in good agreement with the literature [17,18]. However, the possibility that the isobutene dimerization reaction may have been at least partially influenced by diffusion cannot be excluded.

The selectivity to MTBE of the resin was more sensitive to temperature than that of the zeolites, and the resin was found to be much less selective to MTBE at a given temperature than either of the zeolites. Due to its thermal instability and corrosion behavior, the applicability of the resin is limited for all practical purposes to $T < 120°C$. The zeolites exhibited good selectivities to MTBE (ca. 80%) at 150°C,

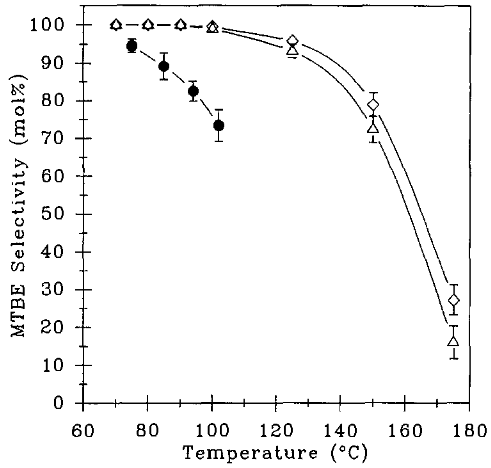

Fig. 2. Effect of temperature on the selectivity to MTBE. (●) Amberlyst-15; (◇) H-ZSM-5; (△) LZ210-12.

a temperature that can be considered within the operational range of any combined syngas-to-alcohols-to-ethers (especially MTBE) process.

In order to more clearly visualize the selectivity differences observed, the selectivity profiles of all the catalysts at 100 and 175°C are presented in figs. 3a and 3b, respectively. The main products identified in this temperature range were MTBE, dimethyl ether (DME) and the isobutene dimers (2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2). In addition, traces of tert-butanol (*t*-BuOH) were found, probably resulting from reaction of isobutene with water produced during the formation of DME. At high temperatures, formation of light alkanes and alkanes was also observed, probably originating from cracking of the isobutene dimers, but the extent of their formation was rather small (< ca. 1%).

It is seen in fig. 3a that all the inorganic catalysts exhibit excellent selectivity to MTBE (greater than 96%) at 100°C. In contrast, at 175°C (fig. 3b) the selectivity to DME and isobutene dimers significantly increased. The selectivity distributions observed for the HY zeolites were the same, within experimental error, in spite of a distinct variation in their acidic properties (table 1). H-ZSM-5 was found to exhibit a slightly higher selectivity to MTBE than the HY zeolites, along with a significantly lower selectivity to the isobutene dimers, and dimethyl ether was the main product at 175°C. A schematic representation of the main reactions in the MTBE synthesis process, based on our experimental observations and literature references [6,16] is given in fig. 4.

The excellent selectivity towards MTBE of the zeolites compared to the resin has been attributed to a shape selectivity effect [9,10]. The apparent inhibition of isobutene dimers formation observed for H-ZSM-5 at 175°C as compared to the HY zeolites and the almost uniform selectivity distribution of the HY zeolites seem to be in agreement with this hypothesis. However, the excellent selectivity behav-

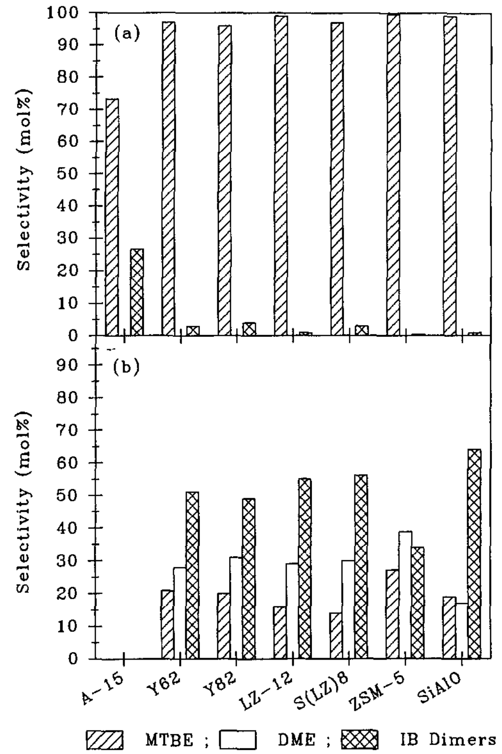

Fig. 3. Comparison of product selectivity for MTBE synthesis at 100°C (a) and 175°C (b).

ior of silica–alumina, which does not have a microporous structure like zeolites and thus cannot exhibit shape selectivity, is likely due to its very low acidity compared to the zeolites.

The variation of product selectivity with reaction time at 175°C for zeolite LZ210-12 is shown in fig. 5a. A small decrease in isobutene dimers selectivity along with increases in dimethyl ether and MTBE selectivity with time was noted. This

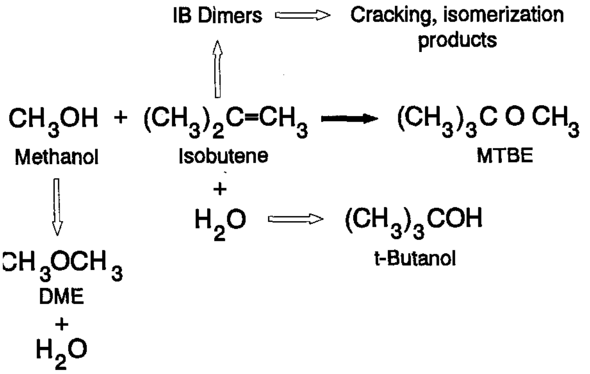

Fig. 4. Schematic of the main reactions involved in the MTBE synthesis reaction process.

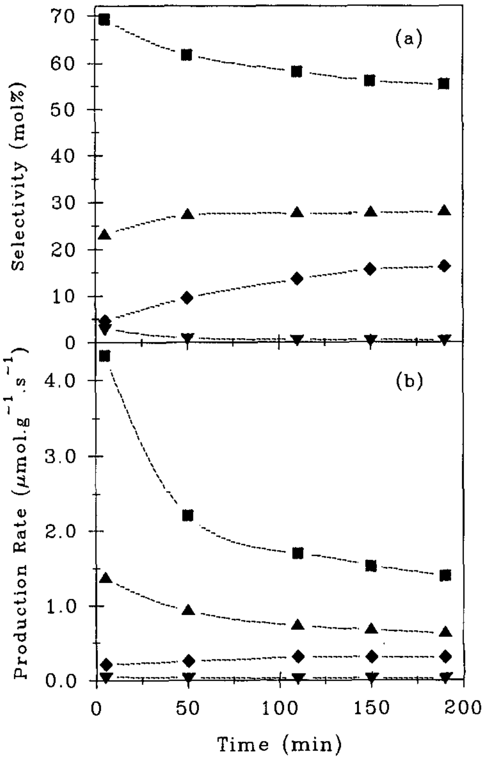

Fig. 5. (a) Effect of reaction time on product selectivity for LZ210-12 at 175°C. (■) IB dimers; (▲) DME; (◆) MTBE; (▼) other. (b) Effect of reaction time on production rate for LZ210-12 at 175°C. (The production rate is expressed in μmol of each product per g of catalyst per second.) (■) IB dimers; (▲) DME; (◆) MTBE; (▼) other.

behavior is typical of all the inorganic catalysts examined. However, the reduction in activity with time due to catalyst deactivation must be taken into account. The rate of product formation on LZ210-12 as a function of reaction time is shown in fig. 5b. It can be seen that, although the extent of formation of isobutene dimers and dimethyl ether decreased with time, the extent of MTBE formation remained nearly constant. These results indicate that the deactivation of a zeolite catalyst appears to be strongly related to the formation of byproducts, in particular of the isobutene dimers. The fact that the extent of formation of MTBE was found to be practically constant with time is not surprising at all, since it was limited by thermodynamic equilibrium under the given conditions, and only an almost complete catalyst deactivation (>99%) could have removed equilibrium limitations on the extent of MTBE formation.

The product selectivity and rate of product formation with reaction time for zeolite H-ZSM-5 are shown in figs. 6a and 6b. The rate curves observed were less steep than the corresponding ones for the HY zeolites, clearly indicating an improved deactivation behavior. The significant suppression of the rate of formation of iso-

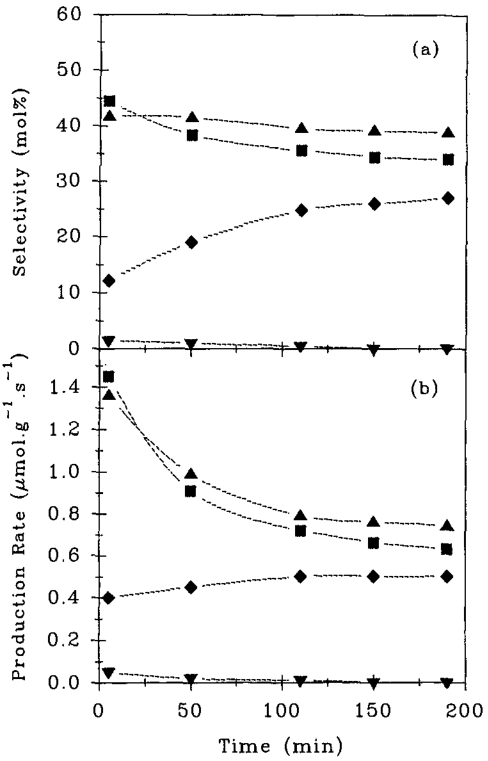

Fig. 6. (a) Effect of reaction time on product selectivity for H-ZSM-5 at 175°C. (■) IB dimers; (▲) DME; (◆) MTBE; (▼) other. (b) Effect of reaction time on production rate for H-ZSM-5 at 175°C. (The production rate is expressed in μmol of each product per g of catalyst per second.) (■) IB dimers; (▲) DME; (◆) MTBE; (▼) other.

butene dimers and the higher selectivity towards MTBE compared to the HY zeolites are two major advantages that make H-ZSM-5 a more favorable catalyst for the synthesis of MTBE at high temperatures.

4. Conclusions

The study of the synthesis of MTBE on various solid acid catalysts at elevated temperatures (up to 175°C) and low pressures (ca. 150 kPa) indicated that the formation of MTBE was limited by thermodynamic equilibrium above ca. 100°C under the experimental conditions applied. All the inorganic catalysts studied exhibited better selectivity towards MTBE compared to the commercially used Amberlyst-15 resin catalyst at the less favorable methanol/isobutene feed ratio of 0.5. The selectivity to MTBE was found to decrease with temperature due to equilibrium limitations on MTBE synthesis and enhanced byproduct formation. Formation of byproducts, in particular of isobutene dimers, appeared to be strongly related to catalyst deactivation.

Of all the catalysts investigated, H-ZSM-5 seems to be the most applicable zeolite for the synthesis of MTBE at high temperatures because of its superior selectivity towards MTBE compared to the larger-pore HY zeolites and because of its very low selectivity towards the isobutene dimers, resulting in slower deactivation.

Acknowledgement

Funding for this work from the US Department of Energy, under Grant DE-AC22-90PC90047, is gratefully acknowledged.

References

[1] F.L. Potter, Fuel Reformulation 1 (1) (1991) 22.
[2] J.E. Peeples, Fuel Reformulation 1 (1) (1991) 27.
[3] G.H. Unzelman, Fuel Reformulation 1 (2) (1991) 50.
[4] W.J. Piel and R.X. Thomas, Hydroc. Proc. 69 (7) (1990) 68.
[5] M.S. Reisch, Chem. Eng. News, Apr. 13 (1992) 16.
[6] G.J. Hutchings, C.P. Nicolaides and M.S. Scurrell, Catal. Today 15 (1992) 23.
[7] M.B. Haigwood, Fuel Reformulation 1 (1) (1991) 52.
[8] T. Takesono and Y. Fujiwara, US Patent 4 182 913 (1980).
[9] R. Le Van Mao, R. Carli, H. Ahlafi and V. Ragaini, Catal. Lett. 6 (1990) 321.
[10] P. Chu and G.H. Kühl, Ind. Eng. Chem. Res. 26 (1987) 366.
[11] P.V. Shertukde, W.K. Hall, J.-M. Dereppe and G. Marcelin, J. Catal. 139 (1993) 468.
[12] A.A. Nikolopoulos, A. Kogelbauer, J.G. Goodwin Jr. and G. Marcelin, submitted.
[13] M. Kojima, M.W. Rautenbach and C.T. O'Connor, J. Catal. 112 (1988) 495.
[14] H.G. Karge, Z. Phys. Chem. NF 122 (1980) 103.
[15] R.H. Perry and D. Green, eds., *Chemical Engineers' Handbook*, 6th Ed. (McGraw-Hill, New York, 1984) T3-181, T3-206;
R.C. Weast, M.J. Astle and W.H. Beyer, eds., *CRC Handbook of Chemistry and Physics*, 64th Ed. (CRC Press, Boca Raton, 1983) D-177;
J.M. Smith, *Chemical Engineering Kinetics*, 3rd Ed., pp. 14–18;
J.M. Smith and H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 4th Ed., pp. 507–514;
C.G. Hill, *Introduction to Chemical Engineering Kinetics and Reactor Design*, p. 570.
[16] J. Tejero, F. Cunill and J.F. Izquierdo, Ind. Eng. Chem. Res. 27 (1988) 338.
[17] W.O. Haag, Chem. Eng. Prog. Symp. Ser. 63 (1967) 140.
[18] T. Ngandjui and F.C. Thyrion, Chem. Eng. Proc. 31 (1992) 1.