Methanol conversion to olefins (MTO) over H-ZSM-5: Evidence of product distribution governed by methanol conversion

Wenzhang Wu [a], Wenyao Guo [b], Wende Xiao [a,b,*], Man Luo [b]

[a] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, China
[b] Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

ABSTRACT

Methanol conversion to olefins (MTO) was investigated in an isotherm fixed-bed reactor at methanol partial pressures ranging from 5 to 50 kPa, water/methanol ratios from 0 to 9 and temperatures from 380 °C to 460 °C over H-ZSM-5 catalyst with a Si/Al ratio of 200. Product distribution was affected by operation conditions remarkably only at low methanol conversions (<80%). When methanol conversion approaches 100%, product distribution is hardly affected by operation conditions. In addition, it was always found that propylene selectivity is enhanced at the expense of hexenes at high methanol conversions. The dependence of product distribution on methanol conversion derives from the change of dominant reaction pathway from olefin methylation and cracking to oligomerization and cracking. Product distribution at low methanol conversions may be determined by the relative rate between olefin methylation and cracking, while at complete methanol conversion product distribution is determined by oligomerization and cracking of $C_4^= $–$C_7^=$ likely.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The current pricing of crude oil gives rise to increasing interest in routines of using coal or natural gas as a feedstock to produce petrochemicals. Methanol to olefins (MTO) process, which enables the transformation of coal or natural gas to light olefins (ethylene and propylene) gains more attention, since methanol can be produced via syngas (CO and H_2) from coal or natural gas using a proven technology [1–3].

Many types of zeolite catalysts have been examined for the MTO process [2,4,5]. Among these catalysts, ZSM-5 zeolite [6,7] is believed to be one of the most suitable catalysts for industrial application of MTO process due to its high resistance to deactivation by coke deposition [8]. This unique property of ZSM-5 facilitates the application of simple fixed-bed reactors for MTO process. It has been concluded that H-ZSM-5 with Si/Al ratio higher than 200 or its modification form is more suitable for MTO reaction with high propylene selectivity [9–12]. Studies on the effects of operation conditions on olefin selectivity in methanol conversion over such high silica H-ZSM-5 were also reported which showed that propylene selectivity is enhanced at high temperature combined with low methanol partial pressure [9].

However, the mechanism for methanol conversion to olefins over ZSM-5 is complicated. Reactions involved in the step of methanol to olefins consist of olefin methylation by methanol [13–17], cracking

of higher olefins [6,15], oligomerization of light olefins [18,19] and olefin formation from "hydrocarbon pool" mechanism [20–24]. The complex reaction network for olefin formation from methanol may probably result in the product distribution (mainly C_2–C_7 olefins) in MTO governed or controlled by methanol conversion [6,25–27]. To figure out whether the olefin distribution is governed by methanol conversion in MTO, studies on the product distribution as a function of methanol conversion are of practical importance. Prinz et al. [26], Dehertog et al. [9,26] and Freiding et al. [12] reported that product distribution in methanol conversion to olefins varied with methanol conversion, but their efforts were mainly concentrated on the selectivity of ethylene and propylene or verifying whether ethylene was the initial product. Kaarsholm et al. [6] provided detailed product distribution of methanol to olefins versus methanol conversion over a phosphorous modified ZSM-5 catalyst and indicated that olefin selectivity was increased at complete methanol conversion due to cracking of C_{6+} species [6,28], but only several sets of reaction condition were investigated. More detailed research on the dependence of product distribution on methanol conversion in MTO at various operation conditions has not been reported, whereas it is of considerable importance to get more insight into the reaction pathway.

In this study, we presented detailed product distributions in MTO as a function of methanol conversion at various methanol partial pressures, water/methanol ratios and temperatures over H-ZSM-5 catalyst with a Si/Al of 200. It was found that methanol conversion does govern the olefin distribution at various reaction conditions. An interpretation for this phenomenon has also been presented.

* Corresponding author at: Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China. Tel./fax: +86 21 3420 3788.
  E-mail address: wdxiao@sjtu.edu.cn (W. Xiao).

2. Experimental

2.1. Catalyst synthesis and characteristics

H-ZSM-5 (Si/Al = 200) was obtained from Shanghai Fuxu Molecular Sieve Co., Ltd Company. The sample had a crystal size of about 1 μm and was made into tablets, crushed and sieved into a fraction of 400–600 μm. Methanol (>99%) is supplied by Sinopharm Chemical Reagent Co., Ltd.

2.2. Experimental setup and procedure

MTO reaction was performed in a tube reactor, which was immersed in a molten salt bath [29]. The reactor tube has a length of 0.5 m and an internal diameter of 0.005 m. It was made of titanium to ensure the absence of wall reactions. The catalyst bed was diluted with quartz powder.

The partial pressure of methanol was varied by diluting the methanol feed with nitrogen or deionized water. Catalyst deactivation by coke deposition was slow at the investigated reaction conditions. The reactor effluent was analyzed on-line by means of a GC equipped with a HP-PLOTQ capillary column (30 m × 0.32 mm i.d.) and a FID detector.

Methanol and DME were treated as a single species, since the dehydration of methanol to form DME over H-ZSM-5 is much faster than the formation of olefins [30]. In fixed bed, it was reported that the conversion of methanol to DME is near equilibrium in MTO reaction [27]. Therefore, DME in the influent was treated as un-converted methanol. Methanol conversion is calculated through Eq. (1):

$$X_{MeOH} = \frac{F_{MeOH,0} - F_{MeOH} - 2F_{DME}}{F_{MeOH,0}} \qquad (1)$$

F_{MeOH} and F_{DME} represent the molar flow rate of methanol and DME in the effluent of the reactor. $F_{MeOH,0}$ represents the molar flow rate of methanol in the reactor inlet.

The selectivity of each carbon of olefins is defined as

$$S_i = \frac{nF_i}{F_{MeOH,0} - F_{MeOH} - 2F_{DME}} \qquad (2)$$

where, F_i represents the molar flow rate of specie i with carbon number of n.

The space time was adjusted by varying the overall feed flow rate to make methanol conversion covering a wide range. The main products observed are C_2–C_7 olefins. Aromatics and C_1–C_4 paraffins are negligible (i.e. ≤3 C%) when methanol inlet partial pressure is kept below 50 kPa.

3. Results and discussions

3.1. Product distribution versus methanol conversion

3.1.1. Effect of methanol partial pressure

Product distributions in MTO as a function of methanol conversion were investigated at methanol partial pressure from 5 kPa to 50 kPa at 460 °C at varying space time. Here, the space time is defined as the ratio of catalyst mass to methanol molar flow rate. As expected, methanol conversion decreases notably with decreasing methanol partial pressure at the same space time, as can be seen in Fig. 1. When methanol partial pressure decreases from 50 kPa to 5 kPa, nearly 5 times more space time is required to maintain 100% methanol conversion.

Product distributions display quite different behaviors at low and complete methanol conversion. At low methanol conversions (i.e. <80%), decreasing methanol partial pressure enhances selectivities of $C_3^=$, C_4 (mainly $C_4^=$) and C_5 (mainly $C_5^=$). Propylene selectivity at
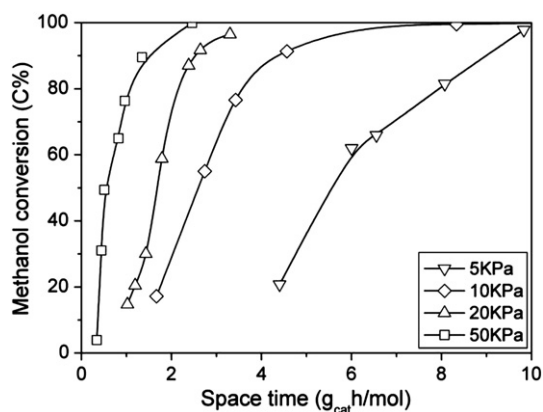

Fig. 1. Methanol conversion versus methanol space time for different methanol partial pressures. Reaction conditions: T = 460 °C, water/methanol = 0, diluent: N_2.

methanol partial pressure of 5 kPa at low methanol conversions is about 40 C%, which is 8 C% higher than that at 50 kPa. $C_2^=$ selectivity remains unchanged with decreasing methanol partial pressure (Fig. 2 (B)) but the selectivity of C_7 (mainly $C_7^=$) decreases remarkably from 8 C% to about 1 C% (Fig. 2 (E)). The selectivity of C_6 (mainly $C_6^=$) undergoes slight decrease (Fig. 2 (A)) when methanol partial pressure is lowered.

At high methanol conversions (i.e. >80%) propylene selectivity is enhanced with increasing methanol conversion, with $C_6^=$ selectivity decreased concurrently, as shown in Fig. 2 (A). Cracking of $C_6^=$ is responsible for the increase of propylene at high methanol conversions. When lowering methanol partial pressure from 50 kPa to 5 kPa at complete methanol conversion, the selectivity of propylene increases moderately from 42 C% to 48 C%. We considered that the decrease of propylene selectivity may partially due to the formation of aromatics at higher methanol partial pressure, since minor amount of aromatics (nearly 3%) at complete methanol conversion at methanol partial pressure of 50 kPa was observed. The fact that propylene selectivity at methanol partial pressure of 20 kPa and 5 kPa tends to converge at high methanol conversion also agrees with this suggestion. Selectivity curves of $C_4^=$ and $C_5^=$ for different methanol partial pressures tend to converge. This means when methanol conversion approaches 100%, $C_4^=$ and $C_5^=$ selectivities are not affected by methanol partial pressure but methanol conversion.

3.1.2. Effect of water to methanol ratio

Product distributions versus methanol conversion at different water/methanol ratio were studied by co-feeding methanol with water in the fixed bed at 460 °C. The inlet methanol partial pressure was kept at 10 kPa. Three water/methanol molar ratios of 0, 1 and 9 were tested, respectively.

At the same space time, increasing water concentration decreases methanol conversion dramatically, as shown in Fig. 3. This behavior can be ascribed to the reduced amount of methanol adsorption on catalyst acid sites caused by competitive adsorption of water. The conversion of methanol is seriously suppressed at extremely high water/methanol ratio.

The effect of water/methanol ratio on olefin distribution at lower methanol conversions also differs from that at complete methanol conversions. At low methanol conversions, ethylene (Fig. 4 (B)) and propylene (Fig. 4 (A)) selectivities increase from 2 C% and 35 C% to about 5 C% and 45 C% when increasing water/methanol ratio from 0 to 9, respectively. In the meantime, selectivity of $C_6^=$ declines dramatically from 18 C% to about 12 C% (Fig. 4 (A)). $C_7^=$ suffers slight decrease when increasing water/methanol ratio at low methanol conversions, as shown in Fig. 4 (E). $C_4^=$ (Fig. 4 (C)) and $C_5^=$ ((D)) also suffer slight decrease in selectivities.

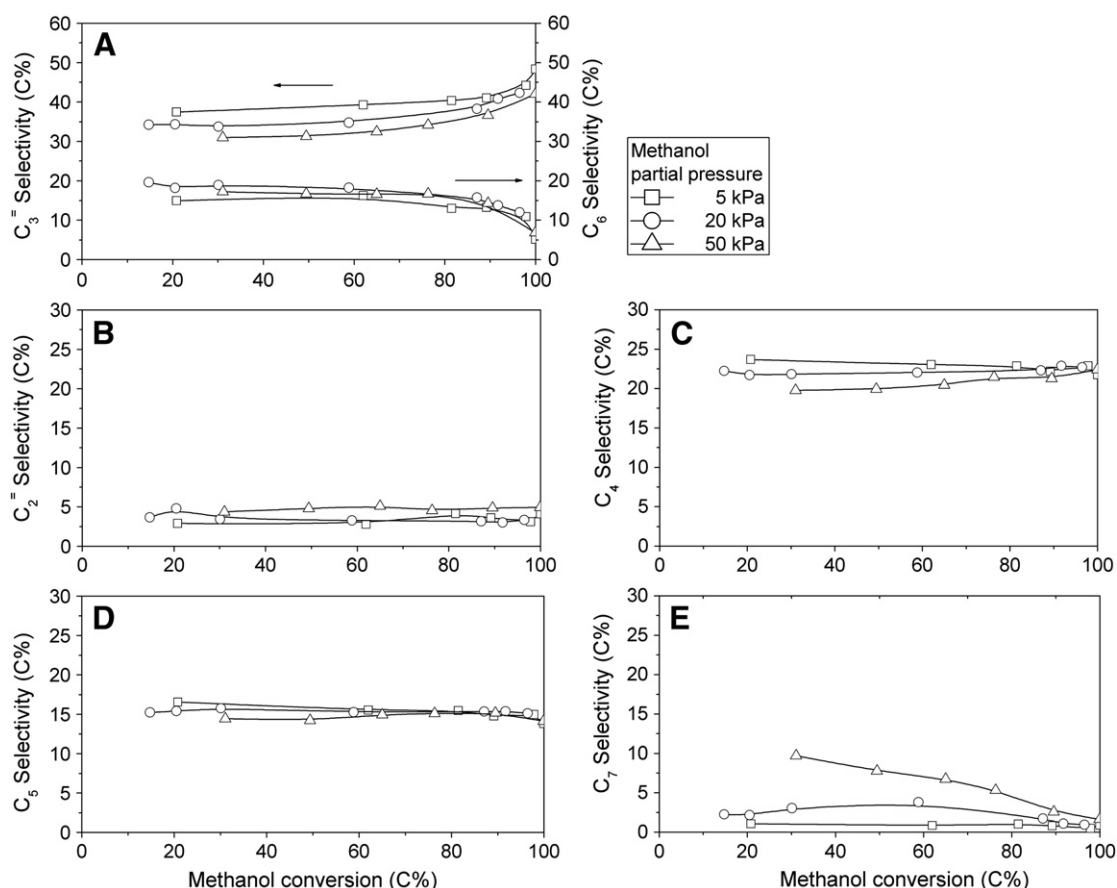Fig. 2. Product distribution versus methanol conversion at different methanol partial pressure. Reaction conditions: T = 460 °C, water/methanol = 0, diluent: N_2.

However, at complete methanol conversion, selectivity curves of $C_3^=$, $C_6^=$ and $C_7^=$ for different water/methanol molar ratios tend to converge, respectively. This fact means selectivities of $C_3^=$, $C_6^=$ and $C_7^=$ are not affected by water co-fed at complete methanol conversion. The phenomenon that propylene selectivity is increased at expense of $C_6^=$ was also observed when water was co-fed with methanol at high methanol conversions. Selectivity curves of $C_2^=$, $C_4^=$, and $C_5^=$ at higher conversions do not tend to converge. The selectivities of $C_2^=$, $C_4^=$, $C_5^=$ seem unchanged with methanol conversion except that $C_5^=$ selectivity declines slightly at 100% methanol conversion. It should be noted that at high water/methanol ratio $C_2^=$ selectivity is increased at expense of $C_4^=$ and $C_5^=$. That is to say, $C_2^=$ is formed mainly form $C_4^=$ and $C_5^=$.
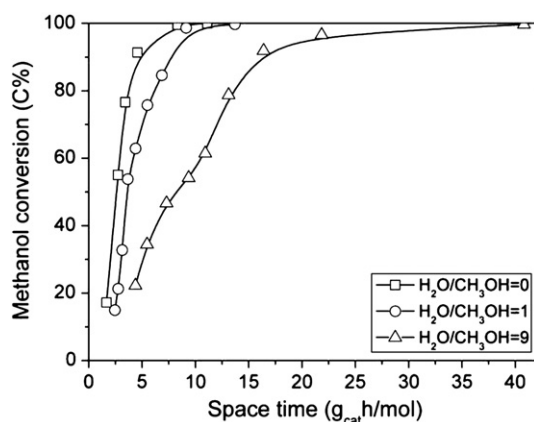

Fig. 3. Methanol conversion versus methanol space time for different water/methanol ratios. Reaction conditions: T = 460 °C, P_{MeOH} = 10 kPa, diluent: N_2.

Change of olefin distribution caused by water co-feeding is quite different from that caused by altering methanol partial pressure. At low methanol conversions, increasing water concentration enhances ethylene formation while decreasing methanol partial pressure does not affect ethylene selectivity virtually. Increasing water concentration results in slight decrease in $C_4^=$ and $C_5^=$ selectivities whereas decreasing methanol partial pressure improves formation of $C_4^=$ and $C_5^=$. At complete methanol conversion, selectivity curves of $C_4^=$ and $C_5^=$ for different methanol partial pressures tend to converge but this is not a hold for the case of very high water/methanol ratio. This may be due to the unique effect of water on methanol conversion to olefins [2,9].

3.1.3. Effect of temperature

Fig. 5 shows the conversion of methanol versus space time at 380 °C, 420 °C and 460 °C at methanol partial pressure of 10 kPa and water/methanol ratio of 1. As expected, increasing temperature gives rise to high methanol conversions at the same space time. When the temperature decreases from 460 °C to 380 °C, nearly twice more space time is required to keep 100% methanol conversion.

Product distributions as a function of methanol conversion at 380 °C, 420 °C and 460 °C are presented in Fig. 6. Again, product distributions at varying temperatures display distinct behavior at low and complete methanol conversions. At low methanol conversions, when temperature increases from 380 °C to 460 °C, the selectivity of propylene decreases from 41 C% to 37 C%; that of $C_6^=$ (Fig. 6 (A)) and $C_7^=$ ((E)) goes through insignificant change. Selectivities of $C_4^=$ and $C_5^=$ increase from 20 C% and 12 C% to 23 C% and 16 C% as shown in Fig. 6 (C) and (D), respectively. $C_2^=$ selectivity declines strikingly from 8 C% to about 2 C%, as shown in Fig. 6 (B).

When methanol conversion approaches 100%, the same reaction behaviors for $C_3^=$ and $C_6^=$ as described in Figs. 2 (A) and 4 (A) were observed. Clearly, the selectivity of $C_3^=$ is increased at the expense of $C_6^=$.

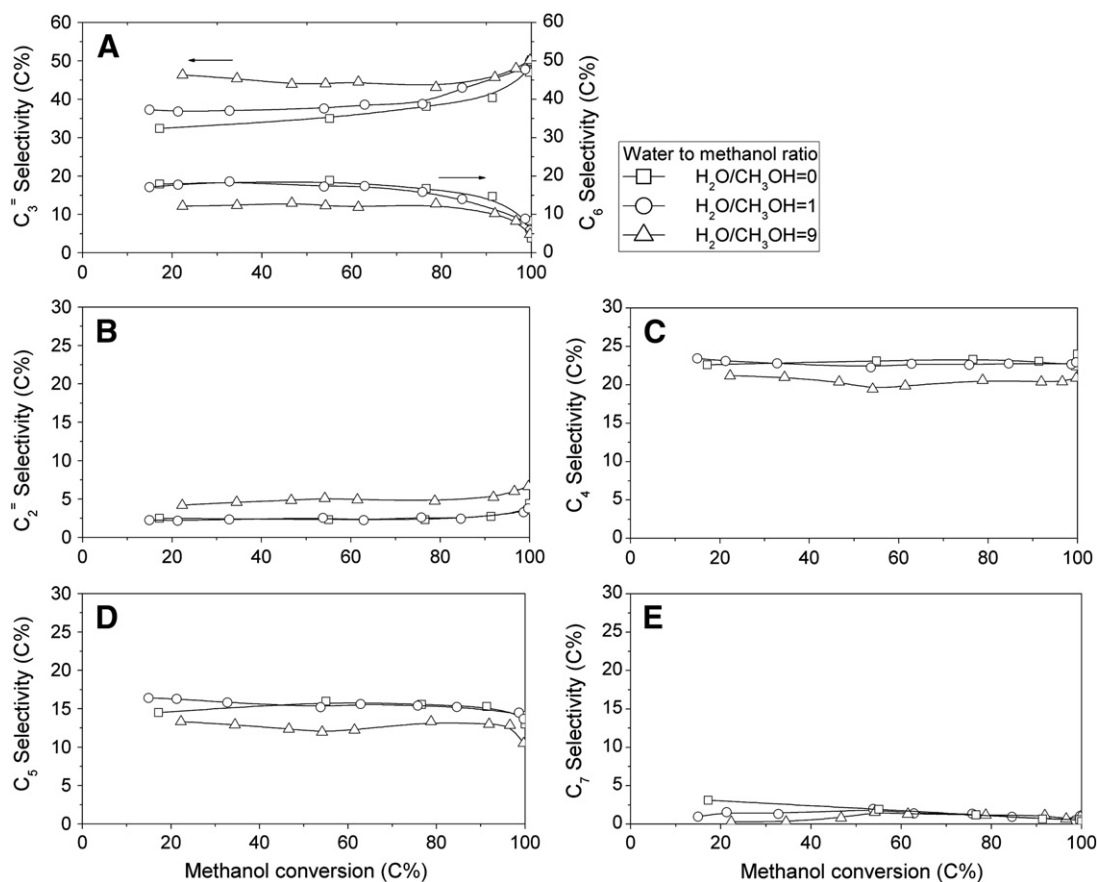**Fig. 4.** Product distribution versus methanol conversion for different water/methanol ratios. Reaction conditions: T = 460 °C, P_{MeOH} = 10 kPa, diluent: N_2.

Selectivities of $C_4^=$ and $C_5^=$ decrease slightly with increasing temperature, while that of $C_3^=$ increases.

The effect of temperature on methanol conversion to olefins over ZSM-5 catalyst has been widely investigated by many authors [2,9]. It is generally accepted that propylene selectivity is enhanced at higher temperature (450–500 °C). In this study, this viewpoint is only valid at complete methanol conversion. At low methanol conversions, it is surprising that propylene selectivity is decreased with increasing temperature. This reverse trend of propylene selectivity with temperature at low and complete methanol conversions suggests that the main reaction pathway may be diverse at different methanol conversion levels.
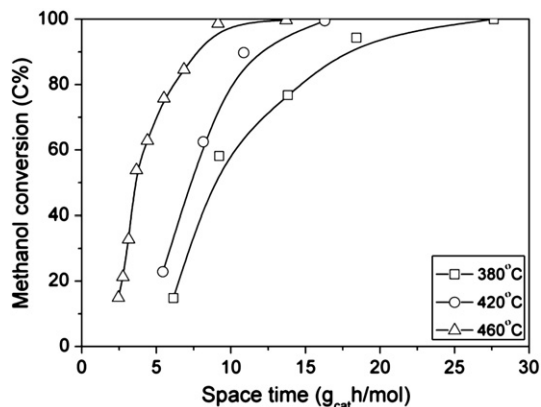

Fig. 5. Methanol conversion versus space time at different temperatures. Reaction conditions: P_{MeOH} = 10 kPa, water/methanol = 1, diluent: N_2.

3.2. Reasons for product distributions governed by methanol conversion

Espinoza [18] pointed out that at low methanol conversions where the oxygenate (methanol and DME) concentration is higher, methylation reaction is dominant; at higher methanol conversions where oxygenate concentration is lower but olefin concentration is higher, olefin oligomerization and cracking reaction dominates. Later, it is found that olefin methylation reactions and cracking of higher olefins, like $C_7^=$ cracking to $C_3^=$ plus $C_4^=$ and $C_6^=$ cracking to $C_3^=$, occur simultaneously [15–17,22,29]. Therefore, the main reaction pathway in methanol conversion to olefins at low methanol conversions is that $C_3^=$–$C_6^=$ are methylated by methanol to form $C_6^=$ and $C_7^=$, which crack to form $C_3^=$ and $C_4^=$ again. Methylation of $C_2^=$ is ignored due to its extremely low methylation reactivity [16,27,29]. These two reverse reactions lead to a steady distribution of $C_3^=$–$C_7^=$ [31].

At higher methanol conversions where olefin concentration is much higher than methanol, oligomerization and cracking reaction become dominant, leading to cracking of $C_6^=$ and $C_7^=$ to $C_3^=$ and $C_4^=$. This is agreed with our experimental results that cracking of $C_6^=$ to formed $C_3^=$ was always observed at higher methanol conversion. Cracking of $C_7^=$ at higher methanol conversions is not notable, due to the low content of $C_7^=$ in all the tests expect in the case where methanol partial pressure is 50 kPa. Oligomerization and cracking of $C_4^=$ and $C_5^=$ may also take place to some degree due to the moderate reactivities of $C_4^=$ and $C_5^=$ [17,29]. Thus the possible dominant reactions involved can be illustrated as follows:

$$C_7H_{14} \rightleftharpoons C_3H_6 + C_4H_8 \tag{3}$$

$$C_6H_{12} \rightleftharpoons 2C_3H_6 \tag{4}$$

$$2C_5H_{10} \rightleftharpoons C_4H_8 + C_6H_{12} \tag{5}$$

$$2C_4H_8 \rightleftharpoons C_3H_6 + C_5H_{10} \tag{6}$$

It is the change of dominant reaction pathway from methylation and cracking to oligomerization and cracking reactions as interpreted above that causes the product distribution governed by methanol conversion.

3.3. Effect of operation conditions on product distributions at the same methanol conversion levels

On the basis of the two different types of reaction pathway existing in the MTO reaction network as discussed previously, we can interpret the effect of operation conditions on product distribution at low and high methanol conversions. Product distribution at low methanol conversions can be elucidated by the relative rate between olefin methylation and olefin cracking. For instance, decreasing methanol partial pressure will suppress methylation reaction rate more than cracking rate, thus the selectivities of $C_3^=$–$C_5^=$ are enhanced at the expense of $C_6^=$–$C_7^=$. Increasing water/methanol ratio also declines methylation rate more than cracking rate, resulting in enhanced $C_3^=$ selectivity. Lowering temperature leads to cracking reaction prevailing methylation reaction, thus the $C_3^=$ selectivity is increased. This may be because that at lower temperature the catalyst surface coverage of olefins is higher than that at higher temperature [32], which results in a relatively higher olefin cracking rate to olefin methylation.

When methanol conversion approaches 100%, cracking reaction of $C_6^=$ (Eq. (4)), oligomerization and cracking reactions of $C_4^=$–$C_5^=$ (Eqs. (5) and (6)) may become significant. Cracking of $C_7^=$ (Eq. (3)) may not play a significant role due to its extremely low content in the effluent. Since Eqs. (3)–(6) are all thermodynamic irreversible reactions, they are influenced by reaction conditions like temperature and pressure. For instance, when temperature is lowered, selectivity of propylene is lowered and those of $C_4^=$–$C_5^=$ are increased since higher olefins are favored by low temperature. Analogously, when methanol partial pressure decreased, propylene selectivity may increase, as is deduced from Eq. (3) by the thermodynamic equilibrium rule. However, selectivities of $C_4^=$ and $C_5^=$ at complete methanol conversion were not influenced by methanol partial pressure. This may be because the oligomerization and cracking of $C_4^=$–$C_5^=$ are equimolar reactions, they are not affected by methanol partial pressure thermodynamically.

As for ethylene at all methanol conversion levels, it can be concluded that the formation of ethylene is enhanced at higher water/methanol ratio and lower temperature. However, one can also found that higher ethylene selectivity is obtained only at high space time ranges. For instance, when the water/methanol ratio rises from 0 to 9, the space times are increased from 10 to 40 g_{cat} h/mol in order to reach complete methanol conversion. Thus we considered that the formation of ethylene is due to the over-cracking of olefins, mainly $C_4^=$ and $C_5^=$ at very high space time. This consideration is in accordance with the hypothesis [14,15,27] that ethylene is formed through re-equilibrium of higher olefins.

The reaction behavior of $C_3^=$–$C_7^=$ at complete methanol conversion is of practical importance in orienting specification of the desired properties of an MTO catalyst with high propylene selectivity. Since propylene is formed mainly through cracking at higher methanol conversions, catalyst possessing properties favoring $C_6^=$–$C_7^=$ cracking will be more suitable. Meanwhile, since propylene selectivity changes with methanol conversion, when selecting promising catalysts for MTO, one should make sure that catalysts should be evaluated at the same conversion levels to eliminate the effect of methanol conversion on olefin distribution.
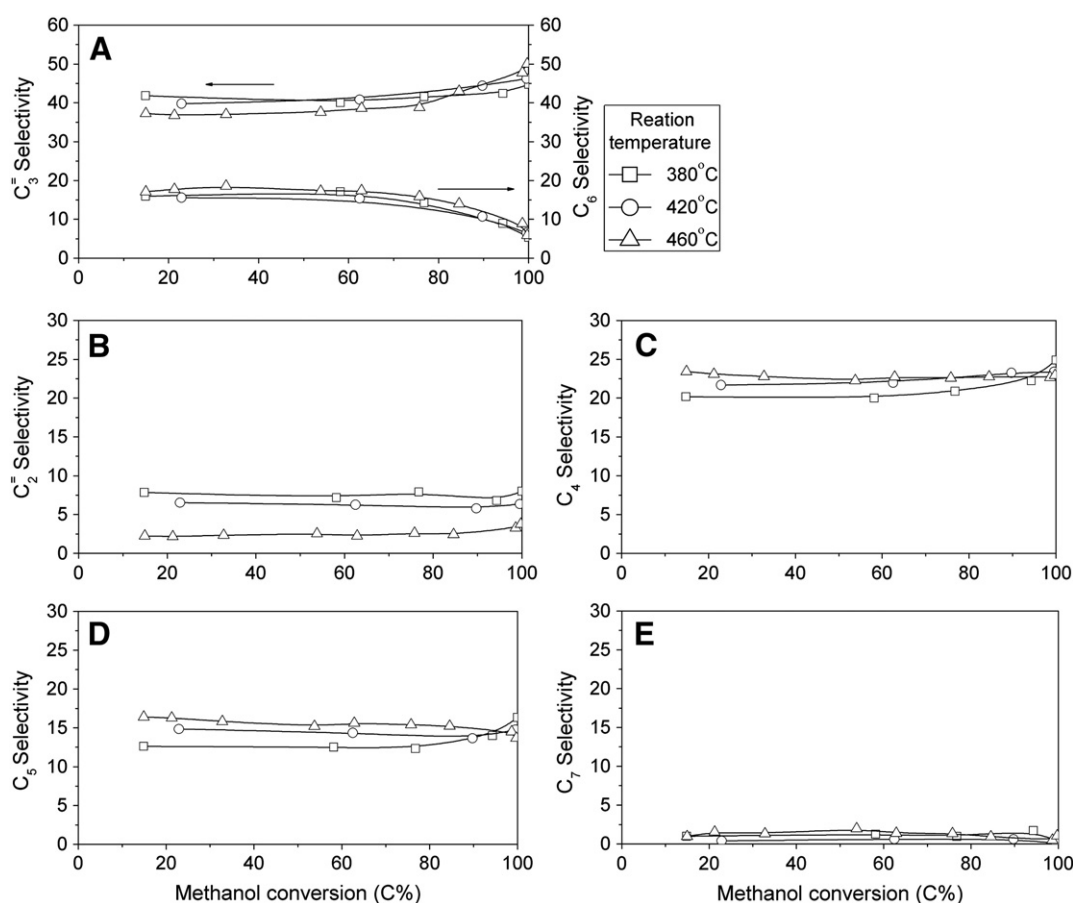

Fig. 6. Product distribution versus methanol conversion at different temperatures. Reaction conditions: $P_{MeOH} = 10$ kPa, water/methanol = 1, diluent: N_2.

4. Conclusions

This paper presents product distributions in MTO versus methanol conversion over high silica ZSM-5 catalyst at various reaction conditions. Product distributions were found governed by methanol conversion in that the distribution of $C_3^=$–$C_7^=$ exhibits distinct behavior at low and complete methanol conversions. At low methanol conversions, methylation and cracking reactions are dominant, and a steady olefin distribution of $C_3^=$–$C_7^=$ is formed due to the methylation of $C_3^=$–$C_6^=$ together with cracking of $C_6^=$–$C_7^=$. This steady olefin distribution was affected by operation conditions evidently at low methanol conversions by changing the relative rate of methylation and cracking. Decreasing methanol partial pressure, increasing water/methanol ratio and lowering temperature facilitate cracking, resulting in higher $C_3^=$ selectivity at the expense of $C_6^=$ and $C_7^=$. At complete methanol conversion, $C_3^=$–$C_7^=$ olefin distribution is determined by oligomerization and cracking, with cracking of $C_6^=$ to give propylene at high methanol conversions being always observed. However, the effect of reaction conditions is not that evident as at low methanol conversions. Ethylene selectivity shows no dependence on methanol conversion. The formation of ethylene is increased significantly only at high space time ranges via over-cracking of olefins, mainly $C_4^=$ and $C_5^=$.

References

[1] F.J. Keil, Methanol-to-hydrocarbons: process technology, Microporous and Mesoporous Materials 29 (1999) 49–66.
[2] M. Stöker, Methanol-to-hydrocarbons: catalytic materials and their behavior, Microporous and Mesoporous Materials 29 (1999) 3–48.
[3] C.D. Chang, Methanol conversion to light olefins, Catalysis Reviews. Science and Engineering 26 (1984) 323–345.
[4] G.F. Froment, W.J.H. Dehertog, A.J. Marchi, A review of the literature, Catalysis 9 (1992) 64 Catalysis 9.
[5] H. Zhou, Y. Wang, F. Wei, D. Wang, Z. Wang, Kinetics of the reactions of the light alkenes over SAPO-34, Applied Catalysis A: General 348 (2008) 135–141.
[6] M. Kaarsholm, F. Joensen, J. Nerlov, R. Cenni, J. Chaouki, G.S. Patience, Phosphorous modified ZSM-5: deactivation and product distribution for MTO, Chemical Engineering Science 62 (2007) 5527–5532.
[7] C. Mei, P. Wen, Z. Liu, H. Liu, Y. Wang, W. Yang, Z. Xie, W. Hua, Z. Gao, Selective production of propylene from methanol: mesoporosity development in high silica HZSM-5, Journal of Catalysis 258 (2008) 243–249.
[8] H. Koempel, W. Liebner, M.S.A.E.F.S.-A. Fabio Bellot Noronha, Lurgi's methanol to propylene (MTP(R)) report on a successful commercialisation, Studies in Surface Science and Catalysis, Elsevier, 2007, pp. 261–267.
[9] W.J.H. Dehertog, G.F. Froment, Production of light alkenes from methanol on ZSM-5 catalysts, Applied Catalysis 71 (1991) 153–165.
[10] T.-S. Zhao, T. Takemoto, N. Tsubaki, Direct synthesis of propylene and light olefins from dimethyl ether catalyzed by modified H-ZSM-5, Catalysis Communications 7 (2006) 647–650.
[11] J. Liu, C. Zhang, Z. Shen, W. Hua, Y. Tang, W. Shen, Y. Yue, H. Xu, Methanol to propylene: effect of phosphorus on a high silica HZSM-5 catalyst, Catalysis Communications 10 (2009) 1506–1509.
[12] J. Freiding, B. Kraushaar-Czarnetzki, Novel extruded fixed-bed MTO catalysts with high olefin selectivity and high resistance against coke deactivation, Applied Catalysis A: General 391 (2011) 254–260.
[13] N.Y. Chen, W.J. Reagan, Evidence of autocatalysis in methanol to hydrocarbon reactions over zeolite catalysts, Journal of Catalysis 59 (1979) 123–129.
[14] M.M. Wu, W.W. Kaeding, Conversion of methanol to hydrocarbons: II. Reaction paths for olefin formation over HZSM-5 zeolite catalyst, Journal of Catalysis 88 (1984) 478–489.
[15] R.M. Dessau, On the H-ZSM-5 catalyzed formation of ethylene from methanol or higher olefins, Journal of Catalysis 99 (1986) 111–116.
[16] S. Svelle, P.O. Rønning, S. Kolboe, Kinetic studies of zeolite-catalyzed methylation reactions: 1. Coreaction of [12C]ethene and [13C]methanol, Journal of Catalysis 224 (2004) 115–123.
[17] S. Svelle, P.O. Ronning, U. Olsbye, S. Kolboe, Kinetic studies of zeolite-catalyzed methylation reactions. Part 2. Co-reaction of [12C]propene or [12C]n-butene and [13C]methanol, Journal of Catalysis 234 (2005) 385–400.
[18] R.L. Espinoza, Oligomerization vs. methylation of propene in the conversion of dimethyl ether (or methanol) to hydrocarbons, Industrial & Engineering Chemistry Product Research and Development 23 (1984) 449–452.
[19] R.L. Espinoza, C.M. Stander, W.G.B. Mandersloot, Catalytic conversion of methanol to hydrocarbons over amorphous or zeolitic silica–alumina, Applied Catalysis 6 (1983) 11–26.
[20] J.F. Haw, J.B. Nicholas, W. Song, F. Deng, Z. Wang, T. Xu, C.S. Heneghan, Roles for cyclopentenyl cations in the synthesis of hydrocarbons from methanol on zeolite catalyst HZSM-5, Journal of the American Chemical Society 122 (2000) 4763–4775.
[21] J.F. Haw, W. Song, D.M. Marcus, J.B. Nicholas, The mechanism of methanol to hydrocarbon catalysis, Accounts of Chemical Research 36 (2003) 317–326.
[22] S. Svelle, F. Joensen, J. Nerlov, U. Olsbye, K.-P. Lillerud, S. Kolboe, M. Bjørgen, Conversion of methanol into hydrocarbons over zeolite H-ZSM-5: ethene formation is mechanistically separated from the formation of higher alkenes, Journal of the American Chemical Society 128 (2006) 14770–14771.
[23] I.M. Dahl, S. Kolboe, On the reaction mechanism for propene formation in the MTO reaction over SAPO-34, Catalysis Letters 20 (1993) 329–336.
[24] W. Wang, Y. Jiang, M. Hunger, Mechanistic investigations of the methanol-to-olefin (MTO) process on acidic zeolite catalysts by in situ solid-state NMR spectroscopy, Catalysis Today 113 (2006) 102–114.
[25] C.T.W. Chu, C.D. Chang, Methanol conversion to olefins over ZSM-5: II. Olefin distribution, Journal of Catalysis 86 (1984) 297–300.
[26] D. Prinz, L. Riekert, Formation of ethene and propene from methanol on zeolite ZSM-5: I. Investigation of rate and selectivity in a batch reactor, Applied Catalysis 37 (1988) 139–154.
[27] K.P. Möller, W. Böhringer, A.E. Schnitzler, E. van Steen, C.T. O'Connor, The use of a jet loop reactor to study the effect of crystal size and the co-feeding of olefins and water on the conversion of methanol over HZSM-5, Microporous and Mesoporous Materials 29 (1999) 127–144.
[28] M. Kaarsholm, B. Rafii, F. Joensen, R. Cenni, J. Chaouki, G.S. Patience, Kinetic modeling of methanol-to-olefin reaction over ZSM-5 in fluid bed, Industrial & Engineering Chemistry Research 49 (2010) 29–38.
[29] W. Wu, W. Guo, W. Xiao, M. Luo, Dominant reaction pathway for methanol conversion to propene over high silicon H-ZSM-5, Chemical Engineering Science 66 (2011) 4722–4732.
[30] M. Kaarsholm, F. Joensen, R. Cenni, J. Chaouki, G.S. Patience, MeOH to DME in bubbling fluidized bed: experimental and modelling, The Canadian Journal of Chemical Engineering 89 (2011) 274–283.
[31] T. Behrsing, T. Mole, P. Smart, R.J. Western, Homologation of olefins by methanol over ZSM-5 zeolite, Journal of Catalysis 102 (1986) 151–159.
[32] P. Borges, R.R. Pinto, M.A.N.D.A. Lemos, F. Lemos, J.C. Vérine, E.G. Derouane, F.R. Ribeiro, Light olefin transformation over ZSM-5 zeolites: a kinetic model for olefin consumption, Applied Catalysis A: General 324 (2007) 20–29.