

Co-reaction of Ethene and Methylation Agents over SAPO-34 and ZSM-22

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Abstract Co-reaction of ethene and different methylation agents (i.e. methanol and chloromethane) was carried out over SAPO-34 and ZSM-22 and the results are compared. It was found that the enhancement of ethene conversion was achieved by co-feeding it with methylation agents. In the ethene–chloromethane system, the methylation of ethene by chloromethane was more prominent compared with that of the co-reaction of ethene and methanol. The reasons for the differences between ethene–methanol and ethene–chloromethane co-reaction system are discussed. Complete suppress of direct conversion of methanol or ethene could be achieved over ZSM-22 by pre-coking, and propene selectivity higher than 80% was obtained at lower conversions.

Keywords SAPO-34 · ZSM-22 · Ethane · Methanol · Methylation · Catalysis

1 Introduction

Propene is a versatile building block for a variety of important monomers, polymers and intermediates. Conventionally, propene took the second place after ethene in the global olefin market. However, the world propene demand has experienced a rapid growth in recent years,

owing to the increasing demands for its derivatives, especially polypropylene. The demand for propene, which is expected to grow faster than supply, has aroused the interests of developing new processes for propene production [1, 2]. The primary sources of propene have been as a by-product of ethene production in steam crackers and from refinery FCC streams. Much effort has been made to conventional technologies for higher propene yield. On the other hand, new technologies for on-purpose propene production, such as propane dehydrogenation, olefin metathesis [3, 4], catalytic cracking of higher alkenes [5], methanol conversion to light olefins (MTO) [6, 7] and MTP—a methanol-to-olefins process optimised for propene yield [8], have been developed.

Among these novel technologies, the ones of producing more propene at the expense of ethene may be more practical or economically advantageous, depending on the demand and alternative value for ethene versus propene. The examples of these technologies include metathesis between ethene and 2-butene into propene [9], highly selective direct conversion of ethene to propene [4], and so on.

Another candidate for producing propene from ethene is the co-reaction of ethene and methylation agents such as methanol or chloromethane, to which less report has been published except several patents [10, 11]. By this route, propene product is expected to come mainly from the methylation of ethene, instead of the direct conversion of ethene or methanol/chloromethane where the selectivity for propene is usually lower. The advantage of this route lies in that the added atom of carbon chain comes from relatively cheaper methanol or chloromethane, which can be produced from methane/coal via syngas as intermediate or directly from methane through oxyhydrochlorination over a supported CuCl catalyst [12]. This process should be

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more economical if cheap ethene source like dry gas from FCC process is used.

Co-reaction of ethene and methanol over molecular sieves has been studied by some researchers with interests in the mechanism understanding of methanol conversion to light olefins. Dahl and Kolboe [13, 14] studied the co-reaction of ethene and methanol, using ethanol as source for ethene. They fed [^{13}C] methanol/ethanol/water onto SAPO-34 at 400 °C. The molar ratio of ethanol to methanol was 1:2, and the reactant (the MeOH/EtOH/H₂O mixture) feed rate (WHSV) was 4.0 h⁻¹. They found that the majority of the propene molecules are formed directly from methanol, and that only a minor part was formed by methylation of ethene. Ronning et al. [15] studied the co-feeding of ethene and methanol on ZSM-5 with isotopic labelling, and deduced that ethene was unreactive and that its methylation cannot be an important part in the reaction network. In a study by Wu and Anthony [16], the effects of adding ethene to methanol feed on conversion of methanol to olefins were investigated over SAPO-34. The reaction conditions were as follows: 400 °C, methanol WHSV = 0.5 h⁻¹ and at constant water/methanol mol ratio of 4.0, with C₂H₄ concentration in the feed of 3.5 and 9.7 mol%, respectively. They reported that when ethene was fed with methanol and water, the selectivity for ethene decreases, while the selectivity for propene and butenes increased. They inferred that ethene and propene react with methanol over SAPO-34 to form propene and butenes, respectively. Tau and Davis [17] investigated the co-feeding system by isotopic tracer method at 300 °C. The catalyst was Silicalite S-115 of Si/Al ratio of ~800. The results showed that ethene was converted by adding a C₁ species derived from methanol to produce higher carbon number compounds. Recently, Svelle et al. [18] studied the co-reaction of [^{13}C] methanol and ethene over H-ZSM-5 (Si/Al = 45). Most of their experiments were carried out at 350 °C employing the partial pressures $P_{\text{methanol}} = 50$ mbar and $P_{\text{ethene}} = 50$ mbar. The conclusion was that the methylation of ethene to form propene dominated at the lowest conversions.

It could be found that the conclusions drawn by different researchers are quite different, sometimes even opposite for the same reaction system. We observed that different catalyst or reaction conditions were used in their studies. That might be the reason for the contradiction. The objective of the present study is to comparatively investigate the role of the methylation plays in the co-reaction system of ethene and methylation agent over different catalyst or under different reaction conditions. Methylation agents of different activity, i.e. methanol and chloromethane were used to co-feed with ethene. Two different catalysts were used—SAPO-34, the small pore size of which was expected to decline the formation of higher olefins, and ZSM-22, a TON type molecular sieve. For the implication of ZSM-22

in “Hydrocarbon Pool Mechanism” has been suggested to explain the failure of the MTO reaction on it [19], it was expected in the present study that the direct conversion of methylation agents be suppressed.

2 Experimental

2.1 Catalyst Preparation and Characterization

SAPO-34 was synthesised hydrothermally as described elsewhere [20, 21] using triethylamine (from Shenyang Chemical Reagents) as the template. Pseudoboehmite (from CNPC Fushun Petrochemical), 85 wt% orthophosphoric acid (Shenyang Chemical Reagents) and 25% colloidal silica (Shanghai Hengxin Chemical Reagent Co., Ltd.) were used as the sources of aluminium, phosphorus and silicon, respectively. In a typical synthesis, pseudoboehmite and phosphoric acid were added to vigorously stirred water in a glass beaker. After stirring, colloidal silica was added to this mixture, which was then stirred for a further 30 min before triethylamine was added. The resulting gel was stirred until homogeneous, and then was transferred to a Teflon-lined stainless steel autoclave. The crystallization was carried out under autogeneous pressure at 473 K for 24 h. The product was filtrated, washed, dried at 393 K for 12 h, and calcined at 823 K for 3 h. The catalysts were prepared by binding the calcined H-SAPO-34 with silica. ZSM-22 was kindly provided by another group of Dalian Institute of Chemical Physics. The NH₄-ZSM-22 was obtained by ion-exchange with solution of ammonium nitrate from calcined sample. After the ion-exchange, the sample was washed with deionized water, dried at 110 °C and finally calcined at 550 °C for 3 h to achieve H-ZSM-22.

The phase purity of the molecular sieves was confirmed by powder XRD patterns recorded with a D/MAX-b X-ray diffractometer with Cu K α radiation ($\lambda = 1.5206$ Å).

The nitrogen adsorption isotherms were measured at 77 K using a NOVA 4000 gas adsorption analyser (Quantachrome Corp.). Before measurement the catalysts were degassed at 623 K for 4 h. The total surface area was calculated according to the BET isothermal equation, and the micropore volume and surface area were evaluated by the *t*-plot method.

2.2 Co-reaction of Ethene and Methylation Agents

The catalytic reactions were carried out in a fixed-bed stainless steel tubular reactor (9 mm i.d.) at atmospheric pressure. Quartz sand was filled in the upper part of reactor to get a plug flow of the mixed feed. Methanol was charged

by passing the carrier gas through a saturator containing methanol. Ethene and chloromethane were fed into the reactor through a mass-flow meter, with helium as dilute gas. After the reactants were charged into the reactor, a sample was taken at a given time on stream and analysed using on-line gas chromatography (Varian GC3800) equipped with a FID detector and a PoraPLOT Q-HT capillary column. In all the reaction runs with chloromethane, HCl was observed in the products as a balance of Cl from chloromethane (not listed in the product distribution).

3 Results and Discussion

3.1 Co-reaction of Ethene and Methanol over SAPO-34

Table 1 presents the reaction results of co-feeding ethene and methanol at different proportion. The effect of methanol proportion was studied by varying the flow rate of methanol while fixing the weight hourly space velocity (WHSV) of ethene, with helium flow being changed to keep a constant total flow rate. Reactions with sole methanol or sole ethene feeding were carried out respectively for comparison and the results were also listed in Table 1. In the case of sole ethene feeding, the conversion was rather low (1.48%) and propene was the major product at a selectivity of about 60%. Although higher ethene conversion over SAPO-34 has been reported in literature [4] and also archived in our previous study, herein the certain reaction conditions were chosen to suppress the direct conversion of ethene. When sole methanol was fed at $\text{WHSV} = 1.0$, but with the other reaction conditions as the same as in co-feeding, the conversion of methanol was complete and the dominant products were ethene (30.5%) and propene (43.2%). It was interesting to notice that, when

ethene was co-fed with a small proportion of methanol, the ethene concentration in the out-let was prominently lower than that in the case of sole ethene feeding. That is to say, adding methanol promoted the conversion of ethene in the feed, though the direct conversion of methanol is incident and produces ethene as one of the main products. When methanol proportion was 3.6%, the observed ethene conversion was 4.66%. Increase of methanol content of the co-feeding mixture to 5.9% resulted in a roughly proportional increase in ethene conversion (8.52%), while the conversion of methanol remained complete. The selectivity for propene ranged from 56% to 60% at these methanol proportions, much higher than that in direct methanol conversion. Whereas, when the methanol proportion was further increased to 9.4% and 15.3%, the ethene conversion decreased to 6.91% and 1.63%, respectively.

Ethene and methanol are both active reactants over SAPO-34 [4, 7]. The conversions of them are related to complicated reaction networks. In spite of that, we may still roughly sort the reactions involved in the co-reaction system into three types—the direct conversion of ethene, the conversion of methanol and the interaction of ethene and methanol. For the reactants and products of each reactions are interwoven, the three types of reactions in fact cannot be distinctly separated from each other and the real reaction network should include all the reactions. The overall “ethene conversion” was the summation of the consumptions and productions of ethene in all the reactions. Under the chosen reaction conditions in the present study, the direct conversion of ethene was suppressed, while the direct conversion of methanol, well known as MTO conversion, produces ethene as one of the main products. It's reasonable to deduce that the increase of the observed ethene conversion in co-feeding should be resulted from the interaction of ethene and methanol. We suggest that the dominant interaction between ethene and methanol be the methylation reaction, on the basis of the

Table 1 Effect of methanol proportion in the feed mixture of co-reaction of ethene and methanol

<i>Inlet/C-mol%</i>						
C_2H_4	100	96.4	94.1	90.6	84.7	0
CH_3OH	0	3.6	5.9	9.4	15.3	100
<i>Outlet/C-mol%</i>						
C_2H_4	98.5	91.9	86.1	84.4	83.31	30.5
$\text{CH}_3\text{OH}/\text{CH}_3\text{OCH}_3$	—	0	0	0.01	0.01	0.11
C_3H_6	0.89	4.83	7.89	9.07	10.0	43.1
C_4^+	0.49	2.90	5.29	5.60	5.74	23.1
$\text{C}_1^0\text{--C}_3^0$	0.07	0.39	0.73	0.95	0.94	3.19
C_2H_4 conv. %	1.48	4.66	8.52	6.91	1.63	—
CH_3OH conv. ^a %	—	100	100	99.9	99.9	99.9
C_3H_6 Sel. C-mol%	60.3	59.5	56.8	58.1	59.9	43.2
C_4^+ Sel. C-mol%	33.1	35.7	38.0	35.9	34.4	23.1

$T = 723 \text{ K}$, ethene
 $\text{WHSV} = 5.5 \text{ h}^{-1}$ (fixed), total
 flow = 110 mL min^{-1} , time on
 stream (TOS) = 6 min

^a Conversion was calculated
 with CH_3OCH_3 included

high selectivity for propene in the co-feeding. When only a small amount of methanol was added into the reaction feed, the direct MTO conversion should be suppressed by the competition of the methylation reaction, and the increase in ethene conversion should be attributed to the ethene consumption of the latter. However, further adding of methanol would enhance the competing MTO conversion which produced more ethene, compensating part of the ethene consumption in methylation and decrease the overall ethene conversion.

The product distribution of the co-feeding system provided some proof for the suggestion of the important role of methylation reactions. The selectivity for higher hydrocarbon products in co-feeding was much higher than that in sole methanol feeding. These higher products in co-feeding should mainly come from further methylation of olefin products. When the methanol proportion in the feed was increased from 3.9% to 5.6%, the selectivity C_4^+ products increased from 35.7% to 38.0%, accompanied by the decrease in propene selectivity. This phenomenon should be explained by the increase of the opportunity for the methylation of propene and further methylation of olefins to higher hydrocarbons at increased methanol concentration.

The effect of contact time (CT) on the co-reaction was investigated by varying flow rate of the dilute gas (helium) while fixing ethene and methanol weight hourly space velocity to 5.5 h^{-1} and 0.55 h^{-1} , respectively. The higher ethene/methanol ratio was chosen to suppress the competition of MTO conversion. The conversion and product distribution at different reaction contact time are illustrated in Fig. 1. The methanol conversion remained almost 100% in all the cases, while the ethene conversion increased with

increasing contact time. Shorter CT favoured propene selectivity. The selectivity for saturated hydrocarbons (C_1^0 – C_3^0) showed little changes with CT and the product distribution was shifted mainly by decreasing propene and increasing heavier products with increasing CT. This tendency towards heavier products with CT should be caused mainly by the enhancement of the direct conversion of ethene, such as oligomerization, instead of by further methylation of propene, for the latter should have consumed more methanol, competing with methylation of ethene and decreasing the overall ethene conversion.

The competition among different types of reactions in the ethene/methanol co-reaction system was influenced by reaction conditions. A series of co-reactions of ethene and methanol were carried out with prolonged time on stream (TOS) and at varied temperatures in the range of 673–773 K. The results at different reaction temperatures are displayed in Fig. 2. The ethene conversion decreased with raised reaction temperature, while the conversion of methanol remained complete. Although the MTO conversion was suppressed at lower methanol proportion, it still seemed to play an important role in the co-feeding system—the observed decrease of ethene conversion should be reasonably ascribed to the compensation of the ethene produced from the competing MTO reactions, in which higher reaction temperature favours the selectivity for ethene [6, 7]. The increased propene selectivity with reaction temperature could be explained by the enhancement of cracking of heavier products like butenes and C_5^+ hydrocarbons.

The effects of TOS on the conversion and product distribution of the co-reaction are illustrated in Figs. 3 and 4.

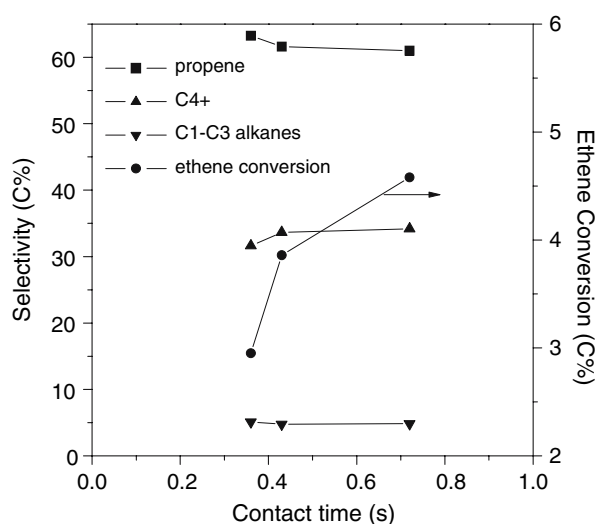


Fig. 1 Effect of contact time on ethene conversion and product distribution of co-reaction of ethene and methanol. $T = 723\text{ K}$, ethene WHSV = 5.5 h^{-1} , methanol WHSV = 0.55 h^{-1}

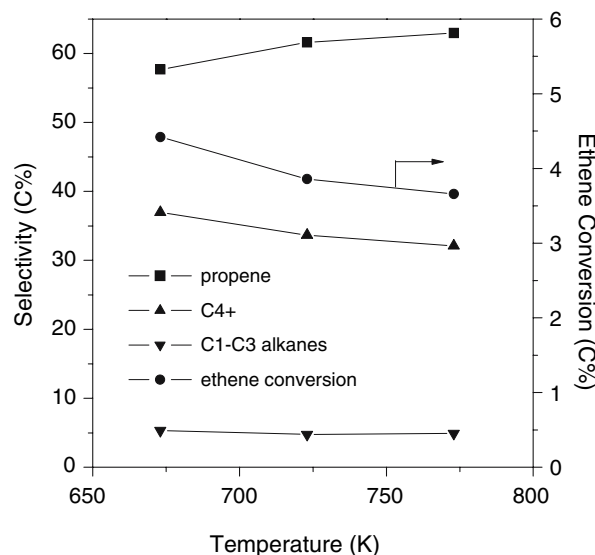


Fig. 2 Effect of temperature on ethene conversion and product distribution of co-reaction of ethene and methanol. Ethene WHSV = 5.5 h^{-1} , methanol WHSV = 0.55 h^{-1} , total flow = 210 mL min^{-1}

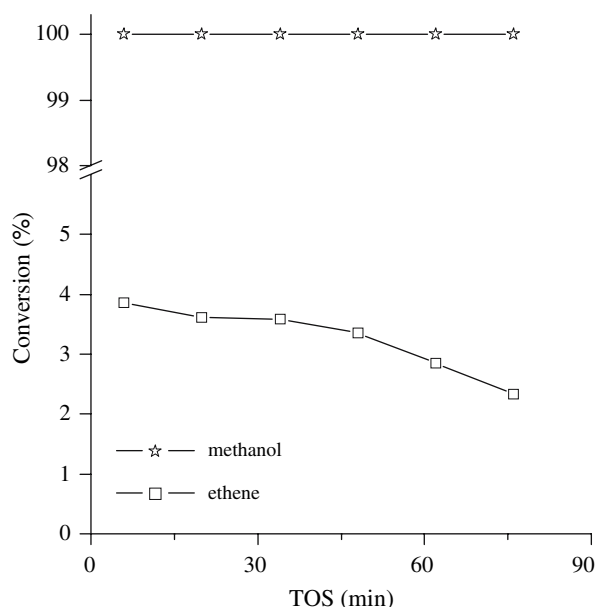


Fig. 3 Effect TOS on conversion of co-feeding ethene and methanol. $T = 723$ K, ethene WHSV = 5.5 h^{-1} , methanol WHSV = 0.55 h^{-1} , total flow = 210 mL min^{-1}

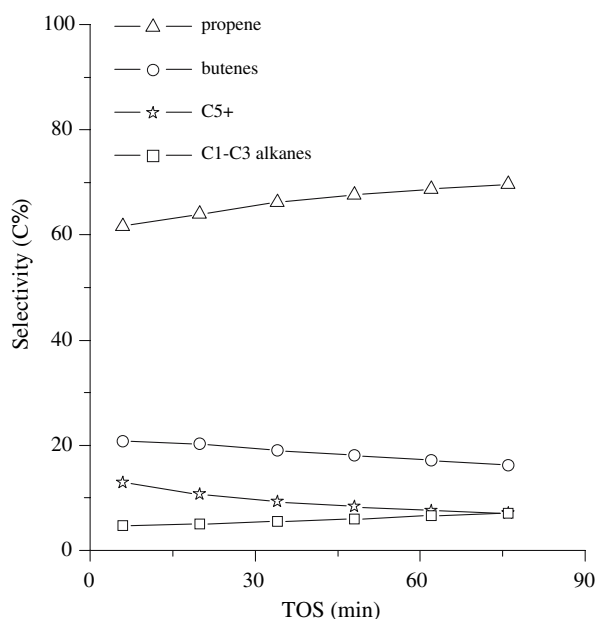


Fig. 4 Effect of TOS on the product selectivity of co-feeding ethene and methanol. $T = 723$ K, ethene WHSV = 5.5 h^{-1} , methanol WHSV = 0.55 h^{-1} , total flow = 210 mL min^{-1}

The conversion of methanol in the co-feed was almost complete within the investigated reaction time, while the observed ethene conversion decreased gradually with increasing TOS, as shown in Fig. 3. As reported in many literatures [6, 22, 23], the product distribution in the MTO conversion over SAPO-34 changes fast with increasing coke level on catalyst and the selectivity for light olefins

such as ethene and propene increases owing to enhancement of shape selectivity by the pore blockage effect of the coke. Besides the catalyst deactivation, the increase of ethene production from the competing MTO reaction, which compensated the amount of ethene consumed in methylation, might contribute to the decrease of ethene conversion with increasing TOS. This explanation could be proved by the fact that propene selectivity increased, while C_4^+ products decreased with increasing TOS, as shown in Fig. 4.

3.2 Co-reaction of Ethene and Chloromethane

As we have discussed in the above section, the direct conversion of methanol played an important role in the ethene/methanol co-reaction system, especially by compensating the ethene consumption in methylation. In view of methylation reaction, the activity of the methylation agent, both in its direct conversion and in methylation, has important influence on the co-reaction behaviour. In one of our precious study, a less active chloromethane was substituted for methanol as methylation agent to co-feed with ethene over SAPO-34 [24]. Herein, part of the data were reorganised and presented for comparison with those of the ethene/methanol co-reaction system.

Table 2 presents the reaction results of the chloromethane/ethene mixture of different proportions. For chloromethane is less active on SAPO-34, the conversion of chloromethane was low (11.3%) when it was fed alone. Our research group have reported the conversion of chloromethane over SAPO-34 [25–27] and the products usually include HCl and hydrocarbons distributed as ethene, propene, C1–C3 alkanes and C_4^+ hydrocarbons. Under the present reaction conditions, the obtained propene

Table 2 Effect of C_2H_4 proportion in the feed mixture of co-reaction of ethene and chloromethane

Inlet/C-mol%					
C_2H_4	100	91.3	85.6	74.8	0
CH_3Cl	0	8.7	14.4	25.2	100
Outlet/C-mol%					
C_2H_4	98.5	87.0	84.3	75.0	1.33
C_3H_6	0.89	5.39	4.94	6.09	5.43
C_4^+	0.49	3.01	2.32	2.72	3.86
CH_3Cl	–	3.01	8.14	15.9	88.7
$\text{C}_1\text{--C}_3$	0.07	0.26	0.20	0.17	0.35
Coke	0.04	0.13	0.11	0.11	0.32
C_2H_4 conv. %	1.48	4.65	1.52	–0.27	–
CH_3Cl conv. %	–	52.1	43.4	36.9	11.3
C_3H_6 Sel. C-mol%	60.3	61.3	65.3	67.1	48.1

$T = 723$ K, CT = 0.78 s (for chloromethane), TOS = 6 min

selectivity of chloromethane conversion was 48.1%. When ethene and chloromethane were co-fed, the reaction behaviour was similar to that of the ethene/methanol system. Adding a small amount of chloromethane resulted in increase in ethene conversion and the selectivity for propene ranged from 61% to 66%, higher than those in the ethene/methanol system. Also, a sharp increase in chloromethane conversion was observed, and the chloromethane conversion increased with increasing ethene proportion. It was reported that there exists an obvious induction period in the conversion of chloromethane over SAPO-34, and it was also found that the induction period might be shortened by adding a small amount of propene to the reactor before admission of the chloromethane feed [28]. A test was designed to make it clear whether the increase of chloromethane conversion observed in the co-reaction caused by the shortening of the induction period owing to the existence of ethene. The results showed that, although the induction period of chloromethane was indeed shortened by co-feeding with ethene, it was not the dominant reason for the increase of chloromethane conversion in co-feeding [24]. As chloromethane is a capable methylation agent, and its conversion to olefins over SAPO-34 bears a strong resemblance to the methanol to olefins reaction [28], it is reasonable to deduce that the methylation of ethene played the similar role in the ethene/chloromethane system as methanol did in the ethene/methanol system. The differences in conversion and product distribution could be explained by the different activities of methanol and chloromethane.

3.3 Co-reaction of Ethene and Methanol over ZSM-22

As observed in the above results, the effects of the direct conversion of methanol or chloromethane over SAPO-34 could not be efficiently suppressed, even at higher ethene proportions. The direct conversion of methanol or chloromethane influences the behaviour of the co-reaction in two aspects. First, it would produce ethene as a main product and compensate the consumption of ethene feed. Second, it would lower the propene selectivity in co-feeding by producing propene at lower selectivity.

Cui et al. [19] have studied the MTO conversion over several zeolites, including ZSM-11(MEL), ZSM-22(TON), SAPO-34(CHA) and SAPO-5(AFI) by pulse reaction. The methanol conversion over ZSM-22 was found dramatically different from the other three catalysts. ZSM-22 showed a low but appreciable production of light olefins during the first few pulses of methanol, but then quickly decreased to essentially zero—the product was only dimethylether. The failure of ZSM-22 to convert methanol into olefins was ascribed to its implication in the MTO mechanism which is

usually referred to as “Hydrocarbon Pool Mechanism” [29–31]. The C1 species (from methanol) bind to certain organic intermediates (hydrocarbon pool) from which primary olefin products dissociate. The author suggested that the channel space that ZSM-22 can offer (0.57 nm) be smaller than what the cyclic organic intermediates involved in the hydrocarbon pool mechanism require, and the initial MTO activity of ZSM-22 might have come from impurity ZSM-11 and/or external acid sites which were quickly deactivated by coking.

These results clued us on how to eliminate the effect of the direct conversion of methanol in the co-reaction system. The MTO conversion on ZSM-22 could be blocked by appropriate pre-coking on the outer surface, with enough acid sites in the channel left for the methylation conversion. We designed a test of ethene/methanol co-reaction over ZSM-22: three reaction runs were carried out successively with methanol, ethene, and ethene/methanol mixture without changing catalyst sample. The results are displayed in Table 3.

In the first run, only methanol was fed over the catalyst. The dimethylether, generated from dehydration of methanol over the catalyst, was also taken as feed to calculate the conversion. The first sampling at 6 min presented a conversion of 96.5% (including methanol and dimethylether) with hydrocarbon products distributed as ethene, propene, C1–C3 alkanes and C_4^+ hydrocarbons. Then the catalyst was then quickly deactivated of converting methanol or dimethylether to olefins. At the third sampling (87 min), the conversion of methanol/dimethylether was below 1%.

After the reaction of sole methanol (Run 1), the catalyst bed was blown with helium, and then the sole ethene was fed (Run 2). In two sampling within the TOS of 25 min, the conversion of ethene was rather low. That is to say, the direct conversion of ethene was suppressed on the present catalyst.

After the reaction Run 2 and the following helium blowing, the conversion of ethene/methanol was examined without changing catalyst sample (Run 3). The first sampling presented dramatically high conversions of ethene (21.6%) and of methanol/dimethylether (71%) to hydrocarbons with a propene selectivity of 44%. The high conversions of both reactants of course came from the methylation of ethene and methanol, because the direct conversion of ethene or methanol was very low over the catalyst after Run 1 and Run 2. With prolonged TOS, the conversion decreased while the propene selectivity increased gradually. After 60 min on stream, the propene selectivity increased to 83% and the conversion of ethene and methanol decreased to 1.7% and 6.6%, respectively.

Frankly, it was disappointed that the high propene selectivity was only obtained at very low ethene and methanol/dimethylether conversion. As observed, C_4^+

Table 3 Reaction results of methanol, ethene and co-feed of them over ZSM-22

Run no.	1			2			3		
Feed/mL/min									
CH ₃ OH	20			0			20		
C ₂ H ₄	0			40			40		
He	40			20			0		
TOS/min	6	60	87	6	25		6	33	60
Outlet/C-mol%									
C ₂ H ₄	12.3	0.23	0.22	98.7	98.8		61.8	73.8	77.5
C ₃ H ₆	29.0	0.10	0.06	0.11	0.09		14.1	5.62	2.35
C ₄ ⁺	51.1	0.37	0.13	1.18	1.08		17.6	3.94	0.37
CH ₃ OH/CH ₃ OCH ₃	3.47	98.5	99.2	–	–		6.11	16.5	19.7
C ₁ ⁰ –C ₃ ⁰	4.13	0.80	0.42	0.04	0.03		0.31	0.16	0.11
CH ₃ OH conv. ^a %	96.5	1.51	0.83	–	–		71.0	21.7	6.60
C ₂ H ₄ conv. %	–	–	–	1.33	1.21		21.6	6.51	1.78
C ₃ H ₆ Sel. C-mol%	30.0	6.80	6.64	8.15	7.47		44.0	57.8	83.0

$T = 773$ K, ethene WHSV = 18 h^{-1} , methanol WHSV = 10 h^{-1}

^a Conversion was calculated with CH₃OCH₃ included

product took a larger proportion in the reaction outlet when the conversion was high. These heavier products should come from the further methylation of propene. At first, we had taken it for granted that the methylation of ethene by methanol would take place in the channels of the pre-coked ZSM-22 and the space district of 10 member ring would reduce the occurrence of further methylation of propene. However, when we measured the surface area and pore volume of a pre-coked ZSM-22 sample prepared under the same reaction conditions as used in the above-mentioned Run 1, we were surprised to find that both the micropore volume and the micropore surface area of the catalyst samples were zero (see Table 4). This indicates that the channels of the pre-coked catalyst were totally blocked by coke and the methylation of ethene by methanol in fact took place on the outer surface. This explained why the high propene selectivity could be obtained only at very low conversion. Some acid sites on the outer surface had survived in pre-coking. The capability of converting methanol to dimethylether provided a proof of the survival of the outer acid sites. The methylation reactions catalysed by these outer acid sites were not shape-selective. High propene selectivity could only be obtained when the conversion was low and the low concentration of propene

restrained its further methylation. However, the deactivation in co-feeding remained unknown.

4 Conclusions

The behaviour of the co-reaction of ethene and methylation agents reveals the important role of methylation reaction in the co-feeding system. However, the competition from the direct conversion of the methylation agents, i.e. methanol or chloromethane influences the co-reaction behaviour in both conversion and propene selectivity. Over SAPO-34, the direct conversion of methylation agents could not be efficiently suppressed, whenever methanol or less active chloromethane was used as methylation agent. On pre-coked ZSM-22, the direct conversion of methanol was blocked, while the methylation conversion taking place on the outer surface played the dominant role in the co-reaction. Propene selectivity higher than 80% was obtained when conversion was low.

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Table 4 Texture properties of fresh and MTO deactivated ZSM-22

Catalyst	S_{BET} (m ² /g)	S_{micro} (m ² /g)	V_{total} (cm ³ /g)	V_{micro} (cm ³ /g)
Fresh	198	97	0.22	0.05
Deactivated	63	0	0.13	0

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