



## Co-reaction of ethene and methanol over modified H-ZSM-5

Jinzhe Li<sup>a,b</sup>, Yue Qi<sup>a</sup>, Lei Xu<sup>a</sup>, Guangyu Liu<sup>a,b</sup>, Shuanghe Meng<sup>a</sup>, Bing Li<sup>a</sup>, Mingzhi Li<sup>a</sup>, Zhongmin Liu<sup>a,\*</sup>

<sup>a</sup>Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

<sup>b</sup>Graduate University of the Chinese Academy of Sciences, Beijing 100049, PR China

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### ABSTRACT

Co-reaction of ethene and methanol was carried out over HZSM-5, P-La modified ZSM-5 (PLaHZ) and hydrothermal-treated PLaHZ catalysts. Hydrothermal treatment at high temperature sharply reduced the acidity of the catalyst, on which the direct conversion of ethene or methanol/dimethyl ether was almost completely suppressed. Co-feeding of ethene and methanol over the said catalyst resulted in considerable conversion of both reactants. Meanwhile, high propene selectivity (ca. 80%) was obtained at lower conversions. The methylation of ethene by methanol was responsible for the enhancement of conversions and propene selectivity in the co-reaction system. The further methylation of propene and the cracking of higher olefins were also operative under current reaction conditions.

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### 1. Introduction

Propene is conventionally by-produced from steam crackers in production of ethene and FCC units. Driven by the consumption of the derivatives such as polypropylene, the demand for propene is recently growing faster than that of ethene [1], leading to an increased interest in developing new technologies for propene production [2]. Among the newly developed technologies, those mainly focusing on the utilization of non-oil based chemicals or intermediates have drawn much attention. These processes include conversion of methanol to light olefins (MTO) over SAPO-34 molecular sieve catalyst, which produces roughly equal amount of ethene and propene [3]; a process known as MTP (methanol-to-propene) by optimizing the propene yield in MTO process over ZSM-5 catalyst through recycling the heavier products [4]; and direct conversion of ethene to propene [5,6]. The formation of propene by methylation of ethene with methanol is a relatively less noticed reaction that could be useful in adjusting propene to ethene ratio in MTO process and in the economic transformation of dilute ethene in FCC dry gas. The advantage of this reaction lies in that the added atom of carbon chain comes from methanol, which can be produced from cheaper resources such as coal or natural gas.

Co-reaction of ethene and methanol has been studied by some researchers with the purpose of better understanding the MTO reaction mechanism [7–10]. Tau and Davis [7] investigated the

co-reaction of ethene and methanol over Silicalite S-115 by isotopic tracer method and concluded that ethene was converted by adding a C1 species derived from methanol to form heavier compounds. However, Ronning et al. [8] drew the conclusion, in a study on co-feeding of ethene and methanol with isotopic labeling over ZSM-5 catalyst, that ethene is unreactive and its methylation could not be an important part in the reaction network. Recently, Svelle and co-workers [9] studied the ethene-methanol co-reaction on H-ZSM-5 using isotopic labeling technology. The authors found that the methylation of ethene to form propene was dominating at very low conversions, but it was eclipsed by other pathways once there was an appreciable amount of hydrocarbon products.

In the co-feeding reaction system of ethene and methanol, it should be noted that both methylation and so-called “MTO conversion” are acid-catalyzed reactions and require an appropriate nature of acid sites. The above contradictory conclusions from different researchers may come from the different catalyst they used. In the present study, ZSM-5 catalysts prepared by various modification methods were used to investigate the influence of the acidity on the behavior of the co-reactions of ethene and methanol.

### 2. Experimental

#### 2.1. Catalyst preparation

H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 38$ ) was obtained from Nanda Catalyst Co., Ltd Company and was designated as HZ. The P/La modification

\* Corresponding author. Tel.: +86 411 84685510; fax: +86 411 84691570.  
E-mail address: [liuzm@dicp.ac.cn](mailto:liuzm@dicp.ac.cn) (Z. Liu).

of HZ was carried out as follows. First, the parent HZ was impregnated with  $H_3PO_4$  aqueous solution under stirring, and the suspension was evaporated, dried at 373 K overnight and then calcined at 823 K for 4 h. The resulting powder was then modified with La by the similar procedure. The resulting P-La modified sample was designated as PLaHZ. The nominal contents of phosphorus and lanthanum were 3% and 2%, respectively. The PLaHZ was hydrothermally treated at 1073 K for 5 h in flowing 100% steam to prepare the steamed sample (designated as PLaHZ-st).

## 2.2. Characterization

The phase structure of the samples was characterized by powder X-ray diffraction (RIGAKU D/max-rb powder diffractometer) with Cu  $K_\alpha$  radiation.

The nitrogen adsorption isotherms were measured at 77 K on a NOVA 4000 gas adsorption analyzer (Quantachrome Corp.). Before measurements 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  $t$ -plot method.

The acidity of the catalysts was determined by temperature programmed desorption of ammonia ( $NH_3$ -TPD). A catalyst sample of 0.14 g was loaded into a stainless U-shaped micro-reactor and pre-treated at 873 K for 30 min in flowing He. After the pre-treatment, the sample was cooled to 423 K and saturated with  $NH_3$  gas. The  $NH_3$ -TPD was carried out from 423 to 873 K in a He flow of 20 ml/min at a constant heating rate of 20 K/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatography equipped with a TCD detector.

## 2.3. Catalyst evaluation

The reactions were performed in a fixed-bed stainless steel tubular reactor (9 mm i.d.) at atmospheric pressure. A catalyst sample of 0.5 g (20–40 mesh) was loaded into the reactor. Quartz sand was filled in the upper part of reactor to get a plug flow of the mixed feed. Fresh catalyst was used for each run. The methanol was charged by passing the carrier gas (helium) through a saturator containing methanol. Ethene was fed into the reactor through a mass-flow meter with helium as dilute gas. The molar feed ratio of  $He:C_2H_4:MeOH$  was 1:1:0.54. The products were analyzed using on-line gas chromatography (Varian GC3800) equipped with a FID detector and a PoraPLOT Q-HT capillary column.

## 3. Results and discussion

The X-ray diffraction (XRD) patterns of the ZSM-5 catalysts before and after modification showed that the intrinsic lattice structure of ZSM-5 was preserved and no other phase was observed. The relative crystallinity and texture properties of the catalysts are listed in Table 1. The relative crystallinity was calculated based on the intensity of the peaks of angle  $2\theta = 22$ – $25^\circ$  in the XRD pattern according to the literature [11,12] using the H-ZSM-5 sample as reference. The relative crystallinity of the catalyst after phosphorus and lanthanum modification (PLaHZ) was only a little lower than that of the unmodified catalyst HZ. However, the hydrothermal treatment at 1073 K resulted in a prominent decrease in the relative crystallinity of PLaHZ-st, which might be attributed to the partial destruction of ZSM-5 structure during high temperature treatment.

The textural properties such as surface area and pore volume of the catalyst samples were calculated on the basis of nitrogen adsorption. As shown in Table 1, HZ presented a BET surface area higher than  $300\text{ m}^2/\text{g}$  and a pore volume of  $0.23\text{ cm}^3/\text{g}$ . The modi-

**Table 1**  
Relative crystallinity and textural properties of catalysts

Catalyst	Relative crystallinity	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{micro}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{micro}}$ ( $\text{cm}^3/\text{g}$ )
HZ	100	358	241	0.23	0.11
PLaHZ	94.5	210	151	0.14	0.07
PLaHZ-st	70.2	255	141	0.17	0.06

fication of P and La resulted in a great decrease in surface area and pore volume. Especially, the micropore surface and the micropore volume decreased to greater extents. Considering the high crystallinity of PLaHZ, the reduced porosity should be due to the channel blockage of P and La into HZSM-5. The micro pore surface area of PLaHZ-st (the hydrothermal-treated sample) was less than that of PLaHZ sample. However, the BET surface area of PLaHZ-st was higher than that of PLaHZ.

The results of  $NH_3$ -TPD of the catalysts are shown in Fig. 1. The TPD curve for HZ exhibits two desorption maxima, which can be assigned to weak and strong acid sites, respectively. The modification with P and La not only sharply decreased the amount of adsorbed ammonia, but also changed the acid strength distribution. The desorption maxima ascribed to strong acid sites was reduced to a great extent. After hydrothermal treatment, only a small amount of weak acid sites were preserved, while the maxima of ammonia desorption for strong acid sites almost disappeared on the profile of PLaHZ-st.

The co-reaction of methanol and ethene over parent and modified ZSM-5 zeolites was carried out at 773 K. For comparison, reactions with sole ethene or methanol feed were also carried out. The typical results over different catalysts are displayed in Table 2.

The conversion of methanol to hydrocarbons over zeolites has been well studied since it was first reported [13–15]. The products usually include hydrocarbons distributed as ethene, propene and higher hydrocarbons. Besides, hydride transfer and cyclization reactions lead to the formation of aromatics, alkanes and coke. On HZ, the high density of acid sites, as revealed by the  $NH_3$ -TPD study, enhanced the hydride transfer and cyclization reactions, resulting in a very high selectivity for C1–C4 alkanes, as well as aromatics and coke (the latter was calculated by the deficit on the balance of H and C).

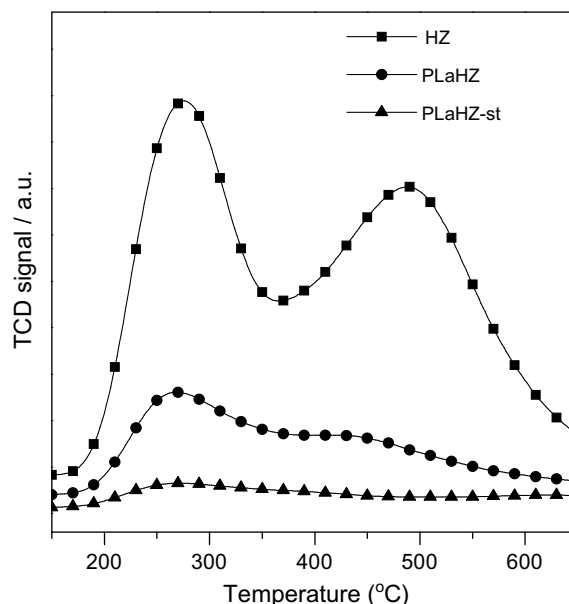


Fig. 1.  $NH_3$ -TPD profiles of the catalysts.

**Table 2**  
Conversion of methanol and/or ethene over different catalysts

Catalyst	HZ			PLaHZ			PLaHZ-st		
	MeOH	Ethene	MeOH+Ethene	MeOH	Ethene	MeOH+Ethene	MeOH	Ethene	MeOH + Ethene
MeOH conv. <sup>a</sup> (%)	100	–	100	100	–	100	2.5	–	60.8
Ethene conv. (%)	–	93.2	92.6	–	83.2	81.6	–	0.4	11.3
Product sel. (%)									
C <sub>1</sub> <sup>0</sup>	2.2	1.7	2.3	1.3	0.6	0.7	27.2	0.6	0.4
C <sub>2</sub> <sup>0</sup>	17.7	–	–	19.4	–	–	8.3	–	–
C <sub>3</sub> <sup>0</sup>	1.5	3.0	3.8	0.3	1.2	1.3	0.3	1.1	0.3
C <sub>3</sub> <sup>0+</sup>	17.3	9.3	8.0	26.4	25.8	24.0	14.4	15.6	52.9
C <sub>3</sub> <sup>0+</sup>	15.5	21.6	24.5	6.5	11.0	12.4	0.0	0.0	0.4
C <sub>4</sub> <sup>0</sup>	6.0	4.7	4.3	9.9	16.6	15.0	8.4	67.9	19.8
C <sub>4</sub> <sup>0+</sup>	8.5	9.6	8.9	9.2	8.7	10.5	0.4	0.0	0.6
C <sub>5</sub> <sup>+</sup> c	3.2	5.8	6.3	9.6	15.0	14.0	11.0	13.7	24.0
BTX <sup>b</sup>	26.1	43.7	41.8	16.6	21.1	21.7	4.4	0.0	1.2
Coke <sup>d</sup>	2.0	0.5	0.2	0.7	–	0.5	25.8	1.1	0.4

T = 773 K, methanol WHSV = 3.5 h<sup>-1</sup>, ethene WHSV = 5.7 h<sup>-1</sup>, time on stream (TOS) = 6 min.

<sup>a</sup> Methanol to hydrocarbon conversion (i.e. considering dimethyl ether as reactant).

<sup>b</sup> Benzene, toluene and xylene.

<sup>c</sup> BTX not included.

<sup>d</sup> Coke selectivity was calculated by the deficit on the balance of H and C.

As for the conversion of ethene over acid catalysts, the formation of olefins, such as butenes and propene should come from oligomerization of ethene and cracking of oligomers [16–19]. Furthermore, the hydride transfer and cyclization reactions will also lead to the formation of aromatics and alkanes at high selectivity. As shown in Table 2, the ethene conversion over HZ was nearly complete and the olefin products reequilibration and cyclization took place rapidly.

When ethene was co-fed with methanol over HZ (Table 2), the methanol conversion remained 100%. The ethene conversion, which is referred to the net lose of ethene after reaction, exhibits a little decrease compared with that of sole ethene feed. Moreover, the product distribution was similar to that of sole ethene feed. The product selectivity of co-reaction, calculated from the distribution of hydrocarbons in the effluent except ethene, presents a propene selectivity of about 8%.

On PLaHZ, the decrease of the acid site density after P/La modification, as shown by the NH<sub>3</sub>-TPD characterization, prominently suppressed the hydride transfer and cyclization reactions. The selectivity for BTX (benzene, toluene and xylene) greatly decreased when compared with that over the parent HZ, in the cases of feeding methanol, ethene, or co-feeding. The selectivity for C<sub>1</sub>–C<sub>4</sub> alkanes also decreased. Meanwhile, the selectivity for propene increased to about 24%.

The reaction results over PLaHZ-st were interesting. When methanol was fed alone, the product was almost dimethyl ether coming from intermolecular dehydration of methanol. When the formed dimethyl ether was also taken as reactant, the conversion to hydrocarbons was very low (about 2%), and the dominant product was methane (27%) and coke (26%). As revealed by the NH<sub>3</sub>-TPD results, hydrothermal treatment at high temperature sharply reduced the acidity of the catalyst - not only the number of acid site was decreased, but also the acid strength was lowered. The low acidity of the catalyst PLaHZ-st should be responsible for its failure to convert methanol into olefins. As presented in Table 2, the conversion of sole ethene feed over PLaHZ-st was also suppressed and the main product was butenes (68%) resulted from the dimerization of ethene, and no aromatics were detected. However, co-feeding ethene and methanol over PLaHZ-st resulted in dramatically high conversions of methanol/dimethyl ether (60.8%) and ethene (11.3%). The dominant products were propene at a selectivity of 53%, and butenes at 20%. Other products were mainly C<sub>5</sub><sup>+</sup> hydrocarbons.

The reactions involved in the co-reaction of ethene and methanol over ZSM-5 could be roughly sorted into three types: the direct conversion of ethene, the direct conversion of methanol and the interaction of them. Propene in the products might originate via different routes. Furthermore, the direct conversion of methanol could also produce ethene as a major product. So the reactants and products of each reaction are interwoven, and the three types of reactions in fact can not be distinctly separated from one another. The real reaction network over unmodified ZSM-5 should include all the reactions. In the present case, for the direct conversion of ethene or methanol/dimethyl ether over PLaHZ-st was depressed, it is reasonable to deduce that the formation of propene in co-feeding should be resulted from the interaction between ethene and methanol. We suggest that the dominant interaction between ethene and methanol be the methylation reaction, on the basis of the high selectivity for propene.

The evolutions of conversion and product distribution of the co-reaction over PLaHZ-st with time on stream (TOS) are illustrated in Fig. 2. Though the acidity of the catalyst was very weak, there was still coking and deactivation in the case of co-feeding. The conversion of methanol/dimethyl ether and ethene decreased gradually with increasing TOS. However, the propene selectivity increased with decreased conversion. Especially, the propene selectivity increased to about 80% at 100 min on stream, at low conversions of methanol/dimethyl ether and ethene. The raising tendency of propene selectivity should be explained by the suppression of further methylation of propene when its concentration was low.

The results of the co-reaction of ethene and methanol over PLaHZ-st at varied temperature are listed in Table 3. The reactant conversions increased with increasing temperature. Product selectivities also varied with reaction temperature. When the temperature increased from 723 to 823 K, the propene selectivity increased from 51.3% to 53.6%, and the butenes selectivity also increased from 19.4% to 22% with decreased selectivities for C<sub>5</sub><sup>+</sup>. Meanwhile, C<sub>1</sub>–C<sub>4</sub> alkanes and BTX selectivities presented little change.

The molar ratios of butenes to propene and that of pentenes to butenes at different temperature are plotted against total conversions in Fig. 3. The total conversion was calculated by dividing all the carbon atoms in the products by the total carbon atoms in the feed, i.e. ethene, methanol and dimethyl ether were all considered as unconverted reactant. The total conversion reflected the degree of conversion of co-feeding ethene and methanol. As shown in Fig. 3, the ratios increased with total conversion. This is

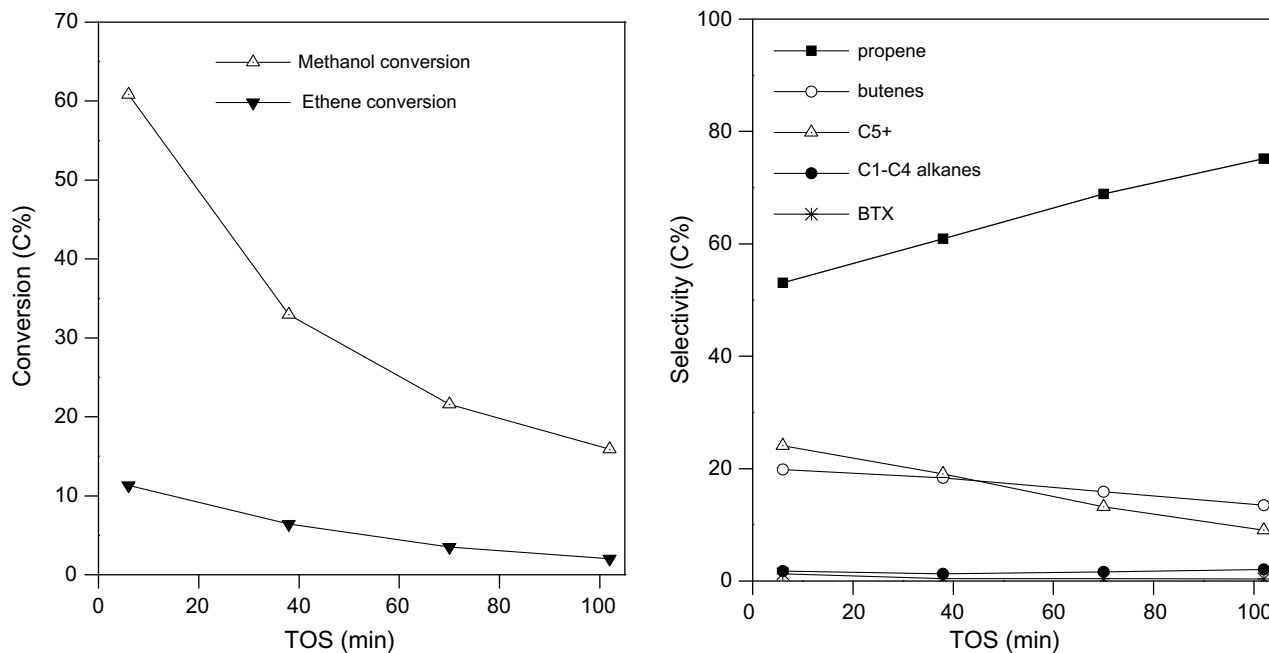


Fig. 2. Time tendency of co-reaction of ethene and methanol over PLaHZ-st.  $T = 773$  K,  $\text{He}/\text{C}_2\text{H}_4/\text{MeOH} = 1/1/0.54$ ,  $\text{WHSV}(\text{methanol}) = 3.5 \text{ h}^{-1}$ .

consistent with the mechanism of consecutive methylation by methanol to produce propene, butenes and pentenes. On the other hand, at the same conversion the ratios decreased with the reaction temperature. This tendency was more obvious for heavier olefins, which is easier to be cracked to light olefins like propene and ethene. This implies that the cracking of higher olefins to form propene and ethene also take place under current reaction conditions and it become more prominent at higher temperature.

The molar ratios of converted methanol to converted ethene at different space velocity are plotted against total conversion in Fig. 4. We found that the ratios are bigger than 1 in all the conditions, and the ratio was nearly 1.5 when extrapolated to zero conversion. This implies that the methylation of ethene by methanol would not be the only dominant reaction in this context and there must be another route for methanol transformation. Because the direct MTO conversion was completely suppressed over this catalyst (PLaHZ-st), we suppose that the further methylation of propene and butenes by methanol play a great role in methanol transformation and a considerable part of propene come from the cracking of the higher alkene originated from the further methylation reactions. This route became more prominent at higher conversion and/or higher reaction temperature, for the cracking reaction was

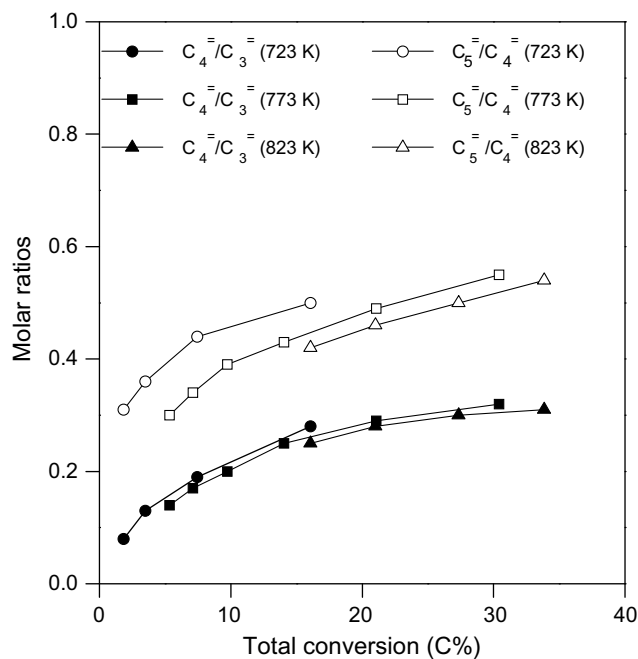


Fig. 3. Molar ratios of olefin products over PLaHZ-st as a function of total conversion at different temperature,  $\text{He}/\text{C}_2\text{H}_4/\text{MeOH} = 1/1/0.54$ ,  $\text{WHSV}(\text{methanol}) = 3.5 \text{ h}^{-1}$ .

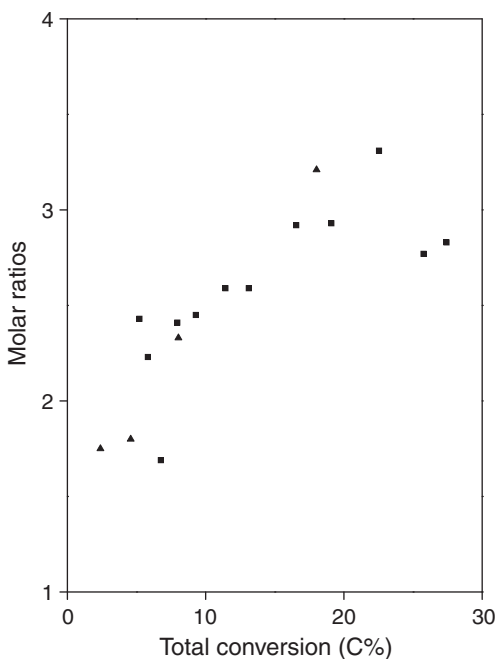
Table 3  
Effect of temperature on catalytic performance of PLaHZ-st in co-reaction

Temperature (K)	723	773	823
MeOH conv. (%)	45.3	60.8	92.1
Ethene conv. (%)	8.1	11.3	18.1
Product sel. (%)			
$\text{C}_0$	0.3	0.4	0.6
$\text{C}_1$	0.2	0.3	0.3
$\text{C}_2$	51.3	52.9	53.6
$\text{C}_3$	0.5	0.4	0.4
$\text{C}_4$	19.4	19.8	22.0
$\text{C}_5$	1.1	0.6	0.3
$\text{C}_6$	25.5	24.0	21.1
BTX	1.4	1.2	1.1
Coke	0.3	0.4	0.5

$\text{He}/\text{C}_2\text{H}_4/\text{MeOH} = 1/1/0.54$ ,  $\text{WHSV}(\text{methanol}) = 3.5 \text{ h}^{-1}$ , TOS = 6 min.

thermodynamically favored at higher temperature with a high selectivity for propene [20]. This type of reaction cycle of alkene methylation and cracking was also recognized by Dessau [21], and was recently emphasized by Bjørgen and co-workers [22] in the MTO conversion over H-ZSM-5.

Fig. 5 shows the olefin yield (C-mol%) at different space velocities as a function of total conversion. It was clear that all of the data at different space velocities were well fitted to the same lines. When we compared these results with the theoretical optimum performance envelopes (OPE) [23,24], we found that the propene



**Fig. 4.** Molar ratios of converted methanol to converted ethene over PLaHZ-st as a function of total conversion.  $T = 773$  K,  $\text{He}/\text{C}_2\text{H}_4/\text{MeOH} = 1/1/0.54$ , (■)  $\text{WHSV}(\text{methanol}) = 3.5 \text{ h}^{-1}$ , (▲)  $\text{WHSV}(\text{methanol}) = 8.75 \text{ h}^{-1}$ .

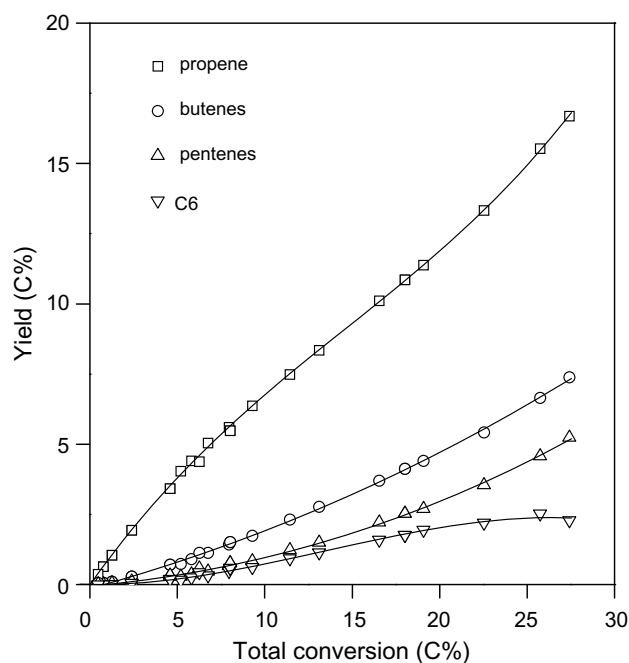
yield curve showed the feature of an unstable primary plus secondary product, the butenes and pentenes yield curves showed the feature of secondary products, and the  $\text{C}_6$  yield curve showed the feature of an unstable secondary product. These findings support the above discussions.

#### 4. Conclusions

The competition of different types of reactions in the co-reaction of ethene and methanol was influenced by the acidity of the catalysts. Lowering the acidity and/or decrease the acid site number of catalyst helped to suppress the direct conversions of methanol or ethene. Over PLaHZ-st, methylation of ethene played a dominant role in producing propene at high selectivity, especially when conversion was lower. However, another route for methanol transformation towards propene over PLaHZ-st in the presence of ethene was the repeated methylation of propene and the cracking of the formed higher olefins. The role of the latter route in the complicated reaction system became more evident with increasing reaction temperature.

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**Fig. 5.** Olefin yields of co-reaction of methanol and ethene over PLaHZ-st as a function of total conversion.  $T = 773$  K,  $\text{He}/\text{C}_2\text{H}_4/\text{MeOH} = 1/1/0.54$ , methanol  $\text{WHSV}$  varied from 3.5 to  $17.5 \text{ h}^{-1}$ .

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