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# Inter-conversion of light olefins on ZSM-5 in catalytic naphtha cracking condition

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#### ABSTRACT

The inter-conversion of light olefins over four types of HZSM-5 based catalysts under cracking conditions was investigated systematically and various methods including XRD, Ar adsorption–desorption, NH<sub>3</sub>-TPD, <sup>27</sup>Al and <sup>31</sup>P MAS–NMR were used to characterize the effects of P modification and steaming on ZSM-5. Regardless the types of catalyst, the same behaviors of light olefin inter-conversion were observed only depending on conversion of light olefins. Also, the conversion and selectivity were not influenced by the presence of hydrogen, suggesting that light paraffins were mainly produced from hydrogen transfer during cracking rather than hydrogenation of light olefins. It can be suggested that the inter-conversion of light olefins occurs through oligomerization of light olefins and then re-cracking of the oligomerized products. To guarantee high light olefin yield in catalytic naphtha cracking, it is strongly required to suppress oligomerization of light olefins during catalytic cracking.

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#### 1. Introduction

Together with BTX (benzene, toluene, and xylene), light olefins such as ethene and propene are important as chemical feed stocks in chemical industry. More than half of light olefins are still produced by thermal cracking of naphtha and a lot of energy is used for their production due to high cracking temperature. Also, due to higher demand for propene than ethene, it is required to produce more propene in naphtha cracking and catalytic cracking is considered as one of good alternative to replace conventional thermal cracking [1–4]. Recently, catalytic naphtha cracking process, applying ZSM-5 based-catalyst and having the name of ACO<sup>TM</sup> was developed by SK Innovation co., KBR co., and KRICT in commercial scale. This catalytic cracking process revealed improved light olefin yield with less energy consumption than conventional thermal cracking process due to the use of acid cracking catalyst and reduced cracking temperature [1]. To guarantee high light olefin yield, especially propene yield, in catalytic naphtha cracking there is no option in selecting catalyst except for ZSM-5. However, the ZSM-5 is still suffered from commercialization due to the lack of hydrothermal stability and low product selectivity. Because the ZSM-5 has intrinsically high activities for the side reactions such as hydrogen transfer, oligomerization and aromatization together with cracking activity, the cracking reaction should be carried out in diluted steam condition at high temperature to prevent side reactions. Therefore high hydrothermal stability of ZSM-5 is required. As an effective modifier to improve hydrothermal stability of ZSM-5, various types of phosphate have been suggested and widely used for the preparation of commercial cracking catalyst [5].

According to our recent study, the light olefins such as ethene and propene produced in catalytic naphtha cracking over ZSM-5 are unstable and considerable amount of them is inter-converted each other through dimerization and re-cracking process. That is, the inter-conversion rate of ethene and propene is relatively high and comparable to that of cracking, which resulted in the transformation of produced light olefins to other light olefins and saturated hydrocarbons such as methane, ethane and propane. Therefore, it was investigated more systematically the inter-conversion behavior of light olefins on ZSM-5 in catalytic naphtha cracking condition and tried to estimate yield pattern of catalytic naphtha cracking based on the behavior of light olefin inter-conversion.

Already, it is known that oligomerization and isomerization of light olefins occur very fast together with cracking over acidic zeolite catalyst, which leads to the formation olefinic products







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with different carbon numbers. Also, irreversible cyclization and hydrogen transfer reactions are responsible for the formation of cycloolefins, alkyl aromatics and paraffins. However, most of the previous studies are focused on the transformation of light olefins for the production of aromatics or heavy hydrocarbon fuel in the low temperature range of 200-450 °C [6-16]. Therefore, it is not easy to estimate the behavior of light olefins at the reaction temperature higher than 650 °C. According to Garwood et al., the shape-selective oligomerization of  $C_2-C_{10}$  olefins occurs more favorably at the temperature lower than 400 °C over ZSM-5, which leads to the formation of aromatics [6]. Quann et al. also reported that distillate-range olefins with high quality fuel properties are produced through oligomerization from  $C_{3=}$  to  $C_{6=}$  olefins over ZSM-5 at 200-300 °C and relatively high pressure of 30-100 bar and lower molecular weight olefins are produced at higher temperature and lower pressure due to high cracking rates of olefins [8]. As the temperature increased, the consumption of ethene and propene decreased, whereas that of butene increased [9]. The activity of oligomerization of light olefins is also strongly influenced by the acidity of zeolite and reaction temperature. The light olefins such as ethene, propene and i-butene are transformed more easily on more acidic zeolite [10]. According to Berg et al., the ethene oligomerization occurs only on strong Brönsted acid sites at low temperature of 27 °C but weak acid sites become active at high temperature. The formed oligomers begin to crack from 127 °C and the rate of cracking becomes faster than that of oligomerization at T>227 °C [11].

According to our study, the behavior of light olefins on ZSM-5 at high temperature is much different from that at low temperature and it is important to interpret the behavior of catalytic naphtha cracking with consideration of inter-conversion of light olefins. That is, in catalytic naphtha cracking, the produced light olefins are unstable and considerable amount of them are transformed irreversibly to other side products through oligomerization and recracking processes. To suppress the side reactions and maximize light olefins yield in catalytic naphtha cracking, understanding the behavior of produced light olefins is quite importance.

However, there has been no detailed study for the behavior of light olefins in catalytic naphtha cracking condition over ZSM-5 based catalysts. Therefore, the reactivity of ethene and propene was investigated thoroughly depending on the types of catalyst in catalytic naphtha cracking condition and it was tried to suggest a generalized mechanism for light olefins inter-conversion.

#### 2. Experimental

#### 2.1. Preparation of catalyst

For activity test of light olefins, four types of ZSM-5s were prepared in the following preparation conditions.

- (i) HZSM-5: parent HZSM-5 (Si/Al = 14.5) was obtained from Albemarle.
- (ii) St-HZSM-5: the parent HZSM-5 was steamed at 770°C in 100 vol% steam flow for 24 h. The steam treatment was carried out in a fixed bed reactor after loading 4 g of catalyst while flowing evaporated water at WHSV of 10 h<sup>-1</sup>. The temperature was programmed from 70 to 770°C for 70 min, maintained at 770°C for 24 h, and then cooled down quickly to room temperature after steaming.
- (iii) P/HZSM-5: the parent HZSM-5 was modified with phosphoric acid by impregnation method. The amount of P corresponding to the Al/P atomic ratio = 1 was loaded on HZSM-5, where Al means framework Al of ZSM-5. After impregnation of P, it was dried at 100 °C for 24 h and then calcined at 650 °C for 6 h.

(iv) St-P/HZSM-5: the P/HZSM-5 was steamed at the same condition as that of St-HZSM-5.

#### 2.2. Characterization of catalyst

#### 2.2.1. XRD analysis

The XRD analysis was carried out on Bruker D5000 operated at 50 kV and 30 mA, with Cu K<sub> $\alpha$ </sub> monochromatized radiation ( $\lambda$  = 0.15468 nm).

#### 2.2.2. Pore analysis

The specific surface area, pore volume were measured by Ar adsorption–desorption isotherms (ASAP 2010, Micromeritics Ins. Corp.). Prior to the measurement, all samples were degassed at  $250 \,^{\circ}$ C until a stable vacuum of ca.  $10^{-3}$  Torr was reached.

#### 2.2.3. Pyridine adsorption

FTIR spectra were taken at room temperature in the range of 400–4000 cm<sup>-1</sup> using an AVATAR 360 Nicolet spectrophotometer in a vacuum cell. Prior to pyridine adsorption, the samples were degassed under vacuum ( $10^{-3}$  Pa) at 400 °C for 24 h. Then the samples were exposed with pyridine for 30 min and degassed for 1 h under vacuum at increasing temperatures (150, 250 and 350 °C), followed by IR measurement. The relative ratio of Brönsted and Lewis acidity was derived from the area of the IR bands at 1550 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>, respectively.

#### 2.2.4. Solid MAS NMR

The <sup>27</sup>Al MAS NMR spectra were obtained on a Bruker AVANCE 500 spectrometer at a <sup>27</sup>Al frequency of 130.325 MHz in 4 mm rotors at a spinning rate 12.0 kHz. The spectra were obtained with an acquisition of ca. 3000 pulse transient, which were reported with a  $\pi/4$  rad pulse length of 5.00  $\mu$ s and a recycle delay of 1.0 s. The <sup>27</sup>Al chemical shifts were referenced to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> solution. The <sup>31</sup>P MAS NMR spectra at a spinning rate of 11.0 kHz were obtained on the same spectrometer at a <sup>31</sup>P frequency of 202.450 MHz with an acquisition of about 100 pulse transients, which were repeated with a  $\pi/2$  rad pulse length of 5.0  $\mu$ s and a recycle delay of 30 s. The <sup>31</sup>P chemical shifts were referenced to H<sub>3</sub>PO<sub>4</sub> solution.

#### 2.3. Reactions

The reactivity of light olefins was evaluated in quartz microreactor. 0.05 g catalyst was loaded into the micro-reactor and reactions were carried out at 675 °C in the WHSV range of 4–128 h<sup>-1</sup>. As a reactant, three types of ethene, propene and both of them were used and hydrogen was also introduced together in the case of seeing the effect of hydrogenation. Because the product volume ratio of C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub> in catalytic naphtha cracking is 20/15/5, the reactivity of light olefins were evaluated in the following reactant volume compositions: (i) C<sub>2</sub>H<sub>4</sub>/He = 20/80, (ii) C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>/He = 20/5/75, (iii) C<sub>3</sub>H<sub>6</sub>/He = 15/85, (iv) C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/He = 15/5/80, (v) C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub>/He = 20/15/65, and (vi) C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/He = 20/15/5/60, respectively. The products were analyzed with GC (6890, Agilent) equipped with NP-1 column and FID detector.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

#### 3.1.1. XRD analysis

All of P-free and P-modified HZSM-5s revealed typical XRD patterns of MFI structure with no other extra peaks regardless of steaming at 770 °C for 24 h. However, in the case of HZSM-5,



**Fig. 1.** XRD Patterns of (a) HZSM-5, (b) St-HZSM-5, (c) P/HZSM-5 and (d) St-P/HZSM-5.

slightly decrease of intensity at  $2\theta$  of  $24^{\circ}$  was observed and relative crystallinity was decreased to 96% due to the dealumination of framework Al by steaming. Different from HZSM-5, P-modified HZSM-5 showed no change in XRD peak intensity and relative crystallinity even after steaming (Fig. 1). These results indicate that the main framework of HZSM-5 is scarcely damaged by steaming and P modification. Also, no XRD peaks corresponding to the extra framework alumina or AlPO<sub>4</sub> were observed over the steamed St-P/HZSM-5. However, according to Ramesh et al., it would not be ruled out the formation of ultrafine particles of extra framework alumina and AlPO<sub>4</sub> lower than 40 Å in particle size on the surface of zeolite crystals [17].

#### 3.1.2. Ar adsorption-desorption

Textural properties of four different types of ZSM-5s are presented in Table 1. All the samples except St-HZSM-5 revealed the adsorption–desorption isotherms of type I (Fig. 2). In the case of St-HZSM-5, an adsorption–desorption hysteresis loop can be seen, which can be attributed to the formation of mesopores due to heavy dealumination of framework Al of HZSM-5 by steaming at 770 °C for 24 h. Therefore, the steaming treatment of parent HZSM-5 resulted in a decrease of both micropore volume ( $V_{micro}$ ) and surface area ( $S_{BET}$ ) but an increase of external surface area ( $S_{ext}$ ) and



**Fig. 2.** Adsorption-desorption isotherms of Argon: (a) HZSM-5, (b) St-HZSM-5, (c) P/HZSM-5 and (d) St-P/HZSM-5.

total pore volume ( $V_{total}$ ). However, after P modification (P/HZSM-5),  $S_{BET}$ , micropore area ( $S_{micro}$ ),  $S_{ext}$ ,  $V_{micro}$  and  $V_{total}$  decreased, suggesting the formation of polymeric phosphate species located in inside of zeolite pore channels or over the external surface of zeolite and blocks the channel. If the P/HZSM-5 was steamed, the  $S_{BET}$ ,  $S_{micro}$ ,  $V_{micro}$  and  $V_{total}$  increased compared with P/HZSM-5 due to the removal of free phosphorus species and the hydrolysis of polymeric phosphate species during steaming. According to our previous study, hydrolysis and re-polymerization of polymeric phosphate species occurs simultaneously by steam and the phosphate species are reassembled in the P modified catalyst [16], which finally leads to the increase of surface area and pore volume.

#### 3.1.3. Pyridine adsorption

The acid property of samples was monitored by FT-IR after pyridine adsorption and then outgassing at different temperatures (Table 1). The increase of outgassing temperature leads to the removal of weakly coordinated pyridine and only pyridine adsorbed on strong acid sites exists. The spectra outgassed at 150, 250 and 350 °C reveals information of total, medium + strong, and strong acid sites of the samples, respectively. Parent HZSM-5 shows the strongest acid strength, and 96% of total Brönsted acid sites and 1/3 of total Lewis acid sites appear as strong ones. Meanwhile, total Lewis acid sites of HZSM-5 are more than total Brönsted acid sites, which agrees well with the previous result that a large fraction of acid sites would be transformed to Lewis sites by calcination at 650 °C [18]. If HZSM-5 was steamed at 770 °C for 24 h, nearly all the Brönsted acid sites disappeared due to heavy dealumination by severe hydrothermal treatment, and half of its total Lewis acid sites was lost and only small amount remain as strong sites. The impregnation of phosphate (P/HZSM-5) also brought an obvious decrease of both strong Brönsted and Lewis acid sites. Especially, the strong Brönsted acid sites decreased preferentially due to the neutralization by phosphate species, and the medium and weak Brönsted acid sites increased caused by the increased P–OH group. The steaming of P/HZSM-5 brought further decrease of Brönsted acid sites, different from steamed HZSM-5 (St-HZSM-5), about 47% of total Brönsted acid sites still remained even after steaming. This means that some improvement in hydrothermal stability could be found by phosphorus modification, which is caused by preventing dealumination from framework [16]. As we know that the cracking capability is directly related to the Brönsted acid sites, their relative quantities were observed to decrease as follows: HZSM-5 > P/HZSM-5 > St-P/HZSM-5 > St-HZSM-5.

#### 3.1.4. Solid-state MAS NMR

Various types of Al and P species were observed in NMR depending on treatment conditions (Fig. 3). Before steaming, most of Al exists as tetrahedral-coordinated Al at 53 ppm, Altetra in zeolite framework but the framework Al comes out from the framework of zeolite by steaming and the intensity of Alterra at 53 ppm decreased almost to zero regardless of phosphate modification (Fig. 3(A)). However, the degree of dealumination by steaming is more severe in phosphate-free HZSM-5 (St-HZSM-5) than in phosphate-modified one (St-P/HZSM-5). If the phosphatefree HZSM-5 is steamed (St-HZSM-5), most of the tetrahedral Altetra species at 53 ppm transformed to other various Al species and Al MNR spectra of broad and low intensity were observed. However, different from St-HZSM-5, new Al peak with high intensity at 40 ppm assigned to distorted framework Al with either tetra- or penta-coordination was observed in the steamed phosphate-modified HZSM-5 (St-P/HZSM-5) [19]. These distorted Al species are formed through the interaction of framework Al with introduced phosphate and they are thought to prevent dealumination of framework Al and enhance hydrothermal stability of ZSM-5. This NMR result is well coincided with that of pyridine

Table 1	
Textural and acid properties of HZSM-5 and	phosphate modified HZSM-5.

Catalysts	$S_{\text{BET}}(m^2/g)$	Micropore area (m²/g)	External surface areas (m²/g)	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )			Lewis acid site			Brönsted acid site		
				Micro	Meso	Total	150°C	250°C	350°C	150°C	250 °C	350 °C
HZSM-5	447	432	15.3	0.15	-	0.17	109	51	37	100	97	96
St-HZSM-5	408	379	29.1	0.13	0.05	0.18	58	13	5	0	0	0
P/HZSM-5	271	268	3.36	0.10	-	0.12	70	11	9	78	44	31
St-P/HZSM-5	357	357	0.05	0.13	-	0.13	81	18	3	47	32	19

adsorption that the relative amount of strong Brönsted acid sites of four catalyst is HZSM-5 > P/HZSM-5 > St-P/HZSM-5 > St-HZSM-5. Also, over the all phosphate-modified HZSM-5s (P/HZSM-5 and St-P/HZSM-5), new Al species at -11 ppm assigned to extraframework AlPO<sub>4</sub> appeared with the disappearance of octahedral Al species at 0 ppm assigned to extra-framework Al<sub>2</sub>O<sub>3</sub>. Therefore, this extra-framework AlPO<sub>4</sub> is thought to be formed through the interaction of non-framework octahedral Al<sub>2</sub>O<sub>3</sub> with introduced phosphate.

Over the phosphate-modified HZSM-5s, many kinds of P species were observed in  $^{31}$ P MAS NMR spectra (Fig. 3(B)). After steaming, low field peaks at 0.9, -6, -16 and -25 ppm decreased dramatically or even disappeared and higher field peaks in the region of -32 to -46 ppm assigned to polyphosphates became dominant.



Fig. 3. (A)  $^{27}\text{Al}$  MAS NMR spectra and (B)  $^{31}\text{P}$  MAS NMR spectra of (a) HZSM-5, (b) St-HZSM-5, (c) P/HZSM-5 and (d) St-P/HZSM-5.

This means that P species become more condensed after steaming [7,20–22].

From the results of characterizations, the followings could be suggested. Even the HZSM-5 is unmodified with phosphate, it maintains MFI structure after steaming but loses all of its acidity and mesopore is formed due to the dealumination of framework Al. If the HZSM-5 is modified with phosphate, some of its acidity is maintained even after steaming and hydrothermal stability is enhanced due to prevention of dealumination.

### 3.2. The behavior of light olefins inter-conversion in catalytic naphtha cracking condition

Typically, catalytic cracking of naphtha is carried out in the reaction conditions of 650–700 °C and WHSV of  $16-32 h^{-1}$  over phosphate-modified HZSM-5 and, as mentioned in Section 2.3, light olefins of about 20 vol% ethene and 15 vol% propene are produced together with 5 vol% H<sub>2</sub>. Therefore, the behavior of light olefins inter-conversion was monitored in this product composition and reaction condition with and without catalyst (Table 2).

The light olefins such as ethene and propene produced in catalytic naphtha cracking are quite reactive and about 22.0% and 55.0% of ethene and propene are transformed selectively to other types of light olefins even at high WHSV of  $32 h^{-1}$  in the presence of catalyst through inter-conversion. That is, the selectivity of propene is 62.9 mol% from ethene and 67.1 mol% of ethene selectivity was obtained when feeding propene. However, if the reaction is carried out thermally without catalyst, the light olefins are quite stable and the conversion of ethene and propene were only 2.3% and 5.8% could be obtained.

Also, quite different product distributions are obtained in the absence/presence of catalyst. In the presence of catalyst, other type of light olefin was produced preferentially with only small fraction of saturated hydrocarbons such as methane, ethane, and propane; i.e. propene was produced mainly when ethane was fed and ethene was the main product of propene reaction. However, in thermal cracking condition without catalyst, hydrogenation reaction occurred dominantly and saturated hydrocarbons were produced preferentially together with considerable amount of higher hydrocarbons ( $C_4-C_6$  fraction). The different reaction pathways in thermal and catalytic conditions could be seen clearly from the product distributions depending on the type of reactants.

In thermal cracking condition, if ethene was used as a reactant, ethane, propene and  $C_{4s}$  would be produced selectively without any methane and propane, but if propene as the feed, methane, ethene, propane and  $C_{4=}$  and small fraction of  $C_{6=}$  were produced without any ethane. This means that saturated hydrocarbons are formed directly from olefin through hydrogenation reaction under thermal cracking conditions. Another thing to be considered in the product distribution is that higher hydrocarbons such as  $C_{4=}$  and  $C_{6=}$  can be formed also from ethene and propene through dimerization reaction even though its rate is not so high in thermal reaction condition;  $C_{4=}$  and  $C_{6=}$  are formed preferentially by the dimerization of ethene and propene, respectively. However, because the formed  $C_{6=}$  are more reactive than  $C_{4=}$ , more complicated product

Reaction condition	Reactant	Conv. (%)	Product selectivity (mole %)									
			CH <sub>4</sub>	$C_2H_4$	$C_2H_6$	$C_3H_6$	$C_3H_8$	C4	C <sub>5</sub>	C <sub>6</sub>	BTX	
Thermal cracking	C <sub>2</sub> H <sub>4</sub> <sup>c</sup>	2.3	0	-	53.0	12.3	0	34.6	0	0	0	
	C <sub>3</sub> H <sub>6</sub> <sup>d</sup>	5.8	11.0	25.9	0	-	18.6	40.1	0	3.7	0.7	
Catalytic cracking <sup>b</sup>	C <sub>2</sub> H <sub>4</sub> <sup>c</sup>	22.0	10.3	-	3.4	62.9	1.5	11.8	1.2	0.3	8.5	
5	$C_3H_6^d$	55.0	8.5	67.1	1.5	-	5.0	10.1	0.6	0.2	6.9	

The degree of inter-conversion of olefins in thermal and catalytic cracking conditions.<sup>a</sup>

<sup>a</sup> Reactions were carried out at 675 °C and WHSV of 32 h<sup>-1</sup>.

<sup>b</sup> HZSM-5 as the catalyst.

<sup>c</sup> The feed is  $C_2H_4/He/H_2 = 20/75/5$  (vol. ratio).

<sup>d</sup> The feed is  $C_3H_6/He/H_2 = 15/80/5$  (vol. ratio).

distribution is obtained in the reaction of propene due to the recracking of formed C<sub>6=</sub>. That is, the formed C<sub>6=</sub> by dimerization of propene are re-cracked, which leads to only small fraction of C<sub>6=</sub> in propene reaction. It was found that the produced ethene and C<sub>4=</sub> is not equal in moles in the reaction of C<sub>3=</sub> although the dimerization of propene to C<sub>6=</sub> and then re-cracking to C<sub>2=</sub> and C<sub>4=</sub> are dominant reaction. It is thought that this is due to the complicated side reactions including dimerization, hydrogen transfer, cyclization and aromatization. So, equal mole of C<sub>2=</sub> and C<sub>4=</sub> can only be formed without these side reactions. In the real condition, the dimerization of C<sub>2=</sub>-C<sub>4=</sub> occurs quickly together with main reaction, however, C<sub>4=</sub> is difficult to crack directly to C<sub>2=</sub> under monomolecular cracking mechanism, which probably lead to higher selectivity to C<sub>4=</sub> than that of C<sub>2=</sub>.

The different pattern of methane formation in the reaction of ethene and propene provides good information about the intrinsic stability of light olefins. In the absence of catalyst under the cracking conditions, ethene and its dimer  $C_{4=}$  is stable enough not to crack further to methane; but propene can dimerized into  $C_{6=}$ , which is most likely to recrack into methane (11.0 mole%) and other light hydrocarbons. This means that methane is formed not by cracking of ethene and its dimer, but by further cracking of  $C_{6=}$ , the dimer of propene.

Different from thermal reaction, more complicated product distribution was obtained in the catalytic reaction (Table 2). The inter-conversion rate of light olefins in the presence of catalyst is very high and even comparable to that of naphtha cracking. That is, considerable amount of ethene is inter-converted selectively to propene (62.9 mol%) and propene to ethene (67.1 mole%) in catalytic naphtha cracking condition through dimerization  $\rightarrow$  recracking process. Therefore, to estimate product distribution more correctly in catalytic naphtha cracking, it is required to understand the behavior of light olefins inter-conversion in catalytic naphtha cracking condition. Therefore the behavior of light olefins was investigated more thoroughly depending on the reaction condition and the type of catalysts.

#### 3.3. The stability of light olefins

To estimate the degree of light olefins inter-conversion in catalytic naphtha cracking condition, the inter-conversion rates of ethene and propene were compared with that of  $n-C_4H_{10}$  cracking over HZSM-5 catalyst while changing reaction temperature (Fig. 4). The inter-conversion of light olefins and  $n-C_4H_{10}$  cracking showed opposite dependence on the reaction temperature. As temperature increased, the rate of cracking increased and the higher conversion of  $n-C_4H_{10}$  was obtained (Fig. 4c). However, the inter-conversion rate of light olefins deceased and the lower conversion was obtained. Only 5% of  $n-C_4H_{10}$  was converted at 500 °C and increased to 80% as the temperature increased to 700 °C (Fig. 4(c)). Different from  $n-C_4H_{10}$ , however, conversion of light olefins decreases with temperature (Fig. 4(a and b)). The reason for



**Fig. 4.** Conversion of (**■**)  $C_2H_4$ , (**●**)  $C_3H_6$ , (**♦**)  $n-C_4H_{10}$  in their corresponding reaction and conversion of (**▼**)  $C_2H_4$  and (**▲**)  $C_3H_6$  in the reaction of  $C_2H_4$  and  $C_3H_6$  mixture depending on temperature over H-ZSM-5 (*T*: 675 °C, WHSV: 32  $h^{-1}$ , reactant composition (vol%):  $C_2H_4/H_2/He = 20/5/75$ ,  $C_3H_6/H_2/He = 15/5/80$ ,  $n-C_4H_{10}/He = 10/90$ ,  $C_2H_4/C_3H_6/H_2/He = 20/15/5/60$ ).



**Fig. 5.** The effect of hydrogen on the conversion of ethene and propene; (•)  $C_2H_4$  with  $H_2$ , ( $\bigcirc$ )  $C_2H_4$  without  $H_2$ , (**\blacksquare**)  $C_3H_6$  with  $H_2$ , and ( $\square$ )  $C_3H_6$  without  $H_2$  (catalyst: St-P/HZSM-5, *T*: 675 °C, reactant composition (vol%):  $C_2H_4/H_2/He = 20/5/75$ ,  $C_2H_4/He = 20/80$ ,  $C_3H_6/H_2/He = 15/5/80$ ,  $C_3H_6/He = 15/85$ ).

Table 2



**Fig. 6.** The effect of hydrogen on selectivity in ethene and propene reaction; (a)  $C_2H_4$  with  $H_2$ , (b)  $C_2H_4$  without  $H_2$ , (c)  $C_3H_6$  with  $H_2$ , and (d)  $C_3H_6$  without  $H_2$  (catalyst = St-P/HZSM-5,  $T = 675 \degree$ C, reactant composition (vol%):  $C_2H_4/H_2/He = 20/5/75$ ,  $C_2H_4/H_2/He = 20/80$ ,  $C_3H_6/H_2/He = 15/5/80$ ,  $C_3H_6/He = 15/85$ ).

the decrease of conversion of light olefins at high temperature can be explained by the increased rate of cracking compared with that of polymerization. That is, at low temperature the rate of polymerization is higher than that of cracking, so that the conversion of light olefin is high. However, relatively low conversion of olefins is obtained at high temperature due to the increased cracking activity. Also, quite different reactivity was observed depending on the type of light olefins. The conversion of propene decreased gradually from 70% to 55% as the temperature increased from 400 °C to 700 °C (Fig. 4(b)). However, the conversion of ethene decreased more rapidly from 49% to 23% as the temperature increased (Fig. 4(a)). This means that the conversion of propene is higher than that of ethene in catalytic naphtha cracking condition. For more precise comparison of inter-conversion rate of ethene and propene, the reaction was carried out using a mixture of 20 vol% ethene and 15 vol% propene (Fig. 4(d and e)). The ethene and propene revealed big difference in reactivity. At lower temperature below 500 °C, almost the same conversions of ethene and propene were obtained but higher conversion of propene was obtained than ethene at high temperature. The conversion of ethene and propene was around 50% and 50% at 500 °C, respectively but it decreased to 3% and 43% at 700 °C. That is, ethene is more stable than propene at high temperature. This means that the ethene exists as it is once it is formed in catalytic naphtha cracking but the formed propene transforms more easily to other products through inter-conversion reaction. Therefore, it is required to maintain short contact time in catalytic naphtha cracking to guarantee high light olefin yield by preventing especially secondary reaction of produced propene.

As can be seen in the patterns of  $n-C_4H_{10}$  cracking and light olefins inter-conversion, because the activities of cracking and inter-conversion are trade-off each other, it is required to carry out catalytic naphtha cracking at relatively high reaction temperature to guarantee high light olefin yield by increasing cracking activity and prohibiting inter-conversion of light olefins. However, if the cracking temperature is too high, a lot of undesired saturated hydrocarbons such as methane, ethane and propane will be formed irreversibly due to the secondary re-cracking of high hydrocarbons and direct hydrogenation of light olefins by thermal reaction. Therefore, the reaction temperature should be optimized in catalytic naphtha cracking to guarantee high light olefin yield and to minimize saturated hydrocarbon formation.

#### 3.4. The effect of hydrogen in inter-conversion of light olefins

Because the economy of process is closely related to the light olefin yield in catalytic naphtha cracking, it is required to produce light olefins such as ethene and propene selectively and to minimize the formation of invaluable saturated light hydrocarbons such as methane, ethane and propane. Therefore, it is quite meaningful to figure out where these saturated light hydrocarbons are originated.

Normally, considerable amount of hydrogen is produced (about 5 vol% in product) during catalytic naphtha cracking. Therefore, the effect of hydrogen on the formation of saturated light hydrocarbons was monitored. The inter-conversion reaction of ethene and propene was carried out without hydrogen and with 5 vol% extra hydrogen in the reactant over steamed P/HZSM-5 (Figs. 5 and 6).

The conversions of light olefins and product distribution were not influenced much by hydrogen, which agrees well with that of 2methylpentane cracking reported by Zhao et al. that the presence of molecular hydrogen would not affect cracking capability [23]. This suggests that the saturate hydrocarbons produced were mainly caused by hydrogen transfer reaction, not by direct hydrogenation of olefin. Only slight difference exist in the product distribution of ethene conversion in the absence/presence of hydrogen; while almost same product distribution was obtained in the reaction of propene even in the presence of hydrogen. This means that small amount of ethane may be caused by the hydrogenation of ethene (reaction (1)).

$$C_{2=} + H_2 \rightarrow C_2 H_6 \tag{1}$$

Another interesting thing found in the product distribution is that relatively large amount of oligomers are formed in the reaction of light olefins;  $C_4s$  are formed preferentially in the reaction of ethene and some fraction of  $C_6s$  are formed preferentially in the reaction of propene (Fig. 6).

In the reaction of ethene, the fraction of  $C_4s$  reached to about 80% when the contact time decreased (WHSV of  $32 h^{-1}$ ). With the increase of contact time, conversion of ethene increased, while selectivity to  $C_4s$  decreased and propene selectivity increased. If the propene is formed by hydrocracking of dimerized ethene, i.e.  $C_{4=}$ , through the following reaction (2), equal mole of CH<sub>4</sub> should be formed. However, there is no CH<sub>4</sub> in the product when WHSV is higher than  $16 h^{-1}$ .

$$C_{4=} + H_2 \rightarrow CH_4 + C_3H_6 \tag{2}$$

Therefore, it is thought that the propene,  $C_{3=}$  is formed by recracking of the trimer ( $C_{6=}$ ) or even higher oligomers of ethene, which also indicating that butene is more difficult to follow monomolecular cracking mechanism. As shown in reactions (3)



**Fig. 7.** Conversion of (a) ethene, (b) propene and (c) ethene and propene mixture depending on the types of catalysts; ( $\blacksquare$ ) HZSM-5, ( $\bullet$ ) St-HZSM-5, ( $\bullet$ ) P/HZSM-5 and ( $\checkmark$ ) St-P/HZSM-5 ( $T=675 \degree C$ , reactant composition (vol%): C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>/He = 20/5/75, C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/He = 15/5/80, C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/He = 20/15/5/60).

and (4), because the cracking of  $C_{6=}$  to two  $C_{3=}$  or  $C_{2=}$  and  $C_{4=}$  proceeds more easily than  $C_{4=}$ , only small fraction of  $C_{6=}$  is observed in the product. Increasing the contact time finally leads to the interconversion of ethene to propene selectively and 62% of propene is obtained at WHSV of 4 h<sup>-1</sup>.

$$C_{6=} \rightarrow 2C_3H_6 \tag{3}$$

$$C_{6=} \rightarrow C_2 H_4 + C_{4=}$$
 (4)

As mentioned before, because propene is more active than ethene, more dimer,  $C_{6=}$ , is formed at the same contact time. However, only small amount of  $C_{6=}$  was observed in the product even at short contact time due to the re-cracking to the shorter hydrocarbons through the reactions of (3) and (4). Therefore, the same as in the reaction of ethene, the propene is selectively inter-converted to ethene at long contact time through series reaction steps of oligomerization  $\rightarrow$  re-cracking and 66% of ethene was obtained selectively at WHSV of 4 h<sup>-1</sup>.

From the above results, the following conclusion can be obtained that propane and ethane are mainly produced by hydrogen transfer during cracking of oligomerized hydrocarbons or



**Fig. 8.** Selectivity of (a) CH<sub>4</sub>, (b)  $C_2H_6$ , (c)  $C_3H_6$ , (d)  $C_3H_8$ , (e)  $C_4s$ , (f)  $C_5s$ , (g)  $C_6s$  and (h) BTX depending on the conversion in the reaction of ethene over different types of catalysts; (**a**) HZSM-5, (**a**) P/HZSM-5 (**a**) P/HZSM-5 (T=675 °C, reactant composition (vol%):  $C_2H_4/H_2/He = 20/5/75$ ).

naphtha, although small part of ethane is produced from ethene through direct hydrogenation. And another important thing to be considered is that the inter-conversion of ethene and propene is the dominant reaction in catalytic naphtha cracking and should be considered seriously in interpretation of catalytic naphtha cracking. With these backgrounds, the following experiments were carried out to figure out how much the inter-conversion of light olefin is influenced by the types of catalyst.

#### 3.5. The inter-conversion depending on the types of catalyst

The higher inter-conversion of light olefins means the higher secondary reaction in catalytic naphtha cracking. Because the cracking activity is strongly influenced by the types of catalyst in catalytic naphtha cracking it was investigated whether the inter-conversion of light olefins is also influenced by the types of catalyst. The inter-conversion was carried out over four different types of catalyst: HZSM-5, P/HZSM-5, St-P/HZSM-5, and St-HZSM-5 (Figs. 7 and 8). The inter-conversion activity was strongly influenced by the types of catalyst as expected. The catalyst having higher naphtha cracking activity revealed the higher inter-conversion activity for all the reactants of ethene, propene and mixture of ethene + propene over the full range of contact time.

Different from activity, however, the selectivity was not influenced by the types of catalyst and almost same product distribution was obtained at the same conversion of ethene, propene and mixture of ethene + propene regardless the types of catalyst.

### 3.5.1. The inter-conversion activity depending on the types of catalyst

The catalyst having higher naphtha cracking activity also revealed the higher inter-conversion activity for all the reactants of ethene, propene and mixture of ethene+propene; HZSM-5>P/HZSM-5>St-P/HZSM-5>St-HZSM-5 (Fig. 7). Also, the inter-conversion activity is well correlated with acidity of catalyst as that of naphtha cracking (Table 1). The HZSM-5 having higher acidity revealed higher inter-conversion activity than that of P/HZSM-5. The acidity of St-HZSM-5 decreased dramatically and almost all of Brönsted acid sites disappeared due to the dealumination of framework aluminum and revealed lowest inter-conversion activity. However, the hydrothermal stability of P/HZSM-5 catalyst is improved; and higher inter-conversion activity of St-P/HZSM-5 can be obtained than St-HZSM-5 due to good hydrothermal stability after P modification. To sum up, inter-conversion activity of four types of catalyst reveal can be ordered depending on the acidity: HZSM-5 > P/HZSM-5 > St-P/HZSM-5 > St-HZSM-5.

Another thing to be considered is that the intrinsic interconversion activity is strongly influenced by the types of olefins. As Garwood et al. suggested in the oligomerization reaction [6], the higher conversion was obtained in the oligomerization of propene than ethene at the same reaction condition. This means that propene is easier to oligomerize than ethene. However, if the ethene and propene exist together in the reactant, the interconversion rate will be lower than that of single reactant itself. Different from 55% propene and 22% ethene conversions from the single reactant of propene and ethene, 44% propene and 12% ethene conversions were obtained from the mixture of propene and ethene over HZSM-5 at WHSV of  $32 h^{-1}$  (Fig. 7(c)). That is, the conversion of ethene and propene are inhibited to a certain degree by the inter-conversion of propene and ethene.

### 3.5.2. The inter-conversion selectivity of ethene depending on the types of catalyst

As mentioned in previous section, the inter-conversion activity is strongly influenced by the types of catalyst. That is, the conversion of light olefins is function of catalyst activity and contact time of reactant with catalyst. The higher inter-conversion of light olefins is obtained at long contact time or over the fresh catalysts.

However, different from activity, product selectivity was not influenced by the types of catalyst. If the product distribution is plotted based on the conversion, quite expectable general trends in product distribution can be obtained regardless the types of catalyst and contact time (Figs. 8 and 9). That is, quite interestingly, the same product distribution is obtained at the same conversion regardless of the types of catalyst and contact time (Fig. 8).



**Fig. 9.** Product distribution of  $C_4$ s depending on the conversion in the reaction of ethene over HZSM-5 (*T*=675 °C, reactant composition (vol%):  $C_2H_4/H_2/He = 20/5/75$ ).

At very low conversion of ethene,  $C_4s$  and ethane were dominantly formed and then decreased rapidly with increasing contact time. This means that  $C_4s$  are initially formed by dimerization of ethene (reaction (5)) and ethane by direct hydrogenation of ethene with hydrogen (reaction (1)), respectively.

$$2C_{2=} \rightarrow C_{4=}$$
 (5)

As the conversion increased, propene,  $C_5s$ , and  $C_6s$  were begun to be formed as secondary products and revealed a maximum at certain conversions. The formation of higher olefinic hydrocarbons from ethene can be explained by following reactions; the  $C_6s$  are formed by further oligomerization of initially formed  $C_4s$  with ethene (reaction (6)) and then the formed  $C_6s$  are recracked to propene (reaction (7)) and the  $C_5s$  by dimerization of formed propene with ethene (reaction (8)). However, the fraction of  $C_5s$  and  $C_6s$  is quite low (<1%) compared with propene (>40%) because the re-cracking rate of  $C_5s$ , and  $C_6s$  is much higher than that of oligomerization. That is, through the reaction of oligomerization  $\rightarrow$  re-cracking, considerable amount of ethene is inter-converted to propene because all of the H-ZSM-5 catalysts have relatively high oligomerization activity comparable to that of cracking.

$$C_{4=} + C_{2=} \rightarrow C_{6=}$$
 (6)

$$C_{6=} \rightarrow 2C_{3=} \tag{7}$$

$$C_{3=} + C_{2=} \rightarrow C_{5=}$$
 (8)

Different from these olefinic species, the fraction of methane, propane, and BTX increased linearly with initial induction time as the conversion increased. This means these saturated hydrocarbons and aromatic species are tertiary products and produced irreversibly through hydrogen-transfer or aromatization of the formed olefinic species (reactions (2), (9), (10)).

$$C_{6=} + 3C_{3=} \rightarrow C_6H_6 + 3C_3$$
 (9)

$$C_{6=} \rightarrow C_6 H_6 + 3 H_2$$
 (10)

Because many kinds of isomer are produced during the inter-conversion reaction, the distribution of produced  $C_4$ s was monitored depending on the conversion (Fig. 9). Olefinic  $C_{4=}$ s such as 1-butene, trans-butene, cis-butene, and iso-butene were preferentially formed with only small fraction of saturated  $C_4$ s. The concentration of  $C_4$  isomers has following order: iso-butene



**Fig. 10.** (a) Conversion and (b) product selectivity in the reaction of 1-butene over HZSM-5 ( $T = 675 \circ C$ , reactant composition (vol%): 1-C<sub>4</sub>H<sub>8</sub>/H<sub>2</sub>/He = 10/5/85).

(33%) > 1-butene and trans-butene (21%) > cis-butene (17%) > cyclobutane  $(5\%) \gg 1,3$ -butadiene (trace amount). Also, the product distribution at short contact time is same as that at long contact time. That is, the product distribution is almost same without change regardless of contact time. This suggests that the isomerization of C<sub>4=</sub> occurs very quickly and reach to an equilibrium prior to further cracking to more light hydrocarbons. This result agrees well with the previous results that the rate of isomerization of C<sub>5</sub>-C<sub>8</sub> alkenes is faster than that of their cracking over H-ZSM-5 [25].

Compared with olefinic  $C_4$ s, the faction of saturated  $C_4$ s including butane and i-butane is very low (generally less than 1%), so it can be suggested that the hydrogenation or hydrogen transfer reaction of  $C_{4=}$  occurs very slowly and can be neglected in catalytic naphtha cracking.

For further understanding of inter-conversion behavior of ethene and propene, the reaction of 1-butene was carried out at the same reaction condition of ethene over HZSM-5 (Fig. 10). 1-butene revealed higher reactivity than ethene and propene and the higher conversion was obtained; 1-butene  $\gg$  propene > ethene.

In product selectivity, also quite predictable result was obtained as that of ethene reaction. At short contact time of  $256 h^{-1}$  corresponding to the low 1-butene conversion, isomerized C<sub>4</sub>s (45%) were obtained preferentially together with cracked product of ethene (17%) and propene (21%). This means that the isomerization rate is higher than that of oligomerization and cracking.

1-butene can be oligomerized to olefinic hydrocarbons higher than  $C_{8=}$  but they are not detected in the product because their cracking rate is much higher than that of formation. During this oligomerization  $\rightarrow$  re-cracking process, ethene and propene are selectively produced the same as the reaction of ethylene.

Also, as a secondary product, BTX were produced through dehydrogenation of olefinic oligomer to alkadiene and then cyclization as the contact time was increased. That is, the increase of contact time brought linear increase of BTX and  $H_2$  together with decrease of  $C_{4=}$  isomer. This means that the contact time in catalytic naphtha cracking should be optimized to guarantee high light olefin yield by minimizing the formation of BTX because they are irreversible product.

In the reaction of 1-butene, the light olefins such as ethene and propene were mainly produced by further cracking of dimer of  $C_{4=}$ s, more ethene than propene was produced as the contact time increased due to higher stability of ethene than propene at high temperature.

The distribution of hydrocarbon products observed from ethene conversion was the same and there is no obvious difference in their selectivity over the four different catalysts. Propene, as the dominant product, can be regarded as a secondary product produced by re-cracking of the ethene oligomers. Therefore, its initial selectivity was quite low at short contact time and then reached to a maximum with increase of contact time due to further reaction of produced propene. Butene, the dimer of ethene, showed higher selectivity and maximum at short contact time and decreased gradually with increasing contact time. Methane mainly comes from the thermal cracking of ethene oligomers, increased linearly with contact time, which indicating that the concurrence of catalytic cracking and radical cracking under catalytic naphtha cracking condition. C<sub>5</sub>s and C<sub>6</sub>s olefins were produced both as secondary products, so their selectivity are low at short contact time, then increased to maximum and finally decreased due to re-cracking.

The formation of saturates is due to hydrogen transfer reactions catalyzed by strong Brönsted acid sites. Ethane selectivity decreased with increasing contact time due to the decreasing concentration of ethene. Propane appears only when propene selectivity reaches the maximum at higher conversion of ethene, suggesting that propane is produced from propene and increased with contact time. BTX, mainly formed irreversibly by hydrogen transfer reaction, increased linearly with contact time.

## 3.5.3. The inter-conversion selectivity of propene depending on the types of catalyst

The selectivity depending on propene conversion also shows the same trends over different catalysts (Fig. 11), indicating that the reaction mechanism of inter-conversion also does not change depending on the acidity of ZSM-5.

In propene reaction, ethene is formed predominantly and its fraction increases with contact time. Because ethene stability is relatively high compared with other hydrocarbons, once it is formed, it is maintained as it is without further conversion to other hydrocarbons and about 70% selectivity is obtained even at long contact time. Propane selectivity from propene was high at short contact time but it decreased rapidly due to the decrease of propene concentration with increasing contact time. However, the other saturates e.g. methane and ethane, increased with the conversion of propylene. C<sub>4</sub>s come from the cracking of propene oligomers or the dimerization of produced ethene, increased to maximum and then decreased with increasing contact time due to re-cracking.



**Fig. 11.** Selectivity of (a)  $CH_4$ , (b)  $C_2H_4$ , (c)  $C_2H_6$ , (d)  $C_3H_8$ , (e)  $C_4s$ , (f)  $C_5s$ , (g)  $C_6s$  and (h) BTX depending on the conversion in the reaction of propene over different types of catalysts; ( $\blacksquare$ ) HZSM-5, ( $\bullet$ ) St-HZSM-5, ( $\bullet$ ) P/HZSM-5 and ( $\checkmark$ ) St-P/HZSM-5 ( $T = 675 \degree C$ , reactant composition (vol%):  $C_3H_6/H_2/He = 15/5/80$ ).

The inter-conversion of propene occurs dominantly through the following pathway (reaction (11)).

$$2C_{3=} \rightarrow C_{6=} \rightarrow C_{2=} + C_{4=}$$
 (11)

Same as in ethene reaction, the dimerized product of  $C_{6=}$  is formed preferentially at the initial stage of reaction and then decreased with increasing contact time due to the further secondary reaction of re-cracking and aromatization (Fig. 11(g)). The



Fig. 12. Selectivity of (a) CH<sub>4</sub>, (b) C<sub>2</sub>H<sub>4</sub>, (c) C<sub>3</sub>H<sub>8</sub>, (d) C<sub>4</sub>s, (e) C<sub>5</sub>s, (f) C<sub>6</sub>s and (g) BTX depending on the conversion in the reaction of ethane and propene mixture over different types of catalysts; (■) HZSM-5, (●) St-HZSM-5, (▲) P/HZSM-5 and (▼) St-P/HZSM-5 (T = 675 °C, reactant composition (vol%): C<sub>2</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/He = 20/15/5/60).



(a) Catalytic inter-conversion network of ethene



(b) Catalytic inter-conversion network of propene



(c) Catalytic inter-conversion network of ethene & propene mixtures

Fig. 13. Catalytic inter-conversion networks of light olefins at high temperature over acidic zeolite.

formed  $C_{6=}$  is quite reactive and re-cracked to most stable ethene. Once ethene is formed other dimerized products such as  $C_{4=}$  and  $C_{5=}$  begin to be formed (Fig. 11(e and f)). However, the level of dimerized fraction is not so high because they are re-cracked to ethene again as the contact time is increased.

Different from the dimerized products, the selectivity of BTX increased linearly with contact time same as in the ethene reaction (Fig. 11(h)). The two routes for the formation of BTX can be suggested such as hydrogen transfer reaction by strong Brönsted acid site and dehydrogenation over stronger Lewis acid site. Therefore, the highest yield of BTX is obtained over parent HZSM-5 with the highest strong acid sites.

From the result of propene reaction, it can be seen also clearly that the propene is inter-converted preferentially to ethene though the series reaction of oligomerization and re-cracking.

### 3.5.4. The inter-conversion selectivity of ethene and propene mixture depending on the types of catalyst

For better understanding of light olefin inter-conversion, reaction was carried out with a mixture of ethene and propene over four different catalysts with different WHSV of stream (Fig. 12). An interesting result was obtained with the mixture different from single reactant. Because the ethene and propene exist together at the initial stage of reaction it was expected to observe all types of dimerized products such as such as  $C_{4=},\,C_{5=}$  and  $C_{6=}$  even at short contact time. However, only  $C_{5=}$  and  $C_{6=}$  were observed at short contact time without  $C_{4=}$  (Fig. 12(d-f)). This means that the dimerization rate of propene is higher than that of ethane. Because propene is reactive enough to dimerize even with ethene as well as propene itself, the dimerized C<sub>5=</sub> and C<sub>6=</sub> are formed preferentially from the beginning of reaction but  $C_{4=}$  begins to be formed after some of propylene is used for dimerization and have a maximum at a certain degree of conversion. This result agrees well with previous result that the copolymerization of ethene with propene is faster than the dimerization of ethene itself over SAPO-34 zeolite [24].

The concentration of methane increased linearly with contact time and reached to 40% at the conversion of 60%. This level of methane formation is about two times higher than that in the reaction of single reactant because of increased concentration of light olefins. According to the previous study, methane is usually regarded as the product of radical cracking, which may be associated with the acidity from extra-framework aluminum (IV) [26], so the St-HZSM-5, most severely dealuminated steamed HZSM-5, induces more favorably the radical cracking of dimerized light olefins and revealed the highest methane formation among the four types of catalyst (Fig. 12(a), red filled circle).

All the other paraffins and BTX product would increase with the contact time, and the St-P/HZSM-5 always showed the lowest selectivity for paraffins and BTX. That is, the St-P/HZSM-5 revealed lower by-products formation at the same feed conversion due to the decreased hydrogen transfer reaction, which suggesting that the modification of HZSM-5 with P will reduce the secondary reaction of light olefins catalytic naphtha cracking.

### 3.6. Catalytic reaction network in the inter-conversion of light olefins

As discussed in previous sections, the inter-conversion of ethene and propene is not negligible in catalytic naphtha cracking condition and the following four main reaction steps should be considered in the inter-conversion of light olefins: (1) oligomerization of light olefins, (2) re-cracking and isomerization of oligomers, (3) copolymerization of mixture of light olefins, and (4) re-cracking and isomerization of copolymer. Except for the main reaction of oligomerization or copolymerization of light olefins and re-cracking of oligomers and copolymers, the other reactions such as hydrogen transfer, isomerization, dehydrogenation, cyclization and aromatization also occur simultaneously to form a complex reaction network. So the following complicated catalytic reaction networks of interconversion of light olefins could be suggested over HZSM-5 based catalyst in naphtha cracking condition (Fig. 13).

#### (1) The conversion of ethene

The inter-conversion of ethene over acid zeolite occurs through the following procedures. Ethene is dimerized firstly to  $C_{4=}$ , which is difficult to undergo monomolecular cracking and then the formed  $C_{4=}$  is further polymerized to  $C_{6=}$ . In naph-tha cracking condition, because the cracking rate of  $C_{6=}$  is faster than the formation rate,  $C_{3=}$  is formed dominantly as an inter-conversion product.

(2) The conversion of propene

The inter-conversion of propene over acid zeolite occurs through the following procedures. Propene is dimerized firstly to  $C_{6=}$  and then the formed  $C_{6=}$  is re-cracked to  $2C_{3=}$  or  $C_{2=}$  and  $C_{4=}$ . The formed  $C_{3=}$  and  $C_{4=}$  is further dimerization and then recracked to  $C_{2=}$  and  $C_{3=}$  at longer contact time (see Fig. 11). The main product in inter-conversion of propene is ethene because the formed propene is neglected as the reactant.

- (3) The conversion of ethene and propene mixture
  - When the mixture of ethene and propene is used as the reactant, the reaction of ethene and propene will undergo oligomerization and copolymerization simultaneously to form  $C_{4=}$ ,  $C_{5=}$  and  $C_{6=}$ . The formed  $C_{4=}$  and  $C_{5=}$  will be further dimerized to higher olefins and then they are re-cracked to small olefins while  $C_{6=}$  undergoes monomolecular cracking. More methane is formed due to the increased concentration of light olefins.

In catalytic naphtha cracking, quite similar light olefin distributions are obtained regardless of catalyst types and reaction conditions, which means that inter-conversion of light olefins through oligomerization  $\rightarrow$  re-cracking occurs simultaneously together with naphtha cracking. Therefore, it is difficult to control the selectivity of ethene and propene in catalytic naphtha cracking.

#### 4. Conclusions

The inter-conversion of light olefins was carried out over four different types of ZSM-5 based catalysts in catalytic naphtha cracking condition and the following conclusions were obtained.

The presence of hydrogen did not affect activity and selectivity in the inter-conversion of ethene and propene, suggesting that light paraffin would formed mainly by hydrogen transfer reaction in catalytic naphtha cracking.

The inter-conversion of ethene and propene is dominant side reaction in catalytic naphtha cracking. That is, the dimerization rate of light olefins is comparable to that of cracking and the inter-conversion occurs through the procedure of oligomerization  $\rightarrow$  re-cracking. The product distribution in inter-conversion of light olefins was not influenced by the types of catalyst and reaction conditions and almost the same product distribution was obtained at the same conversion, which suggests that the inter-conversion of light olefin follows the same reaction mechanisms.

Finally, to guarantee high light olefin yield in catalytic naphtha cracking the catalyst and reaction conditions should be optimized to minimize inter-conversion of light olefins.

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