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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_3-TPD, ^{27}Al and ^{31}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.

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^{TM} 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 re-cracking 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^{-1}. 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_α 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 °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^{-1} 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^{-1} and 1450 cm^{-1}, respectively.

2.2.4. Solid MAS NMR

The ^{27}Al MAS NMR spectra were obtained on a Bruker AVANCE 500 spectrometer at a ^{27}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 μs and a recycle delay of 1.0 s. The ^{27}Al chemical shifts were referenced to $Al(H_2O)_6{}^{3+}$ solution. The ^{31}P MAS NMR spectra at a spinning rate of 11.0 kHz were obtained on the same spectrometer at a ^{31}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 μs and a recycle delay of 30 s. The ^{31}P chemical shifts were referenced to H_3PO_4 solution.

2.3. Reactions

The reactivity of light olefins was evaluated in quartz micro-reactor. 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^{-1}. 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 $C_2H_4/C_3H_6/H_2$ in catalytic naphtha cracking is 20/15/5, the reactivity of light olefins were evaluated in the following reactant volume compositions: (i) C_2H_4/He = 20/80, (ii) C_2H_4/H_2/He = 20/5/75, (iii) C_3H_6/He = 15/85, (iv) C_3H_6/H_2/He = 15/5/80, (v) C_2H_4/C_3H_6/He = 20/15/65, and (vi) $C_2H_4/C_3H_6/H_2$/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,