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Investigation of Deep Catalytic Cracking of Various Model Compounds of Different Classes of Light Hydrocarbons on a Mesoporous Catalyst Based on ZSM-5 Zeolite[1]

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Abstract—The catalytic cracking performance of light hydrocarbon model compounds (1-hexene, *n*-octane, *i*-octane, ethylcyclohexane and ethylbenzene) over a mesoporous catalyst based on ZSM-5 zeolite was analyzed and compared using a microscale apparatus with a fixed-bed reactor. The effects of reaction temperature and weight hourly space velocity (WHSV) on feed conversion and the yields of ethene and propene were investigated. The results showed that with increased reaction temperature, the conversion of model compounds increased monotonically, and that of 1-hexene was close to 100% above 660°C; the yield of ethene plus propene of *n*-octane, *i*-octane and ethylcyclohexane increased continuously, while that of 1-hexene and ethylbenzene passed through maximum. With increased WHSV, the yield of ethene plus propene of ethylbenzene increased continuously, and that of the other model compounds decreased continuously. Through comprehensive analysis of the data, it is indicated that 1-hexene exhibited the highest cracking performance, followed by *n*-octane and ethylcyclohexane, whereas *i*-octane and ethylbenzene exhibited the lowest.

Keywords: catalytic cracking, light hydrocarbon, ethene, propene, model compounds

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Ethene and propene are important basic organic chemical raw materials [1–3]. Steam cracking is the main process in ethene and propene production but has a high energy consumption. The control range of the yield ratio of propene to ethene (P/E) is limited, and the P/E ratio depends greatly on the feed type [4–6]. The production capacity of steam cracking is unable to meet the growing demand for light olefins worldwide, especially propene [7–9].

Catalytic cracking of hydrocarbons has several advantages such as low energy consumption, high yields of olefins and high P/E ratio compared with steam cracking, thus making it a beneficial supplement to steam cracking [10, 11]. Zeolite catalysts are widely used in catalytic cracking. Among them, the ZSM-5 catalyst has remarkably improved light olefin yields [12–17]. Several mature preparation methods for ZSM-5 zeolite exist. Preparation methods mainly include hydrothermal synthesis [18] solvothermal synthesis [19], dry gel conversion method [20], ionothermal synthesis [21] and solvent-free synthesis [22]. The diversity of mature preparation methods of ZSM-5 catalysts allows the study and application of the cracking catalyst. Catalytic cracking feedstocks mainly include light hydrocarbons and heavy hydrocarbons [23–28]. Among them, light hydrocarbons have high light olefin yields and low coking rate. Naphtha is an important catalytic cracking feedstock of light hydrocarbons. The group compositions in naphtha include alkanes, alkenes, naphthenes and aromatics.

Muraza et al. studied the reaction process of propene production by n-hexane catalytic cracking over a hierarchical porous MTT molecular sieve catalyst with high activity, and achieved a P/E ratio of 2.5 [29]. The kinetics of n-hexane catalytic cracking over an MFI zeolite at 475 to 650°C was studied by Nakasaka et al., and the activation energy at high temperatures (550–650°C) was greater than that at low temperatures (475–550°C) [30]. Corma et. al. examined the effect of steam on n–heptane catalytic cracking. Although the presence of steam negatively affected the performance of the catalyst, it could greatly reduce the formation of hydrogen, methane and coke precursors [31]. Many studies reported on the catalytic cracking performance of light alkanes, but only a few compared the cracking performance of different kinds of light hydrocarbons [32]. Systematic research on the cracking performance of different hydrocarbons will contribute to the deeper understanding of light hydrocarbon cracking and the development of new types of cracking catalysts and processes.

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[1] The article is published in the original.

Table 1. Physicochemical properties of the catalyst

Parameter	Value
Diameter, mm	2.0
Length, mm	2.5
Particle density, g/cm^3	1.274
Packing density, g/cm^3	0.754
SiO_2/Al_2O_3 molar ratio[a]	33.6
Specific surface area, m^2/g	371
Total pore volume, cm^3/g	0.38
Mesopore volume, cm^3/g	0.24

[a] Measured by XRF.

In the present paper, the catalytic cracking performance of various model compounds of different classes of naphtha compositions was studied systematically. The effects of reaction temperature and weight hourly space velocity (WHSV) on feed conversion, the yields of ethene and propene, and the composition of the liquid products were investigated. The catalytic cracking performance of different model compounds was analyzed and compared.

1. EXPERIMENTAL

1.1. Feedstock and Catalyst

n-Octane (AR, Tianjin Fuchen Chemical Reagents Factory), *i*-octane (2,2,4-trimethylpentane, 99%, Aladdin Industrial Corporation), 1-hexene (97%, Aladdin Industrial Corporation), ethylcyclohexane (99%, Aladdin Industrial Corporation) and ethylbenzene (99.8%, Anhydrous Grade, Aladdin Industrial Corporation) were selected as the model compound of straight-chain alkanes, branched alkanes, alkenes, naphthenes and aromatics of naphtha group compositions, respectively. The catalyst was a mesoporous catalyst based on ZSM-5 zeolite developed specifically by China University of Petroleum for cracking light hydrocarbon feedstocks in a fixed-bed reactor. The preparation method of the catalyst was reported in the literature [33, 34]. The main physicochemical properties are summarized in Table 1.

1.2. Experimental Apparatus and Procedure

The experiments for the catalytic cracking of light hydrocarbons were performed in a microscale fixed-bed reactor. The apparatus includes five main sections: oil and steam input mechanisms, a reaction zone, a temperature control system, a product separation system and a collection system. The reactor is 40 cm long with a diameter of 1.3 cm.

Experiments were conducted in batches. Ten grams of the catalyst was placed in the reactor. Distilled water and feedstock were kept in separate vessels and pumped by different pumps. When the catalyst bed temperature reached the setting temperature, a variable amount of distilled water was pumped into the furnace to form steam, which then entered the reactor. The light hydrocarbon feed was pumped into the reactor once the reactor temperature stabilized. Cracking reactions took place as the feed came into contact with the catalyst. Gas and liquid collection was started, and time was recorded once reaction temperature stabilized again. The reaction product was cooled and separated into liquid and gas samples via the product separation and collection systems. The liquid sample was collected in a condensate bottle, and the gas sample in a gas collecting bottle. The equipment exhibited good repeatability and stability, with a mass balance of over 97 wt %.

The activity stability of the catalyst was verified at a WHSV of 4.2 h^{-1} and a steam to oil weight (S/O) ratio of 0.36 using 1-hexene as the feedstock. The catalyst maintained good activity and selectivity of ethene and propene, and the coke yield was lower than 0.1 wt % after the input mass of 1-hexene reached 12.5 times of the catalyst mass. In other studies, the handling mass of light hydrocarbons was much lower than that of 1-hexene in the verification experiment, thus the deactivation of the catalyst and the coke yield were neglected.

1.3. Analytical Methods

The gas sample was analyzed using an Agilent 6890 gas chromatograph equipped with a HP—PLOT Al_2O_3 capillary column (50 m × 530 μm × 15 μm), a 1.8 m × 1/8 molecular sieve packed column, a 3 m × 1/8 molecular sieve packed column, a 1.8 m × 1/8 porous polymeric packed column, a 0.9 m × 1/8 porous polymeric packed column, a thermal conductivity detector (TCD), a flame ionization detector (FID) and a ChemStation software. Volume percentages of gas components could be obtained. The state equation of ideal gas was then used to convert the volume percentages to weight yields with the gas sample volume.

The liquid sample was analyzed using an SP 3420 gas chromatograph fitted with a PONA capillary column (50 m × 250 μm × 0.25 μm) and a FID. PONA analytical software was used to obtain the weight percentages of the liquid sample components. Component yields were calculated using the mass of the liquid sample.

2. RESULTS AND DISCUSSION

2.1. Effect of Reaction Temperature on Cracking Performance

The effect of reaction temperature on the feed conversion and the yields of ethene and propene for five model compounds was investigated at a WHSV of 4.2 h^{-1} and an S/O ratio of 0.36.

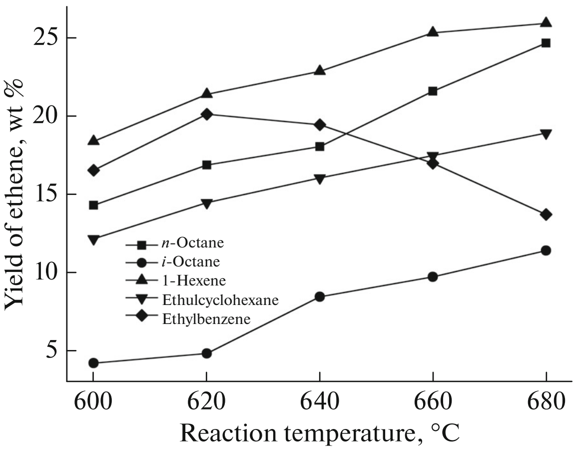

Fig. 1. Effect of reaction temperature on ethene yield (WHSV, 4.2 h^{-1}; S/O ratio, 0.36).

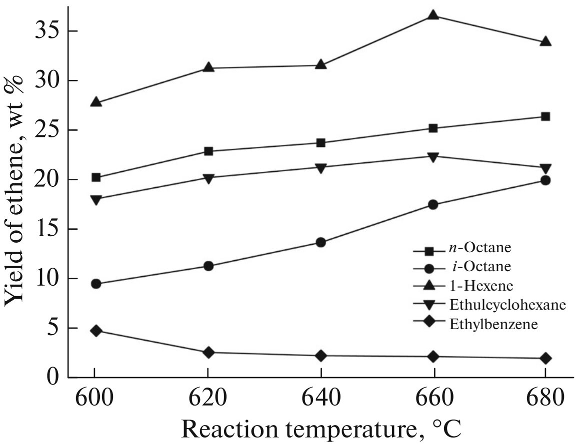

Fig. 2. Effect of reaction temperature on propene yield (WHSV, 4.2 h^{-1}; S/O ratio, 0.36).

With increased reaction temperature, the conversion of n-octane, i-octane, ethylcyclohexane and ethylbenzene increased continuously and reached 97.6, 62.2, 89.2 and 97.8% at 680°C, respectively. Ethylbenzene conversion was high since the cracking reaction of ethylbenzene can take place easily, generating benzene and ethene [35]. The conversion of 1-hexene was high and increased slightly with increased reaction temperature; it approached 100% above 660°C. The rank order of the conversion of the different model compounds was: 1-hexene > *n*—octane > ethylbenzene > ethylcyclohexane > *i*-octane.

The effect of reaction temperature on ethene yield is shown in Fig. 1. With increased reaction temperature, the ethene yield of 1-hexene, n-octane, i-octane and ethylcyclohexane increased continuously, reaching 26.0, 24.7, 11.4 and 18.9 wt % at 680°C, respectively. The ethene yield of ethylbenzene passed through a maximum of 20.2 wt % at 620°C because the side chain scission generating benzene and ethene was the main reaction at a low reaction temperature. Additionally, the secondary reaction degree of ethene increased at a high reaction temperature, resulting in decreased ethene yield. The ethene yield rank order of different model compounds was: 1-hexene > *n*-octane > ethylcyclohexane > *i*-octane.

Figure 2 shows the influence of reaction temperature on propene yield. The propene yield of n-octane and i-octane increased continuously with increased reaction temperature, reaching 26.3 and 19.9 wt % at 680°C, respectively. The propene yield of 1-hexene and ethylcyclohexane passed through a maximum of 36.5 and 22.3 wt % at 660°C, respectively, because secondary reactions of propene intensified at a high reaction temperature. The propene yield of ethylbenzene decreased continuously, and the maximum value was only 4.6 wt % at 600°C. In the catalytic cracking of ethylbenzene, ethene yield was much higher than propene yield, which indicated that the main reaction was the side chain scission generating benzene and ethene. In addition, propene was formed by the secondary reactions of ethene polymerization and then cracking. The rank order of the propene yield of the different model compounds was: 1-hexene > *n*-octane > ethylcyclohexane > *i*-octane > ethylbenzene.

The effect of reaction temperature on the yield of ethene plus propene is shown in Fig. 3. With increased reaction temperature, the yield of ethene plus propene of n-octane, i-octane and ethylcyclohexane increased continuously, reaching 51.0, 31.3 and 40.1 wt % at 680°C, respectively. The yield of ethene plus propene of 1-hexene and ethylbenzene passed through a maximum of 61.9 wt % at 660°C and 22.6 wt % at 620°C, respectively. The rank order of the yield of ethene plus propene of the different model compounds was: 1-hexene > *n*-octane > ethylcyclohexane > *i*-octane. 1-Hexene had the best cracking performance among all model compounds. Ethylbenzene conversion was high, but the yield of ethene plus propene was low. This finding indicated that more by-products were formed when aromatic hydrocarbons were used as feedstocks and that secondary reactions intensified with increased temperature.

The liquid products of *n*-octane were mainly *n*-alkanes, alkenes and aromatics. N-Alkanes were mainly non-cracked feedstock. Alkenes were mainly pentene and hexene. Aromatics were mainly benzene, toluene and xylene. The monomolecular reaction generating octyl carbenium ion was the main reaction in *n*-octane cracking process. The β-cleavage reaction of octyl carbenium ion occured generating alkenes. Secondary reactions such as hydrogen transfer and aromatization occured for small molecular alkenes. The aromatization reactions of different octyl carbenium ions could also occur generating the corresponding aromatics. Therefore, the yields of alkenes and aro-

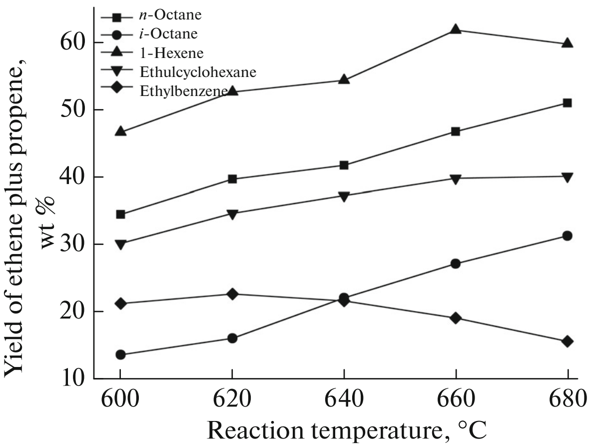

Fig. 3. Effect of reaction temperature on the yield of ethene plus propene (WHSV, 4.2 h^{-1}; S/O ratio, 0.36).

matics in the liquid products of *n*-octane were relatively high. The liquid products of *i*-octane were mainly non-cracked feedstock. With increased reaction temperature, the yield of *i*-octane in the liquid products decreased continuously, which indicated that the cracking ability of *i*-octane enhanced gradually with increased reaction temperature. The liquid products of 1-hexene were mainly aromatics and alkenes. The aromatics were mainly toluene and C_8 aromatics. The alkenes were mainly pentene and hexene. According to the analysis of cracking products of 1-hexene, both the monomolecular reaction and bimolecular reaction occured in 1-hexene cracking process. With increased reaction temperature, the yield of aromatics in liquid products decreased, which indicated that the bimolecular reaction degree of 1-hexene decreased with increased reaction temperature. The liquid products of ethylcyclohexane were mainly naphthenes, alkenes and aromatics. Naphthenes were mainly non-cracked feedstock. Alkenes were mainly pentene. Aromatics were mainly benzene, toluene and xylene. The ring opening reaction generating octyl carbenium ion was the main reaction in ethylcyclohexane cracking process. The cracking and aromatization reactions of octyl carbenium ion occured generating pentene, aromatics, et al. The liquid products of ethylbenzene were mainly aromatics, whose relative content was over 97%. The aromatics were mainly benzene and unreacted ethylbenzene. The molar ratio of benzene to ethene in cracking products of ethylbenzene was close to 1 at low reaction temperature. With increased reaction temperature, the molar ratio of benzene to ethene increased, reaching 1.7 at 680°C. The liquid product group compositions of different model compounds at 600°C are shown in Table 2.

2.2. Effect of WHSV on Cracking Performance

The influence of WHSV on ethene and propene yields in the catalytic cracking of model compounds was investigated at a reaction temperature of 660°C and an S/O ratio of 0.36.

Figure 4 shows the effect of WHSV on ethene yield. With increased WHSV, the ethene yield of 1-hexene, *n*-octane, *i*-octane and ethylcyclohexane decreased continuously, reaching 25.4, 21.6, 9.7 and 17.5 wt % at 4 h^{-1}, respectively. WHSV can reflect the contact time between the feedstock and catalyst. For high WHSV, the reaction extent of the feedstock is small. The above results indicated that low WHSV was conducive to the conversion of the mentioned model compounds into ethene; however, the ethene yield of ethylbenzene increased continuously, reaching 19.4 wt % at 6.79 h^{-1}. This showed that large WHSV was beneficial to the cracking of ethylbenzene to ethene. The ethene yield rank order of different model compounds was: 1-hexene > *n*-octane > ethylcyclohexane > *i*-octane. It was consistent with the rank order of ethene yield of different model compounds at different reaction temperatures.

The effect of WHSV on propene yield is shown in Fig. 5. With increased WHSV, the propene yield of n-octane, ethylcyclohexane, and so-octane decreased continuously, reaching 25.1, 22.3, and 17.4 wt % at 4 h^{-1}, respectively. And the propene yield of n-octane and ethylbenzene varied slightly at approximately 25 and 2 wt %, respectively. The above results indicated that low WHSV was conducive to the conversion of the mentioned model compounds into propene. In addition, the ethene yield of ethylbenzene was higher than the propene yield under different WHSV, which indicated again that the side chain scission generating benzene and ethene was the main reaction in the catalytic cracking of ethylbenzene. With decreased WHSV, the

Table 2. Liquid product group compositions of different model compounds at 600°C

Model compounds	Relative content, wt %				
	n-paraffins	*i*-paraffins	olefins	naphthenes	aromatics
n-Octane	53.0	2.5	13.9	0.7	29.9
1-Hexene	1.4	2.5	18.1	1.1	77.0
Ethylcyclohexane	1.5	2.1	8.9	46.1	41.4
Ethylbenzene	0.7	0.2	1.6	0.1	97.5

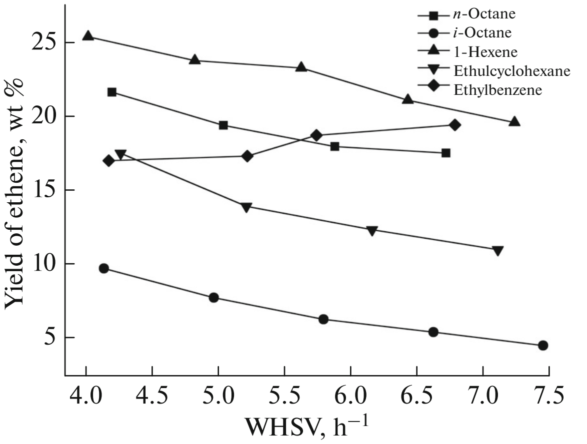

Fig. 4. Effect of WHSV on ethene yield (reaction temperature, 660°C; S/O ratio, 0.36).

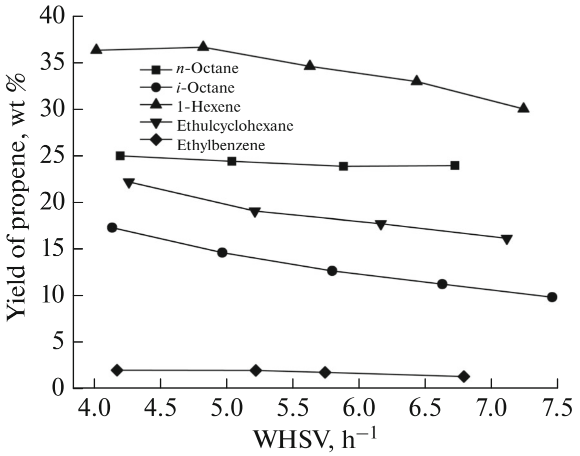

Fig. 5. Effect of WHSV on propene yield (reaction temperature, 660°C; S/O ratio, 0.36).

propene yield of 1-hexene passed through a maximum of 36.8 wt % at 4.82 h^{-1}, which indicated that the yield of propene as the primary product increased firstly and then decreased with increased reaction time because the secondary reaction of propene intensified. Appropriate increase of WHSV could shorten the contact time between the primary product and catalyst, thereby reducing the occurrence of the secondary reaction. Therefore, for 1-hexene, it was necessary to control WHSV at the appropriate level in order to obtain high propene yield. The rank order of the propene yield of the different model compounds was: 1-hexene > *n*-octane > ethylcyclohexane > *i*-octane > ethylbenzene. It was consistent with the rank order of propene yield of different model compounds at different reaction temperatures.

Figure 6 shows the influence of WHSV on the yield of ethene plus propene. With increased WHSV, the yield of ethene plus propene of 1-hexene, *n*-octane, *i*-octane and ethylcyclohexane decreased continuously, reaching 61.9, 46.7, 27.1 and 39.8 wt % at 4 h^{-1}, respectively. This indicated that the mentioned model compounds cracking ability to light olefins was reduced under high WHSV because the contact time between the feedstock and catalyst decreased. The yield of ethene plus propene of ethylbenzene increased slightly, reaching 20.8 wt % at 6.79 h^{-1}. This showed that with increased WHSV, the ethylbenzene cracking ability to light olefins was improved, although the improvement was not obvious. Compared with the other model compounds, the ethylbenzene cracking ability to light olefins was bad. The rank order of the yield of ethene plus propene of the different model compounds was: 1-hexene > *n*-octane > ethylcyclohexane > *i*-octane. It was consistent with the rank order of the yield of ethene plus propene of different model compounds at different reaction temperatures.

3. CONCLUSIONS

(1) The conversion of each model compound increased continuously with increased reaction temperature. The conversion of 1-hexene was the highest, and that of *i*-octane was the lowest among the five model componds.

(2) With increased reaction temperature, the yield of ethene plus propene of *n*-octane, *i*-octane and ethylcyclohexane increased continuously, while that of 1-hexene and ethylbenzene passed through maximum.

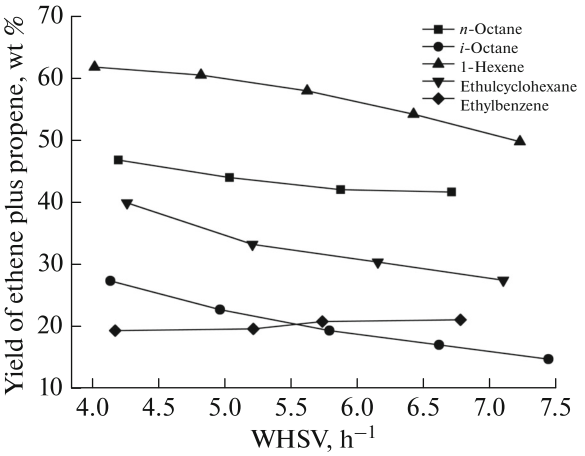

Fig. 6. Effect of WHSV on the yield of ethene plus propene (reaction temperature, 660°C; S/O ratio, 0.36).

(3) With increased WHSV, the yield of ethene plus propene of 1-hexene, *n*-octane, *i*-octane and ethylcyclohexane decreased continuously, and that of ethylbenzene increased slightly.

(4) 1-Hexene exhibited good cracking performance, followed by *n*-octane and ethylcyclohexane; *i*-octane and ethylbenzene exhibited poor cracking performance.

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