Catal Lett (2008) 126:378–382
DOI 10.1007/s10562-008-9636-9

Conversion of *n*-Octene over Nanoscale HZSM-5 Zeolite

Huayun Long · Xiangsheng Wang ·
Wanfu Sun · Xinwen Guo

Received: 12 May 2008 / Accepted: 31 August 2008 /

Abstract Transformation of *n*-octene has been investigated over nanoscale HZSM-5 at different reaction temperature and contact time. The results show that the main reaction was isomerization of *n*-octene over 200 °C. Hydrogen transfer reaction also occurred at 200 °C, but the products were alkanes and cycloolefins instead of aromatics. The aromatization was promoted by high temperature. The maximum selectivity of *i*-paraffins occurred between 300 and 350 °C. Propene, butene and pentene were the primary cracking products. These olefins were oligomerized and cracked to produce a wide distribution of olefins with different carbon atoms. These intermediates then were quickly transformed into aromatics and alkanes by hydrogen transfer over acid sites at high reaction temperature. Propane and butane can be transformed into methane and ethane at long contact time above 400 °C.

Keywords *n*-Octene · Nanoscale HZSM-5 · Reaction temperature · Contact time · Reaction pathway

H. Long · X. Wang (✉) · X. Guo
Department of Catalytical Chemistry and Engineering,
Dalian University of Technology, Dalian 116012,
People's Republic of China
e-mail: wxsdw137@163.com

H. Long
e-mail: longhy@126.com

X. Wang
State Key Laboratory of Fine Chemicals, Dalian University
of Technology, Dalian 116012, People's Republic of China

W. Sun
Fushun Research Institute of Petroleum and Petrochemicals,
Fushun 113001, People's Republic of China

1 Introduction

The rapid development of automotive transportation has brought into question the great increase of fuel consumption and air pollution caused by automobile emissions. In China, approximately 80% of gasoline comes from FCC processes in which the olefin content is usually as high as 50–65 vol.%. The high olefin content of gasoline causes serious automobile emission problem. To reduce the content of olefin and simultaneously preserve the octane number of gasoline, olefins can be converted into aromatics and/or isoparaffins to compensate the loss of octane number in gasoline [1, 2].

Although lower alkanes and alkenes aromatization, such as ethene, propane and propene, have been widely studied over HZSM-5 [3–5] and metal-based ZSM-5 type zeolites viz. Zn/HZSM-5 [6], GaMFI [7, 8] and H-GaAlMFI [9, 10], studies covering the influence of reaction temperature and space velocity on the product distribution in the conversion of larger olefins over HZSM-5 zeolite are scarce. The main components of olefins in FCC gasoline are C_5–C_8 olefins. To understanding the process of FCC gasoline olefins reduction, it is, therefore, important to know the effect of temperature and space velocity on the conversion of these olefins over HZSM-5 zeolite.

In the previous study [11], we have investigated the effect of crystal granularity of HZSM-5 on the decrease of olefins in FCC gasoline and found that the nanoscale HZSM-5 is the most effective catalyst. The better reaction performance of the nanoscale HZSM-5 is assigned to the larger external surface area and the existence of the secondary pores [12] which increases the ability of the zeolite to resist coking during the reaction.

The transformation of olefins over HZSM-5 involves a sequence of following important reactions: oligomerization, cracking, isomerization and hydrogen transfer, etc. The thermodynamic feasibility of these reactions is expected to be controlled by the reaction temperature. In the present work, *n*-octene was chosen as a probe molecule and its conversion over nanoscale HZSM-5 was investigated at different temperature. The effect of contact time on product selectivity was also studied. The reaction pathway of the *n*-octene transformation over nanoscale HZSM-5 has been put forth, based on the results observed in the study.

2 Experimental

2.1 Catalyst Preparation

Nanoscale NaZSM-5 zeolite was synthesized by the hydrothermal crystallization from a gel consisting of sodium silicate, aluminium sulphate, butylamine, sulfuric acid and deionized water in a stainless autoclave at 170 °C for 30 h [13]. The NaZSM-5 was exchanged with 0.4 N ammonium nitrate solution at ambient temperature for 2 h (three times) to convert into NH_4ZSM-5 form. After the exchange, the zeolite was dried at 100 °C for 10 h and calcined at 540 °C for 4 h to obtain the H-form. The catalyst was pressed without any binder and crushed to 10–20 mesh before loading into the reactor.

2.2 Catalyst Characterizations

The crystal size and morphology of nanoscale HZSM-5 were determinated on a JEOL JSM-6700F Scanning Electron Microscope (SEM). The ratio of Si/Al was measured by Elemental analyses (XRF) performed on the Bruker SRS 3400 spectrometer. Nitrogen adsorption and desorption isotherms were measured on Quantachrome Autosorb-1 sorption analyzer.

2.3 Catalytic Reaction

The conversion of *n*-octene was carried out in a continuous flowing fixed-bed reactor under 1.5 MPa. The catalyst (0.5 g) was loaded in the center of the reactor. The molar ratio of N_2/*n*-octene was 4.2. The experimental data, avoiding the catalyst deactivation, were obtained by passing the *n*-octene over a fresh catalyst for a short period (5 min). The absence of catalyst deactivation in the experiment was confirmed by repeating the experiment. The products were analyzed by an online GC with an OV101 capillary column (50 m) connected to a FID. The conversion and selectivity were obtained from the product compositions as following:

$$\begin{aligned} &n\text{-Octene conversion } (\%) \\ &\quad = 100\text{-wt}\% \text{ of } n\text{-octene in the products.} \end{aligned}$$

$$\text{Products selectivity } (\%) = [\text{wt}\% \text{ of a particular product in the products}/(100\text{-wt}\% \text{ of } n\text{-octene in the products})] \times 100.$$

3 Results and Discussion

3.1 Characterizations of Catalysts

Figure 1 was the SEM photograph of the nanoscale HZSM-5 which showed that the crystal size of HZSM-5 was 70–100 nm. The molar ratio of Si/Al obtained by XRF was 14.6. The structure characteristics of the nanoscale HZSM-5 zeolite were presented in Table 1. Nanoscale HZSM-5 has a larger external surface area than traditional microscale HZSM-5 zeolite and the percentage of external surface area reaches 25%.

3.2 Effect of Reaction Temperature on the Conversion of *n*-Octene

Transformation of *n*-octene was carried out over the nanoscale HZSM-5 at several reaction temperatures. The results are presented in Figs. 2–4 and Table 2. The conversion of *n*-octene is nearly 100% for temperature above 250 °C as a result of the high activity of the nanoscale HZSM-5 and the high reactivity of *n*-octene. As showed in Fig. 2 and Table 2, lots of olefins are detected and the main components are isomers of *n*-octene at 200 °C. This

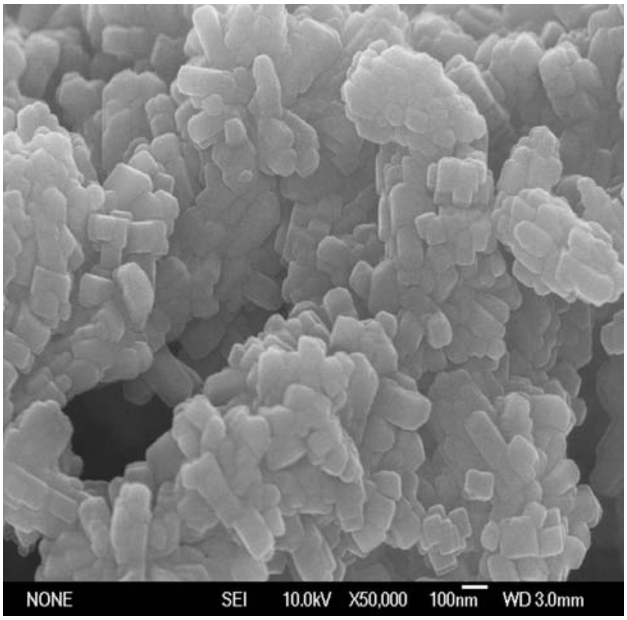

Fig. 1 SEM image of nanoscale HZSM-5

Table 1 Structure characteristics of the nanoscale HZSM-5 zeolite

Sample	SSA ($m^2\ g^{-1}$)	External area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)
Nanoscale ZSM-5	398	100	0.40	0.13

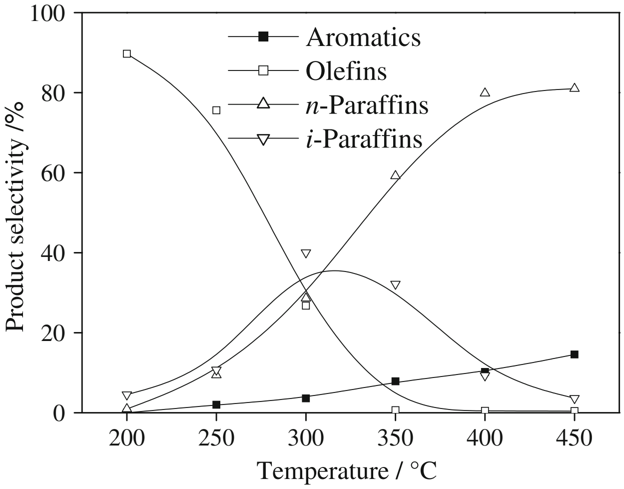

Fig. 2 Effect of temperature on the product distribution of *n*-octene reaction over nanoscale HZSM-5

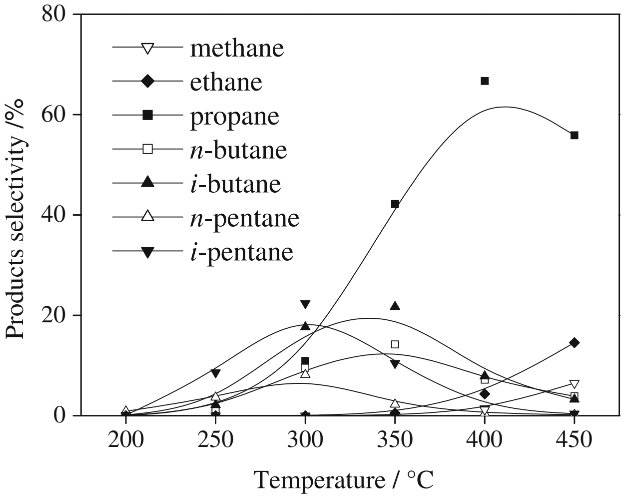

Fig. 3 Effect of temperature on the paraffins distribution

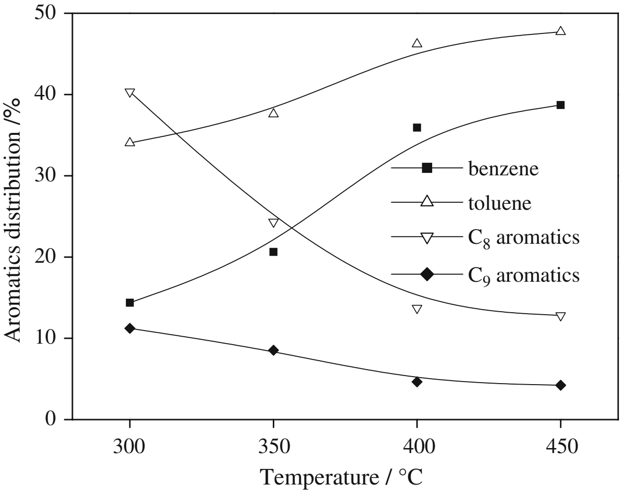

Fig. 4 Effect of temperature on the aromatics distribution

Table 2 Effect of temperature on the olefins distribution

T/°C	$C_3^=$	$C_4^=$	$C_5^=$	$C_6^=$	$C_7^=$	$C_8^=$
200	0.7	2.0	2.7	3.7	5.9	83.9
250	3.3	17.6	20.4	12.7	11.0	13.1
300	2.0	9.8	9.0	2.9	1.8	1.2

demonstrates the main reaction is double bond isomerization and skeletal isomerization of *n*-octene at low temperature. The selectivities of double bond and skeletal isomers reach 42% and 28%, respectively. This shows the double bond isomerization is dominant at low reaction temperature. A small amount of propane and butane are also observed. These alkanes are the products of hydrogen transfer reactions. It is worth noticing that no aromatics but cycloolefins are detected in the products. The selectivity of the cycloolefins is 10%. The results of TPD of benzene over HZSM-5 showed the initial desorption temperature of benzene was found to be ca. 150 °C [14]. It shows that the above observation of no aromatics in the products can not be ascribe to the spatial constraints of HZSM-5 zeolite [15]. These observations implicate that hydrogen transfer reaction can occur at relatively low temperature and the formation of alkanes are accompanied by that of non-aromatics, hydrogen-deficient species (cycloolefins). These intermediates can not be transformed into aromatics further at low reaction temperature, which in accord with previously reported paper [14]. At 250 °C, the cracking and oligomerization of olefins are dominant which results in a wide distribution of olefins in the products as shown in Table 1. With the increase of the reaction temperature, the content of olefins decreases sharply and that of aromatics increases obviously. The selectivity of *i*-paraffins firstly increases and then decreases while that of *n*-paraffins increases with the temperature.

The effect of reaction temperature on the distribution of paraffins is shown in Fig. 3. The most predominant alkane

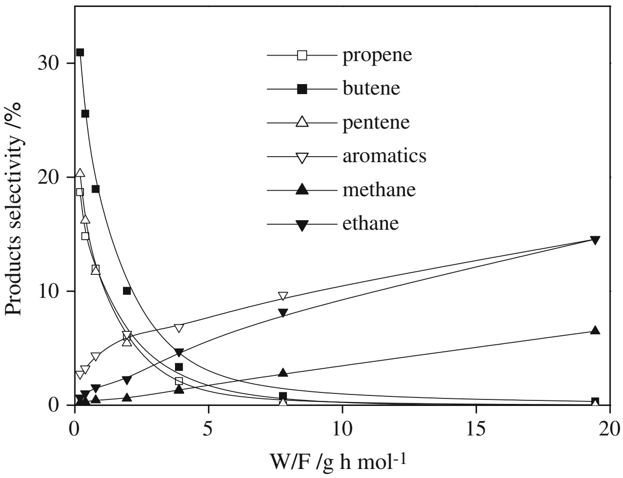

Fig. 5 Effect of contact time on the products distribution over nanoscale HZSM-5 at 450 °C

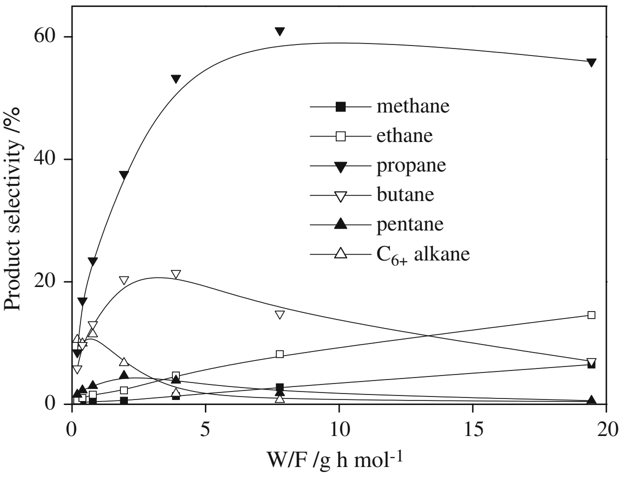

Fig. 6 Effect of contact time on the paraffins distribution over nanoscale HZSM-5 at 450 °C

product above 350 °C is propane, of which selectivity decreases at higher temperature. This indicates that propane once formed can react further at higher temperature. The selectivities of methane and ethane, the most unfavorable products, are negligible below 350 °C and increase sharply when the reaction temperature reaches 400 °C. The selectivities of C_4 and C_{5+} paraffins have maxima and decline faster at higher reaction temperature. The maximum selectivity of *i*-paraffins occurs between 300 and 350 °C. The influence of reaction temperature on the aromatics distribution is presented in Fig. 4. The primary aromatics products are toluene and C_8 aromatics. The selectivities of benzene and toluene increase with the increase of the reaction temperature.

3.3 Effect of Contact Time on Product Distribution

To understand the reaction pathway of *n*-octene transformation, the reaction is carried out over different contact time at 450 °C. The results are shown in Figs. 5–6, where the selectivities of products are plotted as a function of contact time.

At high space velocity, the main products are propene, butene and pentene. The selectivities of these alkenes decrease sharply with the increase of the contact time. No much ethene is observed at low contact time. That means ethene is not a main cracking product of *n*-octene. A small amount of isomers of *n*-octene is also detected. As shown in Fig. 4, contact time has different influence on the distribution of paraffins. The most predominant alkane product is propane. Its selectivity decreases at lower space velocity which shows propane can react further at long contact time. At high space velocity, the formation of alkanes with four and five carbon atoms is appreciable. These alkanes decline with decreasing the space velocity, indicating that their transformation to smaller molecules by cracking is very fast at long contact time. Actually, the selectivities of methane and ethane increase with contact time and reaches 21.1% at $W/F = 19.4$ g h mol^{-1}. It is evident that aromatics are not primary products, since the selectivity of aromatics increases with the increase of the contact time and reaches 14.6% at $W/F = 19.4$ g h mol^{-1}.

3.4 Reaction Path of *n*-Octene Over Nanoscale HZSM-5

Based on the observations a simplified reaction pathway of *n*-octene transformation over nanoscale HZSM-5 is summarized as follows. At 200 °C, the main reaction is the isomerization of *n*-octene including double bond and skeletal isomerization. Low olefins are the cracking products of octene isomers. The oligomerization of these low olefins results in a wide distribution of olefins. The products of hydrogen transfer reaction among olefins are alkanes and cycloolefins. Above 250 °C, cycloolefins can be transformed into aromatics further by hydrogen transfer reaction. The primary aromatics products are toluene and C_8 aromatics. With the increase of the reaction temperature, the selectivities of benzene and toluene increase while those of C_8 and C_9 aromatics decrease. Propane and butane can be transformed into methane and ethane at long contact time above 400 °C.

4 Conclusions

The influences of temperature and contact time on the olefin reaction over nanoscale HZSM-5 are investigated using *n*-octene as a probe molecule. The isomerization of *n*-octene is dominant at low temperature during its conversion over nanoscale HZSM-5. Hydrogen transfer reactions occur at 200 °C, but the products of which are cycloolefins instead of aromatics. These intermediates can not be transformed into aromatics further at low reaction temperature. The selectivity of aromatics increases with the reaction temperature while that of *i*-paraffins firstly increases and then decreases. The maximum selectivity of *i*-paraffins occurs between 300 and 350 °C. The primary aromatics products are toluene and C_8 aromatics. The selectivities of benzene and toluene increase with the increase of the reaction temperature. Propene, butene and pentene are the cracking products. These olefins are oligomerized and cracked to produce a wide distribution of olefins with different carbon atoms. These intermediates then are quickly transformed into aromatics and alkanes by hydrogen transfer over acid sites at high reaction temperature. Propane and butane can be transformed into methane and ethane at long contact time above 400 °C.

Acknowledgment The financially support of China Petroleum & Chemical Corporation (104002) is gratefully acknowledged.

References

1. Hu YK, Zhao LP, Li Y, Zhou Y, Guo HC (2004) J Nonfer Metals (China) 14:317
2. Fan Y, Bao X, Lei D, Shi G, Wei W, Xu J (2005) Fuel 84:435
3. Gnep NS, Doyemet JY, Seco AM, Ribeiro FR, Guisnet M (1987) Appl Catal 35:93
4. Lukyanov DB, Gnep NS, Guisnet MR (1994) Ind Eng Chem Res 33:223
5. Lukyanov DB, Gnep NS, Guisnet MR (1995) Ind Eng Chem Res 34:516
6. Anunziata OA, Pierella LB, Orio OA (1991) React Kinet Catal Lett 43:67
7. Giannnetto G, Montes A, Gnep NS, Florentino A, Cartraud P, Guisnet M (1993) J Catal 145:86
8. Choudhary VR, Sivadinarayana C, Kinage AK, Devadas P, Guisnet M (1996) Appl Catal A 136:125
9. Choudhary TV, Kinage A, Banerjee S, Choudhary VR (2006) J Mol Catal 246:79
10. Choudhary VR, Banerjee S, Panjala D (2002) Microporous Mesoporous Mater 51:203
11. Zhang PQ, Wang XS, Guo HC (2003) J Dalian Univ Technol (China) 43:571
12. Zhang WP, Han XW, Liu XC, Lei H, Liu XM, Bao XH (2002) Microporous Mesoporous Mater 53:145
13. Wang XQ, Wang XS, Guo XW (2000) C.N. Patent. 1,240,193
14. Song YQ, Zhu XX, Xu LY (2006) Catal Commun 7:218
15. Schulz H, Wei M (2004) Stud Surf Sci A Catal Part C 2133