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Conversion of light paraffins for preparing small olefins over ZSM-5 zeolites

Linsheng Wang [1], Maosong Xie and Longxiang Tao

Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
PO Box 110, Dalian 116023, PR China

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The conversion of C_3–C_9 paraffins to small olefins over ZSM-5 zeolite is investigated. The small olefins are primary products and are usually converted into other more stable secondary products such as aromatics on the ZSM-5 zeolites. Thermally treated HZSM-5, K/HZSM-5 and Ba/HZSM-5 catalysts were developed and favourable oxidative conditions were introduced for the conversion process to maximize selective conversion of light paraffins to small olefins at the relatively low temperature of 873 K. The role of K and Ba is to minimize bimolecular hydrogen transfer reactions and enhance the dehydrogenation activity of the catalysts. Meanwhile, the oxygen in the gas phase is effective to improve the olefin selectivity and yield. C_2–C_4 olefin selectivities of 70.4 and 66.8% have been obtained for propane and *n*-hexane feedstocks, respectively, at a temperature of 873 K.

Keywords: ZSM-5 zeolites; light paraffins; small olefins; selectivity; cracking

1. Introduction

The small olefins are valuable materials which find increasing usage in the chemical industry. They are usually obtained from the pyrolysis of various hydrocarbon feedstocks at high temperature. The high temperature required for the reaction causes many problems [1]. Recently, several studies concerning the production of light olefins via the catalytic cracking of hydrocarbons over oxides supported by refractory oxides have been reported [2–9], but the reaction temperature required is still very high (1022–1173 K). A bifunctional synthetic mordenite (containing Cu, Ag, Co) zeolite type catalyst was proposed by Pop et al. for hydrocarbon pyrolysis [10]. For *n*-butane feedstock the selectivity of small olefins can be up to 55.9% with conversion of 49.4% at a relatively low temperature of 923 K. Small olefins also are partially available from the FCC process of cracking heavier petroleum fractions. It is reported that the olefin to paraffin ratio of the cracking gas can be

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[1] To whom correspondence should be addressed.

improved by the addition of ZSM-5 zeolite to Y-type zeolite catalysts [11]. However, the FCC process is limited for the light paraffin feedstocks because the cracking of the light paraffins under the FCC conditions is very difficult. Over the past years, the catalytic conversion of light paraffins into aromatics over ZSM-5 type zeolites has been extensively studied and the Cyclar process has been developed [12]. It is well known that the formation of aromatics is initiated by the formation of small olefins. The small olefins are difficult to make and secondarily converted into more stable aromatics. Hitherto, little attention has been paid to the ZSM-5 zeolites which are suitable for the selective conversion of light paraffins to small olefins. Recently, considerable efforts have been made for the cracking of light paraffins over zeolite catalysts. The cracking of light paraffins over NaK eronites [13], HZSM-5 [14], and aluminosilicates [15] has been reported. The authors only concerned about cracking activity of the zeolites, but little attention was paid to small olefin selectivity. Most of the cracking products over the zeolites are saturated hydrocarbons. In the present paper, some means for inhibiting H-transfer activity and enhancing the dehydrogenation activity of ZSM-5 zeolite catalysts, and favourable oxidative conditions for light paraffin conversion, were applied to maximize the olefin selectivity and yield. Some factors controlling and improving the selectivity of small olefin products have been revealed.

2. Experimental

2.1. CATALYST PREPARATION

The ZSM-5 zeolites were supplied by Nankai University and are commercially available ($SiO_2/Al_2O_3 = 25, 38, 50$). Firstly, the ZSM-5 zeolites were converted into their ammonium forms (NH_4ZSM-5) by repeated ion exchange (four times) with 1 N NH_4NO_3 aqueous solution at about 368 K for 1 h. They were then dried at 383 K for 4 h. HZSM-5 catalysts were prepared by calcining NH_4ZSM-5 at 773 K for 4 h. M/HZSM-5 ($M = K, Ba$) were prepared by impregnating NH_4ZSM-5 with the nitrate aqueous solution of M, then drying at 383 K for 4 h and calcining at 773 K for 4 h. Finally, the catalysts were pressed, crushed and sorted into sizes of 10–30 mesh.

2.2. CATALYTIC TESTS

The catalytic tests were performed with 1–2 g catalyst placed in a fixed bed continuous-flow stainless steel reactor. The catalyst zone was heated under an air stream to 773 K and held at 773 K for 0.5 h and then heated to reaction temperature. At reaction temperature, the stream was switched from air to paraffin feeds. Gaseous feeds were introduced into the catalyst bed through a flowmeter with carrier gas. Liquid feeds were supplied by a pump and gasified in a preheater and then introduced with carrier gas into the reactor. Paraffin feed/carrier gas (mol.) = 1 : 0.9. Products were withdrawn periodically from the outlet of the reactor and analyzed by on-line gas chromatography. The products were separated on two parallel columns: a 6 m long squalane column and a 1 m long TDX column with a TCD. The conversion and the selectivity were calculated on carbon number basis.

2.3. MATERIALS

The feedstocks are pure C_3–C_9 paraffins with over 98% purity.

3. Results and discussion

3.1. THE CONVERSION OF LIGHT PARAFFINS OVER PROTONIC ZSM-5 (HZSM-5)

The conversion of *n*-hexane and propane was carried out over HZSM-5 and thermally treated HZSM-5 under various conditions. The results are demonstrated in tables 1 and 2. It is shown in table 1 that very little small olefins can be produced over HZSM-5 at the relatively low temperature of 673 K. The olefin selectivity and olefin/paraffin ratio were drastically increased with the reaction temperature. The saturation of small olefins in cracking products is mainly attributed to bimolecular hydrogen transfer reaction [16], which results in the formation of aromatics and small paraffins. Hydrogen transfer is exothermic because of the formation of aromatics and the cleavage of the C–C bond is endothermic, thus with increasing temperature, the cracking rate to H-transfer rate ratio is increased [17] and the olefin selectivity and the olefin/paraffin ratio are enhanced. Moreover, much higher olefin selectivity and olefin to paraffin ratio are obtained over thermally treated HZSM-5. The role of thermal treatment is to isolate adjacent acid sites and inhibit the bimolecular hydrogen transfer reaction. Table 2 shows the results for propane conversion over the thermal treated HZSM-5 when oxygen is present and absent, in

Table 1
Conversion of *n*-hexane over HZSM-5 [a]

Reaction temperature (K)	Pretreatment	Conversion (%)	Selectivity (%)					O/P [b]
			C_2H_4	C_3H_6	C_4H_8	$C_2^=$–$C_4^=$	Ar	$C_2^=$–$C_4^=$ / C_2^0–C_4^0
673	–	76.5	1.2	0.9	3.9	6.0	3.8	0.07
773	–	93.8	7.3	8.1	4.4	19.8	8.5	0.28
873	–	100.0	17.5	11.7	3.7	32.9	19.2	0.82
873	1123 K for 1 h	84.7	16.9	20.0	9.2	46.0	11.6	1.2
873	1023 K for 7.5 h	100.0	24.0	21.6	8.2	53.7	0	1.4

[a] Weight space velocity (WSV) = 10 h^{-1}, SiO_2/Al_2O_3 of HZSM-5 = 50.
[b] Olefin/paraffin ratio.

Table 2
Conversion of propane over thermally treated HZSM-5[a]

Carrier gas N_2/O_2	Conversion (%)	Selectivity (%) $C_2^=$–$C_4^=$	Product distribution						
			CO_x	CH_4	$C_2^=$	C_2^0	$C_3^=$	$C_4^=$	C_4^0
1/0	31.4	56.7	0	29.6	39.8	13.4	12.7	3.8	0.6
5/1	36.3	64.8	5.2	11.5	41.5	16.2	17.9	5.5	1.4

[a] Reaction temperature = 873 K, WSV = 5.7 h^{-1}, SiO_2/Al_2O_3 = 50.

the gas phase. The selectivity of small olefins for the catalytic conversion of propane at 873 K under non-oxidative conditions is up to 56.7%, which can be compared to that for the propane pyrolysis at 1113–1143 K in table 3. Under oxidative conditions the olefin selectivity and propane conversion can be further improved and the formation of methane is greatly minimized. The role of oxygen in the gas phase is to promote dehydrogenation and cleavage of the C–C bond. At least one third of products for the direct cracking of propane is methane. When oxygen is present in the gas phase, the cracking of propane most possibly proceeds through the dehydro-dimerization process. Therefore, methane is diminished and olefin selectivity is high.

3.2. CONVERSION OF LIGHT PARAFFINS OVER K AND Ba LOADED ZSM-5

The results for the conversion of *n*-hexane over K and Ba loaded ZSM-5 are demonstrated in tables 4 and 5 respectively. The data shows that the enhanced small olefin selectivity can be obtained over K/HZSM-5 and Ba/HZSM-5, and the formation of aromatics is reduced. The selectivity of small olefins increases with increasing loadings of K and Ba, however high K-loading may render catalyst activity to be reduced, but high Ba-loading (up to 16%) has little effect on the catalyst activity. Therefore, the high yield of small olefins is obtained over Ba/HZSM-5 zeolites. The ion exchange properties of ZSM-5 were studied by Matthews et al. [18]. It was observed that univalent K can be more easily exchanged into the ZSM-5 framework than divalent Ba. K exchanged into the framework partially to poison B-acid sits of HZSM-5 as reported by Nicolaides et al. [19]. As a result, some adjacent acid sites are isolated and bimolecular hydrogen transfer reaction is inhibited. Moreover, the effects of oxygen in the gas phase on the conver-

Table 3
Production distribution from propane pyrolysis[a]

Temperature (K)	Conversion (%)	Selectivity (%) $C_2^=$–$C_4^=$	Product distribution						
			CH_4	$C_2^=$	C_2^0	$C_3^=$	$C_4^=$	C_4^0	others
1113–1143	90.8	55.2	26.4	38.0	6.4	16.1	1.1	0.03	12

[a] According to the data in ref. [22].

Table 4
Conversion of *n*-hexane over K/HZSM-5 [a]

K content (%)	Conversion (%)	Selectivity (%)					Olefin/paraffin $C_2^=-C_4^=/C_2^0-C_4^0$
		$C_2^=-C_4^=$	Ar	C_2H_4	C_3H_6	C_4H_8	
0	100	32.9	19.2	17.5	11.7	3.7	0.8
0.5	100	44.7	7.2	20.8	17.4	6.5	1.1
1.5	91.3	50.5	3.4	18.3	22.3	9.9	1.3
2.0	75.0	57.7	1.1	16.1	28.0	11.2	1.5

[a] Reaction temperature = 873 K, WSV = 10 h^{-1}, carrier gas: N_2.

sion of light paraffins over K/HZSM-5 and Ba/HZSM-5 are shown in table 6. The conversion of light paraffin and the light olefin yield are improved by the presence of oxygen in the gas phase. The dehydrogenation and cleavage of C–C bonds are promoted under oxidative conditions. Thus, the conversion of light paraffins and the olefin selectivity are increased. The results for the conversion of C_3–C_9 paraffins over thermally treated K/HZSM-5 under oxidative conditions are summarized in table 7. It indicates that paraffin conversion and olefin yield are increased with the increase of the carbon chain length of feed paraffins. Higher olefin selectivity (70.4%) for propane conversion under the given conditions is obtained, which is much higher than that for propane pyrolysis (55.2%). The very stable catalyst can be obtained by metal ion modification and thermal pretreatment of ZSM-5. The conversion and the olefin selectivity exhibit very good maintenance with time on stream. Table 8 lists the results of *n*-hexane conversion over thermally treated K/HZSM-5 in 20 h.

3.3. CHARACTERIZATION OF THE ROLE OF K AND Ba BY THE CYCLOHEXENE MODE REACTION

The effects of K and Ba loaded in ZSM-5 on dehydrogenation and hydrogen transfer activity of catalysts are characterized by using the mode reactions [20] of cyclohexene. The results are given in table 9. Cyclohexene can be converted to ben-

Table 5
Conversion of *n*-hexane over Ba/HZSM-5 [a]

Ba content (%)	Conversion (%)	Selectivity (%)					Olefin/paraffin $C_2^=-C_4^=/C_2^0-C_4^0$
		$C_2^=-C_4^=$	Ar	C_2H_4	C_3H_6	C_4H_8	
2	100	41.9	4.9	19.7	16.0	6.2	0.9
8	93.4	48.6	3.3	18.2	20.7	9.7	1.0
16	94.4	53.0	3.4	20.7	22.8	9.5	1.3

[a] Reaction temperature = 873 K, WSV = 10 h^{-1}, carrier gas: N_2.

Table 6

Effect of oxygen in the gas phase [a]

Catalyst	Carrier gas N_2/O_2	Conversion (%)	Selectivity (%)						Olefin/paraffin $C_2^=-C_4^=/C_2^0-C_4^0$
			C_2H_4	C_3H_6	C_4H_8	$C_2^=-C_4^=$	Ar	CO_x	
2% K/HZSM-5	1/0	77.2	16.6	27.4	13.2	57.1	0.6	0	1.47
	5/1	81.3	18.5	26.4	12.4	57.3	0.7	1.2	1.54
8% Ba/HZSM-5	1/0	93.4	18.2	20.7	9.7	48.6	3.5	0	1.12
	5/1	95.7	22.5	20.3	7.9	50.7	6.6	0.7	1.48

[a] Reaction temperature = 873 K, WSV = 10 h^{-1}, paraffin feed: *n*-hexane.

Table 7

Conversion results of different paraffin feeds [a]

Paraffin feed	Conversion (%)	Selectivity (%)				Yield of $C_2^=-C_4^=$ (%)
		C_2H_4	C_3H_6	C_4H_8	$C_2^=-C_4^=$	
n-C_3	27.0	45.6	18.5	6.3	70.4	19.0
n-C_5	83.0	24.6	23.5	7.0	55.1	45.8
n-C_7	89.3	21.2	21.9	9.3	52.4	46.8
n-C_9	100	21.4	21.9	9.3	53.1	53.1

[a] Reaction temperature: 873 K, catalyst: thermally treated K(0.5%)/HZSM-5, carrier gas: $N_2/O_2 = 5/1$.

Table 8

Activity and olefin selectivity maintenance of catalyst with time on stream [a]

	Time on stream (h)				
	1	5	10	15	20
n-hexane conversion (%)	55.2	56.2	64.1	63.3	58.5
$C_2^=-C_4^=$ selectivity (%)	66.1	66.6	66.8	66.5	66.5
CO_x selectivity (%)	1.2	1.2	0.9	0.8	0.9

[a] Catalyst: thermal treated K(0.5%)/HZSM-5, carrier gas: $N_2/O_2 = 5/1$, reaction temperature: 873 K, WSV = 10 h^{-1}.

Table 9

Effect of K and Ba loaded in ZSM-5 on H-transfer and dehydrogenation activity of cyclohexene [a]

Catalyst	Conversion (mol%)	Selectivity (mol%)		Reaction fraction (mol%)	
		cyclohexane	benzene	H-transfer	dehydrogenation
HZSM-5	23.5	49.6	50.4	74.4	25.6
Ba/HZSM-5	24.4	29.0	71.0	43.5	56.5
K/HZSM-5	40.5	2.5	97.5	3.8	96.2

[a] Reaction temperature = 523 K, WSV = 10 h^{-1}, cyclohexene/N_2 = 1/0.9.

zene by dehydrogenation and can be converted to cyclohexane and benzene by bimolecular hydrogen transfer reaction in a parallel way,

$$3\,\text{cyclo-C}_6\text{H}_{10} \left\{ \begin{array}{ll} \longrightarrow 3\text{C}_6\text{H}_6 + 6\text{H}_2 & (1) \\ \longrightarrow 2\,\text{cyclo-C}_6\text{H}_{12} + \text{C}_6\text{H}_6\,. & (2) \end{array} \right.$$

The fractions of reactions (1) and (2) can represent dehydrogenation and hydrogen transfer activity respectively. According to (1) and (2), the fraction of dehydrogenation = benzene selectivity $- \frac{1}{2}$cyclohexane selectivity, and the fraction of H-transfer = 1 − dehydrogenation fraction. Table 9 shows that K and Ba loaded in HZSM-5 can enhance the dehydrogenation activity and inhibit the H-transfer activity, which is responsible for the saturation of small olefins and the formation of aromatics [21]. Therefore, the selectivity of small olefins can be greatly improved by K and Ba modification of HZSM-5.

4. Conclusion

Thermally treated HZSM-5, K and Ba modified HZMS-5 exhibit a potential to be applied in producing small olefins from light paraffins. The selectivity and the yield of small olefins can be enhanced under oxidative conditions. K and Ba loaded in HZSM-5 can enhance the dehydrogenation activity and inhibit the bimolecular hydrogen transfer activity of the catalysts.

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