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Butene catalytic cracking to propene and ethene over potassium modified ZSM-5 catalysts

Xiangxue Zhu[a,b], Shenglin Liu[a,b], Yueqin Song[a,b], and Longya Xu[a,b,*]

[a]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 110, 116023, P. R. China*
[b]*Graduate School of Chinese Academy of Sciences, P. R. China*

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Catalytic cracking of butene over potassium modified ZSM-5 catalysts was carried out in a fixed-bed microreactor. By increasing the K loading on the ZSM-5, butene conversion and ethene selectivity decreased almost linearly, while propene selectivity increased first, then passed through a maximum (about 50% selectivity) with the addition of ca. 0.7–1.0% K, and then decreased slowly with further increasing of the K loading. The reaction conditions were 620 °C, WHSV 3.5 h^{-1}, 0.1 MPa 1-butene partial pressure and 1 h of time on stream. Both by potassium modification of the ZSM-5 zeolite and by N_2 addition in the butene feed could enhance the selectivity towards propene effectively, but the catalyst stability did not show any improvement. On the other hand, addition of water to the butene feed could not only increase the butene conversion, but also improve the stability of the 0.7%K/ZSM-5 catalyst due to the effective removal of the coke formed, as demonstrated by the TPO spectra. XRD results indicated that the ZSM-5 structure of the 0.07% K/ZSM-5 catalyst was not destroyed even under this serious condition of adding water at 620 °C.

KEY WORDS: butene; catalytic cracking; K modification; propene; ethene; ZSM-5 catalyst.

1. Introduction

Propene is one of the fastest growing petrochemicals, driven primarily by the high growth rate of polypropene [1,2]. Traditional methods for propene production cannot meet the growing demand of propene [3]. For example, the production of the co-producing propene from steam cracking is determined largely by the feed state, and most of the new steam cracking capacity is based on ethane feed, which produces little propene [3]. In FCC units, propene is obtained with a relatively low yield, and increasing of the yield has been proven to be expensive and limited [4,5]. Another two on-purpose propene technologies are available, such as propane dehydrogenation and metathesis of ethene and butene, but both of them have seen only limited applications, which depend especially on feedstock economics [1,2,6]. An alternative process is the catalytic cracking of C_4+ alkenes to propene and ethene, of which the feed can be any hydrocarbons containing sufficient amounts of C_4+ alkenes, such as steam cracker by-products, low-value FCC refinery streams, catalytically cracked naphthas and light gasolines, etc. [7–11].

Several patents have been applied on the technology of catalytic cracking of C_4+ alkenes, most of which were carried out on high-silica ZSM-5 zeolites (for example, $Si/Al_2 > 300$) [1,2,4–6]. As the acidities of the high-silica ZSM-5 zeolites are relatively weak, high selectivities of propene and ethene can be achieved along with a suppression of the secondary reactions, mainly the hydrogen transfer reaction of alkenes and the dehydro-cyclization-aromatization of their oligomers to form low carbon alkanes and aromatics. In the literature, studies on the modification of catalyst acidity have been widely reported [12–14], and it is well known that impregnation with an alkali metal ion will result in the poisoning of the zeolite acid sites. However, in the catalytic cracking of C_4+ alkenes to propene and ethene, the effect of alkali metal ion impregnation of ZSM-5 zeolites has not been reported so far. In the present work, we have studied the acidity of the ZSM-5 ($Si/Al_2 = 50$), and its poisoning to different degrees by varying the loadings of potassium ions, and then used the potassium modified ZSM-5 catalysts for butene catalytic cracking.

During the catalytic cracking of hydrocarbons, the major cause for catalyst deactivation is the formation of coke which covers the acid sites or blocks the pores of the catalysts. It has been reported that coke formation can be reduced by means of adding some CO_2 and O_2 to the feed stream, resulting in an improvement of the catalytic performance of the catalyst [15–17]. Analogous to CO_2, H_2O may also be a good reagent that removes coke accumulation on the zeolite catalyst by the reforming reaction ($H_2O + CH\chi$ ($\chi = 0$–4) $= CO + H_2$). However, the addition of water may destroy the structure of the zeolite at high temperatures [18]. In this paper, we also studied the effect of water addition into

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* To whom correspondence should be addressed.
E-mail: lyxu@dicp.ac.cn

the feed on the performance of a 0.7%K/ZSM-5 catalyst in the process of butene catalytic cracking. In addition, the XRD technique was used to determine the structure of the ZSM-5 zeolite before and after the reactions.

2. Experimental

2.1. Catalyst preparation

The HZSM-5 sample, binded with 30 wt% alumina, was obtained from Fushun Petroleum Company, CNPC ($Si/Al_2 = 50$ in the pure HZSM-5 zeolite). The potassium-impregnated HZSM-5 catalysts were prepared by a wet incorporation technique with an aqueous solution of KNO_3 of appropriate concentration at room temperature in vacuum, followed by drying at 120 °C and calcination at 550 °C for 3 h. Hereafter, the K/ZSM-5 catalysts are designated as χK/ZSM-5, where χ is the K loading in weight percent. All the catalysts were crushed and sieved to 20–40 mesh particles before use for butene catalytic cracking.

2.2. Catalyst characterization

The acidities of the catalysts were determined by the NH_3-TPD technique. The sample (0.14 g) was loaded into a stainless steel and U-shaped microreactor and pretreated at 550 °C for 0.5 h in a flowing He. After the pretreatment, the sample was cooled to 150 °C and saturated with NH_3 gas. When the baseline of the gas chromatograph was stable, NH_3-TPD was carried out under a constant flow of He (20 mL/min) from 150 to 650 °C at a heating rate of 18 °C/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatograph with a TCD.

The acid types of the samples were determined by pyridine adsorption using FT-IR spectroscopy. Room-temperature IR spectra were recorded with a Nicolet 710 FT-IR spectrometer from zeolite wafers (10 mg cm^{-2}) mounted in a vacuum cell. Pretreatment of zeolites was performed in the cell at 500 °C and vacuum for 1 h. For the adsorption/desorption studies, pyridine vapor was adsorbed onto the zeolite. The excess of pyridine was removed in vacuum over two consecutive (1 h) periods of heating at 150 and 350 °C, each of them followed by IR measurements.

Powder XRD measurements were performed to identify the component phases as well as to determine the degree of crystallinity of the catalyst. X-ray powder diffraction patterns of the samples were recorded on a Rigaku D/Max RB diffractometer using Cu K_α radiation, operating at 40 kV and 50 mA, with a scanning speed of 8°/min.

Characterization of the coke deposited on the catalysts was conducted by the temperature-programmed oxidation (TPO) method. A catalyst was loaded to a U-type quartz microreactor and pretreated in a helium flow at 500 °C for 30 min to remove the adsorbed water. After that, the temperature was decreased from 500 to 150 °C under flowing He. When the baseline was stable, the helium flow was switched to a flow of 2% O_2 and 98% He at a flow rate of 40 mL/min, with temperature increment of 4 °C/min. The oxidation products (CO_2, CO and H_2O) were monitored by an on-line mass spectrometer.

2.3. Catalytic experiment of butene cracking

Catalytic cracking of butene over the zeolite catalysts was carried out in a plug-flow continuous stainless steel reactor (i.d. 7 mm) provided with a thermocouple in the center of the catalyst bed, using 1-butene (>99.5% pure) as the feed. The catalyst was pretreated at 550 °C for 1 h under a high purity nitrogen flow before starting a reaction run. Then 1-butene and/or nitrogen were passed through the reactor at the desired temperature. If necessary, 1-butene was passed through a water bubbler and fed into the reactor. The bubbler was thermostated at 33, 61, and 76 °C, which will give 5, 20, 40 vol% of water vapor in the feed of butene plus steam at 0.1 MPa, respectively, if thermally equilibrated. In fact, the real concentration of water was 4.7, 19 and 37% after correction when temperatures of the bubbler were kept at 33, 61, and 76 °C, respectively. The reaction products were analyzed by an on-line Varian 3800 gas chromatograph with a 100-m PONA capillary column and a FID.

3. Results and discussion

Butene catalytic cracking is a complicated process, besides the reaction that butene converts to propene and ethene, other reactions can also take place, such as hydrogen transfer, oligomerization, isomerization, aromatization and protolytic cracking. Especially, 1-butene can isomerize rapidly on the zeolite catalyst to *cis*- and *trans*-2-butene isomers, as well as to *i*-butene [19]. Thus, besides ethene and propene, CH_4, C_2H_6, C_3H_8, C_4H_{10}, aromatics, and C_5+ aliphatic hydrocarbons were also formed in the process. For simplicity, we grouped all the types of butene as the feed. And conversion is defined as: Conversion = (C_4H_8% in the feed − C_4H_8% in the products)/(C_4H_8% in the feed). The selectivity of a particular C_xH_y is defined as: $S_{C_xH_y} = (C_xH_y\%$ in the products$)/(\sum C_iH_j\%$ in the products), where all percentages are in weight percent.

3.1. Reaction performance of χK/ZSM-5 catalysts in butene catalytic cracking

The X-ray diffraction patterns for the potassium-impregnated catalysts do not show any appreciable change from that of the parent ZSM-5 sample, which implies that, up to 2 wt% potassium loading, there is no loss of crystalinity of the catalysts due to potassium impregnation. Also no new XRD pattern appears in the potassium-impregnated catalysts, indicating that potassium is well dispersed on the catalysts [12].

The effect of potassium introduction on the catalyst acidity was investigated by means of the NH_3-TPD technique, and the results are shown in figure 1. There are two desorption peaks on the ZSM-5 catalyst, one centers at about 250 °C and the other at about 450 °C, corresponding to the weak and the strong acid sites of the zeolite, respectively. By increasing the K loadings, the amounts of both the strong and weak acid sites over the ZSM-5 show an obvious decrease, and the former changes more apparently than the latter. It should be noted that the strong acid sites are almost absent and only the weak acid sites remain in the catalyst whose K loading is 2.0 wt%. This is consistent with the observations of [13].

The Brönsted and Lewis acidity of the samples have been determined by pyridine adsorption using FT-IR spectroscopy. Figure 2a represents the IR spectra of pyridine adsorption on HZSM-5 catalysts with different K contents. Upon pyridine adsorption at room temperature and outgassing at 150 °C, absorption bands associated with the chemisorbed pyridine were observed at 1547, 1491, and 1454 cm^{-1}. According to previous reports on the IR studies in the pyridine chemisorption [20,21], the pyridine band at 1547 cm^{-1} is assignable to pyridinum ions and the band at 1454 cm^{-1} to Lewis acid-coordinated pyridine, respectively. The band at 1491 cm^{-1} consists of bands due to the Brönsted and

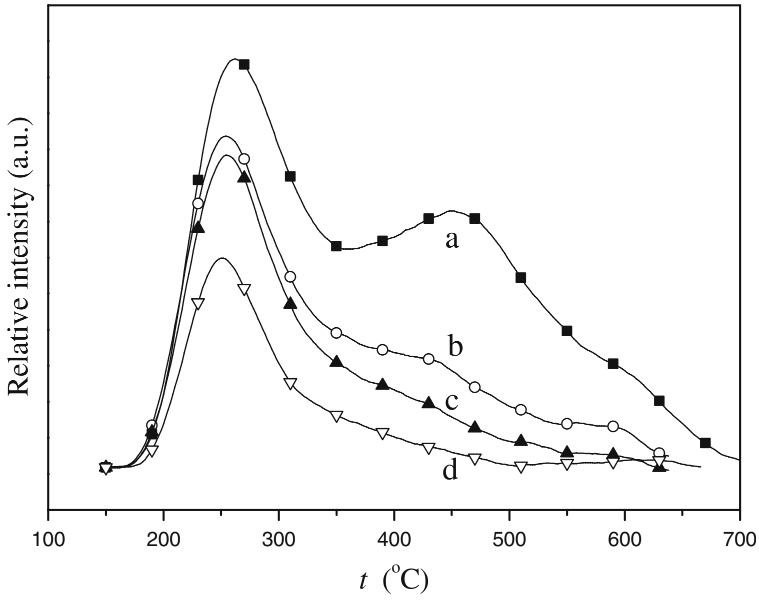

Figure 1. TPD profiles of χK/ZSM-5 samples. (a) ZSM-5; (b) 0.7%K/ZSM-5; (c) 1.0%K/ZSM-5; (d) 2.0%K/ZSM-5.

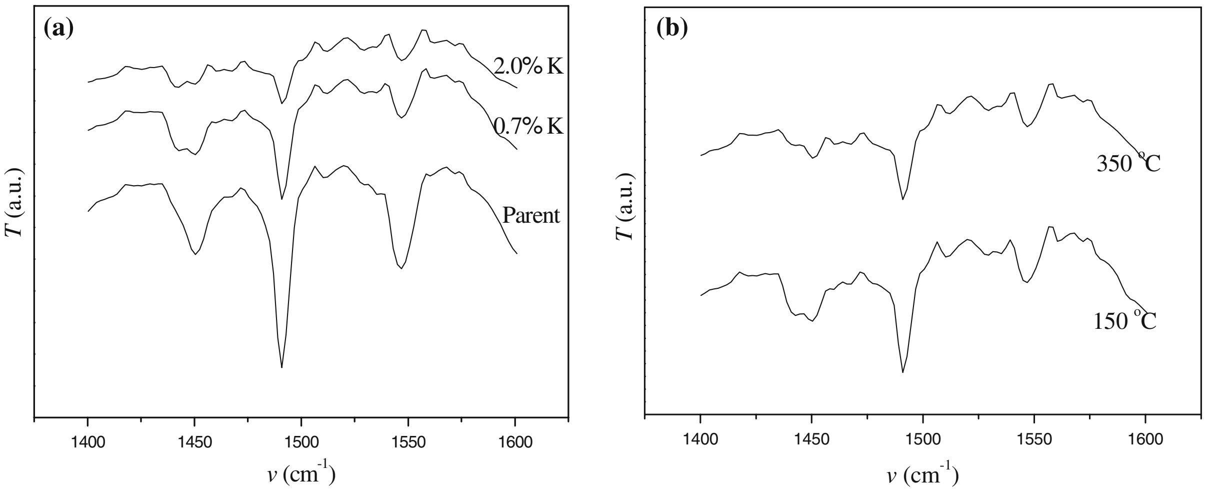

Figure 2. IR spectra of pyridine adsorption on χK/ZSM-5 zeolites (a) Upon outgassing at 150 °C with the samples of K content 0, 0.7 and 2.0%. (b) Upon outgassing at 150 and 350 °C the sample of K content 0.7%.

Lewis sites. From figure 2a it can be seen that with increasing the K content of the ZSM-5 samples from 0% to 2.0%, both the amount of Brönsted acid sites and the amount Lewis acid sites decrease apparently. Moreover, of all the samples, when increasing the outgassing temperature from 150 to 350 °C, the amount Brönsted acid sites shows only a slight decrease, indicating that most of their Brönsted acid sites belong to strong acid sites, while only a small part of the Lewis acid-coordinated pyridine retained at the same time (illustrated by the IR spectra of a sample of 0.7%K/ZSM-5 as shown in figure 2b).

Evaluations of butene conversion, selectivities and yields of propene and ethene relative to the potassium loadings are shown in figure 3a. Thermal conversion of butene was very low and could be neglected under these conditions. By increasing the K loadings on the ZSM-5, butene conversion and ethene selectivity decreased almost linearly, whilst the selectivity of propene first increased, passed through a maximum (about 50%) at ca. 0.7–1.0% K addition, and then decreased slowly with further increasing of the K loadings. Similar trend as the propene selectivity existed for the propene yield (Y C_3H_6), as shown in figure 3a.

Besides ethene and propene, the selectivities of the by-products also changed with the K loadings on the ZSM-5, as shown in figure 3b. When increasing the K loadings, the selectivities of CH_4, C_2H_6, C_3H_8 and

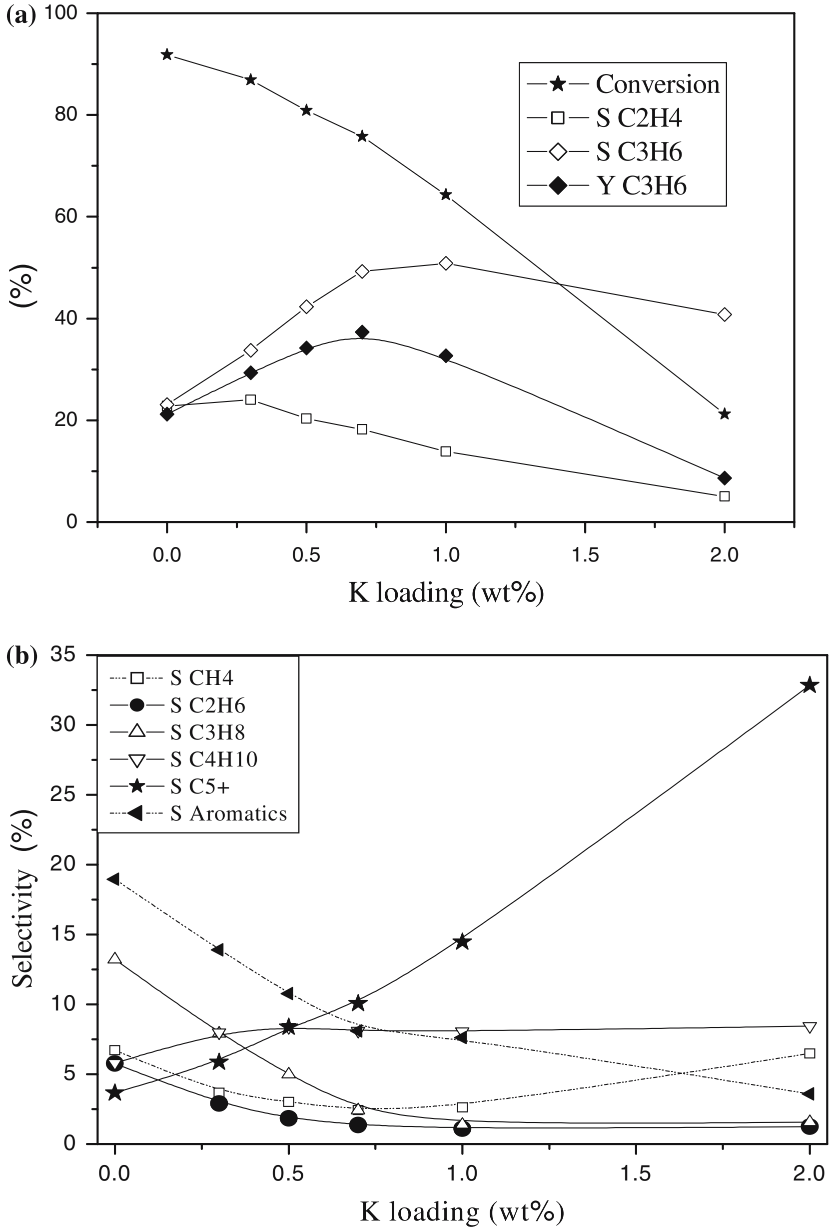

Figure 3. Butene conversion and product distributions on the K-modified ZSM-5 catalysts. Reaction conditions: 620 °C, WHSV of 3.5 h^{-1}, 0.1 MPa of 1-butene pressure and 1 h of time on stream.

aromatics first decreased apparently in the range of 0–0.7%, then decreased slightly upon further increasing of the K loadings, except that the CH_4 selectivity increased slowly, probably due to that the CH_4 selectivity was more influenced by thermal cracking at relatively low conversion levels. Note that the selectivity of C_5+ aliphatic hydrocarbons was apparently enhanced with the increasing of the K loadings, while the C_4H_{10} selectivity was influenced to a smaller extent by the K addition.

According to the above results, a simple reaction pathway for the forming of propene, ethene and the by-products from the catalytic cracking of butene was proposed, as shown in figure 4. First, a $[C_4]^+$ carbenium, formed by the adsorbed butene molecules on the acid sites of the catalysts, dimerizes with another butene molecule to form the $[C_8]^+$ carbenium intermediate, then the intermediate cracks to a propene and a $[C_5]^+$ carbenium *via* the β-scission mechanism (figure 4 (1)). Of course, part of the intermediates may also be converted to aromatics by dehydro-cyclization (figure 4 (2)). The $[C_5]^+$ carbenium so formed can further crack to propene and ethene (figure 4 (3)), or can desorb as $C_5^=$hydrocarbons (figure 4 (4)). The $[C_8]^+$ carbenium, on the other hand, can further oligomerize with a butene molecule to form $[C_{12}]^+$, then the $[C_{12}]^+$ carbeniums can be converted to low molecular hydrocarbons by reactions of cracking, aromatization, etc. Whilst the hydrogen transfer reaction can occur on all alkenes to form the corresponding alkanes and aromatics. CH_4 and C_2H_6 are mainly produced by the dealkylation of the formed aromatics, as well as by protolytic cracking and pyrolysis of the hydrocarbons in the process [22–24].

By considering the product distributions and the K loadings on ZSM-5 zeolite, there exists a relationship between the performance and acidity of the catalysts. As is well known, hydrocarbon cracking is an acidity-controlling reaction. Therefore, butene conversion will decrease with the increasing of the K loadings on the ZSM-5 zeolite. Starting from the parent ZSM-5 to the 0.7%K/ZSM-5, i.e., by decreasing the acidity of the catalyst (figure 1), the formation of aromatics and C_3H_8 (figure 4, (5) and (6)) decreased obviously due to the suppression of the alkenes aromatization and the hydrogen transfer reaction of propene, as the two reactions were more favored on high acidity catalysts [25]. As a result, the selectivity of propene increased apparently.

Relative to the oligomerization of $C_4^=$ to $[C_8]^+$ and their further cracking to propene and $[C_5]^+$, the cracking of $[C_5]^+$ are less energetically favored due to the formation of primary carbenium ions. When the K loadings on the ZSM-5 zeolite was above 1.0%, although the hydrogen transfer and alkene aromatization reaction were further suppressed, the acidity of the catalyst was not strong enough to cause the cracking of $[C_5]^+$ to propene and ethene to occur sufficiently (figure 4, (3)), and a large part of which desorbed as $C_5^=$. Thus, high selectivity of C_5+ aliphatic hydrocarbon, of which $C_5^=$ is the major component, appeared on the 2.0%K/ZSM-5 zeolite catalyst, accompanied by a decrease in propene selectivity, as shown in figure 3a. When the K loadings were between 0.7% and 1.0%, the catalyst possessed suitable acidity both for the cracking of $[C_5]^+$ to propene and ethene and for the effective suppression of the hydrogen transfer and aromatization reaction of alkenes.

3.2. *Influence of reaction conditions on the catalytic performance of 0.7%K/ZSM-5*

Besides the acidity, the performance of the catalyst also depends on the reaction conditions, *viz*., reaction temperature, butene WHSV and butene partial pressure. As the 0.7%K/ZSM-5 catalyst exhibited the best performance in enhancing propene selectivity and yield, it was chosen for studying the effect of reaction conditions on the performance of the catalyst.

3.2.1. *Influence of temperature on the performance of 0.7%K/ZSM-5*

The effect of temperature on butene conversion and product distribution is shown in table 1. Changing the temperature from 540 to 650 °C caused the butene conversion to increase by only 3%, *viz*., from 76.34% to 79.38%. In the reaction pathway shown in figure 4, the reactions of cracking and cyclization-aromatization are enhanced by increasing the temperature, while the hydrogen transfer reaction of alkenes is suppressed.

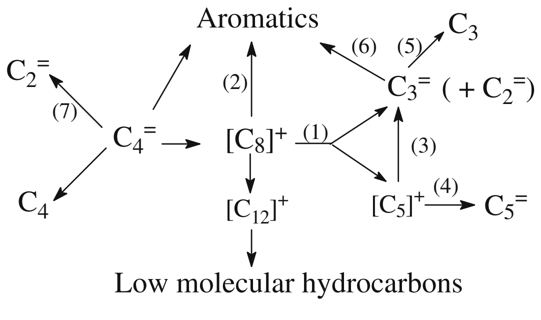

Figure 4. A simple reaction pathway for butene catalytic cracking.

Table 1
Influence of reaction temperature on 0.7%K/ZSM-5 performance

Temperature (°C)	Conversion (%)	Selectivity (%)						
		C_2H_4	C_3H_6	$CH_4+C_2H_6$	C_3H_8	C_4H_{10}	C_5+	Aromatics
540	76.34	13.28	38.90	1.40	6.25	13.93	20.36	5.80
580	77.50	17.49	42.75	2.38	4.60	10.85	13.6	8.34
620	77.53	19.25	46.21	3.70	2.54	9.54	7.66	11.08
650	79.38	21.51	45.35	5.28	1.70	8.35	4.4	13.37

Reaction conditions: WHSV of 3.5 h^{-1}, 0.1 MPa 1-butene pressure and 1 h of time on stream.

These two factors will lead to the fact that butene conversion will be influenced only to a small degree by the temperature. However, the product distribution was apparently influenced by the temperature, as shown in table 1.

As the aromatics dealkylation and the protolytic cracking of hydrocarbons would be enhanced by increasing the temperature, the selectivity of CH_4 plus C_2H_6 increased obviously when the temperature changed from 540 to 650 °C, while those of C_3H_8 and C_4H_{10} decreased apparently owing to the suppression of the hydrogen transfer reaction which was exothermic and thermodynamically unfavorable. Although hydrogen transfer was suppressed, dehydro-cyclization-aromatization of the alkenes oligomers was enhanced with the increasing of the temperature. As a result, the selectivity of aromatics increased with the temperature [23,24]. The increasing cracking severity with temperature resulted in the going down of the selectivity of the C_5+ aliphatic hydrocarbons, as shown in table 1.

Similarly, due to the increasing cracking severity, the ethene selectivity increased steadily with temperature. Besides from the cracking of the C_4 oligomers and other intermediates, ethene can also be produced by the direct cracking of butene, as shown in figure 4.(reaction (7)). Hollander *et al.* [26] has reported that ethene could be formed in the small pores of ZSM-5 from direct cracking of butene/pentene due to the large interaction existed between the adsorbed carbenium ions and the zeolite catalyst, in spite that cracking of butene/pentene was less energetically favorable due to the formation of primary carbenium ions.

The propene selectivity first increased obviously from 38.90% to 46.21% when the temperature was changed from 540 to 620 °C, then the value decreased slightly upon further increasing of the reaction temperature.

According to the product distributions at different temperatures, we can see that higher temperatures (ca. 620 °C) are beneficial for butene conversion and propene/ethene production.

3.2.2. *Influence of the butene WHSV on the performance of 0.7%K/ZSM-5*

Figure 5 shows the effect of 1-butene WHSV on the butene conversion and the selectivities of propene and ethene. By increasing the 1-butene WHSV, butene conversion decreased exponentially, and ethene selectivity

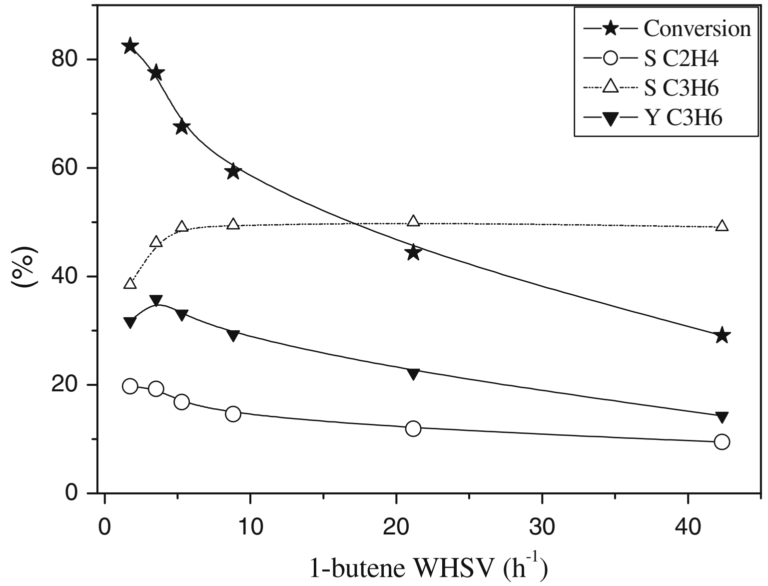

Figure 5. Influence of WHSV on 0.7%K/ZSM-5 performance. Reaction conditions: 620 °C, 0.1 MPa, and 1 h of time on stream.

decreased slowly, while the propene selectivity first increased rapidly from 1.5 to 5.5 h^{-1}, then arrived at a plateau (ca. 50%) between 5.5 and 42 h^{-1}. As a result, the yield of propene first increased with an increasing 1-butene WHSV, then passed through a maximum (ca. 35%) at ca. 3.5 h^{-1}, and decreased slowly with further increasing of the 1-butene WHSV.

As for the other products (not shown here), the selectivities of C_1–C_4 alkanes and aromatics followed similar trends: their selectivities first decreased obviously with the increasing of 1-butene WHSV from 1.5 to 5.5 h^{-1}, then decreased slowly with further increasing of the 1-butene WHSV. All the above results can be explained as follows: the hydrogen transfer reaction and the aromatization reaction, being bimolecular or multiple-step reactions, are more influenced by reducing the contact time with the catalyst [24,27]. In addition, the C_5+ selectivity increased remarkably with the 1-butene WHSV, due to the fact that the contact time was not long enough to let them crack sufficiently.

According to the above results, in order to increase the selectivities and yields of propene and ethene, the butene WHSV should be selected at the range between 3.5 and 5.5 h^{-1} at 620 °C and 0.1 MPa.

3.2.3. *Influence of butene partial pressure on the performance of 0.7%K/ZSM-5*

By fixing the 1-butene flow and changing the N_2 flow in the mixture gas of N_2 and 1-butene, the effect of 1-butene partial pressure on the conversion of the reactant and the selectivities of the products was investigated, as shown in table 2. Butene conversion decreased apparently with the decreasing of the butene partial pressure, due to the fact that dimerization/oligomerization of butene was unfavored by lowering the 1-butene concentration in the feed. Furthermore, low hydrocarbon partial pressures also led to higher dilution of the flowing gas and to higher linear velocities of the reactants and products within the catalyst bed, thus reducing the effective contact time between the hydrocarbons and the catalyst, and this was another reason for the decrement in conversion with decreasing of the 1-butene partial pressure.

With a decreasing of the 1-butene partial pressures, the selectivities of ethene, CH_4 plus C_2H_6, C_3H_8, C_4H_{10} and aromatics all decreased slowly, while the C_5+ selectivity increased apparently. In the meantime, there was a remarkable enhancement in propene selectivity, which can also be explained in terms of the hydrogen transfer reactions, which being bimolecular, were more affected by lowing the reactant concentrations. Furthermore, the decrement in effective contact time and thus the suppression of hydrogen transfer and the aromatization of alkenes as discussed in Section 3.2.2 is another reason for the enhancing of the propene selectivity [27].

According to the above results, the decrement in butene partial pressure suppressed the butene conversion and ethene selectivity, but enhanced the propene selectivity under the conditions of 3.5 h^{-1} of butene WHSV and 620 °C.

3.3. *Influence of steam addition in the feed on the performance of 0.7%K/ZSM-5*

Both K modification (loading of 0.7%K) of the ZSM-5 zeolite and N_2 addition in the butene feed could enhance the selectivity of propene effectively, but the catalyst stability did not show any improvements in butene catalytic cracking (not shown here). However, an obvious difference was observed with the addition of steam to the feed, as shown in figure 6. Contrary to N_2 addition as discussed in Section 3.2.3, steam addition (4.7–37%) enhanced butene conversion by ca. 5%, which was probably due to an acidity enhancement by the adding of steam, since water can regenerate Brönsted acid sites by partial rehydroxylating of the zeolite surface [28], which had been verified by ^{1}H MAS NMR [29]. Also, with the addition of 4.7% water in the butene feed, there was a moderate enhancement in the stability of the 0.7%K/ZSM-5 catalyst, as compared with that of the pure butene feed. By increasing the steam content in the butene feed to 19% and 37%, the stability of the catalyst was markedly improved. For pure butene, butene conversion decreased from 77% to 52% by 25% in 12 h of time on stream on the 0.7%K/ZSM-5, while for the feed with 19% steam added, the butene conver-

Table 2
Influence of butene partial pressure on 0.7%K/ZSM-5 performance

Partial pressure (MPa)	Conversion (%)	Selectivity (%)						
		C_2H_4	C_3H_6	$CH_4+C_2H_6$	C_3H_8	C_4H_{10}	C_5+	Aromatics
0.1	77.53	19.25	46.21	3.70	2.54	9.54	7.66	11.08
0.07	71.39	18.99	49.43	2.77	1.54	8.88	9.00	9.36
0.06	66.07	18.24	50.47	2.65	1.21	8.42	9.81	9.12
0.05	60.46	17.66	53.01	2.29	0.83	7.56	11.44	7.21
0.04	48.56	16.15	52.24	2.43	0.62	7.82	13.79	6.95

Reaction conditions: 620 °C, 1 h of time on stream, 3.5 h^{-1} of 1-butene WHSV.

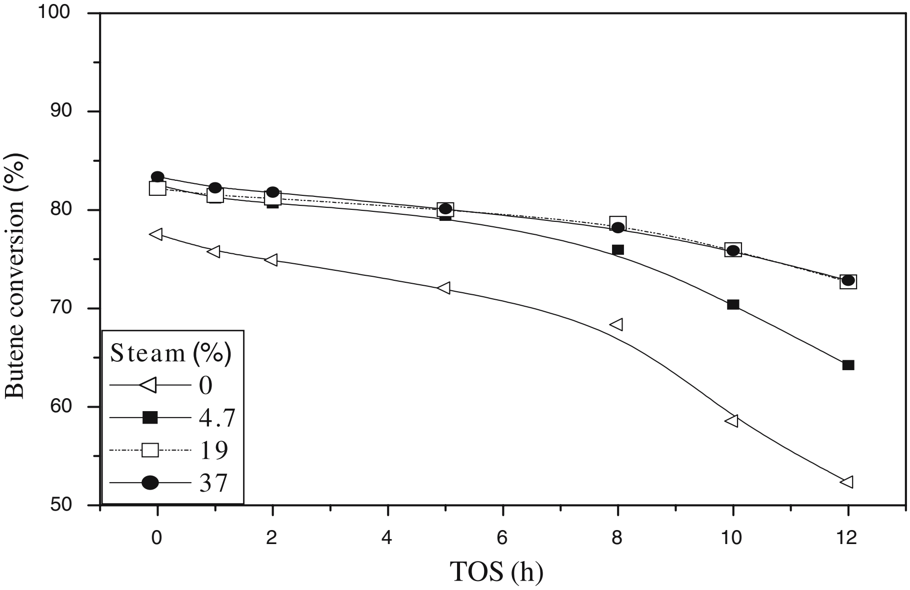

Figure 6. Butene conversion on 0.7%K/ZSM-5 with 0–37% steam in butene feed. Reaction conditions: 620 °C, 3.5 h^{-1} WHSV and 0.1 MPa of total pressure.

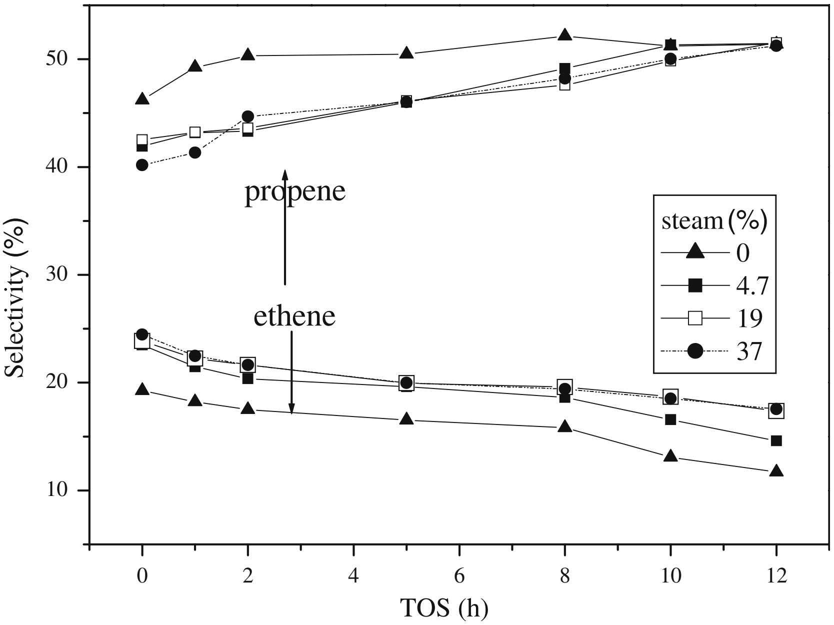

Figure 7. Selectivities of propene and ethene on 0.7%K/ZSM-5 with 0–37% steam in butene feed. Reaction conditions: 620 °C, 3.5 h^{-1} WHSV and 0.1 MPa of total pressure.

sion decreased from 82% to 73%, i.e., only by 9% in 12 h of running time.

Figure 7 shows that the addition of water to the butene feed induced an increase in ethene selectivity. The ethene selectivity changed with time on stream, which was similar to that of the butene conversion, as shown in figure 7. Although the initial propene selectivity decreased somewhat by the addition of steam, it increased slowly as the time on stream was extended. For a time on stream of 12 h, the propene selectivity, no matter there was an addition of water or not, reached to ca. 50%.

The characteristics of coke formed during the reaction on the 0.7%K/ZSM-5 catalyst were evaluated by the TPO technique. Figure 8 shows the TPO spectra as a function of CO formation on the used 0.7%K/ZSM-5, which had reacted at 620 °C for 12 h with various amounts of water added in the reactant flow. The spectra demonstrate that the total amount of coke deposited on the 0.7%K/HZSM-5 catalysts was reduced apparently with the

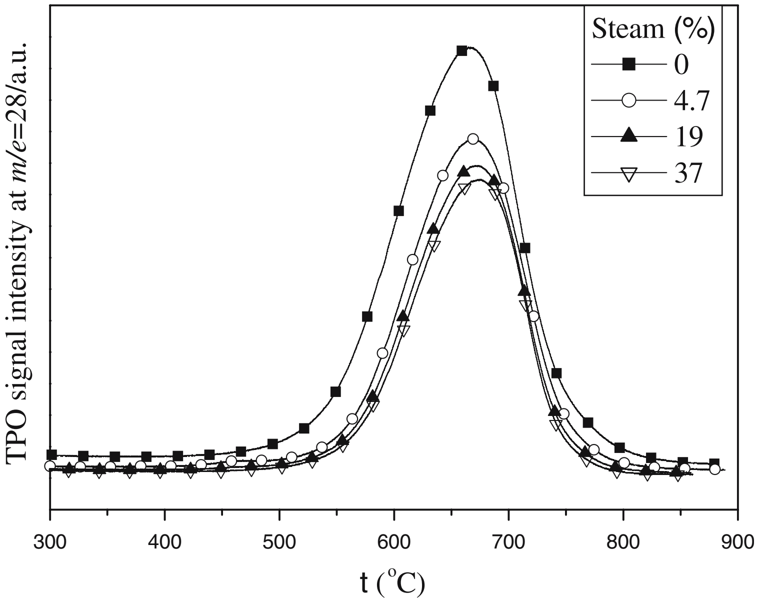

Figure 8. TPO mass spectra at $m/e = 28$ of 0.7%K/ZSM-5 catalyst after the reaction for 12 h with 0–37% steam in butene feed.

addition of water into the butene feed (TPO spectra of CO_2 was just similar to that of CO). The decreasing amount of coke formation by water addition was owing to the effective removal of the surface carbon formed under the reaction conditions [30]. As presented in figures 6 and 8, the stability of the catalyst was not improved with a further increase in water concentration from 19% to 37% in the feed. Also, there was only a slight decrease in the CO TPO spectra in the same range. Both of these results suggested that only part of the coke formed could be removed by the addition of water, and coking was the major cause of catalyst deactivation in the reaction of butene catalytic cracking.

Figure 9 shows the XRD spectra of the 0.7%K/ZSM-5 after the catalytic cracking of butene with or without water in the butene feed. The XRD patterns of all the 0.7%K/ZSM-5 samples are very similar to each other in peak positions and in peak heights, regardless of the concentrations of water (4.7∼37%) in the feed. These results strongly suggest that the ZSM-5 structure had not been destroyed even under such serious conditions of water addition at elevated temperatures.

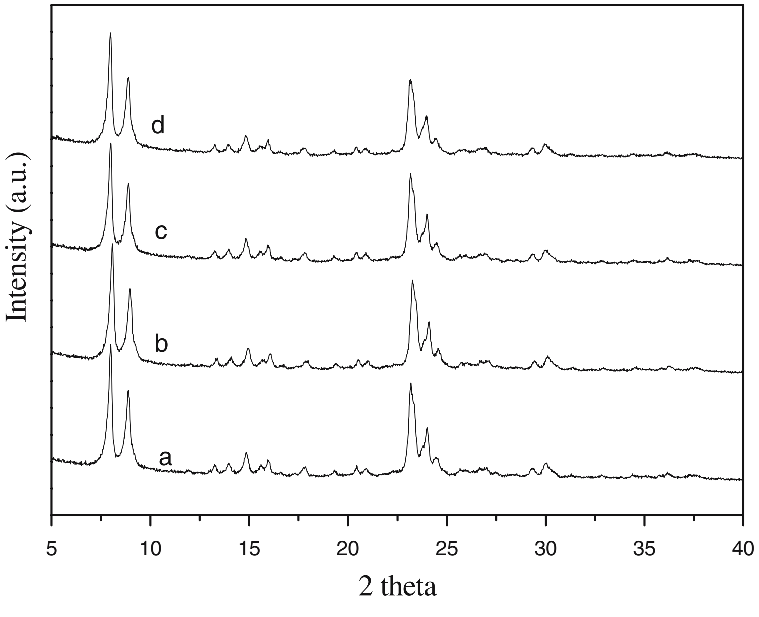

Figure 9. XRD spectra of 0.7%K/ZSM-5 after the reaction for 12 h at 620 °C, under a flowing gas mixture of butene with a: 0, b: 4.7, c: 19, d: 37% of steam.

4. Conclusions

1. There existed a relationship between the performance and the acidity of the χK/ZSM-5 catalysts. Both butene conversion and ethene selectivity decreased with lowering the acidity of the catalyst. K addition up to ca. 0.7~1.0 wt% in the ZSM-5 zeolite could modify the zeolite acidity to an appropriate level for maximizing the yield and selectivity of propene from butene cracking.
2. Butene conversion and product distributions were influenced remarkably by the reaction conditions. The reaction conditions of 620 °C, 3.5~5.5 h^{-1} and 0.05~0.07 MPa were suitable for the production of propene and ethene over the 0.7%K/ZSM-5 zeolite.
3. Steam addition in the butene feed could not only increase the butene conversion, but also could improve the stability of 0.7%K/ZSM-5 catalyst. XRD results indicate that the ZSM-5 structure of the 0.7%K/ZSM-5 was not destroyed even under such serious condition of water addition at 620 °C.

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