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The effect of acidity on olefin aromatization over potassium modified ZSM-5 catalysts

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The transformation of olefin to aromatics over ZSM-5 catalysts with different K-loadings has been investigated both in a continuous flow fixed-bed reactor and in a pulse microreactor. Investigation of variation of olefin aromatization activity with K-loadings shows that strong acid sites are indispensable for the converting of olefin to aromatics. As intermediates of olefin aromatization process, butadiene and cyclopentene not only show much higher aromatization activity than mono-olefins, but also can be transformed into aromatics over relatively weak acid sites of K/ZSM-5. A proposal is put forward, stating that among all the steps experienced in olefins aromatization, the formation of diene or cycloolefin from mono-olefins through hydrogen transfer is the key step and can be catalyzed by strong acid sites.

KEY WORDS: aromatization; zeolite ZSM-5; potassium; acid strength.

1. Introduction

It is well known that the transformation of light hydrocarbon into aromatics over the ZSM-5 catalyst is a complicated acid-catalyzed reaction, which includes oligomerization, cracking, cyclization and hydrogen-transfer. Great interest has been focused on the relationship between the catalyst acidity and its aromatization performance [1–3]. Based on the extent of catalyst poisoning by pyridine, Vikram *et al.* [4] have reported that the extent of aromatization and the distribution of aromatics in butene conversion on the ZSM-5 zeolite depend closely on the strong acid sites. Slinkin [5] observed that the adsorption of 2,4,6-trimethylpyridine over a HZSM-5 did not suppress olefin aromatization due to the dimension of the base molecule, whereas chemisorbed pyridine inhibits the process. Although variation of acidity of ZSM-5 catalyst can be attained by the method of pyridine chemisorption, the chemisorbed molecules will inevitably lead to an increase in the diffusional resistance to the reaction species. In the present work, we investigated in detail the influence of catalyst acidity on aromatization performance of olefins, by introducing potassium into the ZSM-5 catalysts. In addition, we try to elucidate the roles of strong and weak acid sites in the complex aromatization reaction, such as whether or not each step reaction only takes place on the strong acid sites of the K modified HZSM-5 catalysts. The results are reported in this paper.

2. Experimental section

2.1. Catalyst preparation

ZSM-5 zeolite powder with Si/Al molar ratio of 50 (obtained from Fushun catalyst plant) was extruded, with alumina as binder (30 wt%). Then, the extrudate was dried and calcined under flowing air at 550 °C for 5 h to remove the template. The calcined sample was converted into NH_4-form by exchanging with a 0.8 M ammonium nitrate solution for three times at 90 °C. Subsequently, the exchanged sample was washed thoroughly with deionized water to remove the NO_3^- ion and dried 120 °C for 3 h. Finally, the ZSM-5 in NH_4-form was calcined at 530 °C for 3 h to convert into HZSM-5. K/ZSM-5 samples were prepared by impregnating HZSM-5 sample with a KNO_3 solution of appropriate concentration in vacuum, followed by drying and calcination. All the catalysts were crushed and sieved to 20–40 mesh particles before they were loaded into the reactor.

2.2. Catalyst characterizations

XRD: X-ray powder diffraction patterns of the samples were recorded on a Rigaku D/Max RB diffractometer using Ni-filtered CuK_α radiation over 2θ angles ranging from 5 to 40°.

NH_3 temperature programmed desorption (NH_3-TPD): The acidity of the catalysts was determined by NH_3-TPD technique. The sample (0.14 g) was loaded into a stainless U-shaped microreactor and pretreated at 600 °C for 0.5 h in flowing He. After the pretreatment, the sample was cooled to 150 °C and saturated with NH_3 gas. As soon as the baseline in gas chromatograph was stable, the NH_3-TPD was carried out under a

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constant flow of He (20 mL/min) from 150 to 600 °C at a heating rate of 18 °C/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatogram with a TCD.

BET: The specific surface areas of the catalysts were measured by the nitrogen adsorption method (BET method) using NOVA 4000 gas adsorption analyzer (Quantachrome Corp. USA). Each sample was degassed at 350 °C for 3 h under reduced pressure before the measurement.

2.3. Catalytic evaluation

Catalytic reaction was carried out in two modes: continuous flow reaction and pulse reaction. The continuous flow reaction was carried out in a fixed-bed stainless reactor (11 mm i.d.) provided with a thermocouple in the center of the catalyst bed, which represented the reaction temperature. The catalyst was pretreated with a flow of nitrogen at 500 °C for 1 h before the reaction. As the catalyst bed was cooled down to 350 °C, the liquid feed liquefied petroleum gas (LPG) was pumped into the reactor. The reaction conditions were as followed: 350 °C, 0.5 Mpa, 2 h^{-1}. The cooled liquid and gaseous products after 5 h on-stream, were collected and analyzed by Varian-3800 with an FID.

The pulse reaction was performed under atmospheric pressure in a stainless microreactor (i.d = 3 mm, packed with 0.2 g catalyst) with an injection port. Nitrogen was used as carrier gas (flow rate = 20 cm^3 min^{-1}). After the catalyst was pretreated at 500 °C for 0.5 h in nitrogen and cooled down to the reaction temperature (400 °C), a feeding dose of about 0.05 mmol was injected into the microreactor. The products formed were directly detected by an on-line Omnistar mass spectrometer (Blazer Corp, Switzerland).

2.4. Temperature-programmed surface reaction (TPSR)

TPSR was carried out in a stainless U-shaped microreactor, in which the pretreatment condition of the sample was identical to that in the pulse reaction mentioned above. The TPSR differed from pulse reaction in that the catalyst was first saturated with reactant at room temperature and then was heated from room temperature to 500 °C in a nitrogen stream at a heating rate of 10 °C/min. The desorbed products were continuously detected by the Omnistar mass spectrometer.

3. Results and discussion

3.1. Catalyst characterization by XRD, BET and NH_3-TPD

The XRD patterns of the K/ZSM-5 with different potassium loadings are shown in figure 1. An obvious feature is that K_2O crystal phase does not appear and there is almost no decrease in relative crystallinity of the ZSM-5 even if K loading was increased up to 1.9 wt%. This means that K is well dispersed in the ZSM-5. Table 1 presents the dependence of BET specific surface areas of the K/ZSM-5 on K loadings. The specific surface areas of samples decrease somewhat with the increasing of the K-loading. When the K loading was increased up to 1.9 wt%, the surface area changed from 287.2 m^2/g of the HZSM-5 free of K to 273.0 m^2/g. The slight decrease in surface area of only 5% indicates that the pore channels of HZM-5 would not be blocked due to the K introduction.

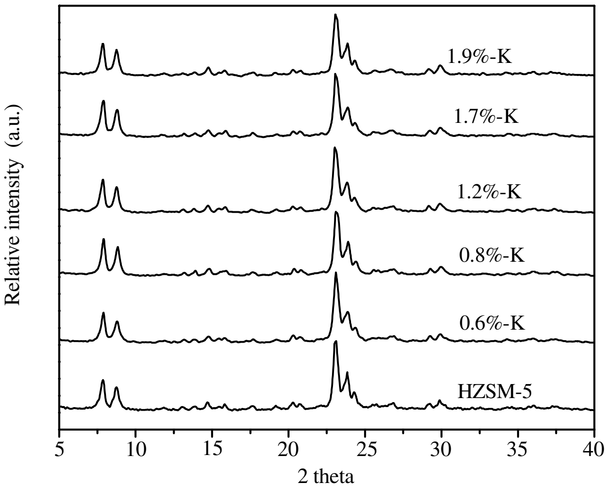

Figure 1. XRD patterns of the K/ZSM-5 with various K-loadings.

Table 1
BET specific surface area over the K/ZSM-5 catalysts with different K-loadings

K-loading wt%	0	0.6	0.8	1.2	1.7	1.9
BET surface area m^2/g	287	285	279	276	274	273

The effect of potassium introduction on the catalyst acidity was measured by NH_3-TPD technique, and the results are shown in figure 2. There are two desorption peaks for HZSM-5. One of the peaks centers at about 250 °C and the other at about 450 °C, corresponding to weak acid sites and strong acid sites, respectively. With the loading of 0.6 wt% K, the number of strong and weak acid sites over the HZSM-5 shows an obvious decrease, and the former changes more apparently than the latter. With the increasing in K-loading, the acid sites of the K/ZSM-5, especially strong acid sites, continued to decrease. Almost all of the strong acid sites disappeared and only part of weak acid sites remained over the 1.9 wt% K/ZSM-5 catalyst.

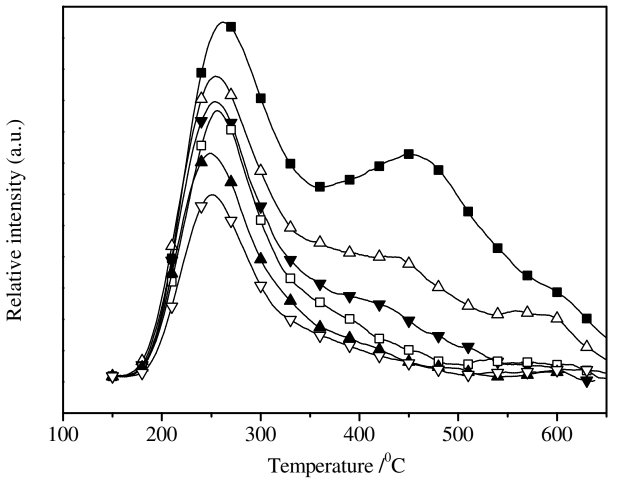

Figure 2. NH_3-TPD profiles of the K/ZSM-5 catalysts with various K-loadings: (■) HZSM-5; (□) 0.6 wt% K/ZSM-5; (▼) 0.8 wt% K/ZSM-5; (□) 1.2 wt% K/ZSM-5; (▲) 1.7 wt% K/ZSM-5; (□) 1.9 wt% K/ZSM-5.

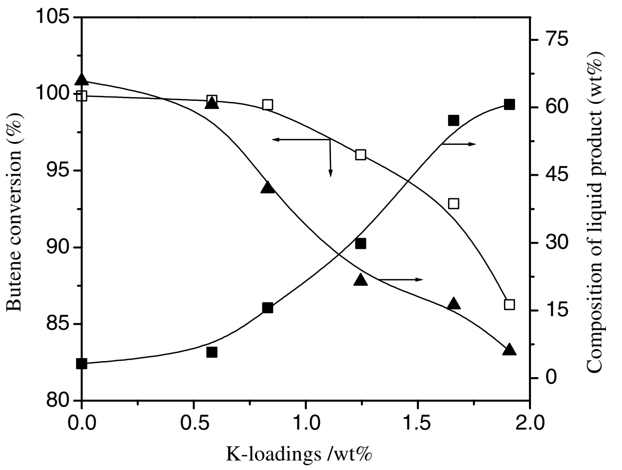

Figure 3. Effect of K-loading over ZSM-5 on the aromatization performance of LPG. (□) butene conversion; (▲) aromatics; (■) olefin; reaction temperature: 350 °C; pressure: 0.5 Mpa; WHSV: $2h^{-1}$; reaction mode: continuous.

3.2. *Effect of potassium loadings over the K/ZSM-5 catalysts on the aromatization activity of LPG in the continuous flow reaction mode*

The aromatization reaction in continuous flow mode was performed at 350 °C, 0.5 Mpa and WHSV 2 h^{-1} of, using a 50 wt% butene-in-LPG feed. The effects of K loadings on butene conversion and the contents of olefin and aromatics in liquid products are shown in figure 3. With the increase of the K-loading over the ZSM-5, butene conversion decreased and the distribution of products also varied, namely, the concentration of aromatics in liquid products decreased, whereas that of olefins increased greatly. The aromatics formed in the liquid products were almost negligible when the K-loading reached 1.9 wt%. Combining the reaction data with the results of NH_3-TPD, it is reasonable to propose that the strong acid sites are absolutely necessary for the transformation of butene into aromatics, while the interconversion of olefins is catalyzed both by strong and weak acid sites, which is in agreement with earlier reports [4,6–8], which state that the transformation of olefins, methanol and ethanol to aromatics is catalyzed by strong acid sites over the ZSM-5. Figure 4 shows the dependence of aromatics distribution on K-loadings on the catalyst. With the increasing of the K-loadings, which corresponded to a decrease of the strong acid sites, the formation of benzene, toluene and C_8 hydrocarbon in aromatics decreases, while that of the large molecular aromatics increases markedly. The distribution of aromatics is controlled to some extent by secondary reactions, particularly dealkylation reaction [3]. Moreover, the dealkylation of poly-alkyl-aromatics is favored with strong acid sites. Consequently, the decrease of the strong acid sites will lead to a decrease in the rate of dealkylation reactions, resulting in a decrease in the formation of benzene, toluene and C_8 hydrocarbon in aromatics.

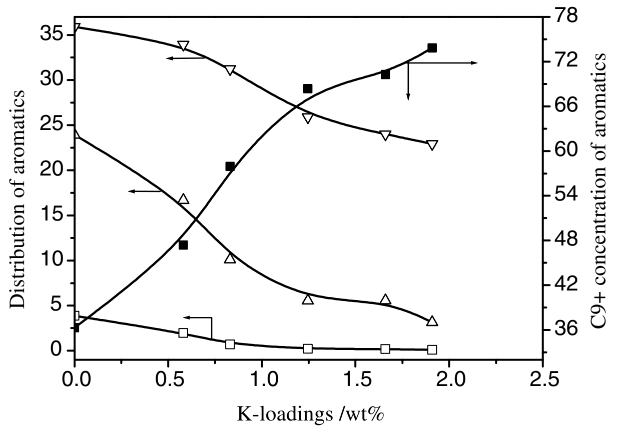

Figure 4. Effect of K-loading over ZSM-5 on the aromatics distribution. (□) Benzene; (□) Toluene; (∇) C8 aromatics; (■) C9+ aromatics; reaction temperature: 350 °C; pressure: 0.5 Mpa; WHSV: $2h^{-1}$; reaction mode: continuous.

3.3. *Effect of potassium loadings over the K/ZSM-5 catalysts on the aromatization activity of different olefins in pulse reaction mode*

The results of continuous flow reaction mentioned above represent an accumulative aromatization performance of the catalyst for 5 h on-stream. During the reaction process, the catalyst may be deactivated slowly due to coke formation, thus affecting the real reaction performance of the ZSM-5 catalyst. In order to avoid the effect of catalyst deactivating, the pulse reaction technique was used to study the effect of the catalyst acidity on the initial activity of aromatization, where the products formed were directly detected by an on-line multi-channel MS. Here, m/e = 91, 78, 92, 106, 120 is denoting to non-benzene aromatics, benzene, toluene,

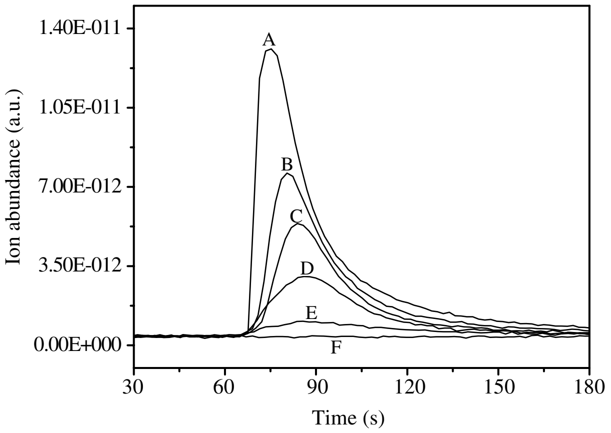

Figure 5. Effect of K loadings on aromatization activity of 1-butene over the K/ZSM-5. (A) HZSM-5; (B) 0.6 wt% K/ZSM-5; (C) 0.8 wt% K/ZSM-5; (D) 1.2 wt%K/ZSM-5; (E) 1.6 wt% K/ZSM-5; (F) 1.9 wt% K/ZSM-5 reaction temperature: 400 °C, reaction mode: pulse.

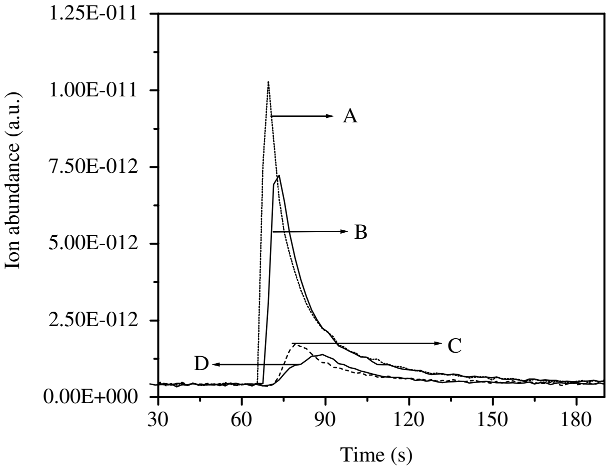

Figure 6. Aromatics distribution during 1-butene aromatization over HZSM-5 catalyst in pulse reaction. (A) benzene; (B) toluene; (C) C_8 aromatics; (D) C_9 aromatics reaction temperature: 400 °C.

C_8 aromatics and C_9 aromatics, respectively [9], and the ion abundance (or the peak area) represents the relative amount of aromatics formed.

The effect of introducing potassium into ZSM-5 on the initial aromatization performance of pure 1-butene is shown in figures 5–7. Clearly, with the enhancement of the K loading, the amount of aromatics formed (i.e. $m/e = 91$) decreased, and almost no aromatics was detected when the K loading was increased up to 1.9 wt% (shown in figure 5), which implies that strong acid sites are essential for the transformation of olefin into aromatics and the activity of olefin aromatization increased with the number of strong acid sites. Figures 6 and 7 show the amount of different aromatics formed over the HZSM-5 and 0.8 wt% K/ZSM-5 catalysts, respectively. Here, for the sake of simplification, therefore, a comparison was carried out only between the HZSM-5 and 0.8 wt% K/ZSM-5. Clearly, 0.8 wt% K introduction resulted in a great decrease in various aromatics formed. However, the amount of benzene and toluene decreased to a larger extent, in comparison to that of C_8 and C_9 aromatics, This suggests that the decreasing of strong acid sites due to the K introduction leads to an appreciable decrease in the concentration of lower aromatics. All these results further prove that there is a close relationship between the performance of olefin aromatization and the number of strong acid sites.

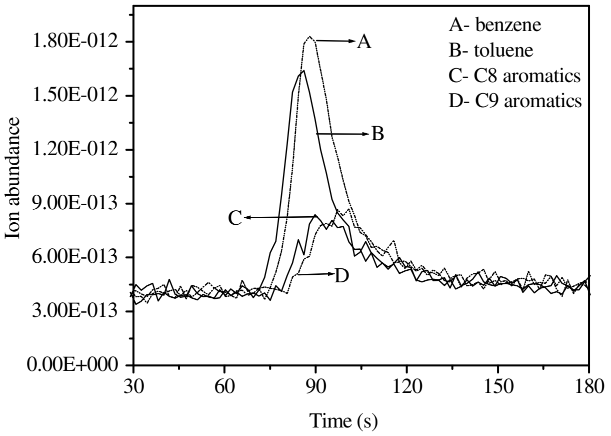

Figure 7. Aromatics distribution during 1-butene aromatization over the 0.8 wt% K/ZSM-5 catalyst in pulse reaction. (A) benzene; (B) toluene; (C) C_8 aromatics; (D) C_9 aromatics reaction temperature: 400 °C.

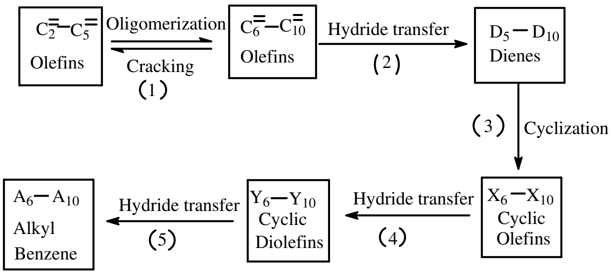

Figure 8. Aromatization pathways of olefin over HZSM-5.

All the above experiment results seem to indicate that the transformation of olefin into aromatics is catalyzed only by strong acid sites over the ZSM-5. However, for this complicated aromatization reaction, the idea that olefin aromatization is carried out only on strong acid sites, while the weak acid sites over the ZSM-5 do not participate in the aromatization of olefins seems to be incorrect. This will be discussed in detail in the following section.

According to a supposed reaction pathway for aromatics formation from light olefin [10] (shown in figure 8), we chose the so-called reaction intermediates (i.e. diene and cycloolefin) as reactants, and the HZSM-5 with lots of strong acid sites and 1.9 wt% K/ZSM-5 only with weak acid sites as two typical catalysts to study the catalytic reactions of strong and weak acid

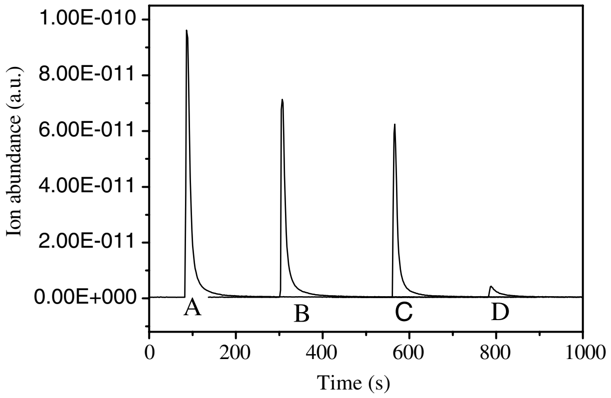

Figure 9. Comparison of aromatization activity of various feeds over the HZSM-5 catalyst. (A) cyclopentene; (B) isoprene; (C) 1,3-butadiene; (D) 1-butene reaction temperature: 400 °C, reaction mode: pulse.

sites in olefin aromatization by means of pulse reaction. The aromatization reactivities of pure 1-butene, 1,3-butadiene, isoprene and cyclopentene over the HZSM-5 and 1.9 wt% K/ZSM-5 are shown in figures 9 and 10, respectively. Reasonably, it is found that a quite larger amount of aromatics was formed over the HZSM-5 than over the 1.9 wt% K/ZSM-5 when 1-butene, 1,3-butadiene, isoprene and cyclopentene were used as the reactants. Isoprene, 1,3-butadiene, and cyclopentene with the same molecular formula C_nH_{2n-2} show much higher aromatization activity than 1-butene both over the HZSM-5 and 1.9 wt% K/ZSM-5 catalysts. These messages indicate that the more hydrogen-deficient hydrocarbons, such as diene or cycloolefin undergo aromatization process more easily than alkenes with the same carbon number during olefin aromatization. This is well in agreement with the previous document reported by Isagulitants [7]. It is worth noting that over the 1.9 wt% K/ZSM-5 catalyst, without any strong acid sites, almost no aromatics were formed when using 1-butene as reactant, whereas a large quantity of aromatics was formed when using 1,3-butadiene, isoprene or cyclopentene as reactants, as shown in figure 10. This implies that diene or cycloolefin, as the so-called intermediates of olefin aromatization [10], may be transformed to aromatics even over weak acid sites of the 1.9 wt% K/ZSM-5 sample. Based on the above results, we suppose that the formation of aromatics during the conversion of olefins (C_nH_{2n}) is mainly controlled by the formation of diene or cycloolefin, and the strong acid sites are responsible for the formation of diene and cycloolefin (i.e. the step (2) shown in figure 8) from olefin [5]. Once diene or cycloolein is formed from olefins over the strong acid sites, it can be transformed into aromatics not only over strong acid sites, but also over weak acid sites.

3.4. TPSR results of 1-butene and 1,3-butadiene over the the HZSM-5 and 1.9 wt% K/ZSM-5 catalysts, respectively

In order to further confirm the above idea that diene and cycloolefin can be transformed into aromatics over weak acid sites, while transformation of mono-olefin into aromatics needs the existences of the strong acid sites, TPSR experimental was designed to hope to provide much more evidental information. From the results of TPSR of 1-butene over the HZSM-5 and 1.9 wt% K/ZSM-5 catalysts as shown in figure 11, the aromatics as product of 1-butene reaction were hardly detected, even at much higher reaction temperature than 550 °C, over the 1.9 wt% K/ZSM-5 catalyst without strong acid sites, But over the HZSM-5 catalyst with strong acid sites, with the reaction temperature rising up to about 225 °C, a larger amount of aromatics were yielded. So it is further evidenced that the strong acid sites over the catalyst are very necessary for aromatization of mono-olefin, the weak acid sites alone could not catalyze the aromatization reaction of mono-olefin directly.

Then again, the 1,3-butadiene can be converted to the aromatics by the weak acid sites of the 1.9 wt% K/ZSM-5 catalyst, just as it can be catalyzed by the strong acid

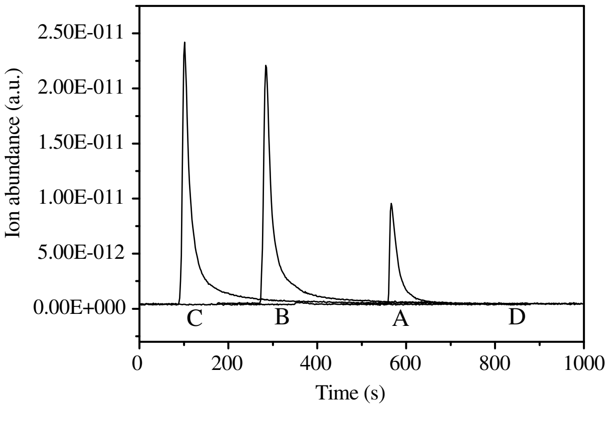

Figure 10. Comparison of aromatization activity of various feeds over the 1.9 wt% K/ZSM-5 catalyst. cyclopentene; (B) isoprene; (C) 1,3-butadiene; (D) 1-butene reaction temperature: 400 °C, reaction mode: pulse.

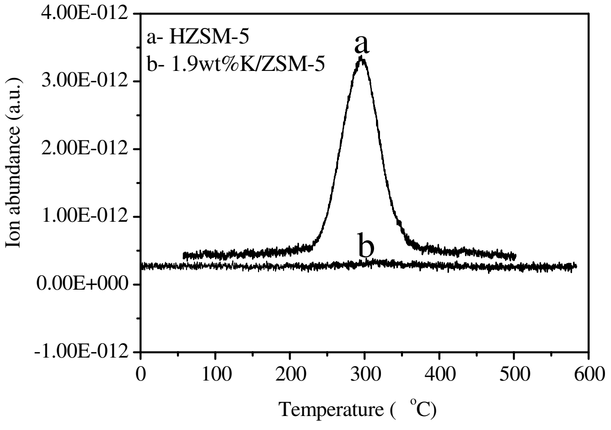

Figure 11. TPSR results of 1-butene over the HZSM-5 and 1.9 wt% K/ZSM-5 catalysts.

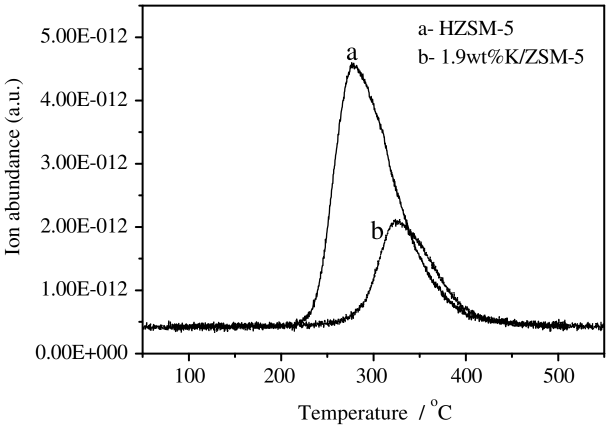

Figure 12. TPSR results of 1,3-butadine over the HZSM-5 and 1.9 wt% K/ZSM-5 catalysts.

sites of the HZSM-5 catalyst, although the aromatization activity of mono-olefin over the 1.9 wt% K/ZSM-5 catalyst was lower. Here, it would be supported by the results of the TPSR of 1,3-butadiene over the HZSM-5 and 1.9 wt% K/ZSM-5 catalysts, as presented in figure 12. Apparently, it is observed that with the reaction temperature increasing up to 260 °C, the absorbed 1,3-butadiene over weak acid sites of the 1.9 wt% K/ZSM-5 catalyst began to transform into the aromatics, and the amount of aromatics formed reached a maximum at 325 °C, whereas, over strong acid sites of the HZSM-5 catalyst, aromatics started to appear at a relative low temperature of 220 °C and reached a maximum at 280 °C. Accordingly, the reactive differences of 1,3-butadiene aromatization between these two catalysts were that aromatization activity of 1,3-butadiene over the 1.9 wt% K/ZSM-5 catalyst was relative lower than that over the HZSM-5 catalyst, and a higher reaction temperature was required for the formation of aromatics from 1,3-butadiene over the 1.9 wt% K/ZSM-5 catalyst.

Generally, the aromatization of olefin is controlled by the formation of its intermediates such as diene or cycloolefin, during the early reaction stage, and then these intermediates convert to aromatics during the following stage.

Furthermore, the results of kinetic study on the process of olefin aromatization indicated that the formation of olefinic carbenium ions (dienes adsorbed on protonic acid sites) by hydrogen-transfer reactions between olefins is the first, and slowest step (shown in figure 6) in the sequence of reaction steps leading to aromatics formation [10]. Once formed, the olefinic carbenium ions can be converted easily into cyclic olefins via cyclization reactions. That is to say the transformation of olefin into aromatics is mainly controlled by diene formation, which means that the activation energy for diene formation through the hydrogen-transfer reaction is rather higher. According to a universal catalytic reaction principle (the higher the reaction activation energy is, the more active sites the reaction requires), stronger acid sites are necessary for the first step of hydrogen-transfer between olefins for the diene or cycloolefin formation. This further supports the present idea that olefin aromatization takes place only over strong acid sites, whereas the as so-called intermediates of aromatization of olefin, i.e. diene or cycloolefin can be transformed into aromatics even over catalysts with only weak acid sites, such as the 1.9 wt% K/ZSM-5 catalyst. Consequently, we suppose that the step of diene formation is the most difficult step during the olefin aromatization process and needs stronger acid sites. However, how to carry out the reaction of dehydrocyclization over strong acid sites of catalyst remains unclear and further studies are required.

4. Conclusions

The introduction of potassium into ZSM-5 resulted in the decreasing of acid sites, especially of the strong acid sties of the catalyst. Even the strong acid sites almost disappeared as the potassium loading was increased up to 1.9 wt%. The activity of aromatization of olefin is directly correlated with the strong acid sites over the catalyst. Especially, the formation of benzene, toluene and C_8 aromatics in aromatics was promoted by the increasing of the strong acid sites. While the weak acid sites alone could catalyze diolefin or cycloolefin, as the intermediates of olefin aromatization, to aromatics, and be unable to transform the mono-olefin into aromatics directly.

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