Effect of Ca/K Modified ZSM-5 on Catalytic Cracking of Low Carbon Olefin

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Abstract. In this paper, the structural and acidic changes of ZSM-5 zeolite modified by K and Ca were studied. Meanwhile we use in-situ FTIR to study the reaction of isobutylene on ZSM-5 zeolite before and after modification, investigating reaction mechanism and optimal reaction time. The results show that the amount of weak acid increases in the modified zeolite. The Ca-ZSM-5 can not only effectively control the hydrogen transfer reaction to inhibit the formation of aromatic hydrocarbons, but also promote the occurrence of dehydrogenation cracking reaction; while the K-ZSM-5 is not effective in the cracking reaction.

1. Introduction
Low-carbon olefins such as ethylene and propylene are important basic raw materials in the petrochemical industry, their demand is increasing with the development of the chemical industry. The traditional method of ethylene production uses a non-catalytic steam pyrolysis process, and the propylene is produced by co-production of ethylene which has limited capacity. In recent years, the low-carbon olefin catalytic cracking process has become the most promising new production technology for its advantages of low reaction temperature, high product yield and flexibility distribution. The key to the cracking process is the catalyst. ZSM-5 is one of the common catalysts used in this process due to its special pore structure, acid properties and good anti-coking ability [1-4]. It has been widely reported that the amount and strength of acid sites are adjusted by element modification to improve the performance [5-8]. The suitable modification method is one of the important factors that directly affect the yield of low-carbon olefins. Therefore, it is necessary to study the effect of different element modified ZSM-5 on catalytic cracking of low carbon olefin.

In this work, ZSM-5 zeolite was modified to investigate the effect of element modification on the pore structure and surface acidity by Ca and K. After that we found the relationship between catalysts and cracking reaction after using the in-situ FTIR.

2. Experimental
2.1 Catalyst preparation

The unmodified ZSM-5 was obtained with ultrafine SiO₂ as carrier and high silica-alumina ratio ZSM-5 as active component, followed by adding the amount of the phthalocyanine powder and the dilute nitric acid. After drying and calcination the gel, all the catalysts were crushed to particles.

Preparation of Ca and K modified ZSM-5 zeolite: The pre-treated ZSM-5 were prepared by a wet incorporation technique with 1% aqueous solution of Ca(NO₃)₂·4H₂O, KNO₃ of appropriate concentration. After drying and calcination, modified catalysts loaded with different elements can be obtained, respectively labelled as Ca-ZSM-5, K-ZSM-5.

2.2. Catalyst characterization

Nitrogen adsorptions were performed with a Micromeritics ASAP 2020 automated gas adsorption analyzer. Prior to analysis, the samples were outgassed at 350°C for 12 h. The specific surface area, pore size and pore volume were calculated according to the isotherm.

The acidities of the catalysts were determined by the NH₃-TPD using a Micromeritics Autochem II 2920 automatic chemical adsorption instrument. The sample (0.10 g) was loaded into a U-shaped quartz tube and pretreated at 600°C for 1 h in a flowing He. After the retreatment, the sample was cooled to 40°C and saturated with NH₃ for 1 h. Subsequently, the physically adsorbed NH₃ was removed in a flow of dry He for 1 h. When the baseline was stable, NH₃-TPD was carried out from ambient temperature to 600°C at a heating rate of 10°C/min, and analyzed by a TC detector.

The acid types of the samples were determined by adsorption of pyridine on a Nicolet AVATAR-360 FTIR. Prior to the measurements, the samples were pressed into self-supporting discs and activated in the IR cell attached to a vacuum line at 500°C for 1.5 h under 10⁻⁶ Torr, then cooled to room temperature where pyridine vapor was introduced into the cell for 1 h. After the adsorption is saturated, the sample was heated to the corresponding temperature, and a spectrum was recorded at each step.

2.3. Evaluation of Catalytic performance

In-situ FTIR transmission spectroscopy was used to characterize the surface information on ZSM-5 in the isobutylene cracking reaction. Prior to the measurements, the samples were pressed into self-supporting discs and activated in the IR cell attached to a vacuum line at 500°C for 1.5 h under 10⁻⁶ Torr. After the sample was pretreated, the isobutylene gas was introduced in situ. When the gas flow rate was stable, the temperature began to heat to 520°C at a heating rate of 12°C/min, and a spectrum was recorded at each step.

TPSR experiment used Micromeritics Autochem II 2920 automatic chemical adsorption instrument with one on-line mass spectrometer(QIC 20, HIDEN) to detect the fragment ion peaks, isobutylene (m/z=56) and propylene (m/z=48) in real time.

3. Results and discussion

3.1 Structure of ZSM-5 zeolites
Fig. 1 and Table 1 highlights the adsorption/desorption isotherms of ZSM-5 zeolite before and after modification. Fig.1 indicates the catalysts have similar pore structures. The volume and specific surface area are fairly close for all three samples in Table 1. The pore size of the Ca-ZSM-5 and K-ZSM-5 decreased slightly, but it was not enough to cause a large change in the pore structure of the zeolite. The BET and microspore surface areas are slightly decreased after Ca modification, attributed the dealumination phenomenon occurs during the modification process. The structure collapses after the skeleton aluminum falls off, resulting in a decrease in specific surface area and pore volume [7].

Figure 1. N2-adsorption/desorption isotherm and pore distribution of zeolites

Table 1. Physical properties of zeolites

| Sample   | $S_{BET}$ (m$^2$·g$^{-1}$) | $S_{micro}$ (m$^2$·g$^{-1}$) | $S_{meso}$ (m$^2$·g$^{-1}$) | $V_{total}$ (cm$^3$·g$^{-1}$) |
|----------|--------------------------|-----------------------------|-----------------------------|-----------------------------|
| ZSM-5    | 362.52                   | 285.54                      | 76.98                       | 0.13                        |
| Ca-ZSM-5 | 338.84                   | 261.01                      | 77.83                       | 0.12                        |
| K-ZSM-5  | 364.77                   | 287.94                      | 76.83                       | 0.13                        |

3.2 Acidic property of ZSM-5 zeolites

The acidity and acid strength of the zeolites were determined by NH$_3$-TPD, and the results are shown in Fig. 2. We sorted acidic properties of zeolites by total acid amounts/(mmol·g$^{-1}$): Ca-ZSM-5(0.50) > ZSM-5(0.45) > K-ZSM-5(0.38). Fig. 2 illustrates the weak acid sites (low temperature desorption) of Ca-ZSM-5 were significantly higher than ZSM-5, but the strong acid sites (high temperature desorption) were lower than ZSM-5. Meanwhile the weak acid sites (low temperature desorption) of K-ZSM-5 are higher than ZSM-5, but the strong acid sites (high temperature desorption) are almost absent.

Figure 2. TPD of NH$_3$ profiles of ZSM-5 zeolites
In order to further detect the acid type of ZSM-5 zeolites, pyridine adsorption FTIR was used to illustrate the acid type and strength. Fig 3. represents the variation of IR bands in 1400-1600 cm\(^{-1}\) region as the increase of the temperature. There are three bands in the region. The one at 1450 cm\(^{-1}\) indicates the presence of Lewis acid sites. The one at 1490 cm\(^{-1}\) is attributed to the Brønsted acid sites. The other at 1440 cm\(^{-1}\) is attributed to the pyridine species interacting with both the two kinds of acid sites. Ca-ZSM-5 (Fig 3B) has an increased amount of Lewis acid and a reduced amount of Brønsted acid compared to ZSM-5 (Fig 3A). It is indicated that Ca-ZSM-5 increases the weak acid and decreases the strong acid. The amount of acid in K-ZSM-5 (Fig 3C) was reduced compared to ZSM-5 (Fig 3A) and the amount of Brønsted acid was significantly less than Lewis acid. This corresponds to the NH\(_3\)-TPD characterization data. The results suggest the introduction of K and Ca can weaken the acid strength and reduce the acidity, and the original strong acid sites of ZSM-5 are converted into weakly acidic sites.

The dehydrogenation cracking reaction mainly occurs in the acidic center of alkaline earth metal modification. The reduction of acidity can inhibit the hydrogen transfer reaction and reduce the side-reaction of the olefin product, thereby promoting the dehydrogenation cracking reaction, which is the main reason for increasing the yield of olefin.

FTIR can give structural information on the surface-adsorbed species, especially the structure information of the adsorbed species under the reaction conditions. High-quality and time-resolved spectra of the catalyst (Fig.4) were recorded by the FTIR spectrometer under real reaction conditions, which provided abundant information about the surface adsorbed species and their evolutions. According to literature, the bands at 2965 and 2860 cm\(^{-1}\) are attributed to the asymmetric and symmetric C-H stretching vibrations of the -CH\(_3\) group, respectively. The band at 2934 cm\(^{-1}\) is associated with the asymmetric C-H stretching vibration of the -(CH\(_2\))- group. The band at 1467 cm\(^{-1}\) is attributed to the C-H bending vibration of the -(CH\(_2\))- group, and that at 1458 cm\(^{-1}\) to the asymmetric C-H bending vibration.
of the \(-\text{CH}_3\) group. Fig. 4A illustrates that the absorption peak 2860 cm\(^{-1}\) which attributed to the methylation vibration gradually increases, from the start of the reaction to 150 min, and the methylene absorption peak (2934 cm\(^{-1}\)) gradually decreases. The characteristic peaks of isobutylene, 1396 and 1386 cm\(^{-1}\), also immediately and continuously decreased in intensity. The reaction temperature increases at a rate of 2°C/min. These spectra suggest as the reaction temperature rises to 300°C, the increase of 2860 cm\(^{-1}\) peak and the decrease of the 1396 and 1386 cm\(^{-1}\) mean that the molecular chain length decrease, It is an important indicator of the progress in the cracking reaction. In addition, after 150 min of reaction, that is, when the reaction temperature was higher than 300°C, the band at 1505 cm\(^{-1}\) related to the C=C vibration of an aromatic ring appeared [10]. The reason is the acid strength of ZSM-5 is high, and the cracked product is re-adsorbed, resulting in the occurrence of side reactions such as aromatization reaction [11]. Isobutylene cracking reaction over Ca-ZSM-5 and K-ZSM-5 were also studied by in-situ FTIR, shown in Fig. 4B and 4C. The cracking reaction occurred on the Ca-ZSM-5 from room temperature to about 300°C, but no characteristic peak associated with the aromatic ring was observed at about 1505 cm\(^{-1}\). This indicates that the acidity of the zeolites modified by Ca can be reduced, and the hydrogen transfer reaction can be inhibited to form aromatic hydrocarbons, while the dehydrogenation cracking reaction can be promoted [7]. K-ZSM-5 hardly undergoes a cracking reaction which is because the amount of Brønsted acid modified by K is much lower than that of Lewis acid, and the acidity is mainly weak acid. It is reported in the literature [12] that the Brønsted acid on ZSM-5 is the active center of the catalytic cracking reaction of olefins. The Lewis acid does not contribute to the activity of the cleavage. At the same time, some scholars do not recommend alkali metals such as K to modify zeolites because in most catalytic reactions, the effect is not obvious [13].

![Figure 4. In-situ FT-IR spectra of isobutylene cracking on the ZSM-5 zeolite surface](A)ZSM-5 (B)Ca-ZSM-5(C)K-ZSM-5)
In order to further verify the reaction conditions of isobutylene on the zeolite, the change of isobutylene (m/z=56) and propylene (m/z=48) fragment ion peaks was detected by TPSR experimental. Fig. 5 shows that when the catalytic cracking reaction is carried out in ZSM-5 and Ca-ZSM-5 zeolites, isobutylene decreases and propylene increases significantly as the temperature rises from room temperature to 300 °C. However, these peaks on K-ZSM-5 did not change, indicating that no catalytic cracking reaction occurred. This is consistent with in-situ FTIR. Thus, we can conclude that the optimal reaction temperature for the catalytic cracking reaction is about 300 °C.

![Figure 5. TPSR of isobutylene cracking on the ZSM-5 zeolite surface](image)

(B)Ca-ZSM-5(C)K-ZSM-5

4. Conclusions

The shaped ZSM-5 was modified by Ca and K. The characterization results shows that the pore volume and specific surface area of zeolites are not much different, but the introduction of K and Ca can weaken the acid strength and reduce the acidity. Meanwhile, in-situ FTIR shows that ZSM-5 had a side reaction such as aromatization, while the Ca-ZSM-5 did not appear related peak and K-ZSM-5 hardly undergoes a cracking reaction. The Ca-ZSM-5 can not only effectively control the hydrogen transfer reaction to inhibit the formation of aromatic hydrocarbons, but also promote the occurrence of dehydrogenation cracking reaction; Furthermore the optimum temperature of the reaction are about 300 °C.

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