

Effect of boron on ZSM-5 catalyst for methanol to propylene conversion

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B-ZSM-5 catalysts were prepared by various modification methods with boric acid, including ion-exchange, impregnation and direct synthesis. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), NH₃-Temperature Programmed Desorption (NH₃-TPD), N₂ adsorption-desorption, Fourier Transform Infrared spectrometry (FT-IR), ²⁷Al and ¹¹B MAS NMR spectra. The results revealed that the weak acidity of catalysts was significantly increased by modification. The catalytic activity was measured in a fixed bed at 460°C for methanol to propylene (MTP) reaction. The results of MTP reaction showed a great increment of the propylene selectivity for the boron modified samples, especially for the directly synthesized B-ZSM-5 which also displayed high activity and selectivity towards C₂=C₄= olefins. It was found that the remarkable selectivity strongly depended on the intensity of weak acidity.

Keywords: methanol to propylene, ZSM-5, boron modification, propylene.

INTRODUCTION

In petrochemical industry, light olefins such as ethylene, propylene and butylene are important intermediates and building blocks, as the essential feedstock for the production of a wide range of petrochemicals. Especially for propylene, due to the growing demands and the shortage of petroleum resource in the future, new processes with a high yield of propylene are required. Methanol to propylene (MTP) process as the process with high yield of propylene is a promising way for the production of propylene instead of petroleum route, since methanol can be easily produced from natural gas and coal¹⁻³. As compared to the methanol to olefins (MTO) process, where ethylene is the main product, high propylene to ethylene ratio is the most distinguishable feature for MTP that enables the high propylene yield in the recirculation process⁴. But achieving a high yield of propylene is still challenging.

ZSM-5 is a kind of high-silica zeolite which shows high selectivity of propylene in MTP reaction. Many works have been done to improve the catalyst activity and selectivity. Stöcker⁵ reviewed the studies of methanol reaction in the past decades and listed many kinds of elements (Cs, Ba, Mg, Sb, Ca, and so on) used for modification by impregnation or substitution on ZSM-5 zeolite, all of which achieved great improvement in methanol conversion or olefin selectivity. Furthermore, mesoporosity zeolite, nano size zeolite, and composite catalysts all bring remarkable improvement in propylene selectivity^{4, 6-8}. Recent studies reveal a much clearer insight into the reaction aspects^{9, 10}. The key step in effective conversion of methanol to propylene lies in controlling the reaction at the olefin formation stage, where the acidity of the catalyst is crucial. Variation of frameworks Si/Al ratio by the pre or post synthesis methods is a generally adopted procedure for tuning the zeolite acidity¹¹. Wei et al.² reported that the density of strong acid sites decreased with the increasing SiO₂/Al₂O₃ molar ratios for ZSM-5 zeolites and the decreased amount of strong acid sites was beneficial to the propylene selectivity. The above mentioned modifications all change the catalysts acidity and make them suitable

for MTP reaction. Typically, Liu et al.³ and Lee et al.¹¹ revealed that phosphorus promoter which had good effect on propylene selectivity, significantly reduced the concentration of catalyst strong acid sites. Moreover, the increase of weak acidity is also important in MTP reaction. The weak acidity can catalyze the reaction such as alkylation and methylation, which plays a vital role in olefin formation¹². Borosilicates with high weak acidity and low strong acidity were discussed by several researchers in different reactions^{13, 14, 15}. In MTG reaction, Unneberg et al.¹³ found that pure B-MFI expressed poor methanol conversion, but Yang et al.¹⁵ found that the B-Al-ZSM-5 catalyst with a 2.0 Al/B ratio showed a positive reaction capability in MTP reaction. Overall, boron used on ZSM-5 in various modification methods in MTP reaction for comparison is rarely reported.

In this work we investigated the influence of three boron modification methods on B-ZSM-5 catalysts performance in MTP reaction. The samples were well characterized by X-ray diffraction, SEM, NH₃-TPD, N₂ physisorption, FT-IR, ²⁷Al and ¹¹B MAS NMR. For the modified catalyst, which gives the remarkable improvement in propylene selectivity, the catalyst structure and acidity were investigated and compared with the B-free catalysts.

EXPERIMENTAL

Catalyst preparation

ZSM-5 zeolite was synthesized by hydrothermally synthesis method, using tetrapropylammonium bromide (TPABr) as the template. The silicon source was silica sol and the aluminum source was NaAlO₂ with NaOH as the alkali source. The molar composition of the gel mixture was SiO₂: (1/300) Al₂O₃: 0.14TPABr: 0.05Na₂O: 30H₂O, with Si/Al ratio of 150. After being stirred for 3 h at room temperature, the mixture was crystallized at 170°C for 48 h. The products were rinsed, dried and then calcined at 550°C for 6 h. Finally the parent ZSM-5 sample was obtained. ZSM-5 was turned into H-form by two consecutive ion exchanges in 1 M NH₄NO₃ solution or H₃BO₃ solution separately with solution/zeolite ratio

of 20 cm³/g at 80°C for 8 h, and then calcined again at 550°C for 4 h, the achieved products were labeled as HZSM-5 and BHZSM-5. The next B-modified catalyst was prepared using incipient wet impregnation method by ZSM-5 with the boric acid solution. After homogenization and an impregnation period of 24 h, followed by drying and then calcinating at 550°C for 4 h, the sample was designated as B₁ZSM-5 containing 2 wt.% of boron. Synthesis of BZSM-5 was in the same way of ZSM-5, except that boric acid was added into the gel with a molar composition of SiO₂: (1/300) Al₂O₃: 0.14TPABr: 0.05Na₂O: 30H₂O: 0.09B₂O₃.

Catalyst characterization

Powder x-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 using Cu K α radiation at 40 kV and 100 mA. XRD patterns were investigated over a 2 θ range of 3–50° and a step size of 0.02°. Scanning Electron Microscopy (SEM) was employed to the morphologic characterization. SEM measurements were performed on a JSM-6360LV electron microscope. Nitrogen adsorption-desorption isotherms were obtained with a Micrometrics ASAP 2020 apparatus. The specific surface areas were determined by the multi-point Brunauer-Emmet-Teller (BET) method. The total pore volume and sizes were evaluated using the standard Barrett Joyner Halenda (BJH) treatment. Fourier Transform Infrared spectrometry (FT-IR) spectra were operated on a Nicolet 6700 Fourier Transform infrared spectrometer in the mid-infrared range of 400–4000 cm⁻¹. The ²⁷Al and ¹¹B MAS NMR spectra were acquired after samples hydration on a Bruker DRX 500 spectrometer, using a 4 mm MAS probe, with a sample spinning rate of 4.0 kHz and at the resonance frequencies of 130.3 and 160.4 MHz respectively. Hydration was performed at room temperature by exposing the material in a closed system of small container with water for several hours. NH₃-TPD was performed on Micromeritics AutoChemII 2920. After pretreatment and NH₃ saturation, NH₃ desorbed from the catalyst sample and was monitored by TCD while temperature linearly increased to 600°C.

Catalytic evaluation

The MTP reaction was conducted in a fixed-bed reactor under the atmospheric pressure at 460°C. Pure methanol was fed by passing N₂ through a saturation evaporator at a weight hourly space velocity (WHSV) of 0.3 h⁻¹. Gas compositions of the products were analyzed online using a gas chromatograph (Agilent GC 6890) equipped with a flame ionization detector (FID) and an HP-Plot Al₂O₃/KCl capillary column. Aqueous and organic phases in liquid products were separated and analyzed on Agilent GC 6820 (TCD, Plot Q) and Agilent 7890A (FID, HP-5), respectively.

Dimethyl ether (DME) was considered to be unconverted reactant and lumped together with methanol in the calculation of conversion and selectivity.

RESULTS AND DISCUSSION

Effect of B on the structure of the catalyst

The XRD patterns of the samples are shown in Figure 1. All the samples exhibit the typical diffraction patterns corresponding to the MFI structure and are well crystallized¹⁶. The intensity of the diffraction peaks of B modified samples is a bit lower than ZSM-5 and HZSM-5. And the crystallinity of BZSM-5 prepared by direct synthesis process is the lowest one in all samples. It is due to its decreased crystallinity, which is caused by the formation of defects. Defects are unavoidable after modification since dealumination is one of its side

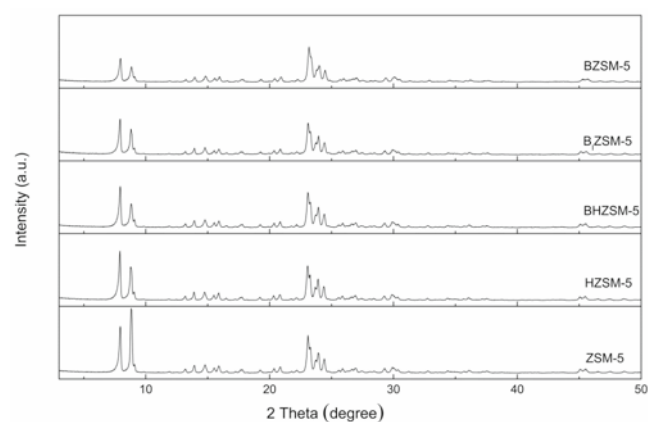


Figure 1. XRD patterns of all samples

effects. The results can be demonstrated in ²⁷Al MAS NMR spectra in the following. And it is worth mentioning that no peak of impurities can be detected after B modification, even in BZSM-5.

The crystal morphologies of samples ZSM-5 and BZSM-5 observed by SEM photographs are displayed in Figure 2. The other three samples show similar morphology as ZSM-5. The crystals of all samples are sphere-like, deposited by the cross-lamellar structure, and the distribution of the particle size seems to be rather uniform. The average crystal size is about 5 μ m in diameter. The external surface of BZSM-5 is rougher than that of others, and its particles exhibit obvious aggregation. Such a complex morphology might be formed by the fusion of a multitude of smaller, possibly primary crystallites¹⁷. The formation of aggregations is due to the small particles size of the zeolite and the addition of the B. It means that the interaction of B is responsible for the change in morphology of the catalyst by direct synthesis.

The N₂ physisorption results of all samples are presented in Table 1. BET surface area and pore volume of ZSM-5 decrease with the modification. On BHZSM-5 and B₁ZSM-5, it is probably due to the progressive blocking

Table 1. Surface characteristic of all samples

Sample	S _{BET} [m ² /g]	V _{total} [cm ³ /g]	V _{micro} [cm ³ /g]	Average Pore Width [nm]
ZSM-5	363	0.22	0.14	2.38
HZSM-5	380	0.23	0.13	2.44
BHZSM-5	360	0.21	0.12	2.39
B ₁ ZSM-5	280	0.17	0.11	2.54
BZSM-5	315	0.18	0.13	2.30

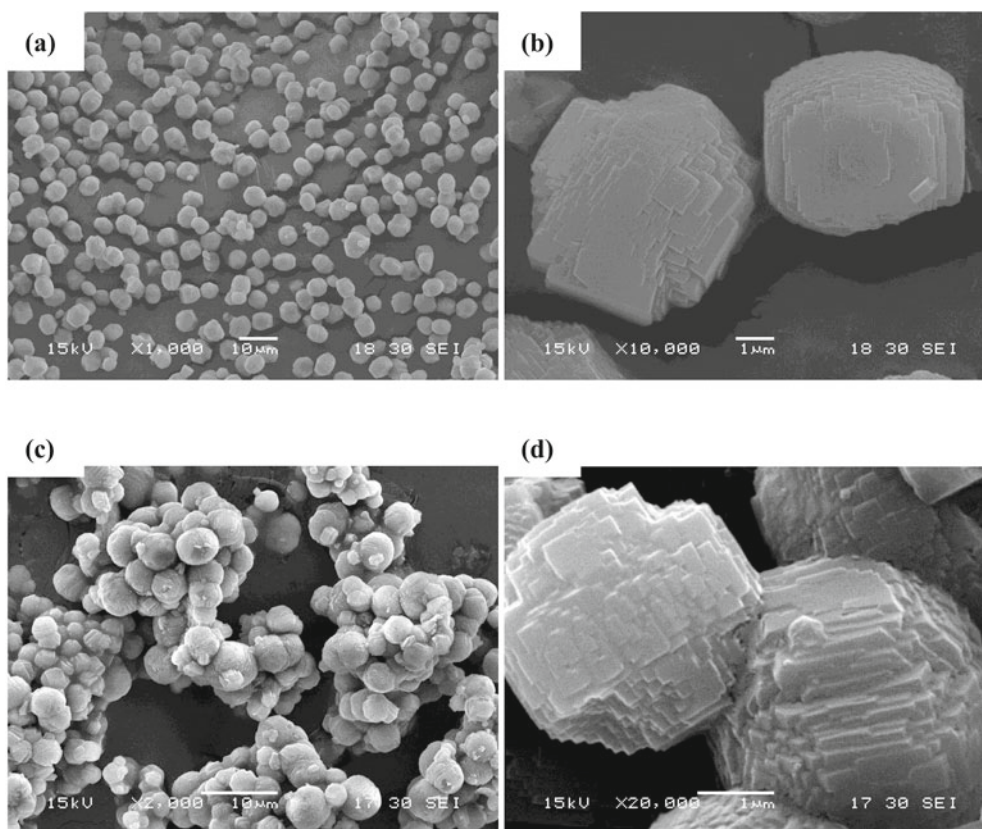


Figure 2. SEM images of representative samples: (a), (b) ZSM-5; (c), (d) BZSM-5

of pores by BO_3^- species inside zeolite channels. And the decrease of S_{BET} on BZSM-5 takes place because of its slightly decreased crystallinity. However, the average pore width shows an opposite trend with various modification methods. The increased pore width for BHZSM-5 and B_1 ZSM-5 probably implies the generation of mesopores due to the dealumination and/or to the washing out of the amorphous species during the modification¹⁸. All indicators of BZSM-5 decrease, which could be attributed to the declined crystallinity and the exframework species blocked of pores.

The IR spectra of all the samples are given in Figure 3. A band at 670 cm^{-1} appears in the IR spectrum assigned to the symmetric bending vibration of Si-O-B band^{19, 20}. The peak at around 920 cm^{-1} is characteristic of the stretching vibration of Si-O-B band. It has been corresponding to tetrahedrally coordinated boron²⁰. This peak is characteristic of B-O-Si linkages for the

borosilicate system²¹⁻²³. The weak peak at 1385 cm^{-1} is assigned to trigonally coordinated framework boron^{24, 25}. From Figure 3 it can be seen that the characteristic peaks are relatively weak on BHZSM-5, whereas stronger on B_1 ZSM-5 and BZSM-5. For BHZSM-5, B atoms have not brought much influence on it. For B_1 ZSM-5, after impregnation, the condensation reaction has occurred during calcinations between boric acid and zeolite acid sites to connect the B atoms with zeolite framework¹⁴. The spectrum of BZSM-5 shows all these bands clearly, indicating that B atoms of BZSM-5 have essentially been incorporated into the framework in combination with Si. These results also can be demonstrated in ^{11}B MAS NMR.

Figure 4(a) shows the ^{27}Al MAS NMR spectra of all the samples. An intense peak at 55 ppm from tetrahedral aluminum in the zeolite framework is observed for all catalysts⁷. The peak intensities of the samples are

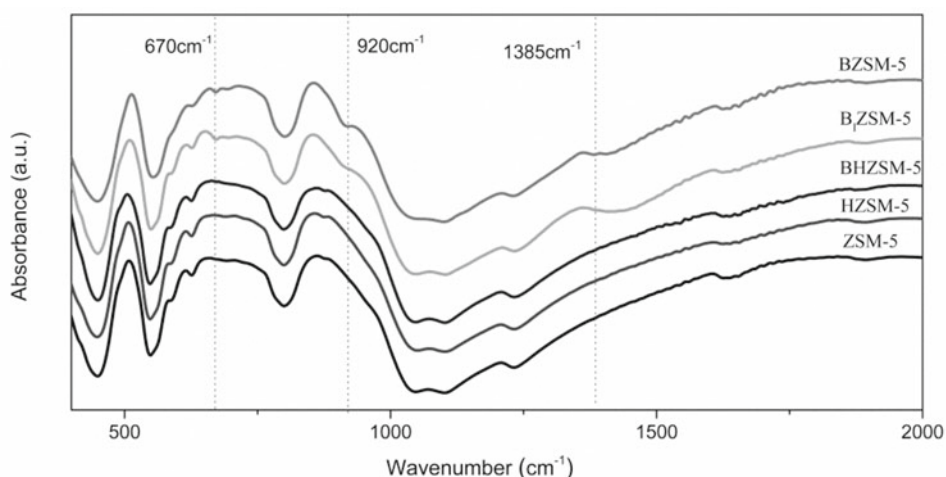


Figure 3. FT-IR spectra of all samples

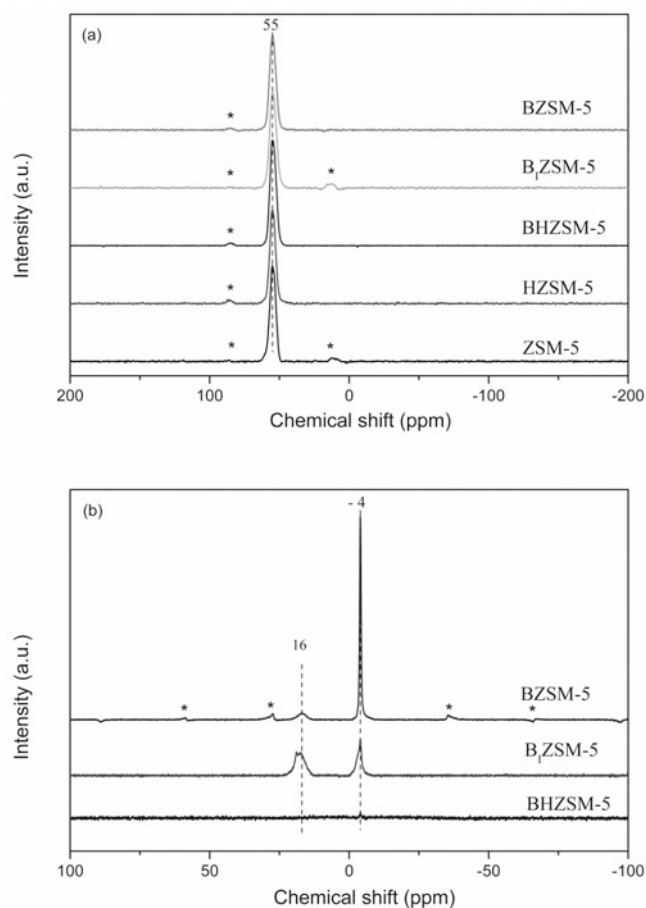


Figure 4. (a) ^{27}Al MAS NMR of all samples and (b) ^{11}B MAS NMR spectra of the B modified samples

almost the same, indicating that all samples have similar crystallinity. Octahedrally coordinated extra-framework Al atoms characterized by a resonance at about 0 ppm are not observed in any sample. The ^{27}Al MAS NMR spectra results show that most of Al species are incorporated into the zeolite framework and B modifications have little influence on the framework of Al.

^{11}B MAS NMR spectra of the B modified samples are shown in Figure 4(b). The main resonance peak at -4 ppm is assigned to tetrahedral framework BO_4 units, and another peak at about 16 ppm is ascribed to the trigonal extra-framework BO_3 units²⁶⁻²⁸. These two peaks are clearly observed for $\text{B}_1\text{ZSM-5}$ and BZSM-5 , but only a slightly signal of -4 ppm appears for BHZSM-5 . The obvious existence of tetrahedral framework boron on BZSM-5 indicates that the B atoms had essentially been incorporated into the framework in combination with Si. Compared with BZSM-5 , most of the boron in BHZSM-5 is within extra-framework, and for $\text{B}_1\text{ZSM-5}$, little influence has been brought by boron. The results are in good agreement with IR results.

Effect of B on the acidity of the catalyst

NH_3 -TPD is used in the characterization of the acidic properties of the samples in this work. The variations in acidity of parent ZSM-5 after B modifications are measured and the results are shown in Figure 5. After peak fitting of the NH_3 -TPD spectra, every spectrum can be divided into 3 or 4 peaks. The parent catalyst ZSM-5 shows 3 broad peaks. Based ZSM-5, it can be found

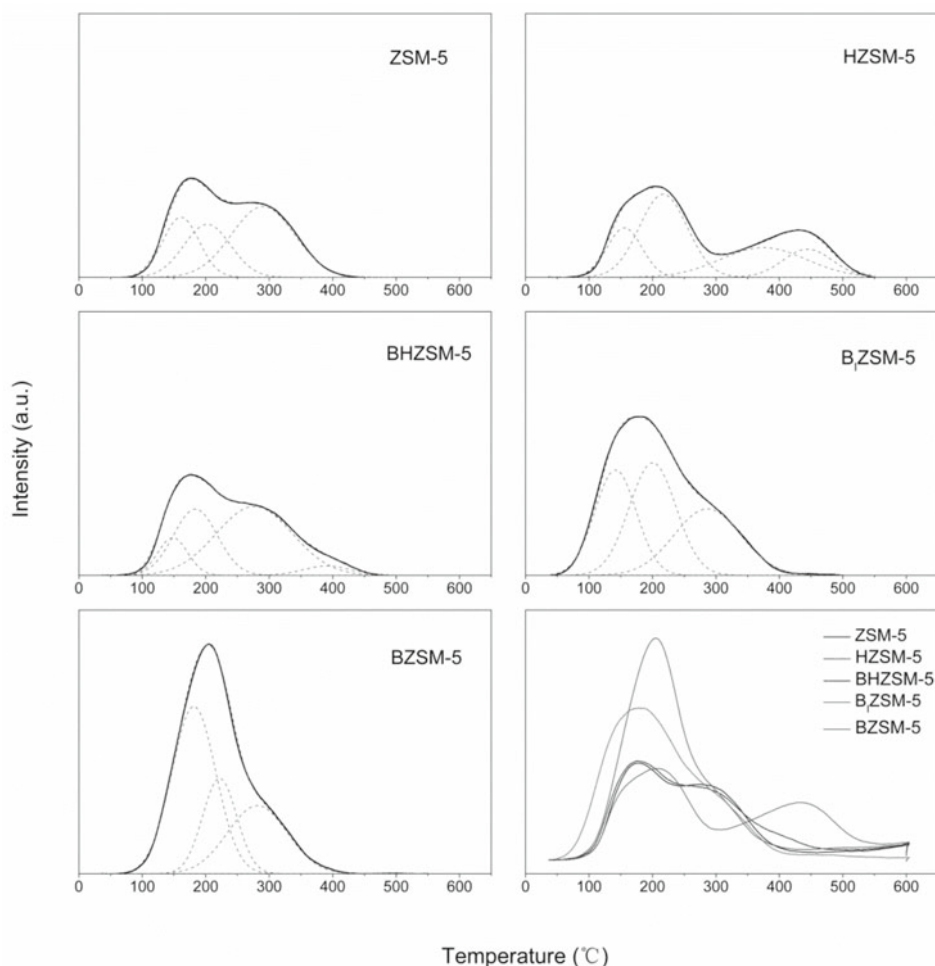


Figure 5. NH_3 -TPD profiles of all samples

that the H-modified samples HZSM-5 and BHZSM-5 show 4 peaks, one peak more than ZSM-5. It is because that the strong acidity of the catalysts increases after H-modification. The strong acid sites of BHZSM-5 are increased, but not obvious. After introduction of B, the intensity of low-temperature peak increases. The spectrum of BHZSM-5 shows a little change in low-temperature peak. The low-temperature peak intensity of B₁ZSM-5 is obviously increasing, indicating the increase of weak acidity, since boric anhydride linked to the zeolite framework via condensation which shows weak acidity after impregnation¹⁴. But impregnation B has only effect on the surface of zeolite, which is different from BZSM-5. The highest low-temperature peak of BZSM-5, meanwhile, shifts toward high temperature, suggesting that the increasing concentration and strength of weak acid sites. It is because B atoms are introduced into the zeolite framework and B acid sites which showing weak acid are generated^{13, 26, 29}.

Effect of B on the catalytic performance of the catalyst

Table 2 shows the results of methanol conversion using the five catalyst samples, tested at T = 460°C; P = 0.1 MPa; and WHSV = 0.3 h⁻¹ with pure methanol as the reactor feed and N₂ as dilute gas. Data were taken after 3 h in reaction. The products obtained are classified into light hydrocarbons (C₁-C₄), light olefins (C₂⁼-C₄⁼), and C₅⁺ hydrocarbons. The reaction result of ZSM-5 and HZSM-5 are comparisons. It can be observed that all samples show high activity toward the high conversions. The catalytic performance of ZSM-5 is ordinary. For HZSM-5, since it contains so many strong acid sites, the higher ethylene selectivity and lower propylene and butylene selectivity are observed apparently. The selectivity to propylene is significantly improved after B modification. For BHZSM-5, the selectivity of ethylene, propylene and butylene are all increased, reaching at 24.80%, 35.35% and 10.49% respectively, while C₂⁼-C₄⁼ olefins selectivity is 70.64%. It may be due to the both increased strong and weak acidity on BHZSM-5, leading the enhancements of the three main olefin products. It is noticed that on B₁ZSM-5 the propylene selectivity increases to 42.27% and the ethylene selectivity decreases to 11.27%, with an increased propylene/ethylene ratio, since its weak acidity is obviously increased and affects the reaction. The selectivity of C₂⁼-C₄⁼ olefins is 68.51%, however the improvement is less than that on BHZSM-5 and BZSM-5. A maximum of 53.53% selectivity to propylene is achieved on BZSM-5 catalyst, while its ethylene selectivity is 16.95%, and the selectivity of C₂⁼-C₄⁼ olefins is as high as 85.21%. The remarkable propylene selectivity is favored by the obviously increasing concentration and strength of weak

acid sites after B addition. Moreover, on BZSM-5 the C₅⁺ selectivity is the lowest of all, which can be ascribed to the suppression of secondary reaction and reduction of aromatics and alkanes amounts by B modification³⁰.

According to the research results in MTP reaction recently, we find that it is very difficult for the single pass selectivity of propylene to achieve 50% or higher, as the literature review published by Stöcker⁵ showed. Also the selectivity reported by Wei et al.² was 45.9%, and in another publication by Yang et al.¹⁵, whose system is borosilicates similar to ours, the propylene selectivity is almost 45%. While impressively, the P impregnation can improve propylene selectivity which can reach over 50%, as Liu et al.³ and Lee et al.¹¹ reported, whose data were 55.6% and 50%, while the selectivity of light olefins were 75% and 81.2% respectively. Comparing with other research results, it can be seen that with our efficient BZSM-5 catalyst, the selectivity of the propylene and light olefins are both remarkably improved, which are 53.53% and 85.21%.

Combined with the catalysts characterization, the main cause for the different product distribution of the samples in MTP reaction could be their difference in catalysts acidity. According to reaction results, the increasing of strong acidity results in an increase in ethylene, whereas the strengthening of weak acidity results in an increment of a little higher olefins, particularly propylene³. After B modification on catalysts the most significant change is the increasing of weak acidity, which efficiently avoids various hydrogen-transfer reaction producing aromatics and aliphatics¹², while propylene selectivity can be improved obviously on these samples. Especially for BZSM-5, plenty of B atoms have essentially been incorporated into the zeolite framework, effectively increasing the concentration and strength of weak acid sites, which caused by BO₄ and BO₃ units. By the appropriate acidity, propylene selectivity on BZSM-5 is improved with pronounced enhancement. BZSM-5 is prepared by boron direct synthesis. In summary, direct synthesis method which fully utilizes the advantages of B addition is the most optimal among the three modification methods—ion-exchange, impregnation and direct synthesis in MTP reaction. In ion-exchange modification, very few B atoms are brought into the catalyst system, while impregnation modification introduces more than the former one and favor the weak acidity increase. But the interaction between B atoms and the zeolite by impregnation is not as obvious as by direct synthesis, which promises excellent reaction results, and also the pores show signs of blockage after impregnation.

From Table 2, butylene selectivity follows the same trend as propylene selectivity, and ethylene selectivity goes against the trend, which corresponds with the

Table 2. Catalytic performance of all samples for MTP reaction

Samples	Conv. [%]	Selectivity [%]					
		C ₁₋₄ ^a	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	C ₅ ^{+b}	C ₂ ⁼ -C ₄ ^{=c}
ZSM-5	99.5	31.69	19.46	29.05	8.61	11.19	57.12
HZSM-5	98.4	13.27	31.71	26.67	6.90	21.45	65.28
BHZSM-5	99.2	14.06	24.80	35.35	10.49	15.30	70.64
B ₁ ZSM-5	95.3	16.37	11.27	42.27	14.97	15.12	68.51
BZSM-5	99.8	7.18	16.95	53.53	14.73	7.61	85.21

^a C₁-C₄ saturated hydrocarbons,

^b C₅ and higher hydrocarbons,

^c C₂⁼-C₄⁼ olefins.

hydrocarbon-pool mechanism^{31,32}. According to this mechanism, there are two possible hydrocarbon pool cycles on ZSM-5 zeolite, methylbenzene cycle and alkene cycle. Ethylene is formed predominantly from the lower methylbenzenes, whereas propylene and higher alkenes are to a considerable extent formed from alkenes methylation and cracking reactions. Our above results show that B modification, especially the direct synthesized catalyst, bringing the appropriate concentration and strength of acid sites favors the alkene route which produced propylene. This is the cause for the excellent propylene selectivity achieved on our B modified ZSM-5 catalyst in the MTP reaction.

CONCLUSIONS

Several kinds of boron modifications had been utilized to prepare B-ZSM-5 zeolites, and the catalysts showed improved reaction activity and propylene selectivity in MTP reaction. The characterization results proved that B modification led to an increase of the weak acidity on the ZSM-5 catalyst without bringing obvious damage of the MFI structure, which result in an improvement of selectivity for propylene. Especially by the direct synthesis method, plenty of B atoms were incorporated into the zeolite framework, and the moderate concentration and strength of acid sites both approach an appropriate level, further improves the propylene selectivity, with pronounced enhancement of propylene selectivity up to 53.53% and C₂=-C₄= olefins selectivity up to 85.21% in MTP reaction.

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