

Conversion of Methanol to Propylene over a High Silica B-HZSM-5 Catalyst

Aina Xu, Hongfang Ma, Haitao Zhang, Weiyong Ying, and Dingye Fang

Abstract—Hydrothermally synthesized high silica borosilicates with the MFI structure was subjected to several characterization techniques. The effect of boron on the structure and acidity of HZSM-5 catalyst were studied by XRD, SEM, N₂ adsorption, solid state NMR, NH₃-TPD. It was confirmed that boron had entered the framework in the boron samples. The results also revealed that strong acidity was weakened and weak acidity was strengthened by the boron added zeolite framework compared with parent catalyst. The catalytic performance was carried out 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 and excellent stability for the B-HZSM-5. The catalyst exhibited about 81% selectivity to C₂= - C₄= olefins with 40% selectivity of propylene as major component at near 100% methanol conversion, and the stable performance in the studied period was 100 h.

Keywords—Methanol to propylene, HZSM-5, boron.

I. INTRODUCTION

PROPYLENE is a versatile building block for important polymers, intermediates and chemicals. Its production is mainly from steam cracking and refineries. Due to the growing demand for propylene and the shortage of petroleum resource in the future, new processes with high yield of propylene are required.

Since the discovery of the methanol-to-gasoline reaction by Mobil Oil, the methanol-to-hydrocarbon (MTHC) technology, mainly the methanol-to-gasoline (MTG) and methanol-to-olefin (MTO) reactions, has been regarded as a new route to convert coal or natural gas into gasoline and

chemicals in general, for methanol can be easily produced from natural gas and coal. Almost anything that can be made out of crude oil can also be acquired with this technology [1, 2]. Methanol-to-olefins (MTO) and methanol-to-propylene (MTP) processes are promising ways for the production of propylene. So, these two new routes have attracted significant attention [2]-[4].

As compared to the traditional MTO process, where ethylene is the main product, high propylene to ethylene ratio is the most distinguishable feature for MTP process that enables the high propylene yield in the recirculation process [5]. But achieving high yields of propylene is still challenging.

Recent studies reveal a much clearer insight into the reaction aspects [6, 7]. 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 plays a vital role. Variation of framework Si/Al ratio by pre or post synthesis methods is a generally adopted procedure for tuning the zeolite acidity [8]. Moreover, many promoters had been impregnated on HZSM-5 and improved the light alkene selectivity observably by leading a significant decrease in acidity, such as phosphorus, lanthanum and silver [7, 9]. Furthermore, from the works made on the improvement of the HZSM-5 stability, modified catalyst with lower strong acidity can successfully reduce coke formation. Blasco et al. [10] found that phosphorus modified HZSM-5 had shown attractive hydrothermal stability and the P/Al ratio in zeolite was important for the hydrothermal stability.

Since the first synthesis of borosilicates with the MFI structure was reported [11], the catalytic properties of the B-ZSM-5 have been discussed by several authors. Unneberg [12] et al. reported that the activity of B modified catalyst in the methanol reaction was very poor compared to pure HZSM-5, for the acidity of B-ZSM-5 was much weaker than the unmodified HZSM-5 catalysts. Yang [13] et al. prepared the B-HZSM-5 catalysts with increased weak acidity and constant strong acidity, which had high activity in methanol conversation reaction. Overall ZSM-5 catalysts after boron addition with high weak acidity would be available in MTP reaction.

In order to involve all advantages over the reported HZSM-5 catalysts, which contains high weak acidity and low strong acidity, a new high silica B-HZSM-5 were synthesized in the present work. The B modified high silica HZSM-5 zeolite was prepared by hydrothermal synthesis method. Samples were well characterized by various methods and used in MTP reaction. For the modified catalyst, which gives the remarkable improvement in propylene selectivity and catalytic

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life, the catalyst structure and acidity were investigated.

II. EXPERIMENTAL

A. Preparation of Catalyst

B modified HZSM-5 zeolite catalyst with Si/Al ratio of 250 were prepared hydrothermally. Certain amount of NaAlO_2 , NaOH and H_3BO_3 was dissolved in deionized water to make a clear solution. TPABr and silica sol was added to the solution under stirring for 3 h to get a translucent gel. The obtained gel with a molar composition of SiO_2 : (1/500) Al_2O_3 : 0.14TPABr: 0.1 Na_2O : 30 H_2O : 0.1 B_2O_3 was stirred for 3 h and then was transferred into a 100 ml stainless-steel autoclave. It was crystallized at 170 °C for 48 h. The precipitated crystals thus obtained were filtered, washed with deionized water, dried overnight at 110 °C and calcined in air at 550 °C for 6 h for removing the template. The zeolite was ion exchanged for 4 h at 80 °C followed by calcination in air at 550 °C for 4 h. Thereby, protonated samples were obtained.

An unmodified HZSM-5 (250) with the molar ratio of SiO_2 : (1/500) Al_2O_3 : 0.14TPABr: 0.1 Na_2O : 30 H_2O was used as benchmark catalyst.

B. Characterization of Catalysts

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 using $\text{Cu K}\alpha$ radiation at 40 kV and 100mA. XRD patterns were obtained over a 2θ range of 3-50 ° and a step size of 0.02 °.

Temperature-programmed desorption (NH_3 -TPD) measurements were carried out on Micrometrics AutoChem II 2920. Prior to the NH_3 -TPD measurements, 0.200 g sample placed in a quartz U-tube reactor was pretreated in He stream at 550 °C for 2.0 h and then cooled to 100 °C. NH_3 -TPD was conducted with a gas mixture of 10 vol. % NH_3 in He at a flow rate of 30 ml/min for 30 min, He flow was passed through the sample to remove weakly adsorbed NH_3 molecules for 60 min. Finally, the He flow (40 mL/min) was passed through the sample with increasing temperatures up to 600 °C at the rate of 10°C/min. The desorbed ammonia was detected on a thermal conductivity detector (TCD).

Scanning Electron Microscopy (SEM) was employed to obtain the surface morphology. SEM measurements were performed on a JSM-6360LV electron microscope.

BET surface areas (S_{BET}) of the ZSM-5 samples were determined by N_2 adsorption-desorption measurements employing the BET-method with a Micrometrics ASAP 2020 apparatus. Total pore volume and sizes were evaluated using the standard Barrett Joyner Halenda (BJH) treatment.

The ^{27}Al and ^{11}B MAS NMR were obtained at a Bruker DRX 500 spectrometer of 99.35 MHz using a short RF pulse length of 4.0 μs and a recycle delay of 8.1 μs .

C. Catalysis Activity

The MTP reaction was conducted in a fixed-bed at 460 °C under atmospheric pressure. Pure methanol was fed into the reactor. The weight hourly space velocity (WHSV) for

methanol was 0.3 h^{-1} .

The analysis of the gas reaction products were performed on on-line gas chromatographs: Agilent GC 6890N (FID, Plot $\text{Al}_2\text{O}_3/\text{KCl}$). Aqueous and organic phases in liquid products were separated. The aqueous phase and the organic phase were analyzed with 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.

III. RESULTS AND DISCUSSION

The N_2 physisorption results of HZSM-5 and B-HZSM-5 catalysts are presented in Table I. BET surface area, pore volume and pore width of catalyst have a little decrease with joining of boron, probably due to the declined crystallinity, caused by the formation of defects after modified for a certain amount of dealumination and the exframework species blocked of pores by inside zeolite channels. Actually, the differences of the two catalysts are slightly, which suggests the textural property is not significantly influenced by B incorporation.

TABLE I
SURFACE CHARACTERISTIC OF HZSM-5 AND MODIFIED HZSM-5 CATALYSTS

| Sample | S_{BET} (m^2/g) | V_{total} (cm^3/g) | V_{micro} (cm^3/g) | Average Pore Width (μm) |
|----------|---|--|---|---|
| HZSM-5 | 365 | 0.21 | 0.11 | 2.32 |
| B-HZSM-5 | 346 | 0.20 | 0.07 | 2.30 |

Fig. 1 shows the XRD patterns of the two prepared zeolites used in this study. Typical diffraction lines corresponding to MFI structure are observed, showing the pure phases of the obtained zeolites. As it is shown in Fig. 1, the intensity of the diffraction peaks of B-HZSM-5 catalyst is a bit lower, indicating that boron addition decreased the zeolite crystalline slightly, but not changed the structure.

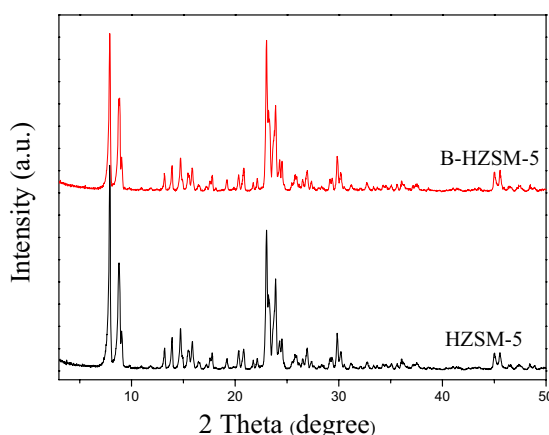


Fig. 1 XRD patterns of the catalysts

Fig. 2 shows the SEM images of the two catalysts. HZSM-5 and B-HZSM-5 exhibited different morphologies along with crystal sizes of 10.0 and 3.5 μm , respectively. The B-HZSM-5 catalyst has the smaller partial size, which is exposed more acid sites and is favorable for reaction. HZSM-5 is an example of the archetype MFI morphology, usually described as twinned prisms. B-HZSM-5 appears to be less complex, appearing as smooth and classical coffin-shape without the side protrusions seen in former [13]. It should be noted that the single crystals are handful composed which leading to the formation of pyramidal boundaries showing on boron modified catalyst [14]. The distribution of the particle size seems rather uniform on both samples, reflecting the well zeolite crystalline.

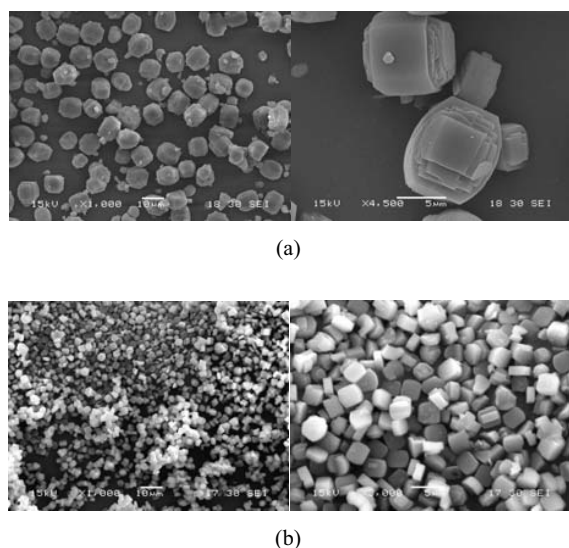


Fig. 2 (a) SEM images of HZSM-5 (b) SEM images of B-HZAM-5

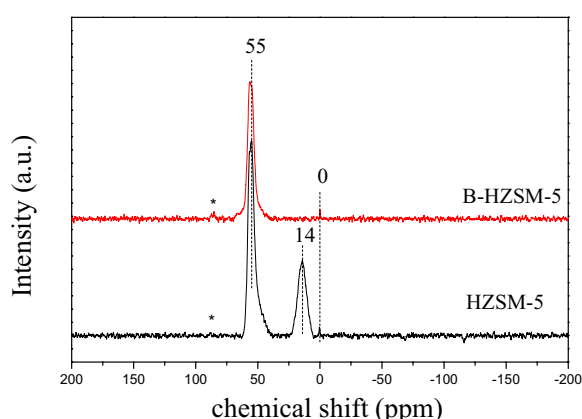


Fig. 3 ^{27}Al MAS NMR spectra of the catalysts

Fig. 3 shows the ^{27}Al MAS NMR spectra of HZSM-5 and boric acid modified catalysts. ^{27}Al MAS NMR spectrum of HZSM-5 sample shows three peaks at 55 ppm, 14 ppm and 0 ppm, respectively. The peak at 55 ppm is ascribed to tetrahedral Al inside the zeolite framework; the peak at 14 ppm can be

attributed to shell octahedral Al and the peak at 0 ppm can be belonged to octahedral Al species of zeolite extra-framework [15, 16]. The peak at 14 ppm completely disappeared upon B modification, suggesting when B is introduced into the zeolite, the shell octahedral Al species had some changes. The intensity of the peak at 55 ppm is lower in B-HZSM-5 catalyst than in HZSM-5, indicating that the zeolite crystallinity decreased with the B addition.

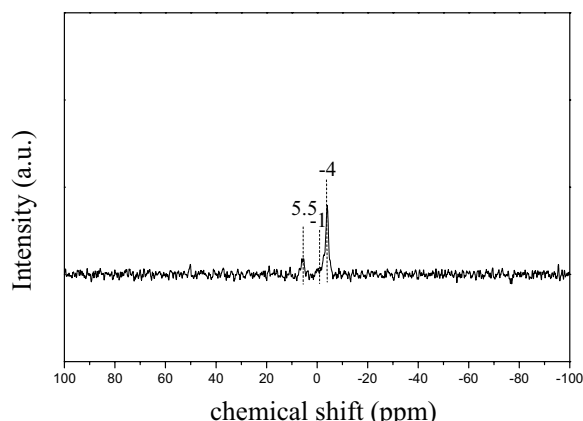


Fig. 4 ^{11}B MAS NMR spectra of B-HZSM-5 catalyst

Fig. 4 shows the ^{11}B MAS NMR spectra of B-HZSM-5 catalyst. As shown in Fig. 5 several peaks appeared at 5.5, -1 and -4 ppm. The main resonance peak at -4 ppm is assigned to tetrahedral framework BO_4 units, and the doublet at -1 and 5.5 ppm has been assigned to trigonally coordinated framework BO_3 [17-19]. The peaks on ^{11}B MAS NMR spectra indicate that B atoms have quantity entered the frameworks combining with Si, which will be in good agreement with NH_3 -TPD results.

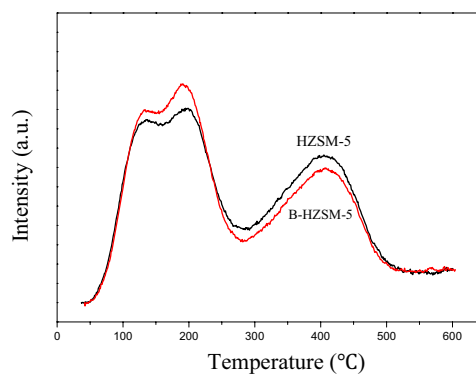


Fig. 5 NH_3 -TPD profiles of the catalysts

Fig. 5 shows NH_3 -TPD profiles of HZSM-5 and B-HZSM-5 catalysts in the temperature range of 50-600 $^{\circ}\text{C}$. The catalysts all exhibit a two-peak pattern: a low temperature peak at 100-200 $^{\circ}\text{C}$ and a high temperature peak at 350-450 $^{\circ}\text{C}$, suggesting weak acid sites and strong acid sites, respectively. Though the signal of NH_3 -TPD is weak for HZSM-5 with a high Si/Al ratio because of the relatively low amount of acid

sites, the variation of desorption peak is clearly observed. Compared to HZSM-5, the desorption peaks of B-HZSM-5 are almost the same peak location while the intensity of low temperature peak is higher and high temperature peak is lower. The NH_3 -TPD results indicate that the weak acid sites increased and strong acid sites decreased with boron addition, clearly emphasizing the effective interaction of B with the zeolite framework. The B atoms in the zeolite framework seem to combine with Si and show weak acidity [17]. Thus the B-HZSM-5 catalyst with the higher weak acidity and lower strong acidity than HZSM-5 is expected to exhibit improved catalytic properties in terms of propylene yield, hydrothermal stability and coke resistance in MTP reaction.

TABLE II
CATALYTIC PERFORMANCE OF CATALYSTS FOR MTP REACTION

| Catalyst | Conv. (%) | Selectivity/ (%) | | | | | |
|----------|-----------|-----------------------------|------------------------|------------------------|------------------------|--------------------------|------------------------------------|
| | | $\text{C}_{1-4}^{\text{a}}$ | C_2H_4 | C_3H_6 | C_4H_8 | $\text{C}_5^{+\text{b}}$ | $\text{C}_2-\text{C}_4^{\text{c}}$ |
| HZSM-5 | 100 | 11.41 | 36.18 | 34.88 | 9.09 | 8.44 | 80.15 |
| B-HZSM-5 | 99.32 | 7.86 | 29.85 | 40.04 | 11.83 | 10.42 | 81.72 |

^a C_1 - C_4 saturated hydrocarbons

^b C_5 and higher hydrocarbons

^c C_2 - C_4 olefins

Table II compares the catalytic performance of the catalyst samples at steady state in MTP reaction, tested at $T = 460^\circ\text{C}$; $P = 0.1\text{ MPa}$; and $\text{WHSV} = 0.3\text{ h}^{-1}$ with pure methanol as the reactor feed and N_2 as dilute gas. Data were taken after 3 h on stream. The products obtained are classified into light hydrocarbons (C_1 - C_4), light olefins (C_2^- - C_4^-) and C_5^+ hydrocarbons. The two catalysts exhibited nearly 100% conversion of methanol, but the products distribution had some differences. With B addition, the following changes are observed in the products distribution: 1. Selectivity of ethylene is decreased. 2. Selectivities to propylene and butylene are both increased. 3. The C_2^- - C_4^- olefin yields increased slightly. These observations suggest the positive role of B in the zeolite framework for improving selectivity of propylene, especially $\text{C}_3^- / \text{C}_2^-$, which can be attributed to the different catalytic acidity of B-HZSM-5 compared to the H-ZSM-5 primary, while the reason for particle size more or less. The study from M. Firoozi, et al. had demonstrated that reduced the crystallite size of the ZSM-5 catalysts could expose more acid sites and get higher performance [20].

Earlier studies indicated that higher Si/Al of zeolite is better for increasing the propylene selectivity [21, 22]. As the acidity decreasing with the increase of Si/Al ratio, the moderate acidity in high Si/Al samples is responsible for the improved formation of propylene. Also the conclusion from phosphorus modified catalysts, the elimination strong acid sites and enhancement propylene selectivity were demonstrated [8, 23]. The improved propylene selectivity obtained in the present study can be ascribed to the decrease in acidity of B-HZSM-5, which caused by BO_4 and BO_3 units. The NH_3 -TPD profiles indeed support the decrease in strong acidity of B-HZSM-5 catalyst. Furthermore, after B addition, the increased catalyst weak acidity, for showing the moderate acidity, are positive for the propylene selectivity.

The changes in products selectivity with time on stream for

the parent and B added HZSM-5 samples are presented in Fig. 6. B modification leads to a distinct improvement in the stability of conversion. The conversion drops to 87.6 % after 50 h on stream for the HZSM-5, and it remains above 98.7 % after 100 h on stream, with no deactivation observed under the same reaction conditions for B-HZSM-5. After B modification, propylene selectivity increases from 34.88 % to 40.04 % and maintains stable in a long period more than 100 h (Fig. 6b). As comparison, it began to decrease at about 30 h for the parent sample.

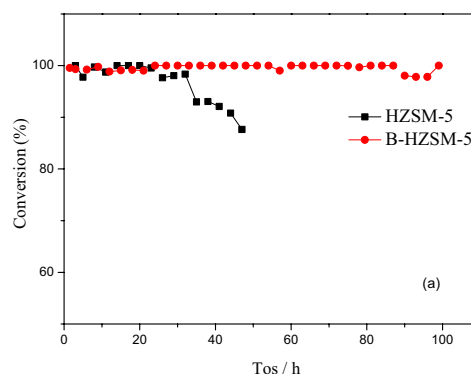


Fig. 6 (a) Comparison of conversion of B-HZSM-5 and HZSM-5 of time on stream

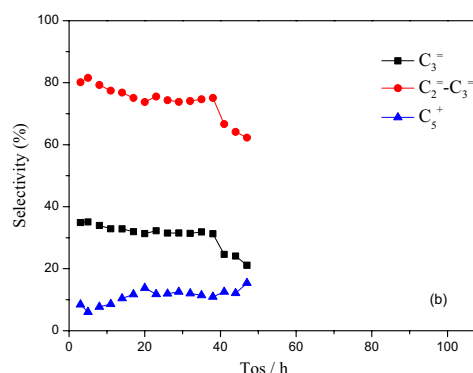


Fig. 6 (b) selectivity of C_3^- , C_2^- - C_4^- and C_5^+ over HZSM-5 of time on stream

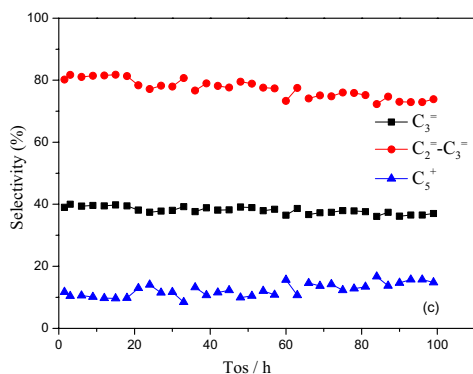


Fig. 6 (c) selectivity of C_3^- , $C_2^-C_4^-$ and C_5^+ over B-HZSM-5 of time on stream

According to the literature, catalyst deactivation is caused by coke deposition [2]. When the coke accumulates to some amount, it would block the micropores of the catalyst and subsequently results in a sharp deactivation. The selectivity of C_5^+ hydrocarbons increases obviously with time on stream (Fig. 6c) for HZSM-5 catalyst, which definitely leads to more coke and accelerates the deactivation process as a result. For B modified catalyst, lower selectivity of high hydrocarbons lasts more than 100 h, which indicates a lower coking rate (Fig. 6b). B-HZSM-5 catalyst with lower strong acidity compared with HZSM-5 can successfully reduce the hydride transfer and cyclization reactions which lead to the formation of high hydrocarbons. Thus, with less coke formation, higher selectivity of propylene and longer time of stability in MTP reaction were obtained. Moreover, the reduction in the crystallite size of the ZSM-5 catalysts suppressed the formation of coke on the surface and/or in the pore, contributing to the slow deactivation, which is another reliable reason for long life time of B-HZSM-5 [24].

IV. CONCLUSIONS

A sample of B modification HZSM-5 catalyst for MTP reaction to produce propylene was prepared by hydrothermal crystallization method. Catalyst with a Si/Al ratio of 250 can effectively convert methanol to propylene. The characterization results demonstrated that B modification had incorporated into the framework and was scarcely damaged the MFI structure. Rather, a decrease in strong acidity and increase in weak acidity were observed in this catalyst for the B addition. By the appropriate concentration and strength of acid sites of B-HZSM-5, olefins selectivity was improved, with pronounced enhancement of propylene selectivity up to 40.0%, at near 100% conversion of methanol. Apart from the product distribution, the presence of B in the framework also caused improved life time of the B-HZSM-5 catalyst and the improved stability with time-on-stream. The catalyst exhibited improved stability in methanol conversion as well as light olefin selectivity in the studied period of 100 h.

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