Effect of acid distribution of B-ZSM-5 on product selectivity in MTP reaction

<u>Subing Fan,</u> **Qixin Wang, Junmin Lv, Yongqiang Cai, Tiansheng Zhao***
State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry & Chemical Engineering, Ningxia University, Yinchuan, 750021, People's Republic of China
**Corresponding author: +86-951-2062393, fansb@nxu.edu.cn*

Abstract: The B-ZSM-5 was successfully synthesized with uniform small crystals by doping B element via isomorphous replacement method and it displayed different acid distribution through modulating the Si/Al ratio and B/Al ratio. The active evaluation showed there existed correlations between the acid distribution and product selectivity in methanol to propylene (MTP) reaction. The internal strong B acid was unfavorable to olefins, especially propylene. The relationships between coking amount and the strong B acid distribution indicate the deactivation is mainly because the blocking of micropores by coking on external surface.

Keywords: acid distribution, product selectivity, isomorphous replacement, methanol to propylene.

1. Introduction

As so far, for methanol to propylene (MTP) reaction, many reaction mechanisms are suggested. Among them, the dual-cycle mechanism is considered to be reasonable for explaining the methanol conversion. And it undergoes many complex processes from methanol to propylene, such as dehydration of methanol, increase of carbon chain, alkylation of olefin, cracking of high olefin, cyclization and dehydroaromatization of high olefin, hydrogen transfer, alkylation and dealkylation of aromatics and so on. However, all these reactions mentioned here are almost relative to the acidity and it has been proved experimentally that the acidity, mainly focusing on acid strength and acid amount tested generally by NH_3-TPD technology in many researches, is vital for the selectivity of propylene.

In this work, the surface acidity of B-ZSM-5 was modified by doping B element via isomorphous replacement method. And the effect of acid distribution on product selectivity in MTP reaction was studied.

2. Experimental

In this work, B-doping ZSM-5 was prepared via isomorphous replacement method. The acid distribution was modulated by adjusting Si/Al ratio and B/Al ratio.

The acidity of prepared samples was characterized on a Bruker Tensor27 FT-IR spectrometer. And the active evaluation of prepared samples in MTP reaction was conducted on a fixed bed reactor under a similar reaction conditions with industrial plant.

3. Results and discussion

Figure 1 shows partial XRD patterns and FT-IR spectra of represented samples with different Si/Al ratio and B/Al ratio. All samples display the MFI topology, indicating the doping of B element doesn't influence their crystal structure. The appearance of 914 cm^{-1} and 1400 cm^{-1} indicate B element enters into the framework of ZSM-5. And the SEM images show the uniform small crystals.

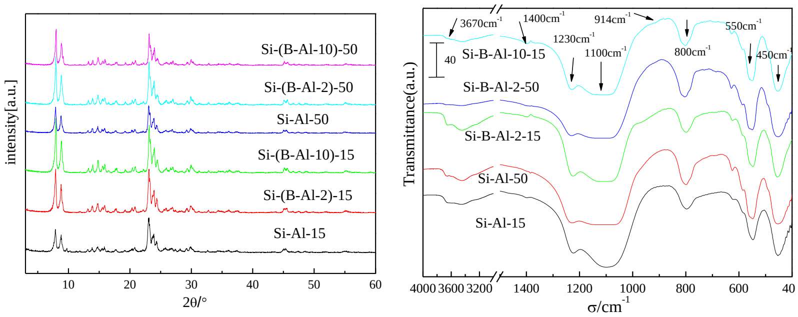

Figure 1. XRD patterns and FT-IR spectra of represented samples

With the decrease of acid amount by increasing the Si/Al ratio, the propylene selectivity increased; and with the decrease of acid strength by increasing the B/Al ratio, the propylene selectivity also increased. And it was also found it has a long lifetime for B-doping ZSM-5. The maximum propylene selectivity reaches above 45% while the aromatics selectivity can be reduced to only 2.3%.

The further research found that actually there have interesting relations between the acid distribution and the product selectivity. Here partial important relationships are simply introduced as shown in Figure 2. It is obvious that the internal strong B acid amount on micropores remarkably influences the product selectivity. With the increase of the strong B acid amount, the production of alkanes is favored, especially for methane, and that of light olefins is unflavored, especially for propylene. That is, the produced primary olefins might undergo the hydrogen transfer reaction in the presence of strong B acid and the internal strong B acid amount should be controlled at a low level. Simultaneously, it was found the selectivity of C_{5+} hydrocarbons and aromatics all had different trend with the internal strong B acid amount. Strong B acid favors the production of C_{5+} hydrocarbons and aromatics. However, they will take secondary reactions, such as dealkylation of aromatics and catalytic cracking of C_{5+} hydrocarbons, when the strong B acid is enough.

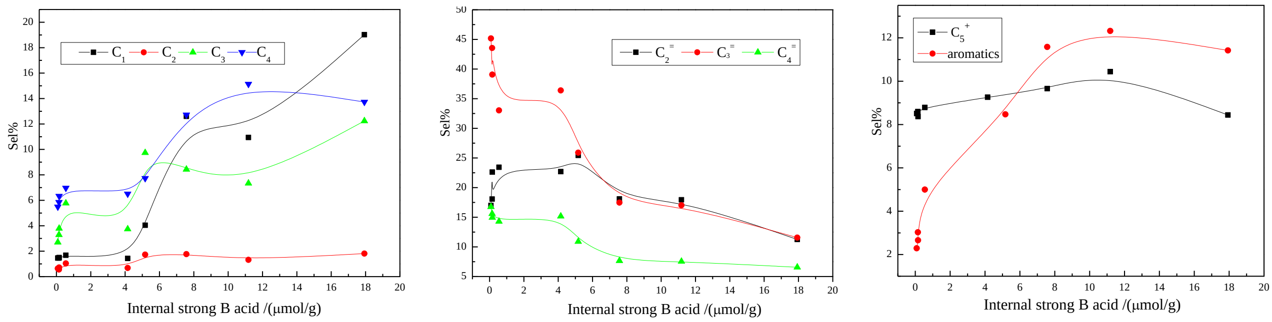

Figure 2. Relationships between internal strong acid amount and product distribution

The correlations between coking amount and strong B acid amount are shown in Figure 3. The coking amount on internal surface increases and finally reaches a balance with the increase of internal strong B acid amount, while that on external surface increases linearly with the external strong B acid amount, indicating the deactivation is mainly because the blocking the micropores by coking on external surface.

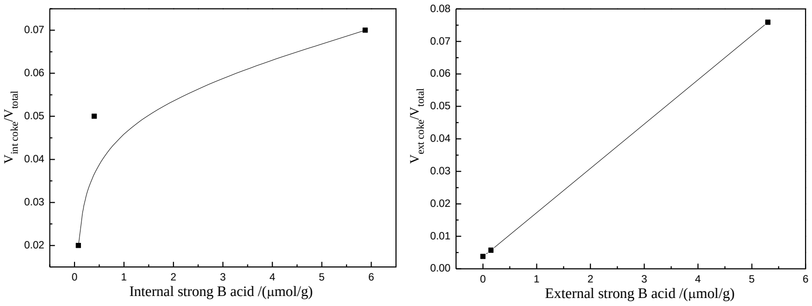

Figure 3. Correlations between coking amount and strong B acid amount

4. Conclusions

There exist close correlations between the acid distribution and product selectivity in MTP reaction. Different acid type, different acid amount and different acid distribution will influence the product distribution and simultaneously influence the coking on internal surface and external surface.

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References (omitted)