

Preparation of boroaluminosilicate zeolite with the AEI structure and its catalytic activity

Yusuke Kunitake¹, Masato Yoshioka¹,
Junko N. Kondo¹, Toshiyuki Yokoi^{1*}

¹ Tokyo Institute of Technology,
Yokohama, Japan

*E-mail: yokoi@cat.res.titech.ac.jp

In recent years, a catalytic conversion of ethene to propene and butenes (ETPB reaction) has received a broad attention because of shale gas revolution. It is well known that 8-membered ring zeolites show high conversion and high selectivities to propene and butenes in the ETPB reaction [1]. However, their catalyst life is generally short. This deactivation is mainly caused by the pore blocking with polycyclic aromatics produced by successive reactions due to high acid amount. Therefore, acid amounts should be optimized to inhibit undesired successive reactions. In this study, the density of acid sites in the AEI-type zeolites was controlled by incorporating boron atoms into the framework instead of Al atoms.

Al-containing AEI (Al-AEI) and B, Al-containing AEI (B,Al-AEI) zeolites were synthesized by using tetraethylphosphonium hydroxide (TEPOH) and USY zeolites as organic structure-directing agent and Si and Al sources, respectively, according to previous report [2].

Typical XRD patterns of the AEI framework structure were observed in as-synthesized Al- and B,Al-AEI zeolites. By SEM observation, both samples showed cubic particles 0.7 - 1.0 μm in each length.

The Si/Al atomic ratio of Al-AEI after the H₂ treatment was ca. 11 (Table 1). B,Al-AEI had Si/Al and Si/B ratios of 29 and 18, respectively; the Si/(Al+B) ratio was calculated to be 11 indicating that approximately 60 % of aluminum atoms in Al-AEI were substituted with boron atoms in B,Al-AEI. The remaining P species in Al-AEI after the H₂ treatment were much lower than those after the calcination in air; the calcination in air resulted in the formation of Al-O-P species and such P species were hardly removed by the calcination. The H₂ flow

treatment is an effective method for removing P species derived from the P-containing OSDA.

The acid amounts estimated by NH₃-TPD were listed in Table 1. The acid amounts of the Al-AEI samples after the calcination in air and H₂ flow treatment were 0.23 and 0.68 mmol/g, respectively. The remaining P species would cover the acid site, resulting in the lower acid amount. The acid amount of the B,Al-AEI after the H₂ flow treatment was 0.25 mmol/g, indicating that the framework B species did not contribute to typical Brønsted acid sites. Thus, the tuning of acid density of the AEI-type zeolite was successfully achieved by the incorporation of B atoms into the framework in place of Al atoms.

Table 1 Components of obtained products.

Sample		Si/Al	Si/B	Si/(Al+B)	P/(Al+B)	Acid amount (mmol/g)
Al-AEI	Air	11	-	-	1.0	0.23
	H ₂ flow	11	-	-	0.4	0.68
B,Al-AEI	Air	28	20	12	1.0	-
	H ₂ flow	29	18	11	0.3	0.25

Figure 1 shows the time course change in the ETPB reactions over the Al-AEI and B,Al-AEI zeolites after the H₂ flow treatment. Both catalysts produced mainly propene followed by butenes. Al-AEI showed a higher ethene conversion than B,Al-AEI at 5 min on time on stream due to the high acid density. The conversions for both catalysts were decreased along with the time. However, the conversion for B,Al-AEI was higher than that for Al-AEI after 30 min on stream. This improvement would be due to the lower acid density.

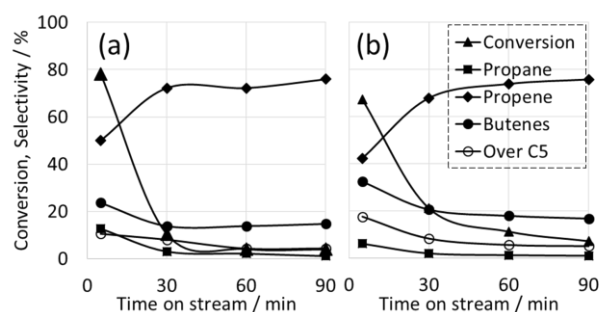


Figure 1 ETPB reaction results of (a) Al-AEI and (b) B,Al-AEI heated under H₂ flow condition.

REFERENCES

- [1] M. Hunger et al., *J. Catal.* 314 (2014) 10
- [2] T. Sano et al., *Chem. Lett.* 43 (2014) 302