The control of acidic property on AEI-type zeolite and its catalytic activity to MTO reaction

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Abstract: To improve the catalytic performance in the Methanol to Olefins (MTO) reaction over the AEI-type aluminosilicate, its acidic property was tuned by incorporating B and Ga atoms into the framework structure. The incorporation of B and Ga atoms was confirmed by several characterizations. Thus prepared zeolites showed different acid strengths, and catalytic lifetime in the MTO reaction, depending on the heteroatoms.

Keywords: **AEI**-type zeolite, MTO reaction, acidic properties.

1. Introduction

Zeolite is well known as the catalyst showed a great performance for MTO reaction. In various framework types of zeolite, small pore zeolite is the notable structure for MTO reaction with the object of selectivity to lower olefins. Especially, **CHA**-type zeolite has been researched passionately to improve the catalyst life and the yield to propylene. In recent years, **AEI**-type zeolite, is similar structure to **CHA**-type, has also been investigated and tried to improve its performance for MTO reaction [1]. However, **AEI**-type zeolite with low acid amount have not been synthesized directly. In this work, synthesis of high silica **AEI**-type zeolite was made an attempt by B and Ga incorporation.

2. Experimental

Al-containing AEI ([Al]-AEI), Al, B-containing AEI ([Al, B]-AEI) and Al, Ga-containing AEI ([Al, Ga]-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]. Thus mother gels were crystallized in an oven at 170 °C for 5 days. The solid products were recovered by filtration, washing with distilled water and drying overnight at 100 °C. After that, all of the products were calcined at 600 °C for 6 h under air atmosphere. The samples were also treated at 600 °C for 6 h under hydrogen flow conditions to remove P species as well as TEPOH. After hydrogen treatment, H-form zeolite was obtained by NH_4^+ ion-exchange and calcined at 600 °C for 3 h. The MTO reaction was performed at 350 °C at a W/F (weight/flow; the weight of catalyst (g) divided by the flow rate of liquid methanol (mol h^{-1}) fed into the reaction system) of 33 g h mol^{-1}. The obtained catalysts were characterized by XRD, ICP, FT-IR, SEM and solid state MAS NMR measurement.

3. Results and discussion

Table 1 Physicochemical compositions of the products

Sample	Products [a]				Acid amount [b] / mmol g^{-1}
	Si/Al	Si/(B or Ga)	Si/T	P/T	
[Al]-AEI	11	-	11	0.4	0.68
[Al, B]-AEI	29	18	11	0.3	0.25
[Al, Ga]-AEI	18	18	9	0.5	0.40

(T = Al, B, Ga), a: ICP, b: NH_3-TPD

Typical X-ray diffraction patterns of the **AEI** framework structure were observed in the as-synthesized [Al]-, [Al, B]- and [Al, Ga]-AEI samples. By SEM observation, [Al]-AEI and [Al, B]-AEI showed cubic particles 0.7 - 1.0 μm in each length, however, for [Al, Ga]-AEI, secondary particles with the size of about 10 μm were observed. The results of ICP elemental analyses and NH_3-TPD were summarize in Table 1. The Si/Al atomic ratio of [Al]-AEI after the hydrogen treatment was ca. 11. [Al, B]-AEI had Si/Al and Si/B ratios of 29 and 18, respectively; the Si/(Al+B) ratio was calculated to be 11, being similar to the Si/Al ratio of [Al]-AEI; approximately 60 % of Al atoms in [Al]-AEI were substituted for B atoms in [Al, B]-AEI. Si/Al and Si/Ga ratios in [Al, Ga]-AEI were ca. 18 and 18, respectively. The acid amount of [Al]-AEI (ca. 0.68 mmol g^{-1}) was higher than that of [Al, B]- and [Al, Ga]-AEI (ca. 0.25 and 0.40 mmol g^{-1}, respectively). The *in-situ* CO-adsorbed FT-IR measurement revealed that there was a marked difference in the acid strength among the samples (Fig. 2). Besides the band at 2140 cm^{-1}, which is attributed to physically adsorbed CO species, [Al]-AEI and [Al, B]-AEI showed a band at 2171 cm^{-1}, which is attributed to the CO species adsorbed on the Brønsted acid sites (BASs) derived from framework Al species. However, the intensity of this band of [Al, B]-AEI was especially lower (Fig. 2(b)) than that of [Al]-AEI (Fig. 2(b)), implying that less acidic OH groups existed in [Al, B]-AEI. Additionally, from the spectra of [Al, B]-AEI, the other band at 2154 cm^{-1} was observed, and this band is attributed to the CO species adsorbed on the BASs derived from framework B species, indicating the formation of weak BASs compared to those derived from framework Al species. These results strongly support the incorporation of B atoms into the AEI framework. According to the spectra of [Al, Ga]-AEI (Fig. 2(c)), a band at 2171cm^{-1} was slightly shifted to lower frequency as the adsorbed CO species increased, indicating that acid site derived from framework Ga atoms existed and its acid strength was weaker than that derived from framework Al atoms.

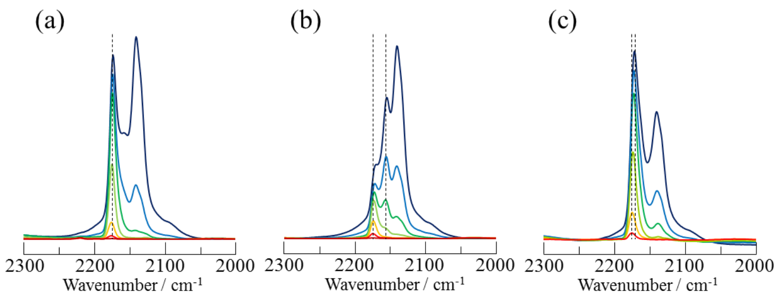

Fig. 2 Subtracted IR spectra measured during CO adsorption at −120 °C on (a) [Al]-AEI, (b) [Al, B]-AEI and (c) [Al, Ga]-AEI.

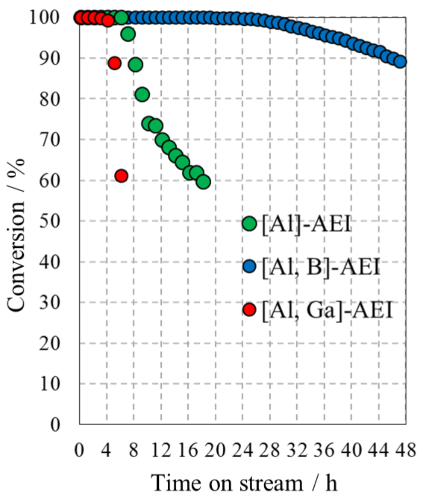

Fig. 3 Methanol reaction results over [Al]-, [Al, B]-, and [Al, Ga]-AEI.

These prepared samples were used as a catalyst for the MTO reaction. Fig. 3 shows the change in the conversion of methanol along with the time on stream. In Fig. 3, [Al, B]-AEI showed a dramatically long lifetime with the conversion of 100 % for 19 h kept, and deactivation occurred gradually after 19 h. By FT-IR measurement, [Al, B]-AEI has acid sites with weak acid strength that cannot convert methanol. Therefore, in [Al, B]-AEI, the active sites for methanol conversion were decreased and pore blocking of coke formation was inhibited. On the other hand, [Al, Ga]-AEI exhibited a shorter catalytic lifetime than [Al]-AEI. In the previous report, Ga containing metallosilicate shows the Lewis acid site [3]. Thus, it is considered that Lewis acid site in [Al, Ga]-AEI promoted aromatics formation, resulting in the rapid deactivation.

4. **Conclusion**

B and Ga atoms incorporation to AEI-type zeolite was carried out to weaken the acid strength and its acidic properties were different from [Al]-AEI by FT-IR. And also, on the MTO reaction, [Al, B]-AEI showed dramatically longer lifetime than [Al]-, [Al, Ga]-AEI.

References

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