Synthesis of CON-type zeolites with trivalent heteroatoms and its Catalytic Application for MTO reaction
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Introduction
The methanol-to-olefins (MTO) reaction over molecular sieve materials has received great attention because of the shortage of crude oil in the foreseeable future. To date, molecular sieve silicaaluminophosphosphate SAPO-34 and ZSM-5 have proven to be uniquely effective catalysts for the conversion of methanol. Their catalysts have high accessibility and diffusibility because of their 3-dimensional channel system. They showed a relatively long catalytic life in the MTO reaction.

Materials and Methods
The metallosilicates with a CON topology were synthesized according to the original recipe of CIT-1 with modifications [1]. In typical synthesis of [Al,B]-CIT-1, aluminum sulfate and boric acid were added to an aqueous solution containing NaOH and N,N,N-trimethyl(-)-cis-myrtylammonium hydroxide (TMMAOH), which was prepared by methylation of (-)-cis-myrtylamine with methyl iodide followed by ion-exchange. Finally, fumed silica was added to the mixture. The molar composition of the reaction mixture was 1.0 SiO2: 0.04 H3BO3: 0.005 Al2(SO4)3: 0.1 NaOH: 0.2 TMMAOH : 60 H2O. Then 2w% of as-made [B]-beta (Si/B = 14 in product) was added to the mixture as a seed. Thus prepared mother gel was crystallized in an oven at 170°C for 21 days. The solid product was recovered by filtration, washing with distilled water and drying overnight at 100°C. In the synthesis of [Ga,B]-CIT-1, Ga(NO3)3· n H2O (n = 7-9) was used as Ga source.

The conversion from sodium-type into proton-type zeolites was conducted by the repeated ion exchange with 2M ammonium nitrate solution and subsequent calcination at 600°C for 6 h. Thus prepared acid-type zeolites were used as catalysts for the MTO reaction.

The MTO reaction, which gives methane (C1), ethane (C2), ethene (C2=), propane (C3), propene (C3=), butenes (C4=), over C5 species and dimethyl ether (DME) as products, was carried out in a fixed bed reactor. The selectivities of the products were calculated on the carbon numbers from effluent of the reactor. The reaction performed at 500°C at a W/F of 6.6 g h mol-1. Typically, 50 mg catalyst was carried at a quartz reactor in a furnace and 12.5% methanol diluted with helium was used as reactant. The catalyst was calcined prior to the reaction at 520°C for 1 h, and then the reactor was cooled to the reaction temperatures.

Results and Discussion
By the XRD patterns, the products synthesized with the Si/Al ratio of 108 to 196 were the pure CON phase with a high crystallinity. On the other hand, the mother gel with the Si/Al ratio below 70 resulted in the amorphous phase. The 29Al MAS NMR spectrum of [Al,B]-CIT-1 exhibited a sharp peak at 58 ppm, which is assigned to tetrahedrally coordinated aluminum. In addition, a small peak at 0 ppm, which is assigned to octahedrally coordinated aluminum was observed.

In the case of gallium, when the Si/Ga ratio of in gel was 200, [Ga,B]-CIT-1 was obtained; its Si/Ga ratio of the product was 73. However, low silica product with the Si/Ga ratio of 70 in gel was amorphous. The MTO reaction were conducted over [Al,B]-CIT-1 (Si/Al = 123) and [Ga,B]-CIT-1 (Si/Ga = 73) (Fig. 1). [AlB]-CIT-1 exhibited an unique catalytic performance in the MTO reaction; the conversion of methanol was kept at 100% until 420 min, and the selectivity to propene, which is a main product, was constantly 60% during the reaction time of 420 min. After 480 min, the conversion was slightly decreased and DME was observed after the reaction time of 900 min. The reason that [Al,B]-CIT-1 showed a long catalytic life and a high propene selectivity would be due to a high diffusibility and weak acidity.

![Figure 1. Selectivity and conversion of the MTO reaction over [Al,B]-CIT-1 with Si/Al ratio of 123.](image)

In [Ga,B]-CIT-1, the conversion of methanol was kept at 100% until the reaction time of 420 min, and the main product was propene with 60% of selectivity in initial stage. After 600 min, the conversion was decreased and the formation of DME was observed at the reaction time of 940 min. The MTO performance of [Ga,B]-CIT-1 was inferior in point of the propene selectivity. However this catalyst showed a low ethene selectivity.

The amounts of the coke formed during the reaction were found to be about 0.05 g ([ALB]-CIT-1) and 0.07 g ([Ga,B]-CIT-1) per 1 g zeolite. These amounts were notably lower compared to ZSM-5 or [Al]-beta, leading to an increase in the catalytic life.

References