Nanosized aluminogallosilicate MFI zeolites in methanol aromatization: the catalytic nature of framework and non-framework Ga species

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Abstract: Methanol aromatization (MTA) is propelled by the burgeoning coal-based industry. Nanoscaled aluminogallosilicate MFI zeolites ([Ga, Al]-ZSM-5) with varying Ga/Al ratio were synthesized. Physicochemical characterizations of catalysts were performed, and the catalytic behaviors of MTA were evaluated. Both Brønsted acids and non-framework Ga species are indispensable in cyclization and dehydrogenation, respectively, of hydrocarbon intermediates to form aromatics. Framework Ga cations are also dehydrogenation-active, but had negligible impact on MTA activity. Approximately 80% aromatics yield can be achieved over an aluminogallosilicate MFI with a Ga/Al ratio of 1/2. This is attributed to the proper concentration of Brønsted acids and non-framework Ga species.

Keywords: Aromatics, Gallium, Methanol, Nanosize, ZSM-5.

1. Introduction

The investigation of methanol conversion to aromatics (MTA) is burgeoning. An effective MTA catalyst should have high dehydrogenation and cyclization activities, together with a 10-member ring space confinement and a low transport limitation. Accordingly, a MFI zeolite with a nanoscaled particle size and containing dehydrogenation-active promoter, e.g., Ga, should be MTA effective. Nonetheless, an in-depth understanding of how framework and non-framework Ga species influence MTA catalysis, and possible contact synergy between Ga cations and Brønsted acids is still missing. This study aims to clarify these unsolved questions.

2. Experimental

A seed-induced crystallization method [1] was employed to prepare nanosized MFI aluminosilicate, aluminogallosilicate, and gallosilicate catalysts. The ratio of tetravalent cation-to-trivalent cation was kept at 40 for all catalysts. Hereafter, the proton-form nanosized [Al]-ZSM-5, [Ga, Al]-ZSM-5 (Ga/Al = 1/2, 1/1, and 2/1), and [Ga]-ZSM-5 were denoted as HnAl, HnGa1Al2, HnGa1Al1, HnGa2Al1, and HnGa, respectively. Acid treatment was employed to selectively extract non-framework Ga species with negligible impact on framework Ga cations [2], and acid-washed catalysts were labeled as HnAl-a, HnGa1Al2-a, HnGa1Al1-a, HnGa2Al1-a, and HnGa-a. Physicochemical characterizations included N2 adsorption, ICP-AES, XRD, SEM, TEM, MAS NMR, NH3-TPD, pyridine-IR, and methanol-TPD-MS were conducted. Catalytic evaluation was executed in a continuous fixed-bed system annexed with an in-line GC under atmospheric pressure [3].

3. Results and discussion

The surface areas of all samples were in 380 to 420 m²/g range. Aggregated microspheres consisting of cubic crystals in a range of approximately 50-150 nm were observed by SEM. The TEM images displayed small crystal size (less than 100 nm), and no Ga clusters were speculated. XRD patterns showed MFI characteristic responses, but a decreasing trend of the relative crystallinity was found by increasing Ga content. The estimated framework Si/M (M= Al and/or Ga) ratio by 29Si MAS NMR decreased following an order as: HnAl (32.7) > HnGa1Al2 (30.7) > HnGa1Al1 (30.2) > HnGa2Al1 (28.5) > HnGa (25.6). The h-peak of NH3-TPD decreased following an order as: HnAl (453 °C) > HnGa1Al2 (413 °C) > HnGa1Al1 (412 °C) > HnGa2Al1 (408 °C) > HnGa (403 °C). All the above results showed that the higher the Ga content, the more the aromatization extent and lower Brønsted acidity can be formed. The acid-treated, Ga-incorporated samples displayed similar morphology, crystallinity, with slightly decreased Lewis acid concentration
compared to their untreated counterparts. The combinative results of ICP, $^{71}\text{Ga}$ MAS NMR, and pyridine-IR showed that the acid treatment extracts most of non-framework Ga species whilst maintains framework Ga cations.

Figure 1 shows the H$_2$ desorption profiles of methanol-TPD-MS of fresh and acid-treated catalysts. Negligible H$_2$ signal was identified for HnAl, while a spike accompanying with a multi-hump response was speculated for each Ga-containing catalyst. The low H$_2$ spike position and strong H$_2$ signal at approximately 460 °C for HnGa$_2$Al$_2$ indicates its relatively high dehydrogenation activity compared to other catalysts. As for each acid-treated, Ga-containing catalyst, the intensity of H$_2$ desorption signal decreased significantly compared to its untreated counterpart. This underlines that Ga species, either in framework or non-framework position, are dehydrogenation-active.

![Figure 1](image1.png)  
**Figure 1.** H$_2$ desorption profile of fresh and acid-treated samples in methanol TPD.

![Figure 2](image2.png)  
**Figure 2.** Aromatic yields in 400, 450, and 500 °C for fresh and acid-treated catalysts in MTA.

Figure 2 displays the aromatic yields of parent and acid-washed catalysts. Substantially high aromatic yield (80%) can be achieved over HnGa$_2$Al$_2$ at 500 °C, in line with its high dehydrogenation activity. This also suggests a proper Brønsted/Lewis (i.e., framework Ga and Al-to-non-framework Ga) ratio (approximately equals to 2) of an aluminogallosilicate MFI catalyst in MTA. Compared to fresh Ga-containing catalysts, aromatic yields of acid-treated catalysts decreased significantly (a fractional decrease of more than 40%). This is related to the removal of dehydrogenation-active, non-framework Ga species. However, as observed in Figure 1, acid-washed catalysts still showed H$_2$ desorption signals, implying that framework Ga cations also play a role in dehydrogenation of hydrocarbon intermediates. Nonetheless, framework Ga species cannot promote aromatic yields in MTA.

4. Conclusions

Nanosized MFI aluminosilicate, aluminogallosilicate, and gallosilicate catalysts, and their acid-treated counterparts, were characterized and evaluated in MTA. A proper Brønsted/Lewis ratio of 2 was discovered, and Ga species, either in non-framework or framework position, were found to be dehydrogenation-active. However, merely non-framework Ga species can enhance aromatics yields.

References