Preparation of Ce-MFI zeolites and their catalytic properties

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MFI zeolites substituted for a variety of other metals are expected to use as catalysts with high activity, because, introduced metal atoms can endow MFI structure so as to influence properties, such as acidity, electron transfer, etc.. In particular, Ce substituted silicates of MFI zeolite (Ce-MFI) have attracted our attention to the catalysts for the methane conversion to higher hydrocarbons. Ce in Ce-MFI is expected to increase Lewis acid sites, or promote oxidization in MFI framework. In this study, we have prepared Ce substituted and Ce, Fe, and Al co-substituted MFI zeolite by the hydrothermal synthesis method. We have also investigated the effect of their introduction on the catalytic activity on the methane conversion.

Ce-MFI was synthesized as follows.. An aqueous solution of $Ce(NO_3)_3$, H_2O, NaCl was added to a Teflon vessel and stirred at room temperature for 5 minutes. Then, an aqueous tetrapropylammonium hydroxide solution was poured into the aqueous solution. The resulting mixture was stirred at room temperature for 10 minutes. After addition of tetraethyl orthosilicate into the reaction solution in the Teflon vessel, the mixture was stirred at 0 ˚C for 6 hours and then at room temperature for 42 hours. The composition of the aqueous solution was adjusted to SiO_2 : CeO_2 : NaCl : TPAOH : H_2O = 1 : 0.02 : 0 - 0.08 : 0.4 : 30. The prepared aqueous solution was treated at 160 ˚C in an autoclave for 120 hours. The solid particles thus obtained was calcined at 540 ˚C for 12 hours.

The XRD patterns were identified as MFI type structure for all the prepared samples. **Figure 1** shows SEM images of Ce-MFI with different Na/Si ratios. Particles with size of 10–30 nm on Ce-MFI were observed, except Na/Si = 0.04. The surface asperity was observed as the Na/Si ratio increased from 0.04 to 0.08. **Figure 2** shows the UV-vis spectra of Ce-MFI with the different Na/Si ratios. The peak at around 260 nm which shows the existence of tetra-coordinate Ce^{4+} was observed, when the Na/Si was adjusted to 0.04 and 0.06. This suggested that the Ce^{4+} was introduced into the framework of MFI. By contrast, when the Na/Si was fixed to 0.08, the peak around 310 nm due to hexa-coordinate Ce^{4+} was observed. This suggested that the Ce^{4+} was out of the framework or on the MFI surface.

In conclusion, Ce-MFI zeolite was successfully prepared by control in the Na/Si ratio. The co-introduction of Ce, Fe, and Al into MFI and their catalytic properties will be presented.

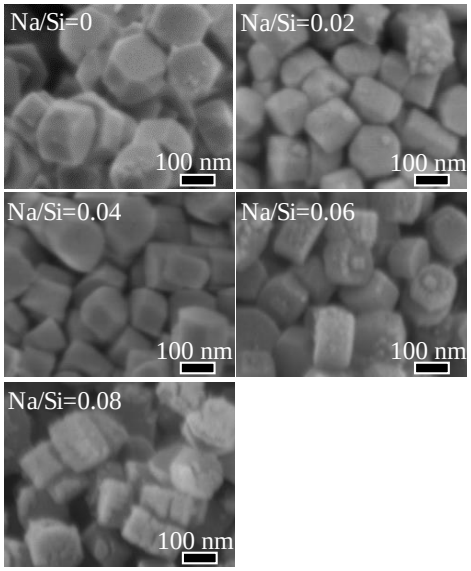

Figure 1 SEM images of Ce-MFI with different Na /Si ratios.

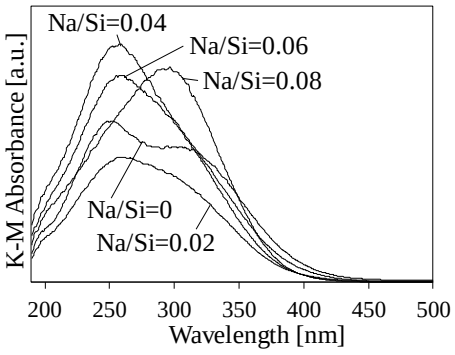

Figure 2 UV-vis spectra of Ce-MFI with different Na/ Si ratios.

REFERENCES

[1] B. Kalita, A. K. Talukdar, *Mater. Chem. Phys.*, **133**, 713–717 (2012).