

Kinetics for 2-methylnaphthalene methylation over MTW-type zeolite with different crystal size and acidity

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2,6-dimethylnaphthalene (2,6-DMN) is a raw material of polyethylenenaphthalate (PEN), which possesses superior properties such as gas impermeability and heat resistance to those of polyethyleneterephthalate (PET). Because DMN possesses 10 isomers with similar boiling point, complex separation process is required to obtain 2,6-DMN. Therefore, development of new process to obtain 2,6-DMN selectively has been required, and production of DMN by isomerization or methylation of 2-methylnaphthalene (2-MN) over zeolite has been expected. Because the pore size of MTW-type zeolite is close to the molecular size of β,β -DMN, it is expected that MTW-type zeolite would be effective for methylation of 2-MN.

The present study is focused on the effect of the crystal size and isomorphous substitution of Al by Fe in the MTW-type zeolite structure on the 2-MN methylation and isomerization rates. To clarify these factors, MTW-type zeolite with different crystal sizes (Si/Al = 100, here after Al-MTW) and ferrisilicate with MTW zeolite structure [1] (Si/Fe = 100, here after Fe-MTW) were hydrothermally prepared and applied for 2-MN methylation under supercritical conditions.

Macro-sized Al-MTW (crystal size: 1000-4000 nm), nano-sized Al-MTW and Fe-MTW (crystal size : 50-100 nm) were hydrothermally synthesized and used as catalyst. A mixture of 2-MN and methanol (2-MN : methanol molar ratio = 0.1) and catalyst were placed in the batch-type reactor. The reactions were conducted at reaction temperatures in the range of 523-583 K and maintained for 90-270 min after the reaction was reached. The pressure in the reactor was 25 MPa, which was monitored with a pressure gauge.

Table 1 summarizes property of MTW zeolites prepared. It was confirmed that the micropore volume and amount of acid site of

zeolites were almost the same value regardless of crystal size and acidity.

Fig. 1 shows Arrhenius plots for rate constants of methylation and isomerization of 2-MN over MTW-type zeolites with different crystal size and acidity. Rate constants for isomerization of 2-MN were almost the same regardless of the crystal size. Conversely, the values over Fe-MTW approximately 5 times lower than that of Al-MTW. Weak acidity of the Fe-MTW zeolite decreased the rate of isomerization of 2-MN. On the other hand, activation energies for methylation and rate constants were decreased with increasing crystal size of zeolite. This is because the diffusivity of 2-MN inside Al-MTW with larger size affected overall rate constant, leading to a decrease in the activation energy. In contrast, these values over nano-sized Al- and Fe-MTW were almost the same regardless of acidity.

Table 1 Properties of MTW-type zeolites

| Zeolite | V_m [cm ³ g ⁻¹] | S_{BET} [m ² g ⁻¹] | S_{EXT} [m ² g ⁻¹] | Amount of acid sites [mmol kg ⁻¹] |
|--------------------|---|--|--|--|
| Macro-sized Al-MTW | 0.13 | 300 | 8.0 | 0.15 |
| Nano-sized Al-MTW | 0.13 | 310 | 45 | 0.15 |
| Nano-sized Fe-MTW | 0.13 | 300 | 40 | 0.15 |

V_m : micropore volume by the t -plot method; S_{BET} : BET surface area by the BET method; S_{EXT} : external surface area by the t -plot method.

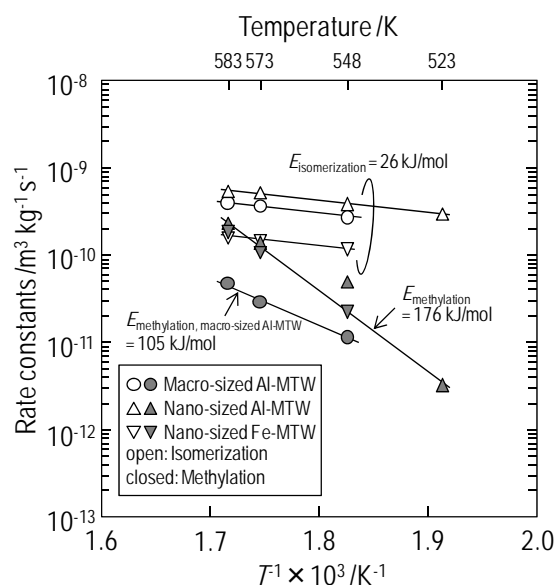


Fig.1 Arrhenius plots of the rate constants of methylation and isomerization

REFERENCES

[1] T. Taniguchi *et al.*, *Catal. Lett.* 146 (2016) 666.