

KINETICS FOR METHYLATION OF 2-METHYLNAPHTHALENE OVER ZSM-12 WITH DIFFERENT CRYSTAL SIZES

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Abstract

Methylation of 2-Methylnaphthalene (2-MN) with methanol over ZSM-12 (Si/Al =100) with different crystal sizes were carried out using autoclave reactor under high pressure reaction condition. 2-MN conversion and dimethylnaphthalene selectivity in products could be improved by decreasing ZSM-12 crystal size. The catalytic activity was maintained for reaction time 270 min regard less of ZSM-12 crystal size due to suppression coke deposition. Rate constants of methylation and isomerization of 2-MN was obtained as the reaction order was first order with respect to 2-MN concentration. Activation energy for methylation over nano-sized ZSM-12 was obtained 176 kJ/mol and higher than that over macro-sized ZSM-12 (105kJ/mol) due to decrease in diffusion resistance within ZSM-12.

Keywords

ZSM-12, methylation, kinetics

Introduction

Polyethylenenaphthalate (PEN) is one of new generation polyester which possesses high properties, such as tensile strength and heat resistance, compared to polyethyleneterephthalate (PET). On the other hands, 2,6-dimethylnaphthalene (2,6-DMN), a raw material of PEN, is industrially produced by multi-step reaction process using alkali metal catalyst and a large quantity of organic solvent. Therefore, selective production of 2,6-DMN with simple reaction step has been desired, and methylation of 2-methylnaphthalene (2-MN) over zeolite is promising. Methylation of 2-MN over ZSM-5 have been reported [Komatsu, et al., 1994], but 2-MN conversion was low because pore diameter of ZSM-5 is close to the aromatic ring. In addition, the catalytic activity rapidly decreased due to coke deposition on strongly acid site of zeolite. It

has been reported [Kondoh, et al., 2015] that coke amount was decreased in upgrading heavy-oil over iron oxide based catalyst under high pressure reaction condition. In this study, ZSM-12 [Chokkaingman, et al., 2013] which have larger pore diameter than ZSM-5 was used for methylation of 2-MN under high pressure reaction condition, and effect of crystal size on the catalytic activity, products selectivity and reaction rate constant were investigated.

Experimental

Macro- (crystal size:1000-4000 nm (Figure 1(a)) and nano-sized ZSM-12 (crystal size:50-100 nm (Figure 1(b)) with Si/Al ratio of 100 were hydrothermally synthesized

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using triethylmethylammonium chloride (MTEACl) and tetraethylammonium bromide (TEABr) as OSDA molecule, respectively.

The ZSM-12, ion-exchanged from Na^+ to NH_4^+ form were pelletized, crashed and sieved to yield samples ca. 0.4 mm in diameter, and calcined under air stream at 823 K for 1 h before methylation of 2-MN. 2-MN/methanol mixture (molar ratio of 2-MN to methanol was 0.1) and ZSM-12 were placed into an autoclave reactor. Then, reactor was heated to reaction temperature of 523-583 K and hold for 0-270 min. Reaction products were analyzed using gas chromatography (GC2010, SHIMADZU Corp.) with a FID detector.

Results and Discussion

Table 1 shows 2-MN conversions and products selectivity at reaction time of 90 min and 270 min over macro- and nano-sized ZSM-12. 2-MN conversion and DMN (β,β -DMN and α,β -DMN) selectivity in products were improved by decreasing ZSM-12 crystal size. This result indicates that diffusion resistance of 2-MN within ZSM-12 pore decreased. In addition, 1-MN, formed by isomerization of 2-MN was decreased and α,α -DMN, formed by acid site on external surface, did not confirmed. It is considered that the methylation of 2-MN mainly proceed with in ZSM-12 pore. Coke loading after the reaction was less than 1.1 wt% regardless of crystal size indicating deactivation rarely occurred under high pressure condition.

Rate constants of methylation (DMN formation) and isomerization (1-MN formation) of 2-MN were obtained as the reaction order was first with respect to 2-MN concentration, respectively. Figure 3 shows Arrhenius plots of rate constants of methylation and isomerization of 2-MN over ZSM-12 with different crystal sizes. Isomerization proceeded faster than the methylation of 2-MN regardless of ZSM-12 crystal size. Activation energies for methylation of 2-MN over ZSM-12 were found to be 105 and 176 kJ/mol over macro- and nano-sized ZSM-12, respectively. This is because the diffusivity of reactant within ZSM-12 pore with larger size affected the overall rate constant, leading to a decrease in the activation energy. On the other hands, activation energies for isomerization over ZSM-12 were almost the same regardless of crystal size.

Conclusion

Methylation of 2-MN was carried out over ZSM-12. By decreasing ZSM-12 crystal size, 2-MN conversion and DMN selectivity in products improved because diffusion resistance of reactant within ZSM-12 pore decreased. Rate constants of methylation and isomerization of 2-MN and their activation energies were successfully. Decreasing crystal size of ZSM-12 is effective for improvement of the methylation rate.

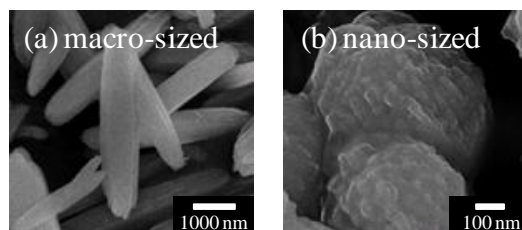


Figure 1: SEM micrographs of (a) macro- and (b) nano-sized ZSM-12

Table 1: Effect of ZSM-12 crystal size on 2-MN conversion and products selectivity at 583 K.

Catalyst	Reaction time [min]	2-MN conversion [mol%]	Products selectivity [mol%]			
			1-MN	β,β -DMN	α,β -DMN	α,α -DMN
macro-sized	90	4.1	89.9	4.5	5.6	0
	270	11.9	88.5	5.1	6.4	0
nano-sized	90	6.8	69.9	13.5	16.6	0
	270	18.5	70.5	13.2	16.3	0

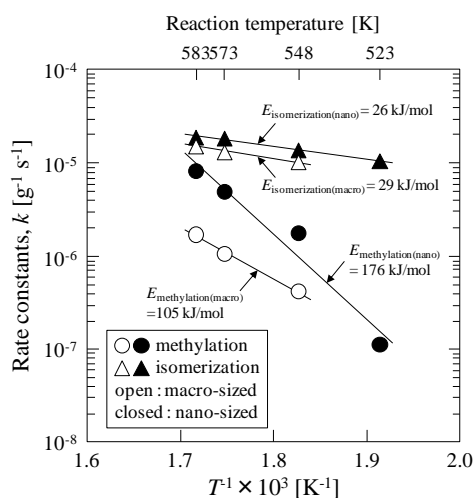


Figure 3: Arrhenius plots of the rate constants of methylation and isomerization of 2-MN over ZSM-12 with different crystal sizes.

Acknowledgments

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