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Shape Selective Catalysis by ZSM-5 in Disproportionation of 2-Methylnaphthalene

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Disproportionation of methylnaphthalene(MN) was carried out on ZSM-5 catalysts. The external acid sites were eliminated by dealumination with $(NH_4)_2SiF_6$. The dealuminated ZSM-5 gave 2,6- and 2,7-dimethylnaphthalene(DMN) from disproportionation of 2-methylnaphthalene(MN), due to its shape selective property.

Shape selectivity has been an important concept in heterogeneous catalysis. The most popular shape selective catalyst is ZSM-5 zeolite, which has a particular pore structure. Thus, shape selective synthesis of p-xylene from alkylation and disproportionation of toluene, and from isomerization of xylenes has widely been investigated using ZSM-5 catalyst.[1-3] In contrast, there have been few studies concerning the shape selective conversions of naphthalene derivatives over ZSM-5 catalyst. It was reported by Neuber and co-workers[4] that 2-MN could not diffuse into the pore of ZSM-5. Fraenkel et al.[5] studied the alkylation of naphthalene and 2-MN with methanol using ZSM-5 catalyst, and reported that the mixture of 2,6- and 2,7-DMN was selectively formed over ZSM-5 catalyst. They proposed that ZSM-5 has half cavities on the external surface and the acid sites in the half cavities are responsible for the selective formation of 2,6- and 2,7-DMN.

It was shown in our previous paper[6] that the catalytic activity of ZSM-5 for disproportionation of 2-MN was stable against deactivation, while those for disproportionation of 1-MN and isomerization of MN became deactivated. We thus proposed that disproportionation of 2-MN proceeded in the pore of ZSM-5. The purpose of this paper is to manifest the shape selective catalysis by ZSM-5 in disproportionation of 2-MN.

Na-type ZSM-5 supplied by Tosoh Co. Ltd. was exchanged 5 times with 1×10^{-3} mol dm^{-3} NH_4Cl solution for 6 h at 70 °C. Thus obtained NH_4-type ZSM-5 was calcined at 540 °C to form the H-type. ZSM-5 was dealuminated

Table 1. Activities of ZSM-5 catalysts in the conversion of 2-MN[a)]

Catalyst	HZSM-5	HZSM-5	HZSM-5
Dealumination	----	$SiCl_4$	$(NH_4)_2SiF_6$
SiO_2/Al_2O_3	24.7	25.4	26.4
%Conversion of 2-MN	18.5	4.9	4.8
Yield/mol%			
Naphthalene	2.1	0.3	1.1
1-MN	15.2	4.5	3.0
DMN	1.1	0.1	0.7
TMN	0.1	---	---

a) Reaction conditions: temperature, 300 °C; W/F, 8000 g-cat.min/mol. Data were taken in the initial 10-20 min of run.

using $SiCl_4$ or $(NH_4)_2SiF_6$ according to the method reported by Namba et al.[7)] or Breck et al.[8)] Disproportionation of 2-MN was carried out at 300 °C in a continuous flow system with a fix bed of catalyst. The reaction products were collected in an ice trap attached to the bottom of the reactor. Products on liquid phase were analyzed by means of gas chromatography using a flame ionization detector. DMN isomers were resolved using DB-1, FFAP, and OV-101 separation columns. The activities for cracking of cumene and 1,3,5-triisopropylbenzene (1,3,5-TrIPB) were determined at 300 °C using a pulse technique.

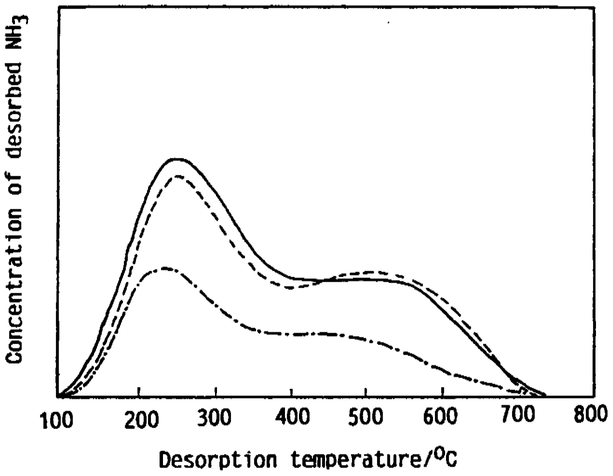

Fig. 1. NH_3-TPD spectra of ZSM-5: ——, non treated; —·—, treated with $SiCl_4$; ----, treated with $(NH_4)_2SiF_6$.

The activities of ZSM-5 and dealuminated ZSM-5 for the conversion of 2-MN were determined using data taken in the initial 10-20 min of run. The results are summarized in Table 1. ZSM-5 had a low disproportionation activity, and 2-MN was predominately isomerized to 1-MN. Naphthalene was more abundantly produced than DMN, showing that demethylation occurred over ZSM-5. The catalytic activities were affected by dealumination. ZSM-5 exhibited a low isomerization activity after dealumination with $(NH_4)_2SiF_6$, while the disproportionation activity changed a little. In contrast, dealumination with $SiCl_4$ reduced the disproportionation activity as well as the isomerization activity.

Figure 1 shows the ammonia-TPD spectra from ZSM-5. There was no appreciable difference in the acidity between ZSM-5 and ZSM-5 dealuminated with $(NH_4)_2SiF_6$, whereas dealumination with $SiCl_4$ reduced the acidity. As shown in Table 2, these results were in good agreement with the results on

Table 2. Cracking activities of ZSM-5 catalysts[a)]

Catalyst	HZSM-5	HZSM-5	HZSM-5
Dealumination	----	$SiCl_4$	$(NH_4)_2SiF_6$
SiO_2/Al_2O_3	24.7	25.8	26.4
%Conversion of			
cumene	75.0	50.2	76.9
1,3,5-Triisopropylbenzene	8.8	0.8	1.4

a) Reaction temperature, 300 °C.

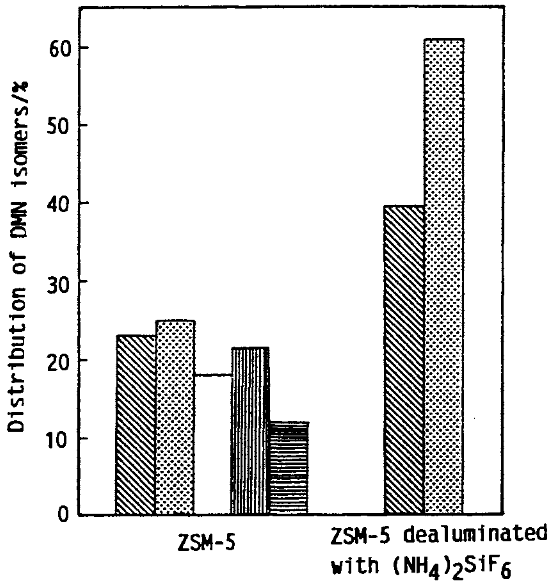

Fig. 2. Distribution of DMN isomers produced on ZSM-5 catalysts: ▨ , 2,6-; ░ , 2,7-; □ , 1,6-; ▥ , 1,7-; ▤ , other DMN isomers.

cumene cracking. The SiO_2/Al_2O_3 ratio of ZSM-5 which was determined by means of X-ray fluorescence analysis, however, hardly changed with dealumination. It has been reported[9)] that part of the aluminum which is substituted in the zeolitic framework by silicon in contact with $SiCl_4$ vapor remains in the solid. It is thus suggested that the ZSM-5 dealuminated with $SiCl_4$ has a higher SiO_2/Al_2O_3 ratio in the framework than the value in Table 1.

ZSM-5 catalysts gave lower level of 1,3,5-TrIPB conversion than that of cumene conversion, although 1,3,5-TrIPB is more reactive than cumene. Cracking of 1,3,5-TrIPB proceeds only on external acid sites because molecular dimension of 1,3,5-TrIPB is large compared with the pore size of ZSM-5. The catalytic activity of ZSM-5 for cracking of 1,3,5-TrIPB was decreased by dealumination with $(NH_4)_2SiF_6$, while the cracking activity for cumene changed little. Dealumination with $(NH_4)_2SiF_6$ is thus considered to remove only external acid sites by substitution of aluminum for silicon. As described above, dealumination with $(NH_4)_2SiF_6$ hardly affected the disproportionation activity of ZSM-5. In contrast, the isomerization activity was reduced markedly after the dealumination. As shown in our previous paper,[6)] the activity of ZSM-5 catalyst for disproportionation of 2-MN was stable against deactivation, while those for disproportionation of 1-MN and isomerization of MN became deactivated. It is thus concluded that disproportionation of 2-MN proceeds in the pore of ZSM-5, while the external acid sites are responsible for the isomerization of 2-MN to 1-MN.

Figure 2 shows the distribution of DMN isomers produced. Although there are ten isomers of DMN, the main DMN products from disproportionation of 2-MN over ZSM-5 were 2,6-, 1,6-, 2,7-, and 1,7-isomers. When the molecular dimension of these DMN isomers is compared on the basis of the position of methyl groups, 2,6- and 2,7-DMN have smaller molecular dimensions than 1,6- and 1,7-DMN. Thermodynamical fractions of 2,6- and 2,7-DMN in DMN isomers are 9.0, and 9.0%, respectively. ZSM-5 gave 2,6- and 2,7-DMN exceeding the thermodynamically attainable level. The selectivities of 2,6- and 2,7-DMN increased from 23.4 and 24.9% to 39.9 and 60.1%, respectively, by dealumination with $(NH_4)_2SiF_6$. As mentioned above, dealumination with $(NH_4)_2SiF_6$ eliminated the external acid sites, and then the activity for isomerization of 2-MN to 1-MN was lowered. It is suggested that the high selectivities of the dealuminated ZSM-5 for 2,6- and 2,7-DMN are attributed to a reduced contribution of isomerization of DMN. ZSM-5 is considered to allow the formation of 2,6- and 2,7-DMN in the pore, due to its shape selective property. 2,7-DMN was formed far more selectively than 2,6-DMN, although no schematic explanation was provided.

We conclude that disproportionation of 2-MN proceeds in the pore of ZSM-5 and yields 2,6- and 2,7-DMN selectively due to its shape selective property, although these DMN isomers are easily isomerized to other isomers on the external acid sites. Isomerization of 2,6- and 2,7-DMN does not occur at all over the ZSM-5 dealuminated with $(NH_4)_2SiF_6$ because of the absence of the external acid sites.

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