SHAPE SELECTIVE DISPROPORTIONATION OF METHYLNAPHTHALENE ON ZSM-5 CATALYST*

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The conversion of 2-methylnaphthalene (2-MN) was studied at atmospheric pressure in a flow--type fixed bed reactor using H-Y, H-beta, H-mordenite, H-ZSM-5, H-ZSM-11 and H-ZSM-48 as catalysts. H-Y and H-beta exhibited high activities for disproportionation and isomerization of 2-MN. H-Mordenite and zeolites having medium size pores were active for the conversion of 2-MN which was mainly isomerized to 1-MN. The low disproportionation activities of these zeolites resulted from their shape selective properties. Disproportionation of 2-MN on the zeolite catalysts gave 2,6- and 2,7-dimethylnaphthalenes (DMN) in higher proportions than the thermodynamically attainable level. H-ZSM-5 was the most selective catalyst to produce these DMN isomers among the zeolite catalysts tested, although 2,7-DMN was formed in a higher proportion than 2,6-DMN. On H-mordenite catalyst, 2,6-DMN was more selectively formed than 2,7-DMN. The selectivity for 2,6-DMN against 2,7-DMN increased with increasing SiO₂/Al₂O₃ ratio of H-mordenite. It is suggested that the composition of DMN isomers produced by disproportionation of 2-MN depends on the acid strength as well as on the shape selective properties of zeolites used.

The advantages of shape selective catalysis have already been proved in a number of industrial processes. Most popular shape selective catalysts are zeolites, of which the pore sizes are comparable with the dimension of many simple molecules. Practically, shape selective reactions on zeolite catalysts have extensively been investigated for conversions of benzene derivatives, e.g. *p*-xylene synthesis by disproportionation or alkylation of toluene and isomerization of xylenes.

In contrast, there are relatively small number of studies concerning the shape selective conversion of polynuclear aromatic hydrocarbons, such as naphthalene derivatives. It was reported by Lee et al.¹ and Sugi et al.² that mordenite exhibited high selectivity for the formation of 4,4'-diisopropylbiphenyl in the alkylation of biphenyl with propene. Solinas and co-workers^{3,4} studied the isomerization of 1-MN and 2-MN on zeolites Y, X, omega, and ZSM-5, and they concluded that these catalysts exhibited no shape selectivity. It was reported by Fraenkel et al.⁵

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that the alkylation of naphthalene with methanol on ZSM-5 gave the slim isomers, namely 2,6- and 2,7-DMN as well as 2-MN. They proposed that such shape selective reactions of naphthalene derivatives occurred on the external surface of ZSM-5, in so-called half cavities. Weitkamp and Neuber⁶ also reported that diffusion of 1-MN and 2-MN into the channel of ZSM-5 was strongly hindered even at 300°C. The purpose of this study is to investigate the shape selective properties of several zeolite catalysts for the disproportionation of 2-MN to DMN.

EXPERIMENTAL

The following zeolites were synthesized according to the methods derived from literatures: zeolite beta⁷, ZSM-11 (ref.⁸), ZSM-48 (ref.⁹). Zeolite Y and ZSM-5 were supplied by Tosoh Corp. and mordenites by the Catalysis Society of Japan. Na zeolites were exchanged 5 times with 0·1M-NH₄Cl solution for 6 h at 70°C. Thus obtained NH₄ zeolites were calcined at 540°C for 4 h to form the H type. Dealumination of NH₄-ZSM-5 was also studied using $(NH_4)_2 SiF_6$ according to the method reported by Breck and co-workers¹⁰.

The acidity of catalysts was determined by means of ammonia temperature-programmed desorption (TPD). In each TPD experiment, a sample was placed in a cell, and was evacuated at 540° C for 1 h. Ammonia was adsorbed at 100° C and evacuated for 1 h. The sample was heated from 100 to 750° C at a rate of 10° C/min. A thermal conductivity detector was used to monitor the desorbed ammonia.

Reactions were carried out at atmospheric pressure in a fixed bed flow-type reactor. A catalyst was loaded into the reactor, and was treated at 540° C for 1 h in a stream of nitrogen prior to reaction, which was peformed at 300° C. An equimolar mixture of 2-methylnaphthalene (2-MN) and benzene was supplied to the reactor from a microfeeder through a vaporizer to mix with nitrogen in a 2:13 molar ratio. Alkylation of 2-MN with methanol was also studied at 270° C, with an equimolar feed of 2-MN and methanol. The reaction products were collected in an ice trap attached to the bottom of the reactor. Liquid samples were analyzed by means of gas chromatography using a flame ionization detector and DB-1 separation column under temperature-programmed heating from 50 to 200° C. As 1,4-, 2,3-, 1,5-dimethylnaphthalene (1,5-DMN) isomers were not separated by the DB-1 column, these isomers were resolved using FFAP and OV-101 separation columns at a constant temperature of 160°C.

The catalytic activities for the cracking of cumene and 1,3,5-triisopropylbenzene (TrIPB) were determined at 300° C using a pulse technique.

RESULTS AND DISCUSSION

The catalytic activities of H-Y, H-beta, H-mordenite, H-ZSM-5, H-ZSM-11, and H-ZSM-48 for the conversion of 2-MN were compared on the basis of data taken in the first 10-20 min of reaction and are shown in Table I. On the H-Y catalyst, 2-MN was consumed by isomerization to 1-MN and by disproportionation to dimethylnaphthalenes (DMN), which were consecutively transalkylated to trimethylnaphthalenes (TMN). Since H-Y has large pores (7.4 Å) and supercages (13 Å) in the channels, it is considered that H-Y allows the diffusion of 2-MN into the channels and the formation of the intermediates required for disproportionation or

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transalkylation. Although H-beta is also a zeolite with large pores, the catalytic activity of H-beta was significantly lower than that of H-Y. The molar SiO_2/Al_2O_3 ratios of H-Y and H-beta were 6.9 and 30, respectively. The low catalytic activity of H-beta seems to be resulted from its less pronounced acidity.

H-Mordenite, H-ZSM-5, H-ZSM-11 and H-ZSM-48 exhibited low activities for the disproportionation of 2-MN, but were active for the isomerization. Isomerization proceeds via a shift of methyl group along the aromatic ring through a monomolecular transition state, whereas a bimolecular transition state is required for disproportionation. Thus, the low disproportionation activities of these zeolites could be attributed to their shape selective properties.

Figure 1 shows the change of catalytic activities with time on stream for the disproportionation of 2-MN. No deactivation was observed on H-ZSM-5, although the catalytic activity was relatively low. The disproportionation activities of H-Y, H-beta, H-mordenite, H-ZSM-11, and H-ZSM-48 gradually decreased with time on stream. It is generally accepted^{11,12} that coke formation leading to deactivation of ZSM-5 hardly occurs in the channels but predominantly on the external surface

TABLE I

Zeolite	н-ү	H- β	H-M	H-ZSM-5	H-ZSM-11	H-ZSM-48	
Pore size, Å	7.4	7.4	7·0	5.4×5.7	5.4×5.7	$5\cdot3 \times 5\cdot6$	
SiO_2/Al_2O_3	6.9	30	19	25	45	150	
Conversion, % Yield, mole %	53.6	22.3	2 9·3	18.4	23.0	8·2	
naphthalene	16.8	4.3	1.0	2 ·1	1 · 1	0.3	
1-MN	18.0	14.8	27.3	15.2	20.9	7.6	
DMN	15.8	2 ·8	1.0	1.0	0.9	0.3	
TMN	3.0	0.4	0.1	0.1	0	0	
Composition of DMN, %							thermodynamical equilibrium
2,6-	18.1	21.9	33.0	26.4	24.9	33.8	9.0
1,6-	15.6	19.3	27.5	17.6	19.9	18.5	18.3
1,5-	1.9	2.9	4.6	0	0	0	9.0
2,7-	18.6	17.3	16.4	27.7	22.2	19.6	9.0
1,7-	15-1	14.2	13.8	17.4	16.2	14.2	18.3
1,8-	0	0	0	0	0	0.2	
2,3-	6.8	8.0	0	5.9	4.6	0	2.9
1,3-	16-9	13.6	3.7	4.4	11.2	11-5	18.3
1,4-	3.5	0	0	0	0	0	9.0
1,2-	3.5	2.8	1.1	0.2	1.3	2.5	5.7

Activities and selectivities of zeolite catalysts for the conversion of 2-methylnaphthalene (2-MN). Reaction conditions: Temperature, 300° C; $W/F = 8\,000$ g-cat. min mol⁻¹

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acid sites. Therefore, the results obtained in this study could be explained if the disproportionation of 2-MN proceeds in the channels. It was shown in our previous work¹³ that the activity of H-ZSM-5 catalysts for the disproportionation of 1-MN decreased with time on stream. As the molecular dimensions of 1-MN and 2-MN are 6.2 and 5.8 Å respectively, it is considered that diffusion of 1-MN into the channels and formation of 1-MN within the channels are restricted by the shape selective properties of H-ZSM-5. The acid sites on the external surface seems to be responsible for the isomerization of 2-MN to 1-MN.

The compositions of DMN isomers produced by disproportionation of 2-MN are displayed in Table I, where the thermodynamic composition¹⁴ is also shown. DMN isomers are classified into three groups based on the position of methyl groups:

α-α: 1,4-, 1,5-, and 1,8-DMN α-β: 1,2-, 1,3-, 1,6-, and 1,7-DMN β-β: 2,3-, 2,6-, and 2,7-DMN

Among them, those having methyl groups at β -positions are the smallest in molecular dimensions, and those at α -positions are the largest.

Selectivity for the α - α isomers was remarkably low on each catalyst, especially on H-ZSM-5. All these catalysts gave the β - β isomers in higher proportions than the thermodynamic equilibrium. As shown in Fig. 2, the selectivity for the β - β isomers decreased in the following orders: H-ZSM-5 > H-ZSM-11 > H-mordenite > H-beta > H-Y. These results can be understood by taking the pore size into consideration.



FIG. 1

Variation in the activities of zeolite catalysts (in yield of DMN, mole %) for disproportionation of 2-MN with time on stream. Catalyst: \Box H-Y; \bullet H-beta; \circ H-ZSM-5; \blacktriangle H-ZSM-11; \triangle H-mordenite

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The selectivity of H-ZSM-5 for the β - β isomers increased with time on stream, while those of other catalysts changed little. Figure 3 shows the variation in the selectivities for 1,6-, 1,7-, 2,6-, and 2,7-DMN on H-ZSM-5 catalyst. The 2,6- and 2,7-DMN selectivities increased with time on stream while those for 1,6- and 1,7-DMN were reduced. The 2,3-DMN selectivity was low compared with those for 2,6- and 2,7-DMN and changed little with time on stream. As previously mentioned, the activity of H-ZSM-5 for the isomerization of 2-MN to 1-MN decreased with time on stream, while that for the disproportionation of 2-MN was stable against







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deactivation. By analogy with these results, the isomerization of DMN on H-ZSM-5 catalyst would decrease with time on stream. If it is the case, the increase in the selectivities for 2,6- and 2,7-DMN with time on stream may be attributed to the reduced contribution of isomerization caused by deactivation. We propose that 2-MN has access to the internal acid sites of H-ZSM-5 and can be disproportionated to 2,6- and 2,7-DMN within the channels.

In order to prove this assumption, the effect of dealumination of H-ZSM-5 on the catalytic activity and selectivity was investigated using $(NH_4)_2SiF_6$ which can react only with Al atoms on the external surface of this zeolite. Table II shows the catalytic activities of H-ZSM-5 and the dealuminated H-ZSM-5 for the conversion of 2-MN, and those for cracking of cumene and 1,3,5-triisopropylbenzene (TrIPB). TrIPB has a larger molecular dimension than cumene and even the pore size of ZSM-5, so that we can expect smaller cracking rate of TrIPB than cumene on H-ZSM-5, as is actually found (Table II). The cracking of TrIPB was further suppressed by the removal of the external acid sites by dealumination, which little decreased the rate of cumene cracking. As there was no appreciable difference in the ammonia-TPD spectra between H-ZSM-5 and the dealuminated H-ZMS-5, it is obvious that dealumination with $(NH_4)_2SiF_6$ removes only external acid sites by substitution of aluminium for silicon.

The dealuminated H-ZSM-5 exhibited a low activity for the isomerization of 2-MN, while the disproportionation activity changed only a little. In Fig. 2, we

Reactant	ZSM-5 (24·7) ^a	Dealuminated ZSM-5 $(26.4)^a$	
2-Methylnaphthalene ^b			
conversion, %	18.5	4.8	
yield, % of naphthalene	2.1	1.1	
of 1-MN	15-2	3.0	
of DMN	1.1	0.7	
Cumene ^c			
conversion, %	75.0	76.9	
conversion, %	8.8	1.4	

TABLE II

Comparison of catalytic properties of H-ZSM-5 and dealuminated H-ZSM-5

^a The value in parenthesis represents molar SiO_2/Al_2O_3 ratio. ^b Continuous flow system at 300°C. ^c Pulse reactor at 300°C.

showed that the selectivities for 2,6- and 2,7-DMN increased from 23 to 40% and from 25 to 60%, respectively, by dealumination with $(NH_4)_2SiF_6$. These results allow us to conclude that 2-MN is disproportionated to 2,6- and 2,7-DMN within the channels of H-ZSM-5, while the external acid sites are responsible for the isomerization of 2-MN or DMN.

On H-ZSM-5 catalyst, 2,7-DMN was formed in a higher proportion than 2,6-DMN. The selectivity for 2,6-DMN against 2,7-DMN on H-mordenite was high compared with that of H-ZSM-5, although H-ZSM-5 exhibited higher selectivity to these DMN isomers than H-mordenite. As there is no difference in the molecular dimension between these DMN isomers, these results cannot be elucidated by the diffusion restriction. It has generally been known that some shape selective reactions are restricted by the dimension or configuration of intermediates, i.e., by so-called transition state restriction. In the case of transition state restriction, product selectivity would be dependent on the type of reaction. Table III shows the activities and selectivities of H-ZSM-5 and dealuminated H-ZSM-5 catalysts for the alkylation of 2-MN with methanol, which requires a smaller intermediate compared with the disproportionation. The dealuminated H-ZSM-5 was less active for this reaction than H-ZSM-5. A comparison with Fig. 2 shows that both alkylation and disproportionation gave similar product selectivities, although disproportionation requires

TABLE III

Catalyst	H-ZSM-5	Dealuminated H-ZSM-5	
Conversion of 2-MN, %	12.4		
Yield, mole %			
naphthalene	0.8	0.4	
1-MN	5.6	1.0	
DMN	4.3	3.2	
TMN	1.6	0	
Composition of DMN, %			
2,6-	26.5	44.2	
1,6-	10.7	0	
2,7-	31.4	55.8	
1,7-	10.8	0	
2,3-	10.8	0	
1,3-	6.0	0	
1,2-	3.8	0	

Activities of H-ZSM-5- and dealuminated H-ZSM-5 catalysts for alkylation of 2-methylnaphthalene (2-MN). Reaction conditions: Benzene/2-MN/methanol, 1/1/1 (molar ratio); temperature 270°C; W/F = 8000 g-cat. min mol⁻¹

a bulky intermediate compared with alkylation. We deduce from these results that the selectivity of 2,6-DMN against 2,7-DMN can not be controlled by shape selectivity properties.

It has been reported¹⁵ that the isomerization of DMN proceeds through the α - β shift of a methyl group, while the shift of a methyl between α - α and β - β positions is prohibited. As shown in Fig. 4, 2,6-DMN was hardly converted on the dealuminated H-ZSM-5, while H-ZSM-5 was active for the conversion of 2,6-DMN. These results indicate that the external acid sites are responsible for the conversion of 2,6-DMN. Figure 5 shows the isomerization and transalkylation products from 2,6-DMN on H-ZSM-5. 2,6-DMN was selectively isomerized to 1,6-DMN and 1,5-DMN, indicating that the methyl shift between adjacent α - α and β - β positions was prohibited. At high levels of 2,6-DMN conversion, however, other DMN isomers were formed. As the formation of these DMN isomers was accompanied by the formation of naphthalene, MN, and TMN, these DMN isomers are considered to be formed by transalkylation through TMN.

Hence, DMN isomers in the initial products could be classified into four groups as shown Scheme 1: 2,6-DMN is isomerized only to 1,6- and 1,5-DMN, but not to the 2,7-DMN group (2,7-, 1,7-, and 1,8-) or the 2,3-DMN group (2,3-, 1,3-, and





Fig. 4





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FIG. 5

1,4-). In this case, the selectivity for 2,6-DMN against 2,7-DMN depends on the relative selectivity for the 2,6-DMN group (2,6-, 2,6-, 1,5-) against the 2,7-DMN group. As is shown in Table I, the 2,6-DMN group was more selectively formed on H-mordenite than on H-ZSM-5. As the acid sites on H-mordenite are relatively stronger than those on H-ZSM-5, there is a possibility that the 2,6-DMN group is more selectively formed on stronger acid sites.



SCHEME 1

In order to investigate the effect of acid strength on the selectivity for 2,6-DMN against 2,7-DMN, disproportionation of 2-MN was performed using H-mordenite with various SiO_2/Al_2O_3 ratios or different degrees of proton exchange. The composition of produced DMN isomers was found to be influenced by the SiO_2/Al_2O_3 ratio and the degree of proton exchange. Figure 6 shows the relationship between the acid strength and the composition of produced DMN isomers. Here, the acid

strength was determined from ammonia-TPD measurements according to the method reported by Sawa and co-workers¹⁶. It seems that the 2,6-DMN group is more selectively formed on H-mordenite having stronger acid sites, and that the selectivities for the 2,3- and 2,7-DMN groups decrease with increasing acid strength.

CONCLUSION

The conversion of ?-methylnaphthalene (2-MN) was carried out using H-Y, H-beta, H-mordenite, H-ZSM-5, H-ZSM-11 and H-ZSM-48 as catalysts. Although these zeolite catalysts were active for the conversion of 2-MN, large differences were found with respect to the selectivities.

The disproportionation activities of H-mordenite and zeolites having medium pores were low compared with those of H-Y and H-beta, and 2-MN was mainly isomerized to 1-MN. H-ZSM-5 was the most selective catalyst to produce 2,6- and 2,7-DMN among the catalysts tested, although these DMN isomers were easily isomerized to other isomers. Isomerization of 2,6- and 2,7-DMN was suppressed by removal of the external acid sites by dealumination using $(NH_4)_2SiF_6$ with the disproportionation activity being unchanged. We conclude that 2-MN is selectively disproportionated to 2,6- and 2,7-DMN within the channel of H-ZSM-5, while isomerization of 2-MN or DMN proceeds on the external acid sites. On H-ZSM-5, however, 2,7-DMN was more selectively formed than 2,6-DMN. The preferential formation of 2,7-DMN against 2,6-DMN on H-ZSM-5 cannot be explained by the shape selectivity because there is no difference in the molecular dimension between these DMN isomers.



FIG. 6

Relation between strength of acid sites on mordenite and composition of classified DMN isomer groups. DMN group: ○ 2,6--DMN; △ 2,7-DMN; □ 2,3-DMN

H-Mordenite exhibited the highest selectivity for 2,6-DMN against 2,7-DMN among the catalysts tested. The composition of produced DMN isomers was found to be influenced by the acid strength of H-mordenite. It is deduced from these results that the composition of produced DMN isomers is changed by the acid strength as well as by the shape selective properties of zeolites.

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