Notes

Methylation of Naphthalene with Methanol over Beta, Mordernite, ZSM-12 and MCM-22 Zeolite Catalysts

Jung-Nam Park, Jun Wang,[1] Chul Wee Lee,* and Sang-Eon Park*

Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology (KRICT),
P.O. Box 107, Yusung, Daejeon 305-600, Korea
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Studies on the gas phase alkylation of naphthalene with methanol over various zeolites are of great practical and fundamental interest. 2-methylnaphthalene (2-MN) is the main raw material in vitamin K synthesis, and 2,6-dimethylnaphthalene (2,6-DMN) is used in the preparation of polyester fibers and plastics with superior properties and of thermotropic liquid crystal polymers.[1] These hydrocarbons can be obtained by alkylation of naphthalene and monomethylnaphthalenes,[2,3] or by isomerization and disproportionation of monomethylnaphthalenes.[4] Methylation of naphthalene has been initially investigated over H-ZSM-5, H-mordenite and H-Y zeolites,[2,5] and it was found that β-selectivity (2-MN) could be obtained over medium pore H-ZSM-5 zeolite, but only with moderate activity. In a recent literature,[6] the acid sites on the external surface of H-ZSM-5 zeolite was selectively neutralized, and this catalyst showed lower initial activity, higher selectivity and longer catalyst life in the methylation of methylnaphthalenes compared with the unmodified one.

More attention has recently been paid to isopropylation and tert-butylation of naphthalene on large pore zeolites and mesoporous aluminosilicates, so as to further improve the β-selectivity and β,β-selectivity.[7] However, 2,6-DMN is a preferable raw material to synthesize 2,6-naphthalene dicarboxylic acid, because it results in a high yield and corresponds well to the atomic economy. Nowadays, BP-Amoco is the only company operating a large-scale industrial process for producing 2,6-DMN, which requires four successive reaction steps starting from o-xylene and butadiene.[8] The commercial utilization of selective zeolite catalysts for methylation of naphthalene still remains an elusive goal and needs further studies.

In this work, the methylation of naphthalene with methanol as the alkylation reagent and 1,2,4-trimethylbenzene (1,2,4-TMB) as the solvent was investigated using a fixed bed gas

phase reactor on the large pore zeolites, such as beta, mordenite and ZSM-12, together with the medium pore zeolite, MCM-22. Catalytic performances are discussed in relation with zeolite pore structures.

Experimental Section

Na-ZSM-12 (Si/Al=44) and Na-MCM-22 (Si/Al=15) were synthesized according to the previous literatures.[9,10] The crystals of ZSM-12 and MCM-22 were confirmed by X-ray diffraction patterns.[11,12] H-Mordenite (H-Mor), H-ZSM-12 and H-MCM-22 were prepared by the repeated ion-exchange of Na-Mordenite (Verikon Zeocat FM-8, Si/Al=6), Na-ZSM-12 and Na-MCM-22, respectively, with the aqueous solution of ammonium nitrate, followed by drying and calcination. H-Beta was obtained by the calcination of NH$_4$-Beta (Zeolyst CP814E, Si/Al=12.5) at 450 ^{o}C for 4 h.

Catalytic tests were performed in a fixed bed microreactor at the atmospheric pressure. The reactant mixture of naphthalene, methanol and 1,2,4-TMB was injected into the reactor through a syringe metering pump. The typical reaction conditions were as follows: reaction temperature = 350 ^{o}C, naphthalene: methanol: 1,2,4-TMB = 1 : 3 : 10 (mole), weight hourly space velocity of reactants = 2.5 h^{-1}, catalyst weight = 0.5 g, flow rate of N$_2$ (carrier gas) = 13 mL/min. Before reaction, the catalyst was pretreated *in-situ* in N$_2$ flow at 450 ^{o}C for 4 h. The products were analyzed by the gas chromatograph (HP 5890 II) equipped with FID and 30 m SE30 capillary column.

Results and Discussion

Table 1 displays the conversions of naphthalene and selectivities of products over the employed zeolite catalysts for the methylation of naphthalene with 1 h time on stream. It can be seen that H-Beta is the most active catalysts among them with a high conversion of 99%, H-Mor and H-ZSM-12 possess the conversions of 42.5% and 51.9%, respectively, and H-MCM-22 has the low activity of only 11.6%. As for the selectivity, comparatively high selectivity for MN is

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*To whom Correspondence should be addressed. E-mail: separk @krict.re.kr or chulwee@krict.re.kr
[1]On research leave from Department of Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China
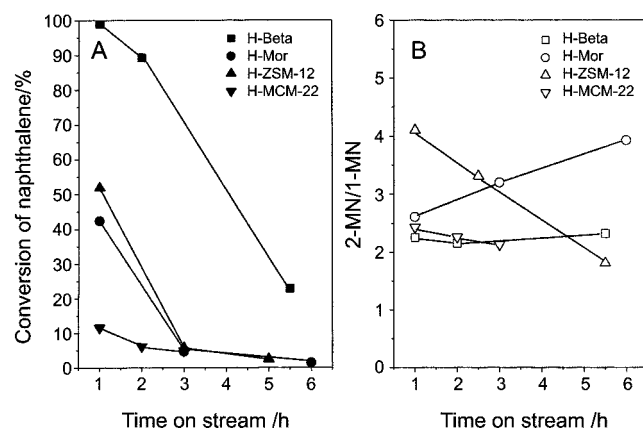
Table 1. Conversion of naphthalene and product selectivity for the methylation of naphthalene with methanol[a]

Catalyst	H-Mor	H-ZSM-12	H-Beta	H-MCM-22
Conversion/%	42.5	51.9	99.0	11.6
Product analysis/wt%				
MN	36.5	40.4	1.8	75.1
EN[b]	3.2	4.1	0.7	0
DMN	30.8	31.9	17.0	15.8
PMN[c]	29.5	23.6	80.5	9.1
MN isomer composition/%				
2-MN	72.3	80.4	69.2	70.8
1-MN	27.7	19.6	30.8	29.2
DMN isomer composition/%				
2,6+2,7-DMN	42.8	55.4	34.5	16.0
others	57.2	44.6	65.5	84.0

[a]time on stream = 1 h; [b]ethylnaphthalene; [c]polymethylnaphthalene.

found on H-Mor, H-ZSM-5 and H-MCM-22, while very low MN and very high PMN are achieved on H-Beta. Furthermore, H-Mor and H-ZSM-12 generate higher selectivities for DMN compared with the other two zeolites. Ethylnaphthalene is also detected in a small amount duo to the ethylation of naphthalene with ethylene or a zeolite-bound ethyl group formed as a side product on methanol conversion which accompanies the methylation reaction.[2] It is also found that, H-Mor and H-ZSM-12 exhibit relatively high selectivities for 2-MN and H-Beta has a 2-MN selectivity comparable to H-MCM-22. The similar result for the selectivity for 2,6+2,7-DMN is observed as that for 2-MN except that H-MCM-22 gives a very low 2,6+2,7-DMN selectivity of 16%.

The behavior of the conversion and the ratio of 2-MN to 1-MN as a function of the experiment duration is illustrated in Figure 1. It is indicated in Figure 1A that the conversions on H-Mor and H-ZSM-12 sharply deactivate to a very low value (*ca.* 5%), by contrast, a relatively slow deactivation rate is revealed in case of H-Beta at least at the early reaction stage. On the other hand, a very slow decrease of conversion

Figure 1. Conversion of naphthalene (A) and ratio of 2-MN to 1-MN (B) for methylation of naphthalene over various zeolites as a function of reaction time on stream.

is observed over H-MCM-22, but in this case its activities are always very low, even at the initial reaction stage. Figure 1B shows a remarkable increase and decrease of β-selectivity for H-Mor and H-ZSM-12, respectively, and the same phenomenon is observed for H-Beta and H-MCM-22, respectively, but with a very slow changing speed. The present observations are somewhat in agreement with previous results,[2,13] in which H-mordenite and H-Y zeolites deactivated rapidly to low conversions (less than 20%) within 2 h of time on stream, while H-ZSM-5 deactivated slowly but always showed low conversions (about 10%). Fraenkel *et al.*[2] found that H-mordenite possessed an activity of 29% and a 2-MN/1-MN of 1.8 after 0.5 h of time on stream, which are lower than what we observed in Table 1, however, they obtained a very high β-selectivity on H-ZSM-5 (2-MN/1-MN = 8.1), which we have not achieved on H-MCM-22 here, who is also a medium pore zeolite like ZSM-5.

Both mordenite and ZSM-12 have large pores with a unidimensional 12MR (12-membered ring) pore system. It is proposed that their high initial activity (Table 1 and Figure 1A) originate from the large pores. However, they undergo rapid deactivation (Figure 1A) due to coking, which is also well known from many other reactions and has generally been attributed to the unidimensional pore system.[14] While the catalyst is on stream, coke is gradually formed and deposits inside the zeolite channel. As a consequence, the diffusion pathways for product molecules increase. Slim molecules, such as 2-MN are less affected than bulkier ones, such as 1-MN. Therefore, the increment of the 2-MN fraction on H-Mor in Figure 1B can easily be rationalized. However, this coke selectivity has not been found on H-ZSM-12, despite its similar pore structure to mordenite. On the contrary, the decrement of 2-MN selectivity on H-ZSM-12 is clearly indicated in Figure 1B. Actually, the previous literature[15] also observed the variation of the β-selectivity on H-ZSM-12 compared with H-mordenite in the gas phase isomerization of 1-MN, and the authors supposed that some unknown factors play a role in case of H-ZSM-12. Here, the Si/Al ratio of the employed ZSM-12 is much higher than that of H-Mor, which leads to the very low density of acid sites. Consequently, it is reasonable to propose here that the deactivation of H-ZSM-12 arise from the coverage of strong acid sites, rather than the blockage of pore channels by coking. It is known[13] that the 1-position in the naphthalenic molecule is more reactive than the 2-position, and it can thus be expected that 1-MN is more favorable to be formed initially and then desorbed out of the unblocked large pore channels in H-ZSM-12 catalysts. This consideration, together with the poor ability of the residual weak acid sites in H-ZSM-12 pores to isomerize 1-MN into 2-MN, account for the increment of 1-MN on H-ZSM-12 with its deactivation.

The very high initial activity on H-Beta (99% in Table 1) corresponds well to its three-dimensional 12MR pore system without super cage. This pore structure also allows a comparatively low deactivation rate for catalyst (see Figure 1A).[6] Moreover, the three-dimensional large pore system is

favorable for the produce of heavy products, with the selectivity of PMN being as high as 80.5%, much higher than those for other zeolites. After partly deactivation of H-Beta at 5.5 h on stream, the conversion drop to 22.9%, while the selectivity for MN increases drastically from initially 1.8% to 54.1%, and 2-MN/1-MN increases slightly, but PMN decreases from initially 80.5% to 22.4%. This observation can also be interpreted reasonably by the concept of coke selectivity.[15]

MCM-22 has a sinusoidal 10MR channel plus large 12MR super cages connected to each other through 10MR windows which form a second independent system of 10MR channels.[16] One would expect that more selective reaction result could be achieved on this medium pore zeolite. However, Table 1 demonstrates that only 16% of the selectivity for 2,6+2,7-DMN could be produced on H-MCM-22. This value is not only much lower than those on the three large pore zeolites, but also even lower than the equilibrium constitution of about 24% for 2,6 and 2,7-DMN.[6] Moreover, for H-MCM-22, the activity is always very low, with the β-selectivity being lower than those on H-Mor and H-ZSM-12. All of these results suggest that the methylation reaction occur on the external surface of H-MCM-22. In principle, the slimmest isomer in products, 2-MN possessed a critical size of 0.58 nm,[2] which cannot diffuse out of the 10MR window of MCM-22 (0.52 nm) to be a real product. On the other hand, it is also possible that acid sites inside the zeolite channel totally deactivate at the very early reaction stage. Consequently, the methylated naphthalene products on H-MCM-22 must be directly generated on its external surface without shape selectivity.

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