

Shape-Selective Alkylation of Naphthalene and Methyl-naphthalene with Methanol over H-ZSM-5 Zeolite Catalysts

DAN FRAENKEL, MARGARET CHERNIAVSKY,† BARUCH ITTAH, AND MOSHE LEVY

Department of Materials Research, The Weizmann Institute of Science, Rehovot, Israel

Received October 22, 1985; revised April 30, 1986

Gas-phase alkylation of naphthalene and 2-methylnaphthalene (2-MN) can be carried out efficiently over H-mordenite (HM), HY, and H-ZSM-5. A high β selectivity is observed with various kinds of H-ZSM-5 but not with HM and HY. At 350°C, with naphthalene:methanol:mesitylene, 1:1:3 (wt) feed and space velocity, WHSV $\sim 0.5 \text{ h}^{-1}$, 15% naphthalene conversion is achievable with 76% selectivity to 2-MN and 2,6/2,7-dimethylnaphthalene (2,6/2,7-DMN). At 400°C, 2-MN can be methylated using a 2-MN:methanol:mesitylene, 1:0.25:3.0 (wt) feed to give 60% 2,6/2,7-DMN at 19% conversion. This shape-selectivity is explained in terms of size differences between relevant molecules and zeolite pores. Nonselective alkylation of naphthalene and 2-MN on HM and HY is suggested to occur in the intracrystalline voids of these large-pore zeolites, which easily accommodate both reactant and product molecules and allow their rapid diffusion. On the other hand, it is postulated that the β -selective alkylation over H-ZSM-5 occurs in external surface sites which perfectly suit small-size naphthalenics; these catalytic sites are too large, however, to allow any *para*-selectivity in the alkylation of toluene with methanol. © 1986 Academic Press, Inc.

INTRODUCTION

The gas-phase alkylation of naphthalene (N) with methanol over heterogeneous catalysts is a well-known process (1). Typical results, summarized in Table 1, show the β -to- α methyl-naphthalene (MN) ratio to be less than 4 at total MN yield of $\approx 75\%$. In view of the recent impressive progress in shape selective catalysis over zeolites (4, 5), especially in ring alkylation of toluene (6, 7), exploring the potential of this class of catalysts in selective alkylation of naphthalene (Scheme 1) to boost the β product, has become a natural step further.

Besides 2-MN, the main raw material in K-vitamin synthesis (8), also 2,6-dimethylnaphthalene (2,6-DMN) is obtainable from β -selective alkylation, either as secondary alkylation product of naphthalene or as the primary product in the alkylation of 2-MN. Being a precursor of 2,6-naphthalenedicarboxylic acid, 2,6-DMN is a potential starting material in the production of polyester

fibers and plastics with superior properties (9, 10).

Our interest in the possibility of β -selective methylation of naphthalene over zeolites was stimulated by the finding during an earlier study (11) that the C_{11} - C_{13} cut of the "gasoline" obtained by methanol conversion on H-ZSM-5 (12, 13) contained almost exclusively methyl- and polymethylnaphthalenes. Interestingly, the β -to- α MN ratio was ≈ 8 which is indicative of a strong β -directing effect that could be attributed to the shape-selective nature of H-ZSM-5. Naphthalene was also detected in significant amounts in the above product mixture. By contrast, zeolite HY and H-mordenite (HM), when used as catalysts in batch experiments of methanol conversion at 400°C, afforded in the C_{11} - C_{13} carbon number region mainly pentamethylbenzene (PMB) and hexamethylbenzene (HMB). These were also the major single products in the organic liquid obtained.

In this article we present our study on the catalytic gas-phase alkylation of naphthalene and 2-MN with methanol over the

† Deceased.

TABLE I
Gas-Phase Heterogeneous Alkylation of Naphthalene with Methanol: Literature Data

Catalyst	Solvent	Reaction conditions				Conversion, %	NM yield, %		β/α	Source
		MeOH/N molar ratio	Temp., °C	Pressure, ^a MPa	Space velocity		α (1-MN)	β (2-MN)		
CATAPAL Al ₂ O ₃	Toluene	4	600	2.75	0.68 ^b	20.4	15.4	59.2	3.8	Ref. (2)
Nikki N-631-L silica-alumina	Benzene	4.16	450	0.1	0.2 ^c	21.0	54.6	2.6	Ref. (3)	

^a 0.101 MPa = 1 atm.

^b LHSV, h⁻¹.

^c ml feed per g catalyst per h.

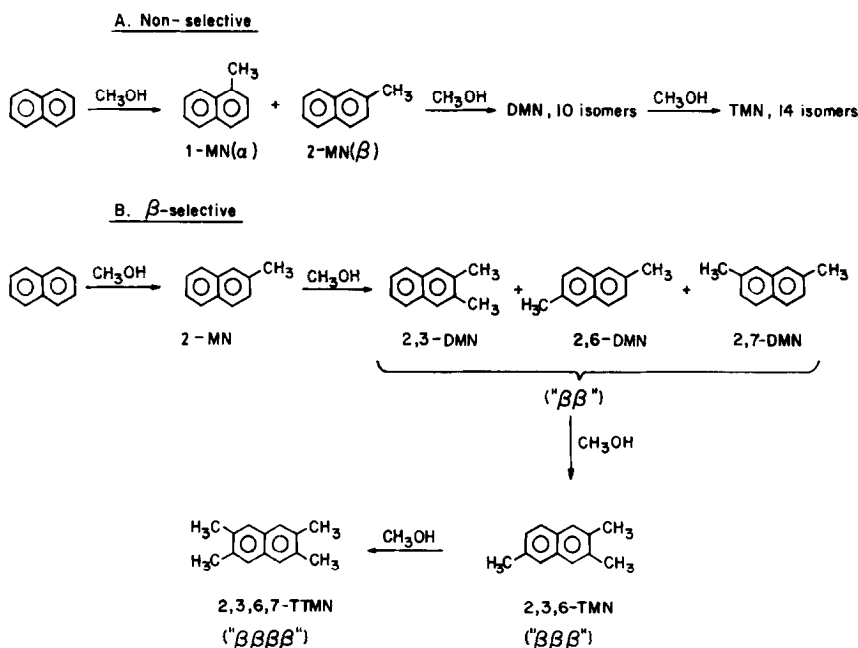
above-mentioned zeolites. An apparently similar work has been just described briefly in the patent literature (14). In discussing our results we relate to mechanistic principles set forth in a previous publication (15).

METHODS

Materials. Absolute methanol (>99.7%) was obtained from Frutarom, Israel. The source of mesitylene was either Fluka (puriss.) or Merck (98%). Naphthalene (>99%) and nitrobenzene (Analar) were

purchased from BDH, and isodurene (90%; 10% durene), tetralin (purum), pseudocumene (purum), 2-MN (>98%) and 1-MN (97%; contains <3% 2-MN) from Fluka. Authentic samples of all DMN isomers, except 1,7, and 2,3,6-trimethylnaphthalene (2,3,6-TMN) were supplied by Fluka.

Catalysts and their characterization. HM is Zeolon 200(H) from Norton Company. HY is SK-40 (Union Carbide) exchanged 6 times with 1 N NH₄Cl solution for 2 h at 90–95°C, then dried at 120°C overnight and



SCHEME 1. Modes of naphthalene methylation

TABLE 2
Chemical Analysis^a of Zeolites

	SiO ₂	Al ₂ O ₃	Na ₂ O	Si/Al		Na/Al	
				Introduced	Obtained	Introduced	Obtained
I	87.4	3.5	0.20 ^b	14.1	21.2	1.2	0.075
II	84.1	7.1	0.37	14.1	10.1	1.2	0.068
III	90.4	2.4	0.22		32.0		0.12

^a In wt%.

^b Possibly includes some K₂O.

calcined *in situ* freshly before use, at 500°C for 16 h. I–VIII are H-ZSM-5-type zeolites from different sources, obtained from their respective NH₄⁺ forms by calcination at 500°C. I and II were prepared according to the original Mobil procedure (16), the former in Pyrex-glass (Sovirel 732.01) ampules and the latter in a Teflon-lined autoclave. Their detailed synthesis was described elsewhere (15). According to their SEM analysis, done on JEOL 35 and on Philips 505 instruments, they have typically 5–10 μm rectangular crystals. I is apparently coated with amorphous silica while II looks almost free of amorphous phase. III is a Mobil sample of very small (~0.5 μm) crystals mostly grouped in large aggregates. IV and V were synthesized using a standard recipe (17) except for the use of 40% (rather than 30%) silica sol (DuPont Ludox HS40), the first at 150°C and the second at 95°C. IV and V have the same morphology of oval-shaped crystals and an average crystal size of ~30 and ~6 μm, respectively. VI was synthesized like II but with 4.4-fold excess of SiO₂; its crystal size and morphology resemble those of III. VII is another version of VI in which the mixture after crystallization is evaporated to dryness before calcination; for all practical purposes, VI and VII may be considered almost identical. VIII was crystallized from a mixture made of 10 g Pyrex glass powder (Sovirel 732.01, 80–100 mesh), 62.5 g 20% tetrapropylammonium hydroxide (Fluka), and 2.0 g B₂O₃, evaporated to a total weight of 62 g, at

155°C during 5 days. This product contains large, "coated" crystals and is similar to I. In their XRD spectra recorded on Philips PW-1011/02 diffractometer, using copper irradiation, I–VIII all have the standard ZSM-5 pattern (16) and exhibit good-to-excellent crystallinity. Chemical analysis of I–III is presented in Table 2.

Catalytic runs and product analysis. Catalytic experiments were performed in a 20-mm-i.d. Pyrex tubular flow reactor surrounded by an electrical heater equipped with a thermoregulator. The catalyst powder, diluted by three times its weight of Pyrex glass powder, was loaded onto the reactor in a folded glass-wool sheet and placed between two 2–3 cm sections of Pyrex glass balls, 3 mm in diameter. Catalyst preactivation (to produce the H-form) was carried out *in situ* at 500°C normally for 1–2 h under air; then under a flow of Ar (~30 cm/min) the reactor was brought to the reaction temperature at which it was allowed to stabilize for an additional half hour. Ar flow was continued throughout the reaction. A naphthalene (or 2-MN)–methanol–solvent feed was injected dropwise into the reactor using a Sage syringe pump. The product mixture was collected in a condenser attached to the bottom of the reactor. Liquid samples taken from the outlet of the condenser, were analyzed on a Tracor 560 gas chromatograph equipped with an FID and operating with a 3390A Hewlett–Packard integrator or a CSI supergrator-3A. The GC columns used routinely for the analysis

TABLE 3
Typical Naphthalene Methylation Results^a

Catalyst	H-ZSM-5 (II)	H-ZSM-5 (III)	HM	HY
Catalyst weight, g	0.5	0.5	5	5
WHSV, h ⁻¹	3.16	3.16	1.18	1.18
Temperature, °C	400	400	400	450
Time on stream, h	0.5	3.33	0.5	1.33
Conversion, %	≈5	9	29	47
Product analysis, wt%				
MN	50.2	65.3	55.5	44.1
EN	10.4	3.9	4.4	1.1
DMN	33.1	20.8	26.1	28.7
TMN	5.6	7.5	10.5	18.7
TTMN ^b	0.7	2.1	2.7	6.3
PMN	—	0.4	0.6	1.1
MN isomer composition, %				
β (2)	89	89	65	63
α (1)	11	11	35	37
DMN isomer composition, %				
2,6 + 2,7	65.6	80.8	35.1	32.2
1,3	14.0	10.2	29.6	30.0
1,6	12.9	7.8	17.9	18.2
2,3 + 1,5(+ 1,4?)	5.4	1.2	11.5	13.3
1,2	2.1	0.0	5.9	6.3
1,8	0.0	0.0	0.0	0.0

^a Feed mixture: N : MeOH : Mes, 1 : 6.61 : 3.57 (mol); Mes = mesitylene. Analysis done with a 30-m SP-2100 capillary column.

^b Tetramethylnaphthalene.

were SE-30 and OV-101 (capillary). GCMS analyses were done on a Finnigan Model 4021 instrument.

RESULTS

(a) Preliminary study

A typical set of experiments with H-ZSM-5 (II and III), HM and HY zeolites, as catalysts is summarized in Table 3. A detailed naphthalenic product analysis is presented. As seen, the methylation of naphthalene over HM and HY gives initially high conversion to a complicated mixture containing a wide spectrum of products from MN's to pentamethylnaphthalenes (PMN's). With II and III much lower conversions were obtained. Figure 1 presents a typical GCMS chromatogram on which the various polymethylnaphthalene groups are seen to be fairly resolved.

DMN isomer identification in this analysis was only partial; it was more complete on the Tracor GC.

(i) *MN products.* The concentration of MN's in the naphthalenic product mixture was 44–65%. The β-to-α ratio (2-MN/1-MN) obtained with HM and HY was ~2 (Table 3). By contrast, the H-ZSM-5 class catalysts, II and III gave a ratio of 8.1.

(ii) *Formation of EN.* To some extent, ethylnaphthalene (EN) is always obtained in the alkylation of naphthalene with methanol. It is apparently produced by ethylation of naphthalene with ethylene or a zeolite-bound ethyl group formed as a side product in methanol conversion which accompanies the methylation reaction. As with MN, high β-selectivity is indicated when H-ZSM-5 is used as catalyst.

(iii) *DMN products.* The higher β-selectivity of II and III in naphthalene methylation, compared to HM and HY is further

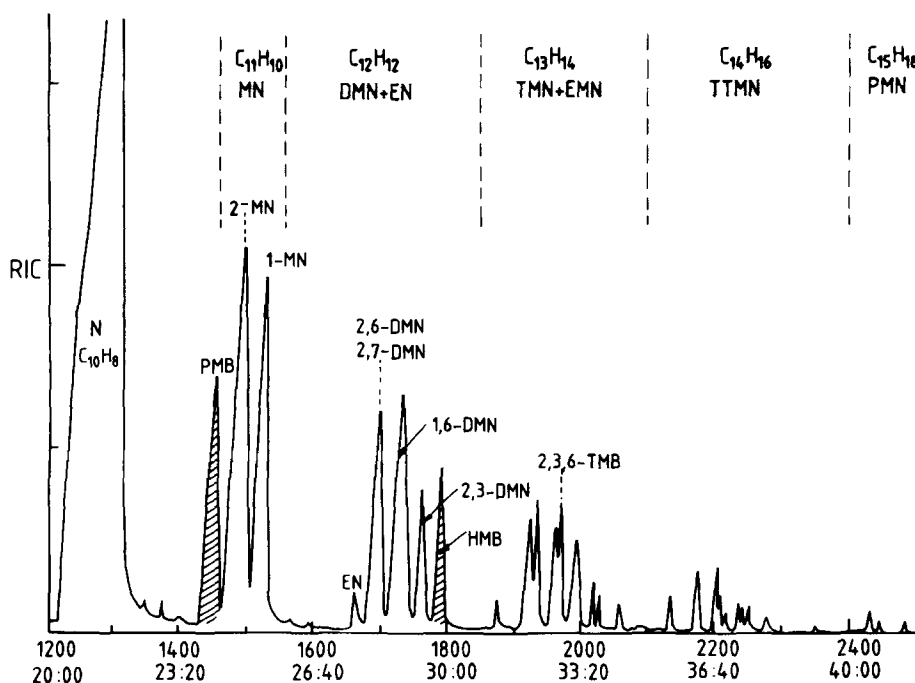


FIG. 1. Typical GCMS analysis (catalyst, HY; column, 30 m capillary SE-54; programming conditions: 45°C, 5 min, 4°C min⁻¹, 200°C).

illustrated in the DMN isomer composition (Table 3). Thus, 2,6/2,7-DMN ("ββ-product") constitutes 65 and 80% of the DMN mixture in the case of II and III, but only 35 and 32% in the case of HM and HY, respectively. The third ββ-product, 2,3-DMN, if at all formed, appears to be a minor product presumably because of the unfavorable steric situation of position-3 of 2-MN with respect to an activated methyl group in the zeolite cavity. 1,8-DMN was not detected in any of the product mixtures analyzed. Perhaps substitution at position-8 is prevented because of the strong steric hindrance imposed by the bulky methyl group in position-1.

(iv) *Higher polymethylnaphthalenes*. Besides their high β-selectivity, II and III exhibit less tendency for polyalkylation than HM and HY.

(v) *Catalyst stability*. Figure 2 presents plots of naphthalene conversion vs time on stream. A rapid deactivation is seen in the case of HM and HY while III appears re-

markably more stable and apparently so is II.

(b) Further Investigation

A systematic experimental work over a wide range of reaction conditions, was done with VI which had been proved superior to other H-ZSM-5-type catalysts

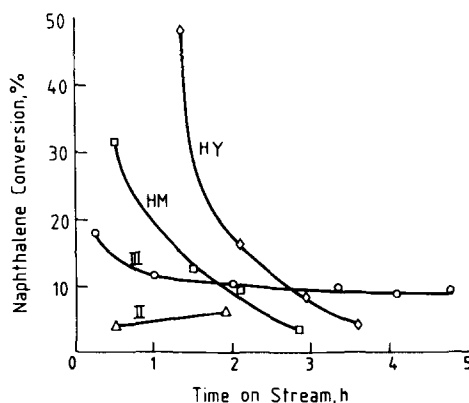


FIG. 2. Naphthalene conversion as a function of time on stream (for reaction conditions, see Table 3).

TABLE 4
 Effect of Catalyst^a

Exp. code	B65	B66	H107	H106	B23	H81
Catalyst	HM ^b	HM ^c	IV	V	VIII	VI
Catalyst weight, g	1	4.5	1	1	1.5	1
WHSV, h ⁻¹ (naphthalene)	0.48	0.38	0.48	0.48	0.44	0.48
Naphthalene conversion, %	2.3	12.5	1.6	5.3	1.3	15.0
Naphthalenics product analysis, wt%						
MN						
2	42.6	38.1	69.3	68.5	69.4	60.6
1	29.0	20.7	— ^d	0.7	2.8	3.8
EN	2.0	11.6	18.5	6.8	3.0	7.4
DMN						
2,6 + 2,7	3.3	4.0	12.2	16.8	21.8	15.3
1,3	4.0	3.7	—	—	—	1.3
1,6	2.3	2.3	—	—	—	1.0
2,3 + 1,5(+ 1,4?)	3.0	1.5	—	—	—	—
1,2	16.5	11.1	—	1.9	—	3.8
Other C ₁₂ ⁺	—	4.2	—	5.2	3.0	6.5

^a Feed ratio N : MeOH : Mes. 1 : 1 : 3 (wt); temp., 350°C, except for Exp. B23 where it was 500°C; time on stream, 0.5 h.

^b 80–100 mesh powder.

^c Pellets (1/16 in.).

^d Nondetectable.

under comparable conditions as demonstrated in Table 4. According to this table, IV, V, and VIII exhibit very high β -selectivity in the formation of both MN and DMN, but low naphthalene conversion. VI, although showing somewhat lower β -selectivity, gives >threefold higher conversion (15%); in addition, unlike the other catalysts, VI exhibits excellent stability. Just for rough comparison, commercial HM, either in pellet or powder form, was used as catalyst under the very same conditions (Table 4); catalyst deactivation was rapid and no β -selectivity was observed.

Effect of solvent. A good solvent should dissolve large amounts of both methanol and naphthalene and remain unreacted under the alkylation conditions; it also should not inhibit catalyst activity (e.g., by poisoning Brønsted acid sites) and not interfere in the GC analysis of naphthalenics. Since mesitylene appears to generally obey these criteria, it was chosen for most experiments. A comparison of different solvents as given in Table 5 reinforces this choice:

Tetralin is very reactive and apparently inhibits naphthalene alkylation. Nitrobenzene behaves similarly. On the other hand, pseudocumene and isodurene give 10–14% conversion of naphthalene but are also quite reactive. With mesitylene about the same naphthalene conversion is achievable with practically no solvent conversion. It should be noted, however, that mesitylene is by no means an inert solvent when passed over catalyst VI at higher temperatures, and reacts readily over HM and HY.

Effect of temperature. The effect of temperature is shown in Fig. 3. Naphthalene conversion is roughly constant between 300 and 400°C then somewhat increases toward 460°C. In parallel, the β -selectivity (expressed in terms of the ratio 2-MN/1-MN) is high and constant from 300 to 350°C, then sharply decreases fourfold toward 400°C and levels off upon further temperature increase. Increasing time on stream slightly improves selectivity at least between 350 and 420°C, as shown by the upper selectivity curve. The effect of time on stream on

TABLE 5
 Effect of Solvent with Catalyst VI^a

Exp. code	H80	H85	B72	H86	H87
Solvent	Mesitylene	Isodurene	Pseudocumene	Nitrobenzene	Tetralin
WHSV, h ⁻¹	0.48	0.45	0.48	0.4	0.45
Conversion, %					
Naphthalene	10.0	10.9	13.8	0.44	0
Solvent	0	13.6	18.1	13.1	30.6
N/Solv.	∞	0.80	0.76	0.03	0
2-MN/1-MN	8.3	12.5	16.3	10.0	—

^a Catalyst weight, 1 g; feed ratio N:MeOH:solv., 1:1:3 (wt); temp., 380°C; time on stream, 0.5 h.

naphthalene conversion seems more complex. At 300°C a sharp drop in conversion is noticed whereas at 350–380°C there is almost no change. At higher temperature conversion appears to slightly improve with time. We attribute the low-temperature drop in conversion to plugging of catalytic sites by large product molecules. At ~350°C these molecules diffuse away from the catalytic sites sufficiently faster thus enabling more reactant molecules to approach the active centers and undergo reaction. At higher temperatures, sites responsible for methanol conversion are presumably deactivated more rapidly than those responsible for the methylation of naphthalene. Therefore, the naphthalene methylation efficiency is improved with time. The delicate balance between the various factors influenced by the temperature dictates the existence of only a narrow temperature inter-

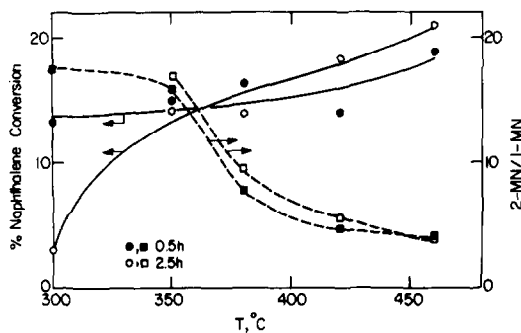


FIG. 3. Effect of temperature on the methylation of naphthalene over catalyst VI. [1 g cat.; N:MeOH:Mes, 1:1:3 (wt); WHSV (naphthalene), 0.48 h⁻¹].

val at which good performance can be expected; 350°C is certainly within this interval. Under the reaction conditions employed, this temperature allowed about 15% conversion, with MN ratio of 16 and only minor changes during 2.5 h on stream.

Effect of methanol concentration in the feed. Keeping a constant mesitylene-to-naphthalene ratio of 3, the effect of the initial N/(N + MeOH) ratio was studied within the range 0.1–0.8. The results are shown in Fig. 4. As seen, naphthalene conversion passes through a maximum at ~0.35. The β -selectivity shows a parallel but opposite behavior, i.e., exhibits a minimum at ~0.35. Increasing time on stream lowers the conversion curve and raises the

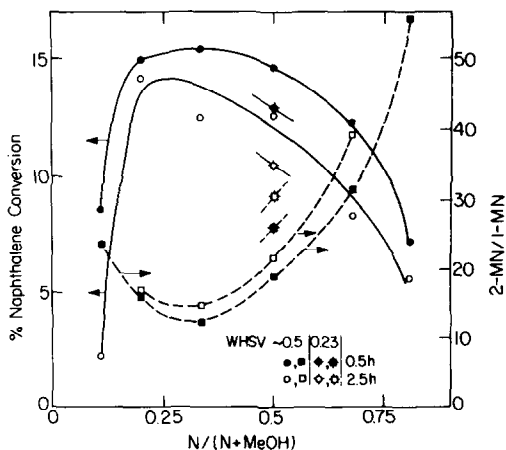


FIG. 4. Effect of feed content on the methylation of naphthalene over catalyst VI. [1 g cat.; N:Mes, 1:3 (wt); 350°C; WHSV (naphthalene), 0.5 ± 0.1 h⁻¹ unless otherwise specified.

TABLE 6
 Alkylation of 2-MN with Methanol

Exp. code	H25	B13	B14	H14	H17	H110	H112
Catalyst ^a	HM ^b	VI	VI	VI	VII	VII	VII
Solvent ^c	Mes	Mes	Mes	Mes	Mes	Mes	1-MN
Feed ratio (wt). 2-MN : MeOH : Solv.	1 : 1.0 : 6.2	1 : 0.5 : 3.0	1 : 0.2 : 3.0	1 : 1.0 : 6.2	1 : 1.0 : 12.5	1 : 0.25 : 3.0	1 : 0.25 : 1.0
WHSV, h ⁻¹ (2-MN)	0.43	0.73	0.82	0.43	0.23	0.58	0.66
Temp., °C	400	500	500	400	400	400	400
2-MN conversion, ^d %	30.1	8.3	8.9	10.8	18.0	18.9	11.6
Naphthalenics product analysis, wt%							
N	6.4	0	2.5	3.8	10.3	4.1	12.4
1-MN	35.7	4.7	18.0	9.7	20.2	9.9	— ^e
DMN							
2,6 + 2,7	15.5	58.0	40.5	54.4	42.3	60.6	66.1
1,3 + 1,6	18.6	13.2	16.7	14.4	14.9	8.5	7.3
2,3 + 1,5 (+ 1,4?)	4.1	4.9	4.6	3.5	3.8	3.5	3.9
1,2	3.5	7.8	9.2	6.9	2.6	—	—
Other C ₁₂ ⁺	16.0	11.4	8.5	7.3	8.5	13.4	10.3

^a 1 g.^b Powder.^c Mes = mesitylene.^d Time on stream, 0.5 h.^e Not included.

selectivity curve, but keeps the basic picture very much the same. The behavior shown in Fig. 4 can be explained in terms of a deactivation effect (pore-plugging or coking) which improves shape selectivity. The maximum in the conversion curve is the result of two opposing factors, (1) the inhibition effect caused by methanol which at high concentrations competes successfully with naphthalene on the catalytic sites, and (2) a mass effect correlating the alkylation activity with the amount of methanol in the feed. As usual in product diffusion controlled processes (vide infra), selectivity changes inversely with conversion. As indicated at $N/(N + \text{MeOH}) = 0.5$, lower space velocity causes decrease in naphthalene conversion and increase in selectivity. Perhaps, these observations may be explained by assuming that as contact time is increased, methanol becomes more strongly involved as reactant, competing with naphthalene on the same acid catalytic sites, hence suppressing catalytic activity with respect to naphthalene.

Alkylation of 2-MN. Typical results of the gas-phase alkylation of 2-MN with methanol over catalysts HM, VI and VII are given in Table 6. As with naphthalene,

HM shows high initial reactivity with poor selectivity and rapid deactivation. The main product is 1-MN obtained by isomerization of 2-MN. Naphthalene—a dealkylation product—is also formed. With VI and VII, 2-MN conversions of ~10% and higher are obtained with appreciable β -selectivity, the 2,6/2,7-DMN fraction in total product being usually well above 0.5. However, some isomerization and dealkylation activity is unavoidable. No EN is formed, in contrast with the methylation of naphthalene. Considering the low methanol-to-2-MN ratio employed (≤ 1) it is also unlikely that substantial amounts of ethylmethyl-naphthalene (EMN) would be produced (although there has been no attempt to identify C₁₃ naphthalenics in the present study). 1-MN was shown to be a convenient solvent (Exp. H112 in Table 6). As reactant instead of 2-MN, with mesitylene as solvent and a 1:0.25:3 feed ratio, 1-MN gave at 400°C and WHSV 0.59 h⁻¹ an initial conversion of 10.6% to a product mixture containing 85% 2-MN, 6% N, and 7.6% 2,6/2,7-DMN. Thus, 1-MN undergoes mainly isomerization under the 2-MN alkylation conditions. It, therefore, presents no problems as potential solvent for this reaction.

TABLE 7

Comparison between the Methylation of Toluene and Naphthalene over H-ZSM-5

Catalyst	I	VIII	II	IV	V	III	VI
Catalyst crystal size ^a	L	L	L	VL and S	L and S	S	S
Morphology	Varying	Varying	Rectangular	Oval	Oval	Irregular	Irregular
"Coating"	Yes	Yes	No	No	No	No	No
Toluene methylation ^b							
Tol. conversion, %	11	8.7	21	25	27	27	25
<i>p</i> -selectivity, %	88	87	49	18	12	9.5	3.3
Naphthalene methylation ^d							
Naph. conversion, %	<1	1.3	~5	1.6	5.3	9	15
β -Selectivity, %	—	89	70	100	100	70	84

^a L, large; S, small; VL, very large.^b I, II, III—for reaction conditions see Ref. (15); IV, V, VI, VIII—450°C; Tol: MeOH, 3:1 (mol); WHSV, 1.2 h⁻¹.^c Calculated from the expression (% *p*-% *p*^{eq}) × 100/(100-% *p*^{eq}), where % *p* is the percentage of *para*-xylene in xylene mixture and % *p*^{eq} is the corresponding value at thermodynamic equilibrium.^d For reaction conditions, see Tables 3 and 4.^e Calculated from the expression (% β -% β ^{HY}) × 100/(100-% β ^{HY}), where % β is the percentage of β -MN in MN mixture and % β ^{HY} is the corresponding value in HY (at 450°C). It is assumed that % β ^{HY} ~ % β ^{eq}, the thermodynamic equilibrium value.

This is a great advantage from a commercial viewpoint since MN isomer mixtures are more readily available, hence are cheaper than pure 2-MN.

DISCUSSION

β -Selectivity in the alkylation of naphthalene may be explained by the fact that "all- β " isomers (Scheme 1B) have the smallest critical molecular size, i.e., 0.58 nm, while isomers with a methyl substituent at position-1 are at least 0.62 nm in critical size (15). Thus, a molecular sieving effect at about 0.60 nm is required for effective β -methylation of naphthalene, while for *para*-selective toluene methylation a sieving effect at \approx 0.55 nm would be adequate. We have recently presented a scale of critical molecular dimensions and nominal pore openings of zeolites in their H-form (15). According to this scale, HM and HY, with a nominal pore opening of 0.70 and 0.74 nm, respectively, should not be selective in naphthalene methylation since all MN and poly-MN isomers produced are sufficiently small to diffuse away easily, as final products, from the zeolitic channels. In addition, the channels of HM and HY are wide enough to allow the production and subsequent diffusion of molecules as large as PMB (0.65 nm) and HMB (0.70 nm). This explains why these compounds are formed

as major products in the HM- and HY-catalyzed methanol conversion (11) but are completely absent in the "gasoline" obtained with ZSM-5, which instead includes MN and DMN. The advantage of mesitylene (0.65 nm) as solvent in the alkylation of naphthalene and 2-MN, and of 1-MN (0.62 nm) as solvent in the alkylation of 2-MN is thus attributed to their relatively large size preventing them from easily reaching ZSM-5 cavity sites. They, however, diffuse rapidly and, therefore, readily react in the large channels of HM and HY.

Because of molecular size differences, an effective catalyst for *para*-selective methylation of toluene should not promote the methylation of naphthalene and 2-MN, whereas if a catalyst is active and β -selective in the methylation of naphthalene and 2-MN it would be also active, but non-*para*-selective in the methylation of toluene. Table 7 compares catalysts I-VI and VIII for their activity and selectivity in the alkylation of toluene and naphthalene with methanol. As seen, large (and "coated") crystals give lower toluene conversion with high *para*-selectivity but whenever small crystals are present the conversion is increased and the selectivity is drastically decreased. The drop in conversion is even more pronounced in the case of naphthalene methylation but there seems to be no

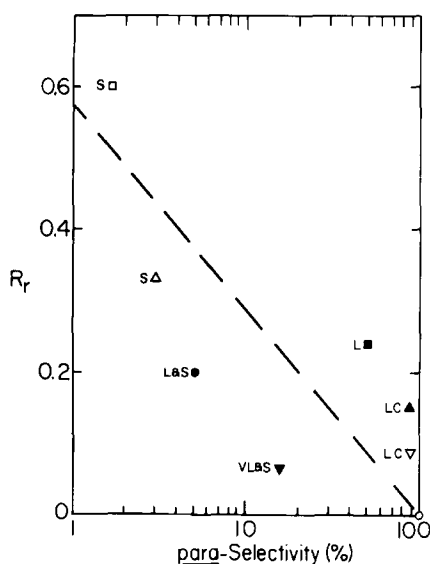


FIG. 5. Correlation between relative rate ratio, R_r , in the alkylation of naphthalene and toluene, and *para*-selectivity. [Point o is based on the assumption that 100% *para*-selectivity should correspond to zero naphthalene conversion. Abbreviations are as described in Table 7 except for LC, indicating large, "coated" crystals].

great effect on the β -selectivity (the drop to 70% is certainly a temperature effect, see Fig. 3; such a temperature effect was not observed in toluene methylation). In Fig. 5, relative naphthalene-to-toluene rate ratios (R_r) based on Table 7, are plotted against and shown to decrease with *para*-selectivity. As seen, small-crystal samples exhibit higher R_r values while large-crystal samples yield smaller values. The results described in Table 7 and Fig. 5 may be rationalized by assuming that in H-ZSM-5 two distinct types of Brønsted acid catalytic sites exist having similar intrinsic nature, one inside the channels, tentatively in the channel intersection cavities (18), the other on the external zeolite surface. The internal site is accessible through 10-rings and therefore exhibits a molecular sieving effect at 0.55 nm which leads to effective *para*-selectivity in the alkylation of toluene. This site operates in all H-ZSM-5-type catalysts. The external site is abundant in III, VI, and VII which have the largest surface area (smallest crystals) but is almost entirely elimi-

nated in I and VIII because these zeolites have large crystals, hence small surface area; furthermore, I and VIII appear to exhibit "coated" crystallites. II appears "uncoated." IV and V have mixtures of large and small crystals in which the large crystals dominate in terms of mass distribution. Thus, II, IV, and V demonstrate intermediate behavior (Table 7). We further speculate that the external Brønsted acid sites are located in "half" channel intersection cavities residing in plane (001) (15); these "half" cavities are characterized by larger-than-10-ring opening hence they can apparently "sieve" molecules up to 0.60 nm. We thus suggest that naphthalene and 2-MN do not practically penetrate the 10-ring channel system of H-ZSM-5 but rather react on catalytic centers located on the zeolite external surface. If such catalytic sites do exist, they can readily explain the high β -selectivity in the alkylation of naphthalene and 2-MN with methanol, as well as the lack of *para*-selectivity in the alkylation of toluene with methanol over small-crystal H-ZSM-5. External surface catalytic activity of ZSM-5 has been previously proposed (6) and a recent article suggests that mesitylene conversion may probe this activity (19). However, external acid sites have not been proposed so far to be shape-selective. Another approach yet experimentally indistinguishable from ours explains shape-selectivity in terms of the average length of the product diffusion pathway (20) assuming that this length is greater in larger or coated crystals. This approach has been recently criticized as not corresponding with the production of *ortho*-rich xylene mixtures over modified ZSM-5 at low temperatures, in an article associating *para*-selectivity with Brønsted acid site concentration (Si-to-Al ratio) of H-ZSM-5 (21). While the latter structural factor and several others (e.g., Al distribution in the crystals, the presence of foreign species in the channels, partial poisoning of external sites, etc.) have not been addressed in the present study, they certainly deserve attention in future related work.

ACKNOWLEDGMENT

This work was supported by the G. M. J. Schmidt Foundation for Pre-industrial Research at the Weizmann Institute (Israel).

REFERENCES

1. Kutz, W. M., and Corson, B. B., *J. Amer. Chem. Soc.* **67**, 1312 (1945).
2. Dodd, J. R., U.S. Patent 4,187,255 (1980).
3. Tso, H. H., Sheu, F. C., and Chen, C. T., *Bull. Inst. Chem. Acad. Sin.* **28**, 71 (1981).
4. Weisz, P. B., *Pure Appl. Chem.* **52**, 2091 (1980).
5. Csicsery, S. M., *Zeolites* **4**, 202 (1984).
6. Kaeding, W. W., Chu, C., Young, L. B., Weinstein, B., and Butter, S. A., *J. Catal.* **67**, 159 (1981).
7. Kaeding, W. W., Young, L. B., and Prapas, A. G., *CHEMTECH* **12**, 556 (1982).
8. Wagner, A. F., in "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd ed., Vol. 21, pp. 585-600. Wiley, New York, 1970.
9. Gaydos, R. M., in "Kirk-Othmer Encyclopedia of Chemical Technology," 3rd ed., Vol. 15, pp. 698-719. Wiley, New York, 1981.
10. Kobayaschi, K., Dogane, I., and Nagao, Y., *Japan. Kokai Tokkyo Koho* 75 0076,054 (1975).
11. Fraenkel, D., Cherniavsky, M., Levitan, R., and Levy, M., unpublished results.
12. Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B., *CHEMTECH* **6**, 86 (1976).
13. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47**, 249 (1977).
14. Eichler, K., and Leupold, E. I., Ger. Offen. DE 3,334,084 (1985).
15. Fraenkel, D., Cherniavsky, M., and Levy, M., in "Proceedings, 8th International Congress on Catalysis," DEHEMA, 1984, IV-545.
16. Argauer, R. J., and Landolt, R. G., U.S. Patent 3,702,886 (1972).
17. Rollmann, L. D., and Valyocsik, E. W., in "Inorganic Syntheses" (Smith L. Holt, Jr., Ed.), Vol. 22, p. 67. Wiley, New York, 1983.
18. Jacobs, P. A., and von Ballmoos, R., *J. Phys. Chem.* **86**, 3050 (1982).
19. Gilson, J. P., and Derouane, E. G., *J. Catal.* **88**, 538 (1984).
20. Wei, J., *J. Catal.* **76**, 433 (1982).
21. Bezouhanova, Cv., Dimitrov, Chr., Nenova, V., Spassov, B., and Lechert, H., *Appl. Catal.* **21**, 149 (1986).