# Transalkylation of naphthalene with mesitylene over H-ZSM-11 zeolite

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The transalkylation reaction between mesitylene and naphthalene has been studied over pentasil zeolites, type H-ZSM-11. The main product was 2-methylnaphthalene. The influence of external and total surface area of the catalysts on catalytic activity and selectivity was investigated. From these observations, it was found that the external surface of zeolites played a key role in the synthesis of 2-methylnaphthalene.

**Keywords:** H-ZSM-11, mesitylene–naphthalene transalkylation, external surface, 2-methylnaphthalene synthesis, vitamin K3

## 1. Introduction

In our previous report [1], mesitylene was chosen as a suitable solvent for the alkylation reaction of naphthalene with methanol over HZSM-11. According to the data obtained in the adsorption studies, the only molecules competing for the same acid sites are mesitylene and methanol. At temperature about 360°C, only 1% w/w of mesitylene was converted into 1,2,4-trimethylbenzene (TMB). Above 400°C, mesitylene is strongly isomerized, especially to the 1,2,4 isomer, and, to some extent, is disproportionated into xylenes and tetramethylbenzenes (TTMB).

At high reaction temperature, mesitylene is not an inert solvent for the reaction and produces methylnaphthalene derivatives in the absence of methanol in the feed [1].

In the course of the catalytic vitamin K cycle, vitamin K is reduced to vitamin KH2 by an enzyme reductase. Vitamin KH2 is then transformed to vitamin K oxide as the carboxylation of glutamate is effected to $\gamma$-carboxyglutamate [2]. In a recent paper Dowd et al. [2] working with 2-methyl-3-phytyl-1,4-naphthoquinone, the blood-clotting vitamin K1, demonstrated that the oxygenation (to form vitamin K oxide) takes place adjacent to the methyl group. Accordingly, this position can be designated the active site of vitamin K1. Taking into account these new results, the synthesis of vitamin K3 (2-methyl-1,4-naphthoquinone) is attracting great interest because it has about three times more antibleeding activity than vitamin K1. 2-methylnaphthalene (2MN) is a raw material for the synthesis of vitamin K3 [3]. In an effort to gain further insight into the process of 2MN synthesis, we report here the results obtained for the transalkylation of naphthalene with mesitylene yielding 2MN as the main product. We also describe the effect of the reaction conditions and the external surface of the catalyst on the mesitylene conversion and on the transalkylation reaction between mesitylene and naphthalene.

## 2. Experimental

Two kinds of H-ZSM-11 zeolite with the same Si/Al ratio (20) but with different external surface were prepared, according to the procedure reported elsewhere [1]. The samples were used to obtain data about the influence of external surface area on the catalytic activity of the catalyst. The proton forms of all catalysts were obtained by ammonium ion exchange using 1 M ammonium chloride solution at 80°C for 40 h followed by 16 h calcination under nitrogen and 10 h under air.

High-purity aromatic hydrocarbons, naphthalene (N) (Aldrich, 99.7%) and mesitylene (Mes) (Aldrich, 99.5%), were employed in the present study. Pure Mes and a mixture of N dissolved in Mes were introduced into the bed through a heat line with a liquid infusion pump at the appropriate flow rate. The N molar fraction was varied in the range 0.1–0.2.

The catalytic tests were carried out using a 45 cm length and 0.7 cm i.d. vertical plug flow quartz microreactor. The reactor was flushed with $N_2$ before introducing the reactants. No change in product distribution was observed after 15 min on line. All samples in the following were taken 15 min or more after establishing steady state of the reaction. Blank experiments, conducted without catalyst and in the range of conditions employed, indicated that uncatalyzed reaction was negligible.

Conversions and product yields were determined by capillary gas chromatography using an AT-1 capillary column (0.54 mm i.d. 30 m length with a film thickness of 2.65 $\mu$m). The conversion of naphthalene or mesitylene is defined as follows:

$$\text{conv.} = \left(1 - \frac{\text{moles of the reactant hydrocarbons in the products}}{\text{moles of the reactant hydrocarbons fed into the reactor}}\right) \times 100, \quad (1)$$

the selectivity of 2MN (S2MN) is:

$$\text{S2MN} = \frac{\text{moles of 2MN species produced}}{\text{moles of (naphthalenics + benzenics) derivatives}} \times 100. \quad (2)$$

## 3. Results and discussion

In order to describe the pathways of the transalkylation reaction of N with Mes over H-ZSM-11 zeolite, we have considered transformations of Mes and a mixture of N and Mes.

### 3.1. Mesitylene conversion

Mesitylene can be transformed by two reaction mechanisms:

(i) By transalkylation generating benzene ring derivatives: benzene (B), toluene (T), xylenes (X), tetramethylbenzene (TTMB), pentamethylbenzene (PMB), hexamethylbenzene (HMB), ethylbenzene (EB), propylbenzene (PB) and butylbenzene (BB).

In this mechanism, the reaction steps are considered as bimolecular steps between two molecules adsorbed on zeolite acid sites or one molecule really adsorbed on zeolite acid sites and another retained in the zeolite by the strong electronic field existing in zeolites [4].

(ii) 1,2,3- and 1,2,4-trimethylbenzene (1,2,3TMB; 1,2,4TMB) formation by a monomolecular isomerization step.

#### 3.1.1. Temperature effect

The effect of the reaction temperature can significantly alter the extent of the various reactions which take place in mesitylene conversion. In figure 1 the yield of the products from mesitylene is plotted as a function of reaction temperature. We used the same space velocity (23 $h^{-1}$) as that employed in the alkylation of naphthalene with methanol in the previous report [1].

As can be seen in figure 1, X are the main reaction products obtained by the bimolecular mechanism in the range of the temperature studied here. In the same way N is not produced by disproportionation of Mes. 1,2,4TMB is the only reaction product detected by monomolecular isomerization and its yield is a function of temperature.

Figure 2 shows the values of the total conversion level for Mes (disproportionation + isomerization) against the conversion by disproportionation only. Under the conditions studied, the disproportionation rate was higher than the isomerization rate and the Mes conversion increases by the above two mechanisms as the reaction temperature increases too.

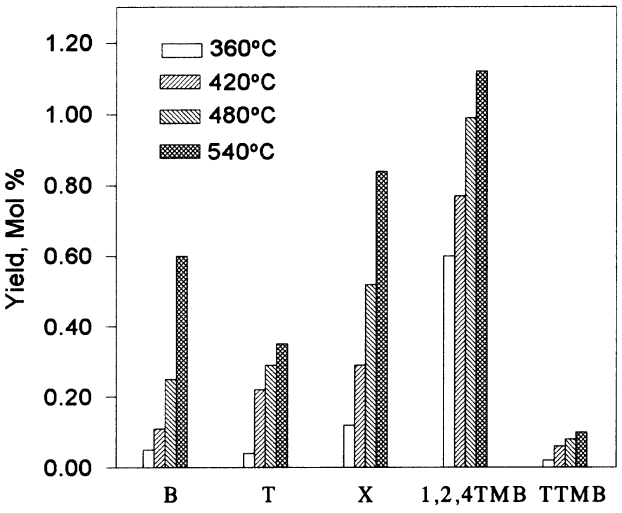


Figure 1. Product distribution for Mes conversion over H-ZSM-11 zeolite at different reaction temperatures and WHSV (Mes) = 23 $h^{-1}$.

#### 3.1.2. Effect of the external surface of the catalyst

Because the zeolite channel diameter in H-ZSM-11 and H-ZSM-5 is smaller than the critical size of Mes (8.4 Å), its interaction is only possible with extra crystalline sites. In the same way, the outer surface of the crystal may play an important role in Mes activation. The effect of the external surface on Mes conversion was studied at 450°C and WHSV = 2.8 $h^{-1}$. Table 1 shows the effect of external surface of H-ZSM-11 and H-ZSM-5 on Mes conversion by isomerization and disproportionation.

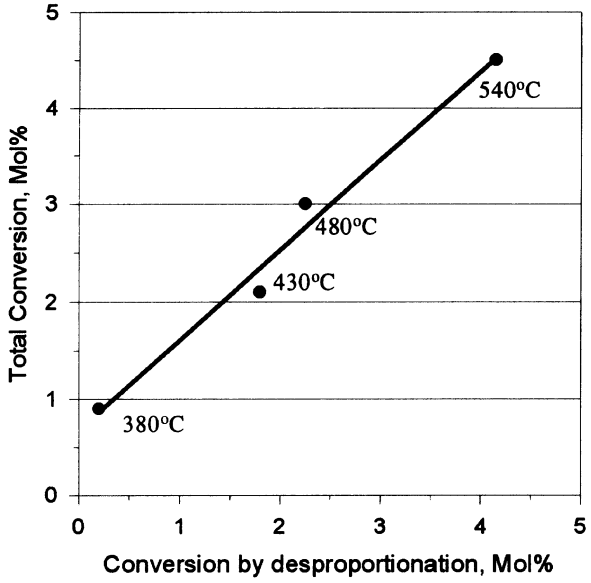


Figure 2. Mes total conversion vs. Mes conversion by disproportionation over H-ZSM-11 zeolite at different temperatures and WHSV (Mes) = 23 $h^{-1}$.

Table 1
Effect of external surface of H-ZSM-11 and H-ZSM-5 on Mes conversion [a]

| Catalyst | Si/Al | | Surface area ($m^2/g$) | | Conversion (%) | |
|---|---|---|---|---|---|---|
| | AA | XPS | total | external [b] | bimol. reaction | monomol. reaction |
| H-ZSM-11 (1) [c] | 20 | 40.5 | 384 | 30 | 4 (33%) | 8 (67%) |
| H-ZSM-11 (2) [d] | 20 | 41 | 415 | 130 | 10 (62%) | 6 (38%) |
| H-ZSM-5 (3) [e] | 17 | 38 | 436 | 32 | 3.8 (32%) | 8.1 (68%) |

[a] Temperature 450°C; WHSV (Mes) = 2.8 $h^{-1}$.
[b] BET, value of uncalcined zeolite containing template ($n$-$Bu_4N^+$; $n$-$Prop_4N^+$).
[c] Silicon source: $SiO_2$, template: $n$-$Bu_4NOH$. Crystallites of 4–5 $\mu$m.
[d] Silicon source: sodium silicate (NWG), template: $n$-$Bu_4NBr$. Average agglomerate particle size 8–9 $\mu$m formed by crystallites of 1–1.5 $\mu$m.
[e] Silicon source: $SiO_2$, template: $n$-$Prop_4NOH$. Crystallites of 4–4.5 $\mu$m.

Taking into account that the bimolecular reaction of disproportionation would demand adjacent acid sites for its catalysis while the monomolecular reaction of isomerization could occur on isolated acid sites, the results obtained with the catalyst with high external surface area (sample 2 in table 1) indicated that the strength of acid sites is not the only parameter that determines their intrinsic activity. The distance between the sites (density) seems to have importance in the case of certain bimolecular reactions. According to Santilli [5], two mechanisms can be proposed for aromatic transalkylation:

(1) The alkyl group (R) on the benzene ring cleaves by acid catalysts. Then $R^+$ adds to another benzene ring.

(2) A dimeric intermediate is formed in which the aromatic rings are bridged by an R group. Subsequent cleavage effects R group transfer from one ring to the other.

If R is a simple alkyl group, pathway 2 would appear to be the lower energy process due to resonance stabilization of the carbonium ion intermediate. The distance between the sites seems to have importance. However, if the intermediate formed in pathway 2 is large relative to the reactants, and its formation may be hindered in small catalyst pores such as in pentasil zeolites, the reaction can proceed via pathway 1. In our case, we work with MES (van der Waals diameter of 0.86 nm) which should render it too bulky for probing intracrystalline catalytic sites. Thus, we suggest that Mes conversion occurs on the external surface of crystallites where the pathway 2 would take place. In this way, this effect is more similar than that shown in metallic catalysts in structure sensitive reactions. According to the data shown in table 1, the Mes conversion occurs on the catalytic sites present on the outer surface of the crystallites; the disproportionation reaction (bimolecular) is a function of external surface and the isomerization reaction is higher on catalysts with lower external surface of HZSM-11 zeolite. Moreover, Mes can be used as a probe molecule to determine the external catalytic activity of the pentasil zeolites [6].

### 3.2. Transalkylation of naphthalene with mesitylene

When N reacts with Mes, three types of reaction pathways are possible: (A) Mes isomerization; (B) Mes disproportionation; (C) N transalkylation with Mes.

#### 3.2.1. Effect of the reaction temperature

Figure 3 shows the effect of the reaction temperature on the transalkylation of naphthalene with mesitylene using H-ZSM-11 zeolite, at the same contact time for mesitylene employed in the Mes reactions without N. The N/(Me + N) was 0.1 and WHSV of N = 2.4 $h^{-1}$. It should be noted that 1,3,5TMB remains unreacted below 360°C (at the temperature chosen for alkylation of naphthalene with methanol in the previous report [1])

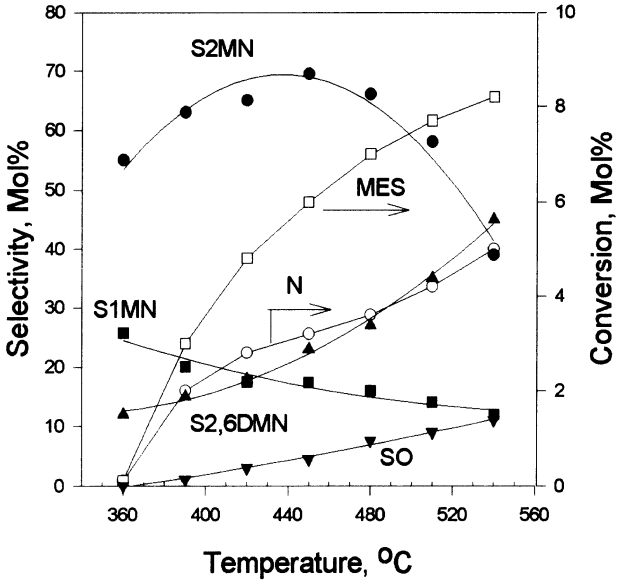


Figure 3. Effect of temperature on Mes conversion, N conversion, and selectivity to 2-methylnaphthalene (S2MN), 1-methylnaphthalene (S1MN), 2,6-dimethylnaphthalene (S2,6DMN) and selectivity to benzene ring derivatives (SO) (excluding 1,2,3- and 1,2,4-trimethylbenzene), at N/(Mes + N) = 0.1 and WHSV (N) = 2.4 and (Mes) = 23 $h^{-1}$.

but, above 400°C, it also produces methylnaphthalene derivatives. N and Mes conversions increase with reaction temperature, Mes conversion being higher than N conversion. Figure 3 shows the 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene selectivities as S2MN, S1MN and S2,6DMN respectively. SO indicates the selectivity to benzenic derivatives (excluding 1,2,3 and 1,2,4TMB). According to the data shown in figure 3, the following aspects can be underlined:

– Reaction temperatures between 380 and 480°C allowed to obtain mono and di-alkylated N derivatives, with high selectivity to 2MN and 2,6DMN.

– At higher temperatures, polyalkylated reaction products derivated from N were detected.

– For benzene ring derivatives, in the whole range of temperature studied, X yields were higher than T and B, increasing the amount of mononuclear aromatic derivatives (excluding 1,2,3 and 1,2,4TMB) with temperature.

### *3.2.2. Effect of the external surface*

According to our previous report [1], the selective synthesis of 2MN by alkylation of N with methanol seems to be consistent with a Rideal type mechanism. The first step in the alkylation reaction of N is the chemisorption of methanol on the Brønsted sites. Methoxonium groups (or a methylcarbenium ion) are formed on the catalyst surface and, according to the TPD analysis [1], N reacts with them impacting, directly from gas phase. The reaction seems to occur on the external surface of the crystallites of the medium pore zeolite. In the same way, we propose that the transalkylation of N with Mes, over H-ZSM-11 at reaction temperatures above 300°C, would be a reaction catalyzed by a single active site.

If our suggestion is correct, catalysts with high external surface area may produce lower yields of naphthalenic derivatives than derivatives obtained by the bimolecular mechanism of disproportionation of Mes. The latter aspect is significantly illustrated by the data shown in figure 4, where the Mes total conversion, Mes conversion by isomerization, Mes conversion by disproportionation and N conversion over two zeolites with different external surface are presented. Thus, the conversion of Mes by isomerization and N conversion (both suggested single-site-catalyzed steps) are higher over the sample with low external surface than the bimolecular disproportionation step. However, the global transformation rate of Mes is higher over catalysts with higher external surface. There has been controversy about the mechanism of alkylation of aromatics with alcohol and light olefins and transalkylation of aromatic over acidic MFI or MEL zeolites [5,7–12]. We could, however, exclude the possibility that the pore size of zeolites in combination with the sizes of the aromatic molecule and of the alkylating agent mainly determine the alkylation mechanism, as Smirniotis [11] recently

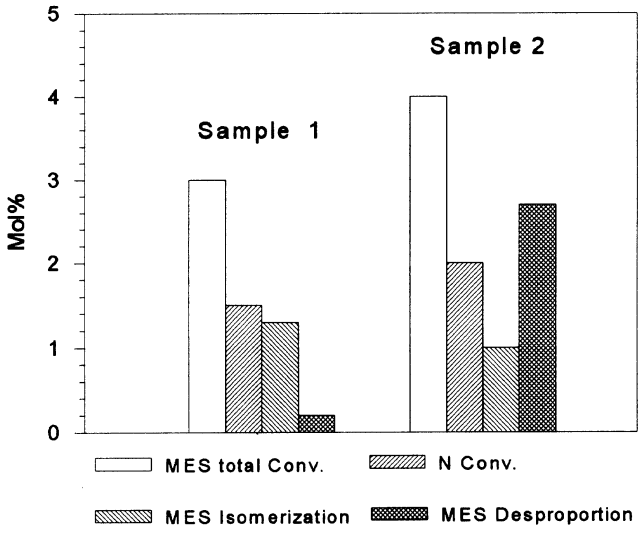


Figure 4. Mes total conversion, Mes conversion by isomerization, Mes conversion by disproportionation and N conversion over H-ZSM-11 zeolite, samples 1 and 2 (see table 1) at 450°C and N/(N + Mes) = 0.2.

reported. We consider that the proton affinity of aromatic hydrocarbons, the electrostatic field of the zeolites and the reaction temperature [9] are the most important parameters to determine the reaction mechanism in both aromatic alkylation and aromatic transalkylation reactions, as N with Mes. In a recent paper, Dougherty [13] evidenced that aromatic systems interact strongly with cations. Although many effects are involved, firstly this p orbital–cation interaction can be considered an electrostatic effect, understanding that the electrostatic interaction between aromatic p orbital and cation involves the quadrupole moment of the aromatic (with permanent dipole moment equal to 0). Not only the critical sizes of aromatic derivatives but also their proton affinity (194.7 kcal/mol for N and 200.7 kcal/mol for Mes [1]) are the reasons of different interaction and adsorption energy of aromatic hydrocarbons.

## 4. Conclusions

The disproportionation activity of the H-ZSM-11 zeolite with low external crystal surface was 20 times lower than the activity obtained with samples with high external surface. This effect can be explained only by an influence of the Brønsted site density. It was concluded that the bimolecular reaction of disproportionation of Mes over pentasil zeolites, would demand adjacent Brønsted acid sites for its catalysis while the monomolecular reaction of isomerization could occur on isolated acid sites. The rate of bimolecular reactions being dependent on the acid density and that of monomolecular reactions being independent, the ratio of these rates can be used for the characterization of the acid site density. The

transalkylation reaction between N and Mes seems to be consistent with the Rideal type mechanism.

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