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Coke precursor formation and zeolite deactivation: mechanistic insights from hexamethylbenzene conversion

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Abstract

Hexamethylbenzene was reacted over zeolite H-beta at 325 °C. The products were C_1–C_5 hydrocarbons, tetra- and pentamethylbenzene. Deactivation was fast. The main attention has been paid to the material retained in the catalyst as deactivation proceeds. The composition of the retained material was determined by dissolving the catalyst in 15% HF and analyzing a CCl_4 extract. Methylated benzenes, dihydro-trimethylnaphthalenes, and hexamethylnaphthalene were found. Naphthalenes were present even at the shortest times on stream, showing that hexamethylbenzene alone is able to form coke species as otherwise observed in reactions involving methylbenzenes, methanol, or olefins. Additional experiments involving [^{13}C]methanol and naphthalene derivatives (either formed in situ or fed separately) gave new insight into the early steps of coke formation. The lowest naphthalene derivative, dihydro-trimethylnaphthalene, is formed from the heptamethylbenzenium ion by a molecular rearrangement and hydrogen transfers. The higher naphthalene derivatives are all formed from dihydro-trimethylnaphthalene by subsequent methylations and hydrogen transfers. Primary alkenes act as hydrogen acceptors. It appears that the main route for deactivation in acid systems where hexamethylbenzene formation takes place is understood.

Keywords: Hexamethylbenzene; Heptamethylbenzenium cation; Dihydro-naphthalene; Hexamethylnaphthalene; Paring reaction; Coke; Beta zeolite; Hydrocarbon pool; Methanol-to-hydrocarbons; MTH

1. Introduction

More than 40 years ago Sullivan et al. described the conversion of hexamethylbenzene (hexaMB) over a nickel sulfide on silica-alumina catalyst and over neat silica-alumina [1]. The reactions were carried out at about 350 °C. Over the nickel sulfide catalysts the reactions were carried out at a quite high hydrogen pressure. Over the silica-alumina catalyst nitrogen was used as carrier gas. HexaMB partial pressure was well above 5 bar. The reaction products over silica-alumina were aliphatics, predominantly isobutane, propane, and isopentane, and lower methylbenzenes. Over the nickel sulfide on silica-alumina catalyst there was also a sizable naphthene formation. The reaction did not give any significant ring rupture, and due to the apparent paring (peeling) of methyl groups from hexaMB, the reaction was named the “paring reaction.” A relatively detailed carbenium ion mechanism involving 5–6 ring shifts and growing side chains was proposed. The aliphatic products were assumed to be formed by breaking the alkyl side chain bonds to the benzene ring.

In isolation, the paring reaction is of limited practical value. However, more generally this reaction has implications on the fundamental mechanistic understanding of product formation and coke formation during arene methylations as well as methanol and olefin reactions in zeolites. Our primary goal was to obtain a deeper understanding of the reactions leading to zeolite deactivation, i.e., ring closure for extension of the aromatic system and hydrogen transfer reactions. The results did, however, also give interesting results relevant to the methanol-to-hydrocarbon (MTH) reaction mechanism.

Since the discovery nearly 30 years ago that methanol reacts over protonated zeolites to give a mixture of hydrocarbons and water, a large amount of work has been carried out to obtain an understanding of the reaction mechanism involved [2,3]. Initially, attention centered on how two or more C_1 entities (e.g., methanol, dimethyl ether, trimethyloxonium ions) could react so that C–C bonds are formed

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[3,4]. During the past 15 years or so increasing evidence has, however, appeared that the reaction actually mainly proceeds by a mechanism where there is a pool of adsorbed hydrocarbons (initially not further specified) that is all the time adding methanol and splitting off ethene, propene, and possibly even higher homologues [5–7]. During the past few years it has become clear that methylbenzenes may play a central role in the MTH reaction and actually be the essential part of the catalytic cycle [2–14]. We also suspected that they may be an essential factor in the coking reactions leading to catalyst deactivation, and we therefore found it of importance to study the reactivity of hexamethylbenzene in a wide-pore zeolite like beta zeolite.

Sassi et al. very recently published an extensive study on the hexaMB reactions in beta zeolite [14]. In their case, however, the primary goal was to throw further light on the MTH reaction mechanism. The line of attack on the problems and the experimental conditions employed were very different from those employed in the work reported here. The two works are complementary. Sassi et al. concentrated their work on analysis of the gas-phase products in the effluent at very short times on stream. The influence of Si/Al ratio, reaction temperature, reactivities of various methylbenzenes, etc., were studied, as were experiments where [^{13}C]methanol and alkylbenzenes were coreacted. In contrast to this line of attack, we concentrated on the confined hydrocarbons formed during the reaction, and less attention has been paid to a detailed analysis of the effluent products and the MTH reaction mechanism.

In order to slow down the reactions we chose to work at 325 °C. Sassi et al. worked mostly at 450 °C, but also at 550 °C. The most prominent feature we observed when hexaMB was reacted over H-beta was a rapid buildup of naphthalene derivatives inside the catalyst framework. These naphthalene derivatives are dominated by a hexamethylnaphthalene (hexaMN). Already after 10–20 min on stream, when the amount of hexaMB that has reached the catalyst is only 10–20% w/w, the amount of hexaMN was larger than pentamethylbenzene (pentaMB), the second most prominent constituent. HexaMN is formed from dihydro-trimethylnaphthalene by methylations and hydrogen transfers. Dihydro-trimethylnaphthalene (dihydro-triMN) is the lowest observed naphthalene derivative and is formed from methylated hexaMB (the heptamethylbenzenium ion) by a molecular rearrangement and hydrogen transfers.

If the hexaMB feed is stopped and the catalyst flushed with carrier gas, hydrocarbon formation (C_1–C_5) goes on for several minutes. The likely source for this hydrocarbon formation, after the first minute or so, is hexaMN. The easy formation of naphthalene derivatives inside zeolite beta may therefore account for parts of the formation of small hydrocarbons. At the same time, the easy formation of condensed benzene rings may explain why deactivation takes place so readily in beta zeolite.

2. Experimental

2.1. Catalyst

A commercially available H-beta (Si/Al = 12) from P.Q. Zeolites B.V. was used in this study. Characterization data of the catalyst are given in Ref. [15].

2.2. Catalytic testing

The catalytic reactions were carried out in a fixed bed Pyrex glass microreactor with internal diameter 3 mm. The catalyst was pressed to tablets that were gently crushed and sieved to obtain particles with sizes in the range 0.25 to 0.42 mm. The experiments were carried out at 325 °C using 40 mg catalyst. The temperature was measured using a thermocouple inserted in the reactor to the bottom of the catalyst bed.

HexaMB (Fluka puriss, mp 164–166 °C, bp 264 °C) and naphthalene (mp 80 °C, bp 218 °C) were both fed by passing nitrogen carrier gas through a heated evaporator with solid hexaMB or naphthalene, and further through a heated line to the reactor. The feed evaporator was kept at 63 and 100 °C for naphthalene and hexaMB, respectively, giving partial pressures of 3 mbar in both cases. The carrier gas flow was maintained throughout at 22 mL/min (STP), giving feed rates (WHSV) of 0.4 h^{-1} (naphthalene) and 0.6 h^{-1} (hexaMB). [^{13}C]Methanol (99% ^{13}C, Cambridge Isotope Laboratories) and naphthalene were coreacted by first passing nitrogen through a methanol saturation evaporator kept at 0 °C, and then the effluent was mixed with another nitrogen stream to give a methanol partial pressure of 20 mbar (i.e., WHSV = 0.9 h^{-1}). The gas mixture was then passed through the naphthalene evaporator. The gas streams were controlled by using calibrated Porter F150 Ball Float flowmeters.

Prior to the start of an experiment, the reactor temperature was set to 325 °C, while the catalyst was flushed with carrier gas. The experiment was started by switching the carrier gas to pass through the evaporator. Gas chromatographic analysis of the reactor effluent was carried out at intervals. At a predetermined time, 5 min to 4 h, the reactor was removed from the oven and the catalyst quickly cooled to room temperature by transferring it to a small glass vessel. Alternatively, the hexaMB feed was stopped by bypassing the evaporator and flushing the catalyst with carrier gas for a set time at the reaction temperature before removal of the reactor and cooling of the catalyst.

The method for calculating the isotopic distributions of the products in experiments where [^{13}C]methanol was involved has been described previously [5,8].

2.3. Analysis of retained material

After being removed from the reactor and cooled to room temperature, a part of the catalyst (15 mg) was transferred to a screw-cap Teflon vessel and dissolved in 0.5 mL 15% HF. Acid treatment for 15 minutes was sufficient to dissolve the catalyst. After having dissolved the catalyst, NaOH solution was added to neutralize the acid and the resulting solution was treated with 0.5 mL CCl_4 (Fluka puriss) to extract the liberated organic molecules from the water phase. The organic phase and the water phase were separated and the CCl_4 solution was analyzed by gas chromatography.

The dissolution procedure does not cause structural transformation of the hydrocarbons as shown by tests carried out with *p*-xylene, 1-octene, and hexaMB impregnated on quartz powder. After going through the same dissolving and extracting procedure (except for a marked increase in HF treatment time from 15 min to 3 and 24 h), no change of the impregnated hydrocarbons could be observed. The technique of dissolving the zeolite crystals in hydrofluoric acid to recover confined constituents by extraction was introduced by Guisnet and co-workers [16].

2.3.1. *Amount of retained material*

Temperature-programmed oxidation (TPO) was employed to quantify the thermally stable coke formed in the zeolite after different reaction times. Twenty milligrams of the spent catalyst was transferred to a quartz microreactor (i.d. 10 mm) in a temperature-program-controlled furnace. The catalyst was heated from room temperature to 700 °C at a linear heating rate of 10 °C/min in a flow of Ar (24 mL/min) and O_2 (2.9 mL/min). The signals $m/z = 40$ and 44, representing Ar and CO_2, respectively, were continuously monitored by an on-line quadrupole MS (Pfeiffer Vacuum OmniStar GSD 300 O, EI 60 eV). In addition, the most prominent methylbenzene signals were monitored to check for compounds desorbing/decomposing before oxidation to CO_2 took place. A 9:1 gas mixture of Ar and CO_2 was used for calibration. The CO_2 flow was plotted vs time in the experiments, and the total amount of CO_2 evolved during the coke oxidation was determined from the areas under these curves.

2.4. *Gas chromatography*

The reactor effluent was analyzed by on-line (heated line) gas chromatography (Carlo Erba, GC6000-Vega series 2, with FID) with a Supelco SPB-5 column (60 m, 0.53-mm i.d., stationary phase thickness 5 µm), applying temperature programming (15 °C/min) from 50 (6 min at the initial temperature) to 260 °C (15 min at the final temperature). In the methanol/naphthalene experiment, the final temperature was kept for 25 min to allow methylnaphthalenes to be eluted. To obtain a complete separation of the light products with respect to alkanes and alkenes, a PLOT-Al_2O_3 column (50 m, 0.53-mm i.d., stationary phase thickness 10 µm) was also used.

The analysis of the organic extract was carried out by GC-MS (Hewlett-Packard HP 6890 with MSD 5973, EI 70 eV), using a HP-5MS column (30 m, 0.25-mm i.d., (5%-phenyl)-methylpolysiloxane, stationary phase thickness 0.25 µm). The following temperature programming was applied: 10 °C/min from 50 (1 min at the initial temperature) to 300 °C (5 min at the final temperature). Injected volume was 1 µL, using an injector split ratio 1:30. The CCl_4 contains a small amount of hexachloroethane that has been used as internal standard. In cases where the NIST98 MS library could not provide clear identifications, high-resolution MS (Micromass Prospec, EI 70 eV) was applied, so that the correct atomic composition could be known.

3. Results

The preceding investigations of the gas-phase products that are formed when hexaMB is passed over an acidic catalyst were carried out under conditions which were rather different from our conditions [1,14]. Despite this, the product spectra in the effluent are broadly speaking similar, but there are also significant differences. We paid particular attention to catalyst deactivation behavior. Simultaneously with monitoring the compounds in the effluent, we studied the compounds that are formed and retained within the zeolite crystals, due to adsorption or confinement. The effect of stopping the feed after some time on stream and then flushing the catalyst with carrier gas was investigated. Changes taking place in the effluent were coupled to the simultaneous change in the compounds confined within the zeolite crystals.

3.1. *HexaMB over H-beta*: *gas-phase products and time on stream*

At short reaction times, (5–10 min) the conversion of hexaMB was around 85%. Chromatogram details of the effluent after 10 min on stream are shown in Fig. 1. In the elution time interval (6.6–19 min) that is not shown, only insignificant peaks were observed. The two chromatograms where 1 and 2 min flushing time was applied are discussed below. Tetramethylbenzene (tetraMB) and pentaMB are the only product polymethylbenzenes of significant concentrations. They constitute 27 and 60 C% of the products, respectively. The distribution of the other products is ethene 2.5 C%, propene/propane 3.6 C%, isobutane 5.4 C%, and 2-methylbutane 1.5 C%. There are no butenes or pentenes in the effluent at this feed rate, but in experiments at 10 times higher feed rates, C_4 and C_5 alkenes appeared.

The catalyst system deactivates rapidly. This is shown in Fig. 2 where the evolution of the effluent composition from TOS = 10 min to TOS = 4 h is displayed. Separate experiments using a PLOT-Al_2O_3 column where propene and propane are well separated showed that the ratio propane:propene that was about 3:2 initially fell to 2:3 in the deactivated catalyst. Although the catalyst is strongly

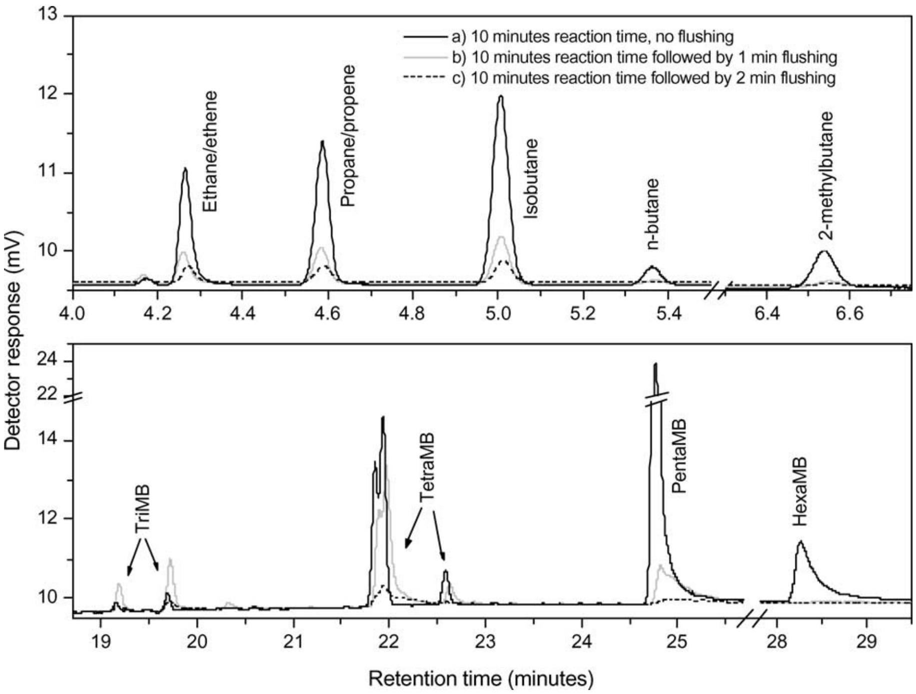


Fig. 1. Chromatogram details (GC-FID) of the effluent after 10 min of hexaMB feeding followed by: (a) no flushing, (b) 1 min flushing, and (c) 2 min flushing. Reactor temperature 325 °C. HexaMB pressure, 3 mbar; WHSV = 0.6 h^{-1}.

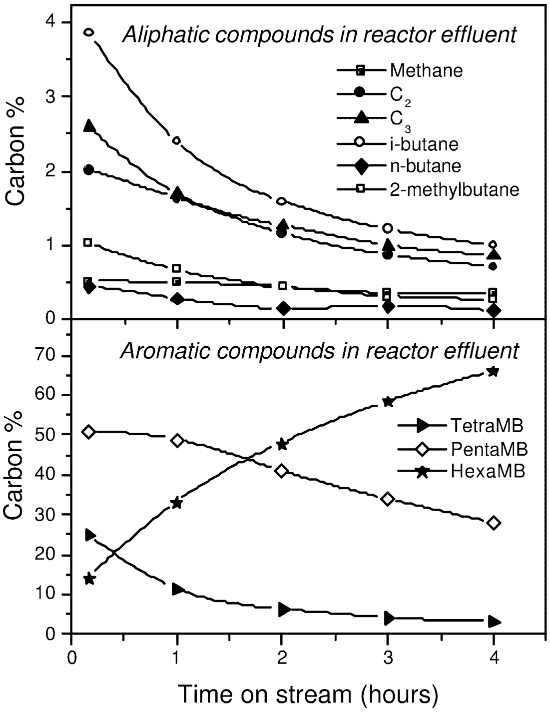


Fig. 2. Evolution of the effluent composition with time on stream when hexaMB was reacted over H-beta at 325 °C. HexaMB pressure, 3 mbar; WHSV = 0.6 h^{-1}.

deactivated after 4 h on stream, the amount of hexaMB that has reached the catalyst is only 2.4 g/g catalyst, and the amount of hexaMB that has reacted and given products is only 1.3 g/g.

3.2. HexaMB over H-beta: retained material and time on stream

Figs. 3a–f show the gas chromatograms of the CCl_4 extract for different reaction times, from 5 min to 4 h. The chromatograms were recorded for 31 min (the last 5 min with column temperature 300 °C), but no detections were made after 19 min so only the segments from 5.5 to 20 min are shown. The sensitivity scale is the same for all chromatograms except for the 4-h sample, which is shown at higher sensitivity (Fig. 3f). The retention time segments 13.5–18 min, where the peaks are small, are shown as insets with increased sensitivity.

The gas chromatograms display surprisingly few compounds; only 5–6 compounds prevail. The first two significant peaks (about 8-min retention time) represent two tetraMB isomers, durene and isodurene. The other methylbenzenes, pentaMB and hexaMB, are eluted at 10.4 and 12.7 min, respectively. As was also the case for the effluent products, pentaMB dominates among the retained polymethylbenzenes. Methylbenzenes were the only alkylbenzenes detected.

The compounds succeeding hexaMB are dihydro-trimethylnaphthalenes and are eluted at 13.5–14 min. The NIST database consistently refers to them as 1,2-dihydronaphthalenes, but the positions of the methyl groups are unclear.

The rather weak signals between 14.5 and 16 min represent dihydro-tetramethylnaphthalenes (dihydro-tetraMN). The peaks eluted at 17–17.5 and at 19 min were not clearly recognized by the NIST library, but were suggested to be compounds containing an oxygen atom. High-resolution MS showed, however, unequivocally that they have compositions $C_{15}H_{18}$ and $C_{16}H_{20}$; i.e., they are hydrocarbons corresponding to pentamethylnaphthalene (pentaMN) and hexamethylnaphthalene. Strictly speaking, one or more of the alkyl substituents might be alkyl groups other than methyl, but we consider this almost certainly not to be the case, because the same compounds are detected when methanol alone or methanol and naphthalene are coreacted over beta zeolite, and compounds with non-methyl alkyl substituents are not observed. In addition, the $C_{15}H_{18}$ and $C_{16}H_{20}$ compounds show fragmentations analogous to those of the lower methylnaphthalenes, i.e., M-15 is the most prominent loss. The positions of the methyl substituents are, however, unknown.

It was shown in Fig. 2 that there is a pronounced deactivation of the catalyst after a rather short time on stream. Looking at Fig. 3 it is clear that the CCl_4 extracts

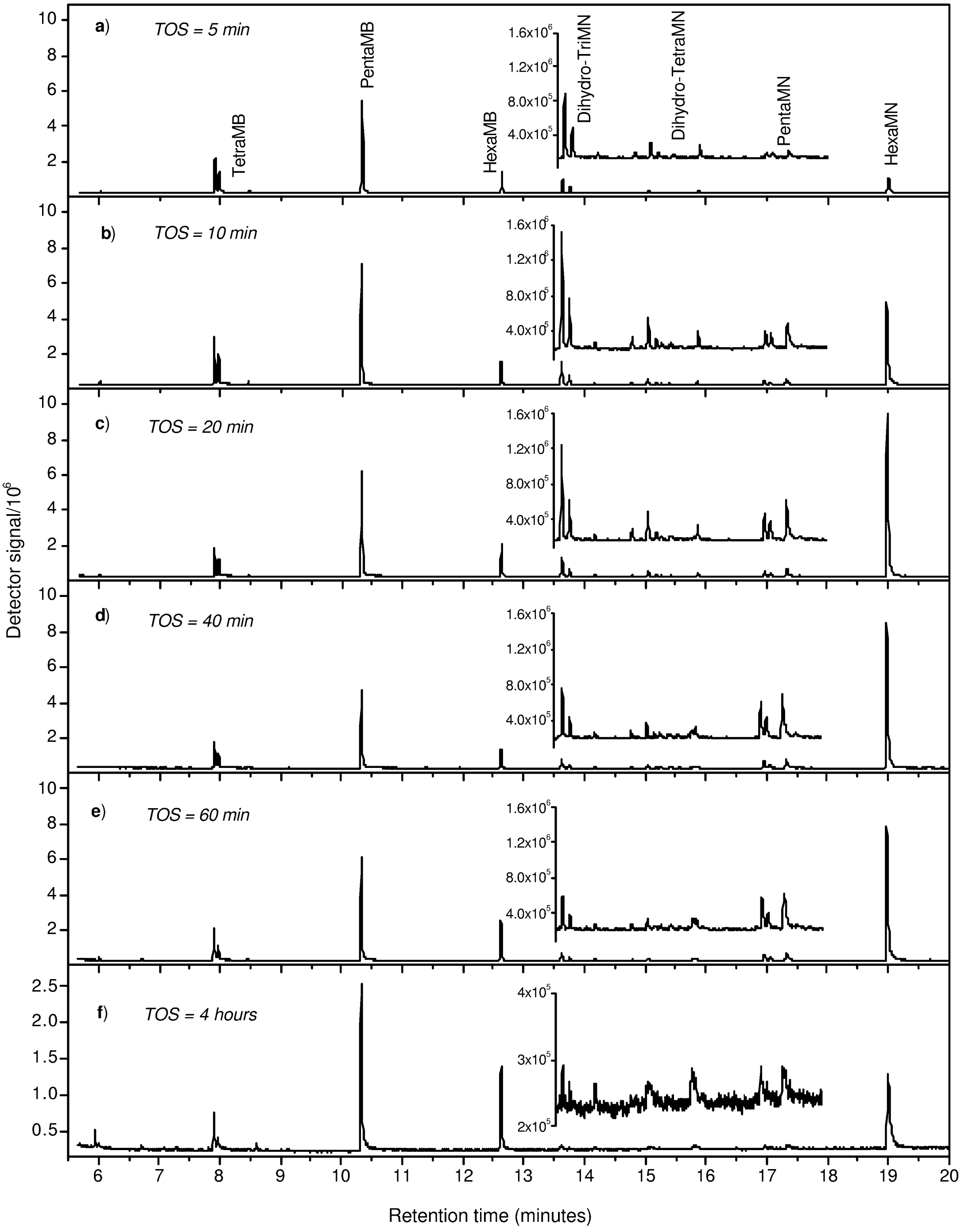


Fig. 3. Chromatogram details (GC-MS) of the CCl_4 extract of H-beta dissolved in HF. Prior to dissolution the catalyst was exposed to hexaMB at 325 °C for: (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 60 min, and (f) 4 h (note the expanded scale). HexaMB pressure, 3 mbar; WHSV $= 0.6\ h^{-1}$.

Table 1
Total amount of thermally stable coke in H-beta after exposure to hexaMB[a] at 325 °C

Time on stream (min)	10	40	60	240
Carbon content (wt%)	0.7	1.0	1.1	2.1

[a] HexaMB pressure, 3 mbar; WHSV = 0.6 h^{-1}.

continue to be dominated by the same compounds during the deactivation process, although quite important changes in relative and absolute amounts are observed.

The most conspicuous feature appears to be the large amount of hexaMN that is formed. After 20 min on stream, it constitutes about 50% of all retained material. However, with further increasing time on stream the amount levels off and starts to decrease, absolutely as well as relative to pentaMB and hexaMB. This effect is clearly seen at TOS = 4 h, where pentaMB is again the most prominent compound. HexaMB is also becoming a major component. It should, however, be noted that the sum of all species that are extracted with CCl_4 upon dissolution of the zeolite, and that can be eluted from a GC column, decreases markedly after 20–40 min on stream.

It appeared unlikely, however, that the amount of retained/confined material actually decreases with increasing time on stream. The color of the used catalyst gets gradually deeper. Previous laboratory experience with the beta zeolite in the MTH reaction, and in alkene reactions, has shown that formation of insoluble material takes place rather rapidly as catalyst deactivation proceeds. The total amount of thermally stable coke was therefore estimated by measuring the amount of CO_2 formed in a TPO apparatus. As shown in Table 1, the results demonstrate that the total amount of thermally stable coke does indeed increase with time. There is evidently formation of material that is not extracted with CCl_4, or not eluted from the GC column.

It is also noteworthy that dihydro-triMN initially is a prominent product. The amount, however, declines already after 10–20 min on stream, and although initially being a major product, it is insignificant after 4 h.

3.3. *HexaMB over H-beta: the stability of the retained material*

In order to obtain information on the stability of the confined hydrocarbons, experiments were carried out where the feed was stopped after 10 minutes, and the catalyst flushed with nitrogen carrier gas. The evolution with flushing time of the effluent composition as well as composition of the material retained in the catalyst were determined.

3.3.1. *Gas-phase products and catalyst flushing*

Effluent analyses were carried out after 1, 2, and 5 min of flushing (the 10-s delay in the transfer line is taken into account). The gas chromatograms in Fig. 1 display the effect of flushing on the effluent. Note the axis breaks. After 1 min of flushing, Fig. 1 (and integrated peak areas) shows a reduction in aliphatic products by 70–75%. After 2 min of flushing, these products were reduced by more than 90%. The internal distribution of the aliphatic products appeared essentially unchanged.

The picture is, however, different for the effluent aromatics and a considerable change in their relative amounts was observed. This is clearly borne out by Fig. 1. HexaMB disappears completely from the effluent and the concentration of pentaMB is reduced by more than 90% after 1 min of flushing while tetraMB is only reduced by 10%. The amount of triMB actually increases by a factor of about 3. After 2 min, the aromatics are barely detectable. After 5 min of flushing (not shown), light products were still detectable in the effluent, but the polymethylbenzenes had vanished.

3.3.2. *Retained material and catalyst flushing*

The effect on the hydrocarbon deposits formed during 10 min reaction time when the catalyst is subsequently flushed with carrier gas is shown in Figs. 4a–e. The figure presents GC-MS total ion chromatograms of the CCl_4 extract obtained after (a) no flushing, (b) 2 min flushing, (c) 3 min flushing, (d) 5 min flushing, and (e) 10 min flushing. Already after 2 min, hexaMB can no longer be discerned in the total ion chromatogram, but an ion chromatogram of the 162 peak shows that, though severely reduced, about 1% of the original amount of hexaMB is still present. Also pentaMB is strongly reduced, but 2% remains. TetraMB is much less reduced by the flushing; 13% remains. The amount of triMB is even less reduced; 65% remains. The dihydro-triMN peaks at 13.75 min retention time are essentially unchanged. HexaMN displays a medium instability; 14% remains after 2 min.

Increasing the flushing time to 3 and 5 min does not introduce striking changes, but it may appear surprising that pentaMB, which during the first 2 min flushing decreased to only 2% of the nonflushed value, only shows a further decrease to 1–1.5% of the original value. Also the amount of tetraMB shows a marked stabilization. Dihydro-triMN still remains essentially unchanged, but hexaMN continues its decline to only 6% of the starting value after 5 min flushing.

Extending the flushing time to 10 min has, however, a pronounced effect. PentaMB disappears (less than one-tenth of the 5-min value), and tetraMB is further reduced to one-third of the preceding value. The naphthalenic compounds, apart from hexaMN, still display only a moderate fall, but hexaMN is still further reduced to about a quarter of the preceding value (at 5 min) to become a nearly negligible species. We believe that the accelerated disappearance of tetra- and pentaMB at this stage is connected with the virtual disappearance of hexaMN.

It should also be pointed out that while the system is being flushed and most retained material is fading away there are compounds whose amount actually increases. TetraMN are barely visible in the unflushed sample, but are easily recognized in the flushed samples. The amount of triMN (at 13.85 min) increases steadily up to 10 min

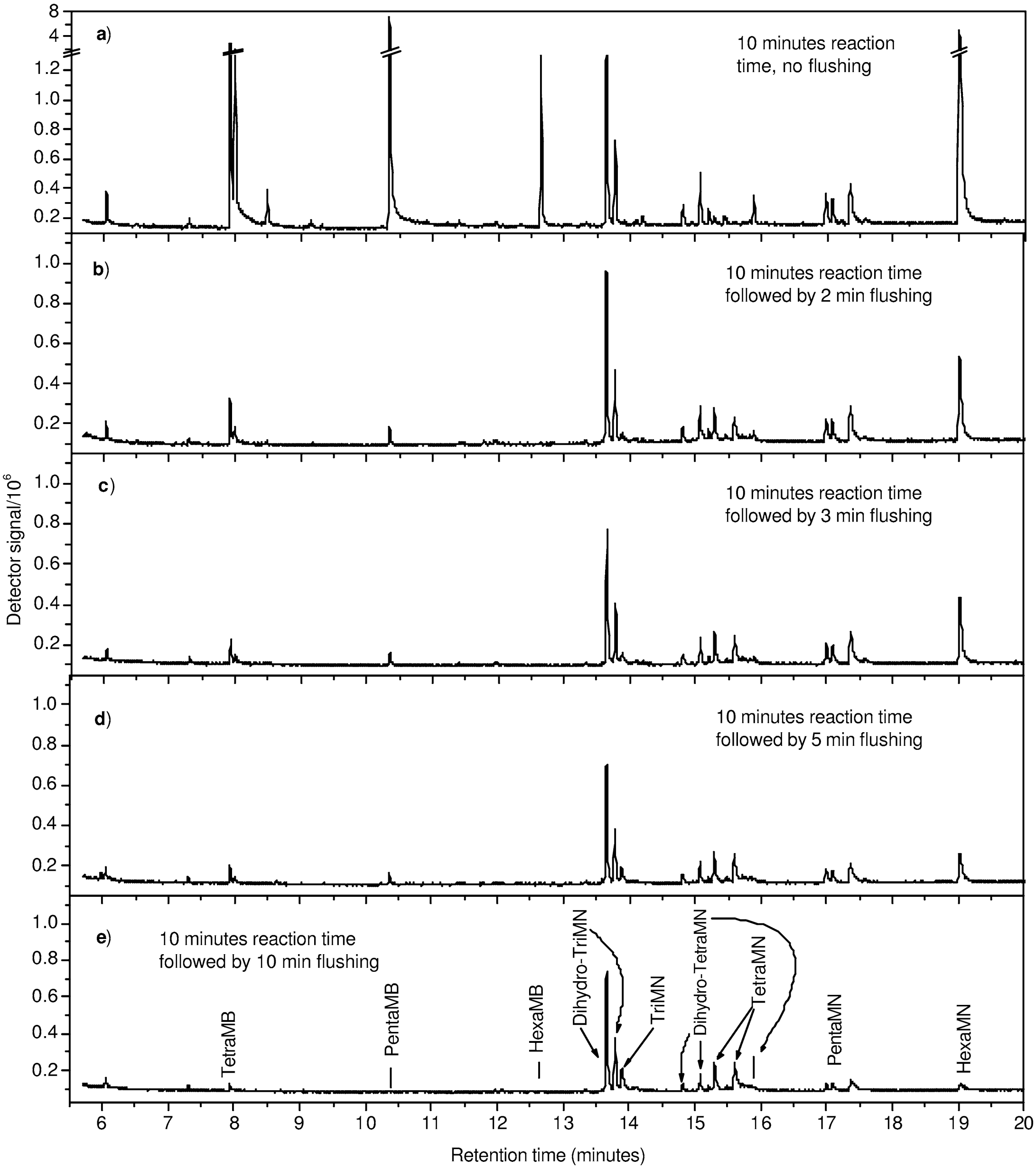


Fig. 4. Chromatogram details (GC-MS) of the CCl_4 extract of H-beta dissolved in HF. Prior to dissolution the catalyst was exposed to hexaMB for 10 min at 325 °C followed by: (a) no flushing, (b) 2 min flushing, (c) 3 min flushing, (d) 5 min flushing, and (e) 10 min flushing. HexaMB pressure, 3 mbar; WHSV = $0.6\ h^{-1}$.

flushing time. After flushing for 10 min, the amount has increased 50-fold. A diMN eluting at 12.1 min (too small to be discernible in the total ion chromatograms—except in Fig. 4e) was shown, by using single ion chromatograms, to increase by a factor 20–25 when the flushing time was increased from zero to 15 min.

3.3.3. Stability of dihydro-naphthalene when methanol is present

The flushing experiments in the previous section showed that dihydro-trimethylnaphthalenes are, in contrast to the other retained molecules, stable under flushing conditions. Experiments were carried out where a methylating agent, in this case [^{13}C]methanol, after flushing under standard conditions for 5 min, was added for 0.5 min—whereupon the reaction was stopped and the catalyst analyzed. They showed that dihydro-naphthalenes are quite reactive in the presence of a methylating agent. After feeding methanol for 0.5 min, the dihydro-triMN peaks were strongly reduced. This is borne out by an overlay of the relevant part of a chromatogram after 5 min flushing and the one obtained in the above experiment. Fig. 5 shows that:

1. Tri- and tetraMN (which were formed during the flushing) disappear.

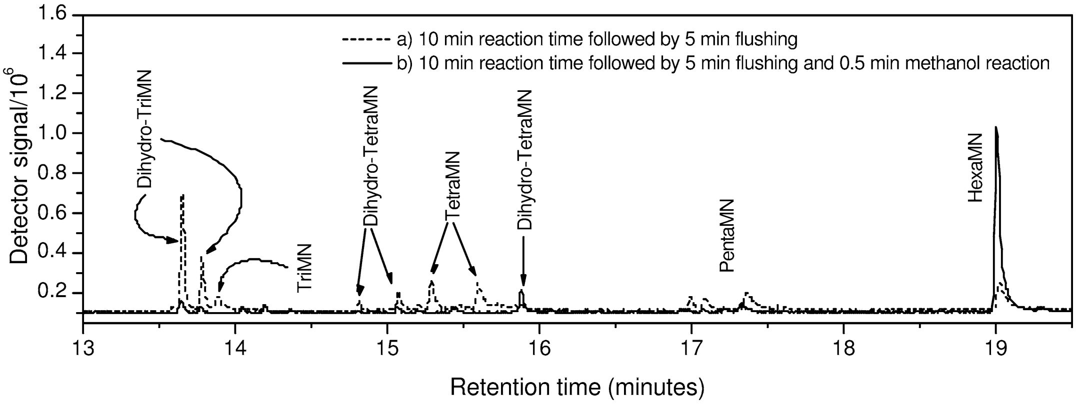


Fig. 5. Chromatogram overlays (GC-MS) of the CCl_4 extracts of H-beta dissolved in HF. Prior to dissolution the catalyst was exposed to hexaMB for 10 min at 325 °C followed by: (a) 5 min flushing and (b) 5 min flushing followed by 0.5 min of methanol feeding. Reactant pressures: methanol, 20 mbar; hexaMB, 3 mbar. Feed rates (WHSV): methanol, 0.9 h^{-1}; hexaMB, 0.6 h^{-1}.

2. The large dihydro-triMN peaks at 13.6 and 13.8 min are strongly reduced, as are also the dihydro-tetraMN around 15-min retention time. A new dihydro-tetraMN at about 15.9 min appears. This compound was present before flushing started (Fig. 4a).
3. HexaMN increases strongly. The increase is in fair agreement with the amount of less methylated compounds that have disappeared during the methanol treatment.

The isotopic composition of the confined molecules was determined after the [^{13}C]methanol addition. The mass spectra show that:

1. The remaining dihydro-triMN at 13.6 and 13.8 min are largely unchanged with respect to [^{13}C]content. Only a small part of the molecules contains ^{13}C atoms beyond the natural ^{13}C content (the two “new” dihydro-triMN peaks around 14.1–14.2 min are richer in ^{13}C).
2. For the most prominent dihydro-tetraMN isomer (15.9 min), the dominating isotopomer contains just one ^{13}C atom (corresponding to methylation of dihydro-triMN by [^{13}C]methanol). This dihydro-tetraMN isomer was not present in the flushed catalyst, but appeared after 0.5 min of methanol addition. The second most common isomer contains only ^{12}C. This compound diminished during flushing.
3. HexaMN displays isotopomers with molecular weights in the range 212–219/220, corresponding to a content of zero to seven or eight ^{13}C. The most common hexaMN isotopomer contains three ^{13}C atoms (corresponding to methylation of dihydro-triMN by three [^{13}C]methanol molecules). (See Figs. A.1–A.3 in Appendix A.)

3.4. *Coreaction of naphthalene and methanol over H-beta*

The large amount of methylated naphthalenes in the retained material and indications that these compounds also take part in the catalytic cycles made it clear that methanol/naphthalene coreaction experiments should be carried out. In addition, methylated naphthalenes are likely to be important factors in catalyst deactivation and coke formation.

3.4.1. *Gas-phase products*

A GC-FID chromatogram of the effluent at TOS = 10 min in the methanol/naphthalene coreaction is shown in Fig. 6. The experiment was performed under the same conditions as the other experiments, using a molar feed ratio methanol:naphthalene of 20:3. Methylnaphthalenes are seen to dominate in the effluent, but there is a fair formation of small aliphatic compounds. Integrated peak areas showed the aliphatic compounds to constitute about 2.5% of the gas-phase compounds. The aliphatic products and their internal distribution are much the same as observed when hexaMB is reacted—with mainly saturated products, except for the C_2 molecules which are dominated by ethene. Fig. 6 also shows that methylbenzenes, although in small amounts, are present in the effluent.

Since it could not be ruled out that the light products and the methylbenzenes were formed entirely from methanol alone, i.e., not involving naphthalene, a parallel experiment using [^{13}C]methanol instead of ordinary [^{12}C]methanol was carried out.

The HP-5MS column is inappropriate for C_2/C_3 analyses and accurate isotopic distributions of these compounds were not obtained. It was, however, clear that the C_3 fraction was not formed entirely from methanol; the molecules were found to contain a significant amount of ^{12}C atoms, about 40%.

For isobutane and isopentane, accurate calculations of isotopic distributions were carried out. Both isobutane and isopentane were isotopically mixed; they contained 67 and 61% ^{13}C, respectively. The remaining 33 and 39% [^{12}C]carbon stem from the reactant naphthalene. The isotopic distributions are shown in Fig. 7. They reveal that in both cases, 90–95% of the molecules contain at least one [^{12}C]carbon.

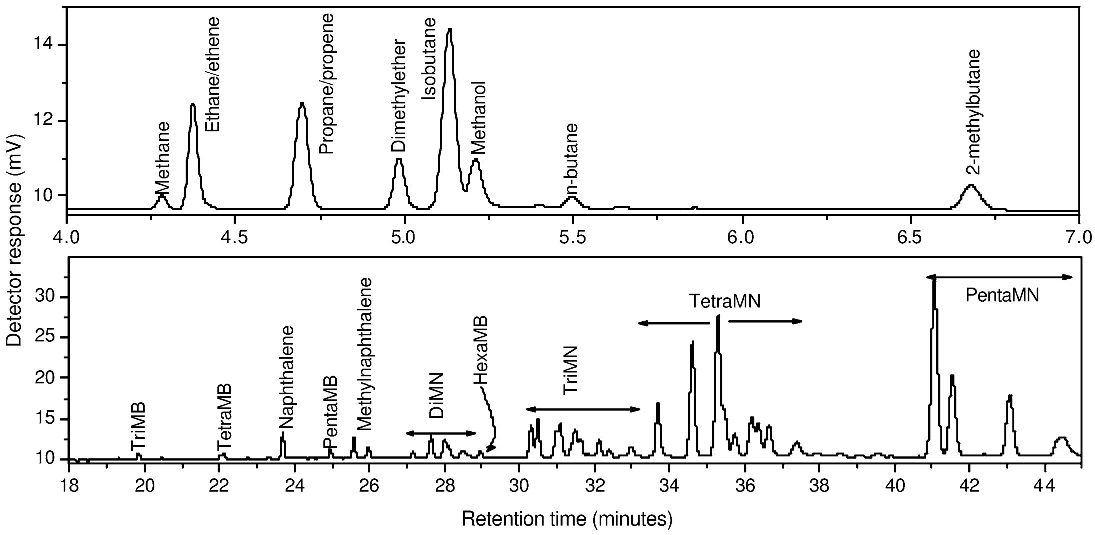


Fig. 6. Chromatogram details (GC-FID) of the effluent when methanol and naphthalene were coreacted over H-beta at 325 °C for 10 min. Reactant pressures: methanol, 20 mbar; naphthalene, 3 mbar. Feed rates (WHSV): methanol, 0.9 h^{-1}; naphthalene, 0.4 h^{-1}.

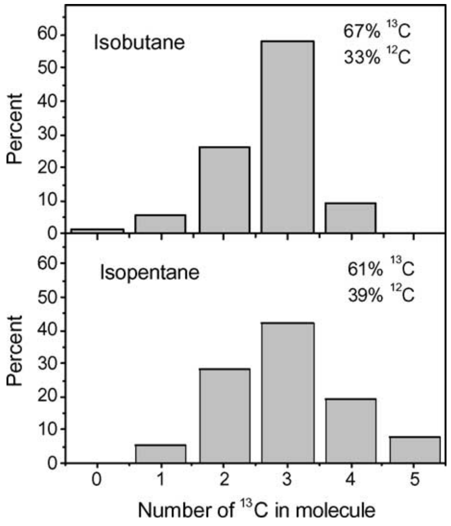


Fig. 7. Isotopic distribution of isobutane and isopentane in the product stream from the coreaction of [^{13}C]methanol and [^{12}C]naphthalene over H-beta at 325 °C. Reactant pressures: methanol, 20 mbar; naphthalene, 3 mbar. Feed rates (WHSV): methanol, 0.9 h^{-1}; naphthalene, 0.4 h^{-1}.

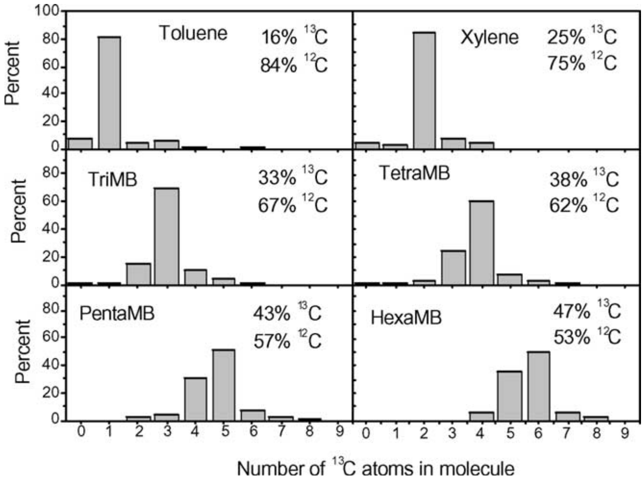


Fig. 8. Isotopic distribution of the methylbenzenes in the product stream from the coreaction of [^{13}C]methanol and [^{12}C]naphthalene over H-beta at 325 °C. Reactant pressures: methanol, 20 mbar; naphthalene, 3 mbar. Feed rates (WHSV): methanol, 0.9 h^{-1}; naphthalene, 0.4 h^{-1}.

The isotopic distributions of the effluent methylbenzenes (C_7–C_{12}) are presented in Fig. 8. An extensive isotopic mixing is seen. The ^{13}C content increases steadily from 16% in toluene to 47% in hexaMB. This means that 84% of the carbon atoms in toluene are ^{12}C and stem from naphthalene, and that 53% of the hexamethylated benzene carbon atoms stem from naphthalene. For more than 80% of the toluene and xylene molecules, the number of ^{13}C atoms corresponds to the number of methyl groups on the benzene ring.

The [^{13}C]methanol experiment did not indicate ^{13}C incorporation into the naphthalene rings. The mass spectra of tri- and tetraMN were, apart from being shifted respectively three and four mass units upward when [^{13}C]methanol was used as methylating agent, essentially undistinguishable from the ones obtained when ordinary methanol was used. The dominating mechanism for methylnaphthalene formation appeared to be neat methylation reactions.

3.4.2. Retained material

Fig. 9 shows a gas chromatogram of the compounds retained in the catalyst after cofeeding methanol/naphthalene for 10 min. An enlargement of the segment from 5.5 to 13 min of retention time is shown as an inset. Methylnaphthalenes dominate strongly, but the enlargement shows that methylbenzenes are detectable among the confined compounds. Isotopic analysis of pentaMB gave an isotopic distribution similar to the one found in the effluent (Fig. 8), but slightly broader. The most common pentaMB species

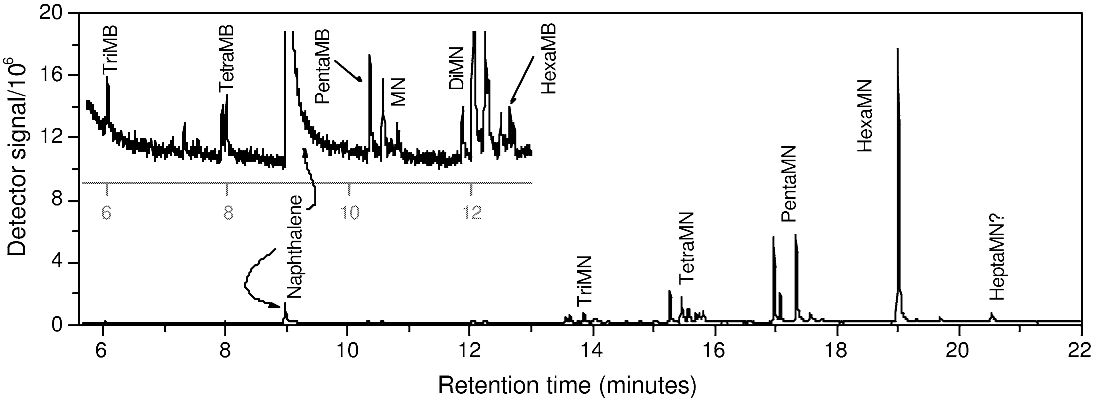


Fig. 9. Chromatogram details (GC-MS) of the CCl_4 extract of H-beta dissolved in HF when methanol and naphthalene were coreacted over H-beta at 325 °C for 10 min. Reactant pressures: methanol, 20 mbar; naphthalene, 3 mbar. Feed rates (WHSV): methanol, 0.9 h^{-1}; naphthalene, 0.4 h^{-1}.

here also consists of five ^{13}C (number of methyl groups) and six ^{12}C.

Similar to the result for tri- and tetraMN in the effluent, hexaMN displayed an isotopic distribution very close to the one expected if there is a clean methylation with little, but not negligible, scrambling. (See Fig. A.4 in Appendix A.)

4. Discussion

The product spectrum in the reactor effluent as given in Figs. 1 and 2 is in broad general agreement with the previous reports by Sullivan et al. [1] and Sassi et al. [14]. They did, however, not investigate catalyst deactivation behavior. A discussion of gas-phase products and catalyst deactivation is best postponed until the properties of the organic material retained in the zeolite cavities have been discussed and is therefore given in Section 4.3.

4.1. Formation of naphthalene derivatives

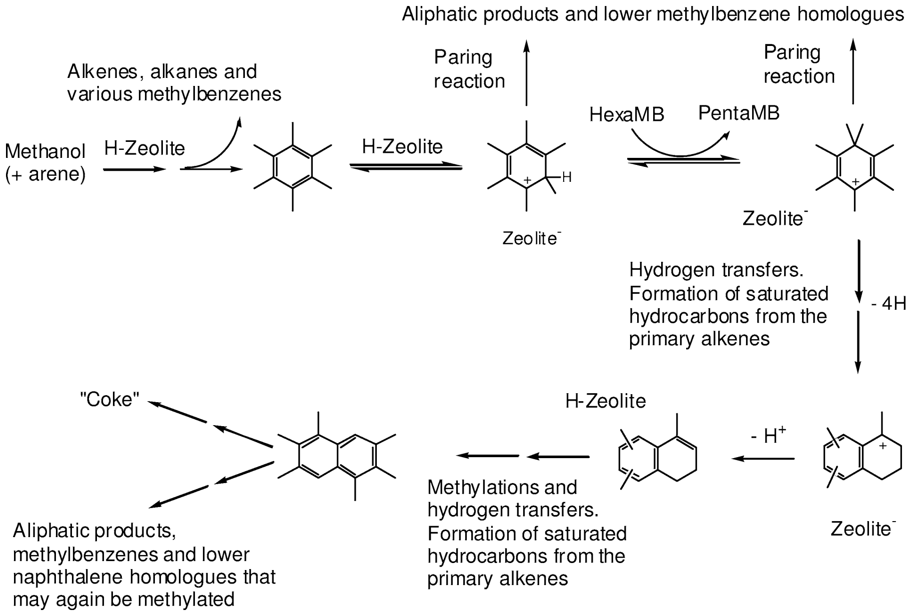
The amount and composition of the organic material retained in the catalyst change substantially with increasing time on stream as shown by Fig. 3. To us the most surprising result is the easy formation of naphthalenic compounds. This extension of the aromatic system is undoubtedly the first step in coke formation and catalyst deactivation. There are two groups of naphthalene derivatives that are quite prominent. Already after 5 min on stream, the products dihydro-triMN (13.75 min) and hexaMN (19 min) are present in essentially the same amount as hexaMB. After 10 min the hexaMN peak is about the same size as pentaMB, and the two constitute 60% of the eluted material.

It is known that hexaMB is a rather basic substance and in a methylating environment can take up a CH_3^+ ion and form a heptamethylbenzenium ion (heptaMB$^+$) [17–19]. Convincing evidence that heptaMB cations also may be formed in protonated zeotype material has recently appeared [14,20]. In the hexaMB reaction system, the initiating step is undoubtedly disproportionation of hexaMB into pentaMB and heptaMB$^+$ ions, i.e., protonated hexaMB transfers a methyl group to another hexaMB molecule. The results obtained here are in excellent accord with an assumption that heptaMB$^+$ may easily form, and bring further evidence that heptaMB$^+$ is an important participant in acid-catalyzed reactions involving methanol, methylbenzenes, and/or alkenes.

Dihydro-triMN has the same number of carbon atoms as a methylated hexaMB, i.e., heptaMB$^+$ or one of its corresponding bases, and might be formed by a molecular rearrangement where four H atoms (and a proton if heptaMB$^+$ is the reacting species) are split off “simultaneously.” Its formation is therefore in excellent accord with the presence of a heptaMB$^+$, and difficult to understand if such a precursor is not present. Speculation on the details of the mechanism for formation of dihydro-triMN is premature. The corresponding tetrahydro-triMN was actively looked for, but was not found. The amount of any tetrahydro-triMN is at most 0.1% of that of dihydro-triMN. It may therefore be concluded that dihydro-triMN is a primary product—not formed from a tetrahydro precursor. Sassi et al. [14] observed trace amounts of tetrahydro-1,4-dimethylnaphtalene and speculated that it could be formed by coupling isopropyl groups ortho to each other. It would then constitute a naphthalene derivative precursor. From our results, it appears unlikely that naphthalene derivatives are formed this way.

It is only initially that dihydro-triMN is an important naphthalene component. The amount increases initially (up to 10 min). From then on, the amount decreases markedly. This shows that it is not a fully inert spectator molecule. It does evidently react further under the prevailing conditions. Fig. 3 suggests that hexaMN is a product from dihydro-triMN (as well as the tetramethylated homologue) since it is the only product gaining in importance as the dihydronaphthalenes decrease.

There are two obvious routes for this reaction sequence. The dihydro-compound might transfer two more H atoms to an acceptor (e.g., an alkene) and form a triMN that in the quite strongly methylating environment might be further methylated to hexaMN. This dehydrogenation-methylation



Scheme 1.

route is, however, highly unlikely because of absence of triMN. Scrutiny of extracted-ion chromatograms allows the conclusion that the ratio triMN/dihydro-triMN is less than 0.002. Also tetraMN is initially absent.

The other possibility is that multiple methylation of dihydro-triMN could take place first and be followed by a dehydrogenation through hydrogen transfer to a hydrogen acceptor. The latter possibility is in accord with the observation that at a short time on stream (5 and 10 min), sizable amounts of dihydro-tri- and -tetraMN are present, but not the corresponding naphthalene(s). The flushing experiment where the reaction was first run for 10 min, where the catalyst was flushed with carrier gas for 5 min and finally exposed to methanol for 0.5 min before being removed from the reactor and analyzed (Fig. 5), is essentially a proof that the reaction proceeds via methylations followed by dehydrogenation. After flushing for 5 min dihydro-triMN (and -tetraMN), which is the only material that is not depleted by the flushing procedure, is shown in Fig. 4d) to constitute by far the larger part of the material left in the catalyst. Fig. 5 shows that by this treatment the dihydro compounds are strongly depleted. (Tri- and tetraMN disappear completely. This is to be expected since they only appeared after prolonged flushing.) By using [^{13}C]methanol and analyzing the isotopic composition of the dihydro-triMN and -tetraMN it was found that the larger part of dihydro-tetraMN had the isotopic composition expected if it is formed by adding one [^{13}C]methyl group from [^{13}C]methanol to [^{12}C]dihydro-triMN. The larger part of the, though markedly reduced, dihydro-triMN is still ^{12}C-atom based. The results are therefore in full agreement with a reaction route where hexaMN is formed by repeated methylations of dihydro-triMN that are followed by dehydrogenation. The correspondence between the decreasing amounts of dihydro-triMN and -tetraMN and the preponderance of hexaMN species with three [^{13}C]methyl groups constitute further evidence that hexaMN is formed via dihydro-triMN. The reactions discussed above are summarized in Scheme 1.

One may wonder why hexaMN is formed in copious amounts while hepta- and octa-MN are not formed. The chromatographic conditions were such that these molecules, and even considerably bigger ones, would be eluted. The experiments where naphthalene and methanol were cofed indicate that heptaMN may possibly form, but only as a very minor product, as shown in Fig. 9. There are several just visible small peaks eluting after hexaMN. They were found to have the right molecular weight, but as there are only two heptaMN isomers, two or more of these peaks are evidently due to other compounds. A likely explanation for the essential absence of heptaMN might be that there are steric constraints leading to a stop at hexaMN (only one isomer is observed). Steric constraints might be due to the confining framework, or they might be caused by methyl groups coming too close together. Quantum chemical calculations carried out in our laboratory indicate that it is harder to methylate hexaMN than the lower methylated homologues, and that hepta- and octaMN are not likely to form under our conditions [21].

Song et al. [11] obtained a selective formation of naphthalene within the chabasite framework in SAPO-34 by converting methanol at 600 °C and thereafter flushing the catalyst with helium carrier gas for 15 min. By cooling the reaction system to 400 °C and restarting methanol feeding, various methylated naphthalenes were obtained, but the upper limit in their case was tetraMN.

As discussed below, hexaMN like hexaMB is likely to be an important part of the catalytic cycle leading to methanol conversion to small alkenes. It should also be pointed out that its formation might be an important step in coke formation and catalyst deactivation. It is clear from Fig. 3 that the amount of hexaMN decreases strongly as the catalyst deactivates. Since it was present in large amounts in the little-deactivated catalyst it is hard to avoid the conclusion that it may react further to products not revealed by our analysis procedure. The increasing amount of coke (Table 1) indicates that this must be the case, as does also the deepening color of the spent catalyst. As a part of a loose speculation, it may be pointed out that if two hexaMN molecules add together by eliminating hydrogen atoms a polymethylated pentacene might result. Such a molecule might be outside the capability of our analysis method. Further condensations would clearly lead to unanalyzable coke.

4.2. *Reactivity of the retained material*

It is now well known that polymethylbenzenes are formed within the SAPO framework when methanol is converted to hydrocarbons (olefins) over a SAPO-34 catalyst. They are by far the major components of the retained material. These molecules are trapped within the framework; they are too big to penetrate the pore openings and escape. If the feeding of methanol is stopped, hexa- and pentaMB disappear quickly, and the amount of tri- and tetraMB appears to increase correspondingly. Simultaneously, ethene and propene leave the catalyst and appear in the effluent stream. Formation of hydrocarbons proceeds via polymethylated benzenes [9,10,12,13].

A similar behavior is observed over beta zeolite using hexaMB as feedstock. One important difference from the SAPO system is that even molecules as big as penta- and hexaMB can diffuse in the beta zeolite pores. As shown in Fig. 1 formation of C_2–C_5 compounds, though declining quite rapidly, go on for some time after cutting the hexaMB feed. The amounts of pentaMB and unconverted hexaMB in the effluent do, however, fall faster. The amounts of tri- and tetraMB display a much slower decline. This observation concurs well with the observation borne out by Fig. 4, where it is shown that essentially all pentaMB and hexaMB disappeared from the catalyst in little more than 1 min. In analogy with the SAPO system one may expect that this rapid disappearance is due to a "cracking" (that probably involves heptaMB$^+$) giving a smaller arene and a C_2–C_5 molecule—as originally proposed by Sullivan et al. [1]. The fast disappearance of penta- and hexaMB means that after the first minute or so of flushing, the C_2–C_5 compounds in the effluent cannot be formed from penta- and hexaMB. The only component present in the beta zeolite framework that disappears/decomposes at a suitable rate after an initial flushing for 1–2 min is hexaMN. It is therefore difficult to avoid the conclusion that hexaMN is splitting off C_2–C_5 compounds. This result is in full agreement with the conclusions reached by Song et al., regarding methylnaphthalenes in SAPO-34 and their assertion that repeated methylation/dealkylation of naphthalenes is part of the catalytic engine in the MTO reaction [11]. It should be noted, however, as is borne out by Fig. 4 that the decline of hexaMN during a flushing experiment is not accompanied by a corresponding increasing amount of less methylated naphthalenes, though their amount does increase. They only appear after a prolonged flushing.

The final proof that hexaMN takes part in catalytic cycles and splits off small aliphatics is given by the methanol/naphthalene coreaction experiments. They showed a fairly normal hydrocarbon formation from methanol. In fact, the results are quite comparable with results obtained when toluene was methylated with methanol over an H-beta catalyst [8]. The larger part of the methanol was consumed by methylation giving not fully methylated arenes. However, all products contained a sizable fraction of atoms from naphthalene (Figs. 6, 7). In addition, the amount of methylbenzenes was negligible, and the aliphatic products bigger than ethene were saturated, so they could not take part in methylation/cracking/remethylation cycles. It may therefore be concluded that naphthalenes are part of a catalytic cycle. The activity of hexaMN for splitting off smaller hydrocarbons cannot easily be directly compared to the corresponding activity of hexaMB, but the fact that it decomposes much slower and that isotopic scrambling also appears to be much slower than has been observed in hexaMB indicate that their catalytic activity is considerably lower. Song et al. arrived at the same conclusion when they investigated methylnaphthalenes in SAPO-34 [11]. In a recent review paper, Guisnet presents several examples from acid catalysis where different coke molecules that are trapped in the zeolite pores can influence the activity and selectivity of the working catalyst [22].

The isotopic analysis of the naphthalene/methanol coreaction products give some hints as to the reaction routes when naphthalene derivatives are fragmentized:

1. The isotopic distributions in the methylbenzenes indicate that hexaMN may split off alkyl groups and retain one intact benzene ring. The fairly large fraction of molecules with one ^{13}C less than the number of methyl groups might be explained by assuming that in some cases a ^{12}C from the broken ring remains attached to the remaining benzene ring.
2. The gas chromatograms displayed in Fig. 6 show that the amount of methylbenzenes that is formed is too small that ring rupture can be the only reaction. In that case there would be more carbon atoms in the methylbenzenes fraction than in the light aliphatics fraction. An equally frequent reaction route may therefore be an analogue to the paring reaction, with ring system retention, as suggested by Sullivan et al. [1] or via methylations of an exocyclic double bond as suggested by Sassi et al. [14]. Scheme 1 summarizes the reactions.

The rapid accumulation of naphthalenic compounds in the zeolite structure shows that systems like H-beta are appropriate for investigating the formation of the condensed aromatic rings, and thus catalyst deactivation and coking. Since hexaMB has been fed alone in this work, a connection between hexaMB and heavier coke species is established. A deeper understanding of the deactivation process is probably a necessity in the development of more deactivation-resistant catalysts.

4.3. *Effluent products and catalyst deactivation*

With knowledge about the reactions that take place inside the beta zeolite pores it is possible to better understand the product spectrum and deactivation behavior. From the results discussed above, it appears that the main route for deactivation in acid systems where hexaMB formation takes place is understood. The catalyst pores must be wide enough to allow formation of heptaMB$^+$ ions and the naphthalenic derivatives. Sassi et al. [14] found that the aliphatics formation was too small to account for the loss of methyl groups in the aromatic molecules. They ascribed this to formation of heptaMB$^+$ ions, which would remain in the vicinity of a zeolite framework anion site, and thus not be free to escape from the zeolite pores. The imbalance between the amount of carbons in aliphatics and the number of methyl groups that have been split off from the aromatic molecules is clearly seen also in our work. It is, however, clear from Fig. 3 that the imbalance is caused by formation of hexaMN and further polyaromatic hydrocarbons (coke). The rapid formation of coke via this reaction route also explains the rapid deactivation. In beta zeolite, it appears that any methylating agent leads to hexaMB formation, and thus rapid deactivation.

The mechanisms for conversion of hexaMB to other methylbenzenes and aliphatics lead to primary formation of alkenes (e.g., C_4H_8) [1,14], yet the aliphatics are to a large extent, or fully, saturated. Sullivan et al. reported only saturated compounds even in the case where the catalyst was silica-alumina, and there was no hydrogen admission. Sassi et al., who worked at a much higher temperature, found about equal amounts of saturated and unsaturated aliphatics. In the present work a very clear excess of paraffinic products was observed, except at very high feed rates. The propensity for alkane formation (caused by hydrogen transfers) is much higher than is observed in the methanol-to-hydrocarbons reaction over, e.g., H-ZSM-5 under corresponding experimental conditions.

The unusually high hydrogen transfer activity can be understood when the reaction where heptaMB$^+$ is transformed into dihydro-triMN is taken into account. This reaction requires the transfer of four H atoms to a suitable hydrogen acceptor—such as an alkene. The uptake of hydrogen by the primary alkenes therefore appears to be mechanistically linked to the formation of naphthalene derivatives.

5. Conclusions

It has been shown that the paring reaction is more complex than hitherto known. Besides having a reaction where hexamethylbenzene is transformed into small aliphatics and less methylated benzenes (in particular pentaMB) there is a quite rapid formation of dihydro-triMN (two isomers dominate), which again are further methylated and split off hydrogen to give hexaMN. Only one of the many possible isomers is observed. HexaMN may also undergo a paring type reaction and produce small aliphatics. During this process there is formation of less methylated naphthalenes, but there are also indications that one of the naphthalene rings may break up, giving an alkylbenzene that is subsequently transformed into a methylbenzene. A more important reaction route may, however, be a self-condensation to much larger aromatic molecules, coke.

In the hexaMB reaction system, the initiating step is undoubtedly disproportionation of hexaMB into pentaMB and heptaMB$^+$ ions. The next step, where dihydro-triMN is formed by a rearrangement from heptaMB$^+$, represents the first step in coke formation and catalyst deactivation. The hydrogen transfers, where saturated hydrocarbons are formed from primary alkenes, appear to be mechanistically linked to the formation of dihydro-triMN and higher naphthalene derivatives from hexaMB. The above reactions explain the observation that the aromatic product in the paring reaction is dominated by pentaMB, and they also explain the imbalance between the amount of carbons in aliphatics and the number of methyl groups that have been split off from the aromatic molecules.

In any methylating environment inside an acidic zeotype material there is a tendency for forming hexaMB, provided the pore system is wide enough, and thus via naphthalenes build up polyaromatic coke. This explains the rapid deactivation of large pore zeolites in the MTH reaction, or in arene methylation reactions.

The reactions that take place in a catalytic system like zeolite H-beta under methylating conditions are summarized in Scheme 1.

Acknowledgment

M.B. thanks the VISTA program of Statoil for financial support.

Appendix A

See Figs. A.1–A4.

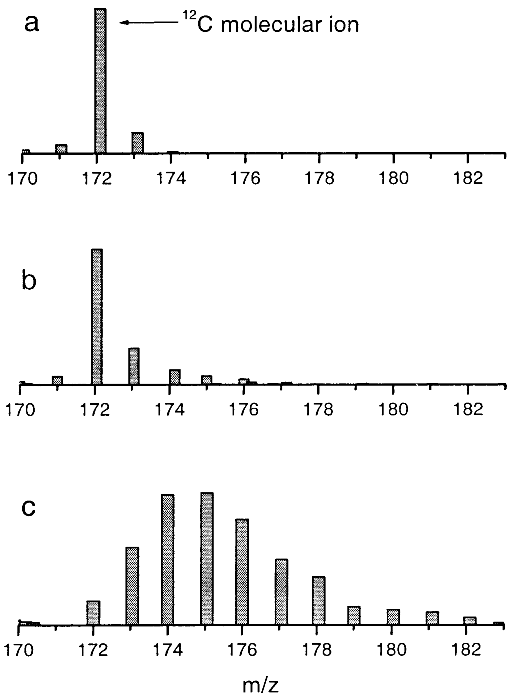


Fig. A.1. Mass spectra of dihydro-triMN retained in the catalyst after: (a) 10 min of hexaMB feeding followed by 5 min flushing, (b) 10 min of hexaMB feeding followed by 5 min flushing and 0.5 min [^{13}C]methanol feeding; the spectrum represents the dihydro-triMN isomer at 13.6-min retention time, and (c) same as (b), but for the dihydro-triMN isomer at 14.2-min retention time.

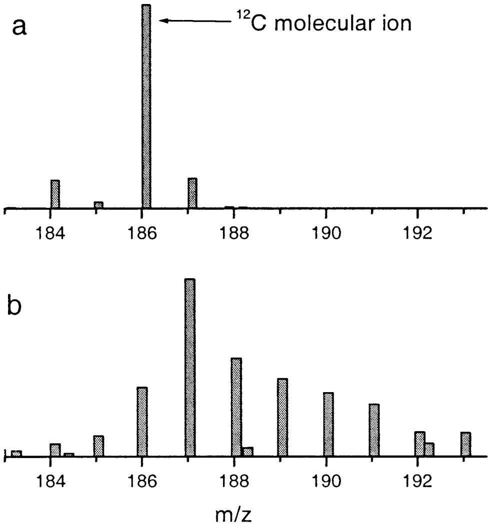


Fig. A.2. Mass spectra of dihydro-tetraMN retained in the catalyst after: (a) 10 min of hexaMB feeding and 5 min flushing, (b) 10 min of hexaMB feeding followed by 5 min flushing and 0.5 min [^{13}C]methanol feeding; the spectrum represents the dihydro-tetraMN isomer at 15.9-min retention time. The figure shows that the most prominent dihydro-tetraMN isomer contains one ^{13}C atom and thus has been formed by methylation of dihydro-triMN.

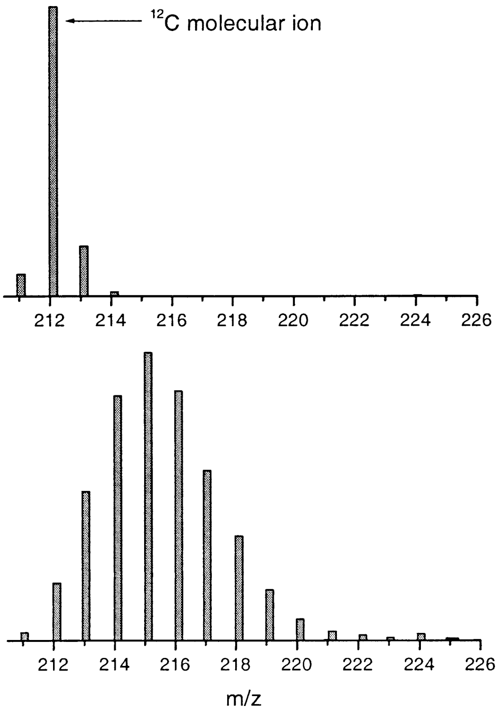


Fig. A.3. Mass spectra of hexaMN retained in the catalyst after: (top) 10 min of hexaMB feeding and 5 min flushing, (bottom) 10 min of hexaMB feeding followed by 5 min flushing and 0.5 min [^{13}C]methanol feeding. The figure shows that the most prominent hexaMN isotopomer contains three ^{13}C atoms and thus has been formed by methylation of dihydro-triMN.

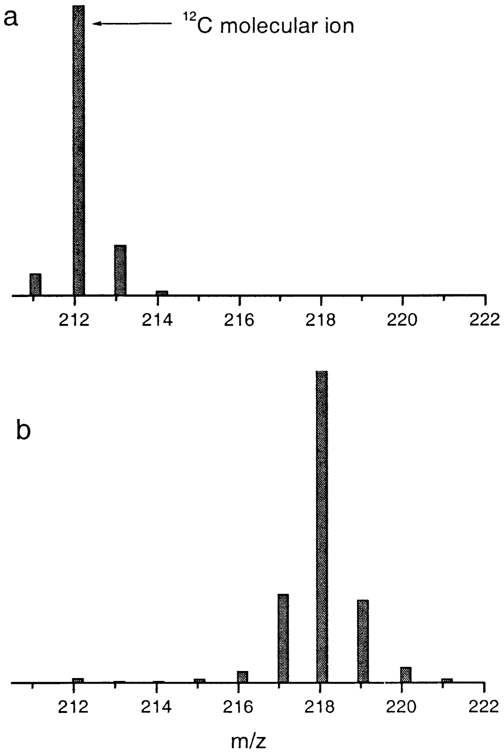


Fig. A.4. Mass spectra of hexaMN retained in the catalyst after: (a) 10 min of hexaMB feeding, (b) 10 min of [^{13}C]methanol and naphthalene cofeeding. The isotopic distribution in hexaMN formed during the [^{13}C]methanol and naphthalene coreaction is close to the one expected if there is a clean methylation with little, but not negligible, scrambling.

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