Conversion of methanol to hydrocarbons: the reactions of the heptamethylbenzenium cation over zeolite H-beta

Morten Bjørgen, Unni Olsbye*, Stian Svelle, and Stein Kolboe

Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway

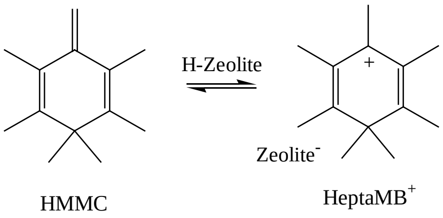
Received 4 September 2003; accepted 2 December 2003

Recent studies have pointed to the heptamethylbenzenium cation as a prominent intermediate in the methanol to hydrocarbons (MTH) reaction. The reactions of the heptamethylbenzenium cation in a H-beta zeolite was studied at 300 °C by feeding its corresponding base (WHSV $= 0.4\ h^{-1}$). The reactant was converted completely into aliphatic products, polymethylbenzenes and coke under the employed conditions. The results testify that the proposed reaction intermediate yields the same product spectrum as methanol. The composition of the material retained in the catalyst micropores after 15 min of reaction was determined by dissolving the catalyst in 15% HF. Polymethylated benzenes (predominantly pentamethylbenzene), dihydro-trimethylnaphthalenes, and hexamethylnaphthalene were the major components. The results also support the idea that the lowest naphthalene derivative is formed from the heptamethylbenzenium cation by a molecular rearrangement. Hence, the heptamethylbenzenium cation is inherently linked to both product formation and catalyst deactivation in the MTH reaction.

KEY WORDS: methanol-to-hydrocarbons; MTH; heptamethylbenzenium cation; beta zeolite; hydrocarbon pool; dihydro-trimethylnaphthalene; hexamethylnaphthalene; coke.

1. Introduction

A variety of protonated zeolites and zeotype materials have been reported to catalyse the reaction where methanol is converted into hydrocarbons and water [1–3]. The reaction is generally referred to as the methanol-to-hydrocarbons (MTH) reaction and represents a possibility for upgrading natural gas and coal to light olefins and higher hydrocarbons. After almost 30 years of research effort, details of the reaction mechanism still need to be clarified. The description of the main reaction path as a "hydrocarbon pool mechanism", is, however, gaining general acceptance. In the hydrocarbon pool mechanism, olefins are believed to be eliminated from a so-called hydrocarbon pool to which methanol is constantly added in a catalytic cycle [3]. The heptamethylbenzenium cation (heptaMB$^+$, scheme 1), which is the terminal benzene methylation product, appears to be of particular importance as a hydrocarbon pool species [4,5].



Scheme 1.

Two mechanisms have been considered to explain the role of heptaMB$^+$ as a hydrocarbon pool compound: the first, the "paring reaction", was originally proposed by Sullivan *et al.* [6] to explain the formation of aliphatic products from hexamethylbenzene (hexaMB). According to this mechanism, heptaMB$^+$ is believed to split off olefins after appropriate rearrangements under formation of lower methylbenzenes that again are remethylated by methanol. In this way, the reaction centre is continuously being regenerated [5,6]. The second mechanism type, initially introduced by Mole *et al.* [7,8] and further elaborated by Haw and coworkers [9], is based on the formation of an exocyclic double bond after a deprotonation of heptaMB$^+$. Subsequent methylations of this exocyclic double bond by methanol results in formation of an alkyl group that may be eliminated as an alkene.

Besides being a vital part of the catalytic cycle in the MTH reaction, heptaMB$^+$ might also play a central role in the reactions leading to catalyst deactivation. Previous and present results point to a relation between hepta-MB$^+$ and the lowest observed naphthalene derivative, dihydro-trimethylnaphthalene (dihydro-triMN) [4].

The aim of this study has been to further elucidate the role of heptaMB$^+$ in the MTH reaction cycle. Hepta-MB$^+$ was fed as its corresponding base, 1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene (HMMC, scheme 1). HMMC is expected to be immediately protonated, forming heptaMB$^+$, when introduced into a protonated zeolite [10]. To the best of our knowledge, this is the first direct study of the reactions of heptaMB$^+$ (fed as HMMC) in a zeolite.

---

* To whom correspondence should be addressed.
E-mail: unniol@kjemi.uio.no

1011-372X/04/0300–0037/0

HeptaMB$^+$ yields a gas phase product spectrum that is similar to that seen in the MTH reaction. Polymethylated benzenes, dihydro-triMN, and hexaMN were the major components retained inside the zeolite pores after 15 min of reaction at 300 °C.

2. Experimental

Experimental details on the catalyst characterization, the catalytic testing, the zeolite dissolution procedure and the gas chromatography have been described previously [4].

2.1. Catalyst and catalytic testing

A commercially available H-beta (Si/Al = 12) from P.Q. Zeolites B.V. has been used in this study.

The experiments were carried out in a micro reactor at 300 °C, using 40 mg catalyst. The nitrogen carrier gas flow was maintained at 22 mL/min (STP). HMMC was fed by passing the carrier gas through a heated evaporator (50 °C), and further through a heated line to the reactor. The resulting feed partial pressure was 2.0 mbar giving a feed rate (WHSV) of 0.4 h^{-1}. The vapor pressure was measured using GC-FID.

2.2. Synthesis of HMMC

The procedure is based on the work of von E. Doering *et al.* [11]. Fifteen gram pentamethylbenzene (Fluka, ~97%) was dissolved in 150 mL cyclohexane (Fluka, >99%) in a 500 mL three-necked flask equipped with a thermometer, a Liebig cooler and a gas inlet line. Thirty gram aluminium trichloride (Fluka, ≥99%) was added and methylchloride (Fluka, ~99%) was passed through the mixture (30 mL/min STP) under vigorous stirring. The mixture was refluxed at 80 °C for 36 h. The dark red mixture was cooled to 0 °C and transferred to a 1000 mL separating funnel containing 150 mL ice water. NaOH was added to basify the water phase. The two phases were separated; the organic phase being left in the funnel. In order to protonate the formed HMMC selectively, 35% HCl (Kebo Lab, purum) was added to the separating funnel. The HCl phase, now containing heptaMB$^+$, was separated from the organic phase and neutralized by adding a saturated NaOH solution cautiously at 0 °C. The aqueous solution was extracted with diethyl ether. Orange, needle shaped crystals appeared after evaporation of the ether. ^{1}H- and ^{13}C-NMR confirmed the product to be HMMC [5]. The purity was 97%, the main impurity being hexamethylbenzene.

3. Results

After feeding HMMC for 12 min at 300 °C over the beta zeolite, GC-FID effluent analyses were carried out. The effluent composition is presented in table 1 together with previously measured data where hexamethylbenzene was reacted [4]. Polymethylbenzenes constituted 80% (on carbon basis) of the effluent and the dominant aliphatic product was isobutane (9%) when HMMC was reacted. Unconverted reactant was not detected in the effluent.

Table 1
Gas phase products (GC-FID) formed from HMMC (300 °C, 12 min reaction time) or hexaMB (325 °C, 10 min reaction time) over H-beta

Compound	HMMC (C%)	HexaMB (C%)[a]
Ethene	3.8	2.5
Propene/propane	4.0 (1.6/2.4)	3.6 (1.4/2.2)
Isobutane	9.2	5.0
n-butane	0.6	0.4
Isopentane	3.1	1.5
Tetramethylbenzene	8.8	27.0
Pentamethylbenzene	47.6	60.0
Hexamethylbenzene	22.9	–

[a] Data obtained from Ref. [4].

In the recent reports on MTH chemistry, the focus has been on the compounds being confined within the zeolite voids during the reaction. The confined material can be analysed by dissolving the catalyst in HF. After having fed HMMC for 15 min, the reaction was quenched by quickly removing the catalyst from the reactor and cooling it to ambient temperature. The catalyst was subsequently dissolved in 15% HF, and the liberated organic compounds were extracted from the aqueous phase with CCl_4. Figure 1a shows the GC-MS total ion chromatogram of the CCl_4 extract. The chromatogram shows two classes of compounds: polymethylbenzenes and polymethyl(dihydro-)naphthalenes.

Pentamethylbenzene (pentaMB) dominates among the methylbenzenes. TriMB is present only in minute amounts. The highest polymethylbenzene, hexaMB, precedes the second class of compounds that was confined in the zeolite pores; the naphthalene derivatives. Consistent with previous studies on similar reaction systems [4,5], dihydro-trimethylnaphthalenes (dihydro-triMNs) are the lowest observed naphthalene derivatives. The dihydro-triMN isomers are succeeded by their methylation products, the dihydro-tetramethylnaphthalenes (dihydro-tetraMNs). The dihydro-tetraMNs are the highest observed dihydro-naphthalenes; the higher bicyclic systems are completely conjugated penta- and hexamethylnaphthalenes (pentaMN, hexaMN).

4. Discussion

Polymethylbenzene chemistry in zeolite and zeotype catalysts is a high priority issue in MTH studies. In particular, deeper insight into the reactions of heptaMB$^+$ appears vital for further progress on the mechanistic understanding of the MTH reaction. By feeding its corresponding base, heptaMB$^+$ has, for the first time, been studied in a zeolite system free from any other compounds than those formed from heptaMB$^+$ itself.

Unconverted HMMC was neither observed in the effluent nor among the compounds being trapped in the zeolite cavities, and the conversion was thus complete. A high conversion will limit the amount of mechanistic information inferable from the current data. However, in this preliminary study, a high conversion was desired in order to facilitate analysis of both the retained material and the products in the effluent.

The effluent was composed of 21% of aliphatics, indicative of alkene formation from heptaMB$^+$. The distribution of the aliphatic products formed when heptaMB$^+$ is reacted over zeolite H-beta, has a close resemblance to the product spectrum seen when either methanol or hexamethylbenzene are reacted over the beta zeolite. This finding supports the idea that heptaMB$^+$ is formed as a reaction intermediate in the methanol conversion.

In order to explain the distribution of the polymethylbenzenes reported in table 1 and figure 1(a), two aspects must be considered: (1) transmethylations between polymethylbenzenes, and (2) the reactions leading to olefins.

When heptaMB$^+$ transfers a $CH_3{}^+$ ion to a suited acceptor, such as a methylbenzene (or a naphthalene), the hexaMB molecule is formed. Bjørgen *et al.* (submitted for publication) have shown very recently that hexaMB may be protonated on a ring carbon by the beta zeolite. Accordingly, in a similar manner, protonated hexaMB, hexaMB$^+$, may also undergo a transmethylation reaction. Any other significant methyl group donors in addition to hexaMB$^+$ and heptaMB$^+$ are hard to imagine for this reaction system.

As mentioned in the introduction, two reaction paths, the paring mechanism and the side chain methylation, have been proposed to explain olefin formation via heptaMB$^+$ in the MTH reaction. In any case, formation of polymethylbenzenes is linked to olefin formation [5,6,9]. Penta- and hexaMB are the polymethylbenzenes expected to result from the side chain mechanism. These compounds are formed from hexaMB$^+$ and heptaMB$^+$ when methyl groups are transferred to an exocyclic double bond during side chain growth. HexaMB will additionally be formed after elimination of a side chain. Indeed, high concentrations of penta- and hexaMB were measured.

In contrast to the side chain methylation mechanism, a paring type mechanism will lead to formation of tri- and tetraMB when propene and butene are formed. As can be seen from table 1 and figure 1(a), only modest amounts of tri- and tetraMB are observed. However, taking transmethylations into account, we suggest that any possible tri- and tetraMBs, associated with C_4 and C_3 formation via a paring mechanism, will be remethylated to form higher methylbenzene homologues. Hence,

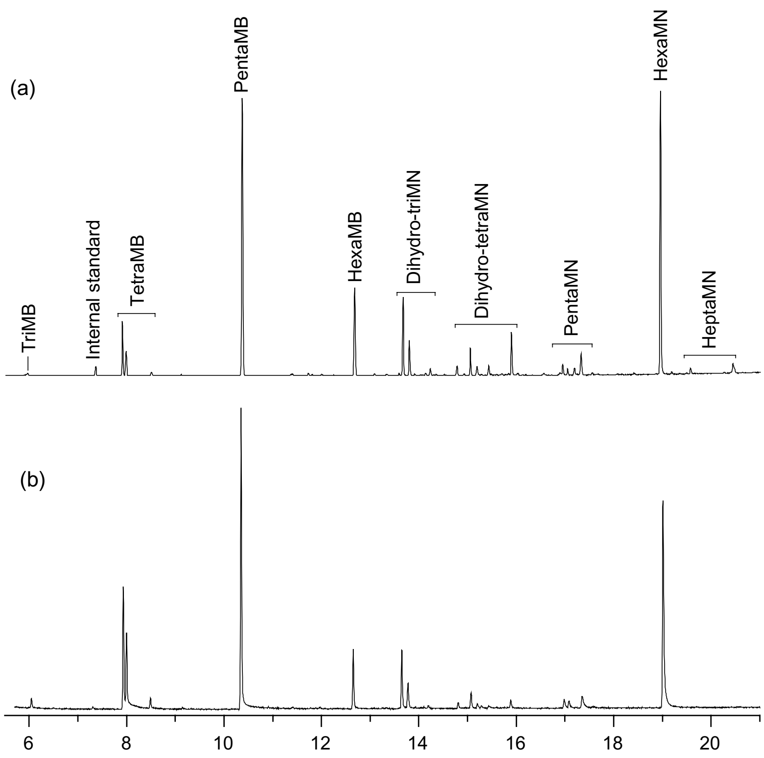


Figure 1. Chromatogram details (GC-MS) of the CCl_4 extracts of H-beta dissolved in HF. Prior to dissolution the catalyst was exposed to: (a) HMMC for 15 min at 300 °C; (b) HexaMB for 10 min at 325 °C, from Ref. [4].

the present data do not permit discrimination between the paring and the side chain methylation mechanisms.

In addition to olefin formation and transmethylations between the various polymethylbenzenes, a rather large part of the methyl groups must be consumed by the extensive methylations of dihydro-triMNs. Previous isotopic labelling experiments have shown dihydro-triMN to be a precursor of the higher naphthalene homologues, i.e. dihydro-tetraMN, pentaMN and hexaMN [4]. The large amount of hexaMN observed within the zeolite pores (figure 1a) is explained by a reaction route where hexaMN is formed by repeated methylations of dihydro-triMN.

We have earlier studied the conversion of hexaMB over the beta zeolite. The reactivity of hexaMB was explained by suggesting a disproportionation of hexaMB into pentaMB and heptaMB$^+$ [4]. The composition of the trapped material formed when hexaMB was the reactant is shown in figure 1b for comparison. The close similarity between the two chromatograms strongly favours the previously proposed disproportionation [4].

As noted, dihydro-triMN is the lowest methylnaphthalene derivative found, and this species has the same number of carbon atoms as heptaMB$^+$. Methylnaphthalenes with less than three methyl groups were actively looked for, but were absent. This is in agreement with earlier studies on similar systems [4,5]. Accordingly, it appears that dihydro-triMN is the primary bicyclic compound. The absence of lower methylnaphthalene derivatives makes heptaMB$^+$ the most likely precursor to dihydro-triMN. Tetrahydro-triMN might be a possible intermediate in the rearrangement of heptaMB$^+$ to dihydro-triMN, but was not detected.

Acknowledgment

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

References

[1] M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3.
[2] C.D. Chang, in: *Shape-Selective Catalysis: Chemicals Synthesis and Hydrocarbon Processing*, eds. C. Song, J.M. Garcés and Y. Sugi, ACS Symposium Series 738 (Washington, DC, 2000).
[3] J.F. Haw, Phys. Chem. Chem. Phys. 4 (2002) 5431.
[4] M. Bjørgen, U. Olsbye and S. Kolboe, J. Catal. 215 (2003) 30.
[5] M. Bjørgen, U. Olsbye, D. Petersen and S. Kolboe, J. Catal. 221 (2004) 1.
[6] R.F. Sullivan, C.J. Egan, G.E. Langlois and R.P. Sieg, J. Am. Chem. Soc. 83 (1961) 1156.
[7] T. Mole, J.A. Whiteside and D.J. Seddon, J. Catal. 82 (1983) 261.
[8] T. Mole, G. Bett and D.J. Seddon, J. Catal. 84 (1983) 435.
[9] A. Sassi, M.A. Wildman, H.J. Ahn, P. Prasad, J.B. Nicholas and J.F. Haw, J. Phys. Chem. B 106 (2002) 2294.
[10] B. Arstad, personal communication.
[11] W. von E. Doering, M. Saunders, H.G. Boyton, H.W. Earhart, E.F. Wadley, W.R. Edwards and G. Laber, Tetrahedron 4 (1958) 178.