Available online at www.sciencedirect.com

Journal of Catalysis 221 (2004) 1–10

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

The methanol-to-hydrocarbons reaction: insight into the reaction mechanism from [^{12}C]benzene and [^{13}C]methanol coreactions over zeolite H-beta

Morten Bjørgen, Unni Olsbye, Dirk Petersen, and Stein Kolboe *

Department of Chemistry, University of Oslo, PO Box 1033, N-0315 Oslo, Norway

Received 16 April 2003; revised 13 June 2003; accepted 13 June 2003

Abstract

[^{13}C]Methanol and [^{12}C]benzene were coreacted over zeolite H-beta at different reaction temperatures, ranging from 210 to 330 °C. The main attention was paid to the material being trapped within the zeolite pores. Hexamethylbenzene and the heptamethylbenzenium cations were easily formed by methylation reactions. The arene methylation reactions leading to hexamethylbenzene and the heptamethylbenzenium cation were much faster than the reactions leading to isotopic scrambling, and the isotopomers $^{12}C_6(^{13}CH_3)_6$ and $^{12}C_6(^{13}CH_3)_7^+$ could be synthesized in situ. This achievement was used to elucidate new details in the MTH mechanism. The heptamethylbenzenium cation was the major compound being retained within the pores of the beta zeolite at 250 °C. When the reaction temperature was increased, this species soon vanished and polymethylbenzenes and -naphthalenes became the dominating components. The isotopic distribution observed in both gaseous products and retained material is in excellent agreement with a reaction mechanism where rearrangement of the heptametylbenzenium cation, followed by dealkylation, is the major reaction route for olefin formation in the MTH/MTO reaction over the H-beta zeolite.

© 2003 Elsevier Inc. All rights reserved.

Keywords: Methanol-to-hydrocarbons; MTH; Hydrocarbon pool; Heptamethylbenzenium cation; Beta zeolite; Paring reaction; Benzene; Methanol

1. Introduction

For nearly 30 years it has been known that methanol can be converted to a mixture of hydrocarbons and water over protonated zeolites. During this time a large amount of work has been carried out to obtain an understanding of the reaction mechanism involved [1–4]. The attention first focused on how two or more C_1 entities (e.g., methanol, dimethyl ether, trimethyloxonium ions) could react so that C–C bonds are formed [3,4]. Ten years ago evidence did, however, appear that the reaction mainly proceeds by a mechanism where there is a pool of adsorbed hydrocarbons that is all the time adding methanol and splitting off ethene, propene, and possibly even higher homologues [5–7]. This hydrocarbon pool was initially not further specified, but during the last few years, it has become clear that polymethylbenzenes play central roles in the hydrocarbon pool mechanism and are essential parts of the catalytic cycle.

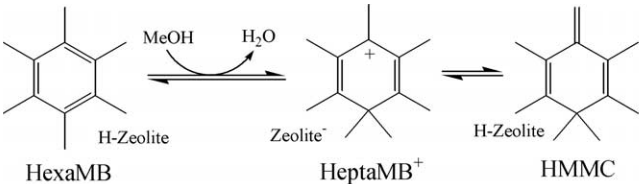
Haw et al. in 2000 showed that cyclopentenyl cations might play an important role in the MTH reaction, and that they are easily transformed into benzene derivatives [8]. The same year, Mikkelsen et al. showed that the formation of ethene and propene in the MTH reaction takes place via an arene or some arene derivative [9]. Information about which arenes are involved and mechanism details were not available. More recently, Haw and co-workers, and Kolboe and co-workers obtained results showing that the catalytic cycle is based on repeated methylations of arenes leading, in particular, to pentamethylbenzene (pentaMB) and hexamethylbenzene (hexaMB), which under the reaction conditions are unstable and split off ethene or propene (in SAPO-34), and are thereby transformed into methylbenzenes with two or three fewer methyl groups [10–14]. Butylbenzene reactions have also been studied [15]. Very recently, it has become increasingly clear that benzene methylation may proceed even further and that the final methylation product may be heptamethylbenzenium ions (heptaMB$^+$) (Scheme 1).

Song et al. showed, by using solid-state NMR spectroscopy, that heptaMB$^+$ may exist in an H-beta zeolite [16]. The very recent works by Sassi et al. and by Bjørgen et al.

---

* Corresponding author.
E-mail address: stein.kolboe@kjemi.uio.no (S. Kolboe).

0021-9517/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/S0021-9517(03)00284-7



Scheme 1.

have explicitly acknowledged the existence of heptaMB$^+$ and utilized it for interpreting the experimental results obtained [17,18]. The heptaMB$^+$ was first isolated and identified as the final stable product in the Friedel–Crafts methylation of benzene, leading to catalyst deactivation, by von E. Doering et al. [19]. The corresponding base to heptaMB$^+$ is 1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene (HMMC) (Scheme 1). A theoretical investigation on methylbenzene methylation by methanol on a zeolite cluster model, carried out in conjunction with our work on the MTH reaction, predicted heptaMB$^+$ to be easily formed, provided the pore system is wide enough [20].

Clearly, investigating the formation and reactivity of heptaMB$^+$ and its corresponding base HMMC is a high priority issue in MTH chemistry. The study on methylbenzene chemistry presented by Sassi et al. shed important light on the hydrocarbon pool mechanism [17]. The authors interpreted their observations to indicate that the MTH reaction mainly proceeds by side-chain methylation of the exo-cyclic methylene group of HMMC. This may form an ethyl or isopropyl group that is subsequently split off as ethene or propene from the ring. The study focused on the gas-phase effluent compounds, and possible active species like HMMC/heptaMB$^+$ being trapped in the pores of the zeolite were not looked for. Very recently, Bjørgen et al. obtained complementary results by liberating and analyzing the compounds that were trapped in the pores during the reaction where hexaMB was the reactant [18]. The study pointed to methylation of hexaMB to heptaMB$^+$ as a central reaction step for forming aliphatic products as well as “coke.”

In an MTH reaction system, methylbenzenes show an extensive interchange of carbon atoms between the ring and the methyl substituents [9,11,17]. This distinctive characteristic is not an obvious consequence of the proposed side-chain methylation mechanism noted above. Other reaction paths leading to this carbon atom interchange must run in parallel. The “paring” mechanism, that was introduced by Sullivan et al. in 1961, was proposed in order to explain the observation that hexaMB apparently splits off aliphatic products (in particular, isobutane) when being reacted over acidic catalysts [21]. The paring mechanism suggests alkyl side-chain growth by ring expansion/contraction, and will, in contrast to a simple side-chain methylation, lead to a carbon atom interchange between the ring and the substituents.

In this study, we obtained information on the olefin formation from reactions involving methylbenzenes consisting of a [^{12}C]benzene ring and [^{13}C]methyl groups. The experiments confirmed a further methylation of hexaMB to heptaMB$^+$. The composition of the organic material retained in the working zeolite was identified by stopping the reaction, dissolving the catalyst in hydrofluoric acid, and analyzing an organic extract of the liberated hydrocarbons. [^{13}C]Methanol and [^{12}C]benzene were reacted over the beta zeolite for 90 s prior to the dissolving and extracting procedure. Our findings clearly show that heptaMB$^+$ is the major compound being retained inside the micropores of the zeolite at 250 °C. The amount of heptaMB$^+$ gradually diminishes as the temperature is increased, and at 315 °C polymethylbenzenes and -naphthalenes are the dominating retained compounds. At the lower reaction temperatures, the isotopic distributions in the gas-phase products propene and isobutane suggest a paring-type mechanism to dominate in the olefin formation. It can now be stated that heptaMB$^+$represents the most conspicuous constituent of the hydrocarbon pool observed thus far.

2. Experimental

Experimental details on the catalyst characterization, the catalytic testing, the zeolite dissolution procedure, and the gas chromatography have been described previously [18,22,23].

2.1. Catalyst

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

2.2. Catalytic testing

The experiments were carried out in a microreactor at 210–330 °C, using 40 mg catalyst. Methanol, either ^{13}C-enriched (Cambridge Isotope Laboratories, 99% ^{13}C purity according to the producer, 97.2% according to our analysis) or ordinary [^{12}C]methanol (BDH Laboratory Supplies, $> 99.8\%$), and benzene (Riedel–deHaën, $> 99.5\%$) were both fed by passing separate nitrogen carrier gas streams through saturation evaporators kept at 0 °C. The carrier gas flow was maintained at 5 mL/min for benzene and 31 mL/min for methanol. The saturated gas streams were mixed and led to the reactor. Resulting feed partial pressures were 5 and 34 mbar for benzene and methanol, respectively, giving corresponding feed rates (WHSV) 0.9 and 2.5 h^{-1}.

2.3. NMR spectroscopy: sample preparation and acquisition parameters

NMR spectroscopy was applied for an adequate structure identification of one of the major peaks in the GC-MS chromatograms (Fig. 1c, No. 4). To get sufficient material for ^{1}H and ^{13}C NMR, an experiment using 4 g of catalyst at 230 °C, with reaction time 20 min, was carried out. The amount of HF and CCl_4 used in the dissolution procedure was scaled correspondingly. After extraction, water in the organic phase was adsorbed on a dehydrated 3 Å molecular sieve (zeolite LTA). Due to the instability of the compound, vaporization of the organic solvent was carried out under reduced pressure

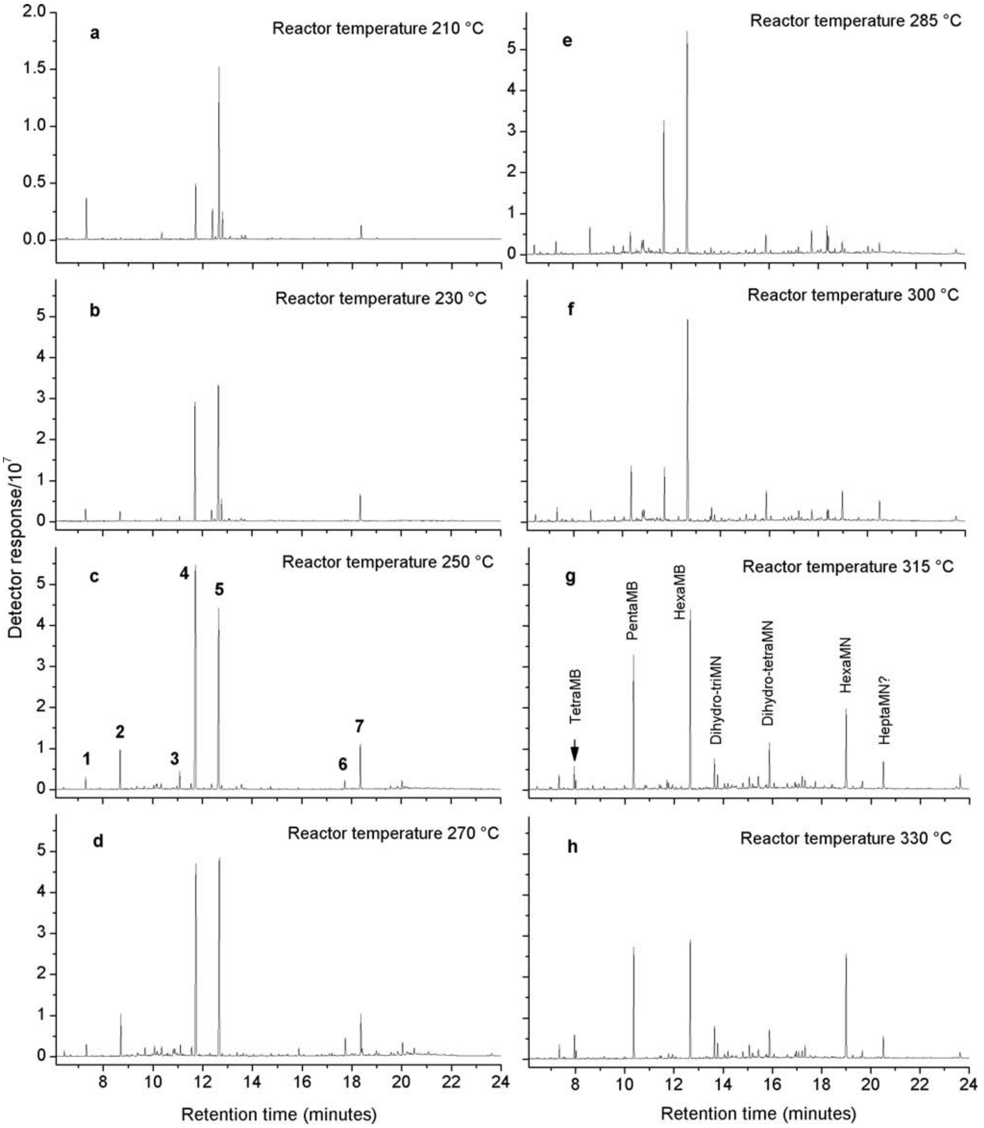


Fig. 1. Chromatogram details (GC-MS) of the CCl_4 extract of H-beta dissolved in HF. Prior to dissolution the catalyst was exposed to methanol and benzene for 90 s at different reactor temperatures.

without heating in a Rotavapor. The residue was dissolved in 0.5 mL $CDCl_3$. This sample was kept at −20 °C when out of the spectrometer.

^1H and ^{13}C NMR spectra were recorded at 0 °C using a Bruker Avance DRX 500 spectrometer at 500 and 125 MHz, respectively.

3. Results

3.1. Identification of the retained organic material formed at different reaction temperatures

Fig. 1 presents the GC-MS total ion chromatograms of the CCl_4 extract for different reaction temperatures, ranging from 210 to 330 °C. Benzene and [^{13}C]methanol were fed for 90 s before the catalyst was removed from the reactor, cooled to room temperature, and dissolved in hydrofluoric acid. The sensitivity scale is the same for all chromatograms except for the 210 °C sample (Fig. 1a), which is shown at higher (3×) sensitivity. Peaks that are prominent in Figs. 1a–1e, covering experiments carried out in the temperature range 210–285 °C, are marked 1 to 7 in Fig. 1c. Two peaks are seen to be clearly dominating. The second of those peaks (No. 5) is hexaMB ($C_{12}H_{18}$), the obvious product after multiple methylations of benzene. The first one (No. 4), has a molecular ion $m/z = 176$, corresponding to a $C_{13}H_{20}$ molecule. The mass spectrum, shown in Fig. A1, gives a very satisfactory match to 1,2,3,4-tetramethyl-5-isopropylbenzene in the NIST98 database, and a slightly less good match to a couple of other alkylbenzenes in the database. However, the compound turned out to be unstable at room temperature and disappeared from the CCl_4 extract after a few days. This observation essentially ruled out the possibility that the compound was an ordinary alkylbenzene. Haw and co-workers have shown that heptaMB$^+$ is present in beta zeolite under

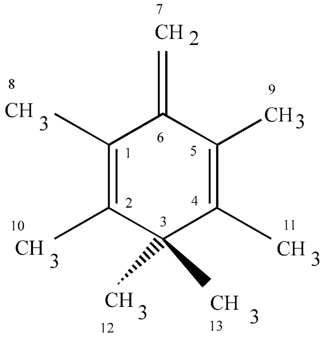
MTH conditions [16]. Its deprotonation product, HMMC, has the same mass as the unknown peak, i.e., 176.

The first attempts to identify the unknown compound by ^{1}H and ^{13}C NMR spectroscopy failed due to the instability of the compound and the small amount available. By scaling up the experiments, from 40 mg catalyst to 4 g, and increasing the reaction time to 20 min, we obtained enough material for NMR experiments. By lowering the temperature in the NMR spectrometer to 0 °C, the decomposition rate was slowed down and several ^{1}H and ^{13}C NMR spectra (COSY, NOESY, HMQC, HMBC [24]) were acquired. The NMR results are given in Table 1. The spectra clearly show that the compound does not contain a benzene ring and confirm that it is actually HMMC. The experiments do, however, not tell whether the HMMC is present as such within the zeolite cavities, or possibly as heptaMB$^+$ ions (discussed below). The important point is that under the right experimental conditions heptaMB$^+$/HMMC can be the most dominating constituent within the zeolite lattice, and we can thereby study its reactions and elucidate further details of the MTH reaction.

The other less prominent peaks marked by numbers in Fig. 1c are less precisely identified, but are closely related to HMMC. (Peak 1 is an internal standard, C_2Cl_6.) Peaks 2 and 3 are isomers of HMMC. Like HMMC, they give a good fit with alkylbenzenes. In particular, peak 3 gives a virtually perfect fit with 1,2,3,4-tetramethyl-5-isopropylbenzene. Peaks 4 and 5 were discussed above. Peak 6 (with molecular mass 298) is unidentified. Interestingly its mass spectrum displays no peaks in the region from $m/z = 298$ to 177 showing loss of a radical with mass 121; from then on the mass spectrum is virtually indistinguishable from the HMMC spectrum. Peak 7 (with a molecular ion at $m/z = 278$, and an intensity pattern in the range $m/z = 278$ to 284 showing three chlorine atoms) is also clearly related to HMMC. It might be caused by an unknown impurity in the CCl_4 that reacts with HMMC; the mass spectrum shows a loss of a CCl_3 radical from the molecular ion.

The chromatograms are seen to become more complex as the temperature is increased. Except for hexaMB, the compounds that are dominating up to about 270 °C gradually vanish, while new peaks appear. At 300 °C, and above, the chromatograms are mainly showing polymethylbenzenes, dihydro, tri- and -tetramethylnaphthalenes, and hexamethylnaphthalene. The most important constituents in this temperature range are marked in Fig. 1g. The confined products that were dominating at the lower temperatures are evidently reacting further to methylbenzenes and -naphthalenes at the higher temperatures. The organic material formed and retained under similar conditions at 325 °C has been thoroughly discussed earlier [18].

Table 1
^{1}H and ^{13}C NMR[a] assignments of HMMC according to the designations in **1**



Atom No.	^{13}C (m)	H (m,J)	HMBC coupled H No. (^{n}J)
1[b]	142.3 (s)		H-8 (^{2}J)
2[b]	138.7 (s)		H-10 (^{2}J), H-8 (^{3}J), H-12/13 (^{3}J)
3	41.5 (s)		H-12/13 (^{2}J), H-10/11 (^{3}J)
4[b]	138.7 (s)		H-11 (^{2}J), H-9 (^{3}J), H-12/13 (^{3}J)
5[b]	142.3 (s)		H-9 (^{2}J)
6	124.4 (s)		H-7 (^{2}J), H-8/9 (^{3}J), H-10/11 (^{4}J)
7	102.6 (t)	4.88 (s)	H-10/11 (^{5}J, w)[f]
8[c]	14.8 (q)	1.87 (q, 0.8)[d]	
9[c]	14.8 (q)	1.87 (q, 0.8)[d]	
10[c]	15.9 (q)	1.84 (br m)[e]	H-7 (^{5}J, vw)[f]
11[c]	15.9 (q)	1.84 (br m)[e]	H-7 (^{5}J, vw)
12	24.7 (q)	1.12 (s)	H-13 (^{3}J), H-8/9 (^{5}J, w), H-7 (^{6}J, w)
13	24.7 (q)	1.12 (s)	H-12 (^{3}J), H-8/9 (^{5}J, w), H-7 (^{6}J, w)

[a] Unknown amount of the compound in $CDCl_3$; values in ppm, relative to $\delta_C = 77.0$ and $\delta_H = 7.24$ for $CDCl_3$. Assignments are inferred from COSY, NOESY, HMQC, and HMBC spectra.

[b] Assignments of the ^{13}C pairs C-1/5 and C-2/4 are not strictly proven and must therefore be considered as interchangeable regarding the somewhat exceptional (^{5}J-, even ^{6}J-couplings!) spin–spin coupling situation caused by the conjugated π-electron system. However, there are strong indications for the assignment given, as the neighborhood of the conjugated methylene double bond should give a low-field shift for the pair C-1/5 due to a negative anisotropic shielding in the ring plane. Further, the alternative assignment would involve a ^{3}J-coupling from H-8/9 to C-2/4 (instead of ^{2}J to C-1/5), as well as a ^{4}J-coupling from H-12/13 to C-1/5 (instead of ^{3}J to C-2/4) which is considered being less likely.

[c] Correct assignments of the ^{1}H and ^{13}C NMR resonances of C/H-8/9 and C/H-10/11 were verified by NOESY experiment.

[d] Homo-allylic ^{5}J-coupling between H-8 and H-10/H-9 and H-11, verified by COSY experiment.

[e] Broad unresolved multiplet, homo-allylic ^{5}J-coupling and further ^{6}J-coupling(s) (< 0.8 Hz) to H-7, verified by COSY experiment.

[f] w, weak; vw, very weak.

3.2. Isotopic analysis of the retained organic material formed at different reaction temperatures

Previous reports have revealed that hexaMB is a very reactive species that is of central importance in the hydrocarbon pool mechanism [10,11,17,18]. The results presented in this work will therefore mainly focus on hexaMB and the methylation of this compound to an even more reactive intermediate, i.e., heptaMB$^+$.

3.2.1. The isotopic composition of hexaMB

Fig. 2 presents the mass spectra (limited to the ions in the vicinity of the molecular ion) of confined hexaMB formed from the benzene and methanol coreaction at the different temperatures, from 210 to 330 °C. Fig. 2a shows the mass spectrum of hexaMB formed from ordinary benzene and

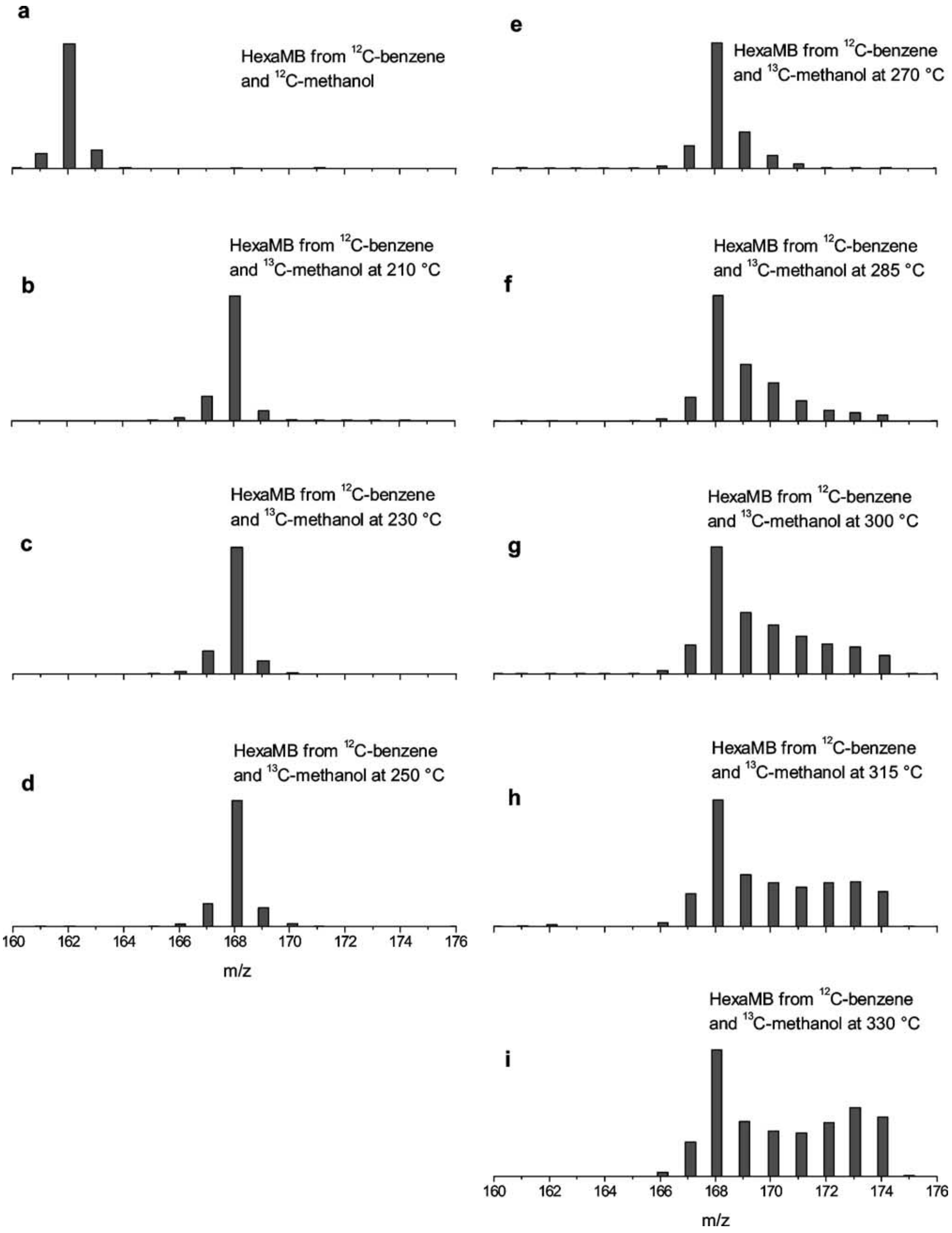


Fig. 2. Mass spectra (in the vicinity of the molecular ion) of hexaMB retained in the catalyst after 90 s of methanol/benzene cofeeding at the different temperatures: (a) [^{12}C]methanol and [^{12}C]benzene, (b)–(i) [^{13}C]methanol and [^{12}C]benzene.

methanol (i.e., only a natural ^{13}C content of 1.1%). The molecular ion is at $m/z = 162$ ($C_{12}H_{18}$). As this species only has the natural ^{13}C content, about 13% of the molecules contain one ^{13}C atom and 11 ^{12}C atoms (the $M + 1$ peak).

Fig. 2b shows the mass spectrum of hexaMB formed from ordinary benzene and ^{13}C-enriched methanol (97.2% ^{13}C) at 210 °C. The mass spectrum looks much the same as the one presented in Fig. 2a, except for being shifted six mass units upward, corresponding to six ^{13}C-methyl groups on the benzene ring.

Increasing the reaction temperature to 230 °C (Fig. 2c) does not introduce any striking changes, but results in a slightly higher ^{13}C content; 9.9% of the hexaMB molecules now contain seven ^{13}C carbons, still very close to the natural contribution of 6.6%. At these low temperatures, the isotopic scrambling is essentially negligible and the hexaMB molecules have been formed from quite clean methylation reactions. When the mass distribution of the molecular ion is compared to the distribution of the ($M - CH_3$) masses it becomes clear that more than 95% of the methyl group carbons derive from the methanol; i.e., scrambling between ring and methyl carbons is insignificant.

At 250 °C (Fig. 2d), the scrambling is still modest, but the amount of ^{13}C in hexaMB starts to increase; 15.9% of the hexaMB molecules have seven ^{13}C carbons, so about 2.5% of the ring carbons are ^{13}C. A further increase in temperature

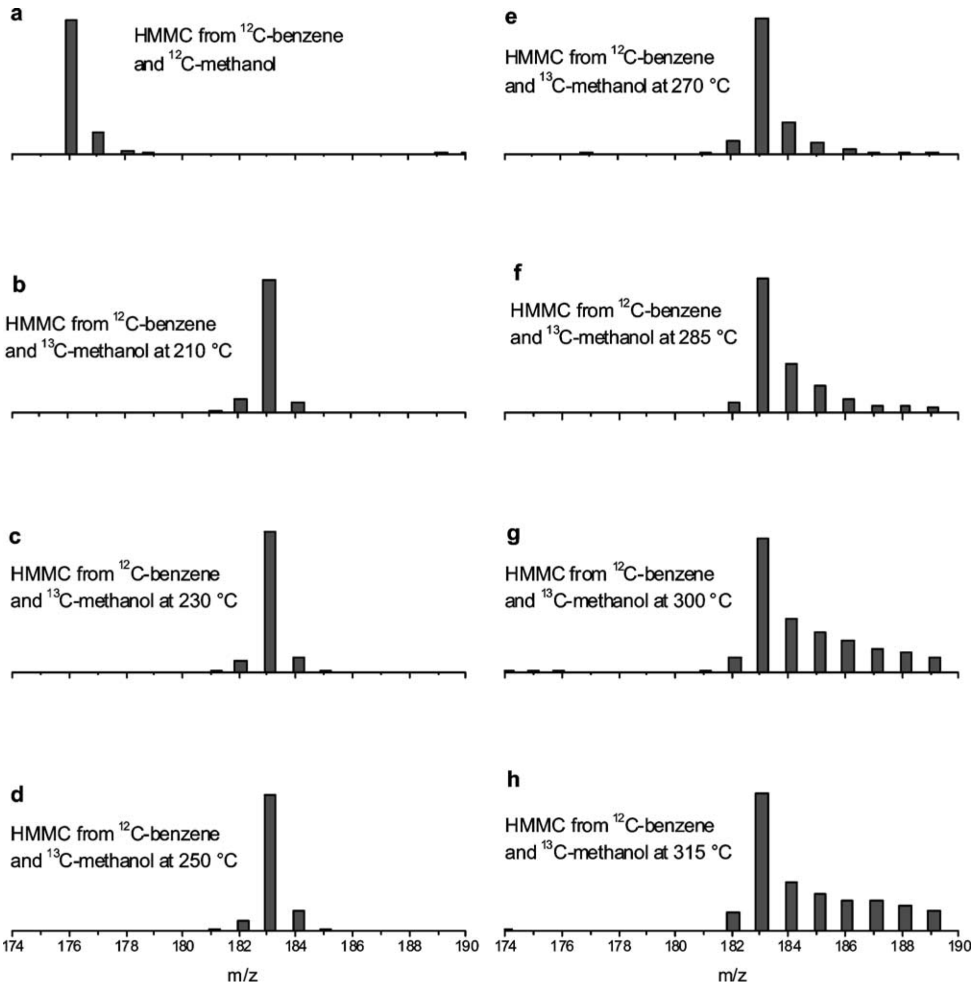


Fig. 3. Mass spectra (in the vicinity of the molecular ion) of HMMC retained in the catalyst after 90 s of methanol/benzene cofeeding at the different temperatures: (a) [^{12}C]methanol and [^{12}C]benzene, (b)–(h) [^{13}C]methanol and [^{12}C]benzene.

results in broader isotopic distributions and the ^{13}C content increases steadily. At 330 °C (Fig. 2i), 72% of the hexaMB molecules have at least seven ^{13}C-labeled atoms.

3.2.2. *The isotopic composition of HMMC*

The success of the low-temperature in situ synthesis of hexaMB containing six ^{12}C atoms and six ^{13}C atoms enabled us to study a possible further methylation of hexaMB. This further methylation is expected to give a species containing seven ^{13}C-labeled carbon atoms.

Fig. 3 shows partial mass spectra of HMMC formed from benzene and methanol coreactions at a series of reaction temperatures. Fig. 3a shows the mass spectrum of HMMC formed from ordinary benzene and methanol. The molecular ion is at $m/z = 176$, and the $M + 1$ peak corresponds to the natural ^{13}C content. Fig. 3b shows the mass spectrum of HMMC formed from ordinary benzene and [^{13}C]methanol at 210 °C. The $M - 1$ peak is caused by ^{12}C impurities in the ^{13}C-enriched methanol. As was also the case for hexaMB, this mass spectrum is essentially the same as the corresponding ^{12}C spectrum (Fig. 3a), except for being shifted seven mass units upward, giving a molecular ion $m/z = 183$. At 210 and 230 °C (Figs. 3b and 3c) the fraction of isotopomers with eight, rather than seven, ^{13}C atoms is in full accord with the value to be expected from the natural ^{13}C content in benzene. Comparison of isotopomer distributions in the M and ($M - CH_3$) spectrum parts showed essential absence of ring and methyl carbons interchange also in HMMC. At higher reaction temperatures broader isotopic distributions and higher ^{13}C contents are gradually observed. This evolution is clearly seen in Fig. 3.

3.3. *Exploration of HMMC side-chain methylation at 250 °C*

Our method of dissolving the zeolite in hydrofluoric acid in order to study the retained organic material does not provide a direct identification of possible carbenium ions present in the working zeolite. Possible cations will not be recovered as such, but be deprotonated and identified as their corresponding bases after the dissolution procedure. An immediate distinction between heptaMB$^+$ and its corresponding base, HMMC, can therefore not be made. Depending on

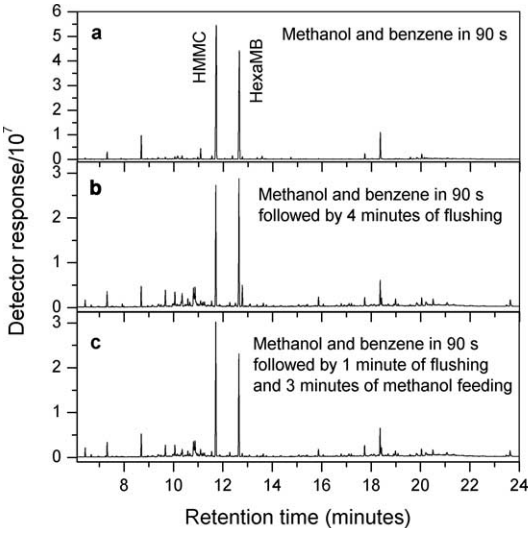


Fig. 4. Chromatogram details (GC-MS) of the CCl_4 extract of H-beta dissolved in HF. Prior to dissolution the catalyst was exposed to methanol and benzene for 90 s at 250 °C followed by: (a) No additional treatment, (b) 4 min flushing, and (c) 1 min flushing and 3 min of methanol feeding.

the acid strength of H-beta, the larger part of the HMMC that we isolate may actually be present as heptaMB$^+$ in the working zeolite. However, the possible HMMC that is present in the catalyst at the reaction temperature will be expected to undergo an easy methylation under methylating conditions (see below). An experiment where methanol was added after 1 min of catalyst flushing was conducted to get information about the HMMC/heptaMB$^+$ ratio in the zeolite at 250 °C. After 1 min of flushing the catalyst was presumably free from benzene. Methanol added after this flushing time would accordingly not be consumed by benzene methylations. If a significant amount of methylated hexaMB is present as HMMC and not as heptaMB$^+$, a decrease in the HMMC peak in the total ion chromatogram is expected after methanol addition.

The effect on the hydrocarbon deposits formed during 90 s of methanol/benzene reaction at 250 °C when the catalyst was subsequently flushed and reacted with methanol is shown in Fig. 4. The figure presents GC-MS total ion chromatograms of the CCl_4 extract obtained after the reaction and:

(a) no flushing,
(b) 4 min flushing, and
(c) 1 min flushing followed by 3 min of methanol reaction.

Fig. 4b shows that catalyst flushing only has a modest effect on the confined hydrocarbons at 250 °C; after 4 min of flushing HMMC and hexaMB have declined to 55 and 72% of their nonflushed values. Several minor components actually increase and new peaks appear as a result of catalyst flushing. Relatively pronounced changes/appearances can be seen between 9.5 and 11 min retention time. We have not been able to identify these compounds, but the majority of them have the same molecular mass as HMMC.

When methanol was added for 3 min after 1 min of flushing (Fig. 4c), a small increase in HMMC is observed while hexaMB decreases. Combined with the expected ease of HMMC methylation [25], the results presented in Fig. 4c make the possibility that significant amounts of HMMC are present in the zeolite at 250 °C less likely.

The difference between flushing for 1 min followed by methanol admission for 3 min and flushing for 4 min is quite small. The methanol treatment appears to cause some more hexaMB to be converted to HMMC, though. Flushing alone made pentaMB (10.35 min retention time) appear as a constituent of the retained material. It did not appear after the methanol treatment (transformed to hexaMB/HMMC). A similar experiment where benzene admission was cut after 90 s, while methanol admission was continued for 4 more min, produced a result very similar to that in Fig. 4c.

When HMMC is methylated (and deprotonated to form the neutral species), once or twice, compounds with molecular weights 190 and 204 will be formed. Only insignificant amounts of these masses have been found. They are too small to be seen in the ion chromatograms, and spectra could not be determined.

3.4. *Effluent analyses*

GC-FID effluent analyses were performed after 90 s of [^{13}C]methanol/[^{12}C]benzene reaction at 250, 270, and 330 °C. At 250 °C, the effluent consisted mainly of unconverted reactants. Methanol/dimethyl ether (in internal equilibrium) represented 50% (on carbon basis) and benzene 44% of the effluent. The remaining 6% were mainly isobutane (1%), toluene (2%), and hexaMB (4%). At 330 °C the effluent composition was 3.5% unconverted methanol/dimethyl ether and 27% benzene, with main products being ethene (8%), propene (6%), isobutane (23%), pentane (8%), and hexaMB (19%).

The HP-5MS column used in the GC-MS analyses is inappropriate for C_2 analyses and isotopic distributions in ethene/ethane were not obtained. Propene and propane were not completely separated, but well enough to get propene mass spectra. The propene isotopic composition was determined at 270 and 330 °C. The isotopic distribution at the two temperatures is shown in Fig. 5. At 270 °C the isotopomer $^{12}C^{13}C_2$ is seen to be dominant. The amount is significantly above a random distribution, whereas at 330 °C the distribution cannot be distinguished from a random one.

The isotopic composition of isobutane could be determined also at 250 °C. The results are given in Fig. 6. At 250 and 270 °C the isotopomer $^{12}C^{13}C_3$ dominates strongly, and the distribution is, in contrast to the result at 330 °C, clearly nonrandom.

4. Discussion

The methylation product of hexaMB, heptaMB$^+$, is undoubtedly a very central intermediate in the MTH reaction.

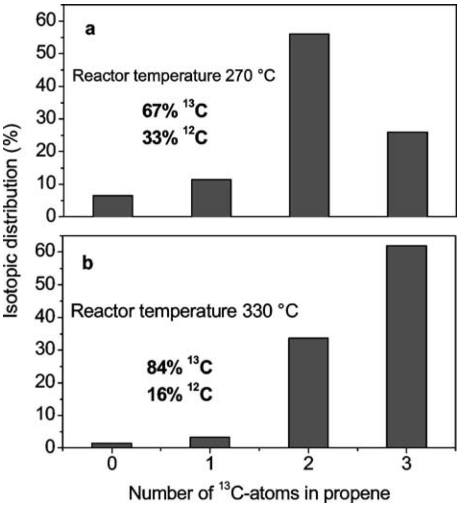


Fig. 5. Isotopic distribution of propene in the product stream from coreaction of [^{13}C]methanol and [^{12}C]benzene over H-beta for 90 s at: (a) 270 °C and (b) 330 °C.

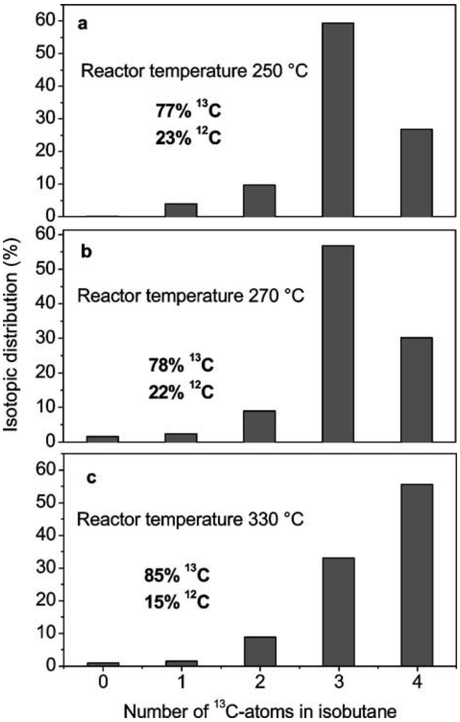
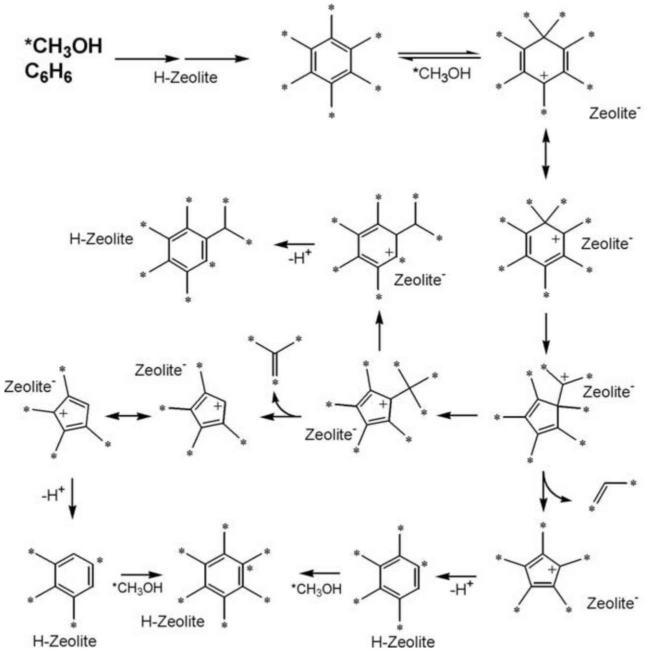


Fig. 6. Isotopic distribution of isobutane in the product stream from coreaction of [^{13}C]methanol and [^{12}C]benzene over H-beta for 90 s at: (a) 250 °C, (b) 270 °C, and (c) 330 °C.

We have for the first time shown that it may, under the right circumstances, be the most prominent compound inside the zeolite porous system.

The first clear evidence that heptaMB$^+$ may actually be formed inside the zeolite cavities (H-beta zeolite) was obtained very recently by Haw and co-workers by means of NMR spectroscopy [16]. Literature reports on the catalytic reaction system suggest two different routes for the further conversion of heptaMB$^+$ into lower hydrocarbons: The first route involves exo-cyclic methylation of the deprotonation product of heptaMB$^+$, HMMC, and a subsequent elimination of ethene or propene [17]. The other route involves intramolecular rearrangements of heptaMB$^+$ according to the paring reaction mechanism, as proposed by Sullivan et al. [21].



Scheme 2.

Sassi et al. concluded that exo-cyclic methylation is the dominating route to olefin formation over zeolite H-beta at 450 °C [17]. The observations we have made are not easily reconciled with a mechanism based on exo-cyclic methylation of HMMC, with subsequent bond breaking. Figs. 5 and 6 make it clear that at 250 and 270 °C the large majority of propene and isobutane product molecules contain carbon atoms (^{12}C) from the benzene ring. The isotopic distribution is in full accord with the distribution to be expected from the paring reaction model. A detailed reaction scheme is given in Scheme 2. The scheme even predicts that the typical propene molecule should contain two ^{13}C and one ^{12}C atom. Likewise the typical isobutane (split off as isobutene) might contain three ^{13}C and one ^{12}C atom. The actual outcome is seen to reflect this prediction well.

The exo-cyclic methylation pathway, on the other hand, does not directly predict the presence of ^{12}C atoms in ethene or propene product molecules. The appearance of ^{12}C atoms from the benzene ring cannot be excluded, however, provided independent scrambling rearrangements take place. Such scrambling would, however, provide an independent access to higher alkyl side chains—and thus be an independent, paring reaction type, route to products formation.

The experiments reported in Section 3.3 were carried out to see if the stability of HMMC/heptaMB$^+$ depends on the presence of methanol. As is borne out by Fig. 4, the effect of adding methanol after a 1-min flush in order to remove benzene from the reaction system produced only marginal changes relative to a flushing with carrier gas for the same time. These results show—independently of the isotopic experiment referred to above—that at 250 °C there are no indications that an exo-cyclic methylation takes place. This interpretation is further corroborated by the absence of compounds with molecular weights 190 and 204 (resulting from methylation of HMMC once or twice) after such a methanol treatment. These observations have two obvious explanations:

(1) Despite the expected ease of methylation, HMMC is not easily methylated.
(2) The basicity of HMMC is so large that the concentration of free HMMC molecules inside the zeolite is effectively zero.

HMMC is known to be basic, from experiments [19], and from quantum chemical calculations [25], so the second alternative is probably the explanation.

Sassi et al. studied the MTH reaction over the H-beta zeolite at 450 °C, and proposed side-chain methylation as the main route to light hydrocarbon formation [17]. Our results were obtained in the vicinity of 250 °C, and it is therefore of interest to consider whether there might be a switch in the main reaction path when the temperature goes from 250 to 450 °C.

When HMMC strongly tends to exist in its protonated form, heptaMB$^+$, this implies that transferring a proton from heptaMB$^+$ back to the zeolite is a highly endothermic process and it takes energy to transfer the proton. By increasing the temperature the relative concentration of free HMMC molecules will therefore increase. But there is no reason to assume that there is a large entropy effect connected with the protonation/deprotonation. The concentration of HMMC will then always be lower than the heptaMB$^+$ concentration, and they will only tend to become equal at extreme temperatures.

Figs. 2 and 3 show that the amount of ^{13}C in hexaMB and HMMC increases strongly with temperature. At 210 °C both compounds contain “exclusively” ^{12}C in the ring, and ^{13}C methyl carbons. At 270 °C about half the rings contain one or more ^{13}C atoms. The mass spectra were studied in detail. It was taken into account that the starting material, benzene, contains 1.1% ^{13}C, and that the [^{13}C]methanol has an isotopic purity of 97.2%. The number of ^{13}C atoms beyond the natural ^{13}C content can thus be determined. The reaction time is in all cases the same (90 s), so the excess ^{13}C is proportional to the exchange rate (provided there is no large excess). An Arrhenius plot then allows an estimation of the activation energy for the exchange processes that lead to ^{13}C incorporation in the ring. The result is an activation energy of ca. 105 kJ/mol. Because replacement of one ^{13}C by another ^{13}C is not observable, the estimate is on the low side. In order to minimize this effect, only the experimental results obtained from 210 to 270 °C were used to estimate the rates. This activation energy implies that at 450 °C, which was the temperature employed by Sassi et al., the time needed to obtain the same incorporation as observed in Fig. 3 at 285 °C is less than 0.5 s. Rate estimates for these rearrangements have previously not been accessible.

Sassi et al. concluded that the MTH reaction proceeds by methylation of the exo-cyclic methylene group of HMMC. The conclusion was to a large extent based on the finding that when a reaction mixture of [^{13}C]methanol and arene passed the catalyst, the ethene and propene products contained relatively more ^{13}C than the reaction mixture; it was more like the ^{13}C content of the methyl groups in the feed. This finding might preclude the paring mechanism. Such a conclusion may, however, not be fully warranted because the scrambling at 450 °C is so fast. The scrambling rate was unknown at the time and could not be taken into account. We also feel that the copious production of isobutane over H-beta (Section 3.4, and Ref. [26]), argues for a considerable participation of reactions of the paring mechanism type. Isobutane/isobutene is not an obvious consequence of the reaction path relying on exo-cyclic methylations. The issue is at the heart of the MTH chemistry, and definitely merits further investigation.

It may, however, not be concluded that exo-cyclic methylations are never important. When the MTH reaction is conducted over SAPO-34 catalysts, it is well known that ethene and propene are the main products. If the isobutyl carbon skeleton were the main primary product over this narrow pore catalyst, it would remain trapped inside the pore system. A rapid filling up and deactivation would be expected. This catalyst system does, however, not deactivate particularly fast. Arstad and Kolboe studied the substances retained within the SAPO-34 framework [10,11]. While isobutane was one of the trapped substances in the catalyst, it was not a dominant component. At the same time it is well known that SAPO-34 is a much weaker acid than H-beta zeolite. For this reason it is to be expected that the amount of free HMMC within the SAPO-34 framework may be far from negligible. Exo-cyclic methylation of HMMC might then lead to a fast formation of ethene and propene at the expense of isobutene formation.

5. Conclusion

The results presented in this work are in broad general agreement with previous works on the hydrocarbon pool mechanism. We can now state on an experimental basis that, provided the pore system is wide enough, hexaMB is easily methylated and forms the heptaMB$^+$ ion upon methylation. Furthermore, heptaMB$^+$ is the most conspicuous constituent that is retained within the pores of the beta zeolite at 250 °C. HeptaMB$^+$ is highly reactive under realistic MTH conditions, and can hardly be detected in zeolite H-beta at 330 °C. At the higher temperatures, heptaMB$^+$ is replaced by more stable compounds, and methylbenzenes and -naphthalenes become the dominating constituents. The arene methylation reactions leading to hexaMB and heptaMB$^+$ are much faster than the reactions leading to isotopic scrambling.

This allowed synthesis of hexaMB and heptaMB$^+$ with ^{12}C atoms in the ring, and^{13}C-methyl carbons by working at low temperatures. The results of the isotopic labeling experiments are in excellent agreement with a mechanism where heptaMB$^+$ ions rearrange and form alkyl side chains that are eliminated as olefins. The activation energy for scrambling ring and methyl carbons has been determined to be about 105 kJ/mol.

Acknowledgment

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

Appendix

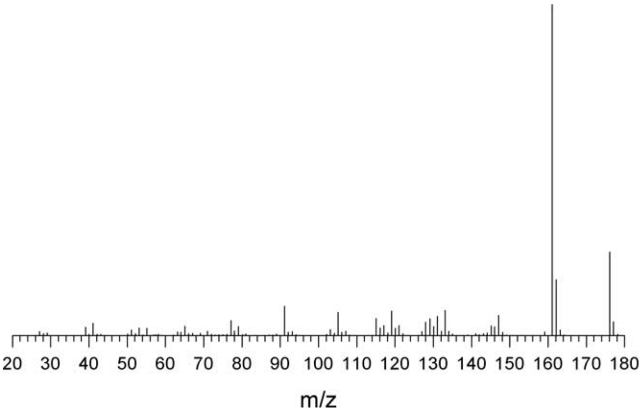


Fig. A1. Mass spectrum of HMMC, 70 eV.

References

[1] J.F. Haw, Phys. Chem. Chem. Phys. 4 (2002) 5431.
[2] C.D. Chang, Catal. Rev. 25 (1983) 1.
[3] M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3.
[4] C.D. Chang, in: C. Song, J.M. Garcés, Y. Sugi (Eds.), Shape-Selective Catalysis: Chemicals Synthesis and Hydrocarbon Processing, in: ACS Symposium Series, Vol. 738, Washington, DC, 2000.
[5] I.M. Dahl, S. Kolboe, Catal. Lett. 20 (1993) 329.
[6] I.M. Dahl, S. Kolboe, J. Catal. 149 (1994) 458.
[7] I.M. Dahl, S. Kolboe, J. Catal. 161 (1996) 304.
[8] J.F. Haw, J.B. Nicholas, W. Song, F. Deng, Z. Wang, T. Xu, C.S. Heneghan, J. Am. Chem. Soc. 122 (2000) 4763.
[9] Ø. Mikkelsen, P.O. Rønning, S. Kolboe, Micropor. Mesopor. Mater. 40 (2000) 95.
[10] B. Arstad, S. Kolboe, Catal. Lett. 71 (2001) 209.
[11] B. Arstad, S. Kolboe, J. Am. Chem. Soc. 123 (2001) 8137.
[12] W. Song, H. Fu, J.F. Haw, J. Phys. Chem. B 105 (2001) 12839.
[13] W. Song, H. Fu, J.F. Haw, J. Am. Chem. Soc. 123 (2001) 4749.
[14] W. Song, J.F. Haw, J.B. Nicholas, C.S. Heneghan, J. Am. Chem. Soc. 122 (2000) 10726.
[15] A. Sassi, M.A. Wildman, J.F. Haw, J. Phys. Chem. B 106 (2002) 8768.
[16] W. Song, J.B. Nicholas, A. Sassi, J.F. Haw, Catal. Lett. 81 (2002) 49.
[17] A. Sassi, M.A. Wildman, H.J. Ahn, P. Prasad, J.B. Nicholas, J.F. Haw, J. Phys. Chem. B 106 (2002) 2294.
[18] M. Bjørgen, U. Olsbye, S. Kolboe, J. Catal. 215 (2003) 30.
[19] W. von E. Doering, M. Saunders, H.G. Boyton, H.W. Earhart, E.F. Wadley, W.R. Edwards, G. Laber, Tetrahedron 4 (1958) 178.
[20] B. Arstad, S. Kolboe, O. Swang, J. Phys. Chem. B 106 (2002) 12722.
[21] R.F. Sullivan, C.J. Egan, G.E. Langlois, R.P. Sieg, J. Am. Chem. Soc. 83 (1961) 1156.
[22] M. Bjørgen, S. Kolboe, Appl. Catal. A 225 (2002) 285.
[23] P. Magnoux, P. Roger, C. Canaff, V. Fouche, N.S. Gnep, M. Guisnet, Stud. Surf. Sci. Catal. 34 (1987) 317.
[24] S. Braun, O.-H. Kalinowski, S. Berger, 150 and More Basic NMR Experiments, Wiley–VCH, New York, 1998.
[25] B. Arstad, J.B. Nicholas, J.F. Haw, J. Am. Chem. Soc., to appear.
[26] Ø. Mikkelsen, S. Kolboe, Micropor. Mesopor. Mater. 29 (1999) 173.