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Mechanistic insight into the methanol-to-hydrocarbons reaction

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Abstract

For nearly 30 years, it has been known that methanol may 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 [C.D. Chang, Catal. Rev. 25 (1983) 1; M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3; C.D. Chang, Shape-selective catalysis: chemicals synthesis and hydrocarbon processing, in: C. Song, J.M. Garcés, Y. Sugi, (Eds.), ACS Symposium Series, vol. 738, Washington, DC, 2000; J.F. Haw, Phys. Chem. Chem. Phys. 4 (2002) 5431; J.F. Haw, W. Song, D.M. Marcus, J.B. Nicholas, Acc. Chem. Res. 36 (5) (2003) 317]. We here aim at presenting some major contributions to today's rather unified view on the MTH reaction mechanism, and, based on this detailed knowledge, to point at possible options for optimizing the performance of MTH catalysts.

Keywords: Hydrocarbons; Methanol; MTH reaction; Mechanism

1. The hydrocarbon pool

Initial work on the MTH mechanism 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 [1–5]. Ten years ago evidence did, however, appear that the reaction mainly proceeds by a mechanism where a pool of adsorbed hydrocarbons is all the time adding methanol and splitting off ethene, propene and possibly even higher homologues (Fig. 1) [6–8]. Today, the importance of the initial C–C bond formation is considered to be minor [9] and the hydrocarbon pool mechanism is gaining general acceptance [4].

The hydrocarbon pool was initially not further specified, but during the last few years, it has become clear that methylbenzenes play central roles in the hydrocarbon pool mechanism and are essential parts of the catalytic cycle: already in 1983, Mole et al. observed that toluene acts as a "cocatalyst" for the MTH reaction over H-ZSM-5 [10,11]. In 2000, Mikkelsen et al. observed isotopic scrambling in the olefinic products when cofeeding ^{12}C-toluene and ^{13}C-methanol over H-ZSM-5 [12]. In a parallel study, Sassi et al. showed that polymethylbenzenes fed over H-beta zeolite are active for olefins formation [13]. In 2001, Arstad and Kolboe studied the organic material trapped inside SAPO-34 after switching from a ^{12}C-methanol feed to a ^{13}C-methanol feed [14]. They observed isotopic scrambling in all polymethylbenzenes, especially the higher homologues. Further, they analysed the olefinic products after the ^{12}C/^{13}C switch and observed that the isotopic distribution of the olefinic products changed only gradually, strongly pointing to polymethylbenzenes as being the active hydrocarbon pool in the SAPO-34 catalyst.

An interesting feature when considering the cited contributions is that similar conclusions have been drawn for quite different zeotype systems. *The role of polymethylbenzenes as the major hydrocarbon pool species appears to be independent of the zeotype catalyst chosen.* The exact nature of the hydrocarbon pool species may however depend on the catalyst type and reaction conditions, and polymethylnaphtalenes and cyclopentadienyl species have also been shown to function as hydrocarbon pool species [4].

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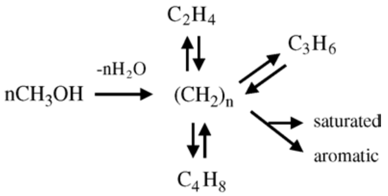


Fig. 1. The hydrocarbon pool mechanism. From Ref. [7].

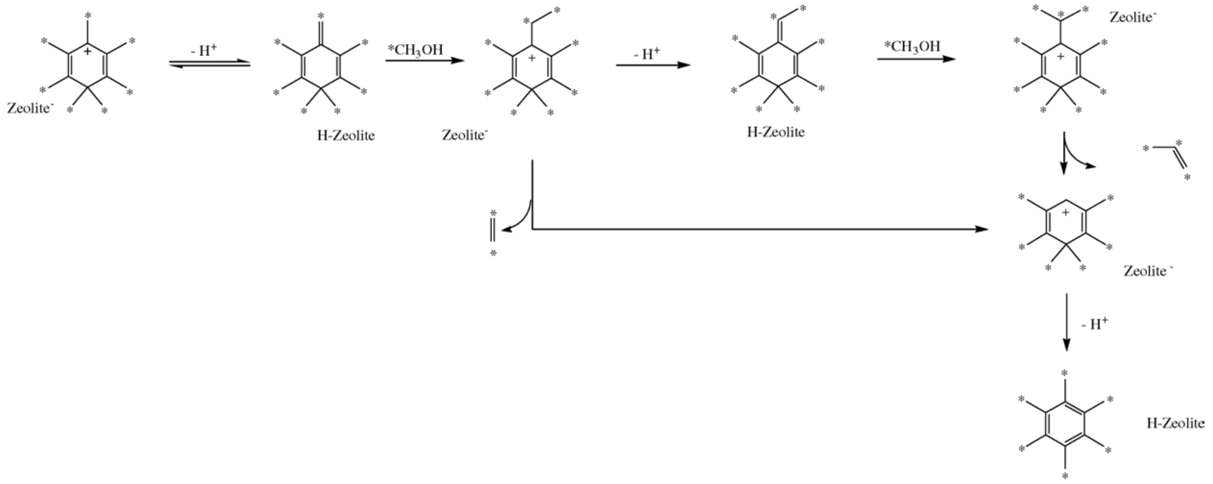
2. Product formation

Most detailed studies of the reactivity of polymethylbenzenes have been carried out over H-beta zeolite, not least because the 12-ring pore structure allows direct feeding of polymethylbenzenes. In H-beta zeolite, it has been shown that hexamethylbenzene has, by far, the highest reactivity for product formation, compared to lower polymethylbenzenes [13]. It has further been shown that the amount of hexaMB retained inside the pores during the MTH reaction decreases dramatically when stopping the methanol feed and flushing the zeolite with inert gas [15]. The decrease is accompanied by continued production of gas phase products.

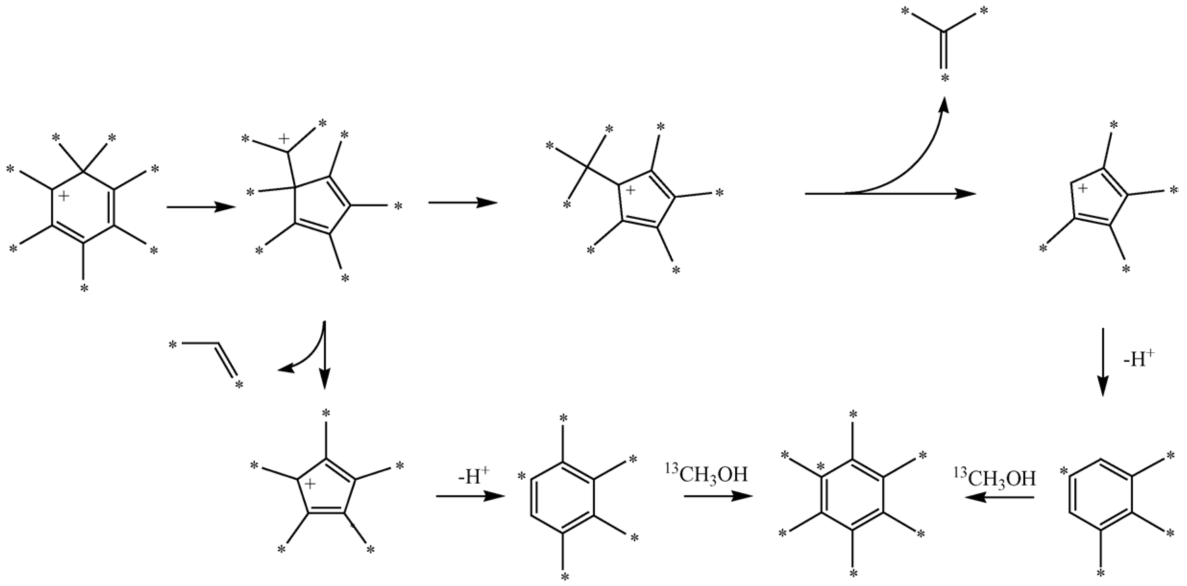
Under methylating conditions, hexaMB may take up a CH_3^+ ion and form the heptamethylbenzenium ion (heptaMB$^+$). This was demonstrated in 1958 by Doering and co-workers who studied the Friedel-Craft methylation of benzene [16]. They also observed an equilibrium between heptaMB$^+$ and its corresponding base, 1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene (HMMC). In 2002, Song et al. observed the heptaMB$^+$ ion inside H-beta zeolite by NMR spectroscopy [17]. One year later, Bjørgen et al. isolated heptaMB$^+$ trapped inside H-beta during (methanol + benzene) reaction, as HMMC, and analysed it ex situ by NMR spectroscopy [18]. Recently, protonation of polymethylbenzenes in H-beta zeolite has been used to probe its acid strength, as measured by IR- and UV–vis spectroscopy. It was shown that tetraMB and higher homologues are protonated, while triMB is not, inside the H-beta zeolite micropores [19,20].

The acid strength of the zeolite is a key parameter in discussing possible reaction paths of the formed heptaMB$^+$ ion. Two main reaction paths have been proposed, the exocyclic methylation route, and the ‘‘paring’’ reaction. In the exocyclic methylation route, first proposed by Mole et al. [10,11] and later refined by Haw et al. [5], heptaMB$^+$ is deprotonated into HMMC. The exocyclic double bond then undergoes reaction with an incoming methanol molecule, resulting in an ethyl group on the benzene ring, which is subsequently dealkylated as ethene (Scheme 1). Also propene formation is possible from this reaction scheme, while butene formation is not, due to steric hindrance [21]. Theoretical calculations indicated that the rate-determining step in the exocyclic methylation route is deprotonation of the HeptaMB$^+$ ion, and that the essential intermediate in the MTH cycle is two *gem*-methyl groups attached to the aromatic ring [21]. Evidence was found that the ethene-to-propene ratio could be increased by decreasing the number of methyl groups on the aromatic ring [21].

The ‘‘paring’’ mechanism, introduced by Sullivan et al. in 1961 [22] suggests alkyl side chain growth by ring contraction/expansion (Scheme 2). The paring mechanism will lead predominantly to propene and isobutene formation. It will further lead to a carbon atom interchange between the ring and the substituents (Scheme 2). In a recent study, methylbenzenes consisting of a ^{12}C-benzene ring and ^{13}C-methyl groups were obtained by reacting ^{13}C-methanol and ^{12}C-benzene over zeolite H-beta. The isotopic distribution of the gas phase products strongly suggested a paring type mechanism to dominate in the olefin formation over this zeolite [18]. However, it might be possible to favour the exocyclic methylation route, and thereby adjust the reaction selectivity, by using a catalyst with sites having a lower acid strength.



Scheme 1. The exocyclic methylation reaction. Adapted from Ref. [5].



Scheme 2. The paring reaction. Adapted from Ref. [18] (* denotes ^{13}C in both schemes).

3. Parallel reactions

In the 1980s, Dessau and co-workers suggested that the MTH reaction proceeds via sequential methylation of light olefins into higher olefins, which are easily cracked into lower olefins that are again methylated [23,24]. Recently, Svelle et al. studied the methylation of ^{12}C-ethene, -propene and -butene with ^{13}C-labelled methanol at low contact times over a H-ZSM-5 catalyst [25,26]. It was observed that the methylation reaction is first order in the olefin and zero order in methanol, for all olefins studied, and that the methylation rate increases in the order ethene < propene < butene. A major finding was that alkene interconversion reactions are severely suppressed by the presence of methanol. The isotopomer distribution in the products further confirmed that methylation, oligomerisation, polymethylbenzene (hydrocarbon pool) formation and cracking reactions all take place in parallel in the catalyst, again underlining the extremely complicated reaction pattern that constitutes the MTH reaction.

4. Catalyst deactivation

Coking is a major challenge in MTH processes. The individual influence of catalyst topology, acid strength and acid site density, respectively, on coke formation is not yet fully understood. Dahl et al. compared the stability of SAPO-34 and its zeolite analogue, chabazite, with different Si/Al ratios, for the MTH reaction. They concluded that the acid site density was the most important parameter for the deactivation behaviour, although a smaller influence of acid strength was also observed [27]. When topology permits (SAPO-34 and H-beta zeolite), methylbenzenes may be converted to polycyclic aromatics and, finally, to coke, with time-on-stream [15,28,29]. Isotopic labelling studies of the methylaromatic products retained inside the pores of H-beta zeolite under MTH-like conditions, strongly indicated that the lowest naphthalene derivative, dihydro-trimethylnaphtalene is formed from the heptaMB^{+} ion [15]. This result may imply that the heptaMB^{+} ion is an important intermediate not only for gaseous product formation, but also for coke formation.

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