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Conversion of methanol to hydrocarbons over zeolite H-ZSM-5: On the origin of the olefinic species

Morten Bjørgen [a,*], Stian Svelle [b], Finn Joensen [a], Jesper Nerlov [a], Stein Kolboe [b], Francesca Bonino [c], Luisa Palumbo [c], Silvia Bordiga [c], Unni Olsbye [b]

[a] *Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark*
[b] *Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway*
[c] *Department of Inorganic, Physical and Materials Chemistry, NIS Centre of Excellence, and Centro di Riferimento INSTM, University of Turin, Via P. Giuria 7, I-10125 Torino, Italy*

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Abstract

This study examined the reaction mechanism with respect to both catalyst deactivation and product formation in the conversion of methanol to hydrocarbons over zeolite H-ZSM-5. The reactivity of the organics residing in the zeolite voids during the reaction was assessed by transient $^{12}C/^{13}C$ methanol-switching experiments. In contrast to previously investigated catalysts (H-SAPO-34 and H-beta), hexamethylbenzene is virtually unreactive in H-ZSM-5 and is thus not a relevant reaction intermediate for alkene formation. However, the lower methylbenzenes are reaction intermediates in a hydrocarbon pool-type mechanistic cycle and are responsible for the formation of ethene and propene. An additional reaction cycle not applicable for ethene also must be taken into account. The C_{3+} alkenes are to formed through rapid alkene methylation and cracking steps to a considerable extent; thus, methanol is converted to hydrocarbons according to two catalytic cycles over H-ZSM-5. Moreover, in contrast to what occurs for large-pore zeolites/zeotypes, molecules larger than hexamethylbenzenes are not built up inside the H-ZSM-5 channels during deactivation. Thus, deactivation is explained by coke formation on the external surface of the zeolite crystallites only. This is a plausible rationale for the superior lifetime properties of H-ZSM-5 in the methanol-to-hydrocarbon reaction.

Keywords: ZSM-5; MFI; MTO; MTH; MTG; Methanol; Zeolite; Mechanism; Hydrocarbon pool; Coking; Deactivation

1. Introduction

The current pricing of crude oil has led to increased interest in the use of natural gas or coal as a feedstock for the production of gasoline and petrochemicals. Methanol can be made from such feedstocks via synthesis gas and further converted into gasoline-range hydrocarbons or alternatively light, possibly polymer-grade alkenes. The zeolite-catalyzed conversion of methanol to hydrocarbons is commonly referred to as the MTH reaction, but because process conditions and catalyst choice alter product selectivity, the abbreviations MTO (methanol to olefins) and MTG (methanol to gasoline) are frequently used depending on the desired products.

The MTH chemistry and its commercial potential have been known for decades. The energy crisis in the 1970s sparked new interest in MTG technology. In the late 1970s, the New Zealand government decided to build the world's first facility for producing gasoline from natural gas via methanol [1]. In 1986, a plant with a planned annual gasoline production of 600,000 tons over a H-ZSM-5 catalyst was started up, but, due to the subsequent drop in crude oil prices, only the methanol synthesis step was left on stream. The Topsøe integrated gasoline synthesis (TIGAS) process of Haldor Topsøe AS, also based on H-ZSM-5 as the catalyst, was demonstrated on a pilot scale in the mid-1980s [2]. However, the TIGAS process was never scaled up due to the situation in the global energy market. Later, more attention was paid to the MTO reaction, and the manufacturing of polymer-grade ethene and propene from methanol using the UOP/Norsk Hydro technology was demonstrated in a demo

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[*] Corresponding author.
E-mail address: mobj@topsoe.dk (M. Bjørgen).

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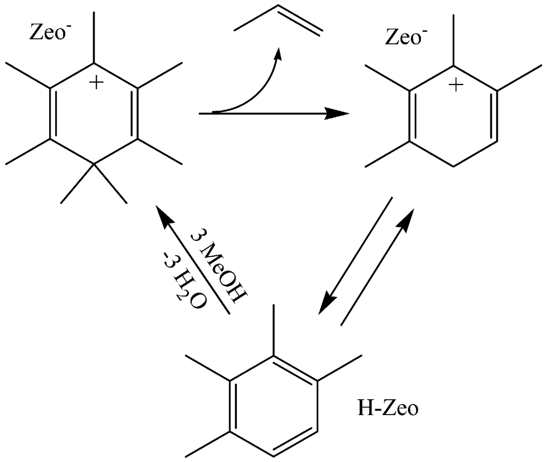
plant [3]. The catalyst choice for the UOP/Norsk Hydro MTO process is the silicoaluminophosphate H-SAPO-34. Lurgi developed a process specifically aiming at selectively converting methanol into propene (MTP) over H-ZSM-5, and the process was demonstrated in a joint Lurgi/Statoil demo plant.

Today, commercial interest in MTG is again increasing, and activities involving both natural gas and coal as feedstocks are emerging. New-generation methanol plants designed to produce larger amounts of product at significantly lower cost are due to come online within the next 5 years, which will increase the profit and interest in methanol downstream activities.

Over the years, the complex mechanism of the MTH reaction has posed a challenge to catalysis investigators. In a simplified route of the MTH reaction, methanol is dehydrated under formation of dimethyl ether and water, followed by formation of alkenes from this equilibrium mixture of oxygenates. The longstanding question has been the specific mechanism behind this latter step, in which C–C bonds are formed from oxygenates (methanol/dimethyl ether). There is presently strong evidence disfavoring direct mechanisms in which methanol/dimethyl ether molecules are combined to form, for example, ethene during steady-state conversion [4–6]. Hunger and co-workers [7,8] have published data indicating that a direct route from methanol/dimethyl ether to hydrocarbons may operate during an induction period. However, this direct route most likely operates at a rate so low as to be eclipsed by even trace impurities of higher alcohols/hydrocarbons in the methanol feed, the catalyst, or the carrier gas.

On the other hand, an all-dominating indirect route known as the "hydrocarbon pool mechanism" has been gradually accepted in recent years. The hydrocarbon pool mechanism was conceptually introduced by Dahl and Kolbe in the early 1990s [9,10], and more recent independent contributions [11–24], have led to an in-depth description of the MTH reaction mechanism. The hydrocarbon pool has been described as a catalytic scaffold composed of larger organic molecules adsorbed in the zeolite to which methanol/dimethyl ether is added and from which alkenes and water are formed in a closed cycle, in which high-energy intermediates are avoided.

The identity and the operation of the hydrocarbon pool have been fairly well described for some specific systems, in particular zeolite H-beta [16–21] and H-SAPO-34 [13–15]. For these catalysts, the hydrocarbon pool has been identified as highly methyl-substituted benzene rings ("polymethylbenzenes") or the benzenium cations derived thereof. In the wide pore beta zeolite, the terminal benzene methylation product (i.e., the heptamethylbenzenium cation) is unquestionably the species responsible for the major part of alkene formation. According to the hydrocarbon pool mechanism over the beta zeolite, the heptamethylbenzenium cation splits off (at least) propene and butene under a concomitant formation of the tetra- and trimethylbenzenium ions, respectively. The heptamethylbenzenium cation is then reformed by subsequent methylation of these lower polymethylbenzenium ions (after deprotonation) by methanol/dimethyl ether, thus completing the cycle. A simplified representation of this reaction cycle is outlined in Scheme 1. The hexaMB plays a similar role in H-SAPO-34.



Scheme 1. Suggested hydrocarbon pool mechanism for propene formation from the heptamethylbenzenium cation over zeolite H-beta.

To date, the most extensive fundamental mechanistic understanding has been attained for the H-SAPO-34 and H-beta catalysts, and many aspects may vary with, for example, pore architecture and also possibly catalyst acidic strength/density. In the present contribution, the mechanism of the MTH reaction over H-ZSM-5, the archetype MTH catalyst, was pursued. Main attention was given to the buildup and reactivity of the organics trapped within the zeolite voids. This work demonstrates that the reaction scheme for alkene formation from methanol over H-ZSM-5 is different than those drawn previously for H-beta and H-SAPO-34. In addition to a modified hydrocarbon pool mechanism, wherein ethene is formed from the lower methylbenzenes, a parallel C_{3+} alkene methylation/cracking cycle is operative. We mentioned this latter property in a recent communication [25]; the present work supplements this with more extensive data and a more thorough discussion.

2. Experimental

2.1. Catalyst and catalyst characterization

A commercially available H-ZSM-5 (Si/Al = 140) from Zeolyst International was used in this study. Powder X-ray diffraction (XRD) was performed in Bragg-Brentano parafocusing geometry using a Philips X'Pert Pro vertical T-T diffractometer and Cu$K\alpha$ radiation. The FTIR transmission spectra were collected using a cryogenic cell allowing high-temperature treatment of the sample in vacuum. The sample was pretreated at 500 °C for 1 h and kept at −213 °C during the subsequent CO adsorption/desorption. A detailed description of the cryogenic cell (consisting of a modified closed-circuit liquid He Oxford CCC 1204 cryostat) is available elsewhere [26]. The spectra were acquired at a resolution of 1 cm^{-1} by averaging 128 interferograms on a Bruker Equinox-55 FTIR spectrometer. The BET surface area was obtained from a Quantachrome Autosorb by N_2 adsorption at −196 °C. The sample was outgassed at 350 °C for 18 h before the N_2 adsorption measurement.