

## Conversion of Methanol into Hydrocarbons over Zeolite H-ZSM-5: Ethene Formation Is Mechanistically Separated from the Formation of Higher Alkenes

Stian Svelle,<sup>†</sup> Finn Joensen,<sup>‡</sup> Jesper Nerlov,<sup>‡</sup> Unni Olsbye,<sup>†</sup> Karl-Petter Lillerud,<sup>†</sup> Stein Kolboe,<sup>†</sup> and Morten Bjørgeren<sup>\*†</sup>

*Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark, and Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway*

Received August 10, 2006; E-mail: mobj@topsoe.dk

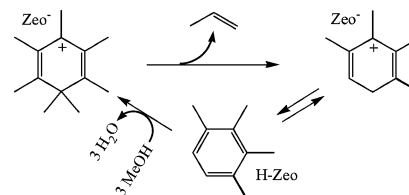
Understanding and obtaining product control have always been a major challenge in the development of heterogeneous catalysts. On the basis of fundamental mechanistic findings, this work outlines ways of controlling the product selectivity in the conversion of methanol to hydrocarbons. Methanol can be produced from natural gas or any gasifiable carbonaceous material, such as petroleum, coal or biomass. The conversion of methanol to hydrocarbons is generally denoted as the MTH reaction, but as process conditions and catalyst choice affect the selectivities, the abbreviations MTO (methanol to olefins), MTP (methanol to propene), and MTG (methanol to gasoline) are often used.

The MTH reaction mechanism has been debated intensively for decades.<sup>1</sup> It is well documented that methanol molecules cannot be coupled directly into hydrocarbons at rates relevant to steady-state conversion,<sup>2–4</sup> and recent results from the groups of Haw and Kolboe are clearly in favor of an indirect reaction route.<sup>5,6</sup> An indirect route, known as “the hydrocarbon pool mechanism”, was outlined in the early 1990s.<sup>7,8</sup> The hydrocarbon pool was described as a catalytic scaffold, constituted by large organics adsorbed in the zeolite, to which methanol is added and olefins are eliminated in a closed catalytic cycle. Hence, an active MTH catalyst can be viewed as an organic–inorganic hybrid material constituted by the inorganic zeolite and the organic hydrocarbon pool. For H- $\beta$ <sup>9</sup> and H-SAPO-34,<sup>10</sup> the main catalytic engines of the hydrocarbon pool are the higher methylated benzenes or their cationic derivatives. For H- $\beta$ , the heptamethylbenzenium cation displays the greatest reactivity, whereas hexamethylbenzene behaves similarly in H-SAPO-34. A simplified representation of this cycle, exemplified by propene formation from heptamethylbenzenium over H- $\beta$ , is outlined in Scheme 1.

Clearly, the detailed reaction mechanism varies with, for example, pore architecture and possibly also catalyst acid strength. H-ZSM-5 is the archetype MTG catalyst and also the catalyst in Lurgi’s MTP process, and in this report we show that for H-ZSM-5 (1) the higher methylbenzenes are present in the zeolite pores, but they are virtually unreactive; (2) ethene appears to be formed exclusively from the lower methylbenzenes; (3) propene and higher alkenes are to a considerable extent formed from alkene methylations and interconversions (e.g., cracking reactions). The two latter statements, implying that the ethene formation is mechanistically separated from the formation of higher alkenes, are of utmost importance for understanding and possibly controlling the ethene/propene selectivity in MTO/MTP catalysis.

Methanol (WHSV = 7.0 gg<sup>−1</sup>h<sup>−1</sup>) was reacted from gas-phase (130 hPa) over 60 mg H-ZSM-5 (Si/Al = 140) in a fixed bed reactor at 350 °C. <sup>12</sup>C methanol was fed for 18 min before switching to <sup>13</sup>C methanol (99% purity) and reacting further for a predetermined

Scheme 1



time. The time evolution of the <sup>13</sup>C content in the effluent was determined from GC–MS analyses performed 0.5, 1.0, and 2.0 min after the <sup>12</sup>C/<sup>13</sup>C methanol switch. Corresponding isotopic data for the organic material retained in the zeolite pores during reaction were obtained from three parallel experiments by thermally quenching the reaction after 0.5, 1.0, and 2.0 min of <sup>13</sup>C methanol reaction. These three catalyst samples were dissolved in 15% HF, and the liberated organics were extracted from the aqueous phase with CH<sub>2</sub>Cl<sub>2</sub> and analyzed with GC–MS.

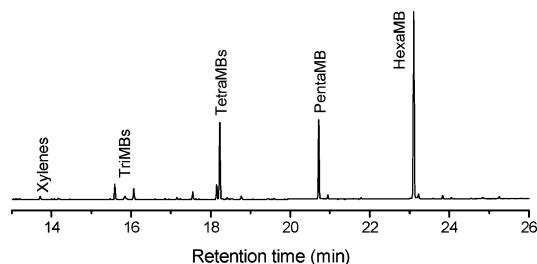
The major products in the effluent, as determined by GC–FID at 20 min on stream were C<sub>2</sub> (10 C %, mainly ethene), C<sub>3</sub> (30 C %, mainly propene), butenes (14 C %), butanes (5 C %), C<sub>5+</sub> alkenes and aromatics (40 C %), and traces of methane. The conversion of methanol/dimethyl ether was 73% (see Supporting Information, Table S1 for further details). These results are typical for low aluminum H-ZSM-5 under the conditions employed.

The material retained within the catalyst was also analyzed after 20 min on stream by the HF dissolution procedure, and the GC–MS chromatogram of the CH<sub>2</sub>Cl<sub>2</sub> extract is shown in Figure 1. The chromatogram is dominated by a few compounds, all of them are methylbenzenes (MBs), ranging from minor amounts of xylenes via triMBs to larger amounts of tetra-, penta-, and hexaMB. TetraMB (durene) is the largest hydrocarbon able to diffuse out of the zeolite pores (detectable in the effluent), implying that penta- and hexaMB are truly trapped within the catalyst, probably residing in the channel intersections. The chromatogram in Figure 1 is representative for a wider range of reaction conditions and H-ZSM-5 catalyst samples. Finally, for this sample, the compositions of the gas phase and the retained material remain stable for several days under these conditions.

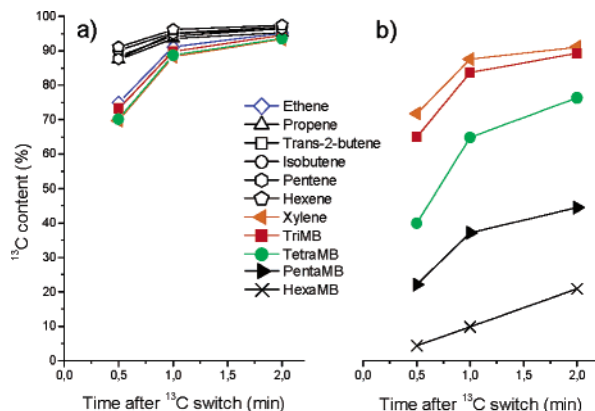
The pathway of methanol incorporation into both gas-phase products and retained compounds was investigated using <sup>13</sup>C labeling as described above. The time evolutions of total <sup>13</sup>C content for the gas phase and retained hydrocarbons are shown in Figure 2a and 2b, respectively. Strikingly, 0.5 min after <sup>12</sup>C/<sup>13</sup>C methanol switch, the gas-phase products are divided into two groups (Figure 2a). The <sup>13</sup>C contents in the C<sub>3</sub>–C<sub>6</sub> alkenes are very similar (87–91%), whereas the second distinct group, that is, ethene and the aromatics, contain considerably less <sup>13</sup>C (70–75%). The same grouping is discernible also after 1 min, but the difference has

<sup>†</sup> Center for Materials Science and Nanotechnology.

<sup>‡</sup> Haldor Topsøe A/S.



**Figure 1.** Chromatogram (GC-MS) of retained compounds. Prior to HF dissolution, the catalyst was exposed to methanol for 20 min at 350 °C.



**Figure 2.** Time evolution of  $^{13}\text{C}$  content in effluent (a) and retained material (b) after  $^{12}\text{C}/^{13}\text{C}$  methanol feed switch.

become smaller and disappears after 2 min of  $^{13}\text{C}$  methanol reaction, as the system approaches complete isotope exchange.

Xylenes and triMB are present both in the effluent and among the retained material (Figure 2b). The isotopic composition of the xylenes is virtually identical in both cases, whereas the  $^{13}\text{C}$  content in triMB is slightly lower for the retained molecules. Further, Figure 2b shows an evident trend in the  $^{13}\text{C}$  content in the higher methylbenzenes: The incorporation of  $^{13}\text{C}$  is slower as the number of methyl groups increases. The low rate of  $^{13}\text{C}$  incorporation of hexaMB in particular, is in stark contrast to data obtained in a similar manner for H- $\beta$  and H-SAPO-34 where hexaMB unquestionably has the highest reactivity.<sup>9–11</sup> As a direct implication of this, it may be stated that a hydrocarbon pool mechanism involving the highest methylbenzenes, proven to be all dominating for H- $\beta$  and H-SAPO-34, cannot be applicable to the H-ZSM-5 catalyst. Rather, on the basis of the practically identical  $^{13}\text{C}$  contents and time evolutions, ethene formation proceeds via the xylenes and/or the triMBs. Ethene formation from xylenes and triMBs is in accord with results from Haw and co-workers,<sup>12,13</sup> showing that the lower methylbenzenes yield predominantly ethene, whereas the higher analogues favor propene. The exact mechanism for ethene elimination cannot be assessed based on the current data, but Haw and co-workers<sup>14,15</sup> have also shown that methylated cyclopentenyl cations are integral to alkene formation on H-ZSM-5 and suggested that these compounds are equilibrated with other, active carbon species. No five rings are found among the retained compounds in our experiments, even so it seems likely that both five- and six-membered rings are involved in alkene formation.<sup>9</sup>

The higher  $^{13}\text{C}$  content in the  $\text{C}_3$ – $\text{C}_6$  alkenes (Figure 2a) compared to ethene (and the aromatics) must be attributed to  $^{13}\text{C}$

incorporation by another mechanism, and the only satisfactory explanation is alkene methylations followed by cracking of the larger alkenes thus formed. For example, immediately after  $^{12}\text{C}/^{13}\text{C}$  methanol switch, a  $^{12}\text{C}_3$  propene may be methylated repeatedly four times, yielding a  $^{12}\text{C}_3^{13}\text{C}_4$  heptene, which may in turn be cracked into  $^{13}\text{C}$  enriched propene and butene. This cycle of  $\text{C}_3$ + alkenes methylation/cracking reactions is related to the scheme originally proposed by Dessau.<sup>16</sup> However, according to that scheme ethene is reequilibrated with the higher alkenes, and cracking is the only route for ethene formation. This is not in compliance with our data as the discrepancy between the  $^{13}\text{C}$  content in ethene and the  $\text{C}_3$ – $\text{C}_6$  alkenes excludes any measurable ethene formation via this alkene based cycle, that is, ethene is not an alkene cracking product.

The above discussion leads to an interesting question regarding mechanistic understanding and selectivity control: *Do the  $\text{C}_3$ + alkene cycle and the aromatics/ethene cycle run independently?* This is probably not the case for H-ZSM-5, as the constant production of aromatics during methanol conversion means that some of the  $\text{C}_3$ + alkenes continuously form new aromatics. This means that for H-ZSM-5 the aromatics/ethene cycle cannot run without the  $\text{C}_3$ + alkene cycle. Inversely, on the basis of the low reactivity of ethene toward methanol relative to that of propene and butenes,<sup>17</sup> the contribution to the  $\text{C}_3$ + alkenes involving ethene is very small and might not be required for the  $\text{C}_3$ + alkene cycle to occur. Finally, the significance of propene formation from the methylbenzenes cannot be evaluated at this point.

In conclusion, if it were possible to separate these two cycles, by sterically suppressing the formation of the larger aromatics (e.g., by altering the topology) and allowing product formation to occur only via the  $\text{C}_3$ + alkenes, formation of ethene might be avoided in an MTP application.

**Supporting Information Available:** Product details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) Stöcker, M. *Microporous Mesoporous Mater.* **1999**, *29*, 3–48.
- (2) Song, W.; Marcus, D. M.; Fu, H.; Ehresmann, J. O.; Haw, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 3844–3845.
- (3) Marcus, D. M.; McLachlan, K. A.; Wildman, M. A.; Ehresmann, J. O.; Kletnieks, P. W.; Haw, J. F. *Angew. Chem., Int. Ed.* **2006**, *45*, 3133–3136.
- (4) Lesthaeghe, D.; Van Speybroeck, V.; Marin, G. B.; Waroquier, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1–10.
- (5) Haw, J. F.; Song, W.; Marcus, D. M.; Nicholas, J. B. *Acc. Chem. Res.* **2003**, *36*, 317–326.
- (6) Olsbye, U.; Bjørger, M.; Svelle, S.; Lillerud, K.-P.; Kolboe, S. *Catal. Today* **2005**, *106*, 108–111.
- (7) Dahl, I. M.; Kolboe, S. *Catal. Lett.* **1993**, *20*, 329–336.
- (8) Dahl, I. M.; Kolboe, S. *Stud. Surf. Sci. Catal.* **1995**, *98*, 176–177.
- (9) Bjørger, M.; Olsbye, U.; Petersen, D.; Kolboe, S. *J. Catal.* **2004**, *221*, 1–10.
- (10) Arstad, B.; Kolboe, S. *J. Am. Chem. Soc.* **2001**, *123*, 8137–8138.
- (11) Bjørger, M.; Olsbye, U.; Kolboe, S. *J. Catal.* **2003**, *215*, 30–44.
- (12) Song, W.; Fu, H.; Haw, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4749–4754.
- (13) Arstad, B.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 2991–3001.
- (14) Haw, J. F.; Nicholas, J. B.; Song, W.; Deng, F.; Wang, Z.; Xu, T.; Heneghan, C. S. *J. Am. Chem. Soc.* **2000**, *122*, 4763–4775.
- (15) Goguen, P. W.; Xu, T.; Barich, D. H.; Skloss, T. W.; Song, W.; Wang, Z.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 2650–2651.
- (16) Dessau, R. M. *J. Catal.* **1986**, *99*, 111–116.
- (17) Svelle, S.; Rønning, P. O.; Olsbye, U.; Kolboe, S. *J. Catal.* **2005**, *234*, 385–400.

JA065810A