Methanol-to-Olefin Process

DOI: 10.1002/ange.200602488

Insights into the Mechanism of Methanol-to-Olefin Conversion at Zeolites with Systematically Selected Framework Structures[**]

Zhi-Min Cui, Qiang Liu, Wei-Guo Song,[*] and Li-Jun Wan[*]

Methanol-to-olefin (MTO) conversion[1,2] is essentially about how an initial ethylene C–C bond is formed from a C_1 species. In recent years, a hydrocarbon pool mechanism proposed by Dahl and Kolboe[3] has gained wide supports for post-induction-time MTO chemistry.[4–13] The organic intermediates, which are referred to as the hydrocarbon pool, serve as platforms to which C_1 species can bind and from which primary olefin products can dissociate. Polymethyl benzenes are the most active hydrocarbon pool species on HSAPO-34.[8,11,13,14] On ZSM-5, cyclopentenyl cations play an important role.[4] Though there is little doubt that ethylene is dissociated from some much larger organic species when the reaction proceeds beyond induction time, with possible routes include paring and side-chain-growth mechanisms,[6,10,15,16] the exact mechanism of how ethylene is formed is still not clear largely as a result of complications from secondary reactions, which make it hard to differentiate primary products from secondary products.

There is an ongoing debate about what happens during the induction time.[13,17–21] Besides the hydrocarbon pool mechanism, several direct mechanisms have been proposed to explain at least the initial olefin formation during the induction time.[2] A direct mechanism involves only C_1 species to form the C–C bond. Haw and co-workers argued that organic impurities in the methanol feed were responsible for forming the initial small amount of hydrocarbon pool species.[19] The contribution from certain direct mechanisms was questioned by H/D exchange studies on dimethyl ether.[21] A recent theoretical study by Waroquier and co-workers found a prohibitively high energy barrier for direct C–C bond formation from various C_1 species.[20] In contrast,

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[*] Z.-M. Cui, Q. Liu, Prof. W.-G. Song, Prof. L.-J. Wan
Beijing National Laboratory for Molecular Sciences (BNLMS)
Institute of Chemistry
The Chinese Academy of Sciences
Beijing, 100080 (P.R. China)
Fax: (+86) 10-6255-7908
E-mail: wsong@iccas.ac.cn
wanlijun@iccas.ac.cn

[**] The authors thank the Natural Science Foundation of China (20121301), the Ministry of Science and Technology of China (2006CB806101), and the Chinese Academy of Sciences for financial support. Z.-M.C. and Q.L. thank Professor Chun-Li Bai for valuable advice.

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Hunger and co-workers contended that C–C bonds could be formed directly from surface methoxy groups.[17,18]

Herein, we approach these issues from a new angle by using zeolites with systematically selected framework structures. We report that the MTO reaction takes place only on zeolites that allow the hydrocarbon pool mechanism to work. In the absence of complications from secondary reactions, H/D exchange was observed on toluene even when no olefins were produced, thus implying a paring-type mechanism for the MTO process.

The zeolites used in this study included ZSM-11 (MEL), ZSM-22 (TON), SAPO-34 (CHA), and SAPO-5 (AFI). The pore structures of these zeolites are schematically illustrated to highlight the essence of each framework in Figure 1. These zeolites were selected on the basis of the maximum diameter of a sphere that could be included in the framework.[22] ZSM-11 and ZSM-22 have similar pore openings; however, the channel intersections in ZSM-11 enable it to accommodate a sphere with a diameter of 0.77 nm, as compared to 0.57 nm for ZSM-22, which has parallel channels. SAPO-5 also has parallel channels, but a sphere as big as 0.82 nm can be fitted into the framework. SAPO-34 has small pore openings of 0.38 nm, yet its cagelike framework allows a sphere with a diameter of 0.73 nm to be encapsulated.

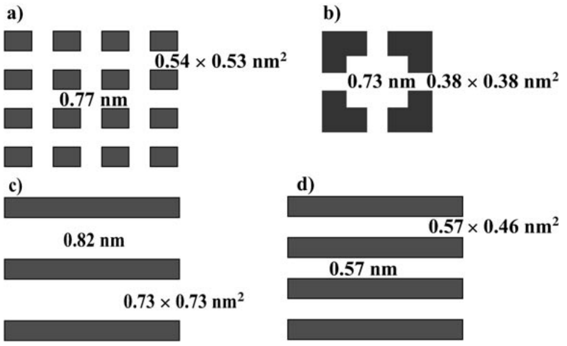


Figure 1. Illustration of zeolite pore structures: a) MEL structure of ZSM-11; b) CHA structure of SAPO-34; c) AFI structure of SAPO-5; and d) TON structure of ZSM-22. The values inside the pores indicate the maximum diameter of a sphere that can be included in the framework, and those outside the pores indicate the size of the pore openings.[22]

Gas chromatography (GC) profiles following the 20th pulse of methanol on zeolites at 400 °C are depicted in Figure 2. Prior to that, the catalysts were pretreated with 19 identical pulses of methanol to ensure that the catalysts were in stable working conditions. ZSM-11, SAPO-34, and SAPO-5 showed various MTO activities. Methanol conversion on SAPO-34, ZSM-11, and SAPO-5 was about 80 %, 90 %, and 70 %, respectively (Figure 2 a–c). Meanwhile, methanol conversion on the TON framework (ZSM-22) was dramatically different from the other three catalysts. ZSM-22 showed a low but appreciable production of olefins during the first few pulses of methanol, probably as a result of an impurity ZSM-11 phase and/or external acid sites. However, the amount of olefins quickly decreased to essentially zero when most of those active sites were deactivated after a few pulses (Figure 2 d).

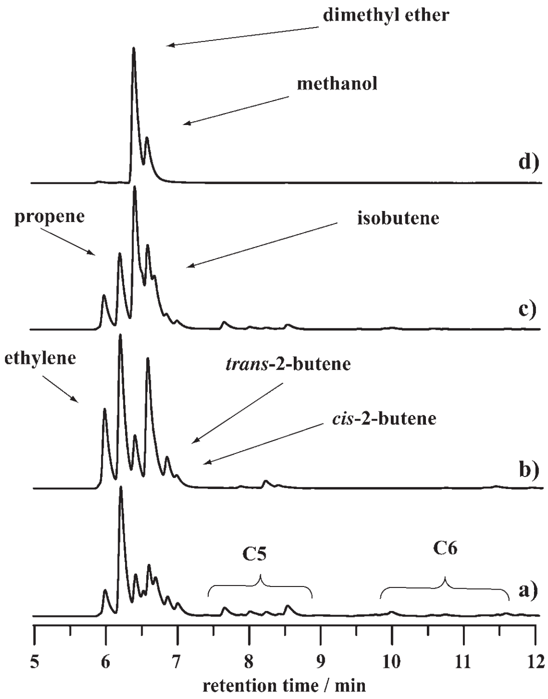


Figure 2. GC profiles of methanol pulsed onto various zeolites at 400 °C. a) ZSM-11; b) SAPO-34; c) SAPO-5; and d) ZSM-22. Samples were taken 8 seconds after methanol pulses. All signals are from a FID detector.

A mixture of methanol and toluene (10:1 v/v) was pulsed onto SAPO-5, ZSM-11, and ZSM-22 at different temperatures (SAPO-34 was excluded from these experiments because its channel opening of 0.38 nm did not allow toluene to enter its cage). At 250 °C, essentially no olefin was produced using any of the catalysts, although various aromatics were detected from the gas stream or from acid-digested catalysts. At 350 °C and 400 °C, methanol conversion was about 90 % on SAPO-5 and ZSM-11. However, no olefins were detected from ZSM-22; only a small amount of xylene was detected.

The failure of ZSM-22 to convert methanol into olefins even with toluene present is mechanistically significant. Parker and Bibby reported that KZ-2 (a zeolite that also has a TON framework) did not show appreciable MTO activity,[23] but at the time of that study the authors could not relate its inactivity to its implication in the MTO mechanism. Mole et al. proposed that toluene takes on a role as co-catalyst in the MTO process,[24] which may explain the high conversions on SAPO-5 and ZSM-11 (90 %) at 350 °C. The major difference between a very active MTO catalyst, ZSM-11, and a non-active MTO catalyst, ZSM-22, is the absence of channel intersections on the latter, which limits the size of the intermediates that can be formed inside the pores to 0.57 nm or less. The hydrocarbon pool mechanism is a space-demanding process, which involves cyclic organic intermediates that require a space larger than that which ZSM-22 can offer (0.57 nm). Thus, ZSM-22 cannot accommodate a complete hydrocarbon pool mechanism cycle and consequently is not an active MTO catalyst. Meanwhile, SAPO-5 has the same type of 1D channel as ZSM-22 but with much larger pore sizes (0.82 nm), thus it is a very active MTO catalyst.

Zeolites are known for their shape selectivity, and the present results are an elegant example of transition-state shape selectivity. ZSM-22 failed as an MTO catalyst because the hydrocarbon pool mechanism did not work on this catalyst. These findings further support the arguments that the hydrocarbon pool mechanism might be the only working mechanism for methanol conversion under these reaction conditions.[19–21] Thus, ZSM-22 provides a pore system to study MTO mechanisms in detail without complications from secondary reactions.

CD_3OH was used to study H/D exchange in methanol and toluene co-injection experiments. A very informative H/D exchange pattern was observed on toluene in the volatile products. At 250 °C, when no olefin was produced from any of the catalysts, no H/D exchange of toluene was observed on SAPO-5, but substantial H/D exchange was observed with ZSM-11 and ZSM-22. The ion-mass distribution of toluene at 250 °C is shown in Figure 3. At higher temperatures, toluene showed more extensive H/D exchange; for example, on ZSM-22 more than half of the toluene molecules present contained one or more deuterium atoms at 350 °C. Table 1 reveals the temperature dependence of H/D exchange of toluene on ZSM-22, ZSM-11, and SAPO-5.

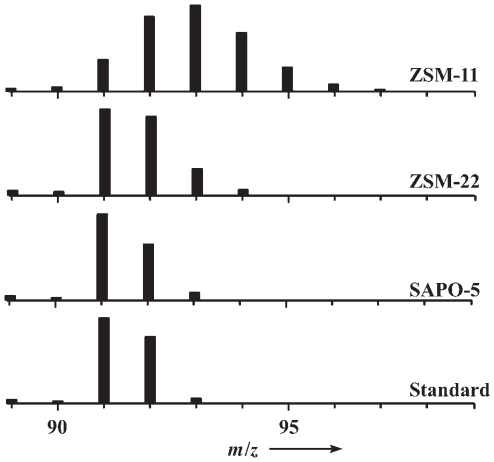


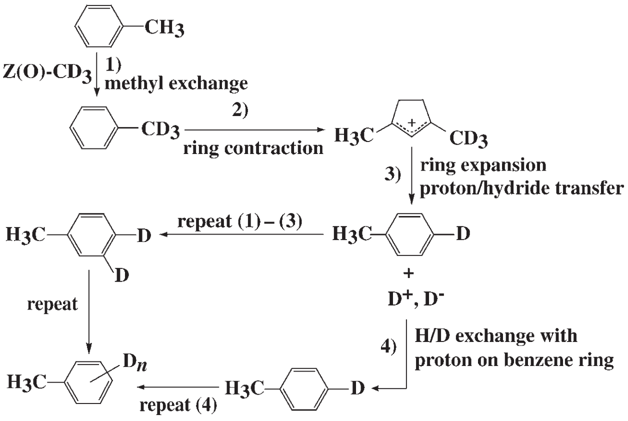
Figure 3. Mass distributions of toluene ions obtained from co-injection of CD_3OH and toluene at 250 °C onto various zeolites.

These findings, especially from the toluene H/D exchange study on ZSM-22 at all temperatures at which no olefin was produced, might provide clues to the detailed mechanism of MTO conversion. 1) As surface methoxy groups or the methyl group on methanol cannot directly undergo H/D exchange with acid-site protons,[25] toluene H/D exchange did not result from direct H/D exchange between protons on the benzene ring and deuterated acid sites. 2) As no olefin was produced on ZSM-22, partially deuterated toluene could not be derived from other highly methylated benzenes that have undergone H/D exchange.[11] 3) The deuterium atoms were incorporated into toluene one by one and not as CD_3 (Figure 3 shows that the [M+3] peak did not dominate). This means that, aided by toluene, the C–D bond on CD_3OH was activated for H/D exchange, but the process did not produce any olefin.

Table 1: Isotopic distribution of deuterium on toluene from H/D scrambling at different temperatures.

Zeolite	T [°C]	Distribution of [D_n]toluene [%]					
		[D_0]	[D_1]	[D_2]	[D_3]	[D_4]	[D_5]
ZSM-22	250	75.4	20.5	3.5	0.3	0	0.3
	350	41.8	39.3	14.7	3.7	0.5	0
	400	25.8	40.6	23.0	4.6	6.0	0
ZSM-11	250	17.7	34.2	30.1	14.3	3.7	0
	350	10.4	23.4	32.6	23.4	0.6	1.3
	400	0.8	19.5	32.2	25.9	11.1	2.5
SAPO-5	250	100	0	0	0	0	0
	350	59.6	16.9	17.2	3.0	3.3	0
	400	28.0	24.3	24.4	16.3	5.5	1.5

Here we propose an indirect mechanism for toluene H/D exchange on ZSM-22. The simplified mechanism is illustrated in Scheme 1. CD_3OH readily forms surface methoxy groups on ZSM-22 acid sites.[13] When toluene is adsorbed inside the pore, because of the confinement effect due to the well-matched sizes of the toluene molecule and the ZSM-22 pore,[26] some of the toluene undergoes methyl exchange with surface methoxy groups to produce [D_3]toluene ($C_6H_5CD_3$). This then undergoes a partial paring mechanism, that is, ring contraction and expansion (steps 2 and 3 in Scheme 1), but stops short of producing any olefin. Steps 2 and 3 involve multiple proton- and hydride-transfer steps, and D^+ and D^- in step 3 could also undergo H/D exchange with toluene. Indeed, deuterium atoms were thus incorporated into toluene as observed in the H/D exchange study. The extent of H/D scrambling increased significantly from 250 °C to 400 °C, as expected from the process shown in Scheme 1. The choice of CD_3OH as donor of deuterium atoms was crucial in



Scheme 1. Mechanism for toluene H/D exchange. Z = zeolite.

experimental design; facile exchange between acid-site protons, benzene protons, and methanol hydroxy protons was not observed as it involved the same isotope.

The same mechanism could be applied to ZSM-11 at 250 °C. No H/D exchange on toluene was observed on SAPO-5 at 250 °C, probably because the pore size of SAPO-5 was too large and the benefit of the confinement effect was minimal. Weaker acid sites on SAPO-5 might also lead to no H/D exchange. At higher temperatures, owing to complications from secondary reactions, results from ZSM-11 and SAPO-5 were difficult to interpret.

Scheme 1 suggests that C–H bonds on methanol groups were activated—which is an essential step in the MTO process—in the presence of toluene through a paring mechanism. The paring mechanism is thus supported as a possible mechanism for MTO conversions. Kolboe and Haw have speculated on the role of the paring mechanism for the MTO process.[6,10,16] In the present study, parts of the paring mechanism were observed in the MTO process for the first time in the absence of complications from secondary reactions.

More detailed studies are underway for a better understanding of MTO mechanisms. It seems that on ZSM-22 and similar zeolites, as a result of their pore structures, the hydrocarbon pool mechanism could proceed to a certain extent depending on the reaction conditions, but stops prior to the olefin formation step. It might be possible to find more detectable intermediates that are involved in hydrocarbon pool mechanisms without complications from secondary reactions, so as to develop a more detailed MTO reaction sequence. This invites joint efforts from both theoretical and experimental studies.

Experimental Section

All zeolite samples were synthesized according to reported methods.[8,27,28] See Supporting Information for details.

The MTO reaction was conducted on a home-built pulse quench reactor. In a typical pulse experiment, 30-mg samples of catalyst were loaded into a 6-mm (OD) stainless-steel tube, which was then heated to reaction temperature and maintained at that temperature for 1 hour under 100 SCCM nitrogen flow prior to the reaction. In pulse experiments, methanol (2 equiv) was pulsed onto the catalyst and GC samples were taken 8 seconds after the injections. The volatile compounds were analyzed with an Agilent 6890 GC equipped with a 50-m capillary column and a FID detector using published response factors.

In H/D scrambling studies, samples were analyzed offline. Volatile products were collected by bubbling exhaust gas into a liquid chloroform trap, while five identical pulses were injected into the reactor. Samples were analyzed with a Shimazu QP2010 GC-MS system equipped with a DB-5 30-m capillary column.

Received: June 21, 2006
Revised: July 21, 2006

Keywords: heterogeneous catalysis · isotopic labeling · methanol-to-olefin process · reaction mechanisms · zeolites

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