

The Role of Methoxy Groups in Methanol to Olefin Conversion

Zhi-Min Cui,^{†‡} Qiang Liu,^{†‡} Shao-Wei Bain,^{†‡} Zhuo Ma,^{†‡} and Wei-Guo Song^{*,†}

Beijing National Laboratory for Molecular Sciences, Chinese Academy of Sciences, Beijing 100080, People's Republic of China, and Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

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In a methanol-to-olefin conversion mechanism (MTO) study, by using zeolite ZSM-22's one-dimensional channels to exclude the hydrocarbon pool mechanism as well as secondary reactions, we found very low olefin yield during an extended reaction time under normal MTO conditions. More significantly, no H/D exchange between the acidic proton and the hydrogen atoms on methoxy groups was observed, even at elevated temperatures as high as 500 °C, suggesting no C–H activation for methoxy groups under normal MTO reaction conditions. In comparison, substantial H/D exchange was found on ethoxy groups. These results confirmed that methoxy groups are energetically not favored to form C–C bonds directly.

1. Introduction

Methanol-to-olefin (MTO) mechanisms have been intensively studied because of their importance in understanding solid acid catalysis and the potential of MTO process in providing basic chemical feed stocks for the chemical industry in the near future.^{1–5} On active MTO catalysts such as zeolite ZSM-5 and SAPO-34, the primary product of MTO is ethene. The hydrocarbon pool mechanism is now well accepted to explain the ethene formation,^{2–4,6–10} but how initial olefins (such as ethene and/or propene) and the earliest hydrocarbon pool species (such as polymethyl benzenes) are formed during the induction time of MTO process remains vague because of secondary reactions, which produce longer chain olefins, paraffin, and aromatics. During the so-called induction time in the MTO process, a very small amount of initial olefins is produced. The yields of the initial olefins are negligible compared to that of the olefins produced after induction time, but the initial hydrocarbon species are formed from these olefins.¹¹ The mechanism of how these initial olefins are formed is one of the central issues in solid acid catalysis, in that it not only concerns how hydrocarbon pool species are generated for MTO, but also relates to two fundamental processes in catalysis beyond MTO itself: C–C bond formation and C–H bond activation.^{12–15}

Surface methoxy groups are formed when methanol molecules react with acid sites of the zeolites. The role of methoxy groups in MTO reactions is an ongoing debate. Several researchers proposed mechanisms that involved methoxy-type species directly forming the initial ethene molecules,^{16–18} while others questioned such a role for the methoxy groups.^{19–21} However, in previous studies, zeolites such as ZSM-5 and SAPO-34 were used. The difficulty of studying the role of methoxy groups with these catalysts is that the induction time of MTO is very short (a few seconds), and, after induction time, secondary reactions dominate the MTO process, making it hard to track possible reactions between methoxy groups while other reactions are happening at much higher rates. In order to study the role of methoxy groups, we need to extend the induction time or

exclude the secondary reactions. On zeolite ZSM-22, because of its channel size restriction, hydrocarbon pool species are inhibited, so that the apparent induction time is infinitely long and there is no secondary reaction.²²

In this paper, we report our investigation of the methoxy groups' role during the MTO reactions, especially whether C–C bonds are readily formed directly from them. By using ZSM-22 to exclude the hydrocarbon pool mechanism, we found very low olefin yield during an extended reaction time at elevated reaction temperatures. More importantly, isotopic exchange results revealed no H/D exchange between the acidic proton and the hydrogen atoms on methoxy groups at temperatures as high as 500 °C, suggesting no C–H activation for methoxy groups under normal MTO reaction conditions. In comparison, substantial H/D exchange was found on ethoxy groups. These results confirmed that methoxy groups are energetically not favored to form C–C bonds directly under normal conditions.

2. Experimental Section

Materials and Reagents. Methanol (99.5%), potassium hydroxide (99.5%), and aluminum sulfate (99.5%) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.; 1,8-diaminooctane (98%) was bought from Acros; CD₃OH (99.5%), CH₃OD (99%), C₂H₅OD, and D₂O (99.8%) were supplied by Cambridge Isotope Laboratories, Inc. All chemicals were used as received without further purification. ZSM-22 (SiO₂/Al₂O₃ = 90) was synthesized as previously reported.²² The mean crystal size of the product obtained was about 500 nm.

Catalytic Testing. The MTO reaction was conducted on a home-built flow-and-pulse-type continuous reactor. In a typical experiment, a 30 mg catalyst sample was loaded into a 6 mm o.d. stainless tube, which was then heated to the desired reaction temperature and maintained at that temperature for 1 h under a 100 sccm nitrogen flow prior to the reaction.

In continuous flow experiments, reactants were introduced into the reactor by flowing 100 sccm nitrogen through a methanol bubbler. Assuming saturated vapor, the methanol feed rate was 48 h^{–1} WHSV. Gas chromatography (GC) samples were taken every 20 min during the time on stream experiments.

* Corresponding author. E-mail: wsong@iccas.ac.cn.

[†] Beijing National Laboratory for Molecular Sciences.

[‡] Graduate School of Chinese Academy of Sciences.

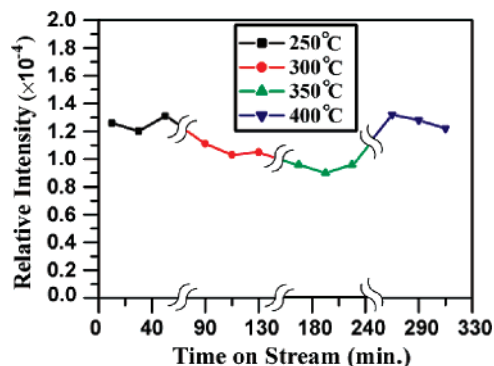


Figure 1. Propene's time on stream relative intensities to DME plus methanol at various temperatures when methanol was flowed onto ZSM-22 constantly.

The volatile compounds were analyzed by an Agilent 6890 GC system equipped with a 50 m capillary column (stationary phase: AT-PONA) and a flame ionization detector (FID).

In pulse-type experiments, desired reactants were pulsed into the reactor by continuous helium flow (100 sccm), and gas chromatography–mass spectrometry (GC-MS) samples were taken 8 s after the pulses. For isotopic exchange experiments, two sets of pulse experiments were carried out. The first set pulsed 2 equiv of CD_3OH (0.9 μL) onto HZSM-22 at a desired temperature, and GC-MS samples were taken 8 s after the injections. Then excessive CD_3OH (5 μL) was pulsed onto the catalyst three times with 5 min intervals to produce CD_3 -ZSM-22. After purging the reactor with helium for 30 min, 1 μL of H_2O was pulsed to liberate the methoxy group and produce dimethyl ether (DME) and methanol. For the second set of the experiment, excessive D_2O was first introduced into the catalyst bed to produce DZSM-22, and the system was then purged for 30 min, then either CH_3OD (0.5 μL) or $\text{CH}_3\text{CH}_2\text{OD}$ (0.7 μL) was pulsed onto the catalyst at various temperatures. The isotopic distribution of all volatile products were analyzed online by a Shimadzu QP2010S GC-MS system equipped with a 100 m capillary column (stationary phase: methyl silicone), and helium was the flowing gas in all pulse experiments.

3. Results and Discussions

Zeolite ZSM-22 is central to this work. Its one-dimensional parallel pores consist of channels with 0.57×0.46 nm pore mouths, and are able to accommodate 0.57 nm spheres inside the channels. We have shown that the hydrocarbon pool mechanism did not work on ZSM-22 since certain intermediates are too large to be able to fit inside the ZSM-22 channel. Since the hydrocarbon pool route is the main route for post induction time MTO process, inhibiting the hydrocarbon pool route will effectively stop the olefin formation and minimize the secondary reactions. Thus ZSM-22 can provide a ideal pore system for detailed studies on non-hydrocarbon-pool mechanisms.²²

In flow-type experiments at various temperatures, methanol was bubbled into the reactor at different temperatures. GC analyses results showed that essentially no olefin was produced from methanol flow on ZSM-22. However, trace amount of olefins (ethene and propene) can still be detected by FID. Figure 1 showed the time on stream relative intensities of propene to DME plus methanol (after response factor correction for FID²³) during the temperature series experiments. The propene to DME-plus-methanol ratio was used to roughly estimate propene yield as the combined yield of DME and methanol was stable. From 250 to 400 °C, the propene yield was constantly very low at

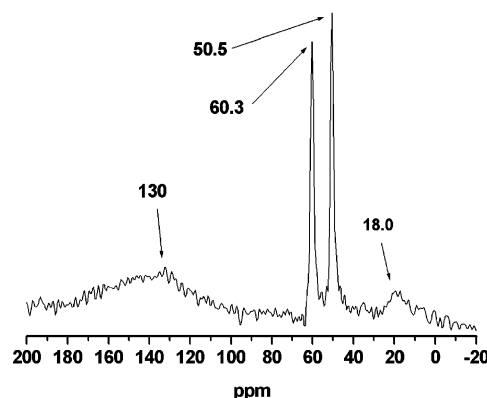


Figure 2. ^{13}C CP-MAS spectrum of ZSM-22 after a methanol- ^{13}C and toluene (5:1, v/v, 2 μL) pulse at 300 °C. Peaks are assigned to the rotor background signal (130 ppm), the surface methoxy group and adsorbed DME (60.3 ppm), adsorbed methanol (50.5 ppm), and methyl benzene (18.0 ppm). The spectrum was acquired at room temperature with a 2 ms contact time, a 2 s pulse delay, and 14 000 scans.

about 0.02% relative to that of DME plus methanol. The fact that the olefin yield is relatively constant in the temperature range from 250 to 400 °C indicates that the propene was not likely to be formed from catalytic reactions involving high-energy barriers. It is likely to be formed from impurities in the methanol (99.5%, with acetone as the major impurity compound). If propene were formed from a catalytic reaction involving methanol, its yield should have increased at higher temperatures.

Similar results were observed for ethene; however, the ethene yields were hard to measure from the GC data because of the presence of formaldehyde. Ethene has almost the same retention time as formaldehyde, which is from the oxidation of methanol by trace oxygen in the flow gas. GC spectra of the gaseous products from the temperature series experiments can be found in the Supporting Information.

On ZSM-22, although almost no olefin was detected, the catalyst was able to catalyze methanol dehydration to DME for quite a long time without any noticeable deactivation. Methylation of toluene was also facile on this zeolite. When methanol- ^{13}C and toluene were co-injected into the reactor, no olefins were formed as reported before,²² but xylene was detected from the volatile product. Solid-state NMR spectrum (Figure 2) of the catalysts showed methyl groups (ca. 20 ppm) from polymethyl benzene, and dominating peaks from surface methoxy groups (ca. 60 ppm) and methanol (ca. 50 ppm) on the zeolite, indicating methylation of the acid sites. Pulsing water to such methylated catalyst produced methanol and DME. Acid digestion of the zeolites also generated a substantial amount of methanol (hydrolysis product of methoxy groups). All these findings indicated the formation of a methoxy group on ZSM-22, as Hunger et al. have reported on other zeolites.¹

The role of these methoxy groups is the focus of this study. Methylation of the acid sites is inevitable and might even be necessary for MTO.¹⁷ It has been reported that surface methoxy groups could react with other C1 species to directly form ethene.^{1,17} In this study, since there was no olefin contribution from the hydrocarbon pool mechanism, an accurate measurement of olefins formed from methoxy groups reacting with other C1 species could be obtained. As Figure 1 showed, olefin formation on ZSM-22 was very low at normal MTO reaction temperatures. It seemed that forming C–C bonds directly from two methoxy type C1 species was difficult, if not impossible. The reason for such difficulty may due to the high-energy barrier of C–H activation on the methoxy groups.

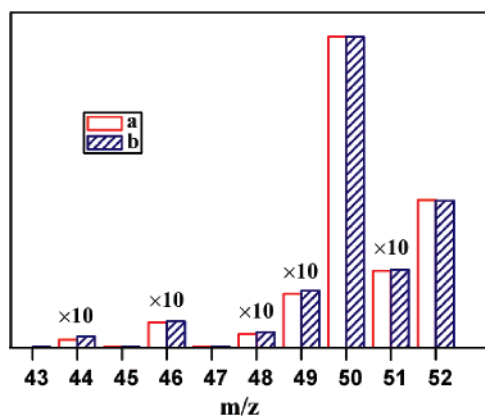


Figure 3. Molecular ion mass distribution for DME when (a) CD_3OH is pulsed onto HZSM-22 at 350 °C, and (b) for DME produced by pulsing H_2O onto HZSM-22 after pulsing 5 μL of CD_3OH three times at 350 °C. The intensities of the small peaks are enhanced 10 times as labeled.

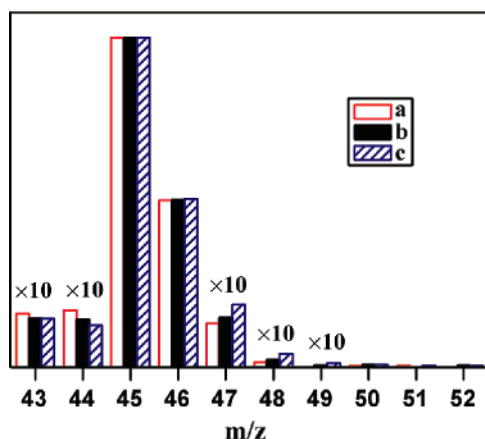


Figure 4. Molecular ion mass distribution for DME product when CH_3OD is pulsed onto DZSM-22 at 200 °C (a), 400 °C (b), and 500 °C (c). The intensities of the small peaks are enhanced 10 times as labeled.

C–H bond activation is at the heart of catalysis. If a methoxy group was involved in forming ethene with other C1 species, it must undergo C–H activation. C–H activation will lead to H/D exchange, and the extent of such an exchange will increase at higher temperatures.^{19,20} Thus we carried out H/D exchange experiments. Two sets of experiments were designed: the first set was CD_3OH pulses onto HZSM-22; the second set was CH_3OD onto DZSM-22 (generated by pulsing excessive D_2O onto HZSM-22). DME was chosen as the probe molecule for two reasons: its formation involves the methoxy groups, and acidic protons are involved in the formation of methoxy groups. In this study, DME is essentially the only product in the gas stream, so that determining the extent of H/D becomes straightforward and unambiguous.

Figures 3 and 4 show the molecular ion mass distributions of DME from the two sets of experiments mentioned above. In the first set of experiments, DME was produced when CD_3OH was pulsed directly onto HZSM-22. After pulsing CD_3OH onto HZSM-22 three times, H_2O was pulsed to liberate methoxy groups, and DME was also formed. The DME from the different experiments showed exactly the same mass pattern (Figure 3), and quantitative hydrogen distribution showed no sign of H/D exchange (Table 1). The finding that there was no H/D exchange on DME from the water pulse is significant. In this experiment, the DME was generated from the methoxy groups, which have a long resident time inside the ZSM-22 channel and plenty of

TABLE 1: Quantitative Results of the Number of H Atoms in Product DME in Various Situations

	H ₀	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆
a ^a	98.5	0.7	0.01	0.01	0.01	0.8	0.01
b ^b	98.1	1.1	0.01	0.01	0.01	0.8	0.01

^a Product DME produced by pulsing CD_3OH onto HZSM-22 at 350 °C. ^b Product DME produced by pulsing H_2O onto HZSM-22 that was treated by 5 μL of CD_3OH three times at 350 °C.

TABLE 2: Quantitative Results of the Number of D Atoms in Product DME Produced by Pulsing CH_3OD onto DZSM-22 at Various Temperatures

	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆
200 °C	98.0	1.1	0.8	0.01	0.1	0.01	0.01
300 °C	98.0	1.2	0.7	0.01	0.1	0.01	0.01
400 °C	97.9	0.9	1.0	0.01	0.2	0.01	0.01
500 °C	97.7	1.0	1.1	0.01	0.2	0.01	0.01

opportunity to undergo H/D exchange with protons on the acid sites nearby, so the lack of H/D exchange suggested that C–H activation on the methoxy groups is highly unlikely.

In the second set of experiments, CH_3OD was used. In order to generate a condition for the protons on methyl groups to exchange with the deuterium on acid sites, HZSM-22 was treated with D_2O to produce DZSM-22 prior to the CH_3OD pulses. In temperature series experiments, no H/D exchange was detected from 200, 400, and 500 °C, respectively, when CH_3OD was pulsed onto DZSM-22. Figure 4 shows the same mass pattern of the molecular ion of DME at different temperatures. Deuterium distributions were calculated from the GC-MS data using a computer simulation program and are listed in Table 2. Note that there are small D₁ and D₂ populations in Table 1 and 2. We believe that these populations are not from actual H/D exchange, but rather from the deviations of simulation results from raw GC-MS data. However, the temperature dependences of the extents of H/D exchange were much more decisive than absolute numerical calculation results to determine whether H/D exchange had occurred. Table 2 and Figure 4 show no temperature dependence of deuterium population from 200 to 500 °C, which is beyond the normal MTO reaction temperature range. These data established that there is no H/D exchange and C–H bond activation on methoxy groups.

In a similar study, Marcus et al. observed no H/D exchange on DME using HSAPO-34 as the catalyst.²⁰ Because HSAPO-34 is an active MTO catalyst, during their H/D exchange experiments, the catalyst cages were filled with hydrocarbon pool species, and a large amount of olefins was expected to be generated. The presence of the hydrocarbon pool species and olefin products sidetracks the central question: whether C–H bonds are activated on methoxy groups.²⁴ In the present study, because no olefin and no hydrocarbon pool species were formed on ZSM-22, and the only organic species on ZSM-22 were methoxy groups (as well as physical/chemical adsorbed methanol and DME, all C1 species), the lack of H/D exchange and C–H activation on methoxy groups was conclusive.

The dynamic range of an MS detector is much lower than that of an FID detector, so, in H/D exchange experiments, no olefin was detected. If we were able to detect trace olefins, as figure S1 showed, deuterium distribution of the olefins would have been very informative. On the other hand, since olefins are prone to H/D exchange even at relatively low temperatures,^{14,25} the origins of the olefins cannot be definitely identified simply from their deuterium distributions.

In comparison, when $\text{C}_2\text{H}_5\text{OD}$ was pulsed onto the DZSM-22, besides dominate ethene production (from ethanol dehydra-

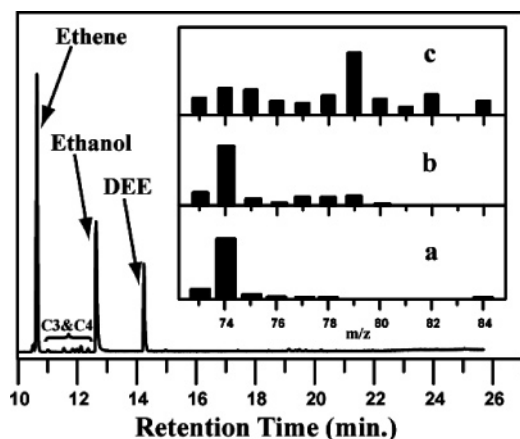


Figure 5. GC profiles of C_2H_5OD pulsed onto DZSM-22 at 300 °C, which has been fully deuterated by D_2O . Inset is the mass distribution for product DEE at (b) 300 °C and (c) 350 °C. Panel a is the standard mass distribution of normal DEE for comparison.

TABLE 3: Quantitative Results of the Number of D Atoms in Product DEE Produced by Pulsing C_2H_5OD onto DZSM-22 at Various Temperatures

	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	D ₉	D ₁₀
250 °C	99.9	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
300 °C	67.0	6.3	1.5	7.9	7.8	9.1	0.4	0.01	0.01	0.01	0.01
350 °C	12.8	11.9	5.5	4.4	8.7	32.6	6.7	2.4	9.3	0.01	5.7

tion), a small amount of diethyl ether (DEE) was detected at 350 °C or lower temperatures, as shown in Figure 5. Mass analyses of these DEE molecules showed substantial H/D exchange on the ethyl groups (Table 3). As expected, the extent of H/D exchange increased observably at higher temperatures. Surface ethoxy groups were found to be relatively stable on the zeolite HY.¹⁸ Apparently, ethoxy groups were also formed on ZSM-22, and C–H bonds on them were readily activated. The main product ethene also showed a certain extent of H/D exchange, but, as mentioned earlier, the H/D exchange on ethene most likely occurred after ethene was formed.

4. Conclusion

C–C bond formation is of particular importance in solid acid catalysis. Theoretical studies have shown that the energy barrier required to form C–C bonds directly from C1 species is very high because of the lack of a means to delocalize electrons.^{19,26} On methoxy groups, the methyl group is directly bonded to an oxygen atom, which is electron negative. The oxygen atom in a methoxy group probably destabilizes the possible intermediate or transition state of the possible C–H activation process. On the other hand, C–H activation on an ethyl group is less influenced by the oxygen, and H/D exchange was observed on DEE. The results in this study are direct and conclusive experimental evidence that supports the previous theoretical doubts on the role of methoxy groups in forming C–C bonds between them under normal MTO conditions. The role of methoxy groups in MTO is to be the methylation agent for the

hydrocarbon species, as studied experimentally and theoretically,^{7,27,28} and is not involved in direct ethene formation.

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Supporting Information Available: GC profiles of methanol flow onto ZSM-22 at different temperatures. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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