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Direct observation of olefin homologations on zeolite ZSM-22 and its implications to methanol to olefin conversion

Zhi-Min Cui [a,b,c], Qiang Liu [a,b,c], Zhuo Ma [a,b,c], Shao-Wei Bian [a,b,c], Wei-Guo Song [a,b,*]

[a] *CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, the Chinese Academy of Sciences, 100190, PR China*
[b] *Beijing National Laboratory for Molecular Sciences (BNLMS), Beijing, 100190, PR China*
[c] *Also in the Graduate School, the Chinese Academy of Sciences, PR China*

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ABSTRACT

In this paper, we studied olefin homologation reactions on zeolite ZSM-22, whose one dimensional pore structure inhibited the hydrocarbon pool mechanism and secondary reactions of the methanol to olefin (MTO) conversion. Homologation of ethylene, propylene and styrene were directly observed between ^{13}C labeled methanol and olefins. Isotopic tracking shows high selectivity for homologation reaction, e.g. from ethylene, propene has one ^{13}C atom, butene has two ^{13}C atoms, and pentene has three ^{13}C atoms. Homologation of styrene's side chain also showed very specific isotopic pattern. The role of olefin homologation is speculated as a key reaction during the induction time of MTO process.

1. Introduction

Methanol to olefin (MTO) process involves perhaps all acid catalyzed reactions, many of which are secondary reactions and have no methanol involved at all [1–4]. A few such examples include olefin polymerization, cracking, aromatization, coking. The dominance of these secondary reactions in MTO process is a major obstacle for chemists to find the detailed mechanism of how methanol is converted to primary olefins.

The hydrocarbon pool mechanism seems to be able to explain the formation of primary olefins [1,5]. In MTO process, ethylene is truly a primary product [6]. The essence of hydrocarbon pool mechanism is the organic intermediate called hydrocarbon pool. Methanol must react first with an organic intermediate, either a polymethyl benzene [7] or a cyclic carbenium cation [8], then the organic intermediates produce the primary olefins. How initial hydrocarbon species are formed is unclear. We have shown that zeolite ZSM-22 with TON framework, due to its relatively small pore channels (0.57 nm, one dimension), is unable to complete the catalytic cycle in the hydrocarbon pool mechanism and is unable to efficiently convert methanol to olefins [9]. On the other hand, since the space inside ZSM-22 is large enough for reactions involving only small species, we hope that such space restriction can provide an ideal condition for studying certain reactions in MTO process without complications from the secondary reactions.

One such reaction is olefin homologation (methylation of the olefin C=C double bond). During the MTO process, methanol can react with olefins, and olefins increase their chain lengths stepwise, i.e. one carbon by one carbon. Olefin homologation was proposed to be a key step in the MTO process by Dessau et al. early in 1980s [10,11]. Several mechanistic studies indicate that olefin homologation reactions exist [12–14]. However, it is very difficult to directly observe the homologation of the olefins because in MTO process, reactions caused by the hydrocarbon pool and secondary reactions overwhelm all other reactions. Recently, Svelle et al. have studied the kinetic of methylation reactions of olefins over ZSM-5. A very small amount of catalyst (2.5 mg) and extremely high reactant (mixture of methanol and short chain olefin) feed rate were used in their experiments, so that the secondary reactions were limited [15,16]. The contributions of olefin homologation in practical MTO reactions using HZSM-5 or SAPO-34 as catalysts are hard to assess, because it is difficult to separate olefin homologations from other reactions.

In our previous study, we found that hydrocarbon pool mechanism and subsequent secondary reactions are inhibited on zeolite ZSM-22 [9]. The smaller pore size of ZSM-22 was believed to be the reason for such inhibition. In this study, we chose zeolite ZSM-22 to study the olefin homologation reaction. On this catalyst, without the complication from side reactions, we directly observed the homologations of simple olefins such as ethylene, propene, butene, and styrene. By labeling methanol with ^{13}C, the homologation products show precise isotope distribution as expected, e.g.

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* Corresponding author at: CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, the Chinese Academy of Sciences, 100190, PR China. Fax: +86 10 62557908.
E-mail address: wsong@iccas.ac.cn (W.-G. Song).

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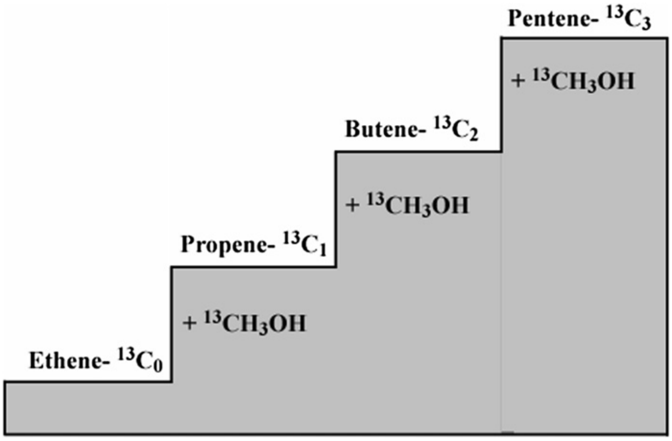

Fig. 1. Schematic illustration of ethylene homologation sequence.

from ethylene, propene has one ^{13}C atom, butene has two ^{13}C atoms, and pentene has three ^{13}C atoms (Fig. 1). Olefin homologation may be a key step during the MTO induction time to generate initial hydrocarbon species.

2. Experimental

2.1. Catalyst

Zeolite ZSM-22 (TON structure, $SiO_2/Al_2O_3 = 90$) was synthesized as reported in the previous report [9]. X-ray Diffraction (XRD) pattern of the zeolite was acquired with a Rigaku D/max-2500 diffractometer (Cu$K\alpha$ target). XRD pattern demonstrated that the obtained zeolite ZSM-22 was a pure crystalline phase with the TON structure. The zeolite was calcined at 600 °C for 10 h to remove the template agent and then converted to proton form by a conventional ion-exchange technique using an aqueous solution of 10 wt% NH_4NO_3.

2.2. Reagents

$^{13}CH_3OH$ (99% ^{13}C) and CD_3OH (99% D) were purchased from Cambridge Isotope Laboratories Inc., and normal methanol (99.5%), ethanol (99.5%), propanol (99.5%), butanol (99.5%) and styrene (99%) were purchased from Beijing Chemical Reagent Co. All chemicals were used as received.

2.3. Catalytic testing

Homologation reaction and MTO reactions were carried out on a pulse type flow reactor. In a typical experiment, 50 mg catalyst sample was loaded into a 6 mm OD (3 mm ID) stainless tube. The reactor was then heated to reaction temperature and remained at that temperature for 1 h under 100 SCCM helium flow; then the reactant were pulsed onto the catalyst using a six-port valve. GC samples were taken 8 s after the pulses. A Shimadzu-QP2010S GC-MS system equipped with a 100 m capillary column (stationary phase: methyl silicone) and a Agilent 6890 GC system equipped with a flame ionization detector (FID) were used to analyze the products.

3. Results and discussions

ZSM-22 is a key catalyst in this study. Its one dimensional parallel pores are consisted of channels with 0.57 × 0.46 nm pore mouth [9]. Its one dimensional pores can only accommodate organic species with the size of 0.57 nm or less. However, some intermediate in the hydrocarbon pool is larger than 0.57 nm, so the hydrocarbon pool mechanism is inhibited. As a result, MTO activity is very low on ZSM-22. Fig. 2a shows that dimethyl ether (DME) was the only major product when MeOH was pulsed onto the catalyst.

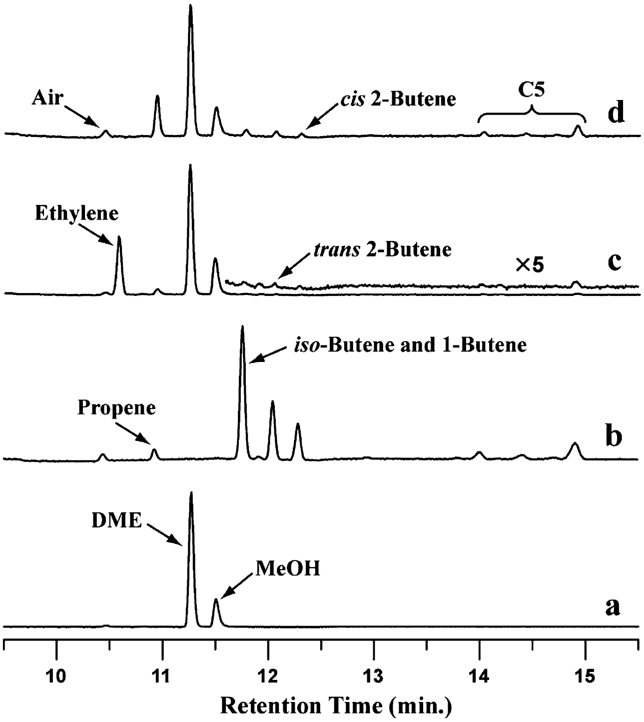

Fig. 2. GC profiles of (a) MeOH pulse; (b) butanol pulse; (c) MeOH/EtOH (5:1, V/V); and (d) MeOH/*iso*-PrOH (5:1, V/V) on ZSM-22. All reactions were carried out at 350 °C.

Though hydrocarbon pool mechanism was inhibited on ZSM-22, and essentially no olefins are produced from MTO reaction, ZSM-22's pores are still big enough for reactions such as olefin oligomerization, cracking and rearrangement. Fig. 2b shows that after a butanol pulse, propene and pentene as well as 1-butene, *iso*-butene, *cis*- and *trans* 2-butene are produced. The presence of propene and pentene was likely due to the dimerization of butene and subsequent cracking of octane. The presence of the 2-butene and *iso*-butene was due to the skeleton rearrangement or double bond shift reactions of 1-butene. However, with excess methanol, olefin oligomerization will be limited because methanol is preferentially adsorbed on the active sites. The olefin uni-molecular rearrangement reactions such as skeleton rearrangements do not change the olefin chain length. These provide ideal conditions for studying the reaction between olefin and methanol.

With no overwhelming secondary reactions on ZSM-22, olefin homologation reaction can be directly observed. Methanol and ethanol (for ethylene) or propanol (for propene) mixture are pulsed onto the catalysts. Primary olefin such as ethylene or propene is generated in situ by dehydration of respective alcohols. Soon after the primary olefin is produced, it homologates with MeOH to extend its olefin chain. Fig. 2c shows that small amounts of propene, butene and pentene along with large amount of ethylene are produced when a mixture of MeOH and EtOH is pulsed onto ZSM-22 at 350 °C. Similarly, after a MeOH/*iso*-PrOH pulse, butene and pentene are produced besides propene (Fig. 2d). The yield of homologations is quite low, especially for ethylene. This agrees well with Svelle et al.'s finding that ethylene is not very reactive in MTO [16].

The best way to examine the olefin homologation is through isotope labeling. If we use ^{13}C labeled methanol, step by step homologation of ethylene and propene can be tracked by the number of ^{13}C atoms on the higher olefin products as illustrated in Fig. 1.

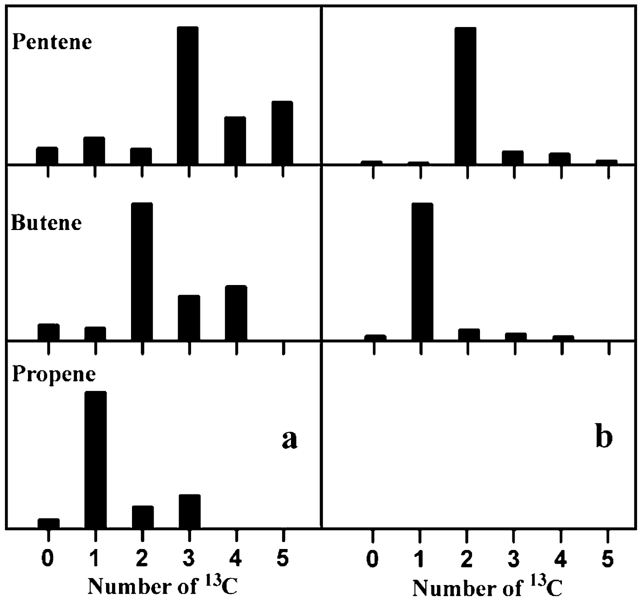

Fig. 3. ^{13}C distribution of olefin products from (a) MeOH–^{13}C/EtOH (5:1, V/V) and (b) MeOH–^{13}C/*iso*-PrOH (5:1, V/V) pulses onto ZSM-22 at 400 °C.

Table 1
^{13}C quantitative isotopomer distribution of olefin homologation products on ZSM-22 at 400 °C

	$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$
Ethylene homologation						
Propene	4.3	**68.5**	10.7	16.5		
Butene	5.7	4.6	**52.4**	16.8	20.5	
Pentene	5.2	8.6	4.9	**45.4**	15.4	20.5
Propene homologation						
Butene	2.5	**85.4**	6.2	3.9	2.0	
Pentene	1.5	1.0	**81.2**	7.7	6.2	2.4

Table 2
^{13}C quantitative isotopomer distribution of olefin homologation products on ZSM-22 at 300 and 350 °C

	$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$
Ethylene homologation						
300 °C						
Propene	9.6	**82.8**	1.7	5.9		
Butene	**60.8**	10.8	17.9	8.3	2.2	
Pentene	7.2	**61.3**	9.3	16.1	0.7	5.4
350 °C						
Propene	5.3	**67.1**	10.3	17.3		
Butene	14.6	3.7	**45.3**	21.8	14.6	
Pentene	4.0	19.0	8.9	**35.6**	16.6	15.9
Propene homologation						
300 °C						
Butene	1.8	**92.9**	1.5	0	3.8	
Pentene	0	8.7	**63.6**	11.3	4.3	12.1
350 °C						
Butene	3.7	**87.3**	4.5	3.4	1.1	
Pentene	3.5	2.3	**82.2**	7.3	3.6	1.1

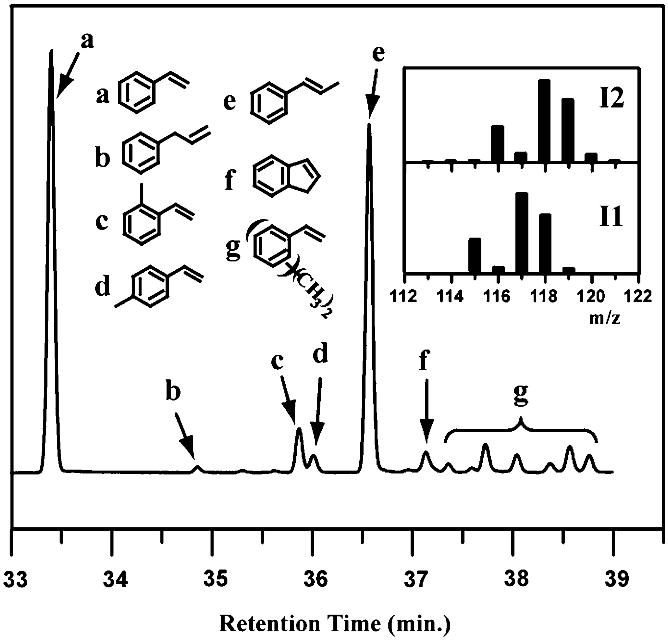

Fig. 4. GC profiles of MeOH/styrene (5:1, V/V) pulse into ZSM-22 at 350 °C. Inset is the molecular ion mass pattern of product **e** for MeOH/styrene (I1) and ^{13}C–MeOH/styrene pulse (I2), respectively, showing the same pattern with mass difference by 1.

After a MeOH–^{13}C/EtOH pulse onto ZSM-22, most propene product has one ^{13}C atom, and most butene has two ^{13}C atoms (Fig. 3a). ^{13}C distribution of pentene also shows that the pentene with three ^{13}C atoms dominates, but there are significant portions of pentene with ^{13}C atom numbers that is not expected from simple homologation, and are most likely from olefin oligomerization and cracking, as mentioned earlier. However, the trend of ethylene homologation through step by step carbon addition is visible (Fig. 3a). Homologation of propene produces butenes and pentene, most of which have one ^{13}C and two ^{13}C atoms, respectively (Fig. 3b), as expected from propene homologation.

Quantitative analyses of ^{13}C distributions of olefin products from MeOH–^{13}C reaction with ethylene and propene on ZSM-22 at 400 °C are listed in Table 1, showing that on ZSM-22, major olefin products are from direct homologation reaction. For comparison, MeOH–^{13}C/EtOH was pulsed onto ZSM-11. Various hydrocarbon products with apparently random ^{13}C distributions for propene, butene as well as pentene were observed (shown in supporting information). Since methanol alone can produce olefins on ZSM-11, most hydrocarbon have high ^{13}C content, indicating that homologation reactions are hidden behind secondary reactions on an active MTO catalyst.

To investigate the temperature influence of homologation on ZSM-22, the mixture of alcohols (MeOH–^{13}C/EtOH or MeOH–^{13}C/*iso*-PrOH) were pulsed onto the catalyst at a series of temperature (250, 300, 350, 400 °C). In both sets of experiments, no homologation product was detected at 250 °C. Pulsing MeOH–^{13}C/*iso*-PrOH mixture into ZSM-22 generated similar isotopic distributions of the homologation products as shown in Fig. 3b. However, when the MeOH–^{13}C/EtOH was pulsed onto the ZSM-22 at different temperatures, interesting isotopic distribution patterns were observed. At 400 °C, a clear trend of adding ^{13}C step by step was observed (as shown in Fig. 3a), such trend became less visible at 350 °C (Table 2). At 300 °C, the ^{13}C distribution of olefin products did not follow expected trend in Fig. 1. Propene has one ^{13}C as expected, but most butene has no ^{13}C and most pentene has one ^{13}C, respectively. The reason for such apparently odd ^{13}C distributions on butene and pentene is perhaps due to the differences in energy barriers and reaction rates for different reactions of olefins on ZSM-22. Svelle et al. have found that the relative rate of alkene interconversion increased with the decreasing reaction temperature [16]. At lower temperature (300 °C), the dimerization reaction of ethylene overwhelmed the homologation reaction, leading to no ^{13}C distribution on butene. One ^{13}C atom on the pentene molecule was actually from the homologation of butene (Table 2).

Styrene is a phenyl group substituted ethylene. The methylation of styrene's C=C double bond may be an important step in

Table 3
Deuterium isotopomer distribution of olefin products from CD_3OH/EtOH (5:1, V/V) pulses onto ZSM-22 at 350 °C

	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
Propene	42.1	35.1	14.8	3.9	3.1	1.0	0.01				
Butene	31.1	40.3	19.3	7.3	0.01	0.01	0.2	1.7	0.1		
Pentene	28.9	40.2	23.0	6.9	0.6	0.01	0.1	0.01	0.01	0.2	0.1

MTO process, since it produces longer side-chain on benzenes, and side chain growth route is one possible route for hydrocarbon pool mechanism [17–19]. When methanol and styrene mixture (MeOH: styrene = 5:1, V/V) was pulsed into the ZSM-22 catalyst at various temperatures, two kinds of styrene methylation were observed, one is methylation of the benzene ring; and the other is methylation of the double bond (homologation). The latter is what we are interested in. Fig. 4 shows that homologation of styrene double bond at β position led to the major product (product **e**). It is worth mention that there is no homologation on the α position of the styrene's side chain, most likely due to the stability of the intermediate species. The space restriction of the ZSM-22's pore may also limit methylation on α position. This is another example of delicate regio-specific control using zeolite pores.

With ^{13}C-labeled methanol/styrene pulse, about 97% product **e** has one ^{13}C atom, indicating that styrene's side-chain was increased by one ^{13}C atom through reacting with methanol-^{13}C. Products **g** is a mixture of aromatics, and 96% of them have two ^{13}C atoms, which may suggests consecutive homologation to styrene's side chain. However, we are unable to assign the individual peaks accurately for product **g**. Note that no ethylene or propene was detected in this experiment, indicating again that hydrocarbon pool mechanism, no matter what the detail process is, was inhibited.

We also studied the homologation of ethylene using CD_3OH and ethanol. The homologation products, including propene and butene, all showed severe isotopic scrambles (Table 3). We believe that the homologation reactions occurred, but the H/D exchange between alkene and the acid site protons as described by Kondo et al. [20], were facile, making it impossible to observe the homologation part of the chemistry.

On ZSM-22, our results show clear step by step olefin homologation. However, it is hard to assess the homologation reactions on MTO-active catalysts, such as ZSM-5, because homologation reaction was covered by hydrocarbon pool reactions and secondary reactions. By choosing conditions that only a minimal olefins can be produced, Svelle et al. had observed similar olefin methylation to higher alkene using ZSM-5 catalyst [15,16]. In their experiments, the mixture of methanol and olefin (ethylene or propene) pass through a small amount of catalyst at an extreme high feed rate, thus hydrocarbon pool reactions and secondary reactions were limited. The selectivity of olefin methylation increased with the feeding rate, while the conversion to hydrocarbons is quite low. This is a clever design and a MTO-active catalyst is used. However, on ZSM-22, hydrocarbon pool reactions and secondary reactions was inhibited by the relatively smaller pores, such extreme reaction conditions is not necessary. Though ZSM-22 is not an active MTO catalyst, since ZSM-22's pore sizes are similar to that of ZSM-5, we believe the homologation reactions observed on ZSM-22 will reflect the homologation chemistry on ZSM-5.

It is reported that ethylene's homologation is not important since it is slower than most of other reactions on SAPO-34 [15,21]. However, olefin homologation may play an important role during the kinetic induction time of the MTO process. It produces the olefins with longer chains, which may explain how initial hydrocarbon pool species are generated. When ethylene and propene molecules are formed (either from impurities in methanol [22] or from direct mechanisms [23]), their concentrations are so low, that the chances of these initial olefin molecules to meet each other and form hydrocarbon pool species (methyl benzenes and carboncations) are very slim. However, with abundant methanol around, each ethylene or propene molecular can homologate several times to form long chain olefins, e.g. octene, which can then form aromatic compounds (hydrocarbon pool species) through a uni-molecular route [24].

4. Conclusion

In summary, with zeolite ZSM-22, the hydrocarbon pool mechanism and secondary reactions are inhibited, which provides an ideal condition for olefin homologation reaction. By labeling MeOH with ^{13}C, we are able to directly observe step by step olefin chain growth. The ZSM-22 catalyst, in spite of being non-active for the MTO reaction, behaves like the MTO-active ZSM-5 with regard to alkene methylation. Direct observation of olefin homologation may explain the formation of initial hydrocarbon species, as homologation may extend the chain length of initial olefins, which then form initial hydrocarbon pool species. The experimental observation may also help theoretical chemists to refine their calculations [25,26].

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Supporting information

The online version of this article contains additional supporting information.

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