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The mechanisms of ethene and propene formation from methanol over high silica H-ZSM-5 and H-beta

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ABSTRACT

Selectivity control is a key issue in the zeolite facilitated conversion of methanol to hydrocarbons. This work addresses: (a) How the zeolite topology (MFI versus BEA) determines the type of intermediate participating in the catalytic cycle thereby controlling the ethene/propene product selectivity in the methanol to alkenes reaction, and (b) to what extent light alkene formation occurs via aromatic and alkene reaction intermediates for H-ZSM-5. Three catalyst samples have been studied in experiments relying on isotopic labeling. For H-beta, penta- and hexamethylbenzene are involved in an aromatics based hydrocarbon pool type mechanism leading predominantly to propene and the higher alkenes (a very low yield of ethene is observed), whereas for H-ZSM-5, the lower methylbenzenes are the aromatic intermediates and represent the major route for ethene formation. For H-ZSM-5, an alkene based and an aromatics based catalytic cycle for product formation are distinguishable. By conducting co-reaction experiments (MeOH + propene or MeOH + *p*-xylene) over H-ZSM-5 we were able to evaluate the relative rates of ethene and propene formation from both the alkene and the aromatics based catalytic cycles.

1. Introduction

The current high and stable oil prices have sparked interest, both commercially and scientifically, in the development of technologies and processes that may utilize natural gas or coal (or even biomass) rather than liquid petroleum as the source of transportation fuels and raw materials for the petrochemical industry. This situation is manifested by the interest in Fischer–Tropsch based technologies for diesel production from natural gas or coal via synthesis gas (H_2 + CO). However, high octane gasoline and light alkenes for polymerization are not the primary products from a conventional Fischer–Tropsch reactor, and other options must be pursued in order to meet increasing demands of these products. Methanol, which may also be manufactured from synthesis gas, constitutes a convenient chemical intermediate in this respect, because when reacted over solid, acidic zeolite catalysts, methanol may be transformed into gasoline (MTG—methanol to gasoline) and/or alkenes (MTO/MTP—methanol to olefins/propene), depending on catalyst choice and process conditions.

The MTG reaction was discovered and later commercialized by Mobil Oil in 1986, when a plant dimensioned for an annual gasoline production of 600 000 tons over a MFI zeolite catalyst came on stream in New Zealand [1]. However, the gasoline part of the MTG plant was later shut down due to decreasing crude oil prices and only the methanol synthesis step remained in operation [1]. Haldor Topsøe A/S later developed the Topsøe integrated gasoline synthesis (TIGAS) process, in which the methanol synthesis and the gasoline synthesis are integrated in one loop [2]. Two alternatives currently exist for light alkenes production from methanol. The Norsk Hydro/UOP MTO process, which is based on the SAPO-34 catalyst, yields a flexible mixture of ethene and propene [3], whereas Lurgi's MFI based MTP alternative predominantly produces propene with some gasoline as by-product [4]. Lurgi recently announced the successful commercialization of the MTP process with a plant expected to come on stream in 2008 [4].

The understanding of the reaction mechanism of the conversion of methanol to hydrocarbons (MTH) has been greatly advanced over the past years [1,5–7]. Current consensus now favors an *indirect* reaction cycle [8–10] known as the hydrocarbon pool mechanism. Rather than being based on coupling of C_1 entities from methanol or dimethylether, this mechanism involves a series of steps where methanol is added to the hydrocarbon pool, resulting in C–C bond formation and subsequent alkene production. Several studies have shown that methylbenzenes may

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constitute the hydrocarbon pool. For example, in H-SAPO-34, propene may be lost from hexamethylbenzene via a series of rearrangements and the resulting trimethylbenzene molecule is then methylated three times by methanol in order to close the catalytic cycle [11]. In the H-beta zeolite, hexamethylbenzene also displays a high reactivity, but the heptamethylbenzenium cation appears to be even more relevant for propene and butene formation [12,13]. Recent research has shown that there are major mechanistic differences from one catalyst topology to another [7]. For H-ZSM-5, we have shown that, *e.g.* hexamethylbenzene is an insignificant reaction intermediate compared to the lower aromatic homologues [7]. Moreover, an additional catalytic cycle, based on repeated alkene methylation and cracking reactions is to some extent in operation over H-ZSM-5. For example, a propene molecule may be sequentially methylated by methanol to give a hexene molecule. Subsequent cracking of this hexene molecule into two propene molecules will result in the net formation of a propene molecule from three methanol molecules.

In this contribution, we compare the mechanisms for conversion of methanol to hydrocarbons over H-ZSM-5 (medium channel dimensions) and H-beta (large channel dimensions) and link the ethene yield to the nature of the active, aromatic reaction intermediates. Further, so far no attempts have been made to address the relative importance of alkenes and aromatics as intermediates within the frame of this recently introduced dual cycle concept [7]. This is addressed by co-reacting ^{13}C MeOH and ^{12}C propene or ^{12}C *p*-xylene over H-ZSM-5, in an attempt to study the reactions of methanol with typical intermediates from each catalytic cycle.

2. Experimental

2.1. Catalysts

Two H-ZSM-5 samples with Si/Al = 50 (ZeoChem AG) and 140 (Zeolyst International) and a dealuminated zeolite H-beta (Si/Al = 120, PQ Zeolites) have been used. H-ZSM-5 (Si/Al = 50) consists of particles of average size ~1 μm, whereas H-ZSM-5 (Si/Al = 140) consists of somewhat larger particles of average size ~3 μm. The H-beta sample consists of particles of average size around 0.2 μm. The H-ZSM-5 (Si/Al = 140) and H-beta samples have been characterized extensively previously [7,14,15].

2.2. Reaction studies

All reactions were carried out at 350 °C in a fixed bed reactor using 60 mg catalyst. The catalyst powder was compressed to wafers that were crushed and sieved to obtain particles in the size range 0.25–0.42 mm. Methanol, either ^{13}C enriched (Cambridge Isotope Laboratories, 99% ^{13}C purity) or ordinary ^{12}C methanol (BDH Laboratory Supplies, >99.8% chemical purity) was fed by passing a controlled He carrier gas stream through a saturation evaporator. Three types of experiments, all involving methanol feed, were performed in order to obtain mechanistic information:

(1) By using two separate and identical feed lines, it was possible to switch from ^{12}C to ^{13}C methanol without otherwise disrupting the experimental conditions. Ordinary ^{12}C methanol (130 hPa, $\text{WHSV}_{\text{MeOH}} = 7\ \text{g g}^{-1}\ \text{h}^{-1}$) was reacted for 18 min at 350 °C. After switching to ^{13}C methanol feed, the isotopic compositions of effluent compounds were determined at increasing ^{13}C methanol reaction times (0.5, 1, and 2 min). Immediately after the final effluent analysis (*i.e.* after ~ 2 min of ^{13}C methanol reaction), the reaction was quenched and the material retained inside the zeolite channels was analyzed (see below).

(2) ^{13}C-methanol (130 hPa, $\text{WHSV}_{\text{MeOH}} = 7\ \text{g g}^{-1}\ \text{h}^{-1}$) was reacted alone for 18 min at 350 °C. Then, a minor flow of pure ^{12}C-propene (0.17 N mL/min) was added as a co-reactant to the He/methanol stream, resulting in a propene partial pressure of 4.3 hPa and a ^{13}C:^{12}C carbon ratio of 10. The propene flow was kept small in order keep the system as equal to the pure methanol system as possible. After a total of 20 min on stream (2 min of co-reaction) effluent analyses were carried out and immediately after, the reaction was quenched and the organic material retained in the zeolite was analyzed (see below).

(3) Finally, co-reaction experiments with ^{13}C methanol and ^{12}C *p*-xylene were performed, also at 350 °C. In this case, both reactants were fed from the beginning of the experiment and the methanol feed rate ($\text{WHSV}_{\text{MeOH}}$) was increased to $25\ \text{g g}^{-1}\ \text{h}^{-1}$. *p*-Xylene was fed ($\text{WHSV}_{\text{xylene}} = 2.5\ \text{g g}^{-1}\ \text{h}^{-1}$) by saturating part of the He stream. The obtained partial pressures of methanol and xylene were 90 and 2.7 hPa, respectively, giving a ^{13}C:^{12}C carbon ratio of 4. Effluent analysis was carried out after 20 min of reaction.

2.3. Analysis of organic material retained in the zeolite

After being removed from the reactor and rapidly cooled to room temperature, a part of the catalyst mass (40 mg) was transferred to a screw-cap Teflon vial and dissolved in 1.0 mL 15% HF. Thereafter, 1.0 mL CH_2Cl_2 (Fluka puriss) was added to the thus obtained solution to extract the liberated organic molecules from the aqueous phase. After phase separation, the CH_2Cl_2 extract was analyzed using GC–MS. The technique of dissolving the zeolite crystals in HF to recover confined constituents by extraction has been used earlier in related studies [7,16] and was introduced by Guisnet and co-workers [17].

2.4. Chromatography

The reactor effluent was analyzed by an on-line GC–FID. The isotopic compositions of the retained compounds (extracted from the HF aqueous phase) and effluent were analyzed on two GC–MS set-ups in order to obtain adequate separation of all compounds, from C_2 to C_{12}. A thorough description of the chromatographic set-up has been given previously [7].

3. Results and discussion

As pointed out in Section 1, previous research has indicated fundamental differences between ethene and propene in the MTH reaction, both with respect to formation and further reaction [7]. In the present study, we have conducted several experiments to obtain a more complete description of the formation mechanisms and roles as intermediates played by the light alkenes and the methylbenzenes. First, we study the incorporation of methanol into both the gas phase products and the reaction intermediates trapped within the zeolite voids by switching from ^{12}C to ^{13}C methanol for both H-ZSM-5 and H-beta. Based on the findings thus obtained, co-reaction of ^{13}C methanol and ^{12}C propene or ^{12}C *p*-xylene was carried out over H-ZSM-5, in order to study the reactions of methanol species selected to be representative for two groups of reaction intermediates within the dual cycle concept [7].

3.1. Composition of retained hydrocarbons and gas phase products for H-ZSM-5 and H-beta

Table 1 lists conversion and selectivity data (carbon based) for the two H-ZSM-5 samples and the H-beta sample after 15 min on stream of methanol conversion ($\text{WHSV} = 7\ \text{g g}^{-1}\ \text{h}^{-1}$) at 350 °C. The two H-ZSM-5 samples give fairly similar results, except that

Table 1

Methanol conversion, propene to ethene ratio, and product selectivities (C%) measured for H-ZSM-5 (Si/Al = 50), H-ZSM-5 (Si/Al = 140), and H-beta (Si/Al = 120) after 15 min on stream at 350 °C and WHSV = 7 h^{-1}.

Catalyst	Conversion (%)	C_3/C_2 ratio (C%)	Product selectivities (C%)					
			C_2	C_3	$C_4^{=}$	C_4^{-}	C_5	C_{6+}
H-ZSM-5 Si/Al = 50	95.3	5.1	4.9	25.0	15.8	7.2	14.5	32.4
H-ZSM-5 Si/Al = 140	73.0	3.1	9.9	30.4	14.3	5.2	11.7	28.4
H-beta Si/Al = 120	54.9	21	1.1	22.7	26.4	10.5	11.7	27.6

the conversion is higher for the more aluminum rich material, as expected. For both H-ZSM-5 catalysts, C_3 (mainly propene) is the dominant single product and the C_3/C_2 ratios are 3.1 and 5.1. H-beta gives lower reactivity, even when compared to the H-ZSM-5 sample with less aluminum, suggesting that the conversion per site is topology dependent, although other factors, such as crystal size and defects may also play a role. Propene is a major product also for H-beta, but it is noteworthy that C_2 (mainly ethene) is much less prominent, the C_3/C_2 ratio is as high as 21 (the corresponding figures were 3.1 and 5.1 for H-ZSM-5). H-beta yields more C_4 alkanes and alkenes than H-ZSM-5, and the selectivities towards C_5 and C_{6+} are rather similar for all three samples.

In this report, we also pay attention to the build-up and stability of the organic material in the zeolite pores during the reaction. Fig. 1 presents the GC–MS total ion chromatogram of the organics that were present inside the zeolites after 20 min of methanol reaction at 350 °C. The chromatograms in Fig. 1 were obtained using the HF dissolution/CH_2Cl_2 extraction procedure and the intensities were normalized to the most intense signal. It should be noted that on an absolute scale, the integrated intensities for H-beta is about an order of magnitude smaller than for the two H-ZSM-5 catalysts. A lower amount of retained hydrocarbons in H-beta appears reasonable, considering the greater diffusivity for such a large pore, small crystal zeolite. As Fig. 1 shows, the composition of the retained hydrocarbons is similar for all three catalysts and a few compounds are clearly dominant. All the major peaks represent polymethylbenzenes (polyMBs). Hexamethylbenzene (hexaMB) is most abundant, followed by pentamethylbenzene (pentaMB)/tetramethylbenzenes (tetraMBs), trimethylbenzenes (triMBs) and *p*/*m*-xylene. Hydrocarbons with molecular mass higher than hexaMB were not present in appreciable amounts in the H-ZSM-5 samples whereas the large pore beta zeolite allows formation of hexamethylnaphthalene (hexaMN). PolyMBs up to tetraMB were detected in the effluent from the H-ZSM-5 samples, so to be precise, only penta- and hexaMB can be considered to be truly trapped inside H-ZSM-5. For H-beta, however, also penta- and hexaMB is observed among the gas phase products, and again this must be attributed to the less restricted space in beta compared to H-ZSM-5.

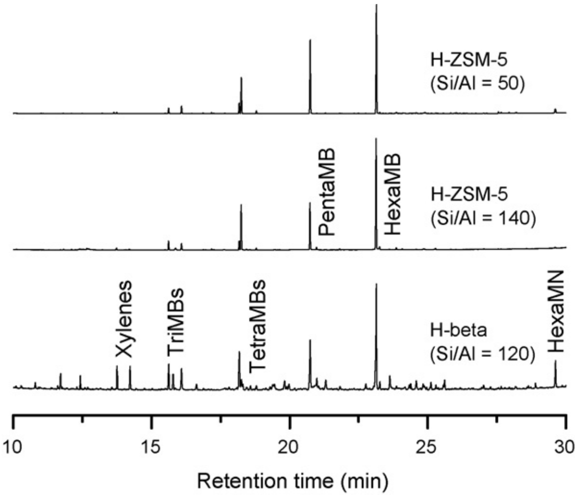

Fig. 1. GC–MS analyses (total ion chromatograms) of the hydrocarbons retained within the zeolite voids, normalized to the tallest peak (hexaMB). Prior to HF dissolution and CH_2Cl_2 extraction, methanol was reacted for 20 min at 350 °C.

3.2. Switching from ^{12}C methanol to ^{13}C methanol for H-ZSM-5 and H-beta

According to the hydrocarbon pool mechanism, methylbenzenes are key precursors for alkene formation. In order to assess the roles of the various methylbenzenes present in H-beta and H-ZSM-5 during the catalytic cycles comprising this mechanism, the reactivity of the species trapped within the pore systems was monitored by the transient ^{13}C incorporation when switching from ^{12}C to ^{13}C methanol. The total ^{13}C contents in the methylbenzenes in the retained material after 18 min of ^{12}C methanol reaction followed by ~2 min of ^{13}C methanol reaction are shown in Fig. 2.

For H-ZSM-5 (Si/Al = 50), a clear trend is observed: The highest rate of carbon incorporation from methanol is seen for the aromatics with the fewest methyl substituents whereas penta- and hexaMB display a much lower reactivity. Reassuringly, exactly the same trend is seen for H-ZSM-5 (Si/Al = 140), except that for most compounds the incorporation of ^{13}C is slower, in line with the lower activity (see Table 1). This conformity shows that the data forming the basis for our further discussion about the reaction mechanism indeed is representative for H-ZSM-5. For H-beta, however, the trend is reversed as penta- and hexamethylbenzene now have the highest rate of ^{13}C incorporation. This implies that different compounds partake as hydrocarbon pool species in H-beta and H-ZSM-5, as discussed in more detail previously [18].

Fig. 3 shows the time evolutions of total ^{13}C content for the C_2–C_6 alkenes and the polymethylbenzenes in the effluent. For H-ZSM-5, the rates of ^{13}C incorporation are significantly slower for ethene and the aromatics compared to the C_3–C_6 alkenes. Gratifyingly, the data are again very similar for the two H-ZSM-5 samples. For the H-beta zeolite, no distinction between the various species is discernible. The grouping of ethene and the lighter methylbenzenes with respect to ^{13}C contents seen for H-ZSM-5 manifests the origin of the ethene from an aromatics based catalytic cycle. The significantly higher ^{13}C content in the C_3–C_6 alkenes is caused by an additional catalytic cycle involving repeated alkene methylations with the incoming ^{13}C methanol. The ^{13}C enriched higher alkenes thus formed subsequently undergo alkene cracking steps, leading to a net production of alkenes from methanol. This dual cycle concept for ethene and propene formation has been discussed in detail previously [7]. As no clear distinctions are seen among the gas phase products formed over H-beta, the analysis is less straightforward. However, Fig. 2 clearly shows that it is the higher methylbenzenes that act as hydrocarbon pool compounds in H-beta, as opposed to the findings for H-ZSM-5 where the lower aromatics are active. Hence, propene and probably butenes also are formed from the aromatics in H-beta rather than ethene, in line with data from Haw and co-workers [19], showing that the lower methylbenzenes yield predominantly ethene, whereas the higher homologues favor propene. These considerations explain the very low ethene yield in H-beta (see

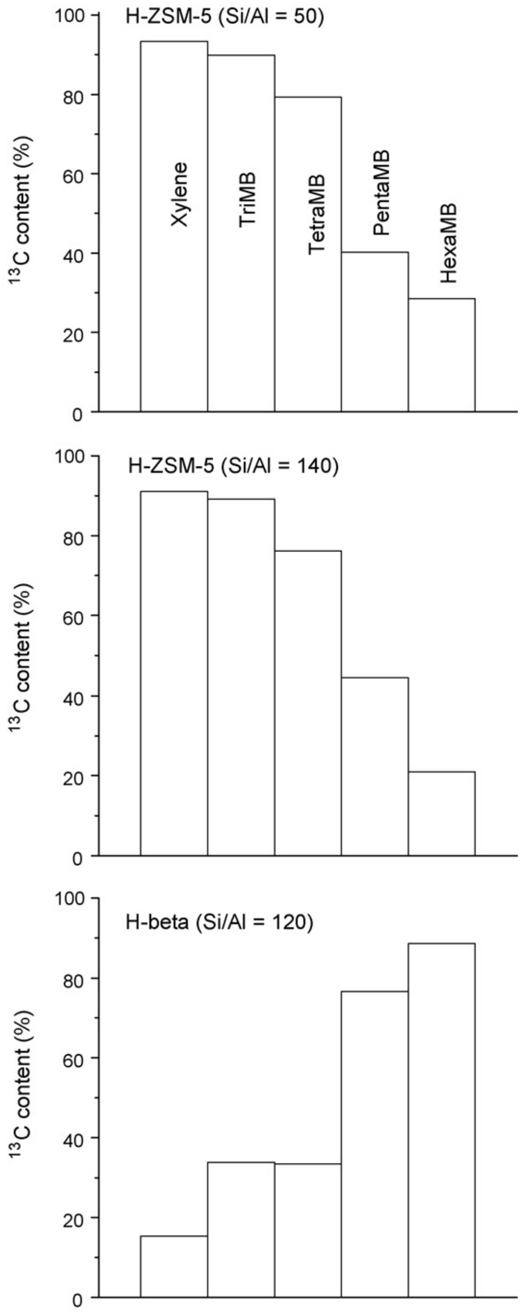

Fig. 2. Total ^{13}C contents in the retained hydrocarbons after 18 min of ^{12}C methanol reaction followed by 2 min of ^{13}C methanol reaction over the three catalysts at 350 °C.

Table 1) compared to H-ZSM-5 under the current set of conditions, as the ethene formation will depend on the actual presence of active, lower methylbenzene intermediates. This does not mean that alkene methylations are insignificant in H-beta. On the contrary, the fact that there is a large, continuous production of C_{5+} alkenes (and subsequently aromatics via cyclizations and hydrogen transfers) is best rationalized by assuming methylation of the lower alkenes, e.g. propene and butene. It seems plausible that the very open H-beta structure allows a more rapid equilibration of C_{3+} alkenes and aromatics, thereby leading to a very similar development in the isotopic composition for all compounds. Two routes are possible sources of the minor amount of ethene produced in high silica H-beta. First, alkene cracking into ethene is in compliance with the isotopic data, but these are apparently slow reactions. Data compiled by Kissin shows that ethene is a minor cracking product from alkenes: In the cracking of 3,4-dimethyl-3-hexene over the Y zeolite at 350 °C the molar yields for propene and butenes have been shown to be 14 and 33 times higher than the yield of ethene [20]. Second, the higher methylbenzenes could be the origin of the ethene, but as already mentioned, Haw and co-workers have shown this to be a minor reaction. Hence, both options for ethene formation are expected to be very slow, in agreement with the fact that very little ethene is produced from high silica H-beta. In summary, it now seems clear that increasing the zeolite channel dimensions allows the hydrocarbon pool catalytic cycle to proceed via larger intermediates (*e.g.* hexaMB), which in turn gives rise to the observed ethene/propene selectivity differences.

3.3. Co-reaction of ^{13}C methanol and ^{12}C propene over H-ZSM-5

Propene is the single most dominant product formed when methanol is reacted alone over H-ZSM-5 (Table 1) under the conditions studied here. From a commercial point of view, propene is also the most desirable light alkene, which has led to the development of Lurgi's MFI based methanol to propene (MTP) process [4]. In the previous section, we showed (Fig. 3) that over H-ZSM-5 one manner in which methanol is incorporated into the products is via C_{3+} alkene methylations and crackings. It is therefore of interest to study in greater detail exactly how propene (the lowest alkene with a reasonable rate of methylation [21–23]) functions as a reaction intermediate. In order to follow how carbon atoms from propene enter into the various hydrocarbons, an experiment was carried out by first reacting ^{13}C methanol for 18 min, in order to build up hydrocarbons from methanol alone, before addition of a minor propene flow (methanol:propene ratio was 10:1 on carbon basis) for 2 min and analyzing the effluent and retained material. Fig. 4 shows the total ^{13}C content in the light alkenes in the effluent (part a) and the retained hydrocarbons (part b). Among the light alkenes (part a), ethene has clearly the highest ^{13}C content, close to 80%. Propene, on the other hand, contains much less ^{13}C, which is reasonable remembering that ^{12}C propene is a reactant. The butenes, pentenes, and hexenes are increasingly richer in ^{13}C compared to propene, but none of the C_{3+} alkenes contain nearly as many carbon atoms originating from methanol as ethene. The retained methylbenzenes (part b) consist mainly of ^{13}C atoms, above 78%. It is noteworthy that xylene and ethene have virtually identical ^{13}C contents, again emphasizing that ethene is formed from the lower methylbenzenes in H-ZSM-5 and not from cracking of the higher alkenes, in agreement with the observations of Rønning et al. [24]. The high ^{13}C content in ethene relative to even the largest alkene analyzed (hexene) strongly indicates that alkene cracking into ethene is a minor reaction under these conditions.

A clearer understanding of the reactions that take place when ^{13}C methanol and ^{12}C propene are co-reacted may be gained by examining the isotopic *distributions* in addition to the total contents of ^{13}C. This information is displayed in Fig. 5, where the observed isotopic distributions (black bars) for the gas phase alkenes (left part) and retained methylbenzenes (right part) are compared with the corresponding random abundances of isotopomers (grey bars). The random distributions were calculated from the actual observed ^{13}C total content for each compound and the number of permutations possible for molecules containing a given number of ^{13}C atoms. For the retained aromatics the center of the distributions are systematically shifted towards the ^{13}C rich isotopomers with increasing molecule size. This essentially conveys the same information as the total ^{13}C contents; the heavier methylbenzenes display the lowest reactivity towards the new ^{12}C atoms from propene. In addition, there is a clear excess of the all ^{13}C isotopomers when compared with the random distributions and a corresponding

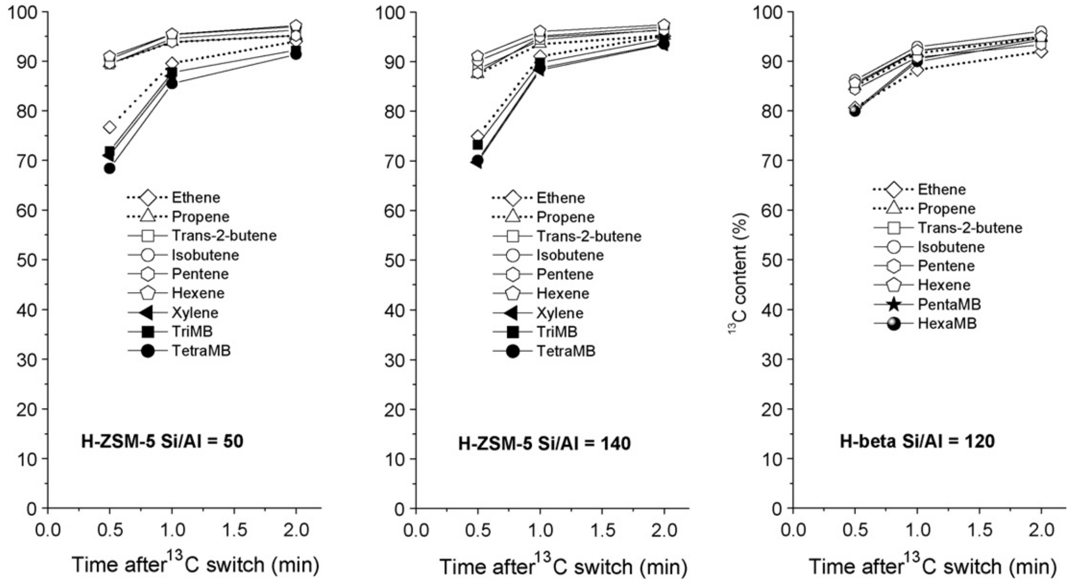

Fig. 3. Total ^{13}C contents in the gas phase alkenes and methylbenzenes after 18 min of ^{12}C methanol reaction followed by 0.5, 1 and 2 min of ^{13}C methanol reaction over the three catalysts at 350 °C.

deficiency of the isotopomers with one and two ^{12}C carbons, *i.e.* there is an excess of molecules built up from carbon atoms coming exclusively from methanol. This observation may be rationalized by considering the reactions that may occur: It is clear that the aromatic rings are relatively reactive towards methanol through methylations, a reaction that involves only ^{13}C methanol carbons and offers no route for ^{12}C incorporation. Alkylation with propene appears to be of little relevance, as there are no detectable amounts of propyl substituted aromatics in the extracts (not shown), and there is no tendency for ^{12}C atoms to be built in units of three. The main route for ^{12}C incorporation from propene into the retained methylbenzenes is most likely the formation of long chain alkenes by multiple propene methylations with methanol followed by cyclizations and hydrogen transfer of these long chain alkenes, eventually leading to the formation of new aromatic rings containing some ^{12}C atoms. Also, it has previously been shown that the build up of methylbenzenes in the H-ZSM-5 pores is indeed slowest for the most substituted isomers [7], in agreement with the trend in ^{13}C content seen for these compounds. Among these three possible reaction routes, the straightforward methylation of aromatic rings is likely to dominate, thereby causing the excess of the all ^{13}C isotopomers.

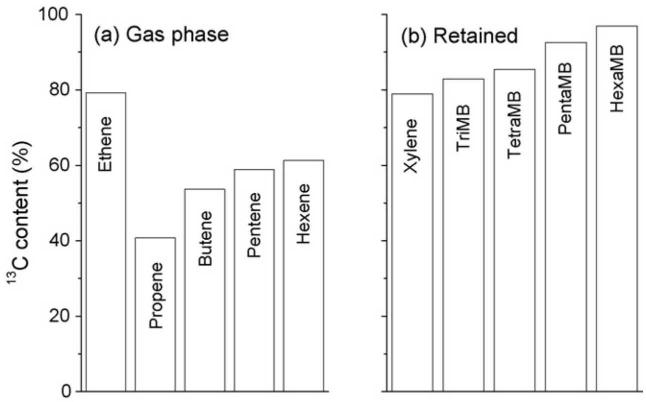

Fig. 4. Total ^{13}C contents in the gas phase alkenes (a) and the retained hydrocarbons (b) after reaction of ^{13}C methanol alone for 18 min and addition of ^{12}C propene for another 2 min at 350 °C over H-ZSM-5 (Si/Al = 140).

The isotopic distribution found for ethene is, in contrast to that seen for the aromatics, in agreement with the calculated random distribution within experimental error. If one accepts that ethene is indeed formed from xylenes and triMBs, as argued above, it may seem counterintuitive that the non-random distribution seen for the aromatics is not inherited by the ethene. This apparent discrepancy may, however, be rationalized by assuming that when ethene molecules are lost from the lower methylbenzenes, there is no distinction between the carbon atoms in the methylbenzene, *i.e.* each methylbenzene carbon atom (ring or methyl group) has the same chance of ending up in the ethene molecule. Such a scenario will lead to ethene molecules with the same overall ^{13}C content, but the ^{13}C atoms will be randomly distributed among the ethene molecules. Arstad et al. studied the loss of ethene from protonated *p*-xylene in the gas phase, *i.e.* without taking a zeolite framework into account, using quantum chemical methods [25]. Their results did to some extent indicate that after an initial highly activated ring expansion, the interchange of ring and methyl carbon atoms could occur within a protonated xylene molecule more easily than the actual loss of ethene. In summary, the present data show that ethene is formed from the lower methylbenzenes and that the ethene formation mechanism equilibrates the carbon atoms from its aromatic precursor prior to the loss of ethene.

The isotopic distribution of propene (Fig. 5, left part) is clearly not random. As already pointed out, ^{12}C propene is a reactant in this experiment and the excess of the all ^{12}C isotopomer indicates that under these reaction conditions, some of the propene molecules do not take part in any reactions at all and remain unconverted. The greater part of the propene molecules in the effluent have, however, undergone one or more reaction steps, as can be seen from the significant shares of molecules with one, two, or three ^{13}C carbon atoms. The mechanistic origin of this labeled propene will be discussed further. Apparently, at most a minor part of the propene stems from ethene methylation. The methylation of ethene would lead to propene isotopomers very rich in ^{13}C, but the abundance of the all ^{13}C propene isotopomers is modest, although not insignificant. More importantly, the rate of ethene methylation is known to be low compared to that of the C_{3+} alkenes, as kinetic investigations have shown that ethene methylation is between one and two orders of magnitude slower than for propene and linear butenes [21,22], and this is further supported by quantum

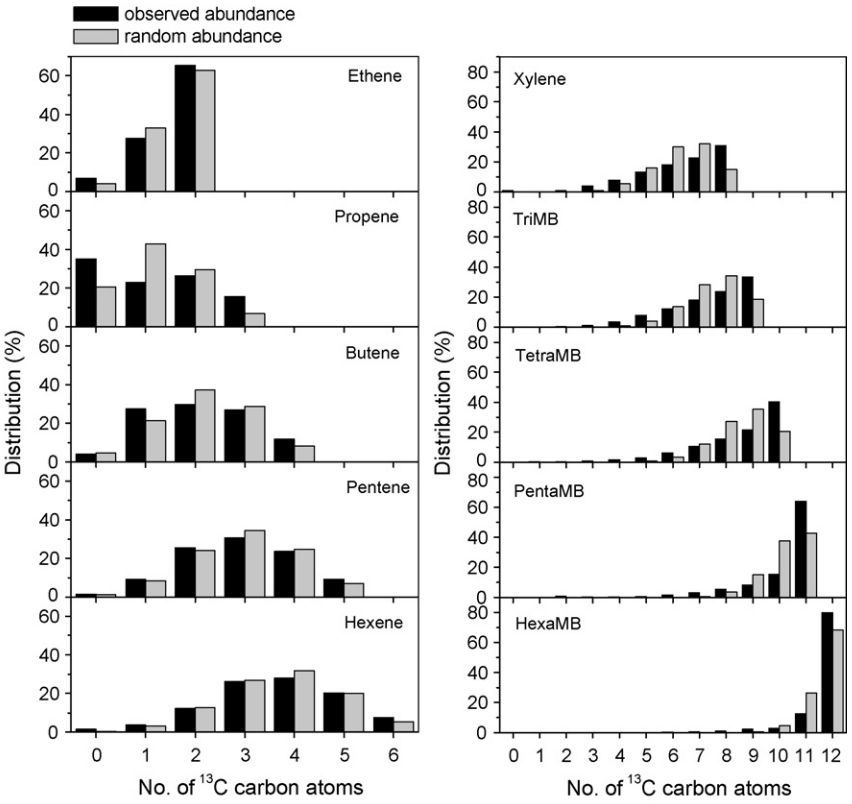

Fig. 5. Detailed isotopic distributions of gas phase products (left) and retained material (right) after reaction of ^{13}C methanol alone for 18 min and addition of ^{12}C propene for another 2 min at 350 °C over H-ZSM-5 (Si/Al = 140). The black bars represent the actual observed distributions, and the grey bars represent the random distributions calculated from the observed total content of ^{13}C in each compound.

chemical studies [23]. Based on a similar argumentation, propene formation from the methylbenzenes is also not a prominent mode of propene formation in this particular experiment, as this would also lead to propene isotopomers very rich in ^{13}C. It should, however, be pointed out that the isotopic distribution of propene is such that neither ethene methylation nor formation from the methylbenzenes can be ruled out entirely, as there is a non-negligible share of the all ^{13}C isotopomers (16%). However, it seems fair to state that both these routes are of minor importance in this propene + methanol co-reaction experiment, which is likely to favor alkene based reactions. Thus, we are left with the alkene methylation/cracking route as the most likely source for most of the propene that is not an unconverted reactant (*vide infra*).

For the butenes, there is an excess of the isotopomer consisting of one ^{13}C atom relative to the random distribution, which may be interpreted as an indication of methylation of some of the ^{12}C propene feed by ^{13}C methanol. Such methylations would also lead to a higher total ^{13}C content in butene than in propene, which is indeed observed (Fig. 4). For the pentenes and hexenes, any such methylation patterns are not discernible in the distributions, which are very close to random for both alkene fractions. Note that the all ^{12}C isotopomer is insignificant for hexene, clearly showing that propene dimerization is insignificant at these reaction conditions (low propene partial pressure).

In general, the isotopic distributions seen for the C_{3+} alkenes become closer to the random distribution with increasing molecular size. This may indicate that the methylation/cracking reactions leading to isotopic equilibration occur quicker for the higher alkenes, in line with the fact that the rates of alkene methylation increase with the size of the alkenes [21–23] and that butene is a more likely cracking product than propene [20], even though for both methylation and cracking, the major difference is seen when comparing ethene and propene. The trend with increasing ^{13}C content seen for the C_{3+} alkenes is also in line with the notion that the larger alkenes are more reactive and therefore undergo more reaction steps than the lower homologues. Ethene, on the other hand, does not appear to partake to a notable extent in these alkene methylation/cracking cycles.

3.4. Co-reaction of ^{13}C methanol and ^{12}C p-xylene over H-ZSM-5

In the previous section we discussed the co-reaction of methanol and propene, representing an intermediate in the alkene based catalytic cycle for methanol conversion. Now, focus will be shifted towards the aromatics based cycle, and the primary objective is to evaluate *which alkenes* that are formed via this cycle and also to *what extent* these reactions take place. As discussed above, ethene appears to be formed predominantly in the aromatics based cycle and a key issue is to determine to which extent propene (and possibly also higher alkenes) is formed by this route. To this end, an experiment was conducted by co-reacting ^{13}C methanol with a minor amount of ^{12}C *p*-xylene (methanol:*p*-xylene ratio was 4:1 on carbon basis) for a total of 20 min and analyzing the effluent. *p*-Xylene was selected as a representative aromatic because xylenes already are present among the products, they display high reactivity (Fig. 3), and diffuse easily into the MFI channels. This experiment was conducted at a high feed rate (WHSV was increased by a factor ~3 compared to the experiments discussed in the previous sections) in order to suppress alkene based reactions and to study alkene formation via the aromatic co-reactant. Fig. 6 shows a chromatogram detail of an effluent analysis after 20 min of co-reaction. Ethene and propene are clearly the two dominating alkene products, with only minor amounts of C_4 and a hardly observable production of C_5. A very limited production of C_{4+} alkenes indicates that the alkene based reaction cycle plays no important role in this experiment. Also, it is significant to note that

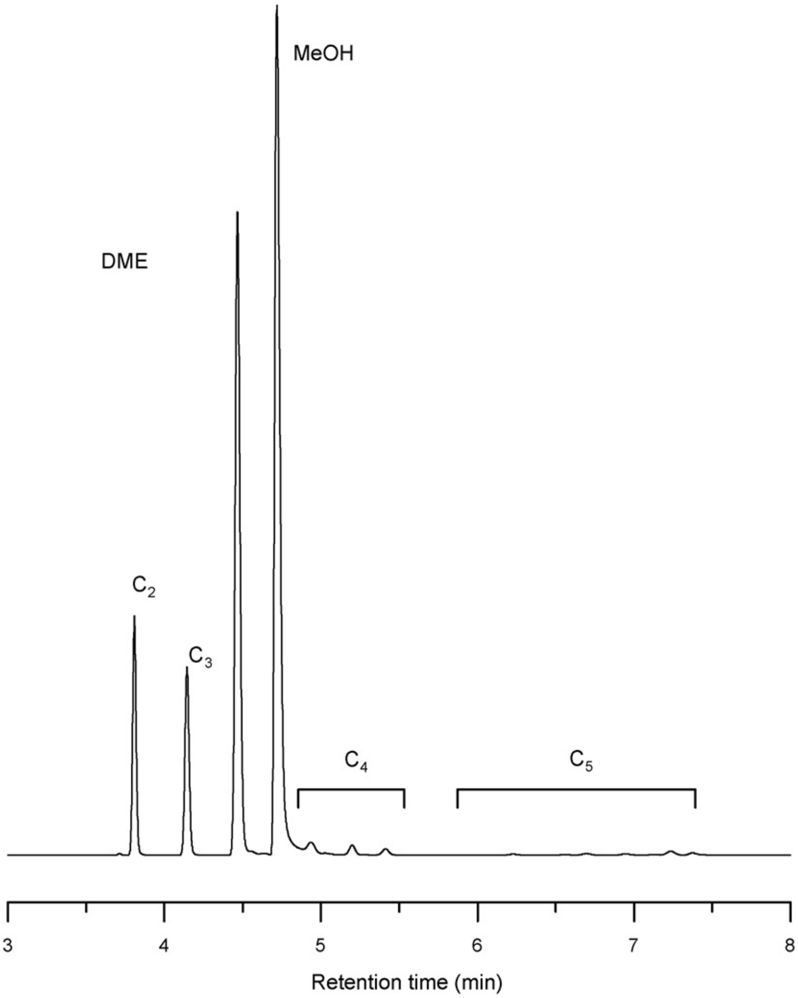

Fig. 6. Chromatogram detail (GC–FID) of the effluent after co-reaction of ^{13}C methanol and ^{12}C *p*-xylene at high feed rate for 20 min at 350 °C over H-ZSM-5 (Si/Al = 140). The main gas phase alkenes are ethene and propene and higher alkenes are barely observable.

because propene methylation into butenes is of little importance (Fig. 6), ethene methylation into propene is virtually non-existent, due to the much lower rate of methylation for ethene compared to propene [21]. This is also in agreement with the very similar total ^{13}C contents of ethene and propene, which were 78 and 81%, in compliance with earlier reports [26]. Based on the observations in this experiment (very little C_{4+} and nearly identical ^{13}C contents in ethene and propene), it may be stated that both ethene and propene are indeed formed from the same precursor, *i.e.* the lower methylbenzenes.

We are now in a position to study the aromatic based catalytic cycle more or less separately from the alkene based cycle. The propene:ethene ratio was close to 1 on carbon basis (0.63 on molar basis). This is in contrast to what is typically observed at appreciable methanol conversion: In the H-ZSM-5 experiments described in Table 1, carbon based propene:ethene ratios of 3.1 and 5.1 were found. However, it may be noted that similar very low propene:ethene ratios have been observed at very low methanol conversion (below 1%) earlier [7], further indicating that this experiment is representative of alkene formation from aromatic intermediates. The very similar ethene and propene yields (Fig. 6) in this experiment, in which the dominant mode of product formation is the aromatics based cycle, imply that the formation rates of ethene and propene from the lower methylbenzenes are comparable or nearly equal. If this is extrapolated to lower more relevant feed rates (higher conversions), when the propene yield is typically several times higher than the ethene yield (Table 1), it appears that the main contribution for propene formation is from the alkene based cycle. Importantly, the ratio between propene and ethene formation rates will not be independent of reaction conditions and catalyst properties, but we have now made the first attempt to quantify the rates of ethene and propene formation from the aromatics based cycle and the alkene based cycle. Ethene and propene are formed at nearly equal rates from the aromatics over H-ZSM-5, whereas ethene is only to a minor extent formed from the alkene route, which is responsible for the major part of the propene production. Understandably, pinpointing the exact sources of ethene and propene is of utmost importance for selectivity control in MTO/MTP applications. The general validity of the above quantification attempt, both with respect to reaction conditions, catalyst properties, and catalyst topology is the scope of further, ongoing studies.

4. Conclusions

In this contribution methanol conversion over two samples of H-ZSM-5 and an H-beta zeolite has been studied. Isotopic labeling has been the primary tool and both effluent and hydrocarbons retained within the zeolite channels have been analyzed. The key issue has been the factors that determine the product selectivity, particularly with respect to ethene and propene which are the target products of methanol to olefin processes. It is found that during conversion of methanol under identical conditions, H-ZSM-

5 yields up to seven times more ethene relative to propene compared to H-beta. The low ethene yield seen for H-beta is a result of the involved hydrocarbon pool aromatic reaction intermediates (penta- and hexamethylbenzene) which tend to yield propene (and butenes) rather than ethene. Due to steric constraints imposed by the zeolite framework, other intermediates (typically trimethylbenzenes) are involved in the reactions taking place in the more restricted H-ZSM-5. Such lower methylbenzene intermediates favor ethene, thus resulting in a relatively high ethene production over H-ZSM-5. In an industrial methanol to propene application, a high ethene yield is not desired, and this report indicates that one route to pursue in order to minimize ethene is to design a catalyst that disallows ethene formation from active lower methylbenzenes, but still maintains a lifetime similar to H-ZSM-5.

In line with earlier investigations, it is observed that on H-ZSM-5 ethene is formed predominantly from the lower methylbenzenes, whereas propene and higher alkenes are to a considerable extent formed from alkene methylations and interconversions. Here, this recently introduced dual cycle concept is consolidated, as the two different H-ZSM-5 samples gave virtually identical results in the mechanistic study, and the mechanistic dual cycle concept is thus not a phenomenon of one specific H-ZSM-5 sample only. Co-reaction experiments (^{12}C *p*-xylene and ^{13}C methanol) conducted at high feed rates were carried out in order to quantify the relative importance of the aromatics based and alkene based catalytic cycles for alkene formation in H-ZSM-5, and under these conditions the aromatics based route produces ethene and propene at similar rates. In addition, the alkene route contributes insignificantly to ethene, but is a highly relevant mode of propene formation for H-ZSM-5. This new insight on the importance of the alkene based catalytic cycle for propene formation from methanol over H-ZSM-5 is of obvious relevance for commercial methanol to propene applications.

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