

Kinetic studies of zeolite-catalyzed methylation reactions

1. Coreaction of [¹²C]ethene and [¹³C]methanol

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Abstract

Coreaction of [¹³C]methanol and ethene has been carried out over H-ZSM-5 (Si/Al = 45). The catalyst has very small crystals. Most experiments were carried out at 350 °C employing the partial pressures $p_{\text{methanol}} = 50$ mbar and $p_{\text{ethene}} = 50$ mbar. The reactor effluents were analyzed using gas chromatography. Isotopic analysis was carried out using GC-MS. A range of feed rates has been used, up to $\text{WHSV} = 292 \text{ h}^{-1}$. This allowed extrapolation of results to zero contact time, giving information about the primary product distribution and the primary isotopic composition of the products. It also allowed the determination of the rate of ethene methylation by methanol. At very high feed rates the dominant coreaction product is propene (approaching 90%). At the highest feed rates the ¹²C₂¹³C₁ isotopomer constituted about 85% of the propene molecules. The reaction order for the methylation of ethene to form propene has been found to be one with respect to ethene and zero with respect to methanol. Measurements have been carried out over an extended range of temperatures, and an Arrhenius plot has been constructed. The apparent activation energy for the methylation of ethene was determined to be 109 kJ/mol. When corrected for the appropriate heat of adsorption for ethene, an intrinsic activation energy of 135 kJ/mol was found. Dimerization of ethene was insignificant under the investigated reaction conditions. Small amounts of aromatics (mainly xylenes) were always detected. These compounds were very rich in ¹³C, containing about 85% labeled carbons.

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1. Introduction

The ability of protonated ZSM-5 (H-ZSM-5) to convert methanol to hydrocarbons (MTH) in the range C₂–C₁₀ and water was discovered and published in 1976. Later it has been found that also other protonated zeolites may have this ability, but they usually deactivate much faster. Industrial processes (methanol to gasoline; MTG, and methanol to olefins; MTO) utilizing this reaction have been developed.

Since the discovery of this reaction a very large number of papers have been published covering virtually every aspect of the reaction—a majority being devoted to clarify the mechanistic aspects. During the years some 20–30 different mechanisms have been proposed. An early comprehensive review was given by Chang, the discoverer of the reaction system [1]. Recently, two quite comprehensive reviews have been given by Stöcker [2] and by Chang [3]. Despite the very

considerable effort, the reaction mechanism of the MTH reaction can still not be regarded a fully settled issue. Since there are extensive reviews, no attempt is made here to give an overview of the large number of papers on the MTH reaction and the various mechanistic proposals.

Over the last few years, the “hydrocarbon pool” mechanism has gained acceptance. As originally proposed by Dahl and Kolboe [4–6], the reaction proceeds via an adsorbate that continually adds reactants and splits off products, in particular C₂–C₄ alkenes. Experiments where benzene or toluene and [¹³C]methanol were coreacted have been performed, and it was clear that ethene, propene, and the arenes in the effluent had indistinguishable isotopic distributions [7]. This strongly indicated that methanol conversion could proceed via repeated methylations and dealkylations of aromatic reaction centers. The specific nature of the hydrocarbon pool has been clarified in a series of publications from Kolboe and co-workers [8–11], Haw and co-workers [12–17] and Hunger and co-workers [18,19]. It has become clear that polymethylbenzenes, polymethyl-

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naphthalenes, and polymethylated cyclopentenyl ions are the main constituents of the hydrocarbon pool.

At the same time it is clear that alkenes, which are important components in the product stream, may be methylated by methanol, once or several times, thereby creating alkenes that are easily cracked to smaller alkenes that are again methylated. These reactions might constitute a competing reaction pathway. Knowledge of the rate of alkene methylation is therefore an important issue. The importance of this alkene methylation/cracking pathway was in particular emphasized by Dessau and co-workers [20,21].

We have previously investigated the reaction system where [^{13}C]methanol is coreacted with ethene or propene over a SAPO-34 catalyst [4,5], the most promising system for an MTO process. This catalyst is very selective toward ethene and propene formation. The pronounced selectivity for C_2 – C_4 formation displayed by the SAPO-34 catalyst is due to the narrow 8-ring pores, which prevent any branched molecules to diffuse out of the catalyst particles into the surrounding gas phase. This study gave no information on the rate of ethene methylation by methanol, and the very narrow pore structure might influence the reactions in a special way. For this reason we consider it necessary to extend the investigation to include also the ZSM-5 catalyst where a much higher diffusivity is present; in addition it is the MTH catalyst archetype.

The rate of alkene methylation by methanol in acidic zeolite catalysts is not easily monitored, and to our knowledge no such measurements have been carried out. The reason for the difficulty of performing these measurements is that alkene interconversion reactions (addition, metathesis and cracking) are not easily distinguished from the reactions caused by methanol. The alkene + alkene reactions might even eclipse the methanol methylation. In addition to this difficulty it must also be kept in mind that the reactions caused by the hydrocarbon pool might well be just as fast, or faster than the methanol + alkene reaction.

By utilizing a reaction system consisting of [^{13}C]methanol and [^{12}C]alkene, and choosing the conditions so that only a minimal conversion to products take place, such information may be obtained. Measuring the rate of methylation of ethene by methanol is the main objective of this paper. In the present work, we have studied the coreaction of ethene and ^{13}C -labeled methanol.

Preliminary experiments indicated that 350 °C is the optimal temperature for extracting the desired information. Extreme feed rates have been employed in order to investigate the primarily formed products and to explicitly study the individual reaction steps that can occur. Methylation of ethene to form propene was then by far the most prominent reaction. Dimerization of ethene to form butenes was at best a very minor, and negligible, reaction. In addition to methylation, a separate reaction pathway, leading to products quite rich in ^{13}C was found to be operative. In our experimental range, the methylation is zero order with respect to methanol and first order with respect to ethene.

We have also determined the apparent activation energy for the methylation step and obtained an estimate for the “true” activation energy. The results are compared with recent theoretical reports on the zeolite-catalyzed methylation of a wide range of alkenes [22] and methylbenzenes [23]. Further experimental work with alkenes other than ethene is in progress.

2. Experimental

2.1. Catalyst

The H-ZSM-5 sample used was a gift from Süd-Chemie AG. The Si/Al ratio is 45. The crystal size is very small, about 50 nm as determined by X-ray line broadening and TEM. This catalyst is quite resistant toward deactivation and the experiments have been performed to minimize and even out any changes in activity over time. A 10 h experiment gave about a 15–20% decrease in catalyst activity. Conversions, and thus also rates, have been corrected for this small deactivation according to the method outlined by Dahl and Kolboe [5,6], but our conclusions do not depend upon this correction.

2.2. Reagents

Ethene with a stated purity > 98% was purchased from Fluka. Gas chromatography (GC-FID)¹ showed ethane to be the main hydrocarbon impurity (~ 0.06%). No higher alkenes could be detected (detection limit: 0.002%). [^{13}C]Methanol was supplied by ISOTEC at a stated chemical and isotopic purity > 99%. GC-MS analysis² showed that traces of ethanol (about 0.2% v/v) were present in the methanol. The isotopic purity was investigated by converting the labeled methanol to hydrocarbons over a zeolite catalyst (in order to remove water and avoid the complications caused by the unknown and quite large content of ^{18}O) and analyzing the isotopic composition of the main products as described below. The average content of ^{13}C atoms was thus found to be 98%.

2.3. Reaction conditions

All catalytic reactions were performed in a fixed-bed Pyrex microreactor (3 mm i.d.). Ethene was fed as a gas, using a needle valve flow regulator and a mass-flow meter. Methanol was fed by passing part of the carrier gas (He, > 99.996%) through a vessel containing the methanol, thus saturating the carrier gas. The partial pressures of ethene and methanol were individually varied from 10 to 100 mbar. Total pressure equaled atmospheric pressure. In order to reduce

¹ Analysis performed with a Siemens Sichromat 2-8 (FID) equipped with a Chrompack PLOT column ($\text{Al}_2\text{O}_3/\text{KCl}$, 50 m \times 0.53 mm \times 10 μm).

² Analysis performed with a Thermoquest GC-MS equipped with a J&W DB-Wax column (30 m \times 0.25 mm \times 25 μm).

the expenditure of [^{13}C]methanol, the feed was admitted to the catalyst for 15 min prior to each analysis. After taking a sample of the effluent for analysis, the feed was stopped (maintaining the carrier gas flow) and the conditions were adjusted to those desired for the next analysis. Separate tests indicated that admitting methanol for 15 min prior to analyzing the effluent was sufficient to reach steady-state activity. The reaction temperature was measured with a thermocouple (0.5 mm diameter) placed in the catalyst bed. Most experiments were done at 350 °C, but reaction temperatures between 305 and 410 °C were investigated. Total gas flow through the reactor was 10–100 mL/min giving feed rates (WHSV) in the range 18–292 h⁻¹. 2.5 mg of catalyst was used to reach the extremely high feed rates necessary to obtain information about the primary reaction products and to minimize secondary reactions. Despite having only a thin layer of catalyst on the glass sinter in the reactor, reactant bypass was negligible. Control experiments carried out at the highest feed rates with 2-butanol as feed, resulted in complete dehydration of the alcohol to form butenes, thus verifying that bypass was indeed insignificant.

2.4. Analysis

Product analysis was performed using gas chromatography. Quantitative effluent composition was determined using an on-line Carlo Erba GC6000 Vega with flame ionization detector (FID) equipped with a Supelco SPB-5 column (60 m × 0.53 mm × 3 μm). Additional analyses were performed on a Siemens Sichromat 2-8 or an HP 6890 equipped with a Chrompack PLOT column (Al₂O₃/KCl, 50 m × 0.53 mm × 10 μm), both with FID. This setup allowed separation of all C₁–C₆ alkenes and alkanes. Products up to C₉ are eluted, if present.

Isotopic composition of the products was determined using an HP 6890 GC with an HP 5973 mass-sensitive detector (GC-MS). Using cryostatic cooling the HP-5MS column (60 m × 250 μm × 0.25 μm) gave adequate separation of all the compounds of interest in this work. Ethene was always dominated by the ¹²C₂H₄ isotopomer from unconverted feed and not amenable for further analysis.

2.5. Calculations

The computational method used for determining the isotopic composition of the products has been outlined previously [4,24]. In order to extract the isotopic composition of a compound it is necessary to know the mass spectrum of the ordinary ¹²C compound (correction for natural 1.1% ¹³C is easily carried out). Standard spectra were obtained by reacting ordinary methanol over the catalyst. To ensure reliable isotopic analysis of the products new standard mass spectra were recorded at intervals. The GC-MS system showed great stability, and variations in the standard spectra were negligible.

3. Results

The main objective for the present work where [^{13}C]methanol and [^{12}C]ethene are coreacted is to collect kinetic data for the methylation of ethene by methanol and to further monitor the role of ethene in the MTH reaction. Attention will focus on experiments where high feed rates have been employed, leading to very low conversions to products. At lower feed rates where higher degrees of reactant conversions are obtained, secondary reactions will eventually dominate, thus making information about the primary processes unavailable. By using a very small amount of catalyst and high gas flows, it was possible to achieve such low conversions at reaction temperatures and a catalyst acid site density that are quite similar to those usually employed for practical MTH purposes.

The reactivities of the individual reactants were investigated prior to the cofeeding experiments. Both methanol and ethene displayed low reactivity when fed alone, and product formation was negligible compared to the coreaction experiments except at the lowest feed rate. The conversion rate of methanol increases very markedly with increasing conversion (the well-known autocatalysis effect). The ratios between the amount of propene formed in the coreaction experiments and that formed when neat methanol was fed (50 mbar methanol and 2.5 mg catalyst in both cases) were ≈ 400, 250, and 3.1 for the carrier gas feed rates: 30, 20, and 10 mL/min. Propene was the main product. At still lower feed rates (lower total gas flows) the conversion of neat methanol appears to approach the conversions observed in the coreaction experiments. Measurements at the highest feed rates may be rendered invalid by the most minute traces of arene impurities in the methanol. A somewhat more detailed treatment of methanol conversion is given in Section 3.5.

3.1. The effect of feed rate (contact time)

A feed mix consisting of 50 mbar [^{13}C]methanol and 50 mbar [^{12}C]ethene was coreacted at a constant reaction

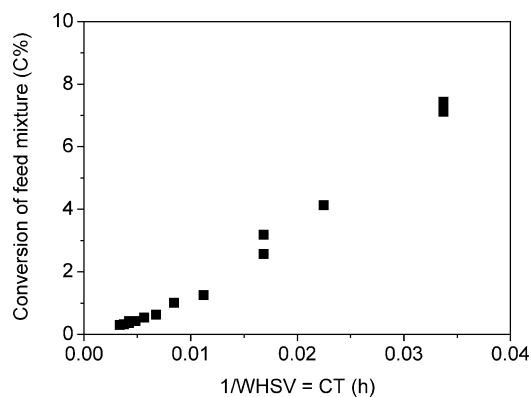


Fig. 1. Conversion of feed mixture: 50 mbar ethene coreacted with 50 mbar methanol; reaction temperature = 350 °C; WHSV varied from 29.4 to 294 h⁻¹.

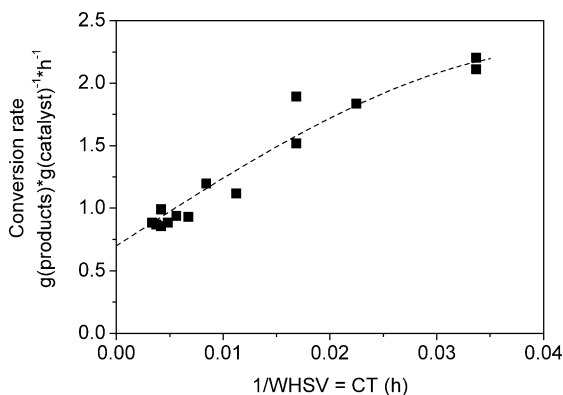


Fig. 2. Conversion rate: 50 mbar ethene coreacted with 50 mbar methanol; reaction temperature = 350 °C; WHSV varied from 29.4 to 294 h⁻¹. The dotted curve shows the extrapolation to CT = 0.

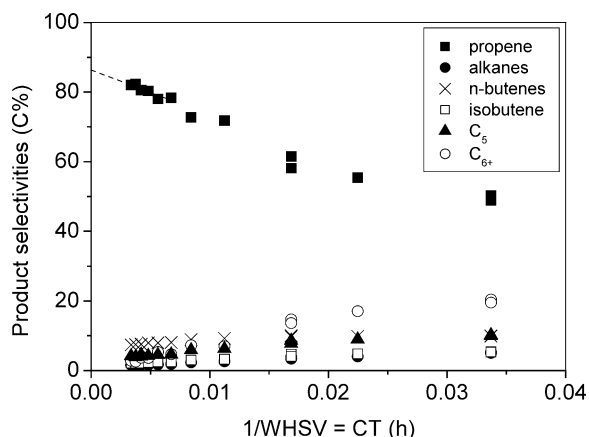


Fig. 3. Product selectivities: 50 mbar ethene coreacted with 50 mbar methanol; reaction temperature = 350 °C; WHSV varied from 29.4 to 294 h⁻¹. The dotted curve shows the extrapolation to CT = 0.

temperature of 350 °C. 2.5 mg catalyst was used, and the total gas flow was varied from 10 to 100 mL/min, thus varying the WHSV between 29.4 and 294 h⁻¹. The “contact time” (CT), defined as 1/WHSV, is a quantity better suited for the further discussion, and it will be used throughout. The space velocity range just mentioned corresponds to the CT range 0.034–0.0034 h.

The conversion to hydrocarbon products obtained in this experiment is displayed in Fig. 1. The degree of conversion is obtained by taking all C atoms in hydrocarbons, except ethene, and then dividing by the total number of C atoms in a given analysis; i.e., ethene, methanol, and dimethyl ether are considered to be unconverted reactant. Note that the maximum conversion in Fig. 1 is about 7.5%. Knowing the conversion and the feed rate, the rate of hydrocarbon formation (C atoms) is obtained by dividing the conversion by CT. The result is displayed in Fig. 2. A clear increase in reaction rate with increasing CT is observed, showing the well-known autocatalysis effect [1–3]. The data in Fig. 2 allow extrapolation to infinite feed rate, or zero contact time. Even though propene was the dominating product, it was

not the only one. Fig. 3 shows the selectivities for the main products. The propene dominance is clearly seen. Extrapolated to zero CT a propene selectivity of nearly 90% is observed.

Since the experiment was carried out with [¹³C]methanol and [¹²C]alkene, the isotopic composition of the hydrocarbon products is of interest. The distribution of the various isotopomers of propene when the contact time is varied is shown in Fig. 4. The isotopomer with one ¹³C and two ¹²C atoms is always dominating, and at the lowest CTs it reaches about 85%, which may also be the value obtained by extrapolation to zero CT. It is noteworthy that the second most common isotopomer is the ¹³C₃ species. Fig. 4 suggests that the amount of this isotopomer may be extrapolated to about 8% at CT = 0. The figure also shows that when the contact time is increased, the amount of this isotopomer increases strongly, and that at the highest contact time, CT = 0.034 h, it is present in nearly the same amount as the ¹²C₂¹³C₁ species. Other experiments not discussed here, and carried out at considerably higher contact times, have shown that this increase continues until the larger part of the methanol has reacted. Under slightly different conditions the following isotopomer distribution was found at a feed rate corresponding to CT ≈ 0.1 h: ¹²C₂¹³C₁; 22%, ¹²C₁¹³C₂; 22%, ¹³C₃; 55%. In this case 96% of the ethene in the effluent still had the original (natural) isotopic composition, but 69% of the methanol was converted to hydrocarbons [24]. The experiment shows that under conditions with a rather high conversion the larger part of the methanol conversion does not involve the ethene.

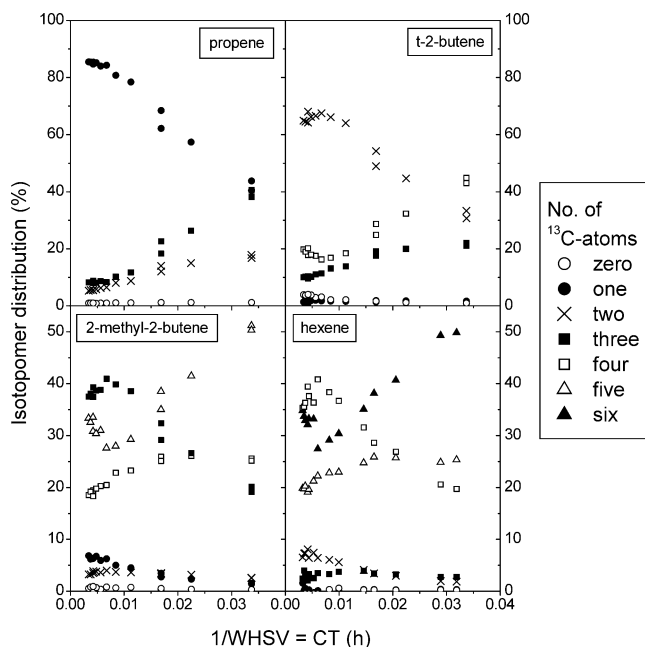


Fig. 4. Isotopic composition of alkene products in the effluent: 50 mbar [¹²C]ethene coreacted with 50 mbar [¹³C]methanol; reaction temperature = 350 °C; WHSV varied from 29.4 to 294 h⁻¹.

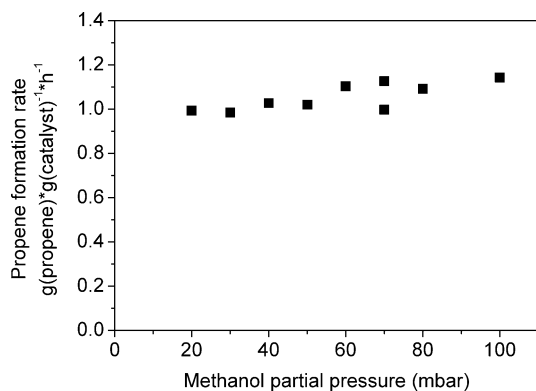


Fig. 5. Rate of propene formation vs methanol partial pressure: 50 mbar ethene coreacted with 20–100 mbar methanol; reaction temperature = 350 °C; total gas flow = 100 mL/min.

3.2. The effect of methanol partial pressure

The effect of varying the methanol concentration in the feed mix was investigated by employing the following reaction conditions: Methanol partial pressure was varied between 20 and 100 mbar (WHSV = 199–448 h⁻¹); ethene partial pressure was fixed at 50 mbar; 2.5 mg catalyst was used; total gas flow through the reactor was held constant at 100 mL/min; the reaction temperature was 350 °C.

The product distribution was independent of the methanol partial pressure, i.e., the same as shown in Fig. 3 at CT = 0.0034 h, and will not be described further. The concentration of hydrocarbons in the effluent was independent of the methanol partial pressure. With a constant gas flow rate this implies that the rate of hydrocarbon formation was independent of the methanol pressure, i.e., the reaction order with respect to methanol is zero. This is shown in Fig. 5.

The isotopic compositions of the products in the effluent were analyzed as above and the results are displayed in Fig. 6. Evidently, the isotopic distributions of the various products are virtually unaffected by the changes in the methanol pressure. The isotopic distributions that are seen from the histograms in Fig. 6 closely resemble those reported for high feed rates in Fig. 4. Methylation reactions are again dominating, but a second, less dominating path-

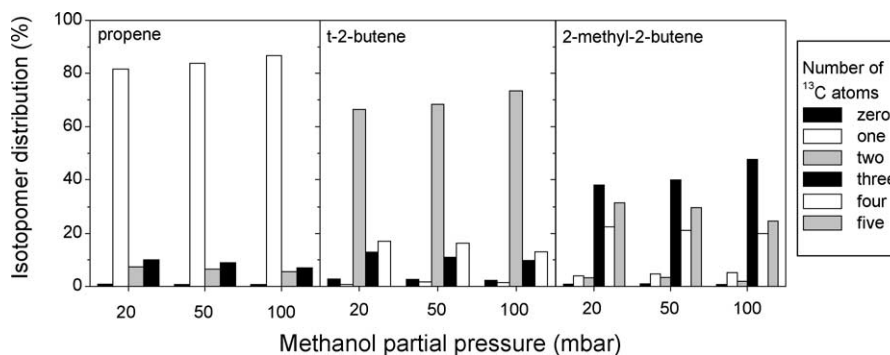


Fig. 6. Isotopic composition of alkene products in the effluent vs methanol partial pressure. 50 mbar [¹²C]ethene coreacted with 20–100 mbar [¹³C]methanol; reaction temperature = 350 °C; total gas flow = 100 mL/min. Additional data points omitted.

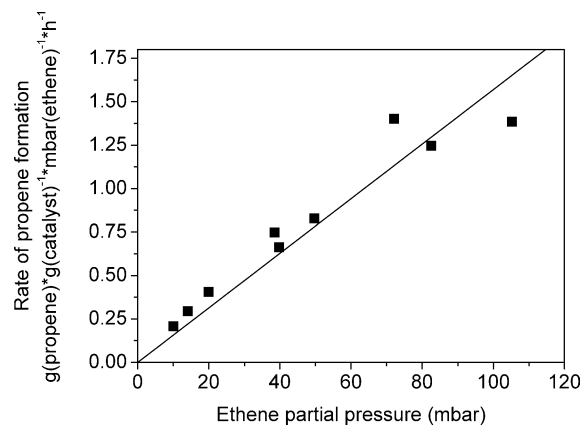


Fig. 7. Rate of propene formation vs ethene partial pressure: 10–105 mbar ethene coreacted with 50 mbar methanol; reaction temperature = 350 °C; total gas flow = 100 mL/min.

way for product formation, leading to alkenes with higher contents of labeled atoms is also operative. The joint *p/m*-xylene product fraction was always very rich in ¹³C.

3.3. The effect of ethene partial pressure

The effect of varying the ethene partial pressure was probed in an experiment analogous to that described in Section 3.2: Ethene pressure was varied between 10 and 105 mbar (WHSV = 183–442 h⁻¹); methanol partial pressure was fixed at 50 mbar; 2.5 mg catalyst was used; total gas flow through the reactor was held constant at 100 mL/min; the reaction temperature was 350 °C. Again, no significant systematic trend in product distribution was found. The concentration of product hydrocarbons in the effluent was proportional to the ethene partial pressure. Hence, with a constant gas flow, the rate was proportional to the ethene pressure. The reaction is first order with respect to ethene, as is seen in Fig. 7.

Isotopic analysis of the products was also carried out here. No striking effect of varying the ethene pressure was observed, but the fraction of isotopomers with only ¹³C declined slightly with increasing ethene partial pressure. In the case of propene, there was almost 10% of the ¹³C₃ iso-

topomer at $p_{\text{ethene}} = 10$ mbar. When $p_{\text{ethene}} = 105$ mbar this fraction fell to about 6%. The minor products displayed a similar trend.

3.4. The effect of reaction temperature

The reaction temperature was varied in order to investigate whether different temperatures would lead to changes in product selectivities or isotopomer distributions, and to construct an Arrhenius plot and determine the apparent activation energy for the methylation of ethene to propene. A feed mix consisting of 50 mbar [^{13}C]methanol and 50 mbar [^{12}C]ethene was coreacted over 2.5 mg catalyst at a total gas flow of 100 mL/min (WHSV = 292 h $^{-1}$). The temperature was varied between 305 and 410 °C. This range covers realistic and practical MTH conditions.

Reactant conversions, rates of products formation, and isotopic compositions were measured. The effect of increasing the temperature, while keeping the contact time constant, on product and the isotopic distributions was much the same as that of increasing the contact time at 350 °C. The product distribution and conversion at 400 °C was virtually identical to the one obtained at 350 °C at CT values somewhere in the range 0.017–0.022 h.

Our primary interest is to determine the activation energy for methylation of ethene by methanol, i.e., the activation energy for formation of the propene isotopomer with one ^{13}C atom. An Arrhenius plot showing the rate of formation of this isotopomer is given in Fig. 8. Even at 410 °C, this isotopomer still constitutes more than 60% of the propene molecules, but at this high temperature one might expect that part of the propene molecules take part in secondary reactions. The apparent activation energy 103 kJ/mol that is extracted from the Arrhenius plot is then somewhat on the low side, but even if the activation energy is estimated on basis of the total amount of propene, the estimate does not rise beyond 114 kJ/mol. The best estimate for the apparent activation energy might be the mean value, 109 kJ/mol.

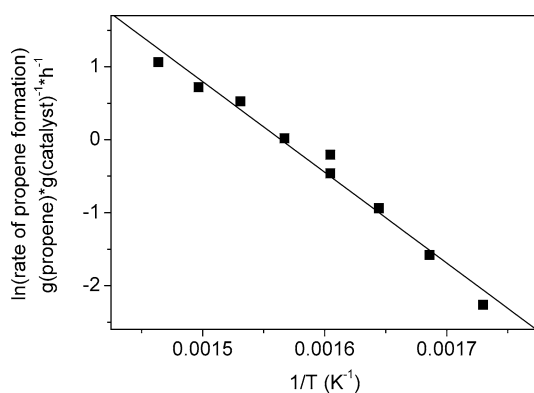


Fig. 8. Arrhenius plot for the formation of singly labeled propene: 50 mbar ethene coreacted with 50 mbar methanol; CT = 0.0034 h; reaction temperature varied from 305 to 410 °C.

3.5. The minor products

It was shown above in Fig. 3 that propene is the main product, which at the lowest CT values constitutes nearly 90% of the products. The remaining 10% comprise many products. They all contain more ^{13}C than propene, but their limiting behavior when $\text{CT} \rightarrow 0$ appears rather diverse and merits a short discussion. For this reason a part of Fig. 3 is reproduced with a much expanded ordinate scale in Fig. 9. Butenes are separated in two groups. *n*-Butenes are lumped separate from isobutene because the two groups have widely different isotopic distributions. C_5 molecules are lumped, but isotopic data have been obtained only for 2-methyl-2-butene. C_{6+} molecules are lumped. Isotopic data are available for one hexene isomer. The isotopic distributions of the minute amounts of *p*-xylene and 1,2,4-trimethylbenzene present in the effluent could be investigated down to $\text{CT} = 0.0067$ h. This analysis was possible because of the simple mass spectra of the polymethylbenzenes, which are dominated by the molecular ion. Isobutene was not adequately separated from 1-butene to allow rigorous determination of the isotopic composition. However, an estimate could be extracted and this is listed in Table 1 together with the results for the aromatics at $\text{CT} = 0.0067$ h. Random distributions for the observed total contents of ^{13}C atoms are included for comparison. The experimental distributions are seen to be fairly close to randomness. The all- ^{13}C isotopomers are, however, in all cases in clear excess relative to the random distribution. For all three hydrocarbons ^{13}C atoms constitute more than 80% of the carbon atoms. Measurements at the longer CTs indicated little variation when CT was changed.

In the $\text{CT} \rightarrow 0$ limit the *n*-butenes, in particular, and also the pentenes remain a sizable fraction of the product hydrocarbons, whereas the C_{6+} fraction is reduced to insignificance. The isobutene and alkane fractions are also reduced, but perhaps less clearly so than C_{6+} .

Fig. 4 shows that at all but the longest contact times the $^{12}\text{C}_2^{13}\text{C}_2$ *n*-butene isotopomer, corresponding to double methylation, is clearly dominating. The second most common species is the $^{13}\text{C}_4$ isotopomer, which at the longest

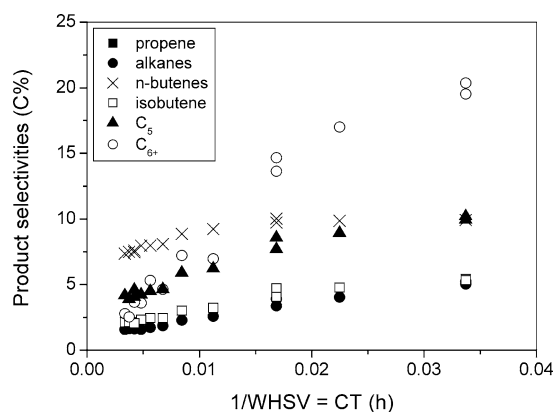


Fig. 9. Product selectivities with expanded Y axis. Propene is outside the scale. Reaction conditions as described in Fig. 3.

Table 1
Isotopic composition of isobutene, *p/m*-xylene, and trimethylbenzene

Number of ¹³ C atoms	Isobutene		<i>p/m</i> -Xylene		Trimethylbenzene	
0	2	(0)	0	(0)	0	(0)
1	3	(2)	1	(0)	0	(0)
2	13	(14)	1	(0)	1	(0)
3	33	(40)	2	(1)	1	(0)
4	49	(43)	6	(3)	2	(1)
5			12	(12)	6	(4)
6			22	(27)	13	(14)
7			24	(36)	22	(29)
8			33	(21)	26	(34)
9					29	(18)
Total ¹³ C content:	81		82		82	

Random distributions for the given total label contents are displayed in parentheses. 50 mbar [¹²C]ethene coreacted with 50 mbar [¹³C]methanol; reaction temperature = 350 °C; CT = 0.0067 h.

contact times becomes the most prominent. Other experiments that are not discussed here at still longer contact times have shown that molecules with 4 and 3 ¹³C atoms eventually become completely dominating at higher methanol conversions [24].

The C₅ molecules show a similar behavior, but this time the most common isotopomer at small CTs is the ¹²C₂¹³C₃ species. At slightly longer contact times molecules with 5 and 4 ¹³C atoms dominate.

Except at the longest contact time, i.e., CT = 0.034 h, the sum of all products formed when methanol was the only reagent was smaller than any of the products discussed in Fig. 9.

4. Discussion

The results described above indicate that two routes for product formation are operative when ethene and methanol are coreacted over H-ZSM-5. Quite clearly, ethene is methylated to form ¹³C₁¹²C₂ propene. Multiple methylations to higher alkenes are also observed. In addition, another mechanism is operative, leading to products very rich in ¹³C.

4.1. Methylation of ethene

Homologation of alkenes via methylation was fairly early proposed to be key reaction steps when methanol is converted to hydrocarbons over acidic zeolites [20,21,25]. Several reports on the coreaction of methanol and various alkenes exist, verifying that such reactions may occur. Wu and Kaeding [26] coreacted unlabeled ethene and methanol over H-ZSM-5, and an enhanced propene production was observed, indicative of ethene methylation. Behrsing et al. [27] coreacted unlabeled hexenes with [¹³C]methanol over H-ZSM-5 and found considerable amounts of mono-labeled C₇ products. Tau and co-workers [28–30] used ¹⁴C labeled reactants to investigate the methylation of ethene

and propene, but no kinetic data were given, and their approach only permitted the determination of the total label content. Iglesia et al. [31] combined [¹³C]methanol with ordinary propene over H-ZSM-5 and did find a large share of singly labeled butenes, but again the kinetics was not investigated. Fairly recently, Rønning et al. [32] published an investigation of the [¹²C]ethene/[¹³C]methanol system, but the conversions were fairly high and the reaction conditions were thus not well suited for kinetic studies.

The results described in the previous section show that by choosing the appropriate reaction conditions, methylation of ethene may be made, by far, the most prominent reaction, and that the rate of methylation can be measured. The limiting rate of formation of the propene isotopomer with one ¹³C atom gives the rate of methylation. Remembering that the reaction is of zero order with respect to methanol and first order with respect to ethene, the kinetic equation describing the methylation of ethene with methanol is given by Eq. (1).

$$r = k p_{\text{methanol}}^0 p_{\text{ethene}}^1 \quad (1)$$

The extrapolated total reaction rate was shown in Fig. 2 to be 0.70 g_{product}/(g_{catalyst} h) at 350 °C and $p_{\text{ethene}} = p_{\text{methanol}} = 50$ mbar. The limiting selectivity propene was shown in Fig. 3 to be 0.90, and the limiting isotopic selectivity to the ¹²C₂¹³C isotopomer was 0.85; thus the rate of formation of the clean methylation product is $(0.90 \times 0.85 \times 0.70 = 0.5355) 0.54$ g/(g h) or 0.013 mol/(g h). The value of k then is 2.6×10^{-4} mol/(g h mbar).

By varying the reaction temperature an apparent activation energy of 109 kJ/mol was found. Assuming that the reaction orders are unchanged over the investigated temperature range, this observed activation energy should be equal to the sum of the true activation energy and the ethene adsorption enthalpy. We have previously published a theoretical report on the mechanism of zeolite-catalyzed methylation of alkenes, using a cluster consisting of four tetrahedral atoms (three Si and one Al) to model the catalyst and utilizing density-functional theory (DFT) to carry out the quantum chemical calculations [22]. According to the calculations the reaction takes place when a methanol molecule is adsorbed end-on onto an acidic site while the alkene is adsorbed in close proximity on a siliceous part of the zeolite, and it proceeds in a concerted one-step process. The same mechanism has been proposed for methylation of arenes by methanol [23]. Hence, the theory suggests that the methylation reaction takes place by a Langmuir–Hinshelwood–Hougen–Watson (LHHW) reaction mechanism type. Based on this mechanism, the experimentally determined adsorption enthalpy of ethene in silicalite-1, the completely siliceous MFI polymorph, may be used as a correction in order to obtain the true activation energy. Choudhary and Mayadevi [33] found an isosteric heat of adsorption of 25 kJ/mol for ethene on silicalite-1, and this value was found to be virtually independent of the ethene coverage. Assuming that the heat of adsorption is unaffected

by the presence of methanol as a coadsorbate, the intrinsic activation barrier for the H-ZSM-5-catalyzed methylation of ethene by methanol should be ~ 135 kJ/mol. This is substantially lower than the value reported in our DFT study [22], where an activation barrier of 183 kJ/mol was found for methylation of ethene. This discrepancy is, however, quite expected. It is well known that the DFT/cluster approach severely overestimates the energies of transition states and charged species, in some cases by as much as 100 kJ/mol [34,35]. Bearing this in mind, the agreement between experiment and theory is acceptable.

Equation (1), as written, is not a LHHW kinetic equation. The adsorption terms are missing. The experimentally found zero and first-order behavior with respect to methanol and ethene means that in our experimental range, methanol is adsorbed on all acid sites, and ethene is extremely sparsely adsorbed. Equation (1) can only be expected to describe the reaction as long as this is valid; i.e., the equation may break down when $p_{\text{methanol}} \ll 20$ mbar, and when $p_{\text{ethene}} \gg 100$ mbar.

The rate constant k of Eq. (1) is given by the Arrhenius expression $k = A \exp(-E_{\text{apparent}}/RT)$. The value of k at 350 °C is 2.6×10^{-4} mol/(g h mbar); hence A has the value 3.5×10^5 mol/(g h mbar) and $k(T) = 3.5 \times 10^5 \times \exp(-13100/T \text{ K}^{-1})$ mol/(g h mbar).

The Si/Al ratio of the catalyst used here is 45, which means that the stoichiometric formula of the zeolite may be written $(\text{SiO}_2)_{45}(\text{AlO}_2)_1\text{H}$, giving a molar mass 2760 g/mol; i.e., there is 3.6×10^{-4} mol/g. There is one proton per molecular unit, so this is also the molar content of active sites per gram catalyst. The preexponential factor A therefore has the value $(3.5 \times 10^5 / 3.6 \times 10^{-4} = 9.7 \times 10^8)$ $A = 9.7 \times 10^8$ mol/(mol h mbar) $= 9.7 \times 10^8$ (h mbar) $^{-1} = 2.7 \times 10^5$ (s mbar) $^{-1}$.

Somewhat simplistically one may say that the preexponential factor expresses the rate that would be obtained if the activation energy were negligible, and it expresses the maximum rate that might be observed for a given reaction. The maximum rate that may be imagined for this reaction is given by the rate by which the ethene molecules hit an active site. It is therefore of interest to compare the value of A , given above, with this collision frequency. According to simple kinetic theory of gases, the number of collisions per unit time and unit area is given by $Z_w = p/(2\pi mkT)^{1/2}$. If the area of an active site is taken to be 0.5 nm², the formula gives that at 350 °C, i.e., 628 K and $p_{\text{ethene}} = 1.00$ mbar the collision frequency per active site is 1.0×10^6 s $^{-1}$, which compares very well with the value $A = 2.7 \times 10^5$ (s mbar) $^{-1}$.

The values obtained above for the rate constant as a function of temperature, $k(T)$, and the preexponential, A , expressed per acid site, should in principle be transferable to other H-ZSM-5 catalysts operating at different partial pressures, reaction temperatures, and Si/Al ratios. However, it should be kept in mind that these rate parameters might not be valid for other catalyst frameworks than MFI.

To what extent does the reaction proceed via ethene methylation when ethene is not added as a coreactant? The data presented here show that although the methylation of ethene does proceed at a nonnegligible rate, it was eclipsed by other pathways once there was an appreciable amount of hydrocarbon products. It was shown (Sections 3.1 and 3.5) that although the number of ^{12}C atoms in the feed was double that of ^{13}C , there was a large excess of ^{13}C atoms in the hydrocarbon products when the CT was increased.

When methanol alone is reacted over a ZSM-5 catalyst, ethene is usually a relatively small product. Using the same catalyst at 350 °C, as here, and a methanol partial pressure 100 mbar only 6% of the products were ethene at 40% conversion [24]. The ethene partial pressure in the effluent was then 1.2 mbar. Since the methylation rate is first order with respect to ethene pressure, the methylation rate was then only 2.5% of the rate obtained when $p_{\text{ethene}} = 50$ mbar. It may therefore be concluded that ethene methylation is only a minor pathway in the MTH reaction. However, if the reactant concentrations are increased by one or two orders of magnitude this conclusion may be less valid.

4.2. Butenes and pentenes

It was shown in Section 3.5 that *n*-butenes and pentenes remain a sizable fraction of the product hydrocarbons in the CT $\rightarrow 0$ limit. The most common isotopomers have two, respectively three, ^{13}C atoms, as one should expect if they are obtained by methylation once or twice of the propene. A question arises. Are these products primary products, or are they secondary products formed by methylation of propene after its desorption from the site where it was formed?

From the ^{13}C atom contents in butene and pentene it is tempting to conclude that they are formed by secondary and tertiary methylations. This may, however, be wrong. In a series of consecutive (irreversible) first-order reactions $\text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{D}$ (ethene \rightarrow propene \rightarrow butene \rightarrow pentene), it is known that in the limit of short reaction time, t , $[\text{B}]$ is proportional to t , $[\text{C}]$ is proportional to t^2 , and $[\text{D}]$ to t^3 . In the limit of $t \rightarrow 0$ one will therefore have the concentration ratios $[\text{C}]/[\text{B}] \rightarrow 0$ and $[\text{D}]/[\text{C}] \rightarrow 0$. The observed ratios did not display this limiting behavior.

If, however, the subsequent methylations of propene take place before the propene molecules can leave the zeolite crystal where they were formed and join the bulk gas phase the concentration ratios become independent of the contact time, CT, because the mean residence time within a crystal is independent of the flow rate.

Alternatively, parts of the butenes and pentenes might be primary products formed from the hydrocarbon pool. Such a formation mechanism would also be in concordance with the finding that the alkene molecules appear to come from two sources. The fraction of propene isotopomers with two or three ^{13}C atoms would also fit in with this explanation, see Fig. 4. Their composition is in agreement with the known

isotopic composition of the arenes, Table 1. No conclusion is presently warranted on this issue. Fig. 4 shows that linear extrapolation to the $CT \rightarrow 0$ limit indicates that the two *n*-butene isotopomers, $^{12}C_1^{13}C_3$ and $^{13}C_4$, constitute 20–25% of the *n*-butenes. The two 2-methyl-2-butene isotopomers, $^{12}C_1^{13}C_4$ and $^{13}C_5$, constitute about 45% of the 2-methyl-2-butene. These isotopomers could not be formed by repeated methylations of ethene. Fig. 9 shows that the limiting value of the fraction of C_{6+} products is zero, so the ^{13}C atom rich *n*-butene and 2-methyl-2-butene isotopomers are not cracking products of C_{6+} . Fig. 4 suggests that the real isotopomer limiting fractions are not obtained correctly by linear extrapolation; the ^{13}C content is even higher. We do not know if this is an artifact, whose origin is unknown, or if it is true. Even if it is a real effect, the conclusions arrived at above become still more valid.

Interestingly, the isotopic composition of isobutene was completely different from that of the linear butenes. The content of ^{13}C atoms is much higher, and the isotopomer distribution is random. It seems probable that isobutene is formed through the hydrocarbon pool mechanism. This is in excellent accord with data reported by Bjørgen et al. [11,36], which show that isobutene/isobutane is the most prominent product formed when polymethylbenzenes are reacted over zeolite H-beta.

5. Conclusions

The coreaction of ethene and [^{13}C]methanol over H-ZSM-5 has been studied at extremely high feed rates. By using a microreactor, it has been possible to collect data at very low conversions, but at a realistic reaction temperature and catalyst acid site density. The isotopic labeling showed that methylation of ethene to form singly labeled propene was dominating at the lowest conversions. Further methylations to form doubly labeled butenes and triply labeled pentenes were also observed. However, more than 20% of the linear butenes, and more than 40% of the pentene, 2-methyl-2-butene, contain more than 2, respectively 3, ^{13}C atoms, and are not formed by multiple methylations of ethene. In the limit $CT \rightarrow 0$ the C_{6+} product fraction becomes zero, and in this limiting case, butenes and pentenes are therefore not the result of cracking of higher alkenes.

The methylation of ethene is zero order with respect to methanol partial pressure and first order with respect to ethene partial pressure. An observed activation barrier for the methylation of ethene of 109 kJ/mol has been found. Correction for the adsorption energy of ethene [33] yields an intrinsic activation energy of about 135 kJ/mol. Dimerization of ethene is a very minor reaction. Superimposed on the methylation pattern is a mechanism and reaction path leading to alkene products very rich in ^{13}C atoms. This mechanism becomes dominating when the conversion exceeds a few percent and hydrocarbons other than ethene are available for reaction with methanol. The results are concurrent with the formation of alkenes with high ^{13}C contents through the hydrocarbon pool mechanism.

Under ordinary MTH reaction conditions, formation of higher alkenes via homologation, starting with ethene, is not an important reaction.

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