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Kinetic studies of zeolite-catalyzed methylation reactions. Part 2. Co-reaction of [^{12}C]propene or [^{12}C]n-butene and [^{13}C]methanol

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Abstract

The co-reaction of propene or n-butene and methanol over an H-ZSM-5 acidic zeolite catalyst has been investigated using isotopically labeled reagents. The main objective has been to obtain kinetic data for the methylation of the propene and n-butene. This study is an extension of our previous investigation of the co-reaction of ethene and methanol [S. Svelle, P.O. Rønning, S. Kolboe, J. Catal. 224 (2004) 115]. At the very high feed rates employed here, the methylation products are dominating, and the isotopic composition is in accord with a methylation formation mechanism. Arrhenius plots have been constructed, and the activation energies, when corrected for the appropriate heats of alkene adsorption, were ∼110 kJ/mol for the methylation of propene and ∼90 kJ/mol for the methylation of n-butene. The results are compared with recent computational studies of the methylation of alkenes. The origin of the products not formed via methylation is briefly discussed. A short survey of the reactivity of propene and n-butene without methanol co-feed is presented. It has been found that alkene interconversion reactions are strongly suppressed by the presence of methanol.

Keywords: H-ZSM-5; Propene methylation; Butene methylation; Methanol-to-hydrocarbons; Propene; Linear butenes; Isobutene; Isotopic labeling

1. Introduction

The methanol-to-hydrocarbons (MTH) process represents a possible route for the upgrading of natural gas or coal to higher value products. Natural gas may be transformed to synthesis gas (CO and H_2), which is subsequently reacted to form methanol. The methanol may then be converted into a mixture of hydrocarbons using acidic zeolite or zeotype catalysts. Mobil was the first to discover and develop this zeolite-based technology, resulting in the methanol-to-gasoline (MTG) process; in which methanol is converted to gasoline over ZSM-5-derived catalysts. Later, Norsk Hydro and UOP jointly developed the methanol-to-olefins (MTO) variant of the reaction, in which ethene and propene are the main products formed over SAPO-34 zeotype catalyst systems. The latest addition to this field is the methanol-to-propylene (MTP) alternative, currently offered by Lurgi. But despite the apparently great potential for industrial application of the MTH reaction, the only full-scale commercial operation to date was the MTG plant in New Zealand in which gasoline production was started in 1986 and later shut down due to a falling price of oil relative to that of methanol [1]. However, an MTO plant is expected to come onstream in Nigeria in 2006, as part of a natural gas to polymers project [2].

In contrast to the maturity of the MTH reaction when it comes to practical applications, the present level of understanding of the underlying reaction mechanism still leaves something to be desired. Initial research focused on the formation of carbon-carbon bonds directly from C_1-units (methanol, dimethylether, or trimethyloxonium ions), but these efforts were all inconclusive, and this reaction is now considered to be of little importance during steady state conversion of methanol to hydrocarbons [3–6]. More indirect mechanism types are currently favored, and experimental

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and theoretical results in favor of the "hydrocarbon pool" mechanism, originally proposed by Dahl and Kolboe [7–9], are mounting. The hydrocarbon pool mechanism proceeds via continuous methanol addition to a hydrogen-poor adsorbate inside the zeolite pores, from which lower alkenes are split off at a later stage of the catalytic cycle. The exact chemical nature of the hydrocarbon pool has been investigated by Kolboe et al. [10–14], Haw et al. [15–21], and Hunger et al. [22,23] and may depend on catalyst type and reaction conditions. Polymethylbenzenes, polymethylnaphtalenes, and polymethylated cyclopentadienyl cations have all been shown to function as hydrocarbon pool species.

In the early 1980s, Dessau et al. [3,5] proposed an indirect reaction mechanism for the methanol conversion based on alkenes as the key intermediates. A considerable part of the hydrocarbons in the product stream are alkenes, and chain growth through via alkene methylation followed by cracking to yield smaller alkenes might constitute a competing mechanistic scheme. Knowledge of the rate of alkene methylation (and ultimately of other species present in the zeolite pores) is therefore an essential step in discriminating between the various proposed mechanisms.

We previously investigated the methylation of ethene by methanol to form propene, at reaction conditions directly comparable to those used in the present study [24]. A central issue in the earlier study was to find the reaction conditions best suited for measuring rate data for the methylation, suppressing any side reactions such as alkene dimerization, alkene cracking, cyclizations, and hydrogen transfer but still operating at a realistic reaction temperature and catalyst acid site density. We found an intrinsic activation energy for ethene methylation of ~135 kJ/mol; the reaction was of first order with respect to ethene partial pressure and of zero order with respect to methanol. The apparent rate constant k was 2.6×10^{-4} mol/(g h mbar) at 350 °C and the pre-exponential A was 3.5×10^{5} mol/(g h mbar).

In this paper we report new results on the kinetics of the methylation of propene and linear butenes by methanol. We used isotopically labeled methanol to follow the individual reaction steps. In contrast to ethene, both propene and the linear butenes display nonnegligible activity when reacted without methanol co-feed even at the very high feed rates used here. It was therefore necessary to address this issue in some detail to gain a better understanding of the results from the co-reaction experiments. Hence the first part of this report concerns the reactivity of propene and the linear butenes alone, with the methylation reactions addressed in subsequent parts.

2. Experimental

The experimental setup and the calculation procedures used have been described in detail previously [24]. We give a brief summary here.

2.1. Catalyst, reagents, and catalytic testing

The H-ZSM-5 catalyst used was a gift from Süd-Chemie A.G. The Si/Al ratio was 45, and the sample consisted of very small crystals (~50 nm). [^{13}C]methanol was supplied either by ISOTEC or Cambridge Isotope Laboratories. Natural isotope abundance propene was supplied by Fluka. Gas chromatography (GC) analysis showed that propane (~0.07%) and 1-butene (~0.05%) were the main impurities. 1-Butene >99% (Fluka) was used for the co-reaction experiments, and 2-butanol >99% (Fluka) was used to study the reactivity of linear butenes without methanol co-feed. 2-Butanol is dehydrated immediately, forming linear butenes in situ. Regardless of the original butene source (2-butanol or 1-butene), the three linear butene isomers in the effluent were always in internal thermodynamic equilibrium, and thus we refer to this feedstock as n-butene in what follows.

A fixed-bed Pyrex microreactor (3 mm i.d.) was used for the catalytic experiments. Propene and 1-butene were fed as gases, and methanol and 2-butanol were fed by passing part of the carrier gas (He, >99.996%) through a vessel containing the desired alcohol, thus saturating the carrier gas. The feed rate [weight hourly space velocity (WHSV)] was varied by varying the total gas flow through the reactor. Typical reaction conditions for the co-reaction of propene and methanol were as follows: methanol partial pressure = 50 mbar, propene partial pressure = 20 mbar, total gas flow = 100 ml/min, reaction temperature = 350 °C, and catalyst mass = 2.5 mg, resulting in a feed rate (WHSV) of 237 h^{-1}. The alkene partial pressure for was slightly lower for n-butene than for propene, typically 13 mbar. The effects of varying the feed rate, reactant partial pressures, and reaction temperatures have been investigated. A key focus has been on studying the catalytic system at low conversion (i.e., high feed rates) but with realistic reaction temperature and catalyst acid site density.

2.2. Analysis and calculations

The effluent was analyzed using a Carlo Erba Vega GC-FID equipped with a Supelco SPB-5 column (60 m × 0.53 mm × 3 µm); the lower response factors for oxygen-containing compounds were taken into account. C1–C4 alkanes/alkenes were separated on a Siemens Sichromat 2-8 (FID) equipped with a Chrompack PLOT column (Al_2O_3/KCl, 50 m × 0.53 mm × 10 µm) or a J&W GS-GasPro column (60 m × 0.32 mm). The isotopic distributions were determined based on analyses made with an HP 6890 GC-mass spectrometry (MS) unit, using a HP-5MS column (60 m × 250 µm × 0.25 µm) or a J&W GS-GasPro column (60 m × 0.32 mm) combined with cryostatic cooling. The computational method used for determining the isotopic composition of the products was outlined previously [24,25].

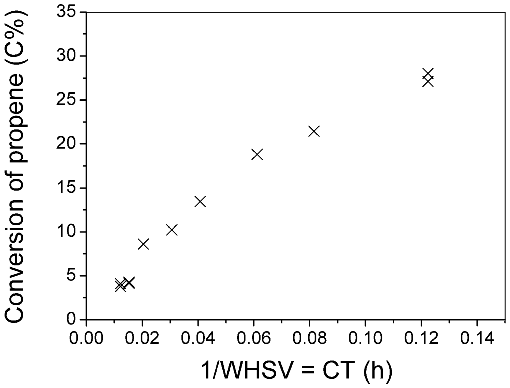

Fig. 1. Conversion of propene versus contact time. 20 mbar of propene reacted alone; total gas flow varied from 10 to 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

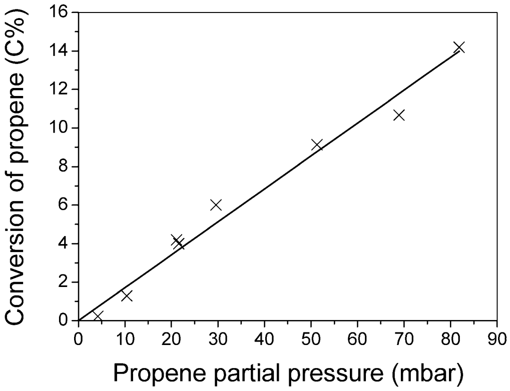

Fig. 2. Conversion of propene versus propene partial pressure. 5–80 mbar of propene reacted alone; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

3. Results

The main objective of the present work was to study and obtain kinetic data for the methylation of propene and linear butenes by methanol. To obtain kinetic data, we needed to operate at very high feed rates and correspondingly low conversions. At higher conversions, (i.e., lower feed rates), secondary reactions rapidly become dominant, and any information concerning the primary reaction steps becomes obscure. The feed rate is usually given as the WHSV, in terms of $g_{feed}/(g_{cat}\,h)$. The inverse quantity, the "contact time" (CT = 1/WHSV) is better suited for the discussion that follows. Using CT rather than WHSV allows extrapolations of rates and selectivities to CT = 0 (or infinite feed rate), thereby providing an estimate for the primary or intrinsic quantities.

Unlike our previously published results concerning the co-reaction of ethene and methanol [24], both propene and n-butene display significant reactivity when fed alone, even at the shortest contact times employed. Therefore, a short survey of the reaction pattern of the alkenes alone will be given before the co-reaction data. As previously described, the reactivity of methanol alone was insignificant [24].

3.1. Propene without methanol co-feed

The effects of varying the contact time on the propene conversion were investigated by reacting 20 mbar of propene over 2.5 mg of catalyst at 350 °C. The total gas flow through the reactor was varied from 10 to 100 ml/min, thus varying the contact time from 0.012 to 0.12 h (WHSV = 81.8–8.2 h^{-1}). The influence on the propene conversion, which increases from 4% to 28%, is displayed in Fig. 1. The nonlinear increase with CT agrees well with the equilibrium content (C%) of propene in a C3–C6 alkene mixture, which is about 35% at an initial pressure of 20 mbar [26], corresponding to 65% conversion. The level of reactivity is in stark contrast to what was observed when ethene was investigated in an analogous manner, the only difference being a higher ethene partial pressure of 50 mbar instead of 20 mbar [24]. The ethene conversion was <0.1% even at the longest CT. The product distribution from propene was virtually unaffected by the changes in feed rate, and the effluent comprised 47 C% n-butenes, 32 C% isobutene, 15 C% C_5 (mainly pentanes), and 4 C% C_6 (mainly hexenes). Hexenes constitute the expected outcome of a primary dimerization reaction, but this product fraction was detected in only small amounts. Clearly, the propene molecules undergo several secondary reaction steps before the products leave the reactor, even at such high feed rates. It is noteworthy that ethene constituted <1% of the products. Traces of butanes were detected. The rate of propene conversion, obtained by dividing the conversion by CT, extrapolates to about 3.5 $g/(g_{cat}\,h)$ at CT = 0 for the chosen conditions.

The degree of conversion depends strongly on the partial pressure. This is displayed in Fig. 2, where the propene partial pressure was varied from 5 to 80 mbar while the total gas flow was held constant at 100 ml/min. The conversion increases, apparently linearly, from <1 to 14% in this range. Because the reaction rate is given by conversion × (feed rate), and both of these quantities are proportional to propene partial pressure, a linear increase in the conversion with pressure demonstrates a second-order reaction. Considering that product formation from propene necessarily involves an interaction of (at least) two propene molecules on the catalyst surface, this behavior may be expected.

Significant changes in product distribution were observed when the feed partial pressure was altered. At 5 mbar, isobutene and n-butene dominated, constituting about 40% and 50 C% of the products, respectively. Modest amounts of pentenes (7 C%) and ethene (3 C%) were also detected. At 80, mbar n-butene still dominated (39 C%) and C_5 had become the second largest fraction (24 C%), followed by isobutene (21 C%) and then C_{6+} (16 C%). Ethene occurred in only trace amounts.

Table 1 lists the propene conversion and product selectivities as a function of reaction temperature. The most striking feature of Table 1 is the pronounced increase in conversion with temperature decrease. This effect is not caused by deactivation at high temperatures; there is hardly any deac-

Table 1
Propene conversion and product selectivities (in C%) versus reaction temperature. 20 mbar of propene reacted alone; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature varied from 250 to 425 °C

Reaction temperature (°C)	C_2	n-C_4	i-C_4	C_5	C_{6+}	Conversion (%)
250	0.1	41	14	35	9.8	12.8
275	0.1	49	19	26	5.8	12.1
300	0.2	53	23	22	2.6	8.9
325	0.4	53	27	18	2.5	6.2
350	0.9	49	31	14	5.1	3.1
350	0.8	50	33	14	3.1	3.8
375	2	47	32	13	6.0	1.9
400	5	45	30	12	8.3	1.2
425	11	42	24	12	11	0.8

tivation, and the experiments were carried out using random temperature settings. The result might seem counterintuitive, but it can be attributed to an increase in the surface coverage at low temperatures. We elaborate on this point in Section 4. The increase in conversion is smaller for the step of 275 to 250 °C than for the other steps in Table 1, indicating that the conversion approaches a maximum value before it drops off as the temperature becomes too low for any reaction to occur. Product formation is insignificant below about 200 °C.

3.2. *n-Butene without methanol co-feed*

The reactivity of n-butene was probed in experiments analogous to those described above for propene. To accurately control the reaction conditions, we used 2-butanol rather than gaseous 1-butene as the precursor for n-butene. 2-Butanol is virtually instantaneously transformed into water and linear butenes. Separate experiments demonstrated that the presence of an equimolar amount of water does not significantly affect butene conversion. There are three isomeric linear butenes, but their interconversion is so fast that an essential equilibrium is always observed. There is a major difference in the possible reactions of n-butene and propene; the linear butenes may undergo a skeletal isomerization, leading to the formation of isobutene, resulting in a slightly more complicated reaction pattern. Conversion and selectivities as a function of contact time are given in Fig. 3. In this figure, n-butene displays greater reactivity than propene. The limiting rate of conversion (conversion divided by CT) can be extracted from the data in Fig. 3; it is about 10 g/(g h), that is, about 3 times that of propene or – if compared at equal partial pressures – a factor about 4.5. Fig. 3 shows only small changes in the product composition when the CT is varied.

Analogously to the foregoing results for propene, the product distribution changes markedly with altered n-butene partial pressure (see Table 2). At the lowest pressures, isobutene is dominant among the products, with selectivity reaching nearly 70 C% at $p_{n\text{-butene}} = 1$ mbar. As was the case for propene, the fractional conversion decreases with decreasing n-butene pressure. But although an almost linear dependence on pressure is apparent, it is not proportional to the butene pressure. Linear regression analysis demonstrates 8.3% conversion at $p_{n\text{-butene}} = 0$.

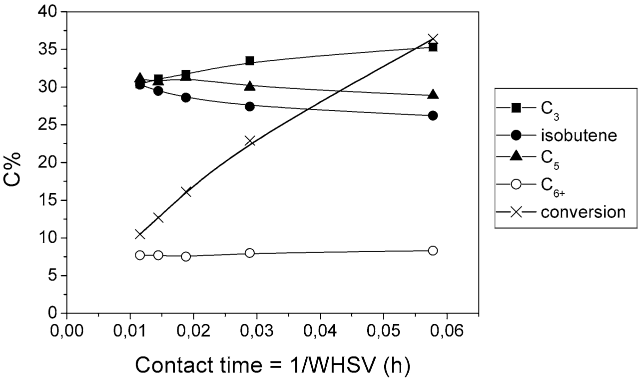

Fig. 3. Conversion of n-butene and product selectivities (in C%) versus contact time. 13 mbar of n-butene reacted alone; total gas flow varied from 25 to 125 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

Table 2
n-Butene conversion and product selectivities (in C%) versus partial pressure. 1–16 mbar of n-butene reacted alone; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C

Partial pressure (mbar)	C_3	i-C_4	C_5	C_{6+}	Conversion (%)
1	15	69	16	–	8.6
2	20	60	20	–	9.3
4	22	54	24	–	9.8
6	31	39	29	1.5	13
10	33	32	31	4.1	15
16	34	28	31	6.7	17

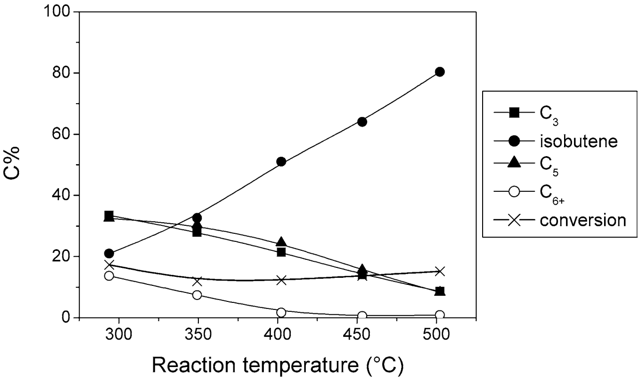

Fig. 4. Conversion of n-butene and product selectivities (in C%) versus reaction temperature. 13 mbar of n-butene reacted alone; total gas flow 75 ml/min; 2.5 mg catalyst; reaction temperature varied from 300 to 500 °C.

The conversion and product distribution at various reaction temperatures are given in Fig. 4. When the temperature rises above 350 °C, isobutene quickly dominates, constituting 80 C% of the products at 500 °C. In the temperature range 300–500 °C, the conversion is essentially constant, although increasing when the temperature falls from 350 to 300 °C. Below about 200 °C the conversion is insignificant, however.

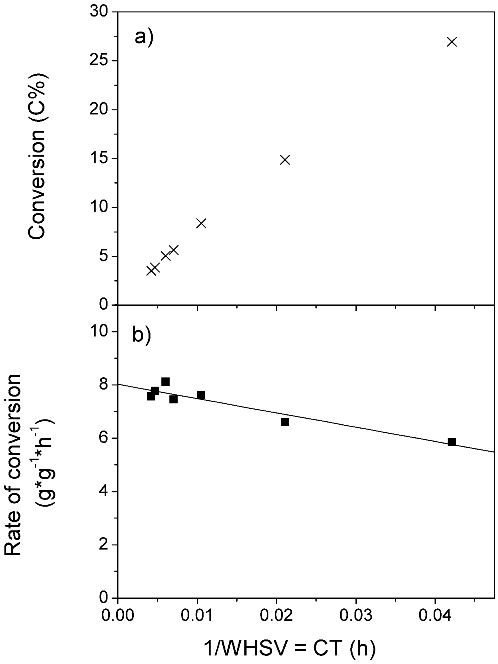

Fig. 5. Conversion (a) and rate of conversion (b) of feed mixture versus contact time. 20 mbar of propene co-reacted with 50 mbar methanol; total gas flow varied from 10 to 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

3.3. Co-reaction of propene and methanol

3.3.1. Influence of the contact time

A feed mix consisting of 20 mbar [^{12}C]propene and 50 mbar [^{13}C]methanol was reacted at 350 °C over 2.5 mg of H-ZSM-5 catalyst. The contact time was varied from 0.0042 to 0.042 h (WHSV = 237–24 h^{-1}) by adjusting the total gas flow. The conversion, determined by considering propene, methanol, and dimethyl ether as unconverted feed, is shown in Fig. 5a. It ranges from 3.2 C% to 27 C%, considerably higher than that observed when ethene and methanol were co-reacted at comparable conditions [24]. Then the conversion ranged from almost 0 to about 7%. Dividing the conversion with CT yields the apparent rate of conversion (see Fig. 5b). Extrapolation to CT = 0 yields a rate of 8.0 g/(g h). The corresponding limiting rate was 0.7 g/(g h) when methanol and ethene were co-reacted at an ethene partial pressure of 50 mbar [24]. The conversion increases slightly less than linearly with increasing CT (the apparent rate decreases), as may be expected because the effective reactant concentrations decrease at high conversions. Hence no autocatalysis is seen in the present case. The product selectivities are shown in Fig. 6. If methylation of propene were the only reaction occurring, then n-butene selectivity would reach 100%, but this is clearly not the case. n-Butene is dominating at the shortest contact times, but other products can always be detected. Extrapolated to CT = 0, an n-butene selectivity of about 70 C% is observed. The other limiting selectivities appear to be 15% C_5, 8% isobutene, and 7% C_{6+}. Ethene and alkanes (butanes) were always present in insignificant amounts.

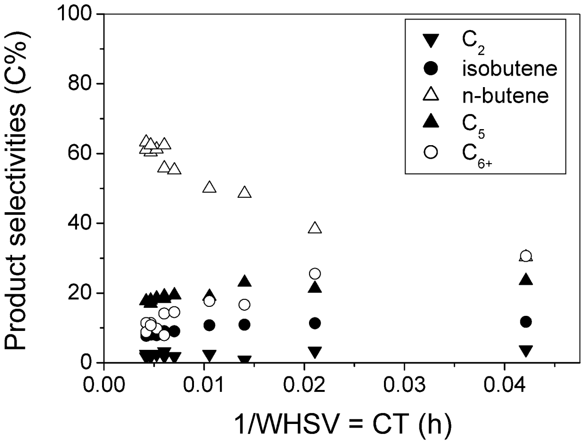

Fig. 6. Product selectivities (in C%) versus contact time. 20 mbar of propene co-reacted with 50 mbar methanol; total gas flow varied from 10 to 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

Because of the quite high reactivity of propene alone, we needed to use isotopically labeled reactants to evaluate the data. The isotopomer distributions of the alkene products are given in Fig. 7. For *trans*-2-butene, which is representative of the linear butene isomers, the $^{12}C_3\,^{13}C_1$ isotopomer is clearly present in excess, demonstrating that methylation is the main pathway for n-butene formation in the co-reaction system. The other n-butene isotopomers are always present, although in smaller amounts, and the extrapolated value for $^{12}C_3\,^{13}C_1$ at CT = 0 is about 90%. The $^{12}C_4$ and $^{12}C_2\,^{13}C_2$ isotopomers both extrapolate to around 5%. When CT is increased, the methylation pattern becomes obscured by secondary reactions, and the isotopomer distributions approach randomness.

The isotopic distribution of 2-methyl-2-butene is strongly dominated by the $^{12}C_3\,^{13}C_2$ species. The amount of this isotopomer greatly exceeds what would normally be expected for a random distribution. Double methylation appears to be the main formation mechanism. The share of pentenes not composed of two ^{13}C and three ^{12}C atoms and thus apparently not formed via methylations was slightly greater than that for the n-butenes. In both cases the limiting amounts of the $^{12}C_2\,^{13}C_3$ and $^{12}C_4\,^{13}C_1$ isotopomers are slightly above 10%, whereas that of $^{12}C_3\,^{13}C_2$ extrapolates to about 65%.

Isotopic data are available for one hexene isomer. No clear differences could be seen when comparing the mass spectrum of this isomer with other less prominent or less well-separated isomers. The $^{12}C_3\,^{13}C_3$ isotopomer, corresponding to triple methylation of propene, is dominant. In addition, when ethene and methanol were co-reacted, isotopic distributions indicating triple and even quadruple methylations were observed [24]. The second most abundant hexene isotopomer is built up exclusively from ^{12}C atoms, which can only be attributed to propene dimerization. Note, however, that the relative content of hexenes becomes very small at the shortest CTs, extrapolating to only 0–5%. Thus

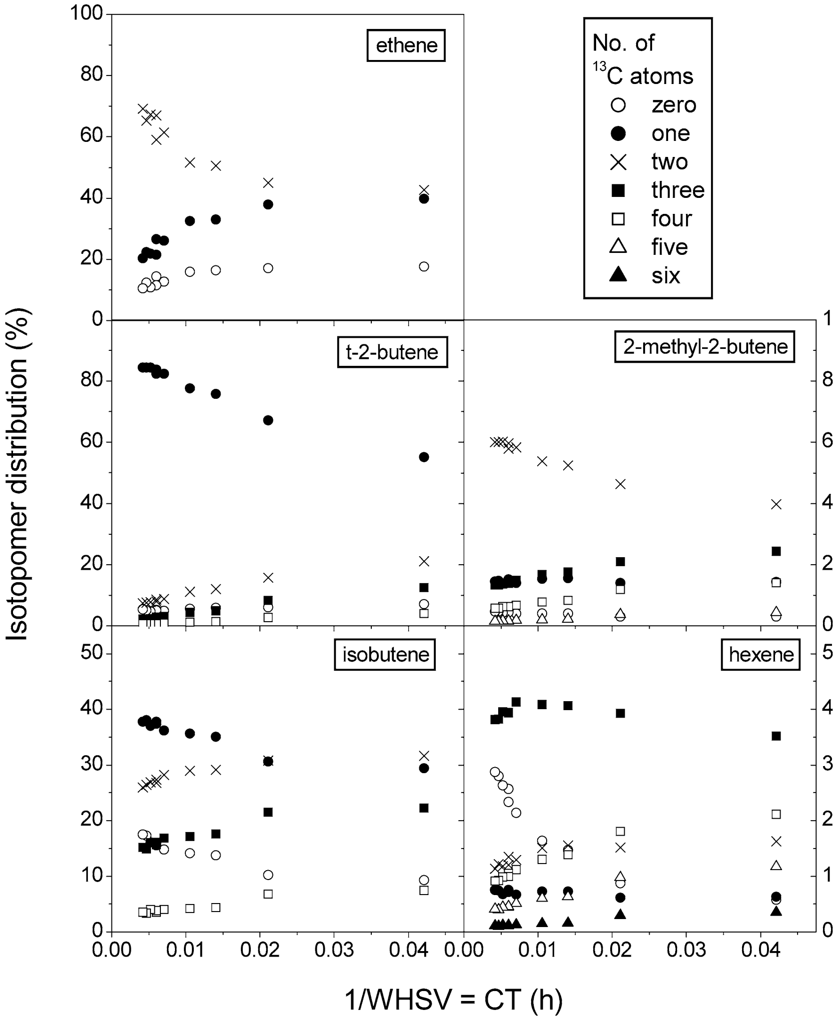

Fig. 7. Isotopic composition of alkene products versus contact time. Note the scale differences. 20 mbar of propene co-reacted with 50 mbar methanol; total gas flow varied from 10 to 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

propene dimerization is a rather unimportant reaction compared with methylation at the conditions maintained in these experiments.

Besides the major alkene products, small amounts of aromatics were always detectable in the effluent. The isotopic composition of the joint p/m-xylene product fraction could be determined due to the simple mass spectrum, which is dominated by the molecular ion peak. The distribution is broad, slightly broader than a random distribution based on the total ^{13}C content, in the sense that the shares of all ^{12}C and all ^{13}C isotopomers are excessive compared with the random distribution. The total content of labeled carbons was high, increasing from 61% at long CTs to 67% at the shortest CT.

No obvious pattern is seen in the isotopic distribution of the ethene molecules in the effluent; it is close to random. Similarly to what was seen for p/m-xylene, the total ^{13}C content is high, increasing from 62% at the long CTs to 79% at the shortest CT. The isotopic composition of isobutene is strikingly different from that of n-butene. The distribution is close to random, and it may be concluded that isobutene is not formed through methylation of propene. Also, the total ^{13}C content is considerably higher, ranging from 37% at CT = 0.0042 h to 47% at CT = 0.042 h, signifying that n-butene is an unlikely immediate precursor for isobutene in this co-reaction system.

Because the isotopic compositions of the products are known, it is possible to evaluate the degree of conversion of propene and methanol individually. By applying this approach to the data collected at the shortest contact time (CT = 0.0042 h), the propene conversion is determined to be 3% and the methanol conversion 2%. Thus the propene conversion is roughly the same as it was when propene was investigated without methanol co-feed (4%, 20 mbar propene in both cases). Even so, the isotopic data show that the reaction steps by which propene is consumed are completely different when methanol is present (methylation) and when it is not (alkene interconversions).

3.3.2. *Influence of propene partial pressure*

We investigated the effects of varying propene partial pressure on the reaction rates and isotopic compositions of

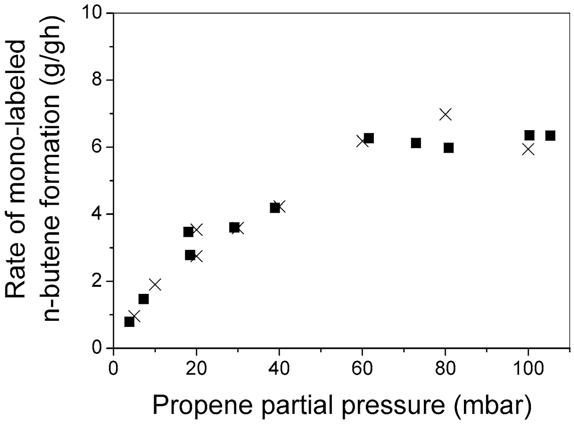

Fig. 8. Rate of mono-labeled n-butene formation versus propene partial pressure. 5–100 mbar of propene co-reacted with 50 mbar methanol; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C. Data obtained in two separate, identical experiments (■ and ×).

the products formed in the co-reaction by conducting the following experiment. The propene partial pressures were varied in the range 5–100 mbar. The methanol partial pressure was kept at 50 mbar with a constant total gas flow of 100 ml/min and 2.5 mg of catalyst. The total conversion of the feed mixture depends on the propene partial pressure; it increased from 1% at 5 mbar to 5% at 100 mbar. The rate of mono-labeled n-butene formation increases with the propene partial pressure up to about 50 mbar, as shown in Fig. 8. At higher propene pressures, the methylation reaction rate levels off and the reaction order approaches zero. As evident from the isotopic distributions (see later), methylation becomes less predominant at higher propene pressures, whereas alkene interconversion reactions become more significant.

Significant effects on the product distribution were also demonstrated in this experiment. The selectivity toward n-butenes decreases with increasing propene pressure; it fell from 55 C% at 5 mbar to 39 C% at 100 mbar. The C_{6+} fraction increased from 9 to 30 C% in the same interval. Only modest shifts were found for the other products, and the selectivities toward C_2, C_5, and isobutene are nearly identical to those presented for the shortest CT in Fig. 6 throughout the investigated range of propene pressures.

Isotopic data are given in Fig. 9. The isotopic composition of the products is dictated by the feed composition. At low propene pressures, the distributions are very similar to those described at the shortest CTs in Fig. 7. But at 100 mbar of propene, the all-^{12}C isotopomer is the most abundant isomer for all of the alkene products except n-butene, for which greater pressure is needed to make $^{12}C_4$ the most prominent isotopomer. Up to 100 mbar of propene, methylation is the most prominent mechanism for n-butene formation. The percent total content of labeled carbons in the n-butenes decreased as the pressure increased, from 29 to 17%. A similar, further enhanced trend can be seen for 2-methyl-2-butene and the hexenes as the shares of ^{13}C atoms decreased from 54 to 16% and from 58 to 9%, respectively. Ethene is richer in ^{13}C than the other alkenes, with an essentially random isotopic distribution. The total ^{13}C content fell from 92 to 43% when the propene pressure was increased from 5 to 100 mbar. The isotopic distribution of isobutene was also close to random. The total content of labeled atoms varied from 58 to 9% in the investigated pressure interval. The aromatics, exemplified by p/m-xylene (not shown), contained mainly ^{13}C atoms, falling from 85 to 46% as the propene pressure increased from 5 to 100 mbar.

3.3.3. Influence of methanol partial pressure

The methanol partial pressure was varied from 10 to 90 mbar in an experiment analogous to that described earlier for the propene pressure effects. Varying the methanol partial pressure had considerably less pronounced effects on conversions, product selectivities, and isotopic distributions than the propene pressure. The methylation reaction may be considered of zero order with respect to methanol at pressures >20 mbar. Below this level, the reaction order may be slightly positive. The product selectivities were virtually unchanged in the investigated range, and thus they are displayed for the shortest CT in Fig. 6. Modest effects on the isotopic compositions can be seen. Decreasing methanol pressure resulted in decreased ^{13}C content of the products and evidently made propene–propene reactions more likely. The general isotopic pattern was usually not changed, but in the case of the hexanes, the share of the all-^{12}C isotopomer grew from about 20 to 41% when the methanol pressure was reduced from 90 to 10 mbar. This isotopomer corresponds to a simple propene dimerization.

3.3.4. Influence of the reaction temperature

In an attempt to determine the activation energy for the methylation of propene, we investigated reaction temperatures between 290 and 400 °C. Reaction conditions were the same as before. The propene partial pressure was 20 mbar, methanol pressure was 50 mbar, and total gas flow was 100 ml/min, resulting in a contact time of 0.0042 h ($WHSV = 237\ h^{-1}$). Reactant conversions, rates of product formation, and isotopic compositions were determined as before. The conversion to products increased from 0.5% at 290 °C to 6.5% at 400 °C. A slight decrease in the selectivity toward n-butene was found at elevated temperatures, coupled with enhanced selectivity toward isobutene, C_5, and C_{6+}. Pronounced temperature effects were also seen when propene and n-butene were studied with no methanol present, as described earlier. We then found that the conversion, and thus the extent of alkene interconversion reactions, increased when the temperature was lowered. This effect was not clearly seen in the co-reaction system, but the isotopic data do reveal that alkene + alkene reactions are of greater relative importance at low reaction temperatures. For the n-butenes, the $^{12}C_3\,^{13}C_1$ isotopomer, indicative of methylation, was always in excess. It constituted 72% of the n-butenes even at 290 °C. At the same temperature, the $^{12}C_4$ isotopomer was the second most abundant, at 23%. As

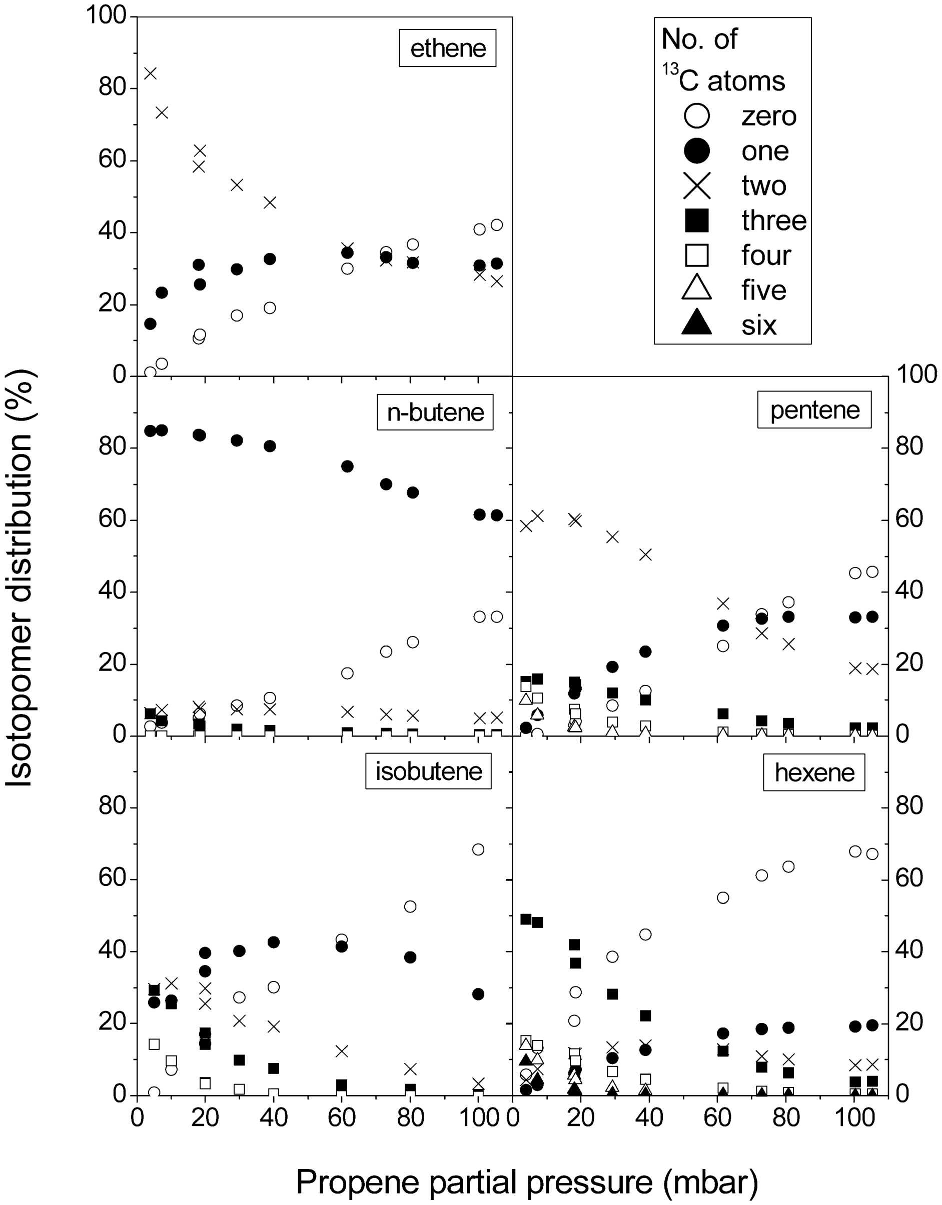

Fig. 9. Isotopic composition of alkene products versus propene partial pressure. 5–100 mbar of propene co-reacted with 50 mbar methanol; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

seen in Fig. 9, at 350 °C the share of $^{12}C_3\,^{13}C_1$ was ~80% and the share of $^{12}C_4$ was only about 4%. For 2-methyl-2-butene, double methylation dominated above 330 °C. Below this temperature, other formation routes, resulting in greater shares of the $^{12}C_4\,^{13}C_1$ and $^{12}C_5$ isotopomers, become increasingly important. A similar but even more pronounced trend was seen for the hexenes. More than 70% of the hexenes were built up exclusively from unlabeled carbons at 290 °C. Correspondingly, the total ^{13}C content was very low (just 7%) at 290 °C, and increased to 54% at 400 °C. The isotopic data for ethene differ markedly from those of the other alkenes; ethene contained almost 80% labeled carbons throughout the investigated temperature range. Isobutene contained between 15% (at 290 °C) and 56% (at 400 °C) ^{13}C, similar to what was observed for the higher alkenes (i.e., pentene and hexene). Little variation was seen in the isotopic composition of the arenes. *p*/*m*-Xylene contained 60–70% ^{13}C, broadly distributed.

A main motivation for the present work was to determine the apparent activation energy and the pre-exponential factor for the methylation reaction by constructing an Arrhenius plot. Such a plot, based on the rate of formation of $^{12}C_3\,^{13}C_1$ isotopomer only, is given in Fig. 10, and an apparent activation energy of 69 kJ/mol can be extracted.

3.4. Co-reaction of *n*-butene and methanol

3.4.1. Influence of contact time

The co-reactivity of *n*-butene and methanol is rather analogous to that described earlier for propene and methanol and

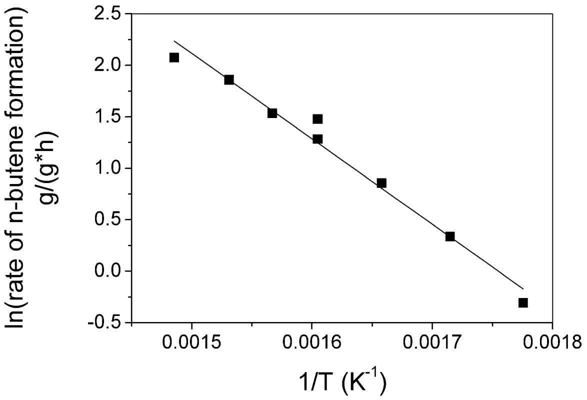

Fig. 10. Arrhenius plot for the formation of mono-labeled n-butene. 20 mbar propene co-reacted with 50 mbar methanol; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature varied from 290 to 400 °C.

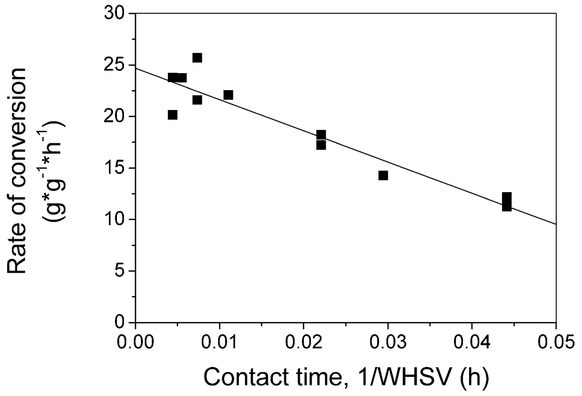

Fig. 11. Rate of conversion of feed mixture versus contact time. 13 mbar of n-butene co-reacted with 50 mbar methanol; total gas flow varied from 10 to 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

Table 3

Conversion of feed mixture and product selectivities (in C%) versus contact time. 13 mbar of n-butene co-reacted with 50 mbar methanol; total gas flow varied from 10 to 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C

CT (h)	C_2	C_3	Isobutene	Butanes	C_5	C_{6+}	Conversion (%)
0.0044	0.9	17	14	2	46	19	8.9
0.0044	0.9	17	14	3	47	19	10.5
0.0055	0.8	17	14	3	45	20	13.1
0.0074	0.9	19	14	3	43	21	15.9
0.0074	1	20	14	3	41	21	18.9
0.0110	1.1	21	14	4	38	22	24.4
0.0221	1.2	24	13	5	32	25	38
0.0221	1	24	14	5	32	24	40.2
0.0294	1.3	24	13	5	31	26	42
0.0442	1.4	25	13	6	29	26	49.7
0.0442	1.3	25	14	6	28	26	53.8

in previous work for ethene and methanol [24]. The following reaction conditions were used: 13 mbar of [^{12}C]n-butene and 50 mbar [^{13}C]methanol were co-reacted at 350 °C over 2.5 mg of H-ZSM-5 catalyst. The contact time was varied from 0.0044 to 0.044 h (WHSV from 226 to 23 h^{-1}) by adjusting the total gas flow between 10 and 100 ml/min. Conversions, product selectivities (Table 3), reaction rates (Fig. 11), and isotopic distributions (Fig. 12) were measured as before. The conversion of the feed mixture ranged from 10 to 54 C% and was thus slightly higher than when propene and methanol were co-reacted. As shown in Fig. 11, extrapolating the rate of conversion to CT = 0 yields a value of 25 g/(g h). Pentenes dominated among the products (see Table 3), and the selectivity for pentenes extrapolates to about 55 C%. At longer contact times, the amounts (C%) of C_3, C_5, and C_{6+} became about equal.

The isotopic data are analogous to those presented earlier for the methylation of propene. For 2-methyl-2-butene, the $^{12}C_4\,^{13}C_1$ isotopomer corresponding to methylation of n-butene, is by far the most prominent, and the abundance of this isotopomer extrapolates to about 85% at CT = 0. Double methylation is the prominent pathway for hexene formation, as is evident from the large content of the double-labeled isotopomer. Trace amounts of aromatics (methylbenzenes) were also detected in this experiment. The total content of ^{13}C atoms in p/m-xylene fell from 58% at CT = 0.0044 h to 42% at CT = 0.044 h, and the isotopic distribution was close to the random distribution. Ethene was also fairly rich in ^{13}C; the total content dropped from 63 to 37% as the CT increased from 0.0044 to 0.044 h. The distribution was close to random. Propene contained considerably fewer labeled carbons than ethene, but in this case the distribution was fairly close to random. Overall, isobutene contained only ∼15% labeled carbons over the investigated range of feed rates. The isotopic distribution of isobutene was fairly close to random, although the $^{12}C_3\,^{13}C$ was somewhat underrepresented (22 compared with 37%). We also analyzed the isotopic composition of *trans*-2-butene; as expected, the n-butene fraction consisted mainly of unconverted reactant. The total content of ^{13}C in t-2-butene increased from 1.7% at CT = 0.0044 h to 5% at CT = 0.044 h.

3.4.2. *Effect of butene partial pressure*

We also investigated the effects of varying the butene pressure on reaction rates and isotopic composition of the products formed in the co-reaction. The experimental conditions were slightly different from the conditions applied earlier. The temperature and amount of catalyst were identical, at 350 °C and 2.5 mg, but in this case the methanol partial pressure was 100 mbar rather than 50 mbar, and the total gas flow was 75 ml/min rather than 100 ml/min. The butene pressure was varied in the range 3–200 mbar.

Also here, as in the methanol/propene co-reaction system, the rates of conversion (Fig. 13a) and mono-labeled pentene formation (Fig. 13b) depended strongly on the alkene pressure. In analogy with the methanol/propene co-reaction system, the product selectivities showed some dependence on the n-butene pressure, but the changes were modest. The most prominent change was seen for the pentene selectivity, which fell from about 41% at very low n-butene pressures to about 34% at an n-butene pressure of 200 mbar. The product spectrum is therefore quite similar to that given in Table 3. The experiments were, like the preceding ones, carried

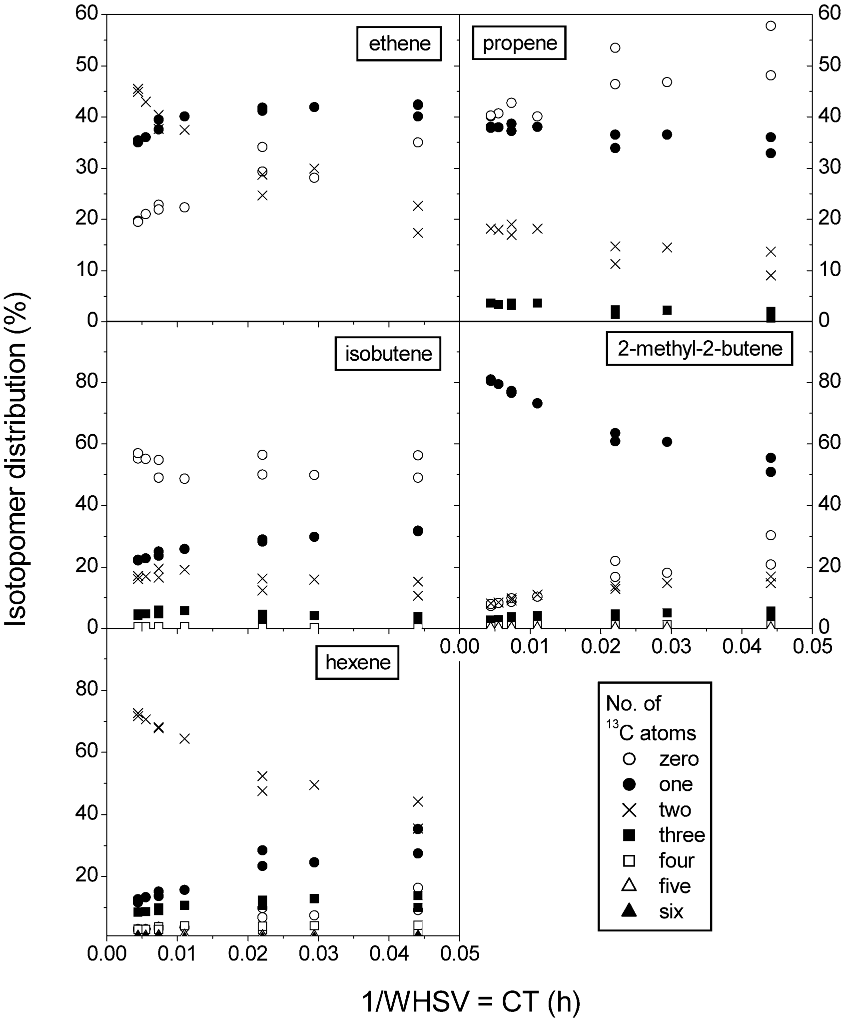

Fig. 12. Isotopic composition of alkene products versus contact time. Note the scale differences. 13 mbar of *n*-butene co-reacted with 50 mbar methanol; total gas flow varied from 10 to 100 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

out with [^{13}C]methanol and ordinary 1-butene. The isotopic composition of the products in the effluent could then be determined. The results are displayed in Fig. 14. Ethene and isobutene were not analyzed.

As in the corresponding co-reaction experiments with methanol/propene, here the isotopic composition of all products underwent a marked change with changes in butene pressure. The gaseous flow rate remained constant and was practically the same as the highest flow rate used in Section 3.4.1 (75 vs. 100 ml/min). The isotopic composition in that case was quite close to the extrapolated limiting composition where isotopic scrambling due to secondary reactions was essentially absent. It is therefore admissible to assume that the observed isotopic composition in this case also closely reflects the primary composition.

It is therefore clear that at the highest butene pressures, alkene/alkene interconversion reactions are less successfully suppressed by methanol. The dominant reaction was formation of pentenes, and at low butene pressures the $^{12}C_4\,^{13}C_1$ isotopomer, obtained by methylation of butene, constituted 80% of the pentene molecules. The remainder of the pentene molecules contained more than one ^{13}C atom. Up to a butene pressure of 25 mbar, the content of the $^{12}C_5$ isotopomer was negligible. At high butene pressures, the content of ^{12}C atoms increased strongly, and at 200 mbar the $^{12}C_5$ isotopomer constituted 50% of the pentene molecules. This isotopomer is formed by alkene/alkene interconversion reactions.

Less directly, Fig. 15, which displays the separate methanol and butene conversion rates versus butene pressure, suggests the same conclusions. The methanol conversion rate initially increased very strongly with increasing butene pressure, but the increase soon tapered off, and above 40–60 mbar, the increase became quite moderate. The butene conversion rate increased essentially linearly with butene pressure. These data were obtained from the known rates of product formation (Fig. 13) and the known isotopic composition of the main products.

The hexene isotopic distribution exhibited an evolution similar to that of pentene (Fig. 14). At the lowest butene pressures, the $^{12}C_4\,^{13}C_2$ isotopomer, corresponding to a double methylation, constituted nearly 80%. At 50 mbar, this isotopomer still constituted about 60%, but now there was >20% of the species with only one ^{13}C atom and >5% with the all-^{12}C species. At 200 mbar, only 20% of the double-labeled isotopomer remained.

Propene, always an important product in this reaction system, with about 20 C% of the products, displayed an isotopic distribution rather close to a random distribution. With increasing butene pressure, ^{12}C atoms constituted an increasingly larger fraction. At 3 mbar, the propene contained 55% ^{13}C; at 100 mbar, only 10%. Propene is probably a product of complex alkene interconversion reactions, as are the hexene isotopomers that do not contain two ^{13}C atoms.

The n-butene that emerged from the reactor had mostly the natural isotope content (about 4.5%) of the $^{12}C_3\,^{13}C_1$ isotopomer. However, at the lowest butene pressures (3 and 6 mbar), the analysis indicated the presence of about 1% of each of the isotopomers with two or more ^{13}C atoms, demonstrating that some butene, like propene and pentene, is formed in reactions involving methanol.

3.4.3. *Effects of the methanol partial pressure*

The influence of the methanol pressure was investigated by varying the partial pressure from about 5 to 105 mbar.

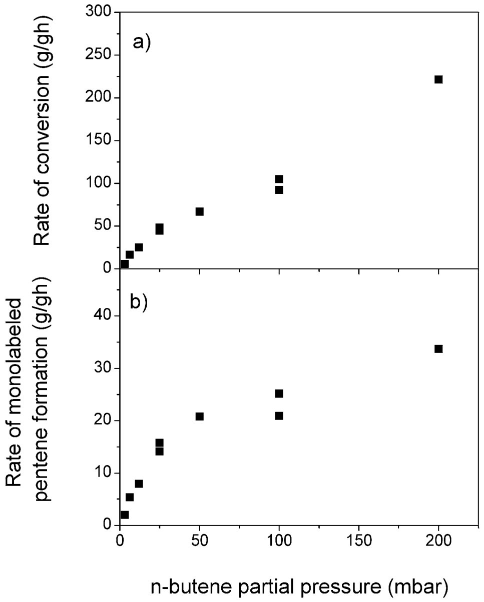

Fig. 13. Rate of feed mix conversion (a) and rate of mono-labeled pentene formation (b). 3–200 mbar of n-butene co-reacted with 100 mbar methanol; total gas flow 75 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

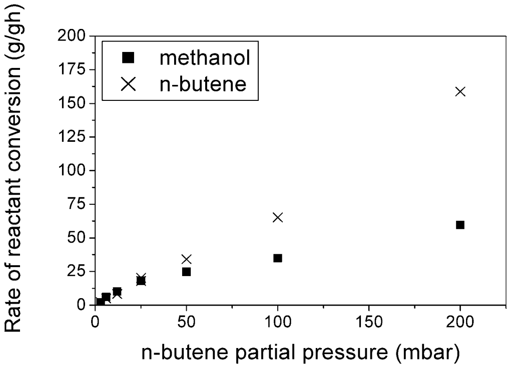

Fig. 15. Rate of conversion of the individual reactants 3–200 mbar of n-butene co-reacted with 100 mbar methanol; total gas flow 75 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

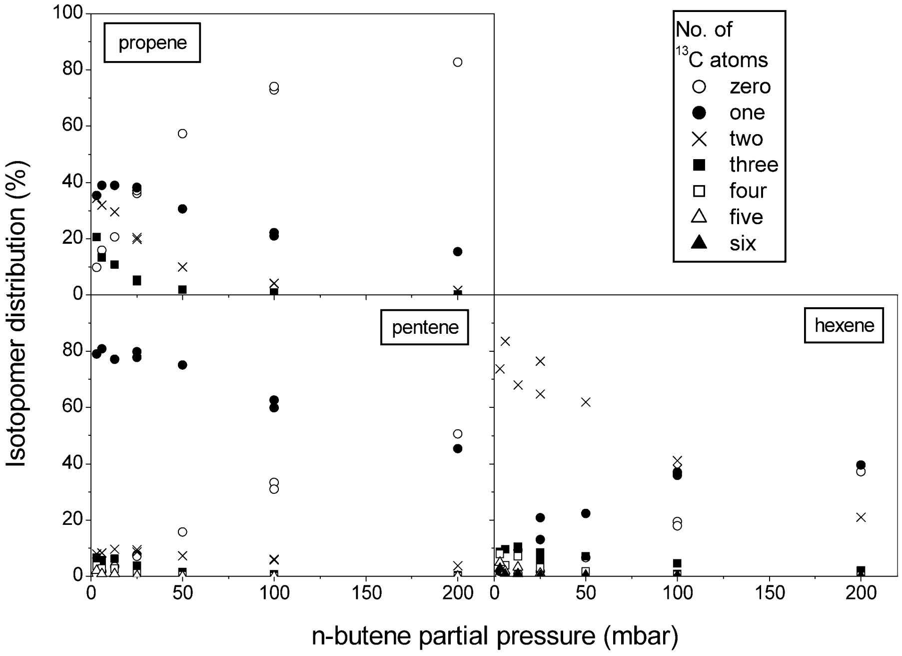

Fig. 14. Isotopic composition of alkene products versus n-butene partial pressure. 3–200 mbar of n-butene co-reacted with 100 mbar methanol; total gas flow 75 ml/min; 2.5 mg catalyst; reaction temperature 350 °C.

The resulting effects on the rate of methylation product formation were moderate. Again, the reaction order was close to zero, but a slightly positive slope was definitely observed. The product selectivities and the corresponding isotopic compositions were measured, and no noteworthy shifts were observed in the investigated pressure range.

3.4.4. *Effects of temperature variations*

Determination of the activation energy of a reaction is a central part of the reaction study. We have therefore studied the reaction system, particularly the rate of ${}^{12}C_4\,{}^{13}C_1$ isotopomer formation, at the following conditions: 50 mbar of methanol, 13 mbar of butene, and a total gas flow rate of 100 ml/min. The isotopic distributions and the effluent composition were determined in two different experiments, spanning two slightly different temperature ranges, 235–450 °C for the isotopic composition and 225–440 °C for the effluent composition. Product selectivities and conversions are given in Table 4. The conversion of the feed mixture increased with the reaction temperature, from around 0.25% to 19%. Pentenes (i.e., the methylation products) were dominant among the products, but less clearly so than for the methylation of propene, and the dominance decreased with increasing temperature. The isotopic distributions are shown in Fig. 16. The pentene isotopomer with one labeled carbon atom is always in excess and increases from a little above 60 to nearly 90% when the temperature is increased from 235 to 450 °C. Double methylation is always the dominant pathway for hexene formation, particularly above 300 °C.

All products except ethene exhibited marked increases in content of the all-${}^{12}C$ isotopomer at the lowest temperatures, indicating a growing relative importance of alkene interconversion reactions at these temperatures. The isotopic distribution in ethene is always close to random, and the total content of labeled carbon atoms fluctuates around 70%.

We also constructed an Arrhenius plot based on the observed rate of mono-labeled pentene formation in this case (Fig. 17). A clear deviation from linearity is seen. We chose the extended temperature range because such behavior was suspected, and we address this issue in more detail in the following section.

Table 4
Conversion of feed mixture and product selectivities (in C%) versus reaction temperature. 13 mbar of n-butene co-reacted with 50 mbar methanol; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature varied from 225[a] to 440 °C

T (°C)	C_2	C_3	Isobutene	Butanes	C_5	C_{6+}	Conversion (%)
225							0.2–0.3
250							0.6–0.8
275	0.5	13	22	1.0	52	12	1.6
295	0.7	15	17	1.4	51	15	2.9
325	0.9	16	15	3.1	47	18	5.1
350	1.0	18	14	3.5	43	20	7.2
350	1.0	19	14	3.5	42	22	8.8
375	1.0	21	13	4.1	40	22	10.5
400	1.1	24	11	3.9	36	23	16.8
440	1.5	26	10	4.2	36	22	19.1

[a] Accurate product selectivities could only be determined above 275 °C, due to poor chromatographic resolution of isobutene and 1-butene. The conversions at 225 and 250 °C are within the tabulated ranges.

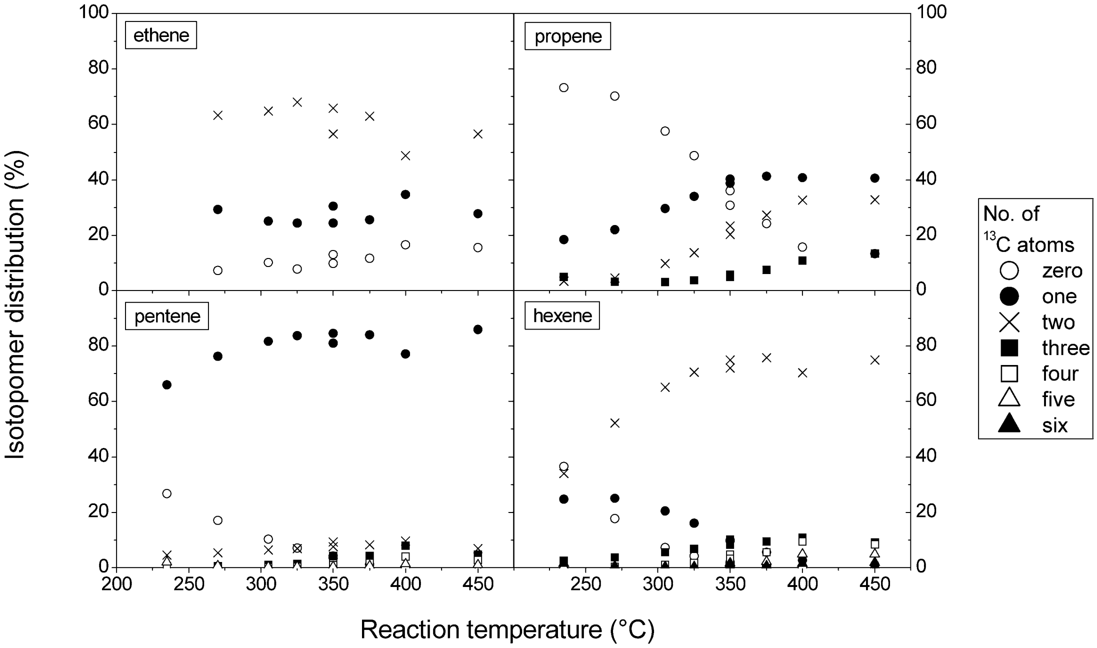

Fig. 16. Isotopic composition of alkene products versus reaction temperature. 13 mbar of n-butene co-reacted with 50 mbar methanol; total gas flow = 100 ml/min; 2.5 mg catalyst; reaction temperature varied from 235–440 °C.

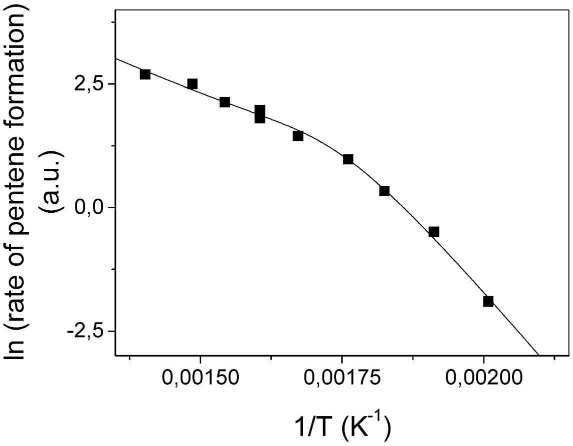

Fig. 17. Arrhenius plot for the formation of mono-labeled pentene. 13 mbar *n*-butene co-reacted with 50 mbar methanol; total gas flow 100 ml/min; 2.5 mg catalyst; reaction temperature varied from 235 to 440 °C.

4. Discussion

4.1. Conversion of alkenes in the absence of methanol

Substantial research efforts have been devoted to the conversion of light alkenes over acidic zeolites [27,28]. However, most of this work has focused on either oligomerization to produce larger hydrocarbons or, in the case of *n*-butene, the skeletal rearrangement reaction leading to isobutene. Hence very little literature data have been obtained at conditions comparable to those used in the present study.

The key observations from our experiments in which propene and *n*-butene were reacted alone can be summarized as follows. The propene conversion decreased with increasing temperature. The yield of products other than isobutene from *n*-butene also decreased when the temperature was raised. At constant temperature (350 °C), alkene interconversion reactions displayed a reaction order slightly below two.

Quite clearly, the formation of products with more or less carbons than the original alkene reactant requires the initial interaction of (at least) two propene or *n*-butene molecules. This consideration may explain both the observed increase in conversion at increasing alkene partial pressures and the increased yields at lower reaction temperatures. Lower temperatures and higher partial pressures inevitably lead to greater surface coverage, which will favor bimolecular events. The decrease in propene conversion at elevated temperatures could also be the result of thermodynamic limitations, as suggested by Bandiera and Ben Taarit [29], but the equilibrium content of propene in a C2–C6 alkene mixture at 425 °C, is around 35% [26], corresponding to 65% conversion. The observed conversion at this temperature (and 20 mbar propene in the feed) is only 1% (Table 1). We therefore consider the kinetic reasoning outlined earlier to provide a more satisfactory rationalization of the observed degree of conversion of propene and also for the decrease in yield of products other than isobutene from *n*-butene at elevated temperatures.

The skeletal isomerization of *n*-butene to form isobutene has been a subject of considerable debate, particularly regarding whether isobutene is formed in a monomolecular, pseudomonomolecular, or bimolecular manner [28]. Isobutene displays a behavior opposite to that of the other major products; the yield increases at elevated temperatures, and the selectivity increases markedly at low alkene pressures. Hence our results indicate that this is mainly a monomolecular reaction under appropriate conditions, that is, very low *n*-butene pressures or elevated temperatures. However, at butene pressures >10 mbar, there are no indications that the monomolecular mechanism overshadows the bimolecular reactions; the product distribution is very much as would be expected from a series of cracking reactions.

We emphasize that even though the degree of alkene conversion is similar with or without the presence of methanol, the isotopic analysis demonstrates that the reactions in which the alkenes are consumed differ greatly. Thus data for alkene conversion collected without a methanol co-feed cannot provide a direct measure of the alkene reactivity when methanol is present. *Alkene interconversions are evidently strongly suppressed by the presence of methanol*.

4.2. Methylation of alkenes

This report is an extension of our previous study on the kinetics of the methylation of ethene [24]. The experimental conditions in that case were essentially the same as those used in the present work. The main part of the experiments was carried out at 350 °C. Ethene and methanol pressures were varied from 10 to 100 mbar. The apparent energy of activation was obtained by varying the temperature from 305 to 410 °C. The reaction was found to be of zero order with respect to methanol and of first-order with respect to ethene. Based on this information, the rate constant 2.6×10^{-4} mol/(g h mbar) was determined at 350 °C with apparent activation energy of 103 kJ/mol. After correcting for the appropriate adsorption enthalpy of ethene, the "true" activation energy was estimated as $\sim$135 kJ/mol.

Extrapolation of the rates of conversion to CT $= 0$ (Figs. 5b and 12) gave 8 and 25 g/(g h) in the propene and *n*-butene co-reaction systems, respectively. The rates of methylation are obtained by multiplying these values by the respective limiting fractional values for the product and isotopic selectivities. This procedure yields 5.0 g/(g h) and 11.7 g/(g h) for the methylation of propene and *n*-butene, respectively. Figs. 8 and 14 show that the propene and *n*-butene methylation rates may be taken as first order with respect to alkene pressure up to 30–40 mbar, although a clear leveling off is seen at higher pressures. The two limiting rates were obtained using different alkene partial pressures and are given on a weight basis. More comparable data are thus obtained by dividing by the partial pressures used and finally converting to molar units. The values then become $k_{\text{propene}} = 4.5 \times 10^{-3}$ mol/(g h mbar) and $k_{n\text{-butene}} = 1.3 \times 10^{-2}$ mol/(g h mbar), and the following ratios may be obtained: $k_{\text{ethene}}:k_{\text{propene}}:k_{n\text{-butene}} = 1:17:50$. These rate constants are apparent rate constants that include the alkene adsorption constants, and the ratios do not strictly apply to the intrinsic rates of methylation.

The apparent activation energy for the methylation of propene (69 kJ/mol) was derived from an Arrhenius plot (Fig. 10) through linear fitting. The results obtained on the temperature dependence of the methylation of n-butene by methanol (Fig. 17) indicate that determining an apparent activation energy for the methylation is not simple, because there is considerable deviation from linearity. But this figure may be interpreted in a fairly straightforward way. With the rather low partial pressures of methanol and butene used, it is to be expected that at high temperatures (well above 350 °C), the coverage by both butene and methanol becomes sparse, so the reaction becomes first order with respect to both reactants. The apparent activation energy then will eventually be $E_{\text{app}} = E_{\text{true}} + \Delta H_{\text{ads,methanol}} + \Delta H_{\text{ads,butene}}$. At the lowest temperatures, it is quite likely that the coverage by butene also will be high. In the case of noncompeting reactions, one might then expect to be able to measure true activation energy. But in the present case there are three competing reactions: methylation, alkene interconversions, and dimethyl ether formation. The three reactions are likely to, at least in part, involve the same sites, so clear-cut conclusions are hardly warranted. The strongly increasing relative amounts of all-^{12}C isotopomers at the lowest temperatures support this point (Fig. 16). Deviation from linearity is seen also in the Arrhenius plot for methylation of propene (Fig. 10), although here it is considerably less pronounced, because the temperature range is narrower. To obtain the best estimate for the apparent barrier, we submitted the data points in the range 295–400 °C in Fig. 17 to linear fitting. This temperature range is nearly identical to that used for propene and previously for ethene [24] and covers the range in which the methylation reaction is closest to first order with respect to the alkene pressure and zero order with respect to methanol. This approach yields an apparent activation energy of 45 kJ/mol.

Assuming that the methylation reactions are approximately first order with respect to the alkene partial pressures and zero order with respect to methanol in a limited temperature interval around 350 °C, the corresponding heat of alkene adsorption should be added to these values to obtain the intrinsic activation energies. Pascual et al. [31] used Monte Carlo simulations and force field methods to calculate adsorption isotherms for several alkenes and found heats of adsorption of 39 kJ/mol for propene and around 45 kJ/mol for the linear butenes on silicalite [31]. Hence the activation barriers become ∼110 and ∼90 kJ/mol. The differences between these activation energies are much larger than the differences in the measured *apparent* rates (1:17:50). Of course, this is caused by the increased adsorption enthalpies as the alkenes become larger, which in turn leads to increases in the surface coverage. These considerations illustrate the need to compare reaction rates at identical degrees of surface coverage or to apply the appropriate corrections for such differences in reaction conditions.

There may be other sources of error besides the assumption concerning the reaction order around 350 °C. At high temperatures, when the conversion is appreciable, some of the alkene originally formed through methylation may be consumed in further reactions, causing the measured rate to be too low. Moreover, it seems to some extent unreasonable to assume that the entire amount of the mono-labeled isotopomers has been formed through methylation at low temperatures. At low temperatures, alkene interconversions are nonnegligible relative to methylation, as is evident from the considerable share of the all-^{12}C isotopomers <300 °C (Fig. 16). Considering the total content of labeled atoms in the higher alkenes (exemplified by the hexenes), it is reasonable to assume that cracking of these would produce some of the mono-labeled isotopomers. These effects also cause the activation energy estimates to be too low. In addition, the adsorption enthalpies used to correct the apparent barriers are measured or calculated for the purely siliceous MFI framework. The presence of aluminum leading to acidic sites and methanol adsorbed onto these sites might affect the strength of the alkene–catalyst interaction to some extent.

We have previously investigated alkene methylation with theoretical methods, using a cluster consisting of four tetrahedral atoms to represent the zeolite combined with the B3LYP/6-31G(d)+ZPE computational scheme [30]. The calculated barriers were 183, 169, and 164 kJ/mol for the methylation of ethene, propene, and n-butene, respectively. The value for n-butene is the average of the calculated values for 1-butene (168 kJ/mol), *trans*-2-butene (162 kJ/mol), and *cis*-2-butene (161 kJ/mol). Gratifyingly, the experimentally observed trend in reactivity is reproduced by the calculations, even though the differences in barriers between the alkenes are slightly smaller in the calculations than in the experiments. The absolute values differ considerably, but this is to be expected, considering the fairly simple cluster used to model the zeolite catalyst [30].

4.3. *The minor co-reaction products*

When propene or n-butene was co-reacted with methanol, nonnegligible concentrations of products other than the simple methylation products were always detected. Moreover, the selectivities toward some of these products did not extrapolate to zero at CT = 0. With respect to the mechanism of the MTH reaction, it is of interest to evaluate possible routes of formation for these minor products. However, it should be kept in mind that the reaction conditions used here are quite different from those usually used during steady-state conversion of methanol to hydrocarbons. This means that even though methylation of alkenes proceeded at appreciable rates in the current experiments, alkenes are not necessarily important reaction intermediates during regular

MTH conditions. At much lower feed rates and correspondingly greater conversions, aromatics will constitute a major share of the products in the effluent. Furthermore, the typical adsorption enthalpy of arenes is greater than that for small alkenes, because of both a larger molecular size and the easily perturbed conjugated π-electrons. Also, the larger aromatic molecules will exhibit much less diffusivity in the fairly small zeolite pores, so the concentration within the zeolite pores will be much higher than in the bulk gas phase. This means that at higher conversions, the internal concentration of arenes and their importance as intermediates might completely overshadow the alkenes, but in the general case both reaction pathways should be taken into consideration.

4.3.1. Ethene

Ethene was always detected in trace amounts in all the co-reaction experiments. It was always fairly rich in ^{13}C, and the isotopic distribution was close to random. Three routes can be envisaged for ethene formation: direct formation from methanol/dimethylether, alkene cracking, and the hydrocarbon pool mechanism. Direct formation from methanol might seem reasonable considering the high share of the $^{13}C_2$ isotopomer detected, but this possibility may be discarded because no detectable amount of ethene was formed when methanol was reacted alone. A direct formation mechanism will not depend on the presence of products in the catalyst pores (i.e., not show any autocatalytic behavior), and the yield of ethene should be unaffected by an alkene co-reactant. Alkene cracking also may be ruled out, because the discrepancy between the total content of ^{13}C in ethene and the higher alkenes (exemplified by hexene) is too large. This leaves the hydrocarbon pool mechanism as the only plausible route for ethene formation. The total label content and the isotopic distribution of ethene matched those observed for p/m-xylene, which may be taken to represent the isotopic composition of the pool species reasonably well.

4.3.2. Propene and isobutene

The total label content of the propene formed in the n-butene + methanol system was considerably lower than for ethene and the aromatics and more in line with (although higher than) that observed for the higher alkenes. The isotopic distribution is fairly close to random, however, the all-^{12}C and -^{13}C isotopomers are overrepresented relative to the mixed isotopomers. This indicates complex (equilibrating) formation pathway, and the data suggest that there are two formation pathways under our operating conditions: formation through alkene cracking and formation through the aromatic hydrocarbon pool. The ^{13}C content of isobutene was less than for propene, indicating that it was formed primarily via alkene cracking and/or monomolecular isomerization of the n-butene feed.

4.3.3. Hexene

In the propene + methanol system, two pathways for hexene formation were easily discernible: propene dimerization and triple methylation. The isotopomers corresponding to these formation routes were present in greater amounts relative to the other isotopomers. When n-butene was the co-reactant, double methylation was dominant. But the other isotopomers were always present as minor components in both systems and did not easily extrapolate to zero at CT = 0. This behavior has been discussed previously [24].

5. Conclusions

[^{13}C]Methanol and [^{12}C]propene or [^{12}C]n-butene have been co-reacted over an H-ZSM-5 catalyst. The primary concern was to obtain kinetic data for the methylation reactions, and methylation and multiple methylations are the main modes of product formation. The previously observed (for ethene methylation [24]) zero-order behavior with respect to methanol pressure and first-order behavior with respect to the alkene pressure were retained, though somewhat weakened as deviations were seen over the investigated partial pressure ranges. Activation energy estimates of $\sim$110 and $\sim$90 kJ/mol were found for the methylation of propene and n-butene, respectively.

At elevated propene or n-butene partial pressures, alkene + alkene reactions were not insignificant for these systems, and the reactivity of the alkenes without methanol present was briefly evaluated. Interestingly, the degree of alkene interconversion reaction increased with decreasing reaction temperature. At high reaction temperatures and low n-butene partial pressures, isobutene was formed through monomolecular isomerization. Alkene interconversions were strongly suppressed by the presence of methanol.

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