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On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34

1. Isotopic Labeling Studies of the Co-reaction of Ethene and Methanol

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^{13}C-Methanol and ^{12}C-ethene (fed as ethanol) have been co-reacted over SAPO-34 in a flow system at 400°C using argon as a carrier (diluent) gas. The feed contained an equal number of ^{13}C and ^{12}C atoms. The products were analyzed by GC–MS, allowing the determination of the isotopic composition of the reactor effluent. The ethanol was immediately converted to ethene, so the reaction system was equivalent to a feed consisting of methanol/ethene/water. While the methanol was completely or almost completely converted to hydrocarbons, the larger part of the ethene emerged unreacted. The products propene and butenes were mostly formed from methanol and contained a large excess of ^{13}C atoms. The ethene effluent consisted mainly of all ^{12}C or all ^{13}C atoms, and only to a small extent of ^{12}C–^{13}C molecules. The reaction system was followed from an initially very active catalyst until the catalyst was sufficiently deactivated that C_1 was not completely converted to hydrocarbons. The tendency for ethene to emerge unreacted, and for all new hydrocarbons to be formed from methanol became more pronounced with progressing catalyst deactivation. The results show clearly that the higher hydrocarbons are, over this catalyst, not formed by successive methylations of ethene. A previously proposed "carbon pool" mechanism can explain the gross effects seen in the product and isotopic distribution. © 1994 Academic Press, Inc.

INTRODUCTION

The conversion of methanol to hydrocarbons may be performed over a variety of acid catalysts, zeolites, and SAPOs. General references can be found in Refs. (1–5). By performing the reaction in structures (zeolites and SAPOs) with channels made up of 8 (Si, P, Al) units, the products are restricted to linear hydrocarbons, as they are the only ones that can be transported out of these channels. Coke (aromatic compounds) will be formed inside the cages of these structures, and in the long run they will fill up the zeolite and deactivate it for further reaction (6). Over SAPO-34 at 400°C, the products are mainly alkenes in the C_2–C_4 range (7, 8) propane being the main side product.

The product spectrum is thus simpler than from, e.g., ZSM-5, where a much wider range of products is found, and so it might be easier to obtain a picture of the reaction pattern.

Several mechanisms have been proposed for the Methanol-to-hydrocarbons reaction (1–5, 9–11). They may be broadly lumped into two groups:

A. Consecutive-type mechanisms:

$$\begin{aligned} &2C_1 && \rightarrow C_2H_4 + 2H_2O \\ &C_2H_4 + C_1 && \rightarrow C_3H_6 \\ &C_3H_6 + C_1 && \rightarrow C_4H_8 \ldots \end{aligned}$$

B. Parallel-type mechanisms:

$$C_1 \left\{ \begin{array}{l} \rightarrow C_2H_4 \\ \rightarrow C_3H_6 \\ \rightarrow C_4H_8 \end{array} \right.$$

In an earlier work, we showed that the consecutive-type mechanisms, insofar as propene formation is concerned, did not appear to be valid (over SAPO-34), and we proposed a modified parallel mechanism type, called the "carbon pool mechanism" (12). By this we mean a group of mechanisms which in broad lines may be represented by Scheme 1.

The nature of the "hydrocarbon pool" is not an issue here. The reaction could proceed via a "rake mechanism" as first proposed by Cormerais *et al.* (11). In this case the hydrocarbon pool would rather consist of ethoxy, propoxy, butoxy groups, etc., formed by methylation of the next lower member. From results obtained in studies of methanol conversion on H–ZSM-5 (9, 10, 13) we be-

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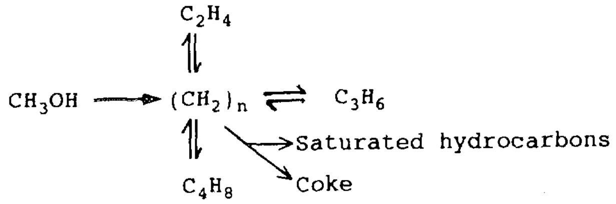

SCHEME 1. Carbon pool mechanism.

lieve rather that the reaction proceeds via an adsorbate which is continually adding and splitting off reactants and products. Work is in progress which will hopefully shed some light on this point.

The objective of the present work is to carry out further measurements on the system ^{13}C–MeOH/^{12}C–EtOH at lower temperatures, and higher space velocities, than was previously done (12). (It has been established by separate experiments that the dehydration of EtOH into C_2H_4 + H_2O is much faster than any other reactions studied: experiments where ethanol was replaced by ethene and water led to the same conclusion.) In this way secondary reactions will be of less importance. It was also considered important to follow the reaction from the initial highly active state, when the catalyst activity is many times higher than needed for complete conversion to hydrocarbons, to the deactivated catalyst, where part of the MeOH/DME emerges unconverted from the reactor. Improvements in the experimental setup, notably the evaporator system, have allowed us to carry out more precise measurements.

EXPERIMENTAL

SAPO-34 was synthesized according to Lok *et al.* (14). Characterization by XRD gave the expected diffractogram. ^{13}C MeOH was obtained from Cambridge Isotopic Laboratories (99% isotopic purity). Ethanol was from A/S Vinmonopolet.

The molar feed ratio of Ar : CH_3OH : C_2H_5OH : H_2O was 6 : 2 : 1 : 1. Thus equal amounts of ^{12}C and ^{13}C atoms were fed to the reactor, and the C : H : O ratios were the same as if the feed were neat methanol. Total pressure was equal to atmospheric pressure. Ethanol served as the ethene source. The combined (methanol-equivalent) liquids were fed by a syringe pump to a specially constructed evaporator of a design as shown in Fig. 1. The temperature in the evaporation zone was kept at 95–100°C by regulating the effect to the heater cartridge. The feed/evaporation system worked well and gave a very smooth feeding of evaporated liquids with no sign of uneven flow. The reactor system has been described earlier (8).

Water, in the feed and formed by the reaction, was partially removed from the reactor effluent before taking samples for analysis by a "cold trap" at 4°C; otherwise the tubing from reactor outlet to the analysis instrument was kept at 100°C to avoid any condensation. The reactor effluent was analyzed by an on-line Hewlett–Packard GC–MS system (12). Analysis of the effluent could be carried out at 20-min intervals.

The experiments were performed at 400°C using 100 mg catalyst. The reactant (the MeOH/EtOH/H_2O mixture) feed rate (WHSV) was 4.00 h^{-1}.

RESULTS

Products

The most important reaction products which were obtained are given in Table 1. The effluent composition is given for 10 analyses at increasing times on stream (TOS). The time covered (216 min) was about the maximum allowed by the feeding pump, but it was also the maximum time for obtaining an essentially complete conversion of C_1 oxygenates into hydrocarbons. The measurements were stopped when the MeOH/DME conversion was about 99%. Once unconverted C_1 oxygenates start emerging from the reactor, complete catalyst deactivation soon takes place (8).

Other reaction products not given in Table 1 are CO, CO_2, CH_4 and C_{5+}. They were, however, formed in smaller amounts than the other products. It was pointed out in a preceding paper (12) that CO_x and CH_4 in a reaction system like the present one are formed almost exclusively from methanol. Otherwise they are of no interest here.

It is seen from Table 1 that during the early stages of the reaction there is a sizeable formation of ethane and propane. These compounds are more hydrogen rich than

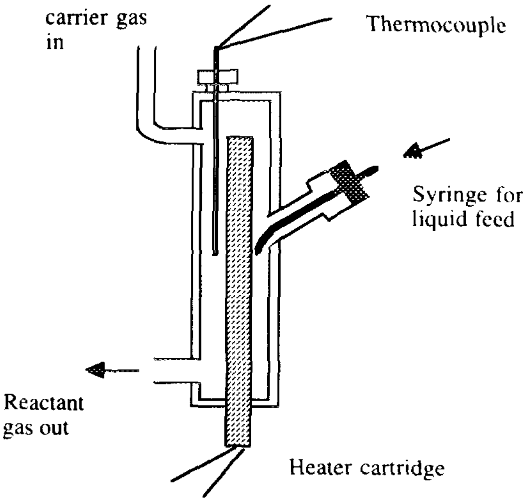

FIG. 1. Schematic drawing of evaporator.

TABLE 1

Hydrocarbons in Reactor Effluent as a Function of Time on Stream[a]

Analysis No.	1	2	3	4	5	6	7	8	9	10
TOS (min) mol%[b]	32	51	74	94	114	135	155	175	196	216
C_2H_4	13.63	14.57	15.68	15.51	15.65	15.87	16.53	16.64	16.53	17.22
C_2H_6[c]	0.35	0.35	0.30	0.30	0.25	0.25	0.20	0.20	0.10	0.10
C_3H_6	7.18	7.73	7.70	7.37	7.42	7.29	7.09	7.13	6.84	6.62
C_3H_8	0.85	0.57	0.45	0.36	0.30	0.27	0.20	0.15	0.15	0.15
ΣC_4s	2.05	1.85	1.83	1.57	1.50	1.34	1.27	1.22	1.25	1.20
ΣC_2	13.98	14.92	15.98	15.81	15.90	16.12	16.73	16.84	16.63	17.32
ΣC_3	8.03	8.30	8.15	7.73	7.72	7.56	7.29	7.28	6.99	6.77
ΣC_4 alkenes	2.05	1.85	1.83	1.57	1.50	1.34	1.27	1.22	1.25	1.20
Carbon sum	60.05	62.14	63.73	61.09	60.96	60.28	60.41	60.40	59.23	59.75

[a] Experimental conditions: temperature, 400°C; carrier gas, 60 mol%; reactant mixture (MeOH + EtOH + H_2O), 40 vol%; atmospheric pressure; 100 mg catalyst (SAPO-34); reactant feed rate (WHSV), 4 h^{-1}.

[b] Most of the water was trapped before analysis, so the water content when the analysis is made is about 1%.

[c] Analysis results well below 0.5% are not precise.

the reactant, and their formation must therefore be accompanied by a simultaneous formation of (hydrogen poor) "coke." With increasing TOS there is a steady increase in ethene concentration in the effluent, and a corresponding decline in propene and butenes.

An impression of the precision of the product concentration measurements given in Table 1 may be obtained from Fig. 2, where the results are plotted together with least-squares fitted quadratic polynomials. It may be pointed out that the product distribution is far from an equilibrium distribution. At 400°C the dominating species at equilibrium would be butenes and to a slightly lesser extent propene (15).

Product Isotopic Composition

A goal of the present work is to measure the isotopic composition of the main products ethene, propene, and butenes (dominated by *t*-2-butene), and the dependence of this composition upon the time on stream (and thereby on catalyst deactivation) using a reaction feed ^{13}C-MeOH/^{12}C-EtOH/H_2O. From these data one may be able to make a choice between consecutive-type reaction mechanisms and parallel- (including carbol pool) type mechanisms.

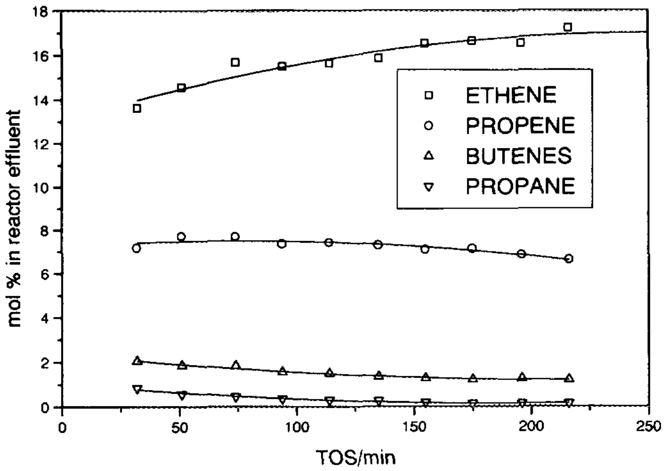

FIG. 2. Product distribution during the experiment.

The procedure used to determine the isotopic composition has been outlined earlier (12). The isotopic compositions of the main products and their time dependences are given in Tables 2–4.

Ethene. There are several conspicuous features regarding the isotopic composition of ethene given in Table 2. It is essentially constant with time, although there is small decrease in the number of molecules with one ^{13}C atom. Otherwise the composition is remarkably independent of time on stream. The precision of the isotopic distribution data is highly satisfactory, as is shown in Fig. 3.

The ^{12}C/^{13}C atom distribution is far from random. For the 216-min point where the ^{13}C content is 28.29%, a random distribution would give 40.6% ethene molecules with one ^{13}C atom, whereas only 8.3% is observed. The divergence from randomness increases slowly throughout the experiment with increasing catalyst deactivation, but as is seen the composition is always very far from random.

Propene. Quite a different result is obtained for propene and butene. The isotopic composition of propene is given in Table 3. Only at short TOS is there a sizeable proportion of ^{12}C atoms in the propene fraction. In the last analysis more than two-thirds of the propene molecules contain only ^{13}C atoms, and the ^{13}C content increases from 67% in the first analysis to 85% at the end of the experiment.

The standard deviation of the analysis results is approx-

TABLE 2

Isotopic Composition of Ethene in Reactor Effluent

Analysis No.	1	2	3	4	5	6	7	8	9	10
TOS (min)	32	51	74	94	114	135	155	175	196	216
0 ^{13}C	66.04	65.73	66.34	66.38	66.41	66.80	66.82	67.49	67.06	67.56
1 ^{13}C	10.80	10.74	10.00	9.82	9.33	9.13	8.95	8.44	8.47	8.29
2 ^{13}C	23.16	23.53	23.67	23.80	24.25	24.07	24.23	24.07	24.48	24.14
% ^{13}C in C_2	28.56	28.90	28.67	28.71	28.92	28.63	28.71	28.29	28.72	28.29

imately 0.5 percentage points. Also, in this case the experimental distribution differs from a random distribution in a mixture with the same $^{12}C/^{13}C$ content. In the first analysis, at TOS = 32 min, the distance from randomness is not far outside the possible error limits, but it increases progressively with TOS and is quite pronounced at the end (216 min). There are more propene molecules with only ^{12}C atoms and more molecules with two ^{12}C atoms than expected, but the two make up only 2 and 9% of the total. There are fewer molecules with one ^{12}C and 2 ^{13}C than expected, but they make up more than 20%. There is an excess of $^{13}C_3$ molecules and they make up two-thirds of the propene fraction.

Butenes. The isotopic content of the butenes evolves in much the same way as is observed for propene. The results are given in Table 4. Only the first few analyses show a sizeable amount of ^{12}C atoms, and it is only in the beginning that a measurable number of C_4 molecules with three and two ^{12}C atoms are found. At the end, where 95% of the atoms are ^{13}C, no molecules with more than one ^{12}C are found. In contrast to the result for propene there are no signs of deviation from a random $^{12}C/^{13}C$ atom distribution.[2]

DISCUSSION

The difference in isotopic composition between ethene on the one hand, which contains 71% ^{12}C, and propene and butenes on the other hand, which at long TOS contain only 15 and 5% ^{12}C, shows that ethene is very unreactive over SAPO-34 under our reaction conditions, once it has been desorbed into the gas phase. The larger part of the ethene molecules emerge unreacted from the reactor. The overwhelming part of the propene and the butene molecules which emerge have been formed from methanol, and it is a rare event that an ethene molecule is being methylated and converted to C_3 or C_4.

It was pointed out above that the $C_2 : C_3 : C_4$ ratio is far from an equilibrium ratio, and that at equilibrium C_3 and C_4 would be present in much larger amounts than C_2. The high concentration of C_2 then implies that the conversion of C_2 to C_{3+} is a slow process. The preponderance of C_{3+} at equilibrium implies that the conversion of C_{3+} to C_2 is an even slower process, so the non-negligible content ^{13}C in ethene cannot come from the higher hydrocarbons (which are rich in ^{13}C). Hence the overwhelming part of ^{13}C in ethene must be formed directly from C_1-oxygenate.

On the basis of the discussion above the following picture emerges. At short TOS, when the catalyst is very active, a differential volume element (which may be regarded as a batch reactor) of reactant gas will be fully converted to a hydrocarbon mixture in a much shorter time than is needed to traverse the catalyst bed. From then on the reactions taking place are hydrocarbon interconversion reactions until the volume element leaves the reactor. From the moment where C_1-oxygenate conversion is essentially complete, the product composition will

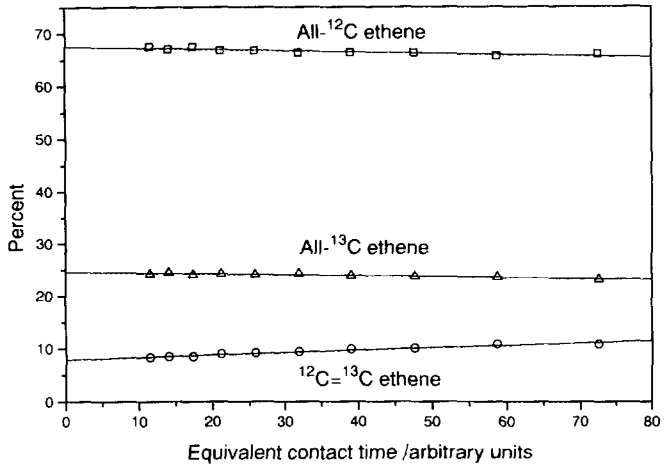

FIG. 3. Evolution of isotopic composition of ethene with equivalent contact time.

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[2] These results actually refer to *t*-2-butene, the larger part of the C_4s. Due to low concentration the other butenes were more difficult to analyze quantitatively, but there were no signs of differing results with *c*-2-butene and 1-butene. The well known facile interconversion between the isomers would also make any difference highly suprising.

TABLE 3

Isotopic Composition of Propene in the Reactor Effluent

Analysis No.	1	Random[a]	2	3	4	5	6	7	8	9	10	Random[a]
TOS (min)	32	(32)	51	74	94	114	135	155	175	196	216	(216)
0 ^{13}C	5.51	3.3	4.41	4.81	4.69	4.48	3.98	4.17	3.52	2.65	2.41	0.4
1 ^{13}C	20.51	20.9	18.52	16.22	14.12	13.65	12.83	11.23	9.46	9.74	8.81	6.0
2 ^{13}C	38.52	44.4	35.77	32.73	29.82	27.19	26.01	23.93	22.64	21.95	20.90	32.9
3 ^{13}C	35.46	31.4	41.31	46.23	51.38	54.68	57.18	60.66	64.38	65.66	67.88	60.9
Σ^{13}C in C_3	67.98 =	67.98	71.33	73.47	75.96	77.36	78.80	80.36	82.63	83.54	84.75	= 84.75

[a] Random distribution for the same ^{12}C/^{13}C content.

differ more and more from the initial composition. (Coke formation may take place at this stage as well as in the first part of the bed, where C_1 species are still present. Coke formation is not a part of this study.)

The discussion of the product spectrum evolution with increasing TOS, and consequently decreasing catalyst activity, might be conducted in terms of catalyst activity. At this stage of knowledge we shall neglect the possible changes in intrinsic catalyst selectivity with deactivation and assume it is constant. The relationship between the time which the volume element (our batch reactor) has spent in the catalyst bed while passing through and the product composition in the batch reactor will then be of the type

$$f(\text{composition}) = k_0Nt, \qquad [1]$$

where f is a so-far unknown function. The main point here is that the term k_0Nt, where k_0 represents the rate constant of a single site and N represents the number of accessible sites, i.e., the variable catalyst activity, is large at short TOS and decreases as TOS increases. Rather than discuss the system in terms of a variable k while keeping t(the time needed for the volume element to pass the catalyst bed) constant, we may discuss it in terms of an imaginary but equivalent system where N is constant and t is variable. The residence time t will then represent what may be called an "equivalent contact time" (ECT). In this way the batch reactor is discussed in terms of the "normal" variable, i.e., time. The equivalent contact time is then in some way inversely related to TOS.

$$\text{TOS small} \Leftrightarrow \text{ECT large}$$

$$\text{TOS large} \Leftrightarrow \text{ECT small.}$$

The above forms a basis for discussing the experimental results. The constancy of the isotopic composition of ethene and the increasing amount of ethene with TOS (which is a decrease with ECT) is to be expected because ethene is converted into higher hydrocarbons with increasing ECT, presumably by a first order process, and the opposite reaction (ethene formation by cracking) is for thermodynamic reasons insignificant.

In order to obtain the maximum information about the reaction route secondary hydrocarbon interconversion reactions should be suppressed as far as possible. The feed rate in this experiment was not a variable, but the above discussion indicates that essentially equivalent information may be obtained by extrapolating to zero ECT. It was pointed out that the exact relationship between TOS and ECT is not known, but it may be argued that the following relationship which satisfies the required inverse relationship between ECT and TOS is likely to be a useful approximation.

$$\text{ECT} = \text{const.} \exp(-\alpha.\text{TOS}). \qquad [2]$$

TABLE 4

Isotopic Composition of Butenes (t-2-Butene) in Reactor Effluent

Analysis No.	1	2	3	4	5	6	7	8	9	10
TOS (min)	32	51	74	94	114	135	155	175	196	216
0 ^{13}C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1 ^{13}C	7.57	6.32	2.74	0.68	0.00	0.00	0.00	0.00	0.00	0.00
2 ^{13}C	24.63	20.27	16.81	14.80	7.33	4.32	2.45	1.06	0.00	0.00
3 ^{13}C	39.83	35.15	32.17	26.26	25.63	21.78	19.72	19.21	18.47	17.03
4 ^{13}C	27.97	38.26	48.28	58.26	67.04	73.90	79.73	79.73	81.52	82.97
% ^{13}C in C_4	72.05	76.33	81.50	85.52	89.93	92.40	93.85	94.67	95.37	95.74

The activity decrease (decreasing N) with TOS which is always observed may then be assumed to be proportional to the number of sites on which carbocation reactions may take place (supported by unpublished laboratory data). Solving the differential equation which then arises, one obtains

$$N = N_0 \exp(-\alpha.\mathrm{TOS}). \qquad [3]$$

If now N in Eq. [1] is replaced by the above expression, it is seen that k_0Nt may be written as $k_0N_0(\exp(-\alpha\,.\,\mathrm{TOS})\,.\,t)$. Consequently we see that the residence time, t, may be replaced by the equivalent contact time, ECT, as given by Eq. [2]. The system may then be treated as if the activity were constant. Any convenient number may be chosen for the unknown "const." We have arbitrarily chosen the value 100. In this way convenient values (in arbitrary units) are obtained for ECT. The "deactivation constant," α, is also not known. We have found, however, that by choosing $\alpha = 0.01$ min^{-1}, i.e., assuming the activity to drop to e^{-1} in 100 min, a generally satisfactory relationship between the observed system behaviour and ECT is obtained. The choice $\alpha = 0.01$ min^{-1} was based upon general knowledge about the deactivation rate for this reaction system. Higher and lower values of α, viz. 0.0025 and 0.025 min^{-1}, have also been tested. Besides being in general disagreement with known system behaviour these values led to unsatisfactory behaviour when extrapolations were carried out.

Treating the ethene results (Table 2) according to the above procedure, Fig. 3 is obtained. The extrapolated values (ECT = 0) are seen to be approximately as follows: all ^{12}C ethene ≈ 67%, ^{12}C=^{13}C ethene ≈ 8%, and all ^{13}C ethene ≈ 24%. A remarkable feature of Fig. 3 is the very small variation in the isotopic composition of ethene with progressing catalyst deactivation (alternatively, decreasing equivalent contact time.) This feature is fully consistent with the result discussed above, viz. ethene is only to a negligible extent formed by the cracking of other hydrocarbons under the prevailing conditions.

Part of the "mixed" molecules, ^{12}C=^{13}C, were actually introduced in the ethene feed, since ethene with a natural isotopic composition was employed. Hence 2.2% of the ethene molecules originally introduced had one ^{13}C-atom. If the feed had been all ^{12}C ethene the above distribution would have been as follows: all ^{12}C ethene 68.5%, ^{12}C=^{13}C ethene 6.5%, and all ^{13}C ethene 24%. Clearly close to two-thirds of the ethene in the reactor effluent is virgin, unreacted ethene.

The corresponding extrapolations for propene are given in Figs. 4a and 4b. Fig. 4a suggests the initial propene to be about 75% all ^{13}C propene, and less than 3% all ^{12}C propene. Figure 4b suggests that the remaining part of the propene molecules consist mainly of ^{12}C ^{13}C$_2$H$_6$, and this species makes up about 17% of the total. ^{12}C$_2$ ^{13}CH$_6$, which would be the initial propene if propene were produced via methylation of ethene, makes up only about 7% of the total.

In the case of butenes it was only in the case of the shortest TOS, i.e., longest ECT, that the contents of molecules with zero, one, or two ^{13}C atoms were high enough to permit quantification. The contents of all ^{13}C butene and butene with three ^{13}C atoms are shown in Fig. 5.

Figure 6 shows the content of ^{13}C atoms in each of the products ethene, propene, and butenes.

The result in all cases is that the initial product consists of propene and butenes which have almost entirely been formed directly from C$_1$ oxygenates and, on the other hand, ethene which is a mixture of two parts (virgin) ^{12}C=^{12}C molecules and one part ^{13}C=^{13}C molecules

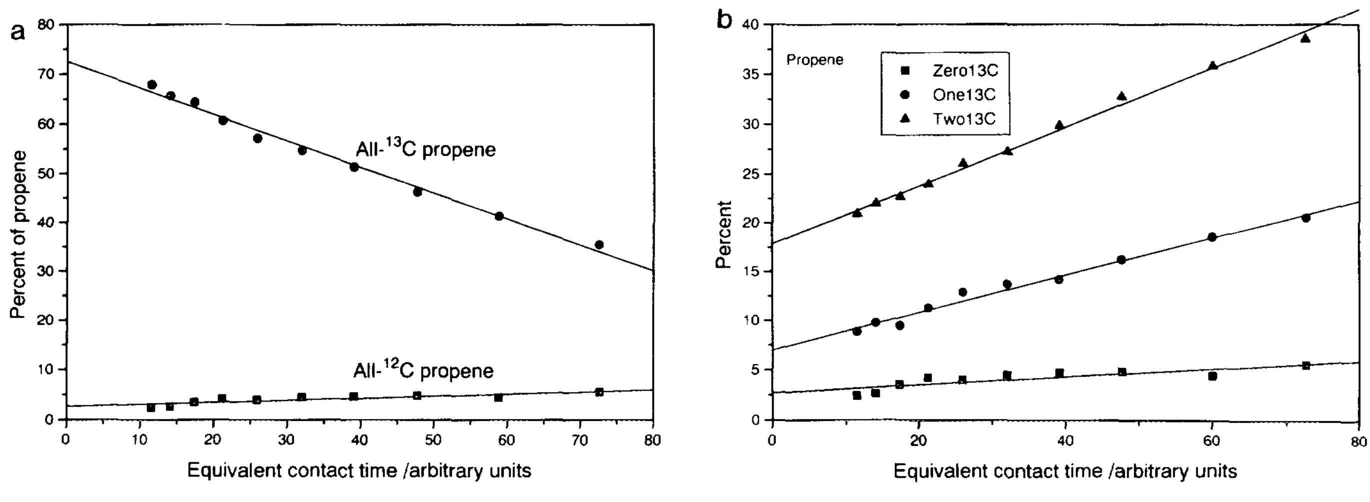

FIG. 4. (a) Part of propene molecules consisting of only ^{13}C or only ^{12}C. (b) Content of propene molecules with mixed isotopic composition.

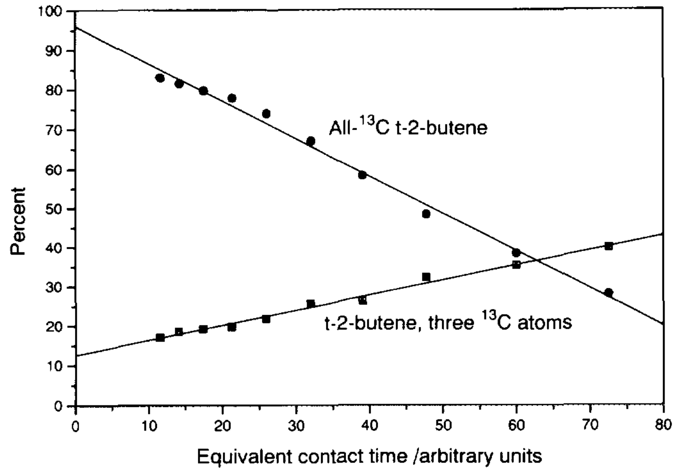

FIG. 5. Isotopic composition of butenes at decreasing equivalent contact time.

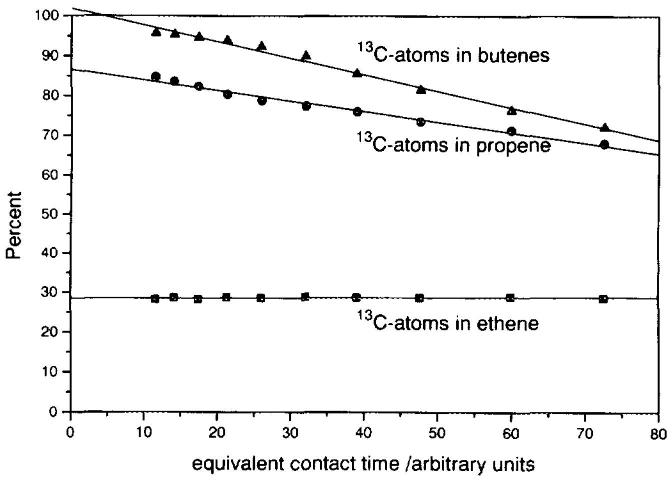

FIG. 6. Content of ^{13}C in ethene, propene, and butenes during the experiment.

made directly from MeOH/DME. The non-negligible content of isotopically mixed molecules at short TOS (long ECT) shows, however, that although C_1 oxygenates are much more reactive than ethene, ethene will take part in the hydrocarbon interconversion reactions at long contact times.

The finding that the isotopic distribution in ethene is always far from random, whereas for propene this nonrandomness is clear only at short equivalent contact times (ECT) and is not visible for butene, supports a carbon pool mechanism, but this result might also arise if propene and butenes are adsorbed, isotopically isomerized, and desorbed at a much faster rate than ethene.

CONCLUSION

The results obtained are in agreement with a carbon pool-type mechanism (parallel mechanism), and ethene is an inert primary product. Thus a consecutive-type mechanism with ethene as primary product which gives higher hydrocarbons by being methylated by MeOH/DME is untenable.

In the co-reaction of ethene and MeOH over SAPO-34, most of the product is made from MeOH, and there is about 90% unconverted ethene remaining at the time when MeOH is fully converted. The propene and the butenes made during the reaction exhibit distributions of ^{12}C and ^{13}C which are nearly random at all times. This observation supports the carbon pool mechanism. Randomness will, however, also result if propene and butenes are adsorbed, isotopically isomerized, and desorbed at a much faster rate than ethene. Further investigation is in progress to shed some light on this issue.

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