JOURNAL OF CATALYSIS **161,** 304–309 (1996)
ARTICLE NO. 0188

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

2. Isotopic Labeling Studies of the Co-reaction of Propene and Methanol

Ivar M. Dahl* and Stein Kolboe†,[1]

Department of Hydrocarbon Process Chemistry, SINTEF SI, P.O. Box 124, N-0314 Oslo, Norway; and †Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway

Received July 11, 1995; revised January 24, 1996; accepted January 31, 1996

[^{13}C]Methanol and [^{12}C]propene (fed as isopropanol, which is immediately converted to propene) have been co-reacted over SAPO-34 in a flow system at 400°C using argon as a carrier gas. The feed was equimolar in ^{13}C and ^{12}C atoms. The products were analyzed by gas chromatography–mass spectrometry, allowing determination of the isotopic composition. While the methanol was completely or almost completely converted to hydrocarbons, the larger part of the propene emerged unreacted. The products ethene and butenes were mostly formed from methanol and contained a large excess of ^{13}C atoms. The propene effluent consisted mainly of all-^{12}C or all-^{13}C molecules and, only to a small extent, isotopically mixed molecules. The tendency for propene to emerge unreacted and all new hydrocarbons to be formed from methanol became more pronounced with progressing catalyst deactivation. The results show that the higher hydrocarbons are, over this catalyst, not formed by successive methylations of bulk gas-phase propene. A previously proposed "carbon pool" mechanism can explain the gross effects seen in the product and isotopic distribution, but it is pointed out that the nonreactivity of propene in SAPO-34 may be caused by slow diffusion of propene in the pores. © 1996 Academic Press, Inc.

INTRODUCTION

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

Several reaction mechanisms have been proposed for this conversion of methanol/dimethyl ether to hydrocarbons (1–8). They may be broadly lumped into two groups: consecutive type mechanisms

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

and 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 earlier work we showed that the consecutive mechanism was not appropriate, and we proposed what we called a "carbon pool mechanism" (Scheme 1), which is a kind of modified parallel mechanism (9, 10). It was shown that methanol is much more reactive than ethene in the reaction, C atoms from methanol being incorporated into the product stream one to two orders of magnitude faster than from ethene. In this work we present results from a similar experiment with isotopically labeled CH_3OH (^{13}C) and unmarked propene (natural isotope composition), from isopropanol. Taking into account that propene is usually more reactive than ethene a more active participation might be expected.

EXPERIMENTAL

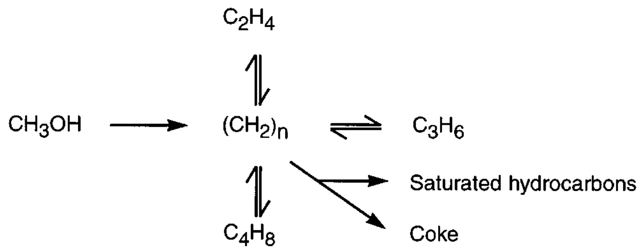
SAPO-34 was synthesized according to Lok *et al.* (11). Elemental analysis was carried out as previously described (12). The product purity was checked by X-ray diffraction (XRD). [^{13}C]MeOH (99% isotopic purity) was obtained from Cambridge Isotopic Laboratories, and isopropanol, from A/S Vinmonopolet.

The experimental setup of the reactor system and the analysis equipment have been described earlier (10, 12). Argon was used as carrier gas. Total pressure equalled at-

---

[1] To whom correspondence should be addressed.

0021-9517/96 $18.00



SCHEME 1. Carbon pool mechanism.

mospheric pressure. The molar feed ratio of Ar : CH_3OH : C_3H_7OH : H_2O was kept at 6 : 2 : 0.67 : 1.33. Thus, the same amounts of ^{12}C and ^{13}C atoms were fed to the reactor, and the C : H : O ratio was the same as if neat methanol were the only feed. The measurements were performed at 400°C with 100 mg catalyst. In the first part of the experiment the metering pump was set of deliver 0.4 g/h ($WHSV = 4\ h^{-1}$). In the second part, it was set to give 0.8 g/h, increasing WHSV to $8\ h^{-1}$.

RESULTS

Products

The most important reaction products obtained are listed in Table 1. The effluent compositions are given for six analyses at increasing times on stream (TOSs). There are other products, e.g., C_{5+}, but they were formed in quantities too small to be analyzed, and they have been neglected. The time covered (145 min) is about the maximum time allowed by the feeding system when the experiment is run as it was done here.

TABLE 1

Composition of the Reactor Effluent during the Experiment

Analysis No.:	1	2	3	4	5	6
TOS (min)[a]:	12	39	65	90	120	145
WHSV (h^{-1}):	4	4	4	4	8	8
	Content (mol%)[b]					
CH_4	0.21	0.21	0.21	0.21	0.17	0.15
CO_2	0.06	0.05	0.05	0.04	0.02	0.02
C_2H_4	3.47	4.39	4.82	4.84	4.82	4.50
C_2H_6	0.07	0.09	0.09	0.08	0.06	0.05
C_3H_6	10.30	12.56	14.08	14.19	14.95	14.93
C_3H_8	2.05	1.09	0.75	0.46	0.15	0.14
$\sum C_4$[c]	3.20	2.26	1.58	1.10	0.85	0.83

[a] The actual time on stream (TOS) is somewhat less than the time indicated. There is a time lag of up to 5 min before the feed reaches the reactor and, later, the sampling valve of the analysis system.

[b] The remainder is argon, about 0.7% H_2O, and negligible amounts of C_4H_{10}, C_{5+}, and CO. In analyses 5 and 6 unconverted methanol and dimethyl ether are also seen.

[c] The C_4 fraction was made up of 1-butene, *trans*-2-butene, *cis*-2-butene, and a small amount of butane, negligible after about 30 minutes. The butenes appear in thermodynamic equilibrium and are dominated by *trans*-2-butene.

It is seen from Table 1 that during the early stages of the reaction there is a sizable formation of propane. The propane is more hydrogen-rich than the reactant, and its formation must therefore be accompanied by simultaneous formation of (hydrogen-poor) "coke." With increasing TOS there is a steady increase in the propene concentration in the effluent and a corresponding decline in butenes (and propane). Ethene formation appears to increase in the early stages (analyses 1 and 2) and thereafter remains fairly stable. The amount of saturated hydrocarbons is larger in this experiment with the methanol/propene feed than in the earlier work where the feed was methanol/ethene (10). In agreement with this, more rapid deactivation was observed in this work.

In analysis 4, a trace amount of unconverted C_1-oxygenates was noted. From then on the feed rate was doubled (to $WHSV = 8\ h^{-1}$) to minimize secondary hydrocarbon interconversion reactions as far as possible, and thereby obtain clearer insight into the primary product distribution. Toward the end (last analysis) 90–95% of the methanol was converted to hydrocarbons.

Unconverted isopropanol was never observed. Separate experiments (laboratory data) have shown that isopropanol dehydration is a very much faster process than methanol conversion to hydrocarbons. It is also important to recognize that the isopropanol molecule is too large to enter the pore system in SAPO-34 with its chabazite-type framework, so the dehydration reaction takes place at the exterior surface of the crystals.

By analogy with previous results when there was a MeOH/C_2H_4 feed, the C_2 : C_3 : C_4 rates is far from an equilibrium ratio. In particular, the C_4's would be the dominant species in an equilibrium mixture (13). The reaction is therefore not thermodynamically limited.

A visual impression of the dependence of the product distribution on TOS and the precision of the measurements may be obtained from Fig. 1, where the effluent content of ethene, propene, and the sum of butenes is plotted versus TOS.

Product Isotopic Composition

As in the preceding work, we are interested in determining the isotopic composition of the main products, viz., ethene, propene, and butenes (dominated by *trans*-2-butene) and the dependence of this composition on the TOS (and, thereby, on catalyst deactivation). This was previously done using a reaction feed [^{13}C]MeOH/[^{12}C]EtOH/H_2O, which behaves like a methanol/ethene mixture. Here we use [^{13}C]MeOH/*i*-[^{12}C]PrOH/H_2O, which behaves like a methanol/propene mixture. The procedure used to determine the isotopic composition was given earlier (9) and is

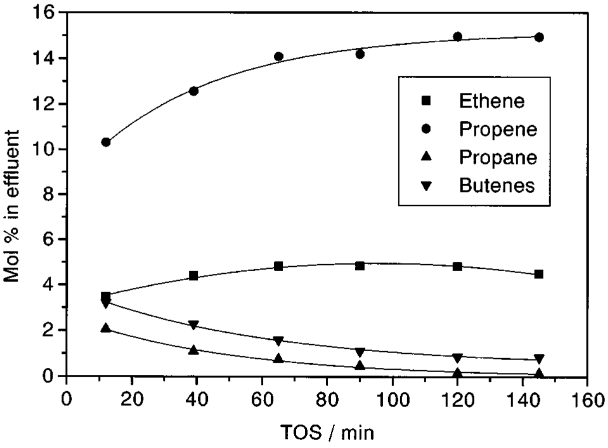


FIG. 1. Content of the products ethene, propene, propane, and butenes in reactor effluent versus time on stream (TOS).

not repeated here. The isotopic compositions and their time dependence are given in Tables 2–4.

Ethene. It is clearly seen that the ^{13}C content of ethene increases steadily with TOS and that the fraction of ethene which may have been formed directly by cracking reactions involving [^{12}C]propene becomes negligible at the longest TOS. In the beginning of the run a nonnegligible part of the propene takes part in reactions which eventually form ethene. Toward the end that part is negligible.

Propene. A noticeable feature of Table 3 is the increase in all-[^{12}C]propene and all-[^{13}C]propene with TOS (analysis 6 excepted) while the isotopically mixed molecules decrease.

Propane. The isotopic composition of propane was also investigated. The obvious strategy would be to base this analysis on the C_3H_x fragments with masses 36–47, but the low concentration of propane and the low probability of forming these fragments made it unfeasible. The most prominent peak in the propane mass spectrum is the C_2H_5 peak with mass 29 (^{12}C). For this reason the mass spectrum in the range 24–31 was used to determine the isotopic composition, but the information is then limited to knowing the fractions of ^{12}C and ^{13}C-atoms in propane, detailed isotope distribution information not being available. However, isotopic analyses showed that there were relatively more ^{13}C atoms and fewer ^{12}C atoms than in propene. In particular, the fraction of all ^{12}C fragments was smaller than in propene. This finding suggests that propane is mainly a direct product from the carbon pool and less a secondary product from propene and H_2. Propane formation soon becomes insignificant.

TABLE 2

Isotopic Composition of Ethene in Reactor Effluent: Percentages of Ethene Molecules with 0, 1, and 2 ^{13}C Atoms

Analysis No.:	1	2	3	4	5	6
TOS (min):	12	39	65	90	120	145
0 ^{13}C (%)	10.60	8.00	6.00	3.70	2.20	0.90
1 ^{13}C (%)	25.60	19.40	16.60	16.90	11.30	10.00
2 ^{13}C (%)	63.70	72.60	77.30	79.40	86.50	89.10
^{13}C in C_2 (%)	76.50	82.30	85.70	87.90	92.20	94.10

TABLE 3

Isotopic Composition of Propene in Reactor Effluent: Percentages of Propene Molecules with 0, 1, 2, and 3 ^{13}C Atoms

Analysis No.:	1	2	3	4	5	6
TOS(min):	12	39	65	90	120	145
0 ^{13}C (%)	29.40	40.80	49.00	53.80	64.90	68.70
1 ^{13}C (%)	32.80	23.50	16.70	13.10	6.20	4.60
2 ^{13}C (%)	24.80	18.10	14.10	10.20	5.10	3.70
3 ^{13}C (%)	12.90	17.60	20.10	22.90	23.80	23.10
^{13}C in C_3 (%)	40.40	37.50	35.10	34.10	29.30	27.00

Butenes. Table 4 shows that the content of all-[^{13}C]-butenes increases strongly with TOS, while all other C_4 molecules decline. In the beginning (analysis 1) the ^{12}C atom content was more than 50%, showing that slightly more than half the C_4's were initially formed by conversion of propene.

DISCUSSION

In the preceding work (10) where the co-reaction of methanol and ethene was studied, it was found that ethene was rather unreactive, so that the reactor effluent consisted essentially of [^{13}C]propene, [^{13}C]butenes, and a mixture of all-[^{13}C]ethene and unconverted all-[^{12}C]ethene. This corresponds to the finding here that the reactor effluent at long TOS consists mainly of [^{13}C]ethene, [^{13}C]butenes, and a mixture of all-[^{12}C]propene and all-[^{13}C]propene.

TABLE 4

Isotopic Composition of the Butene Fraction[a]: Percentages of *trans*-2-Butene Molecules with 0, 1, 2, 3, and 4 ^{13}C Atoms

Analysis No.:	1	2	3	4	5	6
TOS(min):	12	39	65	90	120	145
0 ^{13}C (%)	9.58	10.22	8.97	6.70	2.08	2.22
1 ^{13}C (%)	29.00	23.88	17.94	13.03	6.75	2.71
2 ^{13}C (%)	33.04	26.04	18.21	13.11	7.45	5.31
3 ^{13}C (%)	19.41	19.20	17.81	15.28	12.44	10.87
4 ^{13}C (%)	8.97	20.66	37.06	51.87	71.29	78.89
^{13}C in C_4 (%)	47.30	54.04	64.00	73.15	86.02	90.37

[a] Precise measurements could be made only on *trans*-2-butene (the dominant species), and the data here refer to that compound. Measurements on *cis*-2-butene concurred but showed more scatter.

It was pointed out in the preceding paper (10) that in the early stages, when the catalyst is very active, complete conversion of the methanol takes place at the top of the catalyst bed. In the remaining part of the bed there are only hydrocarbon interconversion reactions, leading to isotopic scrambling. It was furthermore argued that it is reasonable to assume that the main effect of the activity decline because of coke formation is to decrease the number of catalytic sites while the intrinsic activity and intrinsic selectivity of the remaining sites remain unchanged. High-WHSV experiments on MeOH/SAPO-34 (WHSV $= 60$ h^{-1}, $p_{\mathrm{MeOH}} = 70$ mbar) carried out in a different context have shown that to a first approximation the selectivity of SAPO-34 is independent of the degree of coking (deactivation) as long as secondary reactions are largely avoided. It is therefore to be expected that the primary product distribution and isotopic composition (i.e., when secondary reactions have not taken place) is best seen in a deactivated sample, at long TOS. If, however, the isotopic distributions of the products are plotted against TOS, no stationary values are reached; thus, little can be deduced about the primary distribution.

It was shown in the preceding paper that a conceptually simple way of discussing a reaction system such as the present only, where the product spectrum and isotopic composition change with increasing TOS but all other reaction parameters are kept constant, is in terms of an equivalent contact time (ECT). The "true" connection between TOS and ECT is not known, but it was found that the relationship

$$\mathrm{ECT} = 100 \cdot \exp(-\alpha \cdot \mathrm{TOS}), \qquad [1]$$

which corresponds to a first-order activity decay with TOS, worked satisfactorily. The factor 100 was introduced solely to obtain ECT values of a convenient magnitude. The requirement of constancy of all reaction parameters is not really met in this work since the WHSV was increased from 4 to 8 h^{-1} in the last two analyses, with the consequence that the residence time of the imaginary volume element through the catalyst bed is one-half the residence time in the preceding measurements. Varying space velocities may be compensated for by generalizing Eq. [1] to be of the type

$$\mathrm{ECT} = \mathrm{Const.} \cdot \exp(-\alpha \cdot \mathrm{TOS})/\mathrm{WHSV}. \qquad [2]$$

To facilitate any comparison with curves obtained previously, when a methanol/ethanol feed was used, the term Const./WHSV was given the value 100 in cases where WHSV $= 4$ h^{-1}, the feed rate used in the preceding paper (10).

It was pointed out above that the deactivation appeared to be faster here when methanol and propene co-reacted than in the previously reported work. In concordance with this result it was found that α should be assigned a value slightly higher than used previously. $\alpha = 0.015$ min^{-1} appeared to be satisfactory, as compared with $\alpha = 0.01$ min^{-1} used previously. As before, no conclusions depend critically on the precise value assigned to α.

Extrapolation of measured products and their isotopic distributions to ECT $= 0$ may then give information about the primary product spectrum as well as primary isotopic distributions. With this information a choice between various reaction routes and reaction mechanism types might be possible.

The ultimate reason for choosing the above approach to the issue of primary products, rather than the more conventional and obvious one of varying the feed rate enough to obtain widely different conversions of methanol (from only a few percent and upward) is, however, practical. It would not be possible to carry out reliable analyses of the isotopic composition of products having a much smaller concentration than in the actual measurements. In particular, butene formation is of particular interest, but even the most prominent isomer, *trans*-2-butene, is only a minor product under the chosen conditions, and a drastic reduction of its concentration cannot be tolerated. [^{13}C]MeOH is very expensive, and working with much higher feed rates is therefore not economically feasible. The feed rate issue can furthermore not be solved by working at lower temperatures. The system behavior changes markedly a little below 400°C, and the useful lifetime before catalyst deactivation takes place approaches zero.

The fact that the results obtained for the two measurements at the shortest ECT (longest TOS), where the feed rate was doubled, fit neatly with the other points is an argument, in addition to the selectivity independence of coking which was mentioned earlier, that the approach we have been forced to use is valid.

Products

Figure 2 shows the main products when the ECT scale is used. The straight lines are the least-squares lines for

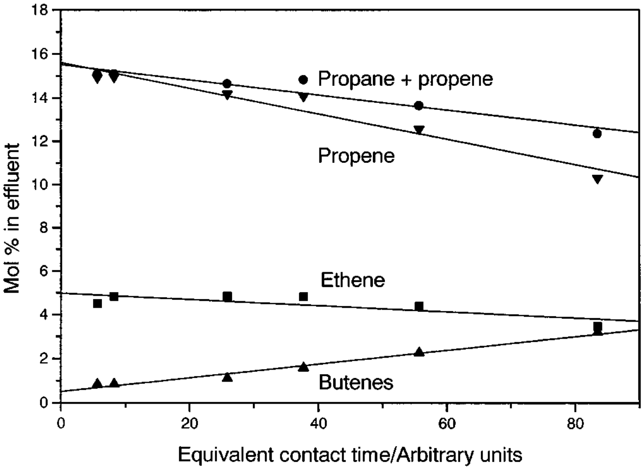


FIG. 2. Content of the products ethene, propene, propane, and butenes in reactor effluent versus equivalent contact time. See text.

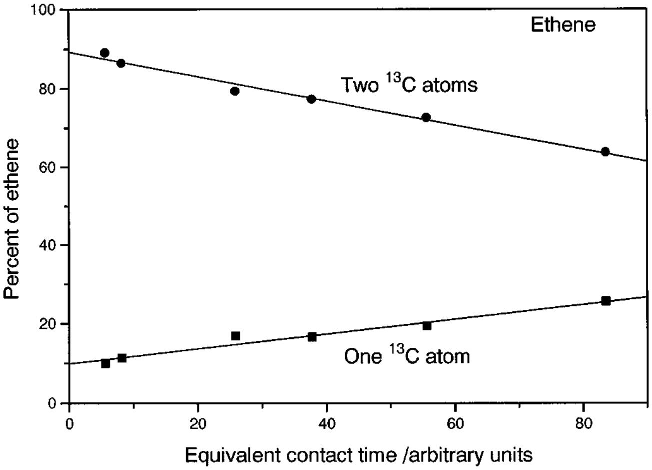


FIG. 3. Isotopic composition of ethene versus equivalent contact time (ECT). The content of ethene molecules with two ^{12}C atoms is not shown, but is ≈ 0 when ECT = 0 and 10% when ECT ≈ 83, corresponding to TOS = 12 min.

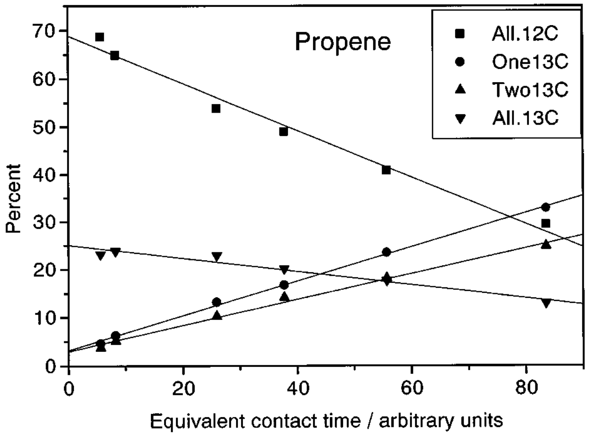


FIG. 4. Isotopic composition of propene versus equivalent contact time.

the given data. They are seen to indicate that the initial composition of the reactor effluent (at complete conversion of C_1 to higher hydrocarbons) is close to $C_2 \approx 5$ mol%, $C_3 \approx 15$ mol%, and $C_4 \approx 1$ mol%, saturated molecules being virtually absent. The propene is only partly formed from methanol; the remainder was part of the feed. See below.

Product Isotopic Composition

Ethene. The percentages of ethene molecules with one and two ^{13}C atoms, respectively, are plotted against ECT in Fig. 3. (The content of all-[^{12}C]ethene is seen from Table 2 to be insignificant at small ECT.) It is clear that virtually all ethene is formed from methanol and only a small fraction is formed by cracking of higher hydrocarbons (derived from propene). The ethene can also not be formed from butenes. For thermodynamic reasons, dimerization of ethene to form butenes must be a much faster process than cracking of C_4 to C_2, and the C_2 concentration is much higher than the C_4 concentration. The observation is, however, in accord with a pool mechanism where C_1 or C_3 may react into the pool, giving the pool (and, thus, also the products) a mixed isotopic composition.

Propene. Figure 4 shows the isotopic composition of propene as a function of ECT. It is immediately clear that at very short ECT, all-[^{12}C]- and all-[^{13}C]propene are the dominant species, while the fraction of molecules with one or two ^{13}C atoms becomes very small at vanishing ECT. At this point it should be remembered that due to the natural 1.1% ^{13}C content in the propene feed, more than 3% of the propene fed contained one ^{13}C atom. Thus, the formation of these molecules in the catalyst bed has been negligible. The content of ^{12}C^{13}C$_2$ is, on the other hand, not correspondingly negligible. It extrapolates to 2.5–3%, which is one-tenth the extrapolated value for the all-[^{13}C]propene. It may be noted that the analyses at the shortest ECT (when methanol was not fully converted) give all-^{12}C values which appear higher than expected and all-^{13}C values which are lower. This is caused by incomplete methanol conversion. Too little propene is formed from methanol, whereas propene in the feed is not influenced by incomplete methanol, conversion. The absence of isotopically mixed molecules shows that propene is much less reactive over SAPO-34 than methanol. The emerging propene molecules either are overwhelmingly virgin feed molecules or have been formed from methanol and are fully ^{13}C-based.

Butenes. Figure 5 shows how the isotopic composition of *trans*-2-butene (=butenes) varies with ECT. At very short ECT the all-^{13}C is dominating, although the ^{12}C^{13}C$_3$ species is also not negligible. The content of species with two or more ^{12}C atoms is seen to vanish. At short ECT

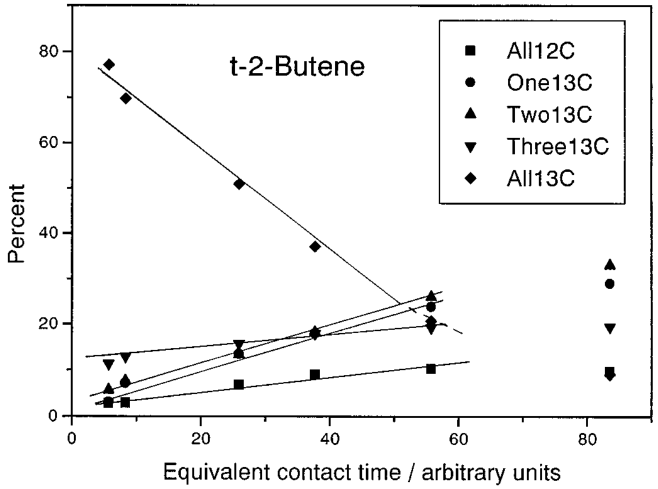


FIG. 5. Isotopic composition of the butenes versus equivalent contact time.

there is thus no sign of butene formed by methylation of propene. The presence of a few molecules with one, or in a few cases two, ^{12}C atom(s) is in accord with the carbon pool mechanism of Scheme 1.

Mechanistic Implications

The experiments carried out here and in preceding work show conclusively that once hydrocarbon molecules like ethene and propene have entered the bulk gas phase, they participate only to a very limited extent in reactions with methanol over SAPO-34.

Could this nonreactivity be caused by slow diffusion of hydrocarbon molecules into the relatively narrow-pore SAPO-34 structure? As far as ethene is concerned this cannot be the case. The small ethene molecule would penetrate the pores at least as easily as methanol (or dimethyl ether). Diffusion of propene could, however, be slower than methanol diffusion. The kinetic diameter of propene is larger than that of methanol, and is about the same as the pore openings in SAPO-34 with its eight-ring chabazite structure (14). Propene and methanol might therefore diffuse at quite different rates. Thus, while it is clear that ethene is hardly reacting with methanol (or dimethyl ether, a similar conclusion concerning the reactivity of propene is not warranted, even though it may well be true. Ongoing co-reaction experiments over H-ZSM-5 and dealuminated H-mordenite suggest that in zeotype materials with larger pore openings, the reactivity of propene toward methanol/dimethyl ether may perhaps not be negligible. However, the observed isotopic distribution appears to be equally well explained by a pool mechanism or by fast hydrocarbon interconversion reactions (15, 16).

The reason for the nonreactivity of bulk gas-phase propene can apparently not be answered at present. More detailed information about diffusion rates would be of interest, and work is in a preparatory stage for a detailed study of the diffusion rates in SAPO-34 or another chabazite framework.

CONCLUSION

Previous results on co-reaction of methanol and ethene showed conclusively that over SAPO-34 the consecutive mechanism is not tenable as a general reaction pathway when methanol is converted to hydrocarbons. The isotopic distribution reported here, where methanol and propene were co-reacted, shows, in accord with the ethene co-reaction results, that bulk gas-phase propene molecules hardly react with methanol over SAPO-34, and is thus in accord with a pool-type mechanism, but whether this nonreactivity is a true nonreactivity or is caused by slow diffusion of propene in the small-pore SAPO-34 cannot be determined.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from the Spung Committee of The Royal Norwegian Council for Science and Technology.

REFERENCES

1. Change, C. D., *Catal. Rev. Sci. Eng.* **25**, 1 (1983); **26**, 323 (1984).
2. Chang, C. D., *Stud. Surf. Sci. Catal.* **36**, 127 (1988).
3. Chang, C. D., *Stud. Surf. Sci. Catal.* **61**, 393 (1991).
4. Hutchings, G. J., and Hunter, R., *Catal. Today* **6**, 279 (1990).
5. Kaiser, S. W., *Arab. J. Sci. Eng.* **10**, 361 (1985).
6. Kolboe, S., *Acta Chem. Scand. A* **40**, 711 (1986).
7. Kolboe, S., *Stud. Surf. Sci. Catal.* **36**, 189 (1988).
8. Cormerais, F. X., Pérot, G., Chevalier, F., and Guisnet, M., *Chem. Res. (S)*, 362 (1980).
9. Dahl, I. M., and Kolboe, S., *Catal. Lett.* **20**, 329 (1993).
10. Dahl, I. M., and Kolboe, S., *J. Catal.* **149**, 458 (1994).
11. Lok, B. M., Messina, C. A., Patton, R. L., Gaiek, R. T., Cannan, T. R., and Flanigen, E. M., *U.S. Patent* 4,440,871 (1984).
12. Nawaz, S., Kolboe, S., Kvisle, S., Lillerud, K. P., Stöcker, M., and Øren, H. M., *Stud. Surf. Sci. Catal.* **36**, 421 (1991).
13. Stull, D. R., Westrum, E. F., Jr., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." Wiley, New York, 1969.
14. Breck, D. W., "Zeolite Molecular Sieves," p. 633. Wiley, New Yrok, 1974.
15. Kolboe, S., and Dahl, I. M., *Stud. Surf. Sci. Catal.* **94**, 427 (1995).
16. Mikkelsen, Ø., Rønning, P. O., and Kolboe, S., to be published.