Catalysis Letters 20 (1993) 329–336

On the reaction mechanism for propene formation in the MTO reaction over SAPO-34

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Received 10 February 1993; accepted 12 May 1993

Three different feeds: methanol, methanol/ethanol/water (2 : 1 : 1 molar ratio) and ^{13}C-methanol/ethanol/water (2 : 1 : 1) have been converted to hydrocarbons over a SAPO-34 catalyst at 420°C using argon carrier gas. The products were analyzed by GC-MS allowing the determination of the isotopic composition of the reaction products. The experiments show that the majority of the propene molecules are formed directly from methanol, and that only a minor part is formed by methylation of ethene.

Keywords: SAPO-34; MTO; MTG; hydrocarbon formation from methanol; reaction mechanism; isotopic labeling

1. Introduction

It has been known since 1977 that H-ZSM-5 is an efficient catalyst for converting methanol (or dimethyl ether) into hydrocarbons [1,2]. Later it has become clear that this reaction may be carried out over a large number of protonated zeolites or other zeo-type materials like SAPO-34 [3–5]. A large number of papers has been published on various aspects of the reaction, but the reaction mechanism is still not clarified [2,6–8]. In the majority of papers the H-ZSM-5 catalyst system has been studied.

As a further means of obtaining additional information on the methanol to hydrocarbons (MTH) reaction over zeotype materials we have investigated the reaction between ^{13}C labeled methanol and (^{12}C) ethene (made in situ from ethanol) over SAPO-34. This catalyst has the advantage that the product consists pre-

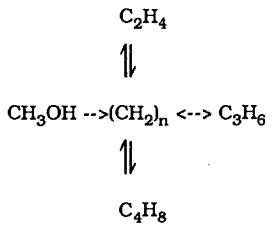
dominantly of C_2–C_4 alkenes [3,4]. The isotopic composition of the reaction products was measured by GC-MS. Because of the unusually high selectivity for ethene (and propene) in this case mechanistic details may differ from those obtained over H-ZSM-5.

From a simplistic view, there are two main mechanism types for olefine formation in the MTH reaction:

(A) A consecutive build up type mechanism with one carbon from methanol adding in each step. (Addition and cracking reactions of the alkene molecules may take place):

$$CH_3OH \rightarrow C_2H_4 \rightarrow C_3H_6 \rightarrow C_4H_8 \rightarrow C_5H_{10} \rightarrow \ldots$$

(B) A "hydrocarbon pool" type mechanism which in a somewhat oversimplified form may be represented by scheme 1.



Scheme 1.

(The "hydrocarbon pool" = $(CH_2)_n$ represents an adsorbate which may have many characteristics in common with ordinary coke, and which might easily contain less hydrogen than indicated. It would perhaps be better represented by $(CH_x)_n$ with $0 < x < 2$.)

This corresponds to a very dynamic situation where one has "big" carbonaceous species inside the cages of SAPO-34 that is all the time adding and splitting off reactants/products.

The consecutive type mechanisms (A) are usually favoured, although it is often acknowledged that propene may be a primary gas phase product alongside with ethene [6–8]. One of us has proposed a reaction mechanism where the hydrocarbons are formed via a hydrocarbon pool, i.e. the B type mechanism [9,10]. A rake mechanism was proposed by Cormerais et al. [11]. Their mechanism may also be consistent with the pool type mechanism.

We have tried to discriminate between the two mechanism types, A and B, by reacting ethanol (as an ethene source) with ^{13}C labeled MeOH to which water is added so that the elemental composition is the same as during the MTO reaction. We have chosen to use the molar ratio MeOH : EtOH = 2 to have equal amounts of labeled and unlabeled carbon. If we then look at the isotopic composition of the propene formed, we should expect from the A type mechanism above to find only singly and triply labeled propene (primary product, scrambling leads to a more

complex pattern). From mechanisms of type B we should expect the ratio 0.125 : 0.375 : 0.375 : 0.125 (for triply : doubly : singly : non-marked propene) if total scrambling in the hydrocarbon pool occurred.

2. Experimental

The reactions have been run at 420°C and 1 bar total pressure with 0.4 g catalyst and a methanol equivalent WHSV of 1 h^{-1}. Argon (99.99%) was used as diluent with partial pressure of 0.6 bar. Methanol: 99% $^{13}CH_3OH$ (Cambridge Isotope Laboratories) or ordinary (non-labeled) reagent grade methanol (Merck). Ethanol: water-free reagent grade.

The SAPO-34 was prepared according to the method given by Lok et al. [12]. Elemental composition was determined using an electron microprobe instrument (EMP-WDX), giving the result that one in eight T-atoms (T-atom: tetrahedrally coordinated Al^{3+}, P^{5+}, or Si^{4+}) was Si. The authenticity and crystalline purity was verified by X-ray powder diffraction.

The experiments were performed using a high precision syringe pump (home-made) for feeding the liquid reagent mixture and a Brooks mass flow controller for the argon diluent. Three different liquid feeds have been used: neat methanol, methanol : ethanol : water = 2 : 1 : 1 (molar ratio) and ^{13}C-methanol : ethanol : water = 2 : 1 : 1. (This ratio gives the same C : H : O ratio as neat methanol.) The reactor system was essentially as described in ref. [4]. The water formed was condensed out (4°C), and the products were analyzed with a Hewlett Packard GC/MS system, model 5890/5970 (equipped with a J&W Scientific DB1, 60 m, 0.2 mm column). The analysis system was calibrated by analyzing a known mixture of all products known to be formed in the reaction system. The reaction was followed for 120 min, i.e. until a moderately deactivated system was obtained. (But oxygenates were still quantitatively converted to hydrocarbons.)

3. Results and discussion

The two feeds, neat MeOH and a MeOH/EtOH/H_2O mixture, lead to similar product spectra, as was to be expected. The product distributions are shown in table 1 which like all other results in this paper refer to a moderately deactivated catalyst system at TOS = 120 min (TOS = time on stream). The most prominent difference being the much higher content of ethene when the ethanol containing feed was employed. This is undoubtedly due to the relative inertness of ethene, as is also evident from the very high content of ^{12}C–^{12}C ethene, shown in table 4.

It is noteworthy that the methanol feed produces more methane than the mixed feed, indicating that methane is mostly (or wholly) formed directly from methanol. Regarding the relative importance of C_3 and C_4 products there is not much differ-

Table 1
Product distributions (% w/w) obtained from MeOH and MeOH/EtOH/H_2O feeds

Product	Feed	
	MeOH	MeOH/EtOH/H_2O
CO [a]	0.9	0.9
CO_2	0.9	0.5
CH_4	1.6	0.7
C_2H_4	25.3	36.1
C_2H_6	1.3	1.6
C_3H_6	34.1	28.2
C_3H_8	12.4	9.6
$\sum C_4$	23.5	22.5

[a] The analysis result for CO represents an upper limit.

ence, but one might speculate that the high content of C_2 when there is ethanol in the feed also leads to a slight preference for formation of C_4 rather than C_3 since the ratio $\sum C_4/C_3H_6$ is slightly higher in this case.

The result suggested by table 1 that methane is formed directly from methanol is further supported by the ion mass distribution in the methane peak. This is seen from table 2 where the ion mass distributions obtained from labeled and non-labeled methanol/ethanol feeds are given. The ion mass distributions are consistent with a ratio $^{13}C : {}^{12}C = 9 : 1$, i.e. about 90% of the methane is formed directly from methanol.

A corresponding result was obtained for carbon dioxide formation. The larger amount which is formed when methanol is the only feed might suggest that it is mainly formed directly from methanol, a result which is again corroborated by the ion mass distributions which indicate that more than 75% of the carbon dioxide has been formed directly from methanol.

Table 1 shows no difference in CO formation from the two feeds. The quantity is, however, so small that the analytical uncertainty cannot be neglected, so there may

Table 2
Ion mass distribution (%) from methane

Ion mass	Feed	
	^{12}C-MeOH/EtOH [a]	^{13}C-MeOH/EtOH
13	0	0
14	11	8
15	44	14
16	44	39
17	0	39

[a] Corrected for natural ^{13}C content.

Table 3
Ion mass distribution (%) of the ethene fraction ($C_2H_x^+$)

Ion mass	Feed	
	^{12}C-MeOH/EtOH [a]	^{13}C-MeOH/EtOH
24	1.88	1.04
25	6.11	3.72
26	28.9	17.2
27	25.8	21.0
28	37.3	33.5
29	0	13.4
30	0	10.1

[a] Corrected for the natural ^{13}C content.

well be a difference. The mass spectra of the labeled and the non-labeled experiment again indicated that CO is formed mostly from methanol (C_1 oxygenate).

The ion masses of the C_2H_x fragments of ethene from the labeled and non-labeled reaction mixtures are given in table 3.

The distribution of molecules with 0, 1 or 2 ^{13}C atoms was calculated from the data given in table 3 (by the same procedure as outlined below for the more complex case of isotope distribution in propene). The result is given in table 4 together with the distribution which would be found if the isotopes were randomly distributed.

The isotope distribution shown in table 4 implies that the C_2 fraction consists of 64.5% ^{12}C atoms and 35.5% ^{13}C.

The ion masses and their frequencies of the propene fraction are given in table 5. Attention may be drawn to the very good reproducibility between separate experiments as evidenced by the essentially identical mass distribution patterns in the two experiments with ^{12}C-MeOH and ^{12}C-MeOH/EtOH.

From the results of the labeled and non-labeled experiments we can calculate the amount of each of the variously labeled propene molecules. The calculation was again based on the assumption that the fragmentation pattern is independent of the particular carbon isotopes in the molecule, so the only effect of introducing ^{13}C atoms into the propene molecule is to shift the ion mass up one unit for each ^{13}C atom introduced. The ion mass distribution for a mixture of propene molecules

Table 4
Isotope distribution (%) in ethene in experiments with labeled methanol

	Found	"Random" [a]
^{12}C–^{12}C	56	41.6
^{12}C–^{13}C	17	45.8
^{13}C–^{13}C	27	12.6

[a] Calculated for the same content of ^{13}C atoms assuming random distribution.

Table 5
Ion mass distribution (%) of the propene fraction ($C_3H_x^+$)

Ion mass	Feed			
	^{12}C-MeOH [a]	^{12}C- MeOH/EtOH		^{13}C-MeOH/EtOH
		obs. [a]	corr. [b]	
36	1.2	1.1	1.1	0.0
37	5.7	5.7	5.8	0.8
38	7.9	7.9	8.0	2.8
39	26.7	26.8	27.4	7.1
40	8.5	8.3	7.7	12.8
41	30.9	31.0	31.7	17.6
42	18.6	18.6	18.2	20.2
43	0.6	0.7	0.0	19.4
44	0.0	0.0	0.0	14.7
45	0.0	0.0	0.0	4.5

[a] The observed ion masses, not corrected for natural ^{13}C.
[b] Corrected for natural ^{13}C content.

containing 0, 1, 2 or 3 ^{13}C atoms may then be calculated for a given ^{13}C distribution and the known fragmentation pattern of ^{13}C free propene given in table 5. The ^{13}C distribution was computed by minimizing (least squares) the difference between the observed pattern from the ^{13}C-MeOH/EtOH reaction mixture and the calculated pattern.

The result of this computation is given in table 6 (experimental distribution), where also the ^{13}C distribution which would arise if the isotopes were randomly distributed is given.

The agreement between the calculated ion mass distribution for the isotopic distribution given in table 6 is given in table 7. The experimental ^{13}C atom distribution is seen to be very nearly random but the deviation from randomness is probably significant.

The ion mass frequencies given in table 5 and the ^{12}C/^{13}C distribution calculated on this basis (table 6) imply that the C_3 fraction consists of 40% ^{12}C atoms and 60% ^{13}C.

Table 6
Distribution (%) of ^{12}C and ^{13}C atoms in the propene molecules formed from ^{13}C-MeOH/^{12}C-EtOH

No. of ^{13}C atoms	Found	Random
0	9	6.5
1	28	29.0
2	39	43.0
3	24	21.5

Table 7
Observed and calculated ion mass frequencies in propene for the $^{13}C/^{12}C$ distribution in table 6

Ion mass	Frequency (%)	
	observed	calculated
36	0.0	0.1
37	0.8	0.8
38	2.8	2.8
39	7.1	7.2
40	12.8	13.0
41	17.6	17.6
42	20.2	20.1
43	19.4	19.3
44	14.7	14.9
45	4.5	4.4

From the results presented above one may conclude that the main route for the formation of propene from MeOH/DME over SAPO-34 is not methylation of ethene (which has been in the gas phase) by methanol.

In a reaction system where water and higher hydrocarbons are present ethene is reacting considerably slower than do C_1-oxygenates to form hydrocarbons. The data allow the estimate that 50–60% of the ethene which was fed left the reactor unconverted even if the activity of the catalyst system undoubtedly was much higher than is needed for a complete conversion of the methanol which is fed. The conversion of methanol into hydrocarbons may well be 10–100 times faster than the methylation of ethene. Hydrocarbon interconversion reactions of ethene are also slow. At equilibrium the conversion of ethene to C_{3+} would be approaching 100% (data from ref. [13]).

The "hydrocarbon pool" mechanism is consistent with the data, but it must be kept in mind that under the experimental conditions chosen, the catalyst has a far higher activity than needed, especially at short TOS. This might explain why we get so close to a random isotope distribution. The experiments should therefore be extended to higher space velocities. Until such experiments where, if needed, the methanol is only partially converted to hydrocarbons have been carried out, one cannot know whether the near random isotopic distribution in propene is significant or not.

4. Conclusion

Only a minor part of the propene molecules may have been formed by addition of methanol to ethene since this would imply a $^{12}C/^{13}C$ ratio >1, so a consecutive build up type mechanism from ethene is not tenable over SAPO-34. The results

are, on the other hand, in accord with a "pool" type mechanism. Methane is mainly formed from MeOH/DME, and only to a minor extent by fragmentation of higher hydrocarbons. As would be expected the same applies to CO and CO_2.

Acknowledgement

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

References

[1] C.D. Chang and A.J. Silvestri, J. Catal. 47 (1977) 249.
[2] C.D. Chang, Catal. Rev.-Sci. Eng. 25 (1983) 1; 26 (1984) 323.
[3] S.W. Kaiser, Arab. J. Sci. Eng. 10 (1985) 361.
[4] S. Nawaz, S. Kolboe, S. Kvisle, K.P. Lillerud, M. Stöcker and H. Øren, Stud. Surf. Sci. Catal. 61 (1991) 421.
[5] S.M. Yang, S.I. Wang and C.S. Huang, Stud. Surf. Sci. Catal. 61 (1991) 429.
[6] C.D. Chang, Stud. Surf. Sci. Catal. 36 (1988) 127.
[7] C.D. Chang, Stud. Surf. Sci. Catal. 61 (1991) 393.
[8] G.J. Hutchings and R. Hunter, Catal. Today 6 (1990) 279.
[9] S. Kolboe, Acta Chem. Scand. A 40 (1986) 711.
[10] S. Kolboe, Stud. Surf. Sci. Catal. 36 (1988) 189.
[11] F.X. Cormerais, G. Perot, F. Chevalier and M. Guisnet, J. Chem. Research (S) (1980) 362.
[12] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gaiek, T.R. Cannan and E.M. Flanigen, US Patent 4,440,871 (1984).
[13] D.R. Stull, E.F. Westrum Jr. and G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969).