Journal of Catalysis **205,** 217–220 (2002)
doi:10.1006/jcat.2001.3376, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Assessment of the Low-Temperature Nonoxidative Activation of Methane over H-Galloaluminosilicate (MFI) Zeolite: A C-13 Labelling Investigation

Claude M. Naccache, Paul Mériaudeau, Gilbert Sapaly, Le Van Tiep, and Younès Ben Taârit[1]

Institut de Recherches sur la Catalyse, CNRS, Conventionné UCB Lyon 2, Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

Received March 26, 2001; revised July 26, 2001; accepted July 26, 2001

Careful investigation of the conversion of various mixtures of propene and methane or ethene and methane over H-galloaluminosilicate (MFI) zeolite under a variety of conditions showed that methane is not inserted into the products. The use of C-13–labelled methane confirmed the absence of methane activation under the reported conditions. © 2002 Elsevier Science

Key Words: **methane activation; isotopic labelling; Ga-MFI; aromatisation.**

INTRODUCTION

In view of the large, worldwide reserves of natural gas, there is considerable interest in activating methane to convert it into a valuable source of chemicals. During the past century, basic and applied research on topics ranging from syngas production to the more recent direct oxidation into methanol (1) or formaldehyde (2) and oxidative coupling to ethane and/or ethylene (3, 4) has been conducted. The latter routes were found to be hampered by unfavourable thermodynamics, which led to deep oxidation when conversions of practical significance were sought.

More recently, methane was successfully converted into benzene and hydrogen over bifunctional catalysts containing molybdenum carbide species and acid-type zeolites (5–7). However, this process too is limited by thermodynamics and rapid deactivation of the catalyst due to deposition of carbonaceous residues.

In principle, however, it should be possible to methanate olefins into the corresponding $n + 1$ alkane at low temperature, as dictated by the thermodynamics of the condensation reaction. Viable reaction rates are seldom obtained, even in the presence of highly acidic catalysts such as sulphated zirconia (8), because the reaction must be conducted at low temperature.

A few years ago, it was claimed that methane could be incorporated into lower olefins, over gallium-modified MFI-type zeolites, to produce aromatics in the gasoline range (9). Surprisingly, it proved necessary to run the reactions at temperatures greater than 450°C, at which methanation of the starting olefin into the corresponding alkane is, thermodynamically, barely possible. However, the dehydrocyclisation of the corresponding alkane into aromatics was claimed to drive the primary equilibrium

$$CH_4 + C_nH_{2n} \rightleftarrows C_{n+1}H_{2n+4}$$

forward.

If aromatics form ($C_{n+1}H_{2n+4} \rightarrow \text{aromatics} + H_2$) and the olefin is *n*-butene, then the free energy change may well reach negative values below −10.6 kcal/mol for benzene. To check this hypothesis, we investigated the conversion of a mixture of methane and ethylene at low and high temperatures.

EXPERIMENTAL AND METHODS

The conversion of mixtures of ethene and methane of various composition was attempted over gallium-modified H-MFI at various temperatures under conditions at which the carbon balance and/or methane consumption could be accurately measured. Because gallium-modified H-MFI, similar to that used by Choudhary *et al.* (9), is subject to deactivation, the square pulse technique was used.

^{13}C-enriched methane (99.5% atom in ^{13}C) from Eurisotop (Gif-sur-Yvette, France) was used without further treatment under the same experimental conditions. All the products were collected in a cold trap (−78°C). The gas phase analysis prior to trapping showed that the composition of the product was the same, regardless of whether natural or ^{13}C-labelled methane was used.

The products obtained with ^{13}C methane were analysed by gas chromatography/mass spectrometry (GC/MS) at

---

[1] To whom correspondence should be addressed. Fax: 33 4 72 44 53 99. E-mail: taarit@catalyse.univ-lyon1.fr.

0021-9517/02 $35.00

the Laboratoire Central d'Analyse of CNRS at Solaize Rhône, France. The mass spectrometer (VG 7070E) was equipped with a dual-focus system. The products were transferred to a 1-L metallic container kept at 60°C and were introduced into the spectrometer via a molecular leak.

The resolution of the spectrometer was adjusted to within 5000, thus enabling the separation of two very close masses of two distinct entities. For example, this resolution enabled the separation of $^{13}CH_3 = 16.027$ u from $^{12}CH_4 = 16.031$ u. In addition, the latter can be safely discriminated from $^{16}O = 15.99491$. Furthermore, the water OH fragment ($OH = 17.003$ u) can be unambiguously separated from $^{13}CH_4 = 17.035$ u.

RESULTS AND DISCUSSION

The results of the conversion of approximately 13 Torr (1.73 kPa) of ethene, both with and without 30 Torr (4.0 kPa) methane, were compared at temperatures ranging from 290 to 500°C (Table 1). These results show that ethene conversions and the product selectivities were identical within the experimental error range and that the carbon balance was always deficient, irrespective of the presence of methane.

Propane, the expected primary product of the methanation of ethene, is not susceptible to conversion at moderate temperatures; its yield was not modified and certainly did not increase in the presence of methane. At higher temperatures, the high yield of aromatics and the increased carbon deficit, in line with an increased production of heavier aromatics and coke, were noteworthy.

Table 2 shows the conversion of ethene in the presence of excess N_2 or CH_4. Here too, temperature had little effect on the reaction. The only indication of possible methane incorporation into the products is the slightly but consistently improved carbon balance in the presence of methane. However, these experiments contrasted with those of Choudhary *et al.*: in our experiments, the olefin partial pressure was very low, whereas Choudhary *et al.* showed that an increase in the olefin to methane molar ratio increased the conversion of methane (9).

Therefore, mixtures with a high olefin partial pressure were used. Mixtures of propene, methane, and nitrogen with a propene to methane ratio of 1 : 1 and a total pressure of 1 atm were reacted over the acidic gallium MFI zeolite at 502°C. The space velocity was the same as that reported by Choudhary *et al.* (9).

The results varied dramatically depending on the time taken to analyse the samples. In one set of experiments, the product stream flowed for 5 min before sampling, while in another set of experiments, the product stream flowed for 10 min before sampling.

A very large excess of carbon was found after 10 min on stream, whereas a large deficit of carbon was observed following 5 min on stream (Table 3). It is not clear whether methane carbon was inserted into the aromatics or into any of the other products. We therefore used ^{13}C methane to determine the presence or absence of the ^{13}C carbon in the aromatisation products.

The $^{12}CH_4$ to $^{13}CH_4$ ratio was found to be 14 : 86 in the evolving stream. The ^{13}C content in a given molecule was measured by comparing the areas of the M^+ ion with those of the $M^+ + 1$, the latter being the representation of one ^{13}C carbon-enriched molecule. Table 4 lists the results for C_6H_6 and C_7H_8, typical of the results obtained for all the detected products, except for methane.

These results show that there was no significant incorporation of ^{13}C into any of the reaction products and that methane is probably not incorporated into the aromatisation products, even though the mass balance may sometimes suggest that the opposite is true.

Indeed, the square pulse technique is a very fine technique when the retention time of the reagents and the products are very close.

TABLE 1

Conversion of Low-Pressure Ethene and Ethene + Methane Mixtures at Different Temperatures and WHSV = 1.06

Temperatures (°C)	$Po_{C_2H_4}$	Po_{CH_4}	$Pf_{C_2H_4}$	C_2H_4 conversion (%)		P_{CH_4}	C_2H_4 balance (Torr)	$P_{C_3H_8}$	$P_{C_3H_6}$	Aromatics selectivity (%)
				Measured	Calculated					
290	13.3	30	6.83	48.6	33.7	28.8	−1.98	0.25	1.17	17
	13.5	0	6.53	52.3	39	—	−1.80	0.22	1.13	14
350	13.8	0	5.85	57.6	53.4	—	−0.57	0.41	1.18	41.3
	13.3	30	5.87	55.9	49.7	29.5	−0.82	0.45	0.88	40.4
400	13.3	30	4.85	63.5	53.2	30.2	−1.37	0.47	0.68	69.7
	13.2	0	4.87	63.1	59	—	−0.54	0.45	0.70	68.8
450	13.3	0	3.80	71.4	56.3	—	−2.0	0.46	0.57	76.3
	13.3	30	3.91	70.6	49.6	30.2	−2.8	0.44	0.54	79.0
500	13.3	30	3.23	75.7	43.7	30	−4.3	0.18	0.34	84.3
	13.9	0	3.26	76.5	60.9	—	−2.2	0.2	0.36	85

TABLE 2

Conversion of Ethene in the Presence of Large Excess of N_2 or CH_4, at Various Temperatures

Temperature (°C)	$Po_{C_2H_4}$	P_{N_2}	P_{CH_4}	$Pf_{C_2H_4}$	C_2H_4 conversion (%)		$P_{C_3H_4}$	$P_{C_3H_6}$	Aromatic selectivity (%)	C_2H_4 balance (Torr)
					Measured	Calculated				
290	13.5	750	—	6.53	52.3	39	0.22	1.13	14	−1.87
	12.5	—	750	7.54	39.7	29.8	0.13	0.68	8.6	−1.23
350	13.8	750	—	5.85	57.6	53.4	0.41	1.18	41.3	−0.58
	12.5	—	750	6.36	49.1	46.5	0.30	1.20	35.3	−0.33
400	13.2	750	—	4.87	63.1	59	0.45	0.70	68.8	−0.54
	12.5	—	750	5.45	56.4	49	0.33	0.78	64.5	−0.93
450	13.3	750	—	3.80	71.4	56.3	0.46	0.57	76.3	−2.0
	12.5	—	750	4.67	62.6	48.4	0.35	0.64	76.4	−1.8
500	13.9	750	—	3.26	76.5	60.9	0.20	0.36	85	−2.17
	12.5	—	750	4.02	67.8	45.1	0.19	0.41	82.9	−2.8

If, as is usually the case, a number of products of various functions are formed, then their adsorption properties will be quite diverse and their retention time will probably vary considerably. This is especially the case when the catalyst is porous, as with zeolites. Therefore, true mass balance is difficult to achieve, especially because the zeolites in our reaction are subject to deactivation. This explains why the square pulse technique is used to minimize the effect of deactivation.

To achieve a more reliable mass balance, the mixture was passed through the catalyst for 2 h, and the condensable products were collected in a cold trap and weighed; the volatile products, C_1–C_4, were analysed to determine the integral carbon.

TABLE 3

Carbon Distribution in the Case of Propene + Methane or Nitrogen Mixtures at 502°C upon Sampling after Different Time on Stream

Sampling time	5 min		10 min	
Carbon mixture	$C_3(74.5) + C_1(25.5)$	$C_3(76.0) + N_2$	$C_3(74.5) + C_1(25.5)$	$C_3(74.5) + N_2$
Compound				
Methane	26.2	4.0	25.7	3.9
Ethane	2.9	4.3	3.2	3.5
Ethene	1.1	1.0	1.1	1.1
Propane	7.4	6.9	6.7	7.4
Propene	0.9	1.0	1.0	0.8
Isobutane	0.3	0.2	0.2	0.2
n-Butane	0.5	0.4	0.5	0.4
Benzene	11.6	11.5	15.5	17.0
Toluene	20.1	20.0	32.5	44.0
C_8	8.8	9.0	20.8	31.3
C_9–C_{12}	12.6	12.7	62.1	73.1
ΣC	92.4	71.0	169.3	182.7
C balance	−7.6	−5.0	+69.3	+108.2
C balance (%)	−7.6	−6.7	+69	+145

After such a long run, the product's carbon content matched that of the converted propene with a small deficit of less than 0.5%. Therefore, methane carbon should not be found in the reaction products, in agreement with the lack of any observable ^{13}C-enrichment, as ascertained by GC/MS.

As mentioned above, the methanation of olefins at these elevated temperatures is not allowed by thermodynamics. In order to account for methane insertion, Choudhary *et al.* (9) suggested the formation of $^+CH_3$ carbenium ions by hydride transfer from CH_4 to a higher carbenium ion. This does not follow the law of thermodynamics, particularly in the case of the secondary propenium ion stabilized by two methyl electron donating groups,

$$CH_4 + (CH_3\text{–}CH\text{–}CH_3)^+ \rightarrow CH_3\text{–}CH_2CH_3 + CH_3^+,$$

and may not occur whatever the catalyst, be it gallium an oxygen. This is especially true for higher carbenium ions. Even the least stable ethenium ion CH_3–CH_2^+, is not amenable to hydride transfer from CH_4. Therefore, our findings are supported by plain chemistry and thermodynamics: methane carbon cannot be inserted into olefin aromatisation products under the reported conditions.

TABLE 4

^{13}C Content of Natural and Reaction Products Benzene and Toluene

Aromatic	C_6H_6	C_7H_8
M^+ peak area	660851	929330
$M + 1^+$ peak area from the $^{13}CH_4$ run	59440	43993
Expected for the natural compound	62823	48308

ACKNOWLEDGMENT

The authors are indebted to Dr Jean-Louis Gass for the GC/MS experiment.

REFERENCES

1. Koenig, G., D.O.S. 3 101 024 (1982).
2. Otsuka, K., and Hatano, M., *J. Catal*. **108**, 252 (1987).
3. Keller, G. E., and Bhasin, M. M., *J. Catal*. **73**, 9 (1982).
4. Ito, T., and Lunsford, J. H., *Nature* **314**, 9 (1982).
5. Wang, D., Rosynek, M., and Lunsford, J. H., *Topics Catal.* **3**, 289 (1996).
6. Wang, L., Tao, L., Xie, M., and Xu, Y., *Catal. Lett*. **21**, 35 (1993).
7. Meriaudeau, P., Tu Ha, V. T., and Van Tiep, L., *Catal. Lett*. **64**, 49 (2000).
8. Scurrell, M. S., *Appl. Catal*. **34**, 109 (1987).
9. Choudhary, V. R., Kinage, A. K., and Choudhary, T. V., *Science* **275**, 1286 (1997).