Catalysis Letters 2 (1989) 249-256

THE IMPORTANCE OF HETEROGENEOUS AND HOMOGENEOUS REACTIONS IN OXIDATIVE COUPLING OF METHANE OVER CHLORIDE PROMOTED OXIDE CATALYSTS

R. BURCH *, E.M. CRABB, G.D. SQUIRE and S.C. TSANG

Catalysis Research Group, Chemistry Department, University of Reading Whiteknights, P.O. Box 224, Reading RG6 2AD, U.K.

Received 19 January 1989; accepted 6 March 1989

The formation of ethene from ethane and methane in a silica reactor has been studied both in the presence and in the absence of chloride-containing catalysts. Some homogeneous conversion of ethane to ethene occurs in the gas phase through direct dehydrogenation, oxidative dehydrogenation, and, when HCl is present, chlorine radical induced reactions. Methyl chloride is detected in the gas phase but has no influence on the conversion of ethane to ethene. It is shown that under typical catalytic conditions, when a chloride-modified catalyst is used, ethane is mostly produced in the catalyst bed.

1. Introduction

Oxidative coupling of methane is emerging as one of the most promising forms of hydrocarbon oxidation, with the real potential of becoming an important industrial process [1]. Many metal oxides [2], alkali-promoted metal oxides [3,4] and mixed metal oxides [5] are claimed to be effective catalysts for converting methane to higher hydrocarbons, principly ethane and ethene. Most effort has been concentrated on optimizing the *total* C_2 selectivity even though ethene is more valuable than ethane. It has been reported, however, that the highest selectivity to ethene is achieved when chloride ions are present in the oxide catalyst [6–9], or if a chlorine-containing compound is introduced into the gas stream during the reaction [10,11].

The mechanism of ethene formation is unknown. However, it has been reported [7] that CH_3Cl is released into the gas phase from chloride-promoted catalysts. This CH_3Cl is believed [7] to catalyse the homogeneous reaction for the formation of ethene from ethane. It is important to establish whether the enhancement of ethene formation in the presence of chlorine is due to homogeneous gas phase reactions or to surface-catalysed reactions. This question is addressed in the present work.

---

* To whom all correspondence should be addressed.

© J.C. Baltzer A.G. Scientific Publishing Company

2. Experimental

The experiments were performed by cofeeding reactive gases into a 5 mm I.D, 26 cm long silica tube reactor. Although most of the current work was done using an empty reactor, for comparison a LiCl/MnO_2 catalyst was prepared as before [10] and tested. (For simplicity the catalyst is referred to as LiCl/MnO_2 even though the oxygen content is not known precisely.), The gases used were: CH_4 (B.O.C. > 99.99%); C_2H_6 (B.O.C. > 99%); C_2H_6 in CH_4 (B.O.C. 5%C_2H_6/95%CH_4); N_2 (B.O.C. > 99%); O_2 in N_2 (B.O.C. 5%O_2/95%N_2); CH_3Cl (B.D.H. > 99.8%); HCl (B.D.H. > 99%). The reaction products were sampled using a gas sampling valve and analysed by gas chromatography (Perkin Elmer Sigma 3 FID, fitted with a 4 m Poropak N column operating at 65 ° C). Analysis of CO and CO_2 was made possible by incorporating a catalytic methanator into the gas chromatograph just before the detector. A quadrupole mass spectrometer (Spectramass Dataquad) was used to analyze the chlorine-containing products.

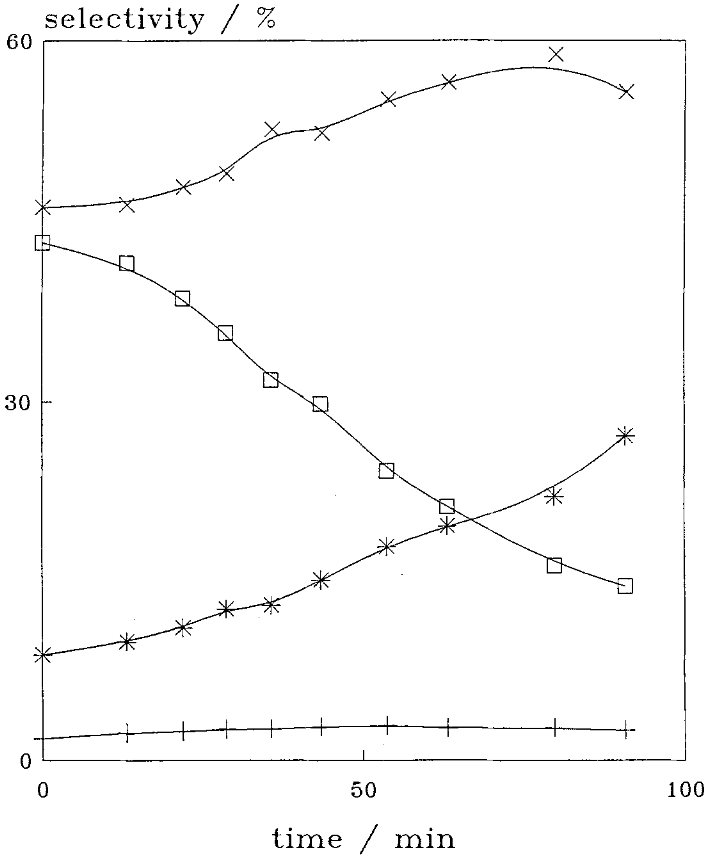

Fig. 1. Selectivity to C_2H_6 (×), C_2H_4 (□), CO (+), and CO_2 (*) as a function of time for the conversion of CH_4 over a LiCl/MnO_2 catalyst.

It is well known [12] that gas phase reactions between CH_4 and O_2 are important under certain experimental conditions (e.g. low CH_4/O_2 ratio, low dilution factor, high residence time and high temperatures). In order to minimise gas phase reactions in our work the CH_4 and O_2 were diluted with N_2 and the CH_4/O_2 ratio was adjusted to 20:1 (50% CH_4/47.5% N_2/2.5% O_2, total gas flow was 60 cm^3 min^{-1}). It was found that under these conditions there was less than 0.1% conversion of the CH_4 in an empty reactor even at 800 ° C.

3. Results and discussion

The $LiCl/MnO_2$ catalyst was tested under our experimental conditions. It was found that promotion of MnO_2 by LiCl at 750 ° C produced a very active catalyst with a C_2 selectivity of 88.3% (C_2H_4 was 43.2%). However, this activity was not maintained and the catalyst deactivated during the first 2 h on stream as shown in fig. 1. Note that the C_2H_4/C_2H_6 ratio decreased as the catalyst became

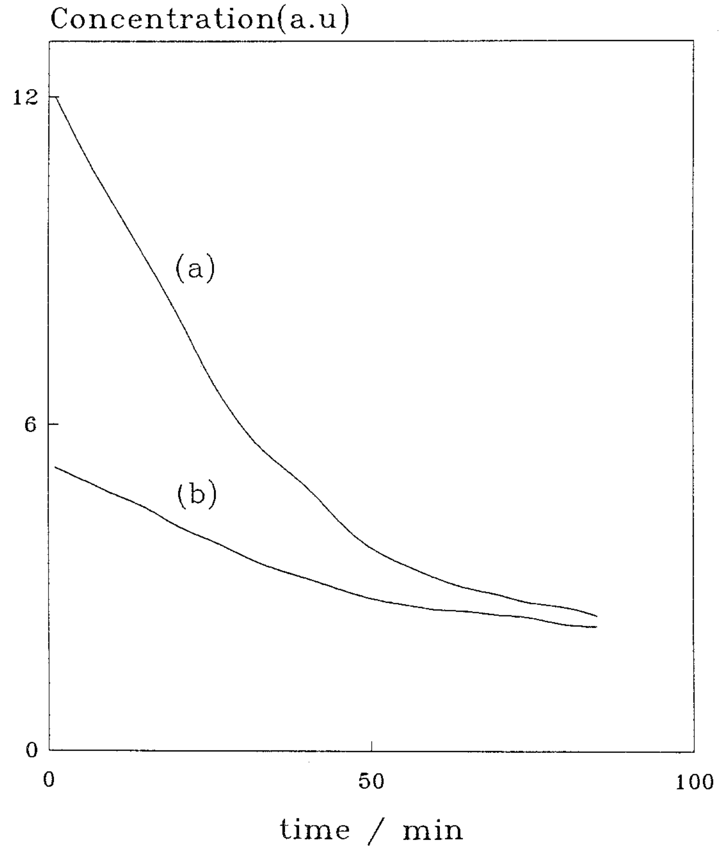

Fig. 2. Evolution of CH_3Cl and HCl as a function of time from a $LiCl/MnO_2$ catalyst during the reaction of CH_4 at 750 ° C. (a) CH_3Cl; (b) HCl.

deactivated. Chlorinated compounds, mainly CH_3Cl and HCl, were detected in the product gases. The amount of CH_3Cl and HCl detected decreased in line with the decrease in the C_2H_4/C_2H_6 ratio, as shown in fig. 2.

These observations are in agreement with the findings of Otsuka et al. [7], who have interpreted their results in terms of the following homogeneous reactions:

$$4\,CH_4 + O_2 \xrightarrow{Li/MnO_2} 2\,C_2H_6 + 2\,H_2O$$

$$\tfrac{1}{2}O_2 + LiCl + CH_4 \rightarrow CH_3Cl + LiOH$$

$$CH_3Cl \rightarrow CH_3\cdot + Cl\cdot$$

$$C_2H_6 + Cl\cdot \rightarrow C_2H_5\cdot + HCl$$

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot$$

$$HCl + H\cdot \rightarrow H_2 + Cl\cdot$$

$$HCl + CH_3\cdot \rightarrow CH_4 + Cl\cdot$$

According to this mechanism chlorine radicals formed from CH_3Cl are responsible for the dehydrogenation of C_2H_6. However, under our experimental conditions the concentration of CH_3Cl was found to be less than 100 ppm and it seemed unlikely that such a small amount of CH_3Cl could account for the high rate of formation of C_2H_4 observed in our experiments. In the course of investigating the role of CH_3Cl in the formation of C_2H_4 we observed that other gas phase reactions may also be of importance. These experiments are now described.

3.1. GAS PHASE REACTIONS IN THE FORMATION OF ETHENE FROM ETHANE ADDITION OF CH_3Cl

Table 1 summarises the results obtained when various gases were passed through the empty silica reactor at reaction temperatures. The results show that pure C_2H_6 can be dehydrogenated to C_2H_4 even at these relatively low temperatures in a silica reactor. (Thermal cracking of C_2H_6 is normally performed in a steel reactor at much higher temperatures.) Thus, at 750 °C about 12% of the C_2H_6 is converted into C_2H_4 with a selectivity of over 97%.

When the C_2H_6 is mixed with a N_2/O_2 stream the selectivity to C_2H_4 is somewhat lower but the activity is much higher. It is apparent that in the presence of a small amount of O_2, such as would be present in the post-catalyst gas volume in a typical methane activation experiment, there can be a substantial homogeneous conversion of C_2H_6 to C_2H_4. These results are consistent with those reported by van Kasteren et al. [13].

The most significant observation in table 1 is that the addition of CH_3Cl has no effect on the formation of C_2H_4 from C_2H_6. CH_3Cl is *not* responsible for the high selectivity to C_2H_4 observed over chloride-containing catalysts. In this

Table 1
Non-catalytic dehydrogenation of ethane in an empty silica reactor.

Gas mixture	$T/°C$	$C/\%$ [a]	Selectivity/% [b]					
			C_2H_4	CO	CO_2	C_1	C_3	C_4
100% C_2H_6	700	2.03	99.1	0	0	0.9	0	0
	750	12.3	97.7	0	0	1.5	0.8	0
	800	36.7	95.6	0	0	2.8	1.6	0
50% C_2H_6/	700	19.2	81.9	4.5	0	4.8	3.7	5.1
47.5% N_2/	750	30.3	89.2	3.4	0	4.3	3.0	0
2.5% O_2	800	53.5	90.8	2.3	0	4.9	2.0	0
100% C_2H_6	700	2.28	98.2	0	0	1.8	0	0
+CH_3Cl [c]	750	12.2	96.2	0	0	2.3	1.4	0
	800	36.9	94.3	0	0	3.7	2.0	0

[a] percentage conversion of C_2H_6.
[b] selectivity is defined as: ((C_2H_6 converted to product i)/(C_2H_6 converted to all products))×100
C_1, C_3 and C_4, refer, respectively, to products containing 1, 3 or 4 C atoms.
[c] flow rate of CH_3Cl was 5 cm^3 min^{-1}.

respect, therefore, our results differ from those by Otsuka et al. [14] who reported that CH_3Cl catalysed the dehydrogenation of C_2H_6 at all temperatures above 650°C. If there is some residual O_2 in the post-catalyst gas stream then there may be a significant amount of C_2H_4 formed from C_2H_6 through homogeneous reactions involving O_2 but *not involving* CH_3Cl.

The post-catalyst gas mixture in our experiments with the $LiCl/MnO_2$ catalyst referred to above, will contain only a small amount of C_2H_6 (about 5%) in excess

Table 2
Non-catalytic dehydrogenation of ethane in the presence of methane in an empty silica reactor.

Gas mixture	$T/°C$	yield/% [a]
95% CH_4/5% C_2H_6	700	1.55
	750	6.70
	800	21.7
95% CH_4/5% C_2H_6+CH_3Cl	700	1.09
	750	5.17
	800	20.4
47.5% CH_4/47.5% N_2/	700	14.2
2.5% O_2/2.5% C_2H_6	750	26.6
	800	41.8
47.5% CH_4/47.5% N_2/	700	12.5
2.5% O_2/2.5% C_2H_6	750	24.3
+CH_3Cl	800	42.3

[a] yield of C_2H_4, defined as (% conversion of ethane×% selectivity)/100.

CH_4. Therefore, in order to further explore the role of homogeneous reactions in the formation of C_2H_4 we have prepared gas mixtures having a large CH_4/C_2H_6 ratio. When these were passed through the empty silica reactor the results shown in table 2 were obtained. (Experiments using pure CH_4 show virtually no reaction under these conditions.)

The results confirm those described in table 1. Addition of a small amount of O_2 increases the yield of C_2H_4 significantly. However, the addition of CH_3Cl has no effect on the yield of C_2H_4 either in the absence or presence of O_2. The conclusion is clear. Under our conditions, gas phase CH_3Cl is not responsible for the high selectivity to C_2H_4 over chloride-containing catalysts.

From the gas kinetic data reported by Karra and Senkan [15] it is apparent that the rate of decomposition of CH_3Cl into $CH_3\cdot$ and $Cl\cdot$ radicals is very slow so it is perhaps not surprising that CH_3Cl is observed to have so little effect on the ethane dehydrogenation reaction. Equally, however, the same kinetic data show that HCl decomposes very readily to produce $Cl\cdot$ radicals. Since HCl is produced over chloride-containing catalysts (see fig. 2) this may be is responsible for the high selectivity to C_2H_4.

3.2. ADDITION OF HCl

Table 3 shows the effect of adding different amounts of HCl to various gas mixtures. It is apparent both in the absence and in the presence of O_2 that when HCl is added the yield of C_2H_4 is greatly enhanced. Indeed when HCl is added at the level of about 1.5% the yield of C_2H_4 is high enough to account for all the C_2H_4 formed in the catalysed reactions referred to above. However, the amount of HCl present in the post-catalyst gas volume was typically < 50 ppm, so although these experiments demonstrate that HCl may have an effect (whereas CH_3Cl clearly does not) they do not confirm that HCl is important under our catalytic conditions.

Table 3
Influence of HCl on the non-catalytic dehydrogenation of ethane.

Gas mixture	HCl flow/$cm^3\ min^{-1}$	yield/% [a]
95% CH_4/5% C_2H_6	0.0	7.58
	0.01	8.58
	0.10	13.8
	1.00	40.4
47.5% CH_4/47.5% N_2/ 2.5% O_2/2.5% C_2H_6	0.0	28.8
	0.01	41.9
	0.10	57.9
	1.00	85.7

[a] yield of C_2H_4, defined as (% conversion of ethane × % selectivity)/100.

Table 4
Influence of post-catalyst volume on ethene selectivity [a]

Catalyst bed position in furnace	C/% [c]	Selectivity/% [b]	
		C_2H_4	C_2H_6
middle	9.36	42.8	47.2
bottom	8.87	38.1	50.5

[a] $LiCl/MnO_2$ catalyst at 750 °C in a 50% CH_4/47.5% N_2/2.5% O_2 mixture.
[b] selectivity is defined as: ((CH_4 converted to product i)/(CH_4 converted to all products))×100.
[c] percentage conversion of CH_4.

3.3. INFLUENCE OF POST-CATALYST VOLUME ON THE SELECTIVITY TO C_2H_4

Under our experimental conditions only a very small amount of O_2 and < 50 ppm of HCl are present in the gas mixture exiting from the bottom of the catalyst bed. From the results presented above we believe that it is very unlikely that the high selectivity to C_2H_4 could be due to post-catalyst homogeneous reactions. However, in order to check out this possibility we have performed some experiments in which we have varied the post-catalyst volume.

Table 4 shows the effect of moving the furnace so that the catalyst bed is either close to the middle, or the bottom of the hot zone. The selectivity to C_2H_4 when the catalyst bed is at the bottom of the furnace corresponds to a situation where the post-catalyst volume at the reaction temperature is very small. Comparison with the C_2H_4 selectivity when the catalyst bed is in the normal middle position shows that only a small amount of the C_2H_4 is produced through gas phase reactions. We believe that the main reason for the enhanced selectivity to C_2H_4 over chloride-containing catalysts is because the chloride modifies the surface of the oxide and either eliminates total oxidation sites [10] and/or creates new types of dehydrogenation site. Sokolovskii et al. [8] have similarly concluded that surface reactions are more important than gas phase reactions in the synthesis of C_2H_4 over their $CaO/CaCl_2$ catalysts.

4. Conclusions

Ethene selectivity enhancement over chloride-containing catalysts, under typical methane-coupling conditions, is mainly due to reactions occurring in the catalyst bed. Gas phase dehydrogenation of ethane may be significant, particularly when there is some residual oxygen in the post-catalyst gas mixture, but methyl chloride has no effect on the conversion of ethane to ethene. HCl can increase the rate of conversion of ethane into ethene in the gas phase. However, this is only an important factor when there is a large partial pressure of HCl. Whether the dehydrogenation of ethane to ethene in the catalyst bed is due purely to a surface catalysed heterogeneous reaction or partly attributable to a homogeneous gas phase reaction occurring just above the catalyst surface is not yet known.

Acknowledgements

We are grateful to British Gas plc for providing financial support for GDS & SCT and to British Gas plc and SERC for funding the equipment used in this research. We are pleased to acknowledge that SCT is in receipt of a S.L. Pao Scholarship from Hong Kong and an ORS award.

References

[1] N.D. Parkyns, Potential of natural gas as a source of future chemicals, in: *Symposium on Energy Production Processes*, April 1988 (Institution of Chemical Engineers, London) p. 35.
[2] G.E. Keller and M.M. Bhasin, J. Catal. 73 (1982) 9.
[3] T. Ito, Ji-X Wang, C-H Lin and J.H. Lunsford, J. Amer. Chem. Soc. 107 (1985) 5062.
[4] R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 43 (1988) 105.
[5] H. Imai and T. Tagawa, J. Chem. Soc., Chem. Commun. (1986) 52.
[6] K. Otsuka, Q. Liu, M. Hatano and A. Morikawa, Chem. Lett. (1986) 903.
[7] K. Otsuka, Sekiyu Giakkaishi 30 (1987) 385.
[8] A.N. Shigapov, M.A. Novozhilova, S.N. Vereshchagin, A.G. Anshits and V.D. Sokolovskii, React. Kinet. Catal. Lett. 37 (1988) 397.
[9] W. Ueda and J.M. Thomas, J. Chem. Soc., Chem. Commun. (1988) 1148.
[10] R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 46 (1989) 69.
[11] H.P. Withers, C.A. Jones, J.J. Leonard and J.A. Sofranko, U.S. Patent, 6, 634, 800 (1987).
[12] G.S. Lane and E.E. Wolf, J. Catal. 113 (1988) 144.
[13] H.M.N. Van Kasteren, J.W.M.H. Geerts and K.V.D. Wiele, preprint in 9th Int. Catalysis Congress, Calgary, 1988.
[14] K. Otsuka, M. Hatano and T. Komatsu, Methane Conversion Symposium, New Zealand, 1987.
[15] S.B. Karra and S.M. Senkan, Ind. Eng. Chem. Res. 27 (1988) 1163.