Catalysis Letters 3 (1989) 331–338

THE SYNTHESIS OF ETHENE DURING THE OXIDATIVE COUPLING OF METHANE *

R. BURCH *,[1], A.A. DOST [1], D.A. RICE [1], S.C. TSANG [1] and G. WEBB [2]

[1] *Catalysis Research Group, Chemistry Department, University of Reading, Whiteknights, PO Box 224, Reading, RG6 2AD, U.K.*
[2] *Chemistry Department, University of Glasgow, Glasgow, G12 8QQ, U.K.*

Received 7 June 1989; revised 11 August 1989

The effect of residence time on the selectivity of a MgO catalyst for the formation of ethene in the methane coupling reaction has been studied. It is found that the variation in ethene selectivity with this time follows opposite trends depending on the experimental conditions. In both cases the results show a positive intercept at zero residence time which may indicate that ethene is a primary product. However, calculations show that gas phase radical reactions just above the catalyst surface could account for the ethene observed even at very short residence times. It is concluded that experiments such as these cannot reliably distinguish between primary and secondary product formation. A SmOCl catalyst was studied and it was found that HCl was released when wet gases were passed over the catalyst at relatively low temperatures. It is concluded that much of the ethene produced over oxychloride catalysts may be produced by gas phase reactions involving chlorine radicals.

1. Introduction

Partial oxidation of methane to produce higher hydrocarbons is one of the most attractive ways of utilising natural gas as a chemical resource. Oxidative coupling of methane to ethane and ethene is currently the subject of considerable research interest [1,2]. Ethene is a more valuable product than ethane so it is desirable to optimise the selectivity for the formation of the unsaturated product. There is as yet no clear agreement as to the mechanism of ethene production. Indeed, many factors affect the selectivity of oxidative coupling catalysts. For example, ethene is favoured at higher temperatures, at high O_2/CH_4 ratios, and at long residence times. The latter effect is indicative that ethene may be produced in a secondary reaction from ethane. However, it has been claimed that ethene is a primary product of the methane coupling reaction [3,4]. Also, it has been reported that chloride-promoted catalysts [5,6] and oxychloride catalysts [7,8] produce large amounts of ethene. Furthermore, there are conflicting claims

---

* Based in part on a paper given at the Royal Society-U.S.S.R. Academy Workshop on Catalysis and Surfaces, Oxford, April 8–10, 1989.

as to the relative importance of surface catalysed versus homogeneous gas phase reactions. This is especially so in the case of chloride-containing catalysts where the role of gas phase chlorine-containing promoters further complicates the overall picture. The purpose of the present work was to investigate the production of ethene under methane coupling conditions.

2. Experimental

The MgO catalyst (B.D.H. Chemicals, Laboratory Reagent) was calcined at 750 ° C for 17 h before use. The SmOCl catalyst was prepared using the method of Wendlandt [9]. The existence of the SmOCl phase has been confirmed by XRD. The catalysts were tested by cofeeding the reaction gases (CH_4, B.O.C. $> 99.99\%$; air, B.O.C. $> 99.99\%$) into a 5 mm I.D., 26 cm long quartz tube reactor. The reaction mixture for the MgO experiments had a CH_4/O_2 ratio of 3.5 : 1 and for the SmOCl experiments the ratio was 5 : 1. The temperature for the MgO experiment was fixed at 710 ° C. In the case of the SmOCl the temperature was programmed from room temperature to 850 ° C at 10 ° C/minute. The reaction products in the MgO experiments were sampled using a gas sampling valve, separated using a 4 m Poropak N column operating at 65 ° C, and analysed using FID detector fitted with a catalytic methanator in a Perkin Elmer Sigma 3 gas chromatograph. The peak areas were determined using an LDC CI10B electronic integrator. For the SmOCl experiments the evolved gases were analysed using a Spectramass Dataquad quadrupole mass spectrometer.

The activity (A) is defined as percentage conversion of CH_4 into all products.

The selectivity for the formation of product i is defined as: $S_i = ((\text{mol } CH_4 \text{ converted to } i)/(\text{mol } CH_4 \text{ converted to all products})) \times 100\%$.

3. Results

3.1. EFFECT OF RESIDENCE TIME ON ETHENE SELECTIVITY

It is normally convenient to explore the formation of primary products over a catalyst by investigating the change in the selectivity as a function of residence time. Extrapolation back to zero residence time should give an indication of which products are formed in a primary reaction and which are formed by secondary reactions. For example, if the concentration of a specific product extrapolates to zero at zero residence time it is valid to assume that it is not a primary product.

Figure 1 shows how the selectivity for the formation of ethene, ethane and total C_2 products varies with residence time under two different sets of experimental conditions. For the results shown in fig. 1(a) the experiments were

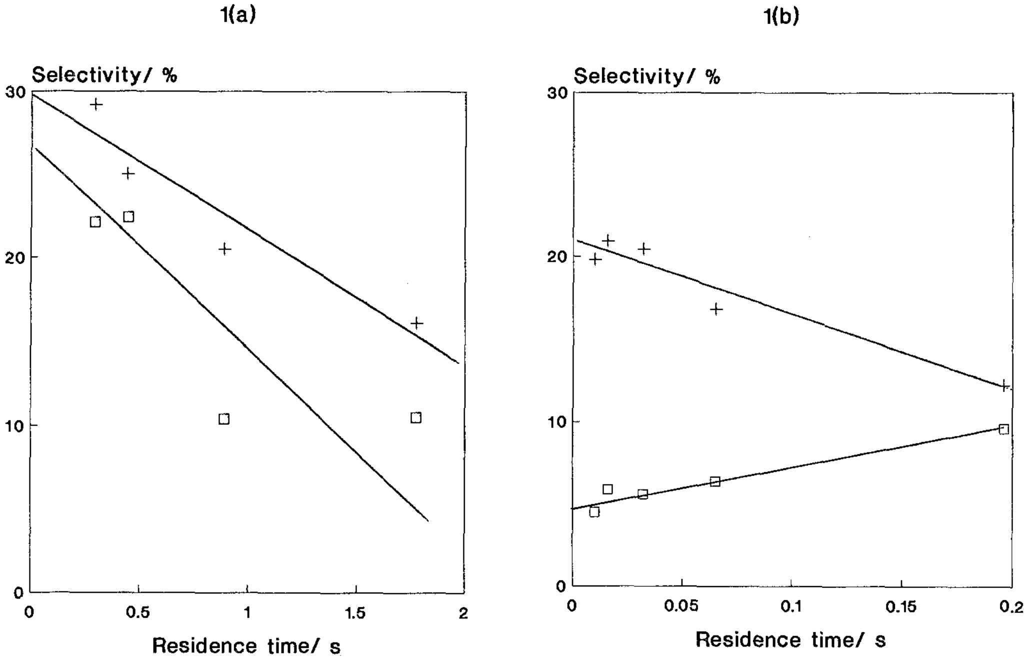

Fig. 1. Ethane (+) and ethene (□) selectivity as a function of residence time during methane coupling over a MgO catalyst at 710 ° C. (a) low residual oxygen partial pressure; (b) high residual oxygen partial pressure.

performed under conditions of long residence time where essentially all the oxygen is consumed, as shown by the data given in table 1. The results shown in fig. 1(b) were obtained under conditions of short residence time where there was a significant amount of residual oxygen (see table 1).

Table 1
Methane and oxygen conversions and product selectivities as a function of residence time [a]

t/s [b]	C_{CH_4}/% [c]	C_{O_2}/% [d]	S_{CO}/% [e]	S_{CO_2}/% [f]	$S_{C_2H_4}$/% [g]	$S_{C_2H_6}$/% [h]
0.01	3.64	13.4	42.5	33.2	4.5	19.8
0.016	5.26	14.2	39.7	33.5	5.9	20.9
0.032	7.12	27.8	38.7	35.3	5.6	20.4
0.065	11.2	35.1	34.5	42.4	6.4	16.8
0.196	20.0	71.5	21.3	56.8	9.6	12.2
0.295	19.2	92.0	18.4	30.3	22.1	29.2
0.446	21.9	98.2	19.4	33.2	22.4	25.0
0.889	19.3	98.0	28.5	40.6	10.4	20.5
1.775	19.5	97.5	25.5	47.9	10.5	16.1

[a] temperature = 710 ° C; $CH_4/O_2 = 3.5:1$; MgO catalyst
[b] residence time
[c] methane conversion
[d] oxygen conversion
[e] selectivity to CO
[f] selectivity to CO_2
[g] selectivity to C_2H_4
[h] selectivity to C_2H_6

Figure 1(a) shows that at small residence times both the selectivity to ethane and to ethene increases. This trend is similar to that reported by Hutchings et al. [3] for experiments performed using similar conditions. These results would appear to support the claim [4] that ethene is a primary product with about 25% of a total of 60% of the C_2 products being ethene produced as a primary product. However, examination of fig. 1(b) shows that the trend in ethene selectivity with residence time is reversed when the experiments are carried out under conditions where the oxygen is not all consumed and where the residence time is short. Clearly, the same catalyst can produce quite different observed trends in ethene selectivity with residence time depending on the exact experimental conditions chosen. Presumably, however, in the experiments where there is unreacted oxygen present some of the ethene formed in the catalyst bed may react further in the post-catalyst gas volume to give total combustion products. Ethene is known to react rapidly with oxygen under coupling conditions so it is conceivable that the intercept at zero residence time in fig. 1(b) underestimates the amount of ethene produced.

The important point to emerge from these experiments is that irrespective of whether the methane coupling reaction is performed under conditions where the oxygen is fully consumed or not there is apparently a significant amount of ethene produced at very short residence times. The critical question is whether

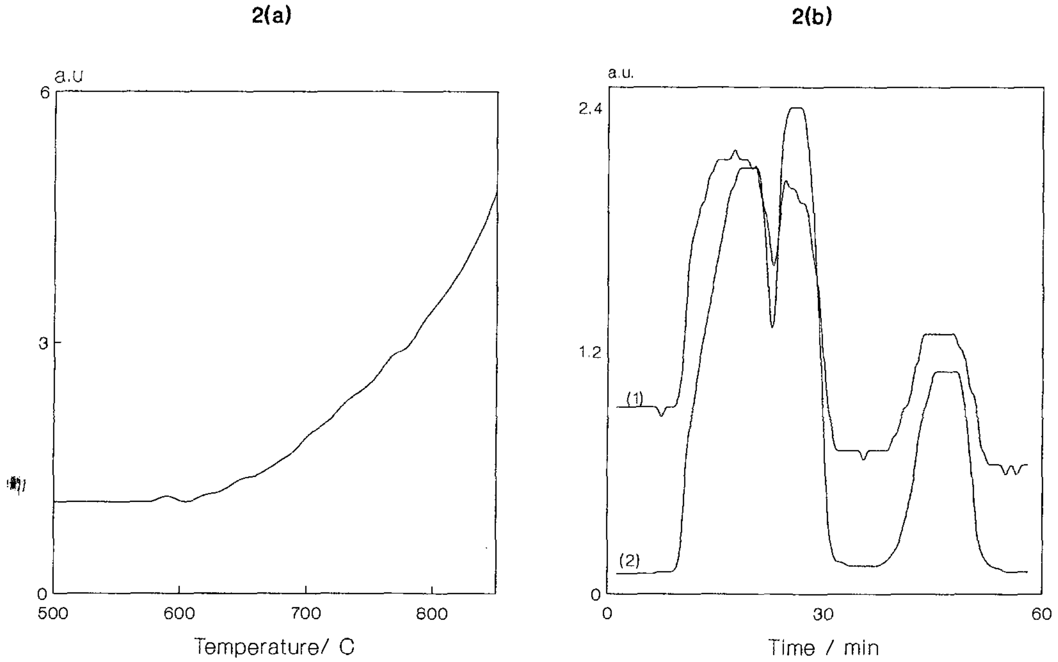

Fig. 2. (a) Evolution of HCl as a function of temperature from a SmOCl catalyst heated in wet CH_4. (b) Influence of H_2O on the release of HCl from a SmOCl catalyst heated in He at 590 °C. (1) HCl; (2) H_2O.

this can be taken as proof that ethene is a primary product in the methane coupling reaction as will be discussed later.

3.2. EFFECT OF HCl ON ETHENE PRODUCTION OVER OXYCHLORIDE CATALYSTS

It is known [10] that HCl, particularly in the presence of oxygen. is effective in the formation of ethene from ethane. It is also known that some oxychlorides [8] are very effective in producing ethene. Many oxychlorides e.g SmOCl are stable even at high temperatures in dry air. However, since water is a byproduct of the methane coupling reaction, it is relevant to investigate the extent to which HCl is released from the surface of oxychloride catalysts under methane coupling conditions. As an example, figure 2(a) shows the effect of heating SmOCl in a stream of wet methane. It is seen that at a temperature of about 600 °C HCl is released from the catalyst and that the rate of evolution of HCl increases rapidly as we approach the temperatures typical of those used in methane coupling experiments. Figure 2(b) shows that there is a direct correlation between the water vapour pressure and the release of HCl when helium containing different partial pressures of water are passed over a fresh sample of SmOCl at 590 °C.

4. Discussion

Ethene can be produced by purely gas phase reactions, such as thermal cracking or oxidative dehydrogenation. These reactions are relatively unimportant at lower temperatures and at short residence times so they do not make a significant contribute to the production of ethene under our conditions.

4.1. PRODUCTION OF ETHENE AT VERY SHORT RESIDENCE TIMES OVER MgO CATALYSTS

The results shown in fig. 1, and those previously reported by Hutchings and co-workers [3] appear to indicate that ethene is a primary product in the methane coupling reaction over a MgO catalyst. However, this interpretation of the results ignores the possible role of gas phase radical reactions of the following type:

$$CH_3. + C_2H_6 = CH_4 + C_2H_5. \tag{1}$$

$$H. + C_2H_6 = H_2 + C_2H_5. \tag{2}$$

$$OH. + C_2H_6 = H_2O + C_2H_5. \tag{3}$$

$$C_2H_5. + O_2 = C_2H_4 + .O_2H \tag{4}$$

$$C_2H_5. = C_2H_4 + H. \tag{5}$$

The rate constants for these reactions are very large [11]. For example, a value of 7.3×10^6 dm^3 mol^{-1} s^{-1} is calculated for reaction (1) at 710 °C. Taking a value for the [CH_3.] of 1×10^{-6} dm^{-3}, from the work of Lunsford and co-workers [12], and a typical value of [C_2H_6] from our experiments of 2.4×10^{-4} mol dm^{-3} we calculate the rate of formation of ethene to be about 1.8×10^{-3} mol dm^{-3} s^{-1}. This may be compared with an estimated rate of formation of ethane over our catalysts of 6×10^{-3} mol dm^{-3} s^{-1}. Although these calculations should not be taken too literally, they demonstrate that the formation of ethene by reaction of methyl radicals with ethane molecules is a reasonable possibility, especially since the total concentration of methyl radicals and ethane molecules just above the catalyst surface will be much higher than the average values used in the above calculations.

Furthermore, other radical reactions, e.g., involving hydrogen or oxygen, have rate constants about three orders of magnitude larger than for the methyl radical reaction described above. These may also contribute to the formation of ethene from ethane in the gas space just above the catalyst surface. What we conclude from this is that radical reactions close to the catalyst surface are so rapid that it is not possible to draw any clear conclusions about the nature of the primary products in methane coupling simply by taking the concentration of products at zero residence time.

4.2. PRODUCTION OF ETHENE OVER OXYCHLORIDE CATALYSTS

For pure oxide catalysts we believe that at very short residence times much of the ethene may be produced by radical reactions close to the catalyst surface. When using chloride-containing catalysts a further complication is introduced by virtue of the fact that HCl is released into the gas phase (see fig. 2). We have shown elsewhere [10] that HCl in the gas phase in the post-catalyst volume has only a marginal effect on the formation of ethene from ethane. However, this does not exclude the possibility of HCl-promoted reactions occurring in the catalyst bed. Thus, the following reaction:

$$CH_3. + HCl = CH_4 + Cl. \tag{6}$$

can occur above the catalyst surface. Similar calculations to those shown above (not repeated here) indicate that even with HCl concentrations as low as 50 ppm the rate of formation of ethene by the reaction of Cl. and C_2H_6 is fast enough to account for much of the ethene formed from ethane over chloride-containing catalysts [13]. For oxychloride catalysts, such as SmOCl, which release much larger amounts of HCl, it is expected that initially the ethene/ethane ratio may greatly exceed unity, as has been reported for bismuth oxychlorides [7,8,14].

In conclusion, we suggest that even at very short residence times ethene production may involve radical reactions triggered by methyl radicals released from the catalyst surface or by other radicals in the gas phase just above the catalyst surface. Consequently, it is dangerous to assume that residence time experiments can differentiate between primary and secondary products in the methane coupling reaction. In the case of chloride-containing catalysts, HCl may react with methyl radicals to produce Cl radicals which can very efficiently convert ethane into ethene.

Acknowledgements

We are grateful to British Gas and SERC for supporting this research and to SERC for providing financial support for A.A.D. We are pleased to acknowledge that S.C.T. is in receipt of an S.L. Pao Scholarship from Hong Kong and an O.R.S. award.

References

[1] M.S. Scurrell, Appl. Catal. 32 (1987) 1.
[2] J.S. Lee and S.T. Oyama, Catal. Rev. Sci. Eng. 30 (1988) 249.
[3] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, J. Chem. Soc., Chem. Commun. (1987) 1862.
[4] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, Catal. Today 4 (1989) 371.
[5] K. Otsuka, Q. Liu, M. Hatano and H. Morikawa, Chem. Lett. (1986) 903.
[6] R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 46 (1989) 69.
[7] W. Ueda and J.M. Thomas, J. Chem. Soc., Chem. Commun. (1988) 1148.
[8] J.M. Thomas, W. Ueda, J. Williams and K.D.M. Harris, preprint Faraday Discussion, Chem. Soc. 87 (1989) paper 87/3.
[9] W.W. Wendlandt, J. Inorg. Nucl. Chem. 9 (1959) 136.
[10] R. Burch, E.M. Crabb, G.D. Squire and S.C. Tsang, Catal. Lett. 2 (1989) 249.
[11] S.B. Karra and S.M. Senkan, Ind. Eng. Chem. Res. 27 (1988) 1163.
[12] K.D. Campbell, E. Morales and J.H. Lunsford, J. Amer. Chem. Soc. 109 (1987) 7900.
[13] R. Burch, G.D. Squire and S.C. Tsang, Catal. Today, submitted.
[14] J. Williams, R.H. Jones, J.M. Thomas and J. Kent, Catal. Lett. 3 (1989) 247.