The Role of Gas Phase Reaction in the Selective Oxidation of Methane

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Partial oxidation of methane at 585 kPa and high temperature gives similar product yields in the presence and absence of catalysts indicating that the requirement for a suitable catalytic material is of secondary importance.

The selective oxidation of methane to useful hydrocarbon and oxygenated products continues to be extensively studied since Bhasin[1] demonstrated that a range of transition metal oxides, *e.g.* MnO, were selective for the formation of C_2H_4 and C_2H_6 *via* oxidative coupling. Since then a considerable number of studies have identifed several alternative oxide systems for this reaction and very high C_2 selectivities have been observed with catalysts based on MgO[2,3] and rare earth oxides,[4—6] particularly Sm_2O_3.[7] Recently alkali promoted MnO catalysts have also been shown to give improved catalytic performance.[8,9] All these recent catalytic studies have been conducted at, or below, atmospheric pressure and at high temperatures, *ca.* 700—800 °C. It is interesting that even when different oxidants are utilised, *e.g.* O_2 and N_2O,[10] the product distribution obtained with these catalysts is broadly similar and consists of H_2, CO_2, CO, C_2H_4, C_2H_6 with a trace of higher hydrocarbons and oxygenated products, *e.g.* MeOH and CH_2O. Under these conditions both the nature of

Table 1.

Expt.	Catalyst	T/°C	P/kPa	CH_4 conv./ %	Yield/mol product per mol CH_4 per h			
					H_2	CO_x	C_2H_4	C_2H_6
1	None	505	185	1.0	Trace	0.010	0	Trace
2	5% Li/MgO	505	185	3.3	0.016	0.031	0.0010	0.0012
3	None	575	185	1.0	Trace	0.009	0	0
4	5% Li/MgO	575	185	17.4	0.084	0.170	0.0015	0.0023
5	None	500	335	1.3	0.007	0.013	0	0
6	5% Li/MgO	500	335	2.0	0.006	0.020	0	0.0007
7	None	540	335	4.3	0.020	0.038	0.0013	0.0032
8	5% Li/MgO	540	335	7.3	0.041	0.069	0.0014	0.0027
9	None	520	585	17.0	0.038	0.16	0.004	0.006
10	5% Li/MgO	520	585	20.1	0.060	0.19	0.005	0.006
11	None	560	585	17.9	0.07	0.17	0.0032	0.0057
12	5% Li/MgO	560	585	22.7	0.04	0.22	0.0031	0.0042
13	MgO	520	585	20.0	0.045	0.19	0.004	0.006
14	5% Ag/α-Al_2O_3	520	585	21.2	0.040	0.20	0.005	0.007
15	10% WO_3/ZSM-5	520	585	20.4	0.045	0.19	0.006	0.008
16	None/quartz liner	525	335	7.6	0.036	0.071	0.0017	0.0031

catalytic oxide[6] and the specific surface area[11] have been shown to affect significantly the product selectivity, and hence the majority of the research effort has been directed at the identification of suitable catalytic materials for the high temperature oxidative coupling reaction. However, this reaction has been known for many years[12] and has been well studied in the absence of catalyst as a homogeneous gas phase reaction when similar products can be observed, but in general the non-catalytic high pressure reaction gives much higher oxygenate selectivities.[13,14] It is currently agreed that the mechanism operating for the low pressure reaction in the presence of oxide catalysts involves the generation of gas phase methyl radicals *via* reaction of gas phase methane with a surface O^- site.[15,16] The radical coupling reaction then occurs in the gas phase. Hence it is apparent that gas phase reactions are of dominant importance in this reaction and to date there has been no study to determine the role of the gas phase non-catalytic reaction at low to moderate reaction pressures. Such a study is necessary to determine the specific role of the identified oxide catalysts or whether such a catalyst is necessary for this reaction. We have now successfully addressed this area and here we report a comparative study of methane oxidation at low to moderate pressures in the presence and absence of catalysts.

MgO, 5% Li/MgO, and 5% Ag/α-Al_2O_3 catalysts were prepared as previously described.[10] 10% WO_3/H-ZSM-5 was prepared by impregnation of H-ZSM-5 with an aqueous solution of ammonium metatungstate using an incipient wetness technique. Catalysts were calcined (24 h, 500 °C) prior to use. Oxidation of methane in the presence and absence of catalyst was carried out in a stainless steel micro-reactor (i.d. 14 mm) at temperatures up to 575 °C and pressures 85—585 kPa.

Experiments were conducted for a range of pressures and temperatures using a fixed CH_4/O_2 molar ratio of 3.5/1 and CH_4 feed-rate of 3.6 l/h; the results are shown in Table 1. At 185 kPa the gas phase reaction (expts. 1,3), *i.e.* no added catalyst, produced only carbon oxides and a trace of hydrogen. Addition of 5% Li/MgO catalyst (4 ml) to the reactor significantly enhanced conversion and product yields at this pressure (expts. 2,4). Hence at this low pressure the non-catalysed gas phase reaction does not play a significant role in line with our previous studies.[10] However, as the reaction pressure is increased to 335 kPa (expts. 5—8) the gas phase reaction in the absence of catalyst becomes significant at 540 °C and similar hydrocarbon yields are observed with and without added catalyst. At 585 kPa the gas phase reaction dominates (expts. 8—12) and there are only minor differences observed when the Li/MgO catalyst is added to the reactor. To demonstrate further the ineffectiveness of added catalysts at 585 kPa, tests were carried out on a range of materials (4 ml) having widely varying catalytic activity and selectivity at 85 kPa[10] and a wide range of surface areas as determined following discharge from the reactor (5% Li/MgO, 2 $m^2 g^{-1}$; MgO, 19 $m^2 g^{-1}$; 5% Ag/α-Al_2O_3, 3 $m^2 g^{-1}$; 10% WO_3/ZSM-5, *ca.* 300 $m^2 g^{-1}$). The results (expts. 9, 10, 13—15) demonstrate that the product yields are not particularly sensitive to the presence of these diverse oxidic materials at 585 kPa. Hence at 585 kPa the catalyst appears to have only a limited effect and in particular enhances the production of carbon oxides and hydrogen, whereas the yields of ethene and ethane are not significantly affected. In addition, comparison of data for the low pressure catalysed reaction (expt. 4) and the high pressure gas phase reaction (expt. 11) shows that, for similar reaction temperatures, improved C_2H_4 and C_2H_6 selectivities are obtained in the absence of catalyst. Stainless steel is known to be an active surface for initiation of the coupling reaction.[12] Additional results obtained using a quartz insert in the reactor (expt. 16) showed similar selectivities and conversions (*cf* expts. 7, 8) and hence the results obtained using the stainless steel reactor are considered to have general significance.

The results of this study demonstrate that increasing the reaction pressure can be as effective as adding a suitable oxide catalyst at lower pressures. The identification of suitable low pressure catalytic materials would therefore appear to have limited significance. The sole requirement for the use of an oxide catalyst may involve the control of selectivity within the hydrocarbon fraction. For example, the level of activity for catalytic oxidative dehydrogenation reactions could be used to regulate the alkene/alkane ratio. In view of these results it is anticipated that more effort will now be applied to the identification of a lower temperature catalytic route which will enable improved product selectivity to be achieved.

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