

## SELECTIVE OXIDATION OF METHANE TO ETHANE AND ETHYLENE OVER VARIOUS OXIDE CATALYSTS

J.A. ROOS, A.G. BAKKER, H. BOSCH, J.G. van OMMEN and J.R.H. ROSS

Department of Chemical Technology, Twente University of Technology,  
P.O. Box 217, 7500AE Enschede, The Netherlands.

### ABSTRACT

Preliminary results are reported for the oxidative coupling of methane to give ethane/ethylene mixtures over a series of different catalyst formulations; the temperature range studied is 650-850°C. A comparison is made of the behaviour of lead/alumina and lithium/magnesia materials. It is found that the former samples give ethane and ethylene plus a predominance of CO<sub>2</sub> whereas the latter give ethane and ethylene plus a mixture of CO, CO<sub>2</sub> and H<sub>2</sub>; at higher temperatures, the lead materials give also H<sub>2</sub> and CO. The lithium-containing materials are much more stable than the lead-containing ones; the latter lose lead, probably by volatilisation of the metal. A number of other oxide materials have also been examined and have been found to be less effective, having lower activities and selectivities than the lead- and lithium-containing systems.

### INTRODUCTION

An area of considerable recent interest is that of direct oxidative conversion of methane into products such as methanol, ethane and ethylene. In particular, a number of publications have appeared in the last few years which show that several types of catalyst can be used to give reasonably high conversions and selectivities towards the formation of the latter two products. This paper presents the first results of a research project which is aimed at gaining a greater understanding of those factors which determine the behaviours of different selective methane oxidation catalysts. The following paragraphs give a brief summary of the most important results reported in the literature to date.

Keller and Bhasin (1) have shown that the coupling of two molecules of methane to give C<sub>2</sub> products can only occur if oxygen (or another oxidant) is present according to the stoichiometric equations:



In oxidising conditions, the following non-selective reactions may also occur:



Also  $C_2H_6$  and  $C_2H_4$  may be non-selectively oxidised to CO and  $CO_2$  in sequential reactions. Using a cyclic operating procedure in which their catalysts were first oxidised by oxygen and then exposed to methane, Keller and Bhasin surveyed a whole range of metal oxides to see if they are suitable as oxidative coupling catalysts. The most promising of these were the oxides of Mn, Cd, Tl, and Pb, all supported on alpha alumina (surface area:  $1 \text{ m}^2/\text{g}$ ). Selectivities of 45% to  $C_2$  hydrocarbons at a  $CH_4$  conversion of 11% could be achieved on the manganese oxide/alumina catalyst. Keller and Bhasin postulated a reduction-oxidation mechanism in which the catalyst is alternately reduced by methane and oxidised by oxygen.

Experiments carried out under continuous flow conditions have also been reported. For example, Hinsen and Baerns (2) have compared the activities and selectivities for the oxidative coupling reaction of various supported catalysts containing the oxides of Pb, Bi, Sb, Sn and Mn. As supported lead oxide turned out to give the best results, they have subsequently examined this system in more detail (3). The most promising materials were found to be  $PbO/\gamma-Al_2O_3$  and  $PbO/SiO_2$ . On the former, a selectivity to  $C_2$  products of 58% was reached at a conversion of  $CH_4$  of 8% ( $740^\circ C$ ;  $CH_4/O_2 = 10$ ); the latter gave a selectivity of 72% but much lower conversions.

Ito et al. (4) have recently reported studies of the reaction over  $Li_2O$ -doped  $MgO$  of methane and oxygen (approximately 2:1) in a helium diluent in which the maximum yield of  $C_2$  products was obtained with a methane conversion of 43% and a selectivity of 45%. Based on investigations of the formation of methyl radicals from methane over the same type of material, they postulated a mechanism in which methyl radicals desorbed from the surface either couple to form  $C_2$  species or react with oxygen to form methoxide radicals which ultimately give rise to the formation of CO and  $CO_2$ .

Otsuka et al. (5) have investigated the reaction over rare-earth metal oxides and also over oxides such as  $PbO$ ,  $Bi_2O_3$ ,  $GeO_2$  and  $CdO$ , all without carrier. The best results were obtained on  $Sm_2O_3$  and  $Dy_2O_3$ ; both gave a selectivity of 93%. It is very difficult to compare these results with the results of the authors mentioned earlier as the reactor feed was in this case very dilute (82% He; total pressure 1 atm.) and a very high  $CH_4/O_2$  ratio of 46 was used, resulting in a very low conversion of methane. No indication of a possible mechanism was given.

Van der Wiele (6) has recently carried out an evaluation of the commercial potential of the reaction and has shown that it might prove to be economically interesting if a total yield of greater than about 24% (i.e. conversion greater than 30%, selectivity greater than 80%) could be achieved. He also reported results for the reaction over a Mn-containing material; this gave yields up to about 7%.

The aim of the present study is to investigate some of the factors which control the activity and selectivity of a range of potential catalysts for the oxidative coupling of methane and also to study such parameters as ageing of the catalysts, etc. Preliminary experiments carried out with catalyst systems similar to those studied by Hinsen and Baerns (2,3) and by Ito et al. (4) showed several new and interesting features and these are reported in this paper together with some results obtained with related catalyst systems. Particular attention is paid to the effect of feed composition and catalyst temperature on the product composition and to changes in activity and selectivity as a function of time in operation. The results of an infrared study of the surfaces of two of the catalysts after use are also given.

## EXPERIMENTAL

### Catalyst Preparation

The catalysts whose behaviour is reported in this paper are shown in Tables 1 and 2. A number of these were impregnated materials which were prepared by wet impregnation of samples of  $\gamma\text{-Al}_2\text{O}_3$  (Ketjen,  $240\text{ m}^2\text{g}^{-1}$  before calcination) or MgO (BDH,  $36\text{ m}^2\text{g}^{-1}$  before calcination). For this purpose, the carrier was added to an aqueous solution of the desired salt and the water was evaporated while stirring until a thick paste remained. The paste was then dried in an oven at  $140^\circ\text{C}$  overnight and calcined in air at  $850^\circ\text{C}$  for approximately 6h. The total areas of these samples after calcination were much lower and are shown in Table 1. The sample designated  $\text{PbO}/\text{Al}_2\text{O}_3(\text{II})$  was prepared by coprecipitation from an aqueous solution of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$  with a second solution of  $\text{Na}_2\text{CO}_3$ , the pH being maintained at 8-9; the same drying and calcination procedure as above was used. The samples designated Si/C, MgO and  $\text{Bi}_2\text{Sn}_2\text{O}_7$  were chemically pure compounds and were heated at  $850^\circ\text{C}$  directly before use; the first was a commercially available ceramic material, the second was obtained from B.D.H Ltd. as a standard reagent and the third was prepared by the solid-state reaction of powders of Bi and Sn oxides brought about by stepwise heating to  $1000^\circ\text{C}$ . A commercially available Fe-Cr- $\text{Al}_2\text{O}_3$  sample, normally used as a high-temperature water-gas shift catalyst, was also investigated. All of the calcined catalyst samples were crushed and sieved to a grain size of 0.3-0.6 mm. before use.

### Catalytic Experiments

The catalytic experiments were carried out in a quartz fixed-bed reactor operated at a pressure of one atmosphere. The temperature of the reactor, heated in an electric oven, is measured by a thermocouple attached to the outside of the reactor. (Later experiments with the thermocouple placed directly above the catalyst bed gave equivalent results and so we conclude that no significant temperature rise occurred in the bed in the measurements reported here). The

internal diameter of the reactor is 4mm. A typical catalyst charge consists of 0.092 g of the catalyst particles mixed with the same weight of quartz particles of the same particle size. For comparison purposes, blank runs have been carried out with the reactor filled with twice the normal amount of quartz without the catalyst. The gas feed to the reactor consists of methane (>99%) and air admitted separately using mass-flow controllers; in a typical experiment, the total flow to the reactor was  $0.42 \text{ cm}^3(\text{STP})\text{s}^{-1}$ . The majority of experiments were carried out with a methane/oxygen ratio of either 5 or 10. All of the gases were analysed by gas chromatography (Carbosieve B: 2.25 m length; 2 mm i.d.) using  $\text{N}_2$  as an internal standard. A carbon balance of 98% was achieved in typical experiments once a steady-state was achieved.

The conversion,  $\alpha$ , of  $\text{CH}_4$  obtained in the kinetic measurements is defined as:

$$\alpha = (\text{mol CH}_4 \text{ s}^{-1} \text{ in feed} - \text{mol CH}_4 \text{ s}^{-1} \text{ in effluent}) / (\text{mol CH}_4 \text{ s}^{-1} \text{ in feed}).$$

The selectivity,  $S$ , to a product  $\text{C}_x\text{H}_y\text{O}_z$  containing  $x$  carbon atoms is defined as:

$$S = x \cdot (\text{mol C}_x\text{H}_y\text{O}_z \text{ formed s}^{-1}) / (\text{mol CH}_4 \text{ s}^{-1} \text{ in feed} - \text{mol CH}_4 \text{ s}^{-1} \text{ in effluent}).$$

These quantities are expressed in the figures and tables as percentages. The  $\text{C}_2$  selectivity is the sum of the selectivities to  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$ ;  $\text{C}_2\text{H}_2$  was observed only at very high temperatures and in relatively small quantities. The yield,  $Y$ , of  $\text{C}_2$  products is given by (methane conversion)  $\times$  (selectivity to  $\text{C}_2$  products). The fraction  $W/F$  is used as a measure of contact time, where  $W$  is the weight of catalyst (in g) and  $F$  is the rate of flow to the reactor (in  $\text{cm}^3 \text{ s}^{-1}$ ). In a typical experiment using 0.092 g of catalyst and a flow of  $0.42 \text{ cm}^3 \text{ s}^{-1}$ , the value of  $W/F$  is  $0.22 \text{ g s cm}^{-3}$ , this corresponds to a contact time in the catalyst bed of approximately 0.6 s.

### Infrared Experiments

The IR-spectra of fresh and used catalysts were taken using a Nicolet MX-S FTIR spectrometer operated in the diffuse reflectance mode; for this, a Barnes reflectance attachment was used. Prior to the measurements, the samples were heated in air in the reflectance cell to approximately  $200^\circ\text{C}$  to remove physically adsorbed water. The IR spectra were then recorded at room temperature.

## RESULTS AND DISCUSSION

### The Influence of Temperature on the Behaviour of the Different Catalysts

Figure 1 shows the conversions of methane and oxygen as a function of temperature for a methane/oxygen feed ratio of approximately 10 for the reactor loaded

with only quartz (A), with  $\text{Li}_2\text{O}/\text{MgO}$ (II) (B) and with  $\text{PbO}/\text{Al}_2\text{O}_3$ (I) (C). The corresponding selectivities are shown in Figure 2. These results are for experiments once a steady-state had been achieved for methane/oxygen ratios of 10. It can be seen for the temperature range studied (approximately 650 to 850°C) that the quartz filling (A) gave measurable activities with selectivities to  $\text{C}_2$  hydrocarbons rising as high as 35%; CO was the major product. The  $\text{Li}_2\text{O}/\text{MgO}$  samples (B) gave slightly higher conversions over the same temperature range but the selectivities to  $\text{C}_2$  products were now considerably higher: a total of better than 60%. The behaviour of the lead-containing catalysts was somewhat different; the oxygen conversion was 100% over the whole range of temperature studied and the conversion of methane increased slightly with increasing temperature. The selectivity to  $\text{C}_2$  products was also relatively high.

With all three sets of experiments shown in Figure 2, the behaviour with respect to the production of ethane and ethylene was similar: the selectivity to  $\text{C}_2\text{H}_6$  decreased with increasing temperature while the selectivity to  $\text{C}_2\text{H}_4$  increased. The optimum  $\text{C}_2$  selectivity of the  $\text{PbO}/\text{Al}_2\text{O}_3$  catalyst was reached at approximately 720°C, while that for the  $\text{Li}/\text{MgO}$  catalyst was found at approximately 780°C. It seems likely that the ethylene is formed as a secondary

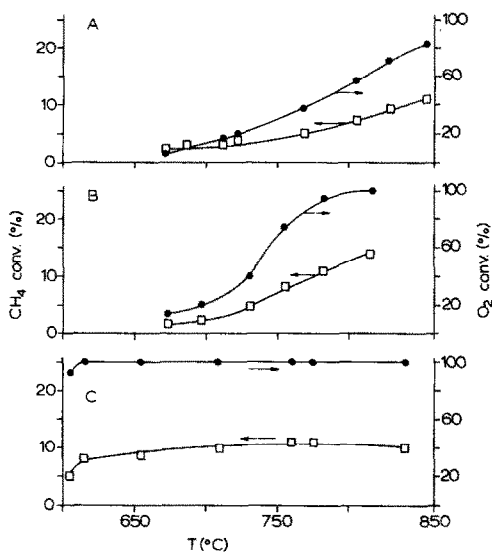


FIGURE 1 Conversions of methane ( $\square$ ) and oxygen ( $\bullet$ ) versus temperature: (A) quartz; (B)  $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ ; and (C)  $\text{PbO}/\text{Al}_2\text{O}_3$ (I).

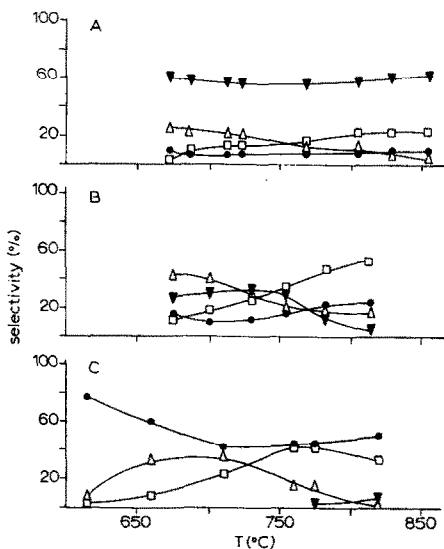


FIGURE 2 Selectivities corresponding to the experiments shown in Figure 2.  $\Delta$  -  $\text{C}_2\text{H}_6$ ;  $\square$  -  $\text{C}_2\text{H}_4$ ;  $\blacktriangledown$  - CO;  $\bullet$  -  $\text{CO}_2$ .

product from the ethane either by direct dehydrogenation (5) or by oxidative dehydrogenation (6):



Hinsen et al. (2,3) have concluded that ethylene is formed from ethane and not directly from methane by reaction (6) and Ito et al. (4) also favour oxidative dehydrogenation of ethane to produce ethylene via  $\text{O}^-$  and  $\text{O}^{2-}$  species on the surface. We cannot at present exclude the possibility that reaction (5) also takes place, at least over the  $\text{Li}_2\text{O}/\text{MgO}$  catalysts, because of our observation of hydrogen as a product (see below).

Larger differences between the samples were found in the production of the two carbon oxides. The selectivity of the  $\text{PbO}/\text{Al}_2\text{O}_3$  catalyst towards CO is very low compared to that of quartz and that of  $\text{Li}_2\text{O}/\text{MgO}$ ; only at high temperature is some CO formed. This can perhaps be explained by the fact that PbO is a much better oxidation catalyst than is  $\text{Li}_2\text{O}$ -doped MgO; any CO formed is immediately oxidised to  $\text{CO}_2$  on the lead-based materials but not on the others (but see below).

An important observation made in this work and which has not been reported previously is that an appreciable quantity of hydrogen was formed in many of the experiments. It was produced over the whole temperature range for both the quartz and  $\text{Li}_2\text{O}/\text{MgO}$  samples even if oxygen was still present at the exit of the reactor. For the lead-containing samples, hydrogen was found only at those temperatures ( $>770^\circ\text{C}$ , see Fig. 2) at which CO was formed, but it became a major product under these conditions. The hydrogen may have been produced by the dehydrogenation of ethane (reaction 5), the water-gas shift reaction:



or by the decomposition of formaldehyde:



Formaldehyde was found as a trace product in the water condensed at the exit of the reactor. In the case of the  $\text{Li}_2\text{O}/\text{MgO}$  catalyst, the water-gas shift reaction was found to be in equilibrium after a period of several hours of isothermal operation. It would seem probable that reactions (5) and (7) occur only in the later parts of the bed, once the oxygen of the reaction mixture has completely (or almost completely) reacted.

If the catalyst is selective for the formation of CO, this CO may then react with the product water according to reaction (7). This results in a gas mixture containing CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O; this is the case with the Li<sub>2</sub>O/MgO catalysts and also with quartz over the whole temperature range studied. However, the lead-containing samples do not produce CO at lower temperatures; it is only possible to form hydrogen by reaction (7) at high temperatures once CO is formed, and this is observed to be the case. It should be noted that a practical consequence of the selective formation of CO<sub>2</sub> over the lead-containing materials is that the conversion of methane for a given consumption of oxygen is always lower (see also Table 1 below). The formation of hydrogen as a product may have some significance in considering the all-over economics of a process based on the oxidative coupling of methane.

We cannot exclude the possibility that the hydrogen is formed directly from the methane or one or both of the C<sub>2</sub> products by a steam-reforming reaction. Further work to elucidate the mode of formation of the hydrogen is planned.

The results of the experiments shown in Figures 1 and 2 are summarised in Table 1 together with results for the same samples at different methane/oxygen ratios (see below); it also includes additional samples of PbO/Al<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>O/MgO. Table 2 gives the results for a series of other materials which will also be discussed briefly below. The coprecipitated lead sample (II) gives slightly improved results compared with those for the impregnated sample (I); this could possibly arise from the inclusion of significant quantities of sodium in this material, as will be discussed more fully elsewhere (7). An increased lithium content has no significant effect on the behaviour of the Li<sub>2</sub>O/MgO samples.

In order to see whether lithium or sodium have any activity or selectivity when used alone, Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> samples were tested; both gave poorer results than quartz alone. Similar results were obtained for calcium supported on alumina. It would therefore appear that a surface with basic properties is not the only requirement of a good oxidative coupling catalyst. We cannot however exclude the possibility that the cations of these materials had become partially or completely buried in the support during the calcination step and that the alumina surface is only slightly modified by their presence. Further work using other supports where less interaction is possible is therefore in progress.

Magnesia alone was also examined and was found to give results similar to those with quartz alone, this is in contradiction to recent results published by Anderson and Tsai (8). The latter workers have reported that only CO and CO<sub>2</sub> were formed in experiments at lower temperatures over similar MgO samples in which O<sub>2</sub> was used as the oxidant; however, this difference may be due to their stainless steel reactor having total oxidation activity.

TABLE 1  
 Compositions and catalytic results (conversion,  $\alpha$ , selectivity to  $C_2$  products, S, and yield of  $C_2$  products, Y) for quartz,  $PbO/Al_2O_3$ , and  $Li_2O/MgO$  samples

Catalyst	Pb or Li content /wt%	Surface area <sub>1</sub> /m <sup>2</sup> g <sup>-1</sup>	Reactant pressures CH <sub>4</sub>	Reactant pressures O <sub>2</sub>	Temp. /K	$\alpha \times 100$ /%	S $\times 100$ /%	Y $\times 100$ /%					
Quartz (blank)	-	-	379	89	712	7	39	2.7					
					787	17	30	5.1					
					844	20	22	4.4					
			Pb/Al <sub>2</sub> O <sub>3</sub> (I)	28.0%Pb	60	515	51	711	3	35	1.1		
								769	5	35	1.7		
								854	11	29	3.2		
Pb/Al <sub>2</sub> O <sub>3</sub> (II)	18.0%Pb (+5.9%Na)	14				374	79	713	19	48	9.1		
								774	17	34	5.8		
								810	18	33	5.9		
			Pb/Al <sub>2</sub> O <sub>3</sub> (II)	18.0%Pb (+5.9%Na)	14	504	53	711	10	57	5.7		
								772	11	56	6.2		
								820	10	43	4.3		
Li <sub>2</sub> O/MgO (I)	3.8%Li	1.0				387	76	713	16	41	6.6		
								766	19	51	9.7		
								822	20	52	10.4		
			Li <sub>2</sub> O/MgO (I)	3.8%Li	1.0	509	52	706	10	52	5.2		
								754	12	65	7.8		
								818	12	64	7.7		
Li <sub>2</sub> O/MgO (II)	5.3%Li	2.0				385	79	692	4	43	1.7		
								721	10	40	4.0		
								742	16	37	5.9		
			Li <sub>2</sub> O/MgO (II)	5.3%Li	2.0	514	52	716	7	56	3.9		
								772	13	72	9.3		
								791	13	76	9.9		
Li <sub>2</sub> O/MgO (II)	5.3%Li	2.0				380	80	723	14	36	5.0		
								778	22	48	10.4		
								803	23	54	12.4		
			Li <sub>2</sub> O/MgO (II)	5.3%Li	2.0	828	80	828	22	45	9.9		
								531	46	730	5	57	2.9
										755	8	55	4.4
782	12	66				7.9							
815	14	70				9.8							



TABLE 2

Compositions and catalytic results for various other catalyst formulations (Except for MgO, only results for the highest temperature studied are given.)

Catalyst	Content additive	Surface area	Reactant partial pressures /Torr		Temp.	x100	Sx100	Yx100
	/wt%	/m <sup>2</sup> g <sup>-1</sup>	CH <sub>4</sub>	O <sub>2</sub>	/K	/%	/%	/%
Quartz (blank)	-	-	379	89	844	20	22	4.4
			515	51	854	11	29	3.2
Na/Al <sub>2</sub> O <sub>3</sub>	1.7%Na	182	393	77	829	15	19	2.9
			507	52	831	9	23	2.1
Ca/Al <sub>2</sub> O <sub>3</sub>	-	-	513	52	839	8	31	2.5
MgO	-	-	508	50	709	8	24	1.9
					760	7	31	2.2
					815	7	27	1.9
					866	8	30	2.4
Cu/MgO	-	-	530	47	840	6	9	0.5
SiC	-	-	490	57	842	7	30	2.1
Bi <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	-	-	382	79	781	13	25	3.3
Bi/Al <sub>2</sub> O <sub>3</sub>	-	-	381	77	749	12	8	1.0
Mn/Al <sub>2</sub> O <sub>3</sub>	7.1%Mn	74	380	78	840	12	6	0.7
Fe/Cr/Al <sub>2</sub> O <sub>3</sub>	-	-	384	77	800	11	7	0.8

A number of miscellaneous samples were examined to test various other possible types of material. The results of Table 2 show that copper supported on MgO is relatively inactive and is selective towards total oxidation. A sample of SiC was very inactive relative even to quartz, the selectivity to C<sub>2</sub> products also being relatively low; it could thus be that this material will be a suitable support for future model studies and that it could also be used for reactor construction. The results of Keller and Bhasin (1) showed that Bi- and Mn-containing samples had some promise. However, the Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> sample was also relatively inactive and unselective and a sample of Bi<sub>2</sub>O<sub>3</sub> supported on alumina was also relatively poor, having a selectivity lower than that of quartz; the same applied to the Mn-containing sample. These observations are strange in the light of the observations of Keller and Bhasin but the difference may arise from the cyclic mode of operation used in their work. It should also be noted that the Bi<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> sample was very unstable and lost most of the Bi over a short period of time. Finally, a sample of a high-temperature shift catalyst (Fe<sub>2</sub>O<sub>3</sub> promoted with Cr<sub>2</sub>O<sub>3</sub> and supported on alumina) was also a poor catalyst. Thus, we find that the catalysts containing metal ions having variable oxidation states give very poor results (Bi/Al<sub>2</sub>O<sub>3</sub>, Mn/Al<sub>2</sub>O<sub>3</sub>, Cu/MgO, Fe/Cr/Al<sub>2</sub>O<sub>3</sub>); PbO/Al<sub>2</sub>O<sub>3</sub> is the only exception to this rule.

### The Influence of $\text{CH}_4/\text{O}_2$ Ratio

In this and the following sections, we give more detailed results for the  $\text{PbO}/\text{Al}_2\text{O}_3$  and  $\text{Li}_2\text{O}/\text{MgO}$  catalysts, showing the effects of reaction conditions as well as describing the ageing effects observed with both types of material.

It can be seen from the results given in Table 1 that an increase in the partial pressure of  $\text{CH}_4$  with a corresponding decrease in the oxygen partial pressure (so that the methane/oxygen ratio is increased from approximately 5 to approximately 10) results in lower conversions of the methane (approximately one half) and higher selectivities to  $\text{C}_2$  products (but not a factor of two) over all those catalysts for which this effect was investigated; the yield (conversion  $\times$  selectivity) is thus reduced by increasing the methane/oxygen ratio. This result is in accordance with the literature data for the  $\text{PbO}/\text{Al}_2\text{O}_3$ ,  $\text{Li}_2\text{O}/\text{MgO}$  and related systems (2,4).

### The Influence of Contact Time

For all the experiments described above, a W/F ratio of  $0.22 \text{ g s cm}^{-3}$  was used. Preliminary measurements have been carried out with one catalyst formulation to show the effect of contact time by variation of the gas flow through the reactor. From these, it was found that the conversion was decreased by lowering the contact time and vice versa as long as the original conversion of  $\text{O}_2$  was less than 100%. Lower contact times also gave improved selectivities to  $\text{C}_2$  products, resulting in approximately equal yields. Ito et al. (4) show that (at a temperature of  $620^\circ\text{C}$ )  $\text{CO}$  and  $\text{CO}_2$  are not derived primarily from ethane or ethylene but from methane. This result, together with the effect of contact time, leads to the conclusion that lowering the contact time lowers the non-selective oxidation of  $\text{CH}_4$  to carbon oxides while the yield of  $\text{C}_2$  products remains unchanged. There is no indication as yet as to whether the non-selective oxidation is homogeneous or heterogeneous. As the variation of the contact time was achieved by variation of the flow, both the homogeneous and heterogeneous reactions may have been affected.

### Ageing Experiments

Figure 3 shows the  $\text{C}_2$  selectivity of the catalysts  $\text{Li}/\text{MgO}(\text{II})$  (upper curve) and  $\text{PbO}/\text{Al}_2\text{O}_3(\text{I})$  (lower curve) as a function of time on stream at  $800^\circ\text{C}$ ; in both cases, the conversion of the oxygen was essentially 100% throughout the duration of the tests while the selectivity varied with time. The  $\text{Li}/\text{MgO}$  catalyst gave a selectivity increase during the first 20 h on stream after which the selectivity decreased to little below the initial level and remained relatively stable. The selectivity of the lead-containing catalyst dropped immediately in an exponential fashion from the start of the experiment due to an increased  $\text{CO}$  production. This

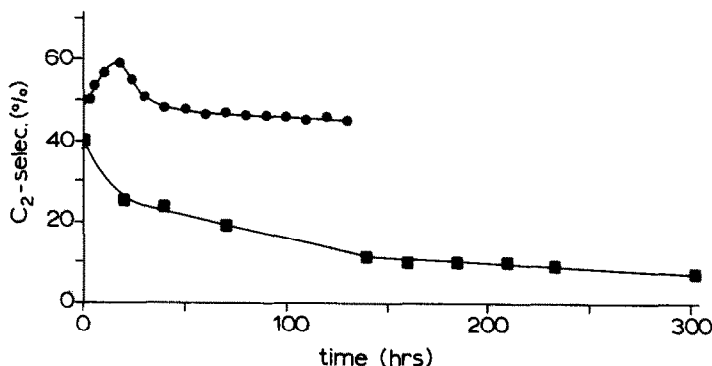


FIGURE 3 The change of selectivity of the  $\text{Li}_2\text{O}/\text{MgO}(\text{II})$  (○) and  $\text{PbO}/\text{Al}_2\text{O}_3(\text{I})$  (■) samples as a function of time at a temperature of  $800^\circ\text{C}$ ; the ratio  $\text{CH}_4/\text{O}_2$  for the former = 10, for the latter = 5.

can be explained by a loss of lead, observed after every run, especially at high temperature ( $750^\circ\text{C}$ ). The lead removed from the catalyst was deposited on colder parts of the reactor and had a metallic appearance; it was therefore probably in the metallic state. The deposit could be converted into the yellow  $\text{PbO}_2$  by flushing the reactor with air at  $850^\circ\text{C}$ . The fact that the catalyst had lost lead was confirmed by elemental analysis: sample I contained 28 wt% Pb before the ageing experiment but only 6 wt% afterwards.

As a result of the loss of lead (oxide) from the catalyst, bare acidic  $\gamma\text{-Al}_2\text{O}_3$  is exposed to the gas phase. According to Baerns et al. (4), acidic surfaces give rise to non-selective oxidation. Our experiments with  $\gamma\text{-Al}_2\text{O}_3$  as catalyst showed low selectivity (ca 10%) and the formation of both CO and  $\text{CO}_2$ . The fact that bare  $\gamma\text{-Al}_2\text{O}_3$  is exposed to the gas phase with the aged lead catalyst thus results in lower selectivity and the formation of CO; the CO may then react with water to form  $\text{CO}_2$  and hydrogen according to the water-gas shift reaction (7). As discussed above, this explains the formation of hydrogen at higher temperatures over these materials.

XRD results show that the  $\text{PbO}/\text{Al}_2\text{O}_3$  catalyst contains PbO and  $\text{PbAl}_{12}\text{O}_{19}$  after calcination (air,  $850^\circ\text{C}$ ). Of these two compounds PbO may be reduced to metallic Pb during a run, especially at high temperatures, in those parts of the bed where no oxygen is present and hydrogen has been formed (see above). The vapour pressure of metallic Pb is a factor of between 2 and 5 larger than that of PbO, depending on temperature. Hence, the volatilisation of both Pb and PbO may be responsible for the loss of lead from the catalyst. The results for the lead-containing catalysts will be discussed in more detail in a subsequent paper (7).

### Infra-Red Results

Preliminary infra-red experiments were carried out in which fresh and used samples of the  $\text{PbO}/\text{Al}_2\text{O}_3$  and  $\text{Li}_2\text{O}/\text{MgO}$  catalysts were examined by a diffuse reflectance technique. The spectra of the used materials were very similar to one another and were different from the original spectra of the two different types of material. The spectra of the used samples contained vibrations characteristic of C-O-C and C-H bonding and we therefore conclude that an oxygen-containing hydrocarbon residue had been formed on the surface. There is as yet no indication as to whether or not this compound takes part in the reaction or provides a special site geometry. According to the radical mechanism proposed by Ito et al. (4), no such surface compound should be formed. However, Garcia et al. have reported (9) the results of cyclic experiments using catalysts containing Ca, Pt and Cr or Ca, Pt and Co, both being supported on a " $\text{CaAl}_2\text{O}_4$ -blocked alumina" in which they have found that a carbonaceous surface species is formed. They suggest that this species acts as an active precursor which eventually evolves ethylene.

### CONCLUSIONS

(i) The  $\text{PbO}/\text{Al}_2\text{O}_3$  system (2,3) shows fair selectivity and activity in the catalytic oxidative coupling of methane to  $\text{C}_2$  products;  $\text{CO}_2$  is formed in preference to CO at most temperatures but CO and  $\text{H}_2$  are observed at high temperatures. The disadvantage of this system is its low stability due to loss of lead from the catalyst.

(ii) Lithium-doped magnesium oxide catalysts show  $\text{CH}_4$  conversions and  $\text{C}_2$  selectivities comparable to the  $\text{PbO}/\text{Al}_2\text{O}_3$  system but are much more stable. Substantial quantities of hydrogen are formed at all temperatures.

(iii) Infrared data indicate that a surface species is formed during reaction on the surface of both the  $\text{PbO}/\text{Al}_2\text{O}_3$  and  $\text{Li}_2\text{O}/\text{MgO}$  catalysts and that this contains carbon, hydrogen and oxygen.

(iv) A decrease in the oxygen partial pressure or the contact time increases the selectivity to  $\text{C}_2$  products but decreases the conversion of  $\text{CH}_4$ . Ethane appears to be the primary product of the selective reaction.

(v) The samples given in Table 2 were much less selective for oxidative coupling of methane.

### ACKNOWLEDGEMENTS

We should like to thank G. Altena for his assistance in constructing and maintaining the equipment and Prof. K. van der Wiele for valuable discussions.

## REFERENCES

- 1 G.E. Keller and M.M. Bhasin, *J. Catal.*, 73 (1982) 9.
- 2 W. Hinsen and M. Baerns, *Chem.-Ztg.*, 107 (1983) 223.
- 3 W. Hinsen, W. Bytyn and M. Bearns, *Proc. 8th. Int. Congr. Catal.*, 3 (1984) 581.
- 4 T. Ito, J-X. Wang, C-H. Lin and J.H. Lunsford, *J. Amer. Chem. Soc.*, 107 (1985) 5062
- 5 K. Otsuka, K. Jinno and A. Morikawa, *Chem. Lett.*, (1985) 499.
- 6 K. van der Wiele, to be published.
- 7 J.A. Roos, A. Bakker, H. Bosch, J.G. van Ommen and J.R.H. Ross, to be published.
- 8 J.R. Anderson and P. Tsai, *Appl. Catal.*, 19 (1985) 141.
- 9 E.Y. Garcia, G.L. Rivera, D.E. Resasco, *React. Kinet. Catal. Lett.*, 28 (1985)