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A comparison of the performances of selected catalysts for the partial oxidation of methane to formaldehyde at elevated pressures

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Abstract

A study of the partial oxidation of methane to methanol and formaldehyde, over various silica supported catalysts, has been undertaken at elevated pressures (up to 1520 kPa) between 500°C and 600°C. C_2 products were observed with O_2 as oxidant; but not with N_2O. O_2 was much more reactive than N_2O in all conditions examined, but no catalytic effect could be observed with O_2. Formaldehyde was generally the major partial oxygenated product observed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Partial oxidation; Selectivity; Nitrous oxide; Oxygen; Elevated pressure

1. Introduction

At atmospheric pressure, many studies of the partial oxidation of methane to formaldehyde have been carried out with silica supported molybdenum [1–4] or vanadium oxides [5,6]. While Gesser et al. [7] have published an extensive review on the high pressure partial oxidation of methane using oxygen with and without catalysts, relatively few publications have appeared concerning the reaction at elevated pressures, in homogeneous conditions, or using unsupported [8], supported [9] and bifunctional catalysts [11] (see Table 1). Prior to undertaking this work, high pressure studies tended to concentrate on using oxygen, at pressures greater than 5000 kPa, below 480°C [8–16].

In this work nitrous oxide was the oxidant, at high pressures in the presence of a catalyst. For comparison purposes, some experiments were performed with oxygen.

2. Experimental

Catalysts which previously gave good results in ambient pressure experiments [1,2,17–19] were chosen for use in the high pressure experiments. These catalysts consisted of a silica support, with or without an added promoter. The catalysts chosen were 7Mo–2Na–cabosil (i.e., 7 wt.% Mo and 2 wt.% Na supported on Cab–O–sil M5), 5Mo–cabosil, 10Mo–2Cu–aerosil, 2V–cabosil and 10Mo–2V–cabosil. They were prepared according to the wet impregnation method reported previously [19].

2.1. Catalyst testing

Catalysts were tested on a high pressure testing system The micro-reactor used consisted of a fixed bed quartz reactor. The temperature of the catalyst bed was measured, and controlled, via a thermocouple, inserted into a thermowell which reached from the reactor inlet to the end of the catalyst bed. Reactants

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Table 1
Literature reports of high pressure oxidation of methane by oxygen

Catalyst	Pressure (kPa)	T (°C)	Methane conversion (%)	HCHO selectivity (%)	CH_3OH selectivity (%)	Ref.
None	5066–15 198	360–390	1.6	(Trace)	10	[8]
None	5066	450	8		81	[12]
MoO_3	5066	460	2.3	2	19	[10]
$MoO_3.UO_2$	5066	460	3.5	2	75	[10]
$CuO.MoO_3$	1915	485	1.4	13	40	[11]
MoO_3/Pumice	2017	458–480		38[a]		[9]
Cu/SiO_2	3040	350	6		92	[13]
SnO_2	3040	247	4		83	
None[b]	1013	225	9.6	22	35	[13]
None	1013–5066	500	5.25		35	[14]
			5		22	
Fe_2O_3/MoO_3	507	700	6.7	41.2		[16]
None		625	15	14.8	19.4	[16]

[a] Yield, no details of conversion were given.
[b] Sensitised with diethyl ether (DEE).

flowed downwards through the reactor. A narrow quartz tube was inserted into the lower section of the quartz reactor to minimise the post-catalytic volume.

Catalyst tests were carried out by placing 0.1 g of catalyst in the reactor. The methane and oxidant (nitrous oxide or oxygen) flow rates were set to their desired values and the system was allowed to stabilise for 20 min. Analysis of the feed and product gases was carried out by on-line gas chromatography [1,2,18,19,21].

Experiments were also carried out in the absence of catalysts, in order to estimate the contribution of homogeneous gas phase and wall reactions.

3. Results and discussion

3.1. Performances of different catalysts at various temperatures with N_2O as oxidant

The influence of temperature (500–600°C) on catalyst performance is illustrated in Table 2. These data indicate that the homogeneous oxidation of methane by nitrous oxide does not occur, to a significant extent, below 600°C.

A general feature to emerge from Table 2 is that methane conversion increased with temperature. 5Mo–cabosil gave the poorest methane conversion, at all temperatures. 7Mo–2Na–cabosil and 10Mo–2Cu–aerosil gave comparable conversions at each temperature examined. The best conversion, at 550°C, was obtained using 2V–cabosil. When the partial oxidation products (CH_3OH and HCHO) were present, the selectivity to HCHO was greater than that to CH_3OH. However, a significant finding is that some methanol was observed, in contrast to the previously published ambient pressure work [1,2,18,19,21]. With 7Mo–2Na–cabosil the selectivity to formaldehyde decreased with increasing temperature (Table 2). The selectivity to methanol, however, increased with temperature. The combined selectivity to the partial oxidation products was approximately constant (4.5–5%) at all temperatures examined. With 5Mo–cabosil an increase in selectivity to HCHO and CH_3OH was noted as temperature increased. When 10Mo–2Cu–aerosil was used, considerable methane conversions were obtained. These conversions, however, did not translate into high yields of HCHO or CH_3OH. The combined selectivity to these products was less than 1%. 2V–cabosil gave the best selectivity to the partial oxidation products at 500°C and 550°C. 10Mo–2V–cabosil gave poorer selectivities than either 7Mo–2Na–cabosil or 2V–cabosil at all temperatures examined.

Table 2
Effect of temperature on catalyst performance at 507 kPa

T (°C)	Oxidation products (%)	Catalyst					
		None	7Mo–2Na–cabosil	5Mo–cabosil	10Mo–2Cu–aerosil	2V–cabosil	10Mo–2V–cabosil
500	Conversion	0	0.21	0.04	0.25	0.24	0.47
	Selectivity HCHO	–	4	0	0	4	0
	Selectivity CH_3OH	–	1	0	0	3	0
	Selectivity CO	–	71	80	83	84	83
	Selectivity CO_2	–	24	20	17	9	17
	Y (CH_3OH+HCHO)	–	0.011	0	0	0.017	0
550	Conversion	0	0.9	0.09	0.83	1.58	1.23
	Selectivity HCHO	–	3.5	3	1	5.5	2
	Selectivity CH_3OH	–	1.5	0	0	2.5	2
	Selectivity CO	–	78	78	81	86	84
	Selectivity CO_2	–	17	19	18	6	12
	Y (CH_3OH+HCHO)	–	0.045	0.003	0.008	0.126	0.049
600	Conversion	0.02	3.25	0.51	3.55		2.4
	Selectivity HCHO	0	2	8	0.5		1
	Selectivity CH_3OH	24	2.5	2	0		1.5
	Selectivity CO	76	82	79	87		88
	Selectivity CO_2	0	13	11	12.5		9.5
	Y (CH_3OH+HCHO)	0.004	0.146	0.051	0.018		0.060

0.1 g catalyst used in each case, pressure=507 kPa, $CH_4/N_2O=5$, $F_{press}=24\ ml\ min^{-1}$.

3.2. *Influence of pressure on the reaction with N_2O as oxidant*

The effect of pressure on the behaviour of 7Mo–2Na–cabosil and 2V–cabosil was examined in the range 101–1520 kPa. A control reaction was carried out in the absence of a catalyst. Negligible conversions were obtained with zero selectivity to the partial oxidation products, even at the highest pressure examined.

Fig. 1 shows that increasing reaction pressure resulted in decreased methane conversion when 7Mo–2Na–cabosil was used. The percentage conversion minimised at 1013 kPa. When 2V–cabosil was used an optimum methane conversion of 1.85% was found at 1013 kPa. 2V–cabosil was considerably more active for methane conversion at all pressures examined, except at ambient pressure.

The influence of reactor pressure on product distribution obtained with each catalyst is shown in Fig. 2. The major product in each case was CO followed by CO_2 (not shown). When 7Mo–2Na–cabosil was used, the selectivity to HCHO increased slightly over the range of pressures examined.

On using 2V–cabosil, the selectivity to HCHO tended to increase with pressure (Fig. 2). Carbon dioxide selectivities (not shown) were comparable at all pressures, over this catalyst.

3.3. *The effect of contact time on the performance of 7Mo–2Na–cabosil*

The effects of pseudo-contact time (*W*/*F*) on the performance of 7Mo–2Na–cabosil, using nitrous oxide, are shown in Fig. 3, which demonstrates that the amount of methane converted was linearly dependent on the residence time in the reactor.

Product selectivities as a function of residence time are also illustrated in Fig. 3. No CH_3OH was observed. HCHO selectivity was favoured at low residence times. As the residence time increased the formaldehyde selectivity decreased to zero with a corresponding increase in carbon monoxide and carbon dioxide selectivity. Similar behaviour was observed with this catalyst when it was previously tested at ambient pressure [1,2].

3.4. *The effect of the amount of feed N_2O on the performance of 2V–cabosil*

The influence of CH_4/N_2O ratio on the behaviour of 2V–cabosil was examined at 1520 kPa. Fig. 4 shows the effect of varying the percentage N_2O in the feed on the conversion of methane. There appeared to be a monotonic relationship between the amount of nitrous oxide present in the feed stream and the amount of methane converted. Enriching the feed in nitrous

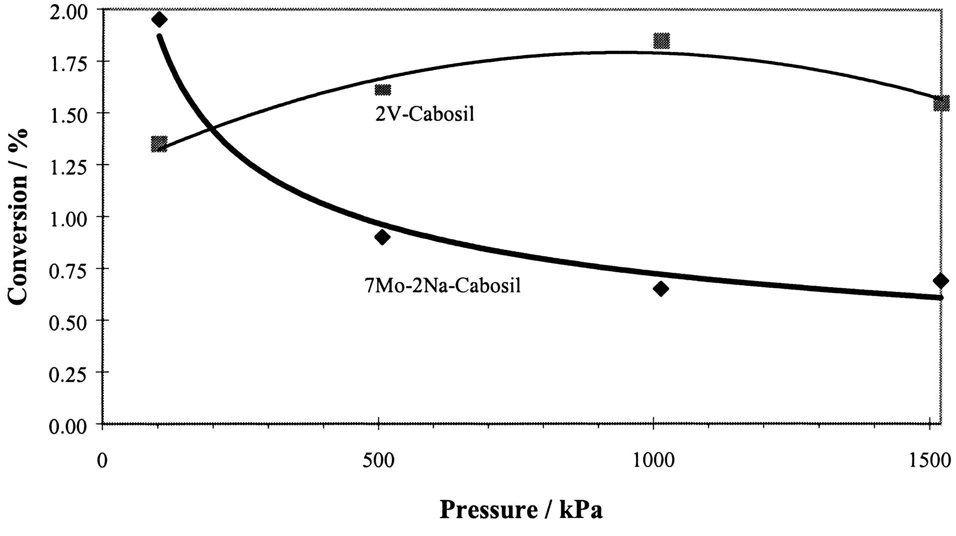

Fig. 1. Methane conversion as a function of pressure. 0.1 g catalyst, F_{press}=24 ml min^{-1}, T=550°C, CH_4/N_2O=5.

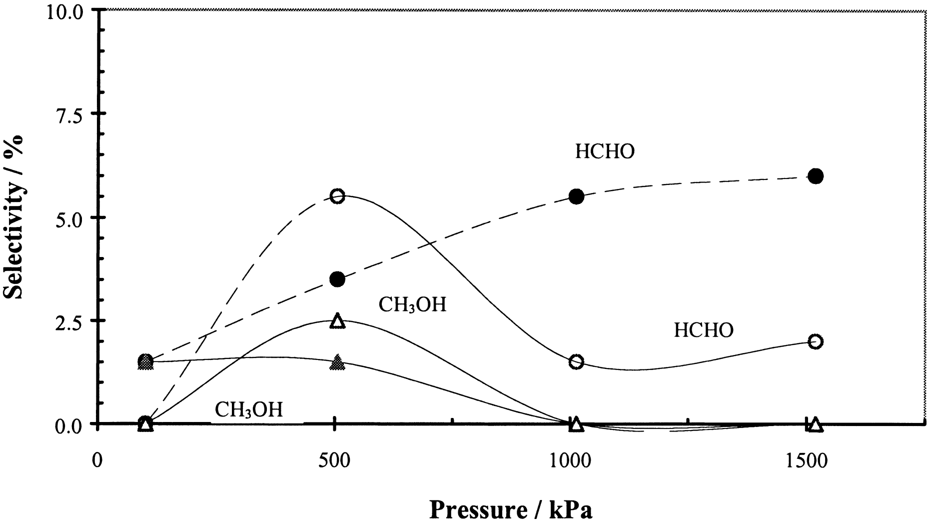

Fig. 2. Selectivity as a function of pressure for HCHO and CH_3OH. Filled symbols refer to 7Mo–2Na–cabosil, open symbols refer to 2V–cabosil. 0.1 g catalyst, F_{press}=120 ml min^{-1}, T=550°C, CH_4/N_2O=5.

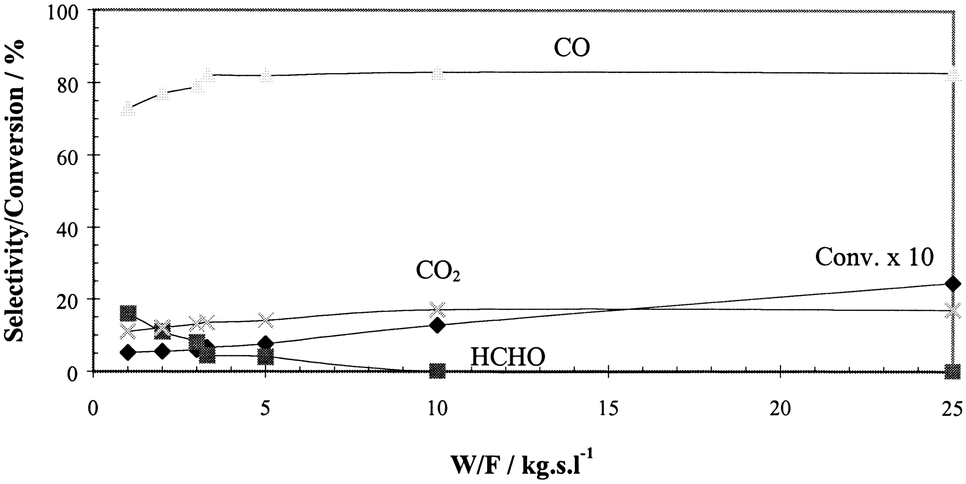

Fig. 3. The influence of W/F on performance of 7Mo–2Na–cabosil. Selectivity to HCHO+CH_3OH, CO and CO_2, and methane conversion×10. 0.1 g catalyst, p=507 kPa, T=550°C, CH_4/N_2O=5.

oxide resulted in increased methane conversion. However, when a 50/50 mixture of methane and nitrous oxide were fed to the reactor, the reaction went out of control after about 10 min. The temperature increased rapidly to 900°C and the system shut-down automatically.

Little or no effect on product selectivities was observed over 2V-cabosil as the N_2O content in the feed was varied. Methanol was not detected.

3.5. The selectivity conversion relationship using N_2O

All of the selectivities obtained from the high pressure experiments outlined above were plotted as a function of conversion, for 7Mo–2Na–cabosil (Fig. 5) and 2V–cabosil (Fig. 6). The curves obtained from ambient pressure work [1,2,18,19,21] are also included (open symbols in each plot). Increasing

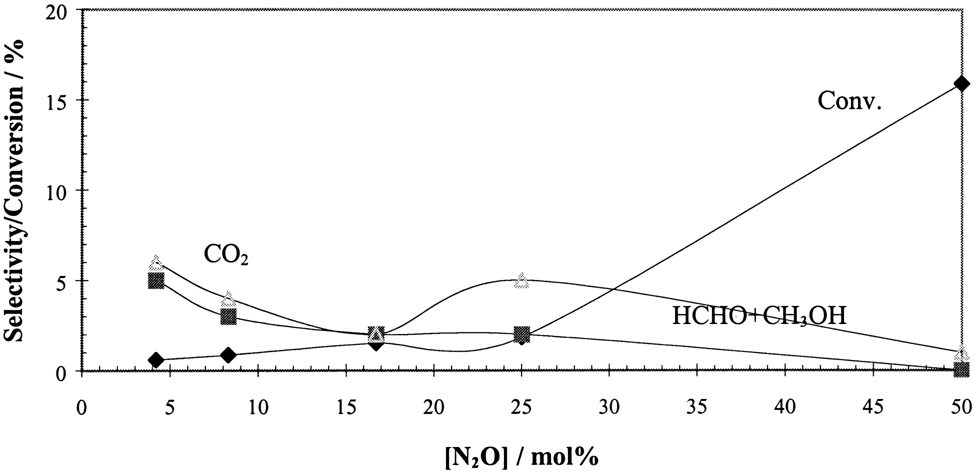

Fig. 4. The influence of feed N_2O content on selectivity to HCHO+CH_3OH, CO and CO_2, and methane conversion×10 over 2V–cabosil. 0.1 g catalyst, p=1520 kPa, T=550°C, F_{press}=24 ml min^{-1}.

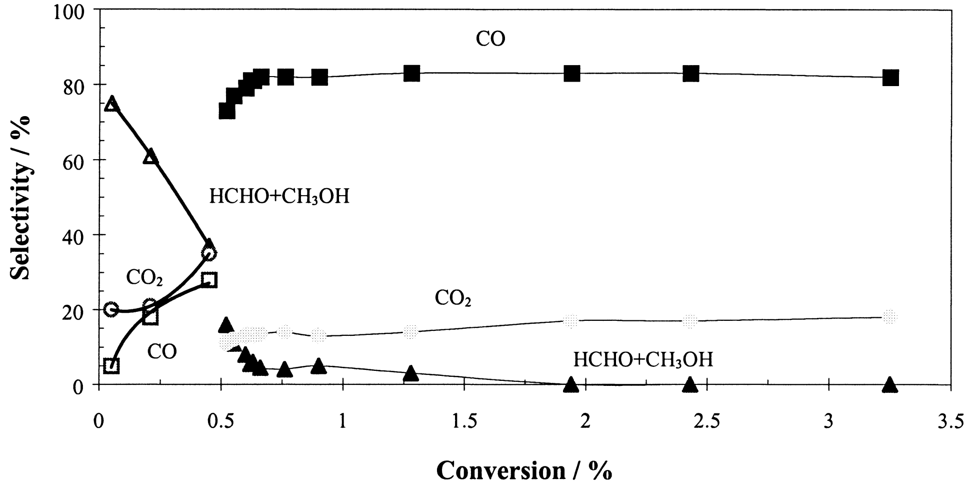

Fig. 5. Selectivities as a function of conversion over 7Mo–2Na–cabosil. Filled symbols refer to high pressure work, open symbols refer to ambient pressure work [1,2,18,19,21]. All data from the high pressure work used, irrespective of temperature or pressure.

methane conversion resulted in decreased formaldehyde selectivity in high pressure cases as was also observed in the ambient pressure work. The percentage conversions obtained in the high pressure experiments were higher than those at ambient pressure. Somewhat lower HCHO selectivities were obtained at high pressures. This agrees with selectivity–conversion relationships commented on previously [1,2,20,21]. Carbon oxide selectivities increased with increasing conversion in high pressure and ambient pressure cases.

3.6. *Partial oxidation of methane at elevated pressures using O_2*

Table 3 summarises the results obtained when oxygen, rather than nitrous oxide, was used as the oxidising agent at a pressure of 1520 kPa. These experiments

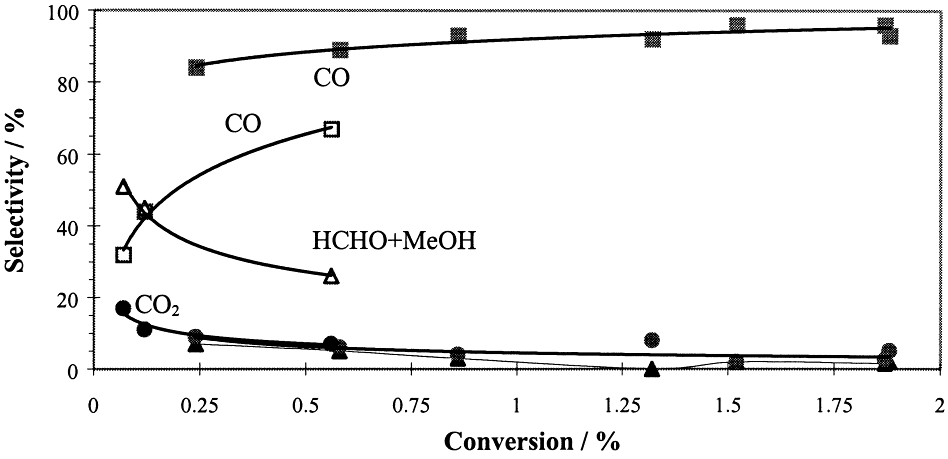

Fig. 6. Selectivities as a function of conversion over 2V–cabosil. Filled symbols refer to high pressure work, open symbols refer to ambient pressure work [1,2,18,19,21]. All data from the high pressure work used, irrespective of temperature or pressure.

were carried out at 550°C, with $CH_4/O_2=5$. A control experiment was carried out with an empty reactor, prior to testing 7Mo–2Na–cabosil and 2V–cabosil in oxygen.

It can be seen that a considerable degree of conversion was achieved in the absence of a catalyst (Table 3). This is in marked contrast to the corresponding tests in the presence of N_2O (Table 2). With oxygen, at 550°C, a conversion of 9.5% was obtained. In cases where a catalyst was used the conversions were 13.8% and 16.6% for 7Mo–2Na–cabosil and 2V–cabosil, respectively (Table 3). These values were larger by a factor of 10 than those obtained using nitrous oxide (refer to Table 2). No coupling products (C_2's or C_{2+}'s) were produced with N_2O, whereas a total selectivity to C_2 of 66% was obtained in the presence of oxygen. Another difference in behaviour of the two oxidants was the production of much more CO as the deeper oxidation product when N_2O was used (compare relative CO and CO_2 selectivities from Tables 2 and 3). With oxygen the dominant deep oxidation product was still CO (Table 3).

3.7. *The effect of pressure on the behaviour of 7Mo–2Na–cabosil with O_2 as oxidant*

Fig. 7 shows the effect of pressure on methane conversion over 7Mo–2Na–cabosil. At lower pressures the conversion was very small. A very small increase in conversion was noted on increasing the

Table 3
Performance of the catalysts using oxygen as the oxidant

Oxidation products (%)	Catalyst		
	None	7Mo–2Na–cabosil	2V–cabosil
Conversion	9.5	13.8	16.6
HCHO selectivity	1	4	2
CH_3OH selectivity	2	1	1
C_2H_4 selectivity	26	19	14
C_2H_6 selectivity	40	28	20
CO selectivity	12	25	41
CO_2 selectivity	19	23	22
Yield products[a]	0.3	0.7	0.5

0.1 g catalyst, $p=1520$ kPa, $T=550°C$, $CH_4/O_2=5$, $F_{press}=24$ ml min^{-1}.

[a] Partial oxidation products (HCHO and CH_3OH).

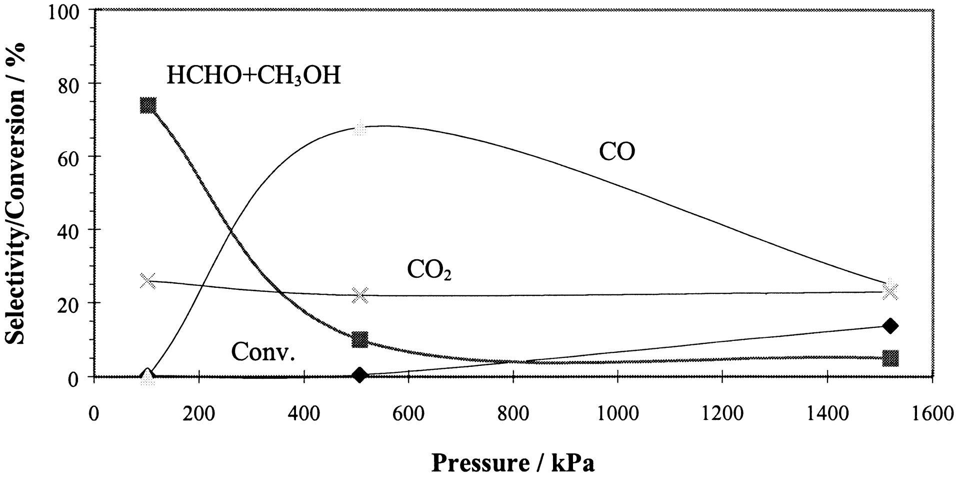

Fig. 7. Selectivities and CH_4 conversion as a function of pressure over 7Mo–2Na–cabosil. 0.1 g catalyst, $CH_4/O_2=5$, $T=550°C$, $F_{press}=24$ ml min^{-1}.

pressure from 101 (0.3% conversion) to 506 kPa (0.5%). On increasing the pressure from 506 to 1520 kPa a large increase in methane conversion from 0.45% to 13.5% was obtained.

The increase in conversion was accompanied by a decrease in HCHO selectivity (Fig. 7). The selectivity to CO_2 decreased slightly with pressure. Carbon monoxide selectivity went to a maximum at a pressure between 506 and 1013 kPa. No coupling products were detected at pressures at or below 1013 kPa. At 1520 kPa C_2 products were detected with a combined selectivity of 58%. The latter products were formed at the expense of CO.

3.8. Reactor temperature profiles

A comparison of the temperature profiles obtained with O_2 at 507 and 1520 kPa and with N_2O at 1520 kPa is shown in Fig. 8. When O_2 was used the temperature profile indicated an increase in temperature as the reactants approached the catalytic zone. At 507 kPa, the maximum (16°C higher than the exit of

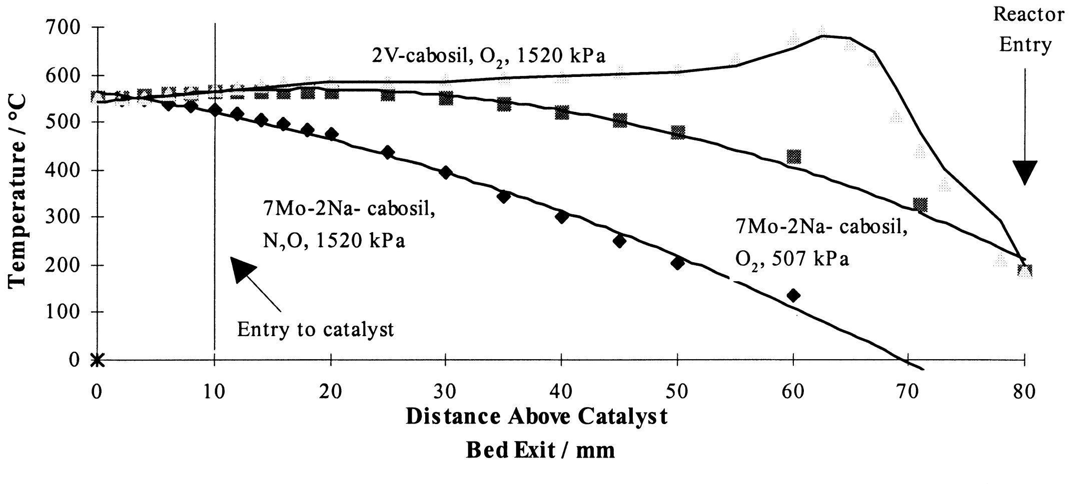

Fig. 8. Temperature profiles across the reactor. 0.1 g catalyst, $CH_4/O_2=5$, $T=550°C$, $F_{press}=24$ ml min^{-1}.

the catalytic region) appeared about 5 mm above the start of the catalyst bed, indicating that some of the reaction took place before the reactants encountered the catalyst body. A slight decrease in temperature was observed as the reactants flowed downwards through the catalyst.

When N_2O was employed at 507 kPa (not shown), the temperature increased until the reactor bed exit was reached. No maximum was noted before reaching the catalyst bed, indicating that heat generated from reaction only occurred in the catalyst bed.

When the profile was recorded for O_2 at 1520 kPa a completely different scenario emerged. As the reactant gas feed flowed down towards the catalyst a sharp increase in temperature was recorded. The maximum temperature (693°C) occurred about 65 mm above the catalyst bed. After this maximum the temperature decreased slowly, to 570°C, as the gas approached the catalytic region. The sharp maximum occurred at the point where the gases entered the heated zone of the furnace. This indicated that the reaction was occurring mainly in the gas phase, prior to contact with the catalyst.

The temperature profiles shown for O_2 at 507 and 1520 kPa show clear temperature maxima before the catalyst bed was encountered by the reactant gases and as such each profile is not dependent on the catalyst choice. The same could not be said of N_2O, where the maximum temperature was only encountered at the reactor exit. Hence, the temperature profiles obtained, at elevated pressures, were determined by the reaction conditions (reactant gas composition and operating pressure) rather than by the catalysts themselves.

4. Discussion

The selectivity-conversion plots shown in Figs. 5 and 6 demonstrate that similar behaviour is observed at ambient pressure and at elevated pressures, and that conversion is the primary factor which determines selectivity for the range of catalysts used in this study.

Oxygen is much more reactive than nitrous oxide. At elevated pressures it is capable of activating methane without the action of a catalyst, as shown by the exotherms in Fig. 8. However, when this activation occurs it is practically impossible to deliver, unreacted, a mixture of oxygen and methane to the catalyst bed. Hence, it is not possible to determine the efficiency of a catalyst in these conditions.

It is interesting to note that methanol was detected only at high pressures in the case of 2V–cabosil or 7Mo–2Na–cabosil. The observed relationship between the use of elevated reaction pressures and the emergence of methanol in the product stream may be explained in the context of the reactions outlined below (Eqs. (1)–(7))

$$CH_3^\bullet + O_2 \rightarrow CH_3O_2^\bullet \tag{1}$$

$$CH_3^\bullet + O \rightarrow CH_3O^\bullet \tag{2}$$

$$CH_3O_2^\bullet \rightarrow HCHO + OH^\bullet \tag{3}$$

$$CH_3O^\bullet \rightarrow HCHO + H^\bullet \tag{4}$$

$$CH_3O_2^\bullet + CH_4 \rightarrow CH_3OOH + CH_3^\bullet \tag{5}$$

$$CH_3OOH \rightarrow CH_3O^\bullet + OH^\bullet \tag{6}$$

$$CH_3O^\bullet + CH_4 \rightarrow CH_3OH + CH_3^\bullet \tag{7}$$

Formaldehyde results from the decomposition of the oxygenated radical species (formed in Eqs. (1) and (2)) via Eqs. (3) and (4), respectively. At low pressures the decomposition reactions are favoured by virtue of the fact that the radical concentrations are low, hence the possibility of further radical reactions occurring is relatively small. However, when the reaction is carried out at elevated pressures the concentration of the radicals and the possibility of radical reactions increases, thus, Eqs. (5)–(7) become significant. Hence, methanol is more likely to be observed in the product stream from the partial oxidation of methane at high pessures than under ambient pressure conditions.

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