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The effect of O_2 addition on the carbon dioxide reforming of methane over Pt/ZrO_2 catalysts

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Abstract

Pt/ZrO_2, Pt/Al_2O_3 and Ni/Al_2O_3 catalysts were found to be active in the temperature range 550–800°C under the conditions for both CO_2 reforming and partial oxidation of methane; of those, the Pt/ZrO_2 material was found to be least prone to deactivation. Combined CO_2 reforming and partial oxidation of methane was used to produce synthesis gas over the Pt/ZrO_2 catalyst. Higher yields of synthesis gas were obtained at lower temperatures than would be obtained with CO_2 reforming of methane alone. Combining the endothermic carbon dioxide reforming reaction with the exothermic partial oxidation reaction, hot spots in the catalyst bed were reduced significantly. Furthermore, the loss of activity of the catalyst with time on stream decreased with the amount of O_2 added to the feed stream; a small amount of carbon deposition occurred in parts of the catalyst bed which were not exposed to oxygen. The reaction pathway for the partial oxidation and the combined partial oxidation and reforming reactions appeared to be methane combustion followed by reforming of the remainder of the methane by the resultant CO_2 and steam.

Keywords: O_2; Carbon dioxide (CO_2); Methane; Pt/ZrO_2 catalysts

1. Introduction

The first reports of carbon dioxide reforming of methane were published in 1928 by Fischer et al. [1] who reported catalyst deactivation due to coking as the main obstacle to the development of the process. However, for both economic and environmental reasons, carbon dioxide reforming has become increasingly important over the past 10 years, and two industrial processes which utilise the reaction, the Calcor and SPARG processes [2–4] have been introduced. Carbon dioxide reforming produces a mixture of hydrogen and carbon monoxide (syngas), which may be used industrially for the synthesis of other products. Traditionally, syngas has been produced by either the gasification of coal or later, by the steam reforming of methane. However, for certain applications, carbon dioxide reforming has some advantages over the conventional steam reforming process which include a lower H_2-to-CO ratio, the possibility of producing higher purity carbon monoxide, possible usage in energy storage and/or transmission systems and superior economics [3].

Almost 100 papers have been published on the topic of CO_2 reforming since the late 1980s. Many of these papers report deactivation due to carbon deposition and thermodynamic calculations indicate that the formation of carbon is favoured when CO_2 and CH_4 are used without additives as a feedstock [5,6]. The

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higher carbon content in the feedstream compared with partial oxidation or steam reforming is also thought to be responsible for the higher level of carbon deposition on CO_2 reforming catalysts. A possible solution to the carbon deposition problem is to add either steam or oxygen to the feed, i.e. to couple methane – CO_2 reforming with methane – steam reforming or with the partial oxidation of CH_4. As CO_2 reforming is a highly endothermic process and thus requires a large amount of energy to proceed, coupling it with the exothermic partial oxidation reaction would also have economic advantages.

Combined catalytic partial oxidation and CO_2 reforming of methane has been reported by Vernon et al. [7]. They reported that transition metals supported on inert oxides are active for combined partial oxidation and CO_2 reforming. They obtained high yields of synthesis gas, without carbon deposition, using a 1% Ir/Al_2O_3 catalyst. They were also able to manipulate the CH_4:CO_2:O_2 ratio in order to achieve a thermoneutral reaction. Choudary et al. [8]. have also reported simultaneous catalytic reactions of CH_4 with CO_2 and O_2 over a NiO–CaO catalyst. They found that while coke formation was a serious problem for CO_2 reforming over this catalyst, little or no coking was found using the coupled process. Conversions above 95% were obtained and the catalyst did not deactivate during 20 h on stream at 850°C for the coupled process. These authors also suggested that it was possible to manipulate the process conditions to achieve a thermoneutral process. Inui et al. [9] carried out reactions using a feed containing CH_4, CO_2, O_2 and H_2O over a Ni–Ce_2O_3–Pt–Rh catalyst. They found that high rates of H_2 formation could be achieved using high flow rates which could not be achieved by partial oxidation or by reforming using steam and CO_2.

Our own research has shown that Pt/ZrO_2 is an active catalyst for the CO_2 reforming of methane; however, some deactivation of the catalyst occurred during the first 300 h of a 1000 h test [10,11]. We have also shown that this catalyst is active with little or no catalyst deactivation for steam reforming, partial oxidation, combined steam reforming and partial oxidation as well as combined steam and CO_2 reforming [12]. Therefore, a study of combined CO_2 reforming and partial oxidation of methane was carried out, the results of which are presented in this paper.

2. Experimental details

2.1. Catalyst preparation

1 wt.% Pt/ZrO_2 and 1 wt.% Pt/Al_2O_3 catalysts were prepared by wet impregnation of the calcined support with a solution of the metal salt. The ZrO_2 support was prepared by calcining $Zr(OH)_4$ extrudates supplied by Mel Chemicals XZ0706/3 in flowing air at 800°C for 15 h. The Al_2O_3 support (Akzo Nobel α-Al_2O_3, 001-3E) was calcined using the same conditions. The calcined sample was then crushed and sieved to obtain particles in the range 212–500 μm. The support was impregnated with a solution of chloroplatinic acid (H_2PtCl_6, PGP Industries). Following equilibration overnight, the excess solvent was removed by rotary evaporation and the sample was then oven-dried at 120°C for 2 h. The catalyst was subsequently calcined in air at 600°C for 6 h. The Ni/Al_2O_3 (ICI Katalco 54-3) catalyst was crushed and sieved to give particles in the range 212–500 μm before use.

2.2. Catalyst testing

Before each activity test, the catalysts were reduced in situ. This was achieved by heating the catalyst in a flow of 20 $cm^3\ min^{-1}$ N_2 and 5 $cm^3\ min^{-1}$ H_2, at a rate of 10°C min^{-1} to 400°C and remaining at this temperature for 1 h; the catalyst was then brought up to the reaction temperature in He and the reaction mixture was introduced. For the catalyst activity measurements the C:O ratio of the feed gases and total flow were held constant at 1 and 175 $cm^3\ min^{-1}$, respectively. The various gas compositions used are listed in Table 1. The activity tests were performed at different temperatures, ranging from 550°C to 800°C in steps of 50°C. The catalyst was kept for 2 h at each temperature, enabling a minimum of five analyses to be made. The loss in catalyst activity at 800°C was monitored for approximately 30 h. 50 mg of catalyst was used in each of these experiments, this being loaded into a quartz reactor with an internal diameter of 4 mm and held in place with quartz wool. The reactor was placed in a furnace which was controlled by a Eurotherm temperature controller. The gases flow rates were regulated by mass flow controllers (Tylan General FC-280). Samples were taken from the reactor effluent

Table 1
The various flow compositions used to investigate the effect of varying the gas composition on the catalyst activity from 550°C to 800°C and deactivation behaviour at 800°C

Test no.	CH_4 ($cm^3\ min^{-1}$)	CO_2 ($cm^3\ min^{-1}$)	O_2 ($cm^3\ min^{-1}$)	He ($cm^3\ min^{-1}$)	Total ($cm^3\ min^{-1}$)
1	25	25	0	125	175
2	30	20	5	120	175
3	35	15	10	115	175
4	40	10	15	110	175
5	45	5	20	105	175
6	50	0	25	100	175

every 20 min and analysed by gas chromatography (Hewlett Packard 5980 Series II).

2.3. Temperature bed profiles

In this series of experiments the conditions used for test numbers 1, 2, 4 and 6 (Table 1) were repeated and the catalyst bed temperatures were measured at intervals of 0.5 cm along the bed. A sample of 50 mg of the Pt/ZrO_2 catalyst was also used in these experiments, but it was diluted with 1.25 g of ZrO_2 (MEL Chemicals XZ0631/3) to give a catalyst bed length of 4.5 cm. A *k*-type thermocouple inside a quartz thermowell was used to measure the temperature along the catalyst bed.

2.4. Dispersion measurements

The platinum dispersions were measured by hydrogen chemisorption; the amount of catalyst used was 50 mg. Pulses which contained 2.4 cm^3 of 1% H_2/Ar were passed over the catalyst and the hydrogen uptake in each was monitored using a Thermal Conductivity Detector (TCD). The Pt dispersion was thence calculated on the assumption that each H atom adsorbs on one Pt atom.

2.5. Carbon deposition measurements

An Intelligent Gravimetric Analyser (IGA, supplied by Hidden Analytical) was used in these experiments. This microbalance can detect weight changes down to 0.1 μg and allows for simultaneous temperature, pressure and flow control. The catalyst was reduced in-situ at 400°C and then heated to 800°C in He before introducing the feed gases. Samples of 50 mg of the catalyst were used in these experiments and the feed compositions used are listed in Table 1 (Test numbers 1, 2, 4 and 6).

3. Results and discussion

3.1. Catalyst testing for CO_2 reforming and partial oxidation of methane

The activities for both the partial oxidation and CO_2 reforming of methane using dilute feeds of three different catalysts, viz., 1 wt.% Pt/ZrO_2, 1 wt.% Pt/Al_2O_3 and a commercial steam reforming Ni/Al_2O_3 catalyst were examined; the deactivation behaviours of the catalysts at 800°C were also investigated. The results of the partial oxidation experiments are shown in Table 2 and those for CO_2 reforming are shown in Table 3.

The Pt/Al_2O_3 catalyst emerged as the most active of the three for partial oxidation and only slight deactivation of the catalyst occurred; however, it was the

Table 2
CH_4 conversion recorded for CH_4 partial oxidation from 550°C to 800°C using 1wt.% Pt/ZrO_2 [12], 1wt.% Pt/Al_2O_3 and Ni/Al_2O_3 catalysts

Temperature (°C)	CH_4 conversion (%)		
	Pt/ZrO_2	Pt/Al_2O_3	Ni/Al_2O_3
550	77.7	81.2	47.9
600	81.5	85.0	50.1
650	85.3	88.6	53.3
700	88.9	91.9	56.7
750	91.9	94.7	59.4
800	94.6	96.7	62.6
Decrease in CH_4 conversion after 25 h at 800°C	0.6	1.2	7.7

Table 3
CH_4 conversion recorded for CO_2 reforming of CH_4 from 550°C to 800°C using 1wt.% Pt/ZrO_2 [12], 1wt.% Pt/Al_2O_3 and Ni/Al_2O_3 catalysts

Temperature (°C)	CH_4 conversion (%)		
	Pt/ZrO_2	Pt/Al_2O_3	Ni/Al_2O_3
550	13.9	6.4	13.3
600	18.1	10.9	17.9
650	30.7	16.8	26.9
700	44.7	31.1	37.5
750	66.3	45.4	50.2
800	74.9	58.5	60.0
Decrease in CH_4 conversion after 25 h at 800°C	3.1	6.6	5.7

least active catalyst of the three for CO_2 reforming and deactivated most rapidly under these conditions. Deactivation of Pt/Al_2O_3 catalysts during CO_2 reforming reported in the literature by van Keulen et al. and Seshan et al. is attributed to carbon deposition [10,13]; both sets of authors experienced significant deactivation of the catalyst in periods less than 25 h. For the case of partial oxidation over Pt/Al_2O_3 catalysts, Claridge et al. [14] reported that no carbon was deposited on this catalyst after 24 h on stream; however, no details of the loss of catalytic activity were given. The Ni/Al_2O_3 catalyst was less active and deactivated more extensively over a period of 25 h at 800°C than did the Pt/ZrO_2 catalyst for either of the two reactions; the deactivation was most likely due to coking. Dissanayake et al. [15] have reported that carbon deposition occurred during partial oxidation over a 25 wt.% Ni/Al_2O_3 catalyst, while Claridge et al. [14] have found that carbon was formed at a rate of 20.32 mg h^{-1} over a British Gas Ni/Al_2O_3 catalyst. As in our results the Pt/ZrO_2 catalyst was quite active and the most stable catalyst of the three samples tested for both the reactions, it was chosen for further study of the combination of CO_2 reforming and partial oxidation reactions.

3.2. *Combined CO_2 reforming and partial oxidation of methane*

In a series of screening experiments with 1 wt.% Pt/ZrO_2 catalyst some of the CO_2 in the reforming feed was replaced by O_2; the C:O ratio was held constant at 1. The effect of oxygen addition on CH_4 conversion at various temperatures between 550°C and 800°C is shown in Fig. 1. The addition of O_2 to the feed increase methane conversion considerably, especially at temperatures <700°C; a conversion of 30.7% was found for CO_2 reforming at 650°C but the value was 74.7% when 9 vol.% O_2 was added. This was almost certainly due to methane being converted by O_2 with a high selectivity towards CO_2 and H_2O, the products of CH_4 combustion, at lower temperatures (Eq. (1)); the

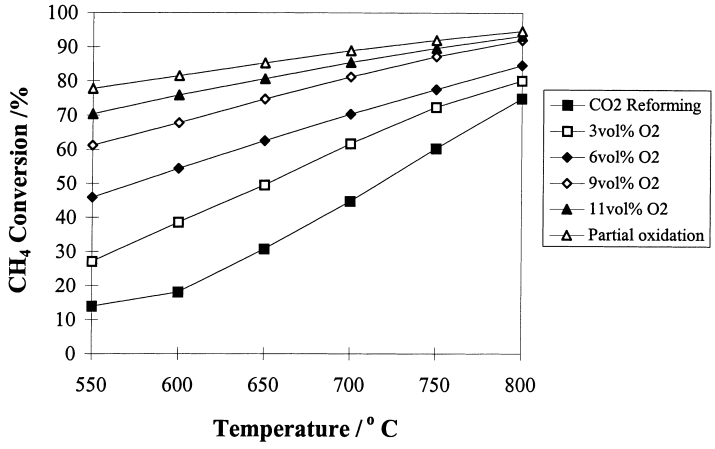

Fig. 1. CH_4 conversion vs. temperature for combined partial oxidation and CO_2 reforming of methane using different gas compositions over the 1 wt.% Pt/ZrO_2 catalyst.

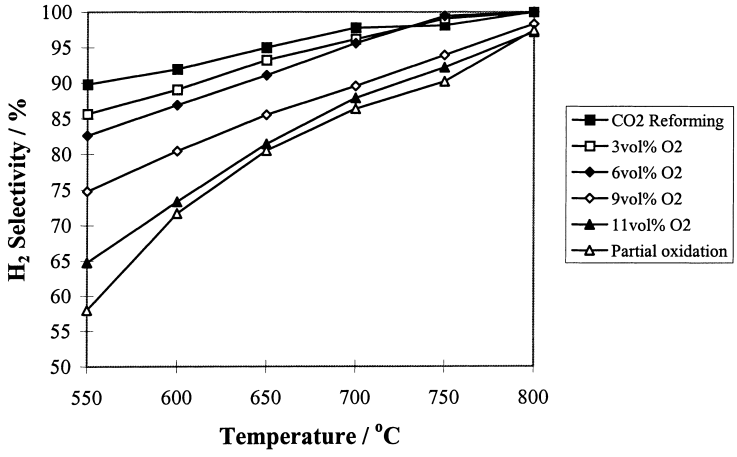

Fig. 2. The H_2 selectivity vs. temperature for combined partial oxidation and CO_2 reforming of methane using different gas compositions over the 1 wt.% Pt/ZrO_2 catalyst.

H_2 selectivities were then calculated to verify this.

$$\text{CH}_4\text{ combustion}: \ \text{CH}_4 + 2\text{O}_2 \Leftrightarrow \text{CO}_2 + \text{H}_2\text{O}$$
$$\Delta H_{298\,\text{K}} = -802\,\text{kJ mol}^{-1} \quad (1)$$

The experimental H_2 selectivities for combined CO_2 reforming and partial oxidation are shown in Fig. 2. The same trend as that predicted by thermodynamic calculations [16,17] was observed here; H_2 selectivity decreased with increased amounts of O_2 in the feed stream, this effect being more pronounced at lower temperatures. This implies that methane combustion occurred to a greater extent at lower temperatures and that this resulted in decreased H_2 selectivity. However, the occurrence of methane combustion at lower temperatures in the case of partial oxidation and the combined reaction feeds does not fully account for the high CH_4 conversions or H_2 selectivities at lower temperatures (e.g. 81.4% CH_4 conversion and 71.7% H_2 selectivity in the case of partial oxidation at 600°C). Methane combustion Eq. (1) is a highly exothermic reaction and therefore would cause an increase in catalyst bed temperature and this in turn would lead to increased CO_2 and steam reforming activity and thus to higher CH_4 conversions and selectivities to syngas. Indeed, large increases in catalyst bed temperature during methane partial oxidation have been reported by many authors [18–20] e.g. Chang and Heinemann [18] reported catalyst temperatures of 1200–1300°C with a furnace setting of 500°C.

3.3. *The reaction pathway of partial oxidation and combined partial oxidation and CO_2 reforming of CH_4*

Catalyst bed temperature profiles were determined in order to help elucidate the reaction pathway. It should be noted, however, that the results obtained were merely qualitative since the true temperature is very difficult to measure accurately: the thickness of an exceptionally hot zone may be very small [20]. The catalyst bed temperature profile obtained for reactions at 800°C are shown in Fig. 3. For partial oxidation, an exotherm was found at the start of the catalyst bed and this was followed by a large endotherm later in the bed. This indicates that the partial oxidation mechanism was methane combustion (Eq. (1)) followed by carbon dioxide and steam reforming:

$$\text{Steam reforming}: \ \text{CH}_4 + \text{H}_2\text{O} \Leftrightarrow \text{CO} + 3\text{H}_2$$
$$\Delta H_{298\,\text{K}} = +206\,\text{kJ mol}^{-1} \quad (2)$$

$$\text{CO}_2\text{ reforming}: \ \text{CH}_4 + \text{CO}_2 \Leftrightarrow 2\text{H}_2 + 2\text{CO}$$
$$\Delta H_{298\text{K}} = +261\,\text{kJ mol}^{-1} \quad (3)$$

Further evidence of this 'indirect' mechanism was provided when the catalyst from the reactor was examined after reaction; ZrO_2 used to dilute the catalyst was white in colour for the first 1 cm of the bed, indicating unreduced ZrO_2, while it was a grey colour in the remainder of the bed, indicating reduced ZrO_2. This was also observed by Hegarty [21] for

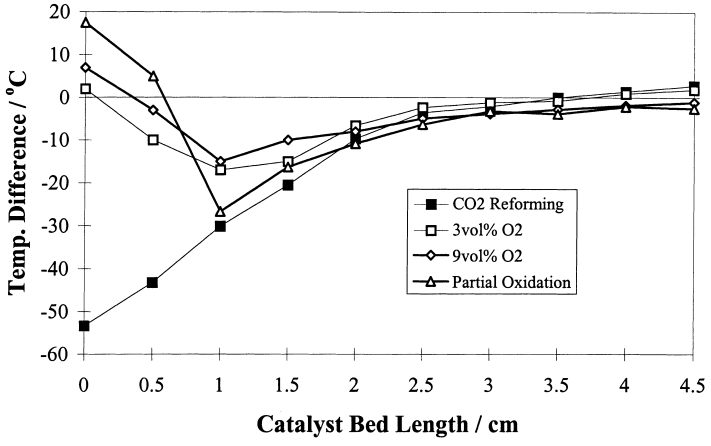

Fig. 3. Catalyst bed temperature profiles measured at a furnace set-point of 800°C for combined partial oxidation and CO_2 reforming of methane; the temperature difference refers to the measured bed temperature minus the furnace set-point temperature.

combined partial oxidation and steam reforming over the same catalyst.

In case of carbon dioxide reforming there was a large endotherm of >50°C at the start of the catalyst bed but the temperature decrease decreased in magnitude further down the bed. For the feed containing CH_4, CO_2 and O_2, both the endotherm associated with carbon dioxide reforming and the exotherm associated with partial oxidation were reduced considerably. This is advantageous as it reduced the temperature of the 'hot spots' in the catalyst bed, one of the main difficulties in operating the partial oxidation process reported in the literature [20,22]. The endotherm observed at the start of the catalyst bed for CO_2 reforming was also eliminated; this is also advantageous as a lowering of the temperature at the start of the catalyst bed increases the thermodynamic potential for carbon deposition; indeed a small amount of carbon was observed at the start of the catalyst bed following the CO_2 reforming test at 800°C, but this was not present following the use of O_2 containing feeds.

3.4. Deactivation studies

The effect of oxygen addition on CH_4 conversion with time on stream at 800°C of the Pt/ZrO_2 catalyst is shown in Fig. 4. For CO_2 reforming, the CH_4 conversion decreased by 4% over 30 h on stream, while for partial oxidation it decreased by only 0.5% over the

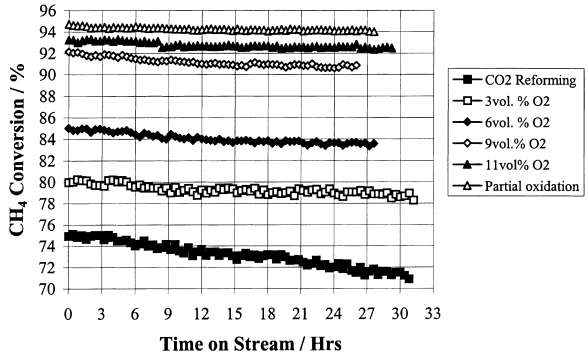

Fig. 4. CH_4 conversion as a function of time on stream at 800°C for combined partial oxidation and CO_2 reforming of methane.

same period of time. For the feed containing CH_4, CO_2 and O_2, methane conversion decreased to a greater extent when less oxygen was present; on addition of 3, 6, 9 and 11 vol.% O_2 CH_4 conversion decreased by 2.1%, 1.7%, 1.2% and 0.75%, respectively. Thus, the addition of oxygen helped to prevent deactivation of the catalyst. This was most probably due to less carbon being formed on the catalyst when O_2 was present in the feed. Similar results have been obtained by Choudary et al. [8] who experienced rapid deactivation of a Ni/CaO catalyst due to carbon deposition during CO_2 reforming, but little or no deactivation in the case of the coupled process after 20 h on stream. While deactivation under CO_2 reforming conditions over the Pt/ZrO_2 catalyst was not as severe as reported

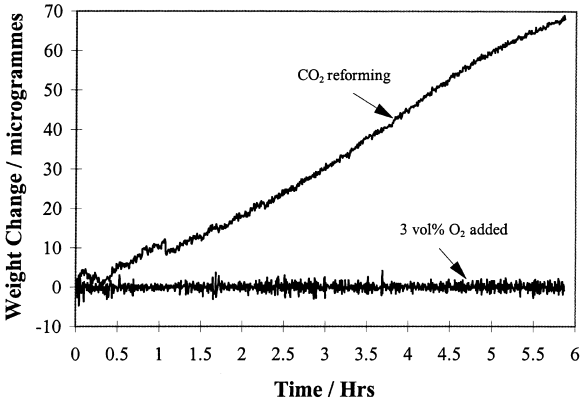

Fig. 5. Weight changes recorded during reaction at 800°C under CO_2 reforming conditions and with 3 vol.% O_2 added to the feed.

by these workers, the general trend of the results is the same.

Microbalance traces were performed to monitor weight changes during reaction for CO_2 reforming, for the coupled reaction with the addition of 3 and 9 vol.% O_2 and for partial oxidation. The results shown in Fig. 5 indicate that there was a constant weight increase as a function of reaction time for CO_2 reforming, but that when the feed contained a small amount of O_2 the weight remained constant. (There was no weight change recorded on addition of 9 vol.% O_2 or for conditions of partial oxidation alone and these results are therefore not shown). The weight gain observed for CO_2 reforming indicates that carbon was deposited on the catalyst during the reaction, with the amount of carbon deposited increasing with time on stream. In contrast, no weight gain was observed when O_2 was added to the feed and this indicates that no carbon was formed on the catalyst under these conditions.

It should be noted, however, that the geometry of the microbalance was not identical to that of the plug flow system used to test the catalyst; in the microbalance, all of the catalyst was exposed to O_2 while, in the plug flow system, all the O_2 appeared to be consumed at the start of the catalyst bed and a large portion of the catalyst did not, as a result, come into contact with O_2. As catalyst stability decreased with decreased amounts of O_2 in the feedstream and thus less of the catalyst was exposed to O_2, it is most likely that some carbon was deposited in the portion of the catalyst bed which was not exposed to O_2 during partial oxidation or combined CO_2 reforming and partial oxidation and that this resulted in slight deactivation.

Table 4
%Pt dispersions of the freshly reduced 1wt.% Pt/ZrO_2 catalyst and after 30 h on stream at 800°C

State of catalyst	Dispersion (%)
Freshly reduced 1 wt.% Pt/ZrO_2	49.3
Aged: CO_2 reforming	31.6
Aged: 3 vol.% O_2 added	26.3
Aged: 6 vol.% O_2 added	23.4
Aged: 9 vol. % O_2 added	21.1
Aged: 11 vol.% O_2 added	16.0
Aged: Partial oxidation	15.5

3.5. *Pt sintering*

Pt dispersion measurements were carried out on the used catalyst after 30 h on stream at 800°C and following 6 h in the microbalance at 800°C; these were compared to the Pt dispersion of the catalyst after reduction at 800°C. The results are presented in Tables 4 and 5. Pt dispersion of the catalyst after reduction was 49.3%, but the value decreased with increased amounts of O_2 in the feed stream; for example, following CO_2 reforming, the dispersion was found to be 31.6%, while, after partial oxidation, the dispersion was less than one-half that of the reduced catalyst. The catalysts which were aged in the microbalance had much lower dispersions than those aged in the plug flow system: when 3 vol.% O_2 was added to the feed, the Pt dispersion was found to be 26.3% on removal of the sample from the plug flow

Table 5
%Pt dispersions of the 1 wt.% Pt/ZrO_2 catalyst after 6 h on stream in the microbalance at 800°C. Also shown are the %Pt dispersions of the different portions of the plug flow reactor catalyst bed following 30 h under partial oxidation conditions at 800°C

State of catalyst	Dispersion (%)
Aged microbalance: CO_2 reforming	33.8
Aged microbalance: 3 vol.% O_2 added	15.8
Aged microbalance: 9 vol.% O_2 added	12.2
Aged microbalance: Partial oxidation	10.7
Aged 30 h: Partial oxidation, first 1 cm of catalyst bed	6.0
Aged 30 h: Partial oxidation, remainder of bed	28.3

system after 30 h, while, following 6 h in the microbalance, a value of 15.8% was obtained.

A possible reason why the Pt dispersion was much less in the case of the samples aged in the microbalance is that the entire catalyst was exposed to O_2, while in the plug flow system only the start of the bed was in contact with O_2. Sintering of Pt in Pt/ZrO_2 catalysts has also been observed by van Keulen [23] who found that extensive sintering of Pt occurred when a Pt/ZrO_2 sample was pre-treated in an oxidising environment at temperatures in excess of 650°C; after O_2 pre-treatment at 800°C, the Pt dispersion was only 3%. He also observed that when the same catalyst was pre-treated under reducing conditions, this extensive Pt sintering did not occur, probably as a result of a SMSI effect. Pt dispersion of the catalyst which had been located in the first 1 cm of the bed following methane partial oxidation (ca. 6%) was found to be considerably less than that of the remaining 3.5 cm of the bed which had a dispersion of 28.3%. As this sintering was most likely caused by the existence of oxidising conditions in the first 1 cm of the catalyst bed, this provides more evidence that all of the O_2 is utilised in combustion at the start of the bed, this being followed by reforming of the remaining methane by the combustion products further on in the bed.

4. Conclusions

Pt/ZrO_2 is both an active and stable catalyst for carbon dioxide reforming, partial oxidation of methane and also for these two reactions combined. High yields of synthesis gas were obtained at lower temperatures than those that would be required for CO_2 reforming, probably due to the occurrence of 'hot spots' in the catalyst bed. Slight deactivation of the catalyst was observed under all the conditions used; the loss of activity with time on stream decreased with the amount of oxygen added to the feed stream. A small amount of carbon deposition may have occurred in parts of the catalyst bed which were not exposed to oxygen. Temperature profile measurements through the catalyst bed indicated that a combination of the exothermic partial oxidation and endothermic carbon dioxide reforming reactions gave a more homogeneous profile than when carrying out either reaction alone. Catalyst bed temperature profiles, together with visual examination of the catalyst after reaction and Pt dispersion measurements, indicated that the reaction pathway for partial oxidation and combined partial oxidation and reforming reactions was methane combustion followed by reforming of the remainder of the methane by the resultant CO_2 and steam.

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