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Syngas production from natural gas using ZrO_2-supported metals

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Abstract

Samples containing 1 wt% of Co, Cu, Fe, Ni, Pd and Pt supported on zirconia have been tested for the steam reforming of methane at temperatures from 400°C to 800°C. The Pt, Pd and Ni materials were found to be the most active. Stability tests at 800°C showed that the Pt sample was the only stable catalyst, significant carbon deposition occurring on the other samples. Partial oxidation and CO_2 reforming of methane were also carried out over the Pt/ZrO_2 catalyst and this material was found to be quite stable under the conditions for these reactions. Additional CO_2 reforming and partial oxidation experiments were carried out using feeds to which steam was added. The H_2/CO ratio could be manipulated, depending on the feed composition used. The addition of steam during partial oxidation gave a much more stable temperature profile through the catalyst bed than was obtained under pure partial oxidation conditions. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Steam reforming; Pt/ZrO_2; Partial oxidation; CO_2 reforming

1. Introduction

The steam reforming of CH_4 is the primary route for the production of syngas [1–3].

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H^0_{298} = +206\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

However, the reaction produces a syngas having a H_2:CO ratio of 3:1 or greater; such a gas composition is only useful for processes requiring a H_2-rich feed such as NH_3 synthesis or iron ore reduction, and so the addition of the water-gas shift reaction is required:

$$CO_2 + H_2 \rightarrow CO + H_2O, \quad \Delta H^0_{298} = +41\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

Alternative syngas compositions can be obtained by processes such as CO_2 reforming or the catalytic partial oxidation (CPO) of CH_4, producing H_2/CO ratios of 1 and 2, respectively.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H^0_{298} = +261\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \quad \Delta H^0_{298} = -36\,\mathrm{kJ\,mol^{-1}} \tag{4}$$

Such H_2/CO ratios are required for processes such as the production of CH_3OH or CH_3COOH [4]. However, there is an increased risk of carbon being deposited on the catalyst under both CO_2 reforming and CPO conditions as compared to steam reforming conditions and this problem has hampered the use of existing steam reforming catalysts for these processes on an industrial level.

This paper gives results on the testing of novel zirconia-based catalysts for the steam reforming process. We have previously reported work on CO_2

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reforming of methane [5] showing that Pt/ZrO_2 is an effective formulation for this reaction. The ultimate aim of the present paper is to show that these zirconia-supported catalysts are effective in processes such as the CO_2 reforming of CH_4, the partial oxidation of CH_4, combined steam+CO_2 reforming and combined CPO+steam reforming. It is considered that the development of alternative catalysts which are more resistant to carbon deposition than are the existing steam reforming catalysts would offer two distinct advantages: firstly, the use of excess steam under industrial steam reforming conditions would not be necessary and hence there would be a reduction in the running costs of a steam reforming plant; secondly, these catalysts might also be used for the production of syngas of varying compositions using CO_2 reforming, CPO, or a combination of these reactions with steam reforming.

2. Experimental

All the catalysts were prepared by wet impregnation of a calcined ZrO_2 support material which also contains 6.8 wt% Al (MEL Chemicals, sample no. XZ0706/3) with a solution of the appropriate metal salt precursor. The precursors used were $Co(NO_3)_2{\cdot}6H_2O$ (BDH), $Cu(NO_3)_2{\cdot}3H_2O$ (BDH), $Fe(NO_3)_2{\cdot}9H_2O$ (BDH), $Ni(NO_3)_2{\cdot}6H_2O$ (Riedel-de Haen), $PdCl_2$ (Johnson Matthey) and H_2PtCl_6 (Johnson Matthey).

Before each activity test, the catalysts were reduced in situ in a mixture of 20% H_2 in N_2 (100 $cm^3\ min^{-1}$) at 400°C for 1 h. In the case of the steam reforming experiments, 130 mg of catalyst was used and the activity was measured at 50°C intervals in the temperature range 400–800°C. The total rate of flow was 130 $cm^3\ min^{-1}$ and the mixture had the following molar ratios: $N_2:H_2O:CH_4:H_2=3.6:2.64:1.0:0.46$; the H_2 was added to ensure reducing conditions throughout the catalyst bed. In the cases of CO_2 reforming, partial oxidation and combinations of those reactions, 50 mg of catalyst was used; the total rate of flow and C:O ratio were kept constant at 175 $cm^3\ min^{-1}$ and 1, respectively, with N_2 used as a diluent. A detailed description of the catalyst testing procedure has been given in a previous paper [5].

In experiments designed to measure temperature profiles in the catalyst bed, a 50 mg sample of catalyst was used, this being diluted with 1.25 g of ZrO_2 (MEL Chemicals XZ0631/3) to give a catalyst bed length of 6.4 cm. A k-type thermocouple inside an axial quartz thermowell was used to measure the temperature profile through the catalyst bed.

3. Results and discussion

3.1. *Testing of catalysts for the steam reforming of methane*

The effects of temperature on the CH_4 conversions were measured under steam reforming conditions for catalysts consisting of 1 wt% Cu, Co, Fe, Ni, Pd, and Pt supported on ZrO_2 and the results are shown in Fig. 1. Table 1 shows the CH_4 conversions obtained at 800°C and the corresponding H_2:CO ratios and cal-

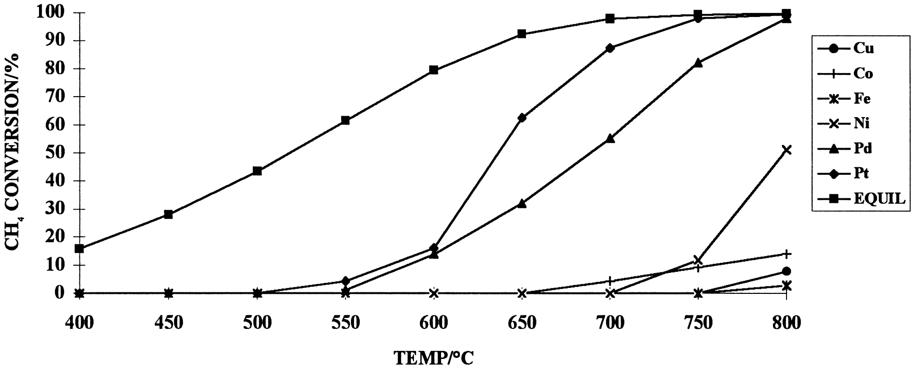

Fig. 1. CH_4 conversions versus temperature for steam reforming over a series of catalysts comprising of group VIII metals supported on ZrO_2; $CH_4:H_2O=1:2.64$, total flow=130 $cm^3\ min^{-1}$.

Table 1
The CH_4 conversions and the corresponding H_2:CO ratios for the steam reforming of methane at 800°C; also shown are the calculated experimental values of the equilibrium constant (K_{exp} WGS) for the WGS reaction based on the gas concentrations in the effluent stream

Catalyst	CH_4 conversion (%)	H_2:CO ratio	K_{exp} WGS
Pt/ZrO_2	98.6	5.6	1.60
Co/ZrO_2	14	7.6	0.09
Fe/ZrO_2	3	31.1	n/c
Cu/ZrO_2	8	16.0	0.18
Ni/ZrO_2	51	4.7	0.23
Pd/ZrO_2	98	3.7	0.55
Equilibrium	99.8	5.2	1.1

culated apparent equilibrium constants (K_{exp}) for the water-gas shift reaction, based on the concentrations of the appropriate gases in the effluent stream; the thermodynamic calculations were carried out using the HSC software package [7]. The 1 wt% Pt/ZrO_2 catalyst had the highest activity over the whole temperature range investigated; the conversion ranged from 4% at 550°C to 98.6% at 800°C. The H_2:CO ratio in the product stream was 5.6, as compared with 5.24 predicted from the thermodynamic calculations. The value of K_{exp} for the water-gas shift reaction over the Pt material was found to be 1.6 and this should be compared with the value of the equilibrium constant (K_{eq}) for this reaction at 800°C of 1.1 calculated using the HSC software [7]. This indicates that the approach to equilibrium for the water-gas shift reaction over the Pt sample was from the CO_2–H_2 rich side; the CO_2 is probably formed by the reaction of steam with CH_4 (reaction (5)) and the CO is then formed via the reverse water-gas shift reaction (reaction (6)). This also accounts for the observation that the H_2:CO ratio over the catalyst had a higher value than that predicted by thermodynamics. It therefore appears that the product composition over the Pt material under these reaction conditions is a function primarily of the reforming reaction and that the water-gas shift reaction does not come to equilibrium.

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2, \quad \Delta H^0_{298} = +163.8\,\mathrm{kJ\,mol^{-1}} \tag{5}$$

$$CO_2 + H_2 \rightarrow CO + H_2O, \quad \Delta H^0_{298} = +41.2\,\mathrm{kJ\,mol^{-1}} \tag{6}$$

The 1 wt% Pd/ZrO_2 catalyst showed (see Fig. 1) the next highest CH_4 conversion, ranging from 2% at 550°C to 98% at 800°C. Table 1 shows that the H_2:CO ratio and the value of K_{exp} for the water-gas shift reaction at 800°C were 3.7 and 0.55, respectively. This indicates, in contrast to the Pt material, that the approach to equilibrium for the water-gas shift reaction for the Pd–ZrO_2 catalyst is probably from the CO and H_2O side, the CO being formed by the reaction of steam with CH_4 (reaction (1)) and CO_2 then being formed via the water-gas shift reaction (reaction (2)).

Of the remaining catalysts, the 1 wt% Ni/ZrO_2 catalyst exhibited the highest CH_4 conversions, ranging from 1% at 700°C to 51% at 800°C. The H_2:CO ratio in the product stream was 4.7 and the value of K_{cal} for the water-gas shift reaction was 0.23, indicating that for this catalyst also the reaction was not at equilibrium under these conditions; as with the Pd material, the approach to equilibrium appeared to be from the CO and H_2O side. In contrast to the catalyst containing Ni-, Pt- and Pd-based catalysts, the remaining materials, Fe, Cu and Co on zirconia, exhibited very low CH_4 conversions at 800°C; the CH_4 conversions were 3%, 8% and 14%, respectively. Further, these three catalysts exhibited significant deactivation at higher temperatures during the screening experiments. It was found that carbon deposition was responsible for this deactivation since regeneration could be achieved by exposing the catalysts to a flow of 50 cm^3 min^{-1} of 20% H_2O/N_2 at 800°C; during the regeneration process, measurable quantities of CO and H_2, presumably formed by reaction (7), could be detected.

$$C + H_2O \rightarrow CO + H_2, \quad \Delta H^0_{298} = +135\,\mathrm{kJ\,mol^{-1}} \tag{7}$$

The activities for the steam reforming of CH_4, determined on the basis of CH_4 conversion, were found to decrease in the order Pt, Pd>Ni≫Cu, Co and Fe, for the series of samples supported on the MEL–ZrO_2 material. This order agrees with that reported by Rostrup Nielsen for MgO-supported catalysts [3]; this author found that Pt and Pd were far more active than Ni for the steam reforming reaction and that metals such as Co and Fe were very inactive.

Fig. 2 shows the results of tests carried out at 800°C using the Pt, Pd and Ni samples for steam reforming in

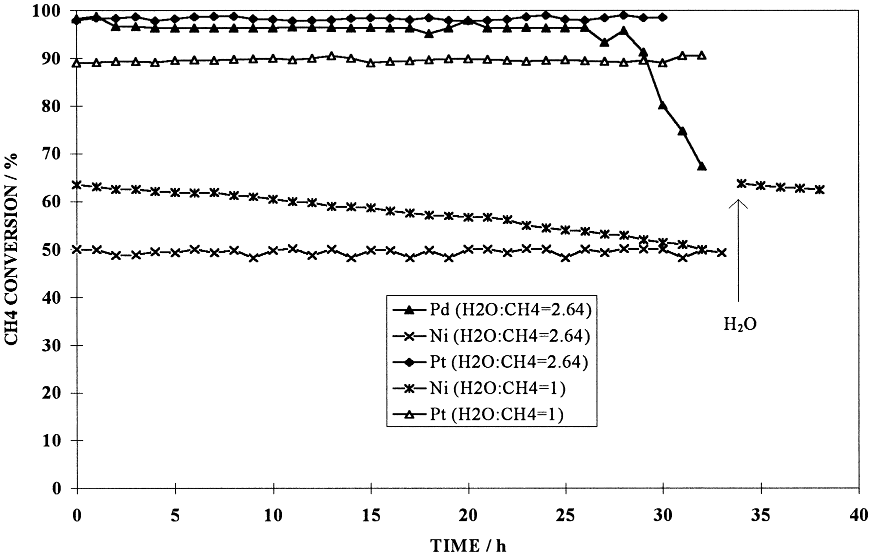

Fig. 2. CH_4 conversion versus time for stability tests carried under steam reforming conditions over Ni, Pd and Pt supported on ZrO_2 using different H_2O:CH_4 ratios (2.64 or 1) at 800°C; the total flow rate used for all the experiments was 130 cm^3 min^{-1}, the arrow indicates that a 20% H_2O/N_2 mixture was passed over the catalyst.

the presence of excess steam (H_2O:CH_4=2.64:1); these experiments were carried out to test the stabilities of the samples under these conditions. The Ni and Pt samples maintained constant conversions throughout the duration of the experiments (ca. 33 h); however, the conversion over the Pd sample, initially ca. 96%, began to drop after about 28 h on stream, reaching a value of 64% after 33 h of use. Attempts to regenerate this catalyst in a flow of 50 cm^3 min^{-1} of 20% H_2O/N_2 at 800°C were unsuccessful. When the sample was removed from the reactor tube, it was a solid black mass, from which it is concluded that the deactivation was due to the deposition of massive carbon. Fig. 2 also shows the CH_4 conversions over the Ni-based and Pt-based catalysts for operation under more extreme steam reforming conditions using a H_2O:CH_4 ratio of 1:1. The Pt sample now gave a conversion of 90% and this remained constant throughout the duration of the experiment (33 h). However, the Ni sample deactivated in a linear fashion during the first 32 h of the experiment, dropping from an initial conversion of CH_4 of 64% to a final value of 51%, apparently again as a result of carbon deposition; the activity could then be regenerated almost completely, to give 63% conversion, by exposing the catalyst to a flow of 50 cm^3(STP) min^{-1} of 20% H_2O/N_2, with the simultaneous production of CO and H_2 (reaction (7)). We conclude that the Pt/ZrO_2 material is considerably more resistant to carbon deposition than the Ni/ZrO_2 material under our reaction conditions.

3.2. *Behaviour of the* Pt/ZrO_2 *catalyst for methane partial oxidation and for* CO_2 *reforming*

The Pt/ZrO_2 catalyst was tested for its activity and stability under both partial oxidation and CO_2 reforming conditions. The results of the activity tests for those two reactions are shown in Fig. 3. At lower temperatures (<750°C) the conversion of CH_4 was much greater in the case of partial oxidation than in that of CO_2 reforming. This appears to be due to the occurrence in the former case of the methane combustion reaction (Eq. (8)) at the lower temperatures, the main products being CO_2 and H_2O.

$$CH_4+2O_2\rightarrow CO_2+H_2O,\quad \Delta H^0_{298}=-802\,\mathrm{kJ\,mol^{-1}} \tag{8}$$

However, at temperatures above about 750°C the

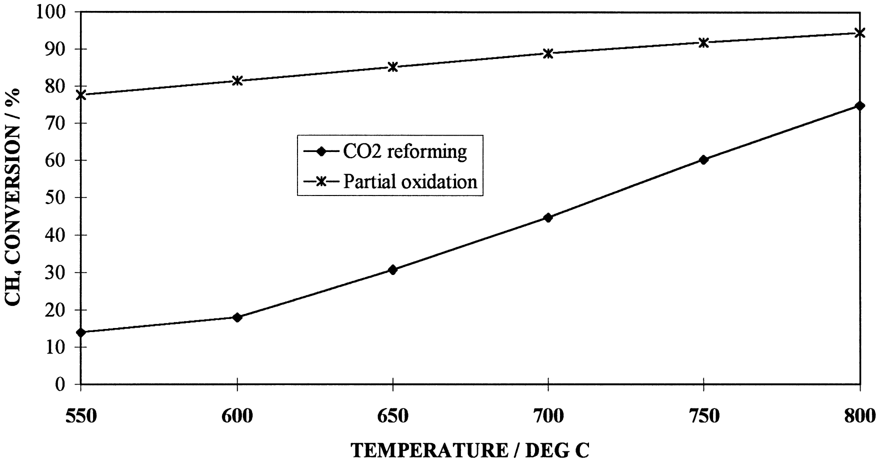

Fig. 3. Activity experiments over a 1 wt% Pt/ZrO_2 catalyst under CO_2 reforming (CH_4:CO_2=1:1) and partial oxidation (CH_4:O_2=2:1) conditions; total flow rate of reactants was 175 cm^3 min^{-1}.

main products of partial oxidation were CO and H_2. These results indicate that the reaction sequence is probably first methane combustion, followed by reforming of the remaining methane by the resultant CO_2 and H_2O; this is in agreement with the conclusions of other studies of methane partial oxidation over supported noble metal catalysts reported in [8,9]. The Pt/ZrO_2 catalyst was also reasonably active for CO_2 reforming under the conditions tested, giving a CH_4 conversion of 75% at 800°C. Data showing the conversions of methane as a function of time over the Pt/ZrO_2 catalyst under both partial oxidation and CO_2 reforming conditions at 800°C are shown in Fig. 4. It can be seen that the catalyst deactivated more under CO_2 reforming conditions than under partial oxidation conditions, there being a decrease in CH_4 conversion of 0.6% after 25 h on stream in the case of partial oxidation and one of 3.1% for CO_2 reforming over the same time span. The results for the CO_2 reforming reaction are similar to those reported by us earlier for the same catalyst using an undiluted feedstock (CO_2/CH_4=2) [5,6]. This work showed that the deactivation in this case was due to carbon deposition. This deposition was much lower than that found with other catalysts such as Pt/TiO_2 or Pt/Al_2O_3. The lower level of deactivation for the CH_4/O_2 reaction was probably

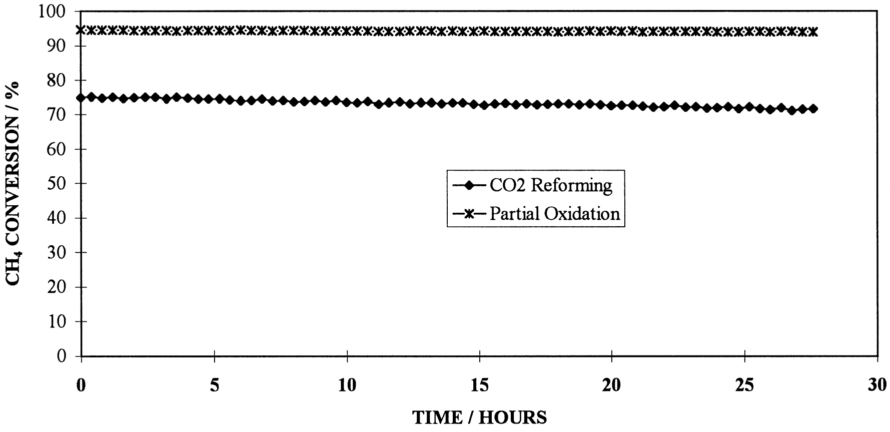

Fig. 4. CH_4 conversion versus time for stability tests carried under CO_2 reforming (CH_4:CO_2=1:1) and partial oxidation (CH_4:O_2=2:1) conditions over a 1 wt% Pt/ZrO_2 catalyst at 800°C; total flow rate of reactants was 175 ml min^{-1}.

Table 2
Calculated and measured CH_4 conversions and H_2:CO ratios for combined partial oxidation and steam reforming of methane at 800°C for different proportions of O_2 and H_2O; vol% CH_4=12.87, balance N_2

H_2O (vol%)	O_2 (vol%)	Equilibrium CH_4 conversion	Actual CH_4 conversion	Equilibrium H_2/CO ratio	Actual H_2/CO ratio
0	6.43	98	97	2.00	1.99
6.69	3.38	97	80	2.60	2.52
10.04	1.56	97	74	3.02	2.81
12.87	0	96	60	3.84	3.05

due to the inhibition of carbon deposition in the presence of oxygen [10].

3.3. *Combined partial oxidation and steam reforming of* CH_4

Since the steam reforming reaction over the Pt/ZrO_2 catalyst showed no loss of activity (see Fig. 2), it was of interest to see whether the behaviour of the Pt catalyst for the partial oxidation and CO_2 reforming reactions would be better with steam added. Table 2 shows the effect of replacing O_2 by various quantities of H_2O on the CH_4 conversions and H_2:CO ratios over the Pt sample at 800°C. Replacing the O_2 by steam resulted in a decrease in the CH_4 conversion and the product composition was also affected by the presence of O_2, the H_2:CO ratio increasing from 2.52 to 3.05. The stability of the Pt catalyst was improved by the addition of O_2, there being no significant deactivation after 15 h for all the feed compositions reported in Table 2. The effect of H_2O addition on the H_2:CO ratio can be explained by the occurrence in parallel of steam reforming and partial oxidation over the Pt sample, the partial oxidation of CH_4 producing a ratio of 2 and steam reforming producing a ratio of 3 or higher due to the effect of the water-gas shift reaction. The increase in CH_4 conversion upon the addition of the O_2 is presumably due to a dual effect: firstly, the rapid combustion of a portion of CH_4 with all of the O_2 present and, secondly, the increased rate of the endothermic reforming reactions as a result of a temperature rise within the bed due to the exothermic combustion reaction. The existence of an exotherm during steam reforming in the presence of O_2 was confirmed by recording temperature profiles through the bed during reaction (Fig. 5).

3.4. *Combined* CO_2 *and steam reforming of* CH_4

Fig. 6 shows the effect of the addition of various amounts of steam to the CO_2 reforming reaction mixture on the CH_4 conversion over the catalysts; steam addition caused an increase in conversion, the effect being more apparent at the higher temperatures.

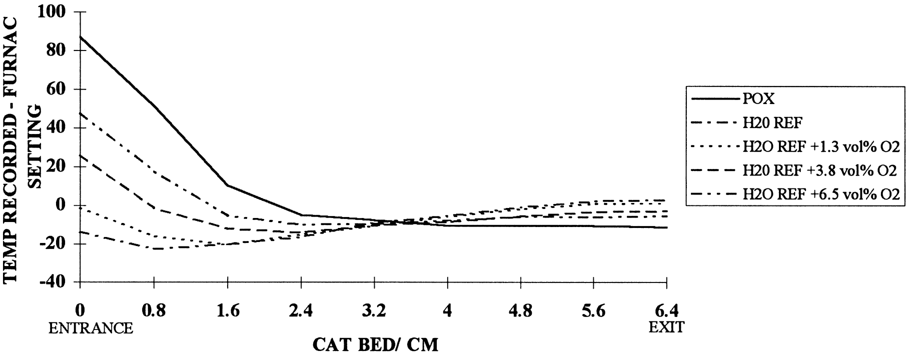

Fig. 5. Temperature profiles in the catalyst bed under combined partial oxidation and steam reforming conditions. The conditions were the same as those for Table 2.

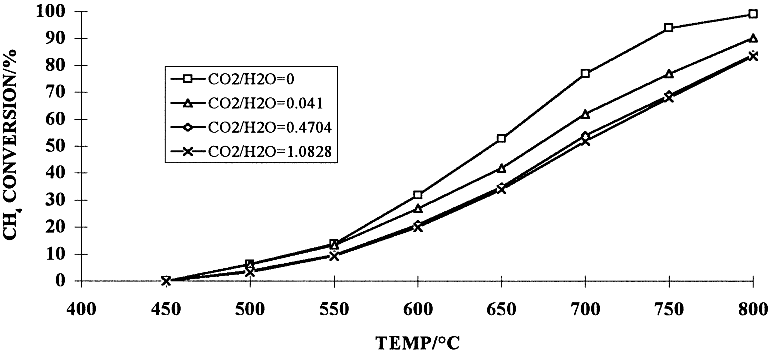

Fig. 6. CH_4 conversion versus temperature under combined CO_2 and steam reforming conditions; the H_2O and CO_2 vol% are listed in Table 2 and vol% CH_4=12.87.

The product composition over the catalysts also varied with varying feed composition. The H_2:CO ratio found for CO_2 reforming at 800°C was 0.90 while that in the presence of 16.3 vol% steam was 1.82. This effect on product composition was observed over the whole temperature range (see Table 3). It can therefore be concluded that it is possible to tailor the product composition (H_2:CO ratio) by varying the CO_2:H_2O ratio in the feed.

The decrease in the H_2:CO ratio is not surprising since the stoichiometric CO_2 reforming reaction produces a H_2:CO ratio of 1 while the steam reforming reaction produces a H_2:CO ratio of 3. It is therefore reasonable to expect that intermediate H_2:CO ratios would be produced on combining the two. The data of the last column of Table 1 show that the water-gas shift reaction was not at equilibrium under reaction conditions; the equilibrium constant (K_{eq}) for the WGS at 800°C is 1.1, while the calculated experimental constant (K_{exp}) for the reaction increased from 1.6 to 4.87 with decreasing steam concentration in the feed. It would be expected that if the WGS reaction occurred to any significant extent over the catalysts under these conditions, the presence of CO_2 in the feed would drive the reaction in the direction of H_2O and CO, leading to a decrease in the value of K_{exp}. However, as this was not the case, it seems that the WGS reaction is far for equilibrium, although it does occur to some extent. It is therefore to be accepted that the WGS reaction does not dictate the H_2:CO ratio in the effluent stream under these conditions and that this ratio is instead a function of the CO_2 reforming and steam reforming reactions.

4. Conclusions

The activity for steam reforming over zirconia-supported metal catalysts was found to decrease in the order Pt, Pd>Ni≫Cu, Co and Fe. The Cu, Co and Fe catalysts exhibited significant deactivation, despite the presence of excess steam. The catalysts containing Pt and Ni remained stable in the presence of excess steam; however, with equimolar amounts of H_2O and

Table 3
Calculated and measured CH_4 conversions, H_2/CO ratios and K_{exp} WGS for the combined CO_2 and steam reforming of methane at 800°C for different proportions of H_2O and CO_2; vol% CH_4=12.87, balance N_2

H_2O (vol%)	CO_2 (vol%)	Equilibrium CH_4 conversion	Actual CH_4 conversion	Experimental H_2/CO ratio	K_{exp} WGS
16.13	17.7	99.70	83.6	1.82	4.87
23	11	99.77	86.8	2.91	1.73
36.6	1.4	99.8	90.3	5.06	1.38
34	0	99.9	99.2	5.60	1.60

CH_4, the Ni catalyst deactivated due to carbon deposition while the Pt catalyst maintained its activity. The Pt/ZrO_2 material also proved to be an active and stable catalyst for both CO_2 reforming and partial oxidation of methane. The presence of steam in the partial oxidation feed increased the CH_4 conversion and decreased the H_2:CO ratio in the products. The Pt/ZrO_2 catalyst was found to be stable under all CPO+steam reforming feeds tested. Steam addition to the CO_2 feed increased both the CH_4 conversion and the H_2:CO ratio. It was found possible to tailor the H_2:CO ratio by altering the O_2:H_2O or CO_2:H_2O ratio in the feed.

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