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Partial oxidation and combined reforming of methane on Ce-promoted catalysts

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Abstract

Pt/ZrO_2 and $Pt/Ce_{0.14}Zr_{0.86}O_2$ catalysts containing 0.5 and 1.5 wt.% Pt were studied in order to evaluate the effect of the support reducibility and metal dispersion on the catalyst stability for the partial oxidation and the combined partial oxidation and CO_2 reforming of methane. The $Pt/Ce_{0.14}Zr_{0.86}O_2$ catalysts proved to be more active, stable and selective than Pt/ZrO_2 catalysts during the partial oxidation reaction. No increase in deactivation was observed when the CH_4:O_2 feed ratio was increased from 2:1 to 4:1. In addition, no water formation was observed at the high CH_4:O_2 ratios. The activity of the catalyst is dependent upon both the dispersion and the ability of the catalyst to resist carbon deposition.

The addition of CO_2 resulted in a decrease in the methane conversion and a decrease in the H_2/CO ratio for the $Ce_{0.14}Zr_{0.86}O_2$ and ZrO_2 supported catalysts. Small increases in the temperature of the bed have been recorded during the partial oxidation reaction. However, within a few minutes the temperature stabilizes below the furnace temperature providing indirect evidence for the combined combustion and reforming mechanisms previously proposed. The 1.5 wt.% $Pt/CeZrO_2$ catalyst shows promise for the autothermal reforming reaction based on the stability during transient operation.

Keywords: Partial oxidation of methane; Dry reforming; $Pt/Ce_xZr_{1-x}O_2$ catalysts; Synthesis gas production

1. Introduction

Increasing concern about world dependence on petroleum oil has generated interest in the use of alternative fuel sources. The reforming of many hydrocarbon feeds is currently being investigated including bio-based materials, such as ethanol, sunflower oil, and biomass derived oils [1–4]. However, the most common feedstock is still natural gas due to the abundance and inexpensive nature.

Many of the natural gas reservoirs are located in remote regions, making the recovery and transportation cost prohibitive [5]. The conversion of natural gas into transportation fuels such as gasoline and diesel is an alternative to the prohibitive transportation costs. The so-called gas-to-liquids technology (GTL) is based on the conversion of natural gas to a synthesis gas prior to the liquid production through the Fischer–Tropsch synthesis [6]. The syngas generation is the most capital and energy intensive part of the production plant, responsible for 50–75% of the capital cost [7]. Therefore, the economic viability of GTL technology depends on optimizing the process for syngas production. Autothermal reforming (ATR) fulfils the requirements to a syngas with H_2/CO ratio of 2, the ratio necessary to GTL plant [8–15]. Moreover, ATR has relative compactness, lower capital cost and greater potential for economy of scale [16]. ATR combines non-catalytic partial oxidation with steam reforming in one reactor. The ATR technology requires the addition of CO_2 or CO_2-rich gas, in order to adjust the syngas composition to the desired H_2/CO ratio [17].

In addition to the problems with carbon deposition during reaction with methane, catalyst stability in the presence of

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O_2, CO_2, and H_2O can be a significant issue. Previous studies have shown that the addition of promoters such as Ce and La to ZrO_2 result in improved catalytic performance for the dry reforming reaction [18]. The increased activity and stability of the mixed oxide is ascribed to both the higher dispersion on the promoted supports and, the ability of the support to facilitate carbon removal from the metal through a support redox mechanism.

The use of CeO_2 as a support and as a promoter has also been studied for the partial oxidation reaction [19,20]. The selectivity to synthesis gas was found to be dependent on the degree of CeO_2 reduction on Pt/CeO_2 and Rh/CeO_2 catalysts [20]. Furthermore, a correlation was seen between the selectivity to synthesis gas and the CeO_2 content of $Pt/CeO_2/Al_2O_3$ [19]. Partial oxidation studies performed on Ni/CeO_2 [21] and $Pt/Ce_{0.75}Zr_{0.25}O_2$ [22] have demonstrated that the stability of the catalyst is dependent upon the metal dispersion. Similar to the dry reforming studies on the Ce–Zr mixed oxides, the stability of the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst was ascribed to the high oxygen storage capacity of the support. The higher amount of oxygen vacancies near the metal particles promotes the mechanism of carbon removal from the metallic surface, which takes place at metal-support interfacial perimeter. Thus, dispersion impacts not only the rate of methane decomposition by also the metal-support interfacial area.

Several studies have been performed on the dry reforming reaction in the presence of oxygen [23–29] over Pt, Ni, and Ir based catalysts. O'Conner and Ross [23] reported that minimal deactivation occurred for the combined partial oxidation and dry reforming reaction on a 1% Pt/ZrO_2 at low space velocities and with a diluted feed. The conversion of methane was found to increase with oxygen content but the selectivity towards H_2 decreased. The decrease in H_2 selectivity was more pronounced at lower temperatures where the formation of CO_2 and H_2O were favored. The reaction mechanism was proposed to proceed through combustion followed by steam and CO_2 reforming.

This paper focuses on the partial oxidation and combined partial oxidation and reforming reactions over $Pt/Ce_{0.14}Zr_{0.86}O_2$ and Pt/ZrO_2. Specifically, the effect of varying the methane, oxygen, and carbon dioxide contents in the feed has been investigated.

2. Experimental

2.1. Catalyst preparation

ZrO_2 and cerium (18 wt.%)-doped ZrO_2 ($Ce_{0.14}Zr_{0.86}O_2$) were obtained from Magnesium Elektron Inc. Prior to the addition of the metal the supports were calcined at 1073 K in a muffle furnace for 4 h. BET single point surface area analysis was carried out in a Micromeritics Gemini II 2370 apparatus after the high temperature calcination. The measured surface areas of the supports are 29 m^2/g for the ZrO_2 and 48 m^2/g for the $Ce_{0.14}Zr_{0.86}O_2$. Pt was added to the supports using incipient wetness impregnation of an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$. The metal loadings investigated were 0.5 and 1.5 wt.%. All of the catalysts were dried overnight at 393 K, and the calcined at 673 K for 2 h in air (50 ml/min).

2.2. Activity studies

Prior to reaction, the catalysts were reduced in situ in H_2 (30 ml/min) at 773 K for 1 h and then heated to 1073 K in He (15 ml/min). The reaction experiments were performed in a 10 mm i.d. quartz reactor at atmospheric pressure and 1073 K. For all of the reactions the catalysts were diluted with a 3:1 ratio of SiC to catalyst to minimize heat effects. The total metal loading for each reaction was held constant by using 20 and 60 mg of catalyst for the reactions on the 1.5 and 0.5 wt.% catalysts, respectively. The total flow rate of the reaction mixture was 100 cm^3/min. For the partial oxidation studies, $CH_4:O_2$ ratios of 2:1, 3:1 and 4:1 were investigated. Two sets of the combined dry reforming and partial oxidation experiments were performed. The first set fixed the C:O ratio at 1:1 and the total flow rate at 100 ml/min. The $CH_4:CO_2:O_2$ ratios studied were 4:2:1 and 3:1:1. The second set of experiments fixed the $CH_4:(CO_2 + O_2)$ ratio at 1:1 and the total flow rate at 120 ml/min. The C:O ratios studied were 1, 0.88, and 0.84. The reactor effluent was analyzed using an SRI GC equipped with a TCD and a Supelco Carboxen 1010 Plot capillary column (30 m, 0.53 mm i.d.). Quantification of the species in the effluent was performed by using calibration injections of known mixtures. Verification of the calibration was performed before every experiment using the reaction mixture flowing through a bypass line.

2.3. Catalyst characterization

Since H_2 and CO adsorption can occur on Ce-containing supports [30] it is not possible to accurately determine the Pt dispersion using chemisorption. In order to measure the Pt dispersion on the catalysts investigated, Transmission electron microscopy (TEM) was performed at the University of Kansas Electron Microscopy Laboratory on a JEOL 1200 EXII microscope. The samples were exposed to the reduction at 773 K in hydrogen and then heated to 1073 K in Ar under identical conditions as stated in the reaction pretreatment. The samples were then cooled to room temperature in Ar after which a small portion of the sample was prepared for TEM analysis. Micrographs of the catalysts were taken at 120 keV with magnifications of 100–500 K. Average particle sizes were determined by counting over 100 particles from at least 15 different areas on each catalyst. The average dispersion was then calculated by assuming uniform spherical particles.

Oxygen storage capacity (OSC) measurements were carried out in a micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). The samples were reduced under H_2 at 773 K for 1 h and heated to 1073 K in flowing He. Then, the samples were cooled to 723 K and a 5% O_2/He mixture was passed through the catalyst until the oxygen uptake was finished. The reactor was purged with He and the dead volume was obtained by switching the gas to the 5% O_2/He mixture. Finally, N_2 pulses were injected in order to calculate the amount of oxygen consumed on the catalysts taking into account a previous calibration of the mass spectrometer.

Temperature-programmed oxidation (TPO) of the carbon deposited during the reaction was carried out in a microreactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). The sample was heated to 1073 K in a 5% O_2/Ar mixture (20 ml/min) while the carbon dioxide and carbon monoxide in the effluent was recorded. Quantification of the carbon monoxide and carbon dioxide was performed using calibration injections of known mixtures.

3. Results

3.1. Catalyst activity

3.1.1. Partial oxidation

The initial methane conversions for the 1.5 wt.% Pt/ZrO_2 and $Pt/Ce_{0.14}Zr_{0.86}O_2$ catalysts during the partial oxidation reaction at 800 °C with a 2:1 ratio of CH_4:O_2 are shown in Table 1. The initial conversions are similar to values that we have previously observed for the partial oxidation reaction with a 2:1 feed ratio [31]. Furthermore, in agreement with previous studies [31,32], the deactivation of the Pt/ZrO_2 catalyst is significant, with the activity after 24 h being approximately 33% of the original conversion. The $Pt/Ce_{0.14}Zr_{0.86}O_2$ catalyst exhibits less deactivation with a 9% decrease in the CH_4 conversion during the 24 h reaction observed.

The effect of varying the CH_4:O_2 ratio was investigated on the 1.5 wt.% $Pt/Ce_{0.14}Zr_{0.86}O_2$ catalyst and the methane conversion obtained during the partial oxidation reaction at 1073 K and CH_4:O_2 ratios of 2:1, 3:1 and 4:1, is shown in Fig. 1. When the CH_4:O_2 feed ratio was increased from 2:1 to 3:1 the initial conversion decreased to 47%. However, the increase in the feed ratio resulted in no significant increase in the deactivation with only an 11% decrease in the methane conversion observed during the 24 h experiment. Further increasing the feed ratio to 4:1 resulted in a larger decrease in the initial conversion to 39%, but also slightly increased the stability with only a 5% loss in methane conversion during the reaction. A significant decrease in the CO_2 selectivity was observed when the feed ratio was increased, with values after 24 h for the 3:1 and 4:1 ratios, of 15 and 7%, respectively. As a result, the CO selectivity increased significantly with the increasing feed ratio with values after 24 h of 85 and 92%, respectively. Finally, minimal water formation was observed when the feed ratio was increased from 2:1 to 4:1.

Table 1
Initial CH_4 conversion, H_2, CO_2, and CO selectivities, and H_2/CO ratio for the 1.5 wt.% Pt/ZrO_2 and $Pt/Ce_{0.14}Zr_{0.86}O_2$ catalysts during the partial oxidation reaction with a 2:1 CH_4:O_2 feed ratio

Catalyst	CH_4 conversion (%)	Selectivity			H_2/CO ratio
		H_2	CO_2	CO	
1.5 wt.% $Pt/Ce_{0.14}Zr_{0.86}O_2$	55	94	22	77	2.4
1.5 wt.% Pt/ZrO_2	50	90	25	74	2.4

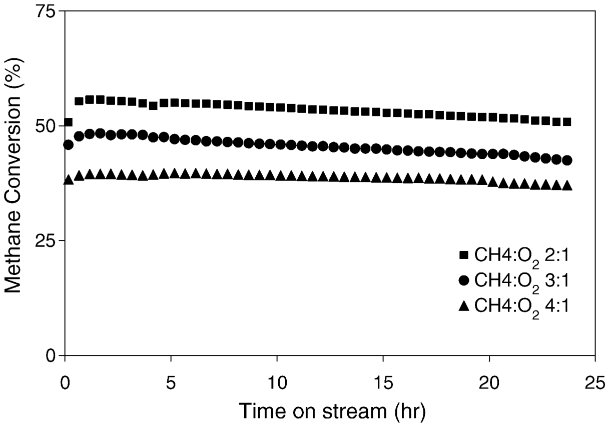

Fig. 1. CH_4 conversion during the partial oxidation of CH_4 at 1073 K and at 2:1, 3:1 and 4:1 ratios of CH_4:O_2. Reactor loading of 20 mg; total flow 100 ml/min.

3.1.2. Combined partial oxidation and dry reforming

3.1.2.1. C:O ratio at 1:1. To study the effects of the addition of CO_2 to the partial oxidation feed, two experiments were performed in which the total flow rate was held constant at 100 ml/min and the C:O ratio in the feed was fixed at 1:1. The corresponding CH_4:CO_2:O_2 feed ratios for the two experiments were 4:2:1 and 3:1:1. Fig. 2 shows

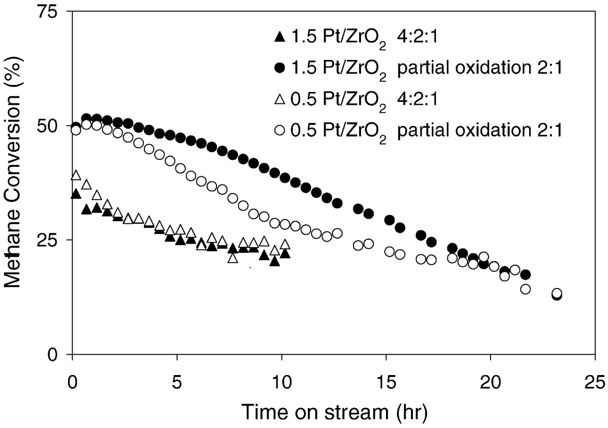

Fig. 2. CH_4 conversion during the partial oxidation reaction at a 2:1 ratio of CH_4:O_2 and the combined dry reforming and partial oxidation of CH_4 at CH_4:CO_2:O_2 ratio of 4:2:1 for the 1.5 and 0.5 wt.% Pt/ZrO_2 catalysts. Reactor loading of 20 mg for 1.5 wt.% catalyst and 60 mg for 0.5 wt.% catalysts; total flow 100 ml/min.

Table 2
Effect of addition of CO_2 to the reactant feed on the CH_4 conversion and the H_2:CO product ratio for the 1.5 wt.% Pt/ZrO_2 and 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst

Catalyst and CH_4:CO_2:O_2 feed ratio	Percentage of CH_4 conversion after			H_2:CO ratio after		
	0.5 h	5 h	10 h	0.5 h	10 h	15 h
1.5 wt.% Pt/ZrO_2, 4:2:1	30	26	20	1.44	1.45	1.24
1.5 wt.% Pt/ZrO_2, 3:1:1	63	55	47	1.64	1.67	1.67
1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$, 4:2:1	54	50	47	1.4	1.42	1.46

The flow rate was constant at 100 ml/min and the temperature was 1073 K.

the results of the 0.5 and 1.5 wt.% Pt/ZrO_2 catalysts when the feed ratio is changed from partial oxidation to 4:2:1. The addition of CO_2 to the feed resulted in a decrease in the initial methane conversion to 35%. Although the rate of deactivation appears to be slightly faster on the 0.5 wt.% catalyst compared to the 1.5 wt.%, the methane conversion at the end of the 4:2:1 reaction and the partial oxidation reaction is the same for both metal loadings.

Table 2 compares the CH_4 conversion and the H_2/CO product ratio for the 4:2:1 and the 3:1:1 reactions on the 1.5 wt.% Pt/ZrO_2 catalysts. When the ratio of CH_4:CO_2:O_2 was increased to 3:1:1 the methane conversion on the 1.5 wt.% Pt/ZrO_2 catalyst increased to 63% and the H_2/CO ratio increased from 1.4 to 1.64. Furthermore, the H_2/CO ratio was more stable remaining near 1.6 for the 10 h experiment. The CO_2 conversion observed on the 1.5 wt.% ZrO_2 catalyst was initially 24% for the 3:1:1 feed ratio. However, the conversion of CO_2 rapidly decreased and CO_2 production was observed after 3 h of reaction. For comparison, the methane conversion and the H_2/CO ratio obtained during the 4:2:1 reaction on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ are also shown in Table 2. The initial methane conversion for the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst (54%) is much higher than the conversion for the 1.5 wt.% Pt/ZrO_2 catalyst (30%) during the reaction with the 4:2:1 feed ratio. In addition to being more active, the Ce-containing catalyst is also more stable during the 10 h experiment.

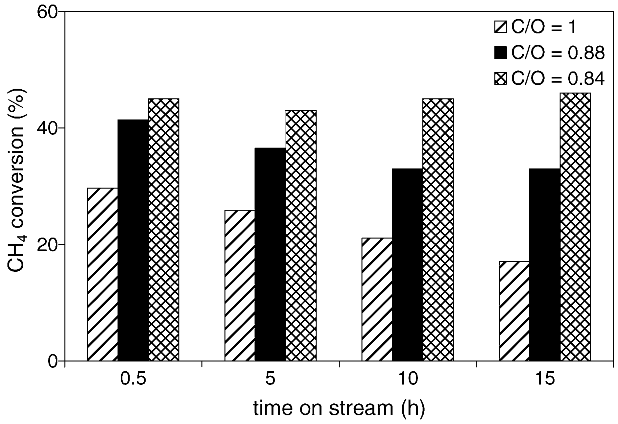

Fig. 3. CH_4 conversion during the combined dry reforming and partial oxidation of CH_4 at 1073 K and a CH_4:(CO_2:O_2) fixed at 1:1 on the 0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst. The C:O ratio varied from 1 to 0.84. Reactor loading of 20 mg; total flow 120 ml/min.

3.1.2.2. Varying C:O ratio. Studies were also performed on the combined dry reforming and partial oxidation reactions with varying amounts of CO_2 and O_2 and a 1:1 ratio of CH_4:(CO_2 + O_2) on the 0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst. The reactions were carried out at 1073 K and atmospheric pressure with a total flow rate of 120 ml/min. The CH_4:CO_2:O_2 ratios studied were 1:1:0 (dry reforming), 1:0.75:0.25, and 1:0.67:0.33, corresponding to C:O ratios of 1, 0.88, and 0.84, respectively. Fig. 3 shows the CH_4 conversion for the catalyst under each reaction condition at 0.5, 5, 10, and 15 h of reaction. Deactivation is observed on the 0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst during the dry reforming reaction, with the conversion decreasing from approximately 30 to 17% after 15 h. With the addition of oxygen, the deactivation is significantly reduced, such that at the higher oxygen content, no deactivation is observed. Table 3 contains the corresponding H_2:CO product ratio and the CO_2 conversion for the same experiments. The presence of oxygen in the feed resulted in a significant increase in the H_2:CO product ratio compared to the dry reforming reaction, however, increasing the oxygen content even further, resulted in only minor increases in the syngas ratio produced. Comparison of the CO_2 conversion for the reactions with oxygen to that for the dry reforming reaction reveals a significant decrease in the CO_2 conversion as a function of time for the 0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst when the CH_4:O_2 ratio reaches 3:1. In addition, a considerable amount of water formation was observed at the higher CH_4:O_2 ratios.

3.1.3. Catalyst stability during transient operation

The 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst was tested for the ability to change the feed conditions during operation in order to obtain different H_2:CO product ratios. The reactor temperature was held constant at 1073 K and the total flow of the reaction mixture was 100 ml/min. Each reaction was performed for three hours before switching to the subsequent reactant feed ratio. The CH_4:CO_2:O_2 ratios employed, listed in order of the reaction, are as follows: (a) 2:0:1 (partial

Table 3
Effect of addition of changing the C/O ratio in the feed on the H_2:CO product ratio and the CO_2 conversion for the 0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst

C:O ratio in feed	H_2:CO ratio after			Percentage of CO_2 conversion after		
	0.5 h	10 h	15 h	0.5 h	10 h	15 h
1	0.82	0.75	0.70	44	36	36
0.88	1.25	1.36	1.38	10	12	10
0.84	1.45	1.5	1.5	11	4	0

The CH_4:CO_2:O_2 compositions were 1:1:0, 1:0.75:0.25, and 1:0.67:0.33. The flow rate was constant at 120 ml/min and the temperature was 1073 K.

oxidation), (b) 4:2:1, (c) 1:1:0 (dry reforming), (d) 3:1:1, and (e) 2:1 (partial oxidation). The catalyst was exposed to Ar at 1073 K for 10 min prior to switching the feed ratio to allow the reactant feed flow rates to stabilize.

The methane conversion observed for the series of reactions is shown in Fig. 4a. The conversion of methane during the first partial oxidation reaction is initially 67% and decreases slightly to 63% after 3 h. The addition of CO_2 to the feed resulted in a reactant ratio of 4:2:1 and a decrease in the conversion of methane to 58%. An increase in the rate of deactivation is also observed with the final conversion after 3 h of the combined reaction at a 4:2:1 ratio at 45%. The next reaction was the dry reforming reaction with a stoichiometric feed of methane and carbon dioxide. The conversion of methane started at 41% and decreased to 37% after 3 h. When the oxygen was again added to the feed in the ratio of 3:1:1, the methane conversion increased and very little deactivation was observed. Finally, the partial oxidation reaction was resumed and the conversion of methane increased back to the final value of the first partial oxidation reaction period.

The H_2:CO product ratios corresponding to each reaction period were calculated and the results are shown in Fig. 4b.

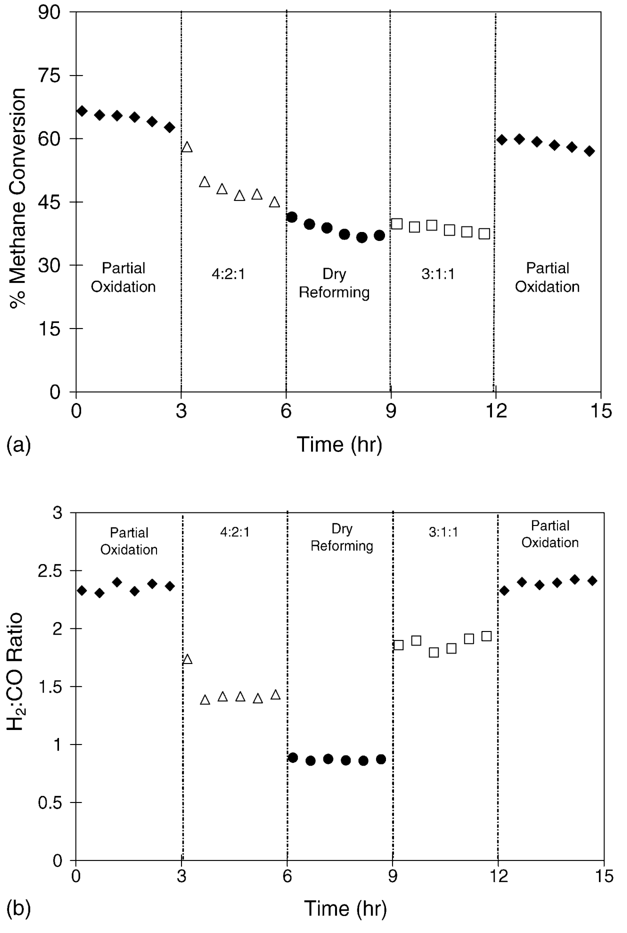

Fig. 4. (a) CH_4 conversion, and (b) H_2:CO ratio during the different reactions at 1073 K on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst. Reactor loading of 20 mg; total flow 100 ml/min.

The product ratio observed for both partial oxidation reactions is 2.4, while the ratio for the dry reforming ratio is closer to 0.8. The reactions performed in the presence of CH_4, CO_2, and O_2 had ratios that were in between the partial oxidation and dry reforming ratios, near 1.4 and 1.8 for the 4:2:1 and 3:1:1 cases, respectively.

3.1.4. *Temperature profile of catalyst during reaction*

A final reaction experiment was performed as an attempt to investigate the temperature of the catalyst under the different reaction conditions employed in this study. The catalyst used for this experiment was the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst. For all of the reactions the total flow rate of the reactants was held constant at 100 ml/min. The reactor was loaded with 20 mg of catalyst which was diluted with a 3:1 ratio of SiC to catalyst. The reactor temperatures studied were 413, 523, 773, 873, 973, and 1073 K. For this experiment, the catalyst was exposed to the normal pretreatment including heating to 1073 K in Ar. The reactor was subsequently cooled to 413 K and the catalyst was exposed to the combined reforming and partial oxidation reactions with a CH_4:CO_2:O_2 feed ratio of 4:2:1. The temperature inside of the reactor was recorded as a function of time using a second thermocouple that was placed in direct contact with the catalyst bed. The total height of the catalyst bed was approximately 3 mm and the tip of the thermocouple was placed into the catalyst. After 5 min of reaction, a sample of the reactor effluent was analyzed for the product composition and reactant conversion. The catalyst was then exposed to Ar and the temperature of the reactor was increased to the next reaction temperature, where the process was repeated.

Fig. 5 shows the temperature difference between the catalyst bed temperature before the reaction and the temperature of the catalyst bed during the combined dry

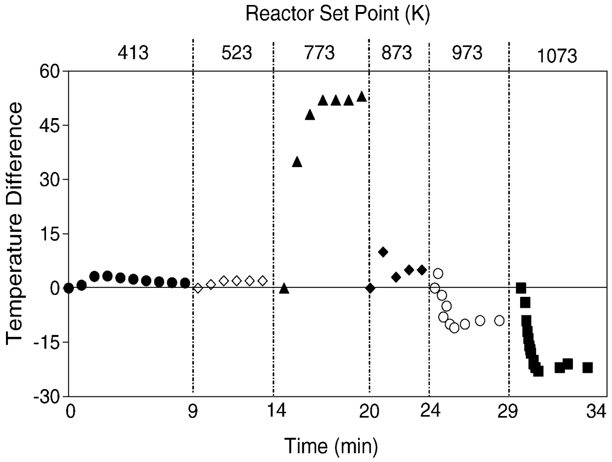

Fig. 5. Temperature difference between catalyst temperature during reaction and catalyst temperature before reaction during combined dry reforming and partial oxidation of CH_4 at different temperatures and at CH_4:CO_2:O_2 ratio of 4:2:1 on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst. Reactor loading of 20 mg; total flow 100 ml/min.

reforming and partial oxidation reactions with a 4:2:1 CH_4:CO_2:O_2 feed ratio. When the reaction was performed at 413 and 523 K, no significant conversion of the methane was observed and only a 2–3° increase in the temperature occurred. When the reactor temperature was increased to 773 K, a significant increase in the temperature was observed at the start of the reaction, with a temperature difference of 35 K within 1 min. The temperature difference stabilized at 53 K after 3 min.

Increasing the reactor temperature to 873 K also resulted in an increase in the temperature of the catalyst. However, the temperature difference reached a maximum of 10 K after 1 min and then decreased slightly. The temperature stabilized after 3 min with a difference of 5 K. Similarly, at 973 K a maximum temperature difference was observed, however, the time to reach the maximum decreased to 15 s and the maximum temperature reached decreased to 4 K. Unlike the lower temperature cases, after 30 s of reaction at 973 K the temperature dropped below the temperature of the bed before reaction and finally stabilized at approximately 10 K below the set point temperature. The final temperature studied for the combined partial oxidation and dry reforming reactions with a 4:2:1 feed ratio was 1073 K. In contrast to the lower temperature reactions, no increase in the temperature of the catalyst bed was observed. The final temperature of the bed was approximately 22 K below that of the set point. The conversion of methane was measured after 5 min of reaction for the different temperature. No conversion was observed for the reaction below 773 K. At 773 K the conversion of methane was approximately 7%. With every 100 K increase in temperature the conversion nearly doubled so that the final conversion at 1073 K was 45%.

Following the combined reaction with a 4:2:1 feed ratio, the catalyst was exposed to Ar and the temperature of the catalyst bed returned to the original set point value. The catalyst was then exposed to the combined reactions at a ratio of 3:1:1 and the partial oxidation reaction with a stoichiometric feed of methane and oxygen. Fig. 6 shows the temperature differences as a function of time for the three cases at 1073 K. The partial oxidation reaction is the only reaction in which a temperature increase is observed. Comparison of the three ratios demonstrates that as the oxygen content is increased, the rate at which the temperature of the catalyst bed decreases, and the total difference between the initial and final temperatures, is reduced. In addition, the conversion measured after 5 min of reaction increased from 45% at the 4:1:1 ratio, to 48% at the 3:1:1 ratio, and 55% under partial oxidation conditions.

3.2. Catalyst characterization

3.2.1. Metal dispersion

TEM was used to determine the average Pt dispersion for the catalysts used in this study and the results are presented in Table 4. All of the samples were reduced at 773 K in hydrogen and then heated to 1073 K in helium prior to the TEM analysis. Analyzing the particle size after exposure to the reaction pretreatment provides the opportunity to obtain an accurate measurement of the Pt atoms exposed at the start of the reaction. The smallest particles were observed on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ (Fig. 7a) with an estimated dispersion of 30%. The particles on the 0.5 and 1.5 wt.% Pt/ZrO_2 catalysts after exposure to the reaction pretreatment (Fig. 7b) were slightly larger with the average size being 5.1 nm. Based on the average of the particle sizes and the assumption of spherical particles of the estimated dispersion on the ZrO_2 support is 21%. The dispersion of the 0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst was slightly higher at 23%.

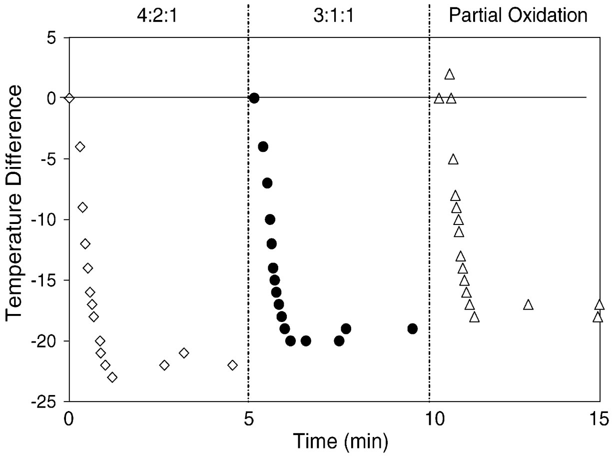

Fig. 6. Temperature difference between catalyst temperature during reaction and catalyst temperature before reaction during combined dry reforming and partial oxidation of CH_4 at 1073 K and CH_4:CO_2:O_2 ratios of 4:2:1, 3:1:1, and 2:0:1 on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst. Reactor loading of 20 mg; total flow 100 ml/min.

3.2.2. Temperature-programmed oxidation of carbon deposits

Temperature-programmed oxidation of the carbon deposited during 10 h of reaction was performed to determine the effect of the oxygen content on the formation of coke. Following the reactions, the catalysts were cooled to room temperature in Ar and then heated to 1073 K at 8.5 K/min in a 5% O_2/Ar mixture (20 ml/min). Fig. 8 shows the carbon dioxide profiles obtained during the TPO for the 1.5 wt.% Pt/ZrO_2 catalyst after reaction at a CH_4:CO_2:O_2 feed ratio of 4:2:1 and 3:1:1. The profile for the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst after reaction at a CH_4:CO_2:O_2

Table 4
Pt metal dispersion as estimated from TEM after reduction at 773 K for 1 h in hydrogen (30 ml/min) and heating to 1073 K in 30 ml/min of Ar

After reaction pretreatment	TEM analysis	
	Range of particle sizes (nm)	Estimated dispersion (%)
0.5 wt.% Pt/ZrO_2	2–12	21
0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$	3–12	23
1.5 wt.% Pt/ZrO_2	2–18	22
1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$	2–10	30

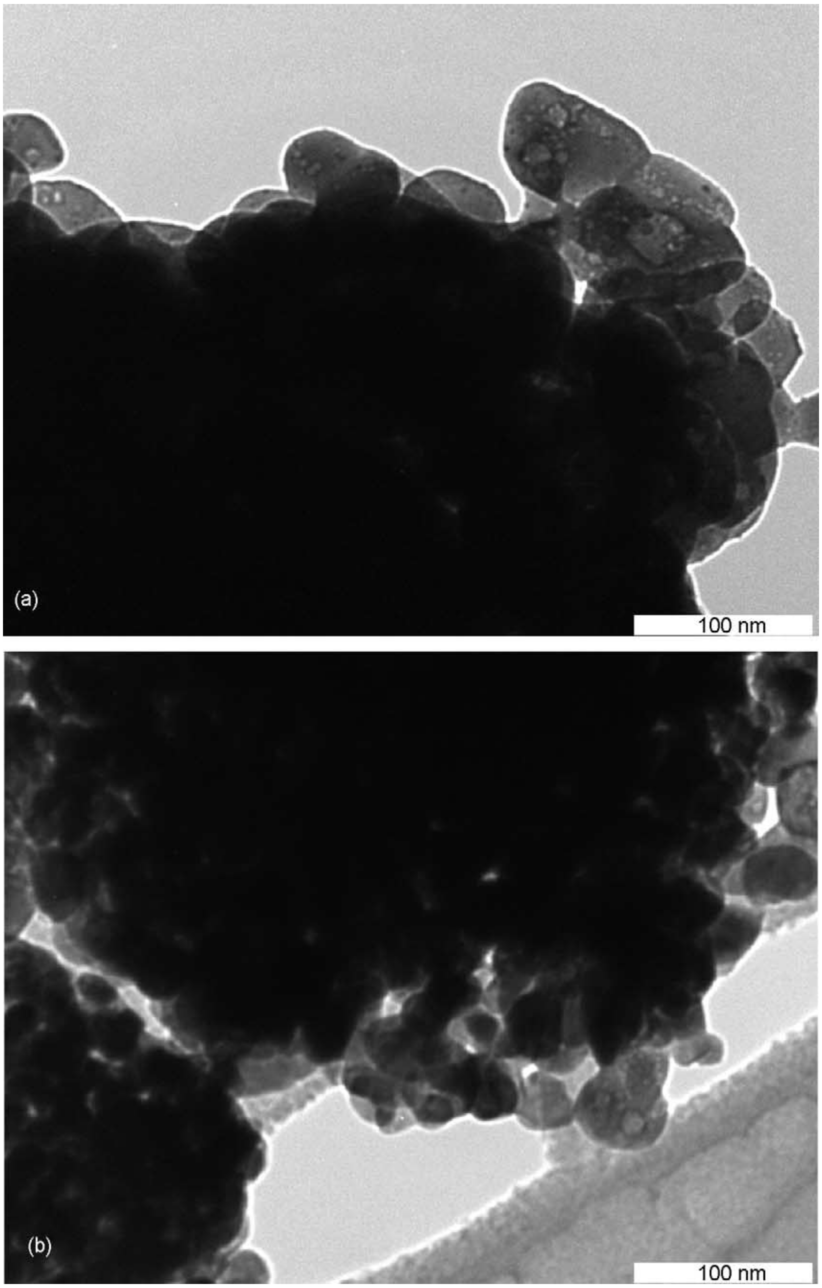

Fig. 7. TEM micrographs of: (a) 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ after pretreatment and (b) 1.5 wt.% Pt/ZrO_2 after pretreatment.

feed ratio of 4:2:1 is also shown. Calibration injections of known amounts of CO_2 were used to quantify the amount of carbon formed after 10 h of the respective reactions. The amount of C, on a per gram of Pt basis, was calculated to be 0.0, 0.15, and 0.20 g, for the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ after reaction at 4:2:1 and the 1.5 wt.% Pt/ZrO_2 catalyst after 4:2:1 and 3:1:1, respectively. For all of the temperature-programmed oxidations performed, no significant carbon monoxide was observed.

3.2.3. Catalyst reducibility

Table 5 presents the oxygen uptakes measured for the catalysts. The oxygen consumption of the Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalysts is considerably higher than that measured for the Pt/ZrO_2 catalysts. The values of O_2 consumption obtained on the Pt/ZrO_2 and the Pt/$Ce_{.14}Zr_{0.86}O_2$ catalysts agree with those reported by others in the literature [31,33].

Table 5
O_2 uptakes measured at 723 K

Catalyst	O_2 uptake (μmol/g_{catal})
0.5 wt.% Pt/ZrO_2	0
0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$	168
1.5 wt.% Pt/ZrO_2	9
1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$	220

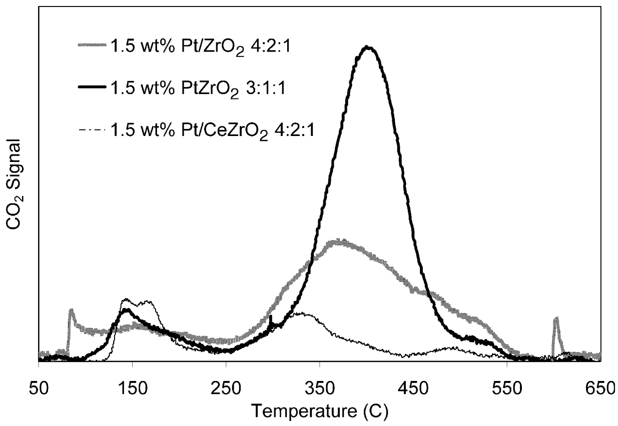

Fig. 8. CO_2 production during the TPO of carbon deposits on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ and ZrO_2 catalysts after 10 h of reactions with 4:2:1 and 3:1:1 CH_4:CO_2:O_2 feed ratios.

4. Discussion

4.1. Partial oxidation reaction: effect of CH_4:O_2 ratio

We have previously studied the reaction mechanism of partial oxidation of methane on Pt/ZrO_2 and Pt/$Ce_xZr_{1-x}O_2$ catalysts [31,32]. The selectivity profiles of CO and CO_2 during the reaction and temperature-programmed surface reaction studies have demonstrated that the mechanism follows an indirect route, in which methane combustion occurs followed by the steam and CO_2 reforming of methane. This mechanism has been also been observed by others [16,17,23,34–37]. Previous studies have shown that the support plays an important role in the CO_2 reforming of CH_4 [18] and thus, a similar role should be observed for partial oxidation. We have demonstrated that Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalysts show greater stability than the Pt/ZrO_2 or Pt/Al_2O_3 catalysts [32]. These results were attributed to the higher reducibility and oxygen storage/release capacity of Pt/$Ce_xZr_{1-x}O_2$ catalysts, which favored a continuous removal of carbonaceous deposits from the active sites and improved the stability of the catalysts. For Pt/ZrO_2 catalysts, the increase of carbon deposits around or near the metal particle inhibited the CO_2 dissociation, which based on the two-step mechanism, resulted in a decrease in the activity due to an eventual buildup of carbon [32].

The higher initial activity observed on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst is most likely due to the differences in the metal dispersion. Fig. 2 shows that the deactivation on the Pt/ZrO_2 catalyst was severe. Comparing the performance of the Pt/ZrO_2 catalyst and the Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst demonstrates that the Ce-promoted catalysts are more stable for the partial oxidation reaction. The OSC values obtained (Table 4) support the increased ability of the $Ce_{0.14}Zr_{0.86}O_2$ support to provide oxygen to the surface of the particle for removal of carbon from the metal. The higher dispersion on the promoted catalyst also leads to a greater metal-support interfacial area which directly impacts the carbon removal efficiency.

Increasing the ratio of CH_4:O_2 resulted in a decrease in the catalyst activity, but did not significantly affect the stability of the catalyst. Furthermore, at CH_4:O_2 ratio of 3 and 4, no water formation was observed and the CO_2 production was significantly reduced. Zhu et al. [38] performed a thermodynamic study of the partial oxidation of methane for synthesis gas production. The effects of CH_4:O_2 ratio and reaction temperature were examined. Their results showed that at 1073 K and CH_4:O_2 ratios higher than 2, the equilibrium products involve only H_2, CO and CH_4. Then, water formation is not expected under these reaction conditions, in agreement with our results. The stability of the catalyst in the presence of higher CH_4:O_2 ratios could be due to the suppression of water formation. We have previously reported that the strong deactivation of a Pt/ZrO_2 catalyst on partial oxidation of methane could be assigned to disappearance of the oxygen vacancies of support caused by water, which is produced during the first step of the mechanism proposed for partial oxidation [39]. Otsuka et al. [40] also showed the reoxidation of the reduced cerium oxide by water. Thus, the lack of water formation in the presence of excess methane could result in the stability of the catalyst remaining high. The operation at this reaction condition appears to be very interesting in terms of operational cost reduction due to lowering the required oxygen content.

4.2. Combined partial oxidation and dry reforming

In this work, the Pt/ZrO_2 catalysts exhibited a strong deactivation during the partial oxidation of methane with a CH_4:O_2 ratio of 2 (Fig. 2). The metal loading had no effect on the final activity of the catalyst for the partial oxidation and combined partial oxidation and dry reforming reactions. The addition of CO_2 resulted in a decrease in the methane conversion and an increase in the initial rate of deactivation compared to the partial oxidation reaction. Changing the feed ratio from 4:2:1 to 3:1:1 (Table 2) did result in an increase in the methane conversion and an increase in the H_2/CO but no significant change in the rate of deactivation was observed during the first 10 h of reaction. It should be noted that deactivation that we observed is greater than what has been previously reported in the literature for a 1 wt.% Pt/ZrO_2 catalyst [23,26] during the partial oxidation and combined reforming reactions. However, the conditions under which we operate are more severe because no diluent is added to the feed for our reactions.

The deactivation of the Pt/ZrO_2 catalyst with the addition of CO_2 has been previously attributed to carbon formation on the metal particle [23,32]. The results of the temperature-programmed oxidation studies (Fig. 8) show that the amount of carbon that is formed during reaction at 4:2:1 and 3:1:1 are similar on the 1.5 wt.% Pt/ZrO_2 catalyst. These results are consistent with the deactivation profiles that are observed for the two reactions. TPO and XPS studies performed on Pt/ZrO_2 and Pt/$Ce_xZr_{1-x}O_2$ after the dry reforming reaction [41] have shown that the CO_2 located near 700 K is due to carbon that is located near the metal particle not to a different form of carbon. Thus, more carbon is formed on the unpromoted catalyst which can explain the deactivation observed.

Promotion of the support with Ce resulted in a catalyst that exhibited much higher methane conversions and stability for the combined reactions with a feed ratio of 4:2:1 (Table 2). Unlike the Pt/ZrO_2 catalyst, the product ratio was very stable even with higher CO_2 contents in the feed. Previous studies [18] on the dry reforming of methane have demonstrated that $CeZrO_2$ supports facilitate the dissociation of CO_2 via a bifunctional mechanism. The first step is the decomposition of methane on the metal particle followed by the reaction of carbon with oxygen from the support near the metal-support interface. The second step is the dissociation of CO_2 resulting in the replenishing of the support oxygen and the formation of CO.

Several studies [42,43] have reported that cerium oxide has an oxygen exchange capacity, which is associated with the ability of cerium to act as an oxygen buffer by storing/releasing O_2 due to the Ce^{4+}/Ce^{3+} redox couple [42]. The incorporation of ZrO_2 into a CeO_2 lattice was shown to promote the CeO_2 redox properties due to the high oxygen mobility of the solid solution formed. Thus, the Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst has a greater capacity to form oxygen vacancies compared to the Pt/ZrO_2 catalyst, and would be capable of functioning without significant deactivation at higher levels of CO_2.

Similar increases in methane conversion (Fig. 4) and the product ratio (Table 4) were observed when O_2 was added to the dry reforming feed on a 0.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst while decreasing the C:O feed ratio from 1 to 0.84. Increasing the oxygen resulted in a significant decrease in the CO_2 conversion. Furthermore, significant water formation was observed at the highest oxygen content. The formation of water and the decrease in CO_2 conversion is indirect evidence for the occurrence of the two-step mechanism previously proposed.

It is important to stress that CO_2 addition decreased the H_2/CO ratio for all of the catalysts studied. Then, the presence of CO_2 can be used to adjust the H_2/CO ratio to the desired value. In fact, this is one of the steps of syngas generation technology from Haldor Topsoe to synthetic fuels production (GTL technology). However, the ability of the catalyst to maintain the desired product ratio is very important and thus the Ce-promoted catalysts appear to be more suited for this application.

4.3. Tuning the H_2/CO product ratio

The results presented in Fig. 5 demonstrates that the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst is capable of operating under a variety of feed conditions without significant deactivation. Even after exposure to the dry reforming reaction and the combined reforming reactions, the activity for the partial oxidation reaction was as would be predicted from previous experiments. More importantly, the ability of the catalyst to generate synthesis gas ratios ranging from 0.8 to 2.4 provides for flexibility in the combination of the syngas generation unit and the Fischer–Tropsch reactor. For example, Fe-based catalysts for FT synthesis work best at H_2/CO ratios of 0.6–1.5, due to water gas shift reactivity [44]. In contrast, cobalt based catalysts exhibit optimal performance at ratios between 1.5 and 2.2. Thus, depending on the downstream application and catalyst being employed, the H_2/CO ratio could be easily modified by varying the CO_2 and O_2 content in the feed without significantly impacting catalyst stability. These results suggest that the Pt/$CeZrO_2$ catalysts are very promising for synthesis gas production for GTL technology.

4.4. Effect of reaction conditions on catalyst temperature

Several studies have shown that operating the partial oxidation or combined reactions at lower temperatures results in the formation of CO_2 and H_2O, due to the occurrence of the combustion reaction without the subsequent reforming reactions [18,32]. The results of our studies on the 4:2:1 reaction at different temperatures shows that no significant reaction occurs on the 1.5 wt.% Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst at temperatures below 773 K. The largest exotherm is observed at 773 K, with a difference of 53 K. The conversion of methane was very low (8%) but the H_2/CO ratio was 2.5 and water formation was observed indicating the combustion reaction is occurring. As the temperature increased, the endothermic reforming reactions started to occur as evidenced by the reduction in the exotherm and the eventually appearance of an endothem at temperatures above 973 K. Furthermore, the product ratio decreased with the increase in temperature starting out a 2.5 at 773 K and decreasing to 2, 1.7, and 1.7 at 873, 973, and 1073 K, respectively. The decrease in the product ratio from 773 to 873 K could also be caused by the simultaneous occurrence of the reverse water gas shift reaction.

A primary advantage to performing the combined partial oxidation and reforming reactions is the ability to couple the endothermic reforming reaction and the exothermic partial oxidation reaction. One of the greatest challenges in the partial oxidation process is the formation of localized high temperature regions or hot spots in the catalyst [45]. O'Conner and Ross [23] have measured the temperature profile within a 4.5 cm catalyst bed, and they find that in the presence of oxygen, an exotherm is formed at the beginning of the bed followed by and large endotherm. The profile is described as indirect evidence for the two-step mechanism in which combustion occurs at the front of the bed followed by the endothermic reforming reactions.

The catalyst bed used in our study is only 3 mm tall so we do not observe a profile with bed length but rather the change in the temperature of the bed as a function of time. The results presented in Fig. 7 show that even under the partial oxidation conditions a significant increase in the temperature of the catalyst bed is not observed. When CO_2 was added to the feed, no increase in the bed temperature is observed at a reaction temperature of 1073 K. In all cases the catalyst bed stabilized at a temperature lower than the reactor set point. However, a decrease in the endotherm and the time to reach the stable temperature decreased when the amount of oxygen increased.

It is interesting to note that the changes occurring in the temperature of the bed happen very rapidly, with the bed temperature stabilizing after 3 min. This data suggests that an accurate observation of the initial catalyst performance may not be possible when the reaction is allowed to proceed for several minutes before sampling the effluent from the reactor.

5. Conclusions

The results of this study demonstrate that the Pt/$Ce_{0.14}Zr_{0.86}O_2$ catalyst is more active and stable for both the partial oxidation and the combined partial oxidation and dry reforming reactions compared to Pt/ZrO_2. The Ce-promoted catalyst is stable even at CH_4:O_2 ratios of 4:1. No effect of the metal loading was observed on the ZrO_2 support, with the 0.5 and 1.5 wt.% catalysts exhibiting similar long-term activities. Deactivation of the Pt/ZrO_2 catalyst was observed even in the presence of oxygen. The deactivation is ascribed to carbon deposition. Temperature-programmed oxidation studies indicated that the amount of carbon formed on the 1.5 wt.% Pt/ZrO_2 catalyst at 4:2:1 and 3:1:1 was similar. This is consistent with the deactivation profiles observed. The increase in the stability of the Ce-containing catalyst is related to the increase oxygen storage capacity and the ability to facilitate carbon removal from the metal particle. Monitoring the catalyst temperature as a function of time inside the reactor provides further evidence that the reaction mechanism proceeds through combustion followed by combined dry and steam reforming as opposed to via direct partial oxidation. The Ce-promoted catalysts are very stable in transient operation and are promising catalysts for application in GTL technology.

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