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Partial oxidation and CO_2 reforming of methane on Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce–ZrO_2$ catalysts

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Abstract

The partial oxidation and CO_2 reforming of methane were studied on Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce–ZrO_2$ catalysts. The reducibility and the oxygen transfer capacity were evaluated by oxygen storage capacity (OSC). The effect of the support on the cleaning mechanism of the catalyst surface was investigated by the sequence of CH_4/O_2 and CH_4/CO_2 pulses. The $Pt/Ce–ZrO_2$ catalyst showed the highest stability on both partial oxidation and CO_2 reforming of methane. The results were explained by the higher reducibility and oxygen storage/release capacity of $Pt/Ce–ZrO_2$ catalysts, which allowed a continuous removal of carbonaceous deposits from the active sites, favoring the stability of the catalysts, as revealed by the CH_4/O_2 and CH_4/CO_2 pulses. For Pt/Al_2O_3 and Pt/ZrO_2 catalysts, the increase of carbon deposits around or near the metal particle inhibits the CO_2 dissociation on CO_2 reforming of methane. This effect on the CO_2 reforming of methane affects the partial oxidation of methane, which comprehends two steps: combustion of methane and CO_2 and steam reforming of unreacted methane.

Keywords: Partial oxidation of methane; CO_2 reforming of methane; $Pt/Ce–ZrO_2$ catalysts; Oxygen storage capacity

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1. Introduction

Increasing concern about world dependence on petroleum oil has generated interest in the use of natural gas. However, the majority of these reserves are located in remote regions, which leads to high transportation costs. Then, the conversion of natural gas into transportation fuels, such as gasoline and diesel, is considered to be an alternative to make the use of this gas economically viable. The so-called gas-to-liquid (GTL) technology is based on the conversion of natural gas to a synthesis gas (syngas) prior to the liquid production through the Fischer–Tropsch Synthesis [1]. The syngas production is the most costly part of the GTL plant, amounting to approximately 50–75% of the total capital cost [2]. Therefore, the reduction of the cost of the syngas generation is needed in order to enhance and sustain the economic competitiveness of GTL technology.

The principal commercial technology for syngas production is catalytic steam methane reforming (SMR) [2]. Since this reaction (Eq. (1)) is a highly endothermic reaction, it is necessary to use high temperatures and pressures. These severe reaction conditions cause the deactivation of the catalysts due to carbon deposits on its surface. In order to avoid this deactivation, a high steam/hydrocarbon ratio should be used, which leads to high capital and operation costs. Furthermore, SMR produces a syngas with an H_2/CO ratio higher than that required for the Fischer–Tropsch Synthesis ($H_2/CO = 2$). Then, alternative routes to the synthesis gas production from methane to GTL applications have been examined:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

Autothermal reforming (ATR) and partial oxidation of methane (Eq. (2)) are technologies that fulfill the requirements for a gas with $H_2/CO = 2$, the ratio necessary for GTL [2]:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \tag{2}$$

The ATR technology combines noncatalytic partial oxidation with SMR in one reactor. In this process, the endothermic reforming reactions occur with the assistance of the internal oxidation of a portion of methane. Moreover, 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 of the FT synthesis [3]. Then, during the ATR process, the CO_2 reforming of methane (Eq. (3)) occurs:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{3}$$

The major obstacle associated with the CO_2 reforming reaction is the deactivation of the catalysts due to carbon deposition. Several studies have shown that Pt/ZrO_2 catalysts are very stable for the CO_2 reforming of methane [4,5]. More recently, we have reported that the use of promoters such as cerium oxide improves the activity and stability of Pt/ZrO_2 catalysts under severe deactivating reaction conditions [6,7]. The CO_2 reforming of methane has been explained by a two-step mechanism that involves the occurrence of CH_4 decomposition on metal particle and of CO_2 dissociation on oxygen vacancies of the support at the same time [8]. Increasing the reducibility of the support, there is an increase in the number of oxygen vacancies formed near the metal particle, improving the ability of the support to dissociate CO_2 and the subsequent cleaning capacity. Therefore, a higher degree of reduction results in a catalyst with higher activity and stability during the CO_2 reforming of methane. The addition of cerium oxide to zirconia increases the reducibility and oxygen-transfer ability of the support, improving the activity and stability of the catalyst.

The partial oxidation of methane is also an interesting alternative to synthesis gas production from methane to GTL applications [9–16]. The main advantage of this process is that the partial oxidation is an exothermic reaction, which leads to a significant reduction of the costs. Furthermore, the presence of oxygen avoids the carbon deposition at high temperatures. However, the main disadvantage of this process is the high cost related to the separation of oxygen from air. The use of air as oxidant is still controversial because it leads to an increase in energy consumption and flow through the units, and a dilution of the syngas with N_2 [3]. The use of oxygen-permeable ceramic membranes has been considered as a good alternative for the separation of oxygen from air [17–19].

Several authors have reported that the addition of CeO_2 to Pt/Al_2O_3 catalyst increases its activity and stability during the partial oxidation of methane [20]. Furthermore, Pt/ZrO_2 catalysts have shown higher activity and stability than Pt/Al_2O_3 catalysts during this reaction [21,22]. These catalysts presented a higher capacity of oxygen storage, which avoids the carbon deposition.

The aim of this work is to compare the performance of the Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce–ZrO_2$ catalysts on the CO_2 reforming and the partial oxidation of methane. The role of the support on the catalytic activity of both reactions is evaluated and compared.

2. Experimental

2.1. Catalyst preparation

Al_2O_3 and ZrO_2 supports were prepared by the calcination of alumina (Engelhard Catalyst) and zirconium hydroxide (MEL Chemicals) at 1073 K for 1 h in a muffle furnace. The $Ce_{0.75}Zr_{0.25}O_2$ support was obtained by a co-precipitation method [23]. An aqueous solution of cerium(IV) ammonium nitrate and zirconium nitrate (Aldrich) was prepared with 75 and 25 mol% of CeO_2 and ZrO_2, respectively. Then, the ceria and zirconium hydroxides were co-precipitated by the addition of an excess of ammonium hydroxide. Finally, the precipitate was washed with distillated water and calcined at 1073 K for 1 h in a muffle furnace. Then, the catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of H_2PtCl_6 (Aldrich) and were dried at 393 K. The samples Pt/ZrO_2 and $Pt/Ce_{0.75}Zr_{0.25}O_2$ were calcined under air flow (50 cm^3/min) at 673 K for 2 h. The sample Pt/Al_2O_3 was calcined under air flow (50 cm^3/min) at 973 K for 2 h. All samples contained 1.5 wt.% of platinum.

2.2. Oxygen storage capacity (OSC)

Oxygen storage capacity measurements were carried out in a microreactor 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 (AGA) 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 by the catalysts, taking into account a previous calibration of the mass spectrometer.

2.3. CO chemisorption

The dispersion was calculated from CO chemisorption by using pulses of a mixture containing 10% CO/He at room temperature. This experiment was performed on an apparatus similar to the one described for the OSC measurements and the same pretreatment was used.

2.4. CH_4 and O_2 or CO_2 pulse experiments

Pulse experiments using CH_4 and O_2 or CO_2 were performed in a microreactor coupled to a quadrupole mass spectrometer (Balzers; Omnistar) using 50 mg of catalyst. The samples were reduced under H_2 at 773 K for 1 h. After reduction, the samples were heated to 1073 K in flowing He and then were exposed to sequences of CH_4/O_2/CH_4 and CH_4/CO_2/CH_4 pulses (500-μl pulses). The area of CH_4, CO, and H_2 obtained for each pulse was converted to moles using a conversion factor, which was determined from a previous calibration of the mass spectrometer.

2.5. Partial oxidation of methane and CO_2 reforming of methane

Reactions were performed in a quartz reactor at atmospheric pressure. Prior to reaction, the catalyst was reduced under H_2 at 773 K for 1 h and then heated to 1073 K under N_2. The CO_2 reforming of methane was performed at 1073 K with a CH_4/CO_2 ratio of 2:1 and a flow rate of 150 cm^3/min. The partial oxidation of methane was carried out at 1073 K and a reactant mixture containing a CH_4/O_2 ratio of 2:1 at a flow rate of 100 cm^3/min. On the experiments of combined dry reforming and steam reforming, water was injected continuously through a syringe pump (SARGE Instruments) at a flow rate of 15 cm^3/min. On the steam reforming reaction, argon was added in place of CO_2 in order to keep the same space velocity. The exit gases were analyzed using a gas chromatograph (Agilent 6890) equipped with a thermal conductivity detector and a CP carboplot column (Chrompack).

3. Results and discussion

3.1. Catalyst characterization

CO chemisorption uptakes are displayed in Table 1. Pt/Al_2O_3 and Pt/$Ce_{0.75}Zr_{0.25}O_2$ presented similar CO/Pt ratios close to 0.1, while Pt/ZrO_2 presented a higher value (0.24).

The reducibility of the catalysts was measured by OSC experiments. The oxygen uptakes obtained for the catalysts are shown in Table 1. The oxygen storage capacity of the

Table 1
CO irreversible chemisorption and O_2 uptakes measured for all catalysts at 723 K

Catalyst	CO uptake (μmol/g_{catal})	CO/Pt	O_2 uptake (μmol/g_{catal})
Pt/Al_2O_3	7.6	0.10	0.0
Pt/ZrO_2	18.4	0.24	8.5
$Pt/Ce_{0.75}Zr_{0.25}O_2$	6.5	0.08	625.6

$Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst is much higher than the one of the Pt/Al_2O_3 and Pt/ZrO_2 catalysts (Table 1). The O_2 consumption observed for the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst is similar to those reported in the literature [24–26]. The amount of Ce^{3+} estimated from O_2 uptake was around 53%. Several studies reported that cerium oxide has a very high oxygen exchange capacity [27,28]. This capacity 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 [28]. The incorporation of ZrO_2 into the CeO_2 lattice promotes the CeO_2 redox properties. The presence of ZrO_2 strongly increases the oxygen vacancies of the support due to the high oxygen mobility of the solid solution formed, which was identified by X-ray diffraction (XRD) data reported in a previous work for $Ce_{0.75}Zr_{0.25}O_2$ support [29].

3.2. Partial oxidation of methane

Fig. 1 shows the methane conversion in the partial oxidation of methane (Eq. (2)) at 1073 K. The initial CH_4 conversions were similar for Pt/ZrO_2 and $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts. The Pt/Al_2O_3 catalyst presented the lowest initial CH_4 conversion. Furthermore, a strong deactivation was observed on the Pt/Al_2O_3 and Pt/ZrO_2 catalysts, whereas the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst practically did not lose its activity after 24 h of time on stream (TOS).

The H_2/CO ratio obtained on the partial oxidation of methane is presented in Fig. 2. Comparing these results with those shown in Fig. 1, it was observed that the H_2/CO ratio decreased as methane conversion decreased, for Pt/Al_2O_3 and Pt/ZrO_2 catalysts. This result could be attributed to a contribution of the reverse water gas shift reaction (Eq. (4)), which is favored at low conversions [30]. This reaction converts H_2 and CO_2 to CO and water. On the contrary, the H_2/CO ratio was about 2 and very stable for the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst:

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{4}$$

The CO and CO_2 selectivities on partial oxidation of methane for all catalysts are presented in Fig. 3. A significant change in the selectivity towards CO and CO_2 was observed on the Pt/Al_2O_3 and Pt/ZrO_2 catalysts during the reaction (Fig. 3). The production of CO_2 increased and the selectivity to CO decreased as the CH_4 conversion decreased. This effect is much less significant on $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts.

These results could be explained through the two-step mechanism proposed for the partial oxidation of methane [31–34]. According to this mechanism, in the first stage, combustion of methane occurs, producing CO_2 and H_2O. In the second step, synthesis gas is produced via carbon dioxide and steam reforming reaction (Eqs. (1) and (3)) of the unreacted methane. We have studied the mechanism of partial oxidation of methane on the

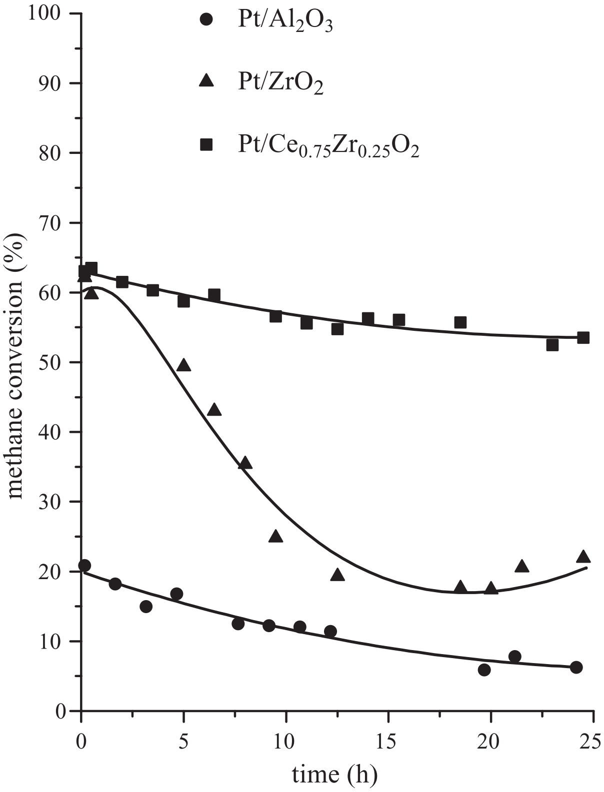

Fig. 1. Methane conversion on partial oxidation of methane versus time on stream for Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts. Reaction conditions: $T = 1073$ K; CH_4/O_2 ratio = 2:1.

Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts, using Temperature-Programmed Surface Reaction (TPSR) experiments [29]. The TPSR results are in agreement with this two-step mechanism of the partial oxidation of methane, as it was observed that the combustion of methane was followed by CO_2 and H_2O methane reforming.

Since the production of CO_2 increased in the Pt/Al_2O_3 and Pt/ZrO_2 catalysts during the reaction (Fig. 3), the second step of the mechanism was inhibited. In order to explain these results, the performance of these catalysts on CO_2 reforming of methane was evaluated.

3.3. CO_2 reforming of methane

The conversions of methane on the CO_2 reforming reaction (Eq. (3)) at 1073 K are shown in Fig. 4. The Pt/Al_2O_3 catalyst had a low initial activity and rapidly deactivated due to coke deposition. The Pt catalysts supported on unpromoted zirconia and ceria-doped zirconia exhibited much higher activity and stability than the Pt/Al_2O_3 catalyst.

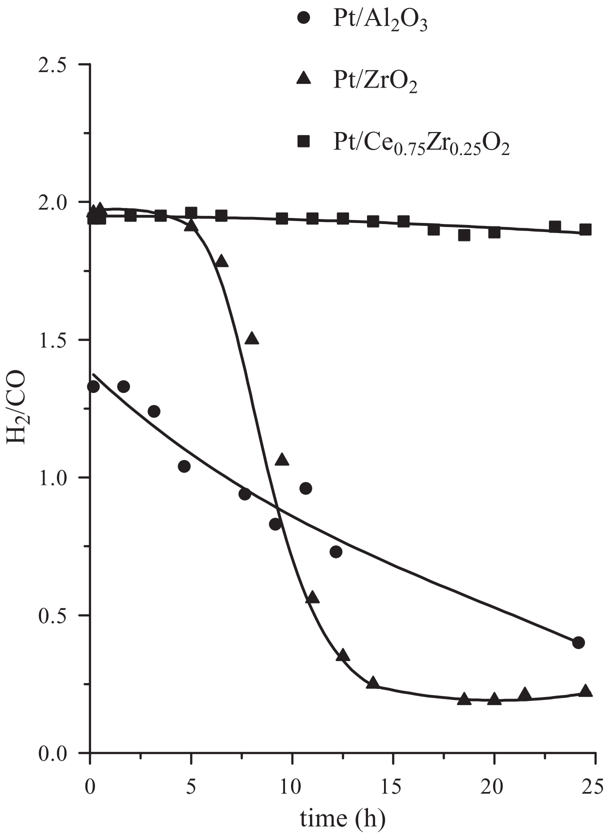

Fig. 2. H_2/CO ratio obtained from partial oxidation of methane versus time on stream for Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts. Reaction conditions: $T = 1073$ K; CH_4/O_2 ratio = 2:1.

Fig. 5 presents the H_2/CO ratio obtained from CO_2 reforming data. In all cases, the H_2/CO ratio was lower than 1. This result could be attributed to a contribution of the reverse water gas shift reaction (Eq. (4)) [30].

Several authors have reported that Pt/ZrO_2 catalysts exhibit good stability on the CO_2 reforming of methane while a strong deactivation is observed on Pt/Al_2O_3 and Pt/SiO_2 catalysts [5,35–37]. The performance of the Pt/ZrO_2 catalyst has been associated with a low carbon deposit. Furthermore, many studies have shown that the addition of promoters, such as CeO_2 to ZrO_2 support, promoted the activity and stability of the Pt/ZrO_2 catalysts [6,7,38]. According to CO_2 reforming mechanism, the first reaction path comprehends the decomposition of CH_4 on the metal particle, resulting in the formation of carbon and hydrogen. Carbon formed can partially reduce the oxide support near the metal particles, generating CO_x species and oxygen vacancies. In the absence of a reducible oxide, carbon will deposit on the metal particle. The second path is the dissociation of CO_2 from the support followed by the formation of CO and O, which can reoxidize the support. Then, CO_2 replenishes the oxygen vacancies and makes the support able to carry out the redox

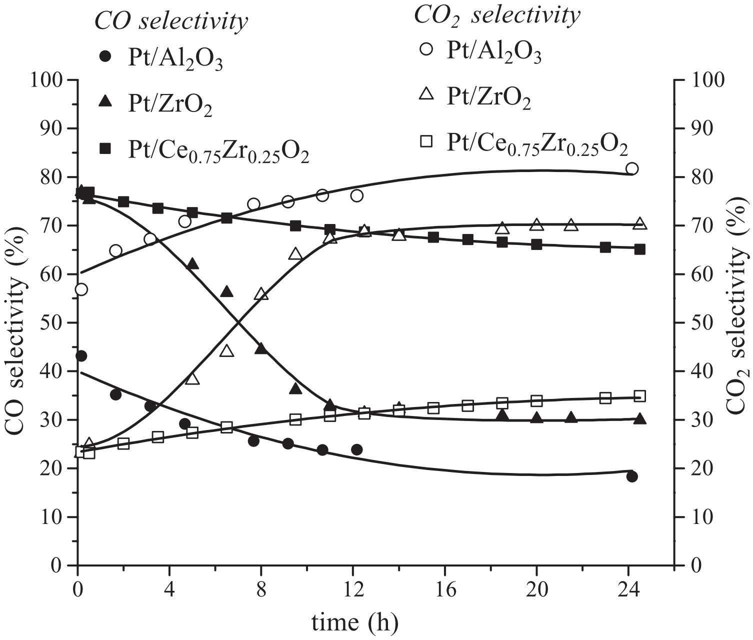

Fig. 3. CO and CO_2 selectivity on partial oxidation of methane versus time on stream for Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts. Reaction conditions: $T = 1073$ K; CH_4/O_2 ratio = 2:1.

mechanism for continuous cleaning, promoting the carbon removal. Therefore, the CO_2 reforming mechanism involves the occurrence of these two paths at the same time. The balance between the rate of methane decomposition and the rate of oxygen transfer determines the overall stability of the catalyst. The addition of cerium oxide to zirconia increases the reducibility and oxygen transfer ability of the support, improving the activity and stability of the catalyst.

In this work, the increase of carbon deposits around or near the metal particles on Pt/Al_2O_3 and Pt/ZrO_2 catalysts affects the CO_2 dissociation and inhibits methane conversion on the CO_2 reforming. The enhancement of the activity and stability on the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst could be assigned to the higher amount of oxygen vacancies in the proximity of metal particles as revealed by the OSC measurements (Table 1). The addition of ceria to zirconia support greatly increases the rate of oxygen transfer and consequently the carbon removal.

According to these results, the increase of carbon deposits around or near the metal particle affects the CO_2 dissociation and inhibits the CO_2 reforming step of the partial oxidation of methane on Pt/Al_2O_3 and Pt/ZrO_2 catalysts. Regarding the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst, the selectivity towards CO practically has not changed during the reaction due to the redox mechanism of carbon removal promoted by the support, as revealed by the OSC measurements (Table 1).

The deactivation of the Pt/ZrO_2 catalyst was stronger on partial oxidation of methane as compared to that observed on CO_2 reforming of methane. As described previously,

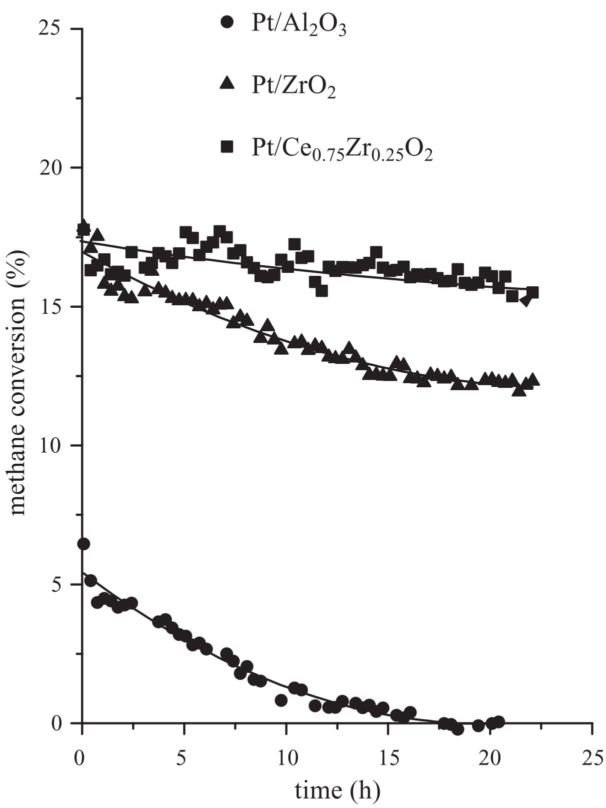

Fig. 4. Methane conversion on CO_2 reforming of methane versus time on stream for Pt/Al_2O_3, Pt/ZrO_2, and $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts. Reaction conditions: $T = 1073$ K; CH_4/CO_2 ratio = 2:1.

the second step of the partial oxidation of methane involves the occurrence of both CO_2 and steam reforming of methane. Then, the CO_2 reforming of methane in the presence of water was studied in order to evaluate the effect of water on the stability of Pt/ZrO_2 catalyst.

3.4. CO_2 reforming of methane in the presence of water

Fig. 6 shows the conversion of methane on CO_2 reforming in the presence of water at 1073 K for Pt/ZrO_2 catalyst. Comparing these results with those obtained for dry reforming (Fig. 4), the initial CH_4 conversion was higher and the deactivation was stronger in the presence of water. The higher methane conversion was associated with the occurrence of steam reforming of methane (Eq. (1)), in addition to dry reforming reaction (Eq. (3)). The deactivation could be related to the formation of carbon deposits on the metal, suggesting that the cleaning capacity of the support decreased in the presence of water. In fact, Otsuka et al. [39] showed the reoxidation of the reduced cerium oxide by water. This oxidation decreases the number of oxygen vacancies of the

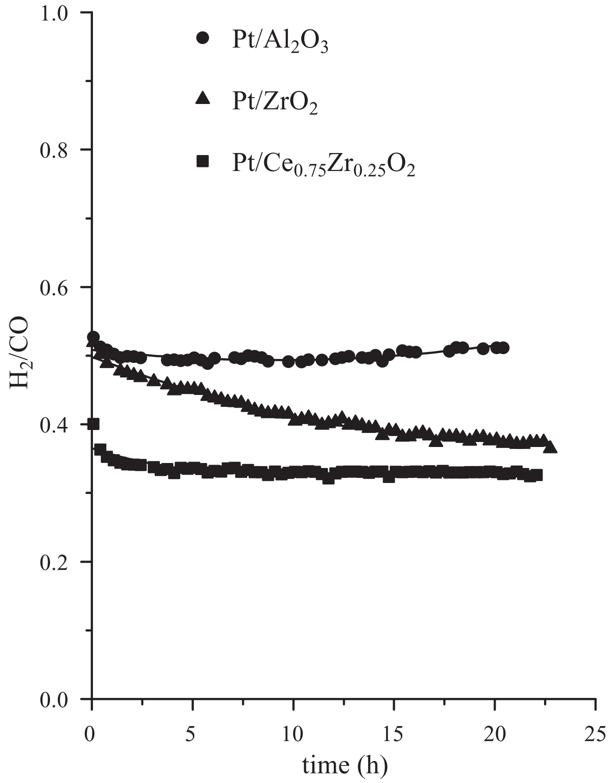

Fig. 5. H_2/CO ratio obtained from CO_2 reforming of methane versus time on stream for Pt/Al_2O_3, Pt/ZrO_2, and Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalysts. Reaction conditions: $T = 1073$ K; CH_4/CO_2 ratio = 2:1.

support. Then, the strong deactivation of the Pt/ZrO_2 catalyst on the partial oxidation of methane could be attributed to the disappearance of the oxygen vacancies of support caused by water, which is produced during the first step of the mechanism proposed for partial oxidation.

On the other hand, the Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalyst is very stable on both CO_2 reforming and partial oxidation of methane. The oxidation of the $Ce_{0.75}Zr_{0.25}O_2$ support in the presence of water should be less significant due to its highest amount of oxygen vacancies, improving the stability of the Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalyst.

3.5. Pulses of CH_4 and O_2 or CO_2

The capacity to remove the carbon of the Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalyst surface was investigated using pulses of CH_4 and O_2 or CO_2. Figs. 7 and 8 showed the consumption of CH_4 during the sequence of $CH_4/O_2/CH_4$ and $CH_4/CO_2/CH_4$ pulses, respectively. The H_2 and CO production is presented in Figs. 9 and 10.

During the first set of CH_4 pulses, only H_2 and CO (Figs. 9 and 10) were produced and each pulse resulted in less H_2 and CO formation. This result can be attributed to coke

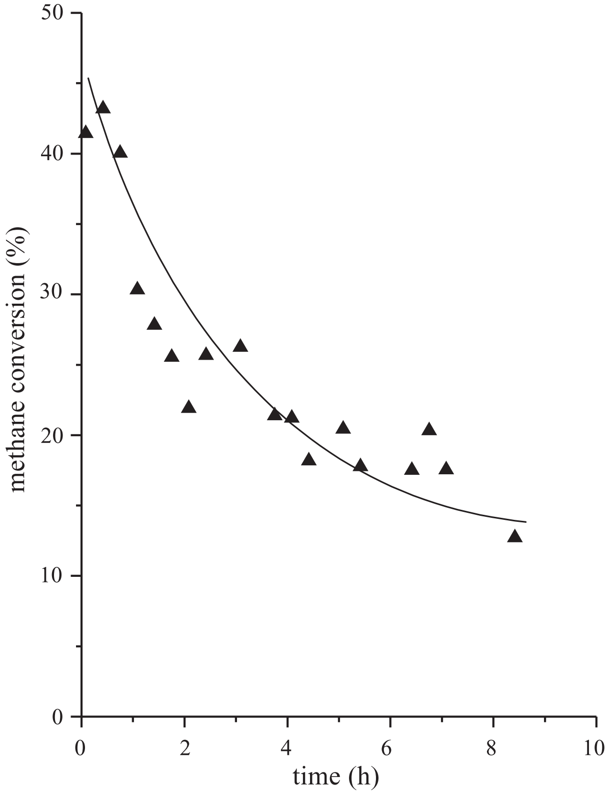

Fig. 6. Methane conversion on CO_2 reforming in the presence of water versus time on stream for the Pt/ZrO_2 catalyst. Reaction conditions: $T = 1073$ K; $CH_4/CO_2 = 2:1$; 15 ml/min H_2O.

deposition. H_2 is formed from methane dissociation while CO should be produced by the reaction between carbon from methane dissociation and oxygen from the supports, since there is no oxygen gas-phase species in the system.

During either O_2 (Fig. 9) or CO_2 pulses (Fig. 10), no H_2 was formed, but CO production was observed. However, during CO_2 pulses, the amount of CO produced was higher. This result could be explained by the CO_2 reforming mechanism described previously [7]. According to this mechanism, the CO formed during CO_2 pulses can be originated from both CO_2 dissociation and carbon removal. However, during the O_2 pulses, CO originates from carbon removal.

In the second set of CH_4 pulses on both sequences of $CH_4/O_2/CH_4$ and $CH_4/CO_2/CH_4$ pulses, the role of support on the removal of carbon is evident. During this set of CH_4 pulses, the CH_4 consumption, H_2 production, and CO formation slightly decreased in comparison to the results obtained in the first set of CH_4 pulses. These results indicate that the oxygen vacancies of $Ce_{0.75}Zr_{0.25}O_2$ support, formed during the first set of CH_4 pulses, were partially replenished during O_2 or CO_2 pulses.

Furthermore, in the first few pulses, CO_2 and H_2O (not shown in Figs. 7–10) were also formed in addition to CO and H_2 on the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst. These results

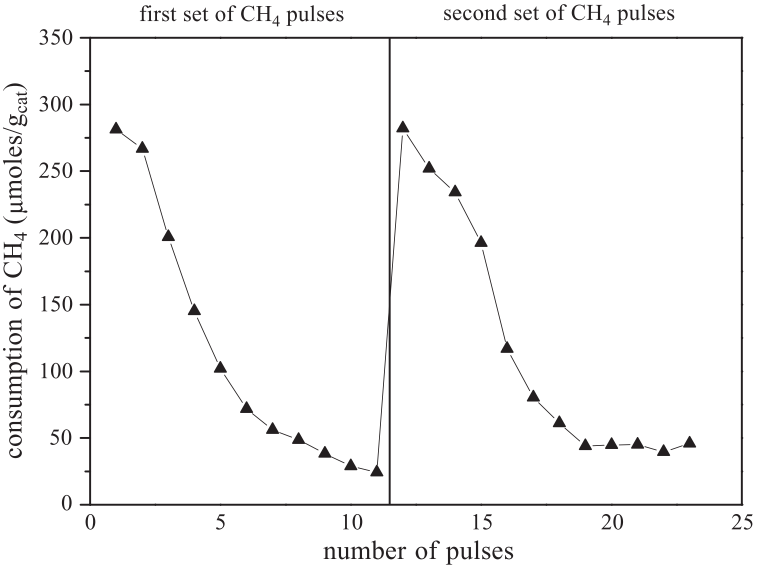

Fig. 7. Consumption of CH_4 during CH_4 pulses at 1073 K over the Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalyst. First set of CH_4 pulses: after pretreatment. Second set of CH_4 pulses: after O_2 pulses.

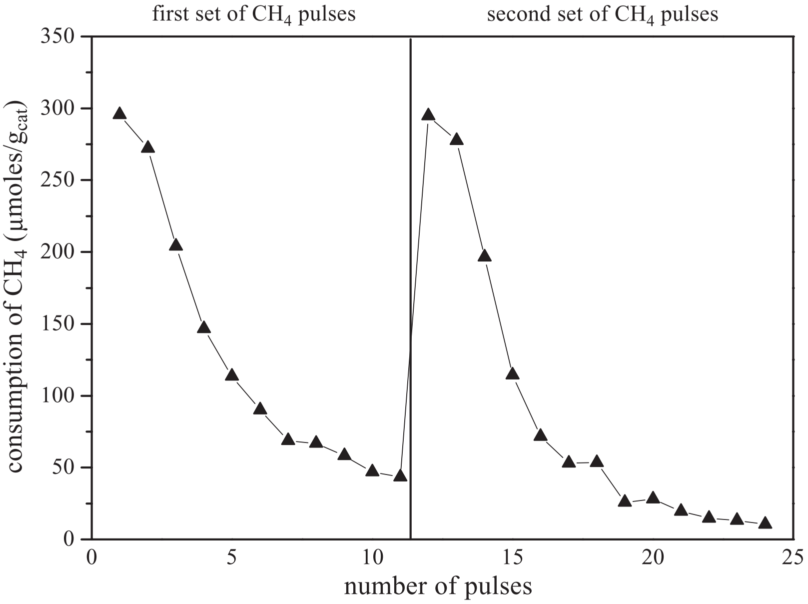

Fig. 8. Consumption of CH_4 during pulses of CH_4 at 1073 K over the Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalyst. First set of CH_4 pulses: after pretreatment. Second set of CH_4 pulses: after CO_2 pulses.

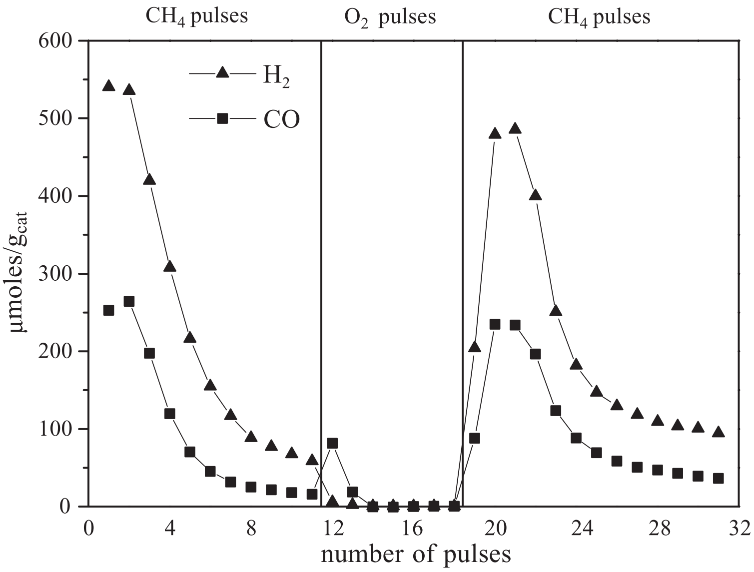

Fig. 9. H_2 and CO production during pulses of either CH_4 or O_2 at 1073 K over the Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalyst.

indicate that a fraction of platinum particles was oxidized during O_2 and CO_2 pulses. Fathi et al. [37] also observed the formation of CO_2, in the first pulse of methane, for the Pt/CeO_2/Al_2O_3-calcined catalyst. However, in the second set of the sequence of CH_4/

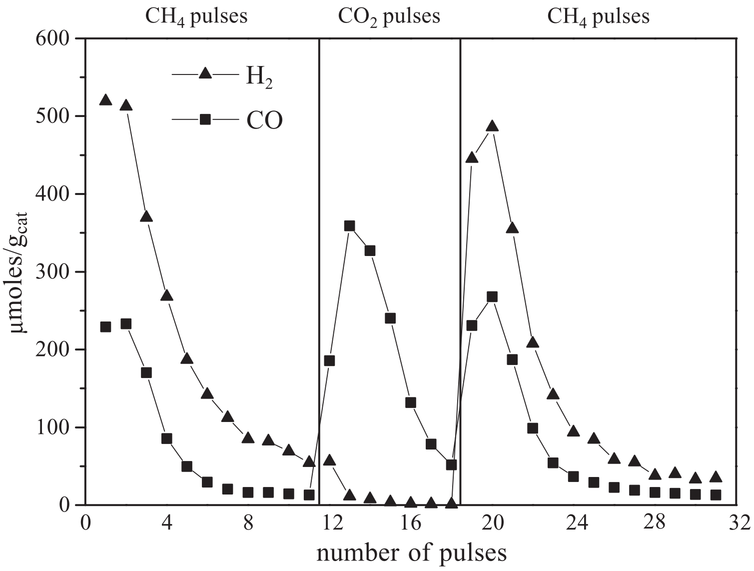

Fig. 10. H_2 and CO production during pulses of either CH_4 or CO_2 at 1073 K over the Pt/$Ce_{0.75}Zr_{0.25}O_2$ catalyst.

CO_2/CH_4 pulses, the production of CO_2 and H_2O was much lower than that observed for the sequence of $CH_4/O_2/CH_4$ pulses, suggesting that the oxidation of metal particles was stronger in O_2 pulses. Moreover, the selectivities to CO and H_2 achieved a maximum around the second pulse and then sharply decreased. These results agree with those obtained by Pantu et al. [40] for Pt/CeO_2 and $Pt/Ce_{0.50}Zr_{0.50}O_2$ catalysts, using CH_4 pulses. According to them, the reaction results in complete oxidation of methane until a certain degree of reduction has been reached, after which the selectivity to CO rapidly increases.

Stagg-Willians et al. [6] obtained similar results for Pt/ZrO_2 and $Pt/Ce-ZrO_2$ catalysts, during a sequence of $CH_4/CO_2/CH_4$ pulses at the same conditions used in this work. They observed that the $Pt/Ce-ZrO_2$ catalyst produced the highest amount of H_2 and CO, during the first set of CH_4 pulses. During CO_2 pulses, the vacancies of the support were replenished. On the second set of CH_4 pulses, the H_2 and CO production was higher on $Pt/Ce-ZrO_2$ catalysts. They concluded that a higher degree of reduction results in an increase of the number of oxygen vacancies near the metal particle and a subsequent increase in the ability to clean the carbon formed on the metal particles. A similar mechanism was proposed by Pantu et al. [40]. According to these authors, the carbon formed from methane dissociation is oxidized by lattice oxygen at or near the contact perimeter between the support and platinum particles, or produce an inactive carbon. Then, in this work, the results obtained during the sequences of $CH_4/O_2/CH_4$ and $CH_4/CO_2/CH_4$ pulses suggest that the addition of CeO_2 to ZrO_2 increased the number of oxygen vacancies formed around the metal particle, increasing the cleaning capacity of the support. These results agree with the OSC experiments.

4. Conclusions

The results of catalytic activity on both the CO_2 reforming and the partial oxidation of methane revealed the important role of the support on the mechanism of these reactions. A strong deactivation was observed on the Pt/Al_2O_3 catalyst in both reactions. The addition of ceria to zirconia greatly promoted the stability of the catalyst due to a higher oxygen exchange capacity of the support. The higher rate of oxygen transfer keeps the metal surface free from carbon. This promotional effect on the CO_2 reforming of methane affects the partial oxidation of methane, which comprehends two steps: combustion of methane and CO_2 and steam reforming of unreacted methane. The strong deactivation observed for the Pt/ZrO_2 catalyst during the partial oxidation of methane could be attributed to the oxidation of the support by water produced during the combustion of methane.

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