Study of the mechanism of the autothermal reforming of methane on supported Pt catalysts

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ABSTRACT

Autothermal reforming of methane was investigated on Pt/CeO\textsubscript{2}, Pt/ZrO\textsubscript{2} and Pt/Ce-ZrO\textsubscript{2} catalysts. Temperature programmed surface reaction experiments (TPSR) showed the reaction proceeds through an indirect mechanism. A carbon removal mechanism was observed for the catalysts that presented oxygen storage capacity, favoring the stability of the catalyst in the reaction.

1. INTRODUCTION

Steam methane reforming (SMR) and non-catalytic partial oxidation has been the commercial technology for producing syngas from natural gas. However, both technologies are not suited to GTL plants due to the required H\textsubscript{2}/CO ratio for FT synthesis. Autothermal reforming (ATR) fulfills the requirements to a syngas with H\textsubscript{2}/CO ratio of 2, the ratio necessary to GTL plant. Moreover, ATR has relative compactness, lower capital cost and greater potential for economy of scale [1]. ATR combines non catalytic partial oxidation with steam reforming in one reactor. The mechanism of the combined reactions (partial oxidation and steam reforming of methane) is not reported in the literature. In order to project good catalysts to the autothermal reforming, it is imperative to know the mechanism of this reaction. The aim of this work is to study the mechanism of the autothermal reforming on supported Pt catalysts.
2 EXPERIMENTAL

2.1. Catalyst preparation

The ZrO₂ support was prepared by calcination of zirconium hydroxide (MEL Chemicals) at 823 K, for 2 h. The CeO₂ support was obtained by calcination of (NH₄)₂Ce(NO₃)₆ (ALDRICH) at 773 K, for 2 h. The Ce-ZrO₂ (18 mol % of CeO₂ and 82 mol % of ZrO₂) was supplied by MEL Chemicals and was calcined at 1073 K for 1 h. The catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of H₃PtCl₆ (Aldrich) and were dried at 393 K. Then, the samples were calcined under air (50 cm³/min) at 673 K, for 2 h.

2.2. Oxygen storage capacity (OSC)

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 H₂ 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%O₂/He mixture was passed through the catalyst until the oxygen uptake was finished.

2.3. Temperature Programmed Surface Reaction (TPSR)

After the activation procedure, the sample (300 mg) was purged in He at 1073 K for 30 min, and cooled to room temperature. Then the sample was submitted to a flow of CH₄/H₂O/O₂/He (4:2:1:25) at 200 cm³/min while the temperature was raised up to 1073 K at heating rate of 20 K/min.

2.4. Reaction conditions

Reaction was performed in a quartz reactor at atmospheric pressure. The reaction was carried out at 1073 K and WHSV = 160 h⁻¹ over all catalysts. A reactant mixture containing methane, oxygen and water (CH₄/O₂ ratio of 4:1 and CH₄/H₂O ratio of 2:1) diluted in helium was used at a flow rate of 200 cm³/min. The exit gases were analyzed using a gas chromatograph (Chrompack CP 9001) equipped with a thermal conductivity detector and a Hayesep D column.

3. RESULTS AND DISCUSSION

3.1. Oxygen storage capacity (OSC)

Table 1 presents the oxygen storage capacity (OSC) measurements. Pt/CeO₂ and Pt/Ce₀.₈Zr₀.₂O₂ catalysts exhibited high and similar oxygen consumption whereas Pt/ZrO₂ catalysts practically did not present oxygen uptake. Cerium oxide has an important oxygen storage capacity [2]. This property is attributed to the ability of cerium to act as an oxygen buffer by storing/releasing O₂ due to the Ce⁴⁺/Ce³⁺ redox couple [2]. The CeO₂ redox properties are
enhanced by the incorporation of ZrO₂ into CeO₂ lattice. The ZrO₂ addition increase the oxygen vacancies of the support due to the high oxygen mobility of the solid solution formed.

3.2. Temperature Programmed Surface Reaction (TPSR)

Figure 1 shows the TPSR curves obtained for Pt/Ce₀.₁₈Zr₀.₈₂O₂ catalyst. The TPSR profiles of all catalysts revealed consumption of methane and oxygen followed by CO₂ and H₂O formation around 720K. However, the production of H₂ and CO was only observed above 790K. These results are consistent to the indirect mechanism. According to this mechanism, in the first step, combustion of methane occurs producing CO₂ and H₂O. In the second one, synthesis gas is produced via carbon dioxide and steam-reforming reaction of the unreacted methane. The same mechanism was observed on the partial oxidation of methane on supported Pt catalysts [3].

![TPSR Diagram](image_url)

**Fig. 1-** Temperature Programmed Surface Reaction of Pt/Ce-ZrO₂ catalyst.
3.3 Autothermal Reforming of Methane

The product distribution on the methane autothermal reforming, as a function of reaction temperature, is shown in Figure 2 for the Pt/ZrO₂ catalyst. The O₂ conversion is 100% over the whole temperature range. The production of steam and CO₂ decreases rapidly as the temperature increases due to the exothermic nature of total combustion. The lower production of H₂ and CO up to 600°C is also related to the occurrence of total combustion. Figure 3 shows the methane conversion versus time on stream (TOS) for all the samples. Pt/ZrO₂ catalyst showed the highest initial conversion but deactivated during the reaction. On the other hand, Pt/CeO₂ and Pt/Ce₀.₁₈Zr₀₈₂O₂ catalysts were quite stable.

Recently, it has been reported in the literature that the support has an important role on the mechanism of the CO₂ reforming [4-6] and the partial oxidation of methane [3,7]. A strong deactivation on the Pt/Al₂O₃ catalyst was observed on both reactions. The performance of Pt/ZrO₂ catalyst depended on the reaction investigated. Several authors have reported that Pt/ZrO₂ catalyst exhibit a good stability on the CO₂ reforming of methane [4-6]. The performance of the Pt/ZrO₂ catalyst has been associated with the low carbon

![Figure 2. Composition profiles for autothermal reforming of methane as a function of temperature over the Pt/ZrO₂ catalyst.](image)
deposit. A two independent path mechanism has been proposed to explain the stability of the Pt/ZrO$_2$ catalyst on the CO$_2$ reforming of methane. This mechanism involves the occurrence of CH$_4$ decomposition on metal particle and CO$_2$ dissociation on oxygen vacancies of the support at the same time [4,5]. 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 [3], the second step of partial oxidation of methane involves the occurrence of both CO$_2$ and steam reforming of methane.

The strong deactivation of the Pt/ZrO$_2$ catalyst on partial oxidation of methane was attributed to disappearance of the oxygen vacancies of support caused by the reoxidation of the reduced zirconium oxide by water, which is produced during the first step of the mechanism proposed for partial oxidation [7]. 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 on the CO$_2$ reforming of methane. The addition of ceria to zirconia greatly promoted the stability of the catalyst due to the higher oxygen exchange capacity of the support. The higher rate of oxygen transfer keeps the metal surface free of 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.

Fig. 3. Autothermal reforming of methane on platinum catalysts at 1073K.
Therefore, the performance of the Pt/ZrO₂, Pt/CeO₂ and Pt/Ce₀.₆Zr₀.₄O₂ catalysts on the autothermal reforming of methane can be explained taking into account the two step mechanism proposed. Since water can reoxidize the reduced support, the deactivation of the Pt/ZrO₂ catalyst could be attributed to the disappearance of the oxygen vacancies of this support. This could inhibit the second step of the mechanism suggested. On the other hand, Pt/CeO₂ and Pt/Ce₀.₆Zr₀.₄O₂ catalysts are very stable. In this case, the oxidation of CeO₂ and Ce₀.₆Zr₀.₄O₂ supports did not affect the stability due to the higher amount of oxygen vacancies of these supports, as revealed by the OSC measurements.

4. CONCLUSIONS

Autothermal reforming proceeds through a two-step mechanism on platinum catalysts supported on CeO₂, ZrO₂ and Ce-ZrO₂: combustion of methane followed by CO₂ and steam reforming of unreacted methane. The OSC capacity showed to be an essential property in order to keep the catalysts stable, as the oxygen released/storage allowed a continuous removal of carbonaceous deposits from the metal surface.

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