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Partial oxidation of methane over rhodium catalysts for power generation applications

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Abstract

The partial oxidation of methane (POM) to syngas, i.e. H_2 and CO, over supported Rh catalysts was investigated at atmospheric pressure. The influence of support material, Rh loading and the presence of water vapor on the methane conversion efficiency and the product gas composition was studied. The catalysts containing ceria in the support material showed the highest activity and formation of H_2 and CO. By increasing the Rh loading, a decrease of the ignition temperature was obtained. The addition of water vapor to the reactant gas mixture was found to increase the ignition temperature and the formation of hydrogen, which is favorable for combustion applications where the catalytic POM stage is followed by H_2-stabilized homogeneous combustion.

Keywords: Catalytic combustion; Partial oxidation of methane; Rhodium catalysts; Ceria

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1. Introduction

Catalytic combustion has been extensively investigated for power generation applications [1,2]. Advantages of this combustion method are low NO_x, CO and soot emissions, as well as the flexibility to perform the combustion reaction over a wide range of fuel-to-air ratios. Palladium (Pd) has been found to be the most active catalyst for methane combustion under fuel-lean reaction conditions. However, Pd-based catalysts suffer from deactivation at higher temperatures due to the phase transition $PdO \rightarrow Pd^0$ and are also strongly inhibited by water [3,4]. An alternative approach is a two-stage process consisting of a catalytic fuel-rich step, where only partial oxidation of the fuel occurs, followed by lean homogeneous combustion. Syngas, i.e. H_2 and CO, is produced under fuel-rich conditions, resulting in a hydrogen-stabilized second stage combustion process. Only limited studies of this combustion concept have been published in the past. Lyubovsky et al. investigated methane combustion under various fuel-to-air ratios for supported Pd, Pt and Rh catalysts demonstrating benefits such as higher activity during fuel-rich operation [5].

Various metals, such as Rh, Pd, Pt, Ru, Ni, Co and Fe, have been investigated as catalysts for partial oxidation of methane (POM) to syngas (1) [6]. Several studies have reported that especially Rh-based catalysts are suitable for this reaction due to their high activity, syngas selectivity and resistance to carbon deposition [7,8].

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2 \quad (1)$$

This paper deals with an experimental study of the catalytic fuel-rich stage described above, i.e. partial oxidation of methane ($\lambda = 0.25$) to syngas. The influence of support material, Rh loading and the presence of water vapor on the methane conversion efficiency and the product gas composition was studied.

2. Experimental

2.1. Catalyst preparation

Supported rhodium catalysts were prepared by the incipient wetness impregnation method using $Rh(NO_3)_3$

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as metal precursor. The metal oxides ZrO_2, Ce–ZrO_2 with 17.5% CeO_2 (MEL Chemicals) and $Ce_{0.9}La_{0.1}O_2$, all previously calcined at 500 °C for 5 h, were used as support material. The Ce–La mixed oxide was prepared by coprecipitation of the corresponding metal nitrates in ammonia. After noble metal impregnation (0.2–1 wt.%), the catalysts were dried at 110 °C followed by calcination in air at 800 °C for 4 h. Finally, ethanol suspensions of the powders were ball-milled and coated on cordierite monoliths (Corning 400 cpsi, length 10 mm, diameter 14 mm).

2.2. Activity tests

Activity tests were conducted in a laboratory-scale quartz glass reactor placed in an electrical furnace. The temperature was monitored by thermocouples inserted before and after the catalyst as well as inside the furnace. The product gas was analyzed for CH_4, O_2, CO_2, CO and H_2. Nitrogen diluted fuel-rich gas mixtures (3.3% CH_4, 1.7% O_2) were introduced to the reactor at a GHSV of 99,000 h^{-1}. Some tests were performed in the presence of 10% water vapor (GHSV 110,000 h^{-1}). Repeated heating and cooling cycles in the temperature range of 200–750 °C were performed for each catalyst whilst measuring the activity.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) analysis was carried out on a Siemens D5000 diffractometer scanning 2θ from 10–90° using monochromatic Cu Kα radiation. Crystal phases were identified by using JCPDS-files. The BET surface area was measured by N_2 adsorption/desorption using a Micromeretics ASAP 2010 instrument. The samples were degassed at 250 °C prior to analysis. Temperature programmed reduction (TPR) experiments and oxygen storage capacity (OSC) measurements were performed on selected catalysts using a Micromeretics AutoChem 2910 instrument. The samples (0.5 g) were oxidized in 5% O_2/He at 700 °C for 30 min prior to reduction. After purging the system with Ar, the reduction was carried out in 5% H_2/Ar (30 ml/min) by heating the sample from room temperature to 800 °C at a heating rate of 10 °C/min. Subsequently, the OSC measurements were conducted by injecting oxygen pulses (1 ml) in a He flow at 450 °C until no more O_2 uptake could be observed.

3. Results and discussion

3.1. Catalyst characterization

X-ray diffractograms of the catalysts are presented in Fig. 1. The monoclinic ZrO_2 phase (peaks at 28.4 and 31.6 °) was detected for all zirconia-supported catalysts after calcination at 800 °C. The XRD pattern of the Ce-doped zirconia was characteristic of tetragonal zirconia (peak at 30.2°). This stabilization of the tetragonal phase by incorporation of another metal cation has been observed previously [9]. For the mixed oxide containing ceria and lanthana, the XRD data indicated that fluorite-type solid solutions were formed (peaks at 28.6 and 33.1°). The X-ray diffractogram of pure CeO_2 (peaks at 28.7 and 33.2°), prepared by the same precipitation method, is also displayed in Fig. 1 for comparison. The position of the peaks was shifted to lower 2θ values when La^{3+} ions were integrated in the CeO_2 crystal lattice due to an increase of the lattice parameter as reported in the past [10]. No segregated phase of lanthanum oxide could be identified. The amount of rhodium in the catalysts was too low to be detected by XRD.

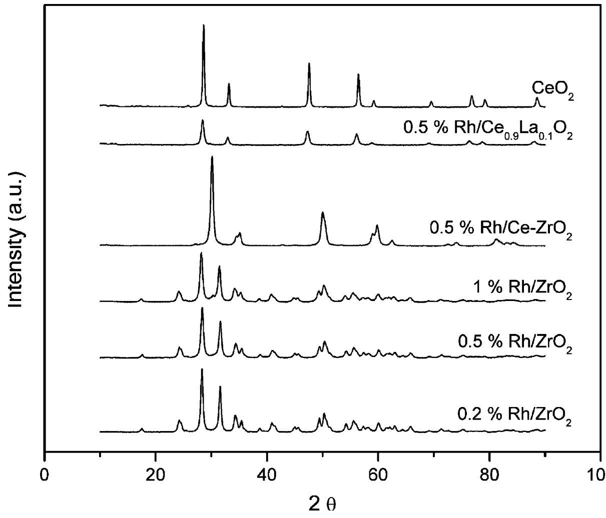

Fig. 1. XRD patterns of Rh catalysts and CeO_2 after calcination at 800 °C for 4 h.

BET surface areas and results from TPR and OSC measurements are listed in Table 1. All catalysts had approximately equal surface areas (30–35 m^2/g) except for 0.5% Rh/Ce–ZrO_2, which had a slightly higher surface area (43 m^2/g). The TPR experiments revealed a strong relationship between support material and reduction temperature. The reduction temperature increased in the order of Rh/$Ce_{0.9}La_{0.1}O_2$ < Rh/Ce–ZrO_2 < Rh/$ZrO_2$for the low-temperature peak, including Rh reduction. A significantly higher intensity of the reduction peaks could be observed for the Ce–ZrO_2- and $Ce_{0.9}La_{0.1}O_2$-supported catalysts when compared to Rh/ZrO_2 indicating that reduction of the support, as well as of rhodium, occurs at lower temperatures.

Table 1
Textural and redox properties of the catalysts after calcination at 800 °C for 4 h

Sample	BET surface area (m^2/g)	TPR peak temperatures (°C)	O_2 uptake (μmol/g)	Ce^{3+} (%)
0.5% Rh/Ce–ZrO_2	43	150,585	264	80
0.5% Rh/$Ce_{0.9}La_{0.1}O_2$	35	65,800	321	25
0.2% Rh/ZrO_2	29			
0.5% Rh/ZrO_2	33	250,530	87	
1% Rh/ZrO_2	34			

A very broad and weak reduction peak corresponding to support reduction was also observed in the high-temperature range for all catalysts. Similar results have been reported previously by Fornasiero et al. [11]. According to their study, the addition of rhodium to CeO_2–ZrO_2 solid solutions was found to promote low-temperature reduction of the support material due to spill-over of hydrogen from the noble metal to the support.

The OSC measurements revealed a significantly higher O_2 uptake for Ce–ZrO_2 and $Ce_{0.9}La_{0.1}O_2$ than for ZrO_2. The degree of reduction is evaluated from O_2 uptake measurements and reported as percentage of Ce^{3+} in Table 1. Note that noble metal oxidation by O_2 uptake is not included in the calculations due to the low metal loading. The amount of Ce^{3+} was estimated to 80 and 25% for Ce–ZrO_2 and $Ce_{0.9}La_{0.1}O_2$, respectively. The high oxygen storage capacity of CeO_2 is related to the ability of the material to shift between reduced and oxidized state, i.e. Ce^{3+}/Ce^{4+} [12]. The addition of dopants, such as Zr and La, to CeO_2 has been reported to increase the OSC and material stability in several studies [13,14].

3.2. Activity tests

The activity tests showed that the rhodium catalysts in this study are active for partial oxidation of methane in the temperature range investigated. The results from the second heating/cooling cycle are always reported in order to obtain a more stable catalytic performance. A slight improvement in activity could be observed during the second heating ramp, probably related to the reduction of Rh_2O_3.An experimental scatter of approximately 5% was thereafter observed. The conversion of methane and oxygen for the catalysts in N_2-diluted air is depicted in Fig. 2. Ignition temperatures, defined as the inlet temperature required for 10% conversion of methane, of 300–480 °C were obtained.

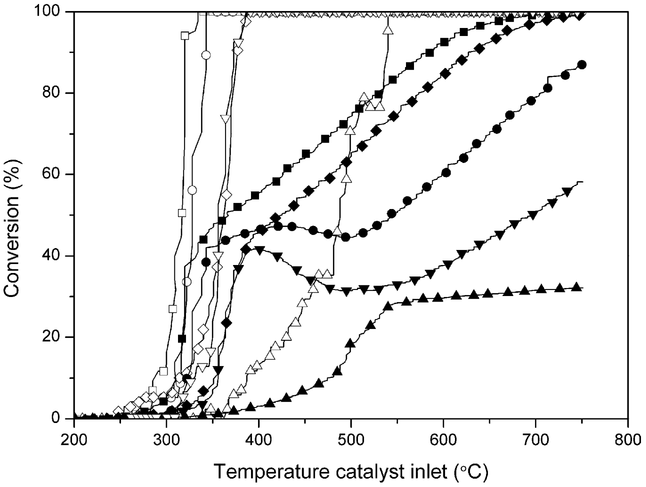

Fig. 2. Conversion of methane (closed symbols) and oxygen (open symbols) in N_2-diluted air vs. catalyst inlet temperature for 0.5% Rh/Ce–ZrO_2 (■), 0.5% Rh/$Ce_{0.9}La_{0.1}O_2$ (◆), 0.2% Rh/ZrO_2 (▲), 0.5% Rh/ZrO_2 (▼) and 1% Rh/ZrO_2 (•).

Both the support material and the Rh-loading had a significant impact on the catalyst performance. The presence of ceria in the support improved the activity, especially at higher temperatures, and complete conversion could be obtained. This behavior is probably related to the high oxygen mobility of ceria. Previous studies have shown that the addition of Ce to ZrO_2 increases the activity and stability of Pt and Ni catalysts for partial oxidation of methane due to an increased CH_4 dissociation and enhanced carbon elimination from the surface [15,16]. Although, carbon deposition should not be a significant problem for the Rh-based catalysts investigated in this work.

The superior activity of the catalysts containing ceria in the support is also explained by the higher rhodium reducibility of these materials compared to zirconia-supported catalysts as revealed by TPR experiments (see Table 1). Metallic rhodium is generally considered to be the active phase of the catalyst. For the ZrO_2-supported catalysts with a Rh-loading of 0.5–1 wt.%, a decrease in methane conversion could be observed at about 450 °C after ignition had occurred. The reason for this behavior has not been studied in detail. However, it could be related to mass transport limitations, which would influence the reaction at higher temperatures, resulting in an insufficient supply of oxygen. This would not occur for catalysts containing ceria since oxygen can be supplied from the support.

The rapid depletion of oxygen and initial high production of CO_2 indicate that complete oxidation of methane occurs initially. Note that the temperature at the catalyst inlet has been recorded and not the actual surface temperature of the catalyst, which obviously is higher due to the strong exothermicity of the complete oxidation reaction. Direct partial oxidation and/or reforming reactions can take place when the oxygen conversion is complete due to the high surface temperature. Increasing the Rh-loading from 0.2 to 1 wt.% significantly affected the CH_4 conversion resulting in a decrease of the ignition temperature by approximately 160 °C.

The product gas composition obtained for the catalysts is presented in Fig. 3. For power generation applications, the absolute values of the product concentrations after the catalyst are of importance in order to evaluate the stability of the following homogeneous combustion stage. Simultaneous H_2, CO and CO_2 production can be observed. The H_2 production follows the same behavior as observed for the methane conversion for all catalysts. The formation of CO_2 occurs mainly at lower temperatures whereas CO is produced at higher temperatures for the tests performed in N_2-diluted air. H_2/CO ratios close to 2 were obtained for these catalysts at 750 °C, indicating that partial oxidation is the overall reaction occurring.

The product gas composition is altered when water vapor is added to the reaction mixture as observed in Fig. 3. Higher amounts of CO_2 are formed in the entire temperature range whereas less CO is formed. Also, at higher temperatures, the formation of H_2 was enhanced by adding water resulting in

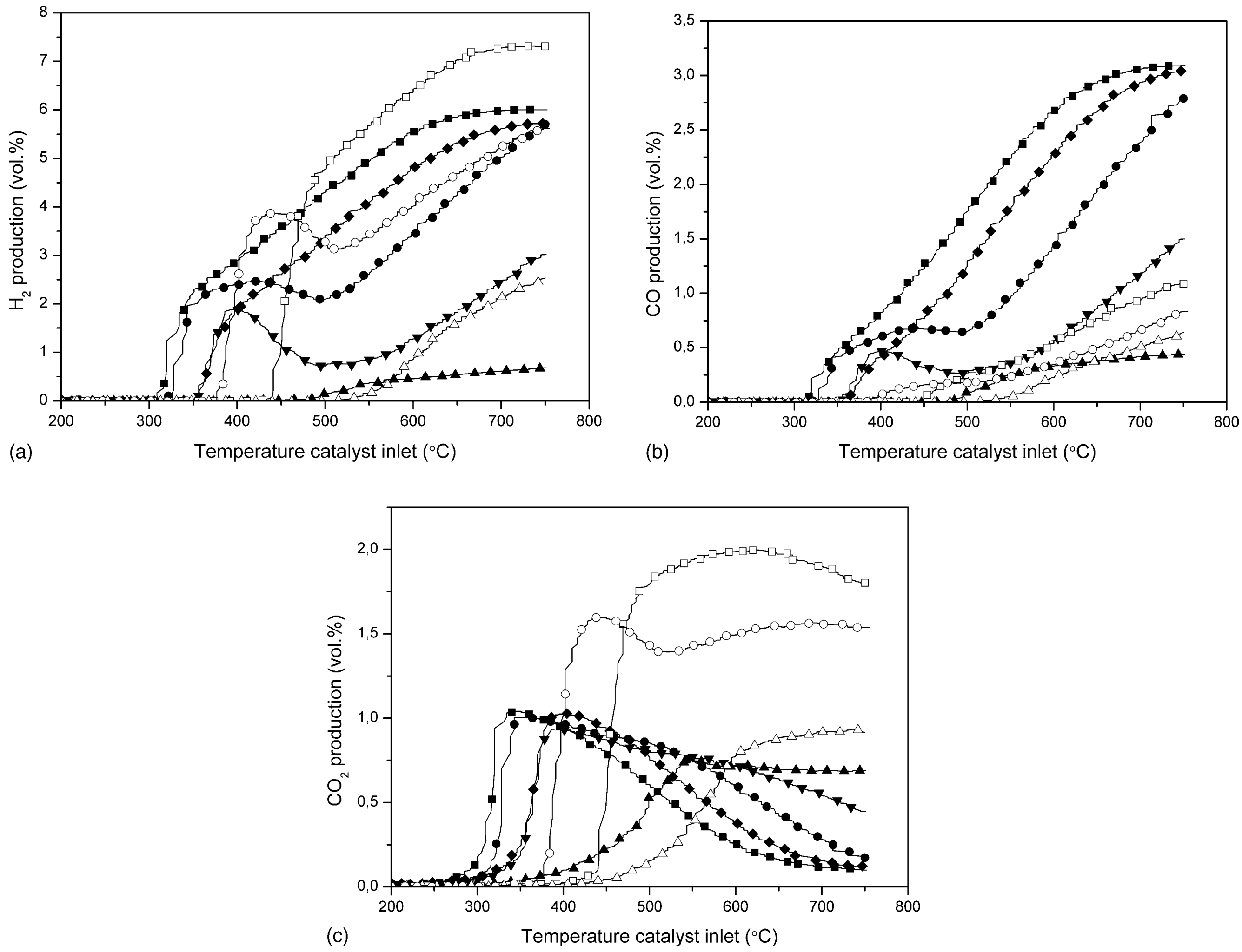

Fig. 3. (a) H_2 production, (b) CO production and (c) CO_2 production in N_2-diluted air (closed symbols) and in 10% H_2O/N_2-air (open symbols) vs. catalyst inlet temperature for 0.5%Rh/Ce–ZrO_2 (■), 0.5% Rh/$Ce_{0.9}La_{0.1}O_2$ (◆), 0.2% Rh/ZrO_2 (▲), 0.5% Rh/ZrO_2 (▼) and 1% Rh/ZrO_2 (•).

H_2/CO ratios higher than 2. Similar trends could be observed for the catalysts not shown in Fig. 3, i.e. 0.5% Rh/$Ce_{0.9}La_{0.1}O_2$ and 0.5% Rh/ZrO_2. The product gas composition is altered due to the water gas shift reaction taking place (2). The high amount of water vapor in the reaction mixture shifts the equilibrium favoring the products H_2 and CO_2. Furthermore, the addition of ceria was found to increase the catalytic activity.

$$CO + H_2O = CO_2 + H_2 \tag{2}$$

For the activity tests conducted in the presence of water, the ignition temperature was increased for all catalysts when compared to the experiments performed in N_2-diluted air (see Fig. 4). The reason for the delay in ignition is presumably due to water adsorbed on the catalyst surface forming hydroxyls, which inhibits the reaction. Additionally, the high-temperature conversion of methane was increased for all ZrO_2-supported catalysts in the presence of water, which could be due to steam reforming of methane.

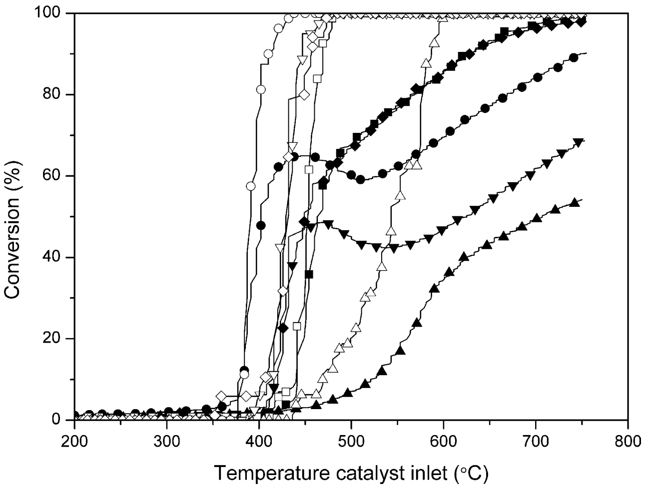

Fig. 4. Conversion of methane (closed symbols) and oxygen (open symbols) in 10% H_2O/N_2-air vs. catalyst inlet temperature for 0.5% Rh/Ce–ZrO_2 (■), 0.5% Rh/$Ce_{0.9}La_{0.1}O_2$ (◆), 0.2% Rh/ZrO_2 (▲), 0.5% Rh/ZrO_2 (▼) and 1% Rh/ZrO_2 (•).

4. Conclusions

In this study, the investigated Rh-based catalysts were active for partial oxidation of methane. The results from the activity tests revealed a significant importance of the support material on the catalytic behavior. The catalysts containing ceria in the support material showed the highest activity and formation of syngas. The amount of rhodium in the catalyst was also found to influence the behavior significantly. By increasing the Rh loading, a decrease of the ignition temperature was obtained.

The addition of water to the reactant gas mixture increased the ignition temperature for all catalysts. Furthermore, the formation of hydrogen was increased in the presence of water, which is favorable for combustion applications where the catalytic POM stage is followed by H_2-stabilized homogeneous combustion.

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