

Catalytic autothermal reforming of methane: Performance of a kW scale reformer using pure oxygen as oxidant

Stefan Rabe^{*}, Thanh-Binh Truong, Frédéric Vogel

Paul Scherrer Institut, General Energy Research Department, Laboratory for Energy and Materials Cycles, 5232 Villigen PSI, Switzerland

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Abstract

The autothermal low temperature catalytic partial oxidation of methane was investigated in a bench-scale reactor (1 kW_{th} power) over a structured ruthenium catalyst (metal monolith support). Pure oxygen was used as the oxidant. Autothermal operation of the reactor was successfully demonstrated. The increase of the O/C ratio increased the average reactor temperature resulting in higher methane conversions. Similar results were obtained for the increase of the space velocity. The product gas generated was rich in hydrogen (65%), nitrogen-free and contained comparably low amounts of carbon monoxide (5%). The results revealed that the oxygen-blown reforming at low temperatures could be a well-suited process for the production of hydrogen in conjunction with a carbon dioxide sequestration.

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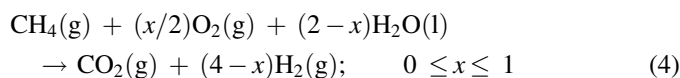
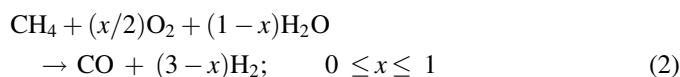
1. Introduction

The catalytic partial oxidation (CPO) of methane to produce hydrogen and carbon monoxide (Eq. (1)) over noble metal catalysts is one of the most studied reactions and has been reviewed several times [1–3]. It is usually conducted at high temperatures (800–1000 °C) and high space velocities [1].



An alternative reforming route is to conduct the catalytic partial oxidation (Eq. (1)) in the presence of water. Thermodynamic calculations reveal that, in contrast to the dry CPO, high methane conversions can be achieved at temperatures below 800 °C in the presence of water [4]. Noble metals as well as nickel catalysts have been applied for this low temperature catalytic partial oxidation (LTCPO) [4–8]. It can be described as a *catalytic autothermal reforming* process combining autothermal reforming (Eq. (2)) and water gas shift reaction

(Eq. (3)) to produce a carbon dioxide rich synthesis gas (Eq. (4)).



The heat of reaction (ΔH_R) depends on the temperature and on the fractions of oxygen and water (Fig. 1). The reaction according to Eq. (4) can be conducted *autothermally* (no external heating is required) if $\Delta H_R \geq 0$. In the ideal case, the reaction can be conducted at the *thermoneutral point* ($\Delta H_R = 0$).

It can be seen that the reaction runs autothermally above temperatures of ca. 500 °C if $x \geq 0.82$. This corresponds to O/C ratios around 0.8 and S/C ratios around 1.2. For lower O/C and higher S/C ratios, the reaction can only be conducted *allothermally* (external heating is required). The reforming efficiency, which can be defined as the ratio of the lower heating value (LHV) of the hydrogen produced and the LHV of the fuel used, reaches its maximum (93.9% based upon the standard

^{*} Corresponding author at: Paul Scherrer Institut, General Energy Research Department, Laboratory for Energy and Materials Cycles, 5232 Villigen PSI, Switzerland. Tel.: +41 56310 2640.

E-mail address: stefan.rabe@psi.ch (S. Rabe).

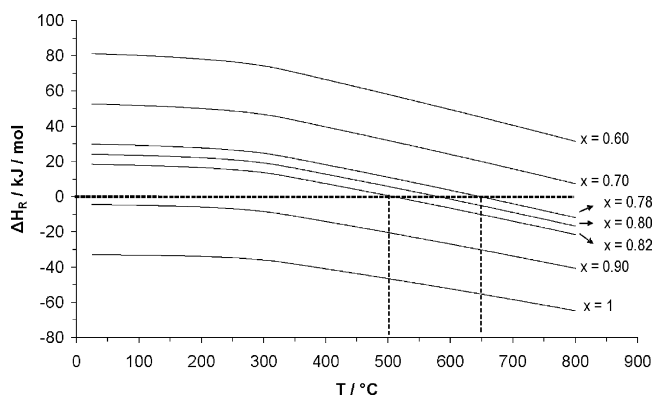


Fig. 1. Calculated heat of reaction (ΔH_R) for different values of x according to Eq. (4) ($p_{\text{tot}} = 0.1$ MPa).

reaction enthalpies at 298 K) at the thermoneutral point [9]. The efficiency increases with increasing temperature. The calculation of the maximum reforming efficiency based on the data presented in Fig. 1 revealed a value of 97% at the thermoneutral point at 645 °C ($x = 0.78$). However, the maximum reforming efficiency cannot be reached in real reaction systems since heat losses occur that reduce the efficiency. Furthermore, more water than calculated for the ideal case needs to be added because the steam reforming requires an excess of water which needs to be heated, reducing the reforming efficiency.

Many of the studies concerning the catalytic reforming of methane were performed on powder catalysts in lab-scale microreactors or in in-situ reaction cells using air or highly diluted oxygen as the oxidant. The autothermal CPO of methane at temperatures of 1000 °C and above over Pt and Rh coated ceramic monolith catalysts using air or pure oxygen as the oxidant was investigated by Hickman et al. [10–12]. A comparison of different active metals on a monolith support was published by Torniaainen et al. [13]. Rhodium revealed high yields of carbon monoxide and hydrogen and an excellent catalyst stability. A study of the CPO of methane over cordierite monolith supported platinum and palladium catalysts in a pilot plant using air as the oxidant was presented by Hochmuth [14]. It was demonstrated that an equilibrium synthesis gas could be produced. Recently, Lee et al. published a paper on the autothermal reforming in an integrated fuel processor consisting of a reforming unit, a sulphur trap and a water–gas-shift unit using air as the oxidant [15]. In most of the studies either air was used as the oxidant or the feed gas was highly diluted with an inert gas in order to avoid the formation of hot spots. As a result, the product gas was diluted as well. For Fischer–Tropsch synthesis as well as for hydrogen production, a diluted syngas will reduce the process efficiency. The need for a reduction of CO₂ emissions has led to a considerable interest in the development of fuel processing technologies which include the sequestration of CO₂. The dilution of the CO₂ containing fuel gas with nitrogen creates problems with respect to an efficient CO₂ separation. The use of pure oxygen as the oxidant could overcome these problems. Following the encouraging results of our earlier work using fixed-bed microreactors [4], we investigated the low temperature catalytic partial oxidation

(LTCPO) of methane using oxygen and water (Eq. (4)) at temperatures <800 °C in a kW scale experimental set-up with respect to a possible application in Fischer–Tropsch synthesis and hydrogen production.

2. Experimental

2.1. Experimental setup

A 1-kW_{th} bench-scale reactor for the autothermal CPO of methane using pure oxygen was constructed (stainless steel, length: ≈20 cm, inner diameter: 3.7 cm). A schematic of the reformer is shown in Fig. 2. A metal monolith catalyst system was chosen to minimize the pressure drop along the reactor and to reduce hot spot temperatures. The reactor was equipped with a thermocouple well and a moveable thermocouple in order to record the temperature profile along the reactor axis. A gas mixing plate was placed in the void volume before the first monolith in order to ensure good mixing of the oxygen with the reactant feed and to establish a uniform flow through the monoliths.

Three monoliths (diameter: 3.5 cm, length: 3.5 cm, 400 cpsi, channel diameter: ca. 0.9 mm, manufacturer: Oberland-Mangold) were used for the experiments. The first monolith was coated with an alumina washcoat (thickness: ca. 30 μm) and impregnated with ruthenium, and the remaining two were blank. A second set of experiments was conducted with two active monoliths. De-ionized water was fed by an HPLC pump to a vaporizer. The water vapor was subsequently mixed with methane. The water/methane feed mixture was further pre-heated to 275 °C. Oxygen was added at room temperature at the reactor inlet section. To start the experiment, the reactor was heated to the catalytic ignition temperature of the feed mixture (approximately 450 °C). After ignition of the reaction, the external reactor heating was turned off.

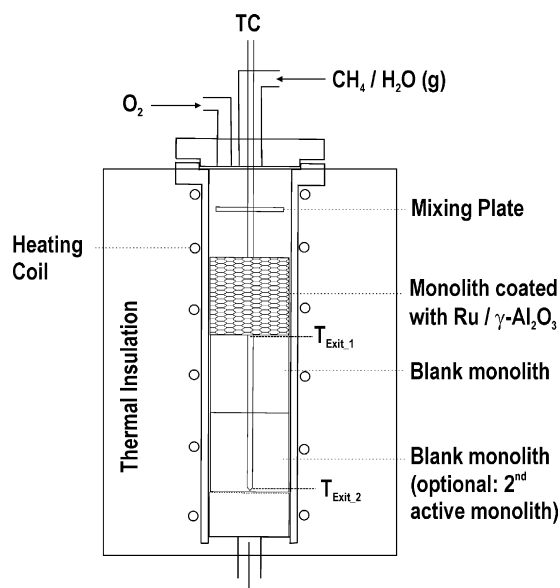


Fig. 2. Schematic of the reactor (TC = Thermocouple well).

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