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Methane catalytic partial oxidation on autothermal Rh and Pt foam catalysts: Oxidation and reforming zones, transport effects, and approach to thermodynamic equilibrium

R. Horn *, K.A. Williams, N.J. Degenstein, A. Bitsch-Larsen, D. Dalle Nogare, S.A. Tupy, L.D. Schmidt

Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

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Abstract

We compare Rh and Pt as catalysts for the partial oxidation of methane to syngas at millisecond contact times. The basis for the comparison are species and temperature profiles, with a spatial resolution of about 300 µm measured along the centerline of an adiabatically operated metal-coated α-Al_2O_3 foam using a capillary sampling technique with mass spectrometric species measurement. Gas temperature profiles are measured with a thermocouple. Investigated stoichiometries range from $C/O = 0.6$ to 2.6 at constant flow rate of 4.7 slpm and atmospheric pressure. Rh and Pt are compared with respect to (i) profile development at syngas stoichiometry, (ii) profile development at varying stoichiometries from $C/O = 0.6$–2.6, (iii) product selectivities and yields in the oxidation zone, (iv) contribution of partial oxidation and steam reforming to the final syngas yield, (v) mass transport limitations, and (vi) approach to thermodynamic equilibrium. Independent of C/O and metal, all profiles show an oxidation zone and a steam-reforming zone. H_2 and CO are formed in the presence of gas-phase oxygen by partial oxidation and in the absence of gas-phase oxygen by steam reforming. CO_2 reforming is not observed. At the same C/O, H_2 and CO selectivities and yields are higher in the oxidation zone on Rh than on Pt. As the C/O ratio increases, the catalyst temperature decreases and selectivities to H_2 and CO in the oxidation zone decrease. The decrease is larger on Pt than on Rh. Because Rh is also the better steam-reforming catalyst, H_2 and CO yields are generally higher on Rh than on Pt. The rate of O_2 conversion at the catalyst entrance is largely mass transport-controlled on Rh but not on Pt. In the oxidation zone on Pt, the methane CPO is kinetically controlled with a constant reaction rate. An average O_2 mass transport coefficient is calculated and compared with literature values on foam catalysts. Finally, exit species flow rates and temperatures are compared with thermodynamic calculations at constant pressure and enthalpy. Rh brings the methane oxidation close to equilibrium if $C/O \leqslant 1.0$, whereas Pt reaches equilibrium only at very high catalyst temperatures if $C/O \leqslant 0.7$. At higher C/O, deviations from equilibrium are observed mainly because steam-reforming slows, but also because water–gas shift equilibrium is not established.

Keywords: Syngas; Catalytic partial oxidation; Methane; Rhodium; Platinum; Mechanism; Spatial profiles; Mass transport; Thermodynamics

1. Introduction

The production of syngas, a mixture of CO and H_2, is of great importance in chemical industry, because syngas is the feedstock for methanol and Fischer–Tropsch synthesis. An important resource for syngas production is natural gas, which consists of 80–90% methane. Unfortunately, natural gas occurs often in remote locations, and costly transportation motivates research to transform it to syngas and finally transportable liquids right at the well head.

Conventional steam-reforming technology is not suited for decentralized syngas production, because steam reformers are large, expensive plants that cannot be scaled down for small-scale operation in a remote gas field. The catalytic partial oxidation of methane to syngas (CPO, Eq. (1)) has received considerable attention because it provides close to 100% methane conversion and >90% syngas yields in millisecond contact times

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[*] Corresponding author.
E-mail address: rumford@gmx.de (R. Horn).

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[1,2] and can be conducted in comparably small reactors ideal for decentralized applications. In addition, the methane CPO supplies a H_2/CO ratio of 2/1, which is favorable for methanol or Fischer–Tropsch synthesis.

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2, \quad \Delta H_r^\circ = -36\ \mathrm{kJ\,mol^{-1}}. \tag{1}$$

Various catalysts on different supports have been reported to be active for the methane CPO. Most catalysts contain a group VIII metal as active component (e.g., Rh, Pt, Ru, Ni) on an oxide support [3]. The present work focuses on Rh and Pt on α-Al_2O_3 foam supports.

An important and open question in methane CPO research is the reaction mechanism and product development in the catalyst bed under autothermal conditions. Direct and indirect mechanisms are proposed [3]. The direct mechanism assumes that H_2 and CO are primary reaction products formed by partial oxidation in the presence of gas-phase O_2. Equation (2) ($0 \leqslant x \leqslant 2$, $0 \leqslant y \leqslant 1$) shows the direct mechanism including the competitive formation of H_2O and CO_2.

$$CH_4 + \left(2 - \frac{x}{2} - \frac{y}{2}\right)O_2 \rightarrow xH_2 + yCO + (2-x)H_2O + (1-y)CO_2. \tag{2}$$

The indirect mechanism postulates a two-zone model with strongly exothermic CH_4 combustion to H_2O and CO_2 at the catalyst entrance (Eq. (3)), followed by strongly endothermic steam- and CO_2-reforming (Eqs. (4) and (5), respectively) downstream.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H_r^\circ = -803\ \mathrm{kJ\,mol^{-1}}, \tag{3}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H_r^\circ = +206\ \mathrm{kJ\,mol^{-1}}, \tag{4}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H_r^\circ = +247\ \mathrm{kJ\,mol^{-1}}. \tag{5}$$

Published mechanistic studies follow essentially two approaches. One approach is to study the methane CPO under realistic conditions (i.e., high catalyst temperatures and atmospheric or elevated pressure) and compare reactor exit data with numerical simulations assuming a reaction mechanism [1,4–9]. Another approach uses well-defined isothermal low-pressure or diluted conditions different from technical applications; examples include TAP experiments in vacuum [10–12], isothermal reactor measurements [13,14], and spectroscopic studies [15]. Depending on the experimental conditions, different product development is inferred and different mechanistic conclusions are drawn. Some authors report a direct mechanism [11,12,15], some find evidence for the indirect mechanism [9,10,13,14] and others advocate for a mechanism in between [8,16].

Our approach to studying methane CPO in as close to industrial conditions as possible is to measure high-resolution (≈300 μm) species and temperature profiles along the centerline of an autothermally operated foam catalyst. Until recently [17–19], high-resolution spatial data were absent in the literature. One earlier study provided spatially resolved data by arranging discrete, Rh-coated metallic screen substrates in a stack and sampling behind each screen [16]. The resolution of this method was limited to 2 mm, however. These data were later compared by another group with numerical simulations [20], but due to the low spatial resolution, H_2 formation was attributed to steam reforming only. No H_2 formation was attributed to partial oxidation, in contrast to our high-resolution measurements showing substantial formation of H_2 in the presence of gas-phase oxygen.

It should be noted here that even though the terms "direct" and "indirect" are commonly used in the literature to discuss the mechanism of methane CPO, Eqs. (2)–(5) describe only a stoichiometrically observed product development in the catalyst bed and give no information about the elementary reaction steps occurring at the catalyst surface. For example, we show in this work that H_2 and CO are formed in the presence of gas-phase O_2 at the entrance section of the catalyst; that is, the reaction there is a partial oxidation according to Eq. (2), but that does not necessarily mean that H_2 formation is the primary event after CH_4 dissociation at the catalyst surface. It is possible that the surface hydrogen atoms H_s are involved in rapid surface reactions with oxygen surface atoms O_s (e.g., $H_s + O_s \rightleftarrows OH_s$ and $OH_s + H_s \rightleftarrows H_2O_s$) before they leave the surface either as H_2 or H_2O. In this case, the reaction would be indirect even though it follows Eq. (2). The actual surface reaction steps can not be inferred from the spatial profiles wherefore we discuss the reaction mechanism only in terms of Eqs. (2)–(5) without using the terms "direct" and "indirect."

The motivation of this work is to present and analyze high-resolution species and temperature profiles for autothermally operated Rh and Pt foam catalysts that give new insight into the reaction mechanism under technically relevant conditions. The high-resolution spatial profiles reveal that on both metals, H_2 and CO are formed partly by partial oxidation (Eq. (2)) and partly by steam reforming (Eq. (4)). CO_2 reforming (Eq. (5)) is not observed in an adiabatic reactor. High catalyst temperatures favor the formation of H_2 and CO in three different ways: (i) by increasing the H_2 and CO selectivities in the oxidation zone of the reactor ($S_{H_2}^{oz} = x/2$, $S_{CO}^{oz} = y$ in Eq. (2)), (ii) by increasing the CH_4 conversion in the oxidation zone (H_2 and CO yields in the oxidation zone increase), and (iii) by increasing the rate of steam-reforming downstream. Because Pt favors total oxidation and does not catalyze steam reforming as efficiently as Rh does, syngas yields are generally higher on Rh than on Pt.

We begin this work by analyzing conventional conversion and selectivity data at the reactor exit (Section 3.1). We then analyze high-resolution spatial profiles measured for syngas stoichiometry (C/O = 1.0, Section 3.2) and for other C/O ratios from 0.6–2.6 (Section 3.3). We discuss mass transport limitations on Rh and Pt in Section 3.4, where we analyze the rate of O_2 conversion at the catalyst entrance. To illustrate how information on mass transport can be extracted from spatial profiles, we calculate an average O_2 mass transport coefficient and compare it with literature values. Finally, we compare exit species flow rates and temperatures with thermodynamic calculations to show how close the reaction is brought to thermodynamic equilibrium on the Rh and Pt foam catalyst (Section 3.5).