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Spatial profiles in partial oxidation of methane and dimethyl ether in an autothermal reactor over rhodium catalysts

Reetam Chakrabarti, Jacob S. Kruger, Richard J. Hermann, Samuel D. Blass, Lanny D. Schmidt *

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

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ABSTRACT

Catalytic partial oxidation (CPO) reactors have complex concentration and temperature gradients which make it difficult to understand the mechanism of autothermal operation. Previous research in the Schmidt group on methane CPO using the capillary sampling technique has shown the existence of two zones – oxidation and reforming [1–4]. Nearly (>90%) all of the oxygen in the feed is converted within the first 2 mm of the catalyst bed. In this paper, temperature and concentration profiles during the CPO of methane and dimethyl ether CH_3OCH_3, an oxygenated hydrocarbon, are presented. Results with the two feeds are compared and the nature of the profiles was similar, with sharp gradients existing in the oxidation zone with slower chemistries in the reforming section. The rhodium catalyst in the oxidation zone during methane CPO was also analyzed using XPS and XRD and shown to be rhodium metal.

1. Introduction

Catalytic partial oxidation (CPO) has been shown to convert a wide range of feedstocks ranging from small molecules such as methane to actual biomass autothermally to a high selectivity thermodynamic equilibrium synthesis gas stream [5–11]. The process takes place over noble metal based catalysts such as rhodium and platinum and typical temperatures in a CPO reactor are on the order of 600–1000 °C with residence times approximately 10–50 ms. CPO involves a combination of oxidation and reforming reactions. CPO was first demonstrated by Hickman and Schmidt in 1993 [5] and comprises of the following reactions involving combustion (Eq. (1)), partial oxidation (Eq. (2)), steam reforming (Eq. (3)), CO_2 reforming (also called dry reforming, Eq. (4)) and water gas shift (Eq. (5)) [3].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_r = -803\,\text{kJ/mol} \tag{1}$$

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

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_r = 206\,\text{kJ/mol} \tag{3}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H_r = 247\,\text{kJ/mol} \tag{4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_r = -41\,\text{kJ/mol} \tag{5}$$

The syngas stream can be upgraded to fuels or chemicals by the Fischer–Tropsch process, methanol, or hydrogen. Due to the short contact times (order of milliseconds), CPO is suitable for portable or small-scale applications like fuel cells unlike conventional steam reformers which have residence times in the order of seconds [1].

The capillary sampling technique has been demonstrated with simple hydrocarbons such as methane [1–4] and ethane [12]. The noble metal catalyst during CPO can be divided into two sections – an oxidation section where oxygen is present in the gas phase and a reforming section downstream without any gas phase oxygen. Knowing the temperature and concentration profiles within the reactor, the mechanism of CPO on different catalysts can be determined. With oxygenated hydrocarbons, a problem with the technique is homogeneous chemistry within the reactor and sampling system which can make it difficult to decouple homoegeneous (gas-phase reactions) and heterogeneous reactions (on catalyst surface). Hence, spatial profiles research with oxygenates is limited. Kruger et al. showed that significant conversion of oxygenated hydrocarbons occur at temperatures in excess of 500 °C which becomes more prominent in the presence of oxygen [11,13]. Dimethyl ether, CH_3OCH_3 (DME) was shown to have negligible homogeneous chemistry even at temperatures in excess of 600 °C indicating its high stability in the gas phase. Therefore, all chemistry can be attributed to the catalyst surface. DME concentration and

* Corresponding author. Tel.: +1 612 625 9391; fax: +1 612 626 7246.
E-mail addresses: chakr027@umn.edu (R. Chakrabarti), kruge084@umn.edu (J.S. Kruger), herma380@umn.edu (R.J. Hermann), blass004@umn.edu (S.D. Blass), schmi001@umn.edu (L.D. Schmidt).

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temperature profiles will help in better understanding the mechanism of CPO of oxygenates and hence of lignocellulosic biomass. As in methane CPO, complete oxidation (Eq. (6)), partial oxidation (Eq. (7)), CO_2 reforming (Eq. (8)), steam reforming (Eq. (9)) and water gas shift reactions (Eq. (5)) take place during DME CPO.

DME is considered as a diesel substitute and has lower NO_x and particulate emissions than diesel fuel [14,15]. DME steam reforming as a source of hydrogen for fuel cells has been reported in the literature [16–18].

$$CH_3OCH_3 + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta H_r = -1329\,\text{kJ/mol} \tag{6}$$

$$CH_3OCH_3 + 1/2O_2 \rightarrow 2CO + 3H_2 \quad \Delta H_r = -38\,\text{kJ/mol} \tag{7}$$

$$CH_3OCH_3 + CO_2 \rightarrow 3CO + 3H_2 \quad \Delta H_r = 246\,\text{kJ/mol} \tag{8}$$

$$CH_3OCH_3 + H_2O \rightarrow 2CO + 4H_2 \quad \Delta H_r = 204\,\text{kJ/mol} \tag{9}$$

In the literature, the interplay between the various reactions was unclear with both a direct and indirect mechanism of CPO being proposed [19–21]. The direct mechanism suggests that syngas products, H_2 and CO are formed directly from partial oxidation (Eq. (2)) while the indirect mechanism suggests the existence of two distinct reaction zones – an oxidation zone producing combustion products (Eq. (1)) and a reforming zone producing syngas (Eq. (3)). Using the spatially resolved measurements by the capillary sampling technique, Schmidt and coworkers showed that all the oxygen is consumed within approximately 2 mm over Pt and Rh based catalysts and syngas production was observed even within the oxidation zone [1–4]. Reaction rates, concentration and temperature gradients were highest in the oxidation zone where oxygen was present in the gas phase (~2 mm). However, as reported by Horn et al. the formation of syngas in the oxidation zone does not confirm the prevalence of a direct mechanism of CPO formation due to the occurrence of multiple surface reactions on the catalyst surface [2]. Detailed numerical simulation studies involving surface reactions taking place during methane CPO suggest that in short contact time reactors, at high temperatures, syngas formation in the oxidation zone takes place mostly by the direct mechanism along with syngas combustion, steam reforming and water gas shift reactions [22–25]. After all the oxygen is consumed, additional syngas is produced by steam reforming.

During CPO, the net environment is strongly reducing due to high amounts of hydrogen produced, hence rhodium exists in a reduced state in the reforming section. However, within the oxidation zone, where oxygen is present, the state of the rhodium catalyst is subject of debate in literature. Grunwaldt et al. showed using in situ X-ray absorption spectroscopy studies at lower temperatures (~400 °C) the presence of an indirect mechanism and in the oxidation zone, rhodium was present in the oxidized state [26,27]. Numerical simulations of short contact time reactors at temperatures similar to CPO (600–1000 °C) suggest that rhodium is most likely to be in the reduced state even in the presence of oxygen [23–25]. The high temperatures in short-contact time reactors during CPO make it difficult to experimentally determine the state of the catalyst. Use of in situ techniques is challenging and it is possible the catalyst might change form while cooling down to ambient conditions. Here, by shutting off methane and oxygen flows simultaneously, we avoid changing the state of the rhodium catalyst while cooling and use XPS and XRD to experimentally determine the state of the rhodium catalyst in the oxidation zone during CPO in short contact time reactors

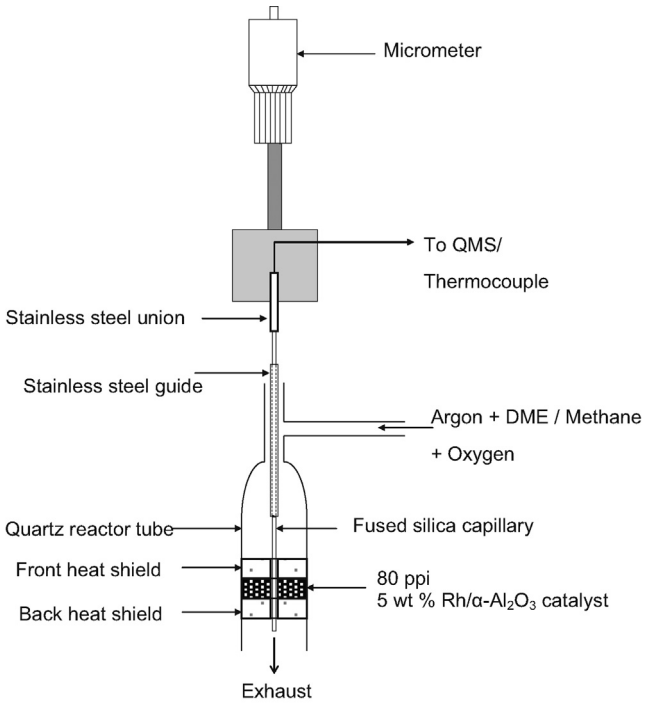

Fig. 1. Experimental setup for measurement of concentration and temperature profiles during methane and dimethyl ether catalytic partial oxidation.

2. Experimental

2.1. Spatial profiles

Methane and DME CPO was carried out in a 19 mm ID quartz reactor. The catalyst consisted of a 80 ppi (pores per linear inch) α-alumina foam monolith (17 mm diameter, 10 mm long) coated with 5 wt% rhodium. Blank 80 ppi α-alumina foams were used as front and back heat shields. The three monoliths (front heat shield, rhodium catalyst, and back heat shield) were wrapped in aluminosilicate cloth to prevent bypassing of gases. A 700 μm hole was drilled along the axis of all three monoliths with a diamond drill bit. Flow rates of gases to the reactor were controlled using mass flow controllers accurate to within ±2%.

Rhodium nitrate was used as the rhodium precursor and catalysts were prepared by the incipient wetness technique as described previously [28], then dried in a vacuum oven and calcined in a furnace in air at 800 °C for 6 h.

Products were analyzed at the exit of the reactor for integral performance data and within front heat shield to test for homogeneous chemistry with a HP 5890 gas chromatograph with a 60 m Plot-Q column. For spatial profile studies, a fused silica capillary (650 μm OD) was connected to a 1/16″ stainless steel union. The other end of the union was connected to a quadrupole mass spectrometer (QMS). The stainless steel union was mounted to a micrometer screw. The fused silica capillary moved along the axis of the reactor through the drilled holes within the three monoliths by turning the micrometer screw. Temperatures were measured by passing a thermocouple (Omega, K-type, 270 μm OD) through the union and the capillary, until the end of the thermocouple was slightly below the end of the capillary, similar to that shown by Horn et al. [1]. The experimental setup is shown in Fig. 1. After turning the micrometer screw, the system was allowed to equilibrate for approximately 5 min. The positions shown are accurate within 0.0125″ (0.3 mm). The profiles along the axis of the catalyst were analyzed with the QMS. Errors in carbon balances were typically within 10%. Hydrogen and oxygen balances each were closed by assuming water as