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Species and temperature profiles in a differential sphere bed reactor for the catalytic partial oxidation of *n*-octane

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Abstract

A method is developed by which temperature and species profiles are measured for the catalytic partial oxidation (CPO) of *n*-octane in a differential manner in a fixed bed of Pt and Rh-coated α-alumina spheres with a minimum resolution of 1 mm (or ~0.4 g) of catalyst over a wide range of feed stoichiometries. Results indicate that two regions of catalytic activity are present in the bed: a short (~1 mm) oxidation zone in the front of the bed and a longer reforming zone downstream. The lengths of the reforming and oxidation zones are dependent on the stoichiometry of the reactor feed. O_2 is consumed rapidly on both Rh and Pt catalysts; however, full O_2 conversion is reached faster on Rh than on Pt. Both steam reforming and dry (CO_2) reforming are observed in the bed downstream of the oxidation zone, but steam reforming is more extensive because higher conversions of H_2O are observed than CO_2 on both Rh and Pt catalysts. The conversion of H_2O and CO_2 in the reforming zone is always higher on Rh than on Pt, therefore Rh is a better reforming catalyst than Pt. Low molecular weight hydrocarbons like methane and ethylene are more readily reformed than octane. Results also indicate that alumina sphere beds are better supports for syngas production than alumina foam monoliths.

Keywords: Catalytic partial oxidation; Rhodium; Platinum; Octane; Profile

1. Introduction

Catalytic partial oxidation (CPO) is a process by which a wide variety of hydrocarbon feedstocks can be autothermally and selectively converted into valuable chemicals like H_2 or olefins in millisecond contact times. In particular, CPO could be used to convert naphtha to olefins for chemical commodities or convert gasoline to H_2 for use in fuel cells. Using *n*-octane as a gasoline and naphtha surrogate, we have previously shown that high selectivity of H_2 can be generated over Rh-coated foams [1], and high selectivity of ethylene and other olefins can be produced on Pt catalysts where H_2 is co-fed as a sacrificial fuel [2]. CPO is a viable alternative to the current industrial processes used to make H_2 (steam reforming) and olefins (steam cracking) because residence times are reduced from 1 s to 10 ms, the process can be scaled up or down according to the size requirements of a particular application, and the reactor does not need to be periodically shut down to remove coke.

Understanding the chemistry of the CPO system is paramount to the design of an efficient reactor that can produce the highest yields of the desired products. We have recently shown that there are significant amounts of both heterogeneous surface chemistry and homogeneous gas-phase chemistry in the CPO of liquid hydrocarbon feedstocks [1]. Specifically, the formation of olefins can be explained as occurring mainly through the homogeneous pyrolysis of the hydrocarbon fuel when H_2, H_2O, CO, and CO_2 are formed through heterogeneous reactions. However, the nature of the surface reactions could not be fully addressed in the experimental or simulation methods. In this work, we have designed an experiment by which these reactions can be explored by inspecting the temperature and species profiles within the catalyst bed by varying the catalyst length.

There is a debate on the role of heterogeneous chemistry in the catalytic partial oxidation process. Some argue that the formation of H_2 and CO is through a direct mechanism whereby hydrocarbon fuel adsorbs on the catalyst surface,

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pyrolyzes into adsorbed C and H atoms that then recombine with adsorbed O atoms to form a combination of H_2, H_2O, CO, and CO_2 depending on the overall stoichiometry of feed stream. Others argue that the formation of syngas is through an indirect route where the hydrocarbon is first completely oxidized to H_2O and CO_2 at the front of the catalyst and then undergoes steam and dry reforming to produce H_2 and CO downstream. Reviews on both the experimental and simulation literature for methane CPO have been recently done that show that arguments can be made for both mechanisms [3,4]. Most recently, a technique has been developed which can measure temperature and species flow rate profiles inside a Rh-coated catalytic foam monolith for the CPO of methane using a moveable direct-sampling capillary that is connected to a mass spectrometer for species analysis [3]. Spatial temperature and flow rate measurements can offer further insight into the chemistry of the reaction because it can be possible to see different reaction zones develop within the catalyst. These results show that syngas is formed through both direct and indirect mechanisms and that there is a significant amount of steam reforming inside the catalyst bed, but an insignificant amount of CO_2 reforming on Rh catalysts when methane is used as the reacting fuel.

In this work, temperature and species profiles are measured within a catalytic sphere bed for the CPO of *n*-octane to examine the heterogeneous chemistry for heavier hydrocarbon fuels. A method is developed whereby the products can be analyzed by gas chromatography (GC), and profiles can be constructed by changing the length of the catalyst bed. The resulting temperature and flow rate profiles are analyzed and the mechanism of the reactions is discussed.

Several different metals have been used to catalyze the partial oxidation reaction including Rh, Pt, Ni, Pd, and Ir. Previous results have shown that Rh and Pt give the best performance because Rh generates high selectivity to syngas while Pt is the best catalyst for olefin production [5–8]. The other metals do not perform as well as Rh or Pt for various reasons including coking, sintering, volatility, and inactivity [6,7,9]. In this work, the contribution of the catalyst metal to the chemistry of the CPO process is examined by measuring temperature and species flow profiles for both Rh and Pt catalysts.

The final variable considered in this work is the effect of feed stoichiometry. Previous results on the CPO of *n*-octane give general trends in relation to the C/O ratio in the reactant stream [1,10]. The maximum selectivity of syngas is usually observed for C/O ratios slightly less than 1.0. In this region, the fuel conversion is 100% and measured catalyst temperatures are approximately 1000 °C. As the amount of O_2 in the feed decreases (C/O increases), reactor temperatures fall to 800 or 900 °C, fuel conversion decreases, syngas selectivity decreases, and the selectivities of ethylene and heavier olefins increase. Measuring the temperature and species flow rate profiles as a function of the inlet stoichiometry offers insight into the changing chemistry in the reactor as the feed becomes more fuel rich.

2. Experimental

Experiments were carried out in a 19 mm inside diameter (i.d.) quartz tube at atmospheric pressure. The upstream portion of the reactor for this experiment was constructed in a similar fashion as has been described and sketched previously [11]. *n*-Octane (>99% purity) was introduced through a low flow automotive fuel injector at the top of the quartz tube and mixed with N_2 and O_2 (in air stoichiometry) introduced through a side port via electronically controlled mass flow controllers. The portion of the reactor tube in this section was wrapped in a Variac-controlled resistive heating tape that vaporized the thin film of fuel produced on the wall from the spray of the fuel injector. A thermocouple was inserted into the reactor after the vaporization and mixing zone and before the catalyst assembly to ensure that a constant vapor preheat temperature of ~160 °C was maintained.

The catalysts used in these experiments were low surface area 1.3 mm diameter α-alumina spheres that were coated with either Rh or Pt metal. The catalysts were prepared via dropwise addition of aqueous metal salt solution ($Rh(NO_3)_3$ or H_2PtCl_6) directly onto the spheres. The total amount of solution was applied to the spheres over the course of several doses where the water was allowed to evaporate and the spheres were thoroughly mixed between applications. Enough solution was added to ensure that the catalysts would contain 5 wt% metal loading based on the initial mass of the spheres. The coated spheres were calcined in a closed furnace at 600 °C for 5 h.

A sketch of the catalyst assembly is shown in Fig. 1. A 1 mm i.d. 2 mm outside diameter (o.d.) quartz sampling tube was pushed through a septum, wrapped in Fiberfrax paper, and inserted into a side port in the quartz reactor so that the end of the sampling tube was in the middle of the reactor. The

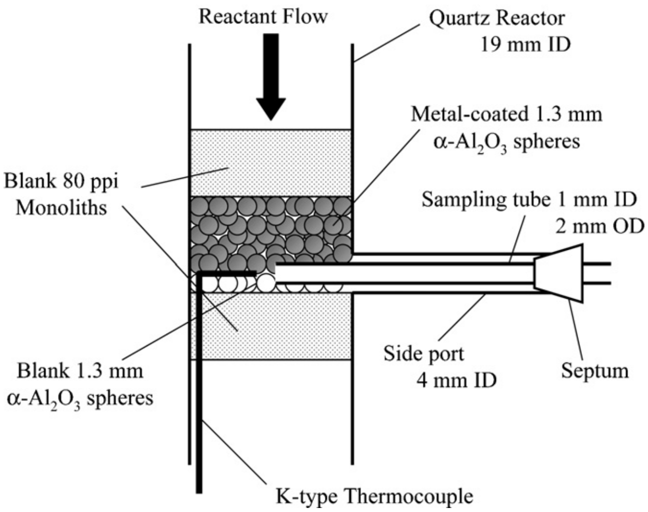

Fig. 1. Schematic of the catalyst assembly. The temperature is measured with a K-type thermocouple and the product gases are sampled with a gas-tight syringe through a quartz sampling tube at the center of the end of the Rh or Pt-coated sphere bed. Since temperatures and species flows are measured at the very end of the catalyst bed, differential temperature and species flow profiles are measured by varying the mass of the bed.