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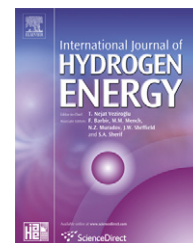
Reactor temperature profile during autothermal methane reforming on Rh/Al$_2$O$_3$ catalyst by IR imaging

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ABSTRACT

Catalytic autothermal reforming of methane was studied over a commercial rhodium catalyst as a function of feed flow rate, feed composition and oven temperature.

The process is carried out in a catalytic fixed bed reactor inserted in a tubular oven. Temperature profile of the catalyst bed was measured by IR thermography and product composition was measured with a continuous gas analyzer.

The effect of water addition at fixed flow rate on catalyst temperature profile was investigated in two ways. In one case, upon water addition, an equivalent amount of nitrogen was removed from the feed in order to keep oxygen and methane concentrations constant. With this protocol nitrogen to oxygen ratio varies as a function of amount of water in the feed. In the other case, upon water addition, nitrogen, oxygen and methane were all reduced to keep total flow rate constant, thus keeping both oxygen to methane and nitrogen to oxygen ratios constant.

The effect of water addition on product composition was investigated as a function of reactor thermal level, regulated by acting on oven temperature.

1. Introduction

The reduction of fossil reservoirs, the ever increasing energy demand, and the environmental concerns are pushing the research to explore new energy sources and energy carriers. The use of hydrogen is one of the most flexible and clean ways to store and transport energy produced from fossil or renewable sources, for mobile and stationary purposes. However, transition to a hydrogen based society is limited by the tremendous investment required to create the infrastructure necessary for hydrogen storage and distribution from large production sites to the final users. In the near future, small scale decentralised hydrogen generation is a reasonable alternative to reduce the distribution and storage issues. Indeed, natural gas or other fuels could be delivered near the final user by using the existing infrastructures, and reformed by small reactors to produce hydrogen on site. Among the most important features of these novel reactors are compactness, rapid dynamic response and durability.

The most efficient process to produce hydrogen from fossil fuels is steam reforming [1–4], however, due to the necessity of external heating at high temperature (800 °C) the technology required cannot be reproduced on a small scale with the same efficiency.

Catalytic partial oxidation (CPO) [5–10] and autothermal reforming (ATR) [11–20] are promising technologies to produce hydrogen on a small scale since they are characterized by compact reactors with internal energy generation. The

efficiency of these processes increases with reactor temperature, which, in turn, is limited by catalyst thermal stability.

Due to the coexistence of exothermic and endothermic reactions, with rather different kinetics, a non-uniform temperature profile develops in the catalyst bed, with a pronounced hot spot in the former part of the catalyst, where the highest thermal stress is concentrated [8–10,21–24]. Water addition to the catalytic partial oxidation mixture decreases reactor thermal level and increases syngas yield [8,25–35]. Numerical simulations performed by De Groote and Froment [8] predicted that the addition of water to the CPO mixture should reduce the difference between maximum temperature and bed exit temperature and should shift downwards the temperature peak. Thiese results were explained by invoking a sooner start of the reforming reactions in the reactor.

Experimental works proved that the predicted effect of water addition is related to the catalyst type [35–40]. For instance, when the catalyst is Ni-based, temperature peak reduction is somewhat limited by the high oxygen affinity of Ni with the result that the exothermic and the endothermic reactions remain rather separate [35–39,41].

When the catalyst is Rh based, the lower oxygen affinity of Rh could improve the superposition of the oxidation and reforming reactions, reducing the temperature peak. This behaviour was shown by investigating the effect of water addition on reactor temperature profile on a Rh catalyst, keeping reactor thermal level above 850 °C [40].

In this work we address the effect of water addition on product composition and reactor temperature profile on a commercial Rh catalyst, maintaining feed preheating within the limits obtainable with typical internal heat recovery reactors, such as reactors with integrated counter current heat exchangers or reverse flow reactors. The effect of feed composition, total flow rate and oven temperature is also presented and discussed.

2. Methods

2.1. Experimental apparatus

The experimental apparatus, schematized in Fig. 1 essentially consists of a 21 mm ID tubular quartz reactor with a catalyst section length of 20 mm placed between two inert alumina sphere sections, (60 mm each).

The gaseous reactants, coming from pressurized vessels, are fed to the reactor by Thermal Mass Flow Controllers (Brooks 5850), while liquid water is fed to a homemade evaporator by a Liquid Mass Flow Controller (Bronckhorst L23V02). Care was taken to insulate the reactor as much as possible, to limit the formation of radial temperature gradients in the catalyst bed. For this reason, the reactor was embedded in a ceramic insulating material (150 mm long) and then inserted into a tubular oven with a heating length of 500 mm.

Reactor pressure is measured with Piezo Pressure Transmitters placed immediately before and after the quartz reactor. Pressure drop in the reactor proved to be negligible.

Product composition was measured by means of an ABB Gas Analyzer, equipped with thermal conductivity sensor Caldos 17, for H_2, infrared sensor Uras 14, for CO, CO_2, and CH_4 and paramagnetic sensor Magnos 106 for O_2. A condenser and a $CaCl_2$ trap were placed before the ABB Gas Analyzer to reduce water content below the limits mandatory for the instrument. Temperature profile in the catalyst bed was measured with an IR thermography equipment (Phoenix, Flir Systems) capable of collecting the radiation emitted in the wavelength range 2–5 μm, with a resolution of 320×256 pixels. Spatial resolution, depending on the distance between the IR thermography equipment and the reactor, was, in this work, 3 pixel/mm.

IR image acquisition was performed by rapidly opening the oven and sliding upwards the ceramic insulating material to visualize the catalyst bed. To minimize reactor temperature drop the entire procedure lasted less than 5 s. Upon exposure to the environment, reactor temperature decreased at a rate of ca. 2 °C/s, as measured by continuous IR acquisition for a time interval of 10 s from oven opening.

Fig. 2 reports a typical IR image of the reactor. Three zones are visible: the inert alumina spheres (very top and bottom of the image); the catalyst bed (central part); the quartz disks used to separate the catalyst bed from the inert alumina spheres.

To convert IR data from photon emission to temperature, a calibration was performed by increasing oven temperature stepwise. For each step, before acquiring the IR image, enough time was allowed to achieve a stable temperature within the catalyst bed, as measured by an axial well k-thermocouple inserted in the reactor. The calibration was performed on the reactor loaded with catalyst and inert alumina spheres, in the same configuration used during the experiments to account for different material emissivity. The values of photon emission detected by the IR camera in the catalyst and in the inert sections were then correlated to the temperature measured by k-thermocouple.

In order to reduce datadispersion, the temperature profiles were always calculated by averaging temperature profiles measured in the catalyst in six different radial positions.

2.2. Catalyst

The catalyst, Rh/Al_2O_3, was purchased from Engelhard (code 4406), and was supplied in 2.4 mm diameter pellets. The pellets were crushed and particles with diameter in the range 1–1.18 mm were separated and used as catalyst. To reach the desired catalyst bed length (20 mm), 5 g of catalyst were loaded in the reactor. Catalyst physical properties are reported in Table 1 (data provided by the supplier). Spheres of α-Al_2O_3, with diameter of 1 mm, were used to create two inert sections before and after the catalyst bed.

Immediately after loading, the catalyst was reduced according to the following procedure: the catalyst bed was brought at 400 °C in N_2 atmosphere, then, while fluxing a stream of H_2 (30%) in N_2, the temperature was raised to 600 °C with a 5 °C/min ramp and kept at 600 °C for 1 h.

After the reduction step, oven temperature was brought to the desired value, however, to avoid coke formation at low temperature, the catalyst bed was heated up to ca. 700 °C by oxidizing a stream of H_2 before feeding the reactants.