

Experimental and modeling analysis of the effect of catalyst aging on the performance of a short contact time adiabatic CH₄-CPO reactor

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Available online 29 September 2007

Abstract

Catalytic partial oxidation of methane at short contact time was studied in a lab-scale packed bed reactor over a 0.5 wt% Rh/A₂O₃ catalyst. Experiments were focused on the investigation of catalyst stability and durability upon repeated start-up/shut-down tests at different inlet temperatures and flow rates. Measurements of the axial temperature profiles evidenced a high sensitivity of the steady state thermal behavior of the reactor on catalyst activity: a decrease of the intrinsic catalytic activity was interpreted as the cause of a progressive over-heating of the bed which, in turn, moderated the loss of methane conversion and syngas productivity. At sufficiently high flow rate the observed temperature rise spread along the whole catalytic bed. Under such conditions both steady state and dynamic reactor performances were affected by the progressive decay of catalyst activity. A rationalization of the observed results was pursued by applying a one dimensional (1D) heterogeneous model of the reactor to the quantitative analysis of experimental results. Model predictions revealed the occurrence of operating surface temperatures up to 1100 °C and allowed to quantify the progressive worsening of reactor performances in terms of a loss of reforming activity localized in correspondence of the catalyst hot spot.

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Keywords: Catalytic partial oxidation; Methane; Rh catalyst; Deactivation; Adiabatic reactor; 1D model analysis

1. Introduction

On-board fuel reforming for the production of hydrogen or synthesis gas faces several challenges. Among them, there is the need of a compact reformer unit, with fast response to load changes. Catalytic Partial Oxidation (CPO) offers in this respect the advantages of an autothermal operation and small reaction volumes; indeed partial oxidation has been proven in the literature as a successful technology for the conversion of liquid hydrocarbons into CO and H₂ mixtures in milliseconds contact time reactors [1,2]. The compactness and simplicity of a single-step CPO reformer could also allow an efficient conversion also of CH₄ for both the small-scale distributed generation of hydrogen and mobile applications [3–5].

Among noble metals, Rh has been mostly studied for the partial oxidation of natural gas and liquid hydrocarbons because of its high activity and selectivity, low tendency to C formation and low volatility [6,7]. Autothermal operation is characterized by extremely high temperatures (even higher than 1000 °C) which can compromise long-term catalytic performances. To counterbalance possible activity losses, due for instance to thermal sintering of the metal clusters [8] or volatilization of the active species, relatively high metal loadings (from 2 to 10% by weight) have been proposed in the literature [1,9].

Data concerning catalyst durability under conditions of continuous operation are reported by Basini et al. [10] who observed stable reactor performances for a time on stream of 500 h; however, the reactor operated at low GHSV close to conditions of thermodynamic equilibrium. Mitri et al. [9] studied the behavior of a reverse flow reactor upon aging of 3–5 wt% Pt, Rh and Ir based catalysts. Within a time on stream of

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25 h they found that Rh did not suffer significant deactivation phenomena. In this work, pieces of evidence were collected on the behavior of a CH₄-CPO reformer, operating under quasi-adiabatic conditions with a 0.5 wt% Rh/Al₂O₃ catalyst within an overall time on stream of 150 h. The low Rh content allowed to better investigate the impact of catalyst activity on the overall performance of the reactor. The stability of the catalyst was monitored within series of repeated start-up/shut-down experiments at different reaction temperatures and flow rates (in the range of tenths of ms contact times) with the aim of identifying critical operating conditions associated to the decay of catalyst activity. The effects of catalyst aging over the behavior of the reactor were investigated in terms of both steady state conversion/productivity and evolution of axial temperature profiles (so far scarcely investigated in the literature). The impact of catalyst deactivation on the start-up dynamics of the process was also studied. A quantitative analysis of the observed deactivation phenomena was pursued by applying a complete model of the adiabatic reformer [11] which incorporates an indirect kinetic scheme of the reaction process based on previous work discussed in ref. [12] and accounts for the combined effect of heat and mass transfer.

2. Experimental

2.1. Lab-scale assembly

The process of CH₄ partial oxidation was studied on a 0.5 wt% Rh/Al₂O₃ catalyst (BET surface area $\sim 40 \text{ m}^2 \text{ g}^{-1}$) prepared by grafting of alumina powders with Rh₄(CO)₁₂ dissolved in *n*-hexane [13,14]. After drying, the catalytic powders were dispersed in an aqueous solution of nitric acid and a slurry was prepared via 24-h ball milling of the dispersion. A thin (20 μm) and mechanically resistant catalyst layer was deposited by dipping over solid alumina spheres with an average diameter of 3.4 mm. A packed bed of coated spheres (about 17 g) was placed inside a quartz tube reactor between two beds of uncoated spheres acting as thermal shields to prevent axial heat dispersion by radiation. A layer of mullite particles upstream from the spheres bed was used to realize the preheating of reactants and to optimize their premixing. Radial insulation of the reacting zone was realized by wrapping a layer of ceramic insulator around the quartz tube in correspondence of the packed bed. The reactor, equipped with an axial sliding thermocouple, was located inside a tubular furnace for the preheating of the system. A detailed description of the geometry and features of the reactor are reported in ref. [15]. Tests were performed at atmospheric pressure with CH₄/air feeds (O₂/CH₄ ratio = 0.56).

2.2. Start-up and shut-down procedures

The process was started-up by delivering at time zero of the dynamics (t_0) the reactant mixture to the reactor previously heated to the initial desired temperature (reported in the following as $T(t_0)$) under static N₂ atmosphere. The temporal evolution of the outlet stream composition was acquired by

means of a continuous ABB AO2000 analyzer, able to measure CH₄, O₂, CO, CO₂ and H₂ volumetric percent; water concentration during dynamics was estimated by closing the oxygen mass balance. Under steady state conditions the analysis of products was repeated by gas chromatography, which also allowed a direct measurement of H₂O. Atomic mass balances to converted C, O and H were closed within 3%.

The reaction was shut-down by diluting progressively the reactant stream with N₂ and, eventually, the reactor was cooled down to initial conditions under pure N₂ flow. Catalytic runs (1.5–2 h long each) were operated daily; by night the reactor was left under static N₂ atmosphere at room temperature. The autothermal behavior of the reactor was investigated in 4–5 h long experiments by switching off the heating furnace after reaching the stable ignited state.

3. Reactor modeling

A previously developed one dimensional (1D) dynamic heterogeneous model of an adiabatic packed bed reactor was applied to the analysis of experimental data. Model equations and assumptions are fully discussed in refs. [12,15]. The model implements a molecular indirect kinetic scheme independently derived over a 0.5 wt% Rh/ α -Al₂O₃ catalyst with a surface area of $\sim 4 \text{ m}^2 \text{ g}^{-1}$ [12]; the model parameters were modified (after a sensitivity analysis developed in ref. [15]) to account for the higher value of surface area ($40 \text{ m}^2 \text{ g}^{-1}$) in the present experiments. To study the effect of localized deactivation phenomena the possibility to assign an axial activity profile of the catalytic bed was herein implemented in the model, which extended the analysis of kinetic sensitivity mentioned above.

The heat exchange between the oven and the reactor along the preheating zone as well as the heat dispersion in the catalytic portion were described by including in the gas phase energy balance a heat transfer term with an overall heat transfer coefficient.

4. Results and discussion

4.1. Steady state performances: experimental results

The reproducibility of the reactor performances upon exposure of the catalyst to different operating conditions was tested by performing experiments in which the preheating temperature was alternatively set at 380 and 610 °C and the flow rate was increased from 140 N L h⁻¹ (representative of an important thermodynamic control on the product mixture, with a significant role of heat dispersion) to 240 N L h⁻¹ (representative of a more kinetically controlled, almost adiabatic operation) [15]. Catalyst stability with time at constant preheating temperature and flow rate was investigated by performing series of consecutive start-up/shut-down experiments, for an overall time on stream of about 150 h.

Concerning steady state results, Fig. 1a and b reports the evolution of CH₄ conversion and of H₂ and CO molar fractions, respectively, observed during the sequence of experimental runs. The conversion of O₂ was complete under all operating

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