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Small-scale H_2 production from gasoline via Catalytic Partial Oxidation: experimental study using spatially resolved sampling probes and modeling analysis

Andrea Carrera, Alessandra Beretta, Gianpiero Groppi*

Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156 Milano
**Corresponding author: alessandra.beretta@polimi.it*

Highlights

- Increasing temperatures are measured in the CPO reactor passing from light to liquid fuels.
- Mass transfer limits the rate of reforming reactions of heavier molecules.
- Gas-phase reactions and C-deposition are also promoted.
- EGR allows for a favorable thermal control and contrasts C-formation.

1-Introduction

The Catalytic Partial Oxidation (CPO) of hydrocarbons is a promising solution for the small-scale production of H_2 and CO/H_2 mixtures. The process involves highly exothermic (oxidation) and highly endothermic (reforming) reactions, which results in the formation of a hot-spot at the very reactor entrance. In the case of logistic fuels (of interest for on-board H_2 applications) critical issues arise or become more severe than for light hydrocarbons, such as the intensity of the hot-spot temperature (>1000°C), the catalyst stability, the onset of gas-phase reactions, the formation of C-deposits. In this work, we analyze the CPO of i-C_8H_{18} (a model molecule for gasoline) on Rh and compare it with the CPO light hydrocarbons: the focus is on the characterization of the thermal behavior, the impact of homogenous chemistry, the coke formation tendency. Spatially resolved sampling techniques and reactor modelling are applied to gain an insight of the complex interplay of physical and chemical phenomena which govern the reactor behavior.

2-Methods

2 wt% Rh/αAl_2O_3 powders were prepared by dry impregnation of $Rh(NO_3)_3$ of the αAl_2O_3 support (10 m^2/g BET SA) and used to washcoat 400CPSI, 2.5 cm diameter cordierite honeycombs. Honeycombs were loaded in an insulated reactor equipped with a system for measurement of spatially resolved temperature and concentration profiles [1]. Tests were typically run at 10 Nl/min with fuel/air mixtures and $O_2/C=0.56$. A previously developed 1 D reactor model was adapted to described the system, by introducing the kinetic scheme for octanes CPO independently estimated from isothermal kinetic tests [2].

3.Results and Discussion

Figure 1 shows the measured temperature and concentration profiles in i-C_8H_{18}-CPO tests. Data were collected by sliding a thin TC, an optical fiber connected to the IR-pyrometer and open capillary connected to the μ-GC. The same qualitative features were observed as in CH_4 CPO and C_3H_8 CPO, previously studied [1]. A hot spot was present on the catalyst wall at the reactor entrance, while a smoother hot spot was formed in the gas phase at some distance from the inlet. The concentration of O_2 dropped to zero within the first 5 mm, while the conversion of the hydrocarbon proceeded along the length of the monolith. H_2O concentration passed through a sharp maximum at the entrance, while CO and H_2 were progressively produced along the catalyst bed. CO_2 was initially formed, then kept almost constant. Notably, despite the tests were performed under diluted conditions (56% added N_2, corresponding to 2% iC_8) in order to prevent catalyst overheating, the temperature profile was very close to that measured in a non-diluted CH_4-CPO test, with an inlet CH_4 concentration of 27%.

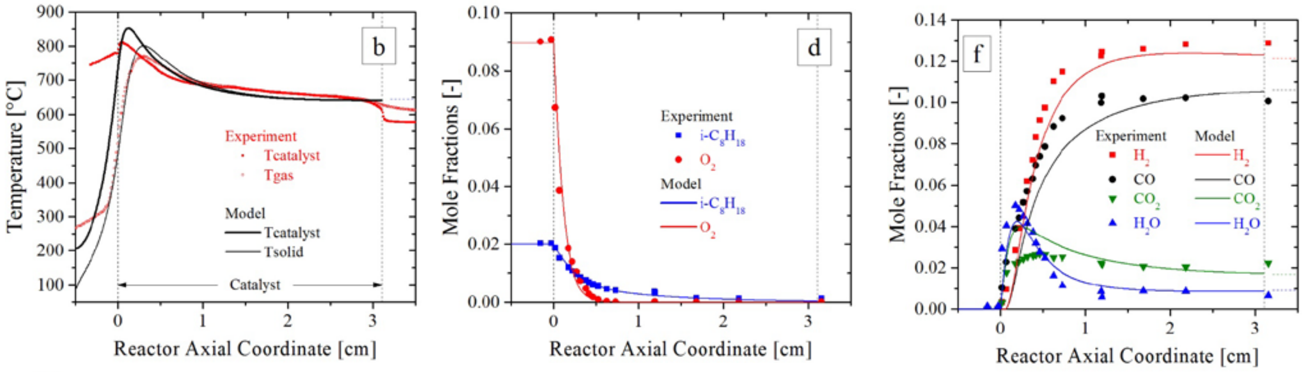

Figure 1 – iC_8H_{18} CPO experiment and simulation. (a) Solid- and gas-phase T-profiles; (b) evolution of the reactants concentration; (c) evolution of the syngas composition.

Simulation performed with a fully predictive 1D adiabatic reactor model provided very satisfactory description of the data (solid lines in Fig. 1). Model analysis confirmed that, as in the case of CH_4-CPO, the consumption of O_2 proceeds under a fully mass transfer controlled regime; however, differently from CH_4-CPO, steam reforming of the C_8 fuel is also markedly affected by diffusional limitations. As a consequence, the balance between exo- and endo-thermic reaction rates is less favorable for the high molecular weight fuel, which is responsible for more severe hot spot at the reactor entrance. Further iC_8-CPO tests at decreasing N_2-dilution showed that the hot spot temperature grows as high as 1100°C when a stoichiometric iC_8/air mixture is used, which inevitably deactivates the Rh-catalyst. At decreasing dilution and increasing reactor temperature, the role of gas-phase reactions was found more and more important. The formation of cracking products (methane, isobutene, butenes, ethylene and propylene) is characterized by a bell-shaped concentration profile along the catalyst bed; indeed, gas phase reaction produce hydrocarbon species in the hot-spot zone, but such species are then consumed at the catalyst surface via reforming reactions.

N_2 dilution of reacting gas, which was adopted in the experimental tests to prevent catalyst overheating, makes coke deposition a critical issue in the CPO of logistic fuels. Significant coke deposition was observed after adiabatic tests, which resulted in a marked deactivation in the reforming zone of the catalyst. As an alternative the dilution with exhaust gas recirculation (EGR) was explored by means of thermodynamic and modelling analysis. The results showed that EGR is a practical solution for obtaining the dilution of fuel/air mixture for on-board applications at the values needed for maintaining the catalyst temperature below the threshold for sintering and deactivation (that we empirically estimated around 900°C) and thus guaranteeing the long term stability of the fuel processor. Additionally, the presence of H_2O and CO_2 in the diluent stream reduces significantly the thermodynamic potential to solid carbon [3].

[1] D. Pagani et al., Ind. Eng. Chem. Res., 53 (2014) 1804.
[2] D. Pagani et al. Chem. Eng. J. 294 (2016) 9-21.
[3] A. Carrera et al. Ind. Eng. Chem. Res. 56 (2017), 4911-4919.

Keywords
Catalytic Partial Oxidation; Rh/Al_2O_3; small scale H_2 production; reactor modelling