A fundamental study of methane pyrolysis on Fe-Al_2O_3 catalyst in a fluidized bed reactor: a combined experimental and CFD investigation

Marco Orsenigo[1], Davide Cafaro[1], Veronica Piazza[1], Chiara Negri[1], Lidia Castoldi[1],
Gianpiero Groppi[1], Matteo Maestri[1], Alessandra Beretta[1]*

1 Politecnico di Milano, Department of Energy, LCCP group, via La Masa 34, 20156 Milano, Italy;

**Corresponding author: alessandra.beretta@polimi.it*

Highlights

- A fundamental study of methane pyrolysis is performed in fluidized bed reactor.
- Carbon accumulation strongly affects the nature of the particles, impacting fluidization.
- Eulerian-Eulerian approach can predict the fluid-dynamic behavior.

1. Introduction

Methane pyrolysis is a valuable process to produce turquoise hydrogen with the simultaneous production of high-value solid carbon. Operations in fixed bed reactors are limited by overpressure and reactor blockage due to carbon deposition, instead, the fluidized bed reactor allows for continuous operations[1]. The aim of this work is to study the fluidization of Fe based catalyst and characterize the effect of carbon build-up on the fluidized reactor performances. An experimental campaign was performed in lab-scale fluidized bed reactor operating in semi-batch mode, to monitor the variation of the solid properties at different operating conditions. Solid characterization analyses and fluidization tests were used to improve a Eulerian-Eulerian (EE) model to guide the reactor design towards continuous operation.

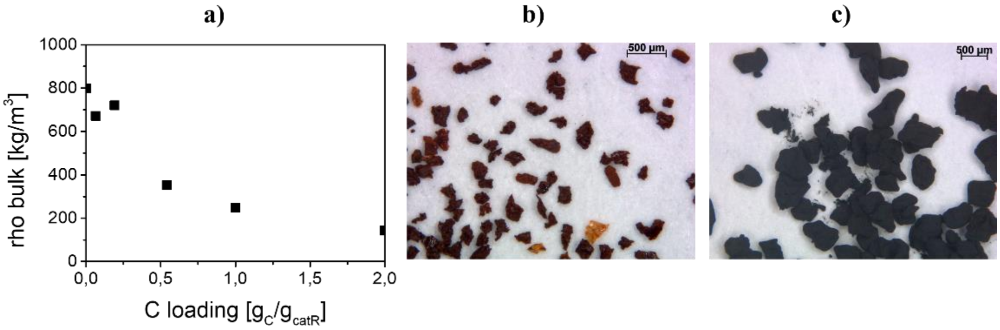


Figure 1. a) Bulk density as a function of the C loading = C/catalyst; b) and c) optical microscope images of the fresh catalyst and of the spent catalyst, after pyrolysis at T=800°C with C loading of 2.

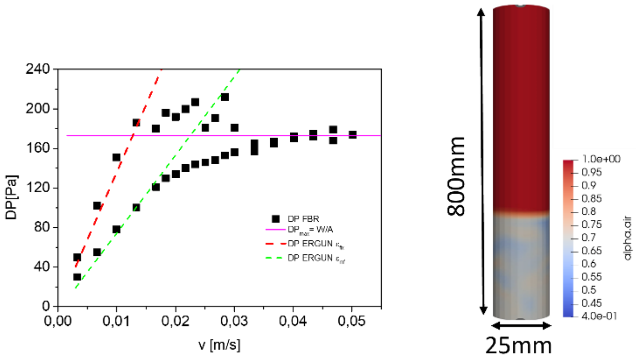
2. Methods

Experiments of methane catalytic pyrolysis were performed in a fluidized bed reactor over Fe-Al_2O_3 catalyst in a powder (100μm)[2]. The experimental campaign was carried out in a quartz reactor (I.D = 25mm, L = 800mm) placed into a vertical tubular oven. The temperature was measured by an axial multi-point thermocouple. Pressure was monitored by a pressure transducer connected to the reactor inlet and a differential pressure transmitter connected to the reactor's terminals. All the methane pyrolysis tests were performed in a batch mode at ambient pressure by varying the operating temperature (800-850°C), GHSV (1-20 NL/h/g_{cat}) and CH_4 inlet concentration (10%-100%). The morphological properties of the fresh and spent catalyst were characterized; the particle size distribution was determined by sieving, whereas the bulk density (ρ_{bulk}) was calculated by measuring the solid height and its weight in a graded cylinder.

Euler-Euler numerical simulations were performed for the solution of the system's governing equations. By adopting this numerical framework, it is possible to provide insights into the interactions between the macro-scale transport phenomena and the catalytic elementary steps at the catalyst sites[3].

3. Results and discussion

Pyrolysis experiments were performed in a fluidized bed reactor over Fe-Al_2O_3 at different operating conditions to collect coked material at different C loading. Fig. 1a illustrates a significant decrease of bulk density with increasing C loading, indicating a variation of particle properties that are relevant for the fluidization behavior. The characterization of spent catalysts discharged at different time on stream revealed important morphological changes. Fig. 1b shows the fresh catalyst with an average particle size of 200 μm, while Fig. 1c displays the catalytic particles with a C loading equal to 2 with an average particle size of 300 μm. The impact of the evolving particle characteristics was experimentally assessed via non-reactive fluidization tests by measuring pressure-velocity curves at growing C-load, allowing to determine the minimum fluidization velocity (v_{mf}) at each C loading. Then, those profiles were fitted using the Ergun equation (Fig. 2a) to determine the void fraction both of the initial tight packing (red line) and the one of the loose packing, after defluidizing the particle bed (green line), and other properties, such as the particle density. The characterization of solid properties based on the different degrees of carbon build-up not only allows determining the fluidization regime in which the reactor is operated but also provides the input parameters for a detailed CFD numerical investigation. The EE approach, adopting solid properties determined from the experimental campaign can predict the fluid dynamic behavior of the system. Fig. 2b displays the results of EE simulation of void fraction in a bed of the spent catalyst at C loading of 2 and a gas velocity equal to the minimum fluidization. This enables the control of the fluidization regime during the operations and improve physical understanding of the phenomena occurring into the unit paving the way for the reactor scale-up.



a) **b)**

Figure 2. a) pressure drops at varying inlet gas velocity for the spent catalyst with C loading of 2; b) Void fraction map of the lab scale reactor by means of a Euler-Euler simulation.

4. Conclusions

The application of fluidized bed reactors to CH_4 catalytic pyrolysis need to address the challenge of drastically evolving properties of the solid. Here we address a fundamental understanding of how C-accumulations changes shape, morphology, density of the particles, thus the fluidization regime and the overall reactor performance.

References

[1] J. X. Quian, L. R. Enakonda, W. J. Wang, D. Gary, P. Del-Gallo, J.-M. Basset, D. B. Liu, L. Zhou, Int. J. Hydrogen Energy 44 (2019) 31700-31711
[2] J.L. Pinilla, R. Utrilla, R.K. Karn, I. Suelves, M.J. Lázaro, R. Moliner, A.B. García, J.N. Rouzaud, Int. J. Hydrogen Energy 36 (2011) 7832-7843
[3] D. Micale, C. Ferroni, R. Uglietti, M. Bracconi, M.Maestri, Chem. Ing. Tech. 94 (2022) 634-651.

Keywords

Methane Pyrolysis; Fluidized bed reactor; Scale-up; Euler-Euler simulations.