Methane pyrolysis on Fe-Al$_2$O$_3$ catalyst for turquoise H$_2$ production: a combined experimental and modeling study on reaction and deactivation kinetics

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Highlights
- Fe/Al ratio strongly affects the structure properties and the catalytic performance.
- Tests in TGA and packed bed reactor provide evidence for initial first order kinetics.
- Deactivation kinetics change with C-load and CH$_4$ partial pressure.

1. Introduction

Hydrogen is gaining increasing attention as a sustainable energy source; a promising production process involves the thermo-catalytic CH$_4$ pyrolysis, resulting in CO$_2$-free turquoise hydrogen. Fe-based catalysts offer an advantageous balance in terms of cost, activity, resistance to deactivation, low toxicity and valuable carbon nanostructures [1-2]. However, the continuous build-up of carbon strongly impacts catalyst performance and challenges the kinetic study. In this work, iron-based catalysts with Al$_2$O$_3$ as textural promoter were prepared, characterized and tested in CH$_4$ pyrolysis at different scales, with the ultimate aim of developing a comprehensive kinetic model accounting for deactivation.

2. Methods

Fe-Al$_2$O$_3$ catalysts with different Fe/Al molar ratios (i.e. 50:50, 75:25, 88:12, 94:6, 97:3) were prepared from nitrate salts using the fusing method, as described by Pinilla and coworkers [2]. The prepared catalysts were characterized by BET, XRD, HR-TEM, FESEM. The same techniques, along with Raman and TPO, were applied to characterize the formed solid carbon from deactivated catalysts.

Experiments of catalytic CH$_4$ pyrolysis were carried out at different scales. Tests in thermobalance under temperature ramp (TG/MS) were used as screening methodology of the various formulations. Selected formulations were then tested in a packed bed reactor, loaded with 750 mg of catalyst powder, using a micro-GC for composition analyses. The effects of temperature (750-850 °C), inlet CH$_4$ (20-95%), space velocity (5-20 NL/h/g$_{cat}$) and H$_2$ co-feed (0-80%) were explored.

The collected data were used to derive a kinetic expression for CH$_4$ pyrolysis. For this purpose, a 1D dynamic reactor model was developed, able to describe the temporal evolution of the phenomena taking place along the axial coordinate of the reactor. This numerical model was implemented in MATLAB® framework, adopting the finite difference method to discretize the system's governing equations.

3. Results and discussion

Analyses on fresh catalyst samples revealed a well-defined crystal structure, mainly associated to hematite phase. The Fe/Al ratio significantly influenced the structure, with BET surface area progressively decreasing with Fe content. During screening in TGA, the 75:25 formulation showed the highest initial pyrolysis rate, but the 50:50 composition tended to the same C-load for prolonged time.

The 50:50 formulation was chosen as reference for packed bed tests. Fig.1a presents in symbols the evolution of CH$_4$ conversion measured at the outlet of the reactor at varying inlet concentration. Each conversion curve was transformed into a corresponding C build-up curve, with quantification of the parameter C* = gC/g$_{cat}$. In all tests, a rapid deactivation caused the decrease of methane conversion; the decline of conversion (and the growth of C-build up) was progressively more pronounced at increasing CH$_4$ feed content. Notably, characterization analyses showed that the formed carbon species were

mainly organized (i.e. graphitic) and with a tubular structure (i.e. nanotubes, $d_{average}$ 50nm ca.), as seen in Fig.1c.
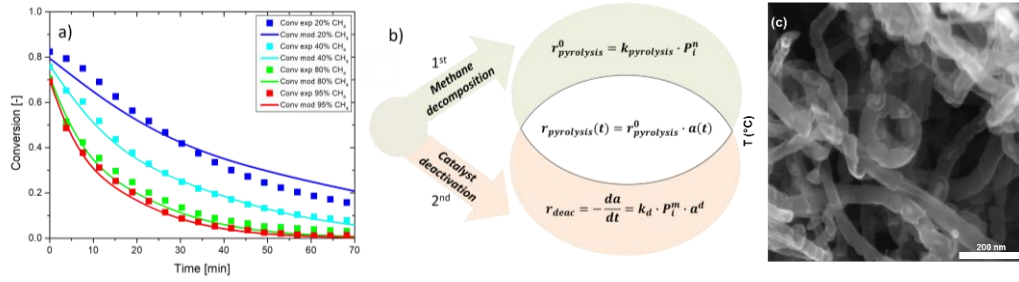

Figure 1. a) Pyrolysis tests at varying inlet CH_4 concentration (800°C, 20 NL/h/g_{cat}). b) Kinetic model for the CH_4 pyrolysis. c) FESEM image of spent catalyst.

To describe the observed phenomena, a dynamic model of the reactor was developed (equations in Fig.2) where the process kinetics was described by accounting for two factors: the initial rate of methane decomposition (r^0, that is the rate of reaction on the fresh C-free catalyst) and the catalyst activity function (a(t)), defined as the ratio between the actual rate of pyrolysis at a generic time and r0. A first order dependence of r^0 on CH_4 was assumed, based on the analysis of the initial conversion data as function of the C-load and their extrapolation at zero C-load (Fig.1b). Concerning the deactivation rate (r_{deac}= -da/dt, detailed in Fig.1b), two distinct laws were incorporated to describe the evolving kinetics in the range of low (<1 gC/gcat) and high (>1 gC/gcat) carbon build-up, respectively

The solid lines in Fig.1a show a good agreement of the model with the experimental measurements and an equally satisfactory result was obtained by predicting independent data, collected under conditions different from those used for deriving the kinetic parameters. Besides enhancing the comprehension of CH_4 pyrolysis kinetics, this model turned out to be a powerful tool to describe the temporal evolution of C* along the axial coordinate of the reactor (see Fig.2), information not accessible from the experiments.

Based on the reactor and kinetic modelling, a generalized activity function was developed that sets an explicit correlation between the catalyst activity and the controlling parameters, that are C* (carbon load) and CH_4 partial pressure. This tool enables the design of reactors that operate under steady state conditions, based on the continuous make up of fresh catalyst and removal of deactivated catalyst.
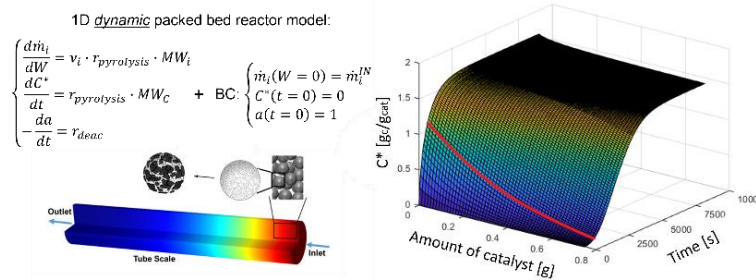
Figure 2. Governing equations of the dynamic reactor model together with the temporal evolution of the carbon build up along the axial coordinate of the reactor.

4. Conclusions

This study provides insights into CH_4 pyrolysis on Fe-Al_2O_3 catalyst, combining characterization, tests across multiple scales and the development of a kinetic model. An analytical expression of the catalyst activity can now be used for the design of different reactor configurations.

References

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