

A multiscale study of CH₄ pyrolysis over Fe-Al₂O₃ catalyst: the challenge of C build-up for the kinetic and the reactor studies

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Significance and Relevance

This work reports a multiscale study of CH_4 pyrolysis on iron catalyst, where the build-up of solid C challenges conventional studies in catalysis and calls for expert lab-scale and modelling methodologies. Tests were performed in thermobalance to identify promising catalyst formulations, in packed bed reactor to quantify kinetics, and in fluidized bed reactor to study the scaling of the process. Macroscale models with intrinsic kinetics and characterization of C-loaded solids (up to an unprecedented 4.5 g_c/g_{cat}) were applied to rationalize observed performance and optimize reactor operation.

Preferred and 2nd choice for the topic: H₂ storage and transportation, green H₂ production, hydrogen vectors; Multiscale modeling and advanced simulation aspects. Preferred presentation: Oral preferred.

Introduction and Motivations

The thermo-catalytic reaction of CH₄ pyrolysis (CH₄ \rightarrow 2 H₂ + C(s), Δ H° = 75.6kJ/mol) is receiving growing interest as source of CO₂-free hydrogen. Fe-based catalysts offer an advantageous balance in terms of cost, activity, resistance to deactivation, low toxicity and valuable carbon nanostructures¹. However, the continuous build-up of carbon not only impacts catalyst performance during reaction, but also poses challenges for the kinetic analysis, reactor design and process scale-up. In this work, iron-based catalysts with Al₂O₃ as textural promoter were prepared and tested in CH₄ pyrolysis at different scales and reactor configurations, integrating experiments with a comprehensive reactor and kinetic modeling to guide process optimization and scale-up.

Materials and Methods

Fe-Al₂O₃ catalysts were prepared by fusion-decomposition method using nitrate salts. Tests on multiple scales were performed in three different lab-scale configurations: a thermobalance (TG, m_{cat} =5 mg), a packed bed reactor (PBR, m_{cat} =750 mg) and a fluidized bed reactor (FBR, m_{cat} =5 g). The effect of temperature (750-850°C), inlet CH₄ (10-95%), space velocity (1-20 NL/h/g_{cat}) and H₂ co-feed (0-80%) on catalyst activity and deactivation was investigated. Experiments were also designed to measure the C-load capacity of the catalyst.

Catalyst testing was coupled with a comprehensive characterization of the fresh, reduced and Cloaded catalyst, including microscopic (e.g., N₂ ads/des, XRD, FESEM, TEM, Raman) and macroscopic (e.g., measurement of density, particle size distribution, minimum fluidization velocity) properties.

Reactor models were developed to simulate experiments: a 1D dynamic reactor model for PBR was developed, able to describe the temporal evolution of the phenomena taking place along the axial coordinate of the reactor. FBR experiments were simulated with a dual modeling approach: Euler-Euler CFD numerical simulations, and Kunii and Levenspiel (KL) macroscopic model².

Results and Discussion

Reactive tests in thermobalance were performed on catalysts with different Fe loadings (12-97 wt%) to identify promising catalyst formulations: the catalyst with Fe:Al molar ratio of 50:50 demonstrated the optimal balance between Fe content and structural promotion by Al_2O_3 .

Tests in PBR were carried out to explore the effect of temperature, GHSV and feed composition on methane conversion and the corresponding C build-up curve ($C^* = g_C/g_{cat}$). In all tests, a rapid decrease



of conversion was observed, becoming progressively more pronounced at increasing methane feed content and temperature. The dynamic reactor model allowed to decouple and quantify the reaction and deactivation kinetics: the initial rate of methane decomposition (r^0 , the reaction rate on the fresh C-free catalyst) was expressed with a first order dependence on CH₄ based on the extrapolation at zero C^* of conversion. An activity function (a(t), defined as the ratio between r(t) and r^0) was then evaluated to account for the observed deactivation: this function establishes a quantitative correlation between the activity and the controlling parameters C^* , CH₄ partial pressure and temperature (Figure 1(a)).

Fluidization measurements and CFD analyses (Figure 1(b)) on fresh and C-loaded catalysts guided the design of experiments in FBR: minimum fluidization velocity and bed expansion were evaluated at increasing C*, and the existence of a bubbling fluidization regime was verified. A wide experimental campaign highlighted trends in line with those observed in PBR. Furthermore, the characterization of unloaded catalyst showed drastic changes of solid properties taking place during the evolution of C build-up: for instance, the bulk density decreased from 700 to 200 kg/m³, accompanied by changes in particle size distribution and void fraction.

A KL macroscale model was developed, with the incorporation of the intrinsic kinetics and the detailed characterization of the C-loaded solids: this model showed good agreement with experimental data (Figure 1(c)), validating the approach and opening to further process optimization.

The further scale-up of this process requires advancements in catalyst shaping to ensure its suitability for fluidization, as well as dynamic modeling of the FBR. Both topics are currently under investigation. An additional challenge lies in carbon valorization: different potential applications are under evaluation (e.g., C-carrier for CO_2 storage, C as reducing agent), coupling the characterization and testing of unloaded catalyst with process analysis to assess the overall feasibility.



Figure 1: (a) Surface map of catalyst activity; (b) Euler-Euler simulation of a catalyst with C-load of 2 g_C/g_{Cat} ; (c) Comparison between experiment in FBR and macroscopic model predictions.

In conclusion, this study investigates CH_4 pyrolysis on Fe-Al₂O₃ catalyst, combining tests across multiple scales, kinetic modelling and reactor modelling. Models and experience can now be transferred at larger scale testing and process analysis.

References

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- 2. Daizo Kunii & Octave, L. Fluidization Engineering. (1991)