A new method for the evaluation of catalyst deactivation phenomena by the moving observer approach.

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Highlights

- Evaluation of catalyst deactivation in fluidized bed reactor is challenging.
- This new method determines the particle trajectory to replicate.
- A moving observer setup is developed to replicate the trajectory in a fixed bed reactor.
- This setup unlocks the potential of *operando* methods for moving particles.

1. Introduction

A comprehensive characterization of catalyst deactivation mechanisms in fluidized bed reactors is essential to understand the stability of the system and to properly evaluate the long-term performance of the reactor.

Presently, researchers face difficulties in evaluating the nature and impact of coking layers on catalysts in systems with moving particles. On one hand, the use of *operando* methods is prevented by the intrinsically erratic particle motions in fluidized bed reactors [1]; on the other hand, the use of ex-situ detection techniques for carbon deposition hinders the time dependence evaluation.

Therefore, the goal of this study is establishing an innovative method to study the evolution of coking layers on catalysts in real time during the fluidized-bed CO2 methanation by a *moving observer* approach. This approach consists in the reduction of the fluidized bed reactor to a non-steady-state fixed bed reactor. Particularly, the focus of the poster will be on the experimental evaluation of coking on the external surfaces of catalyst particles.

2. Methods

The study takes advantage of a bench-scale fluidized bed reactor already available at the Paul Scherrer Institute (PSI), with the twofold intent to gather data on both the motion of particles inside the reactor, and the time-space evolution of composition profiles. The former is done by particle tracking techniques, of which radioactive particle tracking (RPT) is considered among the most reliable and versatile [2], [3].

The experiments in the reactor are focused on obtaining data on both the composition profiles inside the reactor and the evolution of the coking layer on the catalyst particles. This is done by feeding the reactor with a typical methanation mixture consisting of CO_2 and H_2, with the addition of ethylene. Given its tendency to form polymeric structures on solid surfaces at reactive conditions, ethylene is a suitable surrogate of coke precursors.

The experimental results are utilized to derive a comprehensive reactor model, which describe the concentration and temperature profile, as well as the particle movement in the fluidized bed reactor. With this model, it is possible to describe the environment that the particle encounters in its motion in the reactor.

3. Results and discussion

Figure 2 explains how the data on composition may enable the ideal division of the reactor in zones of different average composition, while the data on particle motion makes it possible to determine the average time spent by the particle in each of these zones [4]. The combination of these two sets of information is then used in the moving observer setup to put the catalysts in contact with streams of similar compositions (feeds 1, 2, ..., N in the figure) at the same time spans, in the attempt to closely replicate the real operating conditions to which the catalyst is subjected.

The moving observer setup, being a fixed bed reactor, allows for the application of operando methods for the instant detection and characterization of carbon deposition on catalyst particles, and the evaluation of its development in time. For this scope, the most promising technique appears to be Raman spectroscopy, which has been shown to effectively detect carbonaceous structures [5], [6]. In our presentation, we will describe the operation of this setup, showing how this new approach allows improving the detailed determination of catalyst deactivation phenomena.

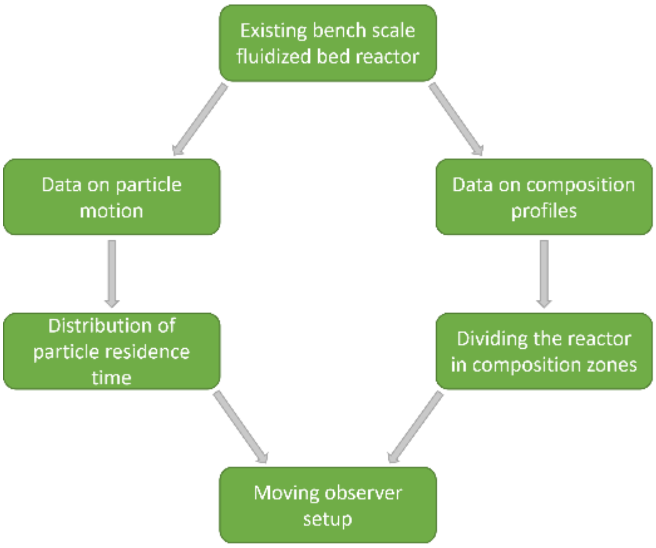

Figure 1: Roadmap of the study.

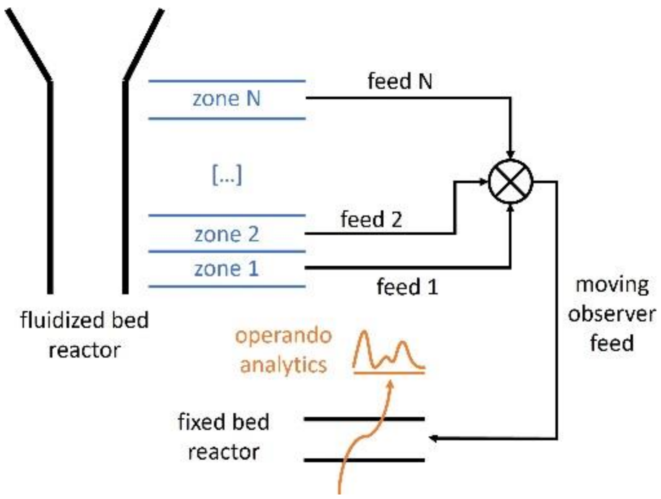

Figure 2: Scheme of the moving observer setup.

4. Conclusions

By combining the moving observer setup with the insight on particle motion in a fluidized bed obtained from particle tracking, it is possible to analyze catalyst deactivation by coking with operando methods.

This theoretically enables to study the evolution of the coking layer in time in a single run, instead of the many runs at different times on stream which are made necessary by the use of ex-situ carbon detection techniques in the case of fluidized bed reactors.

References

[1] H. R. Norouzi, N. Mostoufi, Z. Mansourpour, R. Sotudeh-Gharebagh, and J. Chaouki, "Characterization of solids mixing patterns in bubbling fluidized beds," *Chemical Engineering Research and Design*, vol. 89, no. 6, pp. 817–826, 2011, doi: 10.1016/j.cherd.2010.10.014.

[2] M. Al-Dahhan, S. Aradhya, F. Zaid, N. Ali, and T. Aljuwaya, "Scale-up and On-line Monitoring of Gas-solid Systems Using Advanced and Non-invasive Measurement Techniques," *Procedia Eng*, vol. 83, pp. 469–476, 2014, doi: 10.1016/j.proeng.2014.09.080.

[3] A. Efhaima and M. H. Al-Dahhan, "Assessment of scale-up dimensionless groups methodology of gas-solid fluidized beds using advanced non-invasive measurement techniques (CT and RPT)," *Canadian Journal of Chemical Engineering*, vol. 95, no. 4, pp. 656–669, 2017, doi: 10.1002/cjce.22745.

[4] A. Köhler, D. Pallarès, and F. Johnsson, "Modeling Axial Mixing of Fuel Particles in the Dense Region of a Fluidized Bed," *Energy and Fuels*, vol. 34, no. 3, pp. 3294–3304, 2020, doi: 10.1021/acs.energyfuels.9b04194.

[5] Y. T. Chua and P. C. Stair, "An ultraviolet Raman spectroscopic study of coke formation in methanol to hydrocarbons conversion over zeolite H-MFI," *J Catal*, vol. 213, no. 1, pp. 39–46, 2003, doi: 10.1016/S0021-9517(02)00026-X.

[6] R. Geng *et al.*, "Evolution of carbon deposits during ethylene aromatization over Zn/ZSM-5," *Fuel*, vol. 358, no. PA, p. 130078, 2024, doi: 10.1016/j.fuel.2023.130078.

Keywords

Catalyst deactivation; fluidized bed reactors; moving observer approach.