Uncover the *Secret Life of Catalysts* with Accessible Reaction Engineering Tools: DRM and RWGS

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Abstract

Catalytic reactors are important in many application areas, ranging from hydrogen, fuels, plastics, pharmaceuticals, food products, emission control, and countless others, with reactors and catalysts engineered to minimize unwanted by-products. Catalyst development often involves testing small scale experimental systems that have vastly different heat and mass transfer characteristics as compared to those of commercial-scale reactors. For example, lab-scale powder bed experiments may be minimally affected by internal mass transfer resistances, while narrow tube diameters may limit radial temperature variability inside the packed bed. Catalyst coatings on structured reactors such as monoliths may have a thermal profile that is difficult to measure during testing. Batch autoclave reactors reduce external transport limitations but reveal little about what happens inside a catalyst where concentrations may be very different from those in the bulk mixture. Given these experimental challenges, translating performance between reactor scales, or identifying catalyst performance problems is greatly enhanced by accessible reaction engineering tools, such as DETCHEM PBR and DETCHEM CHANNEL. Dry Reforming of Methane and Reverse Water Gas Shift examples are given, where these tools predict coke within catalyst structures. For the DRM example, SEM EDS analysis confirmed coke formation inside the interior of a catalyst pellet and not in the shell coating surrounding a highly conductive core (HeatPath™), as predicted by DETCHEM PBR. With RWGS, a 50 μm thick catalyst coating was found to suppress coking in an adiabatic monolith, partially due to the surprising side-benefit of methanation supplying sufficient heat to prevent carbon activity exceeding a value of one.

Introduction

The path to decarbonization will require many different technologies (Figure 1A), with catalyst selection and reactor design driving the performance of each of these unique processes. For each of the technologies outlined in Figure 1A (as well as the countless others not listed), a wide range of challenges and constraints must be addressed to have a successful design (Figure 1B). Oftentimes these challenges are not fully addressed, relying on guesses, heuristics, or experience. Other options require extensive experimentation but that can be time consuming and expensive. Another option is to simulate processes using computational fluid dynamics (CFD) or other tools, but oftentimes such codes are expensive or built-in features don't fully describe the physics of the

system of interest. One effect in particular that is often insufficiently analyzed is the mass transfer resistance favoring side reactions that can occur inside porous catalyst structures.

Practical catalysts balance non-linear multi-step reactions with second-order diffusion effects. This interplay can reveal unexpected findings that mask laboratory observations or scale-up problems. Critical diffusion dimensions that affect side reactions depend on the reaction network complexity. These critical diffusion lengths that inhibit side reactions may be on the order of just a few μm, or as large as 1000+ μm. The "secret life of catalysts" occurs inside catalyst structures (e.g., *pellets, powders, and wall coated catalysts*), where transport is controlled by diffusion and where series or series-parallel reactions can dominate. Although this internal region physically contains most catalyst sites, complex reactions inside pore structures are generally poorly analyzed and rarely optimized. Side reactions that run amok inside a catalyst can be conflated with an intrinsic catalyst problem and the catalyst practitioner may move to the next formulation or condition. Reduced performance at scale can become accepted, instead of being understood and improved upon.

The physics of coupled reaction and diffusion is not new, described by (among others) Turing[1], Aris[2] and Fogler[3]. Every undergraduate chemical engineer learns the principles of internal diffusion limitations and a simple effectiveness factor analysis in their reaction engineering class.

The problem lies in the use of simplified analyses. Reality is often more complex and interesting than a simplified analysis might conclude. So why is this known effect of internal diffusional resistance coupled with reaction mostly ignored or oversimplified? Accessible reaction engineering tools are not routinely available nor are results generally expected to challenge the interpretation of laboratory data. Here, accessible means readily usable with little programming or customization needed for the chemical engineer more interested in the application than the theory. Without such reactor simulation tools, it is difficult to see what one doesn't expect to find.

DETCHEM[4] is a suite of accessible reaction engineering tools designed to help to understand what happens inside a catalyst, integrating:
- multi-step reaction kinetics, either from microkinetic models with perhaps hundreds of steps or apparent rates with a few steps, <u>coupled</u> with
- catalyst internal pore diffusion that may be molecular, Knudsen, or mixed, <u>coupled</u> with
- realistic heat transfer models, such as state-of-the art correlations for packed beds, structures, or open channels, to model the flow of heat that results from exterior heating/cooling along with endo- or exothermic heat transfer demands linked with the kinetic mechanisms.

DETCHEM PBR and DETCHEM CHANNEL from the DETCHEM software suite are used for the present work. DETCHEM PBR is a one-dimensional packed bed reactor simulator and DETCHEM CHANNEL is a single channel reactor simulator for structured reactors, such as monoliths and microchannels.

Two examples will be discussed that reveal the secret life of catalysts, and for each of these examples DETCHEM tools will be used to analyze chemistry inside of catalysts. In Section 2, we investigate a Dry Reforming of Methane (DRM) Nickel catalyst that was shown to concentrate CO inside the pellet. In the second example (Section 3), a modeling analysis for RWGS was

completed to show that coke can form inside catalysts, even if the exterior of the catalyst is observed to be coke-free. The RWGS example shows that through modeling, an elegant solution can be found to allow operation in a regime without coke formation.
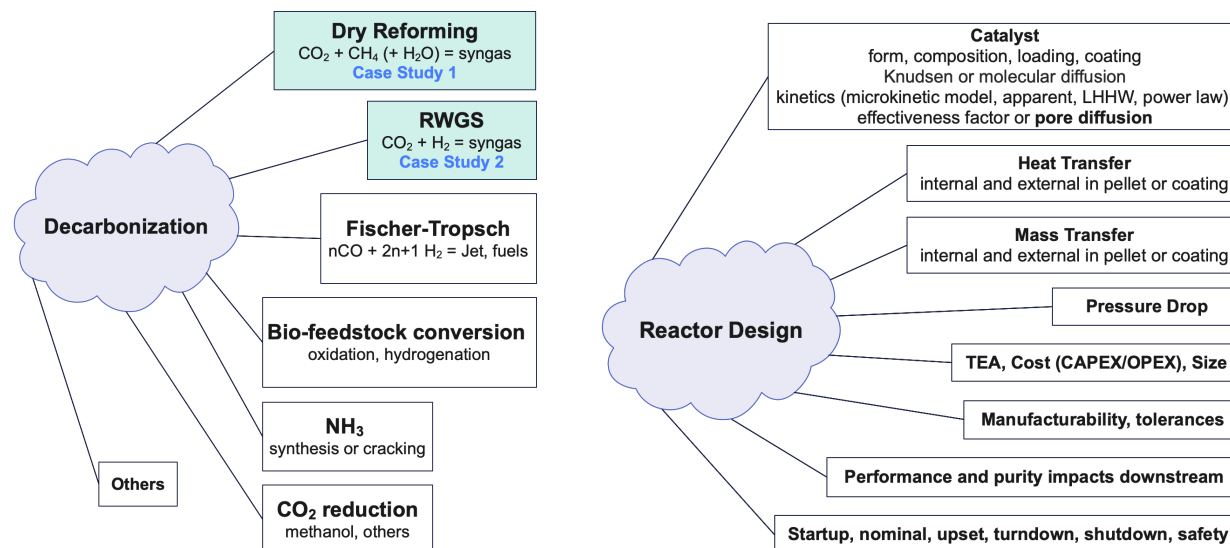

Figures 1A and 1B. A wide range of technologies (1A, left) and analyses (1B, right) are needed to address decarbonization.

Dry Reforming of Methane (DRM)

Summary experimental data for DRM collected with 6 mm Ni/alumina catalyst pellets are shown in Figure 2A. The catalyst deactivated when operated with a S:C below 1.5 and a high pressure of 20 barg but there was no visible external coke. DETCHEM PBR, however, predicted the formation of coke in the interior of the catalyst pellet for most of the catalyst bed (Figure 2B). This was confirmed by SEM EDS (Figure 3). Coke forms in the interior of the catalyst due to the concentrating effect of CO inside the catalyst pellet (Figure 4) which leads to the carbon activity exceeding one. When carbon activity exceeds a value of one, coke is thermodynamically favored to form. DRM modeling was based on an experimentally fit apparent kinetics for a simplified reaction network consisting of DRM, Water Gas Shift (WGS), and Steam Methane Reforming (SMR) steps.

One solution to avoid coke formation in DRM reactors is to use the Nexceris HeatPath^{TM},[5] catalyst, whereby the catalyst is coated on a dense, highly conductive core (Figure 5). At a steam to carbon ratio (S:C) down to 0.3 the catalyst ran for 450 hrs without coke formation (predicted by DETCHEM PBR modeling, and confirmed by SEM EDS of selected pellets, Figures 6A and 6B). Despite the lower volumetric catalyst loading of the 12wt.% Ni doped Al_2O_3-CaO-MgO material when applied as a thin coating on the HeatPath^{TM} catalyst particle, the performance improved (Table 1) due to the elimination of side reactions inside the catalyst pellet. Without the proper accessible tools, such as DETCHEM PBR, finding an engineering solution would be difficult.
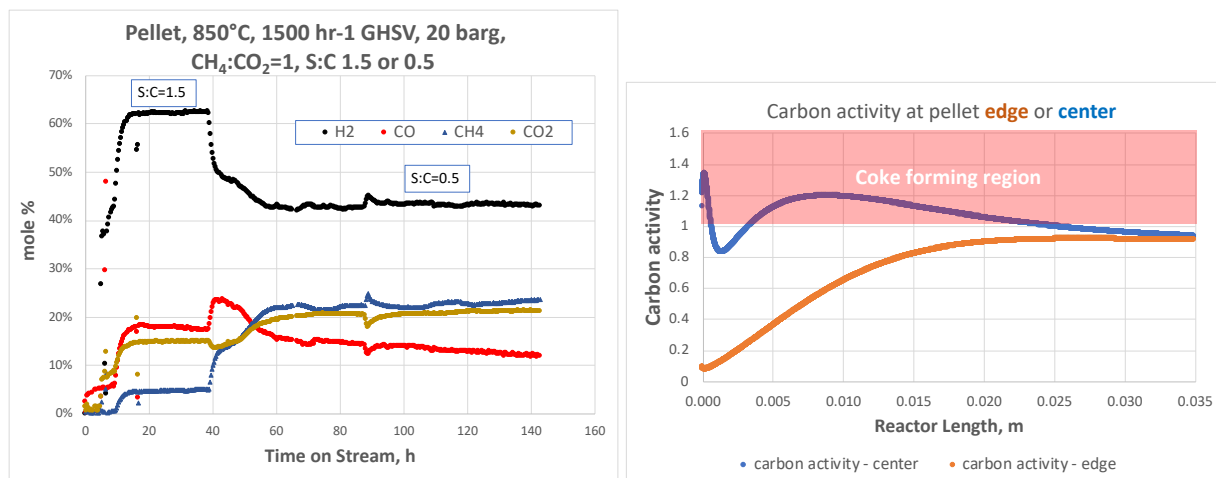
Figures 2A and 2B. DRM data (2A, left) and a DETCHEM PBR modeling prediction that coke under these experimental conditions should form inside the catalyst pellets, not on the exterior of the pellets (2B, right).
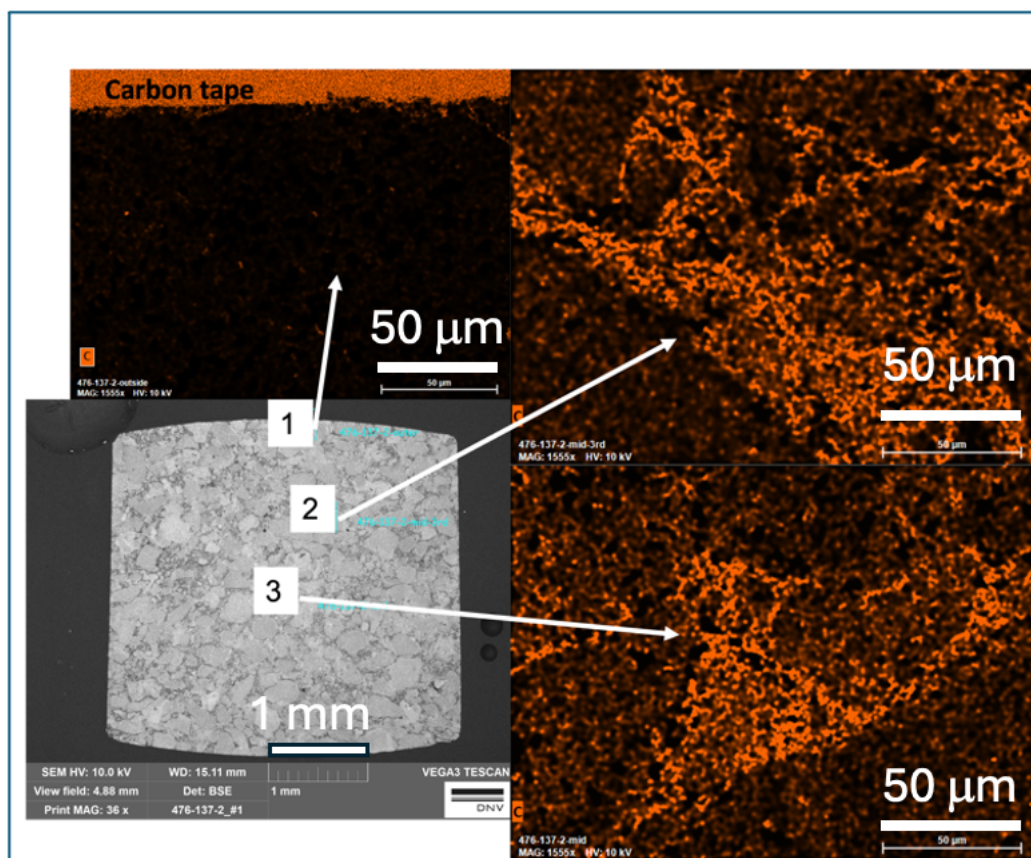
Figure 3. SEM analysis confirms the presence of coke inside, but not on the outside of the catalyst pellet, as predicted by DETCHEM PBR. The length scales have been enhanced for clarity.
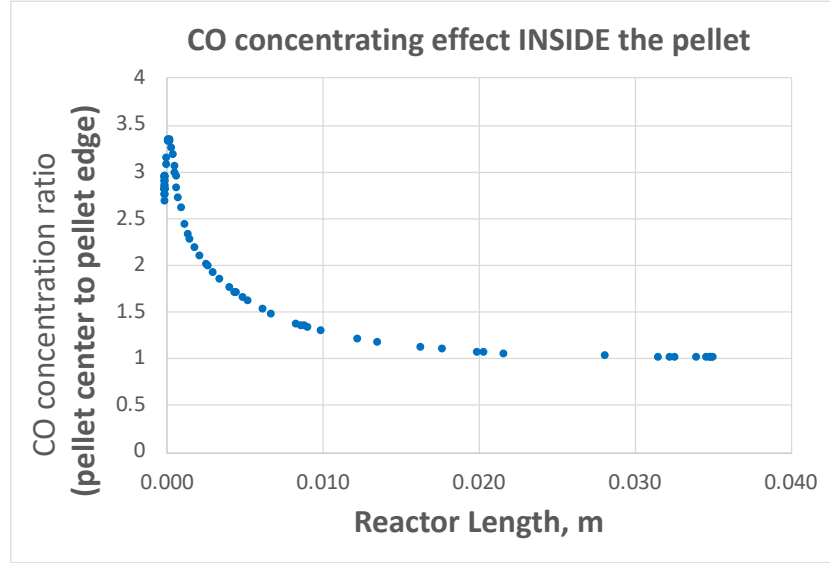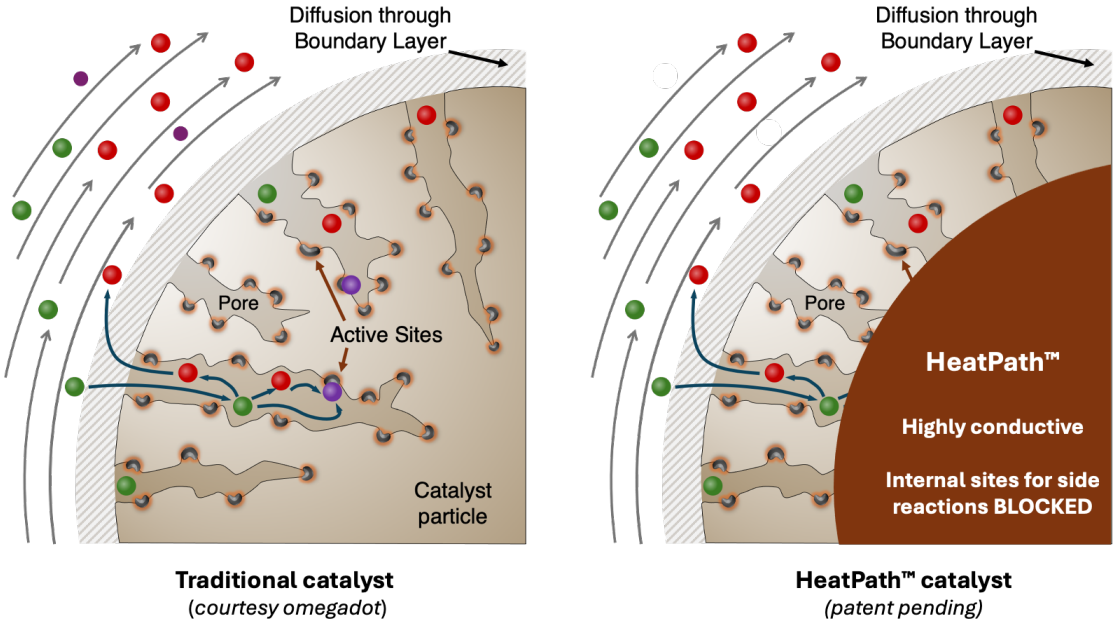
Figure 4. Coke forms due to a concentrating effect of CO inside the pellet, as predicted by DETCHEM PBR.

Figures 5. Conventional pellet catalysts (left) can have intricate pore structures that limit mass transfer. Mass transfer resistances inside a catalyst particle can affect overall reactor performance, but the effect of stagnant zones within the pellet can be mitigated by instead using a thin catalyst coating. Thin shell coatings on highly conductive catalyst cores are possible with Nexceris HeatPath^{TM} (right).
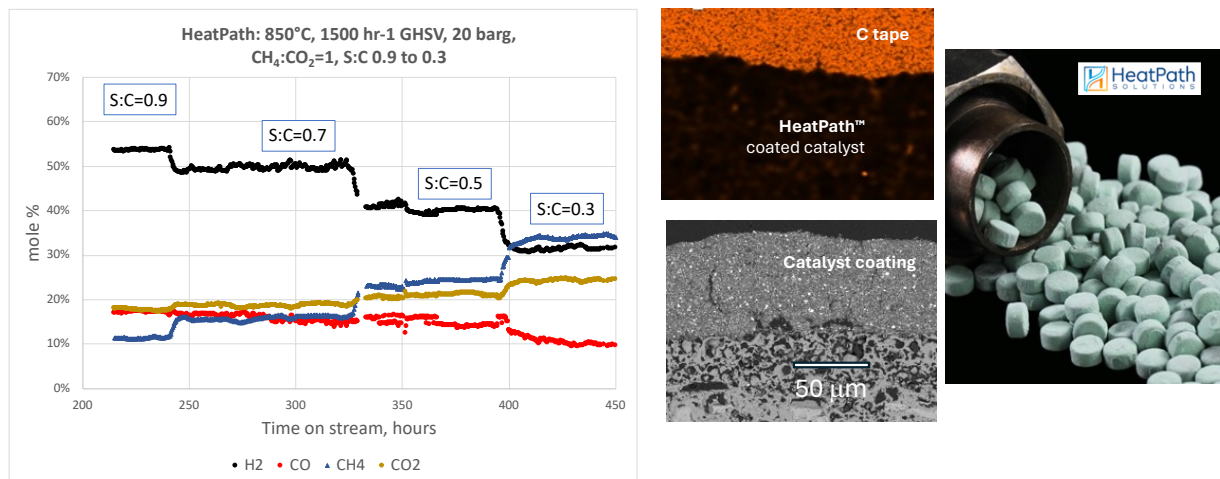
Figures 6A and 6B. DRM tests were repeated with HeatPath™ (6A, left). With the thin shell coating, coke does not form inside the catalyst (6B, right). The presence of carbon in the top of the SEM EDS dot map (orange color) is due to carbon tape, not coke.

Table 1. Summary of DRM results (GHSV=1500 hr^{-1}, P=20 barg, CH$_4$:CO$_2$=1, T=850°C). Despite the thin coating, the HeatPath™ pellet with a shell catalyst coating was more productive than a conventional pellet because the interior of the conventional pellet is where CO concentrated and unwanted side reactions – like coking – occurred.

| System	S:C	g/g/h (CH$_4$)	g/g/h (CO$_2$)
Pellet	1.5	0.15	0.12
Pellet (*pre-coking*)	**0.5**	**0.11**	**0.37**
HeatPath™	1.5	5.88	4.38
HeatPath™	**0.5**	**2.95**	**10.12**

Reverse Water Gas Shift (RWGS)

In another example, a DETCHEM PBR analysis of RWGS on a Nickel-based catalyst was completed to determine how to best configure a catalyst to operate at pressure without coke formation. A microkinetic model with 6 gas phase species, 13 surface species, and 52 surface reactions was used to model the catalyst[6]. Both packed bed and a monolith structured reactor designs are considered in this design study. A packed bed reactor with 5-mm diameter catalyst particles exhibits a strong internal pellet CO concentrating effect and a carbon activity greater than 1 in a 0.5 m long, 4 cm diameter tube. As a result, the carbon activity at the center of the pellet is substantially higher than at the edge of the pellet and internal coking is predicted (Figure 7A).

To evaluate the effect of thin coatings and the potential for coke formation, the same RWGS microkinetics were applied to a model of a wall coated adiabatic monolith reactor using DETCHEM CHANNEL (Figure 7B). Catalyst thickness varied between 10 and 100 microns, with results presented here for two catalyst thicknesses: 50 and 75 μm. A critical catalyst thickness was identified for the structured catalyst, beyond which the carbon activity inside the wall coating can also exceed unity. Surprisingly, the detailed microkinetic model shows a small methane formation rate (selectivity <2%, Figure 8A) for which the highly exothermic methanation reaction can in some cases achieve a sufficiently high internal catalyst temperature (Figure 8B) to maintain a local carbon activity less than one, overcoming carbon formation in the monolith. An alternative catalyst formulation that suppresses methane formation would not benefit from this extra heat and would be more likely to form coke in the slightly colder catalyst interior. A highly conductive coated catalyst pellet could also overcome the predicted carbon formation.
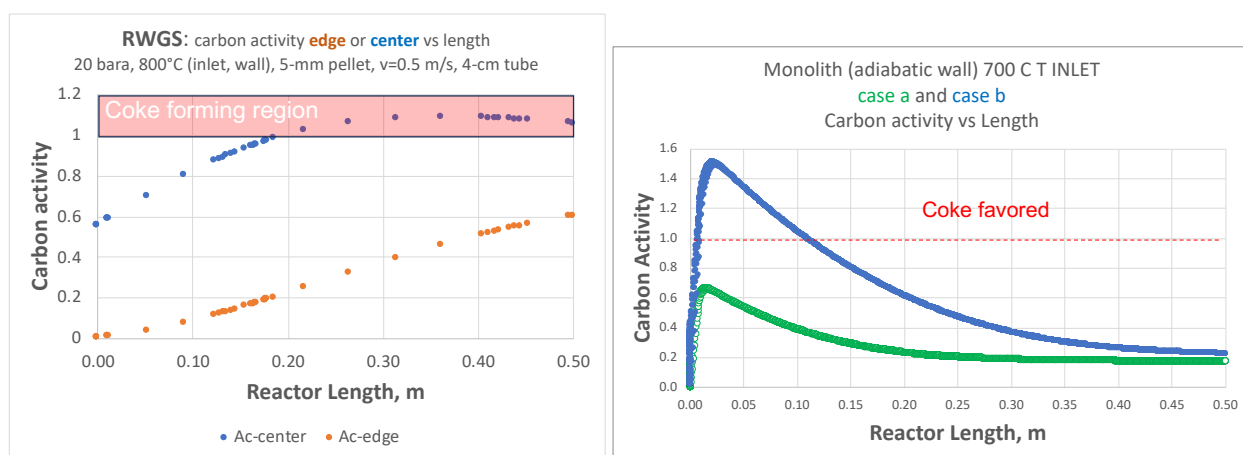
Figures 7A and 7B. DETCHEM PBR predicts coke formation in the interior of catalyst pellets (7A, left), as does DETCHEM CHANNEL for 75 μm thick (case b) coatings (7B, right) in a washcoated monolith. Coke is not predicted, however, for 50 μm thick (case a) washcoated coatings in a monolith.
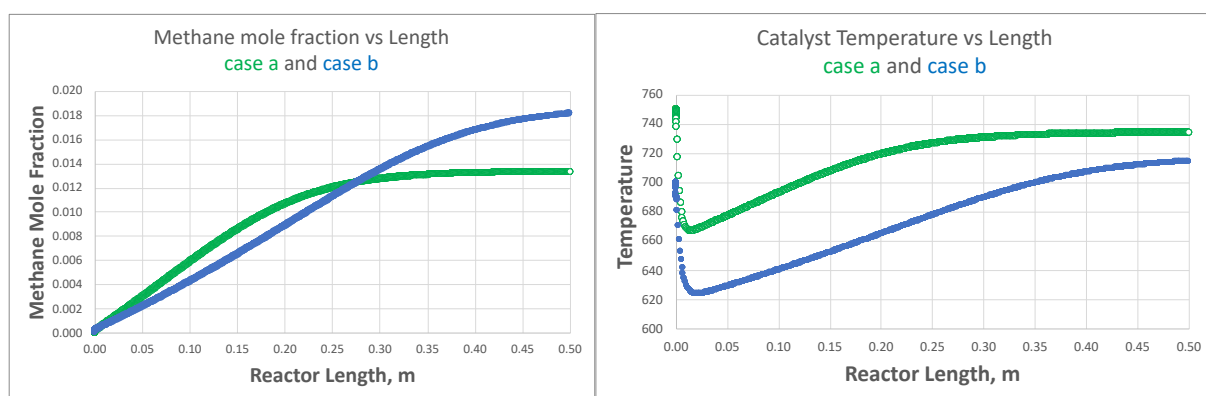
Figures 8A and 8B. With the selected microkinetic mechanism in a monolith configuration, DETCHEM CHANNEL predicts slightly higher methanation in the thinner "case a" catalyst (8A, left), which rases the temperature just enough to aid in the suppression of coke formation (8B, right).

For these cases, direct local temperature measurements are challenging, and the solution to promote a small amount of methanation is only found via simulation. Once again, accessible DETCHEM tools augment development by seeing what is happening inside the catalyst. The secret life of catalysts is no longer hidden, but now understood and problems overcome by changing geometry, operating conditions, thickness, or any other parameter available to the engineer.

Conclusion

The tradeoff of kinetics, pore diffusion, and heat transfer can lead to surprising, counterintuitive, and interesting findings. This secret life of catalysts might be promoting unwanted series or series-parallel reactions that are difficult to understand without supporting reaction engineering tools. In the case of the RWGS catalyst, a small amount of methanation (i.e., an unwanted side reaction) proved to be beneficial. Here, improving a catalyst to reduce methanation could in fact *exacerbate* carbon formation. For a practitioner, experimental observation alone would be challenging to understand why one system failed and the other did not. Development time and cost can be reduced by guiding efforts with useful analysis tools. The use of accessible reaction engineering tools (such as DETCHEM PBR and DETCHEM CHANNEL) speeds development and catalyst optimization, avoids pitfalls of experimentally missing the "sweet spot", reduces scaleup risk, and may solve vexing plant problems.

It is much easier to blame the catalyst for poor performance and move to the next interesting science experiment or accept the industrial expectation that performance deteriorates with scale up. Reaction kinetics are the Rosetta Stone to translate between catalyst geometries and reactor scales. Evaluating catalyst performance with tools that include realistic pore diffusion and reaction coupled with local heat transfer can reveal the true nature of a problem and provide clues on how to find practical solutions.

References

[1] Turing A. The chemical basis of morphogenesis. *Phil. Trans. R. Soc. London* 1952; **237**: 37–72. DOI: https://doi.org/10.1098/rstb.1952.0012
[2] Aris R. The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts: The theory of the steady state. Oxford Clarendon Press; 1975.
[3] Fogler HS. *Elements of Chemical Reaction Engineering*. New Jersey Prentice Hal; 1986.
[4] omegadot software & consulting, GmbH. DETCHEM v3.0 2024. www.omegadot.software . Accessed March 6, 2024.
[5] HeatPath Solutions. https://heatpathsolutions.com . Accessed March 11, 2024.
[6] Delgado KH, Maier L, Tischer S, Zellner A, Stotz H, Deutschmann O. Surface reaction kinetics of steam- and CO_2-reforming as well as oxidation of methane over nickel-based catalysts. *Catalysts* 2015; 5(2): 871-904. DOI: https://doi.org/10.3390/catal5020871del