Technology Offer

Core-shell catalyst design for improved heat management with highly exothermic reactions

File no.: MI1402-5768-LC

Background

Heat management of fixed bed reactors with exothermic reactions is a major challenge for current and future chemical plants. Inadequate heat management can irreversibly destroy the catalyst by sintering or other degradation effects, if a certain temperature is exceeded (e.g. within localized hotspots). However, the most common countermeasures (e.g. feed dilution or fixed-bed dilution) to avoid hotspots in fixed-bed reactors often result in a significant reduction in space-time yield and thus higher process costs.

Especially for discontinuous reactor operation scenarios, a reliable heat management concept is essential to ensure high space-time yields under all possible scenarios. Such scenarios are intensively discussed with regard to Power-to-X processes based on renewable energy sources such as wind and solar.

Technology

Based on the multiscale optimisation of fixed-bed reactors, Prof. Kai Sundmacher and Dr.-Ing. Ronny Zimmermann developed together with co-workers at the Max Planck Institute for the Dynamics of Complex Technical Systems a novel **core-shell catalyst pellet design**. This patented pellet design features a highly active catalyst pellet core surrounded by an inert, low-permeability shell. At low temperatures, the active core mainly determines the reaction rate, while the inert shell has no significant influence, as shown in Fig. 1. At high temperatures, however, the inert shell acts as a mass transport barrier, preventing the reactor from exceeding a certain temperature limit and thus reliably prevents thermal runaways.

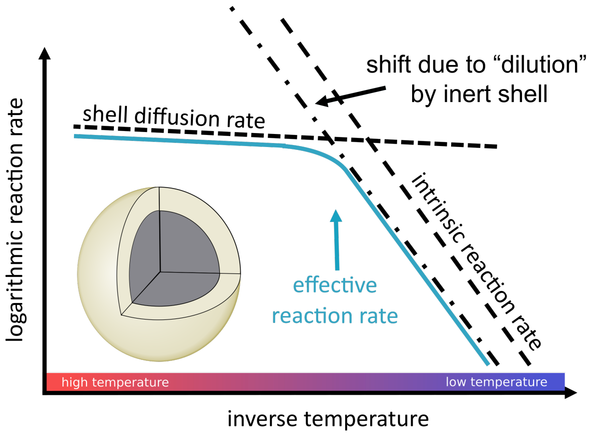

Figure 1: The basic principle of core-shell catalyst pellets (Arrhenius plot): At high temperatures, the mass transport through the inert shell becomes rate-determining, which decreases the effective reaction rate and thus limits hot-spot temperatures and prevents reactor runaways.

Manufacturing Core-Shell Catalysts

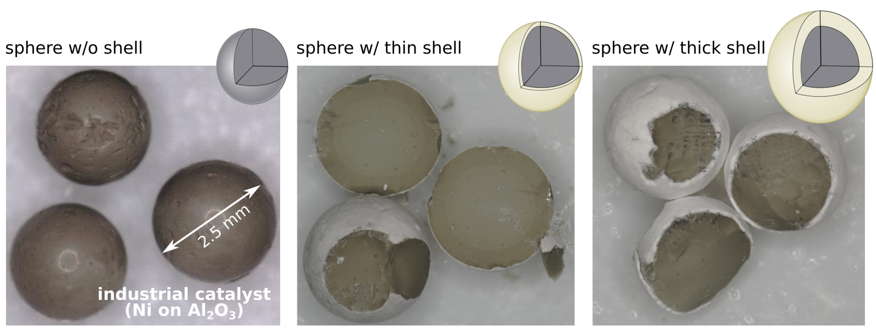

Figure 2: Core-shell catalyst pellet samples produced by fluidized-bed coating.

The core-shell catalyst pellet design **can be produced at low costs and at any scale** using standard coating techniques like fluidized-bed coating. Shell properties such as **porosity, pore size, and shell thickness can be tailored** towards the demands of a given catalyst-reactor system (Fig. 2).

Max-Planck-Innovation GmbH
Arnulfstr. 58
80335 München
www.max-planck-innovation.de

Case Study CO_2 Methanation

Several computational and experimental studies have been conducted to evaluate performance and technical feasibility of the new core-shell catalyst pellet concept [1-5]. CO_2 methanation represents a highly exothermic example case for which **heat management plays a crucial role** for the overall process performance.

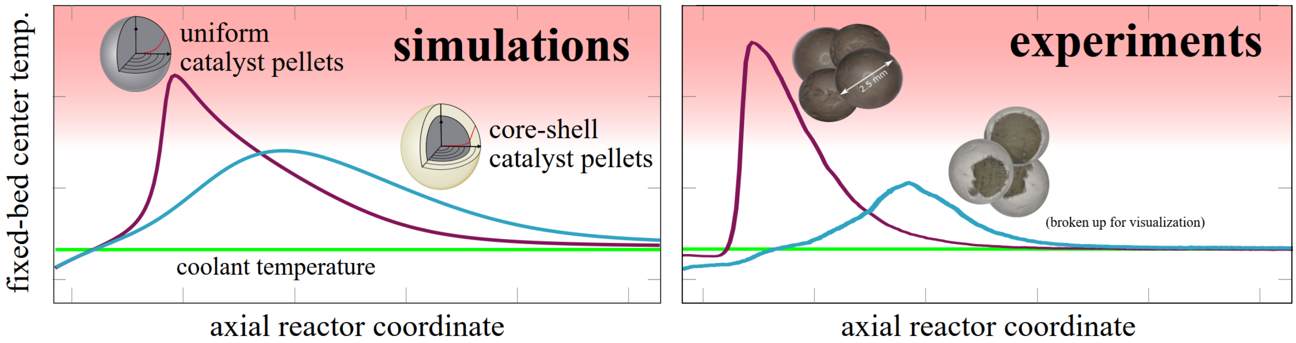

Figure 3: The core-shell catalyst pellet concept applied to CO_2 methanation: Simulation studies (left) and pilot-reactor experiments (right) (tube length: 2 m; tube diameter: 2 cm). In both cases, a significant decrease of the hot-spot temperature is observed.

The temperature profiles obtained from simulations as well as pilot-scale experiments, confirm the significant influence of the shell's **mass transfer limitation at high temperatures**. It **decreases the hot-spot temperature** and results in a well-balanced fixed-bed temperature profile, while simultaneously achieving high methane yields.

In comparison to other state-of-the-art methanation process concepts (using e.g., fixed-bed dilution, recycle compressors, intercooling, distributed feed injection) the novel core-shell catalyst design offers several advantages [2]:

- **Higher space-time-yield:** up to 3x higher compared to fixed-bed dilution
- **Lower pressure loss:** up to 3x lower compared to catalyst dilution
- **CO_2 conversion > 95%** already **after the first reactor stage**
- **Simpler process configuration**: less or no need for recycle compressors, reactor cascades, intercoolers, distributed feed injection
- **Prevents temperatures excursions** causing catalyst deactivation and reliably prevents thermal runaways
- **Reduced thermal sensitivity** with regard to changing operating conditions
- **Increased flexibility:** faster reactor start-up and shut-down and suitable for rapid load changes.

With these features, product qualities as achieved with the widely used TREMP™ technology by Haldor Topsøe (using a recycle compressor and three to four reactor stages with intercooling) also become accessible by the use of a **one-stage multi-tubular fixed-bed reactor** filled with the novel core-shell catalyst pellets. Ultimately, the simpler process configuration will lead to **lower capital and operating costs**, **less downtimes**, as well as significantly **higher load flexibility**.

Max-Planck-Innovation GmbH
Arnulfstr. 58
80335 München
www.max-planck-innovation.de

Further Applications

The novel core-shell catalyst design as a general concept should be also useful for other exothermic processes, e.g., Fischer-Tropsch GTL, sulfuric acid synthesis, methanol synthesis, or ammonia synthesis.

Patent Information

European priority patent application filed in May 2019

PCT patent application filed in May 2020, nationalized in EP, US, CN

EP3972735B1 granted (validated as Unity Patent, CH, GB, ES, IE, NO)

CN114126757B granted, US20220266235A1 under examination

Literature

[1] R. Zimmermann, J. Bremer, K. Sundmacher: "Optimal catalyst particle design for flexible fixed-bed CO_2 methanation reactors", *Chemical Engineering Journal* 387 (2020) 123704

[2] R. Zimmermann, J. Bremer, K. Sundmacher: "Load-flexible fixed-bed reactors by multi-period design optimization", *Chemical Engineering Journal* 428 (2022) 130771

[3] R. Zimmermann, J. Bremer, K. Sundmacher, L. Mörl et al: "Core–shell catalyst pellets for effective reaction heat management", *Chemical Engineering Journal* 457 (2023) 140921

[4] R. Zimmermann, K. Sundmacher: "Core−Shell Catalyst Pellets for Reaction Heat Release Control in Fixed-Bed Reactors", *Ind. Eng. Chem. Res.* 2024, 63, 7556−7564

[5] A. Geschke, R. T. Zimmermann, J., Bremer, K. Sundmacher, Core-Shell Catalyst Pellets for CO_2 Methanation in a Pilot-Scale Fixed-Bed Reactor. *Chemie Ingenieur Technik*. 2024, (in print)

Contact

Dr. Lars Cuypers,
Diplom-Chemiker
Senior Patent- & Lizenzmanager
Telefon: 089 / 29 09 19-21
E-Mail: cuypers@max-planck-innovation.de

Max-Planck-Innovation GmbH
Arnulfstr. 58
80335 München
www.max-planck-innovation.de