Catalysis Engineering - Structuring Catalysts and Reactors for Energy and Atom Efficient Multiphase Operation

Freek Kapteijn, Sina Sartipi, Jorge Gascon, Bart Kaskes, David Vervloet, and J. Ruud van Ommen

Catalysis Engineering, ChemE-Delft University of Technology

f.kapteijn@tudelft.nl

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Many catalytic processes, including recent routes to process renewables, are multiphase operations, comprising mostly a solid catalyst and reactants and products in the gas and liquid phase. Intrinsic reaction kinetics, mass and heat transport processes in the catalyst, GL and LS phase equilibria and reactor hydrodynamics are coupled and determine together the overall process.
Catalyst particle size, pore size and liquid phase determine the diffusion time for molecules to reach the active sites. Hydrodynamics in the reactor control the mass and heat transfer rates between gas and liquid, between liquid and solid catalyst, and with the surroundings. These characteristic transport times should be compatible with the intrinsic catalytic reaction time(s) for an optimal productivity or selectivity. The increasing use of zeolites with strongly restricted diffusion poses even larger challenges.
Various multiphase reactor types are being used, with the slurry bubble column reactor and the trickle bed reactor as the two extremes of the most common operations. In these systems the reaction steps and transport phenomena are strongly coupled. Alteration of one step in a process to improve it affects the other. In an ideal situation one would like to optimize each step in the process independently of the other.

Structured reactors and catalysts

Structured reactor

Structured catalysts and reactors offer high precision in catalysis at all relevant scales of the catalytic process, from that of the catalytic species up to that of the reactor [1,2]. As illustration and classical example, the highly exothermal Fischer-Tropsch synthesis is used. The application of cross-flow structures improves by convection the overall heat transfer of the reactor [3-6], allowing higher operating temperatures or larger reactor diameters without compromising the product slate. Considering mass transport in catalyst particles. the syngas H_2/CO feed ratio should be ~1, much lower than the stoichiometric ratio in order to compensate for the differences in diffusivities, while optimizing the space time yield of C5+ products [7]. This optimal feed ratio is more in-line with that present in syngas derived from biomass, while still being compatible with a high CO selectivity.

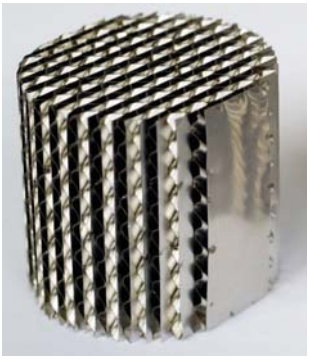

Figure 1. A Closed Cross Flow Structure (CCFS) packing element consists of a stack of corrugated and flat sheets.

Putting all elements together, an optimization of the FTS reactor operation will be presented. Using a closed-cross flow structure (CCFS) packed with catalyst particles [8] a considerable improvement of reactor performance (C5+ space time yield) compared to the base case (random packed bed) can be reached for highly active catalysts [9].

Structured catalysts

The supply of biomass is generally limited and often subject to campaigns in agriculture, so small-scale transportable units are desired for BTL operations. This is also the case for locations where a small physical footprint is required (e.g. oil rigs). With a target of direct liquid (fuel) production, a simple one-step process can be reached with a bifunctional catalyst containing both an FTS functionality and a hydrocracking/isomerization function. The closer these functions are in proximity, the better the performance. Cobalt supported on mesoporous ZSM-5 turned out to be the optimal bifunctional catalyst where the C20+ fraction is nearly completely absent [10-13].

Another bifunctional system, combining catalysis with shape selective membrane separation, namely silicalite-1 coated H-ZSM-5, yields a highly selective production of *p*-xylene in the alkylation of toluene with methanol, eliminating the need of further energy intensive separation of xylene isomers [14,15].

Conclusions

Structuring of catalysts and reactors from the nm to the m scale allows decoupling the scale-dependent and independent phenomena that play a role in multiphase catalytic processes. Following this approach allows optimizing and fine-tuning the reactor operation. This is illustrated for the classical FTS process where a considerable productivity improvement is predicted. The use of bifunctional catalysts further extends the application scope of this approach and may contribute to more sustainable developments. Advances in materials science for the controlled manufacture of such structured systems are crucial.

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