Perspectives on Engineered Catalyst Design and Forming

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Run of Show

Defining the Catalyst

An FCC Case Study

Considerations for Technology Selection & Modeling

An Industrial Perspective

Engineered Catalyst Development in ChemCatBio
An engineered catalyst is a multicomponent catalyst formulation that possesses additives and structural elements required for operation in a commercial reactor

- Physical: mass/heat transfer
- Chemical: functionality
- Mechanical: strength, attrition resistance

• Simplified requirements for commercialization upon successful identification of promising research catalyst candidates
  - Translation of synthesis methods from bench-scale to multi-ton manufacture
  - Identification of appropriate formulation (left)
  - Powder shaping to macroscopic forms

Catalytic Cracking: The Modern FCC (up to 200 kbdp)
A Technology Race

1933
Houdry Process
- Fixed bed reactors
- Swing regeneration
- Pelleted clay catalyst

1941
Thermofor Cat Cracking (TCC)
- Moving bed reactor
- Continuous flow of catalyst via bucket elevators
- Pelleted SiAl catalyst

1942
Fluid Cat Cracking (FCC)
- CRA consortium
- Fluidizable catalyst particles (~100 um)
  - Crushed catalyst
- 1946: Spray drying
- 1960: Zeolites
- Today: ~400 units WW, > 10 Mbpd

Co-development of process and catalyst
FCC Catalyst Market (~$3 B) Requires Large Spraydryers
The FCC Catalyst: A Complex Design Challenge

Non-spherical particles WILL BECOME SPHERICAL in the unit: FINES LOSSES, STACK OPACITY, etc

New FCC catalysts can require lots of spray drying R&D to achieve physical property targets at commercial scale


Charlesworth and Marshall, AIChE J. 6 (1) 1960
**FCC Catalyst Architecture: Heavily Researched**

**Fig. 23** X-ray nanotomography study of an E-cat catalyst particle, revealing the relative spatial distributions of Ni and Fe and their effect on the macropore structure and accessibility. A sub-volume of $16.6 \times 16.6 \times 10 \, \mu m^3$ was selected (b) out of the entire catalyst particle of $44.8 \times 52.7 \times 51.2 \, \mu m^2$ in size (a), including the relative Fe and Ni distributions. Permeability calculation was applied on this sub-volume (c). Mass transport through the sub-volume along the selected axis (red arrow) is visualized using the velocity field of the fluid. The streamlines indicate the magnitude of the velocity field where red represents the highest velocity (i.e., where the pore space constriction is the largest) and blue indicates the lowest velocity. (Reproduced with permission from ref. 170, Copyright American Chemical Society, 2015).

**Fig. 24** (a) Single slice of the X-ray micro-tomogram of E-cat particles inside a polyimide tube, which is the circle around the image. The E-cat catalyst particles have a range of shapes and sizes, and some are hollow. Some of them are indicated by the red circles in the image; (b and c) 2D transmission X-ray microtomography images of sections of two E-cat particles showing different sizes of internal voids, which are the dark colored regions in the images; and (d) equivalent diameter of internal voids in the set of E-cat catalyst particles as investigated with X-ray micro-tomography. (Reproduced with permission from ref. 172, Copyright Wiley-VCH, 2014).

Important Considerations for Technology Selection

• Fluid-solid hydrodynamics
  - Set by reactor type (fixed bed, moving bed, fluid bed, riser)

• Intrapellet mass transfer constraints
  - A relative term! Fast vs slow reactions
    - Ratio of diffusion & reaction rates and the Effectiveness Factor
    - Fast example: cracking at high temperature → FCC catalyst @ SCT
    - Slow example: resid HDS, WHSV ~ 0.5

• Deactivation rate and regeneration requirements
  - Is the reaction endothermic and powered by coke burn, like FCC?

• Thermal considerations
  - Heat integration
  - Intrapellet heat transfer for highly endothermic/exothermic reactions
  - Frequency and severity of coke oxidation regenerations
  - Fast/large temperature swings (like FCC process)
Fluid-Solid Hydrodynamics: $\Delta P$ and $U/U_{mf}$

- **Wen-Yu equation**
- **Ergun equation**

- **Risers**
- **Bubbling Beds**

**Graphs**
- Ambient $N_2$, ABD 760 kg/m$^3$, $\rho_{\text{part}}$ 1260 kg/m$^3$
- $SED = \text{Spherical Equivalent Diameter}$
For complex reaction networks, analytical expressions become intractable, in which case combined pellet-reactor modeling can step in!
The Consortium for Computational Physics and Chemistry (CCPC) is a Bioenergy Technologies Office (BETO) consortium composed of six national labs applying multi-scale computational science to enable and accelerate the bioenergy economy.
CCPC DFO Program 2021-2022
(Direct Funding Opportunity)

Packed bed deployment
Pyran: 1,5 PDO from furfural
Catalyxx: higher alcohols from EtOH (Guerbet)
Integrated Computational/Experimental Approach

**Intrinsic Kinetics**
- Crushed (powder) catalyst
  - Isothermal
  - Gradientless
  - Low conversion

**FF Effects**
- Single (or few) pellet with small gradients

**Bed HT Effects**
- Bed HT tests

**Reactor Effects**
- Prepilot reactor (~100 g catalyst)

**Experiment**
- Forming + Formulating
  - Catalyst mesoscale model
  - Bed HT model
  - Prepilot reactor scale model
Characterization of a modular Temkin reactor with experiments and computational fluid dynamics simulations

Gregor D. Wehinger\textsuperscript{a,}\textsuperscript{*}, Bjarne Kreitz\textsuperscript{a}, Anton Nagy\textsuperscript{b}, Thomas Turek\textsuperscript{a}

A small, well-mixed reactor for high throughput study of commercial catalyst pills

Edward M. Calverley\textsuperscript{a,}\textsuperscript{b}, Edward L. Lee\textsuperscript{b}, De-Wei Yin\textsuperscript{b}, Thomas J. Parsons\textsuperscript{c}

Chemical Engineering Science 151 (2016) 130–138

Heat transfer characteristics of mixed convection in packed beds

Yuelong Qu\textsuperscript{a,b}, Liang Wang\textsuperscript{a,b,c}, Xipeng Lin\textsuperscript{a,c}, Haoshu Ling\textsuperscript{a,c}, Yakai Bai\textsuperscript{a,c}, Shuang Zhang\textsuperscript{a,c}, Haisheng Chen\textsuperscript{a,b,c,}\textsuperscript{*}
Engineered Catalysts: Considering Shape, Size, and Processing

Composition is Crucial, But Far From the Only Concern

Catalyst Composition

What is in the catalyst (elemental composition)

How it is put together
- Mixing, impregnation, precipitation, etc
- Additives, lubricants, burn-outs, etc
- Forming, shaping, sizing
- Thermal treatments (calcination)

How it is utilized
- reactor type
- reactor scale, dimensions, etc
- temperature, pressure, WHSV
- feed, poisons, etc
- disruptions or runaway potential
- pressure drop (DP, ΔP...)

Catalyst Processing History

Reactor Process Conditions
Considering Catalyst Form Factors

1. Reactor scale
   • Catalyst loading: need for efficient packing, mechanical strength to prevent attrition
   • Pressure drop: need for uniform flow, avoidance of “hot spots”, reduced energy consumption
   • Thermal profile: endo vs exo thermic processes, heat management, thermal conductivity

2. Reactor type
   • Fixed bed, fluidized bed, moving bed: can dictate shape, size, & mechanical property needs

3. Phases of matter present
   • Single or multiphase systems: feed, intermediates, products
   • Traditionally, gas phase is most common, but not necessarily for newer trends & technologies

4. Practicality & existing deployed capital assets
   • Economic viability or production
   • Scale & throughput
Clariant Catalysts: Covering a Wide Range of Applications

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<th>REFINERY / FUELS</th>
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CUSTOM CATALYSTS tailor-made for specified applications
Clariant Catalysts: Covering a Wide Range of Applications

- Dehydrogenation
- Emission Control, Oxidation & Zeolites
- Ethylene & Derivatives
- Styrene & MTP
- Fuels
- Hydrogenation & Custom Catalysts
- Polypropylene
- SynChem
Examples: De-NO\textsubscript{x} SCR Using a Wash-Coated Monolith

- Fixed bed
- High WHSV
- No recycle

- Honeycomb is extruded & calcined
- Active metals are wash-coated
Examples: Vanadium Phosphates for Maleic Anhydride Production

**TECHNICAL SPECIFICATIONS**

**SYNDANE® 3102 LA**
Small catalyst rings for short reactor tubes

**SYNDANE® 3122 LA**
Bigger catalyst rings suitable for wide range of process conditions

**SYNDANE® 3142 LA**
Proprietary catalyst shape for long reactor tubes with low pressure drop

**COMPOSITION SYNDANE® LA SERIES**
- Vanadium phosphorus mixed oxide
- Vanadium content > 27 wt %
- Pre-activated
- Specific promoters to decrease by-product formation
- Thermal stability up to approx. 500°C

- Fixed bed
- Thousands of small reactor tubes
- Sensitive to WHSV
- Critical need for thermal management

➢ Shaped catalyst is extruded & calcined
➢ Specific shape is dictated by reactor
Examples: $\text{CrO}_x/\text{Al}_2\text{O}_3$ Dehydrogenation Catalyst

- Fixed bed
- Large single train reactors
- >10,000 tons produced/yr
- >4 year catalyst operating life

- $\text{Al}_2\text{O}_3$ carrier is produced by multi-step process
  - Forming, extruding calcining & steaming are critical
  - Texture required

- Active components impregnated, but carrier physical properties are key to long-term stability & performance
The Challenge: A technical catalyst must faithfully **reproduce the performance** of laboratory preparations and possess the required physical properties **for large scale operation**.

Developing a technical catalyst from benchtop candidates requires **at a minimum**:
- Gram-to-kilo **protocol adaptation**
- Determination of **multi-component formulation**
- **Shaping powders** into reactor specific macroscopic forms

Translation of promising research catalysts to viable technical bodies is a non-trivial research challenge.
Establish Industrial Advisory Board

Identify Catalyst Targets

Phyisco-Chemical Requirements

Industrial Expert Input and Review

Equipment Selection

Assessment of Best Practices

Methods Development & Review

Produce 1st–Gen. Eng. Catalyst

Near-term targets identified within Conversion
Pt/TiO$_2$ (*Catalytic Upgrading of Pyrolysis Products*)

Cu-HBEA (*C1 Building Blocks*)

- Process and reactor configuration dictate form and required performance characteristics
- Forming technologies reviewed with advisory board to ensure industrial relevance, feasibility, and equipment requirements
- Academic and patent literature surveyed for best practices
- Develop processing methods with industrial guidance
- Produce baseline technical catalyst at targeted scale
De-risks conversion technologies

- Enables projects to assess performance at increasing scales
- Go/No-Go decision points ensure performance targets are met at each scale
- Provides a baseline engineered catalyst to accelerate commercialization when licensed to technology provider
Equipment Selection

**Process Requirements**
(1 – 10 kg)

- Dry Mixing
- Wet Mixing
- Extrusion
- Drying
- Calcination
- Tumbling
- Impregnation

- High shear / Orbital Mixers
- 1” Screw Extruder
- Bucket/Cement Mixers
- Rotary and Muffle Furnaces
Equipment Selection

**Commissioned 1–10 kg scale catalyst manufacturing equipment**

*Dedicated in-house equipment* for inert processing, thermal treatment, precipitation, physical forming

*Ability to optimize* translation from research catalyst to engineered catalyst

*Transferable knowledge* for more rapid and simplified contract manufacturing at relevant scales
Pipeline for Emerging Methodologies

Flame-spray pyrolysis (FSP) for tunable Pt speciation

- Industrially deployed at MT/y scale
- One-step synthesis of active phase and support
- Tunable product slate in whole biomass pyrolysis vapor upgrading
CCB Summary

Developed a flexible, engineering-scale catalyst synthesis capability to produce scalable and cost effective next-generation biomass conversion catalysts and mitigate commercialization risk by enabling large-scale performance evaluation.

- **An industry guided** engineering-scale catalyst synthesis capability can significantly reduce the economic investment and time required to verify large-scale performance.

- **Responsive engineering-scale catalyst design** enables the fundamental evaluation of technical catalyst properties and performance.

- **Emerging scale-up methodologies** provide an opportunity for scalable performance enhancement over traditional methods.
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Thank You

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