Micro-Structured Monolithic-Catalyst Bed as Compact and High Throughput Reactor System for Conversion of Syngas to Liquid Fuels

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Presentation at Technical Session of Syngas Production and Gas-to-Liquids

AIChE Annual Meeting

Nov. 11th, 2010

Salt Lake City, UT

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Acknowledgment

- Colleague at Pacific Northwest National Lab

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- This work was supported under laboratory-directed research and development (LDRD) program of PNNL by Energy Conversion Initiative and Energy & Environmental Directorate.

- Pacific Northwest National Laboratory (PNNL) is operated by Battelle for the Department of Energy.

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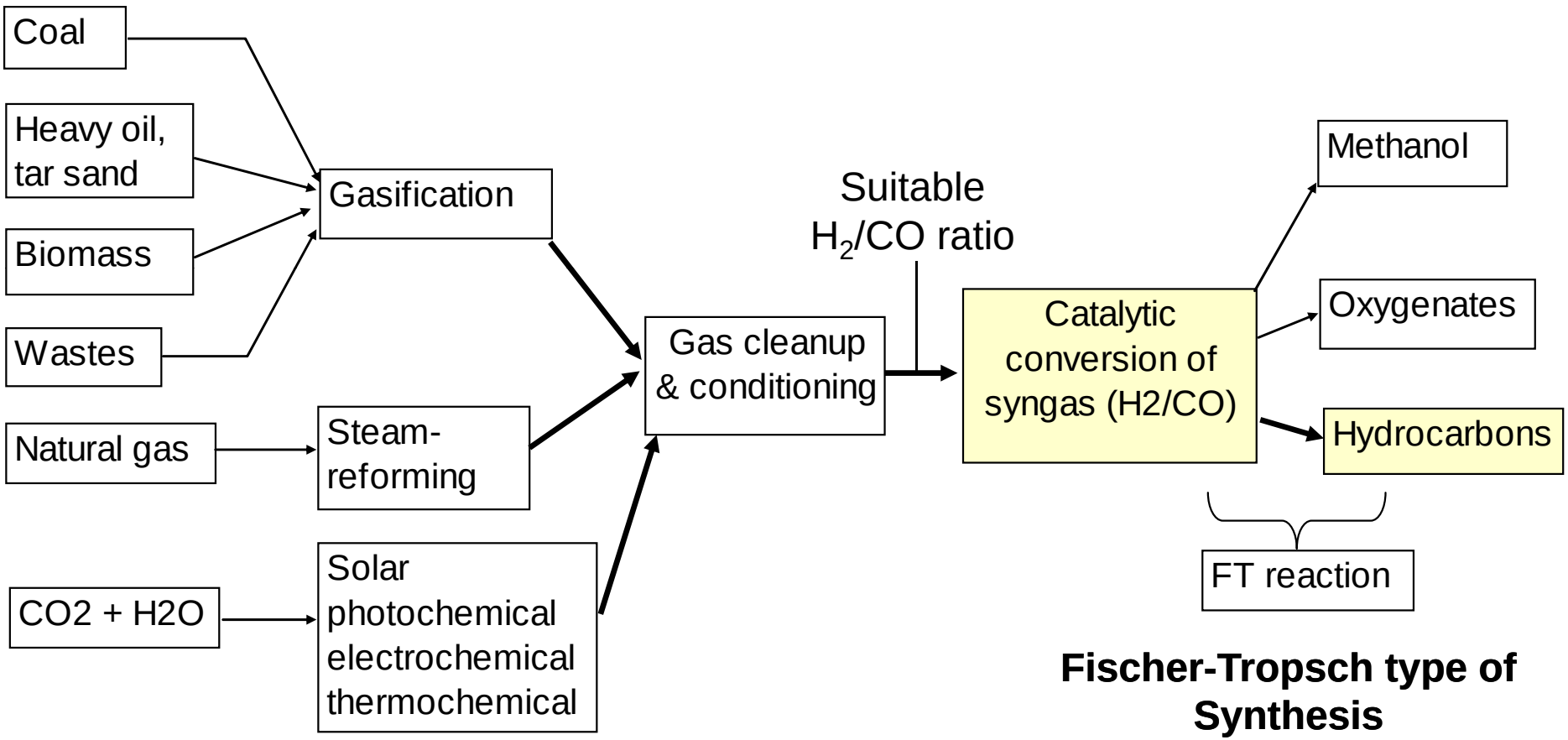
Syngas Conversion Critical to Production of Chemicals or Liquid Fuels from Various Carbon Sources



Fischer-Tropsch type of Synthesis

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Catalysis chemistries studied extensively

Highly exothermic and complex reaction paths

Main reaction:
(ΔH ~ -10 MJ/kg-product)

$$CO(g) + 2H_2(g) \rightarrow H_2O + CH_2^*$$

Chain growth

$$C_nH_{2n+2}(paraffin)$$

$+H_2$

$$C_nH_{2n}(olefin)$$

Coke

Side reaction:

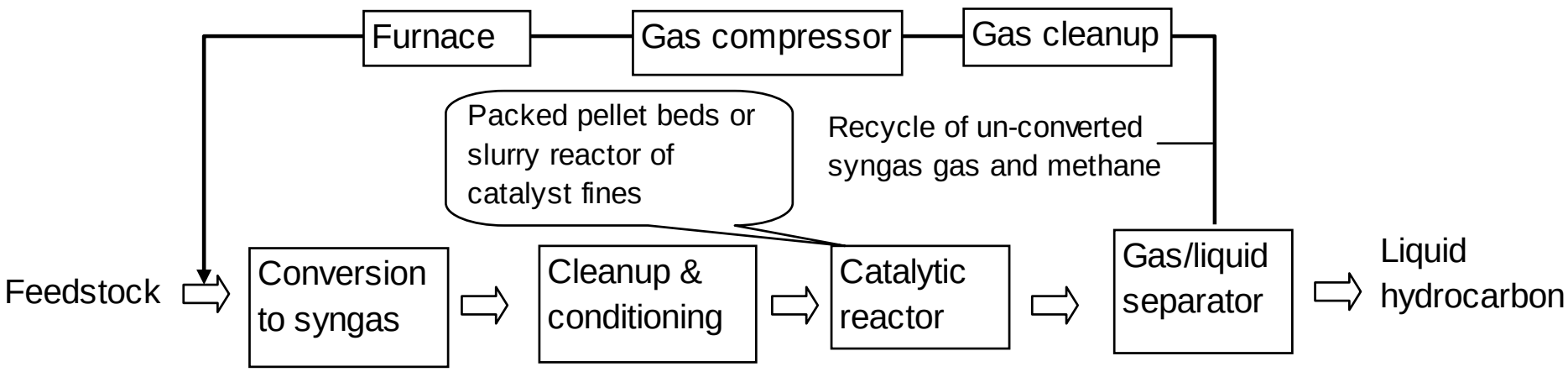
$$CO(g) + 3H_2(g) \rightarrow H_2O + CH_4$$

$$CO(g) + H_2O(g) \rightarrow H_2 + CO_2$$

- **Co-based catalysts for fixed beds**
- **Fe-based catalysts for slurry beds**

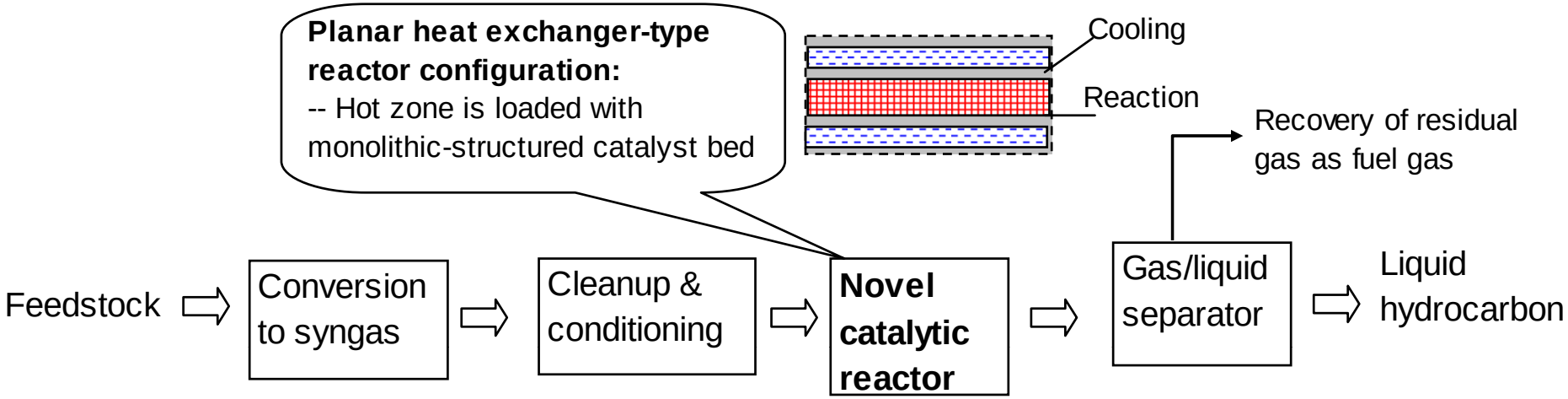
Step-out reactor needed to overcome "scale-economy" barrier for distributed gas-to-liquid conversion

- Current FT reactor commercialized for large-scale, integrated plants. Cost-prohibitive when processing capacities are one or two orders of magnitude smaller than refineries or petrochemical complexes.
- Most today's needs of gas-to-liquid conversion are like distributed production at small capacity scales, coal gasification, biomass gasification, remote natural gases, solid wastes, other renewable energy sources.



Major portion of capital and operation costs is associated with the gas recycle system, beyond the reactor itself

Present objective: compact, high-throughput, modular reactor unit



- Achieve nearly complete syngas conversion at one pass to dramatically simplify process flow diagram, and thus, capital and operation costs

Limitations of conventional reactors (packed or slurry beds):

- CH_4 selectivity is too high at deep CO conversion
- Hydrodynamics, such as back mixing
- Catalyst deactivation

A holistic approach toward catalyst & reactor design

Li & Kwauk "Exploring complex systems in chemical engineering – the multi-scale methodology". *Chem. Eng. Sci.* 58 (2003) 521-535, a powerful approach to all catalytic reactor systems.

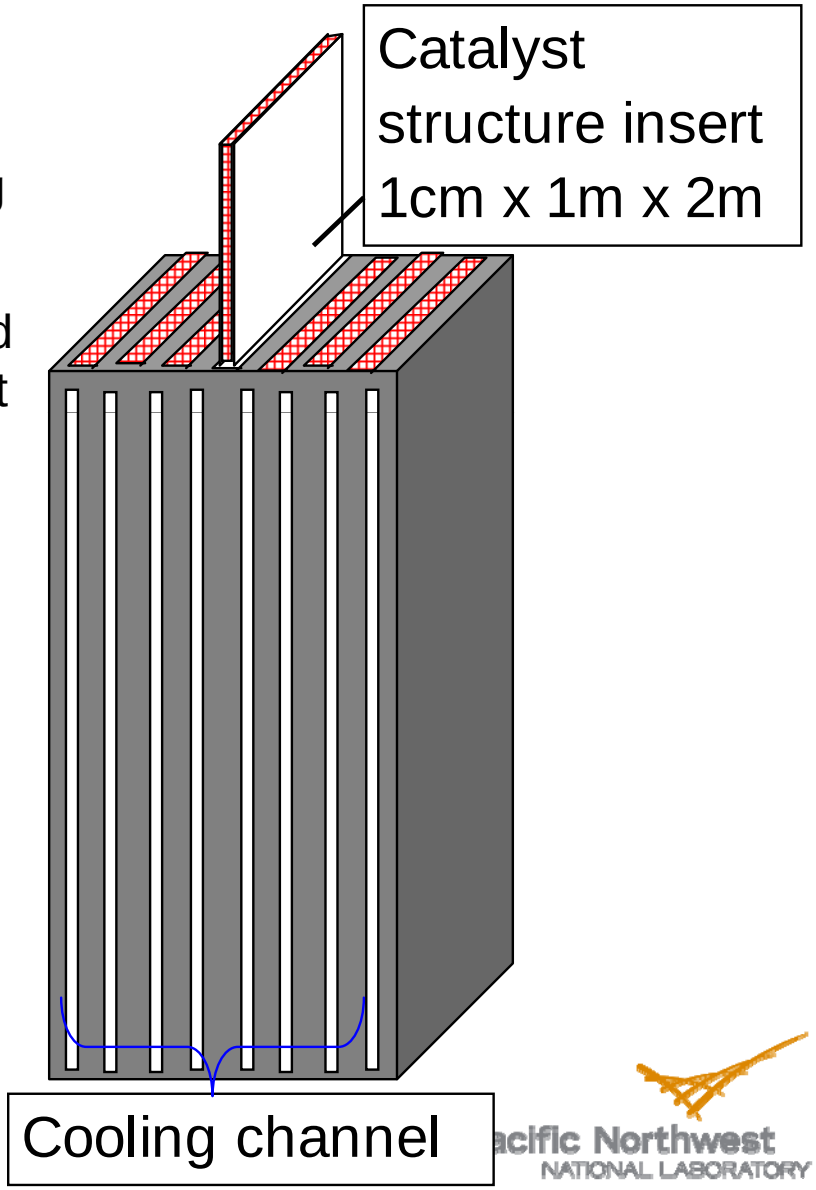
Address mass and heat transfer at

- Reactor scale
- Scale of individual reaction unit
- Catalyst structure scale

Reactor-scale design to address heat management at macro-scale

Planar, heat-exchanger-type design:

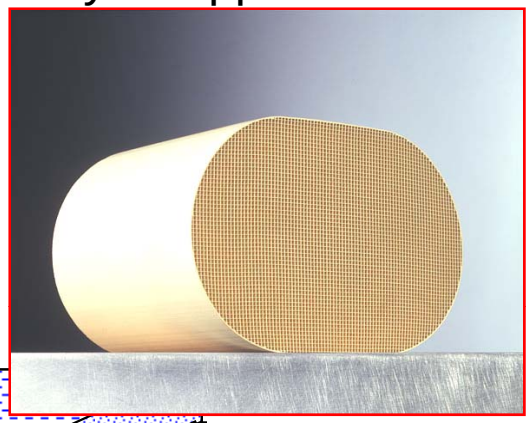
- Take away reaction heat by adjacent cooling streams
- Control temperature profiles by feed gas and cooling fluid distribution, flow rates, and heat exchanging area
- Utilize existing reactor fabrication technologies
- Scale up by numbering up reactor modules

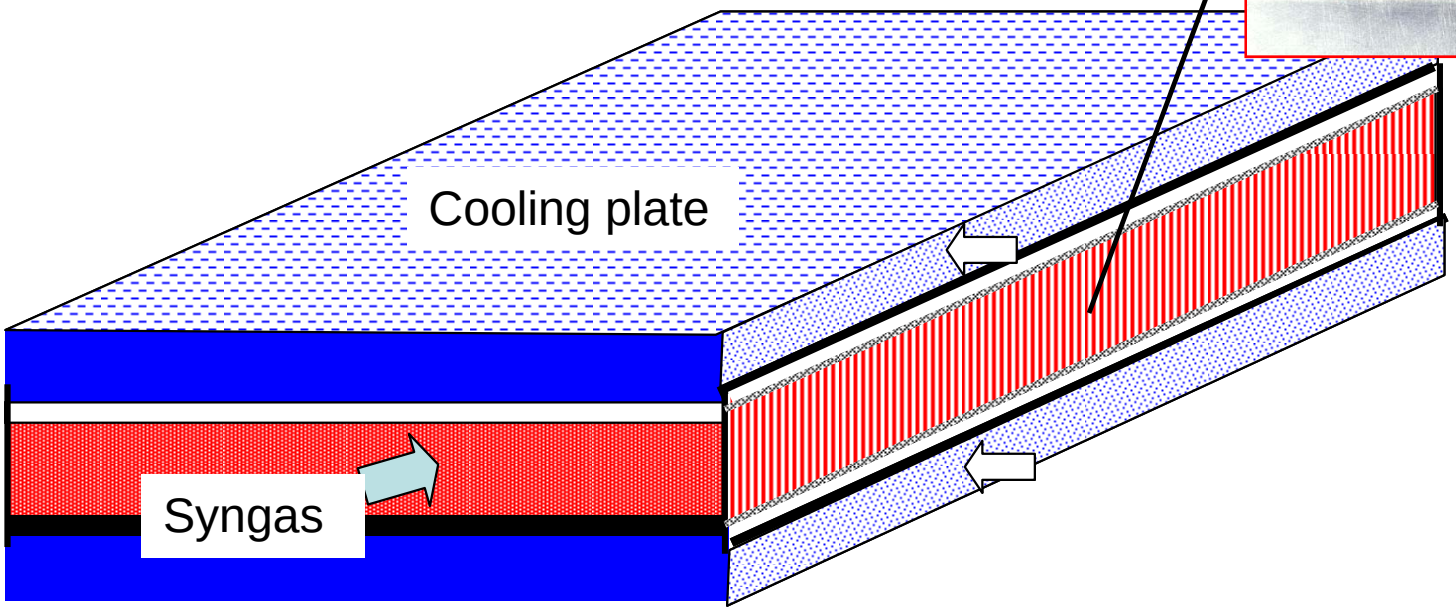


Micro-structured catalyst bed to address heat and mass transport at scale of individual reaction zone

- Structured catalyst bed comprises catalyst coatings on a continuous inert support.
- Support matrix provides 3-D thermal conduction network for rapid heat transfer from catalyst surfaces to the heat exchanging interface.

Ceramic honeycomb as catalyst support structures





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Catalyst channel-scale design to addresses gas/liquid/catalyst mass transport at reaction points

Bulk fluid

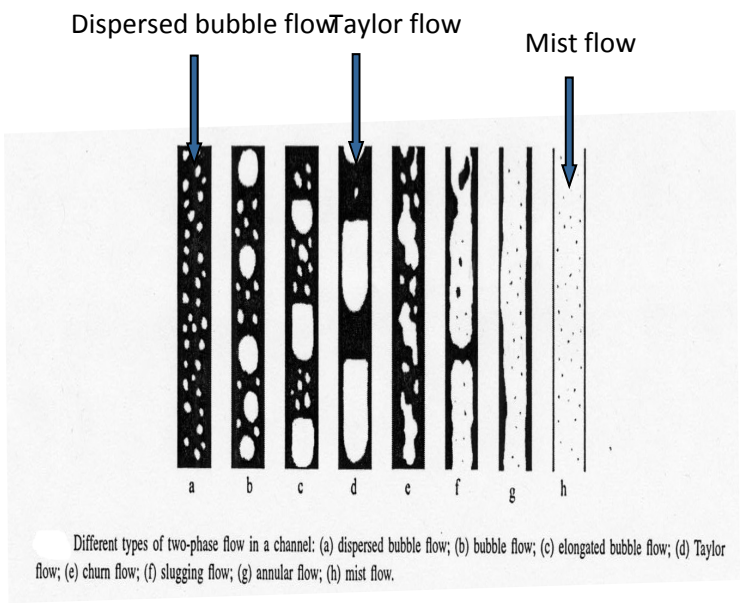
H_2 (g)
CO (g)

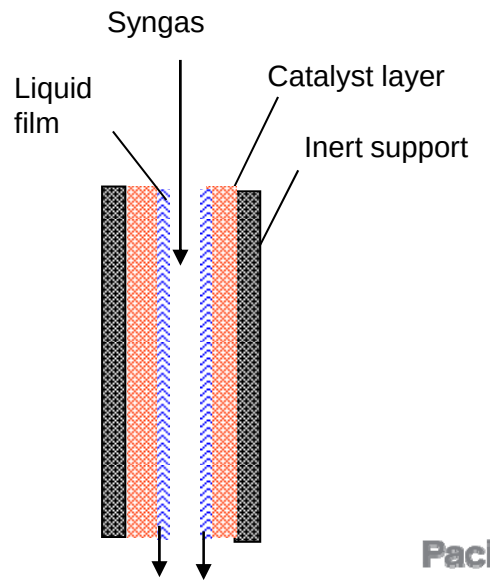
I ⇨ Channel surface ⇨ II ⇨ External surface of catalyst coating ⇨ III ⇨ Catalyst pore ⇨ IV ⇨ H_2O Oil CH_4 Catalyst surface

H_2O
Oil
CH4

Steps I & II can be controlled by channel geometries (size, shape) and flow conditions (Ul, Ug)

Steps III &IV can be optimized by thickness and pore structures of the catalyst coating layer





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Experimental testing of key design principles

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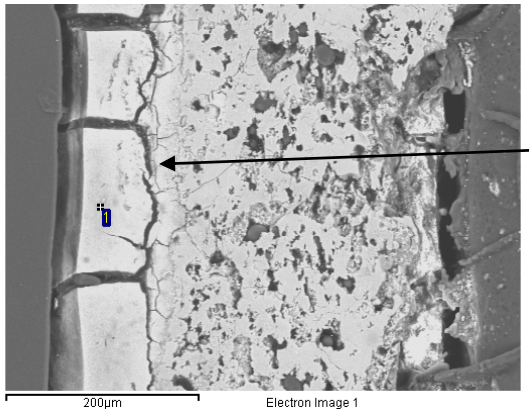
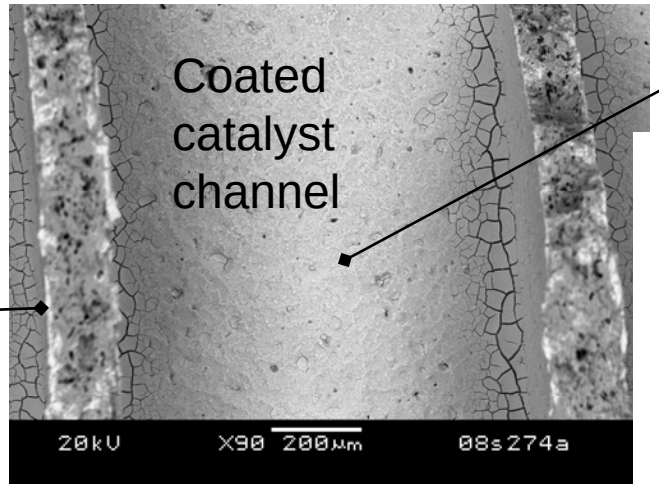
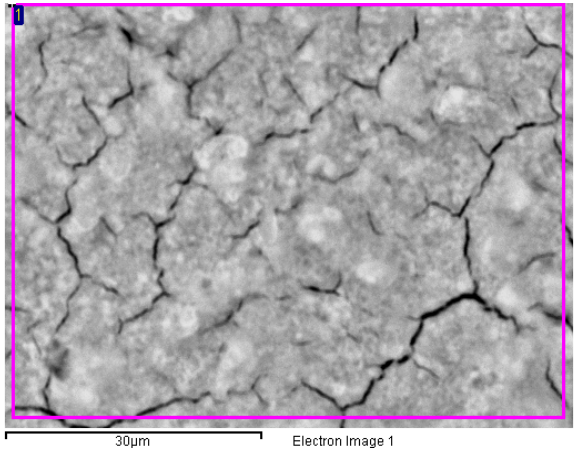
FT catalyst coating on ceramic monolith substrate of 1mm channel size

Cross-sectional view of coating



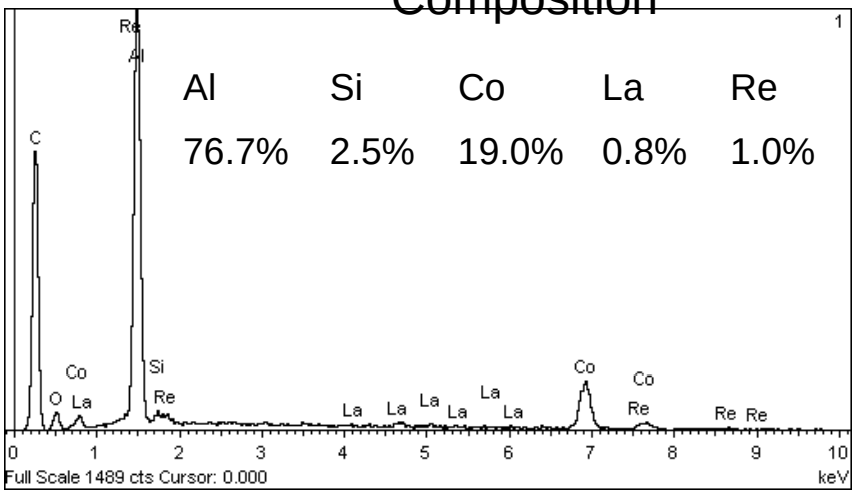


Coating texture of channel surface



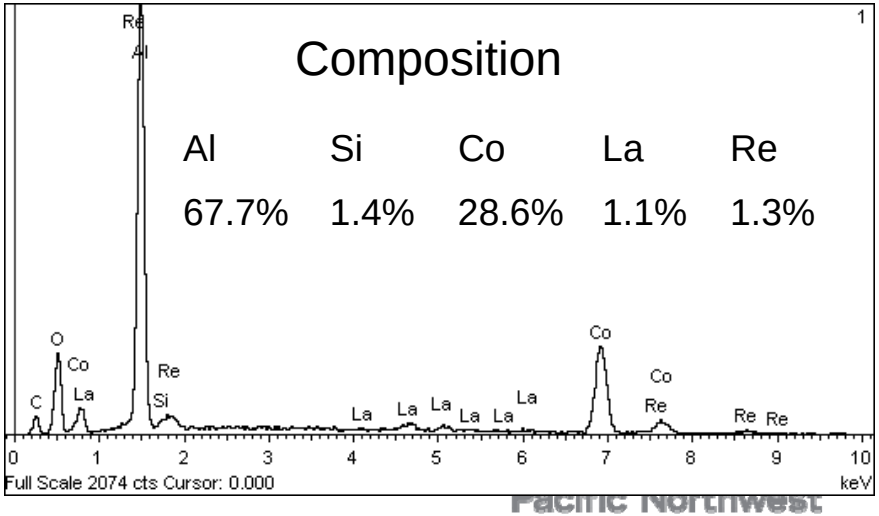
Composition

Al	Si	Co	La	Re
76.7%	2.5%	19.0%	0.8%	1.0%



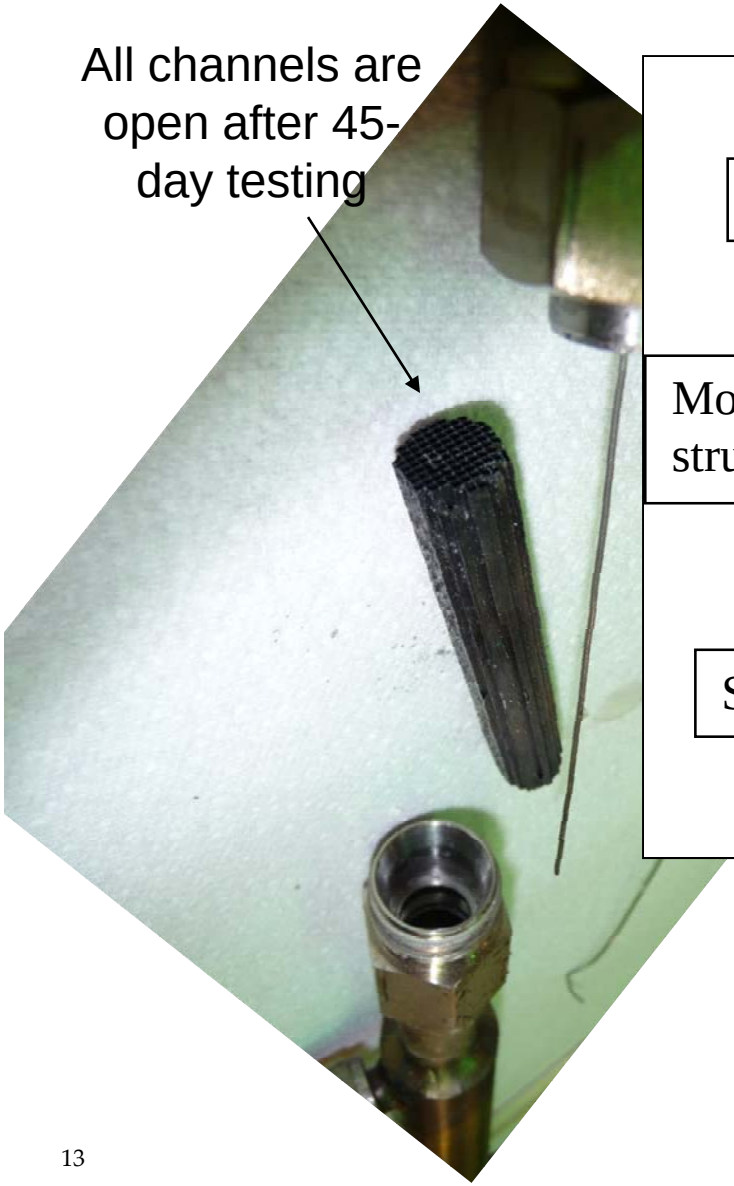
Composition

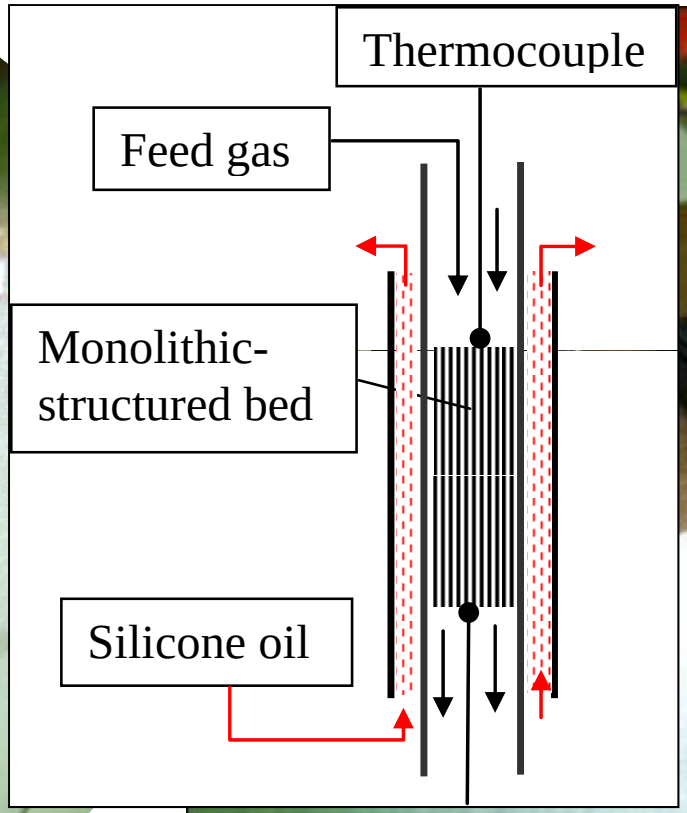
Al	Si	Co	La	Re
67.7%	1.4%	28.6%	1.1%	1.3%

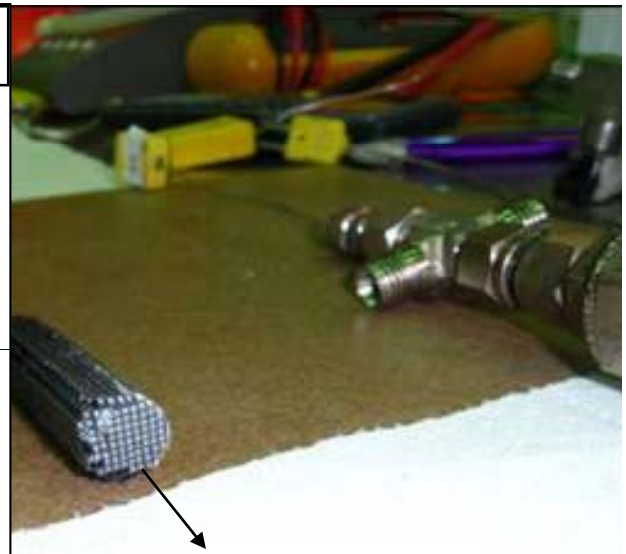


Reaction testing in a ½″ OD stainless steel tube sheathed with silicone oil heat-exchanging fluid

All channels are open after 45-day testing







- After reaction was quenched, existence of wax was found in all channels on bottom of the bed

→Suggest uniform reaction among all channels

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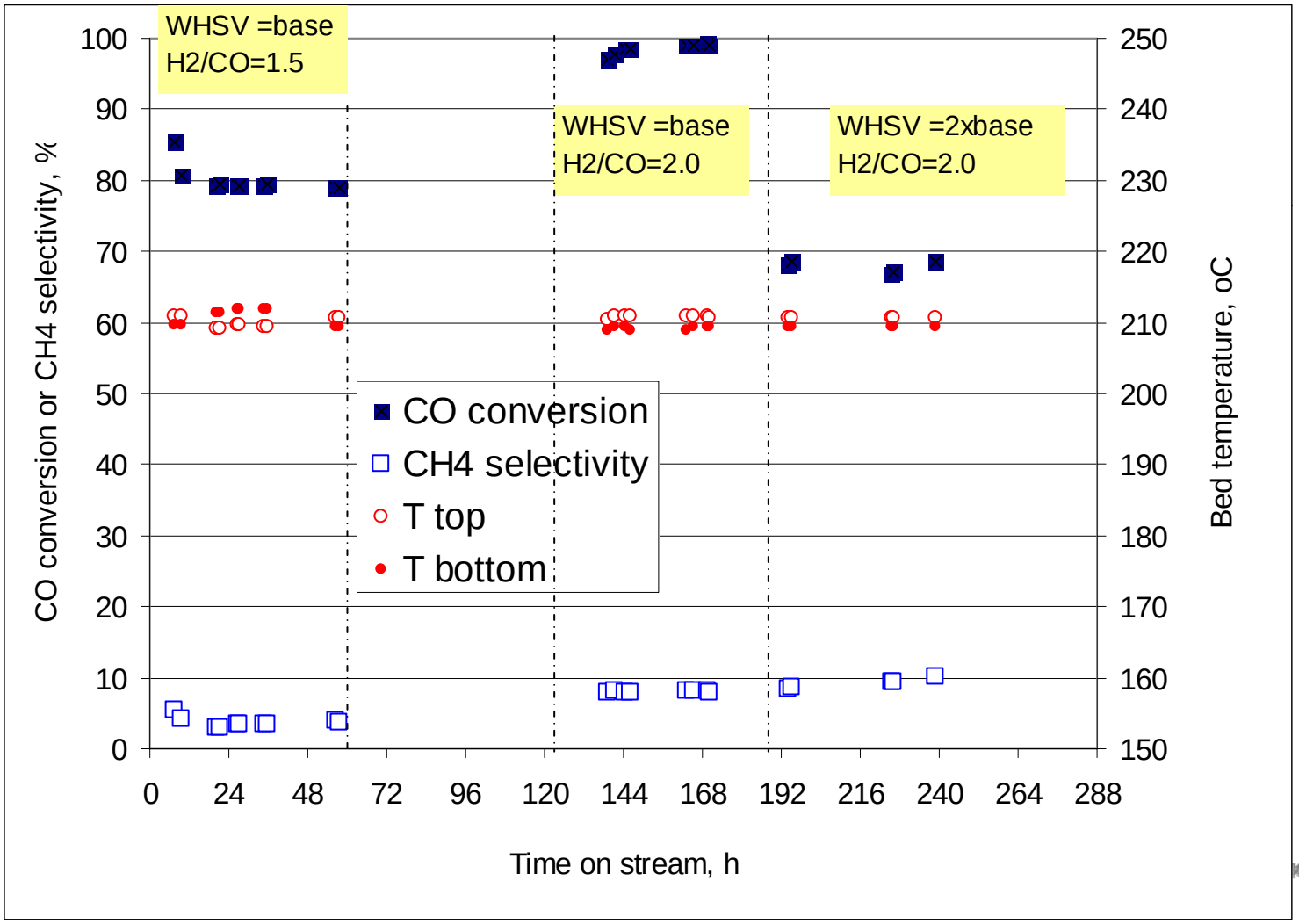
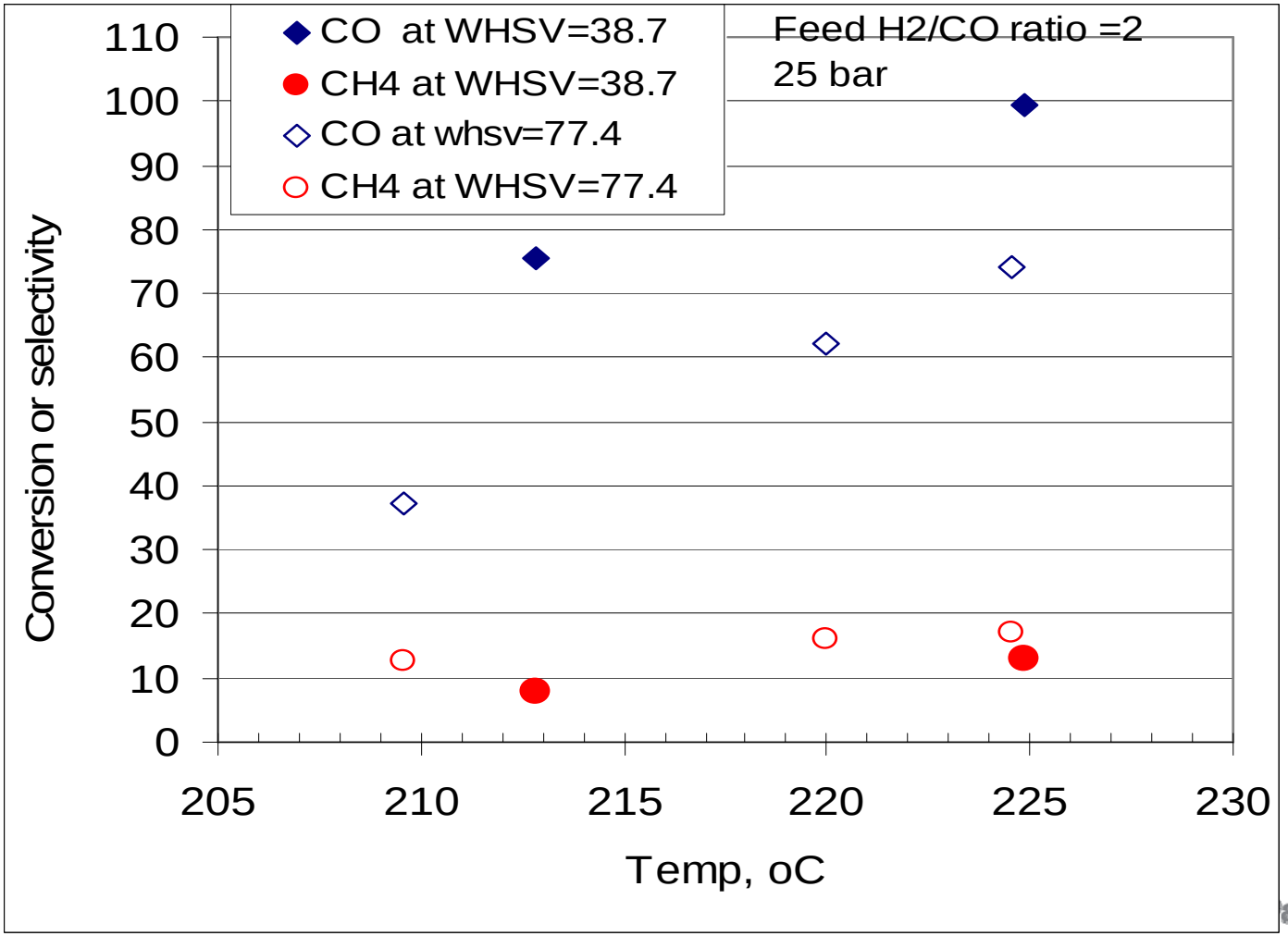
Steady-state performance of monolithic-structured catalyst bed (25 bar, 210°C)

- Nearly complete H_2 or CO conversion at base WHSV at CH_4 selectivity <10 wt%. Stable temperature control



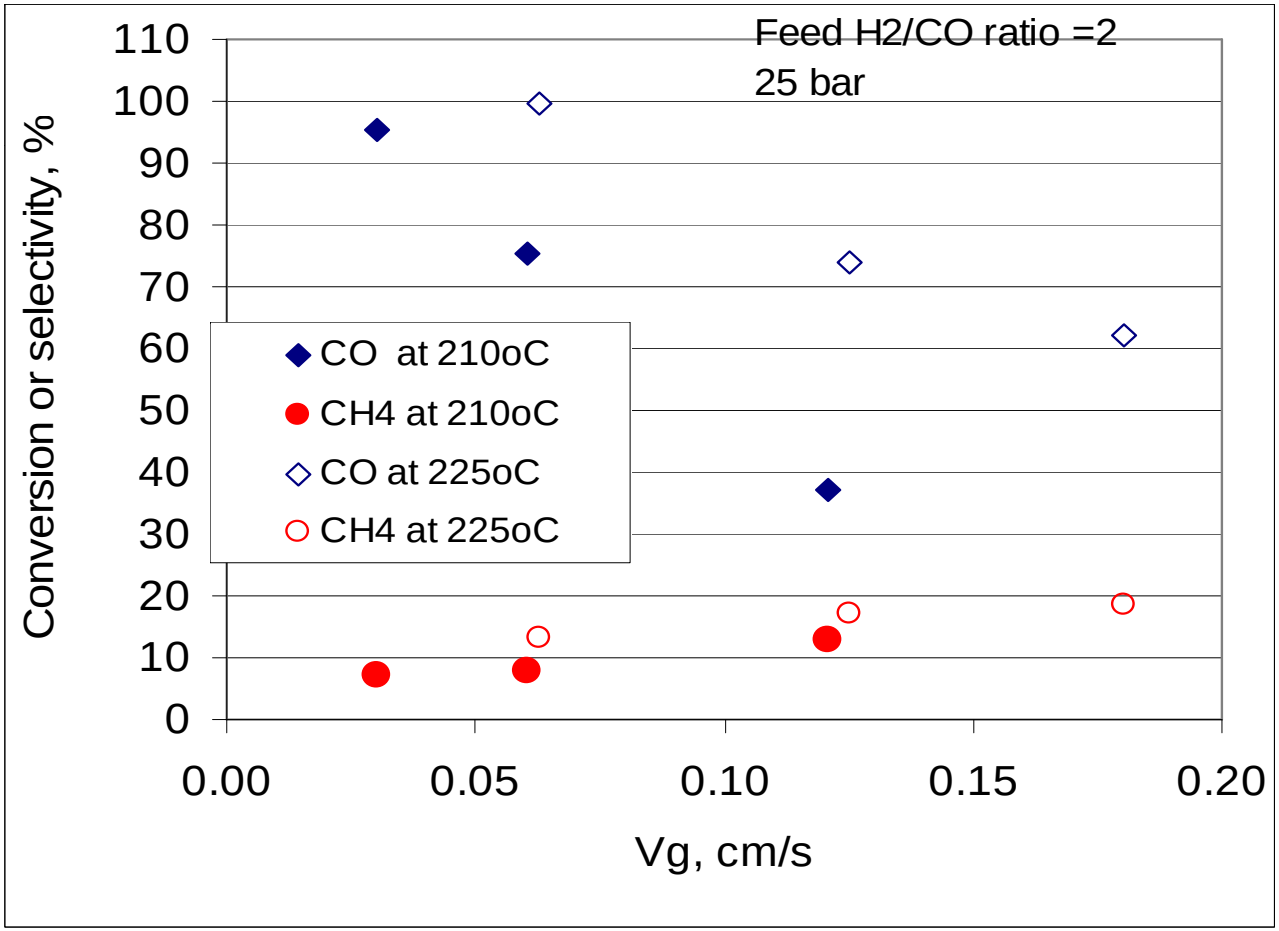
Impact of reaction temperature on performance of structured catalyst bed

- At a given WHSV, CO conversion and CH_4 selectivity increase with temperature, as expected



Impact of feed gas superficial linear velocity on performance of structured catalyst bed

- CO conversion decreases with increasing Vg (= increasing WHSV), as expected.
- CH_4 selectivity increases with Vg → higher CH_4 selectivity at lower CO conversion → opposite to results of conventional slurry or packed particle beds



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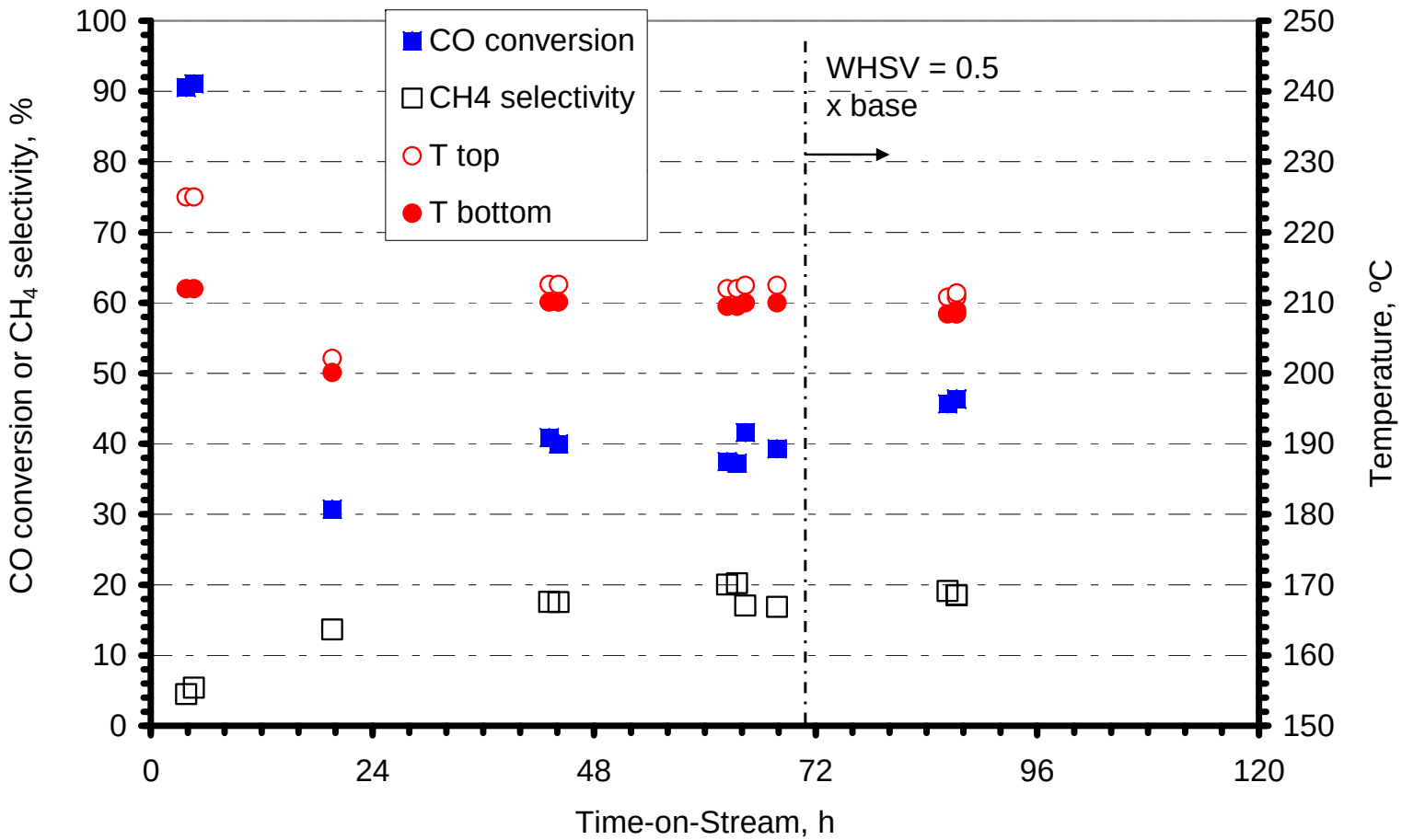
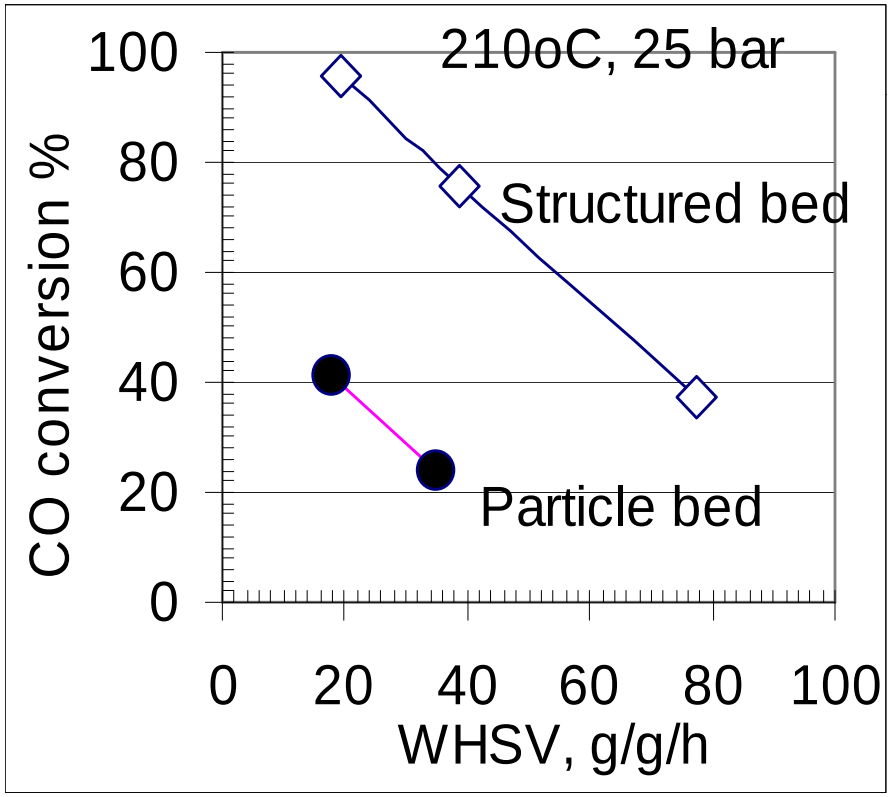
Steady-state performance of crushed monolith catalyst particle

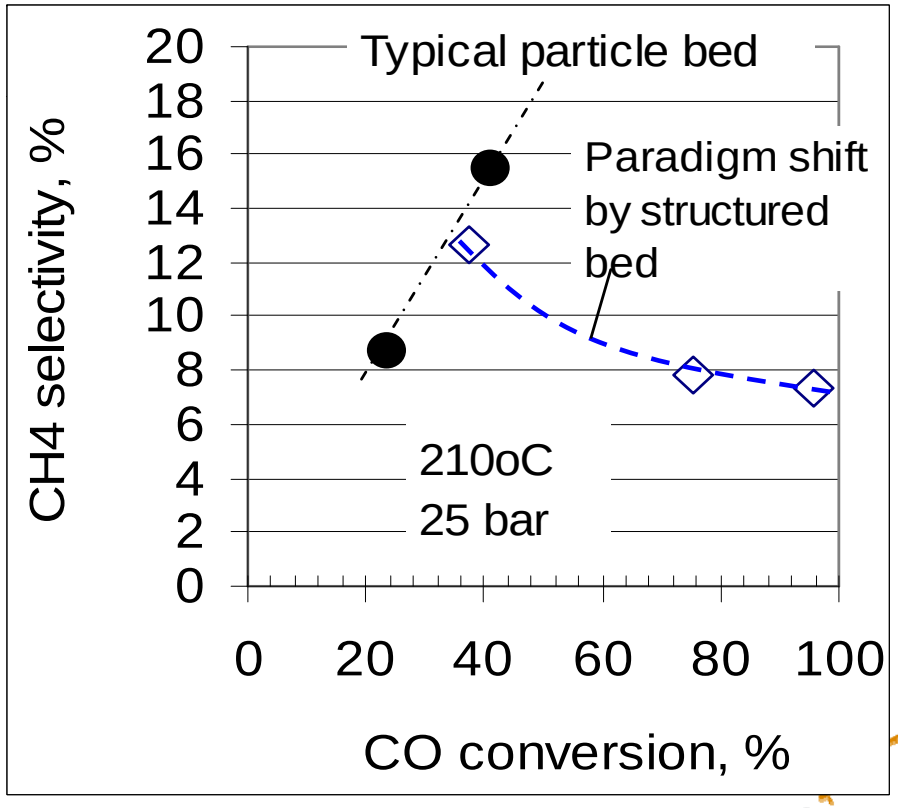
- 60-200mesh (~170um), H_2/CO = 2, 25 bar, 210°C
- Very difficult to control temperature. CO conversion was unstable under const conditions. Very high CH_4 selectivity



Comparison of structured bed to crushed monolith particle bed under same temperature

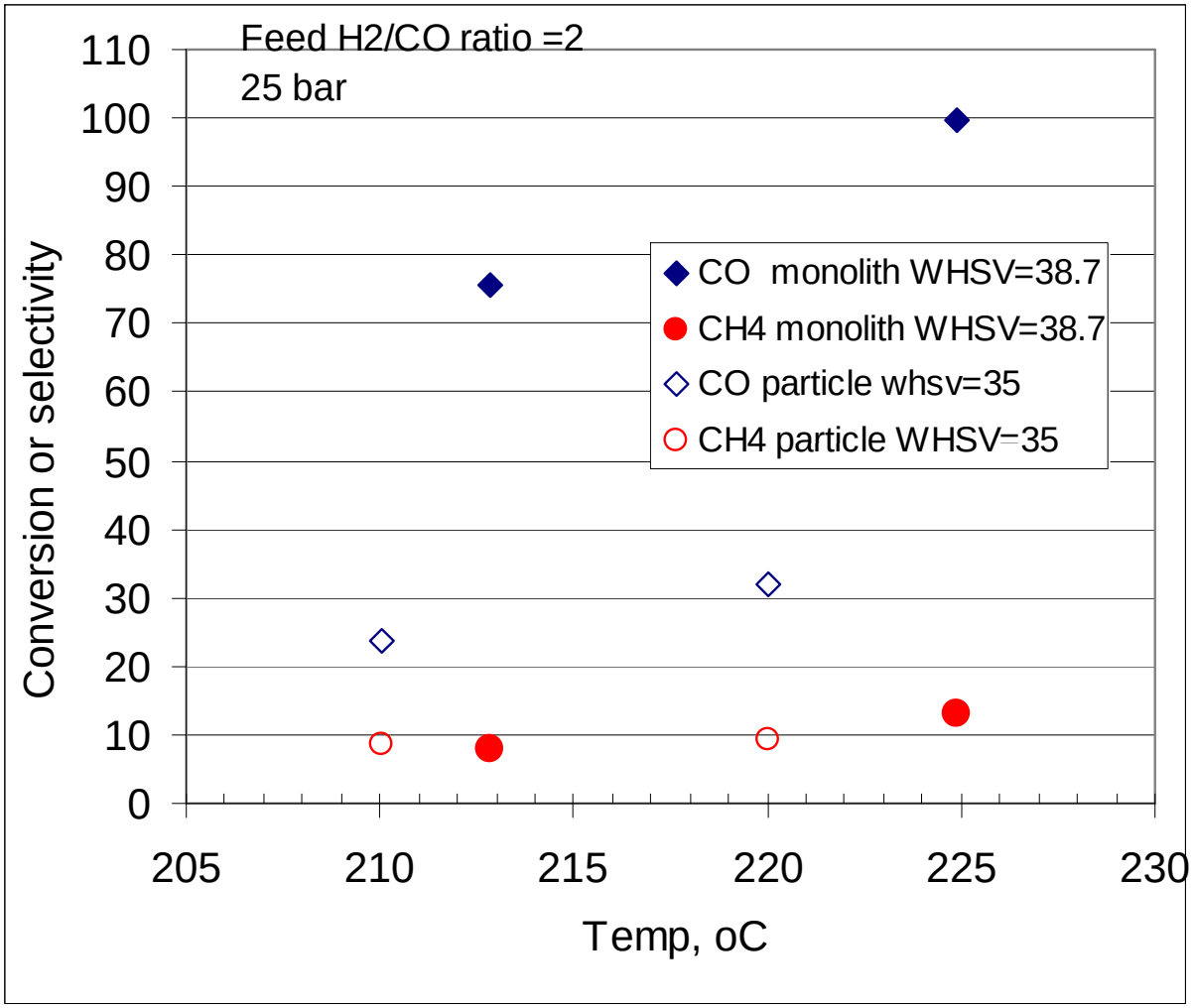
- The structured bed shows CO conversion activity a few times higher than the crushed particle bed.
- The structured bed enables <10% CH_4 selectivity at nearly complete one-pass CO conversion.





Comparison of structured bed to crushed monolith particle bed at different temperature

- Structured bed consistently provides CO conversion a few times higher than the particle bed under the same reaction conditions



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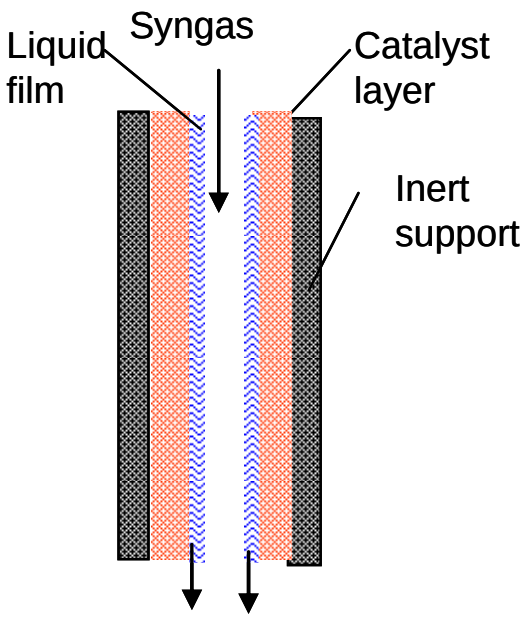
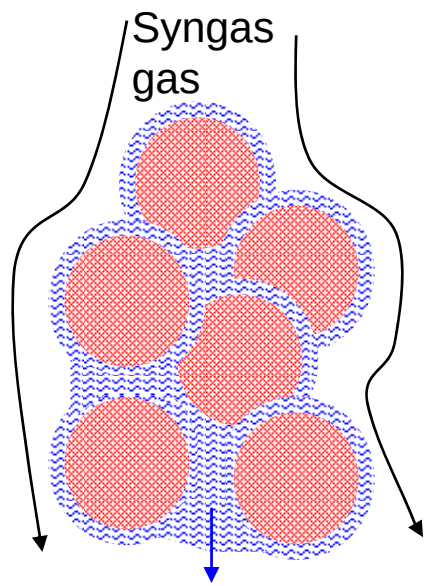
Proposed physical models for multiphase reaction in different catalyst beds

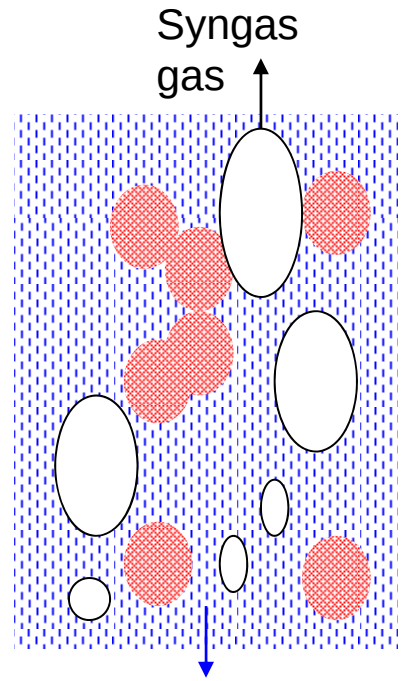
- Packed particle bed or slurry bed may be uniform at macro-scale. Segregation of gas/liquid/solid (catalyst) is inevitable at individual particle scale
- Micro-structured catalyst channel provides uniform contacting of gas/liquid/catalyst
- Catalyst surface coverage by a dynamic, thin liquid film favors for low CH_4 selectivity and high reaction rate.



Structured catalyst channel



Packed catalyst pellets



Slurry bed

Concluding remark

- For gas-to-liquid (FT) reaction, micro-structured catalyst bed designs lead to some unexpected, exceptionally good performance attributes with a common catalyst composition:

- >90% CO conversion at <10% CH_4 selectivity
- A few times of higher activity than the same catalyst material in crushed particle form
- Good temperature control in conventional sizes of reaction tubes (micro-channel reactor is not necessary)
- Catalyst bed free of plugging by wax
- A compact, high throughput gas-to-liquid catalytic reactor is possible

Note: poor performances obtained with conventional catalyst particle or slurry beds may be due to the reactor design issues rather than due to catalyst material itself.