New developments in the area of nonstationary and sorption-enhanced catalytic processes

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NEW DEVELOPMENTS IN THE AREA OF NONSTATIONARY AND SORPTION-ENHANCED CATALYTIC PROCESSES

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Main sources of development of new catalytic technologies

Development of new reaction pathways
   chemistry driven progress

Development of new catalysts
   catalysis driven progress

Development of new process approaches
   engineering driven progress
Development of new process approaches

- Various catalyst bed configurations (packed, tubular, fluidized, moving etc.)
- New catalyst shapes (granules, monoliths, miniliths, foams, fiber-glass fabric etc.)
- Structured beds
- Microreactors
- Multifunctional processes
- Unsteady-state catalytic processes

Shift from static to dynamic paradigm in search of new degrees of development freedom
Temperature cycling – reverse-flow operation

Main idea – periodical reversing of the reaction mixture flow in the fixed catalyst beds
Reverse-flow processes

- decrease of capital cost
- decrease of energy consumption
- improvement of process stability
- commercial experience – hundreds industrial installations worldwide (VOC incineration, sulfur dioxide oxidation, deNOx)
Reverse-flow reactors – past, present and future

Excellent example of engineering-driven technology

A lot of success achieved, more success to be achieved, but general potential of the temperature cycling approach in RFR seems to be spent

Temperature cycling basis of RFR does not mean that only the catalyst temperature is changing. It is just about the developers paradigm.

Some research and practical experience shows that nonstationarity of catalyst surface composition, if not properly accounted at development, may lead to decreased process efficiency
Forced feed composition cycling

A great amount of lab research done in this area

**Simple reactions** – *increase of reaction rates*
Increase mostly 20-30% - not that interesting

**Complex reactions systems** – *selectivity increase is possible*
Interesting

**Thermodynamically limited reactions** – *overcoming the equilibrium limitations*
Interesting

- realization of forced feed composition cycling in practice is technically and technologically complicated procedure
- the positive effect, achieved in lab experiments, may be lost or turned into negative during scale-up: CSTR/plug flow, diffusion limitations, influence of heat effects in the adiabatic conditions
Not simply the way out but the promising basis for the development of new generation of catalytic processes

Temperature cycling

Combined nonstationarity of the catalyst

Forced feed composition cycling
Recent BIC developments in this area

• adsorption-catalytic reverse-process for VOC abatement
• sorption-enhanced steam reforming with super-adiabatic sorbent regeneration
• reverse-process for anaerobic oxidative dehydrogenation of hydrocarbons
Adsorption-catalytic process for incineration of VOCs in low-concentrated waste gases

\[ C_x H_y + [O] \Rightarrow [P] \]
\[ [P] + O_2 \Rightarrow CO_2 + H_2O + [O] \]

Combination of catalytic and adsorption properties of oxide catalysts in respect to VOCs: accumulation of VOC from lean gases at ambient temperature with periodical incineration of sorbed VOC at elevated temperatures

- High VOC removal degree
- Low energy consumption (key criterion for treatment of lean gases)
- Possibility of desorption of VOC during catalyst-adsorbent heating

_UOP, Haldor Topsoe – 1979_
**BIC approach: adsorption-catalytic reverse-process (ACRP)**

Combination of adsorption-catalytic principle with reverse-flow approach

Adsorption cycle is performed under constant gas flow direction, flow reversals are performed only in the regeneration cycle

Mathematical simulation of the regeneration cycle

BIC approach: adsorption-catalytic reverse-process (ACRP)

- extra-low energy consumption
- improved purification efficiency

ACRP was successfully tested at the pilot and semi-industrial scale
New VOC incineration approach: adsorption-catalytic process in the multi-dispersed fixed bed

Different dynamics of heating of micro-fibers (<10 µm) and adsorbent-catalyst pellets (5-10 mm) ⇒ minimization of desorption losses

S.Zazhigalov, N.Chumakova, A.Zagoruiko, 2011. See the poster
Sorption-enhanced steam reforming of hydrocarbons and organic feedstocks

Pioneers: Tessie du Motay, Marechal (1868), Brun-Tsekhovoy (1990), Hufton, Mayorga, Sircar (1999), Ding and Alpay (2000)

Steam reforming reactions
\[ \text{CH}_4 + \text{H}_2\text{O} \Leftrightarrow \text{CO} + 3 \text{H}_2 \quad \text{CO} + \text{H}_2\text{O} \Leftrightarrow \text{CO}_2 + \text{H}_2 \]

With simultaneous chemisorption of \( \text{CO}_2 \)

\[ \text{MeO} + \text{CO}_2 \Leftrightarrow \text{MeCO}_3 \]

- Efficient equilibrium shift
- One-step production of pure COx-free hydrogen
- Small/Medium/Large scale feasibility

**Problem:** no efficient solution for regeneration stage (technological complications, low energy efficiency) – no commercial success yet
BIC approach: SERP + autothermal super-adiabatic regeneration concept

regeneration of the chemisorbent by the heat of exothermic catalytic reaction performed directly in the adiabatic sorbent/catalytic bed

\[
\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (4)
\]

efficiency of regeneration does not depend upon the reactor diameter \(\Rightarrow\) the reactor diameter and unit productivity of the reactor is not limited

Process flow-sheet:
counter-current separate cyclic feeding of Steam-Methane and Air-Methane mixtures
Super-adiabatic heat wave
(BIC - G.K. Boreskov, Yu.Sh. Matros, O.V. Kiselev)
regeneration in the moving heat wave of catalytic combustion reaction
(super-adiabatic mode)

Maximum temperature may significantly exceed the adiabatic one

\[ T_{\text{max}} - T_{\text{in}} \gg \Delta T_{\text{ad}} \]

Efficient transfer of catalyst enthalpy to the reaction zone
(formal contradiction to thermodynamics)

high temperatures, sufficient for efficient chemisorbent regeneration, are achievable under ambient inlet temperature of the air/methane mixture (no gas preheating required) with quite low methane concentrations \( \Rightarrow \) low energy consumption for sorbent regeneration
Simulation: methane reforming stage

Inlet mixture composition (% vol.) - 25% CH₄, 75% H₂O;

\[ u_{in} = 0.3 \text{ m/s}; \quad T_{in} = 20^\circ\text{C}; \quad P = 5 \text{ atm}; \quad l = 1 \text{ m}; \quad T_{init} = 500^\circ\text{C}; \quad X_{init} = 0; \quad v_c = v_s = 0.3. \]
Simulation: methane reforming stage

Inlet mixture composition (% vol.) - 25% CH₄, 75% H₂O; 
\( u_{in} = 0.3 \text{ m/s}; \) \( T_{in} = 20^0\text{C}; \) \( P = 5 \text{ atm}; \) \( l = 1 \text{ m}; \) \( T_{init} = 500^0\text{C}; \) \( X_{init} = 0; \) \( v_c = v_s = 0.3. \)

During first 200-300 sec practically complete conversion of methane is observed, with COx content in produced hydrogen not exceeding 50 ppm.
Simulation: regeneration stage

Inlet mixture composition: 1% CH₄ in air; $u_{in} = 1$ m/s; $T_{in} = 20^0C$; P = 1 atm; initial conditions – the final ones for $t=200$ sec in reforming cycle, mixture feeding direction – opposite to one in reforming cycle.

Efficient and energy-saving regeneration of the CO₂-scavenger in the heat front (superadiabatic heat wave) of the catalytic combustion reaction is possible.
Technological benefits

Simple one stage process flow-sheet with minimized heat-exchange infrastructure, low capital and operating costs, high flexibility to feedstock composition

Compared to conventional (syngas) reforming technologies:
• One-stage production of high purity COx-free hydrogen
  small/medium scale units may be feasible

Compared to conventional SERP technologies:
• Simple reactor design, unlimited unit productivity
• Significant decrease of energy consumption, maximized energy efficiency
  medium/large scale units are feasible

Compared to autothermal reforming (partial oxidation) technologies:
• One-stage production of high purity COx-free (and nitrogen-free) hydrogen
• Simplified process control, elimination of oxygen feeding complications
• No catalyst coking problems
  increased process safety and reliability

The process concept is applicable for production of hydrogen from methane and to other hydrocarbon/organic feedstock (LPG, methanol, ethanol, biofuels etc.)
Selective (anaerobic) oxidation and oxydehydrogenation using catalyst oxygen storage

Anaerobic (from Greek αναερόβιος) – in absence of air

Idea: use of lattice oxygen chemisorbed at the catalyst surface as a mild selective oxidant instead of molecular oxygen

$$C_xH_y + [Ox] \rightarrow C_xH_{y-2} + H_2O + [Red]$$

with periodical reoxidation of the catalyst surface by $O_2$

$$[Red] + \frac{1}{2} O_2 \rightarrow [Ox]$$

High selectivity is expected
Heat effects of the oxidative dehydrogenation reactions

Bulk oxidation:

1) \( \text{C}_x\text{H}_y + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_x\text{H}_{y-2} + \text{H}_2\text{O} \quad \Delta H_1 \approx 100\text{kJ/mol} \)
2) \( \text{C}_x\text{H}_y + n\text{O}_2 \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} \quad \Delta H_2 \approx 800\text{kJ/mol} \)

Anaerobic oxidation:

1a) \( \text{C}_x\text{H}_y + [\text{O}]_{\text{CAT}} \rightarrow \text{C}_x\text{H}_{y-2} + \text{H}_2\text{O} + [\ ] \quad \Delta H_{\text{RED}1} \)
1b) \( \frac{1}{2}\text{O}_2 + [\ ] \rightarrow [\text{O}]_{\text{CAT}} \quad \Delta H_{\text{OX}1} \)

2a) \( \text{C}_x\text{H}_y + 2n(\text{O}) \rightarrow x\text{CO}_2 + \frac{y}{2}\text{H}_2\text{O} + 2n(\ ) \quad \Delta H_{\text{RED}2} \)
2b) \( n\text{O}_2 + 2n(\ ) \rightarrow 2n(\text{O}) \quad \Delta H_{\text{OX}2} \)

Heat effect of anaerobic oxidation reaction (at the catalyst reduction stage 1a/2a) is always lower than that for the bulk oxidation (1/2)

\[ \Delta H_{\text{RED} i} = \Delta H_i - \Delta H_{\text{OX} i} < \Delta H_i \]

The remaining balance heat is produced at the reoxidation stage (1b/2b) when it cannot influence the selectivity of the target reaction

Unique opportunities for the heat management in the anaerobic process (unavailable in the steady-state approach)

• Oxidation stage may be slightly exothermic or even endothermic ⇒ possibility to process concentrated hydrocarbon feedstock in the simple and cheap reactors with fixed catalyst bed (no feedstock dilution, no fluidized beds, tubular reactors, multi-stage reactors with heat withdrawal etc.)

• Heat effect distribution between catalyst reduction/reoxidation stages may be varied by the choice of catalysts with different oxygen bonding energy

• Efficient control of the process temperature in the anaerobic process may additionally improve the product yield for reactions with temperature-dependent selectivity

Alternative anaerobic process flow sheets

Circulating moving bed reactors
(conventional approach)

Swinging fixed-bed reactors
(BIC approach)

Catalyst circulates between anaerobic oxidation reactor and oxidizer-regenerator (also known as CLC – Chemical Looping Combustion flow-sheet)

Multi-reactor counter-current scheme with periodical swinging between catalyst reduction and reoxidation modes in each reactor
Circulating moving vs fixed-bed swing for the anaerobic process

Circulating moving bed reactors

• Catalyst stirring
• Complicated reactor design
• Catalyst circulation ratio depends upon the effective catalyst oxygen storage capacity – low oxygen capacity may lead to unreasonably high energy losses for catalyst transport

Swinging fixed-bed reactors

• No catalyst stirring
• Simple and cheap reactor design
• Catalyst oxygen storage capacity influences the duration of the cycle between reduction/reoxidation switching – insufficient capacity may be compensated by more frequent switching (not leading to the rise of the process capital costs and energy consumption)

Case information: insufficient catalyst oxygen storage in the commercial unit for anaerobic oxidation of butane to maleic anhydride has led to catalyst circulation rate of ~10’000(!) tons/hour with consequent enormously high energy consumption for vertical catalyst transport. The technology was finally considered as unfeasible.

The anaerobic fixed-bed process may be feasible even at moderate oxygen storage capacities of the existing catalysts
Anaerobic process simulation

Case study: propane $\Rightarrow$ propylene (simulation)

Cyclic process in the fixed catalyst beds with separate feeding of reagents:

- high selectivity
- counter-current feeding is preferable
- moderate maximum temperature, process may be performed in the fixed bed without heat withdrawal even with undiluted propane as a feedstock

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Anaerobic vs steady-state technologies

Anaerobic process potential advantages

- High selectivity and product yield — high feedstock efficiency
- Use of undiluted feed — higher concentration of the product — simplification of the downstream separation
- Simple and cheap fixed-bed reactor design, minimized heat-exchange infrastructure — possible decrease of the capital costs
- No catalyst stirring, efficient coke incineration at each reoxidation cycle — possible increase of the catalyst lifetime
- Possibility to use air instead of pure oxygen without downstream problems with nitrogen separation from product stream

Anaerobic process potential problems

- Increased catalyst loading
- More complicated control strategy

The anaerobic process potential looks promising but its actual feasibility needs additional quantitative confirmation, which, in turn, requires additional experimental data and process simulation for estimation of the basic process parameters.
Unsteady-state catalysis – summary

Increased efficiency
- increased conversion, equilibrium shifts, increase of selectivity

New opportunities for heat management
- autothermal processing of lean feedstock (adsorption-catalytic VOC oxidation)
- energy-saving sorbent regeneration in the super-adiabatic heat wave (sorption-enhanced hydrogen production)
- heat redistribution between stages of exothermic reaction (anaerobic oxidative dehydrogenation)

Decrease of capital costs, energy-saving
- simple and cheap fixed bed reactors
- minimized heat-exchange infrastructure
- lower fuel consumption, autothermal operation
- improved feedstock efficiency

Improved process control options
- increased process stability under oscillations of external parameters
Unsteady-state and sorption-enhanced catalysis approach opens new degrees of freedom for creative process engineers.