Simulation of Surface Chemical Reactions

in a Monolith Channel for Hydrogen Production

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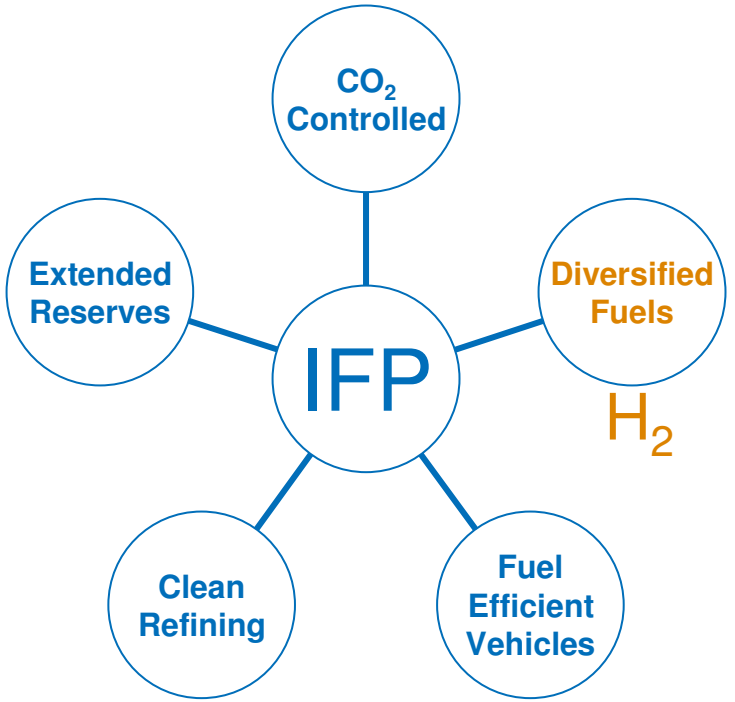
IFP Presentation

- French R&D public institute
- Mission:
  - To **develop** the technologies and materials of the future in field of **energy**, **transport** and the **environment**
- Some numbers about IFP:
  - 2 main locations (Rueil and Lyon)
  - ~1800 workers (~1100 researchers)
  - ~200 PhD and post-doctoral students
- More information at: www.IFP.fr

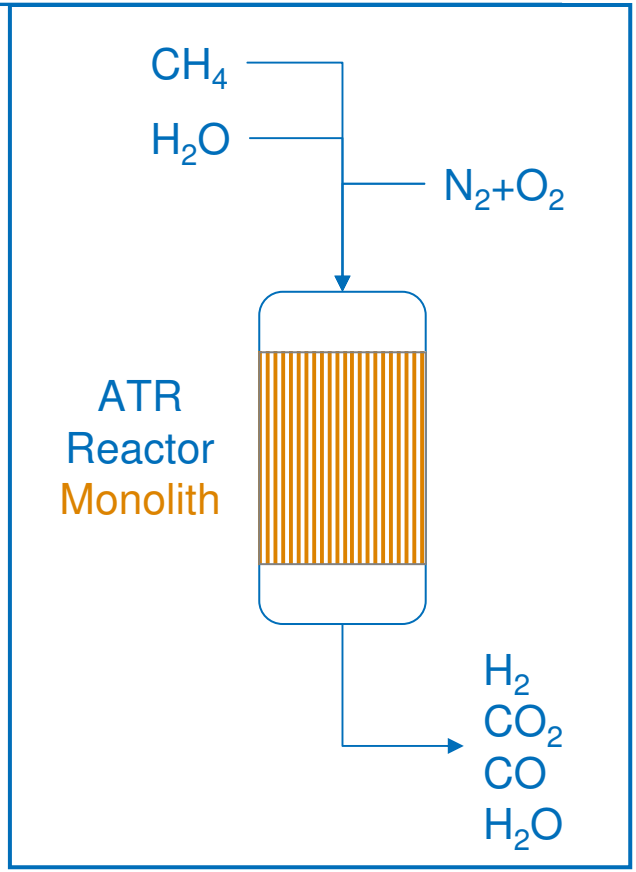
5 strategic priorities



H_2 production from CH_4 by ATR process over monoliths

- In an ATR reactor, three main reactions occurs:
  - Steam Reforming : $CH_4 + 2H_2O \xrightarrow{+\Delta H} 4H_2 + CO_2$
    Energy
  - Partial Oxidation : $CH_4 + 1.5O_2 \xrightarrow{-\Delta H} 2H_2O + CO$
  - Water Gas Shift : $CO + H_2O \longleftrightarrow H_2 + CO_2$

    Thermodynamic Equilibrium Expected



- This system need to be catalyzed
  - In our case: Impregnated monoliths

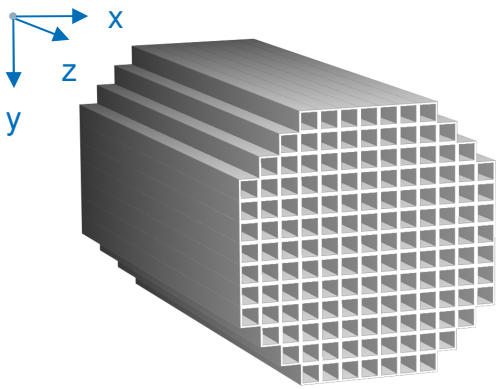
Objectives

- The objective is to build an isothermal reactor model.
- It will be shown:
  - The geometry definition and governing equations
    - Two different approaches to model the catalytic layer
    - The set of 20 mass balance equations
    - Involved with 42 surface chemical reactions
  - The main simulation results
  - The trend evaluations

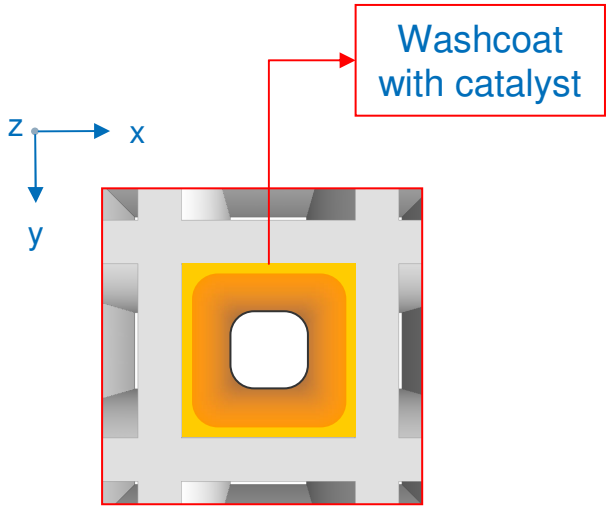
ENSIC

ifp Innovation Energy Environment

Problem Definition: Global Geometry

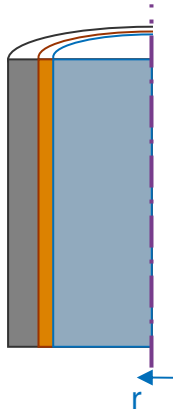


Monolith



Modeling only a channel

Axial symmetric geometry



Half monolithic wall

Catalytic layer

Gas phase

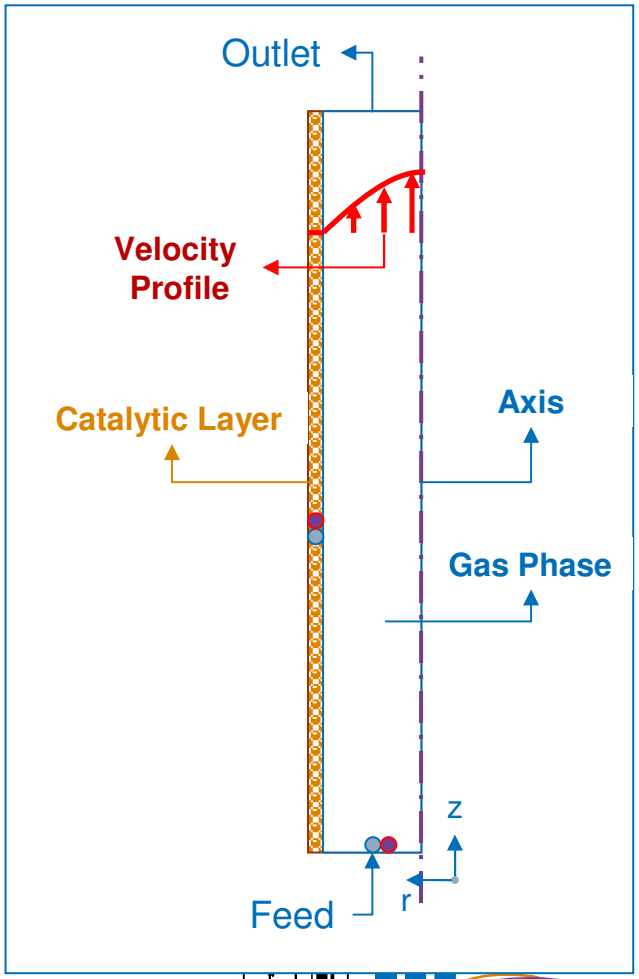
Shape between circle and square
3D

Cylindrical Channel
2D

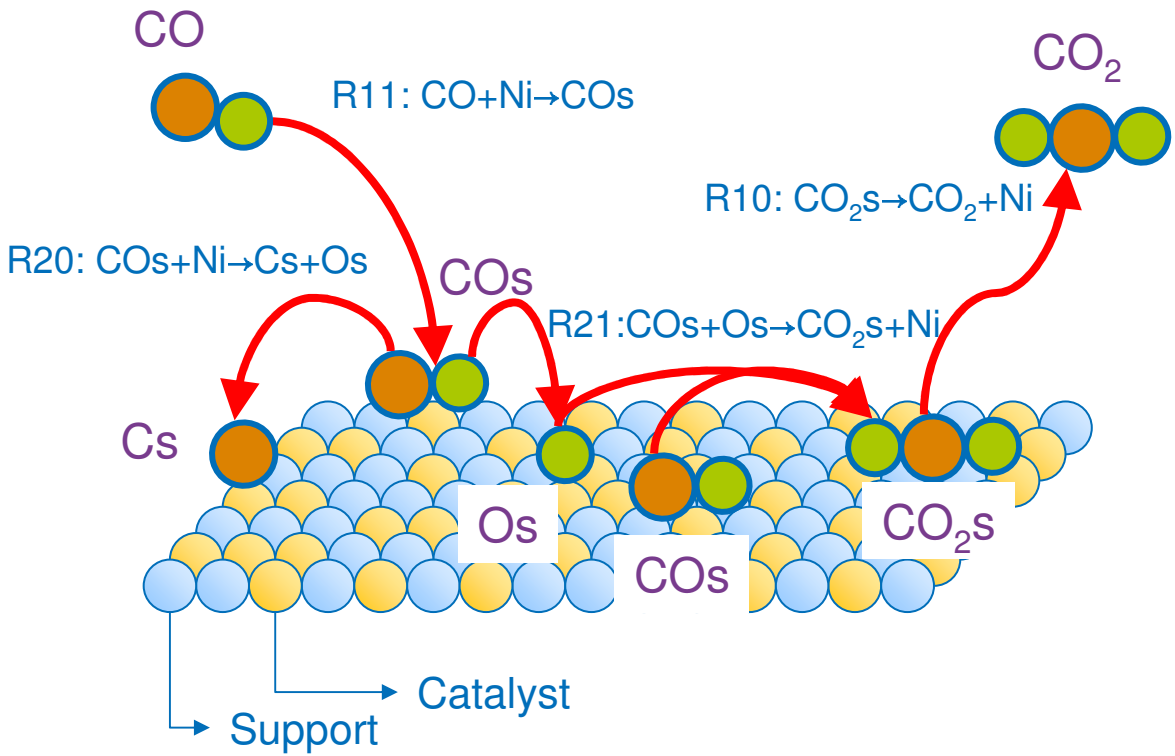
Problem Definition: Governing Equations

- Hydrodynamic:
  - Gas phase: Poiseuille profile
  - Catalytic layer: No velocity
- Masse Balance Equation $\frac{\partial C_k}{\partial t} + \nabla.(-D\nabla C_k + C_k u) = R$
  - For 7 Gas Species (H_2, O_2, H_2O, CH_4, CO, CO_2 and N_2)
    - **Gas Phase** - Convection and Diffusion $\frac{\partial C_k}{\partial t} + \nabla.(-D\nabla C_k + C_k u) = 0$
    - **Catalytic Layer** - Diffusion and Surface Reaction $\frac{\partial C_k}{\partial t} + \nabla.(-D\nabla C_k) = R$
  - For 13 adsorbed species (from a surface mechanism)
    - Only the surface reactions are taken in count (considering the mean field approximation)

$$\begin{cases} \frac{\partial Cs_k}{\partial t} = R, k-1 \\ site\ balance, k \end{cases}$$



Problem Definition: Chemical Reaction Mechanism



	Surface Adsorption/Desorption Reactions						
R1	H_2	+	2Ni(s)	→	2H(s)		
R2			2H(s)	→	H_2	+	2Ni(s)
R3	O_2	+	2Ni(s)	→	2O(s)		
R4			2O(s)	→	O_2	+	2Ni(s)
R5	CH_4	+	Ni(s)	→	CH_4(s)		
R6			CH_4(s)	→	CH_4	+	Ni(s)
R7	H_2O	+	Ni(s)	→	H_2O(s)		
R8			H_2O(s)	→	H_2O	+	Ni(s)
R9	CO_2	+	Ni(s)	→	CO_2(s)		
R10			CO_2(s)	→	CO_2	+	Ni(s)
R11	CO	+	Ni(s)	→	CO(s)		
R12			CO(s)	→	CO	+	Ni(s)
	Surface Reactions (involving O, H and Ni atoms)						
R13	H(s)	+	O(s)	→	Ni(s)	+	OH(s)
R14	Ni(s)	+	OH(s)	→	H(s)	+	O(s)
R15	H(s)	+	OH(s)	→	Ni(s)	+	H_2O(s)
R16	Ni(s)	+	H_2O(s)	→	H(s)	+	OH(s)
R17			2OH(s)	→	H_2O(s)	+	O(s)
R18	H_2O(s)	+	O(s)	→	2OH(s)		
	Surface Reactions (involving O, C and Ni atoms)						
R19	C(s)	+	O(s)	→	Ni(s)	+	CO(s)
R20	Ni(s)	+	CO(s)	→	C(s)	+	O(s)
R21	CO(s)	+	O(s)	→	Ni(s)	+	CO_2(s)
R22	Ni(s)	+	CO_2(s)	→	CO(s)	+	O(s)
	Surface Reactions (involving C, O, H and Ni atoms)						
R23	Ni(s)	+	HCO(s)	→	H(s)	+	CO(s)
R24	H(s)	+	CO(s)	→	Ni(s)	+	HCO(s)
R25	Ni(s)	+	HCO(s)	→	CH(s)	+	O(s)
R26	CH(s)	+	O(s)	→	Ni(s)	+	HCO(s)
	Surface Reactions (involving C, H and Ni atoms)						
R27	Ni(s)	+	CH_4(s)	→	H(s)	+	CH_3(s)
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R32	H(s)	+	CH(s)	→	Ni(s)	+	CH_2(s)
R33	Ni(s)	+	CH(s)	→	H(s)	+	C(s)
R34	H(s)	+	C(s)	→	Ni(s)	+	CH(s)
	Surface Reactions (involving C, O and H)						
R35	CH_4(s)	+	O(s)	→	OH(s)	+	CH_3(s)
R36	OH(s)	+	CH_3(s)	→	CH_4(s)	+	O(s)
R37	CH_3(s)	+	O(s)	→	OH(s)	+	CH_2(s)
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R39	CH_2(s)	+	O(s)	→	OH(s)	+	CH(s)
R40	OH(s)	+	CH(s)	→	CH_2(s)	+	O(s)
R41	CH(s)	+	O(s)	→	OH(s)	+	C(s)
R42	OH(s)	+	C(s)	→	CH(s)	+	O(s)

Deutschmann, O., Tischer, S., Schaedel, B., and Maier, L., Surface reactions: reforming and oxidation of methane on nickel, http://www.detchem.com/mechanisms/nickel.html, (01/03/06)

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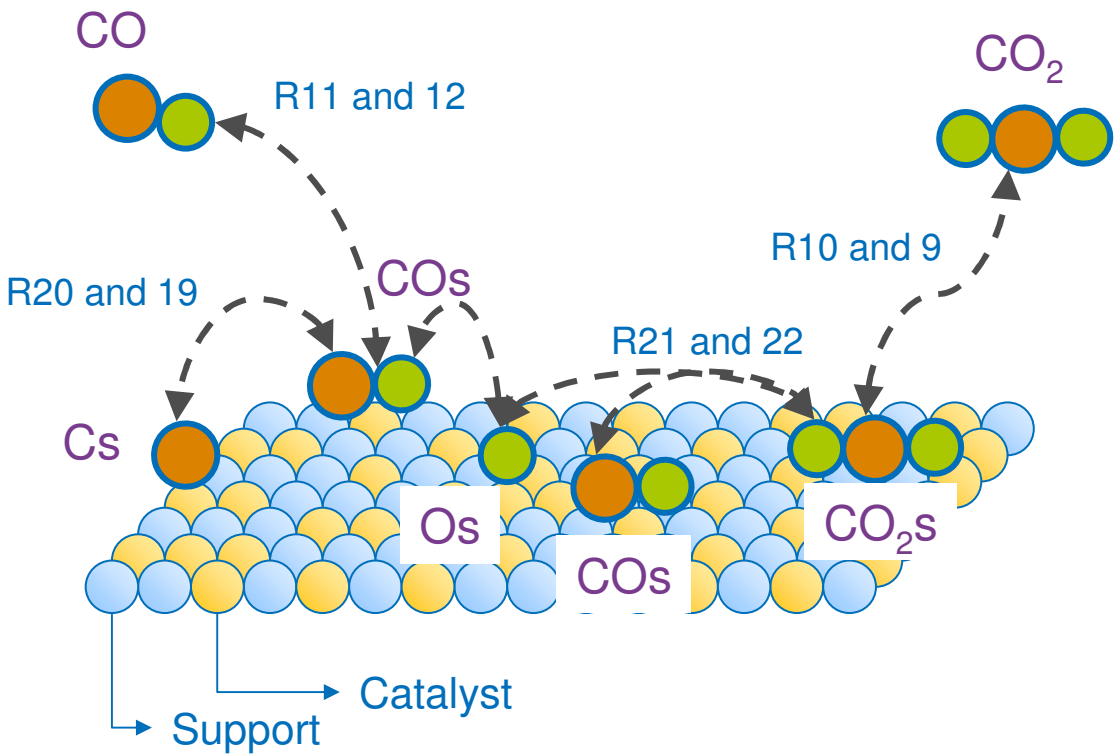

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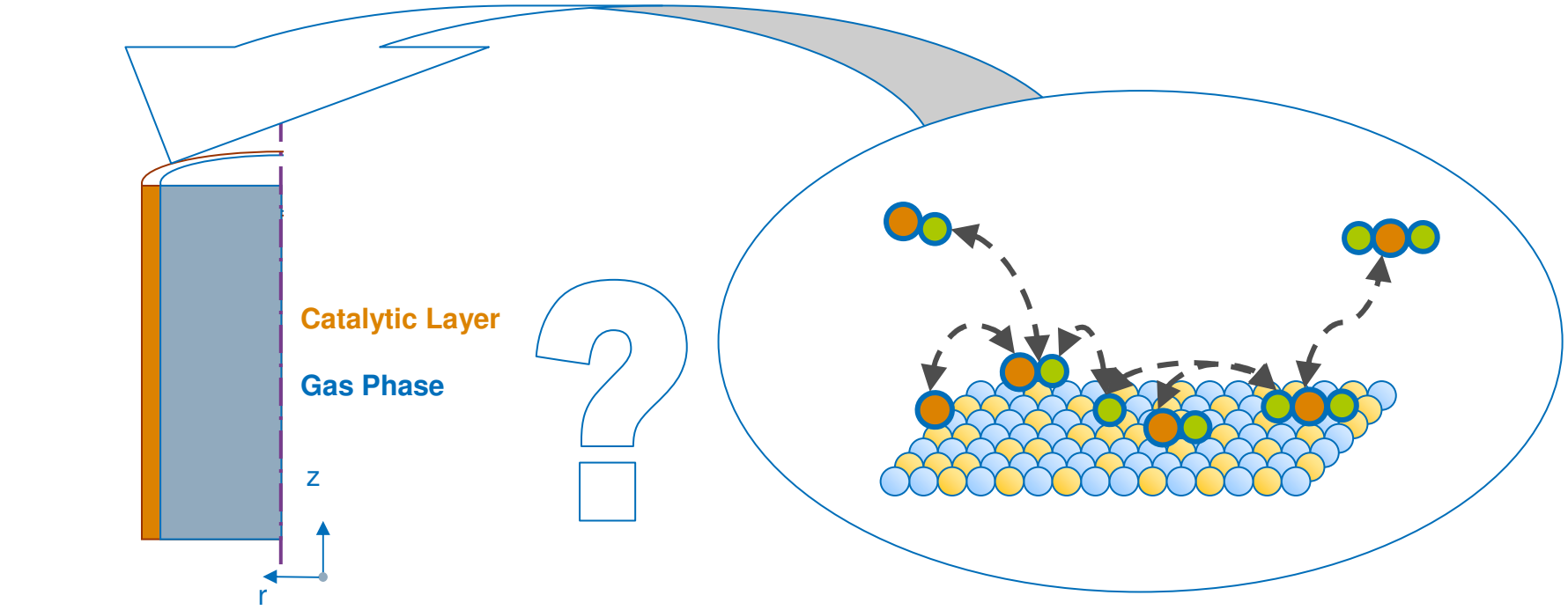


Cylindrical Channel

How the surface reaction mechanism can be integrated in this geometry using COMSOL?

Catalytic Layer Modeling

Two different approaches

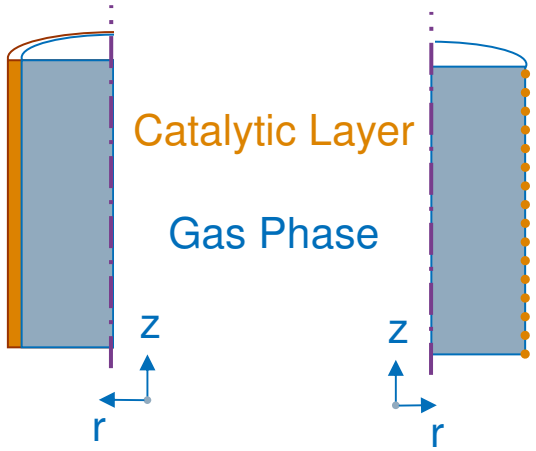
Catalytic Thin Volume (VM)

Easy to model in COMSOL, by using 2 domains

By **conserving** the total **catalytic sites** and the **total Volume**

$$Ni_{Total}\left(\frac{mol}{m^2}\right)\frac{Surf}{Vol}\left(\frac{m^2}{m^3}\right)$$

Conversion of the chemical reaction model from **surface to volume**



Catalytic Surface (SM)

Coupling of 1D/2D domains by, for example: **Boundary weak form**

$$\frac{\partial Cs_k}{\partial t} = R,$$

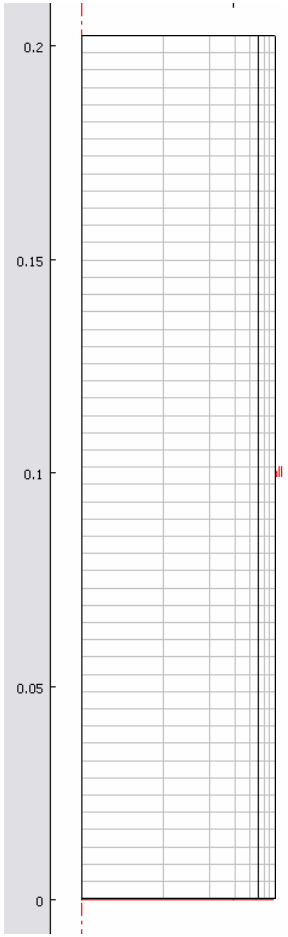
dweak = c_test * c_time

weak = c_test * R

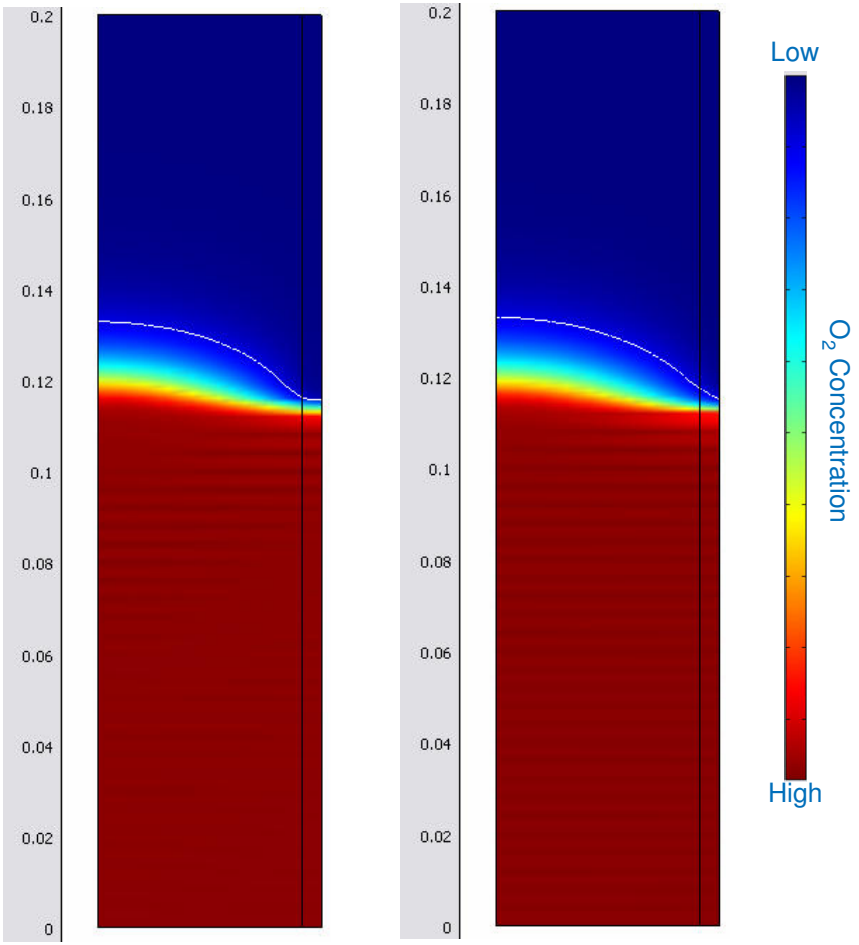
Direct use of the surface **chemical reaction model**

CONCLUSION: Both cases are simulated

Catalytic Layer Modeling: for surface O_2 adsorption



Run Simulation:
- In transient mode
- Up to 1s



Draw and Mesh

VM Case

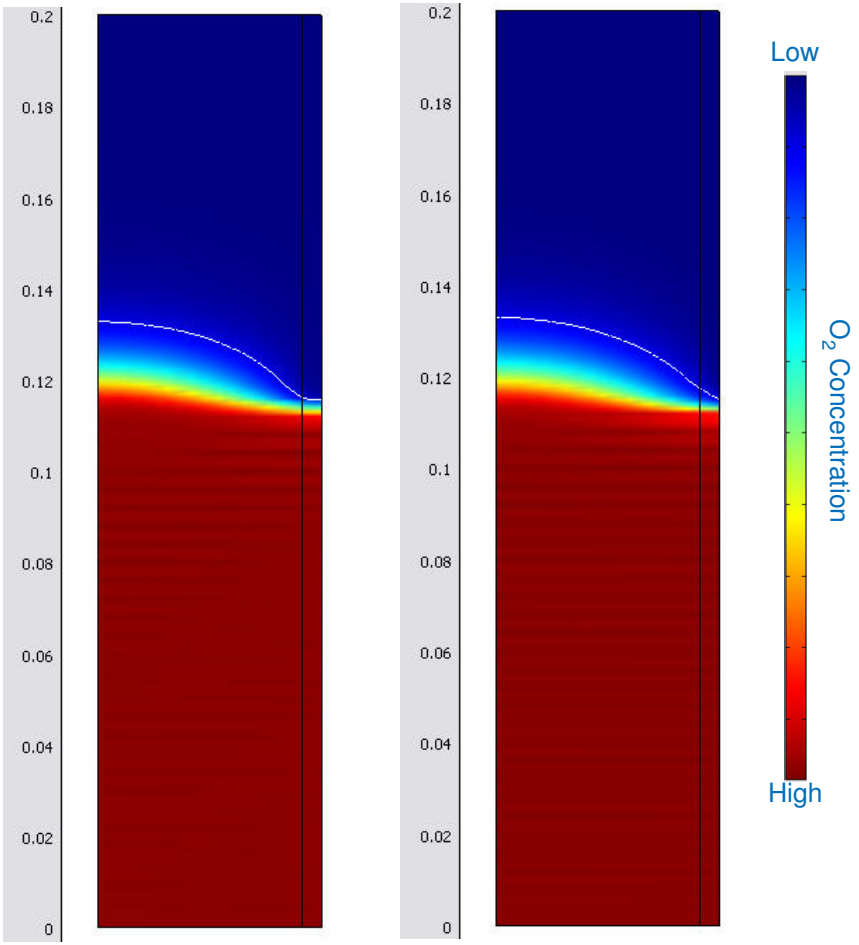
SM Case

Catalytic Layer Modeling: for surface O_2 adsorption

- The results are similar, then:
  - The two approaches are equivalent
  - The chemical mechanism conversion from **surface** to **volume** is reasonable
- The SM is better than VM in terms of calculation time

	COMSOL 3.4
VM	1016
SM	533
Model Comparison	- 48%

$$\frac{t_{SM} - t_{VM}}{t_{VM}}$$



Catalytic Layer Modeling: for surface O_2 adsorption

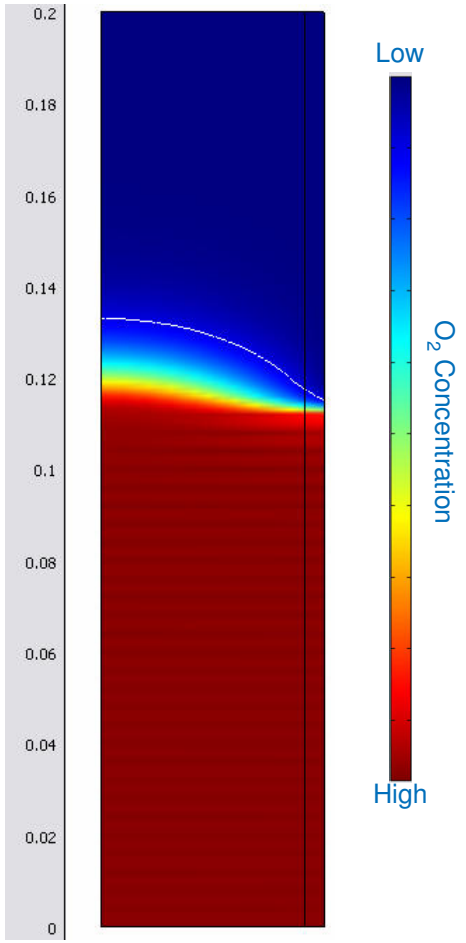
- The results are similar, then:
  - The two approaches are equivalent
  - The chemical mechanism conversion from **surface** to **volume** is reasonable
- The SM is better than VM in terms of calculation time

	COMSOL 3.4	COMSOL 3.5	Version Comparison
VM	1016	337	- 67%
SM	533	126	- 76%
Model Comparison	- 48%	- 63%	

Fails with 42 surface reactions

$$\frac{t_{3.5} - t_{3.4}}{t_{3.4}}$$

$$\frac{t_{SM} - t_{VM}}{t_{VM}}$$



SM Case

Main Objectives

- The Objective is to build an isothermal reactor model.
  - The problem geometry is defined by: ✓
    - Axial symmetric geometry
    - Modeling the catalytic layer as surface using boundary weak form
  - The governing equations are defined by: ✓
    - Hydrodynamic: Poiseuille
    - Mass balance equations
    - Surface chemical reactions
- We will:
  - Show you the main simulation
  - Evaluate the simulator trends

ATR Monolithic Reactor Modeling:

- 7 gas species
  - H_2, O_2, H_2O, CH_4, CO, CO_2 and N_2

  ⇨ 7x $\frac{\partial C_k}{\partial t} + \nabla.(-D\nabla C_k + C_k u) = R$ Convection and Diffusion Chemical Engineering Module

- 13 adsorbed species
  - H_2Os, OHs, Hs, Os, Cs, COs, CO_2s, CH_4s, CH_3s, CH_2s, CHs, HCOs and Ni

  ⇨ 12x $\frac{\partial Cs_k}{\partial t} = R$ dweak = c_test * c_time; weak = c_test * R — Boundary Weak Form PDE Modes

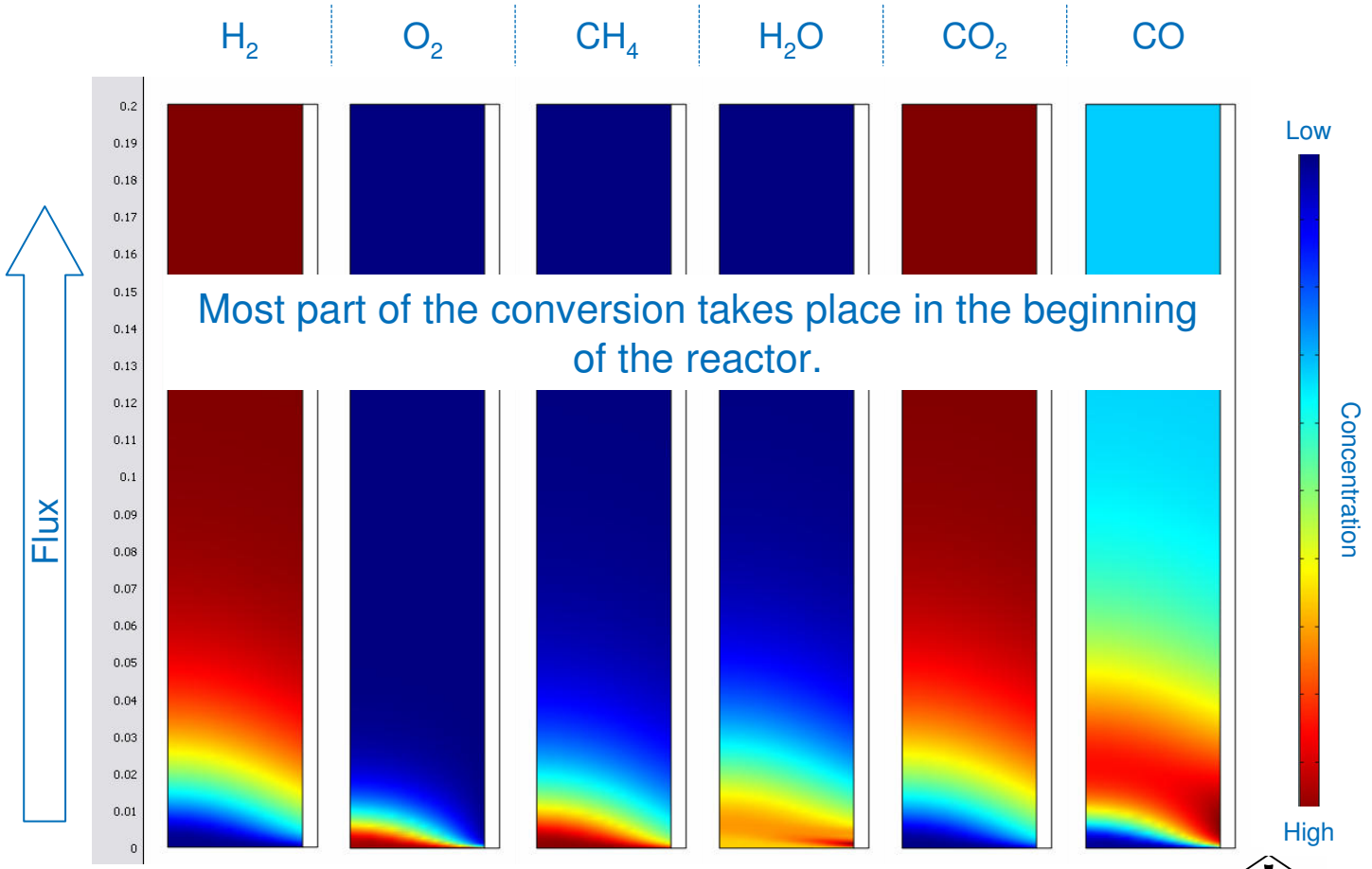
  1x *site balance*

  20 equations

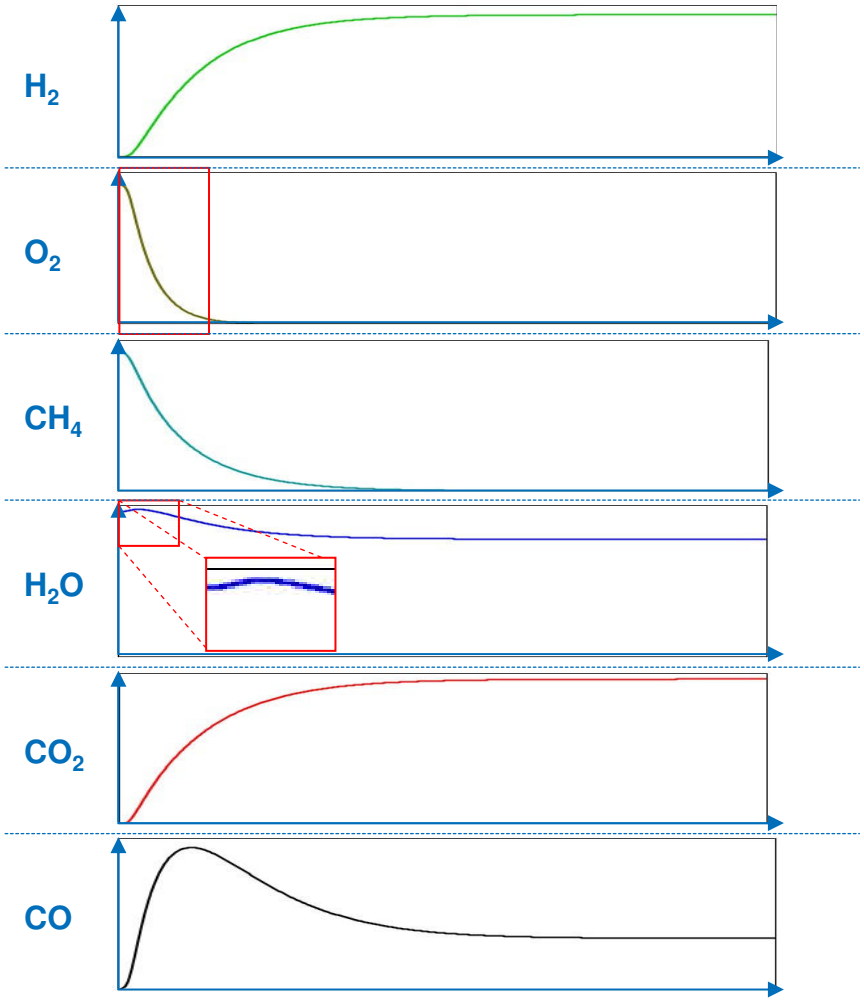
- 42 surface chemical reactions

- Time-dependent solver until the steady state, being the initial values for:
  - All gas species = injection concentration
    - to avoid the concentration front wave calculation
  - Ni = total catalytic site density then all other solid species = 0

ATR Monolithic Reactor Modeling: Simulation Concentration Profiles



ATR monolithic reactor modeling: Concentration profiles in channel axis



- **First observation: Partial Oxidation**
  - The O_2 is totally converted and fast
  - An amount of H_2O and CO is formed

$$CH_4 + 1.5O_2 \xrightarrow{-\Delta H} 2H_2O + CO$$

- **Second observation: Steam Reforming**
  - The H_2O is consumed
  - The CH_4 is almost totally converted
  - CO_2 and H_2 are produced

$$CH_4 + 2H_2O \xrightarrow{+\Delta H} 4H_2 + CO_2$$

- **Third observation: Water Gas Shift**
  - CO and H_2O are converted into H_2 and CO_2 till the equilibrium state

$$CO + H_2O \longleftrightarrow H_2 + CO_2$$

The result trends are as expected

ENSIC

Energy Environment

Main Objectives

- The Objective is to build an isothermal reactor model.
  - The problem geometry is defined by: ✓
    - Axial symmetric geometry
    - Modeling the catalytic layer as surface using boundary weak form
  - The governing equations are defined by: ✓
    - Hydrodynamic: Poiseuille
    - Mass balance equations
    - Surface chemical reactions
  - The main simulation was run: ✓
    - For 7 gas species and 13 adsorbed species
    - Resulting in 20 mass balance equations
    - Interlinked by 42 surface chemical reactions
  - The simulator trends was evaluated by the presence of : ✓
    - Partial oxidation
    - Steam reforming to produce H_2
    - Water gas shift equilibrium

Conclusions

- To model a catalytic surface we suggest using the Boundary Weak Form application
- A simulator of an ATR monolithic reactor is now ready to use and to be improved, namely:
  - by adding hydrodynamic and thermal effects

Acknowledgements

- The authors thank :
  - ANRT for the financial support
  - COMSOL team for help

...and you for your attention