Department of Energy
&
Department of Chemistry, Materials, and Chemical Engineering

POLITECNICO DI MILANO





Matteo Maestri & Alberto Cuoci

CatalyticFOAM

Heterogeneus catalysis within OpenFOAM

HPC enabling of OpenFOAM for CFD applications

November, 26th, 2012

Outline

- ✓ Introduction and motivation
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  - ✓ Governing equations
  - ✓ Numerical methodology
- ✓ Validation and examples
  - ✓ Annular reactor (simple chemistry)
  - ✓ CPO of CH_4 on platinum gauze (complex 3D geometry)
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
- ✓ Extensions
  - ✓ KMC (Kinetic Monte Carlo)
  - ✓ Multi-region solver
- ✓ Conclusions and future works

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Chemical reactor engineering

Catalytic reactor design:

- ✓ Important in chemical industry (~90% of industrial chemical processes are catalytic)
- ✓ Need for an accurate design to provide high yields (€)
- ✓ Need for a deep understanding for advanced design

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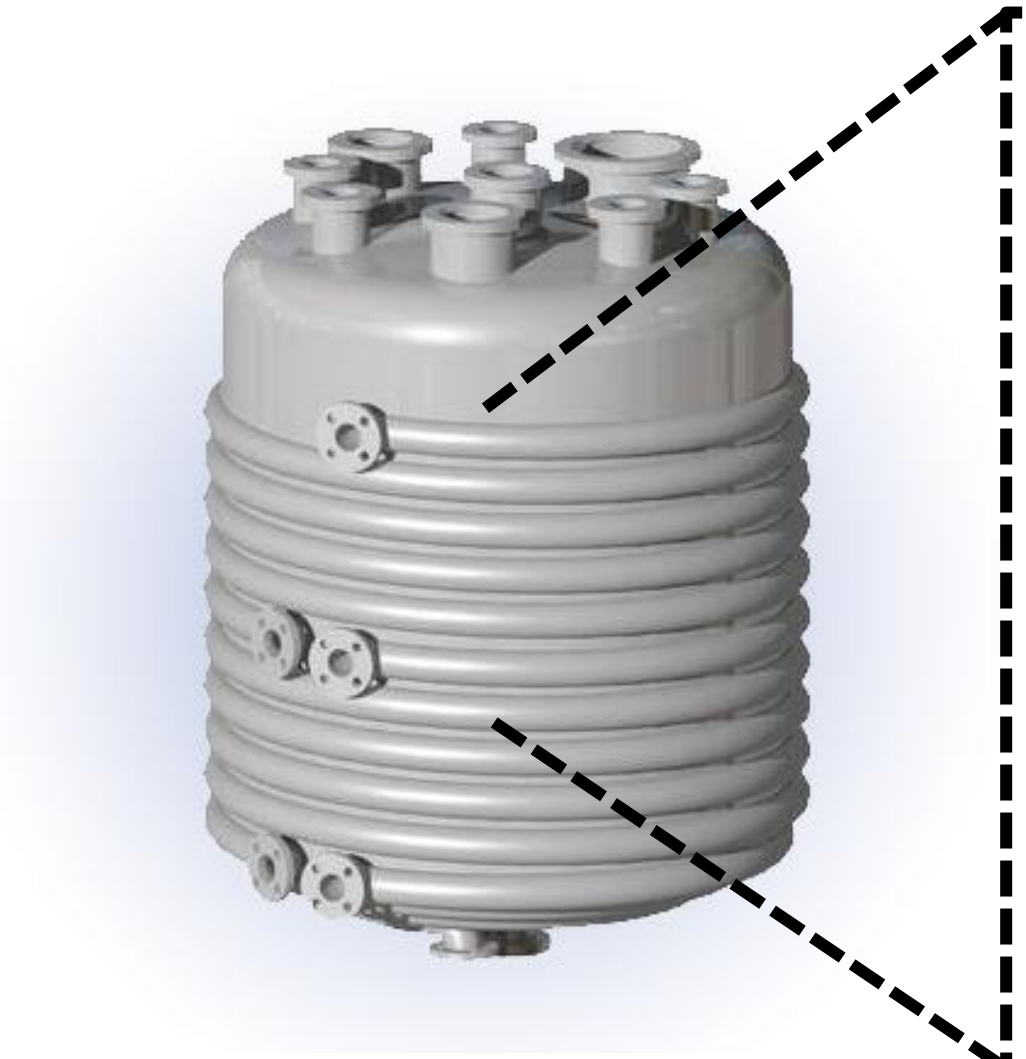

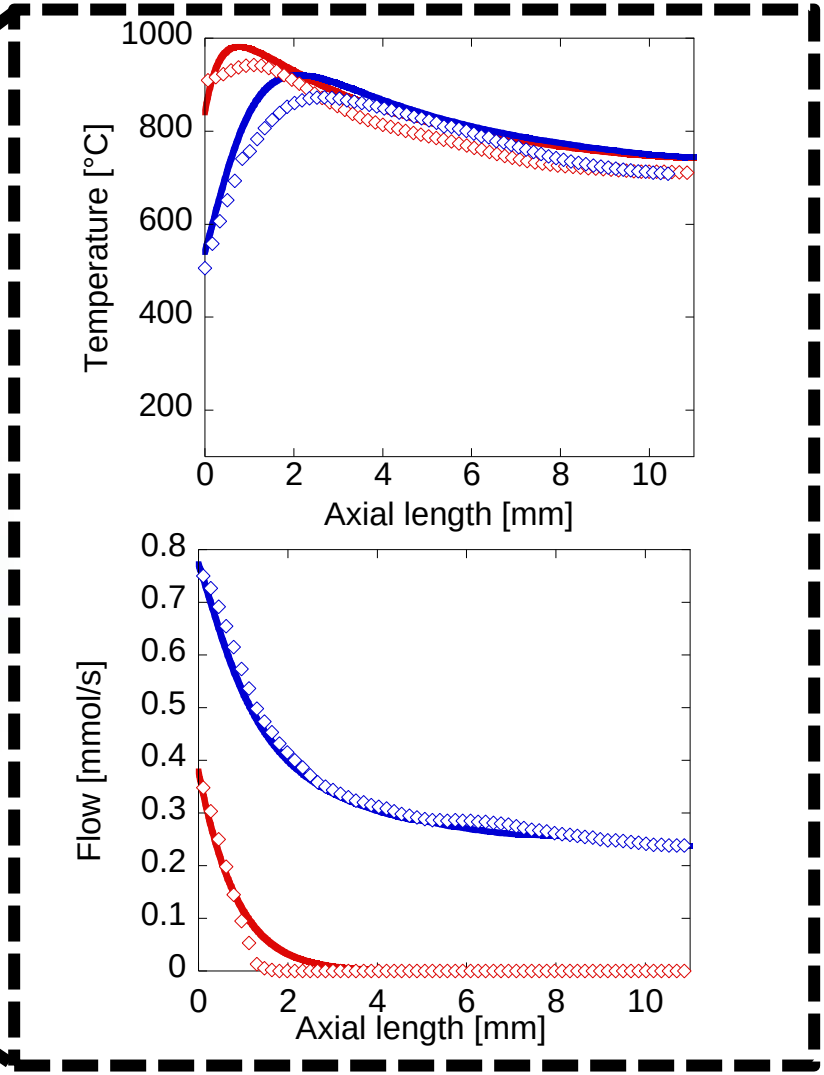

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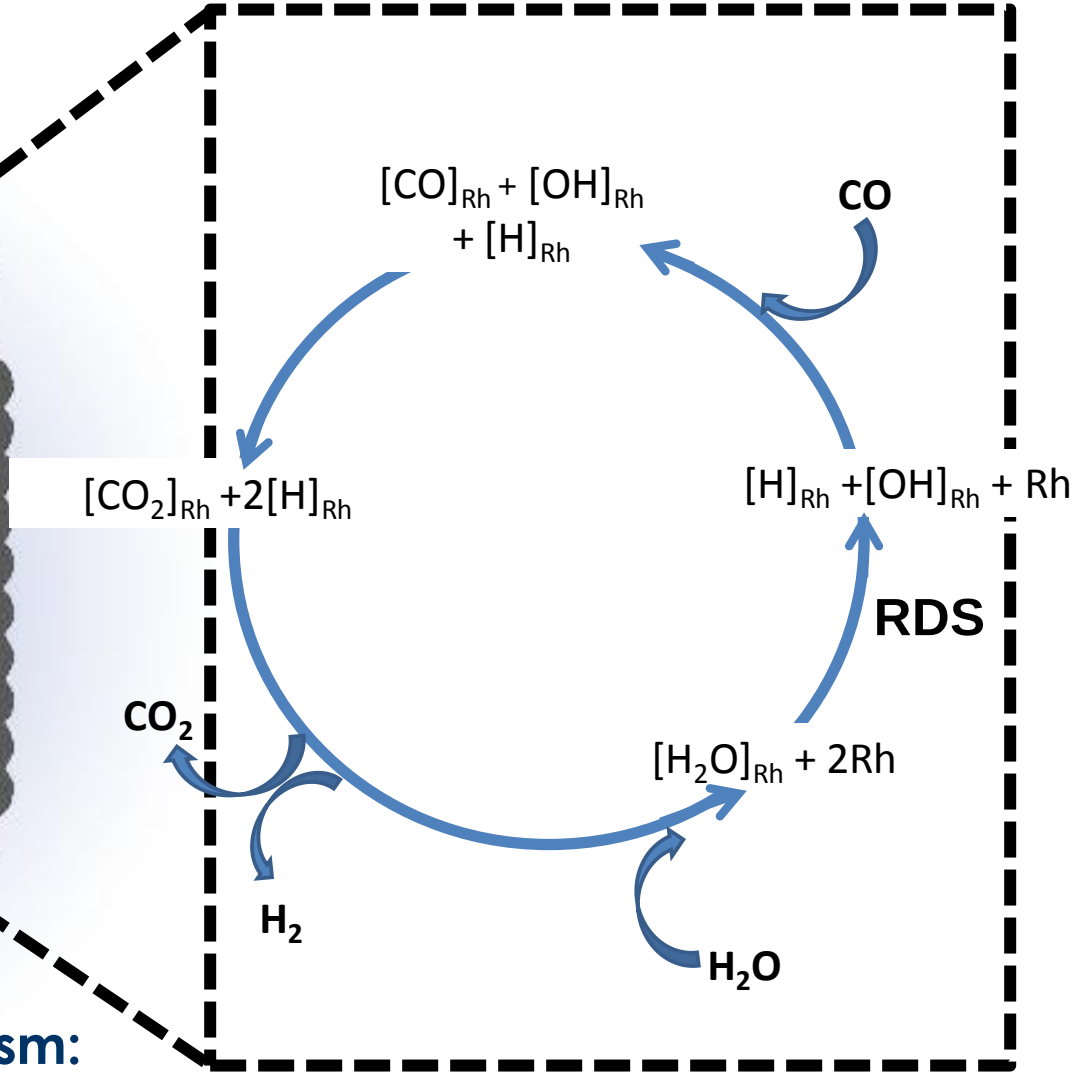

Dominant reaction mechanism: understanding & design

(*) *Microkinetic analysis of complex chemical processes at surfaces*
M. Maestri – in "New strategy for chemical synthesis and catalysis" Wiley, 2011

A multiscale phenomenon

Result of the interplay among phenomena at different scales

Microscale

$COOH^*+^* \rightarrow CO^*+OH^*$
$CO^*+OH^* \rightarrow COOH^*+^*$
$COOH^*+^* \rightarrow CO_2^*+H^*$
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$CH^* + H^* \rightarrow CH_2^* + ^*$
$CH^* + ^* \rightarrow C^* + H^*$
$C^* + H^* \rightarrow CH^* + ^*$
$CH_3^* + O^* \rightarrow CH_2^* + OH^*$
$CH_2^* + OH^* \rightarrow CH_3^* + O^*$
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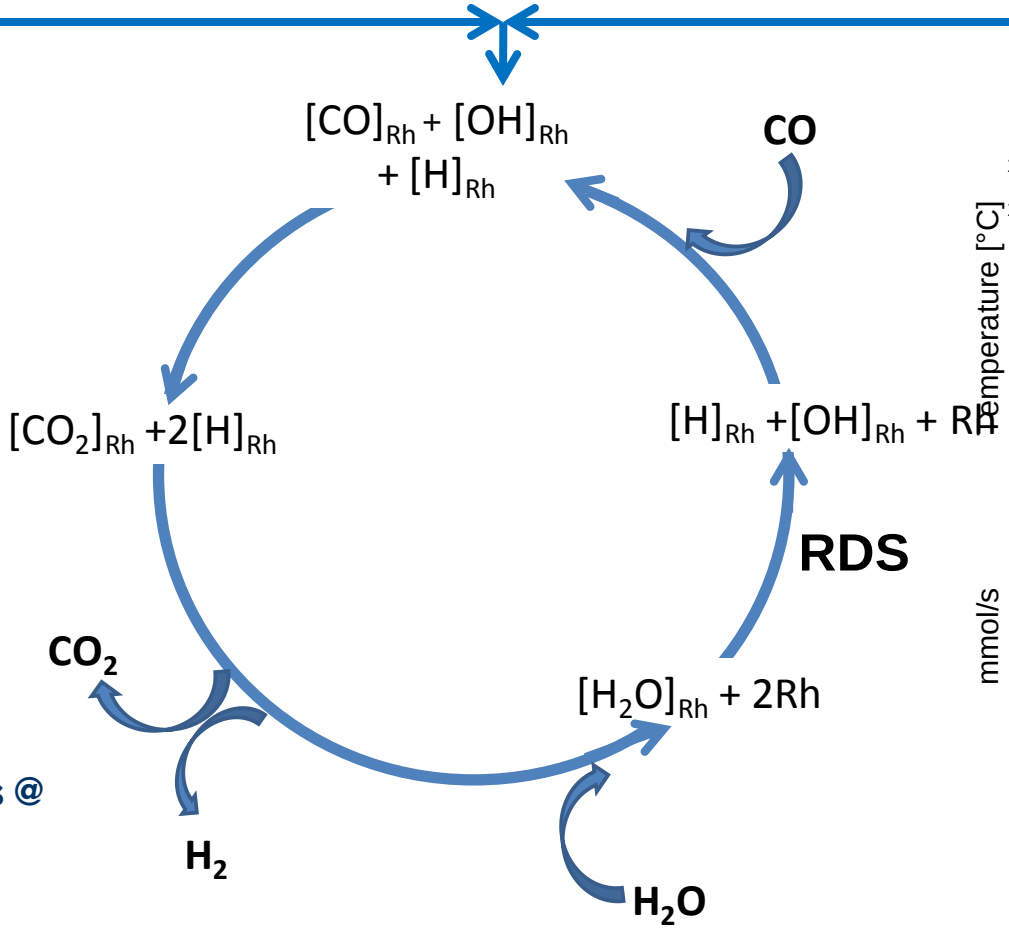
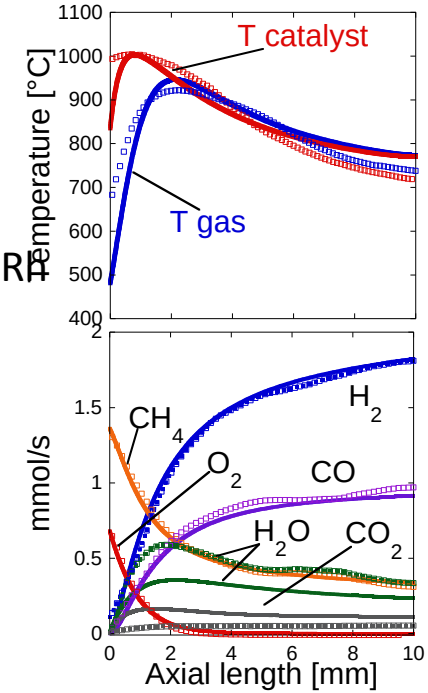
...

~ 10^2 potential steps @ different coverages



Macroscale



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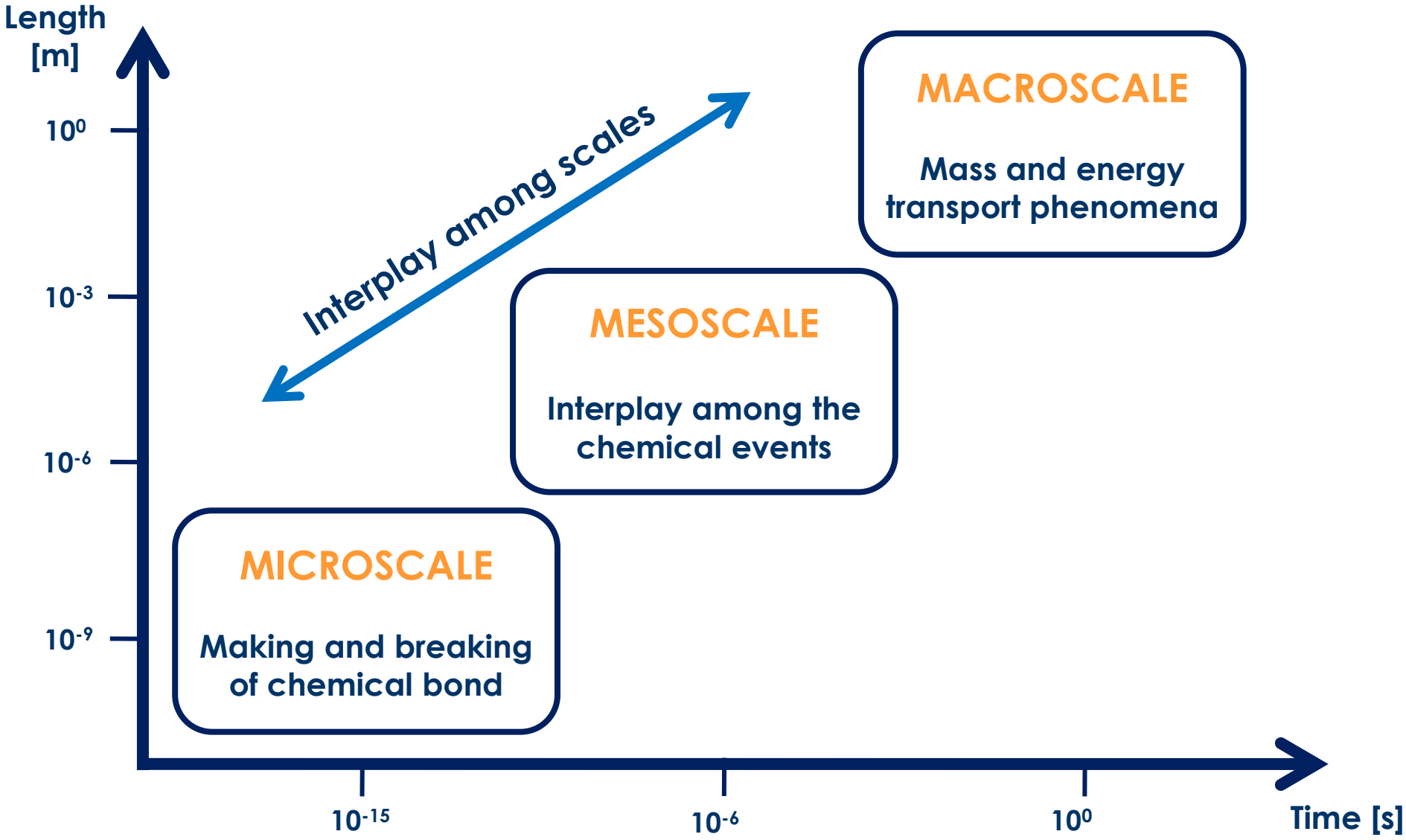

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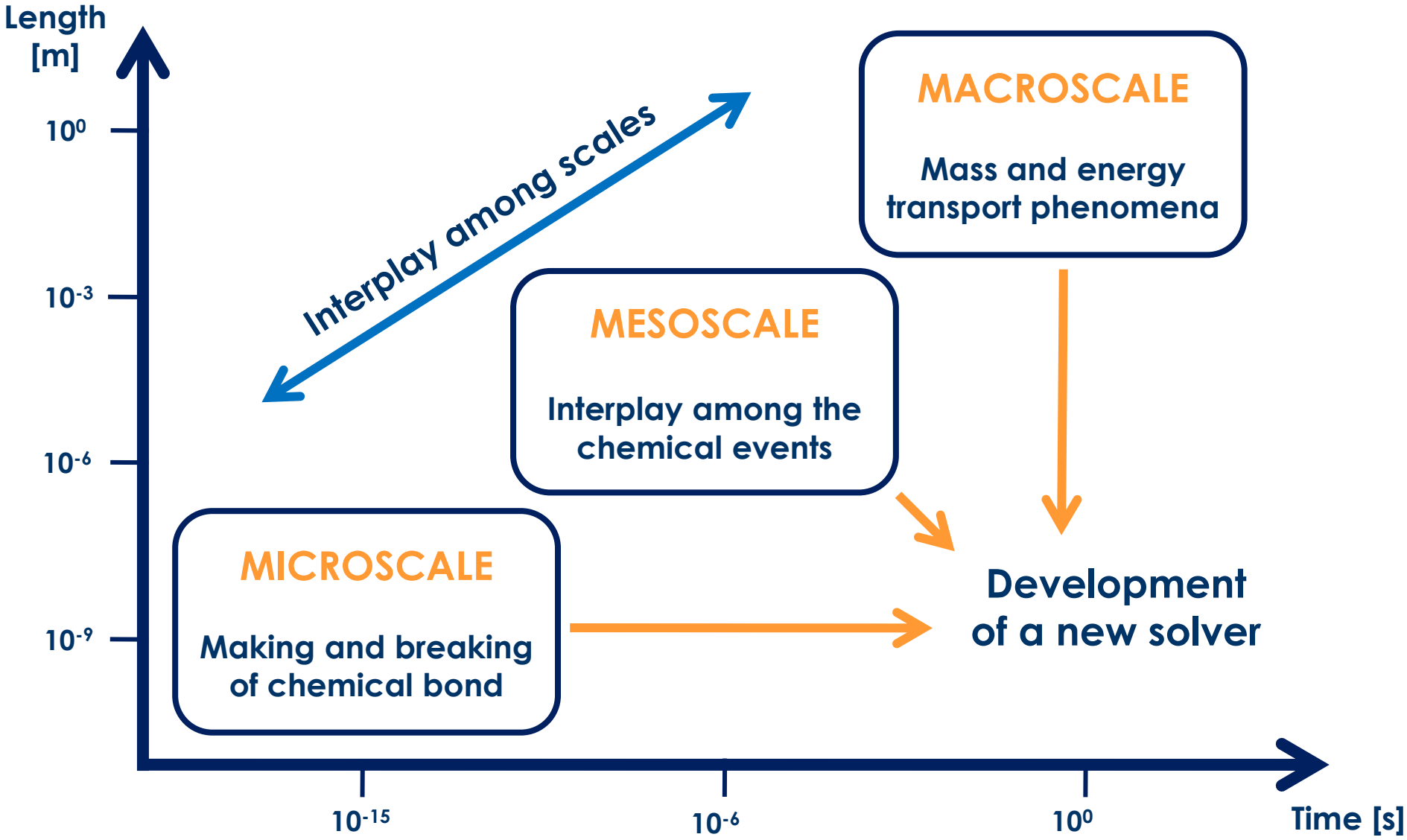
Need of tools for analysis



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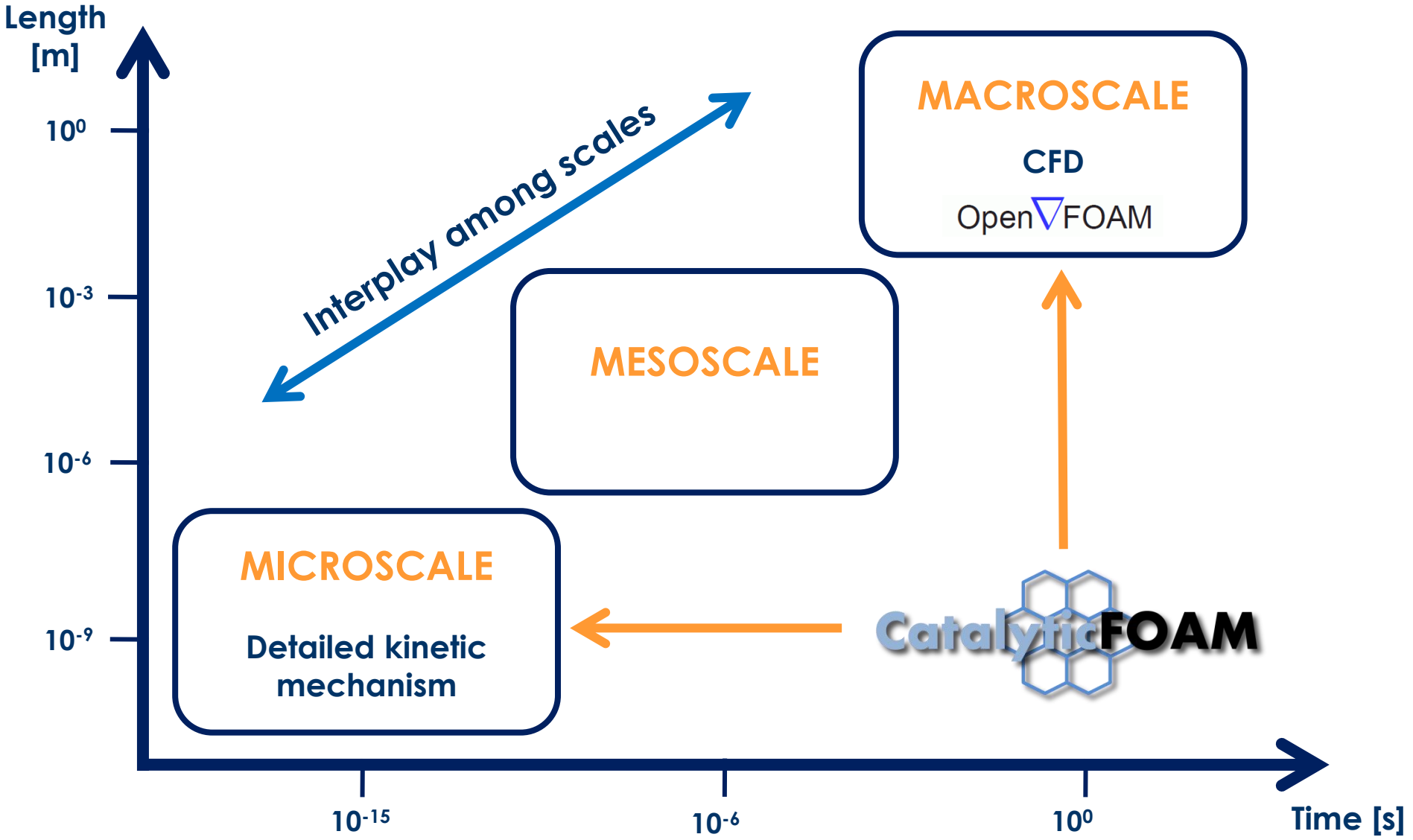

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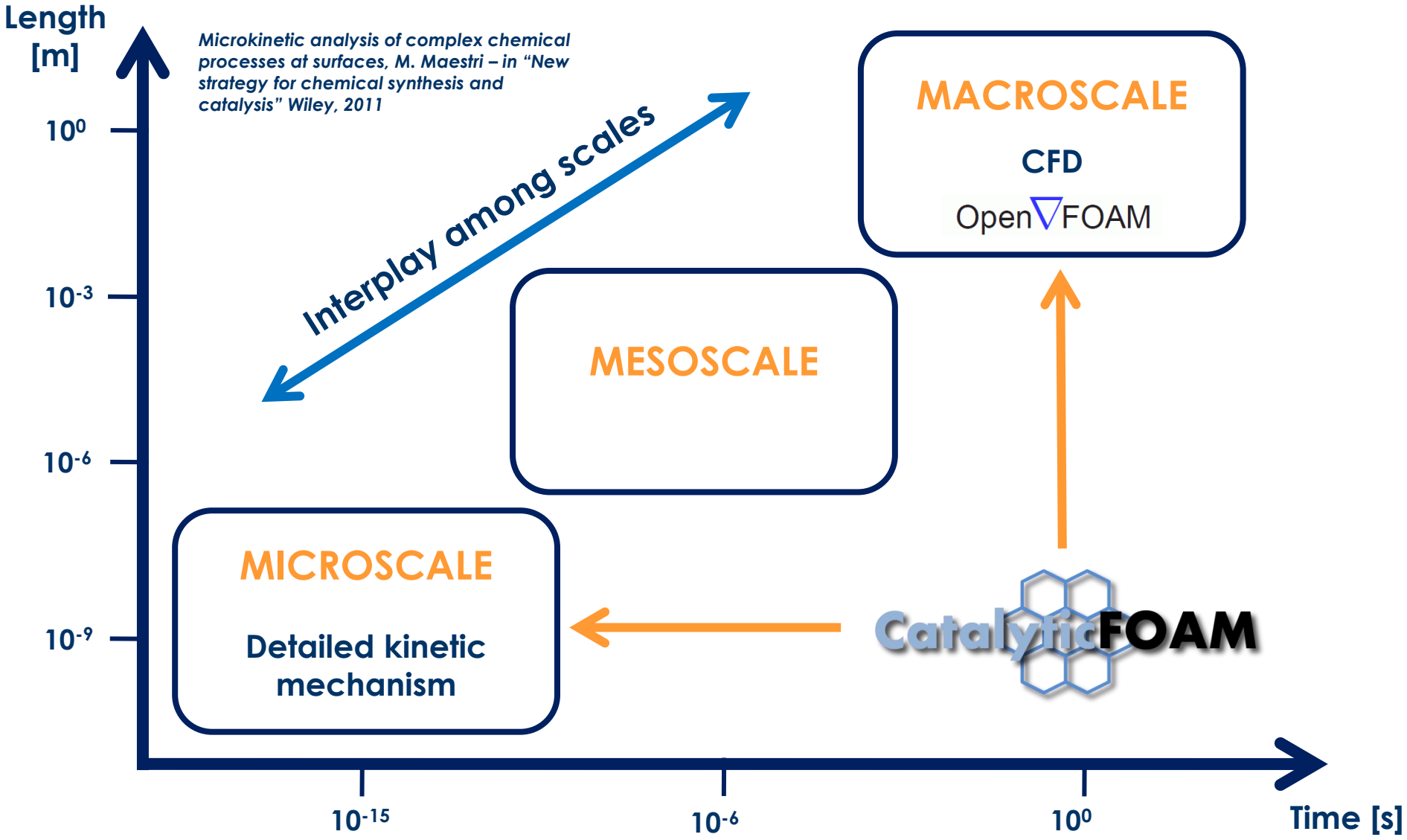
A “first principles” approach to CRE



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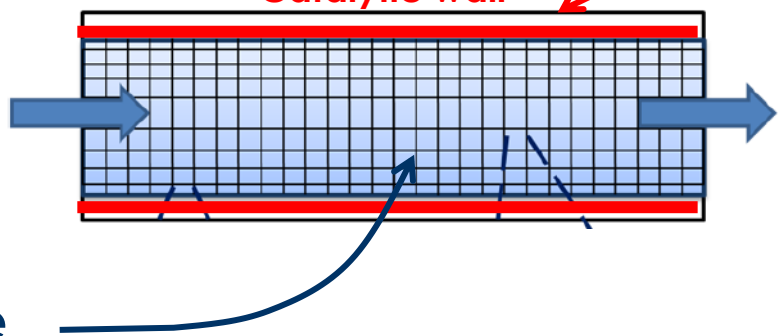
Governing equations



Catalytic walls

$$\sigma_{cat}\frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{het} \qquad i = 1,\ldots,NS$$

Adsorbed (surface) species

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$ **continuity**

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v}\mathbf{v}) = -\nabla p + \nabla \cdot \left[\mu\left(\nabla \mathbf{v} + \nabla \mathbf{v}^T\right) - \frac{2}{3}\mu(\nabla \mathbf{v})\mathbf{I} \right] + \rho \mathbf{g}$$ **momentum**

$$\frac{\partial}{\partial t}(\rho \omega_k) + \nabla \cdot (\rho \omega_k \mathbf{v}) = -\nabla \cdot (\rho \omega_k \mathbf{V}_k) + \dot{\Omega}_k^{\text{hom}} \qquad k = 1,\ldots,NG$$ **gas-phase species**

$$\rho \hat{C}_P \frac{\partial T}{\partial t} + \rho \hat{C}_P \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{P,k} \omega_k \mathbf{V}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}}$$ **gas-phase energy**

Boundary conditions

Non-catalytic walls

$$\nabla \omega_k\big|_{inert} = 0$$

$$T\big|_{inert} = f(t,T)$$

$$\nabla T\big|_{inert} = g(t,T)$$

Catalytic walls

$$\rho \Gamma_{k,mix} (\nabla \omega_k)\big|_{catalytic} = -\alpha_{cat} \dot{\Omega}_k^{het} \qquad k = 1,\ldots,NG$$

$$\lambda (\nabla T)\big|_{catalytic} = -\alpha_{cat} \sum_{j=1}^{NR} \Delta H_j^{het} \dot{r}_j^{het}$$

$$\sigma_{cat} \frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{het} \qquad i = 1,\ldots,NS$$

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Detailed microkinetic models

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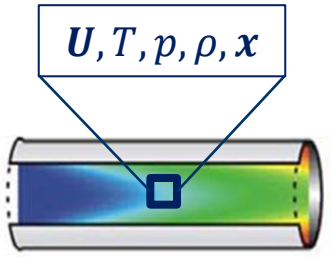
$$r_j = A_j \cdot T^{\beta_j} \cdot \exp\left(-\frac{E_{att,j}(\theta_i)}{RT}\right) \prod_{i=1}^{NC} (c_i)^{\nu_{ij}}$$

Numerical challenges



- ✓ **Dimensions of the system**
  - **Proportional to the number of species**
  - **Proportional to the number of cells**

Numerical challenges

- ✓ **Dimensions of the system**
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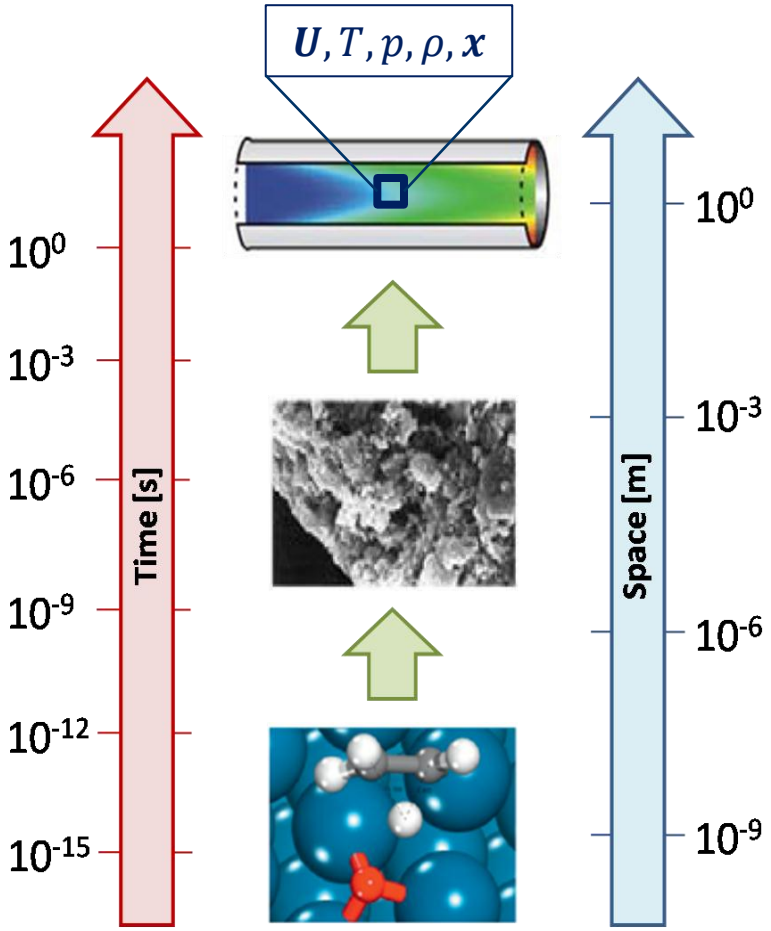
- ✓ **Stiffness**
  - Different temporal scales involved
  - Different spatial scales involved



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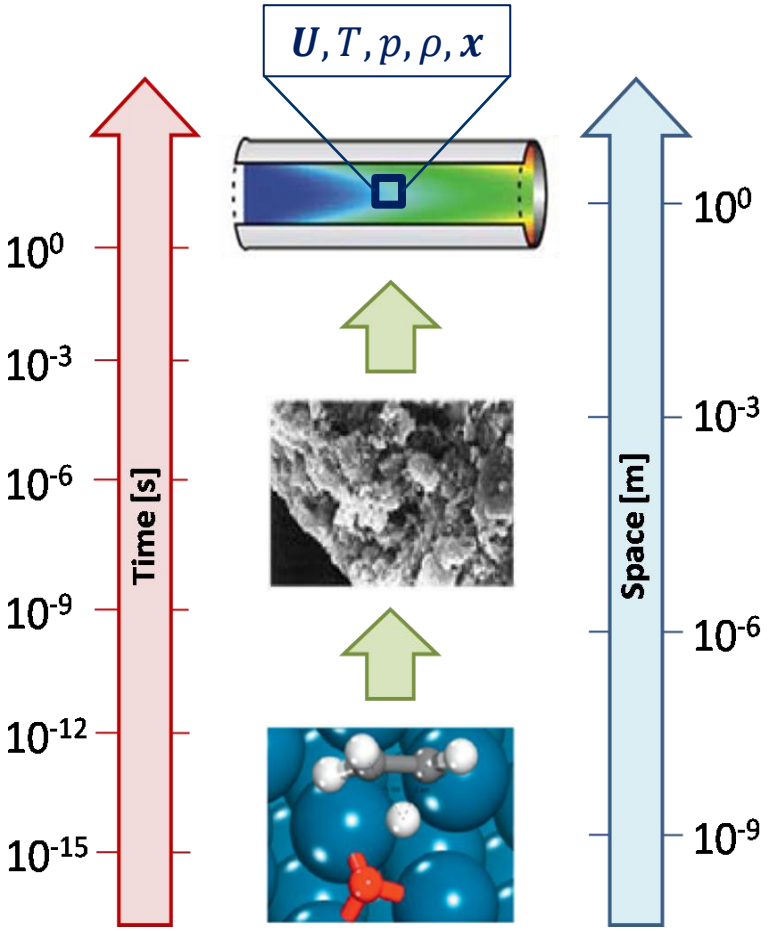
- ✓ **Non-linearity**
  - Source term non linear in concentrations and temperature
  - Coverage dependence of activation energy



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OpenFOAM

segregated approaches are not feasible

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Numerical solution

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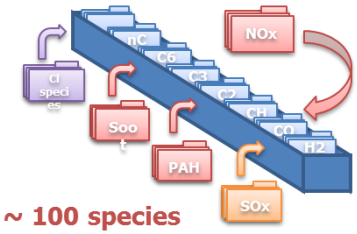
Fully segregated algorithms

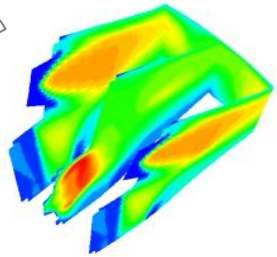
☺ easy to implement and computationally efficient
☹ unfeasible when large, stiff kinetic mechanisms are used

Detailed kinetic schemes



~ 100 species
~ 1000 reactions

Complex geometries



Strong non linearity of reaction terms
High stiffness

Fully coupled algorithms

☺ all the processes and their interactions are considered simultaneously
☺ natural way to treat problems with multiple stiff processes
☹ the resulting system of equations can be extremely large and the computational cost prohibitive

Operator-splitting methods

☺ usually avoid many costly matrix operations
☺ allow the best numerical method to be used for each type of term or process
☹ the resulting algorithms can be very complex and usually differ from term to term

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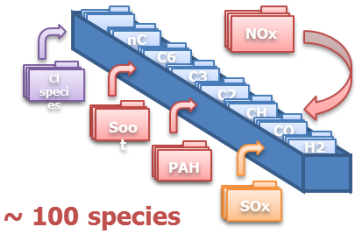

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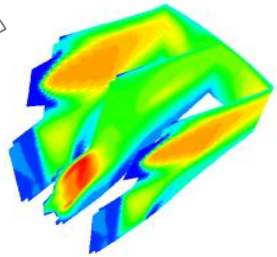

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catalyticFOAM

Operator-splitting algorithm

Stiff reaction terms

PDE

$$\begin{cases} \dfrac{\partial}{\partial t}(\rho\omega_k) = -\nabla\cdot(\rho\omega_k\mathbf{v}) - \nabla\cdot(\rho\omega_k\mathbf{V}_k) + \dot{\Omega}_k^{hom} & k = 1,\ldots,NG \\ \rho\hat{C}_P\dfrac{\partial T}{\partial t} = -\rho\hat{C}_P\mathbf{v}\nabla T + \nabla\cdot(\lambda\nabla T) - \rho\sum_{k=1}^{NG}\hat{C}_{P,k}\omega_k\mathbf{V}_k - \sum_{k=1}^{NG}\hat{H}_k^{hom}\dot{\Omega}_k^{hom} & \\ \sigma_{cat}\dfrac{\partial\theta_i}{\partial t} = \dot{\Omega}_i^{het} & i = 1,\ldots,NS \end{cases}$$

gas-phase species

gas-phase energy

adsorbed (surface) species

Finite volume discretization

After spatial discretization, the original PDE systems is transformed into an ODE system

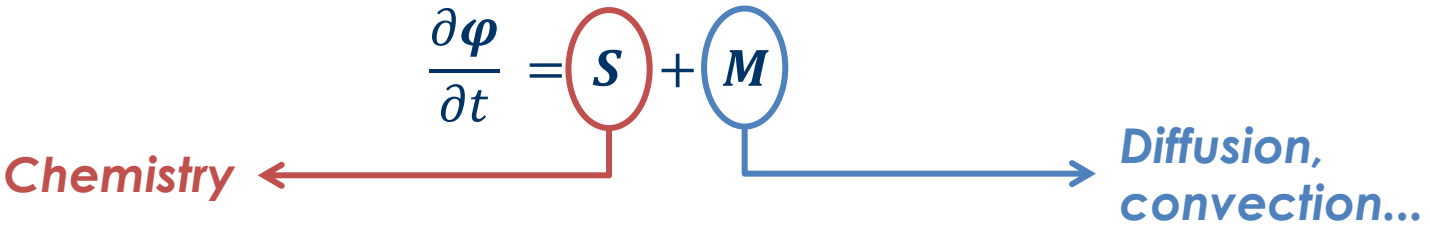
ODE

$$\begin{cases} \dfrac{\partial\omega_k}{\partial t} = M_k + S_k & k = 1,\ldots,NG \\ \dfrac{\partial T}{\partial t} = M^T + S^T & \\ \dfrac{\partial\theta_i}{\partial t} = S_i^{het} & i = 1,\ldots,NS \end{cases}$$

S = terms associated to the stiff processes (homogeneous and heterogeneous reactions)

M = terms involving transport processes (convection and diffusion), non stiff and weakly non linear

Strang splitting (I)



Strang splitting (I)

$$\frac{\partial \varphi}{\partial t} = S + M$$

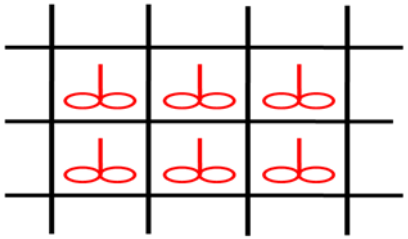
Chemistry

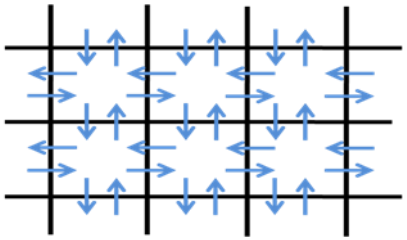
Diffusion, convection...

Strang splitting scheme

Chemical step

$$\frac{\partial \varphi}{\partial t} = S$$





$$\frac{\partial \varphi}{\partial t} = M$$

Transport step

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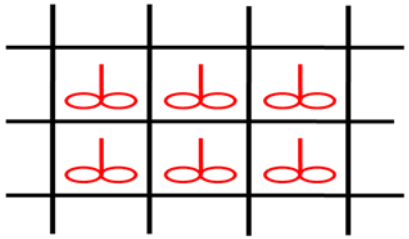

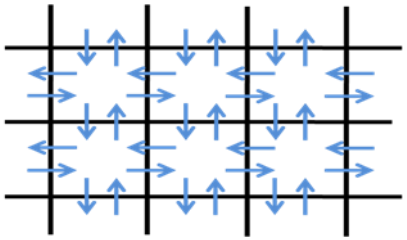

$$\frac{\partial \varphi}{\partial t} = M$$

Transport step

Strang splitting (II)

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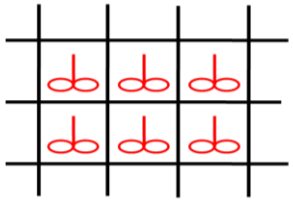
Chemistry

Diffusion, convection...

Chemistry



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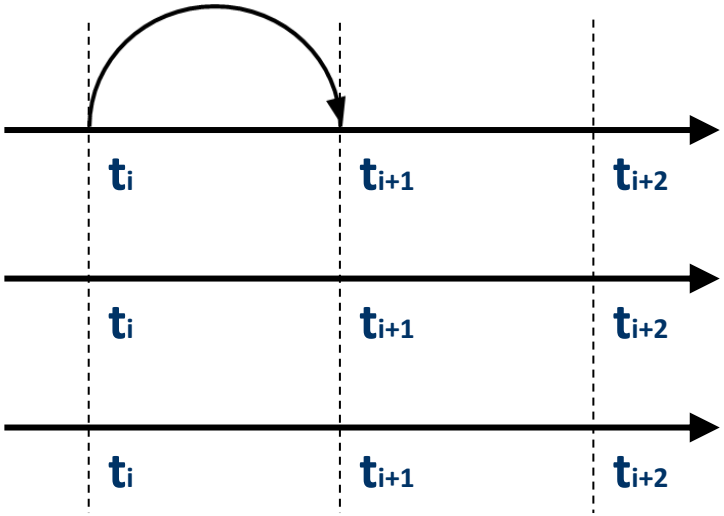

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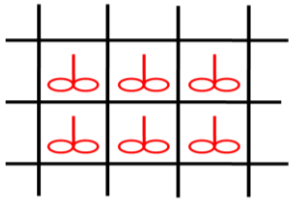

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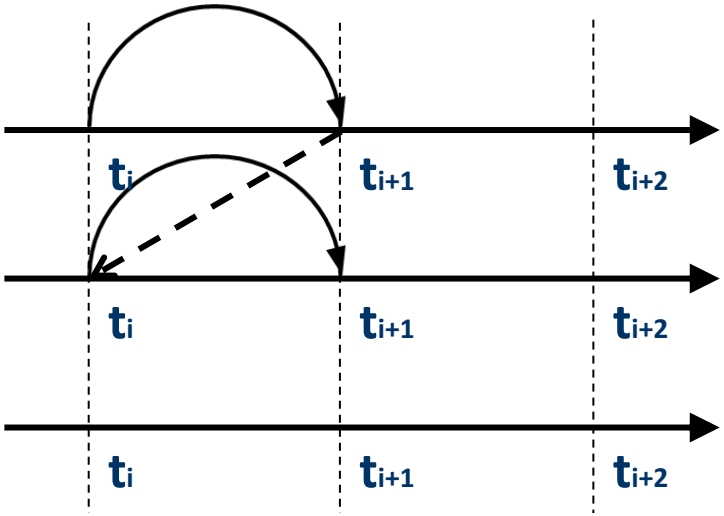

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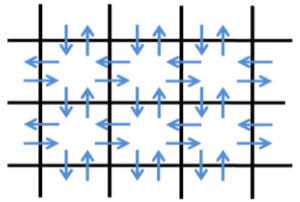

Transport

Strang splitting (II)

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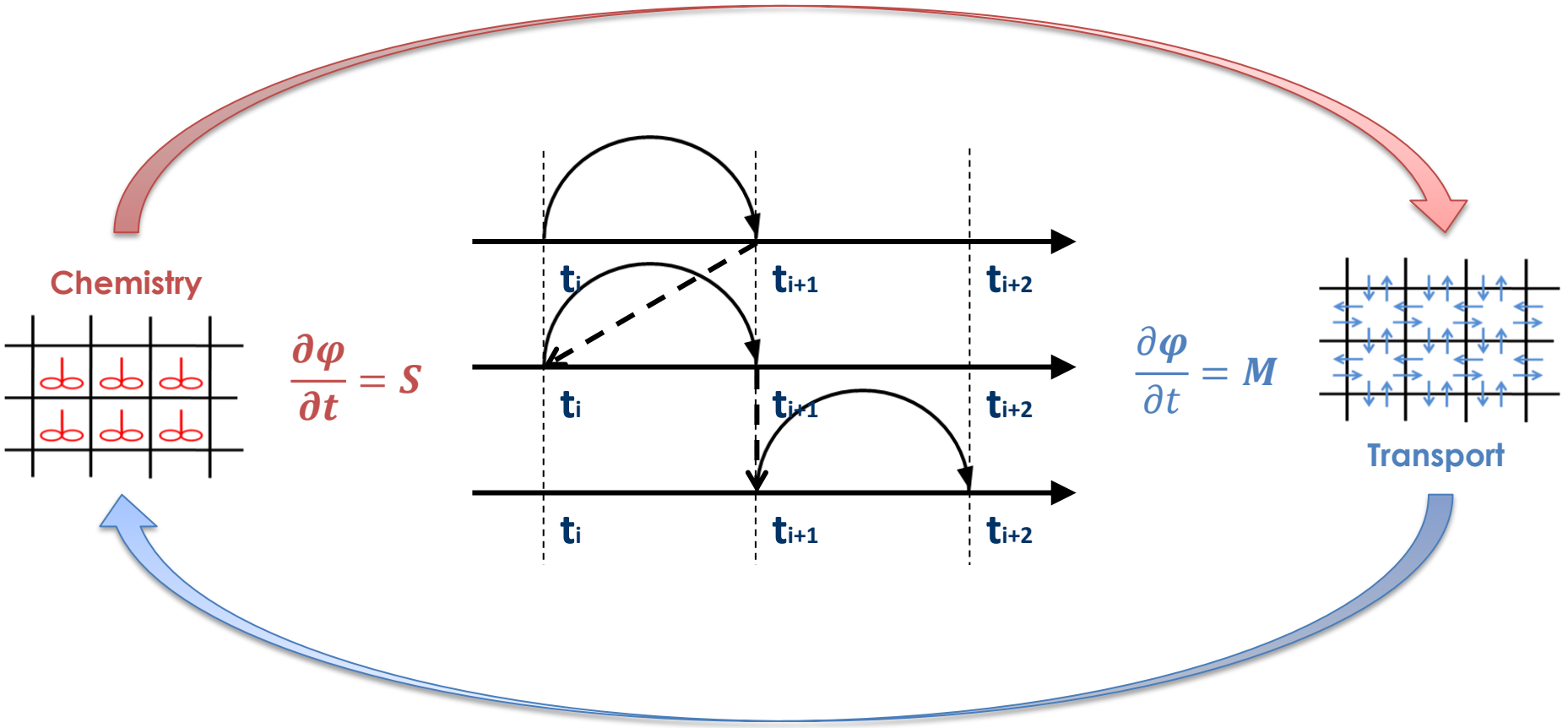
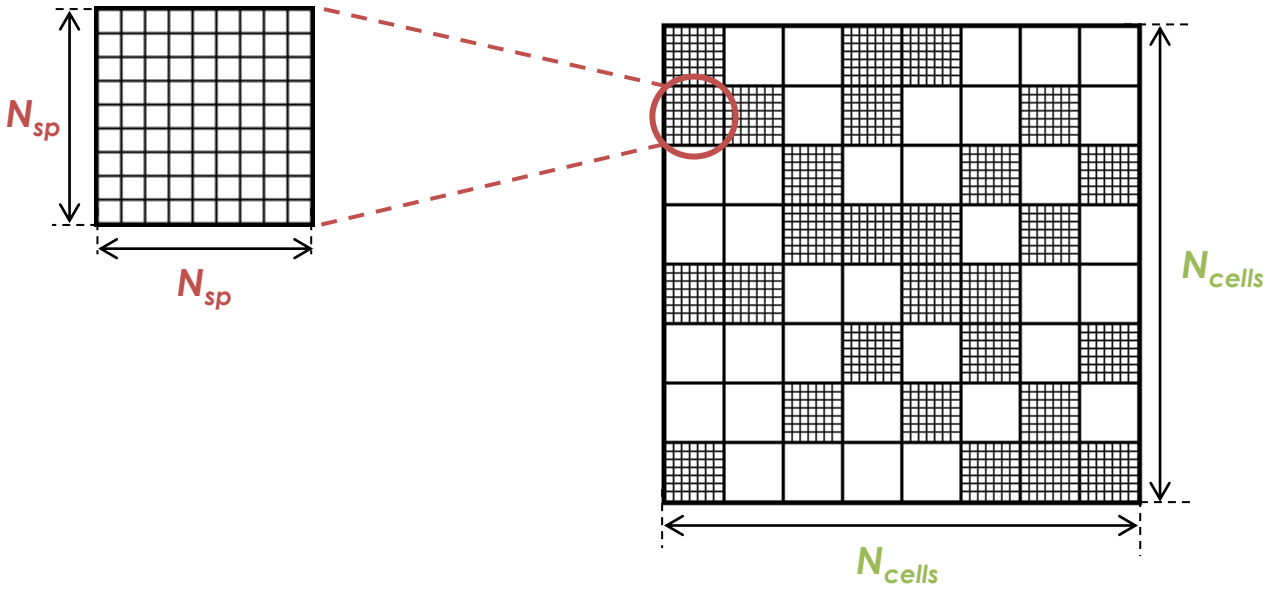
Chemistry

Diffusion, convection...



Operator splitting algorithm (I)



$$\frac{\partial \varphi}{\partial t} = M + S$$

Jacobian matrix:

- ✓ Sparse
- ✓ Unstructured
- ✓ Blocks

Operator splitting algorithm (II)

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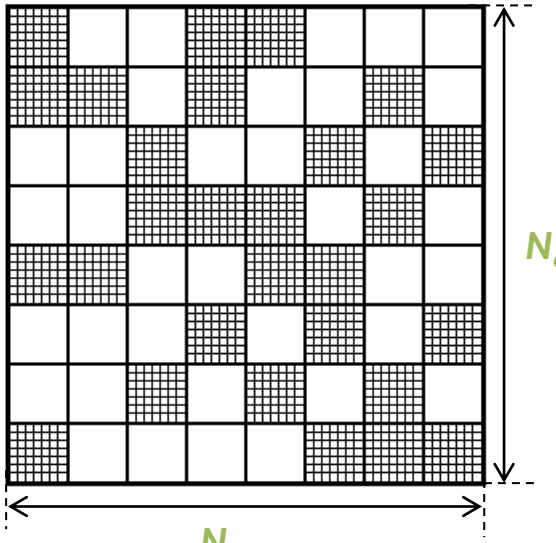
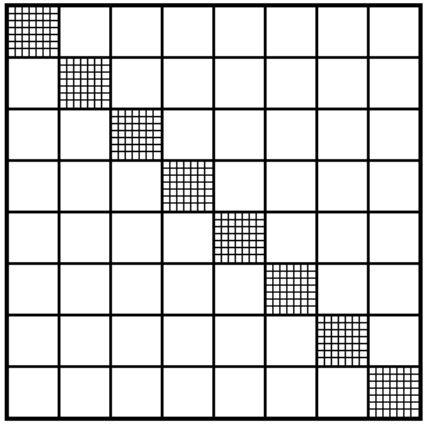
Global system



$$\frac{\partial \varphi}{\partial t} = M + S$$

Source term



$$\frac{\partial \varphi}{\partial t} = S$$

Jacobian matrix:

- ✓ Sparse
- ✓ Diagonal
- ✓ Blocks

Operator splitting algorithm (III)

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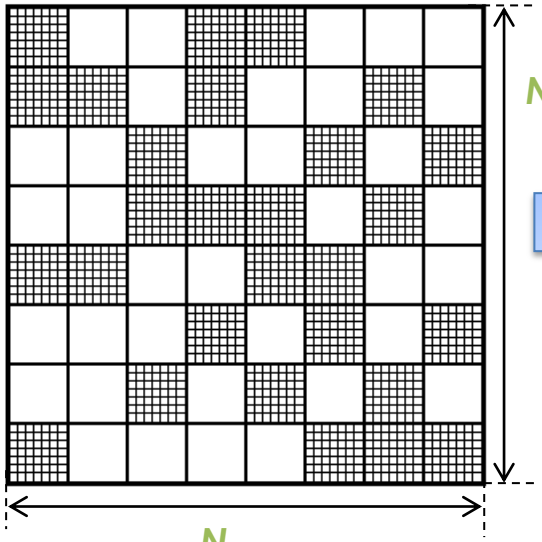
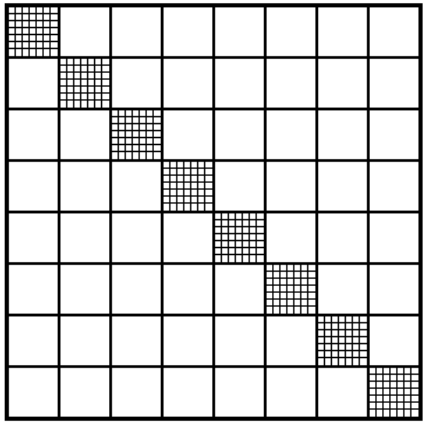
Global system



$$\frac{\partial \varphi}{\partial t} = M + S$$

Source term

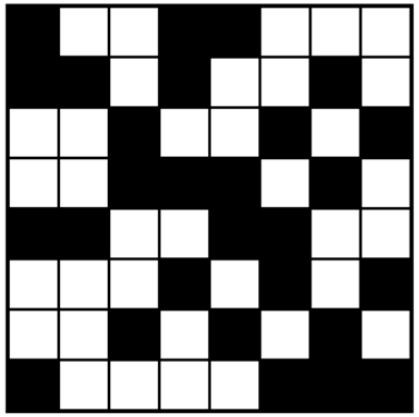


$$\frac{\partial \varphi}{\partial t} = S$$

Jacobian matrices:

- ✓ Sparse
- ✓ Unstructured

Transport term



$$\frac{\partial \varphi}{\partial t} = M$$

Operator splitting algorithm (IV)

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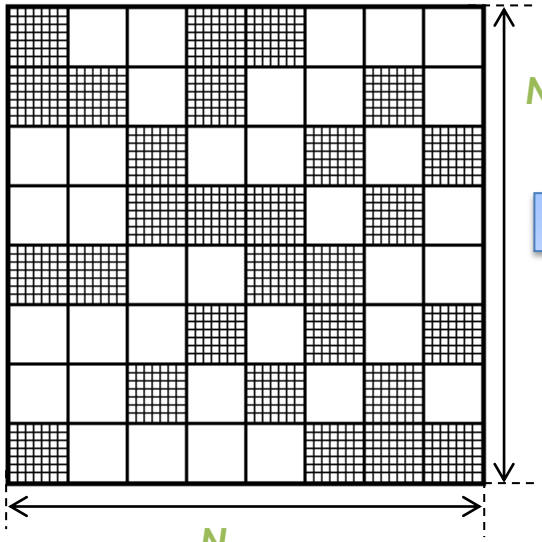
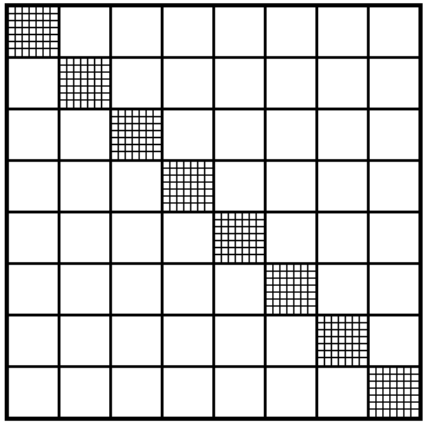
Global system



$$\frac{\partial \varphi}{\partial t} = M + S$$

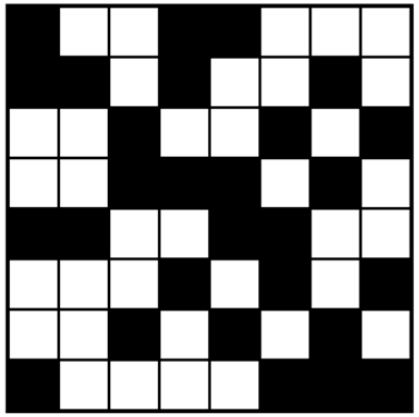
Source term



$$\frac{\partial \varphi}{\partial t} = S$$

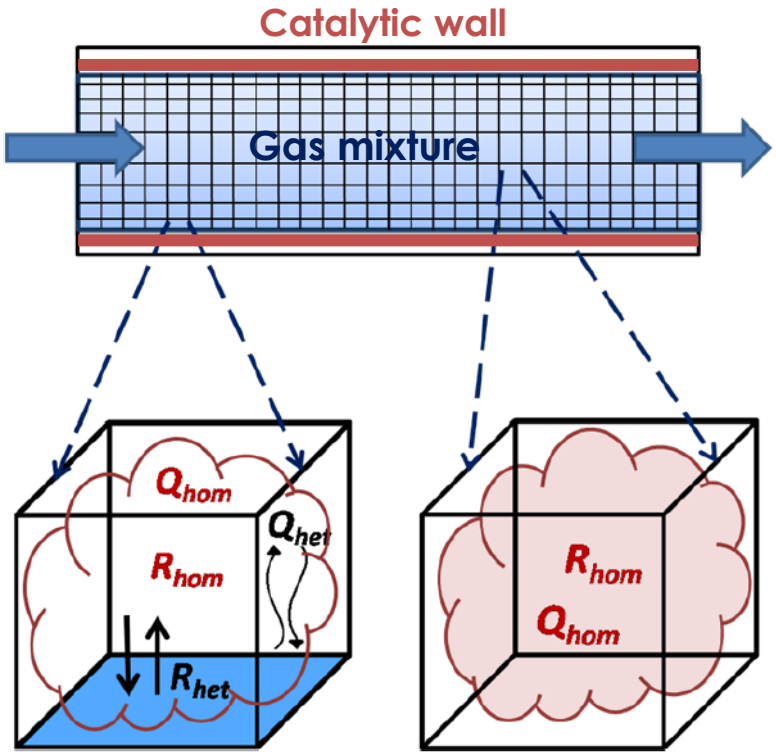
Using a suitable algorithm for each sub-problem

Transport term



$$\frac{\partial \varphi}{\partial t} = M$$

Reactor network



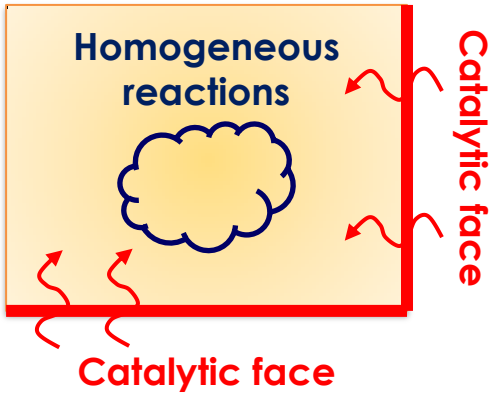
Semi-batch reactor

Batch reactor

Each computational cell behaves as a chemical reactor in the splitting-operator algorithm (chemical step)

Each reactor is described by a set of stiff ODE, which must be integrated on the time step Δt

Heterogeneous reactors



NF = number of catalytic faces

NG = number of gas-phase species

NS = number of adsorbed (surface) species

Equations: $N = NG + 1 + NF \cdot NS$

Semi-batch reactor

$$\begin{cases} \rho \dfrac{d\omega_k}{dt} = \dot{\Omega}_k^{hom} + \dfrac{1}{V}\left\{ \sum_{j=1}^{NF} \alpha_j^{cat} A_j \dot{\Omega}_{k,j}^{het} - \omega_k \sum_{j=1}^{NF} \left[\alpha_j^{cat} A_j \sum_{k=1}^{NG} \dot{\Omega}_{k,j}^{het} \right] \right\} & k=1,\ldots,NG \quad \text{Gas-phase species} \\ \rho \hat{C}_P \dfrac{dT}{dt} = -\sum_{k=1}^{NG} \hat{H}_k^{hom} \dot{\Omega}_k^{hom} - \sum_{k=1}^{NS} \hat{H}_k^{het} \Omega_k^{het} & \text{Gas-phase temperature} \\ \sigma_{cat} \dfrac{\partial \theta_{i,j}}{\partial t} = \dot{\Omega}_{i,j}^{het} & i=1,\ldots,NS \quad j=1,\ldots,NF \quad \text{Adsorbed species} \end{cases}$$

Homogeneous reactors

Homogeneous reactions

~~NF = number of catalytic faces~~

NG = number of gas-phase species

~~NS = number of adsorbed (surface) species~~

Unknowns N = NG + 1 + ~~NF·NS~~

Batch reactor

$$\begin{cases} \rho \dfrac{d\omega_k}{dt} = \dot{\Omega}_k^{hom} + \dfrac{1}{V}\left\{ \sum_{j=1}^{NF} \alpha_j^{cat} A_j \dot{\Omega}_{k,j}^{het} - \omega_k \sum_{j=1}^{NF} \left[\alpha_j^{cat} A_j \sum_{k=1}^{NG} \dot{\Omega}_{k,j}^{het} \right] \right\} & k=1,\dots,NG \\ \rho \hat{C}_P \dfrac{dT}{dt} = -\sum_{k=1}^{NG} \hat{H}_k^{hom} \dot{\Omega}_k^{hom} - \sum_{k=1}^{NS} \hat{H}_k^{het} \dot{\Omega}_k^{het} & \\ \sigma_{cat} \dfrac{\partial \theta_{i,j}}{\partial t} = \dot{\Omega}_{i,j}^{het} & i=1,\dots,NS \quad j=1,\dots,NF \end{cases}$$

Gas-phase species

Gas-phase temperature

Adsorbed species

catalyticFOAM structure

catalyticFOAM structure

- ✓ Implementation of detailed reaction mechanisms for surface kinetics
- ✓ Heterogeneous kinetic models: CHEMKIN®format, UBI-QEP framework

catalyticFOAM structure

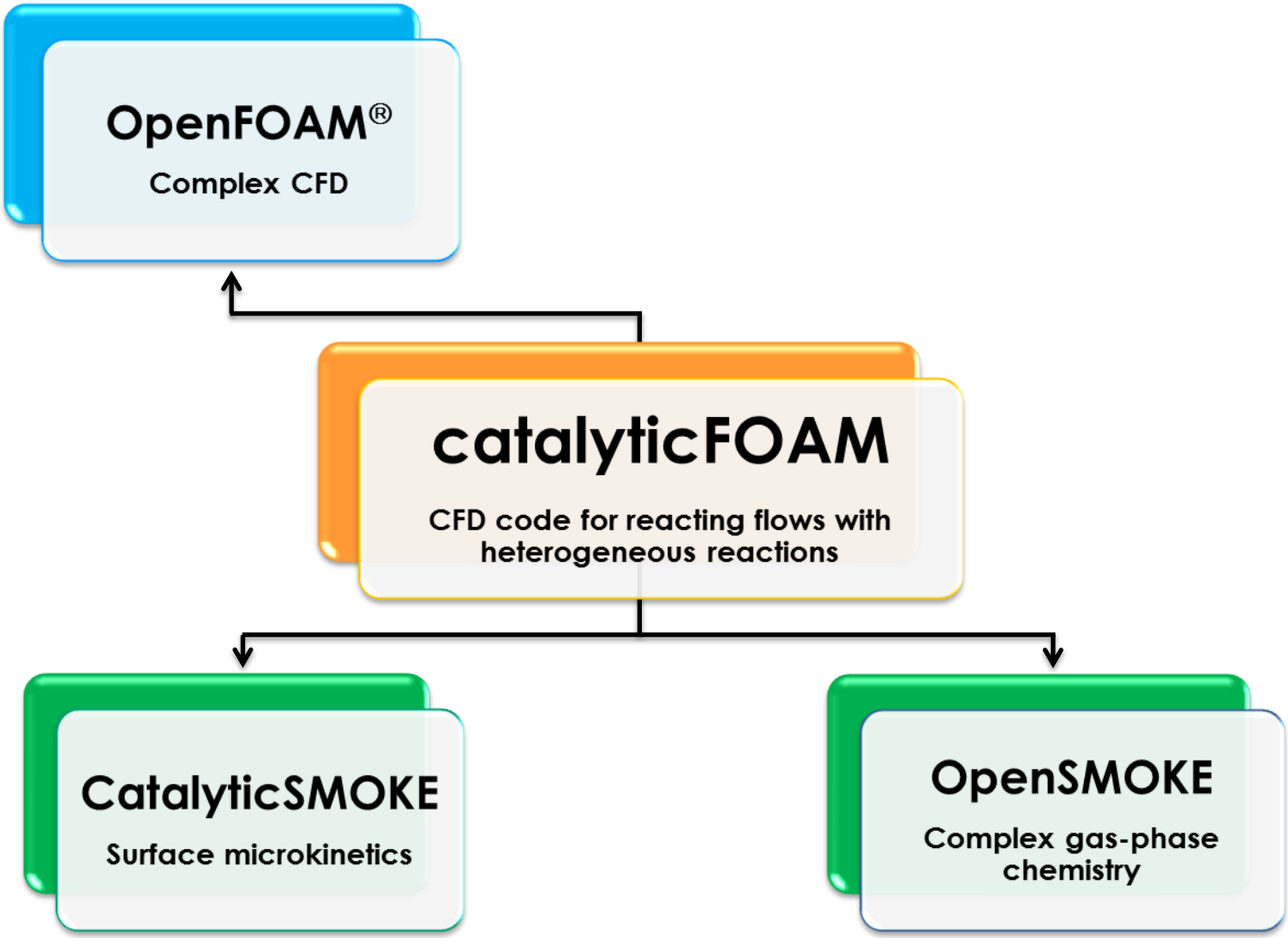
OpenFOAM®
Complex CFD

- ✓ Implementation of detailed reaction mechanisms for surface kinetics
- ✓ Heterogeneous kinetic models: CHEMKIN®format, UBI-QEP framework

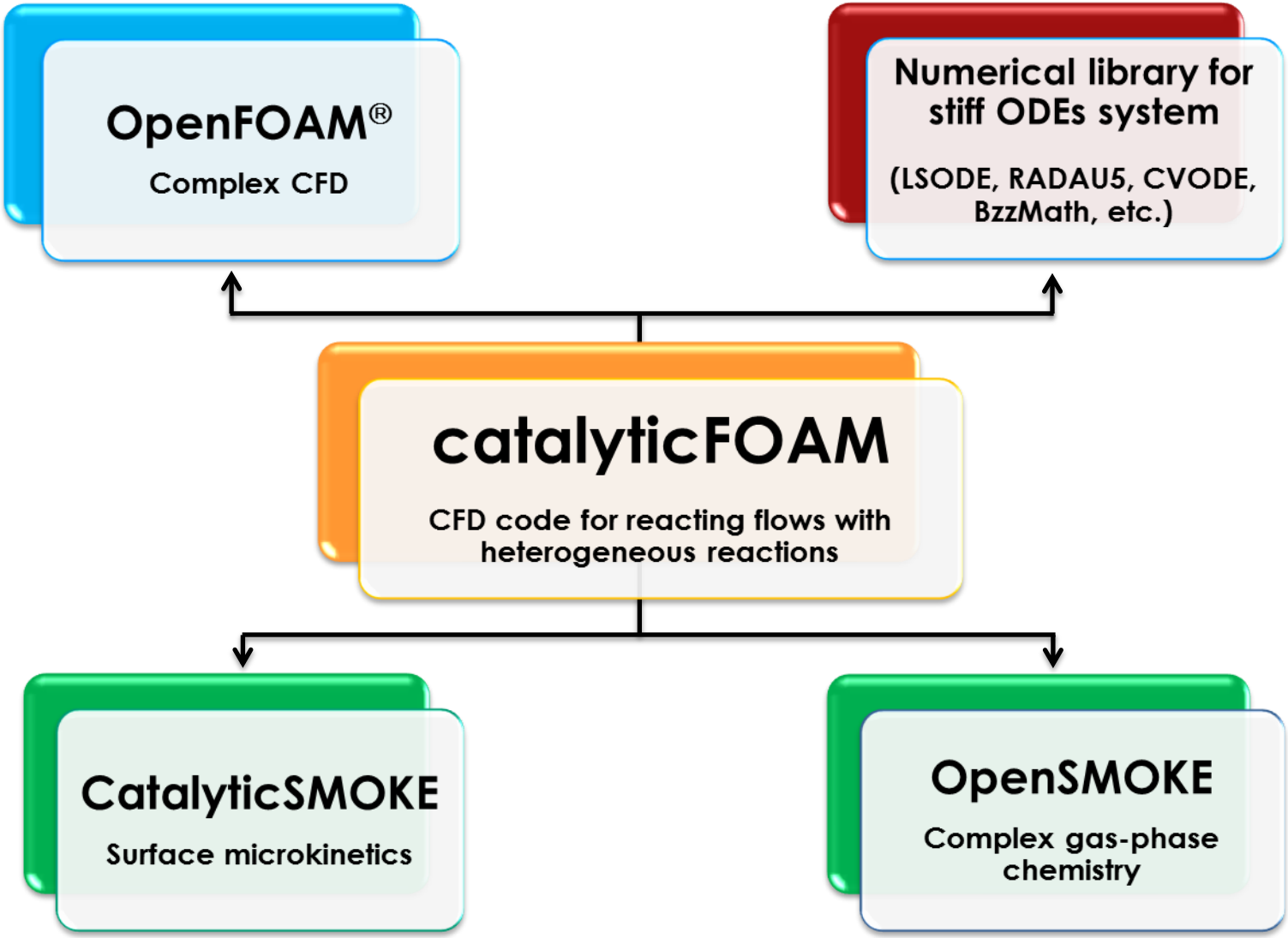
CatalyticSMOKE
Surface microkinetics

OpenSMOKE
Complex gas-phase chemistry

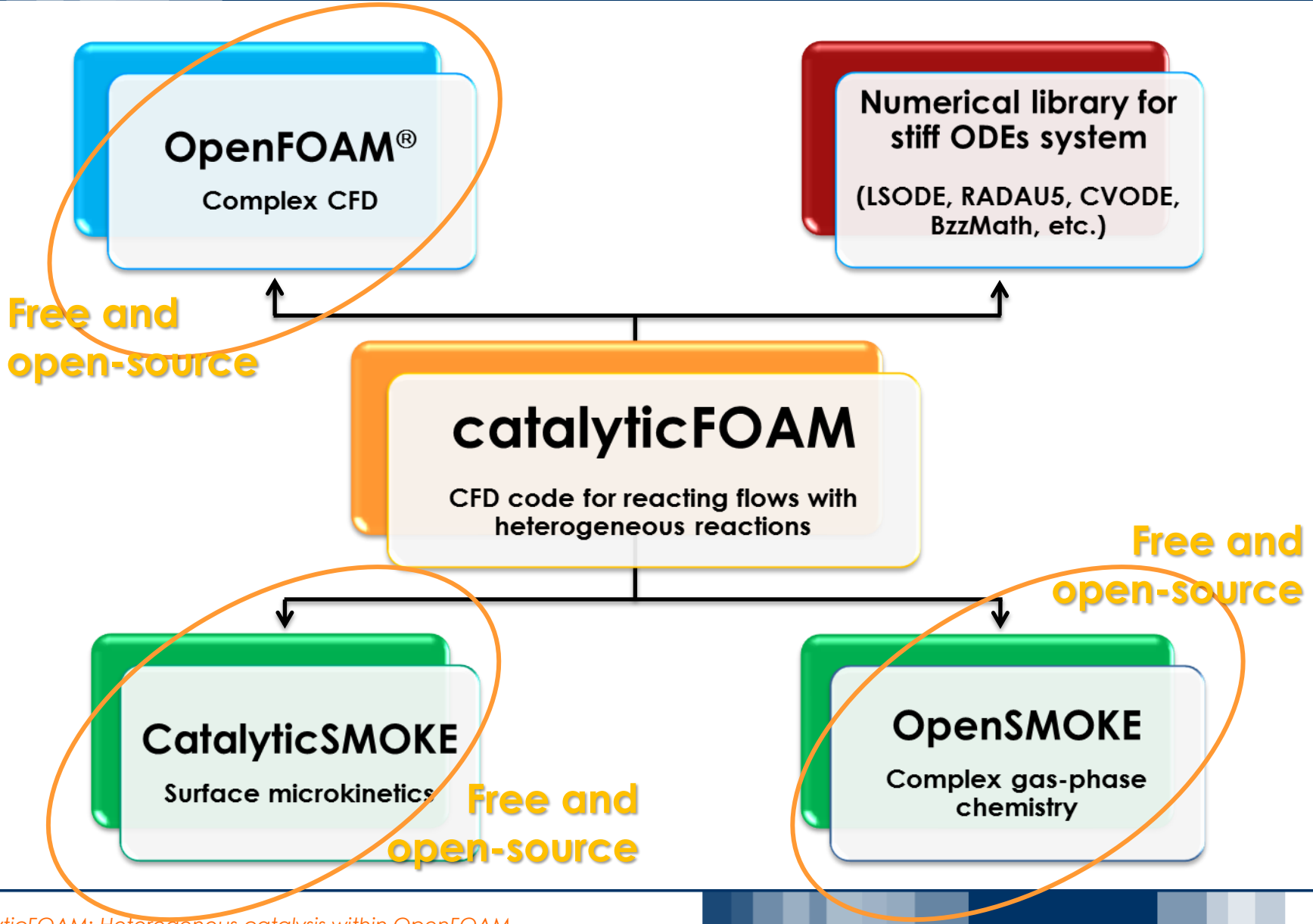
catalyticFOAM structure



catalyticFOAM structure



catalyticFOAM structure



Stiff ODE solvers in catalyticFOAM (I)

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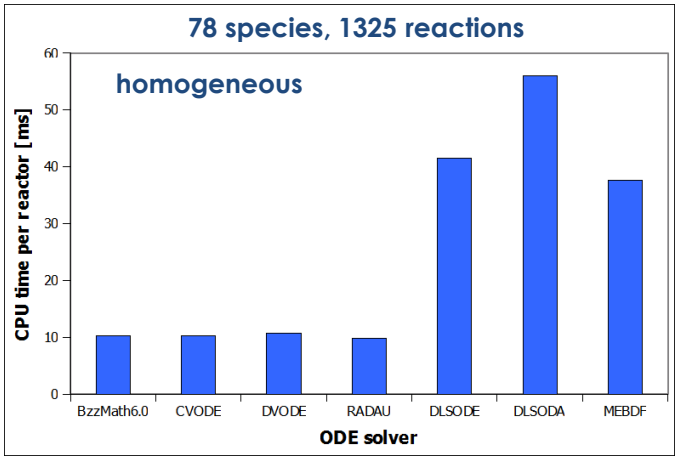
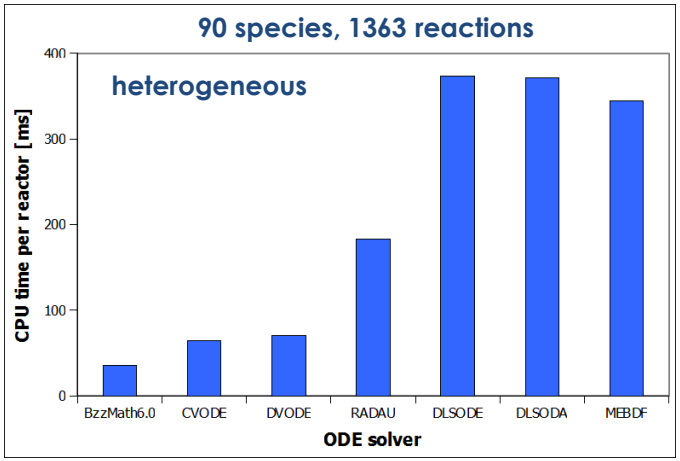
	Language	Linear system solution	Parallel	Code available	License
BzzMath6	C++	Direct	No	No	Free only for academic use
DVODE	FORTRAN	Direct	No	Yes	Free
CVODE	C	Direct/Iterative	Yes	Yes	Free
DLSODE	FORTRAN	Direct	No	Yes	Free
DLSODA	FORTRAN	Direct	No	Yes	Free
RADAU5	FORTRAN	Direct	No	Yes	Free
LIMEX4	FORTRAN	Direct	No	Yes	Free only for academic use
MEBDF	FORTRAN	Direct	No	Yes	Free

Most of the CPU Time (80-90%) is spent for the numerical integration of the ODE systems corresponding to the homogeneous and heterogeneous reactors

The best performances are obtained using the following solvers: BzzMath6, CVODE, DVODE

Performances of stiff ODE solvers: CPU time





Details about the C++ implementation

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For each solver a common C++ interface was created

Creation of ODE System objects

```
ODESystem_BatchReactor_Homogeneous_DVODE *odeSystemObject_Homogeneous;
odeSystemObject_Homogeneous =
        ODESystem_BatchReactor_Homogeneous_DVODE::GetInstance();
```

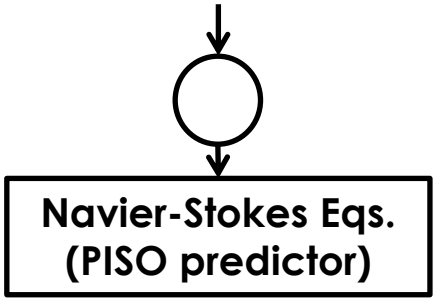
Creation of ODE System Solver

```
OpenSMOKE::OpenSMOKE_DVODE<ODESystem_BatchReactor_Homogeneous_DVODE>
ode_Homogeneous(odeSystemObject_Homogeneous);
```

Loop on every computational cell

```
ode_Homogeneous.SetMaximumNumberOfSteps(100000);
ode_Homogeneous.SetAnalyticalJacobian(false);
ode_Homogeneous.SetAbsoluteTolerance(aTol);
ode_Homogeneous.SetRelativeTolerance(rTol);
ode_Homogeneous.SetInitialValues(t0,Y0);
ode_Homogeneous.Solve(tf);
ode_Homogeneous.Solution(yF);
```

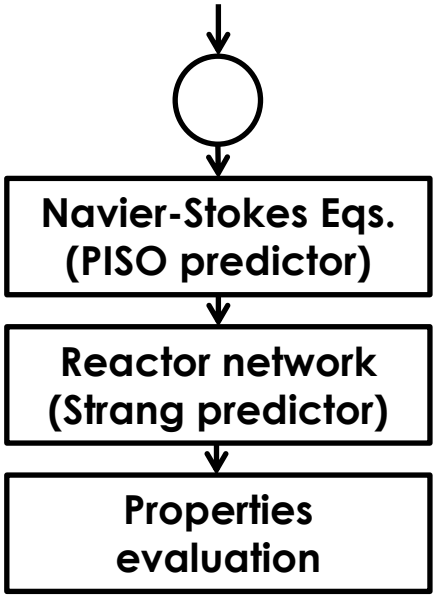
Solution procedure

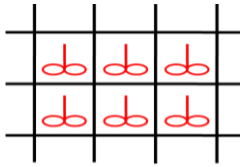


Main features:

- ✓ Solution of the Navier-Stokes equations (laminar and turbulent regime)

Solution procedure

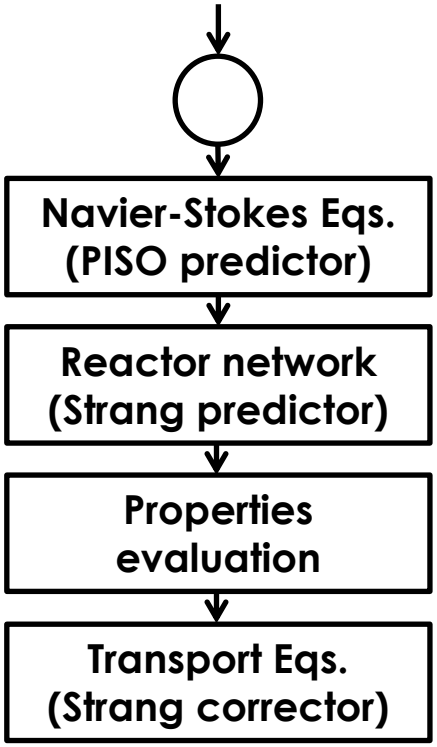


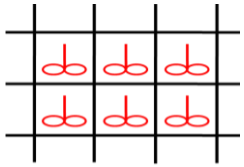


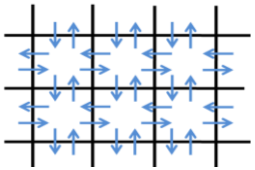
Main features:

- ✓ Solution of the Navier-Stokes equations (laminar and turbulent regime)
- ✓ No limit to the number of species and reactions

Solution procedure



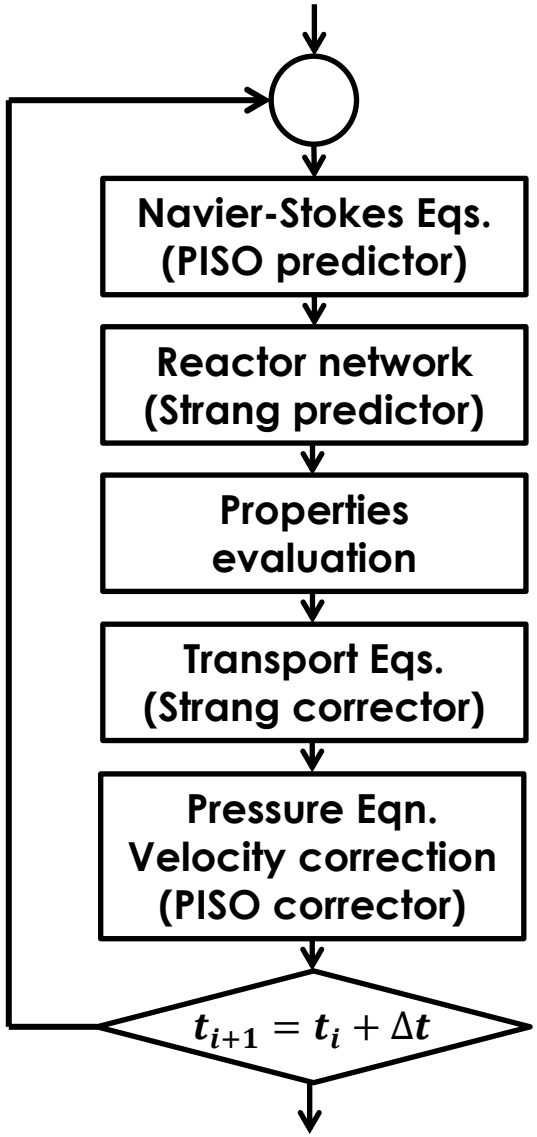


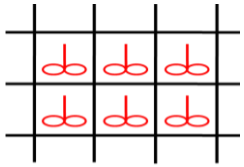


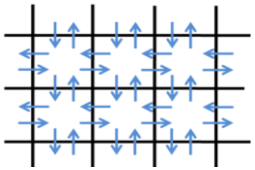
Main features:

- ✓ Solution of the Navier-Stokes equations (laminar and turbulent regime)
- ✓ No limit to the number of species and reactions
- ✓ Isothermal and adiabatic conditions

Solution procedure







Main features:

- ✓ Solution of the Navier-Stokes equations (laminar and turbulent regime)
- ✓ No limit to the number of species and reactions
- ✓ Isothermal and adiabatic conditions

catalyticFoam.C

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```
    ...

while (runTime.run())
{
    #include "readTimeControls.H"
    #include "readPISOControls.H"
    #include "compressibleCourantNo.H"
    #include "setDeltaT.H"

    runTime++;
    Info<< "Time = " << runTime.timeName() << nl << endl;

    #include "rhoEqn.H"

    for (label ocorr=1; ocorr <= nOuterCorr; ocorr++)
    {
        #include "UEqn.H"
        #include "chemistry.H"
        #include "properties.H"
        #include "YEqn.H"
        #include "TEqn.H"

        // --- PISO loop
        for (int corr=1; corr<=nCorr; corr++)
        {
            #include "pEqn.H"
        }
    }

    #include "write.H"
}
...
```

loop

continuity

momentum

Strang (predictor)

Strang (corrector)

PISO loop

Post-processing

Predictor step (chemistry)

```
Loop over all the reactors
{
        if reactor is catalytic
        {
                assembling ODE initial values
                (gas-phase species, temperature, adsorbed species)

                solving the ODE system

                moving the solution to OpenFOAM
        }

        else
        {
                assembling ODE initial values
                (gas-phase species and temperature)

                solving the ODE system

                moving the solution to OpenFOAM
        }
}
...
```

Numerical library for stiff ODEs system

(LSODE, RADAU5, CVODE, BzzMath, etc.)

solverOptions file

```
gasProperties        "H2onRh_UBI_MatteoTDC_2008/idealgas.bin";
gasKinetics          "H2onRh_UBI_MatteoTDC_2008/reactions.bin";
surfaceProperties    "H2onRh_UBI_MatteoTDC_2008/surface.bin";
```

Thermodynamics/Transport properties and kinetic schemes

```
homogeneousReactions        on;
```

Homogeneous reactions on/off

```
energyEquation    off;
```

Gas-phase energy equation on/off

```
viscosityMixingLaw  Herning;
```

Evaluation of dynamic viscosity

```
absoluteTolerance 1.e-12;
RelativeTolerance 1.e-7;
```

Absolute and relative tolerances (ODE solver)

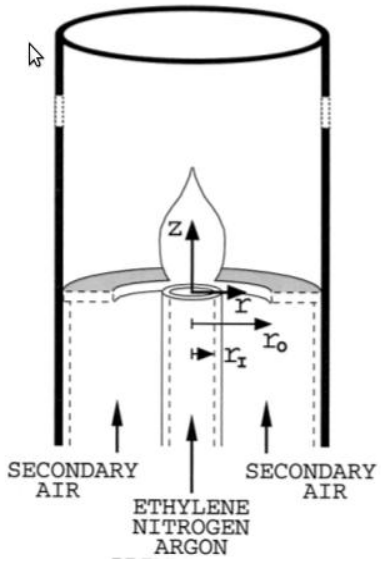
```
AlfaCatalyst 1.5668;
```

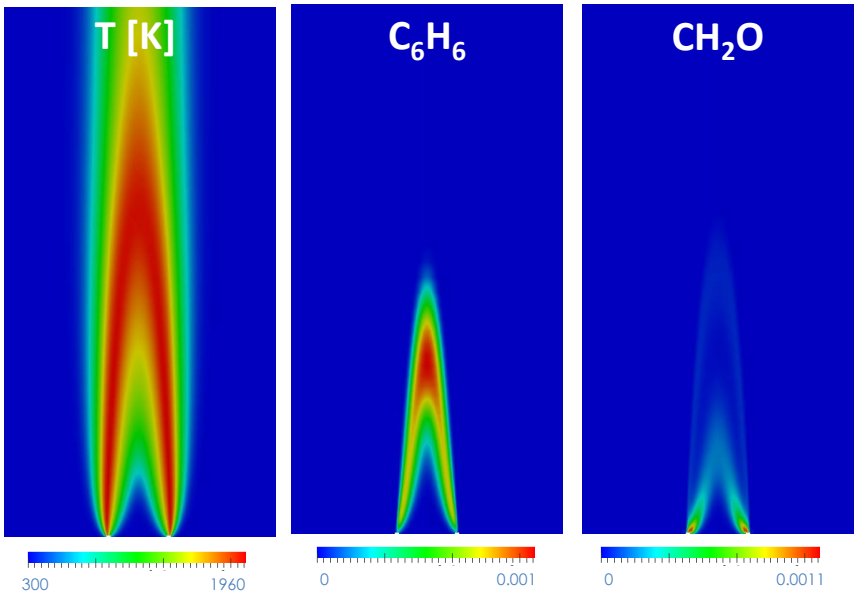
Specific, catalytic surface (dimensionless)

Outline

- ✓ Introduction and motivation
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  - ✓ Governing equations
  - ✓ Numerical methodology
- ✓ **Validation and examples**
  - ✓ Annular reactor (simple chemistry)
  - ✓ CPO of CH_4 on platinum gauze (complex 3D geometry)
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
- ✓ Extensions
  - ✓ KMC (Kinetic Monte Carlo)
  - ✓ Multi-region solver
- ✓ Conclusions and future works

Laminar, coflow flames (I)



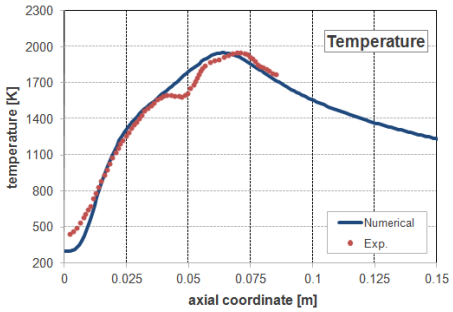


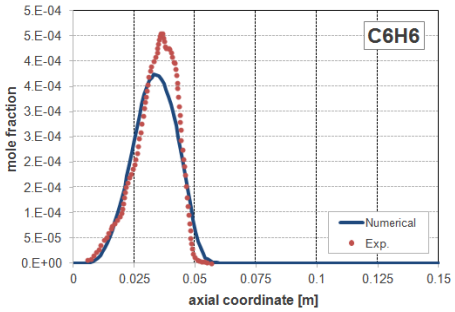
PolimiC1C16HT kinetic scheme
168 species
5400 reactions
Freely available in CHEMKIN format:
http://creckmodeling.chem.polimi.it

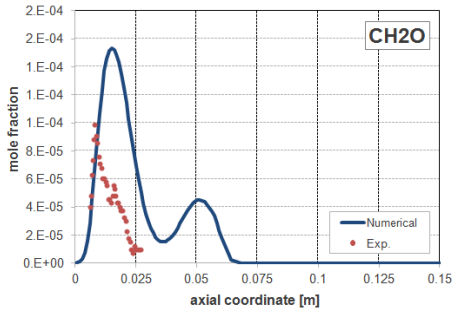
2D axisymmetric (55x200 mm)
Computational grid: ~10,000 cells
Pressure/Velocity coupling: PISO
Discretization: first order upwind

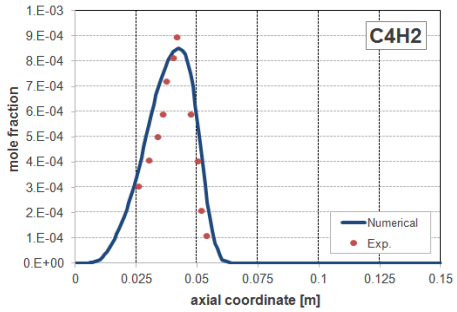
Bennet, B.A., McEnally, C.S., Pfefferle, L.D., Smooke, M.D., Colket, M.B., *Computational and Experimental Study of Axisymmetric, Coflow Partially Premixed Ethylene/Air Flames*, Combustion and Flame (2001)

Measurements along the axis

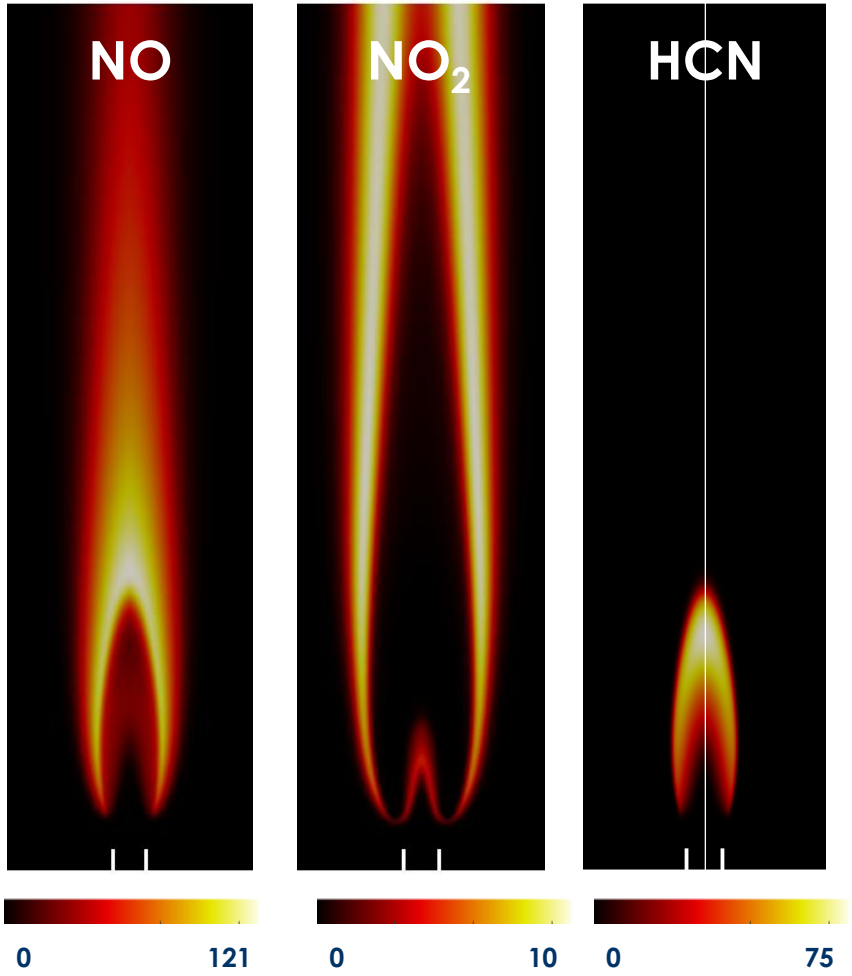




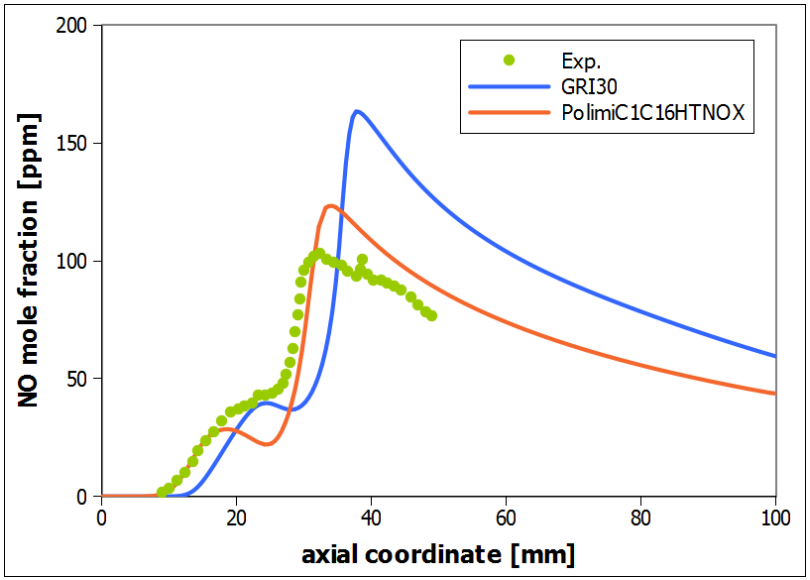




Laminar, coflow flames (II)



mass fractions of NOx (ppm)



M.D. Smooke, A. Ern, M.A. Tanoff, R.H. Mohammed, D.F. Marran, B. Long, *Proceedings of the Combustion Institute*, 26 (1996) 2161-2170.

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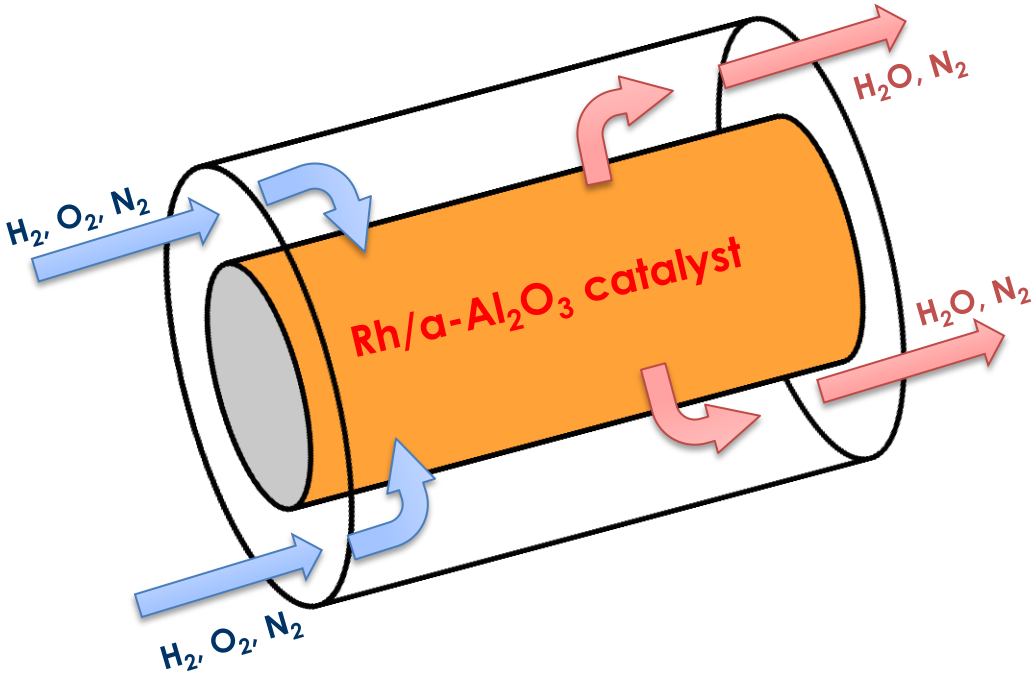
  - ✓ Multi-region solver
- ✓ Conclusions and future works

Numerical tests

The numerical tests have been performed by investigating the combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor (*).

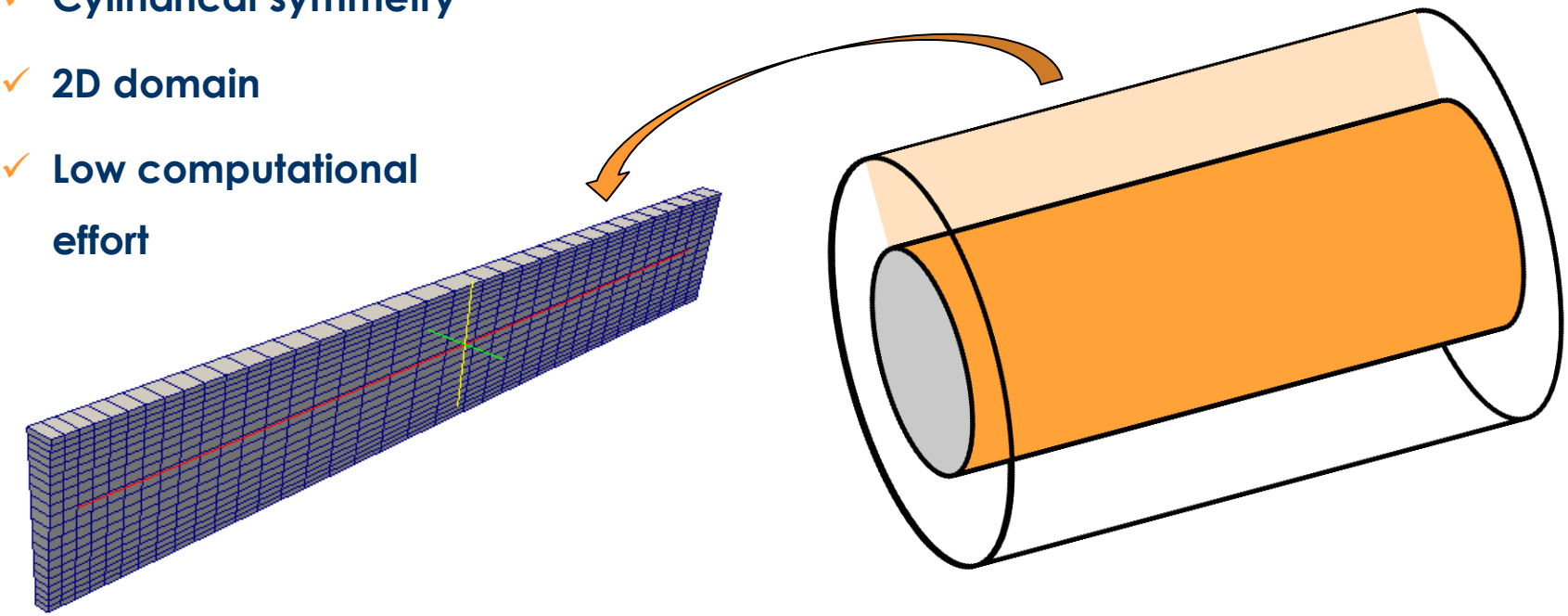
Operating conditions	
Inner radius	0.235 cm
Outer radius	0.450 cm
Reactor length	1.5 cm
H_2 mole fraction	0.04 (-)
O_2 mole fraction	0.01 (-)
N_2 mole fraction	0.95 (-)
Pressure	1 atm
Rh site density	2.49 10^{-9} mol/cm^2
Catalytic surf.	5 cm^{-1}



(*) ***M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos,*** *2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst, Chemical Engineering Science (2008)*

Numerical test

- ✓ Cylindrical symmetry
- ✓ 2D domain
- ✓ Low computational effort



Meshes

2D Axisymmetric Mesh
from 2,000 to 10,000 cells

- Centered (2nd order) spatial discretization
- Implicit Euler time integration
- Max Courant number 0.1

Kinetic schemes

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Heterogeneous kinetics

- 5 Species: Rh(s), H2O(s), H(s), OH(s), O(s)
- 18 Reactions

1. H2+2Rh(s)=>2H(s)
2. 2H(s)=>H2+2Rh(s)
3. O2+2Rh(s)=>2O(s)
4. 2O(s)=>O2+2Rh(s)
5. OH(s)+Rh(s)=>H(s)+O(s)
6. H(s)+O(s)=>OH(s)+Rh(s)
7. H2O(s)+Rh(s)=>H(s)+OH(s)
8. H(s)+OH(s)=>H2O(s)+Rh(s)
9. H2O(s)+O(s)=>2OH(s)
10. 2OH(s)=>H2O(s)+O(s)
11. OH+Rh(s)=>OH(s)
12. OH(s)=>OH+Rh(s)
13. H2O+Rh(s)=>H2O(s)
14. H2O(s)=>H2O+Rh(s)
15. H+Rh(s)=>H(s)
16. H(s)=>H+Rh(s)
17. O+Rh(s)=>O(s)
18. O(s)=>O+Rh(s)

Microkinetic mechanism
Maestri et al., 2008
Mhadeshwar and Vlachos, 2005

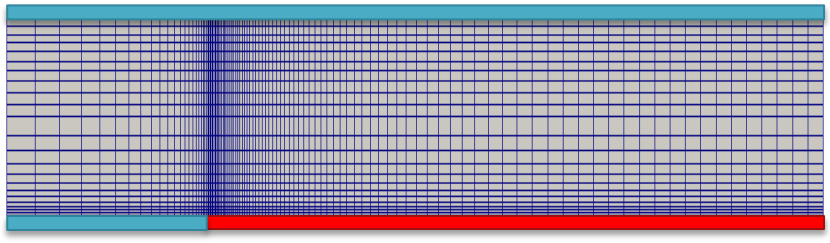
Homogeneous kinetics

- 10 Species
- 21 Reactions

1. H+O2=OH+O
2. O+H2=OH+H
3. H+O2+M=HO2+M
4. H+2O2=HO2+O2
5. OH+HO2=H2O+O2
6. H+HO2=2OH
7. O+HO2=O2+OH
8. 2OH=O+H2O
9. H2+M=2H+M
10. O2+M=2O+M
11. H+OH+M=H2O+M
12. H+HO2=H2+O2
13. 2HO2=H2O2+O2
14. 2OH+M=H2O2+M
15. O+OH+M=HO2+M
16. H+H2O=H2+OH
17. H2O2+H=H2O+OH
18. H2O2+H=H2+HO2
19. HO2+H2O=>H2O2+OH
20. OH+H2O2=>H2O+HO2
21. O+H2O2=>OH+HO2

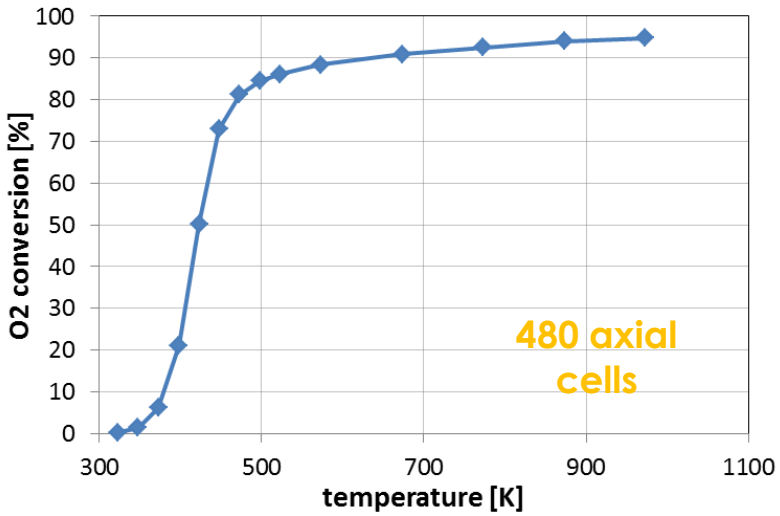
PolimiH2 mechanism (Frassoldati et al., 2006)

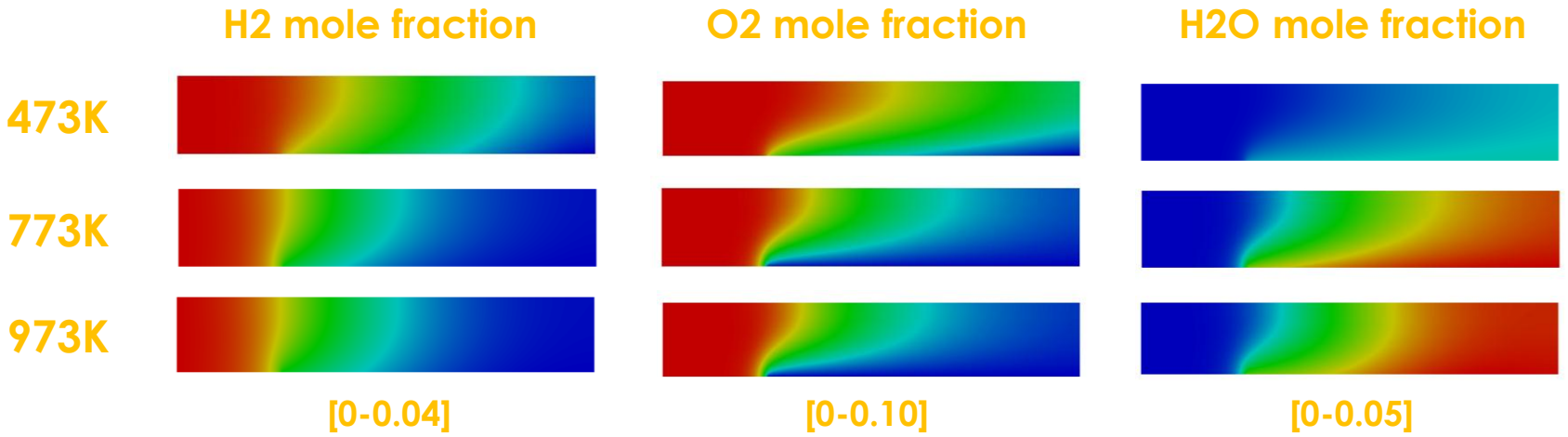
Main results



$\alpha_{cat} = 0$

$\alpha_{cat} = \frac{A_{cat}}{A} = 1.50$

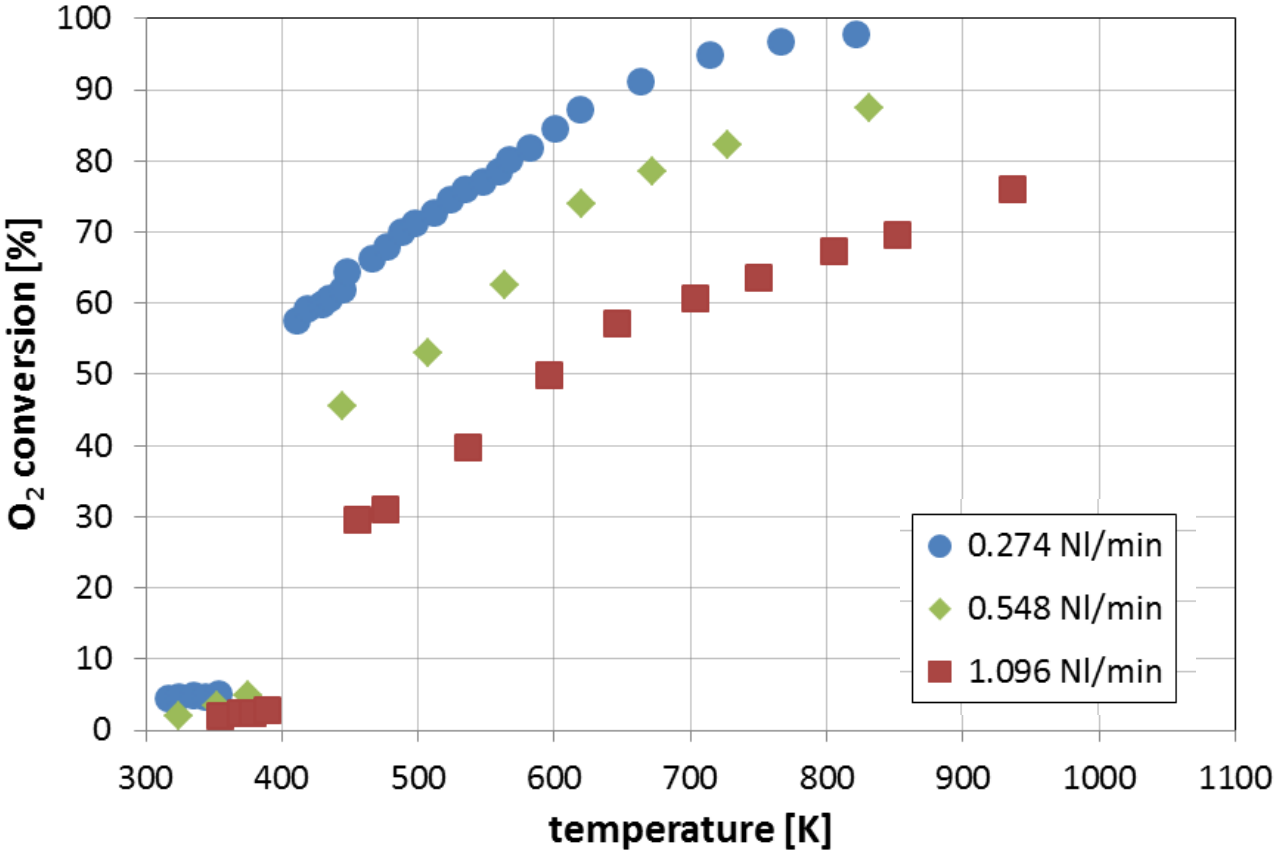




Validation

Comparison with experimental measurements

- ✓ **Flow rate of:**
  - 0.274 Nl/min
  - 0.548 Nl/min
  - 1.096 Nl/min
- ✓ **Inlet:**
  - H_2 = 0.04
  - O_2 = 0.01
  - N_2 = 0.95
- ✓ **Reactor:**
  - R_{in} = 0.235 cm
  - R_{out} = 0.450 cm
  - L = 1.5 cm



(*) **M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos,** *2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst, Chemical Engineering Science (2008)*

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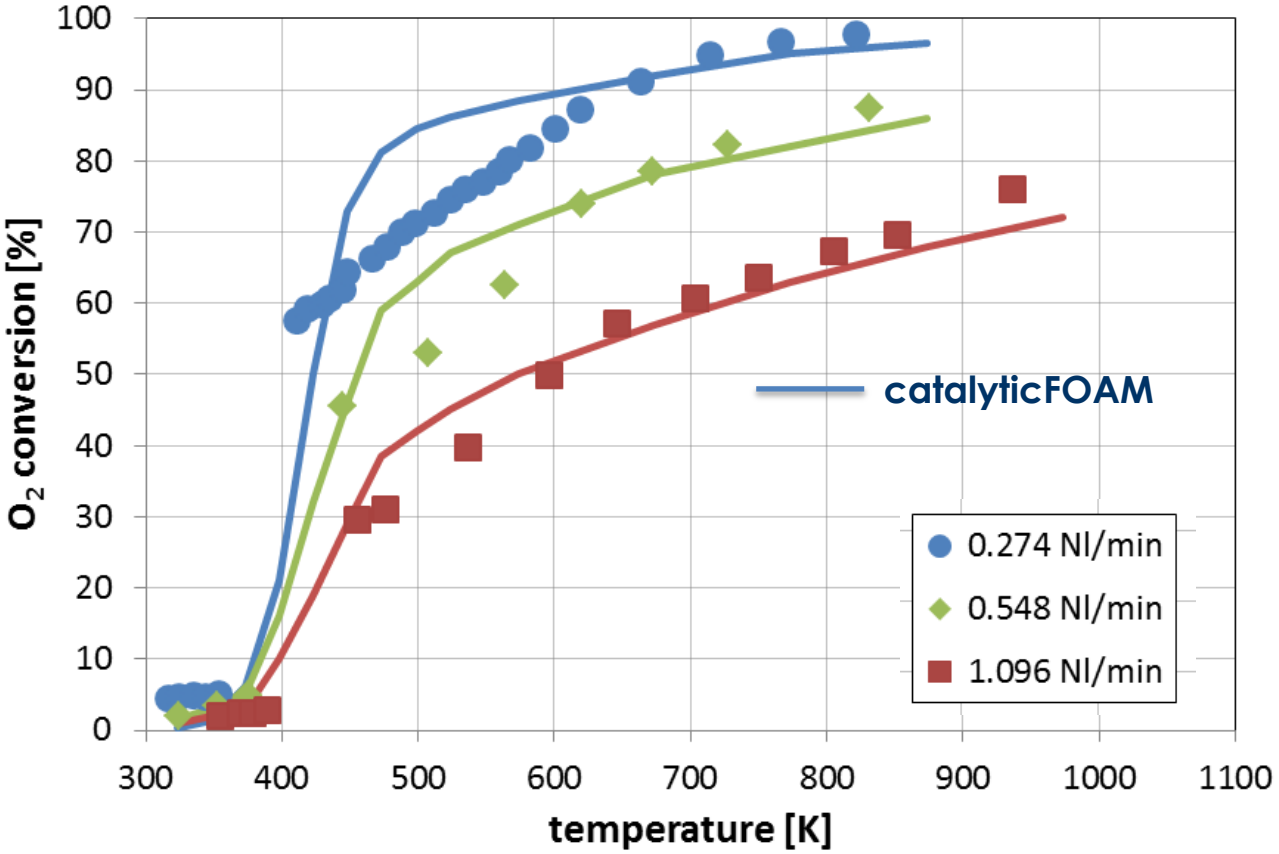

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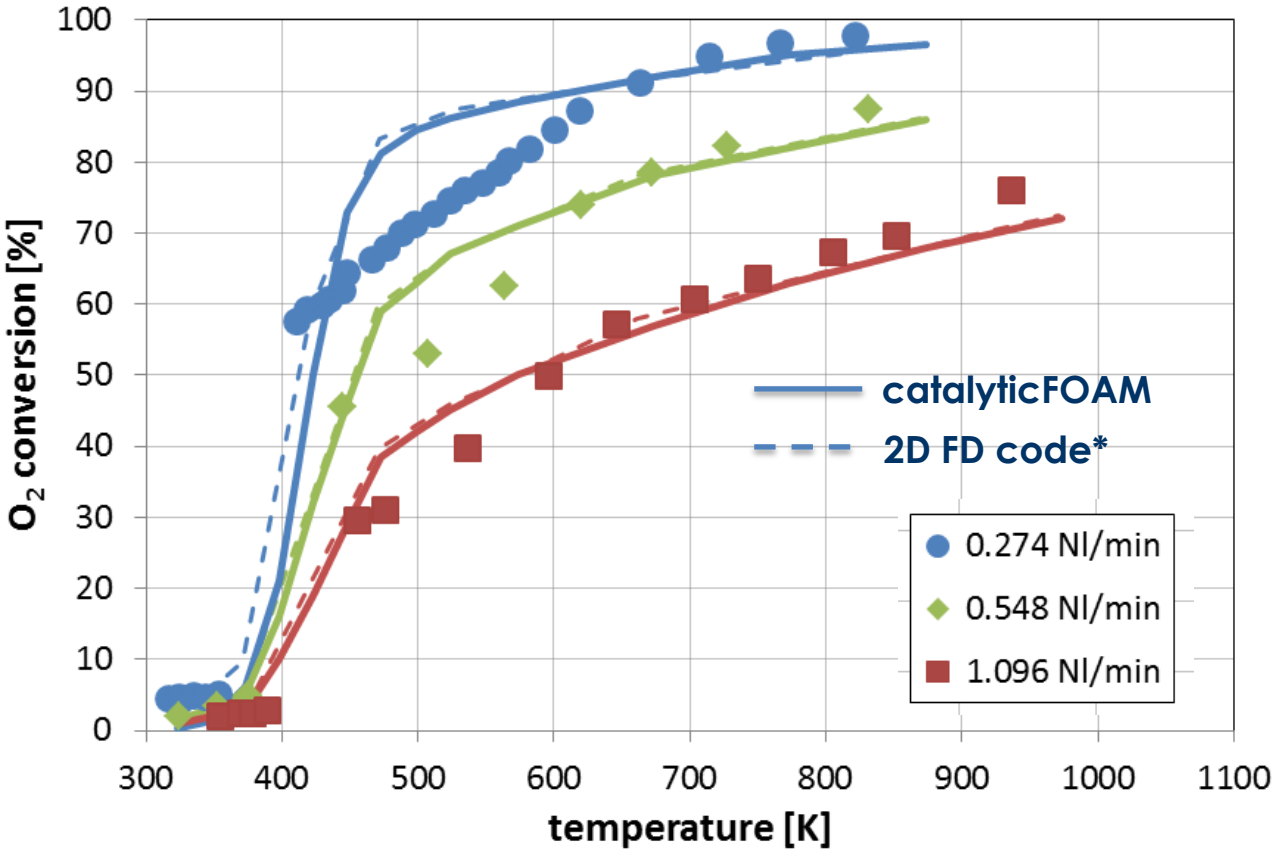

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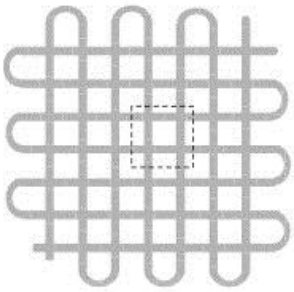
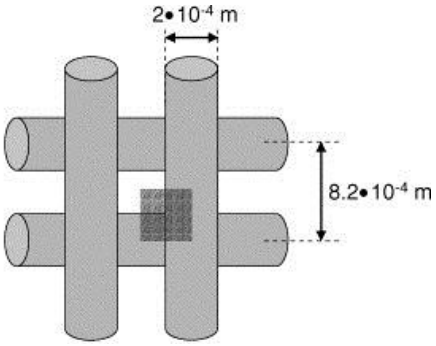
  - ✓ Multi-region solver
- ✓ Conclusions and future works

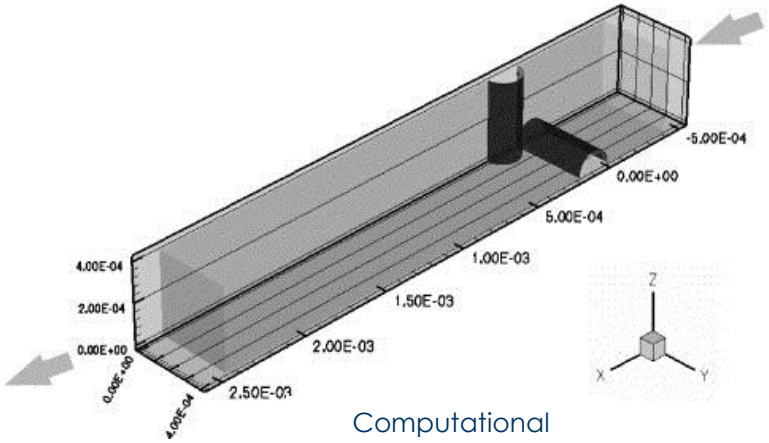
CPO of methane over platinum gauze (I)



Original gauze structure



Detail of wire intersections

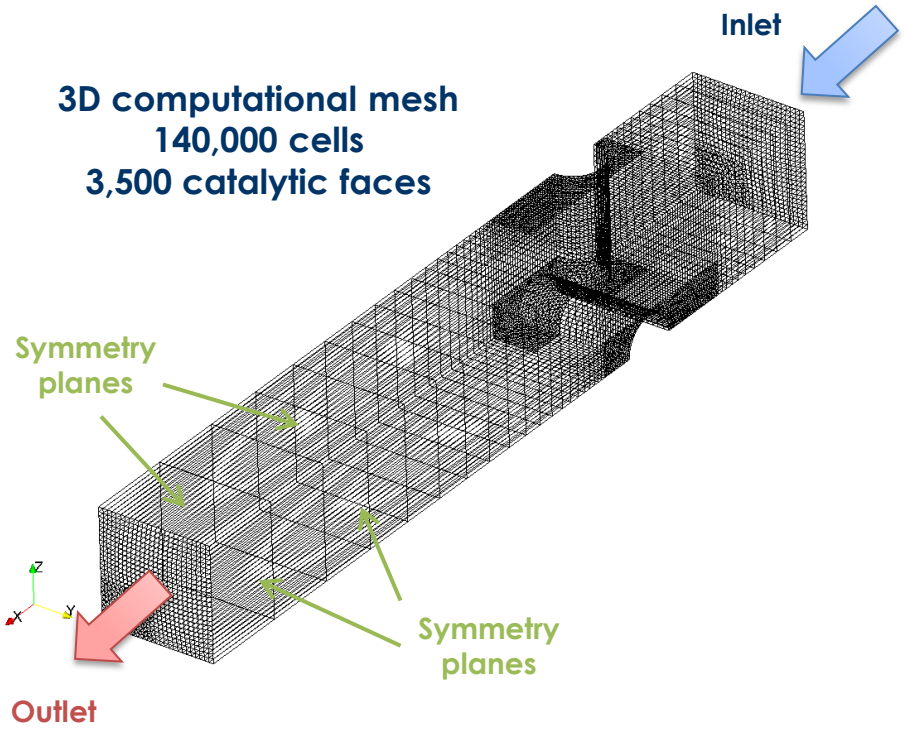


Computational domain

Operating conditions	
Inlet temperature	600 K
Inlet velocity	10 m/s
Gauze temperature	1000-1200 K
CH_4 mole fraction	0.143 (-)
O_2 mole fraction	0.057 (-)
He mole fraction	0.80 (-)
Pressure	1.3 bar
Pt site density	2.72 10^{-9} mol/cm^2
Catalytic surf.	5 cm^{-1}

(*) ***R. Quiceno, J. Perez-Ramirez, J. Warnatz, O. Deutschmann,*** *Modeling the high-temperature catalytic partial oxidation of methane over platinum gauze: detailed gas-phase and surface chemistries coupled with 3D flow simulations, Applied Catalysis A: General 303 (2006) 166-176*

CPO of methane over platinum gauze (II)



- Centered (2nd order) spatial discretization
- Implicit Euler time integration
- Max Courant number 0.05

Heterogeneous kinetics

- 11 Surface Species
- 36 Surface Reactions

www.detchem.com/mechanisms

(*) ***R. Quiceno, et al.,*** *Applied Catalysis A: General 303 (2006) 166-176*

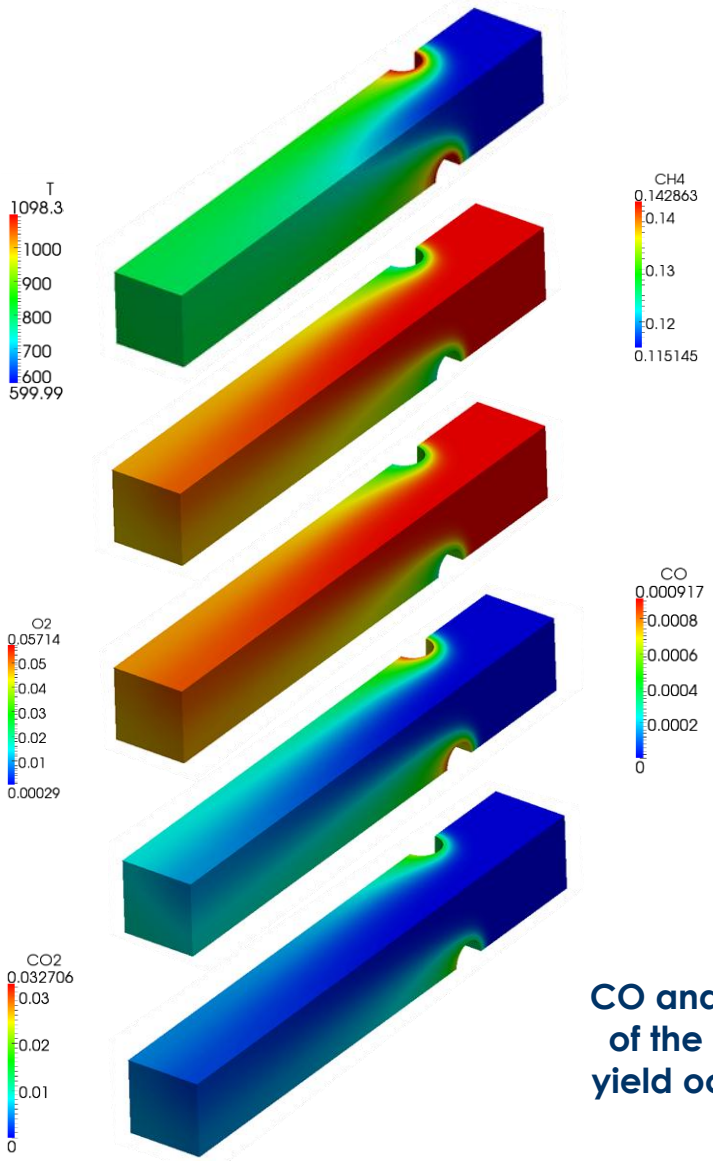
Homogeneous kinetics

- 25 Species
- 300 Reactions

http://creckmodeling.chem.polimi.it/

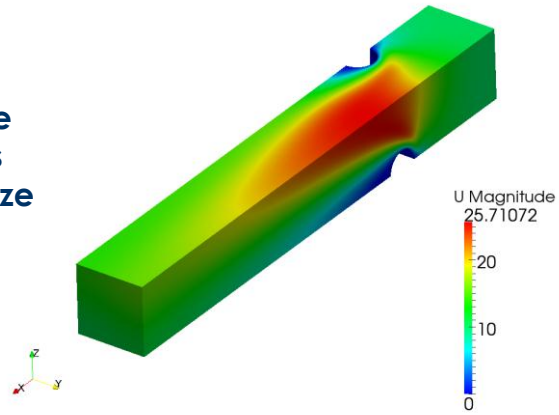
(*) ***E. Ranzi, et al.,*** *Progress in Energy Combustion Science, 38 (2012) 468-501*

CPO of methane over platinum gauze (III)



T_{inlet} = 600K
T_{gauze} = 1000K

The temperature of the mixture becomes uniform at 2-3 wires diameters downstream the gauze



2 days of calculation on 12 cores

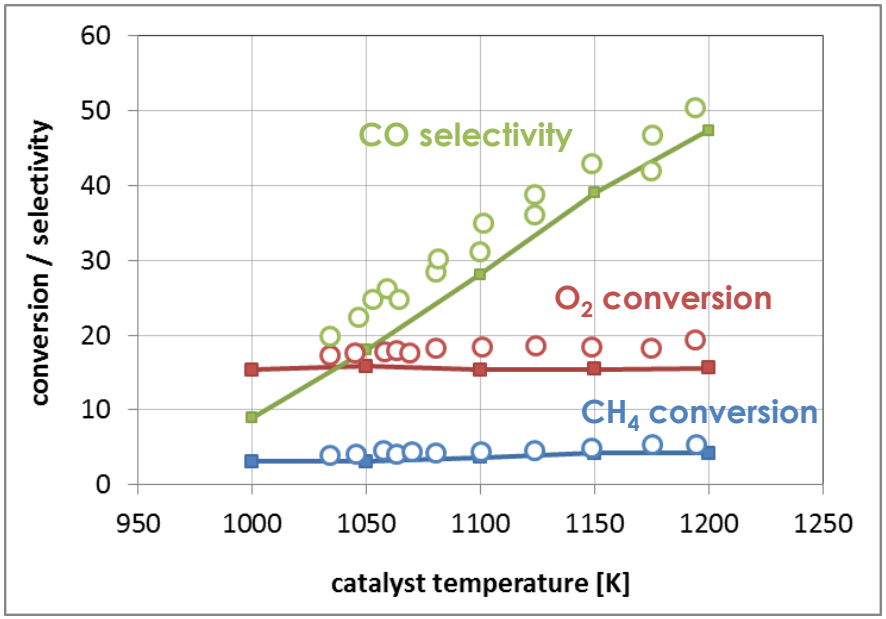
- ✓ Under the conditions used in these tests the homogeneous reactions are not relevant
- ✓ Simulations performed with and without the gas-phase reactions exhibit very similar results
- ✓ The concentration of radical species in the gas phase is negligible

CO and CO2 are produced on the surface of the catalytic wires, with their maximal yield occurring at the crossing of the wires

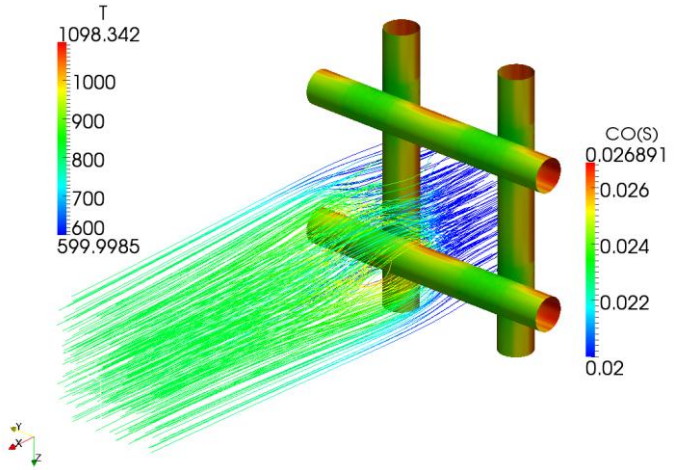
CPO of methane over platinum gauze (IV)

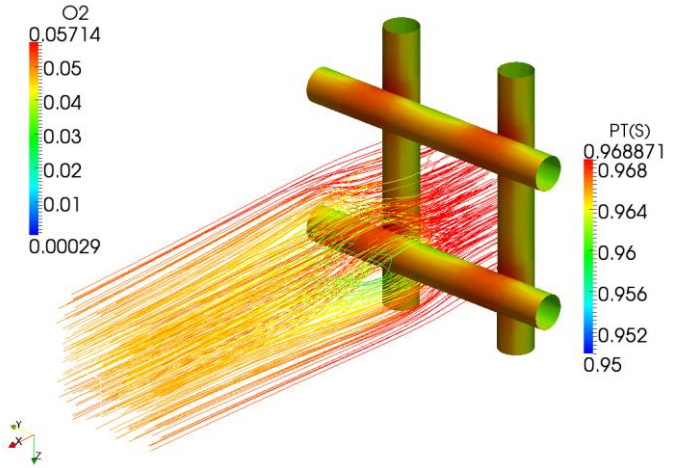
POLITECNICO DI MILANO

Comparison with experimental data



- ✓ CH4 and O2 conversions are not temperature dependent
- ✓ The CO selectivity is strongly influenced by the gauze temperature





- ✓ Mass fraction of main adsorbed species (CO(s), OH(s), etc.) is maximum downstream, where the inlet mixture meet the catalyst wires

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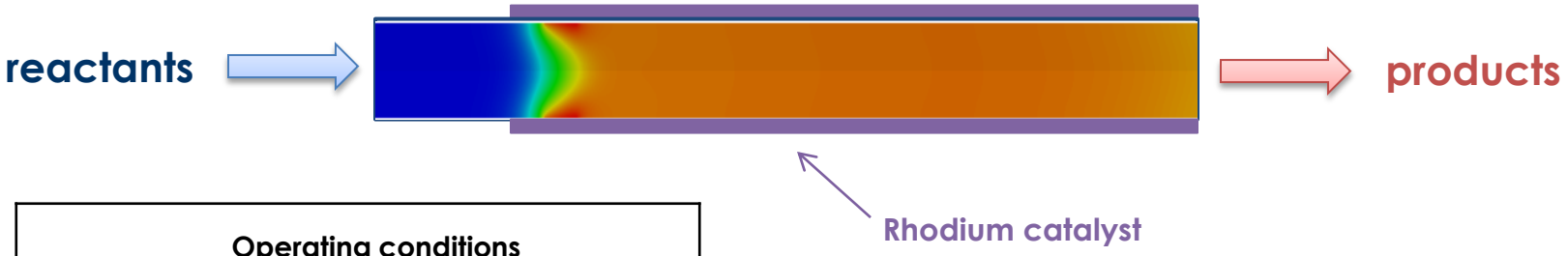
CPO of iso-octane over rhodium catalyst (I)

POLITECNICO DI MILANO

Sketch of a single channel (circular section)



Operating conditions	
Inlet temperature	1076 K
Inlet velocity	0.90 m/s
Wall temperature	1076 K
iC_8H_{18} mole fraction	0.143 (-)
O_2 mole fraction	0.057 (-)
N_2 mole fraction	0.80 (-)
Pressure	1 atm
Rh site density	2.49 10^{-9} mol/cm^2
Catalytic surf.	5 cm^{-1}

Heterogeneous kinetics
- 17 Surface Species
- 56 Surface Reactions

www.detchem.com/mechanisms

Homogeneous kinetics
- 168 Species
- 5,400 Reactions

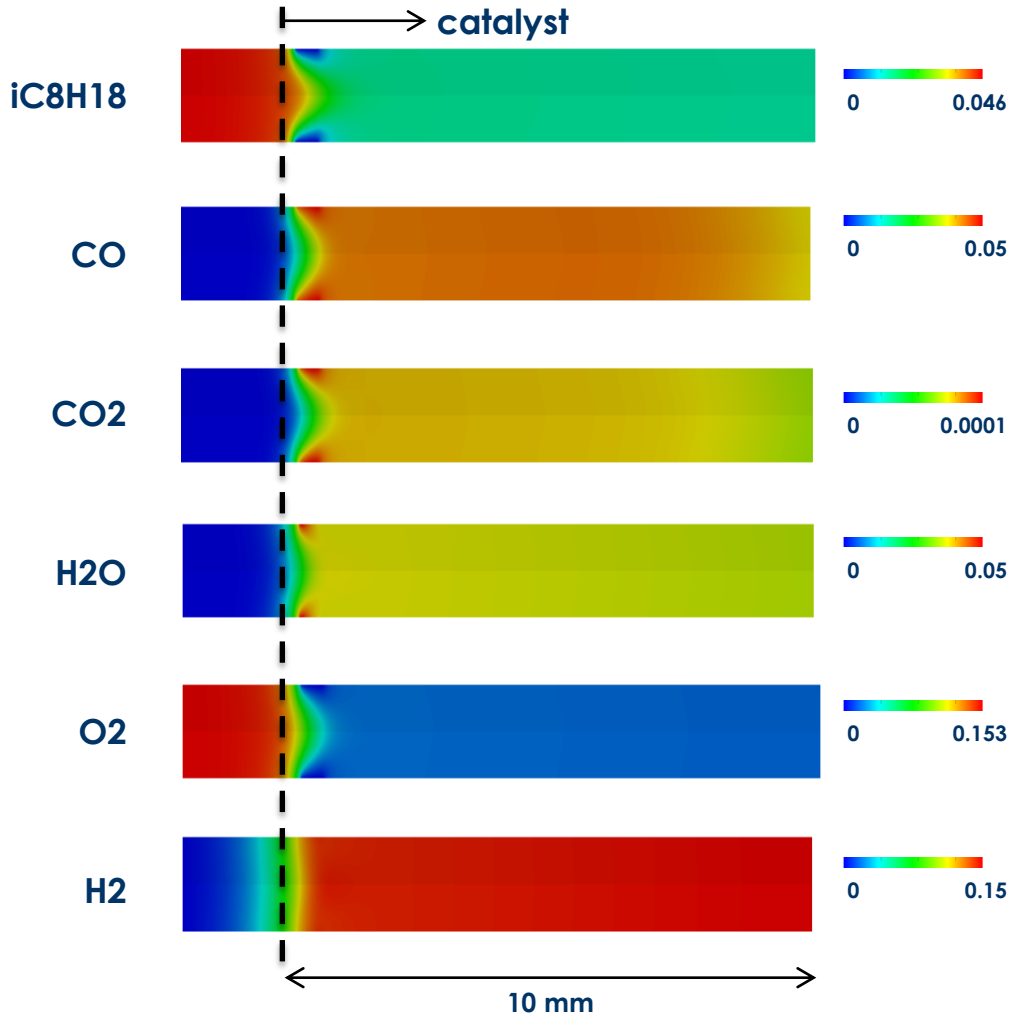
http://creckmodeling.chem.polimi.it/

(*) ***M. Hartmann, L. Maier, H.D.Minh, O. Deutschmann,*** *Catalytic partial oxidation of iso-octane over rhodium catalyst: an experimental, modeling and simulation study, Combustion and Flame 157 (2010) 1771-1782*

CPO of iso-octane over rhodium catalyst (II)

POLITECNICO DI MILANO

Gas-phase main species
2D mesh (4,000 cells)



4 days of calculation on 12 cores

The catalytic surface reaction is very fast in the entrance (first 1 mm)

Strong back-diffusion of H2: importance of diffusion coefficients

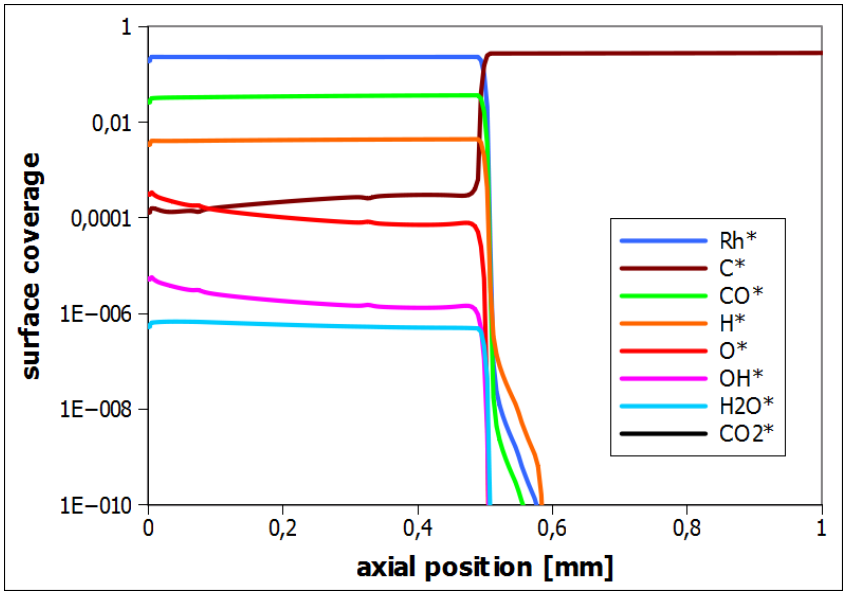
Strong radial gradient are present in the first mm of the reactor

The concentration of iC8H18 and O2 on the surface is practically zero, which means that catalytic reactions are mass-transfer limited

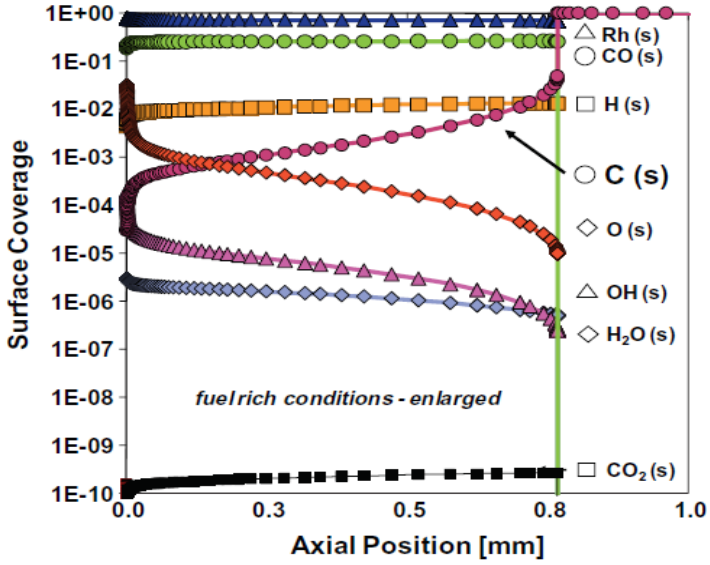
CPO of iso-octane over rhodium catalyst (III)

POLITECNICO DI MILANO

CatalyticFOAM
2D mesh (5,000 cells)

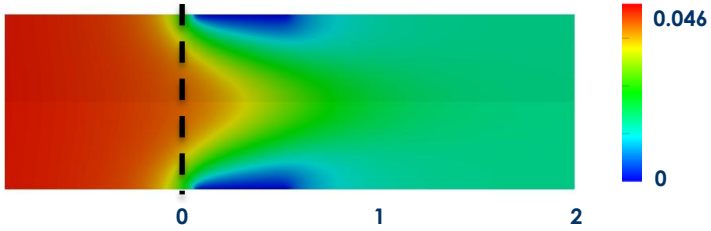


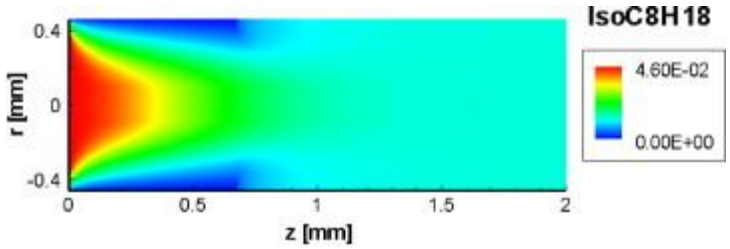
DETCHEM^CHANNEL
www.detchem.com



M. Hartmann, et al., Combustion and Flame 157 (2010) 1771-1782

iC8H18





Outline

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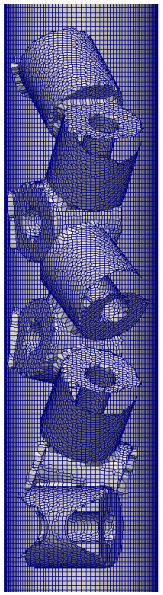
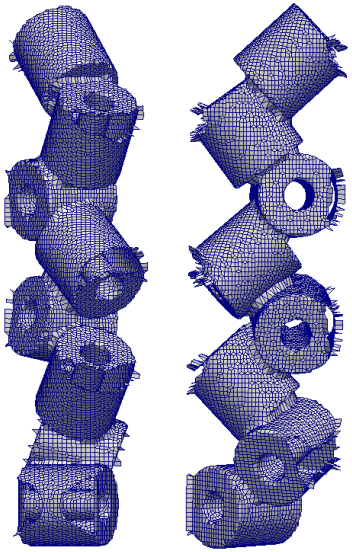
Tubular reactor with Raschig rings (I)

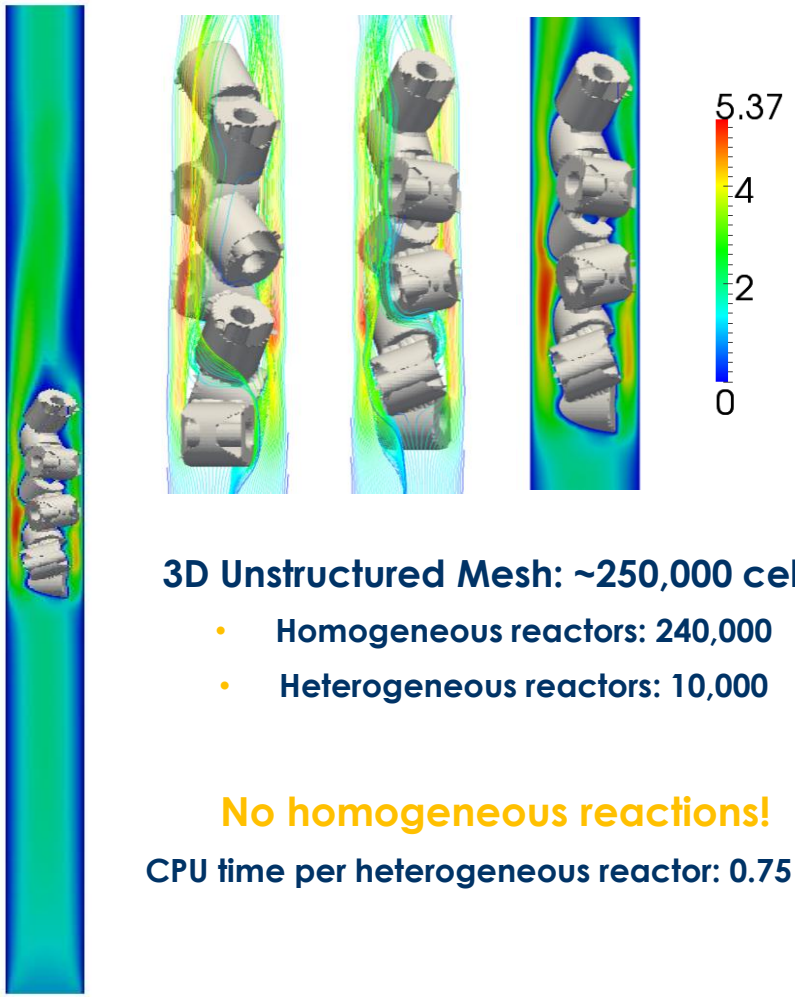




Inlet mixture

Operating conditions	
Internal diameter	1 cm
Total length	15 cm
CH_4 mole fraction	0.100 (-)
O_2 mole fraction	0.056 (-)
N_2 mole fraction	0.844 (-)
Temperature	873.15 K
Residence time	0.15 s

Velocity Field



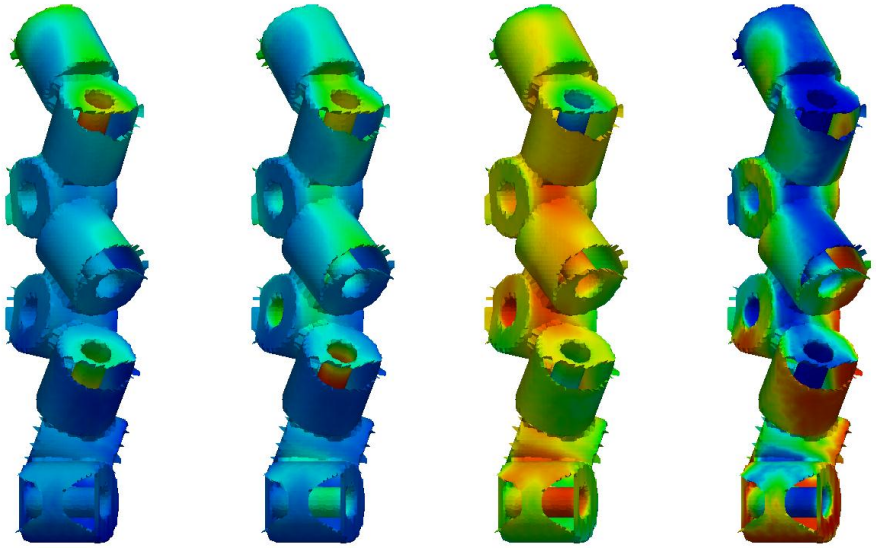
3D Unstructured Mesh: ~250,000 cells

- **Homogeneous reactors: 240,000**
- **Heterogeneous reactors: 10,000**

No homogeneous reactions!

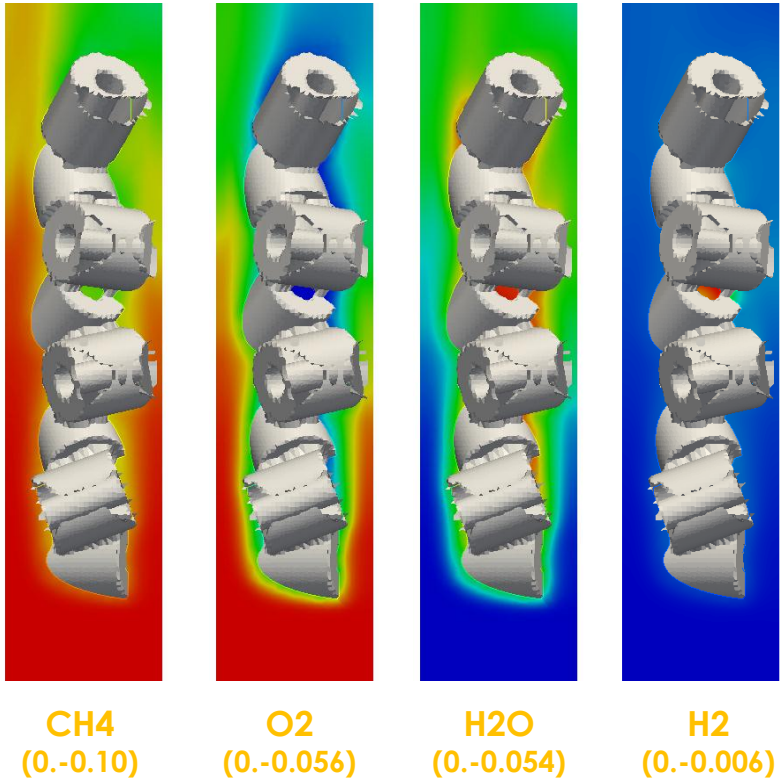
CPU time per heterogeneous reactor: 0.75 ms

Tubular reactor with Raschig rings (II)

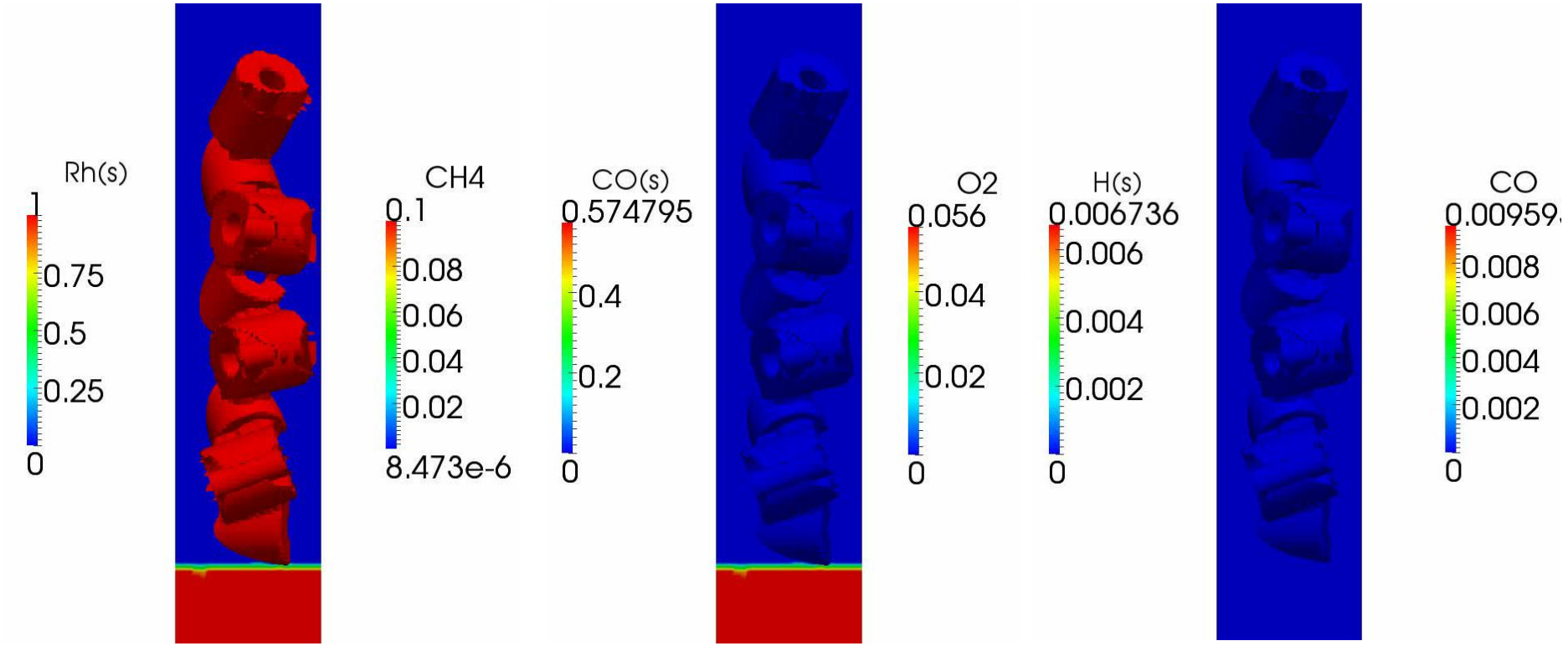


Adsorbed species (mass fractions)

Gas-phase species (mole fractions)



Tubular reactor with Raschig rings (III)



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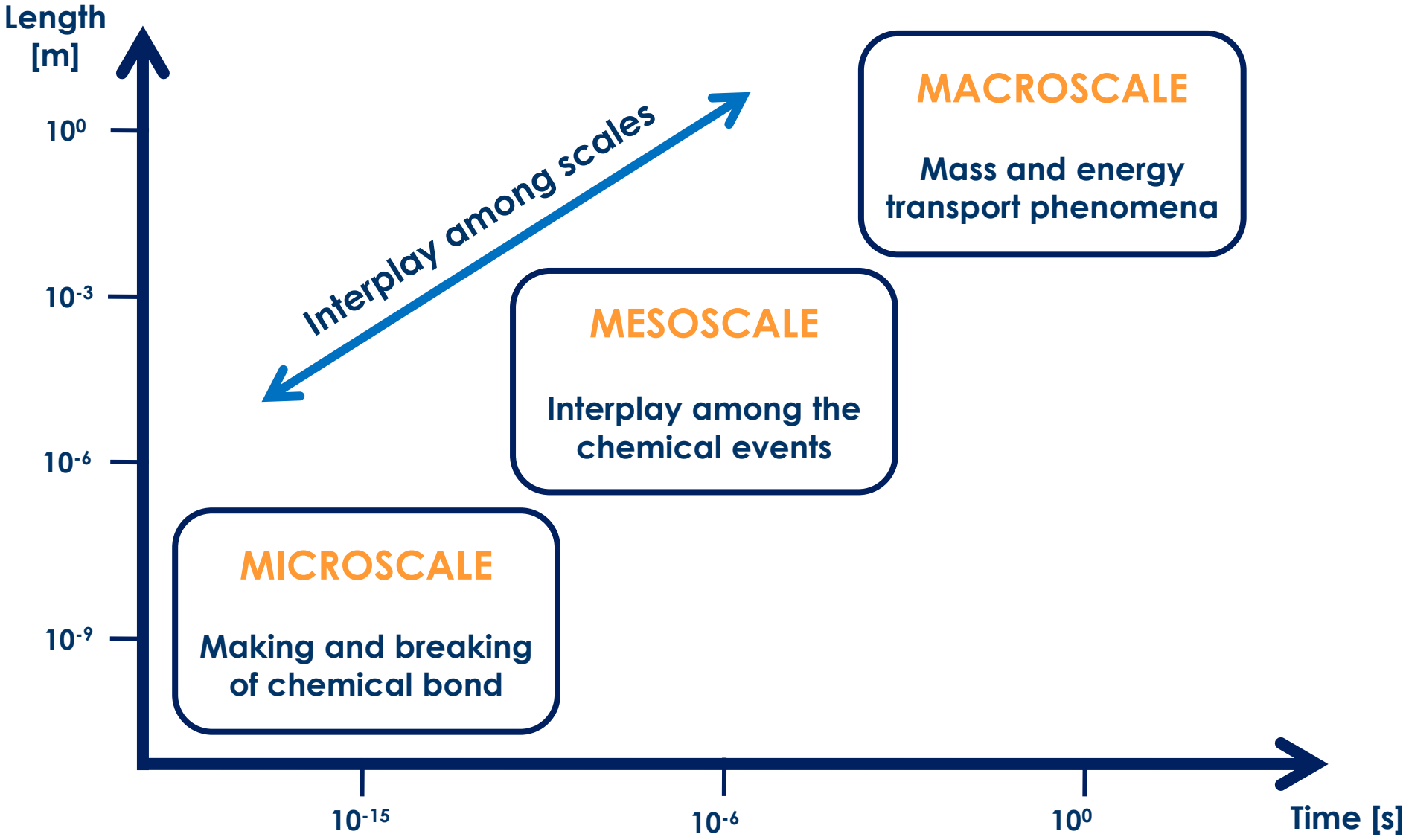
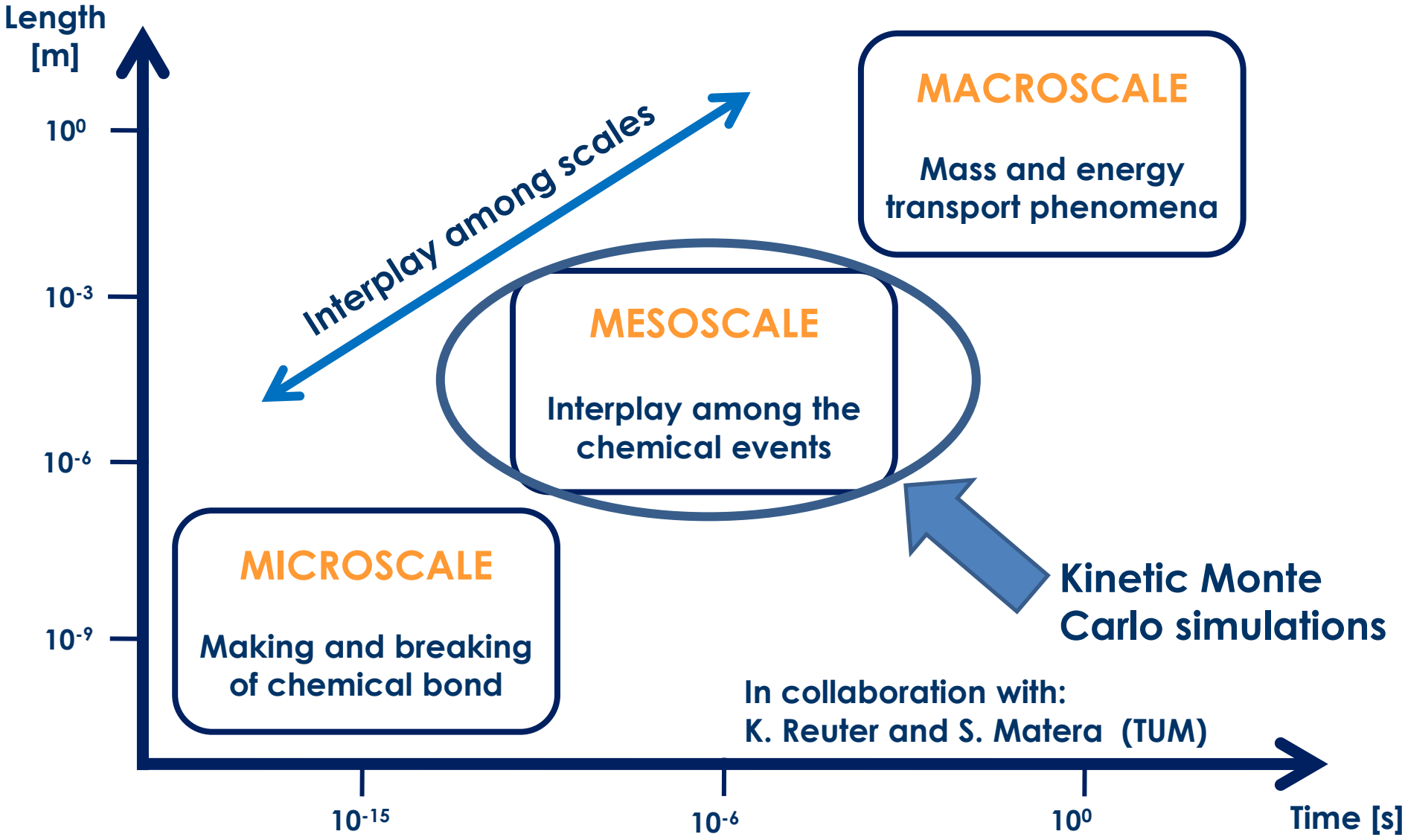
A "first-principles" approach



(*) *Microkinetic analysis of complex chemical processes at surfaces*
M. Maestri – in "New strategy for chemical synthesis and catalysis" Wiley, 2011

A "first-principles" approach



(*) *Microkinetic analysis of complex chemical processes at surfaces*
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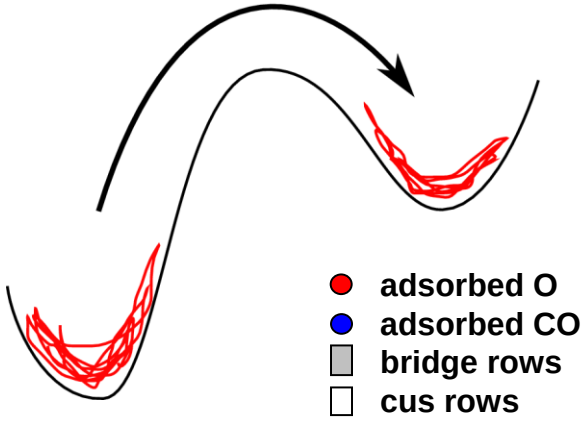
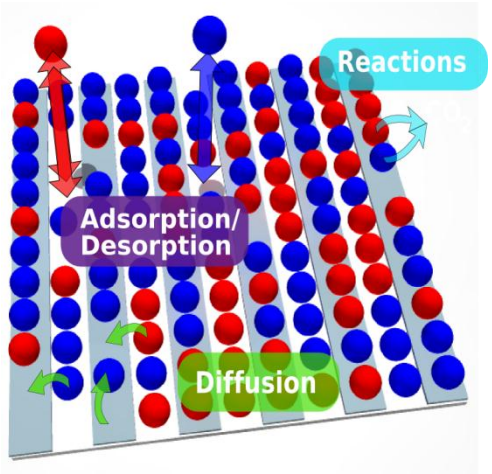
First-principles kinetic Monte Carlo

- ✓ Evaluate the statistical interplay of large number of elementary processes
- ✓ open non-equilibrium system → need to explicitely follow the time evolution
- ✓ rare event dynamics → Molecular Dynamics simulations unsuitable. Map on a lattice model→ Markov jump process description

$$\frac{d}{dt}P(\boldsymbol{x},t)=\sum_{y}k(\boldsymbol{x},\boldsymbol{y})P(\boldsymbol{y},t)-\sum_{y}k(\boldsymbol{y},\boldsymbol{x})P(\boldsymbol{x},t)$$

- ✓ Each site *a* has own entry in x denoting its adsorbate state x_a
- ✓ Simulate trajectories x(*t*) (kinetic Monte Carlo)





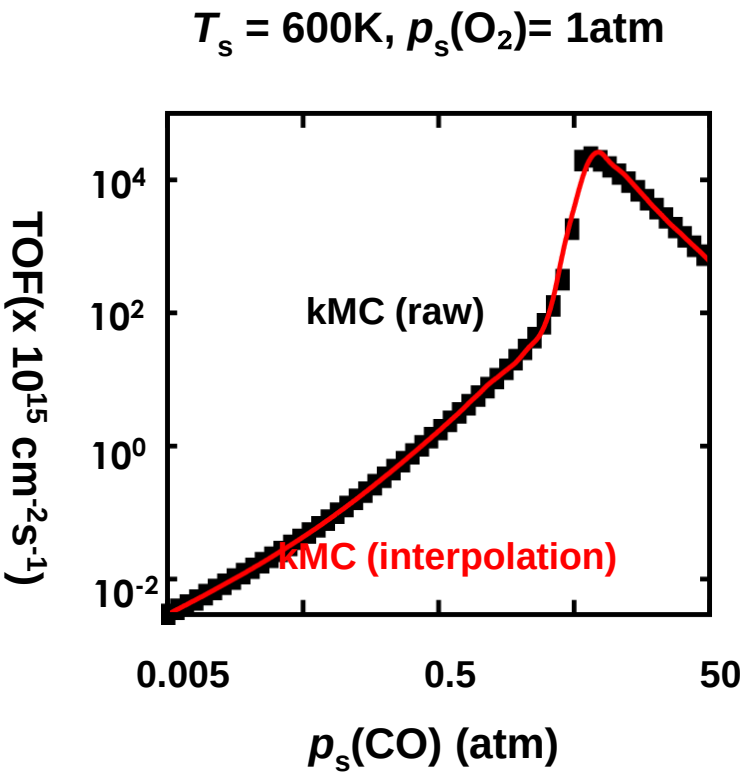
K. Reuter and M. Scheffler, *Phys. Rev. B* 73, 045433 (2006)

"Effective" bridging between the scales

- ✓ Continuum equations need boundary conditions for the mass fluxes j^{α} at the surface:

$$j_n^{\alpha} = \nu^{\alpha} M^{\alpha} \mathbf{TOF}$$

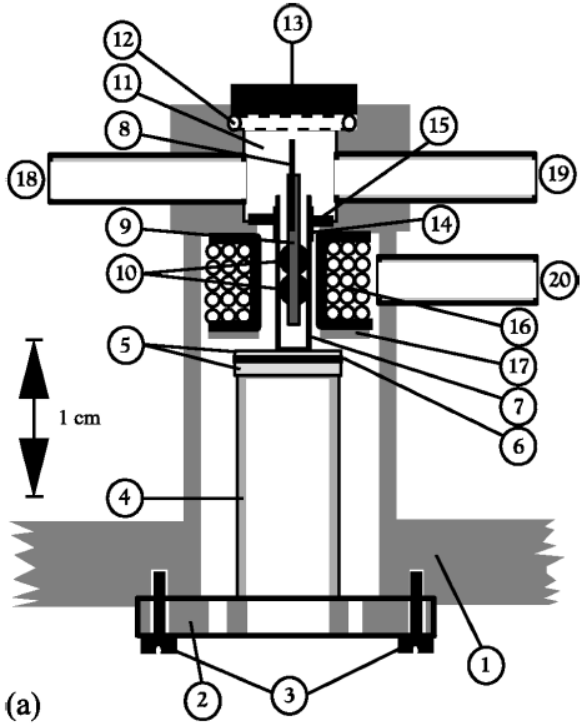
- ✓ **Coupled problem**: to determine the TOF with 1p-kMC the pressures at the surface are needed, but the pressure field depends on the TOF
- ✓ **kMC too expensive** for direct coupling to the flow solver
- ✓ Run kMC beforehand and interpolate (Modified Shepard)
- ✓ Very efficient
- ✓ Easily extendable to more complex geometries



S. Matera and K. Reuter, *Catal. Lett.* 133, 156-159 (2009); *Phys. Rev. B* 82, 085446 (2010).

An example: The reactor STM (I)

The Reactor STM



Rasmussen, Hendriksen, Zeijlemaker, Ficke, Frenken, *The Reactor STM: A scanning tunneling microscope for investigation of catalytic surfaces at semi-industrial reaction conditions*, Review of Scientific Instruments, 69(11), (1998)

CO oxidation on Ru_2O

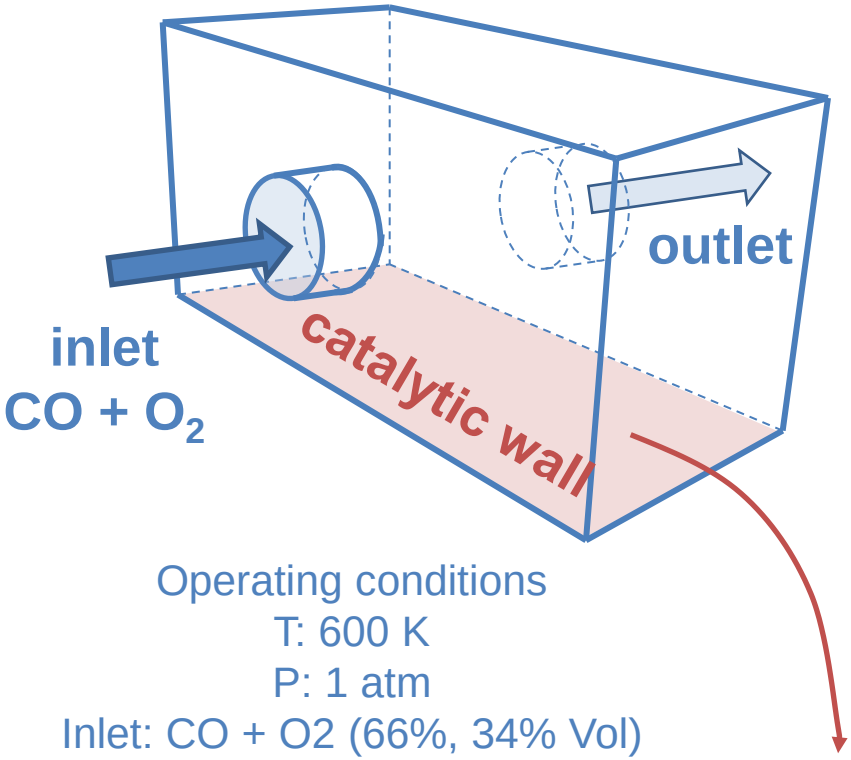
Rate constants $k(x,y)$ from DFT and harmonic Transition State Theory

Model system

- ✓ CO oxidation on $RuO_2(110)$
- ✓ 2 types of sites, bridge and cus

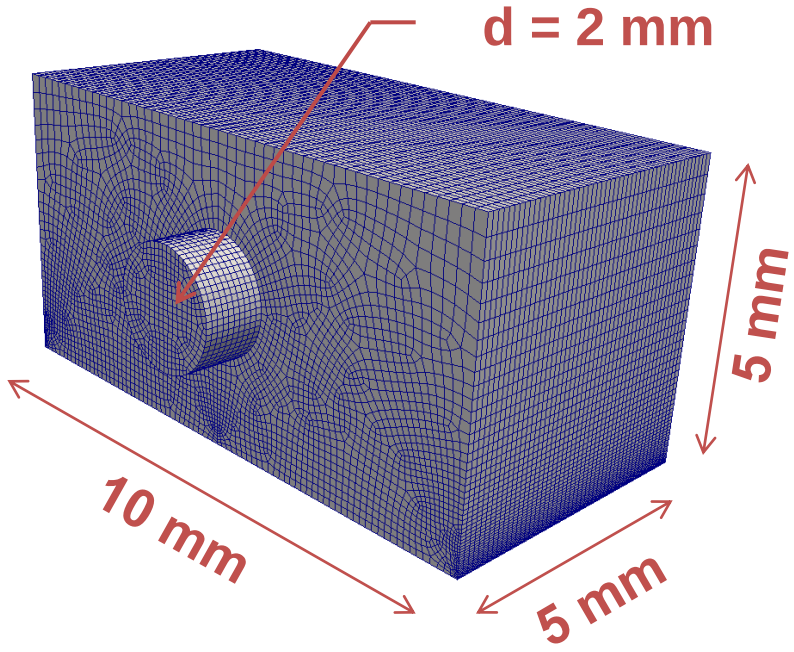
K. Reuter and M. Scheffler, *Phys. Rev. B* 73, 045433 (2006)

An example: The reactor STM (II)



Operating conditions
T: 600 K
P: 1 atm
Inlet: CO + O2 (66%, 34% Vol)
Inlet velocity: 5 cm/s

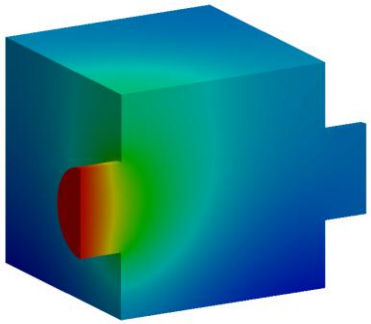
Catalytic Wall
Catalyst: Ru_2O

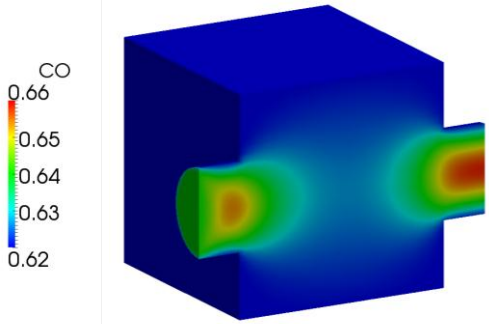


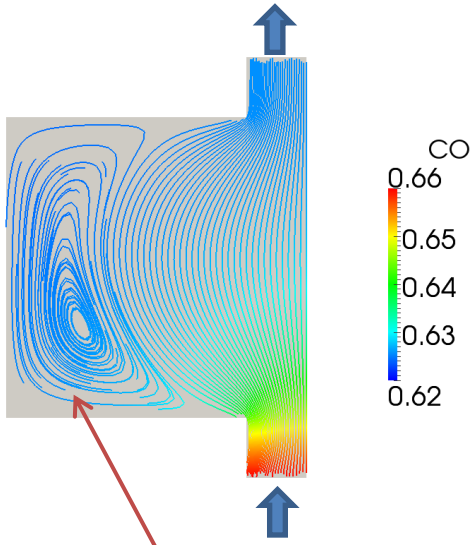
Computational details
Mesh: unstructured, ~90,000 cells
Discretization: 2nd order, centered
Max time step: 10^{-4} s
CPU time: ~2 s per time step

An example: The reactor STM (III)

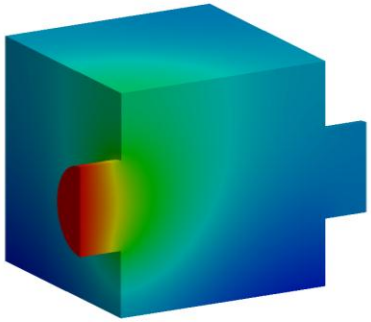
Steady-state results

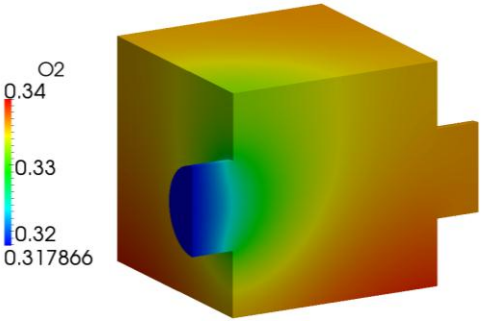






Strong recirculations





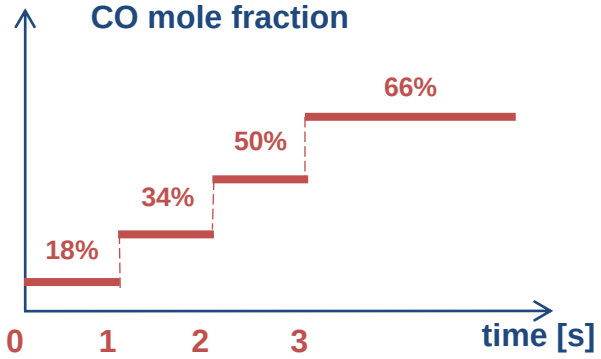
An example: The reactor STM (IV)

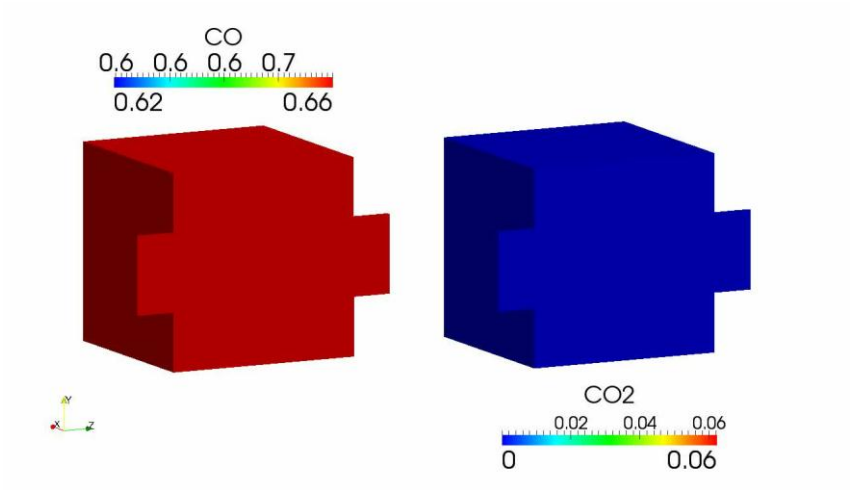
Dynamic results

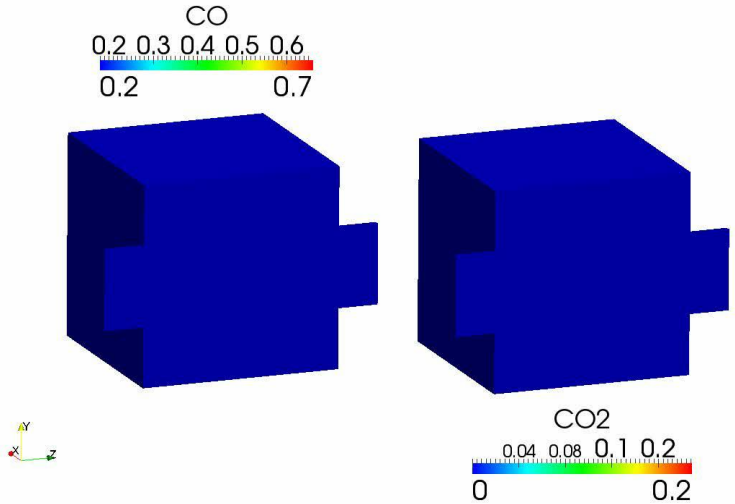
Operating conditions
T: 600 K
P: 1 atm
Inlet: CO + O2 (66%, 34% Vol)
Inlet velocity: 5 cm/s

Initial conditions:
CO + O2 (66%, 34% Vol)

The CO mole fraction in the inlet stream increases during the time



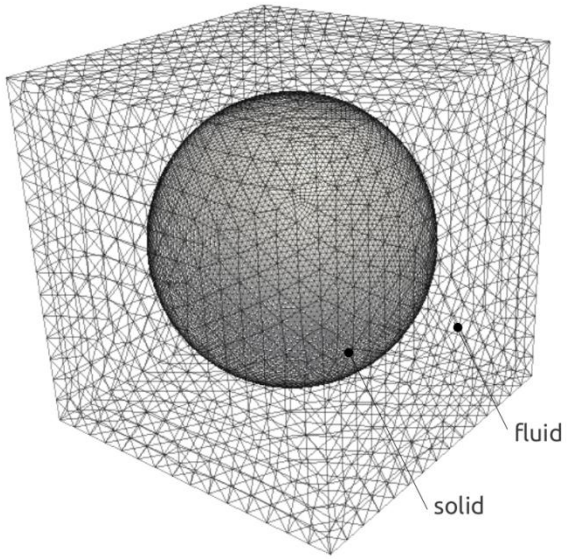


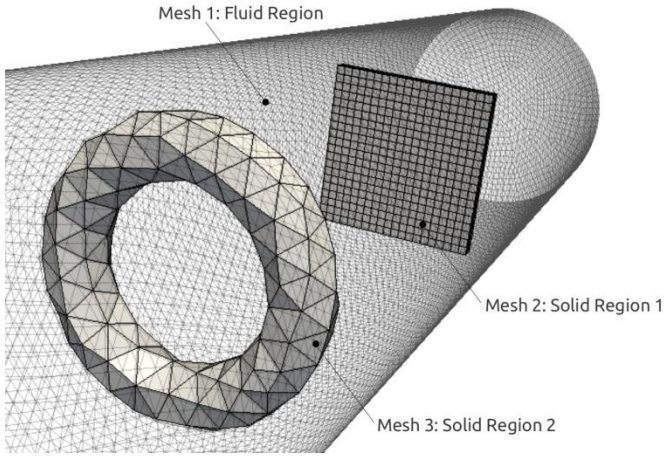


Outline

- ✓ Introduction and motivation
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  - ✓ Governing equations
  - ✓ Numerical methodology
- ✓ **Validation and examples**
  - ✓ Annular reactor (simple chemistry)
  - ✓ CPO of CH_4 on platinum gauze (complex 3D geometry)
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
- ✓ **Extensions**
  - ✓ KMC (Kinetic Monte Carlo)
  - ✓ **Multi-region solver**
- ✓ Conclusions and future works

Motivation





- ✓ In the original version of catalyticFOAM the catalyst morphology is not detailed
- ✓ the presence of the catalyst was accounted for by as boundary condition imposing continuity between the reactive flux and the diffusive flux to and from the catalytic surface.

This approach does not account for diffusive limitations in the solid phase or in general for the intra-solid transport phenomena

Need of a Multi-Region Solver (gas phase + solid phases)

How to couple the regions?

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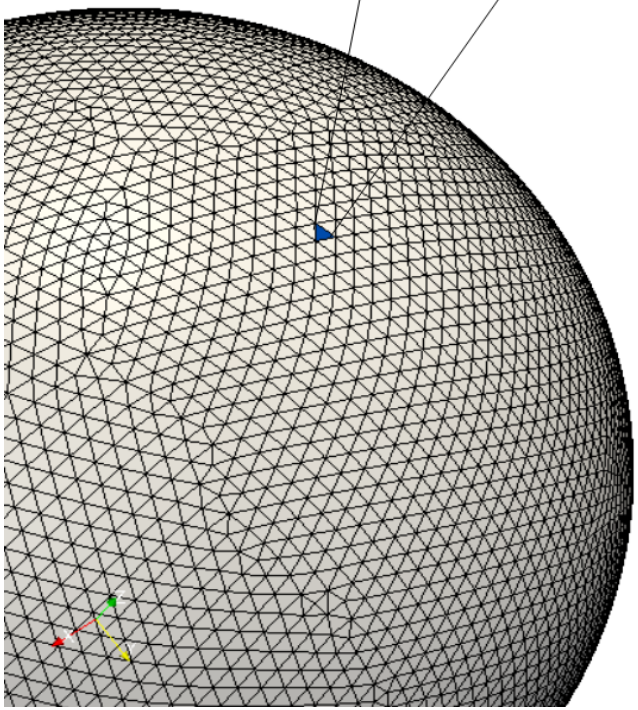
Coupling at the boundary interface:

- ✓ Conjugate heat transfer
- ✓ Conjugate mass transfer

$$\begin{cases} k_{SOL,I}\left(\frac{\partial T_{SOL}}{\partial x}\right)_{(I)} = k_{FLUID,I}\left(\frac{\partial T_{FLUID}}{\partial x}\right)_{(I)} \\ T_{SOL,I} = T_{FLUID,I} \end{cases}$$

$$\begin{cases} D_{SOL}\left(\frac{\partial C_{SOL}}{\partial x_I}\right)_{(I)} = D_{FLUID}\left(\frac{\partial C_{FLUID}}{\partial x_I}\right)_{(I)} \\ C_{SOL,I} = C_{FLUID,I} \end{cases}$$



Partitioned Approach

- ✓ Governing equations are solved in each zone with the appropriate BCs.
- ✓ Mixed BCs for a PDE indicates that different BCs are used on different parts
- ✓ of the boundary of the domain of the equation.
- ✓ The resulting conditions have to be used for each region, according to the
- ✓ updated values in the neighboring one.

The partitioned approach

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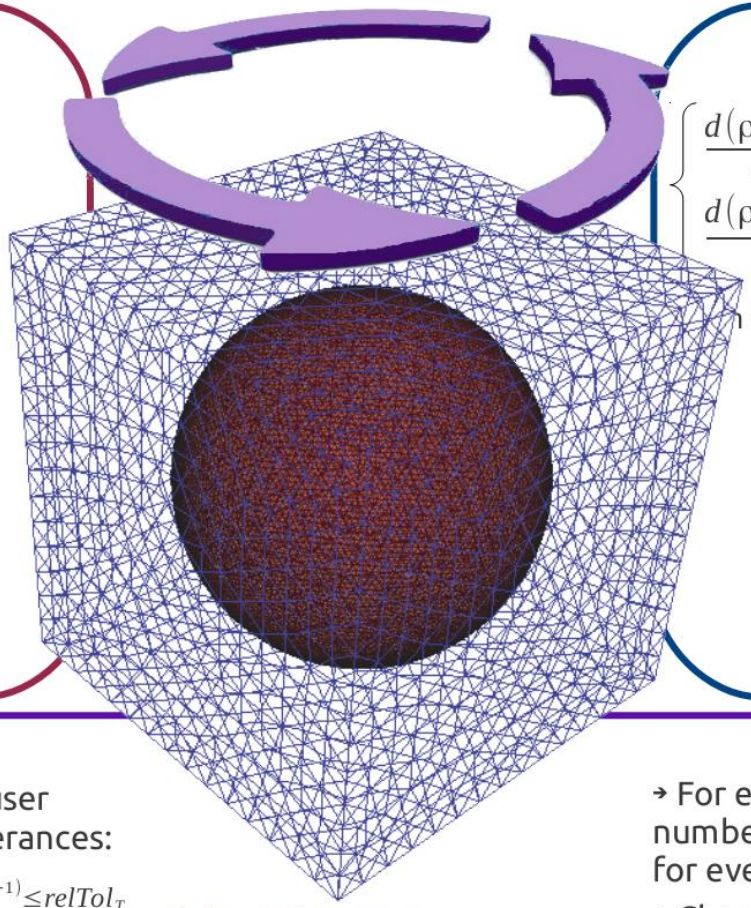
Solid Interface Cells

$$\begin{cases} \dfrac{d(\rho_{mix} Y_i)}{dt} = \nabla(\rho_{mix} D_{\mathrm{mix,i}} \nabla(Y_i)) \\ \dfrac{d(\rho_{mat} c_p T)}{dt} = \nabla(k \nabla(T)) \end{cases}$$

with the mixed BCs on the interface:

$$T_{\mathrm{I,SOL}} = \frac{\frac{k_{SOL} \cdot T_{SOL}}{\Delta_{SOL}} + \frac{k_{FLU} \cdot T_{FLU}}{\Delta_{FLU}}}{\frac{k_{SOL}}{\Delta_{SOL}} + \frac{k_{FLU}}{\Delta_{FLU}}}$$

$$C_{\mathrm{I,SOL}} = \frac{\frac{D_{SOL} \cdot C_{SOL}}{\Delta_{SOL}} + \frac{D_{FLU} \cdot C_{FLU}}{\Delta_{FLU}}}{\frac{D_{SOL}}{\Delta_{SOL}} + \frac{D_{FLU}}{\Delta_{FLU}}}$$



Fluid Interface Cells

$$\begin{cases} \dfrac{d(\rho_{mix} Y_i)}{dt} = \nabla(\rho_{mix} D_{\mathrm{mix,i}} \nabla(Y_i)) - \nabla(\Phi Y_i) \\ \dfrac{d(\rho_{mat} c_p T)}{dt} = \nabla(k \nabla(T)) \end{cases}$$

n the mixed BCs on the interface:

$$T_{\mathrm{I,FLU}} = \frac{\frac{k_{FLU} \cdot T_{FLU}}{\Delta_{FLU}} + \frac{k_{SOL} \cdot T_{SOL}}{\Delta_{SOL}}}{\frac{k_{FLU}}{\Delta_{FLU}} + \frac{k_{SOL}}{\Delta_{SOL}}}$$

$$C_{\mathrm{I,FLU}} = \frac{\frac{D_{FLU} \cdot C_{FLU}}{\Delta_{FLU}} + \frac{D_{SOL} \cdot C_{SOL}}{\Delta_{SOL}}}{\frac{D_{FLU}}{\Delta_{FLU}} + \frac{D_{SOL}}{\Delta_{SOL}}}$$

Convergence Criteria

- Residuals must be lower than user given absolute and relative tolerances:

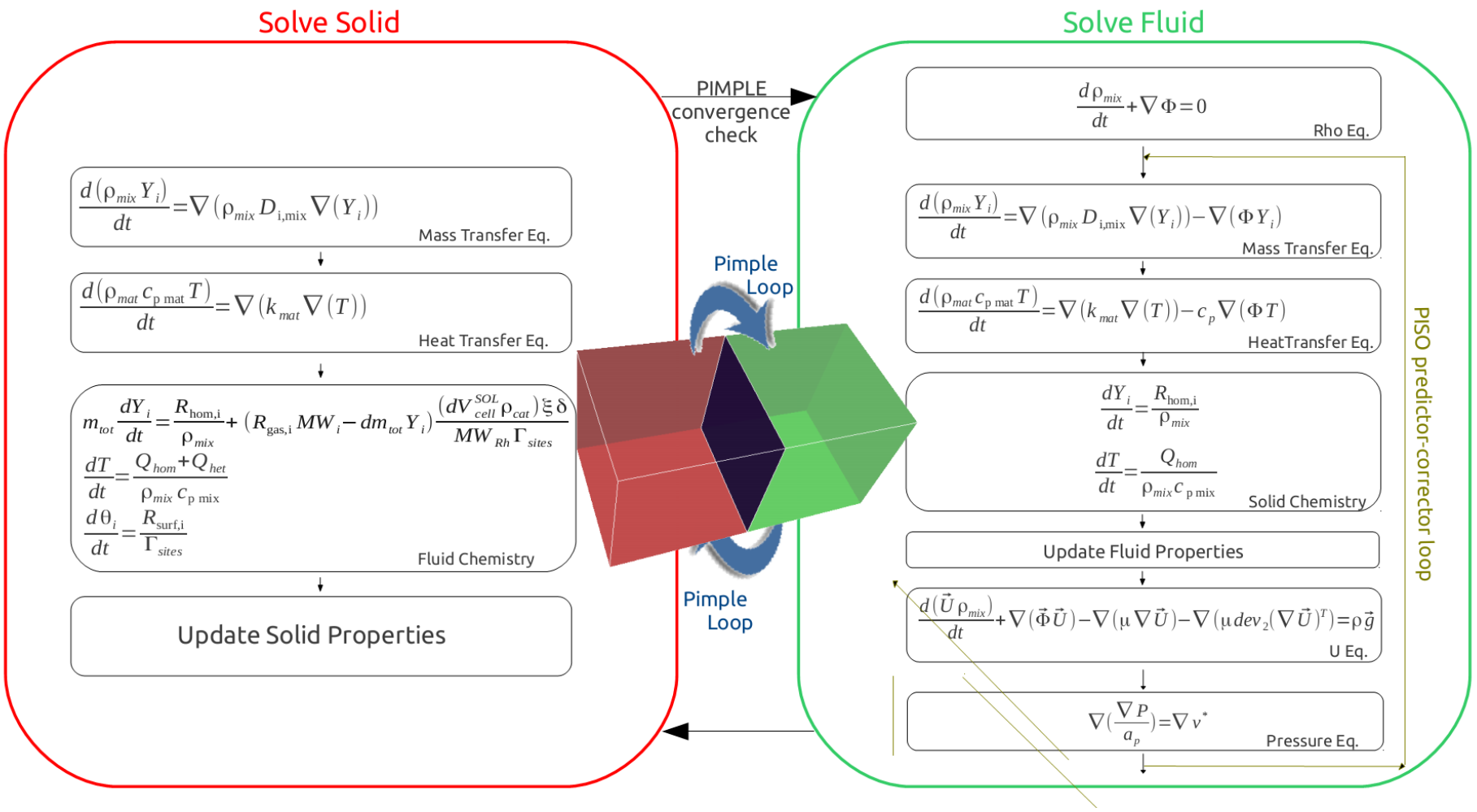
$$\left|T^{(k)} - T^{(k-1)}\right| \le absTol_T \qquad \left|T^{(k)} - T^{(k-1)}\right| \div T^{(k-1)} \le relTol_T$$
$$\left|Y_i^{(k)} - Y_i^{(k-1)}\right| \le absTol_Y \qquad \left|Y_i^{(k)} - Y_i^{(k-1)}\right| \div Y_i^{(k-1)} \le relTol_Y$$

PIMPLE Loop

PIMPLE Method

- For each time step, given a maximum number of iterations, solve alternatively for every cell of the 2 coupled regions
- Check for convergence: when it is reached, proceed to the next time step

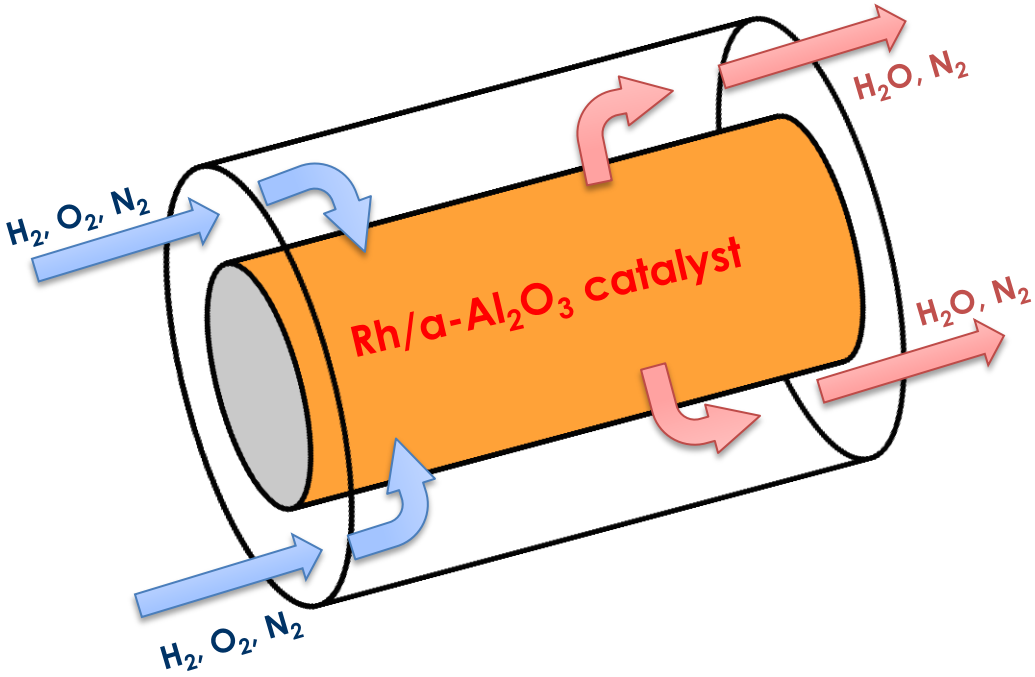
Multi-domain code



Example: annular reactor (I)

The numerical tests have been performed by investigating the combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor (*).

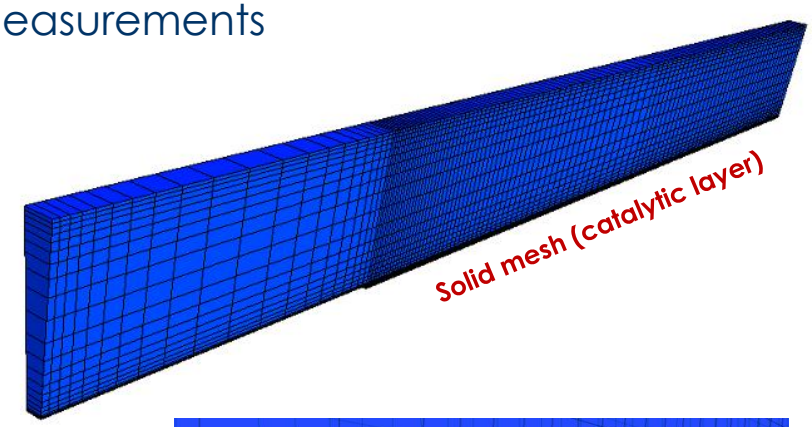
Operating conditions	
Inner radius	0.235 cm
Outer radius	0.450 cm
Reactor length	1.5 cm
H_2 mole fraction	0.04 (-)
O_2 mole fraction	0.01 (-)
N_2 mole fraction	0.95 (-)
Pressure	1 atm
Rh site density	2.49 10^{-9} mol/cm^2
Catalytic surf.	5 cm^{-1}

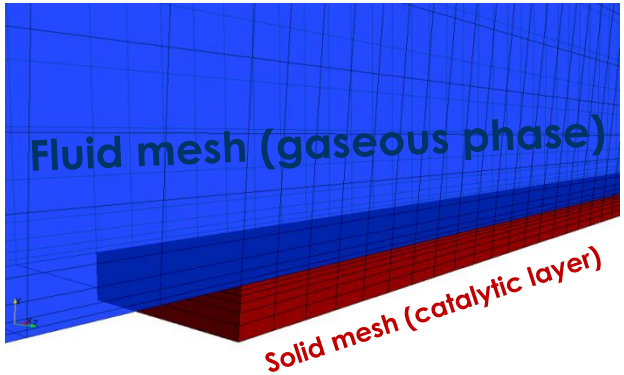


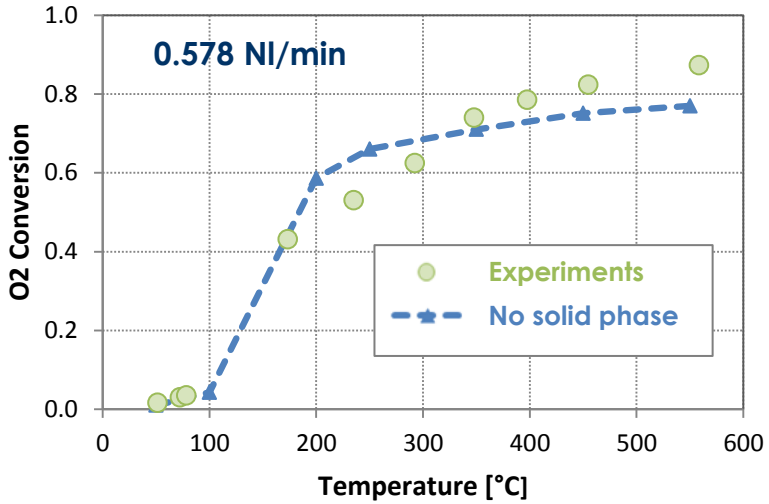
(*) ***M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos,*** *2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst, Chemical Engineering Science (2008)*

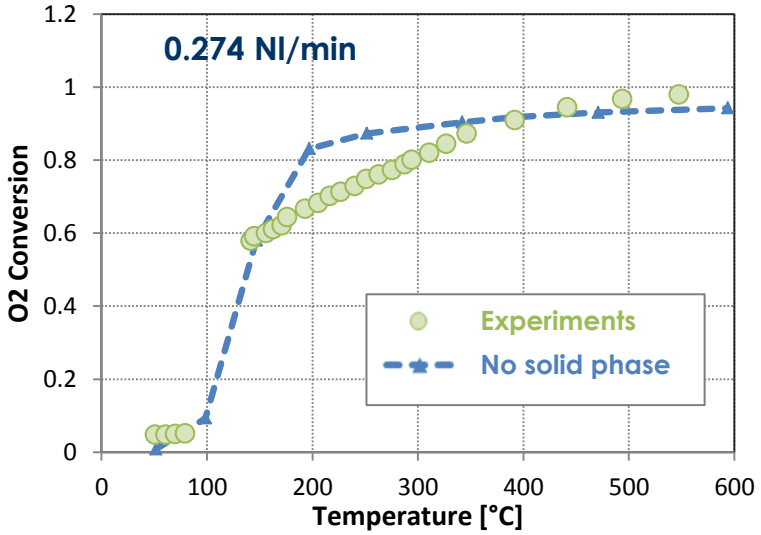
Example: annular reactor (II)

Numerical simulations take into account the solid phase (catalytic layer) in order to model the diffusive limitations and correctly capture the experimental measurements





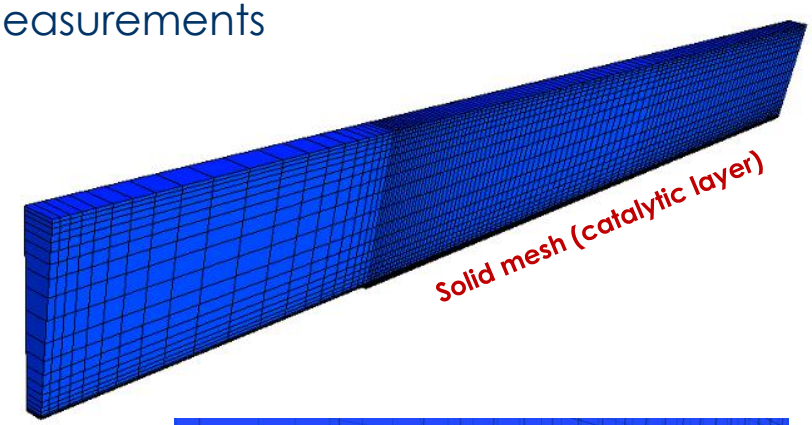


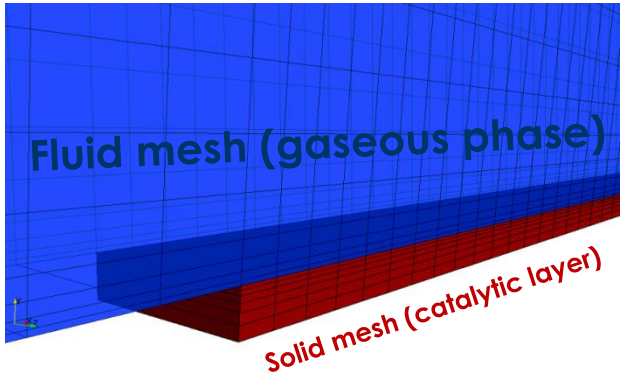


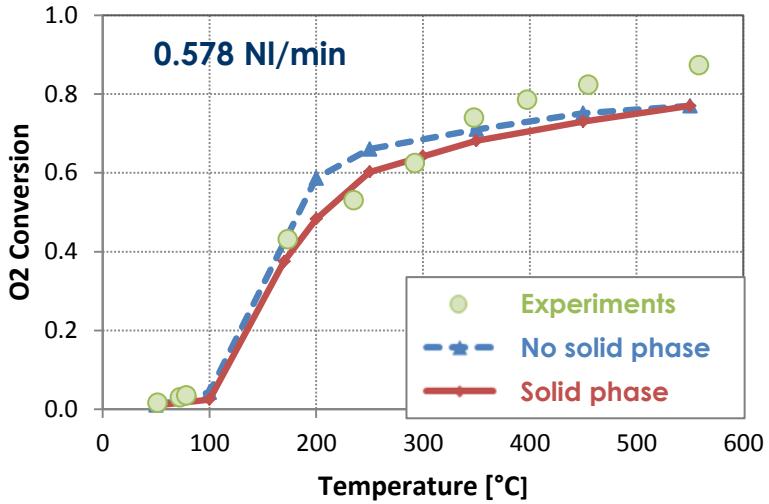
The mesh is thus highly refined near the catalytic wall in the radial direction

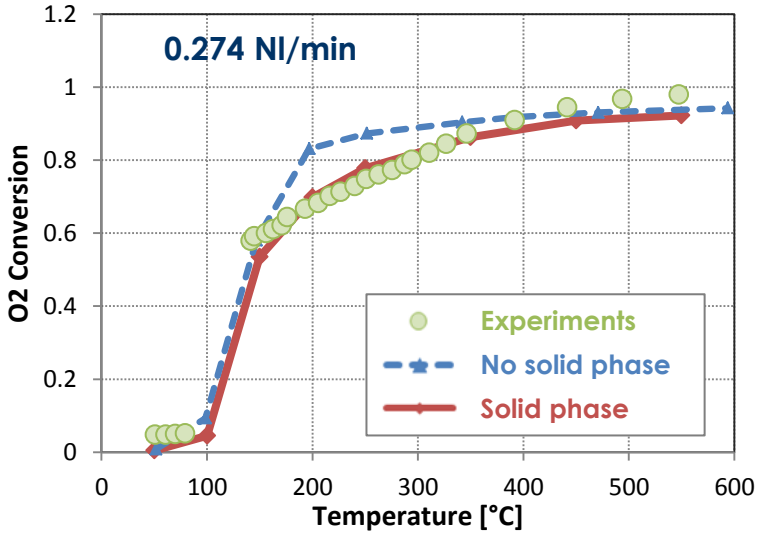
Example: annular reactor (II)

Numerical simulations take into account the solid phase (catalytic layer) in order to model the diffusive limitations and correctly capture the experimental measurements





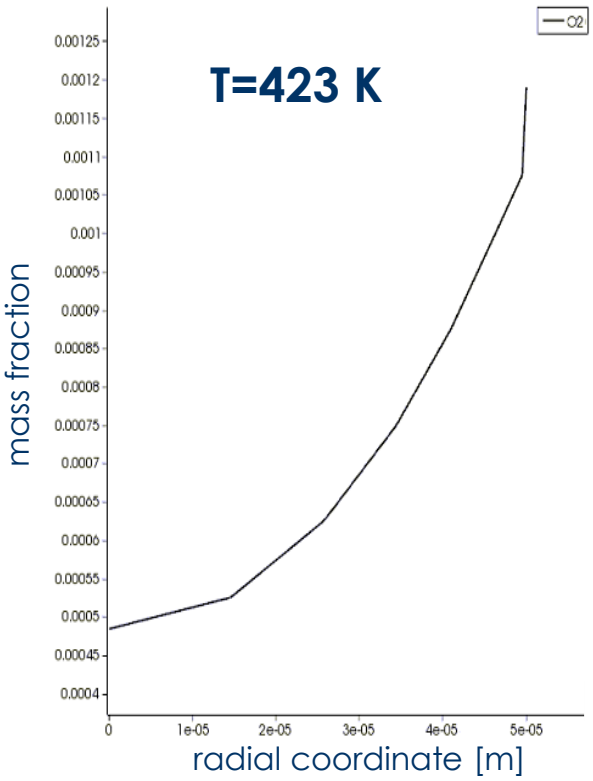


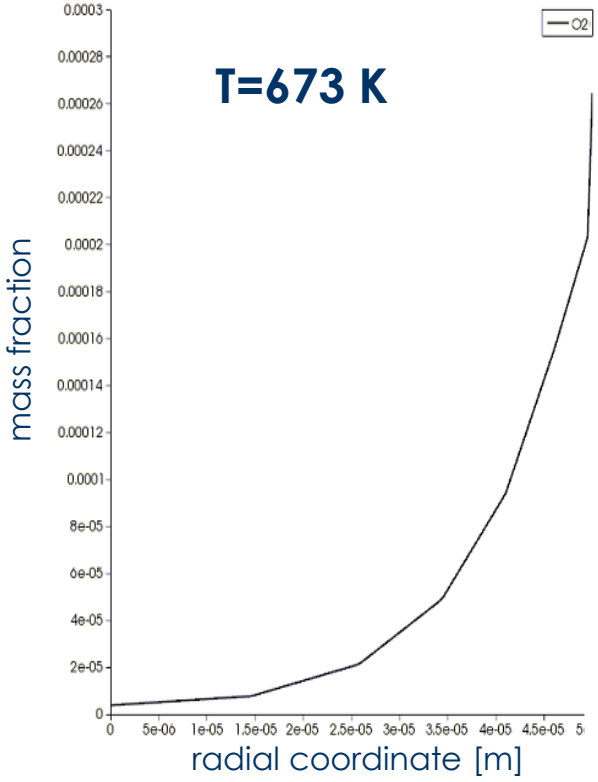


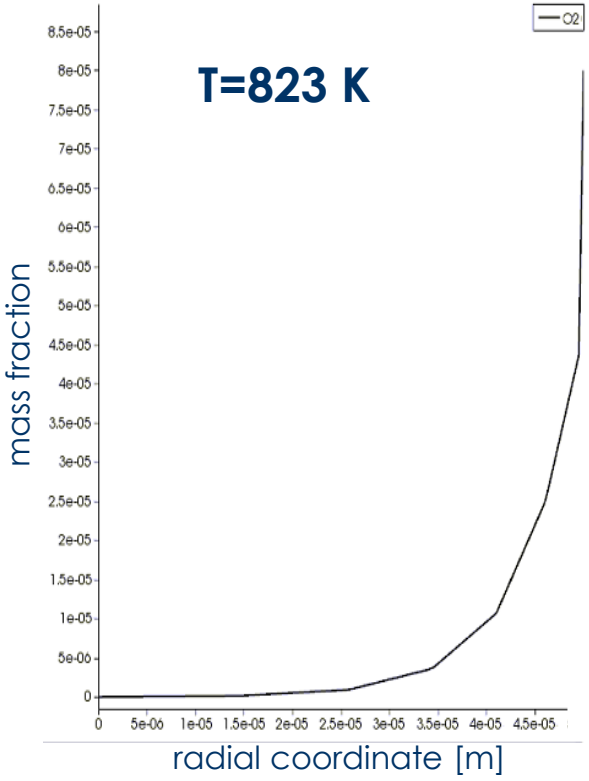
The mesh is thus highly refined near the catalytic wall in the radial direction

Example: annular reactor (IV)

O_2 mass fraction in radial direction in the solid phase







strong influence of diffusive intra-phase limitations inside the 50 μm thick catalytic solid phase in the middle range of temperatures

What we have done…

- ✓ Numerical procedure adopted → Splitting scheme
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework → Implementation of the solution procedure
- ✓ Numerical tests → Optimization of spatial and temporal discretization
- ✓ Validation tests → Reliable description of the system
- ✓ Show-case → Wide applicability

What we are doing/planning to do…

- Description of the solid-phase:
  - Energy transport within the solid and with the environment
  - Mass transport within the solid (diffusion and reaction problem, i.e., detailed assessment of internal mass limitations)
- Validation and extension to turbulent flow
- Kinetic Monte Carlo
- Parallelization of the calculation
- Storage/retrieval methods (e.g. ISAT) for fast numerical integration of ODE systems

Release - Policy

The catalyticFOAM software is fully compatible with OpenFOAM version 2.1.x.

Nevertheless, it is not approved or endorsed by ESI/OpenCFD, the producer of the OpenFOAM software and owner of the OPENFOAM® and OpenCFD® trade marks.

Software will be released under the L-GPL license through an independent webiste: www.catalyticfoam.polimi.it

Acknowledgements

CatalyticFOAM@polimi.it

Students involved in the project:
S. Goisis, A. Osio, M. Calonaci, F. Furnari, G. Gentile,
F. Manelli, S. Rebughini, B. Baran, Y. Niyazi

BASF
The Chemical Company

Additional slides

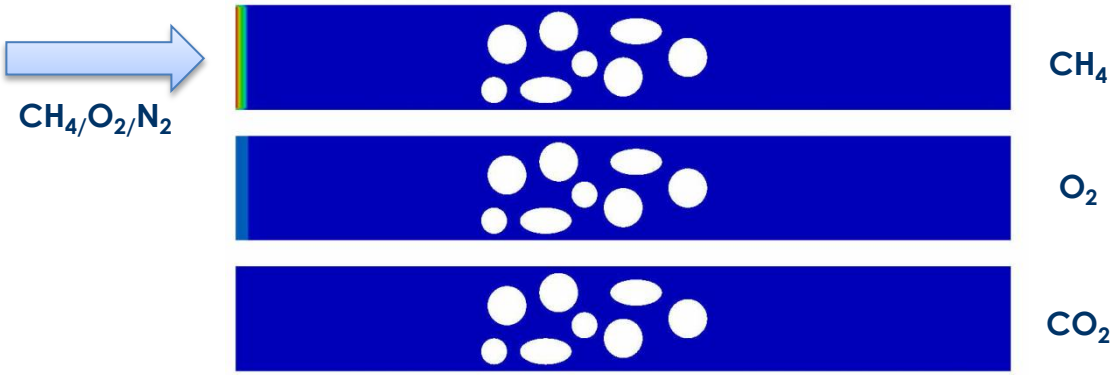
Conclusions

- ✓ **C++ library for homogeneous and heterogeneous chemistry (complex kinetics, thermodynamics, transport properties)**
- ✓ **Development of the catalyticFOAM solver for the OpenFOAM® framework**
- ✓ **Validation tests (lab-scale systems)**
  - ✓ Annular reactor (simple chemistry)
  - ✓ CPO of CH_4 on platinum gauze (complex 3D geometry)
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings

Perspectives

Validation

- ✓ Realistic reactors



Chemistry and Physics

- ✓ Extension to turbulent flow

Numerics

- ✓ Storage/retrieval methods (e.g. ISAT) for fast numerical integration of ODE systems
- ✓ Steady state problems: more efficient strategies
- ✓ Improvement of parallel performances

Acknowledgements

Matteo Calonaci

Federica Furnari

Sandro Goisis

Alessandra Osio

Thank you for your attention!

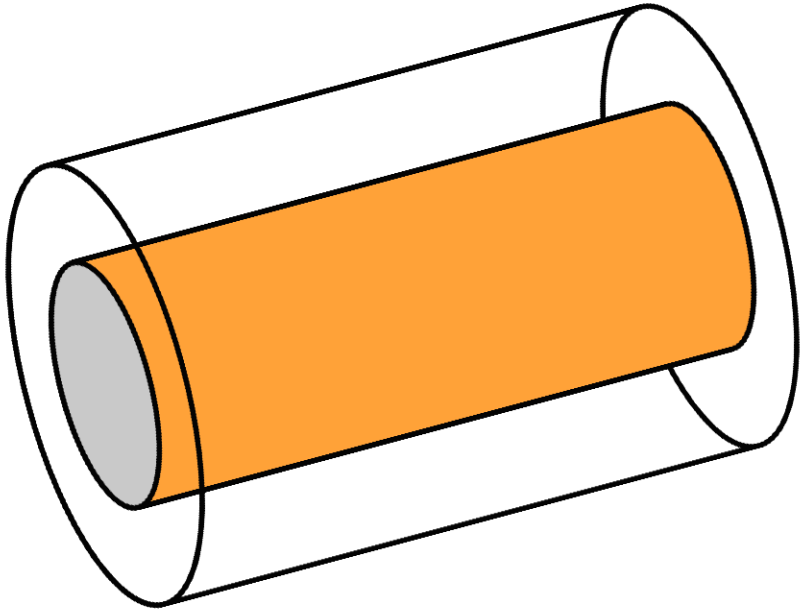
www.catalyticfoam.polimi.it
catalyticfoam@polimi.it

Show case

POLITECNICO DI MILANO

Any geometry with arbitrary complexity can be investigated with catalyticFOAM.

Operating conditions	
Inner radius	0.235 cm
Outer radius	0.450 cm
Reactor length	1.5 cm
H_2 mole fraction	0.04 (-)
O_2 mole fraction	0.01 (-)
N_2 mole fraction	0.95 (-)
Pressure	1 atm



(*) 2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst. M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos – CES 2008

Show case

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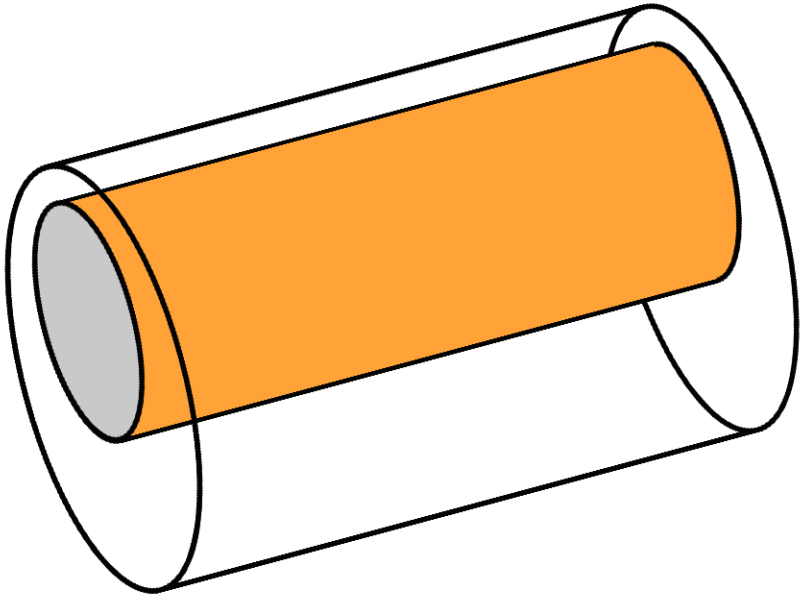
N_2 mole fraction	0.95 (-)
Pressure	1 atm
Eccentricity	50 %



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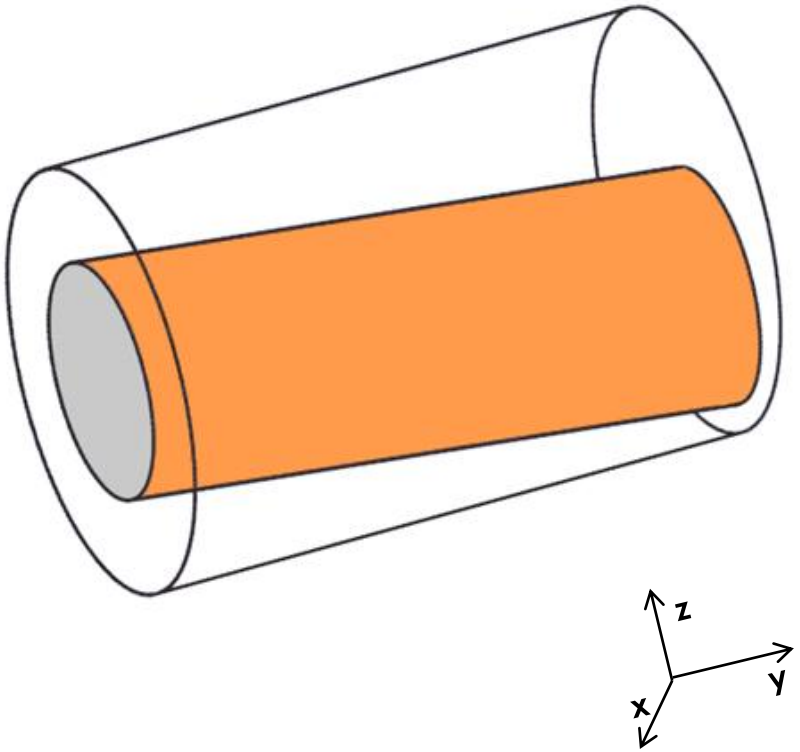
H_2 mole fraction	0.04 (-)
O_2 mole fraction	0.01 (-)
N_2 mole fraction	0.95 (-)
Pressure	1 atm
Slope (x-axis)	2,5°
Slope (y-axis)	2,5°



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The possible eccentricity of the annulus in experimental apparatus has been investigated with catalyticFOAM.

Operating conditions	
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Reactor length	1.5 cm
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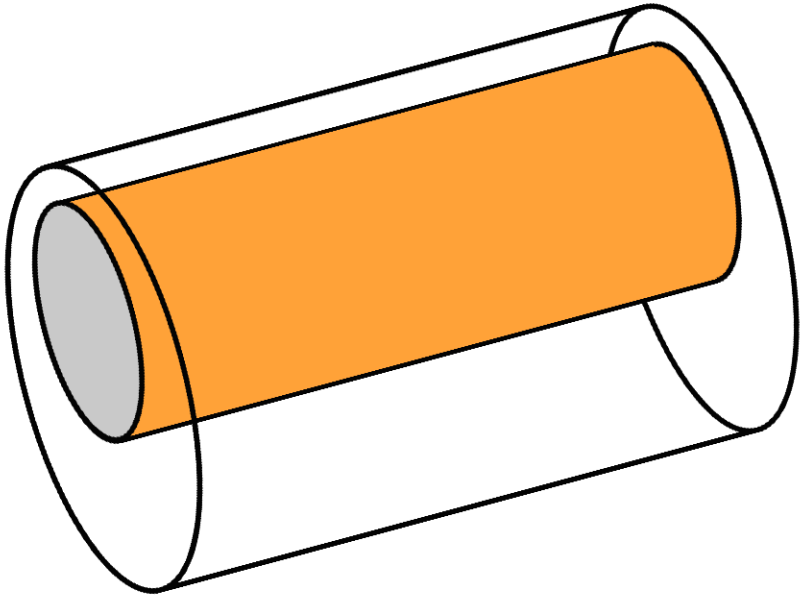
O_2 mole fraction	0.01 (-)
N_2 mole fraction	0.95 (-)
Pressure	1 atm
Eccentricity	50 %



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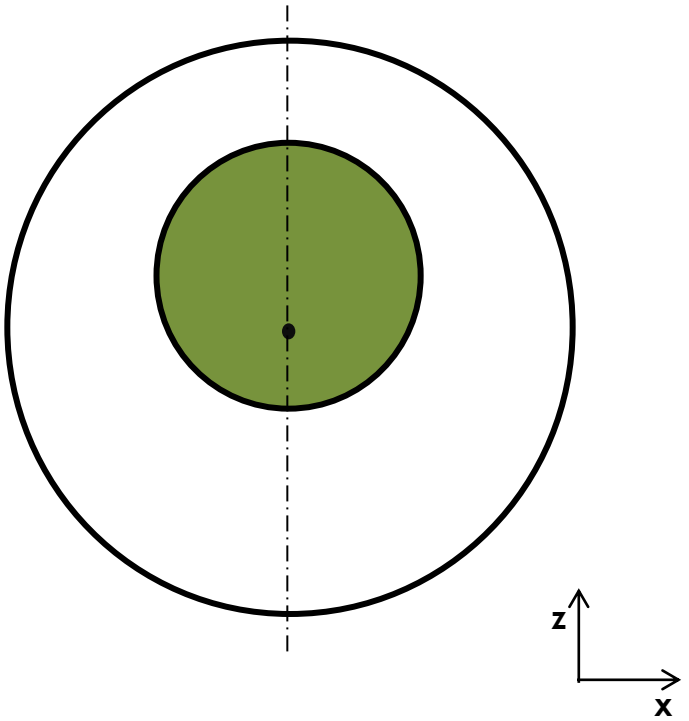
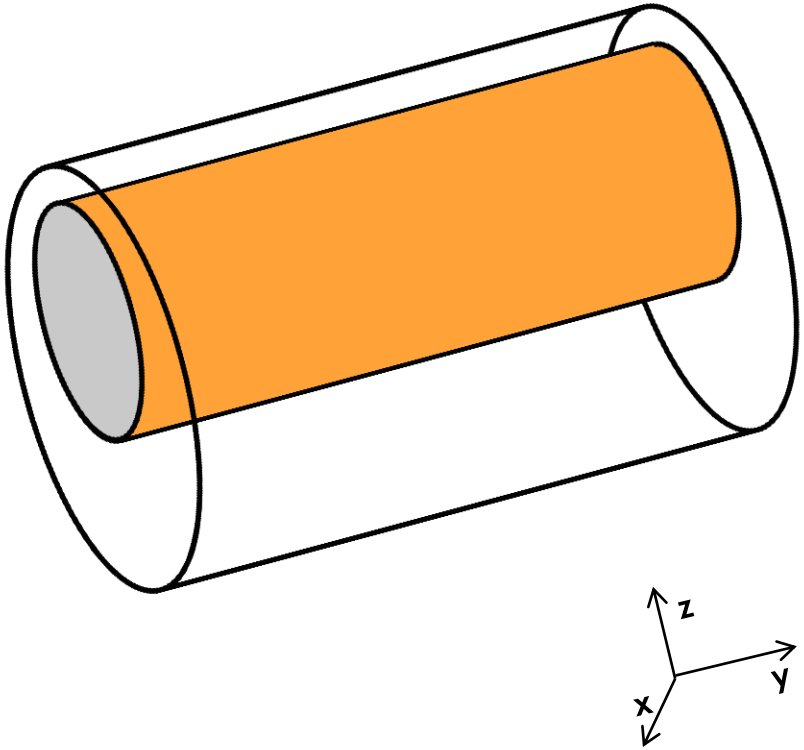
Identification of the calculation domain

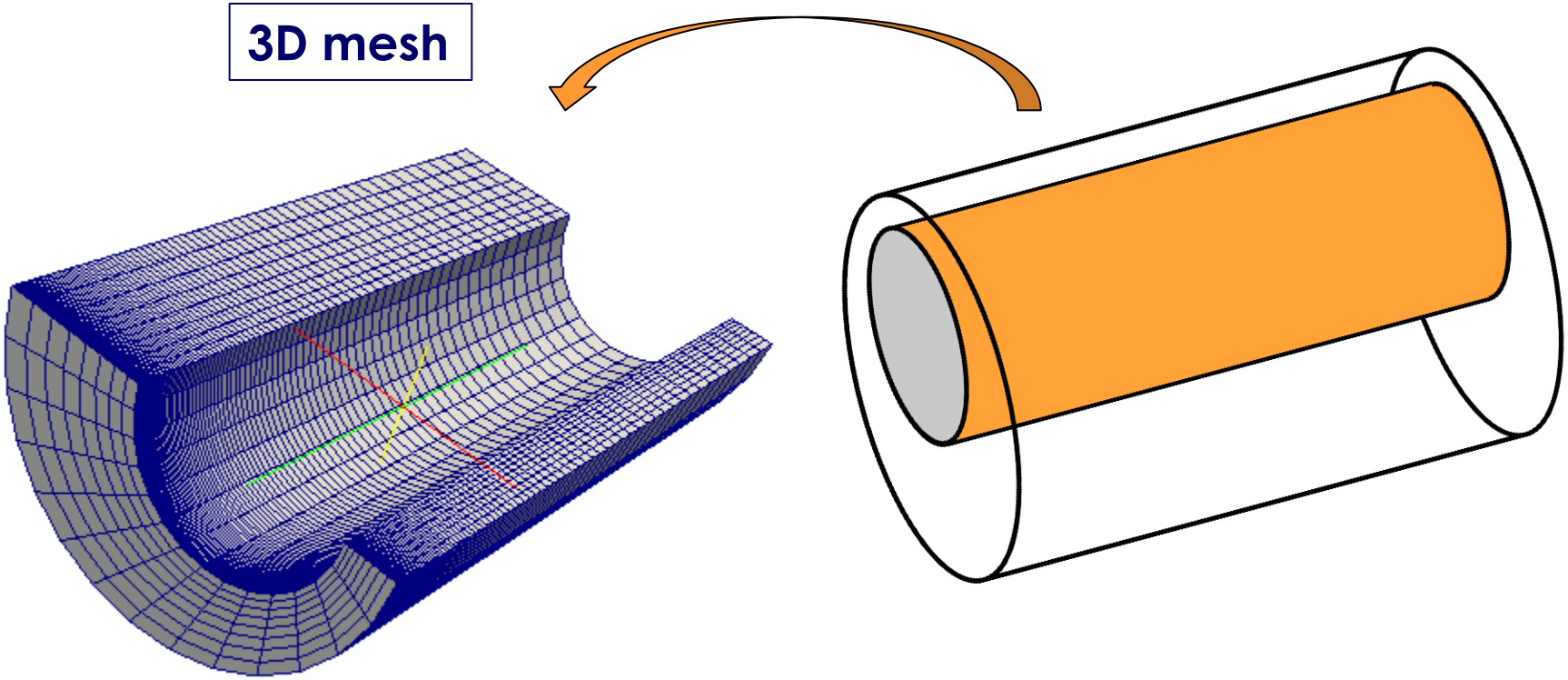
- ✓ Eccentricity of 50%
- ✓ Planar symmetry





Show case

Identification of the calculation domain



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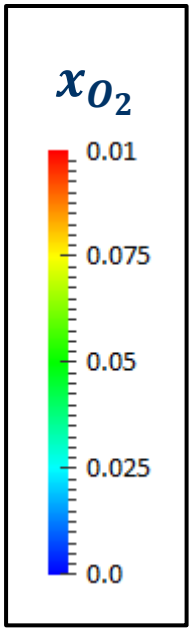
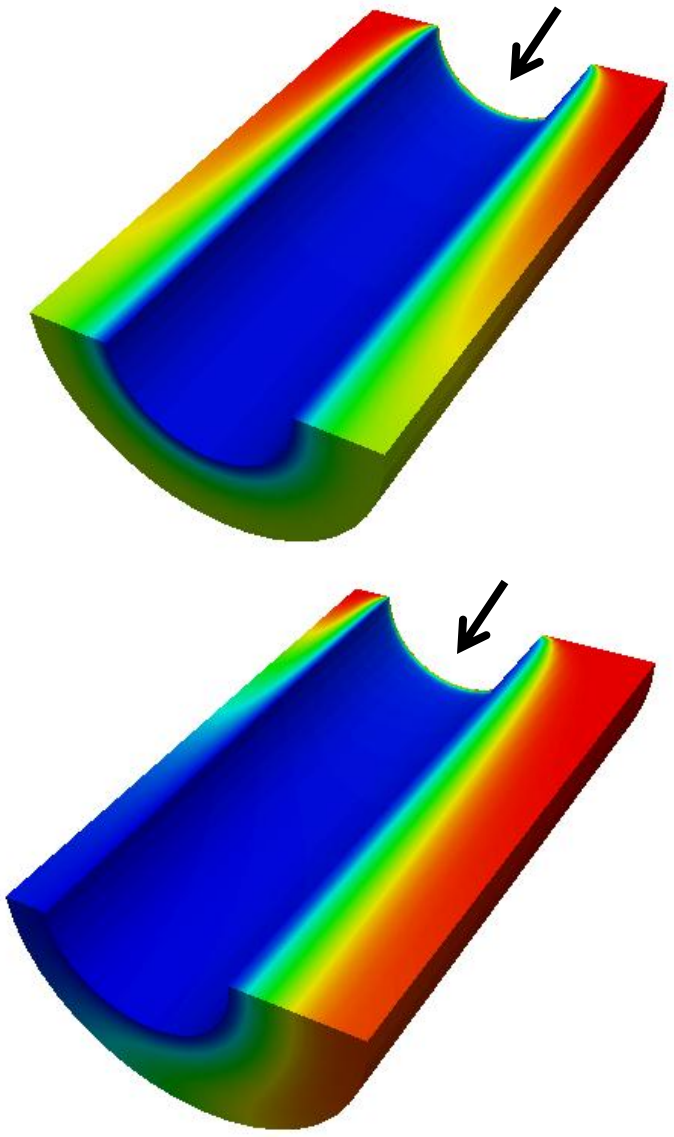
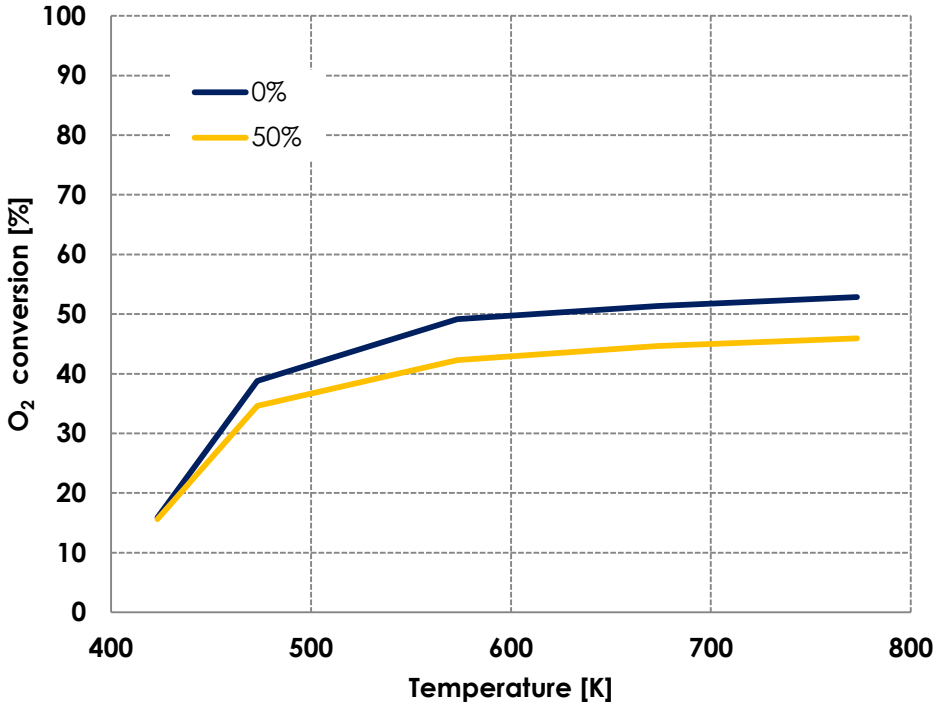
M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos – CES 2008

Show case





Effect of eccentricity on the O_2 conversion at different temperatures



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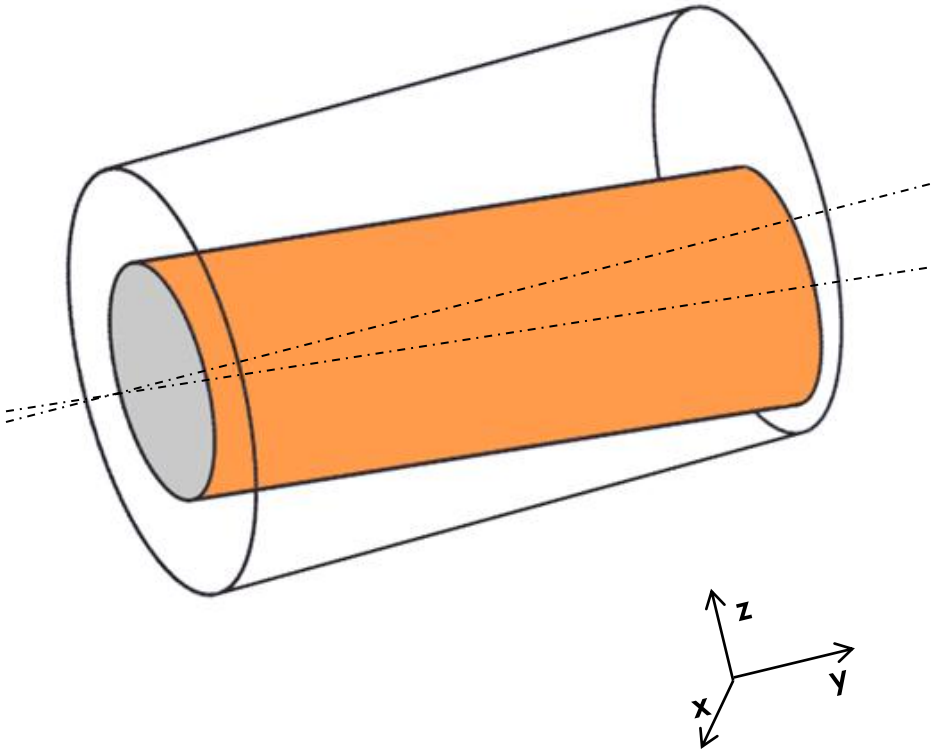
M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos – CES 2008

Show case

POLITECNICO DI MILANO

Any geometry with arbitrary complexity can be investigated with catalyticFOAM.

Operating conditions	
Inner radius	0.235 cm
Outer radius	0.450 cm
Reactor length	1.5 cm
H_2 mole fraction	0.04 (-)
O_2 mole fraction	0.01 (-)
N_2 mole fraction	0.95 (-)
Pressure	1 atm
Slope (x-axis)	2,5°
Slope (y-axis)	2,5°



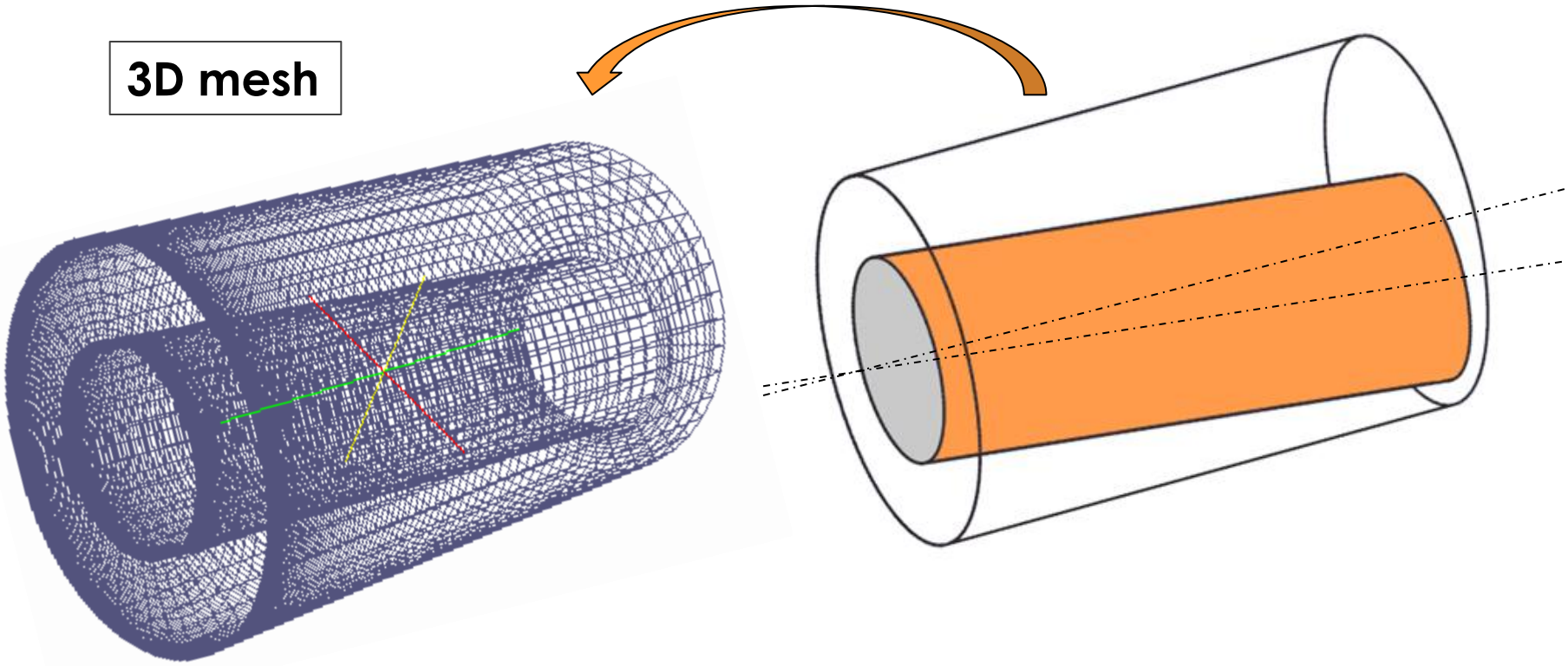
(*) 2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst. M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos – CES 2008

Show case

POLITECNICO DI MILANO

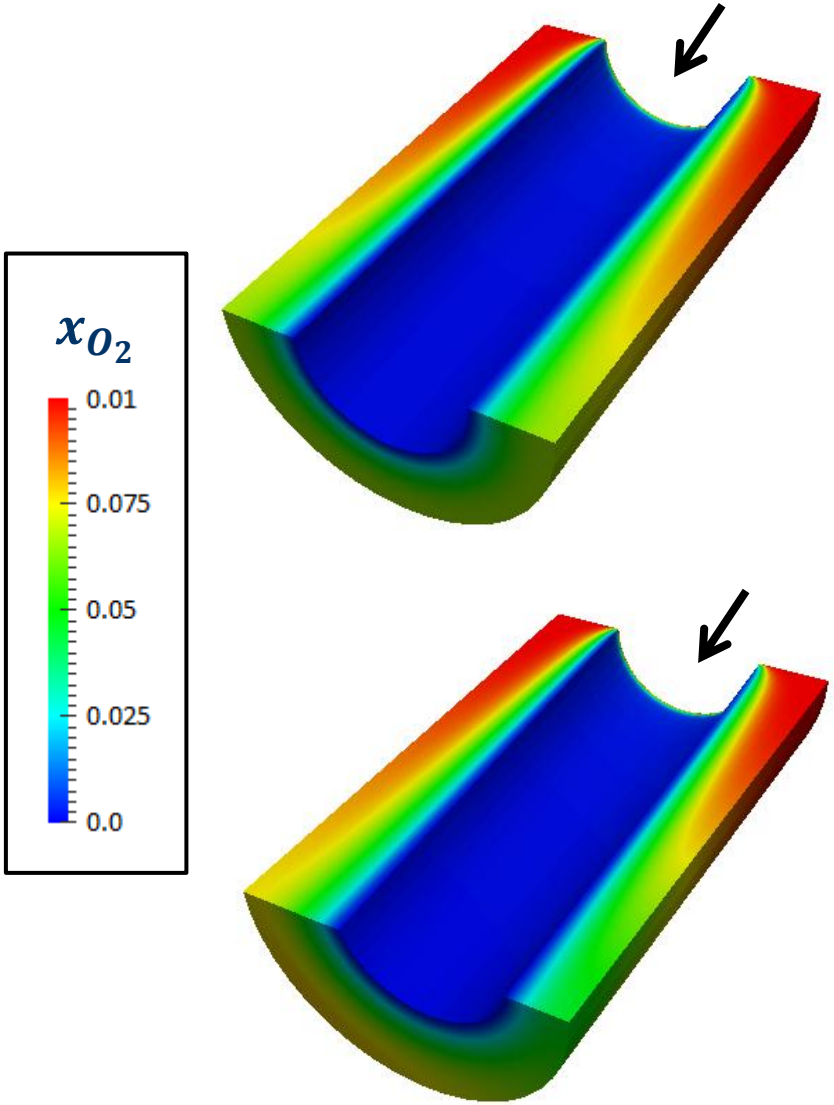
The case of cylinders with incident axis has been studied with catalyticFOAM

3D mesh

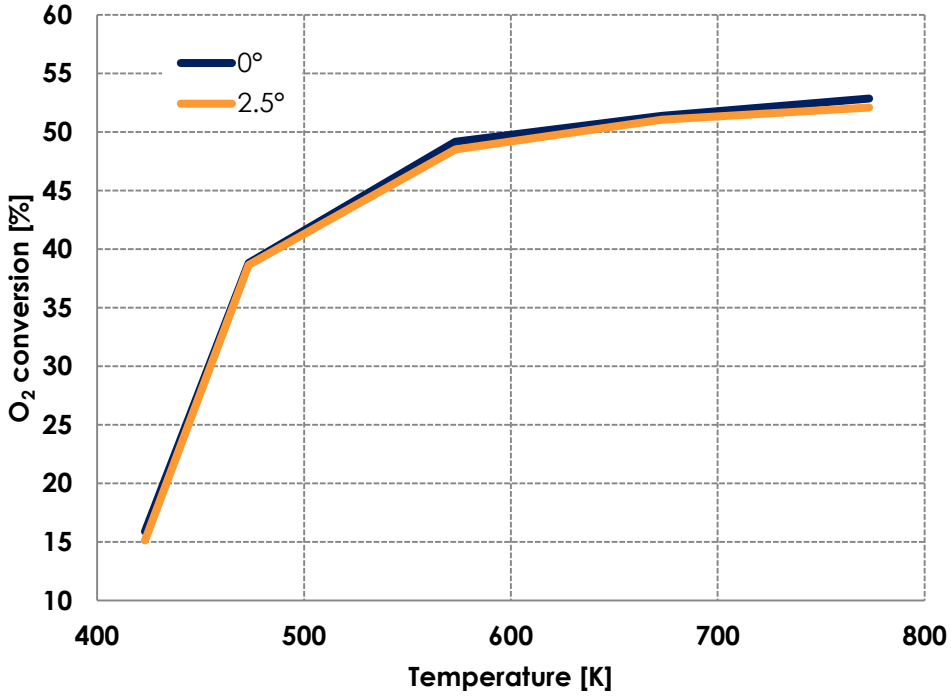


(*) 2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst. M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos – CES 2008

Show case



O_2 conversion at different temperatures for cylinders with incident axis

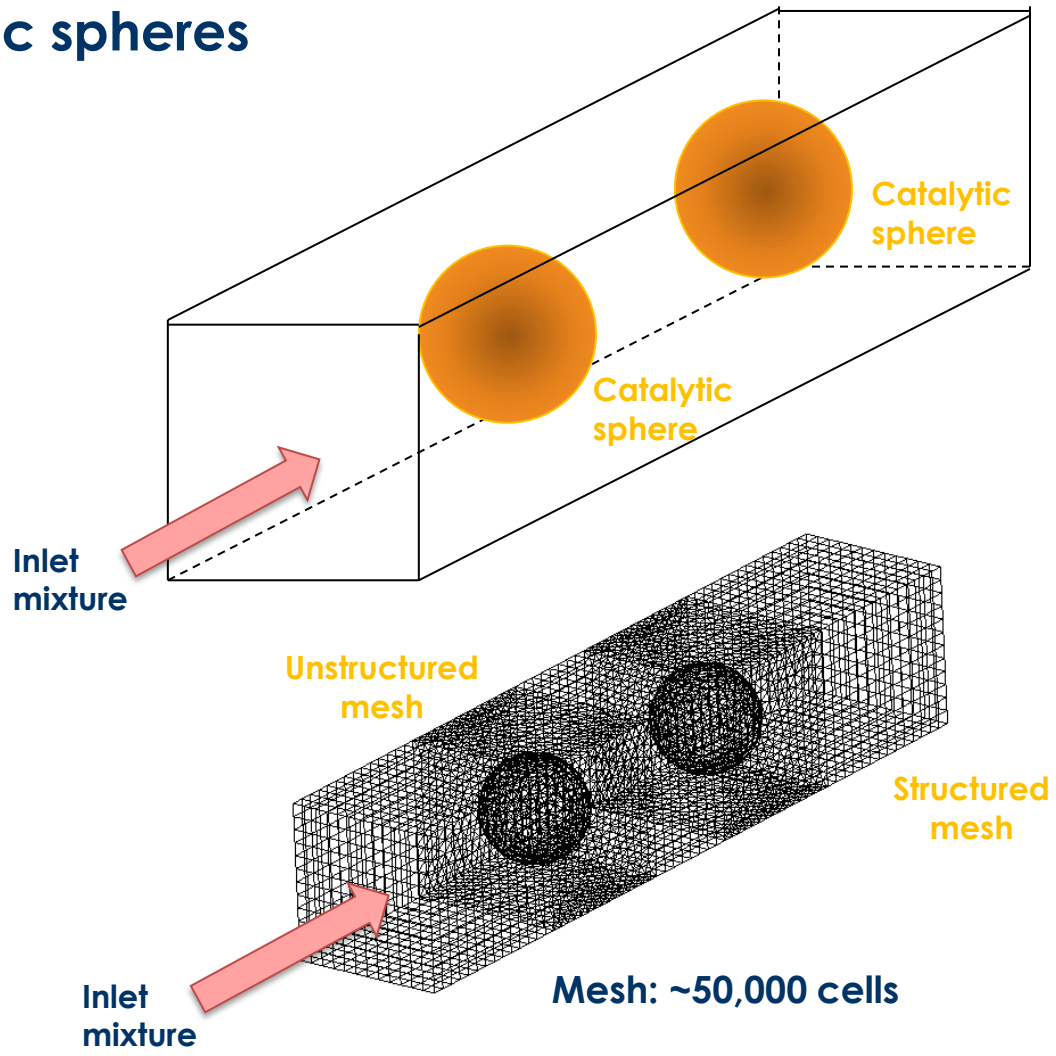


(*) 2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst.
M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos – CES 2008

More Complex Geometries

Square channel with catalytic spheres

Operating conditions	
Channel Side	0.30 cm
Channel length	1.50 cm
Sphere diameter	1.00 cm
CH_4 mole fraction	0.10
O_2 mole fraction	0.056
N_2 mole fraction	0.844
Pressure	1 atm
Temperature	873 K
Inlet velocity	2 m/s
Residence Time	7.5 ms
Reynolds Number	130
Rh site density	$2.49\ 10^{-9}$ mol/cm^2
Catalytic surface	1.566 (-)



Details

POLITECNICO DI MILANO

Heterogeneous kinetics

- 13 Species
- 82 Reactions

Maestri et al., 2009
Mhadeshwar and Vlachos, 2005

Homogeneous kinetics

- 23 Species
- 84 Reactions

DRM19 Kinetic Mechanism

Meshes

- 2X: 696 cells (58 x 12)
- 3X: 2784 cells (116 x 24)
- 4X: 11136 cells (232 x 48)

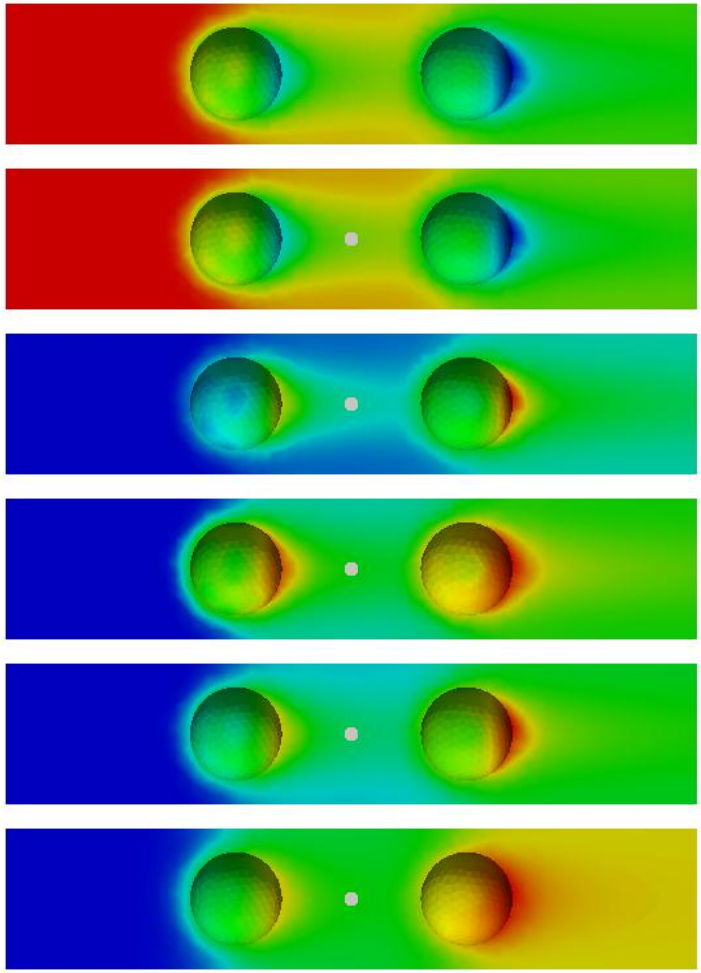
Numerical details

- Centered (2^{nd} order) spatial discretization
- Implicit Euler time integration
- Max Courant number 0.1

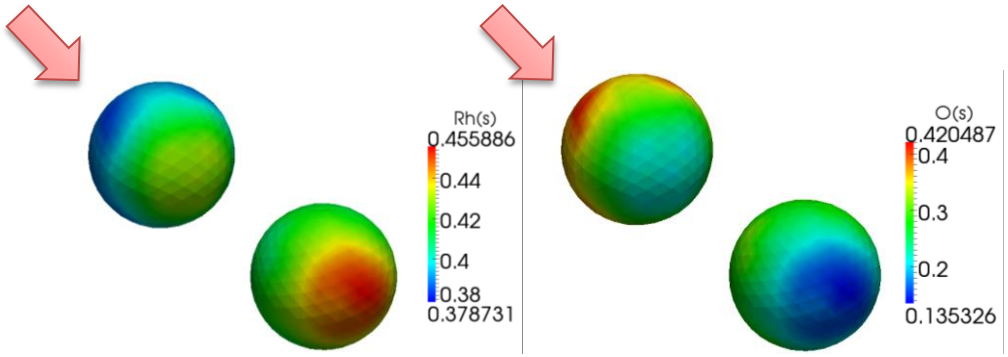
Main results (steady-state)

POLITECNICO DI MILANO

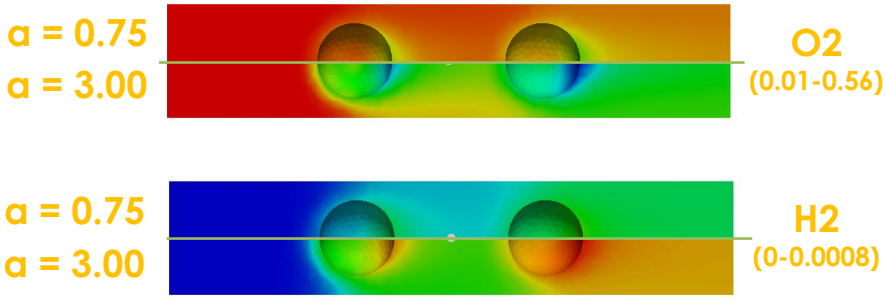
Mole fractions



Adsorbed species (mass fractions)

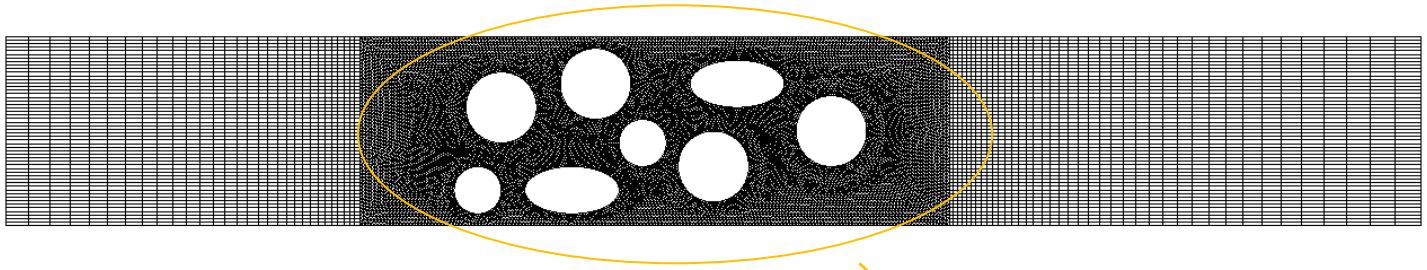


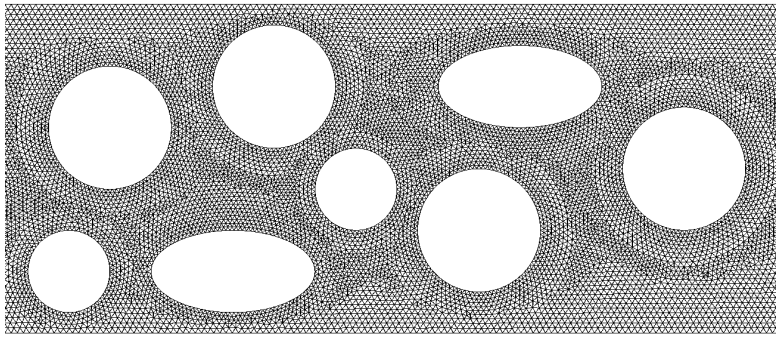
Effect of specific catalytic surface



2D Channel

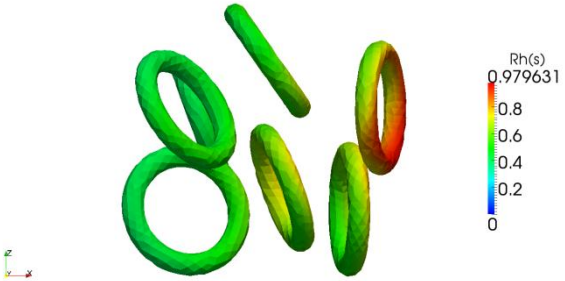
The calculation mesh is divided in structured and unstructured zones

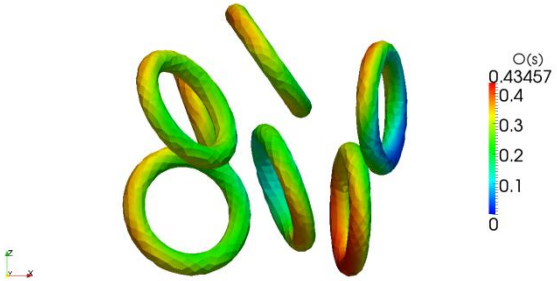


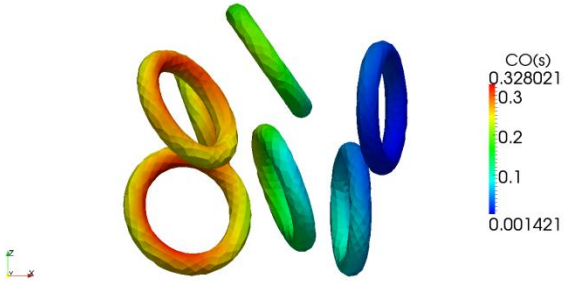


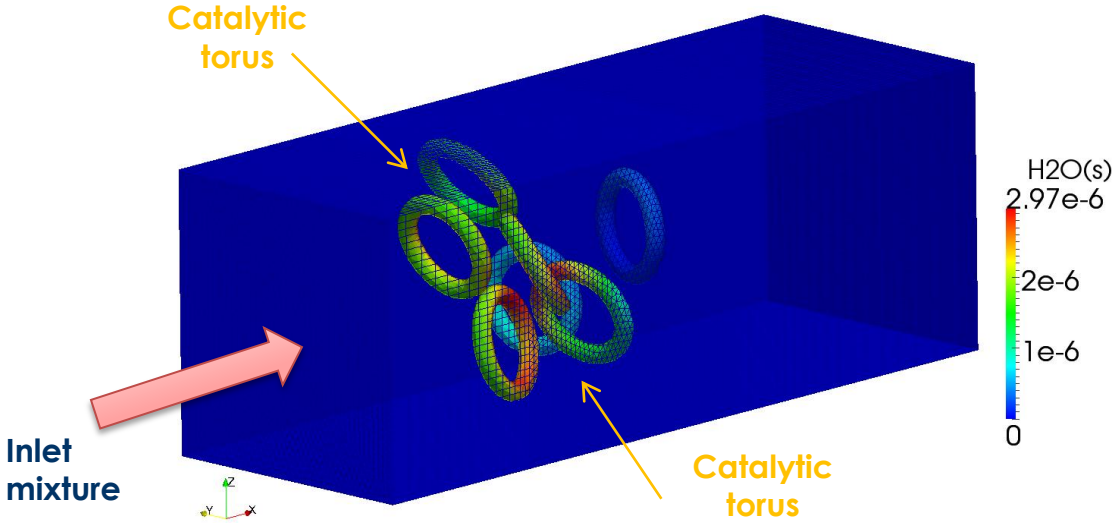
Operating conditions	
Channle thickness	0.8 cm
Channel length	6 cm
CH_4 mole fraction	0.100 (-)
O_2 mole fraction	0.056 (-)
N_2 mole fraction	0.844 (-)
Temperature	873.15 K
MESH	27,000 cells

Channel with catalytic, toroidal elements









3D Mesh: ~450,000 cells

- **Homogeneous reactors: 445,000**
- **Heterogeneous reactors: 5,000**

No homogeneous reactions!

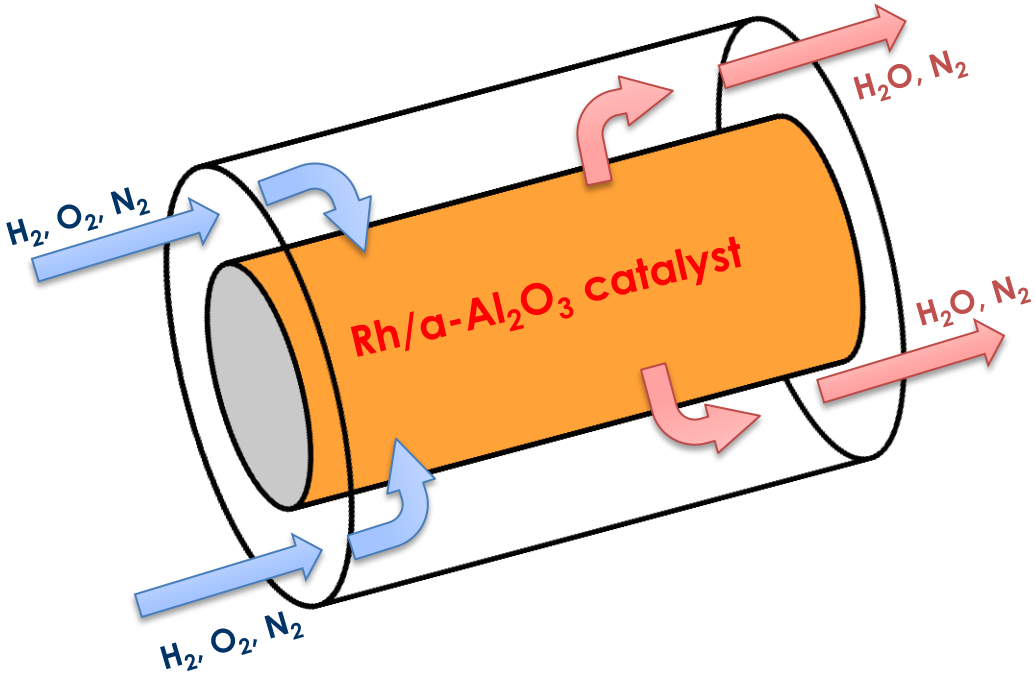
CPU time per heterogeneous reactor: 0.75 ms

This time is weakly dependent on the specific features of the investigated case

Example: annular reactor (I)

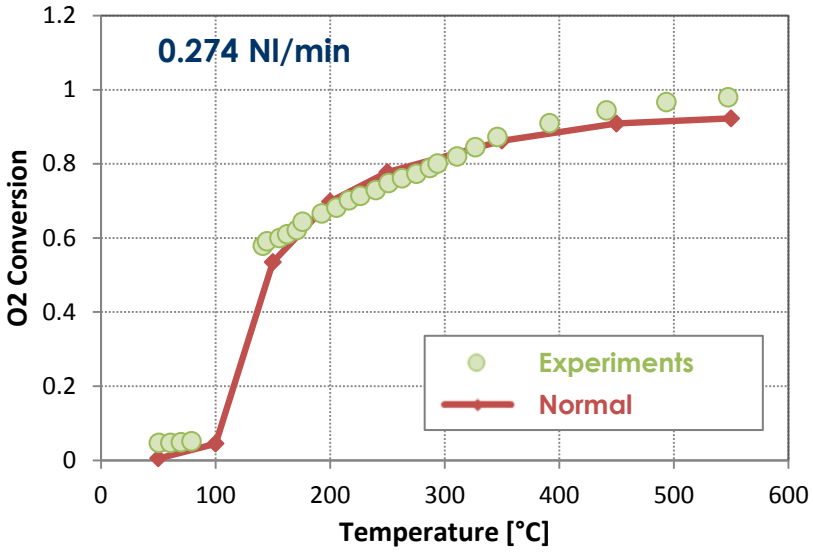
The numerical tests have been performed by investigating the combustion of a fuel-rich H_2 over Rh catalyst in an annular reactor (*).

Operating conditions	
Inner radius	0.235 cm
Outer radius	0.450 cm
Reactor length	1.5 cm
H_2 mole fraction	0.04 (-)
O_2 mole fraction	0.01 (-)
N_2 mole fraction	0.95 (-)
Pressure	1 atm
Rh site density	2.49 10^{-9} mol/cm^2
Catalytic surf.	5 cm^{-1}



(*) ***M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos,*** *2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst, Chemical Engineering Science (2008)*

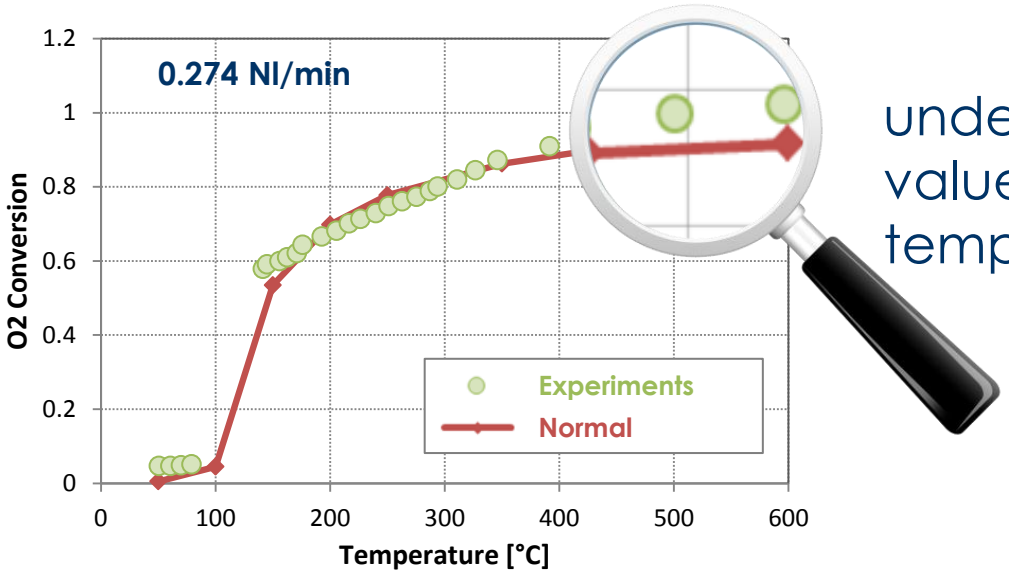
Example: annular reactor (III)



underestimation of conversion values occurring at high temperatures

It is then possible to investigate also the underestimation of conversion values occurring at high temperatures: the "conversion enhancing mechanism" observed in the experimental data cannot be due homogeneous gas phase chemistry playing a role at high temperatures, as the fraction of H* which is predicted to desorb in the gas phase at 500°C is many order of magnitudes lower than the one identified as necessary to trigger gas-phase chemistry.

Example: annular reactor (III)



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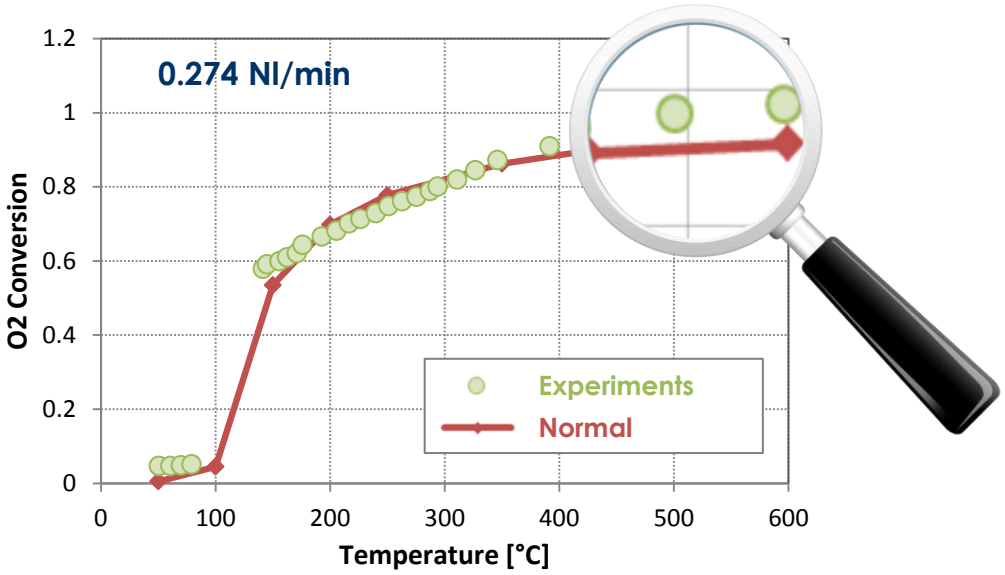
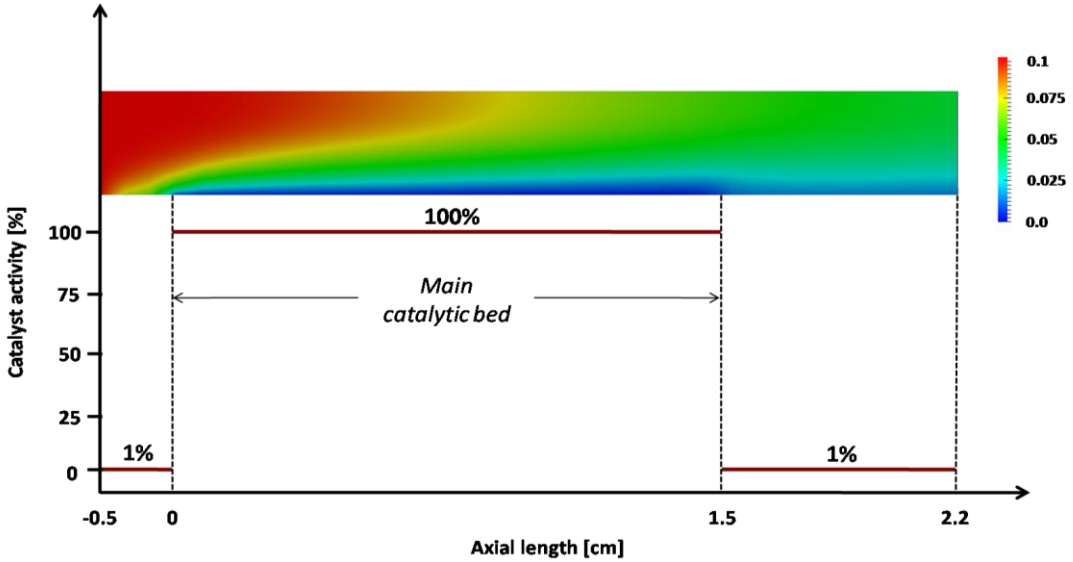
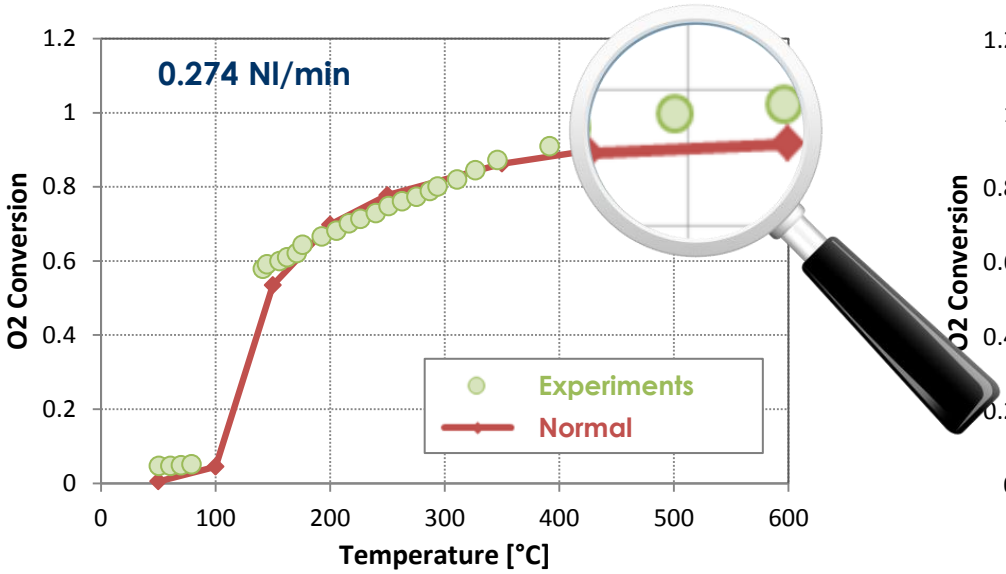


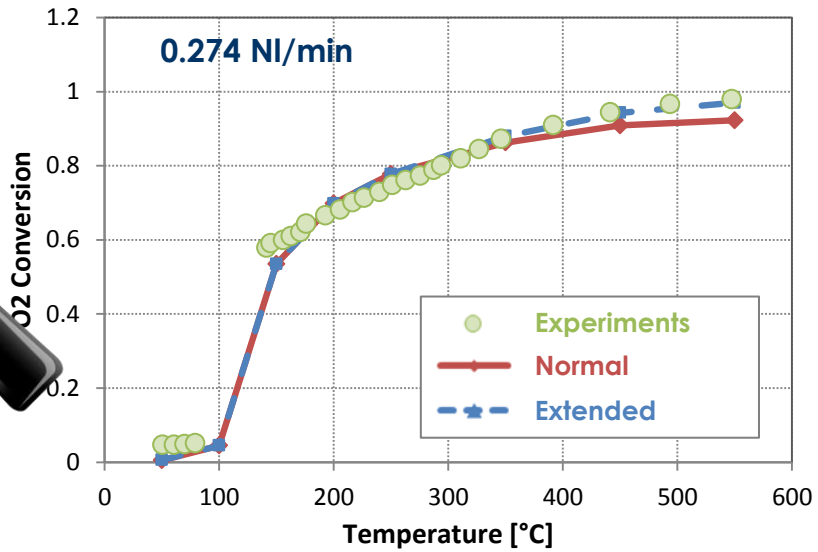
A possible explanation for this has been formulated by Maestri et al. (2008), in terms of **additional zones** of low catalytic activity outside the catalytic bed.

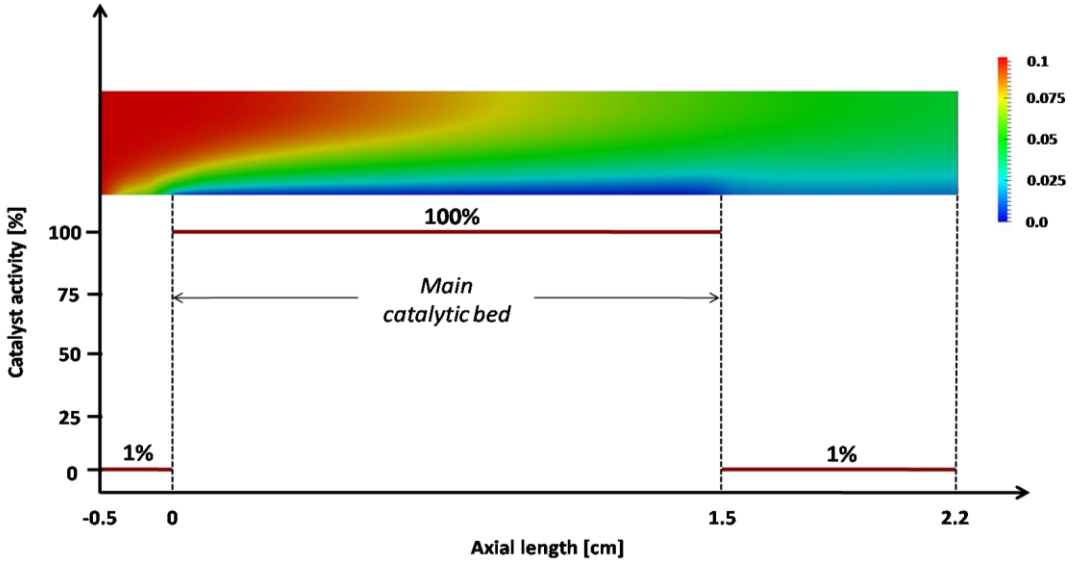


Two section with low catalytic activity up-stream and down-stream the catalytic bed are added to the simulations. A catalyst layer of 2 mm is then added upward the main bed. Another one is added downstream, with a length of 7 mm. The **catalytic activity** of these beds is fixed equal to **1%** of that of the main bed.

Example: annular reactor (III)

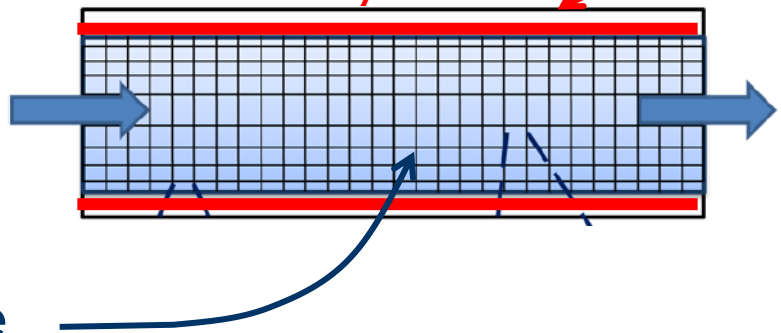






The additional low activity sections (working in chemical regime due to the low amount of catalyst), lead to an **increase of the conversion**. At low temperatures, on the other hand, the contribution is almost negligible.

Governing equations



Catalytic walls

$$\sigma_{cat}\frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{het} \qquad i = 1,\ldots,NS$$

Adsorbed (surface) species

Gas-phase

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$ continuity

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v}\mathbf{v}) = -\nabla p + \nabla \cdot \left[\mu \left(\nabla \mathbf{v} + \nabla \mathbf{v}^T \right) - \frac{2}{3}\mu (\nabla \mathbf{v}) \mathbf{I} \right] + \rho \mathbf{g}$$ momentum

$$\frac{\partial}{\partial t}(\rho \omega_k) + \nabla \cdot (\rho \omega_k \mathbf{v}) = -\nabla \cdot (\rho \omega_k \mathbf{V}_k) + \dot{\Omega}_k^{\text{hom}} \qquad k = 1,\ldots,NG$$ gas-phase species

$$\rho \hat{C}_P \frac{\partial T}{\partial t} + \rho \hat{C}_P \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{P,k} \omega_k \mathbf{V}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}}$$ gas-phase energy

Boundary conditions

Non-catalytic walls

$$\nabla \omega_k \big|_{inert} = 0$$

$$T\big|_{inert} = f(t,T)$$

$$\nabla T\big|_{inert} = g(t,T)$$

Catalytic walls

$$\rho \Gamma_{k,mix} \left(\nabla \omega_k\right)\big|_{catalytic} = -\alpha_{cat}\, \dot{\Omega}_k^{het} \qquad k = 1,\ldots,NG$$

$$\lambda \left(\nabla T\right)\big|_{catalytic} = -\alpha_{cat} \sum_{j=1}^{NR} \Delta H_j^{het} \dot{r}_j^{het}$$

$$\sigma_{cat} \frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{het} \qquad i = 1,\ldots,NS$$

Adsorbed (surface) species

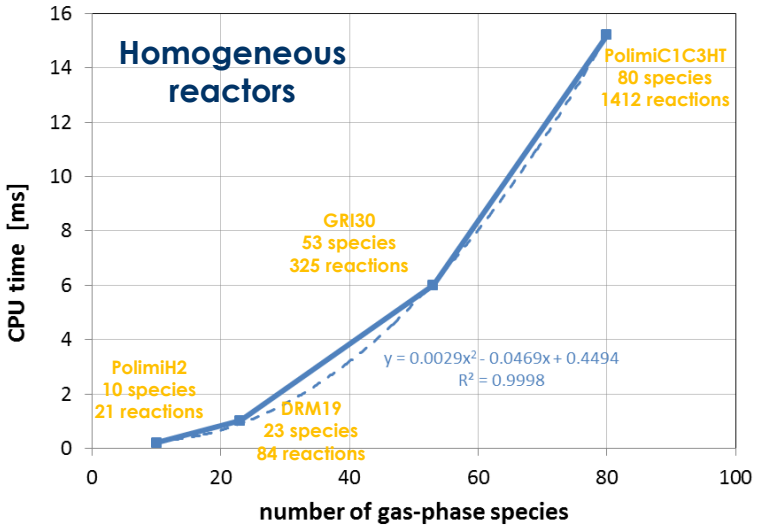
M. Maestri, Microkinetic analysis of complex chemical processes at surface, in "New strategy for chemical synthesis and catalysis", Wiley-VCH (2012)

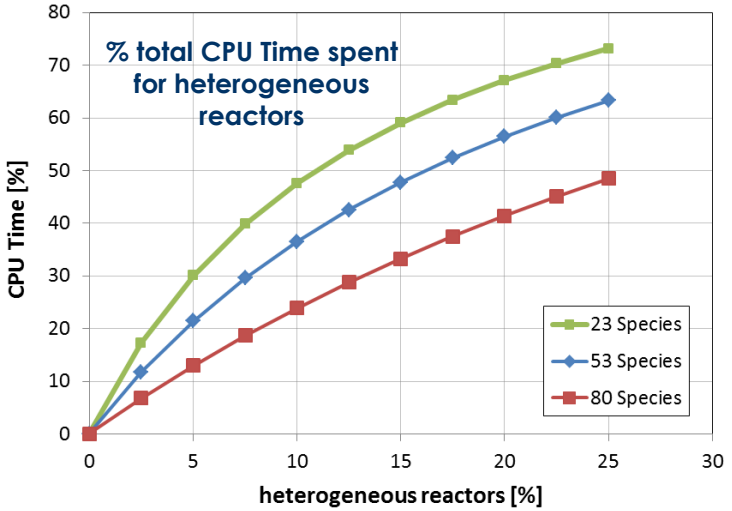
Detailed microkinetic models

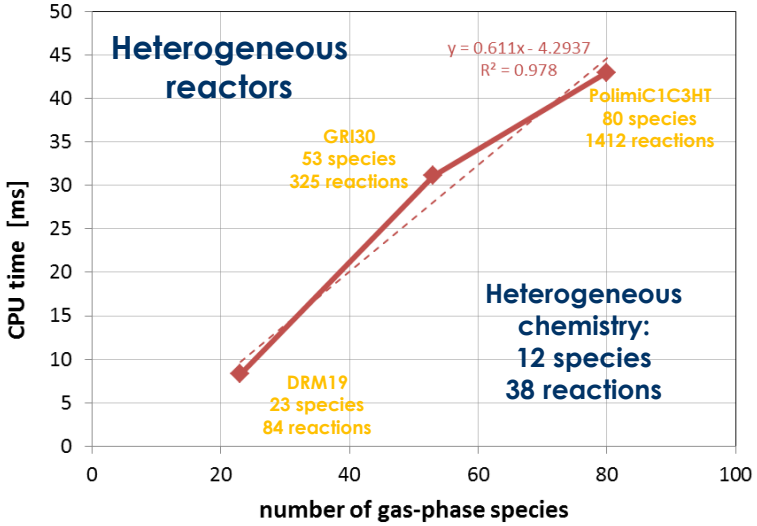
$COOH^* + * \rightarrow CO^* + OH^*$
$CO^* + OH^* \rightarrow COOH^* + *$
$COOH^* + * \rightarrow CO_2^* + H^*$
$CO_2^* + H^* \rightarrow COOH^* + *$
$CO_2^* + H_2O^* \rightarrow COOH^* + OH^*$
$COOH^* + OH^* \rightarrow CO_2^* + H_2O^*$
$CO_2^* + H^* \rightarrow HCOO^{**}$
$HCOO^{**} \rightarrow CO_2^* + H^*$
$CO_2^* + OH^* + * \rightarrow HCOO^{**} + O^*$
$HCOO^{**} + OH^* \rightarrow CO_2^* + H_2O^*$
$CH^* + H^* \rightarrow CH_2^* + *$
$CH^* + * \rightarrow C^* + H^*$
$C^* + H^* \rightarrow CH^* + *$
$CH_3^* + O^* \rightarrow CH_2^* + OH^*$
$CH_2^* + OH^* \rightarrow CH_3^* + O^*$
$CH^* + OH^* \rightarrow CH_2^* + O^*$
$CH_2^* + O^* \rightarrow CH^* + OH^*$
…

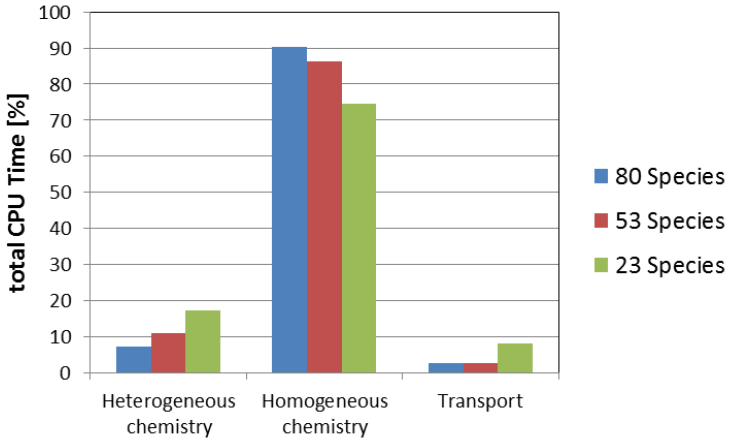
$$r_j = A_j \cdot T^{\beta_j} \cdot \exp\left(-\frac{E_{att,j}(\theta_i)}{RT}\right) \prod_{i=1}^{NC} (c_i)^{\nu_{ij}}$$

CPU time


Homogeneous reactors
PolimiC1C3HT
80 species
1412 reactions
GRI30
53 species
325 reactions
PolimiH2
10 species
21 reactions
DRM19
23 species
84 reactions
y = 0.0029x² - 0.0469x + 0.4494
R² = 0.9998
CPU time [ms]
number of gas-phase species


% total CPU Time spent for heterogeneous reactors
23 Species
53 Species
80 Species
CPU Time [%]
heterogeneous reactors [%]


Heterogeneous reactors
y = 0.611x - 4.2937
R² = 0.978
PolimiC1C3HT
80 species
1412 reactions
GRI30
53 species
325 reactions
Heterogeneous chemistry:
12 species
38 reactions
DRM19
23 species
84 reactions
CPU time [ms]
number of gas-phase species


total CPU Time [%]
Heterogeneous chemistry
Homogeneous chemistry
Transport
80 Species
53 Species
23 Species