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Matteo Maestri & Alberto Cuoci




Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM


HPC enabling of OpenFOAM® for CFD applications
6 April 2016




The catalyticFOAM group




<http://www.catalyticfoam.polimi.it/>
The catalyticFOAM Group







Matteo Maestri
heterogeneous catalysis, multiscale modeling, microkinetic modeling



Alberto Cuoci
CFD, numerical methods



Stefano Rebughini (PhD Student)
Hierarchical analysis of complex reacting systems, microchannel reactors

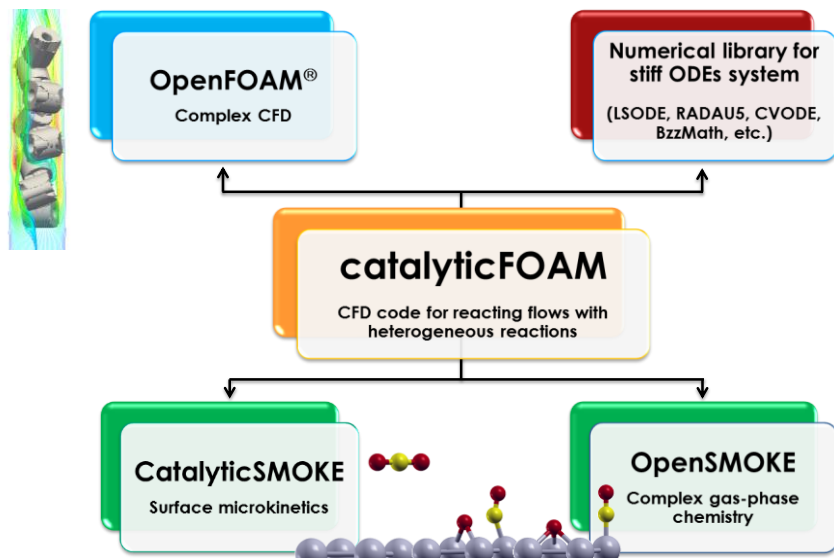


Mauro Bracconi (PhD student)
ISAT, complex geometries, metallic foams

Former Students

Sandro Goisis and Alessandra Osio Development of numerical methodology	Tiziano Maffei Improvement of multi-region solver
Giancarlo Gentile and Filippo Manelli Development of multi-region solver	Salvatore Raffa Automatic generation of meshes for packed bed reactors

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



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

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



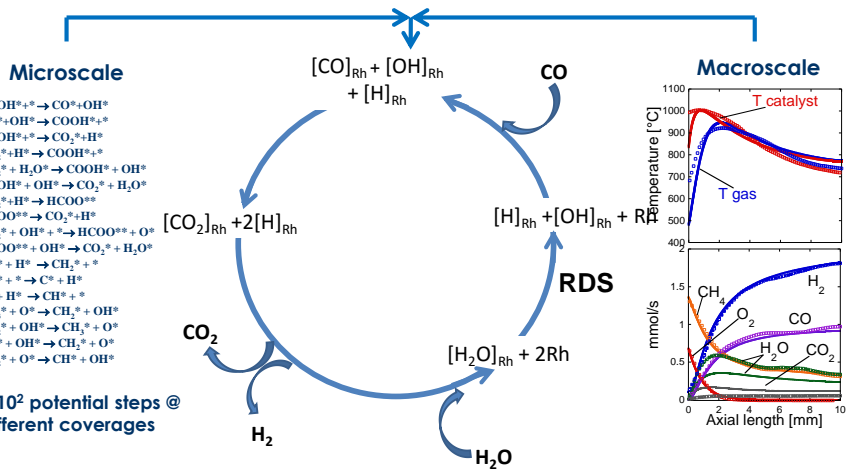
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Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

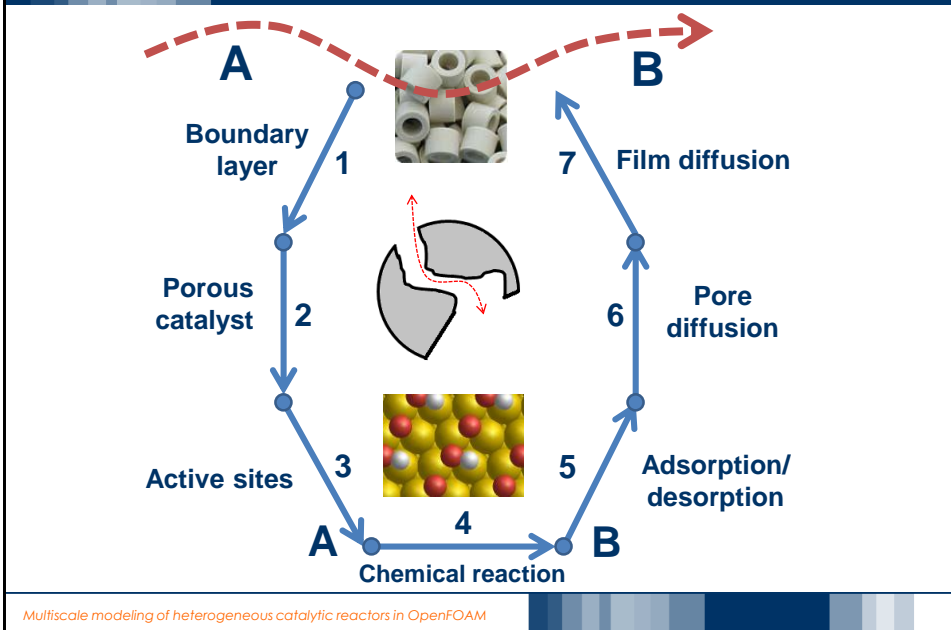


Result of the interplay among phenomena at different scales

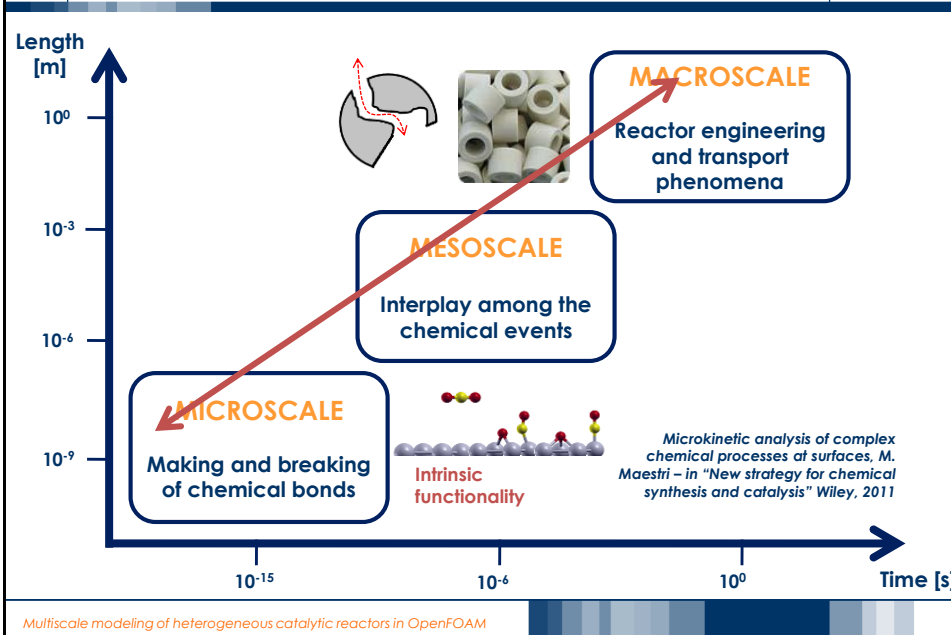


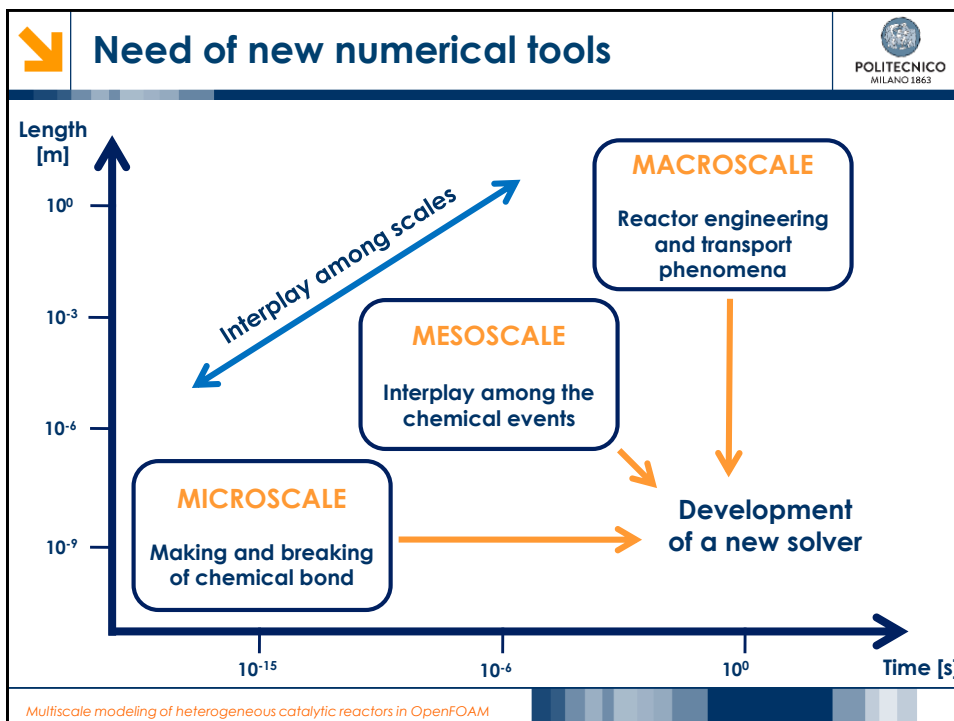
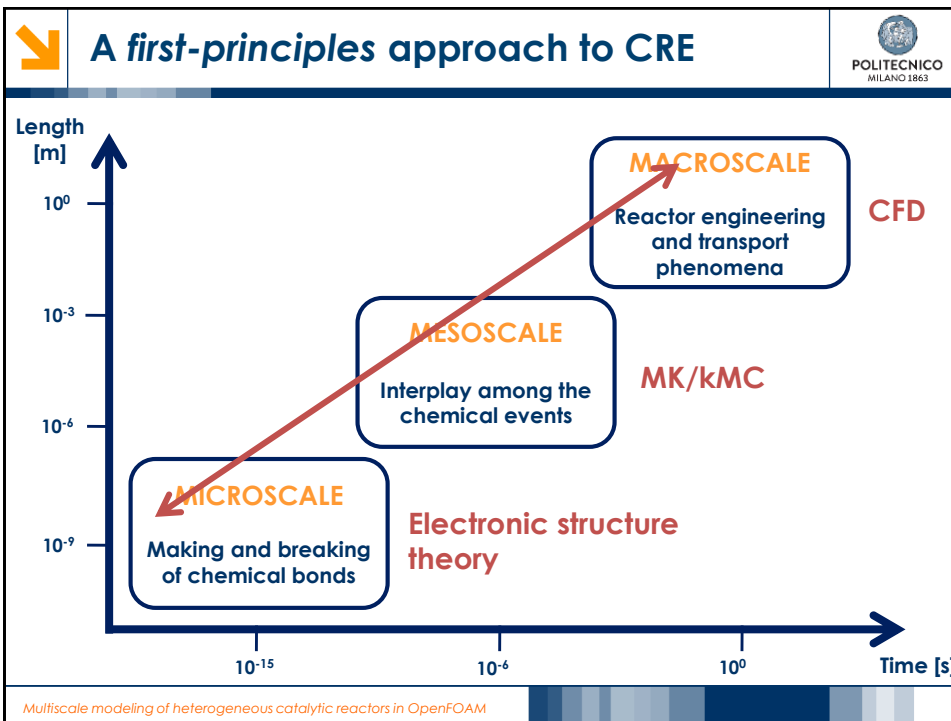
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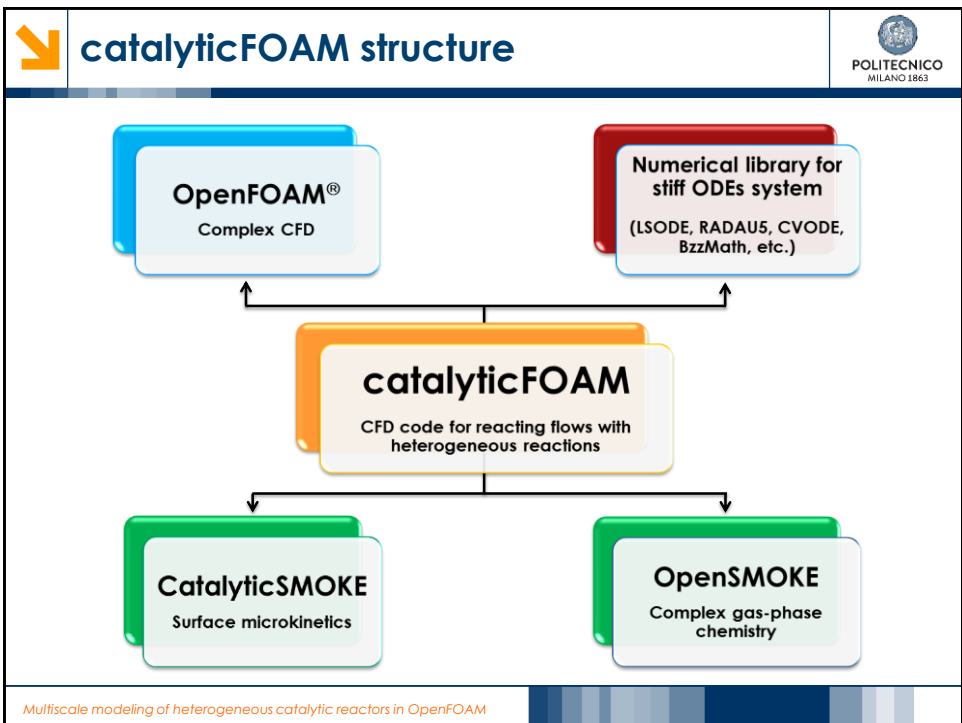
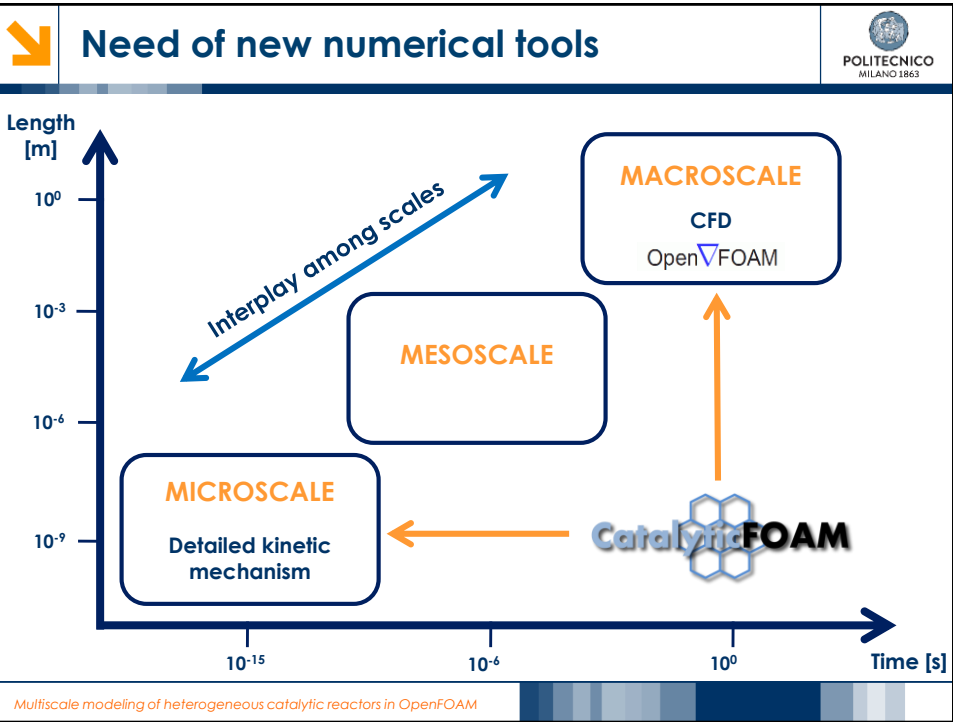
Catalysts at work



Need of bridging between the scales







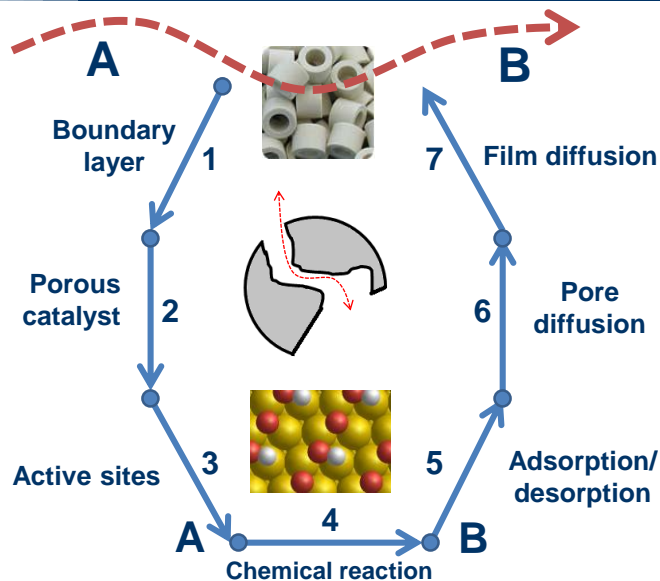


Outline

- ✓ Introduction and motivation
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
 - ✓ Governing equations
 - ✓ Numerical methodology
 - ✓ Simulation with detailed kinetics: stiff ODE solvers and ISAT
- ✓ Validation and examples
 - ✓ Annular reactor
 - ✓ CPO of CH₄ on platinum gauze (complex 3D geometry)
 - ✓ CPO of iso-octane (complex chemistry)
 - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
 - ✓ Packed bed reactors for industrial applications (complex 3D geometry)
- ✓ Extensions
 - ✓ KMC (Kinetic Monte Carlo)

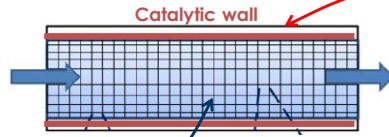


Catalysts at work





Governing equations



Catalytic walls

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

Adsorbed (surface) species

Gas-phase

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

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

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

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

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Boundary conditions

Non-catalytic walls

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

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

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

Catalytic walls

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

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

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

Adsorbed (surface) species

Detailed microkinetic models



...

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

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Numerical challenges (I)

✓ Dimensions of the system

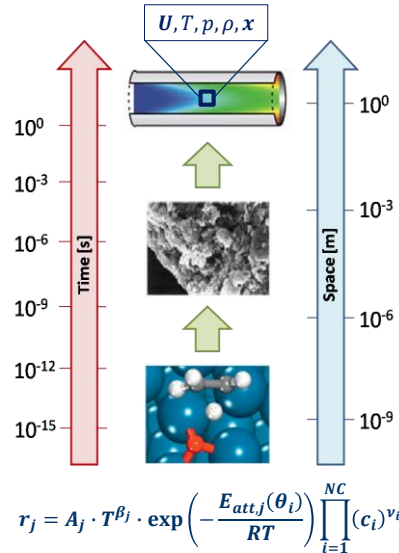
- Proportional to the number of species
- Proportional to the number of cells

✓ Stiffness

- Different temporal scales involved
- Different spatial scales involved

✓ Non-linearity

- Source term non linear in concentrations and temperature
- Coverage dependence of activation energy



Numerical challenges (II)

✓ Dimensions of the system

- Proportional to the number of species
- Proportional to the number of cells

✓ Stiffness

- Different temporal scales involved
- Different spatial scales involved

✓ Non-linearity

- Source term non linear in concentrations and temperature
- Coverage dependence of activation energy

segregated approaches are not feasible

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Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

Numerical solution

Fully segregated algorithms

- ⊕ easy to implement and computationally efficient
- ⊖ unfeasible when large, stiff kinetic mechanisms are used

Detailed kinetic schemes

~ 100 species
~ 1000 reactions

Strong non linearity of reaction terms
High stiffness

Complex geometries

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

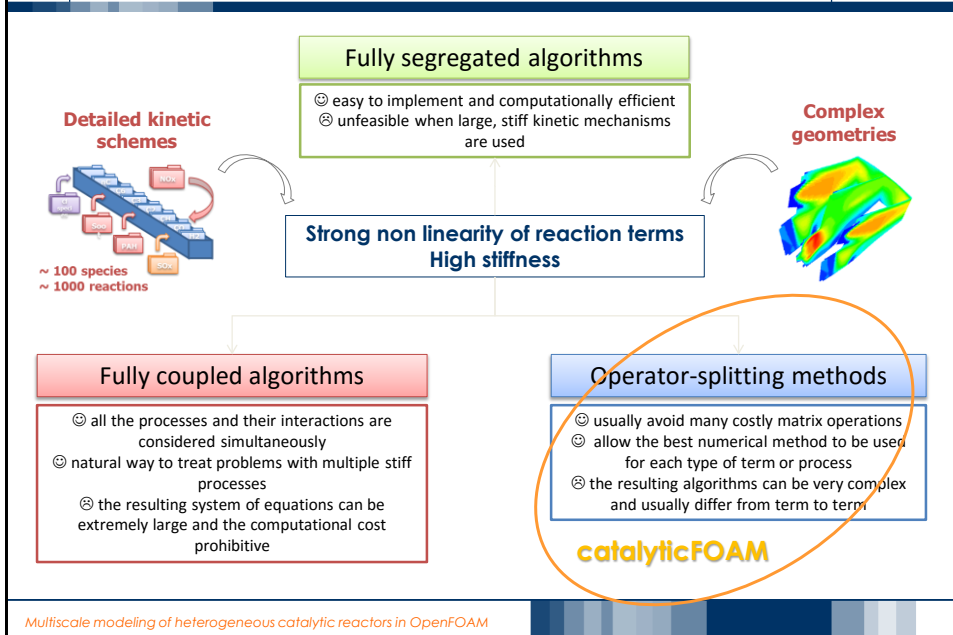
Operator-splitting methods

- ⊕ 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

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Numerical solution



Operator-splitting algorithm

PDE

$$\begin{cases} \frac{\partial}{\partial t}(\rho\omega_k) = -\nabla \cdot (\rho\omega_k \mathbf{v}) - \nabla \cdot (\rho\omega_k \mathbf{V}_k) + \dot{\Omega}_k^{\text{hom}} & k = 1, \dots, NG & \text{gas-phase species} \\ \rho \hat{C}_p \frac{\partial T}{\partial t} = -\rho \hat{C}_p \mathbf{v} \nabla T + \nabla \cdot (\lambda \nabla T) - \rho \sum_{K=1}^{NG} \hat{C}_{P,K} \omega_K \mathbf{V}_K - \sum_{K=1}^{NG} \dot{H}_K^{\text{hom}} \dot{\Omega}_K^{\text{hom}} & & \text{gas-phase energy} \\ \sigma_{\text{cat}} \frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{\text{het}} & i = 1, \dots, NS & \text{adsorbed (surface) species} \end{cases}$$

Stiff reaction terms

Finite volume discretization \downarrow After spatial discretization, the original PDE systems is transformed into an ODE system

After spatial discretization

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

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

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

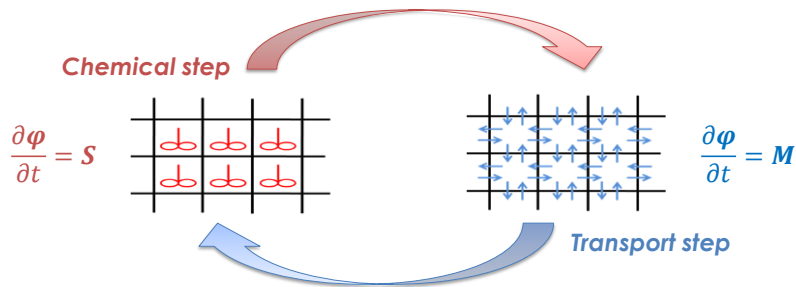


Operator-splitting: an example

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

Chemistry ← (S) + (M) → Diffusion, convection...

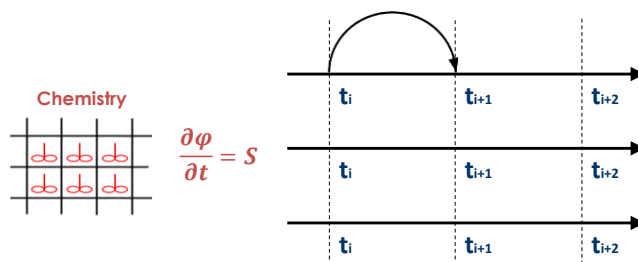
Operator-splitting scheme



Operator-splitting: an example

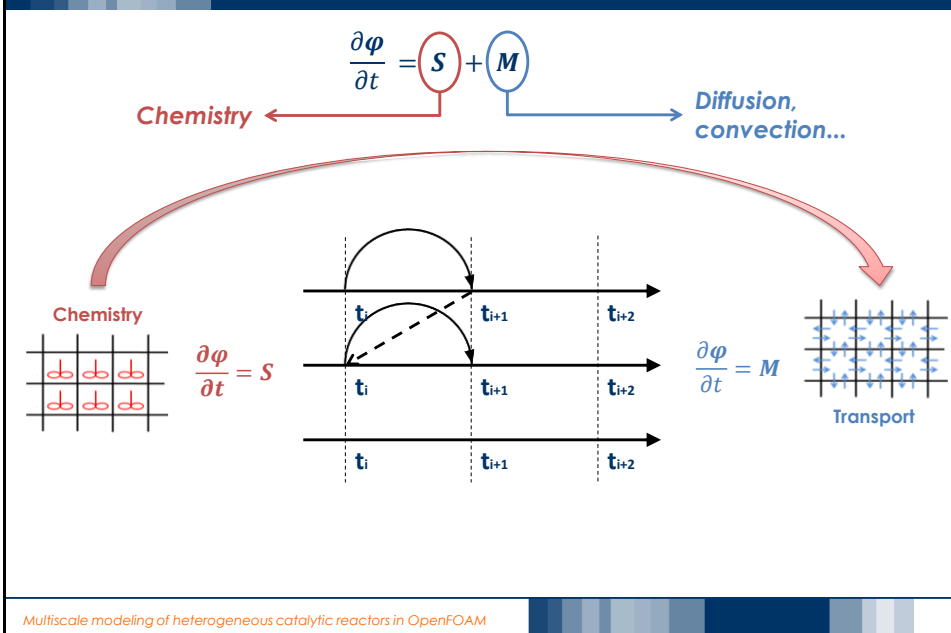
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Chemistry ← (S) + (M) → Diffusion, convection...

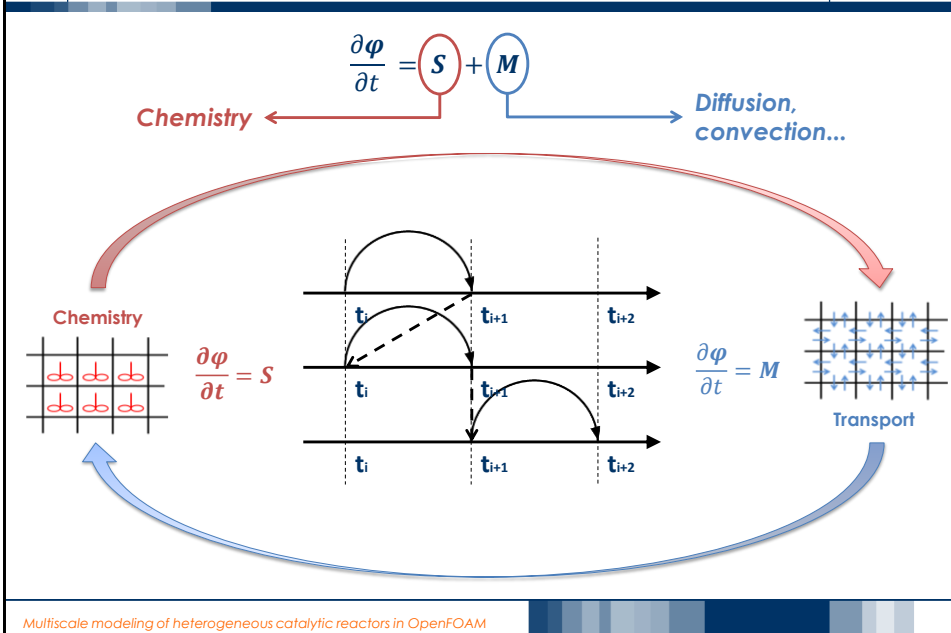




Operator-splitting: an example

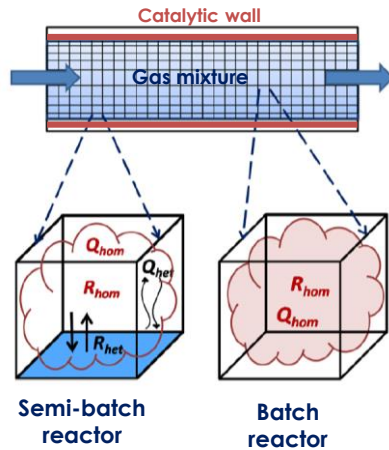


Operator-splitting: an example





Operator-splitting in catalyticFOAM (I)

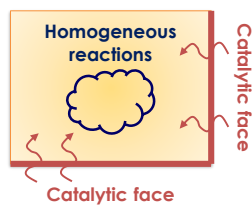


Each computational cell behaves as a chemical reactor in the splitting-operator algorithm (chemical step)

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



Operator-splitting in catalyticFOAM (II)



NF = number of catalytic faces
NG = number of gas-phase species
NS = number of adsorbed (surface) species

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

Semi-batch reactor

$$\left\{ \begin{array}{l} \rho \frac{d\omega_k}{dt} = \dot{\Omega}_k^{\text{hom}} + \frac{1}{V} \left\{ \sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \dot{\Omega}_{k,j}^{\text{het}} - \omega_k \sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \sum_{k=1}^{NG} \dot{\Omega}_{k,j}^{\text{het}} \right\} \quad k=1, \dots, NG \\ \rho \hat{C}_p \frac{dT}{dt} = - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}} - \sum_{k=1}^{NS} \hat{H}_k^{\text{het}} \dot{\Omega}_k^{\text{het}} \\ \sigma_{\text{cat}} \frac{\partial \theta_{i,j}}{\partial t} = \dot{\Omega}_{i,j}^{\text{het}} \quad i=1, \dots, NS \quad j=1, \dots, NF \end{array} \right. \quad \begin{array}{l} \text{Gas-phase} \\ \text{species} \\ \text{Gas-phase} \\ \text{temperature} \\ \text{Adsorbed} \\ \text{species} \end{array}$$



Operator-splitting in catalyticFOAM (III)

Homogeneous
reactions



NF = number of catalytic faces
NG = number of gas-phase species
NS = number of adsorbed (surface) species

Unknowns $N = NG + 1 + \cancel{NF} - NS$

Batch reactor

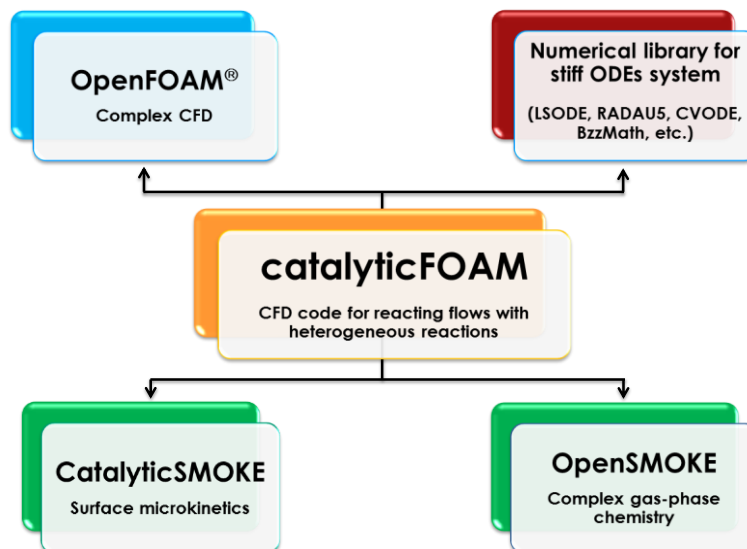
$$\left\{ \begin{array}{l} \rho \frac{d\omega_k}{dt} = \dot{\Omega}_k^{\text{hom}} + \frac{1}{V} \left[\sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \dot{\Omega}_{k,j}^{\text{het}} - \sum_{j=1}^{NF} \alpha_j^{\text{cat}} A_j \sum_{k=1}^{NG} \dot{\Omega}_{k,j}^{\text{het}} \right] \\ \rho \hat{C}_p \frac{dT}{dt} = - \sum_{k=1}^{NG} \dot{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}} - \sum_{k=1}^{NS} \dot{H}_k^{\text{het}} \dot{\Omega}_k^{\text{het}} \\ \frac{\partial \theta_{i,j}}{\partial t} = \dot{\theta}_{i,j}^{\text{het}} \quad i=1, \dots, NS \quad j=1, \dots, NF \end{array} \right. \quad k=1, \dots, NG$$

Gas-phase species
Gas-phase temperature
Adsorbed species

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

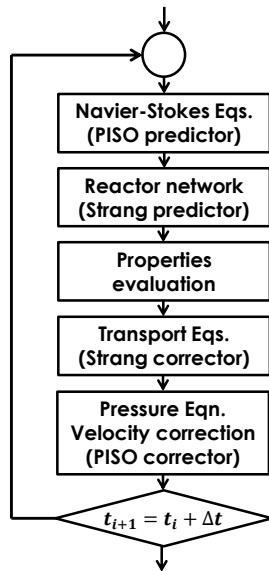


catalyticFOAM structure



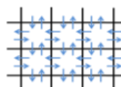
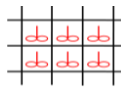
Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

Solution procedure



Main features:

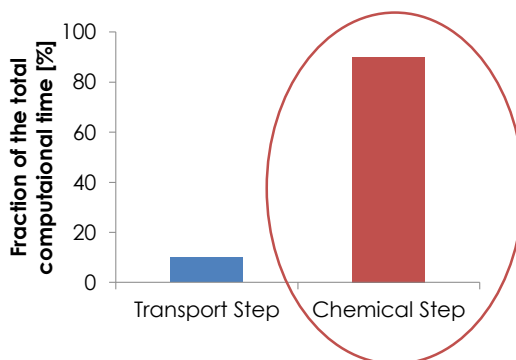
- ✓ Solution of the Navier-Stokes equations (laminar and turbulent regime)
- ✓ No limit to the number of species and reactions
- ✓ Non-isothermal conditions



Where is the computational time spent?

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

diffusion, convection ← M → reaction



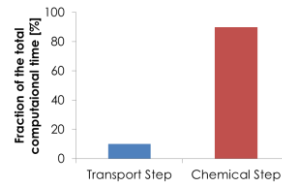
Most of the CPU Time (80- 90%) is spent for the numerical integration of the ODE systems corresponding to the homogeneous and heterogeneous reactors



Where is the computational time spent?

Reaction/Chemical step $\frac{\partial \phi}{\partial t} = S$

- semi-batch reactor describing composition and temperature
- reaction terms for both homogeneous and heterogeneous chemistry
- stiff and highly-non linear
- solved with expensive implicit method



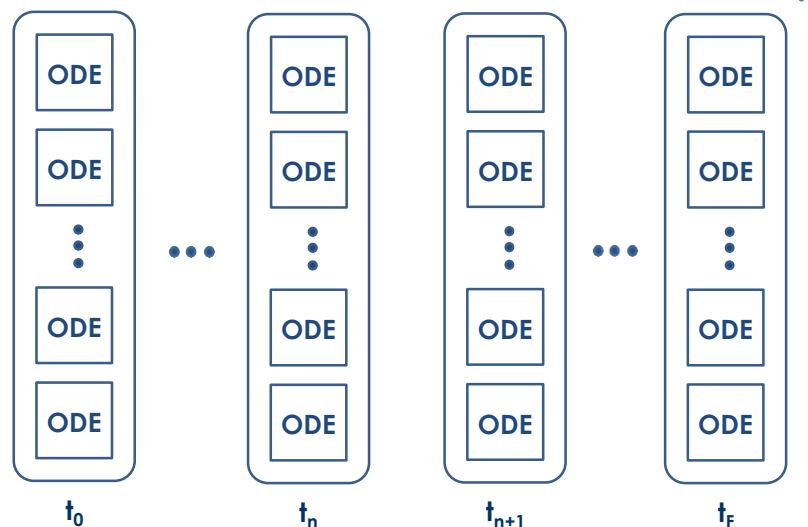
solving the reaction term is the bottleneck of the system



need for speeding up the chemical term



Reaction step = independent ODEs





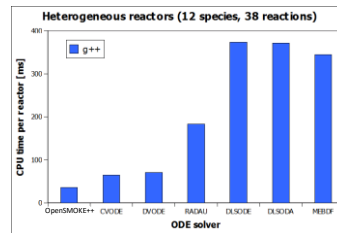
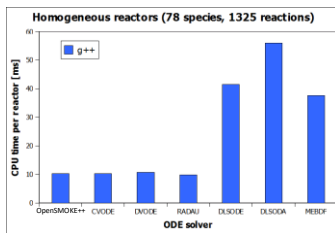
Stiff ODE solvers in catalyticFOAM (I)

	Language	Linear system solution	Parallel	Code available	License
OpenSMOKE++	C++	Direct	No	Yes	Free
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:
OpenSMOKE++, CVODE, DVODE

Performances of stiff ODE solvers: CPU time



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Direct integration vs extrapolation



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

Direct integration vs extrapolation

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The diagram illustrates two methods for solving Ordinary Differential Equations (ODEs) over time. The top section, labeled 'Direct integration', shows a blue arrow pointing from a box labeled ODE_n to a box labeled ODE_{n+1} . To the right, a timeline shows two points, t_n and t_{n+1} , with a blue arrow indicating the progression of time. The bottom section, labeled 'Extrapolation', shows a red arrow pointing from a box labeled ODE_n to a box labeled ODE_{n+1} , suggesting that the solution at t_{n+1} is estimated based on the solution at t_n .

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

Direct integration vs extrapolation

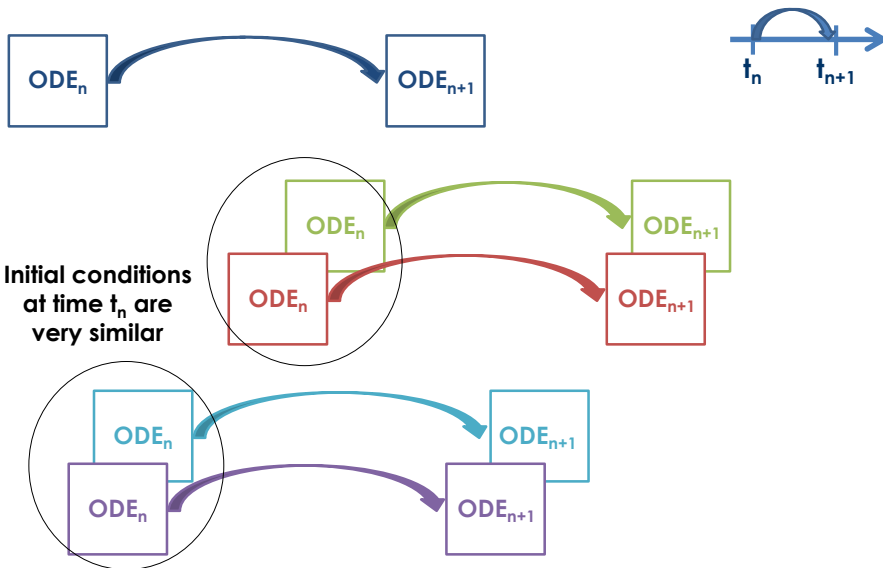
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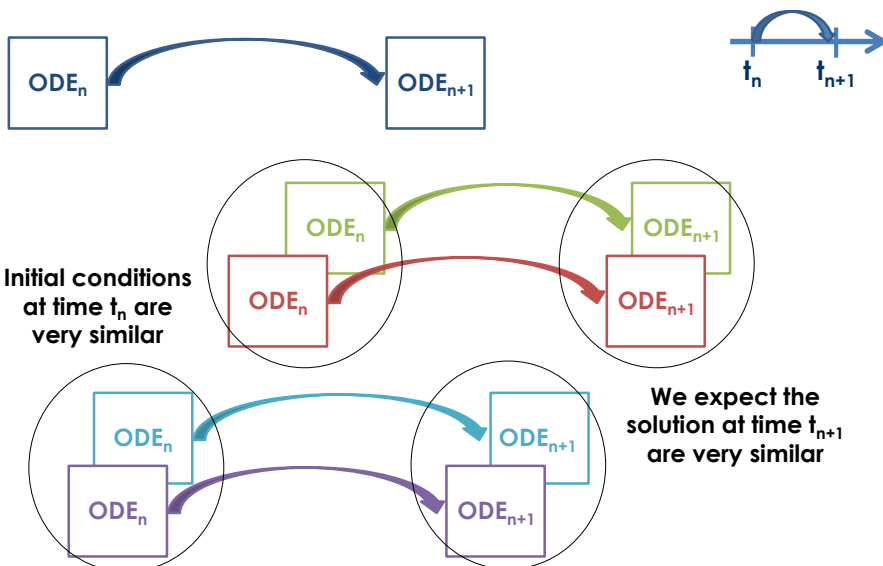
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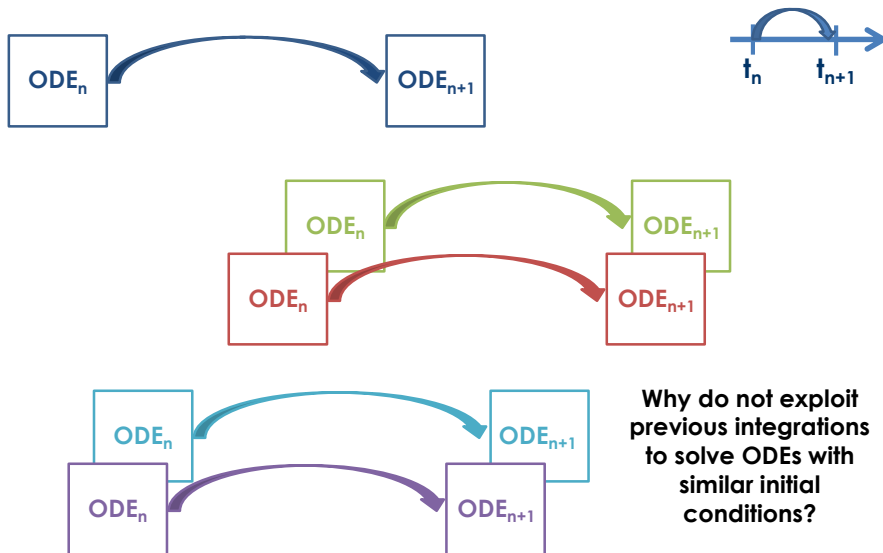
Direct integration vs extrapolation



Direct integration vs extrapolation



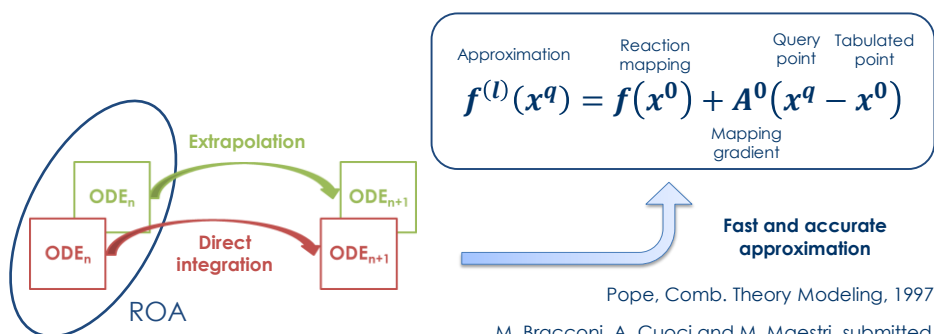
Direct integration vs extrapolation



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

ISAT: In Situ Adaptive Tabulation

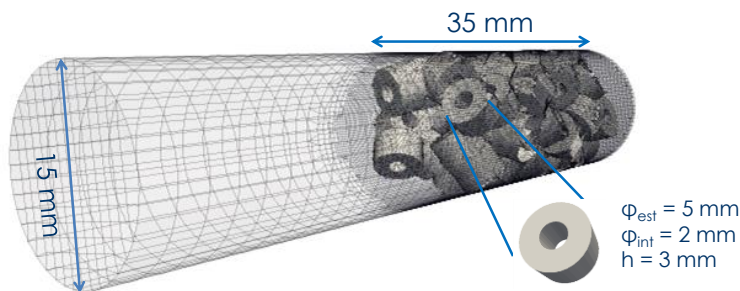
- ODEs integrations are stored in a tree
- exploit stored information to well-approximate ODEs with similar initial conditions by means of linear interpolation
- error control through definition of a trusted approximation region (ROA)



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Example: fixed bed of Rashig rings (I)



Methane – heterogeneous

	n° cells
fluid	~180,000
catalytic	~60,000

13 surface species
82 heterogeneous reactions

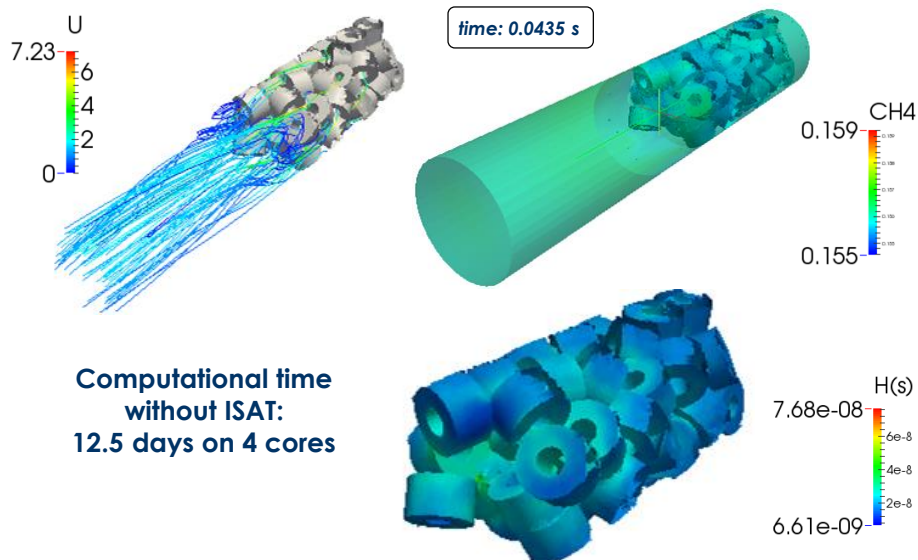
OPERATING CONDITIONS

CH ₄ mass fraction	0.1565
O ₂ mass fraction	0.1753
N ₂ mass fraction	0.6682
Inlet temperature	673.15 K
Outlet Pressure	1.01 bar
Flow velocity	1 m/s

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



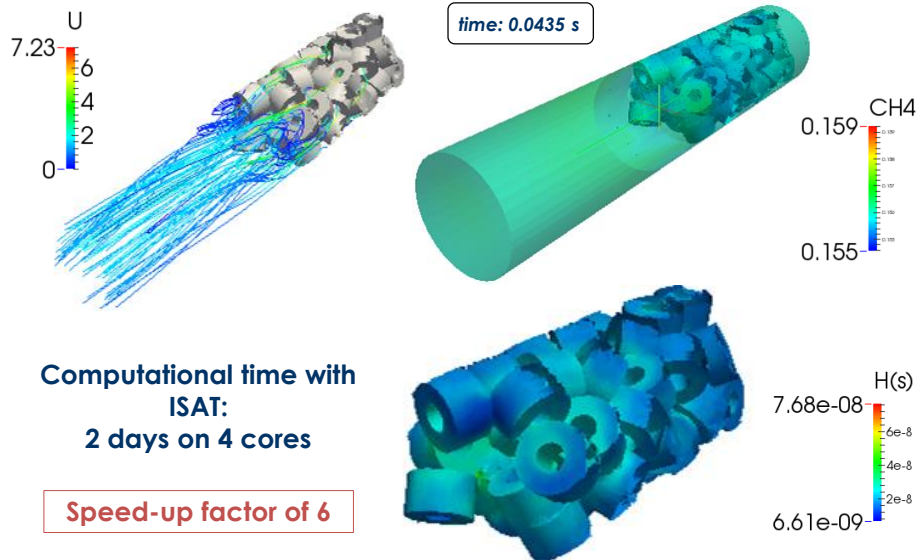
Example: fixed bed of Rashig rings (II)



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Example: fixed bed of Rashig rings (III)



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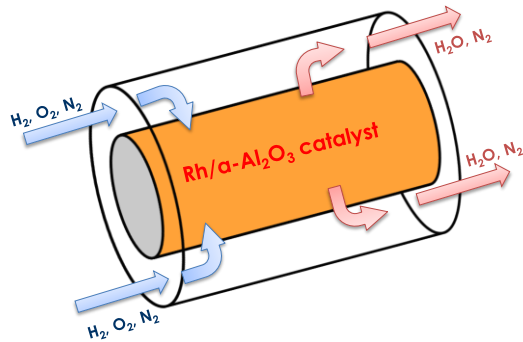
Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



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	$2.49 \cdot 10^{-9}$ mol/cm ²
Catalytic surf.	5 cm^{-1}



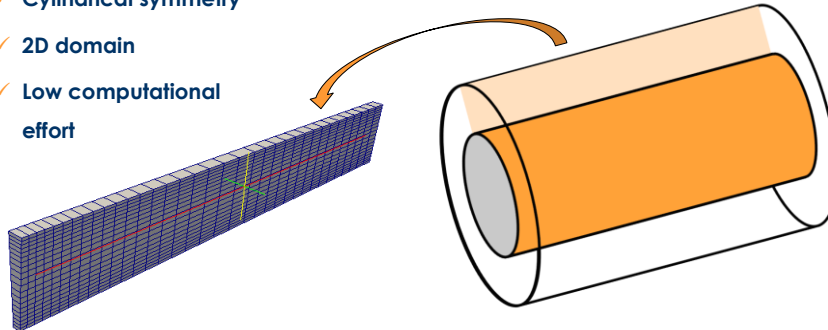
(* M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos, 2D detailed modeling of fuel-rich H_2 combustion over Rh/ Al_2O_3 catalyst, Chemical Engineering Science (2008)

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



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

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Kinetic schemes



Heterogeneous kinetics

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

1. $H_2 + 2Rh(s) \rightarrow 2H(s)$
2. $2H(s) \rightarrow H_2 + 2Rh(s)$
3. $O_2 + 2Rh(s) \rightarrow 2O(s)$
4. $2O(s) \rightarrow O_2 + 2Rh(s)$
5. $OH(s) + Rh(s) \rightarrow H(s) + O(s)$
6. $H(s) + O(s) \rightarrow OH(s) + Rh(s)$
7. $H_2O(s) + Rh(s) \rightarrow H(s) + OH(s)$
8. $H(s) + OH(s) \rightarrow H_2O(s) + Rh(s)$
9. $H_2O(s) + O(s) \rightarrow 2OH(s)$
10. $2OH(s) \rightarrow H_2O(s) + O(s)$
11. $OH + Rh(s) \rightarrow OH(s)$
12. $OH(s) \rightarrow OH + Rh(s)$
13. $H_2O + Rh(s) \rightarrow H_2O(s)$
14. $H_2O(s) \rightarrow H_2O + Rh(s)$
15. $H + Rh(s) \rightarrow H(s)$
16. $H(s) \rightarrow H + Rh(s)$
17. $O + Rh(s) \rightarrow O(s)$
18. $O(s) \rightarrow O + Rh(s)$

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

Homogeneous kinetics

- 10 Species
- 21 Reactions

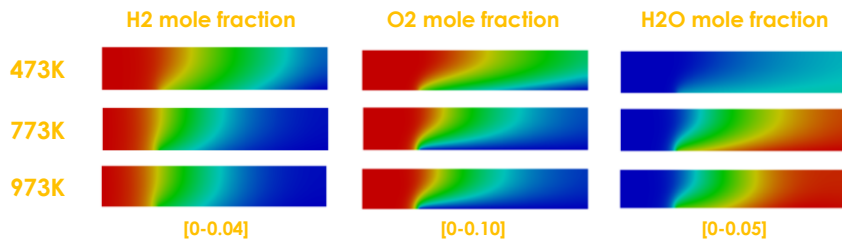
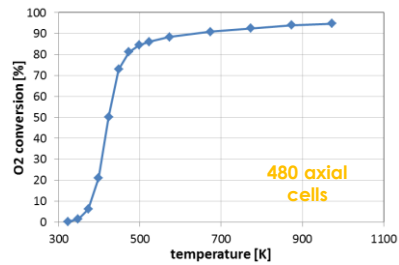
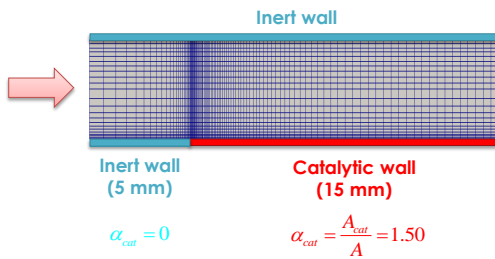
1. $H + O_2 \rightarrow OH + O$
2. $O + H_2 \rightarrow OH + H$
3. $H + O_2 + M \rightarrow HO_2 + M$
4. $H + 2O_2 \rightarrow HO_2 + O_2$
5. $OH + HO_2 \rightarrow H_2O + O_2$
6. $H + HO_2 \rightarrow 2OH$
7. $O + HO_2 \rightarrow O_2 + OH$
8. $2OH \rightarrow O + H_2O$
9. $H_2 + M \rightarrow 2H + M$
10. $O_2 + M \rightarrow 2O + M$
11. $H + OH + M \rightarrow H_2O + M$
12. $H + HO_2 \rightarrow H_2 + O_2$
13. $2HO_2 \rightarrow H_2O_2 + O_2$
14. $2OH + M \rightarrow H_2O_2 + M$
15. $O + OH + M \rightarrow HO_2 + M$
16. $H + H_2O \rightarrow H_2 + OH$
17. $H_2O_2 + H \rightarrow H_2O + OH$
18. $H_2O_2 + H \rightarrow H_2 + HO_2$
19. $HO_2 + H_2O \rightarrow H_2O_2 + OH$
20. $OH + H_2O_2 \rightarrow H_2O + HO_2$
21. $O + H_2O_2 \rightarrow OH + HO_2$

PolimiH2 mechanism (Frassoldati et al., 2006)

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Main results



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



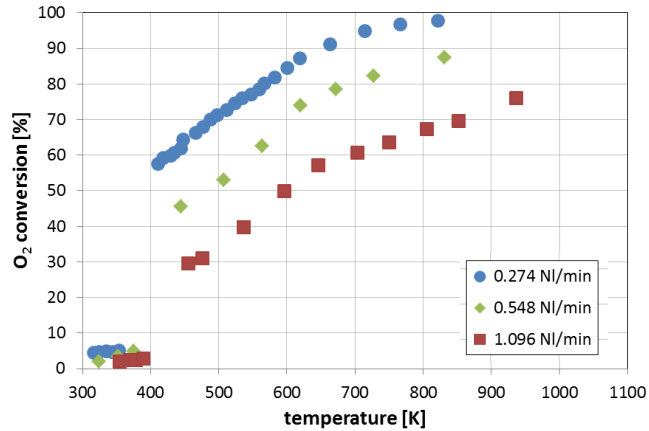
Validation

Comparison with experimental measurements

✓ Flow rate of:
0.274 NI/min
0.548 NI/min
1.096 NI/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)

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



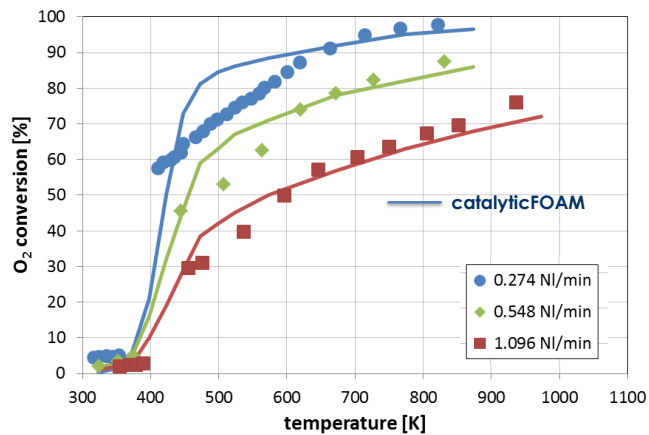
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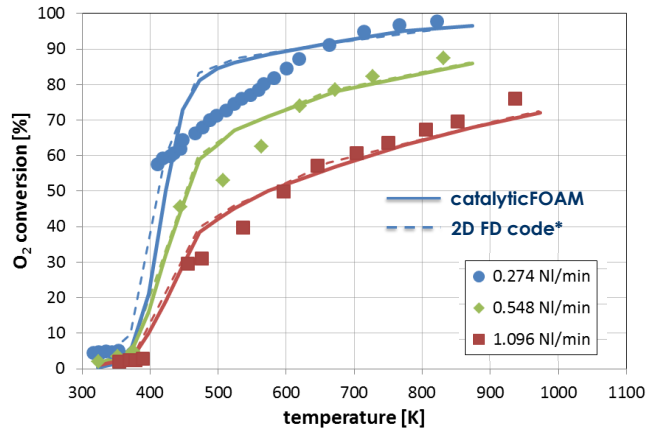
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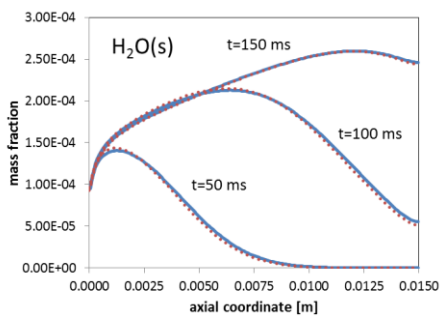
(*) M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi, D. Vlachos, 2D detailed modeling of fuel-rich H_2 combustion over Rh/Al_2O_3 catalyst, Chemical Engineering Science (2008)

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



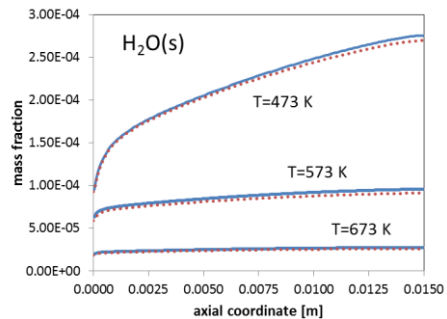
Comparison with Ansys-FLUENT 13.0

Dynamic simulation



Profiles of adsorbed H_2O along the catalytic wall in at 473K at several times

Steady-state simulation



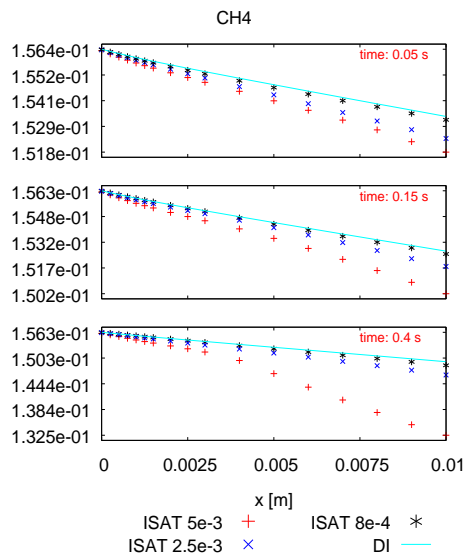
Profiles of adsorbed H_2O along the catalytic wall in steady state conditions at different temperatures

— catalyticFOAM
- - - - - Ansys-FLUENT 13.0

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



ISAT performances



Correct choice of tolerance is of paramount in ISAT in order to have accurate results

A tolerance of $1e-4$ is enough for correctly describing the steady-state behavior
If the transient is of interest, lower tolerances are usually required

A **speed-up factor of 10-12**
(depending on the operating conditions) was measured

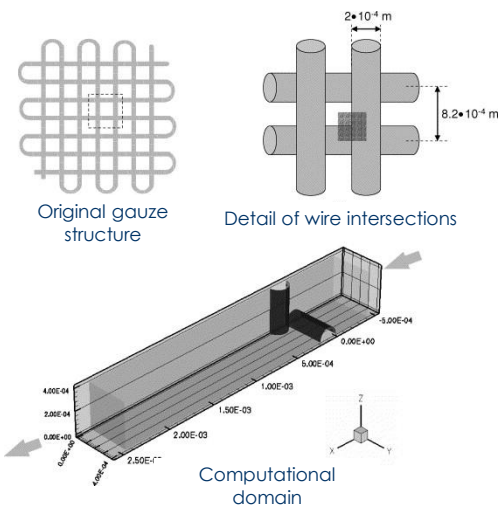


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CPO of methane over platinum gauze (I)



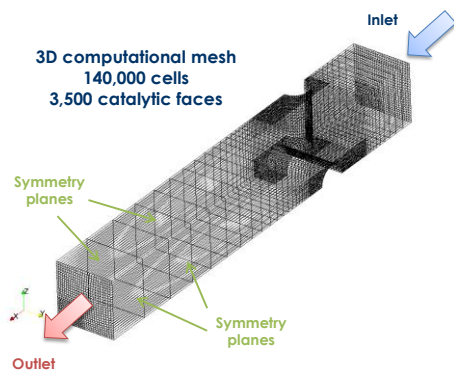
Operating conditions	
Inlet temperature	600 K
Inlet velocity	10 m/s
Gauze temperature	1000-1200 K
CH ₄ mole fraction	0.143 (-)
O ₂ mole fraction	0.057 (-)
He mole fraction	0.80 (-)
Pressure	1.3 bar
Pt site density	$2.72 \cdot 10^{-9}$ mol/cm ²
Catalytic surf.	5 cm ⁻¹

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

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM



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

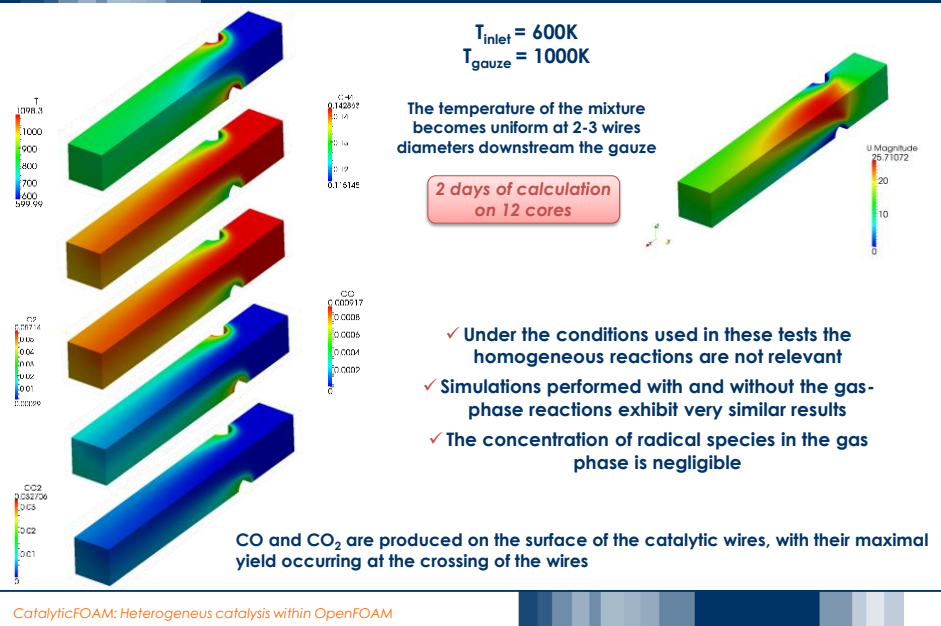
<http://creckmodeling.chem.polimi.it/>

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

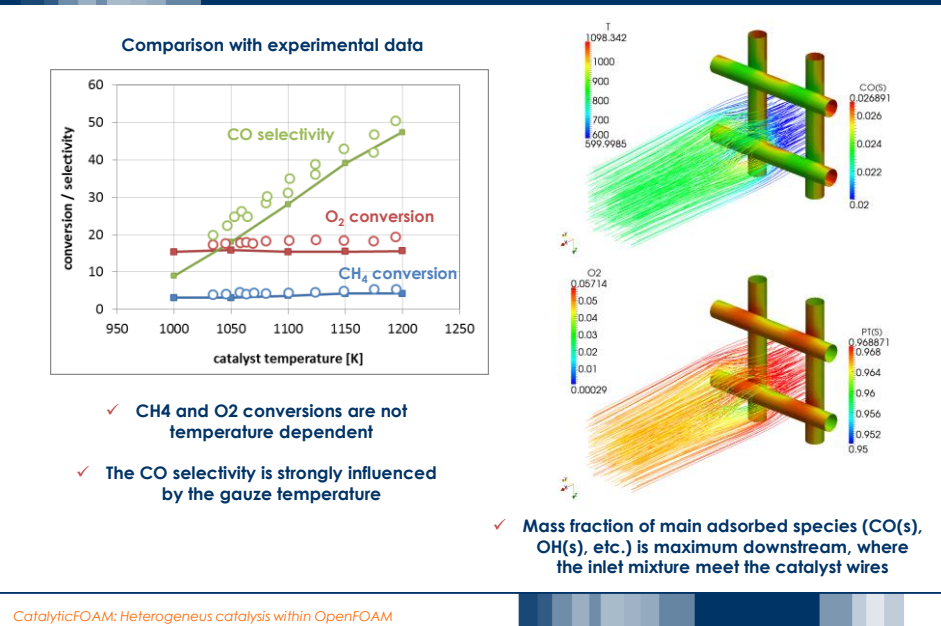
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM



CPO of methane over platinum gauze (III)



CPO of methane over platinum gauze (IV)





Outline

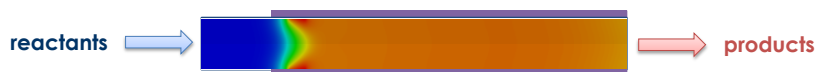
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CatalyticFOAM: Heterogeneous catalysis within OpenFOAM



CPO of iso-octane over rhodium catalyst (I)

Sketch of a single channel (circular section)



Operating conditions	
Inlet temperature	1076 K
Inlet velocity	0.90 m/s
Wall temperature	1076 K
iC ₈ H 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

Rhodium catalyst

Heterogeneous kinetics

- 17 Surface Species
- 56 Surface Reactions

www.delchem.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

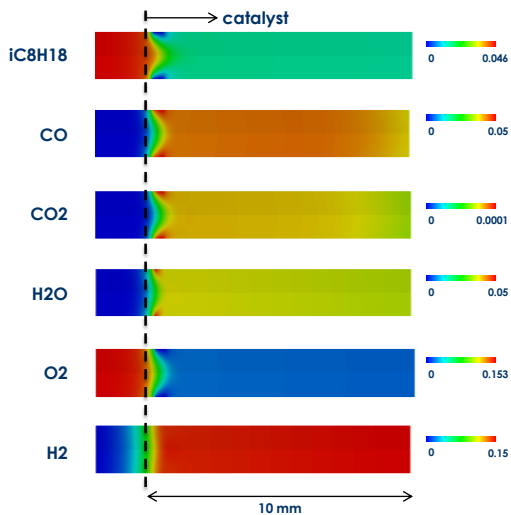
CatalyticFOAM: Heterogeneous catalysis within OpenFOAM



CPO of iso-octane over rhodium catalyst (II)

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

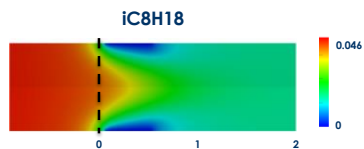
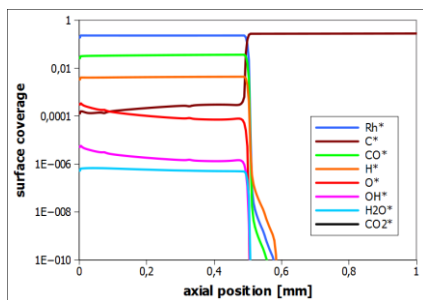
The concentration of iC₈H₁₈ and O₂ on the surface is practically zero, which means that catalytic reactions are mass-transfer limited

CatalyticFOAM: Heterogeneous catalysis within OpenFOAM

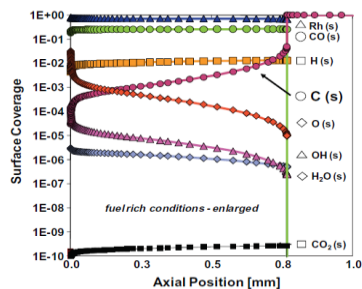


CPO of iso-octane over rhodium catalyst (III)

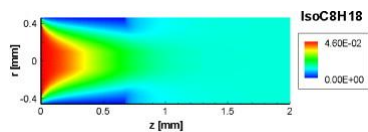
CatalyticFOAM
2D mesh (5,000 cells)



DETCHEMCHANNEL
www.detchem.com



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



CatalyticFOAM: Heterogeneous catalysis within OpenFOAM



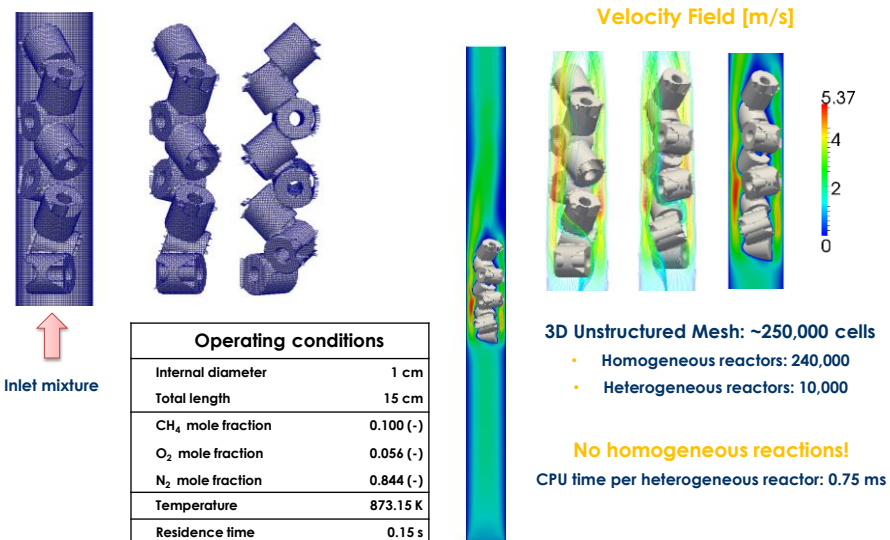
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CatalyticFOAM: Heterogeneous catalysis within OpenFOAM



Tubular reactor with Raschig rings (I)

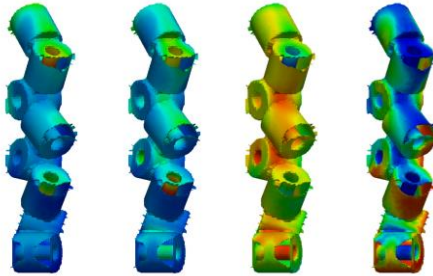


Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Tubular reactor with Raschig rings (II)

Rh(s) (0.37-1.0) H(s) (0.001-0.006) CO(s) (0.-0.57) CO₂(s) (0.-4·10⁻⁹)



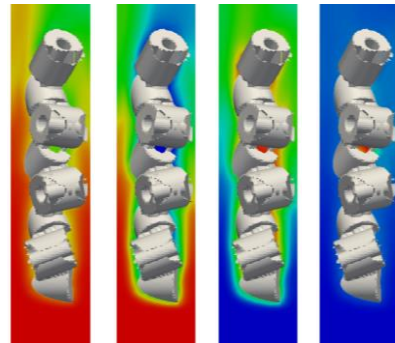
Adsorbed species (mass fractions)

C1 microkinetic model on Rh

82 reaction steps
13 adsorbed species
UBI-QEP and DFT refinement

M. Maestri et al., AIChE J., 2009

Gas-phase species (mole fractions)



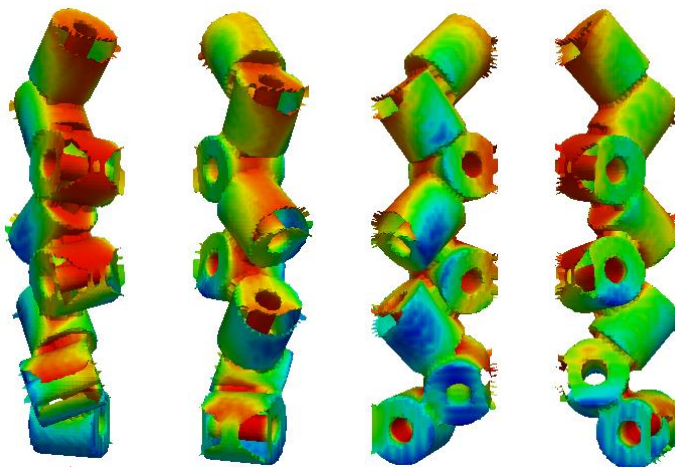
CH₄ (0.-0.10) O₂ (0.-0.056) H₂O (0.-0.054) H₂ (0.-0.006)

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Tubular reactor with Raschig rings (III)

Adsorbed species at the catalyst surface



Inlet mixture

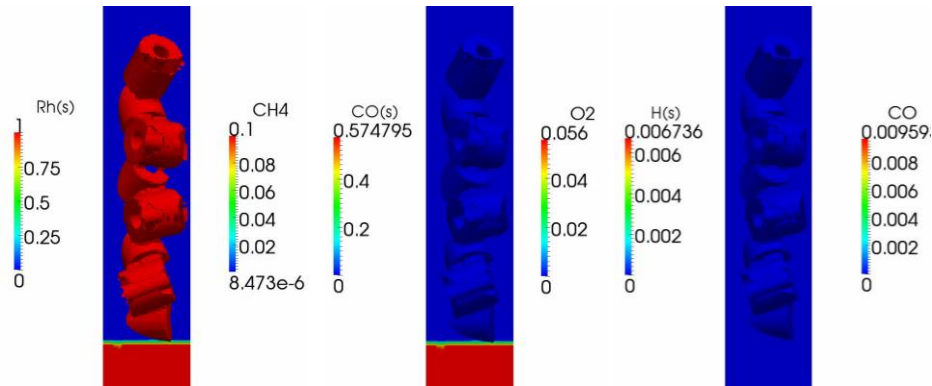
H(s)
0.85
0.84
0.82
0.8
0.78
0.76

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Tubular reactor with Raschig rings (IV)

Dynamics of the system



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



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 - ✓ **Packed bed reactors for industrial applications (complex 3D geometry)**
- ✓ Extensions
 - ✓ KMC (Kinetic Monte Carlo)
- ✓ What's next?
 - ✓ Complex domains relevant to industrial applications

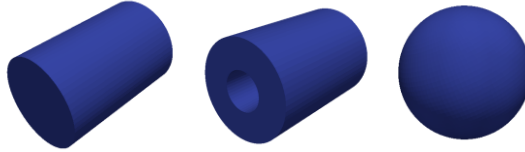
Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Analysis of performances

Investigated structures

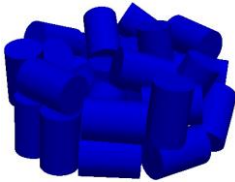
Cylinders
Rings
Spheres



Same catalytic area

	$A_{\text{single element}} [\text{m}^2]$	N
Sphere	1.13×10^{-4}	50
Ring	1.88×10^{-4}	30
Cylinder	1.57×10^{-4}	36

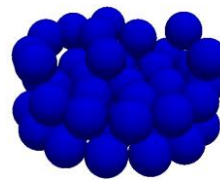
36 cylinders



30 rings



50 spheres

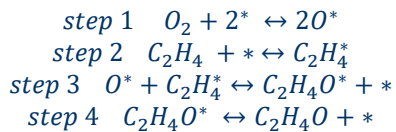


Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



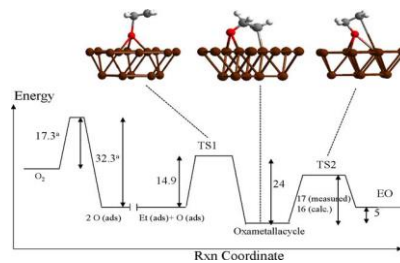
Global kinetic scheme

Micro-kinetic model



Global kinetic scheme

KINETIC MODEL PARAMETERS	
A	$9.85\text{E}5 \text{ 1}/(\text{atm m}^3 \text{ s})$
E_{att}	15 Kcal/mol
m	0.65
n	0.71



Suljo Linc and Mark A. Barbeau, Construction of a reaction coordinate and a microkinetic model for ethylene epoxidation on silver from DFT calculations and surface science experiments, November 2002, Journal of catalyst, pag 200-213

$$r = k_{\text{overall}} (P_{\text{O}_2})^n (P_{\text{C}_2\text{H}_4})^m$$

$$k_{\text{overall}} = A e^{-\frac{E_{\text{att}}}{RT}}$$

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Operating conditions

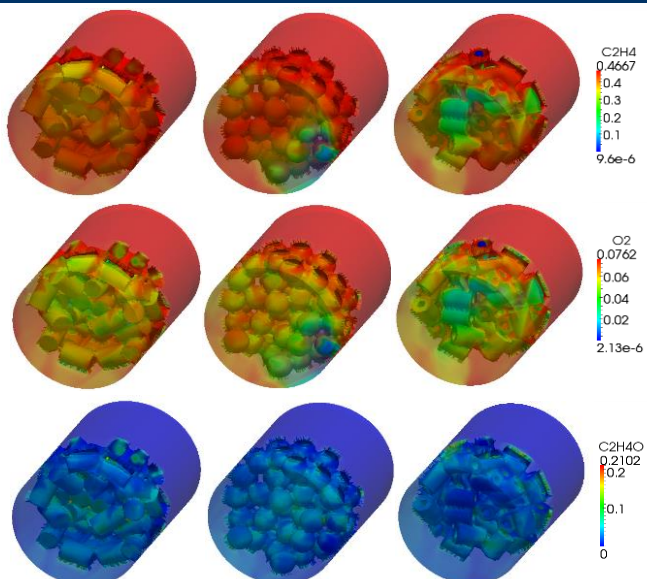
OPERATING CONDITIONS	
C ₂ H ₄ Molar Fraction	35.0 %
O ₂ Molar Fraction	5.0 %
CH ₄ Molar Fraction	60.0 %
Pressure	15 atm
Temperature	432 – 550 K
Inlet Velocity	1 m/s

- ✓ Oxygen based process
- ✓ Methane as inert component
- ✓ Isothermal simulations at 432 K, 490 and 550 K
 - ✓ Adiabatic simulations at 432 K
 - ✓ Multiregion simulations at 490 K

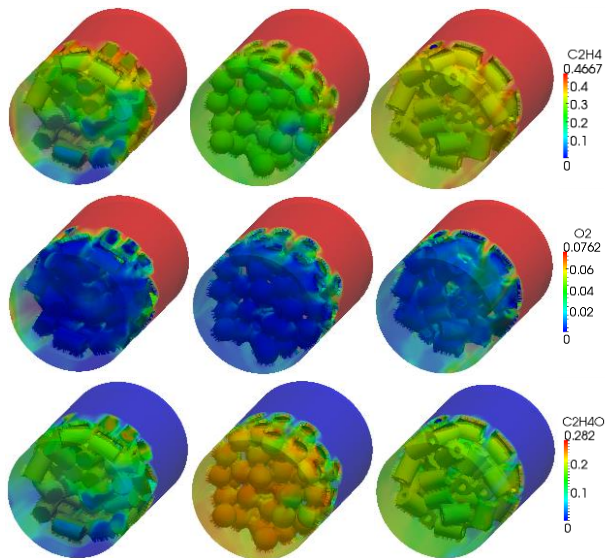


Isothermal simulations: 432 K

The behaviour of the three packed beds is almost the same



Isothermal simulations: 550 K

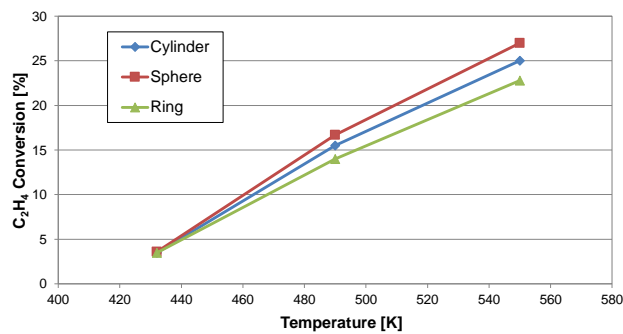


Spheres at high temperature can guarantee the higher conversion

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

Isothermal simulations

C₂H₄ Conversion vs Temperature



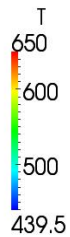
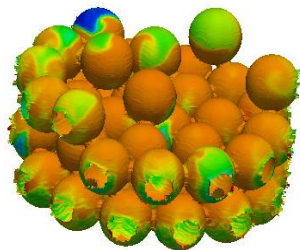
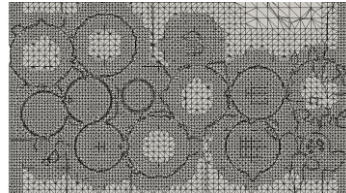
	432 K	490 K	550 K
Cylinders	3.5 %	15.5 %	25.0 %
Spheres	3.6 %	16.7 %	27.0 %
Rings	3.5 %	14.1 %	22.8 %

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Extension to multiregion

Multiregion Mesh: the spheres have been meshed with the same level of refinement of the bulk phase - conformal mesh



Adiabatic simulations
Need to have very fine meshes close to the reactor wall

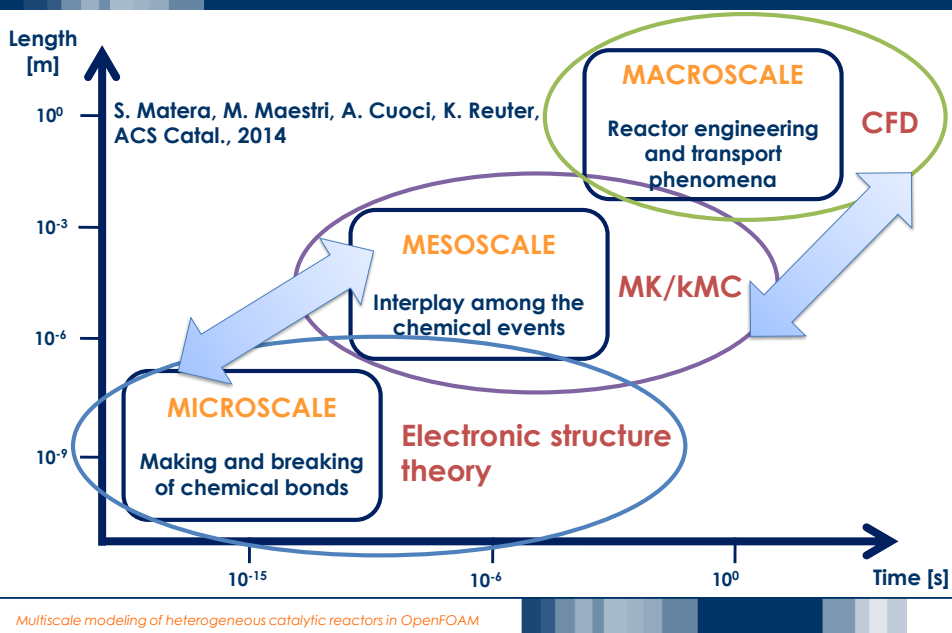


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Extension to kinetic Monte Carlo

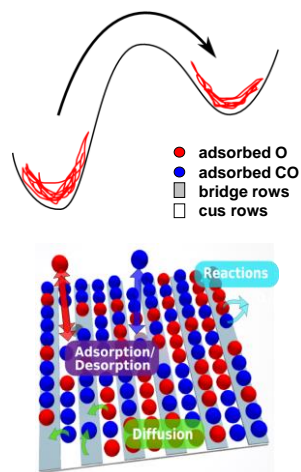


First-principles kinetic Monte Carlo

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

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

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



S. Matera, M. Maestri, A. Cuoci, K. Reuter, ACS Catal., 2014

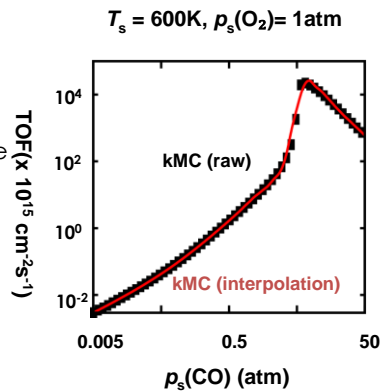


“Effective” bridging between the scales

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

$$j_n^a = v^a M^{ar} \text{TOF}$$

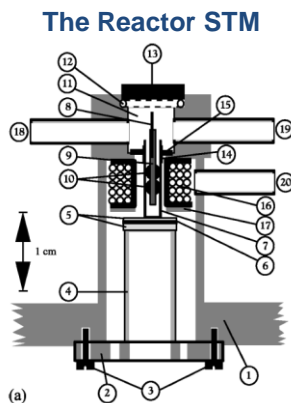
- ✓ **Coupled problem:** to determine the TOF with 1p-kMC the pressures at the surface are needed, but the pressure field depends on the TOF
- ✓ **kMC too expensive** for direct coupling to the flow solver
- ✓ Run kMC beforehand and interpolate (Modified Shepard)
- ✓ Very efficient
- ✓ Easily extendable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



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)

S. Matera, M. Maestri, A. Cuoci, K. Reuter, *ACS Catal.*, 2014

CO oxidation on Ru_2O

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

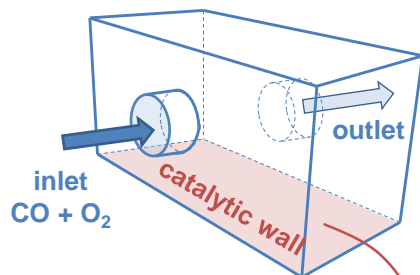
Model system

- ✓ CO oxidation on $\text{RuO}_2(110)$
- ✓ 2 types of sites, bridge and cus

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



An example: The reactor STM (II)



inlet
CO + O₂

outlet

catalytic wall

Operating conditions

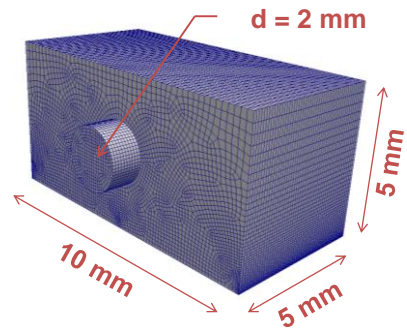
T: 600 K

P: 1 atm

Inlet: CO + O₂ (66%, 34% Vol)

Inlet velocity: 5 cm/s

Catalytic Wall
Catalyst: Ru₂O



d = 2 mm

10 mm

5 mm

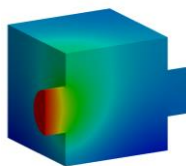
5 mm

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

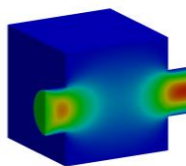


An example: The reactor STM (III)

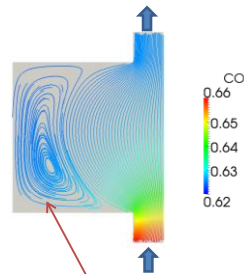
Steady-state results



CO
0.66
0.65
0.64
0.63
0.62

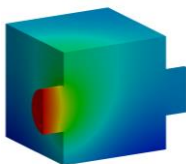


U Magnitud
0.1
0.075
0.05
0.025
0

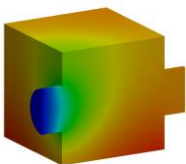


CO
0.66
0.65
0.64
0.63
0.62

Strong
recirculations



O₂
0.34
0.33
0.32
0.317866



CO₂
0.063
0.06
0.04
0.02
0



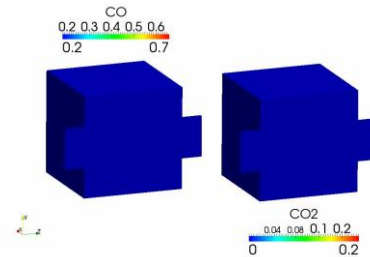
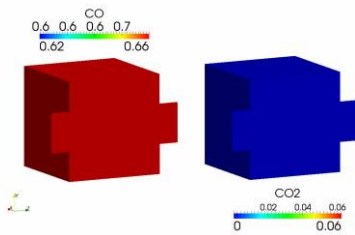
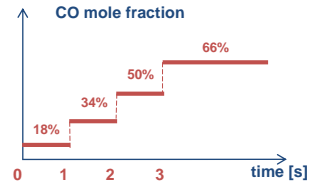
An example: The reactor STM (IV)

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)

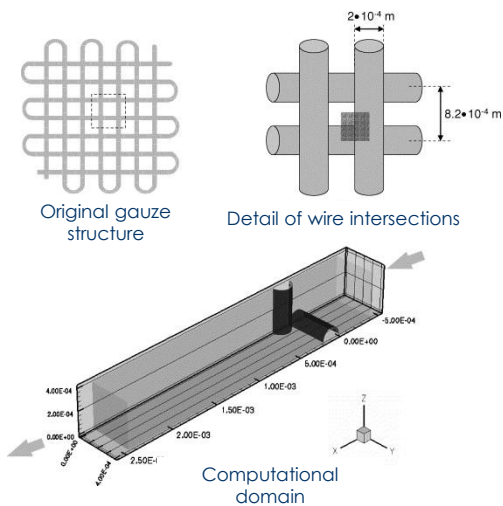
The CO mole fraction in the inlet stream increases during the time



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

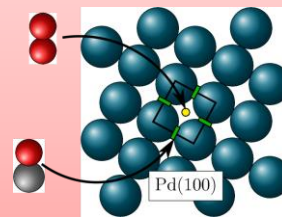


An example: the catalytic gauze (I)



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

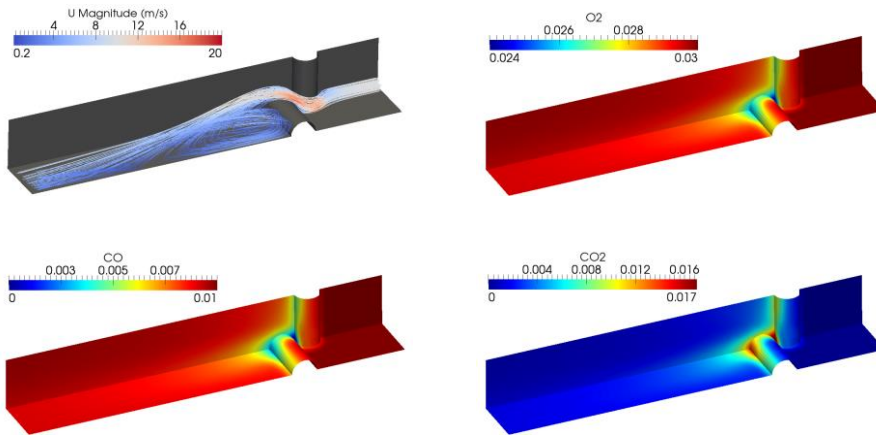
- Model system: CO oxidation on Pd(100):



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



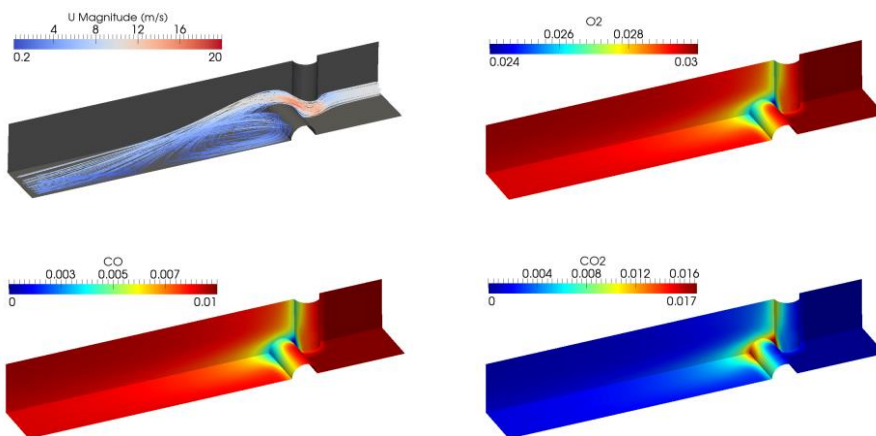
An example: the catalytic gauze (II)



Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



An example: the catalytic gauze (III)



DFT → kMC → CFD

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Outline

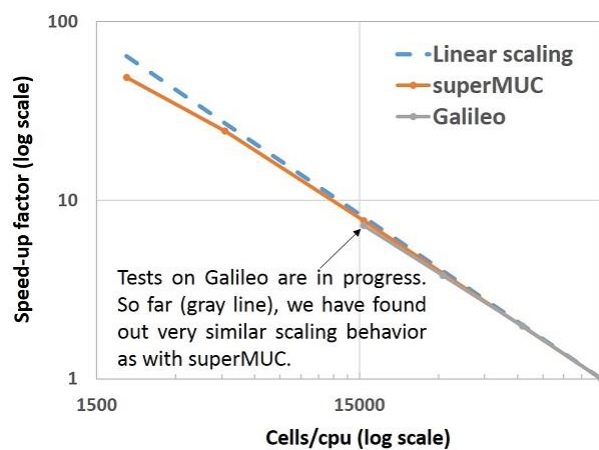


- ✓ Introduction and motivation
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
 - ✓ Governing equations
 - ✓ Numerical methodology
 - ✓ Simulation with detailed kinetics: stiff ODE solvers and ISAT
- ✓ Validation and examples
 - ✓ Annular reactor
 - ✓ CPO of CH₄ on platinum gauze (complex 3D geometry)
 - ✓ CPO of iso-octane (complex chemistry)
 - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
 - ✓ Packed bed reactors for industrial applications (complex 3D geometry)
- ✓ Extensions
 - ✓ KMC (Kinetic Monte Carlo)

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Overall HPC performances



Packed-bed of spheres – 2 Mio Cells

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



Publications on international journals

M.Maestri, A.Cuoci, *Coupling CFD with detailed microkinetic modeling in heterogeneous catalysis*, Chemical Engineering Science 96(7), pp. 106-117 (2013) DOI: [10.1016/j.ces.2013.03.048](https://doi.org/10.1016/j.ces.2013.03.048)

Matera, S., Maestri, M., Cuoci, A., Reuter, K., *Predictive-quality surface reaction chemistry in real reactor models: Integrating first-principles kinetic monte carlo simulations into computational fluid dynamics*, ACS Catalysis 4(11), pp. 4081-4092 (2014) DOI: [10.1021/cs501154e](https://doi.org/10.1021/cs501154e)

Maffei, T., Gentile, G., Rebughini, S., Bracconi, M., Manelli, F., Lipp, S., Cuoci, A., Maestri, M., *A multiregion operator-splitting CFD approach for coupling microkinetic modeling with internal porous transport in heterogeneous catalytic reactors*, Chemical Engineering Journal, 283, pp. 1392-1404 (2016) DOI: [10.1016/j.cej.2015.08.080](https://doi.org/10.1016/j.cej.2015.08.080)

Rebughini, S., Cuoci, A., Maestri, M., *Hierarchical analysis of the gas-to-particle heat and mass transfer in micro packed bed reactors*, Chemical Engineering Journal, In press, DOI: [10.1016/j.cej.2015.12.089](https://doi.org/10.1016/j.cej.2015.12.089)

Rebughini, S., Cuoci, A., Maestri, M., *Handling contact points in reactive CFD simulations of heterogeneous catalytic fixed bed reactors*, Chemical Engineering Science, 141, pp. 240-249 (2016) DOI: [10.1016/j.ces.2015.11.013](https://doi.org/10.1016/j.ces.2015.11.013)

Bracconi, M, Cuoci A., Maestri, M., *In-situ adaptive tabulation for CFD operator-splitting based simulations of heterogeneous reactors*, submitted

Multiscale modeling of heterogeneous catalytic reactors in OpenFOAM



The catalyticFOAM software is fully compatible with OpenFOAM version 3.0.

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.

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