Willkommen
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Materials Science and Technology

Additive Manufactured (AM) Open Cell Structures: Promising substrates for Automotive Catalysts

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Politecnico di Milano, 22.02.2018

- Introduction
- Simulation for accessing potentials of foams
- Comparison honeycomb (HC) / Kelvin cell polyhedra
- Possibilities with AM
- Geometrical Optimization of polyhedral catalyst lattice
- Simulations and measurements on first prototypes
- Manufacturing of vehicle size polyhedral prototypes
- Considerations of real life catalysts

Foam catalyst achieved similar conversion of standard honeycomb using 1/2 of noble metal

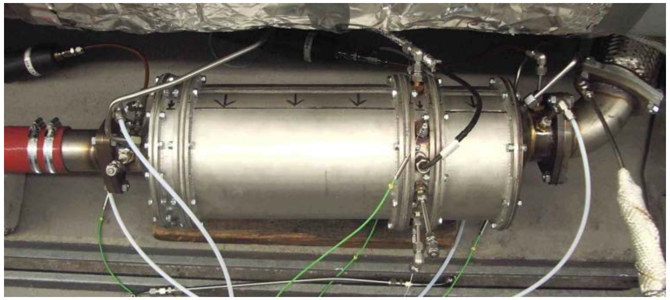
Industrial standard honeycomb

Foam reactor

- Small Heavy Duty truck (Iveco Daily)

- Different coating
- No particular customization

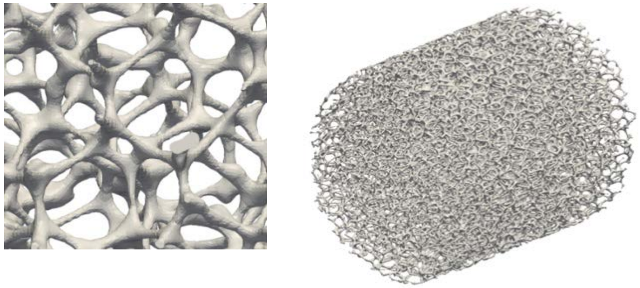
Empa ICEL, test bench,
Bach & al., SAE 2011-24-0179



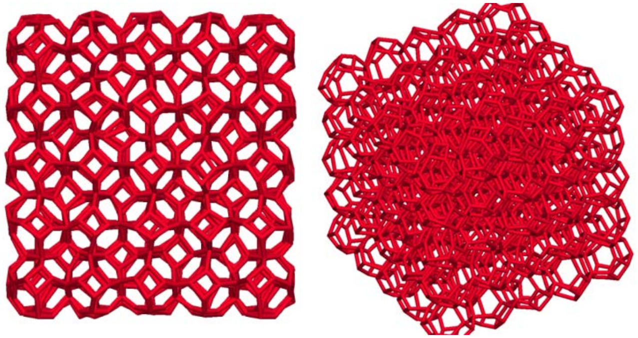
Test Catalyst assembly

CFD Simulations in OpenFOAM of Open Cell structures: real foam CTs and Kelvin cell lattices

Modellization



Real Foam (CT scans at Empa 499)



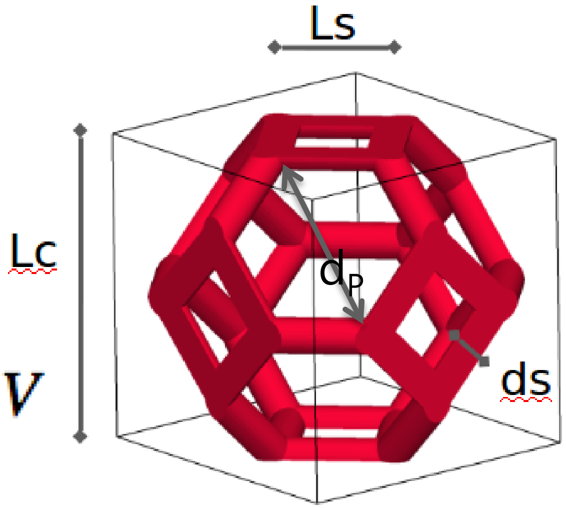
periodicity

⬇

Ideal Foam (CAD 3D)

$$\varepsilon = \frac{V_{void}}{V_{tot}}$$

$$S_W = S_V \cdot V$$



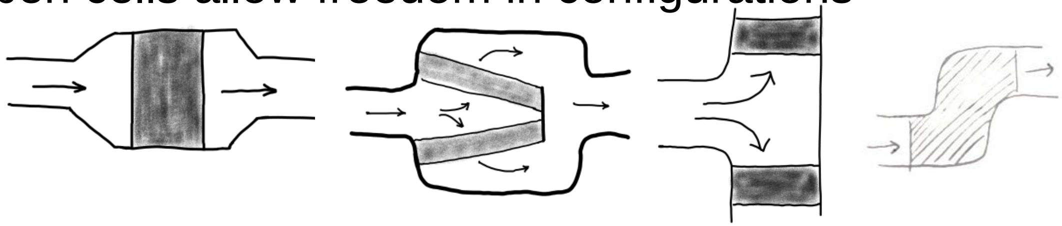
Validation (reference to Literature)
Performances calculated through I*

$$I = \frac{-\ln(1-\eta)}{\Delta P \cdot \rho \cdot U^2}$$

$\uparrow \varepsilon \Rightarrow \downarrow \Delta P$
$\downarrow d_p \Rightarrow \uparrow k$

*Giani (2005)

Open cells allow freedom in configurations



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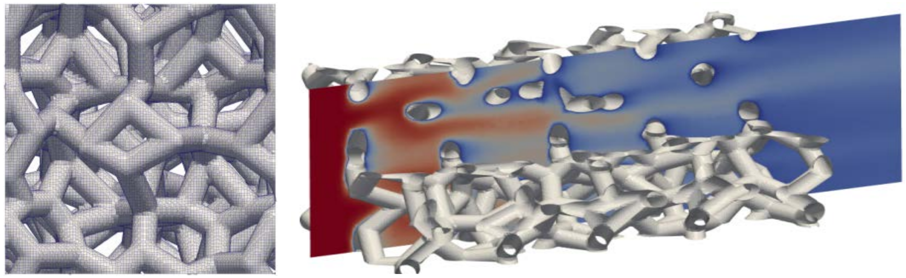
Can Kelvin Cells outperform honeycombs?

Simulations of randomized Kelvin cell lattices and HCs,

Same chemical & fluid dynamic assumptions

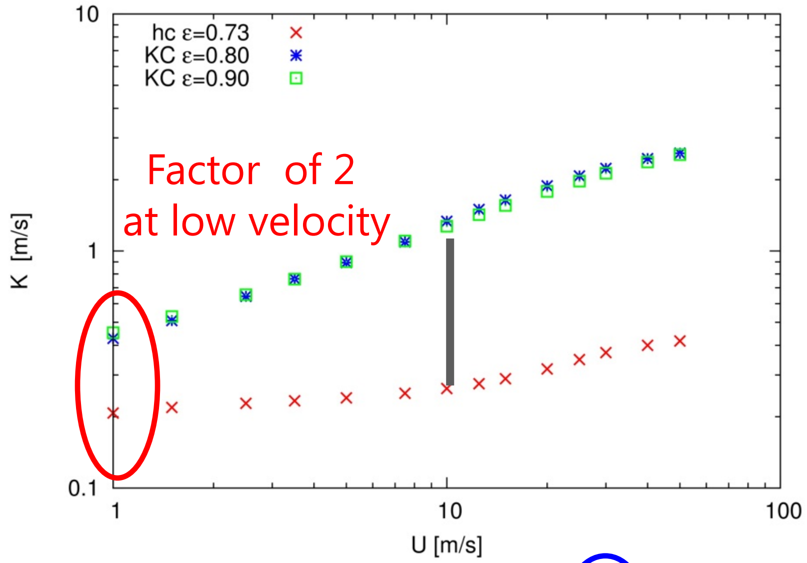


ε = 80-90% Vel(1-50 m/s)

Chan. Size 400-600CPSI, ε = 73%
Vel (1-50 m/s)

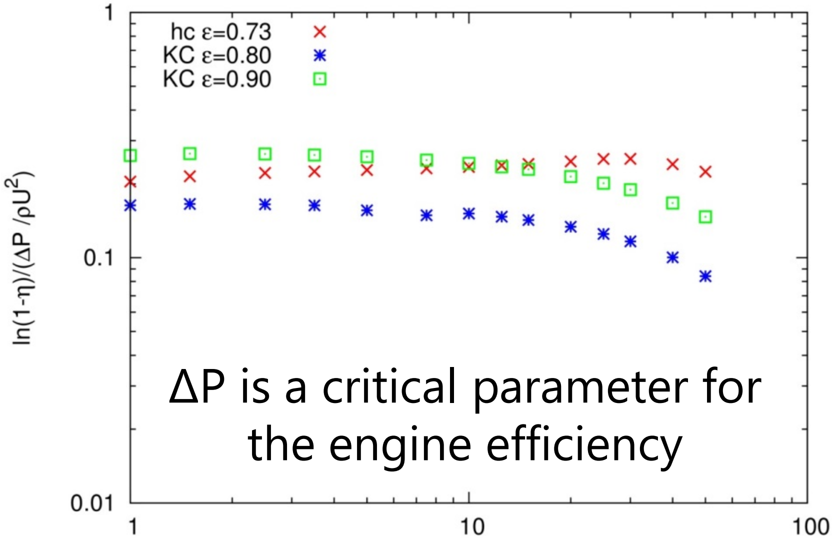
Kelvin Cell needs less surface for the same conversion (lower precious metal amount)

Mass transfer (external surface)



Factor of 2
at low velocity

Conversion/pressure drop trade off



ΔP is a critical parameter for the engine efficiency

From simulations

$$K = -\frac{\ln(1-\eta)}{\frac{S_W}{Q_{in}}}$$

Wetted surface

Volumetric flow rate

$$K \cdot S_V = -\frac{\ln(1-\eta)}{\frac{V}{Q_{in}}}$$

const

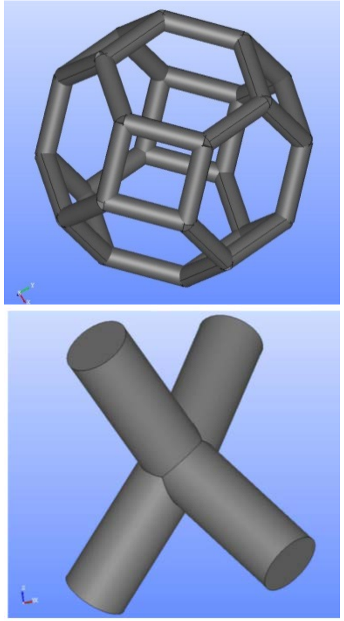
Specific surface

$$S_W = S_V \cdot V \propto \frac{1}{K} \propto$$ Noble Metal quantity

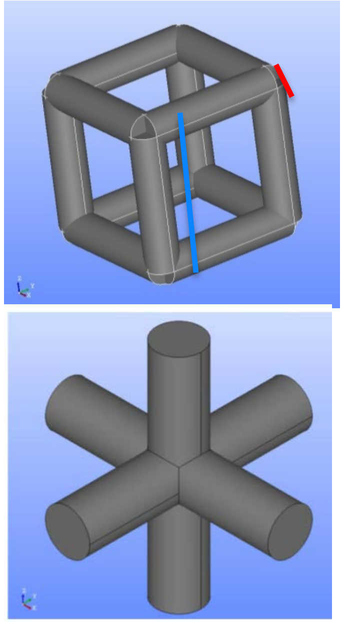
VEL=10m/s
1/10 Sw , 1/2.5 V

- Regular Kelvin cells outperform randomized foams
- Idea of 3D Printing*: design for features, we analyzed different regular cells

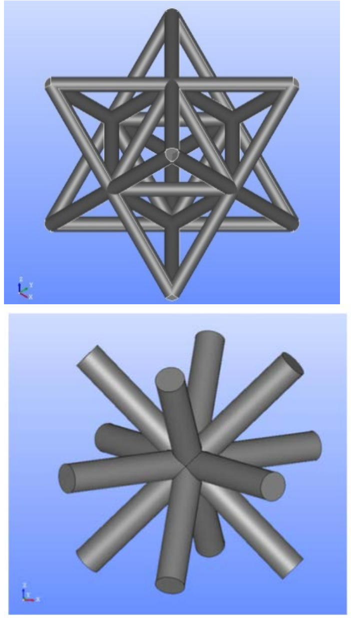
Kelvin



Cubic



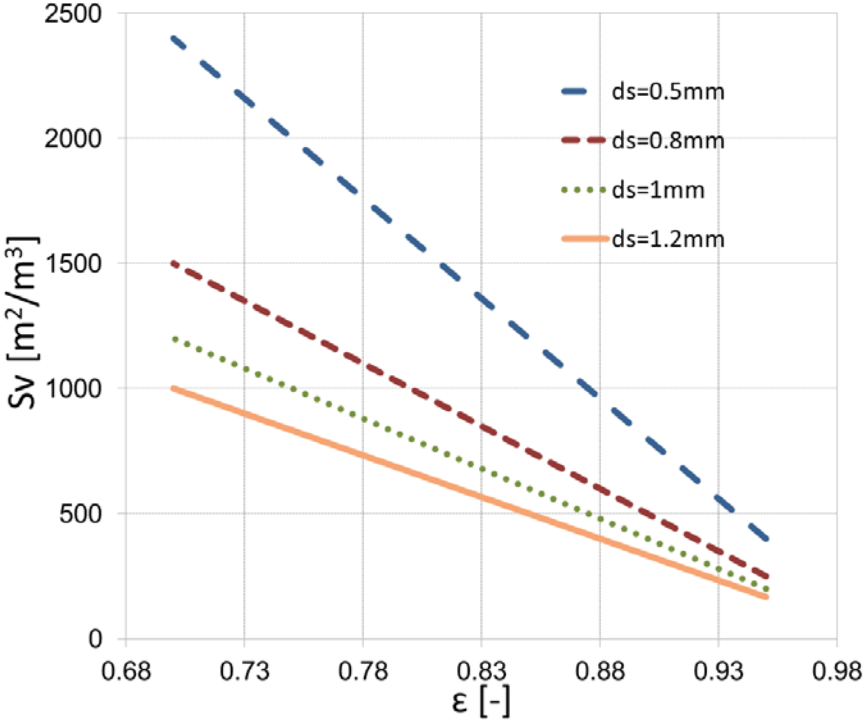
Octet

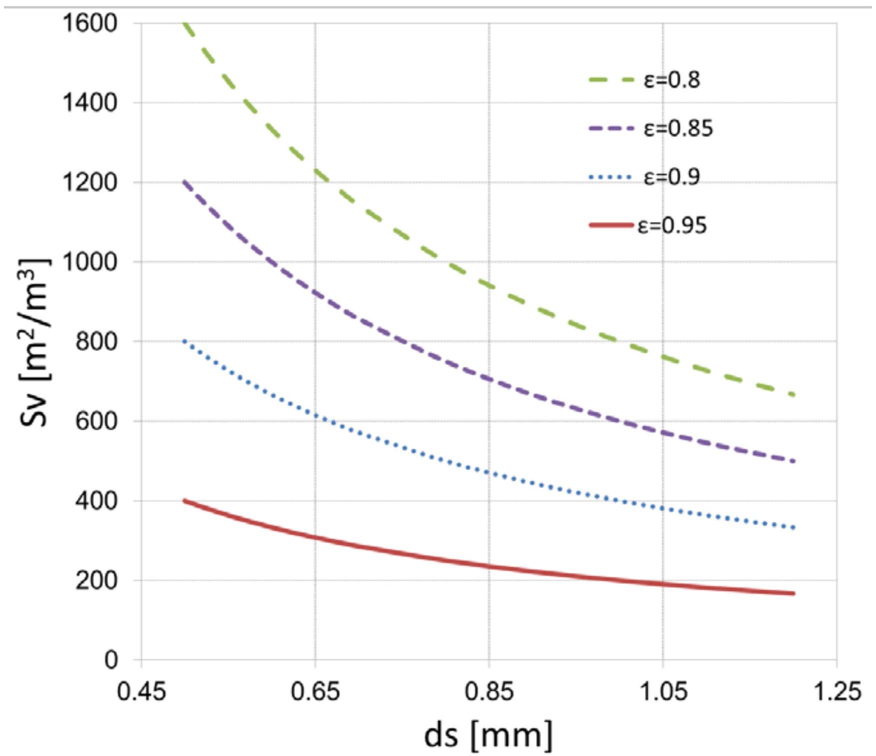


Cubic cells tested with 2 flow direction straight and at 45 degree

*Ultralight, ultrastiff mechanical metamaterials, Xiaoyu Zheng et al. , Science 344, 1373 (2014)

Analytical expressions of **Sv** in function of **ε** and **d_s** are derived



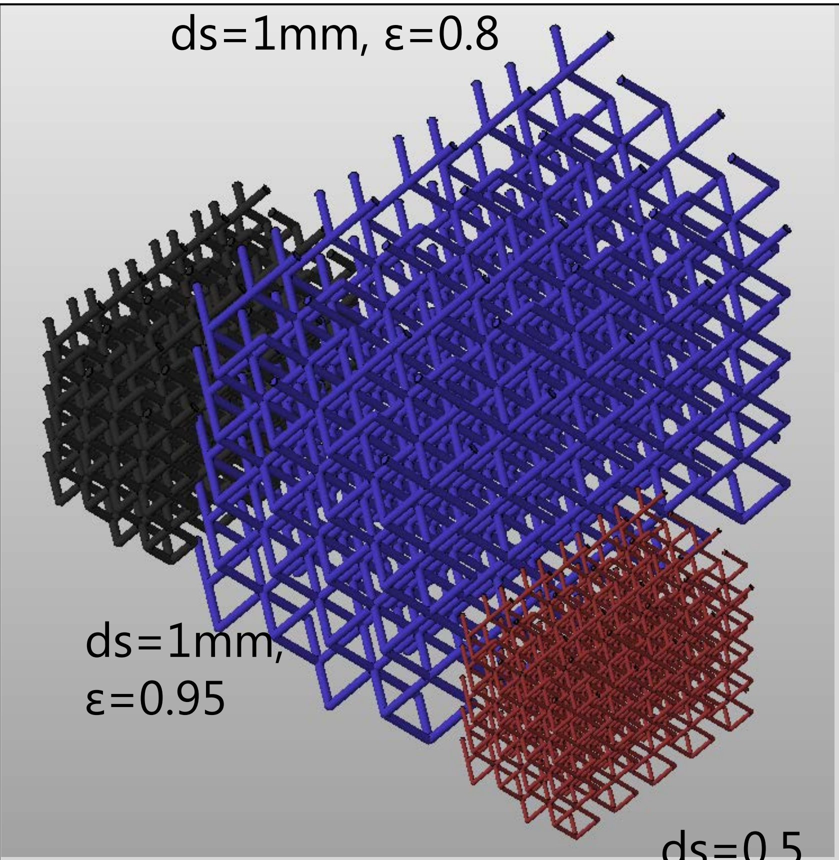


Fixing (ε, d_s), same Sv, but different Lc

Higher ε at fixed d_s → Lower Sv

Higher d_s at fixed ε → Lower Sv

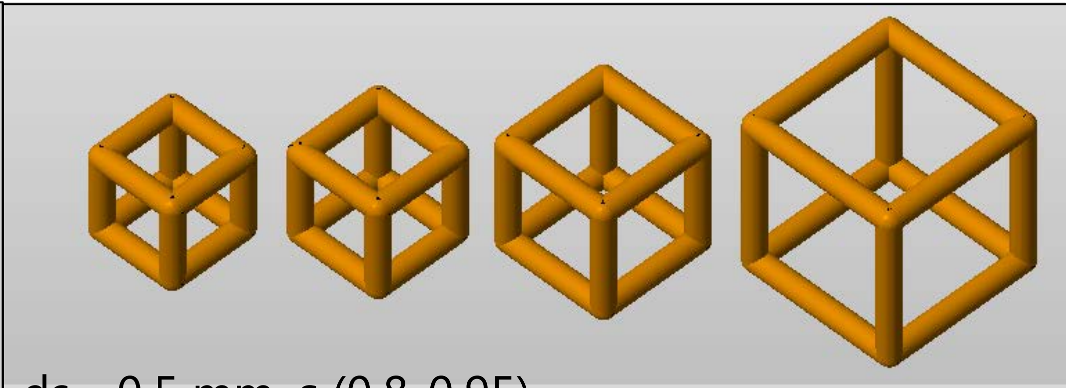
Different porosities, ε, can be achieved by changing either L_s, d_s or both



ds=1mm, ε=0.8

ds=1mm, ε=0.95

ds=0.5 mm, ε=0.95

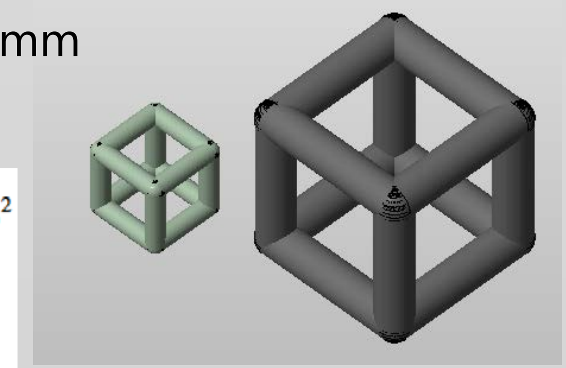


ds =0.5 mm, ε (0.8-0.95)

ε=0.85, ds (0.5/1) mm

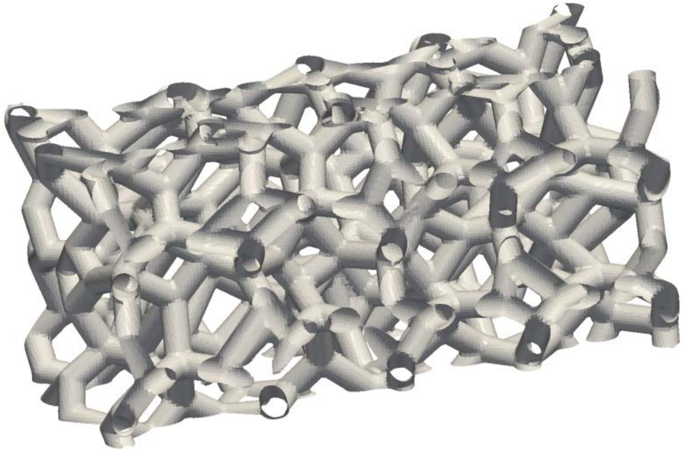
$$\varepsilon = 1 - \frac{3}{4}\pi(r)^2$$

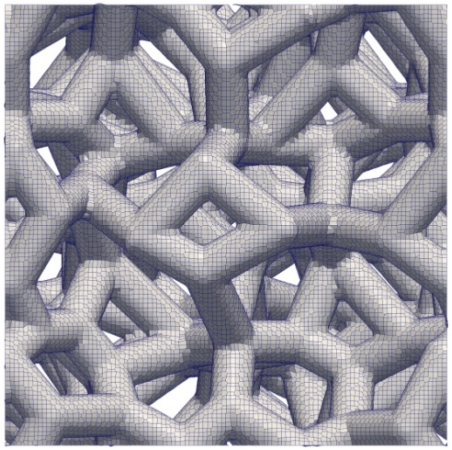
$$r = \frac{d_S}{L_c}$$



4 geometrical configurations, 4 ε (80-95%), 2 d_s (0.5mm,1mm)

Simulations for geometrical optimization: CH_4 oxidation in air is studied





Infinite fast Chemistry, mass transfer limited regime → Steady state

→ reactingSimpleFoam

Single Region No CHT (3°C),

→ T_{in}=700 K T_w=750 K

X_{CH4}=0.1%
Abundance of O_2
$P_{out}=P_{amb}$

Simulations for geometrical optimization: CH_4 oxidation in air is studied

Homogeneous reaction non considered,
Heterogeneous reactions modelled as B.C.

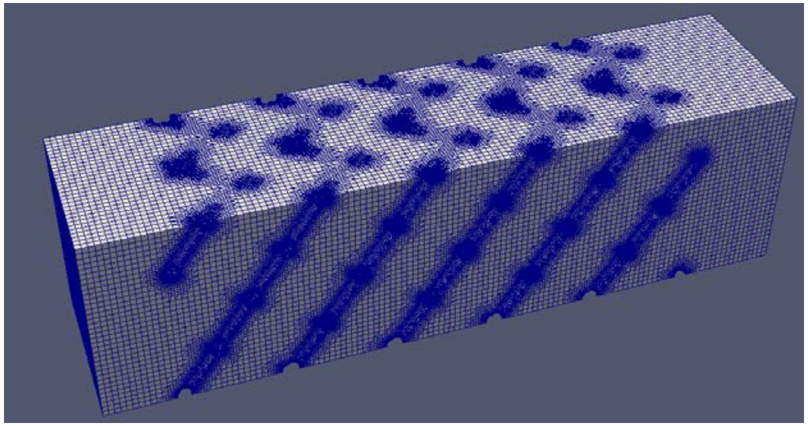
Oxidation of methane

$$X_{sCH4} = 0$$

Other species :

$$\frac{\partial X_i}{\partial \boldsymbol{n}} = \alpha_i \frac{M_i}{M_{CH4}} \frac{\partial X_{CH4}}{\partial \boldsymbol{n}}$$

Inert specie: N_2



Wash coat not modelled (30 %)

4x2x2 Cells + periodic B.C

no instabilities, laminar flow

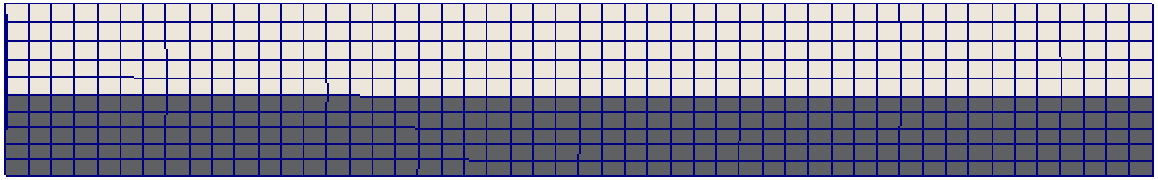
Sc=1, $D_{CH4,air}$=ν

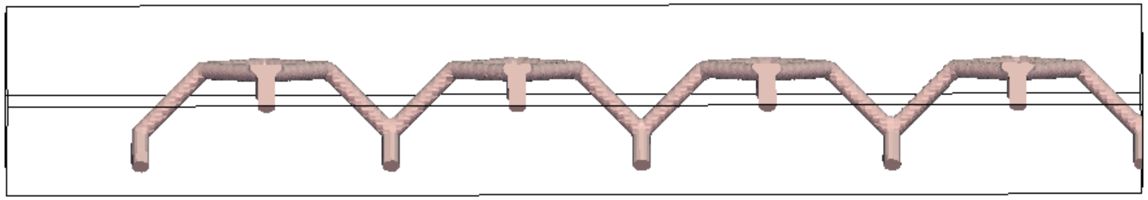
Transport properties: Sutherland

thermal properties: Janaf table

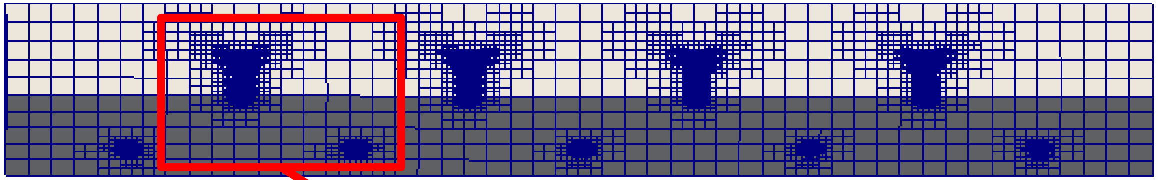
Perfect gas

SnappyHexMesh

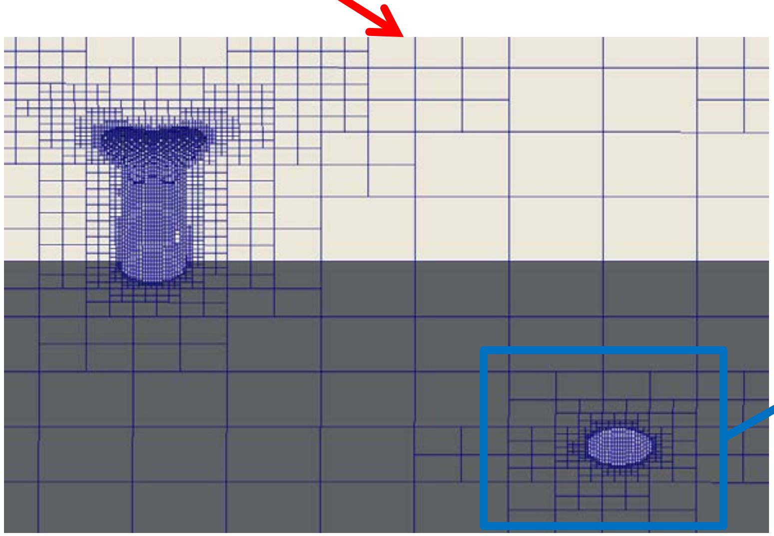


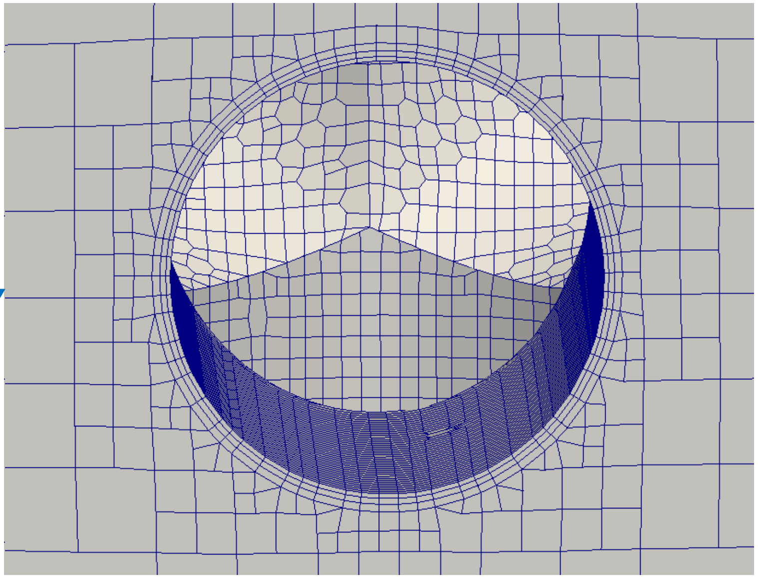


1. Cartesian Block Mesh
2. Foam Surface (STL file)
3. Castellate Mesh
4. Snapp to surface
5. Add Layer

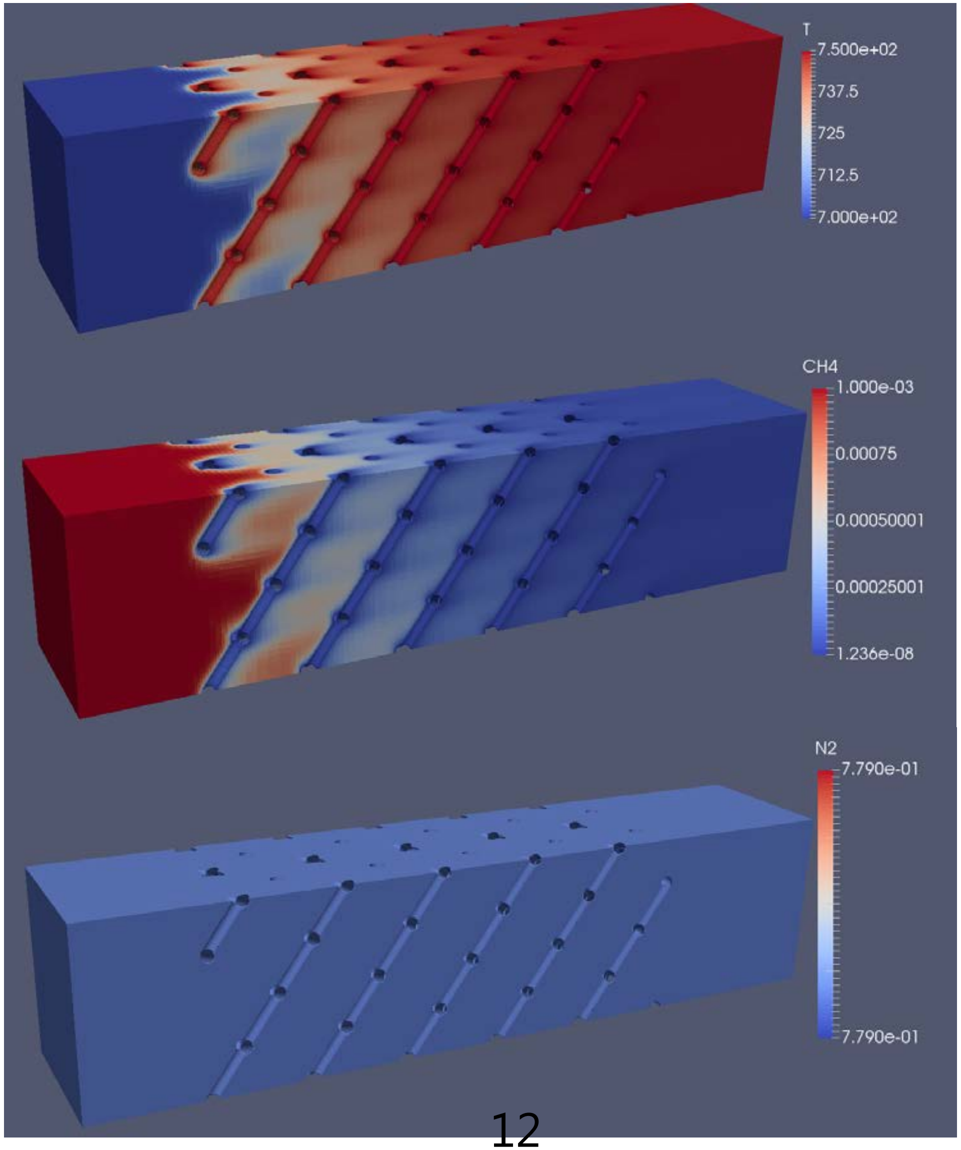


1 Case = (10^6) cells
12 hrs in 1CPU



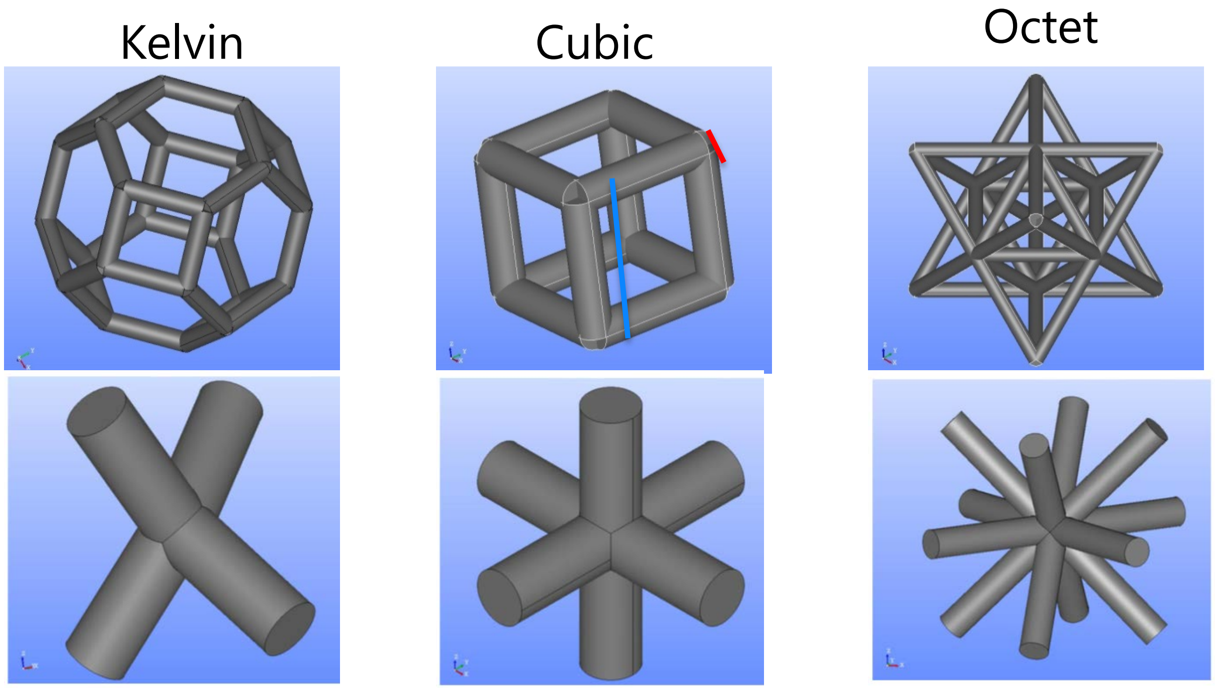


Sample Cubic 45 Cells results:



Inert Specie: N_2

Optimization of the geometry of the cell



Kelvin

Cubic

Octet

Cubic cells tested with 2 flow direction straight and at 45 degree

	CELL	ds	Ls	Lcell	ε	Sv
K2	Kelvin	0.5	2	5.66	0.95	416
C3	Cubic	0.5	3.4	3.36	0.95	416
O6	Octet	0.5	5.6	8.00	0.95	416

Manufacturing limit

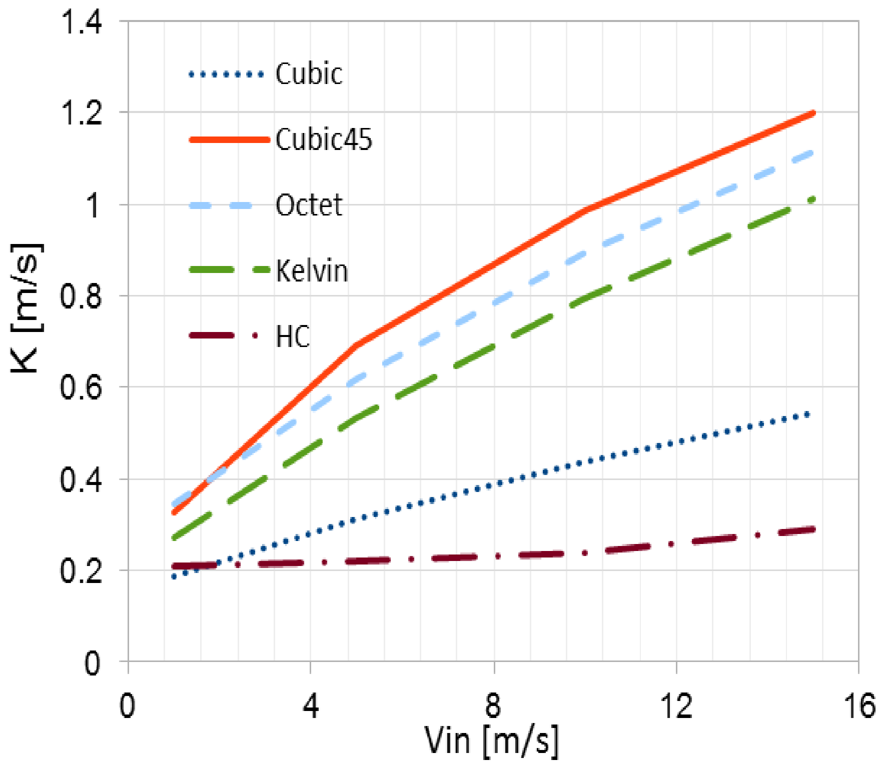
Growing struts L

same ε and Sv

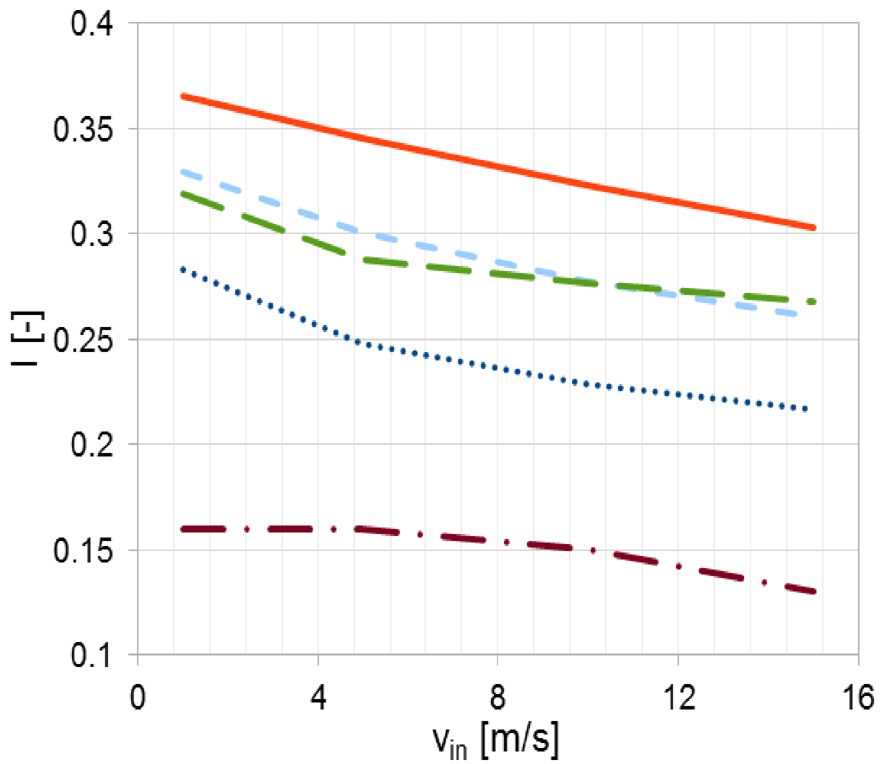
Rotated cubic cell is the optimal cell for a lattice structure, higher K and I at all vel

Vel (1-15 m/s)

Mass Transfer



conversion/pressure trade off



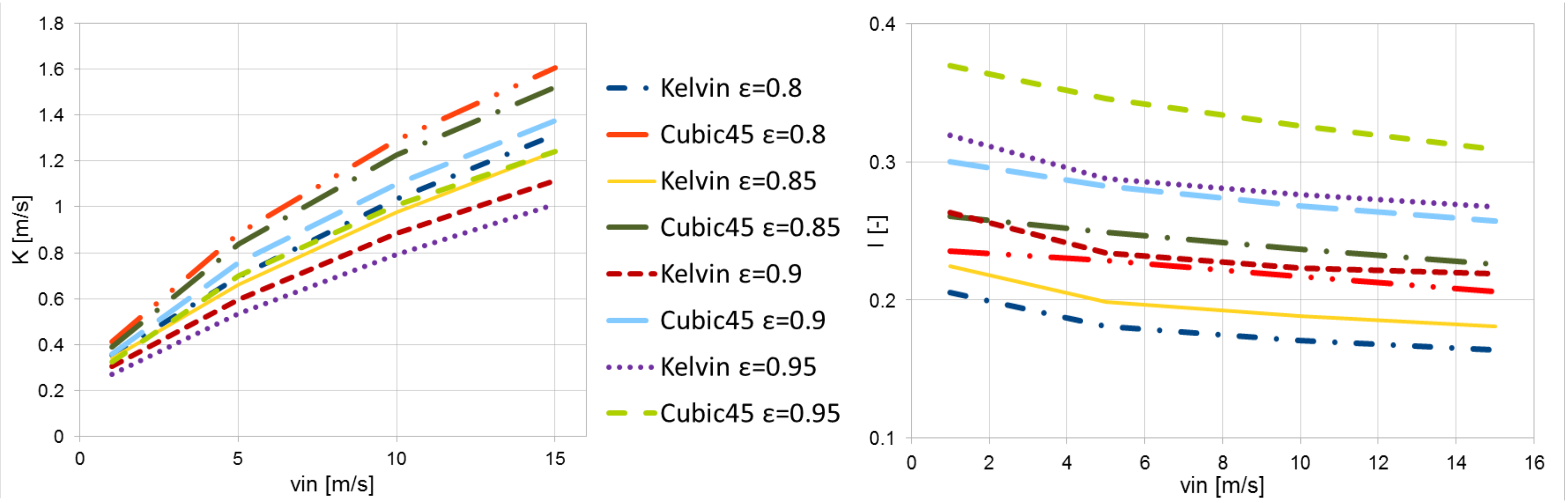
At vel=10m/s Cubic45 requires 4 times less S_w than HC, but 3/2 bigger Volume ($S_{vHC} = 6S_{wCUBIC45}$)

Rotated cubic cell is the optimal cell for a lattice structure at all ε, Higher ε means lower K, but higher I

Same d_s

Mass Transfer

conversion/pressure trade off

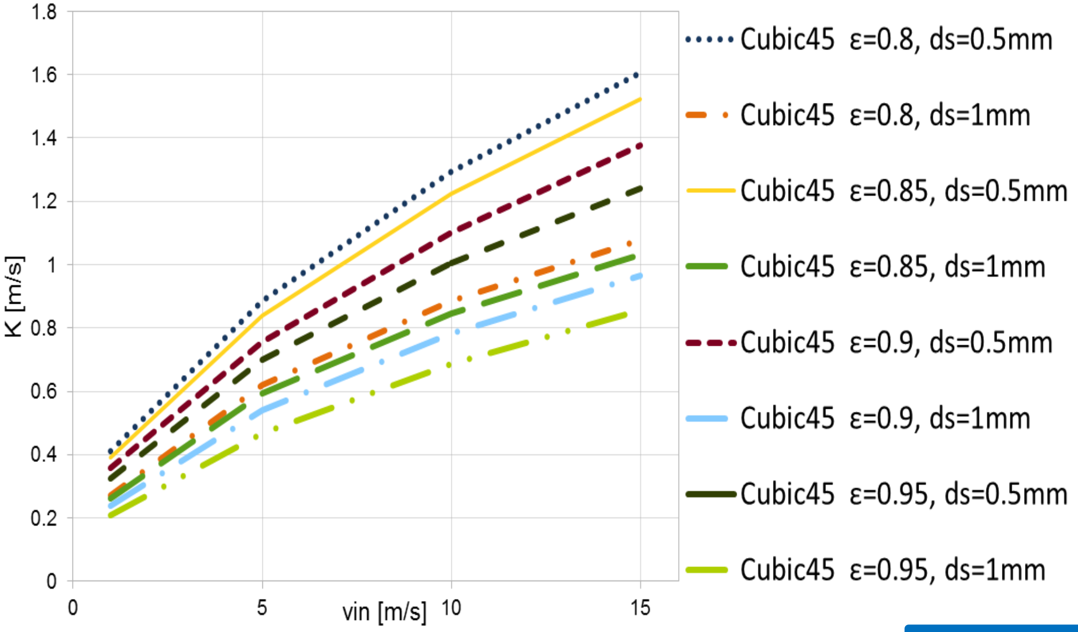


$$K = -\frac{ln(1-\eta)}{S_v\, V/Q_{in}}$$

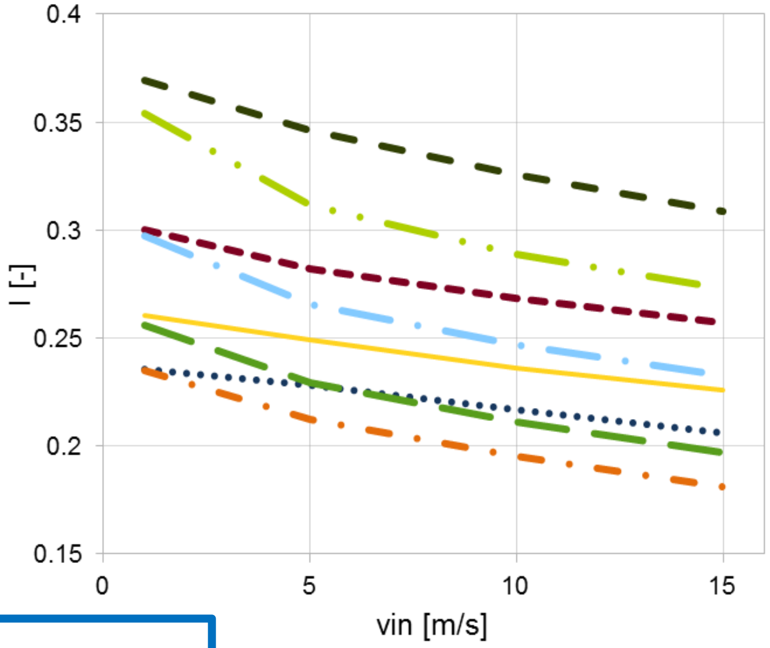
$$S_w = S_v V \ \propto 1/K$$

Higher ds means lower K and lower I

Mass Transfer



conversion/pressure trade off



$$K = -\frac{ln(1-\eta)}{S_v\, V/Q_{in}}$$

$$S_w = S_v V \;\propto 1/K$$

BEST: Cubic45, higher ε, lower d_s

3D printing of Al_2O_3: Matching Photopolymer and photoinitiatior

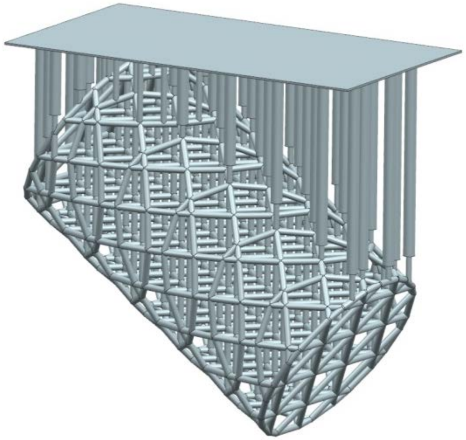
Slurry

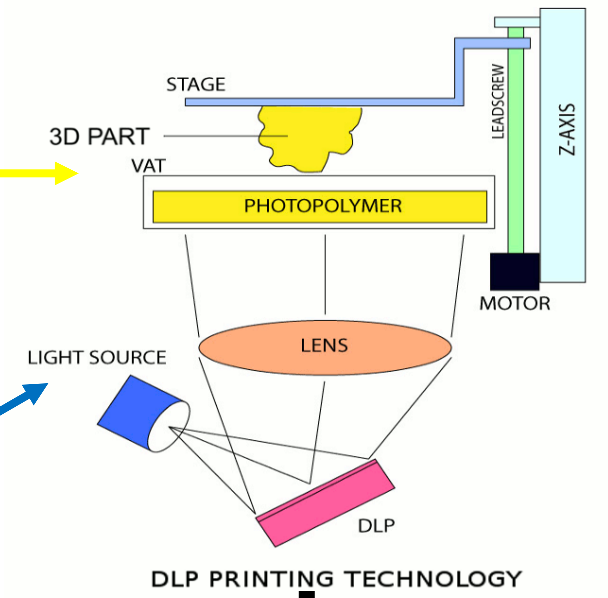
Photosensitive resin

Al_2O_3 ceramic powder

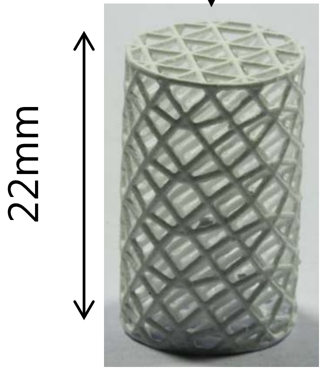
Photo initiator

CAD file

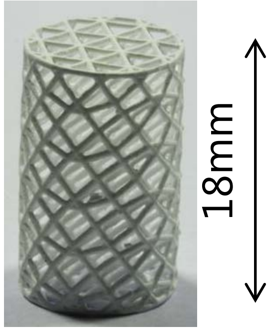




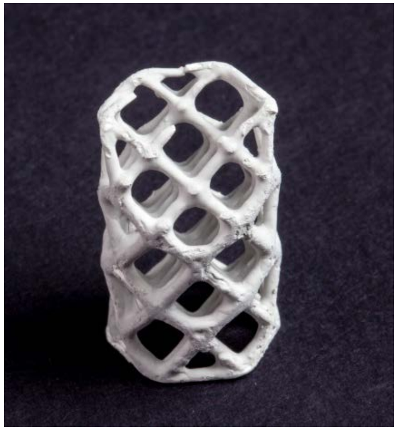
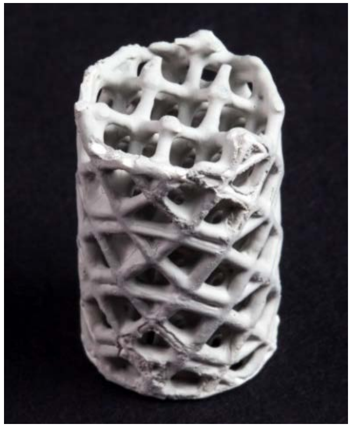
DLP PRINTING TECHNOLOGY



Sintering



Coating in house (J. Tschudin), Coating adhesion: Satisfactory

3D4

$L_s = 4\text{mm}$

$d_s = 600\mu\text{m}$

$\varepsilon = 0.95$

$S_v = 353\text{m}^2/\text{m}^3$

3D3

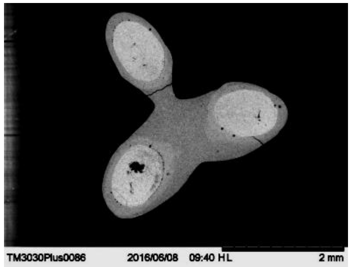
$L_s = 3\text{mm}$

$d_s = 600\mu\text{m}$

$\varepsilon = 0.90$

$S_v = 630\text{m}^2/\text{m}^3$



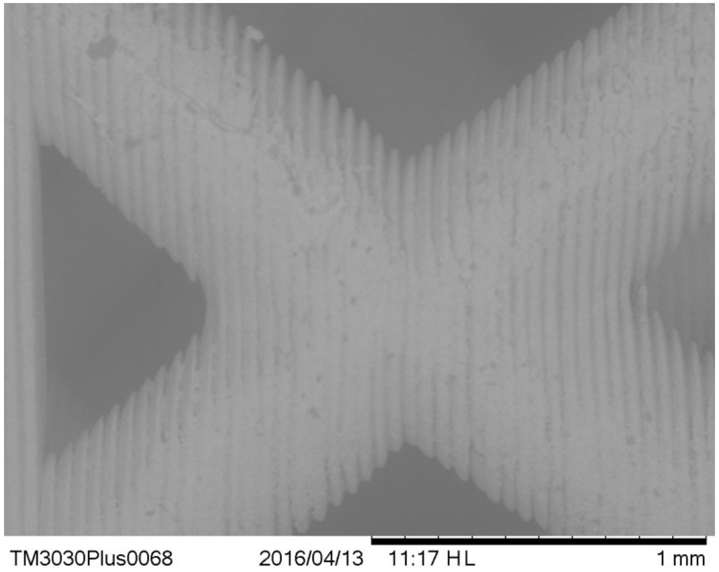


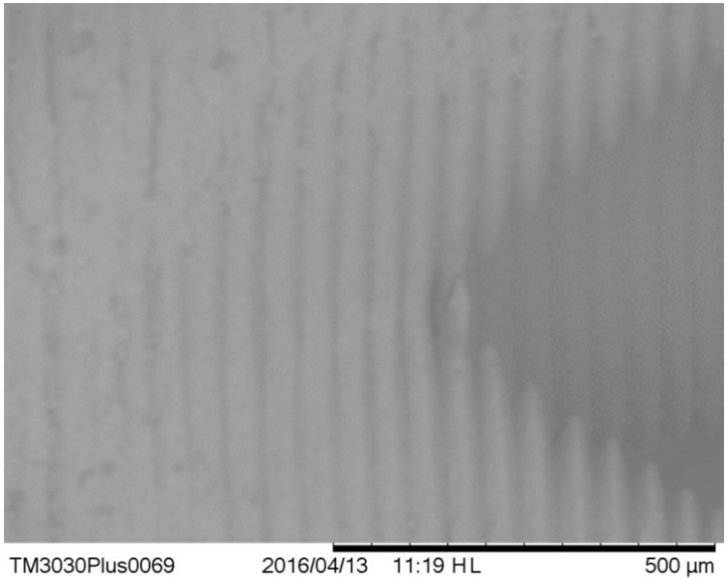
- approx. 40 weight % of coating
- Pt amount: 40-70gr/ft^3,
- BET-surface area: 18m^2/gr (commercial catalysts 48m^2/gr)

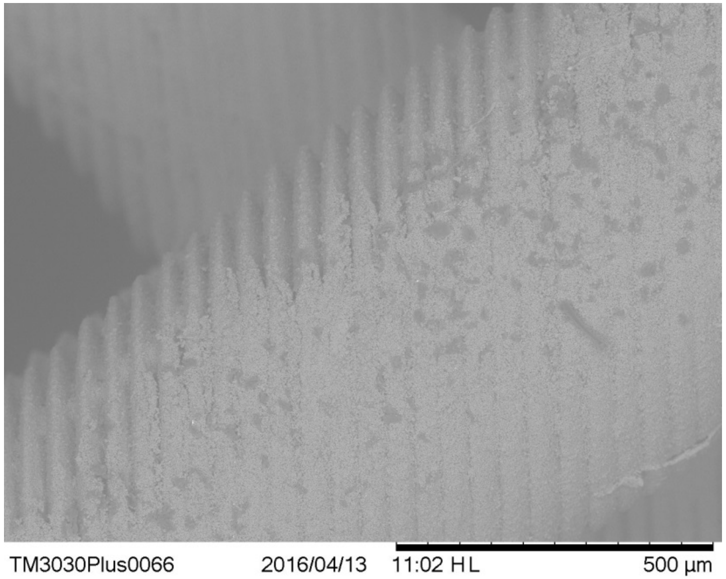
D = 12mm

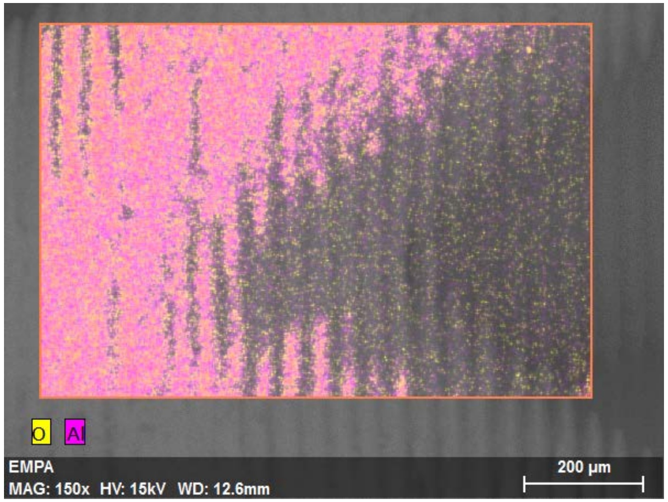
L = 20mm

Struts with 600μm ± 50μm diameter, each layer about 50μm thick, material Al_2O_3





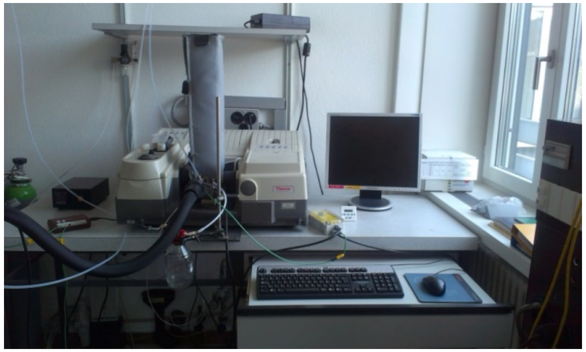


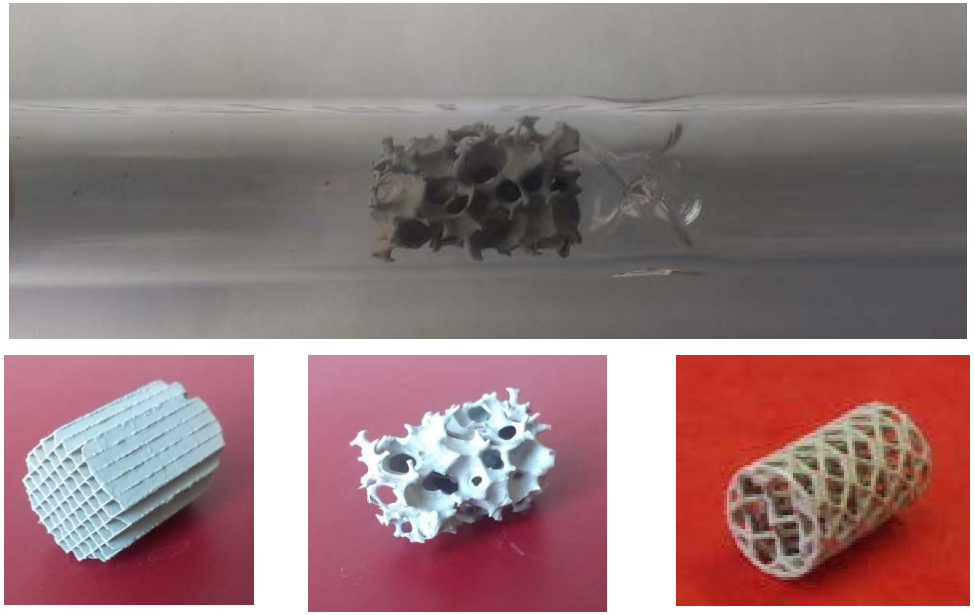


Catalytic performance of samples tested in a model gas reactor

Oven

Infrared spectroscopy





- Small reactor dimensions are unfavorable for the 3D structures with high porosity
- Only low velocities can be tested
- Only small dimensions catalysts can be tested

Measurements confirm simulations: 3D3 with almost identical conversion as HC but ¼ of the wetted surface

- Specific surfaces:

HC S_V~2400 [1/m]
3D S_V~600 [1/m]

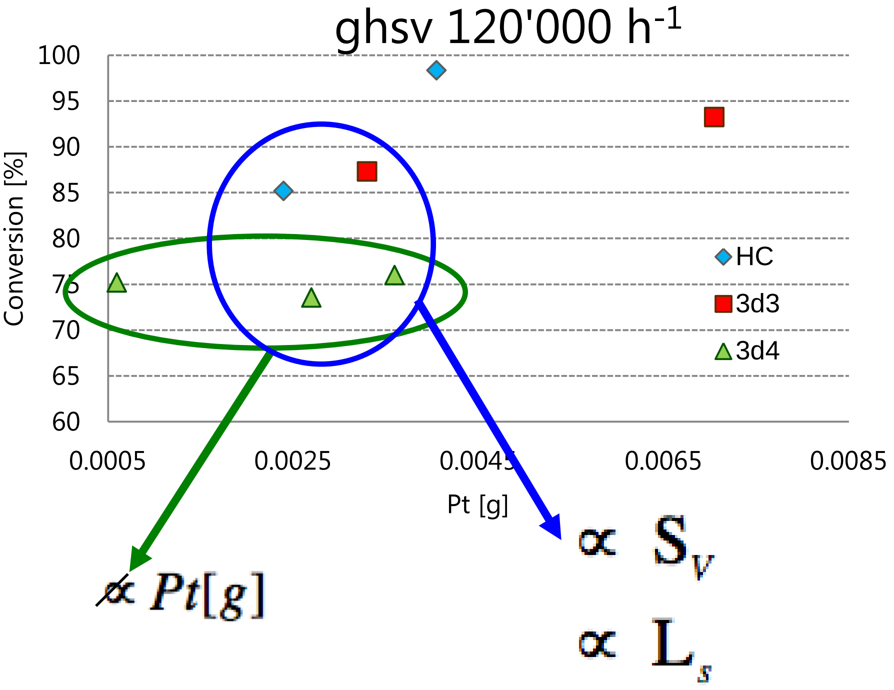
- Similar washcoat (precious metal quantity)

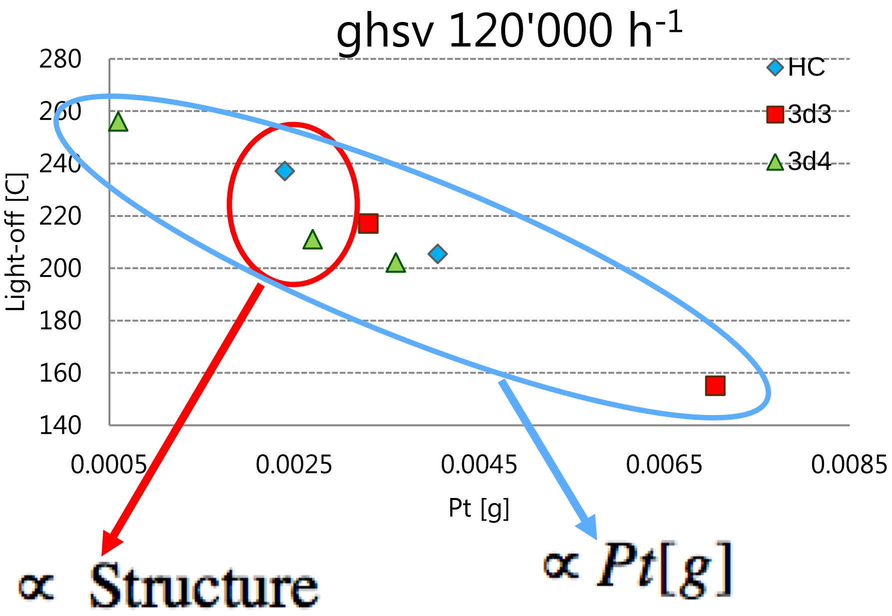
→

3D has thicker (UNUSED) washcoat

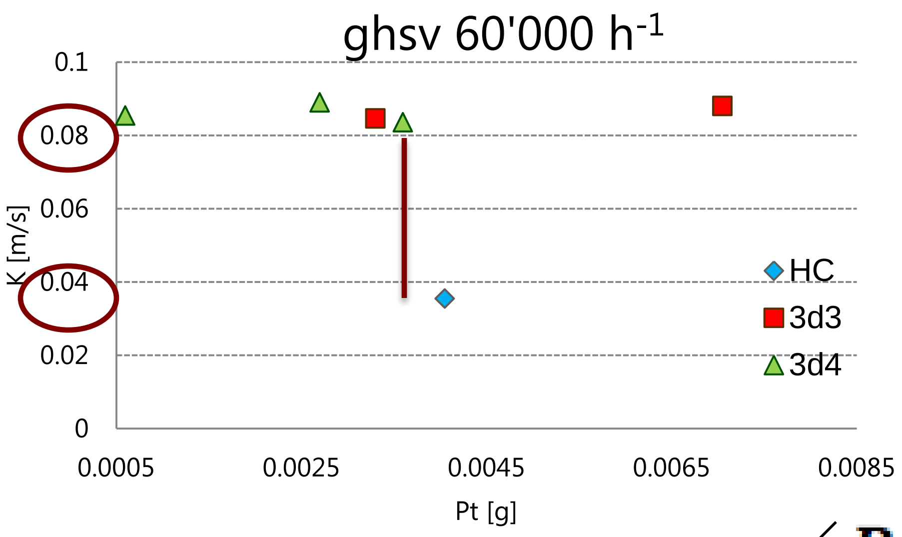
→

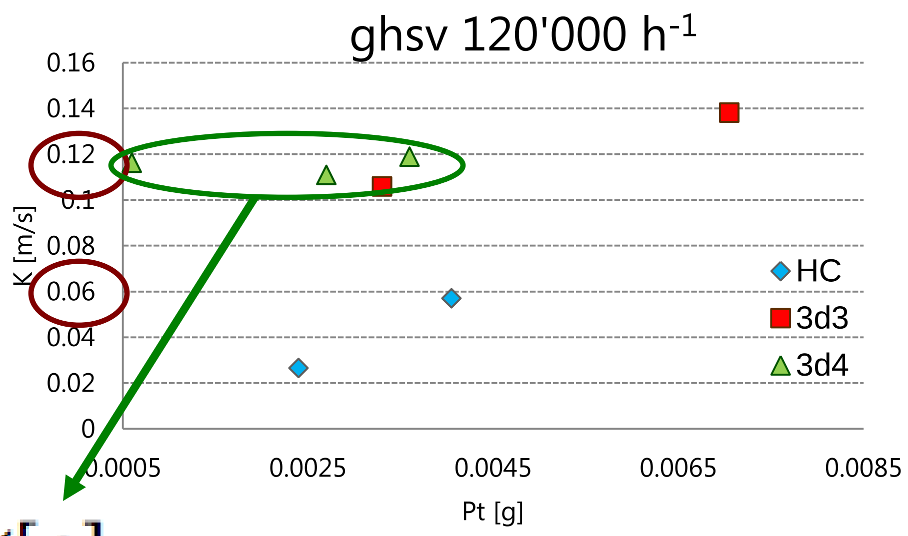
- Good comparison: with SAME thickness
- 3D requires less precious metals





Mass transfer coefficient measurements confirm higher reactivity per surface area





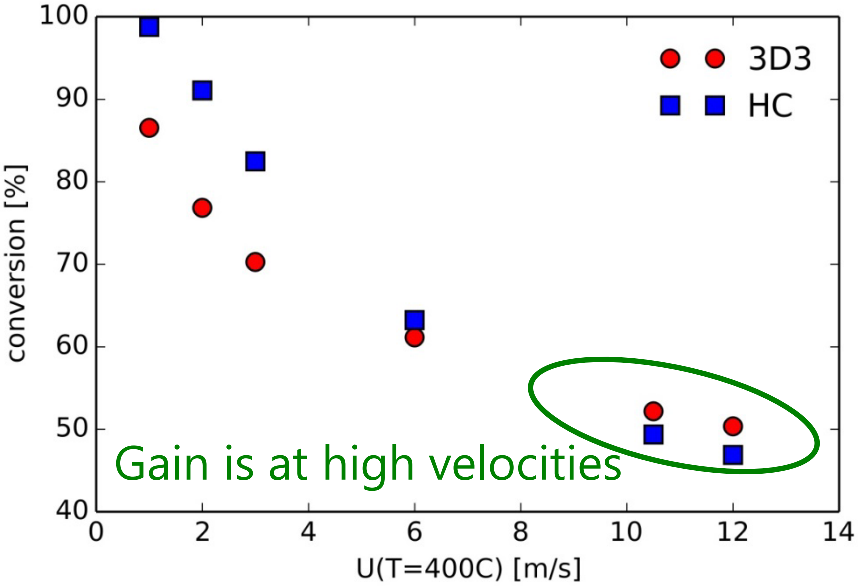
$$\not\propto Pt[g]$$

Reactor	CFD
3D / HC	3D / HC
2.	2.

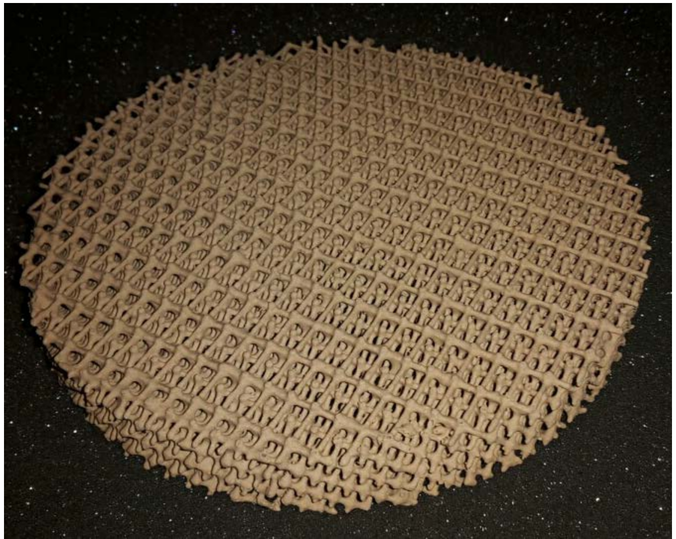
Reactor		CFD
3D 4mm	3D 3mm	3D
0.12m/s	0.13m/s	0.19m/s

Very low velocity, where HC is advantageous because of fully developed flow

3D outperforms HC at high velocities although with ¼ of the surface



Manufacturing vehicle size catalysts is currently an issue



- Manufacturing and stability constraints: restrict possible parameters

$\varepsilon \leq 0.9$

$d_s \geq 1$ mm

Comparison of entire catalysts with identical V: cubic45 higher conversion than HCs with 2 times less surface

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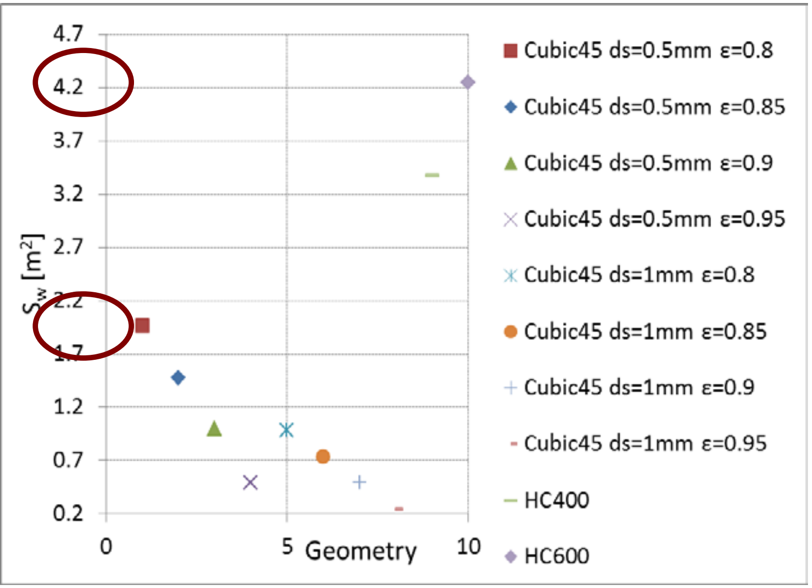

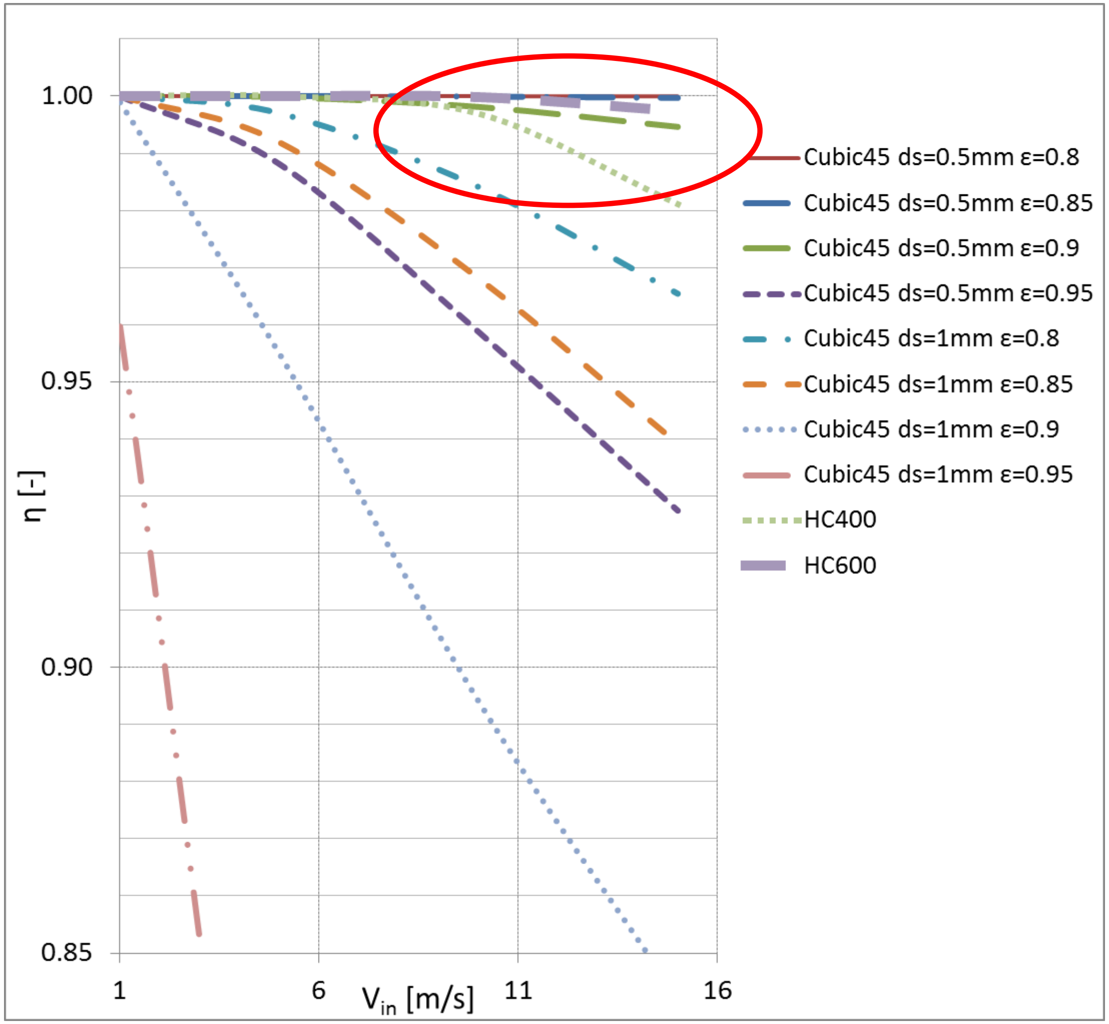

For the simulated configurations, no evident disadvantages in pressure drop

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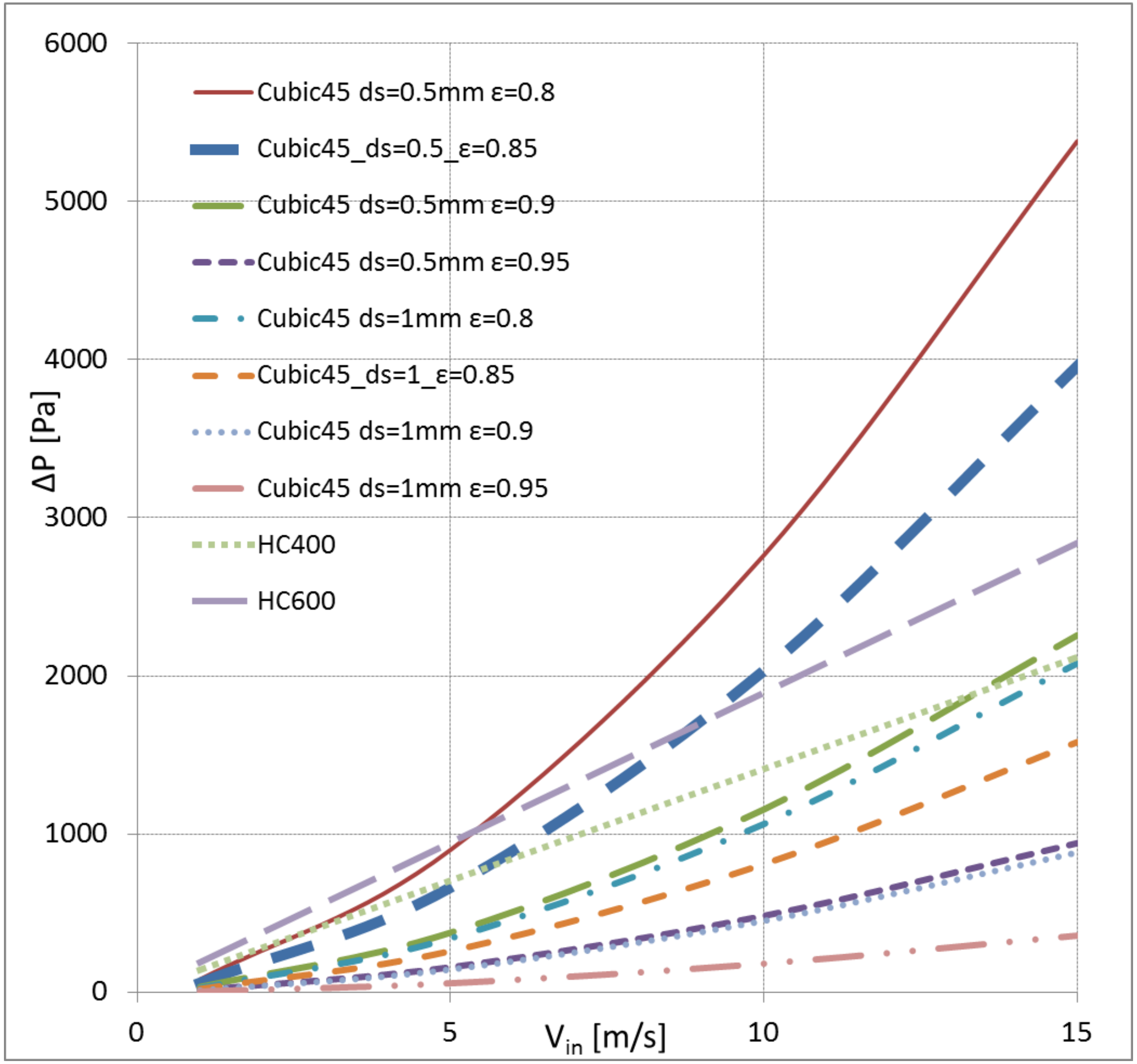
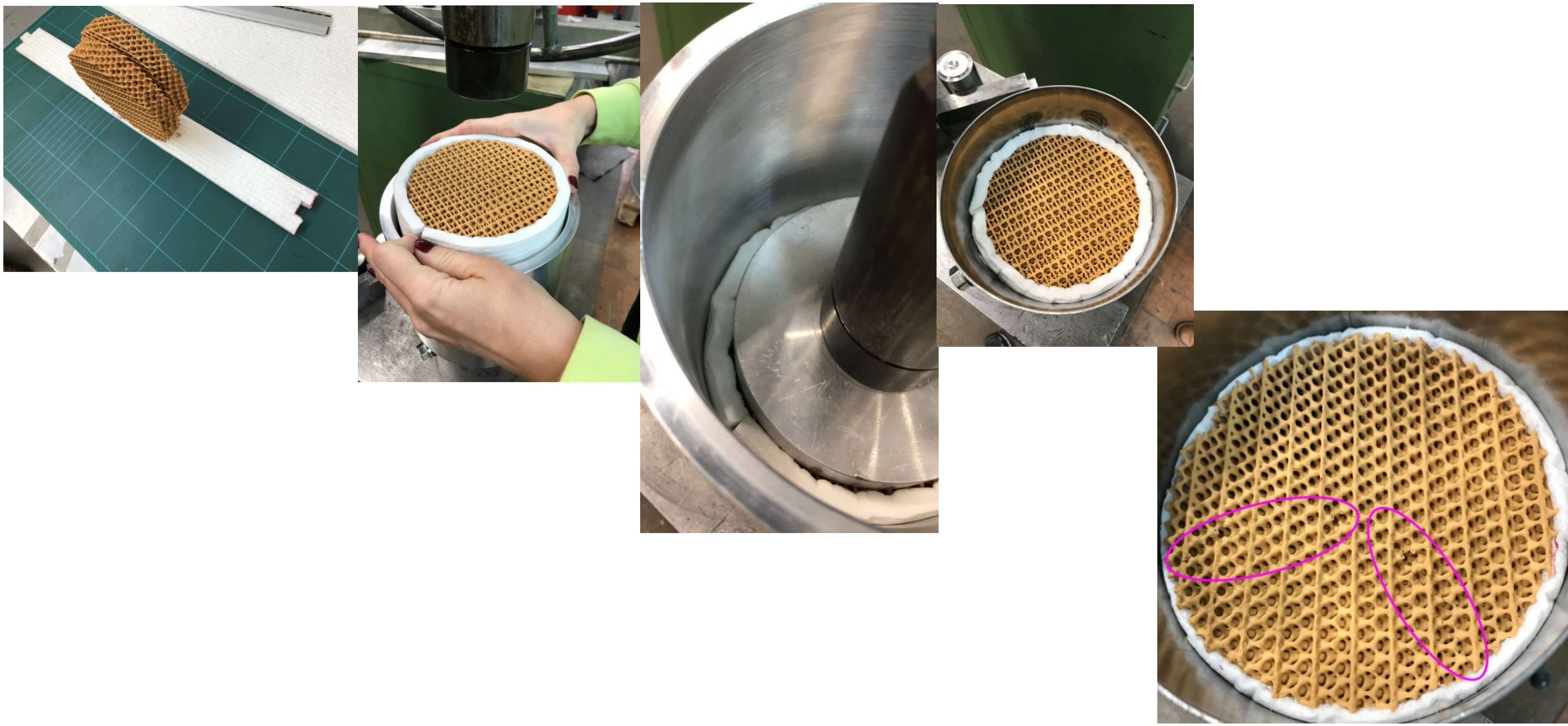


First gasoline vehicle application project



Thank You!

Questions?