EXTRUSION OF HYDRIDE HONEYCOMBS

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Workpackage WP3: Formulation of Hybrid Adsorbents

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AGENDA

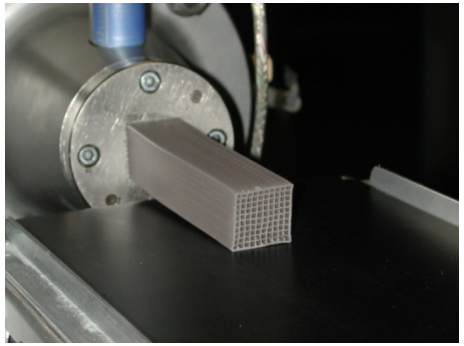
- Introduction to Extrusion
- Reference honeycombs
  - Zeolite honeycombs by Corning
  - Zeolite honeycombs by IKTS
- Advanced honeycombs
  - MOF-honeycombs by IKTS
- Summary

Extrusion

inorganic powders
e.g. zeolite, MOF, carbon

dispersing liquid,
water or organic solvent

(organic) auxiliary agents
mainly: binder, plasticiser
further agents: lubricant, surfactant



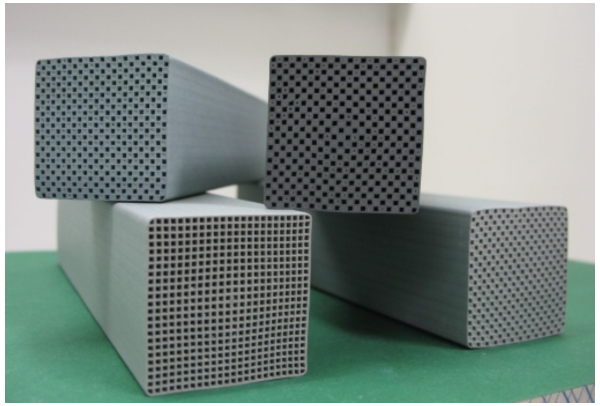
mixing/
plastification

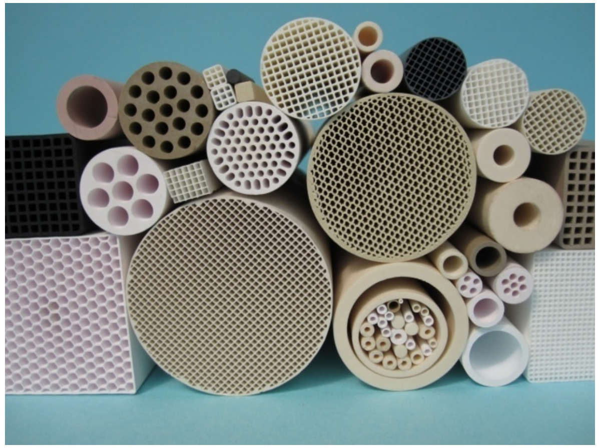
feedstock

extrusion/
cutting to length

drying

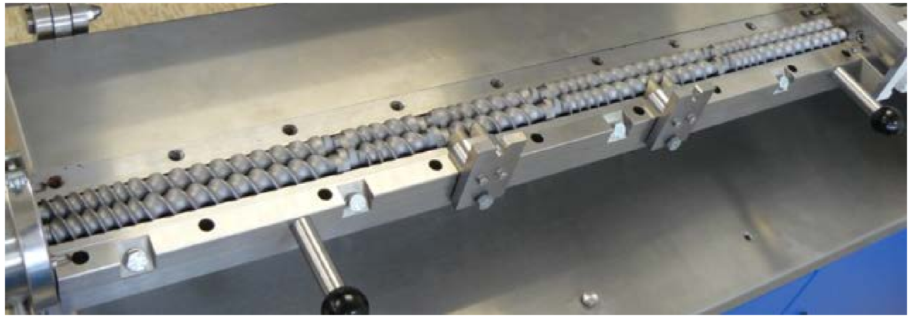
thermal treatment





Extrusion – Feedstock preparation

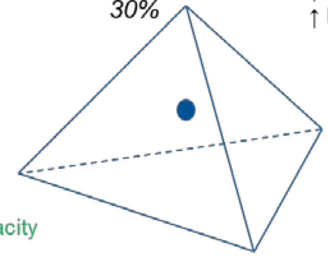
A sufficient good plasticity of the feedstock is the most important property for extrusion. It is achieved by the original plasticity of the raw materials or adjusted by inorganic and/or organic auxiliary agents.



Hybrid Honeycomb Reference Material
Summary of accomplishments (I)

- Optimized reference honeycomb dimensions have been selected
  - 400 cells/inch² & 8 mils (200 µm) wall thickness
  - Trade-off between extrusion capability, geometrical surface area and strength.
- Reference material formulation
  - Extruded zeolite + phenolic resin followed by carbonization heat treatment to obtain zeolite/carbon composite
  - Formulation trade-off
    - extrudability/strength
    - CO_2 Adsorption
    - thermal stability for carbonization
    - electrical conductivity

400/8

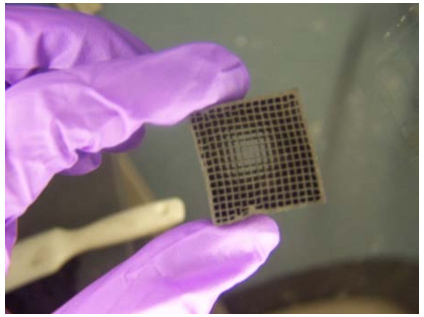


  - <u>preferred choice</u>: **70 wt% ZSM-5 / 30% wt% carbon** obtained after carbonization at 800°C

Hybrid Honeycomb Reference Material
Summary of accomplishments (II)

- Delivery of honeycomb reference material
  - 2 compositions extruded

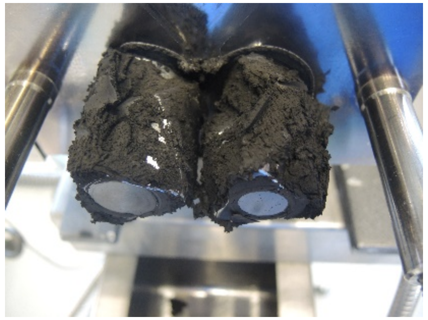
Composition	ZSM-5 Zeolite	Carbon
AOC-170	78 wt.%	22 wt.%
ATI-170	82 wt.%	18 wt.%

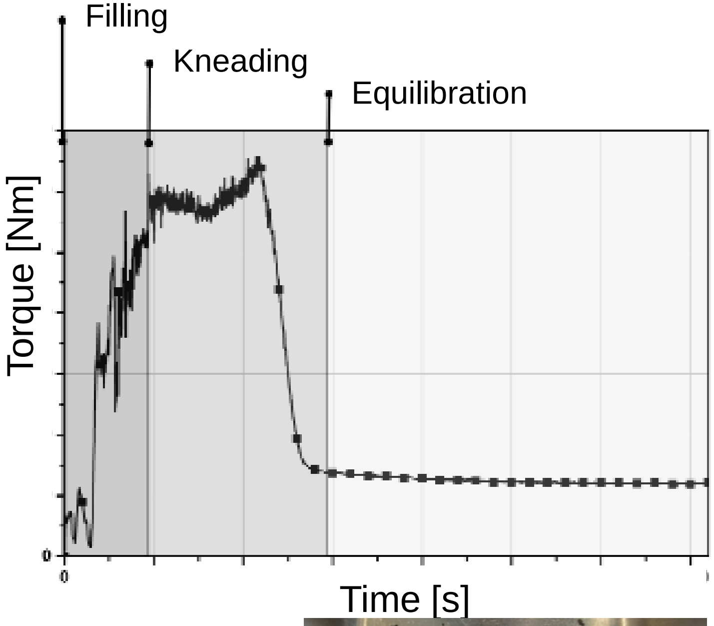


  - Samples delivered to University of Torino , SINTEF, Monash University, University of Melbourne
- Alternative path developed to increase CO_2 adsorption capacity
  - Extruded honeycombs with Na 13X zeolite – phenolic resin – carbon black addition + carbonization at 500°C
  - Na-13X Zeolite lost surface area after carbonization
  - 13X/C honeycombs carbonized at 400°C available for further testing

Feedstock development for extrusion of honeycombs

- Brabender Plastograph for mixing and plastification (torque rheometer) of small amounts (50 cm³)





- adaption of carbon content using zeolit 13X
- development of feedstocks with the MOFs UTSA-16 and CPO-27-Ni

Feedstock compositions

- binder concepts

cold-plastic binder system

processing temperature: room temp. (20 -25 °C)

main binder component

polyvinyl alcohol	hydroxypropyl-methylcellulose	SiO_2
poorly extrudable	plastic feedstock, extrudable,	plastic feedstock, extrudable,

thermo-plastic binder system

processing temperature: ≈ 70 °C

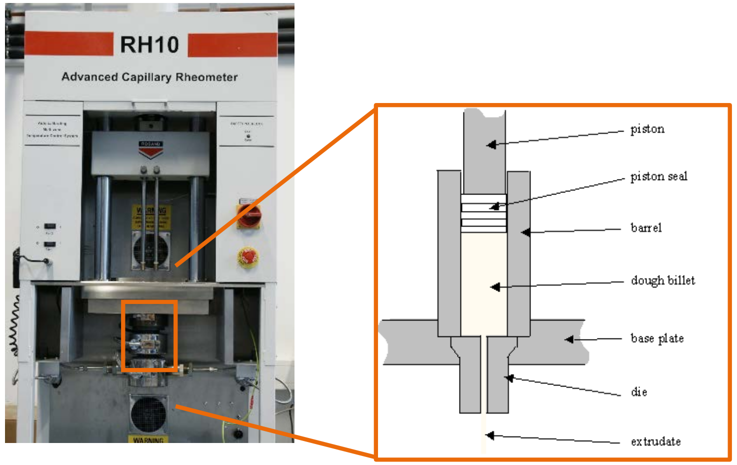
paraffin + LD-polyethylene

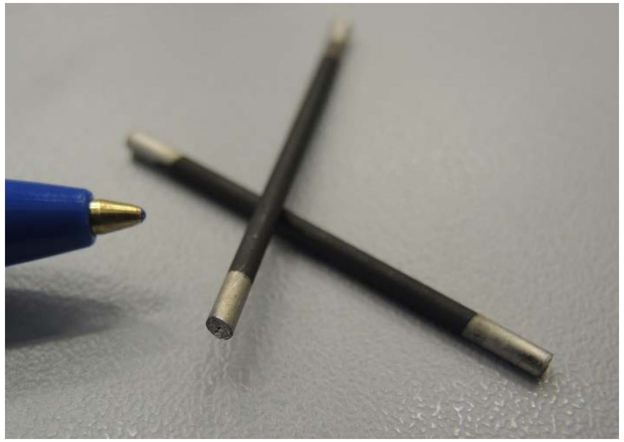
partial de-binding by solvent extrusion to create open porosity

→ low mechanical stability and/or low spec. surface of MOF containing feedstocks/ extrudates

Adaption of carbon content for electrical conductivity

- cold-plastic feedstock
  - Z13X powder + carbon powder + cellulose ether binder + water
- extrusion of 2,0 mm lines by using capillary rheometer





- testing parts with 25 mm length, contacting with conductive silver
  - best results with carbon black
  - 20 wt.-% carbon black: 0,124 Ω·m → basis for further feedstock preparation
    30 wt.-% carbon black: 0,013 Ω·m

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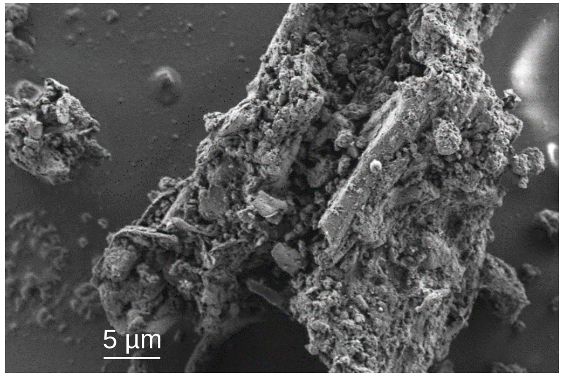
Bio-carbon materials as additives for hybrid honeycomb

- HTC (hydrothermal carbonization) bio-carbon and lignin from BIOKOL
- carbonization HTC-material
  - Ar, 7 K/min -> 950 °C, 30 min dwell time
    - → 121 m²/g
- carbonization lignin
  - Ar, 4 K/min -> 850 °C, 60 min dwell time
    - → 155 m²/g

	C [wt.-%]	S [wt.-%]	O [wt.-%]	N [wt.-%]	H [wt.-%]
lignin	66,3	1,24	29,4	0,69	5,53
carbonized lignin	**95,2**	0,43	2,32	0,54	0,69

- electrical conductivity similar to carbon black,
- very promising carbon materials for substitution carbon black
  - can be used in advanced honeycomb



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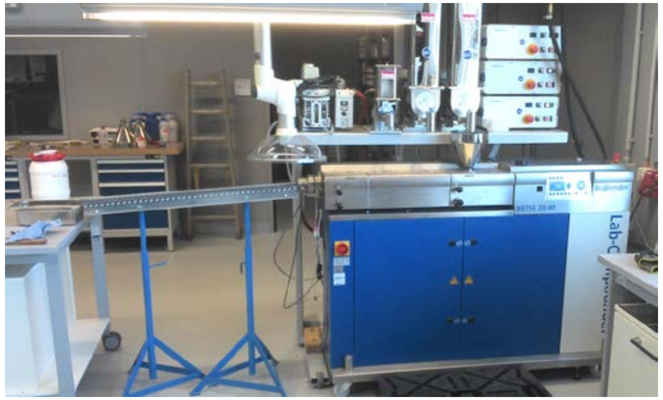
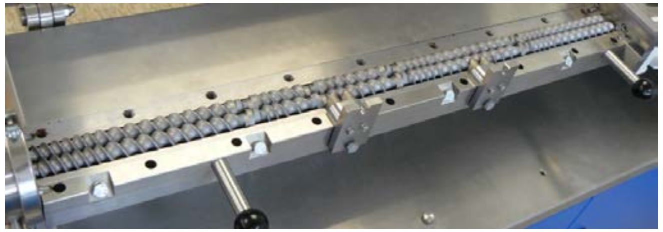
Twin screw extruder

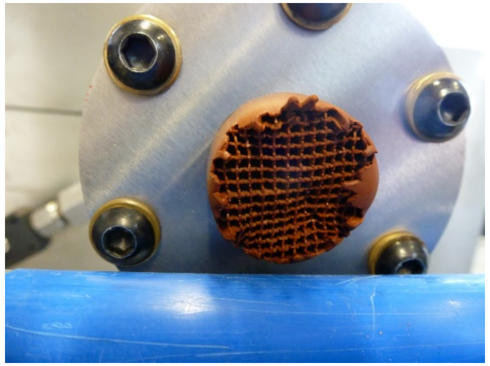
- (mixing), plastification and extrusion in one machine





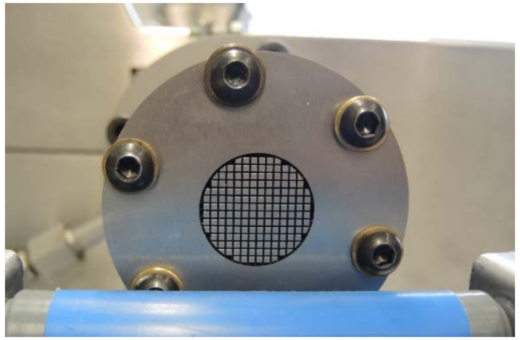
- extrusion tool: 200 cpsi, wall thickness 0,3 mm, diameter 25,4 mm,

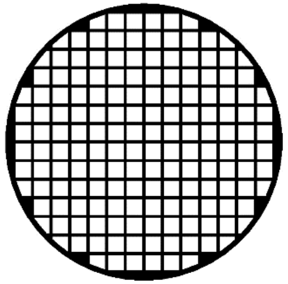
volume to be filled
before feedstock outlet:
45 cm³



Extrusion of zeolite 13X / carbon honeycombs

- tool: 200 cpsi, diameter 25,4 mm

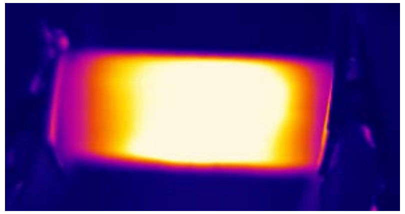


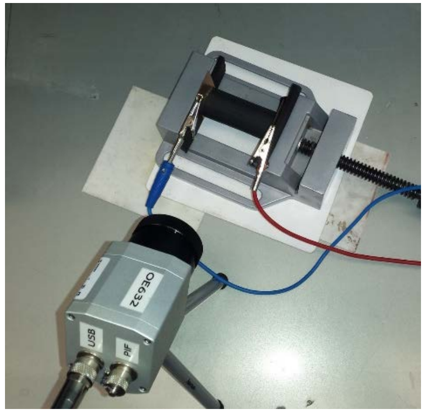


- honeycomb contacted with silver ink
  - $\rho = 0{,}077\ \Omega * m$

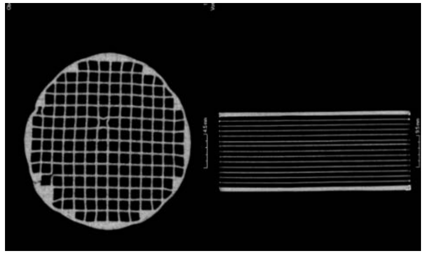
$$A = 0{,}382 * \pi/4 * d^2$$

- electrical heating up to 150 °C
  - 5 cycles (heating+ cooling) ~30 min
  - slightly decrease of mechanical stability
  - R remains constant



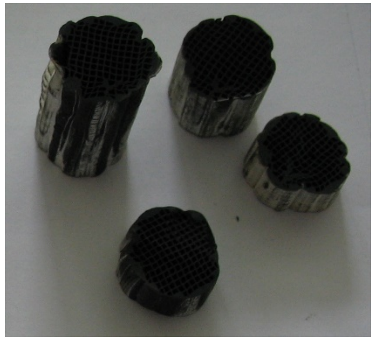
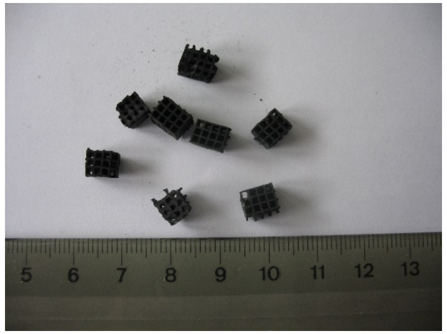


- attention: binder degradation at higher temperatures (> 250 °C) can decreases mechanical stability
- optimization of drying

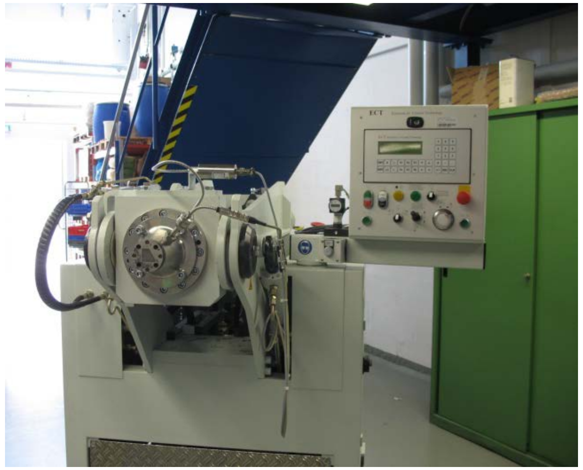


Extrusion of MOF/ carbon monoliths

- adaption of feedstock composition using measuring kneader
- CPO-27-Ni → processed in water
- UTSA-16 → processed in n-propanol/water mixture
- extrusion in double-screw extruder using zeolite feedstock for “banking”

- extrusion with piston extruder using ceramic feedstock for “pushing”



Extrusion of advanced honeycombs – MOF/ carbon

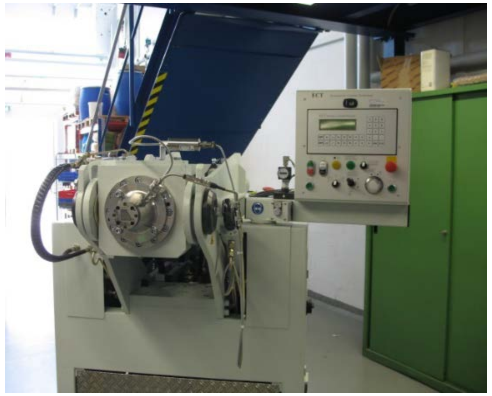
- UTSA-16 + carbon black , CPO-27-Ni + carbon black
  - favoured compositions

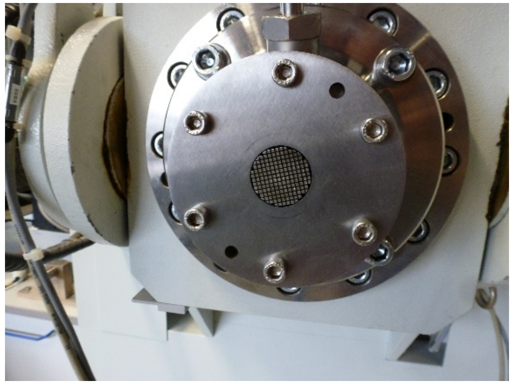
MOF-Material	MOF [wt.-%]	carbon black [wt.-%]	SiO_2-binder [wt-%]	Cellulose-etherbinder [wt-%]	additional organic additives (plasticiser, lubricant, surfactant) [wt.-%]	specific surface area [m²/g]
UTSA-16	63,9	20,5	-	9,1	6,5	402 (866)
CPO-27-Ni	67,0	19,6	5,2	2,7	5,5	400 (921)

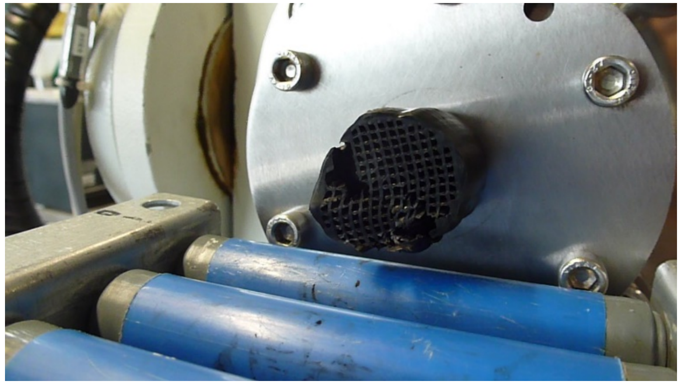
- challenge: maintenance of high specific surface area of starting MOF-material in the honeycomb

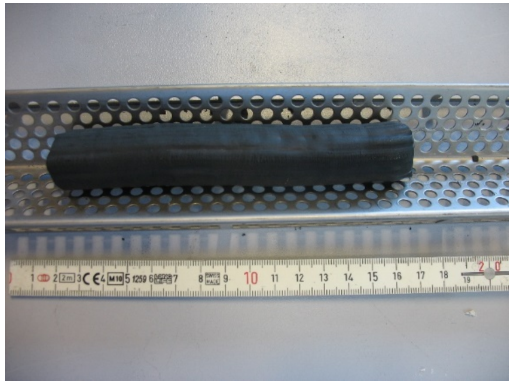
Extrusion of MOF/ carbon monoliths

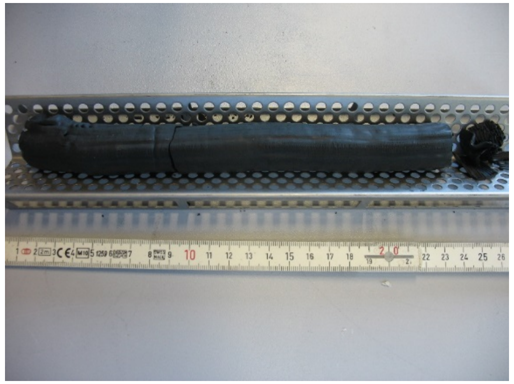
- feedstock CPO-M10
  - promising results, sufficient mechanical stability, some cracks in the outer skin after drying

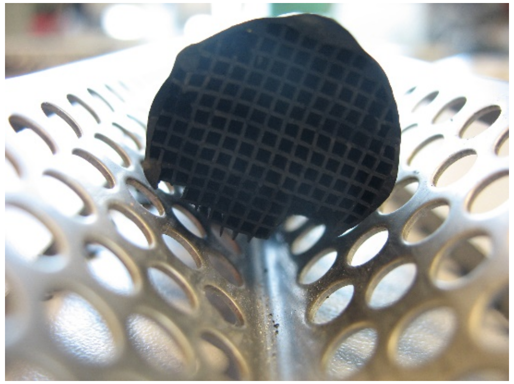






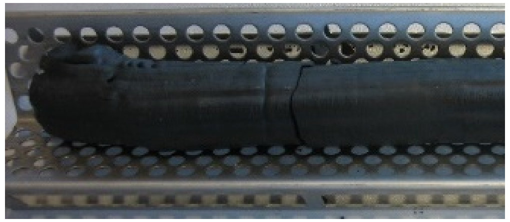
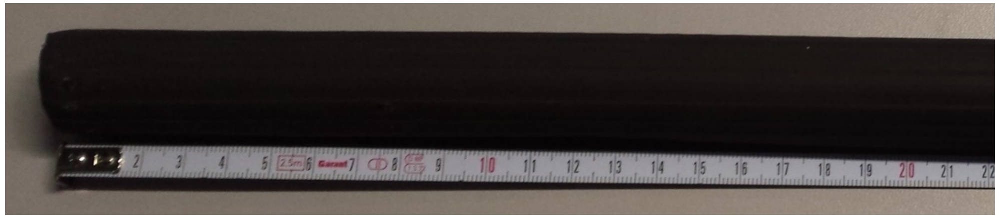






Summary

- reference hybrid honeycombs based on zeolites 13X and ZSM5
  - electrical conductivity, mechanical stability and specific surface area are in target range
- advanced hybrid monoliths based on UTSA-16 and CPO-27-Ni
  - electrical conductivity, mechanical stability are in the target range
  - promising specific area, but not yet reproducible
  - still defect in larger honeycombs (≥ 20 cm)
  - good prospects to come

from  to 

- substituting carbon black by bio-carbon as electrical conductive additive is possible

Thank you!