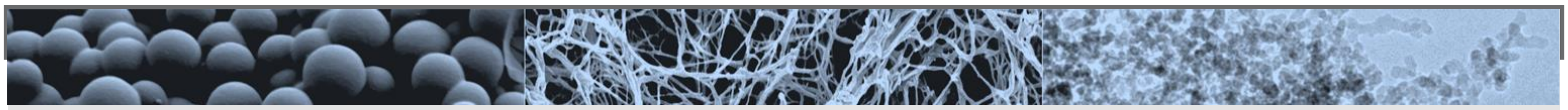
Metalized aerogels for applications in catalysis



Introduction

Background:
- The majority of heterogeneous catalysts are linked to inorganic carrier matrices
- Relatively few aerogel matrices are being used; examples are predominantly restricted to gas-phase reactions [1]

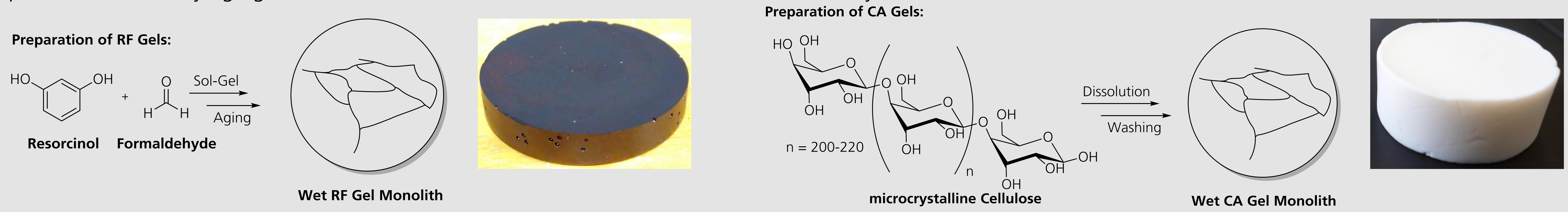
Advantages of organic aerogel matrices:
- Tailored (hierarchical) porosity allows for an optimization of reagent flow
- Different solvent systems are feasible when compared to inorganic carrier systems -> different reactivity/selectivity profiles
- Sustainable Feedstocks may be used

Advantages of (electroless) plating methods:
- Compared to nanoparticle loading a more film-like metal coating is possible -> different reactivity/selectivity profiles in catalysis
- Catalyst bleeding should be less likely compared to nanoparticle loading because of chemical matrix-metal interaction
- Redox-active aerogels backbones may facilitate electroless metal deposition
- Electroless plating is scalable and yields higher loading than electroplating
- In contrast to electroplating electroless plating methodologies may be applied to non-conductive aerogels

Our Goals:
- Use of aerogels as matrix for electroless plating of metals
- Implementation of (bio)organic aerogels as matrices in heterogeneous catalysis
- Further applications of metalized aerogels (thermal management (e.g. heat pipes/ heat pumps) and sensors)

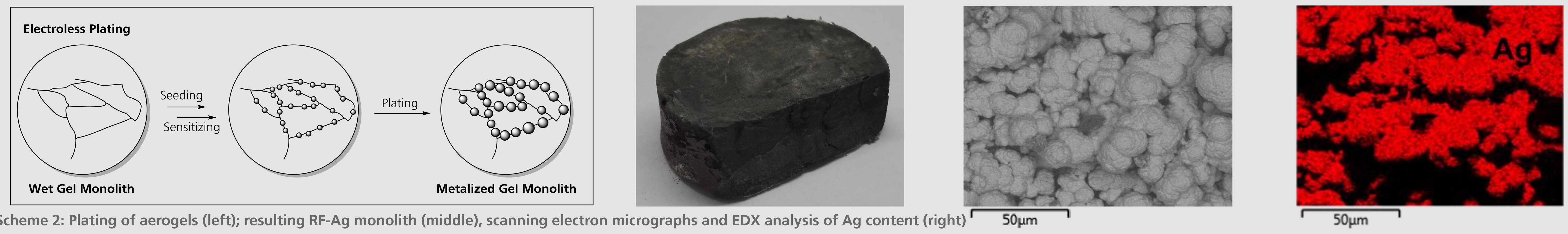
Experimental

Preparation of wet gels:
- Resorcinol-formaldehyde (RF) Aerogels were prepared by sequential sol-gel process followed by aging in an oven
- Cellulose-based gels (CA) were obtained by reversible dissolution with salt melt hydrates[3]



Scheme 1: Preparation of wet gels from RF (left) and Cellulose, respectively (right)

Electroless plating:
- Plating was achieved in two steps: a) seeding with metal nanoparticles/ sensitizing with Sn(II) and b) plating with metal salt/ chemical reductant (e.g. tartrate)
- final drying (RF: ambient conditions; cellulose: supercritical CO_2) afforded metalized aerogels



Scheme 2: Plating of aerogels (left); resulting RF-Ag monolith (middle), scanning electron micrographs and EDX analysis of Ag content (right)

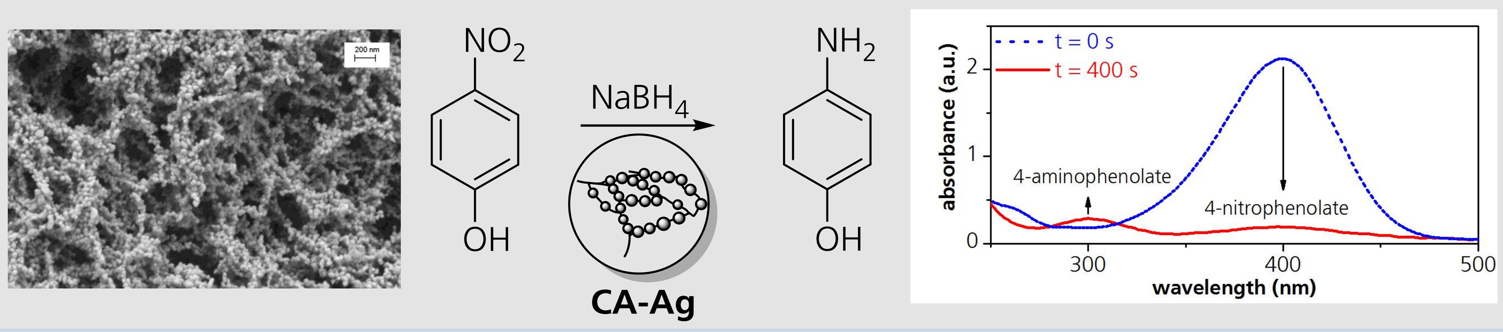
Results

- Composites of Ag, Au, Pt, and NiB were prepared with RF and cellulose gels, respectively (Table 1)
- Composites were characterized with respect to density, porosity, and thermal and mechanical properties (Table 1)

Table 1: Properties of aerogel metal composites

Properties	Envelope density [g/cm³]	Skeletal density [g/cm³]	Porosity [%]	Specific surface area [m²/g]	Gas permeability [µm²]	Thermal conductivity (Hot Disk) [mW/m*K]	Compressive modulus E* (DMA, 1Hz) [MPa]
RF	0.2910	1.5012	80.1	< 1	8.08	70	4.28
RF-Ag	0.6072	3.1283	78.4	1.19	1.88	205	15.51
RF-Au	0.6202	2.7871	77.9	< 1	3.34	124	15.07
RF-Pt	0.6386	3.3025	77.2	0.53	3.07	83	14.68
RF-NiB	0.6990	3.1289	75.1	1.15	2.87	87	19.48
CA (3wt.%)	0.0571	1.4547	96.2	192.13	0.465	32	4.30
CA-Ag	0.0930	2.2494	95.9	98.46	0.410	-	12.41

Preliminary catalytic test:
- reduction of nitrophenol with CA-Ag composite:
- apparent rate k_{app} of ca. $1 \cdot 10^{-3} \cdot s^{-1}$ (high concentrations of $NaBH_4$: pseudo-1st order kinetics)[3]
- comparable to colloidal Ag nanoparticles (k_{app} of ca. $2 \cdot 10^{-3} \cdot s^{-1}$)[4]



Conclusions

Summary:
- Several metal aerogel composites were prepared using wet gels and electroless plating approach
- Ag-plated cellulose gels show competitive performance in the reduction of nitrophenol

Outlook:
→ Other late transition metals will be plated to both cellulose and resorcinol-formaldehyde gels
→ Based on the initial results in catalysis, further studies on synthetically useful reactions (*e.g.* hydrogenations, cross-coupling reactions) are planned

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References
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