Silylation of Monolithic Resorcinol-Formaldehyde Xerogels

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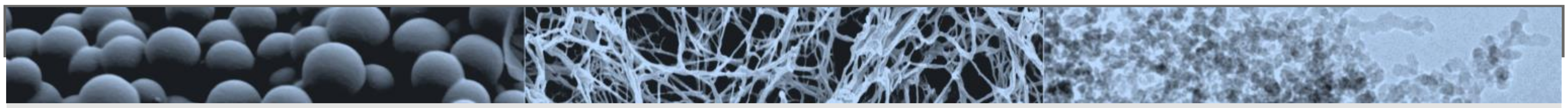
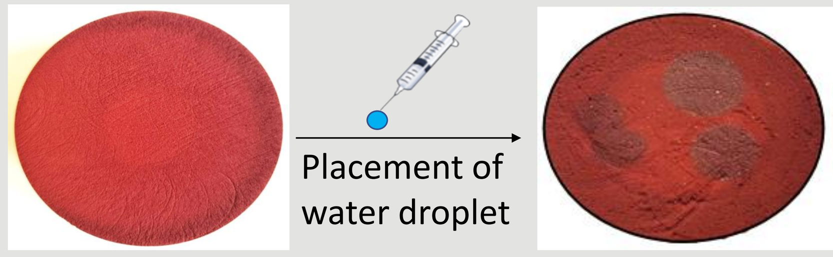


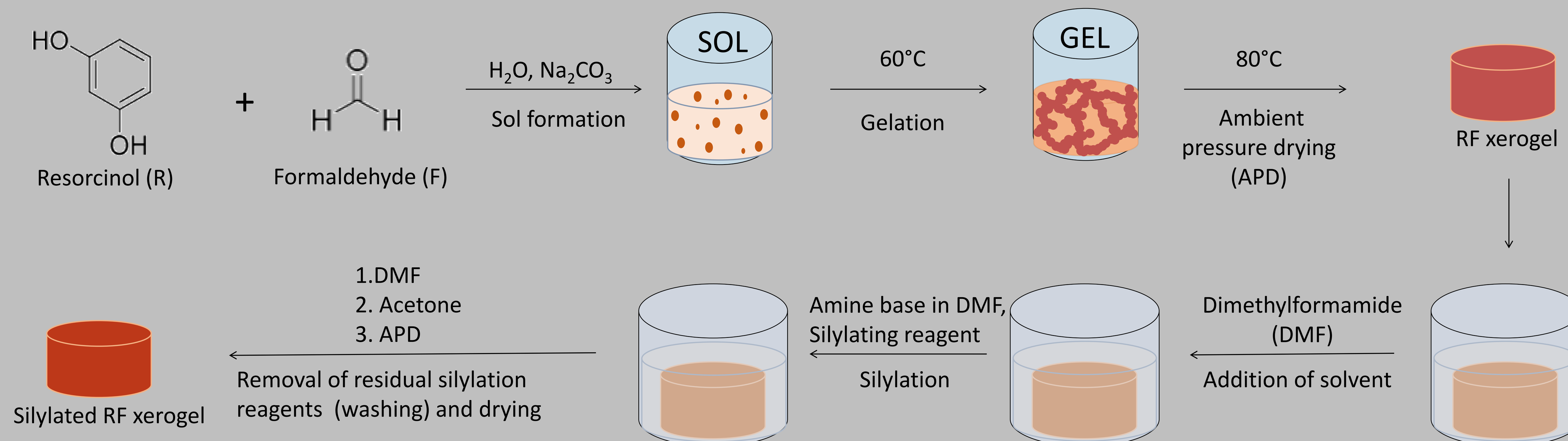
Motivation

- Aerogels and xerogels based on resorcinol-formaldehyde (RF) polymers have promising properties for applications as filters or catalysts[1]
- However, free OH groups of the phenolic gels make them hydrophilic
- Previous publications include post-synthetic silylation of RF gels, but only on powdered materials using small silyl reagents[2-3]
- Our approach is to functionalize monolithic RF xerogels, more specifically to silylate them with sterically demanding silylation reagents to create a long-lasting hydrophobicity.



Experimental

Synthesis of silylated RF xerogels



- Silylation using polar aprotic solvents
- Addition of external base
- Use of sterically demanding silylating reagents
- Variation of Si-counterion (electronically activated triflate)

Sample	Silyl Reagent	Base
TMS-A	Trimethylsilyl chloride (TMS-Cl)	Imidazole
TMS-B	Trimethylsilyl triflate (TMS-OTf)	2,6-lutidine
TBS-A	*tert.*-Butyldimethylsilyl chloride (TBS-Cl)	Imidazole
TIPS-A	Triisopropylsilyl triflate (TIPS-OTf)	Imidazole
TIPS-B	Triisopropylsilyl chloride (TIPS-Cl)	2,6-lutidine
TBDPS-A	*tert.*- Butyldiphenylsilyl chloride (TBDPS-Cl)	Imidazole

Characterization & Results

Elemental analysis:

- Successful incorporation of silicon could be established
- Silicon is present in quantities <2% by weight

→ Not all free hydroxy groups were silylated

→ Chemical reactivity of the phenolic hydroxyl groups in the gel does not seem to be crucial, but rather their accessibility within the pore network.

Sample	Si Content [%] (m/m)
TMS-A	0.61
TMS-B	1.16
TBS-A	1.51
TIPS-A	0.20
TIPS-B	0.27
TBDPS-A	1.23

SEM-EDX-Characterization:

- SEM-EDX images of an RF xerogel treated with RF-TBS-A

→ observing of rather homogeneous distribution of carbon, oxygen and silicon

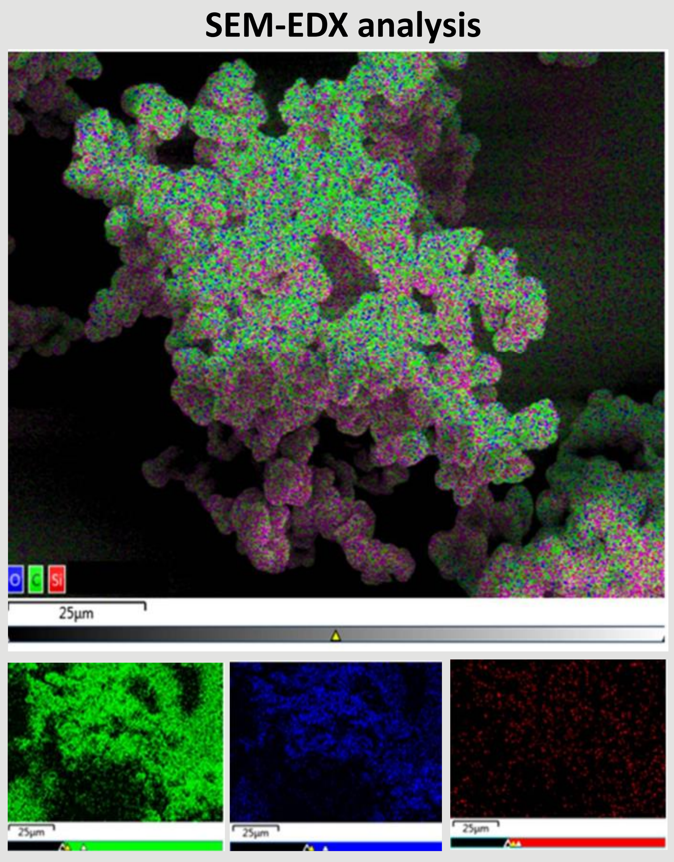
→ The lower relative abundance of Si agrees with the hypothesis that not all phenolic hydroxy groups are silylated

XPS-analysis:

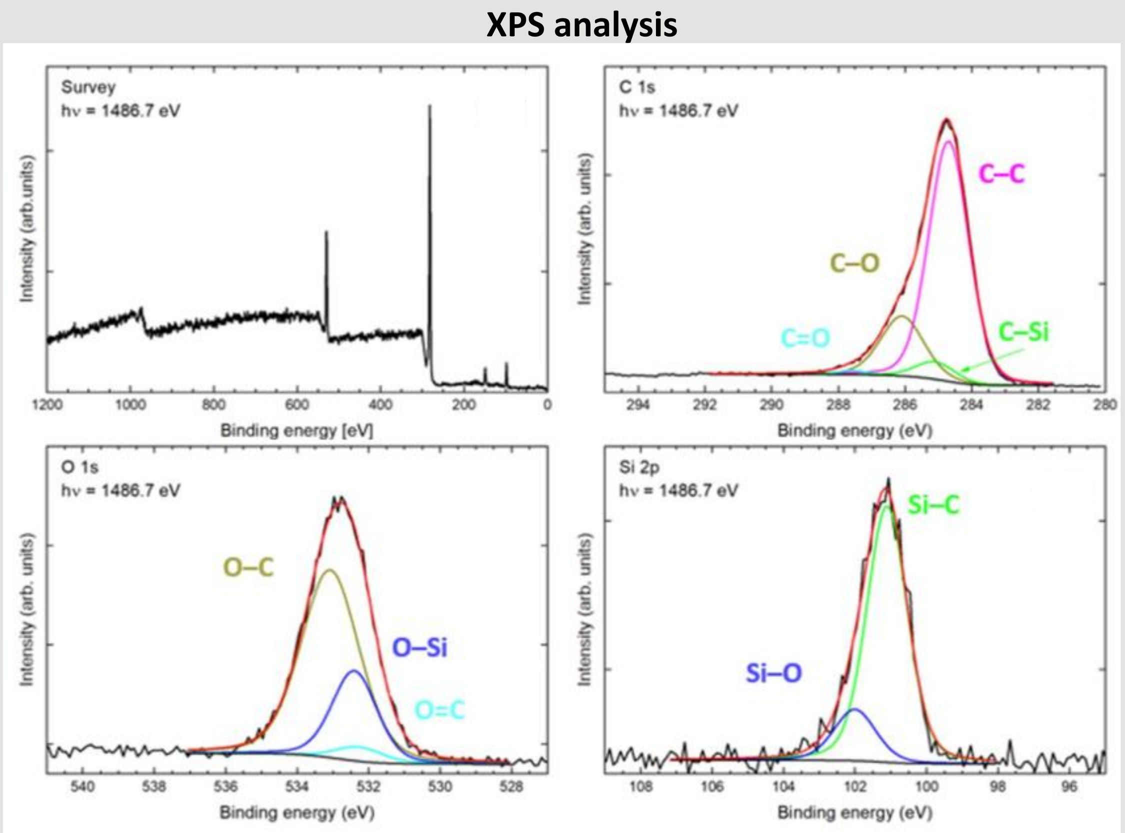
- Resulting bond energies clearly indicate the presence of silicon-oxygen bonds
- Ratio of Si-O bonds to Si-C bonds correspond to expected 1:3 ratio for trialkylsilyl ethers

→ Formation of covalent Si-O bonds

SEM-EDX analysis



XPS analysis



Microstructural properties:

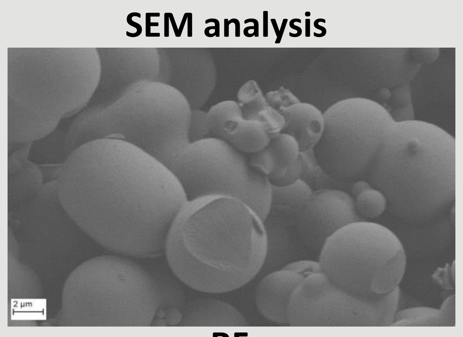
- Pycnometry revealed slight reduction in porosity for silylated samples

→ the pore network is not significantly affected by the functionalization process

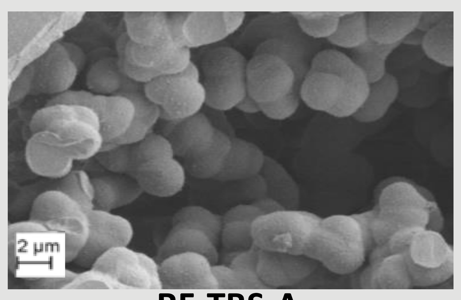
- The treatment with silylating reagents did not significantly affect the microstructure, nor the porous network within the xerogel.

Sample	Density [g·cm^{-3}] Envelope	Density [g·cm^{-3}] Skeletal	Porosity [%]	Inner Surface Area [m^2·g^{-1}]
RF	0.3262	1.44525	77.39	0.676 ± 0.003
RF-TMS-B	0.3213	1.3545	76.28	0.411 ± 0.044
RF-TIPS-B	0.3239	1.3685	76.33	0.423 ± 0.008

SEM analysis



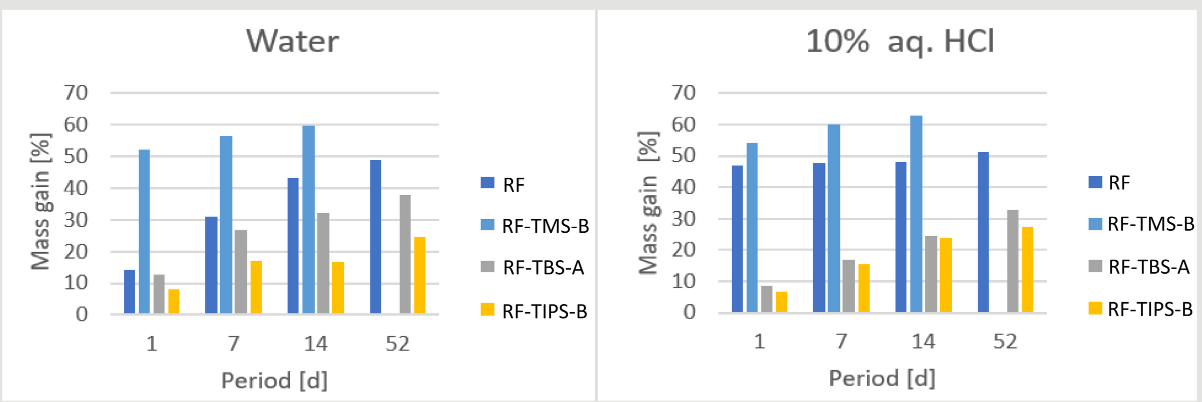
RF



RF-TBS-A

Determination of wetting behavior

- The monoliths in liquid water and 10% aq. HCl were more inert between the silylated variants compared to the RF reference, except for RF-TMS-B.
- The effect was still pronounced after 7 weeks



Static contact angles, as determined using tangent or the LB-ADSA (in brackets) method

sample	1	2	3	4	5	8	11
	time exposed to air / months						
	contact angle/°						
RF	n.a.						
RF-TMS-A	n.a.						
RF-TMS-B	139.5±1.8 (147.5±0,7)	137.2±2.9 (143.0±1.1)	136.5±3.7 (137.1±0.7)	135.7±3.4	n. d.	n. d.	n. d.
RF-TBS-A	136.4±3.0 (140.0±2.9)	136.5±1.5 (142.1±1.0)	135.4±2.1 (142.9±2.5)	135.3±2.4	135.0±1.1	134.5±1.5	134.2±1.3
RF-TIPS-A	142.8±1.2	n. d.	142.6±1.7	n. d.	141.1±2.2	137.9±1.9	136.9±1.9
RF-TIPS-B	143.7±2.0 (151.1±1.1)	143.9±0.4 (149.9±0.6)	140.5±1.8 (146.6±1.7)	139.1±1.3	n. d.	n. d.	n.d.
RF-TBDPS-B	138.3±2.2	n. d.	139.3±3.2	n. d.	139.2±2.2	135.1±1.8	133.9±2.5

Dynamic contact angles, as determined using Wilhelmy method

sample	1	2	3	4	5	8	11
	time exposed to air / months						
	contact angle/°						
RF-TMS-B	152.4±1.4	144.9±12.3	143.6±13.0	144.0±1.1	n. d.	n. d.	n. d.
RF-TBS-A	123.8±15.9	121.6±2.4	123.4±12.8	124.3±2.0	136.1±1.7	132.3±2.9	125.3±16.5
RF-TIPS-A	151.9±8.3	n. d.	150.1±7.4	n. d.	146.2±4.8	132.2±2.4	129.8±2.3
RF-TIPS-B	139.1±8.0	137.9±4.0	138.0±1.9	137.4±1.4	n. d.	n. d.	n. d.
RF-TBDPS-B	101.8±11.3	n. d.	112.5±17.1	n. d.	120.0±6.4	112.8±10.7	119.2±5.9

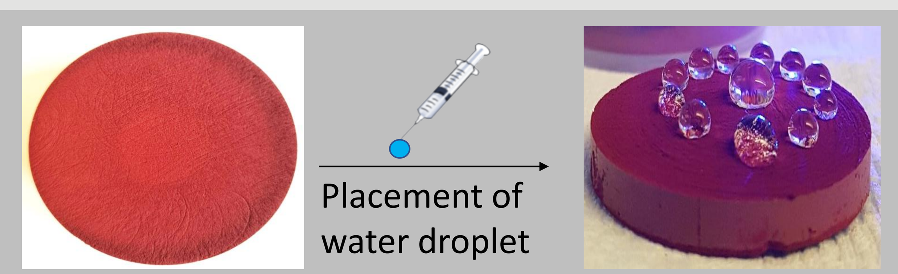
n.a. = not applicable (droplet was absorbed by monolith); n.d. = not determined

Static and dynamic contact angles:

- Static contact angles between surface and the water droplet (tangent method): 133.9 - 143.9°
- Automatized positioning of the tangent using low-bond axisymmetric drop shape analysis (LB-ADSA) consistently achieve higher values (137.1 - 151.1°)
- Contact angles determined by Wilhelmy method in range of 101.8 - 152.4°

Conclusion

- A procedure for the silylation of monolithic resorcinol-formaldehyde xerogels has been established
- Sterically and electronically varied silyl reagents including electronically activated triflates could be applied in solution phase using auxiliary amines as external base
- Xerogels displayed marked hydrophobicity with contact angles consistently exceeding 130°
- The hydrophobic properties remained when the monoliths are exposed to humid air for several months
- RF gels with sterically demanding silyl groups sustained water and even dilute hydrochloric acid for weeks[4]



Acknowledgement

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References

[1] M. A. Aegerter, N. Leventis, M. M. Koebel, *Aerogels Handbook*, Springer New York, **2011**.
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