Supporting Information

Investigation of silica particle growth by incorporation of a pyrene fluorescent probe

Fabian Walther and Dominik Brühwiler*

* Corresponding Author. E-mail: dominik.bruehwiler@zhaw.ch (D. Brühwiler)

ZHAW Zurich University of Applied Sciences, Institute of Chemistry and Biotechnology, CH-8820 Wädenswil, Switzerland

Contents

1. Synthesis of pyrene sulfonyl chloride (PySCl): NMR data

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.07 (d, J = 8.34 Hz, 2H), 8.71 (d, J = 8.35 Hz, 1H), 8.40 – 8.31 (m, 3H), 8.24 (d, J = 8.89 Hz, 1H), 8.17 (d, J = 8.90 Hz, 1H), 8.15 – 8.05 (m, 2H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 136.6, 135.6, 131.9, 131.6, 130.8, 130.0, 128.4, 128.2, 128.1, 127.5, 126.9, 126.3, 125.1, 123.8, 123.6, 122.5 ppm.

2. Size of particles obtained by co-condensation with APTES

APTES was co-condensed with TEOS in a range of molar ratios to investigate whether the presence of APTES would significantly affect the particle size (Fig. S1). Particles obtained with an APTES/TEOS molar ratio between 0.001 and 0.025 did not differ significantly in terms of the particle size. Furthermore, the particles in the APTES/TEOS range of 0.001 to 0.010 had a similar total pore volume compared to the particles synthesized without APTES, which is why co-condensation with PySCl-APTES was carried out in this range.

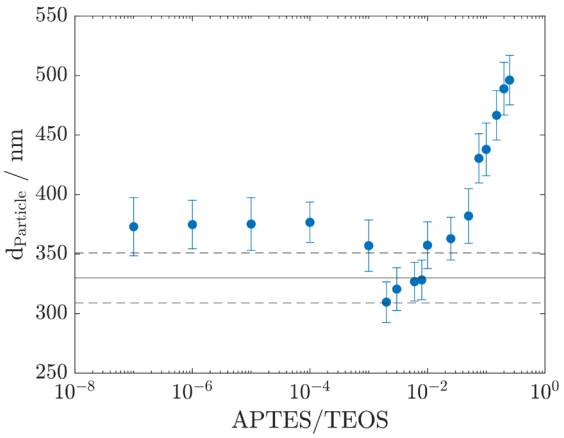


Fig. S1. Particle diameter as a function of the APTES/TEOS molar ratio. The values were determined by measuring the diameter of at least 100 particles from the respective SEM images. The uncertainties are given as standard deviation of the particle measurement. The average diameter of the particles obtained from the synthesis without APTES (solid line) and its uncertainty (dashed lines) are shown as well.

3. Determination of the ideal amount of PySCl and APTES

In a headspace vial (20 mL), PySCl (see Tab. S1 for the amount) in ethanol (99.9 %, 5 mL) was mixed with APTES (see Tab. S1 for the amount) and left to stir for 16 h at 350 rpm and room temperature. TEOS (8 mL) was added and allowed to homogenize at 350 rpm for 10 min (precursor solution). In a polypropylene beaker (250 mL, diameter = 70 mm), which was equipped with a magnetic stir bar (length = 47 mm), a solution of ultrapure water (43 mL), ethanol (98 %, 45 mL) and aqueous ammonia (28 – 30 %, 14 mL) was prepared, covered with

a watch glass, and left to stir at 350 rpm for 10 min (hydrolysis solution). After 10 min, the stirring speed of the hydrolysis solution was increased to 500 rpm and the precursor solution was added quickly (< 3 s). The polypropylene beaker was covered with a watch glass and the mixture was stirred for 4 h at room temperature and 500 rpm. After 4 h, the resulting suspension was transferred to two Falcon tubes (50 mL) and centrifuged at 4000 rpm for 10 min. The particles were washed with water (three times 20 mL per Falcon tube) and ethanol (six times 20 mL). The product was oven-dried at 80 °C for 16 h.

Tab. S1. Amounts of APTES and PySCl used in the synthesis of the samples reported in Fig. 1.

molar ratio APTES/TEOS	V(APTES) / µL	m(PySCl) / mg
0.003	26.1	5.8
0.007	60.0	13.3
0.008	70.0	15.5
0.010	84.1	18.6

4. Influence of the water/ethanol ratio

In a headspace vial (20 mL), PySCl (18.6 mg) in ethanol (99.9 %, 5 mL) was mixed with APTES (84.51 µL) and left to stir for 16 h at 350 rpm and room temperature. TEOS (8 mL) was added to this solution and allowed to homogenize at 350 rpm for 10 min (precursor solution). A polypropylene beaker (250 mL, diameter = 70 mm) was fitted with a magnetic stir bar (length = 47 mm). A solution of ultrapure water (see Tab. S2 for the amount), ethanol (98 %, see Tab. S2 for the amount), and aqueous ammonia 28 – 30 % (14 mL) was added. The polypropylene beaker was covered with a watch glass and the mixture was allowed to stir at 350 rpm for 10 min (hydrolysis solution). After 10 min, the stirring speed of the hydrolysis solution was increased to 500 rpm and the precursor solution was added rapidly (< 3 s). The polypropylene beaker was covered with a watch glass and the mixture was stirred for 4 h at room temperature and 500 rpm. After 4 h, the resulting suspension was transferred to two Falcon tubes (50 mL) and centrifuged at 4000 rpm for 10 min. The particles were washed with water (three times 20 mL per Falcon tube) and ethanol (six times 20 mL). The product was oven-dried at 80 °C for 16 h.

Tab. S2. Amounts of ethanol and water used in the synthesis of the samples reported in Fig. 4.

V(ethanol) / mL	V(water) / mL
88	0
75	13
65	23
60	28
55	33
52	36
48	40
45	43
40	48
32	56
27	61

5. Potential cross-linking of the PySCl-APTES conjugate

To show that the observed excimer emission of the co-condensed particles is not due to the potential cross-linking of the PySCl-APTES conjugates in solution (prior to co-condensation with TEOS), 3 mL of the reaction mixture was taken at specific time intervals and placed in 10 mL of ethanol to quench the reaction. The particles were then separated, and a fluorescence spectrum of the supernatant was measured after appropriate dilution (1:100). No excimer band was observed.

6. Comparison of co-condensed and purely siliceous particles

When using a co-condensed probe molecule to study the growth of silica particles, it needs to be ensured that the incorporation of the probe molecule into the silica framework does not significantly affect the properties of the resulting particles. Fig. S2 shows the diameter and total pore volume of particles prepared with and without PySCl-APTES under different conditions (water/ethanol ratio). The results show that the co-condensation of PySCl-APTES does not have a significant effect on the structural properties of the resulting particles under the conditions investigated in this work.

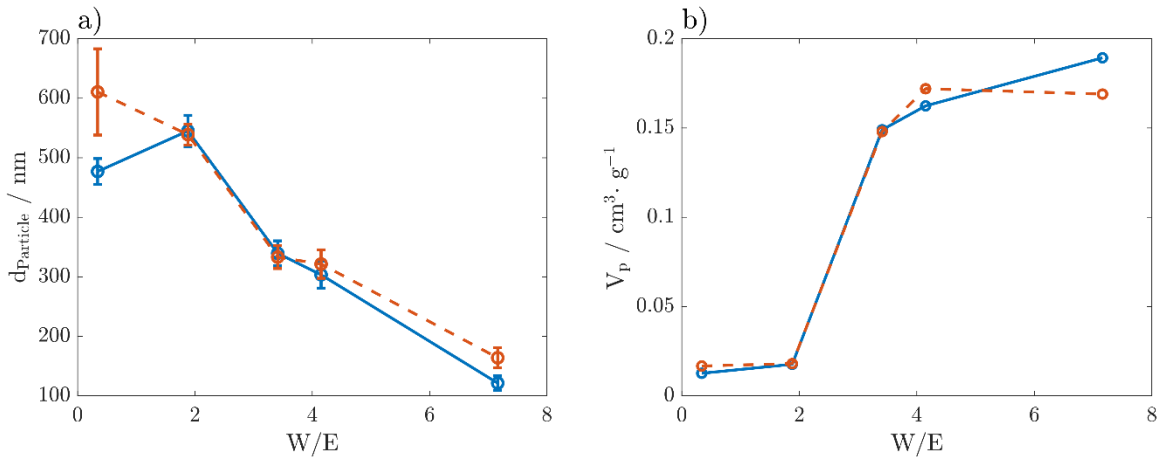


Fig. S2. Comparison of the diameter (a) and total pore volume (b) of silica particles with (solid line) and without co-condensed (dashed line) PySCl-APTES. The particles were prepared using various water/ethanol ratios according to the procedure described in Chapter 2.6.

7. Fluorescence spectra

Fig. S3 shows the fluorescence spectra used for the determination of $I_{Excimer}$ (Fig. 6 and 7).

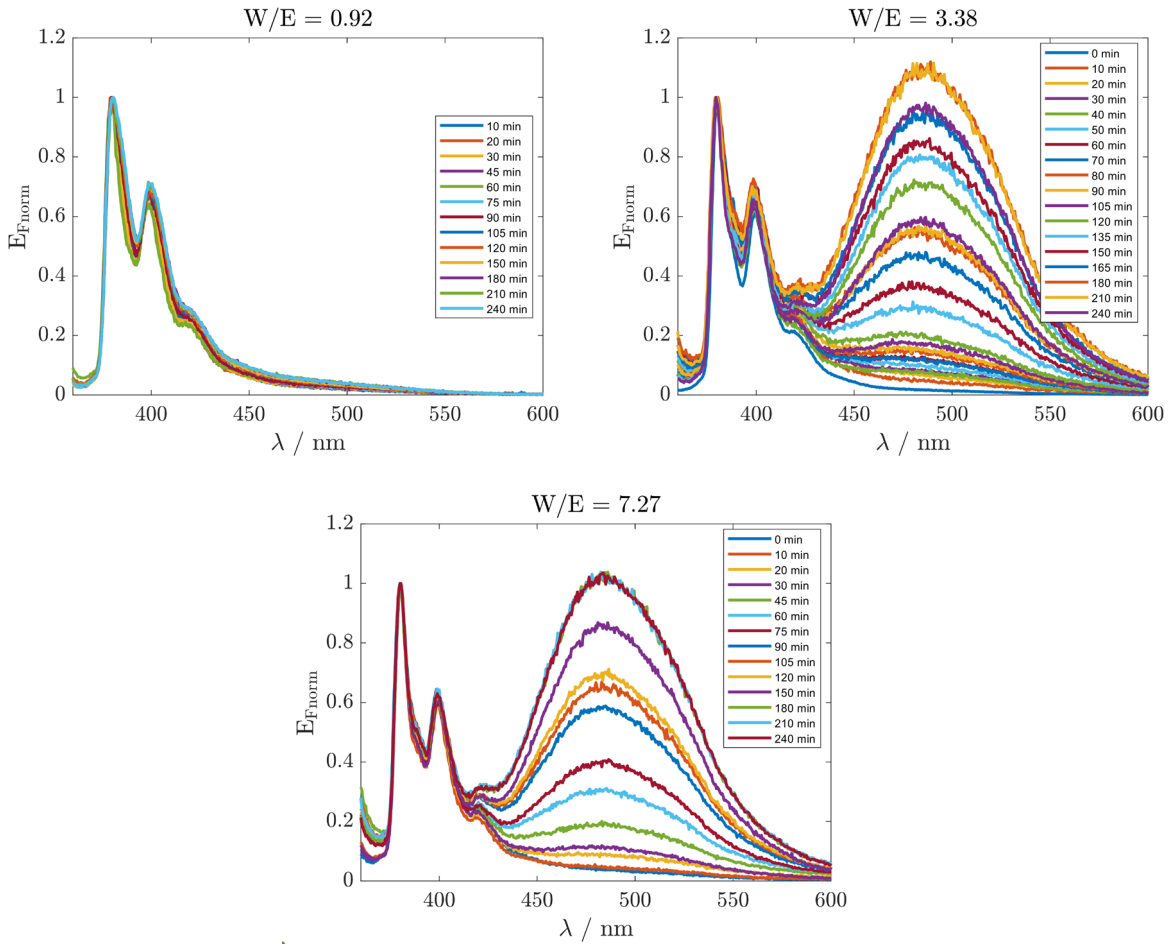
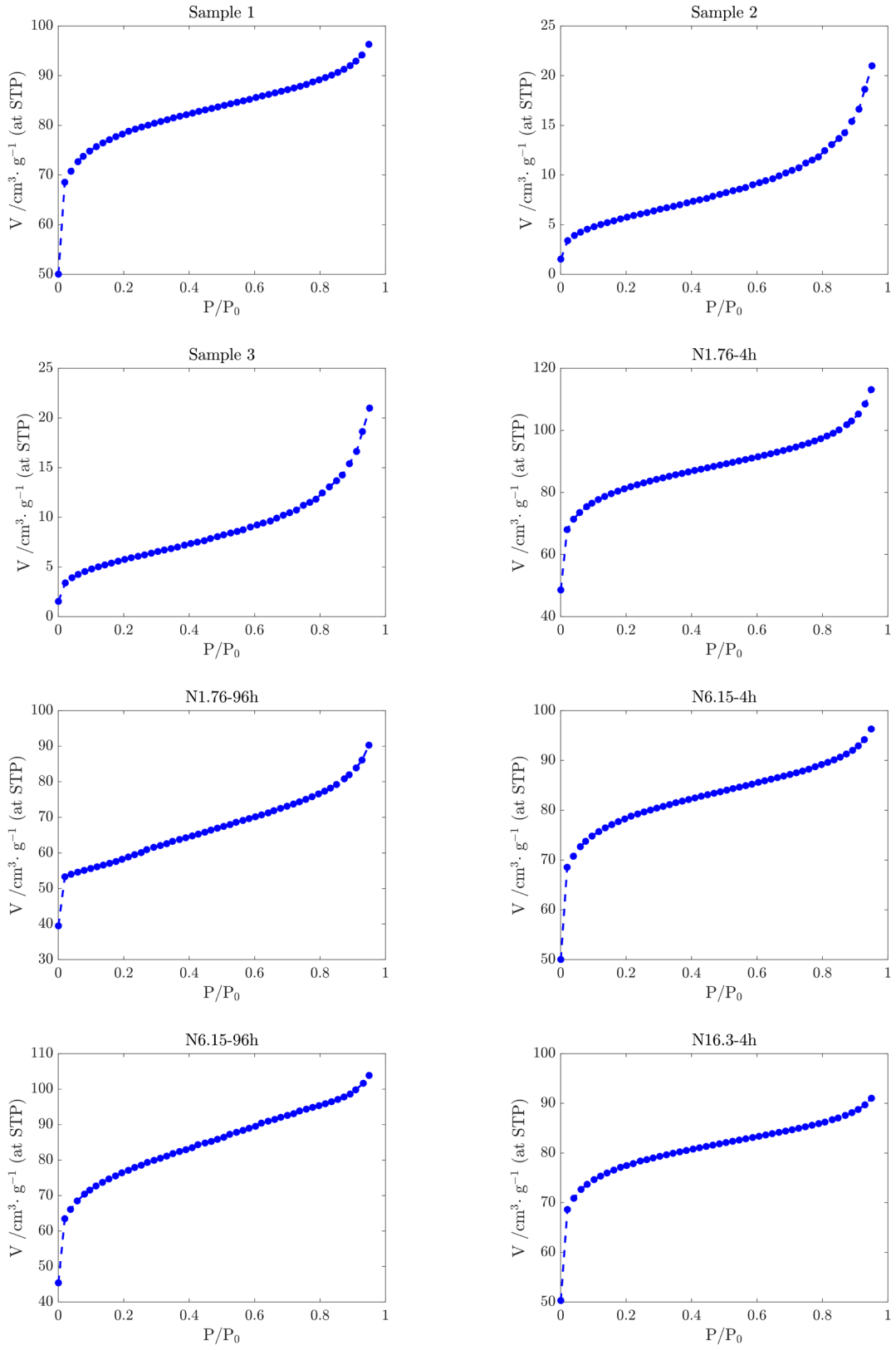
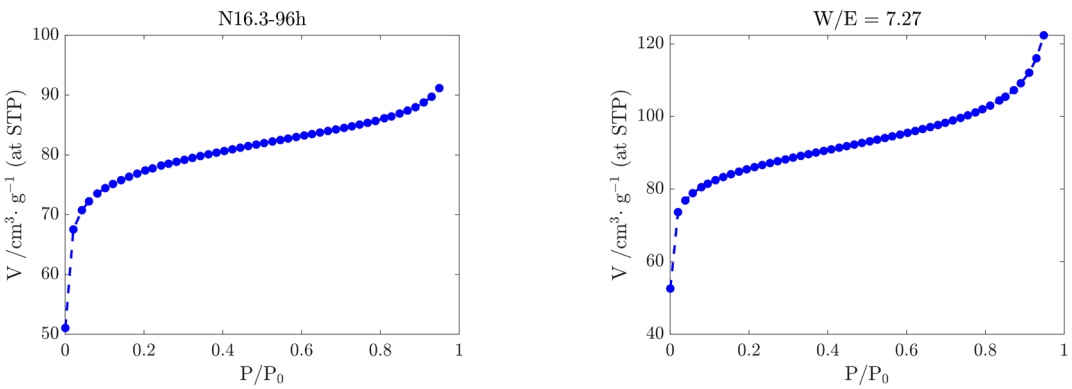


Fig. S3. Fluorescence spectra as a function of time for particle growth conducted at various water/ethanol ratios (given by the respective W/E values). $I_{Excimer}$ reported in Fig. 6 and 7 corresponds to the intensity at 483 nm.

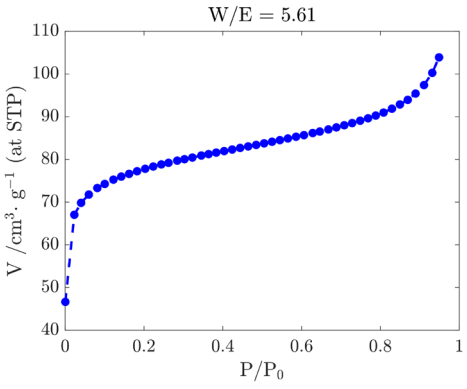
8. Adsorption isotherms

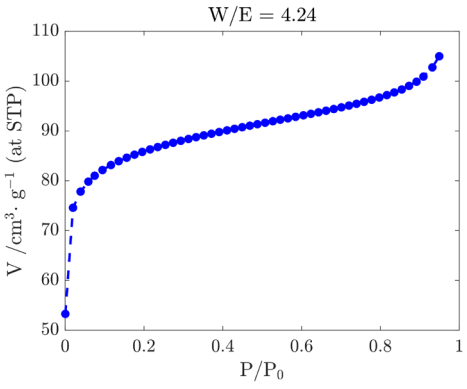
Nitrogen adsorption isotherms (77 K) of all reported samples are given in Fig. S4.

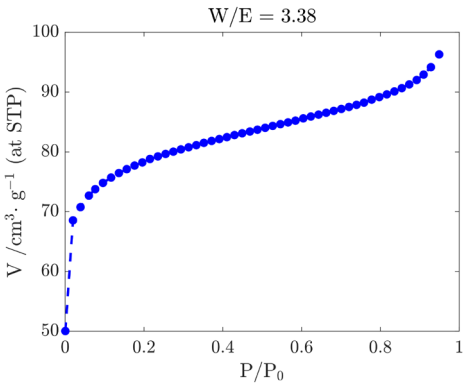


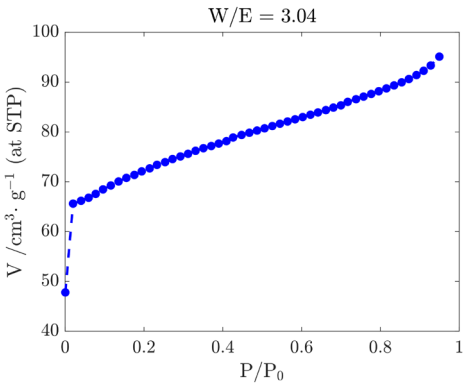

N16.3-96h
V /cm³· g⁻¹ (at STP)
P/P₀

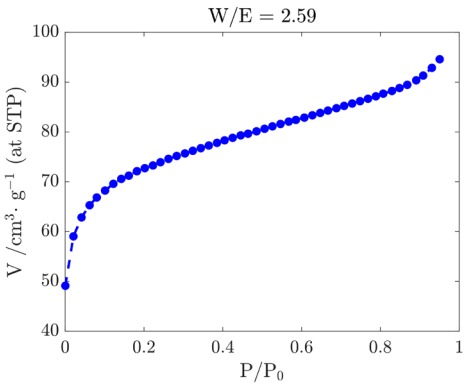
W/E = 7.27
V /cm³· g⁻¹ (at STP)
P/P₀

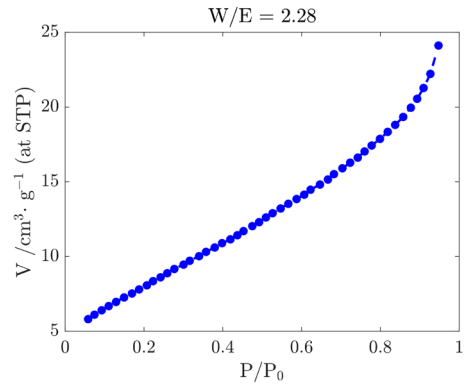

W/E = 5.61
V /cm³· g⁻¹ (at STP)
P/P₀

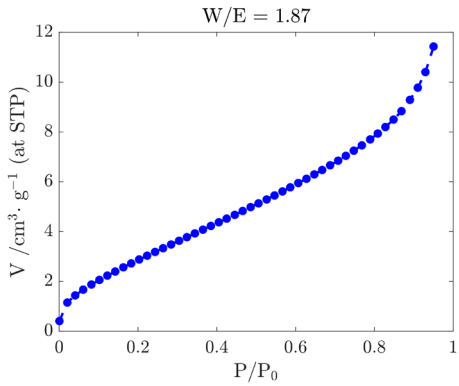

W/E = 4.24
V /cm³· g⁻¹ (at STP)
P/P₀

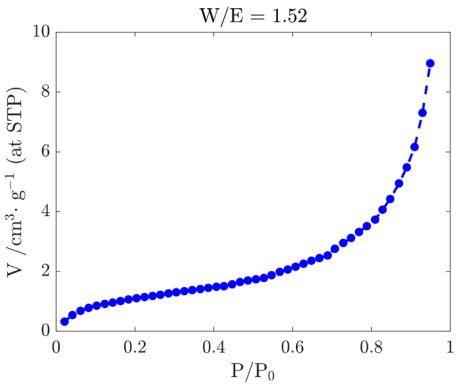

W/E = 3.38
V /cm³· g⁻¹ (at STP)
P/P₀

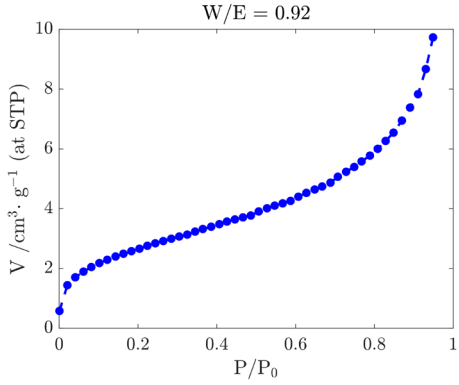

W/E = 3.04
V /cm³· g⁻¹ (at STP)
P/P₀

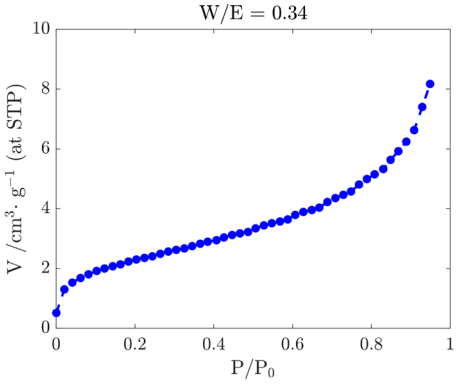

W/E = 2.59
V /cm³· g⁻¹ (at STP)
P/P₀

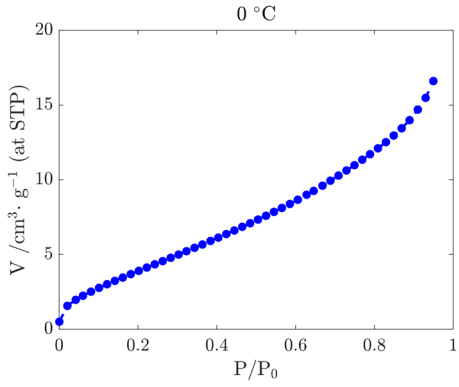

W/E = 2.28
V /cm³· g⁻¹ (at STP)
P/P₀

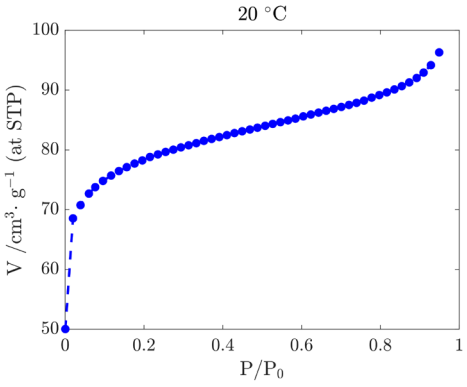

W/E = 1.87
V /cm³· g⁻¹ (at STP)
P/P₀

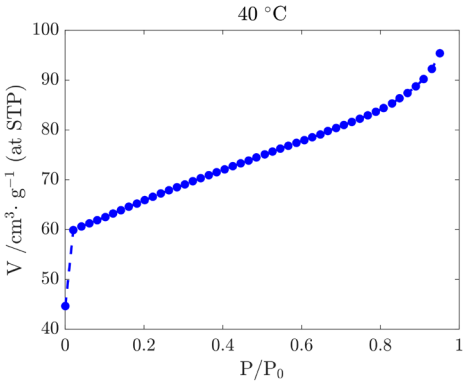

W/E = 1.52
V /cm³· g⁻¹ (at STP)
P/P₀

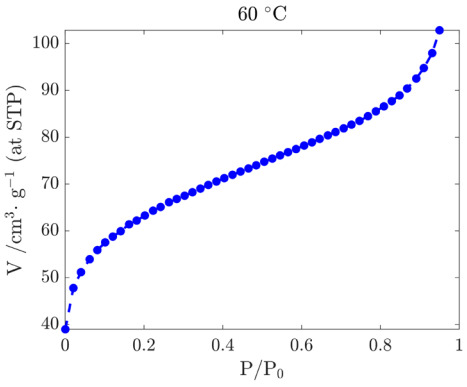

W/E = 0.92
V /cm³· g⁻¹ (at STP)
P/P₀


W/E = 0.34
V /cm³· g⁻¹ (at STP)
P/P₀


0 °C
V /cm³· g⁻¹ (at STP)
P/P₀


20 °C
V /cm³· g⁻¹ (at STP)
P/P₀


40 °C
V /cm³· g⁻¹ (at STP)
P/P₀


60 °C
V /cm³· g⁻¹ (at STP)
P/P₀

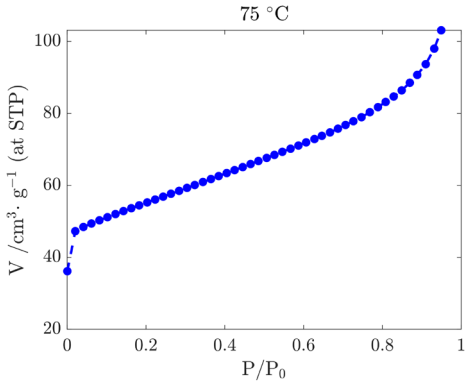


Fig. S4. Nitrogen adsorption isotherms measured at 77 K. The sample names are given above the respective isotherm plot. Samples Nx-4h and Nx-96h are reported in Tab. 2, where x corresponds to the molar equivalents of ammonia (relative to TEOS). We further report the isotherms of the samples synthesized with different water/ethanol (W/E) ratios as well as at various temperatures.

9. Particle size data

Particle size data of the reported samples are summarized in Tab. S3.

Tab. S3. Diameters of the spherical particles obtained from SEM images. Samples Nx-4h and Nx-96h are reported in Tab. 2, where x corresponds to the molar equivalents of ammonia (relative to TEOS). Q is the number of measured particles.

	mean / nm	standard deviation / nm	median / nm	Q
sample 1	340	21	340	109
sample 2	226	21	232	118
sample 3	93	15	91	102
N16.3-96h	433	18	434	112
N16.3-4h	440	15	442	101
N6.15-96h	338	22	340	120
N6.15-4h	340	21	340	109
N1.76-96h	219	14	220	102
N1.76-4h	173	14	173	117
W/E = 0.34	477	22	479	103
W/E = 0.92	433	17	436	108
W/E = 1.52	399	22	401	109
W/E = 1.87	545	26	548	113
W/E = 2.28	430	18	432	117
W/E = 2.59	471	22	472	114
W/E = 3.04	410	21	413	112
W/E = 3.38	340	21	340	109
W/E = 4.24	303	22	302	116
W/E = 5.61	187	19	189	117
W/E = 7.27	121	12	122	108
0 °C	596	36	602	115
20 °C	340	21	340	109
40 °C	263	19	265	121
60 °C	177	12	178	111
75 °C	138	10	138	116
methanol	310	21	310	112
ethanol	340	21	340	109
isopropanol	1063	82	1085	105
acetone	437	41	439	112