**A.1. Results**

**Table S1**. Texture properties of the methyl substituted silica gels.

| Sample (mol% MTES) | Hysteresis Type | Acid Catalysts | DFT (nm) | $S_{BET}^{a}$ (m²/g) | $S_{BET}^{b}$ (m²/g) | $V_{micro}$ (cm³/g) | $V_{total}$ (cm³/g) |
|---|---|---|---|---|---|---|---|
| 0 | H2a | A | 4.72 | 448 | 494 | 0.133 | 0.373 |
|   | H3 | B | 32.65 | 291 | 283 | 0.110 | 0.562 |
| 5 | H2a | A | 3.06 | 563 | 608 | 0.168 | 0.385 |
|   | H2a | B | 13.46 | 669 | 696 | 0.238 | 1.304 |
| 10 | H2a | A | 3.06 | 556 | 604 | 0.166 | 0.360 |
|   | H2a | B | 7.3 | 777 | 813 | 0.266 | 0.945 |
| 20 | H2a | A | 3.06 | 588 | 627 | 0.221 | 0.335 |
|   | H2a | B | 5.09 | 859 | 893 | 0.307 | 0.720 |
| 30 | H2a | A | 2.5 | 541 | 613 | 0.239 | 0.304 |
|   | H2a | B | 4.89 | 930 | 976 | 0.324 | 0.728 |
| 40 | H4 | A | 1.38 | 527 | 603 | 0.248 | 0.299 |
|   | H2a | B | 5.09 | 1059 | 1115 | 0.356 | 0.931 |
| 50 | H4 | A | 1.38 | 457 | 527 | 0.230 | 0.252 |
|   | H2a | B | 5.29 | 851 | 893 | 0.303 | 0.799 |
| 60 | H4 | A | 2.03 | 616 | 695 | 0.269 | 0.351 |
|   | H2a | B | 4.89 | 895 | 938 | 0.332 | 0.704 |
| 70 | H4 | A | 2.03 | 409 | 465 | 0.197 | 0.2378 |
|   | H4 | B | 2.03 | 694 | 722 | 0.275 | 0.482 |
| 80 | H4 | A | 2.03 | 251 | 265 | 0.115 | 0.158 |
|   | H4 | B | 2.11 | 424 | 438 | 0.189 | 0.282 |

a – single point, b - multi point

**Table S2.** Average values of the pores and primary particles size obtained in small angle scattering measurements by fitting data with the unified exponential/power-law model.

| MTES content (%) | Diameter (nm) | | | |
|---|---|---|---|---|
|   | series A | | series B | |
|   | SANS | SAXS | SANS | SAXS |
| 0 | 10.35 ± 0.16 | 8.11 ± 0.19 | 53.59 ± 6.02 | 30.68 ± 4.35 |
| 5 | 7.29 ± 0.09 | 6.34 ± 0.10 | 15.13 ± 0.35 | 11.39 ± 0.50 |
| 10 | 5.64 ± 0.08 | 5.36 ± 0.04 | 9.68 ± 0.17 | 8.37 ± 0.19 |
| 20 | 4.74 ± 0.11 | 4.65 ± 0.07 | 6.84 ± 0.14 | 6.34 ± 0.09 |
| 30 | 8.17 ± 1.06 | 5.59 ± 1.02 | 6.48 ± 0.18 | 5.85 ± 0.15 |
| 40 | 12.0 ± 2.21 | 8.60 ± 2.13 | 8.55 ± 0.31 | 7.59 ± 0.28 |
| 50 | 15.02 ± 2.28 | 28.08 ± 2.18 | 10.54 ± 0.27 | 10.45 ± 0.24 |
| 60 | 5.04 ± 0.63 | 5.38 ± 1.15 | 9.12 ± 0.45 | 9.28 ± 0.50 |
| 70 | 11.17 ± 5.33 | 7.59 ± 3.12 | 8.85 ± 0.86 | 8.48 ± 0.91 |
| 80 | 7.32 ± 1.32 | 6.89 ± 1.29 | 11.10 ± 4.25 | 9.69 ± 3.78 |

**Table S3**. XRD maxima position shift with the MTES mole percent

| Sample | Position | FWHM | Height |
|--------|----------|------|--------|
| A0 | 22.70 | 8.65 | 276.3 |
| A5 | 22.65 | 8.65 | 260.7 |
| A10 | 22.66 | 8.92 | 249.8 |
| A20 | 22.61 | 9.42 | 226.5 |
| A30 | 22.64 | 10.15 | 216.4 |
| A40 | 22.57 | 10.87 | 211.9 |
| A50 | 22.56 | 12.2 | 211.8 |
| A60 | 22.47 | 12.06 | 209.2 |
| A70 | 22.45 | 11.3 | 219.8 |
| A80 | 22.34 | 11.43 | 216.3 |
| B0 | 22.86 | 9.19 | 277.3 |
| B5 | 22.70 | 9.06 | 240.9 |
| B10 | 22.8 | 9.51 | 250.8 |
| B20 | 22.81 | 10.01 | 244.2 |
| B30 | 2.77 | 10.13 | 228.2 |
| B40 | 22.72 | 9.98 | 207.2 |
| B50 | 22.65 | 10.22 | 213.8 |
| B60 | 22.51 | 10.78 | 215.5 |
| B70 | 22.48 | 10.92 | 217.5 |
| B80 | 22.32 | 11.07 | 211.4 |

**Table S4**. Quantitative analysis of $^{29}$Si MAS NMR spectra.

| Sample | $^{29}$Si MAS NMR | | | | | | | | | | | |
|--------|------|------|------|------|------|------|------|-------|-------------|---------------|-------------------|-----------------|
| | $Q^4$ (%) | $Q^3$ (%) | $Q^2$ (%) | Q (%) | $T^3$ (%) | $T^2$ (%) | $T^1$ (%) | T (%) | $Q^4 + T^3$ (%) | $Q^4 + T^3 +$ $Q^3$ (%) | $Q^3 + Q^2 +$ $T^2$ (%) | $Q^2 +$ $T^2$ (%) |
| B0 | 70.5 | 28.70 | 0.82 | 100 | 0 | 0 | - | 0 | 70.53 | 99.19 | 29.48 | 0.82 |
| B5 | 63.3 | 32.30 | 1.51 | 97.20 | T3+T2 = 2.82 | | - | 2.82 | 66.16 | 98.49 | 33.84 | 1.51 |
| B10 | 65.6 | 22.10 | 0 | 87.70 | 10.20 | 2.11 | - | 12.31 | 75.78 | 97.89 | 24.22 | 2.11 |
| B40 | 43.6 | 14.80 | 0.62 | 58.9 | 26.50 | 14.51 | - | 41.05 | 70.11 | 84.86 | 29.88 | 15.13 |
| B60 | 36.6 | 4.82 | 0 | 41.40 | 40.50 | 18.10 | - | 58.58 | 77.08 | 81.90 | 22.92 | 18.10 |
| B80 | 17.4 | 1.58 | 0 | 19.90 | 61.18 | 18.90 | 0.91 | 80.07 | 78.61 | 80.19 | 20.47 | 18.89 |
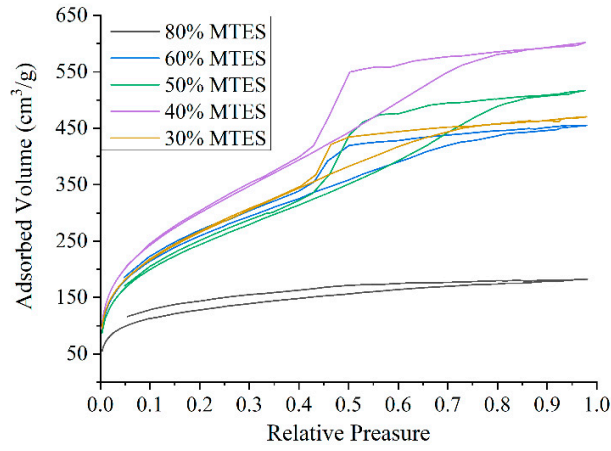
**Figure S1.** Evolution of nitrogen adsorption isotherms with 30-80% of MTES content.
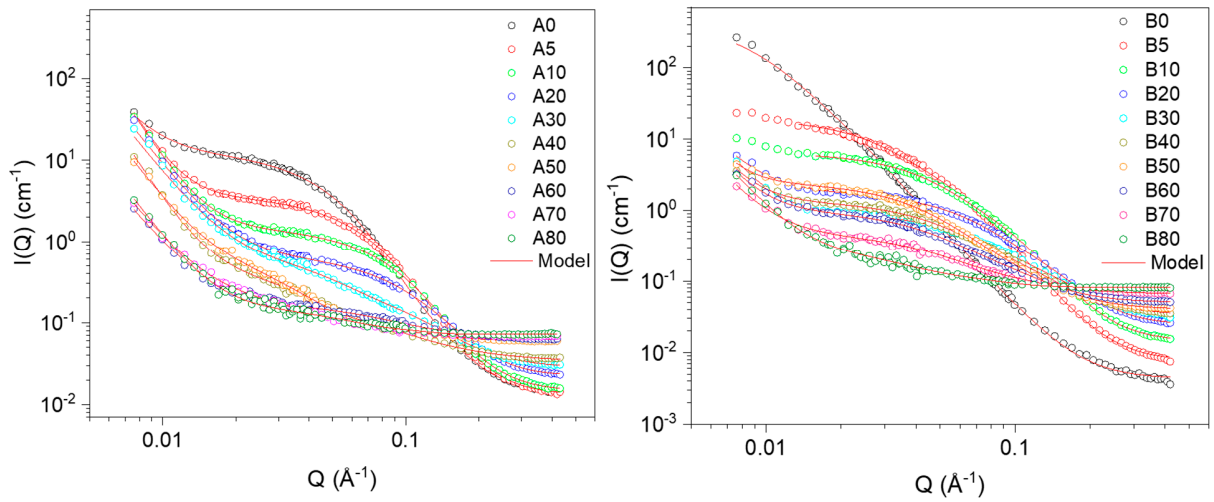


**Figure S2.** SANS profiles of series A (left) and B (right) as the amount of MTES in the reaction mixture increases from 5 % (A5/B5) up to 80 % (A80/B80). The SANS spectra of the TEOS silica precursor are also displayed for comparison (A0/B0). The applied model is also displayed as red lines.
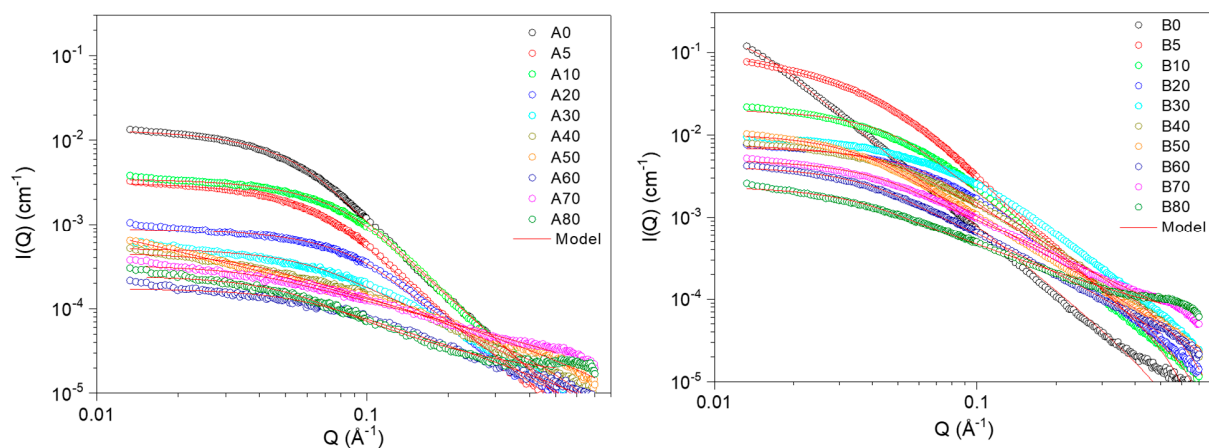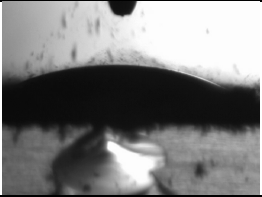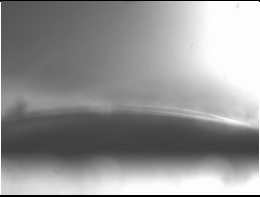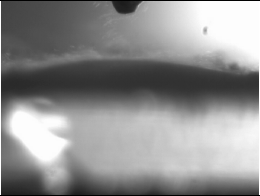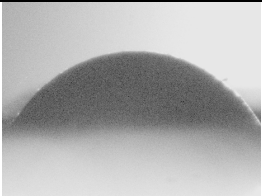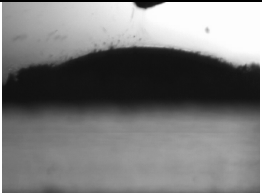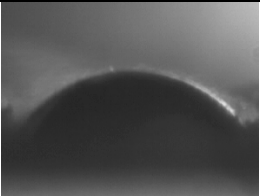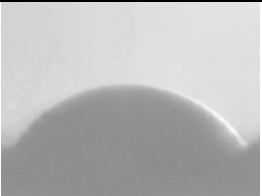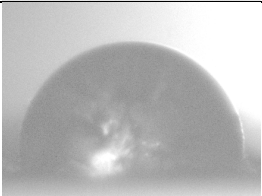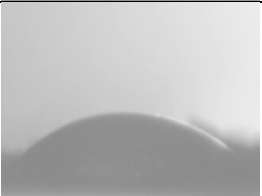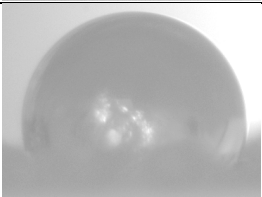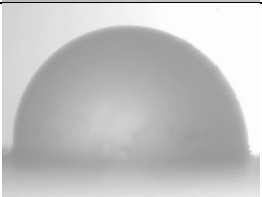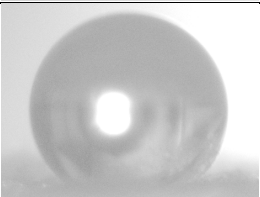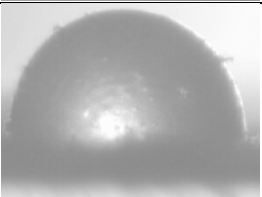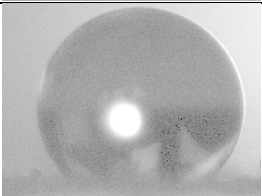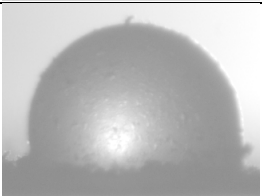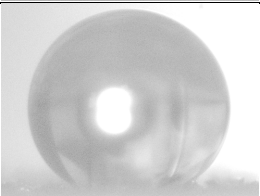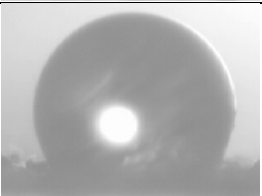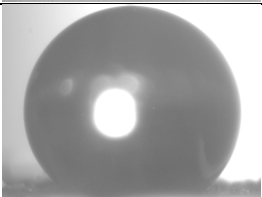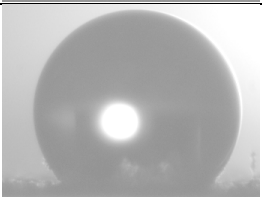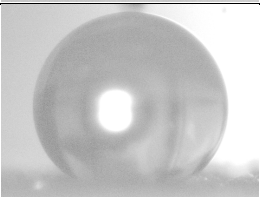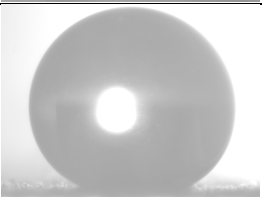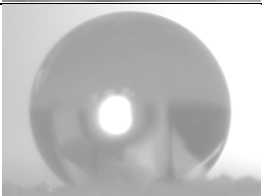
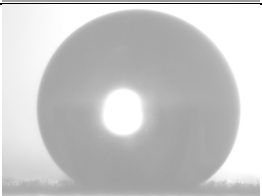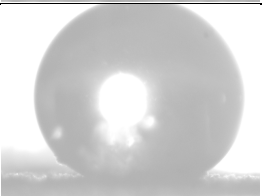**Figure S3.** SAXS profiles obtained for series A (left) and B (right), as the amount of MTES in the reaction mixture increases from 5 % (A5/B5) up to 80 % (A80/B80). The SAXS spectra of the TEOS silica precursor are also displayed for comparison (A0/B0). The applied model is also displayed as red lines.
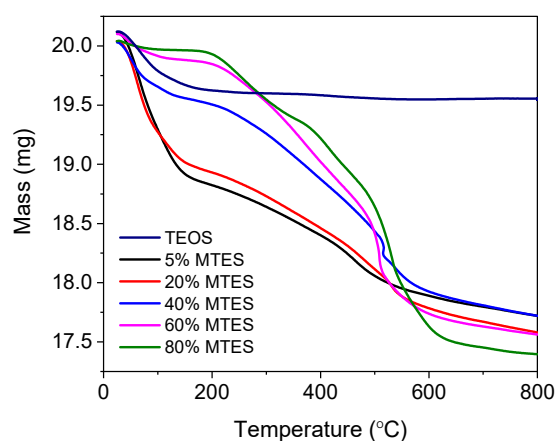


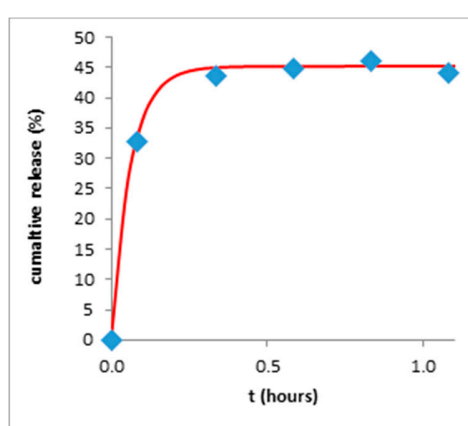**Figure S4**. TG curves of the silica xerogels with different methyl content

| MTES content (%) | series A | | series B | |
| --- | --- | --- | --- | --- |
| | **as-received** | **ground** | **as-received** | **ground** |
| 0 | | | | |

| | | | | |
|---|---|---|---|---|
| 5 | | | | |
| 10 | (no data) | | | (no data) |
| 20 | | | | |
| 30 | | | | |
| 40 | | | | |
| 50 | | | | |
| 60 | | | | |
| 70 | | | | |

| 80 |  |
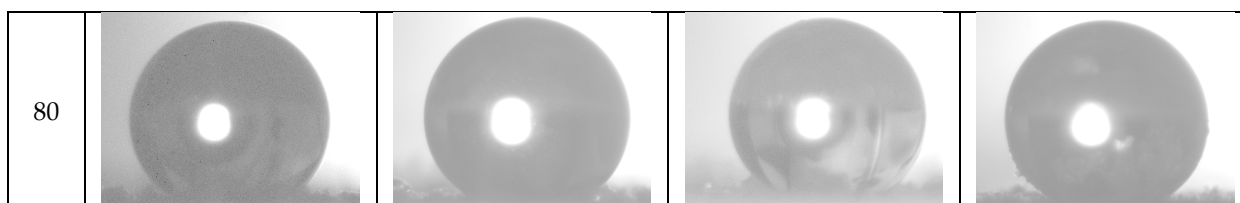


**Figure S5**. Representative contact angle images, one for each sample type, series A, respectively B, both as-received and ground.

**Mathematical modelling of drug release**



**Figure S6**. Fitted drug release curve of carrier A40 silica measured in HCl medium.