Supplementary Information for

Supercritical Fluid Atomic Layer Deposition: Base Catalyzed Deposition of SiO₂

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Figure S1. Scheme for (a) 2-step and (b) 3-step ALD reactions.
Figure S2. Sc-CO$_2$ deposition system connected with a IR cell. Each vessel and the IR cell have a heating jacket and can be separately pressurized and isolated from the system.
Figure S3. (a) Supercritical CO₂ deposition system. Each chamber had a temperature controlled heating jacket and are connected to a sc-CO₂ mainline through separate inlet and outlet valves (b) and (c) vessels configured to run a ALD reaction system in continuous mode.
**Figure S4.** IR spectra recorded after each cycle for the 2-step ALD reaction of TEOS/TEA followed by H₂O/TEA.

Figure S5 is a plot of the relative increase in the Si-O-Si bands at 1116 cm⁻¹ and 1070 cm⁻¹ for SiCl₄ and TEOS, respectively for each cycle using a 3-step SiCl₄ ALD process and a 2-step ALD for TEOS/TEA, then H₂O/TEA. A linear growth rate is obtained for both SiCl₄ and TEOS based reactions. Using an approximation of a similar extinction coefficient, we find that a higher growth level is obtained using SiCl₄.
Figure S5. Relative intensity of the Si-O-Si band at (a) 1116 cm\(^{-1}\) for the 3-step ALD reaction using SiCl\(_4\) and at (b) 1170 cm\(^{-1}\) for the two step reaction (TEOS/TEA then H\(_2\)O/TEA) versus the number of cycles.

FTIR spectroscopy for 2-step ALD on MCM-41 using TEOS

Figure S6 shows the FTIR spectra for MCM-41 and at each step during the first ALD cycle. In section 3.2, we used a fume silica thin film technique to provide access to the region below 1300 cm\(^{-1}\). This region is opaque when recording DRIFT spectra because of the presence of strong bulk silica modes and thus, this region of the spectrum is not shown in Figure S6. In the spectrum of MCM-41 (Figure S6a), the sharp peak at 3745 cm\(^{-1}\) and the broad weak peak at 3670 cm\(^{-1}\) are the SiOH stretching mode of free and interparticles silanols, respectively.\(^1\) The broad peak at 3400 cm\(^{-1}\) is due to H-bonded silanols and adsorbed water. The band at 1627 cm\(^{-1}\) is due to adsorbed water. The peak at 1867 cm\(^{-1}\) is a combination Si-O bulk mode and is used to normalize spectra to take into account differences in the amount of silica probed by the IR beam.
Figure S6b is the spectrum recorded after the first step of ALD reaction, exposing of MCM-41 to TEA/TEOS. The peak due to isolated SiOH groups at 3745 cm\(^{-1}\) is not present, showing that reaction of TEOS had occurred with all of these groups on the silica. Several C-H stretching modes attributed to adsorbed TEOS appear in the region 2984-2846 cm\(^{-1}\). This spectrum is similar to Figure S6 where the same reaction was carried out \textit{in situ} on a thin silica film. Other peaks in the 1600-1500 cm\(^{-1}\) region in Figure S6b are due to carboxamates.

Figure S6c shows IR spectra for the second step of the first ALD cycle (i.e, after exposing the TEOS-treated silica surface to H\(_2\)O/TEA). In this spectrum, the bands due to C-H modes are removed from the silica. This shows that hydrolysis of the adsorbed TEOS layer was complete. This hydrolysis step was slow as bands, due to C-H modes, showed a steady decrease with time but still were present with treatment times of 6 hrs. For this reason, we contacted the powder with the H\(_2\)O/TEA for 12 h. We also note the absence of a peak at 3745 cm\(^{-1}\) due to isolated silanols in Figure S6c. Generation of these silanols is important as they provide surface sites for the next ALD cycle. However, the absence of a band at 3745 cm\(^{-1}\) in Figure S6c is due to the excess amount of water present on the surface, relative to Figure S6a. The intensity ratio of the 1627/1867 cm\(^{-1}\) shows that there is 35% more adsorbed water on the MCM-41-1C compared to the MCM-41. It is the excess amount of water in which hydrogen bonds to the isolated silanols that is the reason for the absence of the band at 3745 cm\(^{-1}\). This was confirmed by the spectrum shown in Figure S6d. Figure S6d is the spectrum of the same sample shown in Figure S6c, after going through the degassing procedure on the ASAP 2020. The bands due to adsorbed water in Figure S6d are reduced relative to Figure S6c, which is accompanied by the appearance of the band at 3745 cm\(^{-1}\). The spectrum in Figure S6d is similar to the spectrum MCM-41, showing that surface silanols are regenerated in the process. From the similarity of Figures S6a and S6d,
one could conclude that the hydrolysis step completely removed the adsorbed TEOS, returning the MCM-41 to its original state. However, this would not be consistent with the observed reduction in surface area and pore size.

Figure S6. DRIFT spectra of (a) MCM-41, b) MCM-41 treated with TEOS/TEA in sc-CO₂, (c) after H₂O/TEA addition, and (d) after N₂ adsorption/desorption process.
Figure S7  N$_2$ adsorption/desorption isotherms for MCM-41-XC, X represents the number of ALD cycles.
Figure S8. Pore size distribution for MCM-41 and MCM-41-XC, X represents the number of ALD cycles.

Table S1. Structural properties from N\textsubscript{2} adsorption–desorption isotherms. The error for surface area values has been calculated with ASAP software.

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area m\textsuperscript{2}/g</th>
<th>Pore Diameter nm</th>
<th>Pore Volume cm\textsuperscript{3}/g</th>
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<tbody>
<tr>
<td>MCM-41</td>
<td>1103±56</td>
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<td>1.68</td>
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<td>MCM-41-7C</td>
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<td>0.52</td>
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</tbody>
</table>
**Figure S9.** DRIFT spectra of MCM-41 and MCM-41-XC, X represents the number of ALD cycles. The broad band around 3400 cm\(^{-1}\) is due adsorbed water H-bond with the isolated silanols.