CrystEngComm

Microwave Assisted Synthesis of Porous Organic Cages CC3 and CC2

Journal:	*CrystEngComm*
Manuscript ID	CE-COM-06-2019-000880.R1
Article Type:	Communication
Date Submitted by the Author:	26-Jun-2019
Complete List of Authors:	Lucero, Jolie; Colorado School of Mines, Chemical & Biological Engineering; Colorado School of Mines Osuna, Carla; Colorado School of Mines Crawford, James; COLORADOSCHOOLOFMINES, Chemical and Biological Engineering Carreon, Moises; COLORADOSCHOOLOFMINES, Chemical and Biological Engineering

COMMUNICATION

Microwave Assisted Synthesis of Porous Organic Cages CC3 and CC2

Jolie Lucero, Carla Osuna, James M. Crawford, and Moises A. Carreon *

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The microwave synthesis of two prototypical porous organic cages, denoted as CC3 and CC2 is demonstrated. CC3 crystals displaying narrow size distribution were synthesized in just few minutes. The fast synthesis of narrow size distribution POC crystals makes microwave a highly appealing synthetic approach for the synthesis of these crystals.

Porous organic cages (POCs) are porous crystals with highly desirable properties, such as uniform pore distributions, high surface areas, and thermal and chemical stability. These properties make POCs appealing for several functional applications. [1-5] Their unique structure and distinctive solid state molecular packing differentiate POCs from conventional porous crystalline materials, such as zeolites, metal organic frameworks, and covalent organic frameworks.[6-8] POCs are made of covalently bonded organic cages that assemble into crystalline microporous materials with three-dimensional connectivity and uniform pore size.[1,2] Typically, POCs are synthesized through cycloimination reactions.[1-3] The most studied POC is CC3,[1-5, 9, 10] formed by the coordination of 1,3,5-triformylbenzene, (TFB), with *trans*-1,2-diaminocyclohexane. Due to CC3's regular crystalline structure with unimodal limiting pore size of ~3.6 Å, CC3 has been mainly used for the separation of several chemicals and gases, [3-5, 11, 12] as a proton conductor, [13] and as a catalytic support.[14] Comprehensive reviews on POCs have been reported elsewhere.[15, 16]

Up to date, POCs have been prepared via batch synthesis (solvothermal synthesis) at room temperature or through a dynamic flow synthesis.[17] Microwave treatment represents an alternative synthetic approach. Microwave heating offers the following distinctive features: [18] (1) higher heating rates than that of conventional heating; (2) no wall or heating diffusion effects; (3) selective heating due to the difference in the way chemicals and contaminants interact in the presence of microwaves; (4) there are no "hot spots". Typically, microwave heating leads to smaller and more uniform crystals, which is highly desirable for many functional applications in which crystals with narrow size distribution is desired. Several porous crystals, including zeolites, [19-21] mesoporous oxides, [21, 22] and metal organic frameworks, [23, 24] have been synthesized via microwave. Herein, we report the successful synthesis of two prototypical types of porous organic cages, denoted as CC3 and CC2. To the best of our knowledge, we demonstrate for the first time the successful synthesis of any porous organic cage synthesized via microwave.

Figure 1 shows the PXRD patterns of CC3 crystals synthesized via microwave as a function of synthesis time (experimental details on the microwave synthesis conditions are given in the Supporting Information). All XRD patterns correspond to the common topology of CC3α crystals. Notably, CC3 crystals were synthesized at times as short as only 5 minutes, which is comparable to a previous study that used optimal dynamic flow to achieve a resonance time of 10 minutes.[17] Additionally, CC3 formation via conventional solvothermal approach requires at least several hours, or days.[25] When the CC3 was synthesized via microwave for 15 minutes, the sample showed a slight XRD peak displacement as compared to the calculated XRD pattern. This inconsistency suggests a small change occurred in the unit cell volume of the porous organic cage crystal.[26] The sample also exhibits a shift in XRD peaks to lower two theta angles, indicating an increase in interplanar spacing. The samples synthesized at 30, and 60 minutes show similar XRD peak positions, as compared to the calculated CC3α XRD pattern. The observed change in interplanar spacings, between the sample synthesized for 15 minutes as compared to the others, illustrate the flexible nature of CC3, as well as the ability to exhibit different packing densities. Our group has observed CC3 flexibility in a contraction-expansion effect for the solvothermal synthesis of CC3.[10]

[a] *Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, Colorado 80401, United States.*

Electronic Supplementary Information (ESI) available: Experimental methods. See DOI: 10.1039/x0xx00000x

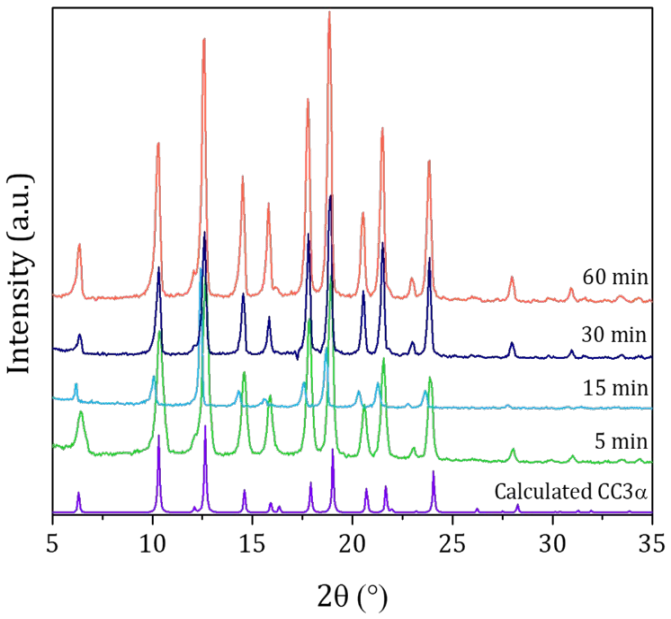

Figure 1. PXRD patterns of microwave synthesized CC3α at 5, 15, 30, and 60 minutes. For comparison the calculated pattern of CC3α is shown.

Figure 2 shows representative SEM pictures of the microwave synthesized CC3 crystals. All samples show highly crystalline faceted octahedral shapes, which is the typical morphology of CC3. The samples synthesized at 5, 15 and 30 minutes show very regular and narrow crystal size distribution. The sample synthesized at 60 minutes shows are broader crystal size distribution. The samples synthesized at short microwave synthesis times displayed the smallest crystal sizes and narrow size distribution. Specifically, the average crystal size (quantified by SEM) for the sample synthesized at 5 minutes and 15 minutes was 0.83 ± 0.2 μm, and 0.78 ± 0.2 μm respectively. At 30 minutes of microwave synthesis the crystal size increased to 1.1 ± 0.3 μm. Finally, at 60 minutes, a considerable crystal growth of 6.7 ± 3.2 μm was observed. From 30 to 60 minutes, there is a considerable increase in crystal size. Sintering, and Ostwald ripening mechanism, [27] in which small crystals disappear at the expense of growing, energetically favorable larger crystals, is likely responsible for this continuous crystal growth. **Figure 3** shows the CC3 average crystal sizes as a function of microwave synthesis time.

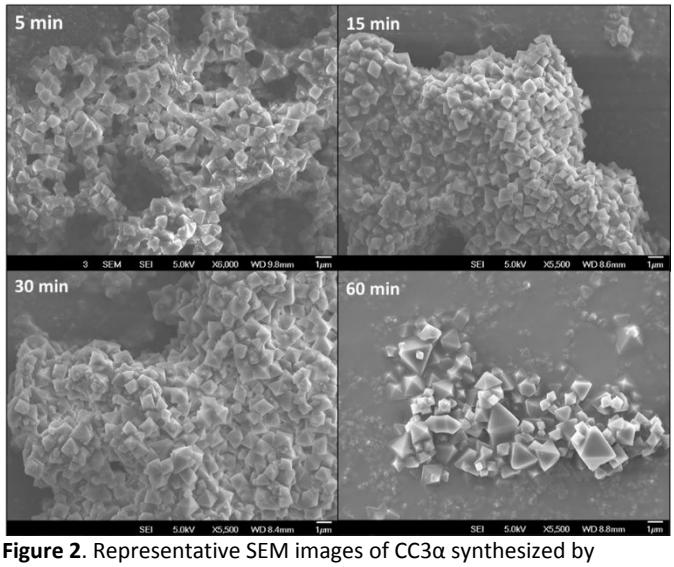

Figure 2. Representative SEM images of CC3α synthesized by microwave for 5, 15, 30, and 60 minutes.

Table 1 summarizes the textural properties of the microwave synthesized CC3 crystals. The BET surface areas extracted from N_2 isotherms, (**Figure S1**), for all samples were in the range of 464-509 m^2/g. The apparent BET surface area, and the simulated BET area for CC3α are in the ~410 - 523 m^2/g range. [10, 26] Interestingly, it has been hypothesized that an increase in surface area in racemic, and quasi-racemic CC3 crystals is related to a reduction in crystallinity.[25] In this report, the authors suggested that the increase in surface area arises from a reduction in long range order, leading to additional extrinsic microporosity between the CC3 cages. **Table 1** shows that the higher surface area samples are those having the largest micropore volume contributions, confirmed by the pore distributions shown in **Figure S2**. The higher BET area of the 60 minutes synthesized sample is likely the result of the inefficient packing of the CC3 cages resulting in the presence of some amorphous agglomerates (**Figure 2**, 60 minutes). In principle, this inefficient packing reduces the density of the material, creating gaps among the cages leading to additional adsorption sites for nitrogen, and therefore to higher surface areas. FT-IR spectra **(Figure S3)**, and details about key bond stretches of the microwave synthesized samples confirm the CC3 structure**. Figure S4** shows 1-D ^{1}H NMR spectra of microwave synthesized CC3 and CC2. Since we are synthesizing the mixed racemate of CC3, which has low solubility in most solvents,[26] the supernatant was analyzed by NMR. The soluble dissymmetric cage reported by Slater *et al*.,[28] is present within the supernatant**.** The ^{1}H NMR spectra confirms the structure of both CC2, and CC3.

During microwave irradiation, energy transfer occurs in

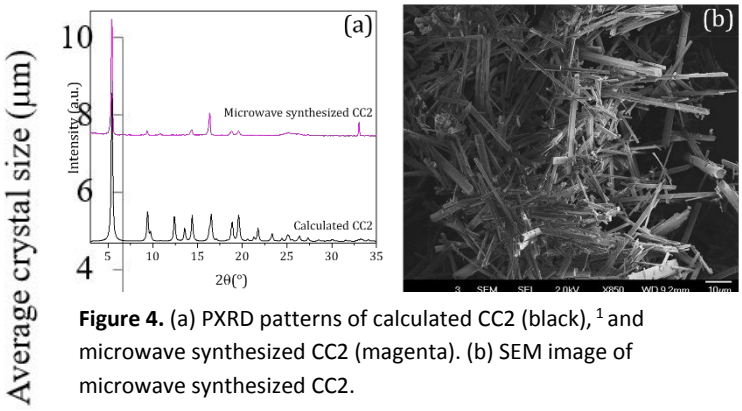

Figure 4. (a) PXRD patterns of calculated CC2 (black), [1] and microwave synthesized CC2 (magenta). (b) SEM image of microwave synthesized CC2.

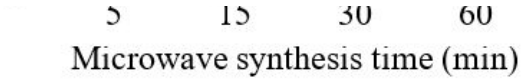

Figure 3. CC3 average crystal size as a function of microwave synthesis time. Numbers above indicate crystal size standard deviation.

nanoseconds, resulting in a high instantaneous temperature of the molecules.[29] This high local temperature, promotes faster reaction rates, as compared to those of conventional heating methods. Therefore, the observed small crystal size of the microwave synthesized CC3 crystals, may be related to a high nucleation rate. Furthermore, microwave leads to an enhancement of the dissolution

of reactants at very short times, leading to the formation of a high concentration of small nuclei. Eventually, crystallization of these nuclei due to the rapid consumption of the reactant leads to small crystals with narrow size distribution. Additionally, the *rac*-CC3 crystal is known to form quickly after CC3 molecule formation.[26] Typically, the room temperature formation of CC3 crystals requires synthesis times of at least 8 hours.[10] **Figure S5** shows a CC3 sample synthesized via solvothermal approach for 8 hours. For direct comparison, this sample was prepared with the exact same precursor composition as the microwave synthesized samples, but a bit more concentrated (16.6 mg/mL TFB/$V_{Tot,DCM}$ vs 2 mg/mL TFB/$V_{Tot,\ DCM}$). High dilution conditions has been shown to be more efficient for this type of cage formation.[25, 30] XRD shows the peaks corresponding to CC3 structure. However, the peaks are broader, indicating low degree of relative crystallinity. Crystal size for this solvothermal synthesized sample was ~ 2 μm with broader size distribution (±1.8 μm), and had irregularly shaped crystals. This size is more than double than the size of the sample synthesized for 5 minutes in the microwave. Although *rac*-CC3 crystals with average size < 1 μm, and narrow size distribution have been reported, [26] these crystals synthesized solvothermally still require ~3-5 days to form the homochiral cages CC3-S, and CC3-R before mixing. [10, 25, 26]

Table 1. Textural properties of CC3 microwave synthesized samples.

Microwave synthesis time (minutes)	Surface Area [$m^2 \cdot g^{-1}$]		Pore volume [$cm^3 \cdot g^{-1}$]		
	S_{BET}[a]	S_{ext}[b]	V_{tot}[c]	V_{micro}[b]	V_{meso}[d]
5	484	237	0.37	0.07	0.30
15	464	255	0.36	0.05	0.31
30	474	175	0.31	0.1	0.21
60	509	221	0.37	0.08	0.29

[a] Specific surface area was calculated by BET method (positive c-value, R^2>0.99), [b] external surface area and micropore volume were calculated by the t-plot method using the Kruk-Jaroniec-Sayari Thickness, [c] total volume was calculated from the quantity adsorbed at P/Po=0.975, [d] mesopore volume = total volume - micropore volume

The microwave synthesis approach was successfully extended for another prototypical type of POC, denoted as CC2. This POC has a limiting pore aperture of ~3.6 Å, (similar to CC3) and is formed by the condensation of 1, 3, 5-triformylbenzene with 1, 2-diaminopropane. **Figure 4** shows the PXRD, and a representative SEM image of CC2 crystals synthesized via microwave. The XRD peaks of this microwave sample synthesized for 8 hours agrees well with the simulated pattern of CC2 (Figure 4a). The Langmuir surface area of this sample was ~620 m^2/g, also in close agreement to the reported Langmuir surface area of 600 m^2/g for CC2.[1] **Figure S6** shows the N_2 isotherm, and pore distribution for this sample. The morphology of this sample (Figure 4b) shows needle-like, or $p\bar{3}$ symmetry. This morphology is characteristic of CC2 crystals[1]. In contrast with CC3, the formation of observed CC2 crystals requires longer synthesis times (8 hours). Nevertheless, CC2 crystals were synthesized in a few hours, as compared to a conventional batch approach, [1] which requires several days. For the formation of discrete cages, rather than oglio- or polymeric byproducts, longer synthesis times are needed for increased reversibility of CC2 formation.[25]

Conclusions

In summary, porous organic cage CC3 crystals were synthesized via microwave-assisted approach. The uniform, fast and localized heating provided by microwave, led to the formation of small crystallites with narrow size distribution. Specifically, the crystallite sizes of CC3 were in the ~ 0.8-1.1 micron size range for microwave times less than 30 minutes. As compared to conventional solvothermal treatment in which several hours are required to form this POC with larger crystal size. For microwave synthesis, only a few minutes were required to synthesize small CC3 crystals with narrow size distribution. The PXRD patterns confirmed the formation of CC3α structure, and a contraction-expansion effect associated to the flexible nature of this POC. The resultant crystals displayed BET surface areas in the 464-509 m^2/g range. To our best knowledge, we demonstrate here for the first time, the successful microwave synthesis of two prototypical porous organic cages. The fast synthesis of narrow size distribution POC crystals makes microwave a highly appealing synthetic approach for the synthesis of these microporous crystals for diverse potential functional applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

M. A. Carreon thanks the National Science Foundation NSF-CBET Award # 1705675 for supporting this work financially. We thank Professors John Falconer and Rich Noble from University of Colorado for allowing us to use the microwave

Notes and references

1. T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner and A. I. Cooper, *Nat. Mater.*, 2009, **8**, 973-978.
2. J. T. A. Jones, T. Hasell, X. Wu, J. Bacsa, K. E. Jelfs, M. Schmidtmann, S. Y. Chong, D. J. Adams, A. Trewin, F. Schiffman, F. Cora, B. Slater, A. Steiner, G. M. Day and A. I. Cooper, *Nature*, 2011, **474**, 367.
3. Q. L. Song, S. Jiang, T. Hasell, M. Liu, S. J. Sun, A. K. Cheetham, E. Sivaniah and A. I. Cooper, *Adv. Mater.*, 2016, **28**, 2629-+.
4. L. Chen, P. S. Reiss, S. Y. Chong, D. Holden, K. E. Jelfs, T. Hasell, M. A. Little, A. Kewley, M. E. Briggs, A. Stephenson, K. M. Thomas, J. A. Armstrong, J. Bell, J. Busto, R. Noel, J. Liu, D. M. Strachan, P. K. Thallapally and A. I. Cooper, *Nat. Mater.*, 2014, **13**, 954-960.
5. T. Hasell, M. Miklitz, A. Stephenson, M. A. Little, S. Y. Chong, R. Clowes, L. J. Chen, D. Holden, G. A. Tribello, K. E. Jelfs and A. I. Cooper, *J. Am. Chem. Soc.*, 2016, **138**, 1653-1659.
6. P. J. Waller, S. J. Lyle, T. M. Osborn Popp, C. S. Diercks, J. A. Reimer and O. M. Yaghi, *J. Am. Chem.Soc.*, 2016, **138**, 15519-15522.

7. B. Zhang, M. Wei, H. Mao, X. Pei, S. A. Alshmimri, J. A. Reimer and O. M. Yaghi, *J. Am. Chem. Soc.*, 2018, **140**, 12715-12719.
8. H. Lyu, C. S. Diercks, C. Zhu and O. M. Yaghi, *J. Am. Chem. Soc.*, 2019.
9. M. Liu, M. A. Little, K. E. Jelfs, J. T. A. Jones, M. Schmidtmann, S. Y. Chong, T. Hasell and A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 7583-7586.
10. J. Lucero, S. K. Elsaidi, R. Anderson, T. Wu, D. A. Gomez-Gualdron, P. K. Thallapally and M. A. Carreon, *Cryst. Growth Des.*, 2018, **18**, 921-927.
11. T. Mitra, K. E. Jelfs, M. Schmidtmann, A. Ahmed, S. Y. Chong, D. J. Adams and A. I. Cooper, *Nat. Chem.*, 2013, **5**, 276-281.
12. A. Kewley, A. Stephenson, L. J. Chen, M. E. Briggs, T. Hasell and A. I. Cooper, *Chem. Mater.*, 2015, **27**, 3207-3210.
13. M. Liu, L. J. Chen, S. Lewis, S. Y. Chong, M. A. Little, T. Hasell, I. M. Aldous, C. M. Brown, M. W. Smith, C. A. Morrison, L. J. Hardwick and A. I. Cooper, *Nat. Commun.*, 2016, **7**, 9.
14. J. K. Sun, W. W. Zhan, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 7063-7066.
15. T. Hasell, A. I. Cooper, *Nat. Rev. Mater.*, 2016, **1**, 16053.
16. J. D. Evans, C. J. Sumby, C. J. Doonan, *Chem. Lett*., 2015, **44**, 582-588.
17. M. E. Briggs, A. G. Slater, N. Lunt, S. Jiang, M. A. Little, R. L. Greenaway, T. Hasell, C. Battilocchio, S. V. Ley and A. I. Cooper, *Chem. Commun.*, 2015, **51**, 17390-17393.
18. Y. Li and W. Yang, *J. Memb. Sci.*, 2008, **316**, 3-17.
19. S. R. Venna and M. A. Carreon, *J. Mater. Chem.*, 2009, **19**, 3138-3140.
20. Z. Xie, M. Zhu, A. Nambo, J. B. Jasinski and M. A. Carreon, *Dalton Trans.*, 2013, **42**, 6732-6735.
21. G. A. Tompsett, W. C. Conner and K. S. Yngvesson, *ChemPhysChem*, 2006, **7**, 296-319.
22. C. A. Deshmane, J. B. Jasinski and M. A. Carreon, *Microporous and Mesoporous Mater.*, 2010, **130**, 97-102.
23. J. Klinowski, F. A. Almeida Paz, P. Silva and J. Rocha, *Dalton Trans.*, 2011, **40**, 321-330.
24. Z. Ni and R. I. Masel, *J. Am. Chem. Soc.*, 2006, **128**, 12394-12395.
25. M. E. Briggs and A. I. Cooper, *Chem. Mater.*, 2017, **29**, 149-157.
26. T. Hasell, S. Y. Chong, K. E. Jelfs, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2012, **134**, 588-598.
27. L. Ratke and P. W. Voorhees, *Growth and Coarsening: Ripening in Material Processing*, Springer, Berlin, 2002.
28. A. G. Slater, M. A. Little, M. E. Briggs, K. E. Jelfs and A. I. Cooper, *Molec. Syst. Des. Eng.*, 2018, **3**, 223-227.
29. N. A. Khan and S. H. Jhung, *Coord. Chem. Rev.*, 2015, **285**, 11-23.
30. Y. Jin, C. Yu, R. J. Denman and W. Zhang, *Chemi. Soc. Rev.*, 2013, **42**, 6634-6654.