Encapsulation of hexanal in calcium-squarate metal organic framework (UTSA-280) for active packaging

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Project outline/ M&M

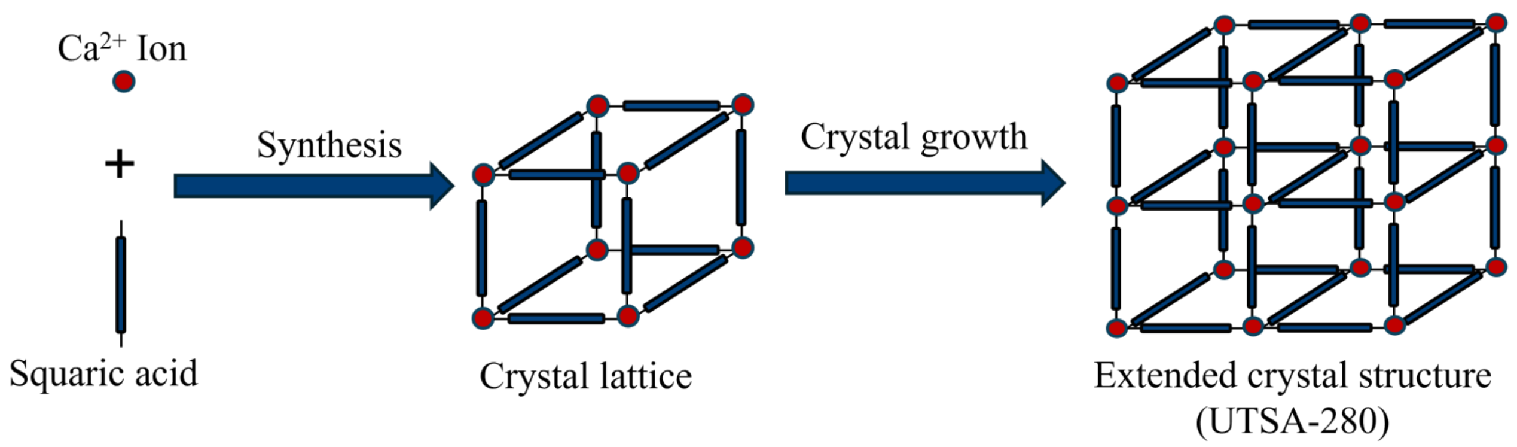


Figure 1: Synthesis of calcium-squarate metal organic framework (UTSA-280) [1]

This study explores the use of metal-organic frameworks (MOFs) as active porous components for extending the shelf life of packaged goods. Specifically, the MOF UTSA-280, a calcium-squarate MOF, was synthesized using a novel mechanochemical method. The pores of UTSA-280 were utilized to encapsulate hexanal, a compound known for its antimicrobial and antifungal properties. The integration of these hexanal-encapsulated MOFs into packaging materials demonstrated a significant increase in the shelf life of the products. This approach leverages the unique properties of MOFs to provide an innovative solution for food preservation and storage [2],[3].

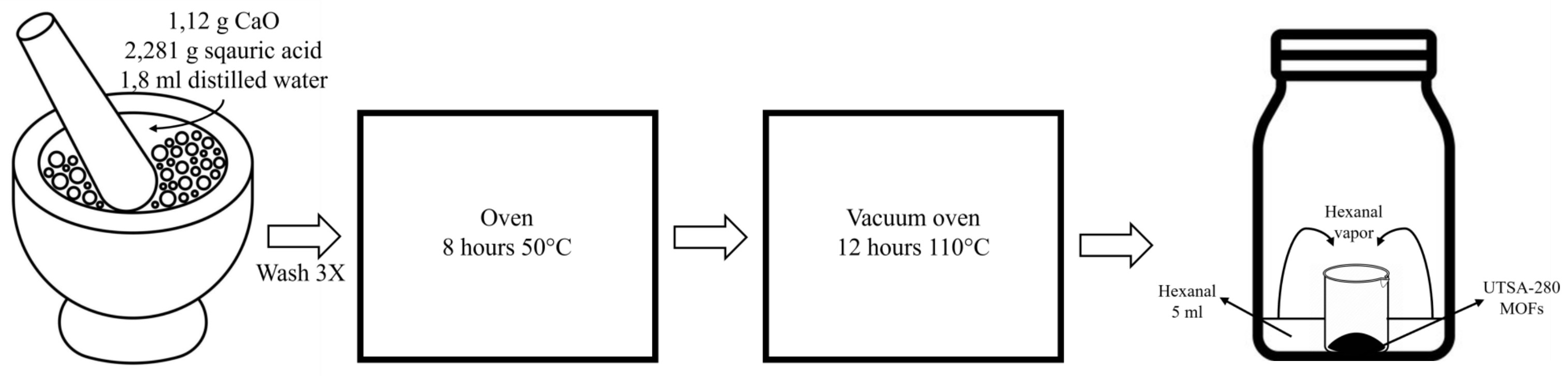
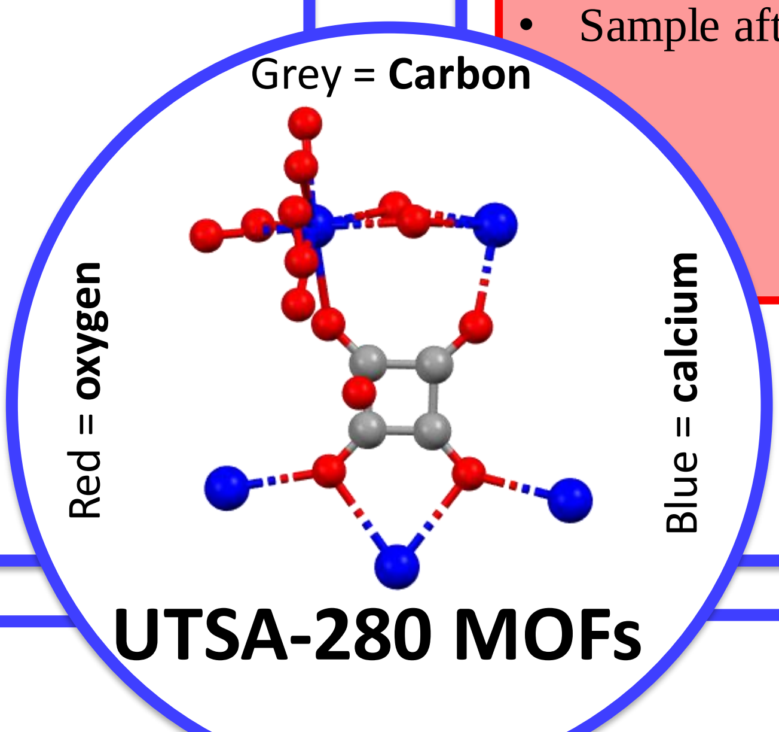


Figure 2: mechanochemical synthesis, activation and encapsulation of hexanal

Calcium oxide (CaO), squaric acid, and water were ground together for 2 minutes using a mortar and pestle. The mixture was then washed three times with distilled water in a 100 ml beaker. The sample was dried in an oven at 50°C for 8 hours and subsequently activated by drying in a vacuum oven at 110°C for 12 hours. Hexanal was encapsulated into the MOF using a vapor diffusion process in a 1.9-liter jar. The MOF was characterized before and after encapsulation with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), and Scanning electron microscopy (SEM). Lastly, the amount of hexanal encapsulated was determined using TGA.



Results and Discussion

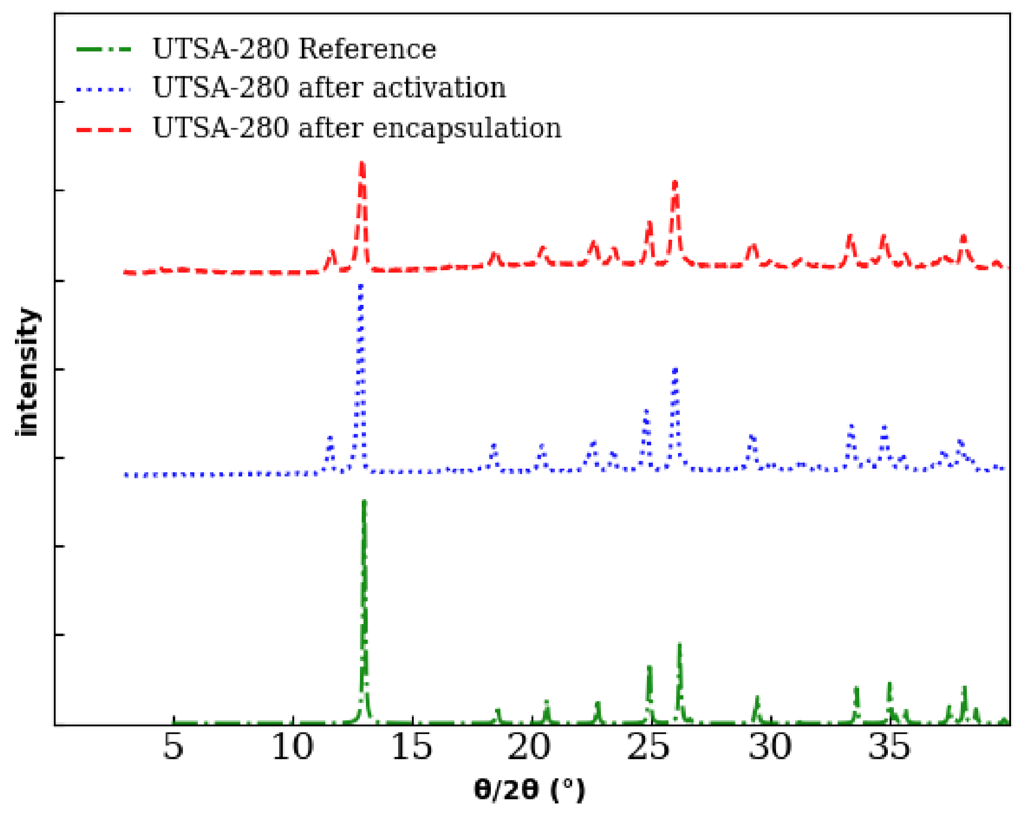


Figure 3: XRD results

- High intensity peaks at different 2θ angles = crystalline structure formed
- Crystalline structure is preserved after encapsulation, as evidenced by similar XRD measurements post-activation and post-encapsulation.
- The peak ratio comparison with reference data indicates that a similar crystal structure is obtained.

- Pure CaO gives no peaks (expected from literature)
- Squaric acid only has peaks in the fingerprint region
- Sample as synthesized
    - Peak at 3500-3000: O-H bonds (water)
    - Peak at 1660: C=O bonds
    - Peak at 1400: C=C bonds
- Sample after activation/ encapsulation
    - Peak at 3500-3000: O-H bonds (water)
    - Peak at 1660: C=O bonds
    - Peak at 1400: C=C bonds

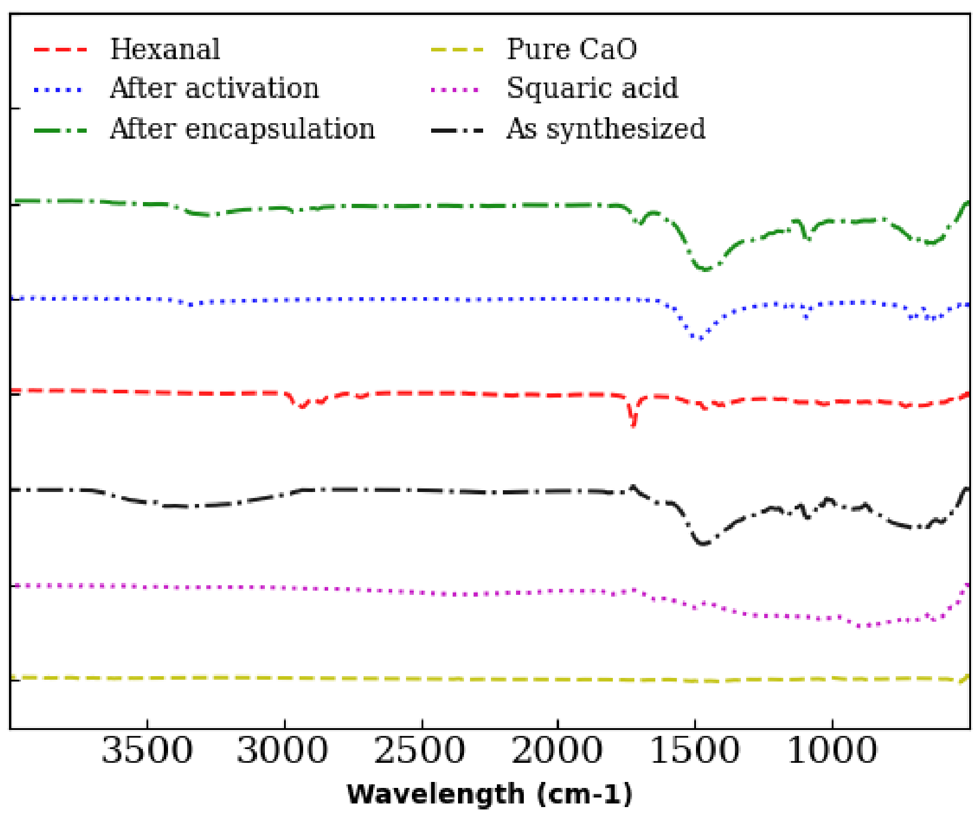


Figure 4: FTIR results

Results and Discussion

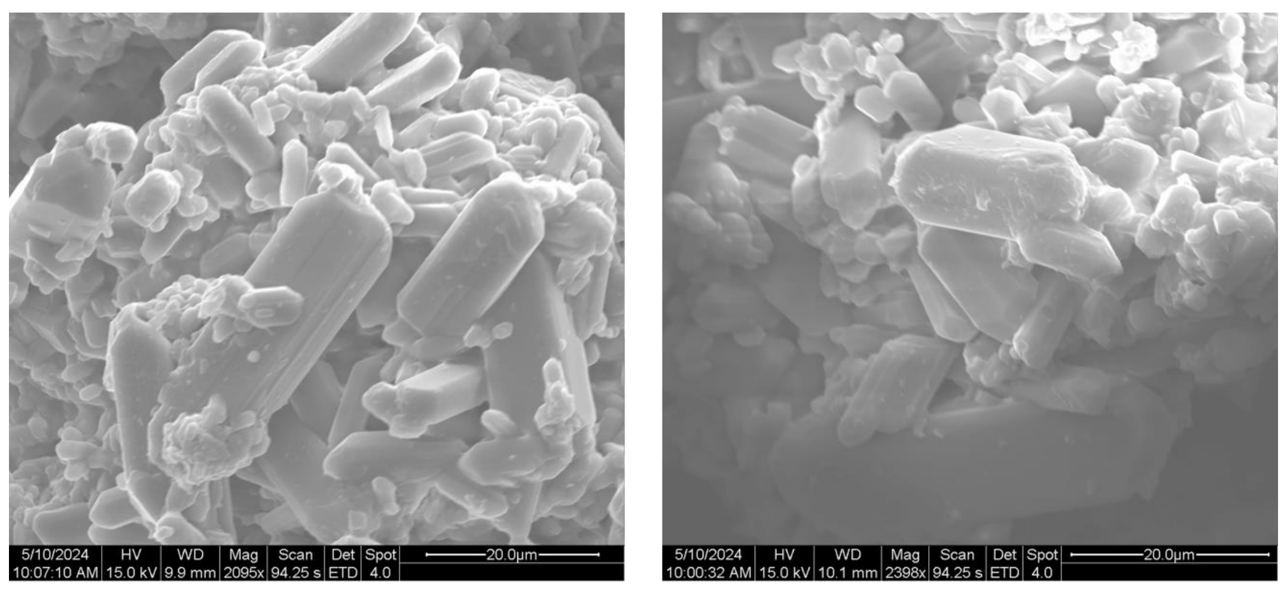


Figure 7: SEM Images

- SEM images visibly displayed the UTSA-280 crystals.
- Crystals retain crystal structure after encapsulation
- Encapsulation is non-destructive for the crystals

Conclusion

- UTSA-280 MOFs synthesized via mechanochemical grinding yield a grey powder, indicating successful formation
- XRD analysis shows that the crystalline structure remains intact during hexanal encapsulation, resembling reference UTSA-280 crystals
- FTIR confirms chemical interactions and MOF formation before activation and after hexanal encapsulation
- TGA and DSC reveal thermal stability and a notable shift in evaporation temperature, with 19.78 wt% hexanal encapsulated
- SEM visually confirms the integrity of UTSA-280 crystals post-encapsulation
- Future applications: incorporate the encapsulated MOFs into food packaging to extend the shelf life of fresh food products

Results and discussion

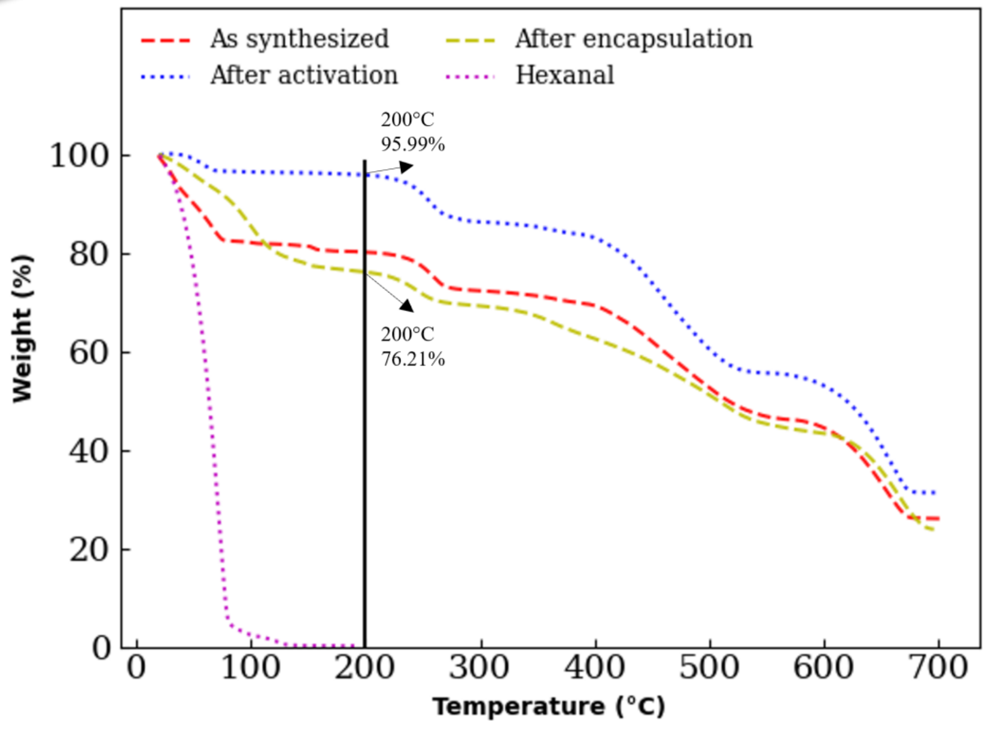


Figure 5: TGA results

- As synthesized: bigger peak around 100°C = water loss
- After activation
    - 150-300°C: H_2O coordinated with Ca^{2+} ions
    - Above 392°C: framework degradation
- After encapsulation
    - Successful encapsulation
    - 150-300°C: hexanal coordinated with Ca^{2+} ions
    - Above 392°C: framework degradation
    - ~20 wt% hexanal encapsulated

- Pure hexanal evaporates at 40°C
- Post-encapsulation, evaporation peak shifts to 100-150°C: successful encapsulation.
- Peak at ~200°C indicates hexanal coordination with Ca2+ ions.
- Post-activation, peak around 100°C: residual water.
- Peak at 150-170°C: strong secondary bonding in the encapsulated structure.

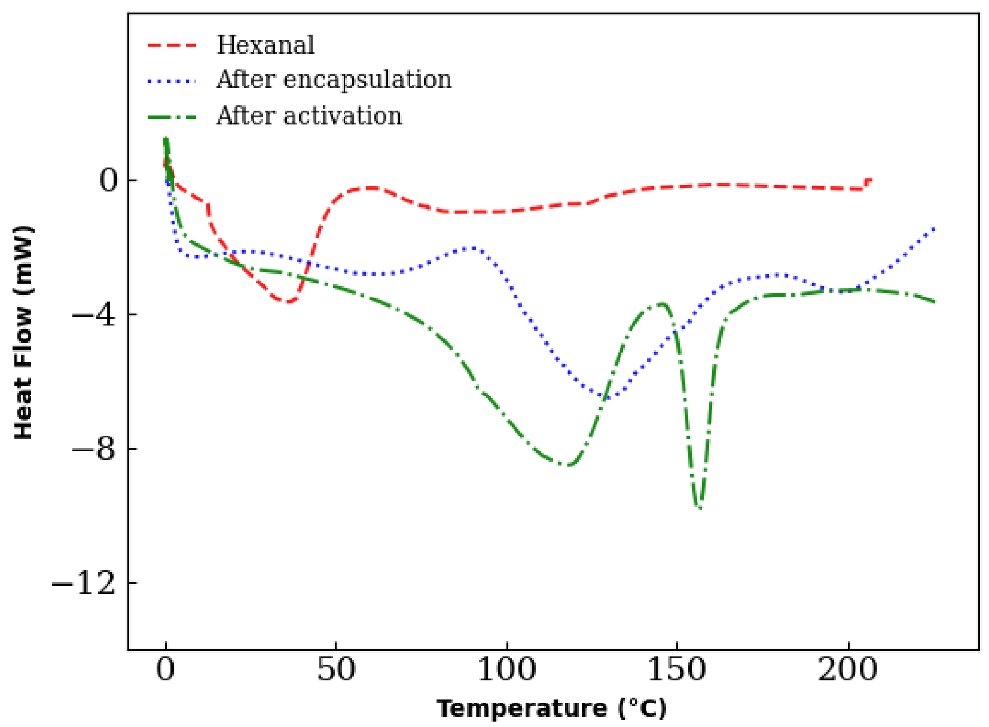


Figure 6: DSC results

Supervisors / Co-supervisors / Advisors: Prof. Dr. Ir Mieke Buntinx/ Prof. Dr. Ajay Kathuria

[1] A. Kathuria, A. El Badawy, S. Al-Ghamdi, L. S. Hamachi, and M. B. Kivy, "Environmentally benign bioderived, biocompatible, thermally stable MOFs suitable for food contact applications," Trends in Food Science and Technology, vol. 138. pp. 323–338, Aug. 01, 2023. doi: 10.1016/j.tifs.2023.06.024.

[2] S. Xian, Y. Lin, H. Wang, and J. Li, "Calcium-Based Metal–Organic Frameworks and Their Potential Applications," Small, vol. 17, no. 22. John Wiley and Sons Inc, Jun. 01, 2021. doi: 10.1002/smll.202005165.

[3] R. H. Shi et al., "Two calcium-based metal organic frameworks with long afterglow as anticounterfeiting materials," Chemical Engineering Journal, vol. 479, Jan. 2024, doi: 10.1016/j.cej.2023.147851.