Transformability of CALF-20 Metal-Organic Framework: Theoretical and Experimental Insights

J. Drwęska[1], F. Formalik[2,3], K. Roztocki[1], R. Q. Snurr[3], L. J. Barbour[4], A. M. Janiak[1]

[1]Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland, [2]Department of Micro, Nano, and Bioprocess Engineering, Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, [3]Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois, 60208, United State, [4]Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa.

agnieszka.janiak@amu.edu.pl

Calgary Framework 20 (CALF-20) is a readily obtained and reproducible zinc-based metal-organic framework that exhibits excellent durability in the CO2 sorption process [1]. In our study, we monitored this process at atomic resolution using in situ single-crystal X-ray diffraction under controlled gas pressure. The experiment revealed slight structural changes in the framework upon gas sorption and allowed us to determine the real positions of carbon dioxide in the pores (Fig. 1).
Recent reports on CALF-20 suggest its susceptibility to humidity [2] and pressure-induced phase transformations [3]. We studied changes in CALF-20 triggered by temperature, including a single-crystal-to-single-crystal transition of the initial phase α-CALF-20 into γ-CALF-20, assisted by solvent included in the pores (Fig. 1). We were also able to capture a transient phase of CALF-20 called τ-CALF-20 (Fig. 1). Interestingly, its calculated powder pattern correlates perfectly with that of the previously reported β-CALF-20 [2] (Fig. 1). However, the crystal structure determined by SC-XRD experiment differs significantly from the structure based on the powder data described in the literature.
Theoretical analysis of CALF-20 has proven that the presence of water molecules is crucial in stabilizing the structure, leading to its exceptional stability. Nevertheless, under anhydrous conditions, the energetically favourable phase is α-CALF-20, as supported by experimental data. Furthermore, a contracted phase is predicted to exist only at extremely low temperatures.

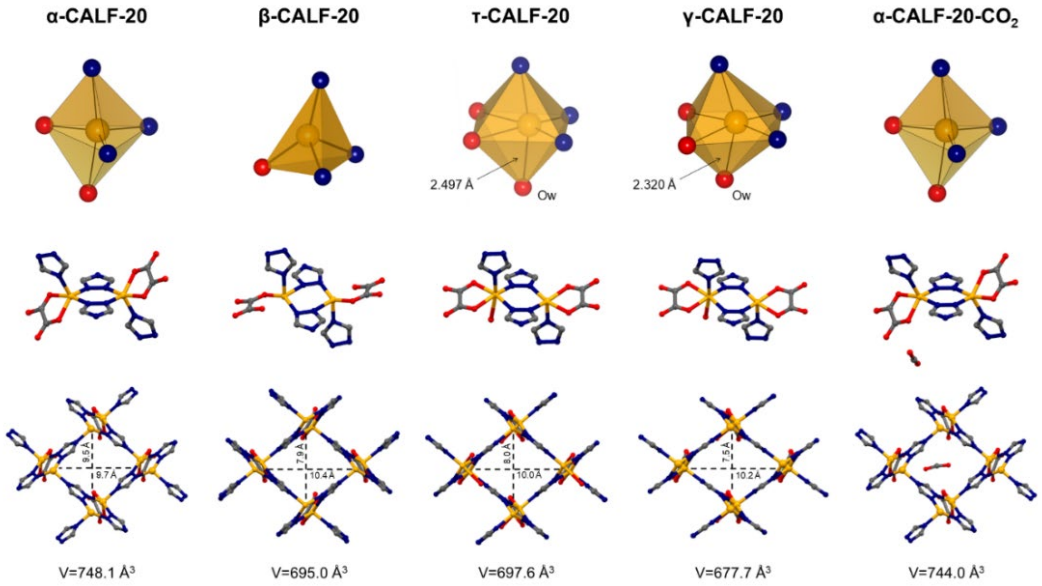

Figure 1. A structural comparison of CALF-20 phases.

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