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Stability improvement of $\text{Cu}_3(\text{BTC})_2$ metal-organic framework under steaming conditions by encapsulation of Keggin polyoxometalate

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$\text{Cu}_3(\text{BTC})_2$ with incorporated Keggin polyoxometalate was demonstrated to be stable under steaming conditions up to 483K, while the isostructural HKUST-1 degrades and transforms into $[\text{Cu}_2\text{OH}(\text{BTC})(\text{H}_2\text{O})]_n \cdot 2n\text{H}_2\text{O}$ from 343K onwards.

Porous hybrid materials such as $\text{Cu}_3(\text{BTC})_2$ metal-organic frameworks (MOFs) have been intensively studied in the last decade^{1, 2} because of their interesting properties such as a large surface area, well-defined micro- and mesoporosity in combination with attractive sorption properties, easily accessible transition metal centers and the ability to arrange them in tailored meso-structures such as thin films³, patterned single crystals⁴, etc. More recently HKUST-1 MOF was identified as candidate for energy storage^{5, 6}, CO_2 capture⁷⁻¹¹ and safe storage and separation of propane and propylene¹². Exploiting its hydrophilic properties, HKUST-1 has been applied for reversible adsorption of water at room temperature and in this context used in humidity sensors¹³. At present $\text{Cu}_3(\text{BTC})_2$ is one of the few MOF that is produced by the chemical industry (BasoliteTM C300 - BASF).

Despite its interesting applications, one of the major concerns impairing industrial application of this material is its low stability in steam conditions. Schlesinger *et al.*¹⁴ showed that the stability of hydrated $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$ deteriorates from 343K onwards. The anhydrous material is stable until 473K, implying that water molecules coordinated to the paddle-wheel units¹⁵ have to be removed carefully before crossing the 343K stability boundary. Catalyst decomposition at 353K also prevented Schlichte *et al.*¹⁶ from optimizing the turnover frequency in HKUST-1 based liquid phase cyanosilylation of benzaldehyde.

Keggin type heteropolyacids (HPAs) have been successfully applied as molecular level template for the formation of $\text{Cu}_3(\text{BTC})_2$ MOFs in water and ethanol solvent mixture at room temperature^{17, 18}. Here we report that the resulting $\text{Cu}_3(\text{BTC})_2$, incorporating Keggin type $\text{PW}_{12}\text{O}_{40}^{3-}$ [$\text{HPA}@\text{Cu}_3(\text{BTC})_2$] is more robust in steam conditions compared to HKUST-1 which is very important in view of applications.

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Supplementary information for this article is available on the www

As described by Bajpe *et al.*¹⁸ $\text{HPA}@\text{Cu}_3(\text{BTC})_2$ was prepared by dissolution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Fluka) in a 10^{-3}M $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Fluka) solution prepared using an 0.1M NaNO_3 in 50% vol. ethanol (VWR)-water solution. Upon complete dissolution, a $1.259 \times 10^{-2}\text{M}$ 1,3,5- H_3BTC (Acros organics) solution in 0.1M NaNO_3 in 50% vol. ethanol-water was added and aged statically for 24h at room temperature. The HKUST-1 sample was prepared according to the modified recipe of Rowsell *et al.*¹⁹. Millipore[®] water was used throughout. After synthesis, the solids were collected, washed twice with absolute ethanol and dried at 343K to remove physisorbed solvents, while retaining the chemisorbed water in the paddle-wheels of the structure. Sealed 0.5mm glass capillaries containing the compounds were subjected to a thermal treatment at 363, 393, 423, 453 and 483K for 24 h.

PXRD patterns were obtained for all samples from 3 to 90 degrees 2θ using a Stadi P ($\text{CuK}\alpha_1$, STOE& Cie GmbH) in θ - 2θ geometry and capillary mode. The data was processed using the STOE Software WinXPOW.

The HKUST-1 structure consists of three types of pores^{1, 20}, small (octahedral) pores in the center of $\text{Cu}_{12}\text{BTC}_8$ units with a diameter of only 6Å, and two larger pores around 11-15Å formed by the organization of these units in the HKUST-1 structure. Due to the hydrophobic character of the benzyl core and the lack of unoccupied metal coordination sites, the small pore exhibits hydrophobic character²¹. In one of the big pores, water molecules are bound to the available copper coordination sites and as consequence this pore shows a highly hydrophilic character. Grajciar *et al.*¹⁵ showed that the Cu-Cu distance in the paddle-wheels is elongated due to the interaction with these water molecules. This phenomenon leads to a square pyramidal coordination of the cations as compared to a square planar coordination in the anhydrous HKUST-1 structure. Upon careful heating, the water molecules can be detached from the paddlewheel without any damage to the original structure. In steam conditions, however, Cu hydrolysis is enhanced²². The hydroxylation of Cu^{2+} in the paddle-wheel changes the local structure and consequently the compound. As shown in figure 1a, the PXRD patterns for heat-treated hydrated HKUST-1 confirm the occurrence of structural changes upon heating from room temperature to 453K. Crossing the 343K stability boundary, the diffraction lines broaden, hence indicating a phase transition. At 393K, an intermediate, currently unidentified phase with low crystallinity is formed which in turn transforms into the green $[\text{Cu}_2\text{OH}(\text{BTC})(\text{H}_2\text{O})]_n \cdot 2n\text{H}_2\text{O}$ structure²³ (supplementary

information). At 423K the formation of this phase is complete and irreversible.

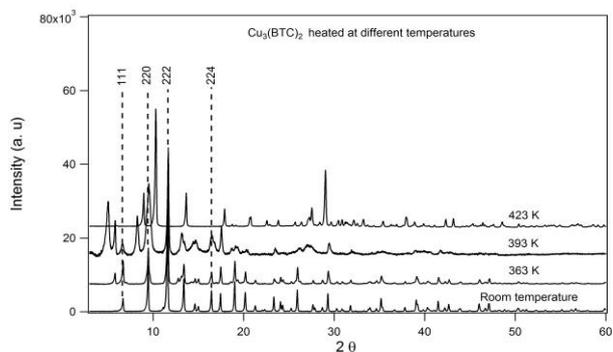


Figure 1a: PXRD patterns of hydrated HKUST-1 as function of temperature.

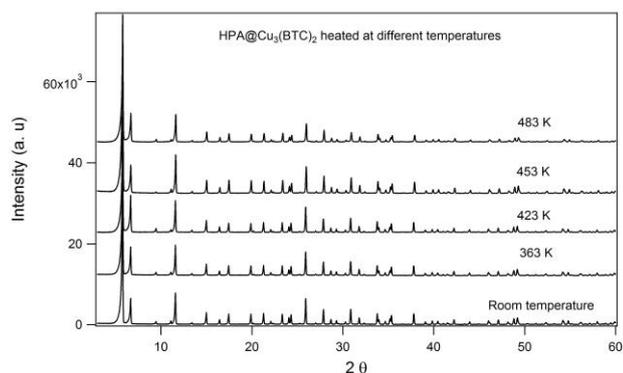


Figure 1b: PXRD patterns of the HPA@Cu₃(BTC)₂ as function of temperature.

The cubic unit cell of HKUST-1 consists of 2D layers constructed from hexagonally organized BTC molecules interconnected by copper pairs (figure 2). These (111) layers are oriented perpendicular to the diagonal in space of the unit cell. Viewed from the side, one set of these 2D layers is connected by the two other sets of these planes intersecting under an angle of 70.53°, creating the cavity system between two consequent parallel layers. Comparison of the PXRD pattern of the material obtained at 393K with that of the intact structure revealed some reflections persisting and remaining sharp during the initial transformation. Some of these persistent reflections are associated with indices $h=k=l$, and hence relate to the distance between parallel 2D layers. In addition, reflections associated with indices $h=k, l=0$ and $h=k, l=2h$ are observed, which both relate to distances in plane of the 2D layers. This indicates that in addition to the distance between at least one set of 111 planes also their dimensions are preserved during the transformation of the structure between 298 and 393K. Further heating the material in steam conditions up to 423K results in the formation of the green $[\text{Cu}_2\text{OH}(\text{BTC})(\text{H}_2\text{O})]_n \cdot 2n\text{H}_2\text{O}$ phase, which is a densely packed layered material with very small interlayer distance ($\pm 3.5\text{Å}$) and altered intra-layer structure as compared to the layers present in HKUST-1 (supplementary information).

Figure 1b shows the PXRD patterns for HPA@Cu₃(BTC)₂ samples after heat-treatment up to 483K in steam conditions. Refinement of this series of identical patterns resulted in unchanged unit cell parameters, confirming the absence of any

structural changes. As expected from the diffraction patterns, no color-changes were observed. In HPA@Cu₃(BTC)₂, one type of the big pores, empty in HKUST-1, is occupied by Keggin ions¹⁷. The presence of these guest species obviously prevents any structural changes observed for empty HKUST-1 under steam conditions.

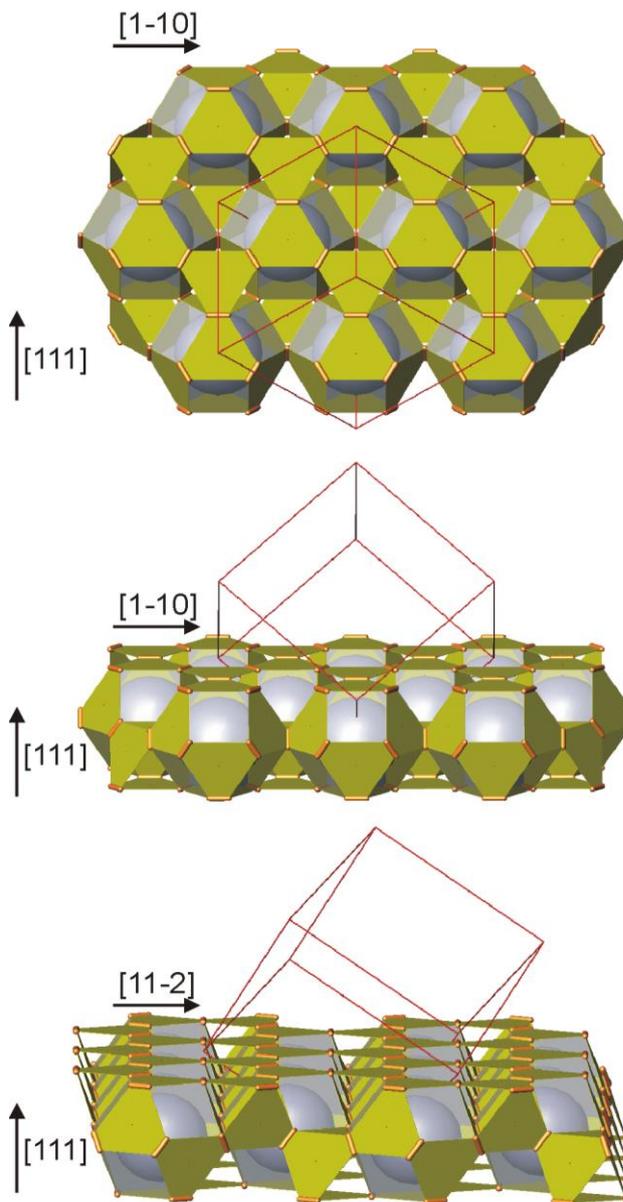


Figure 2: Cubic unit cell of HKUST-1. The parallel (111) layers are composed by hexagonally organized BTC molecules (triangles) interconnected by copper pairs (orange cylinders). The spheres inside the pores represent the HPA.

The structure of the green $[\text{Cu}_2\text{OH}(\text{BTC})(\text{H}_2\text{O})]_n \cdot 2n\text{H}_2\text{O}$ phase obtained after steam treating unstabilised HKUST-1, cannot serve as a host for large species like $\text{PW}_{12}\text{O}_{40}^{3-}$ ($\text{Ø } 11\text{Å}$). The transformation of HPA@Cu₃(BTC)₂ would hence require a complete disassembly of the original structure before the densely packed, layered material could be formed. The structural stability

of anhydrous HKUST-1 (up to 473K)¹⁶, demonstrates the stability of the paddle-wheel geometry in absence of strongly complexing ligands like OH⁻, so a full disintegration of HKUST-1 and reassembly of its components into the dense layered phase would be highly unlikely. Considering that the PXRD patterns obtained at intermediate stages of the transformation indicate the preservation of at least one set of the original 2D layers, it can be concluded that the presence of Keggin ions between parallel layers in the stabilised material prevent any lateral movement and consequently lock the connecting BTC molecules in place. The transformation of the paddle-wheel geometry in HKUST-1 into the dinuclear μ -hydroxy linked copper centres in [Cu₂OH(BTC)(H₂O)]_n.2nH₂O would require significant structural flexibility. In HPA@Cu₃BTC₂, the guest species prevents both this structural flexibility and the re-orientation of BTC linking parallel layers. Although the detailed transformation mechanism for the conversion of HKUST-1 into [Cu₂OH(BTC)(H₂O)]_n.2nH₂O is currently not yet elucidated, the results of this stability study indicate that the transformation only occurs in presence of strong bridging ligands like hydroxyl and that an initial delamination step is followed by a re-arrangement of the BTC linkers.

In summary, we report a study investigating the stability of Cu₃(BTC)₂ MOF in steam conditions. HPA@Cu₃(BTC)₂ is stable until 483K in steam conditions, while the conversion of HKUST-1 to Cu₂OH(BTC)(H₂O).nH₂O starts at 343K. The superior stability of HPA@Cu₃(BTC)₂ compared to the related, isostructural HKUST-1 phase, increases its suitability for practical applications in hydrous, heat conditions with temperatures up to 483K.

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