# - Supplementary Information -

# Crystals for sustainability – structuring Al-based MOFs for the allocation of heat and cold

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SUPPLEMENTARY MATERIAL

This supplementary information file contains all experimental procedures (S.1), characterization of different CAU-materials (S.2), characterization of CAU-10-H on alumina supports (S.3) and characterization of CAU-10-H on metallic aluminium supports (S.4).

## S.1 - Experimental section

2-Aminoterephthalic acid (Aldrich, 99%), 2,5-hydroxyterephthalic acid (Aldrich, 97%), 4,4′-benzophenonedicarboxylic acid (TCI, 95%), isophthalic acid (Aldrich, 99%), 5-aminoisophthalic acid (Aldrich, 94%), 5-hydroxyisophthalic acid (TCI, 97%) $AlCl_3 \cdot 6H_2O$ (Aldrich, 99%), $Al_2(SO_4)_3 \cdot 18H_2O$ (Aldrich, 98%), α-alumina beads (~4mm, Alfa Aesar, 99%), γ-alumina beads (1-3 mm, 000-3p, Akzo Nobel), metallic aluminium foil (0.5 mm thick, Mateck, 99.999%), NaOH (Aldrich, 98%), methanol (Aldrich, 99.8%), DMF (Aldrich, 99.8%), acetic acid (Aldrich, 99.7%) and HCl solution (37% wt., Aldrich) were purchased from respective suppliers and were used without any further purification.

### S.1.1 - Synthesis of different CAU-materials (powder)

#### *S.1.1.1 - CAU-1*

The synthesis of CAU-1 was performed according to literature,[1] by suspending 379 mg of 2-aminoterephthalic acid and 1507 mg of $AlCl_3 \cdot 6H_2O$ in 20 mL of methanol in a 30 mL Teflon insert. The mixture was heated for 5 hours at 125 °C. To sustain the pressure, the insert was put in a steel autoclave. The residue after filtration was a yellow powder. The as-synthesized powder was washed overnight with 500 mL of deionized water three times. The final suspension was filtered and the product was dried in air.

#### *S.1.1.2 - CAU-1-$(OH)_2$*

Again literature procedure was followed to synthesize CAU-1-$(OH)_2$ .[2] A mixture of 1048 mg of $AlCl_3 \cdot 6H_2O$, 299 mg of 2,5-hydroxyterephthalic acid, 36 mg of NaOH and 10 mL methanol was fitted in a 30 mL Teflon insert, which was placed in a stainless steel autoclave. Hereafter, the autoclave was placed in an oven for 5 hours at 125 °C. A yellow product was obtained after filtration. The synthesized product was thoroughly washed five times on the filter paper with demineralized water. The residue was dried in air to obtain CAU-1-$(OH)_2$.

*S.1.1.3 - CAU-8*

The synthesis of CAU-8 was performed according to literature. [3] In a 30 mL Teflon insert, 2000 mg of 4,4′-benzophenonedicarboxylic acid, 2466 mg of $Al_2(SO_4)_3 \cdot 18H_2O$, 8 mL of deionized $H_2O$ and 12 mL of DMF were mixed to a suspension. The insert was placed in an autoclave and heated up in the oven to 140 °C in 1 hour. The autoclave was kept at this temperature for 12 hours and then cooled down to room temperature. The reaction was followed by a filtration step. The obtained powder was thoroughly washed with 40 mL of DMF (Aldrich, 99.8%). After another filtration, the white solid was washed with water. Finally, the powder was dried in air.

*S.1.1.4 - CAU-10-H*

According to literature,[4] CAU-10-H was synthesized by adding 160 mg of isophthalic acid, 640 mg of $Al_2(SO_4)_3 \cdot 18H_2O$, 0.8 mL of DMF and 3.2 mL of $H_2O$ to a Teflon insert, sealed within a stainless steel autoclave. The insert was placed in an oven, which was kept at 135 °C for 12 hours. The product, obtained from filtering, was dispersed in deionized water by sonication. The dispersion was filtered again and the white powder was dried in air under ambient conditions.

*S.1.1.5 - CAU-10-$NH_2$*

A mixture of 360 mg of 5-aminoisophthalic acid (Aldrich, 94%), 477.6 mg of $AlCl_3 \cdot 6H_2O$ (Aldrich, 99%), 1.2 mL of DMF (Aldrich, 99.8%) and 4.8 mL of deionized $H_2O$ was made to synthesize CAU-10-$NH_2$, as described in literature.[4] This mixture was made in a Teflon insert, which was placed in a stainless steel autoclave. The autoclave was kept at 120 °C for 12 hours in an oven. A pale pink solid was obtained. In similarity to the work-up of CAU-10-H, the solid was dispersed in deionized water by sonication for 30 minutes. The dispersion was filtered off and the residue was dried in air to obtain the final product.

*S.1.1.6 - CAU-10-OH*

For the synthesis of CAU-10-OH, as adopted from literature,[4] 4 mL of DMF and 16 mL of deionized $H_2O$ with 1000 mg of 5-hydroxyisophthalic acid and 1352 mg of $AlCl_3 \cdot 6H_2O$ were mixed in a 30 mL Teflon insert within a steel autoclave. The autoclave was placed in an oven which was set to 120 °C for 12 hours. The residue of the following filtration was redispersed in deionized water by sonication for 30 minutes. After a final filtration, the product was obtained by drying in air.

**S.1.2 - Synthesis of CAU-10 supported on alumina supports**

Synthesis of CAU-10-H on either α- or γ-alumina was performed by using the aluminium ions leached from the supports directly, effectively replacing $Al_2(SO_4)_3 \cdot 18H_2O$ by a molar equivalent amount of $Al_2O_3$. To have a satisfying amount of beads and to compensate for the fact that, effectively, not all alumina is involved in the reaction, this equivalent amount is doubled. This results in a Teflon insert filled with ~190 mg of either α- or γ-alumina, 160 mg of isophthalic acid, 0.8 mL of DMF and 3.2 mL of deionized $H_2O$. Additionally, to some of the synthesis mixtures either 0.11 ml acetic acid or 0.16 ml HCl solution (37% wt.) was added. The Teflon insert was then placed in a stainless steel autoclave and kept at 135 $^oC$ for 12 hours inside an oven. As there is an anticipated amount of excess organic linker on the alumina beads after synthesis, these were washed overnight with DMF to remove any unreacted isophthalic acid and subsequently washed overnight with $H_2O$ to remove the DMF. Finally the beads were dried at 100 $^oC$ in air overnight.

**S.1.3 - Synthesis of CAU-10-H supported on metallic aluminium**

An aluminium square plate of 20 by 20 mm (~550 mg) with the corners cut off was placed in a Teflon insert. The molar ratios and reaction conditions were equivalent to the hydrothermal syntheses with γ-alumina (see S.1.2). Thus, again the decision was made to double the amount

of moles of aluminium because evidently not all aluminium present will participate in the reaction. Due to the high molar amount of aluminium, the synthesis liquid volume is enlarged compared to sections S.1.1. and S.1.2. To the Teflon insert containing the aluminium plate (~550 mg), 850 mg of isophthalic acid, 4.2 ml of DMF and 17 ml of deionized $H_2O$ were added. Additionally, to some of the synthesis mixtures either 1.7 ml acetic acid or 1.7 ml HCl solution (37% wt.) was added. The Teflon insert was then placed in a stainless steel autoclave and kept at 135 $^oC$ for 12 hours inside an oven. Subsequently these plates were washed overnight with DMF and subsequently washed overnight with $H_2O$ to remove the DMF. Finally the beads were dried at 100 $^oC$ in air overnight.

**S.1.4 - Equipment**

$N_2$ adsorption at 77 K was measured a Quantachrome Autosorb-6B with equilibration time of 2 minutes. Prior to adsorption measurements, samples were degassed for 16 hours at temperatures varying between 150 °C and 250 °C under vacuum. The exact temperature at which degassing was performed was chosen in accordance with TGA data. $H_2O$ adsorption was measured on a Quantachrome Autosorb-1 with an equilibration time of 10 minutes, with installed vapour capability. Pretreatment was the same as for $N_2$ adsorption. For the repeated adsorption measurements, samples were pretreated *ex situ* between subsequent measurements.

XRD measurements were carried out on a PANalytical X'pert PRO diffractometer. The machine used a CO-Kα X-ray source, operating at 45 kV and 40 mA. Thermo-gravimetric analysis (TGA) was measured on a Mettler Toledo TGA/SDTA 851e. The samples were heated in air from room temperature to 800 °C with a rate of 5 °C per hour. The measurement device is equipped with simultaneous differential thermal analysis (SDTA).

Scanning electron microscopy (SEM) microscopy was performed with either Philips XL20 or Jeol JSM 6010AL.

## S.2 - Characterization of different CAU-materials (powder)

This section contains XRD-patterns (Figure S 1), $N_2$ adsorption isotherms (Figure S 2), comparison of measured pore volumes with values reported in literature (Table S 1), TGA- (Figure S 3) and SDTA-profiles (Figure S 4) of synthesized CAU-1, CAU-1-$(OH)_2$, CAU-8, CAU-10-H, CAU-10-$NH_2$ and CAU-10-OH and SEM images of CAU-10-H powder (Figure S 5).

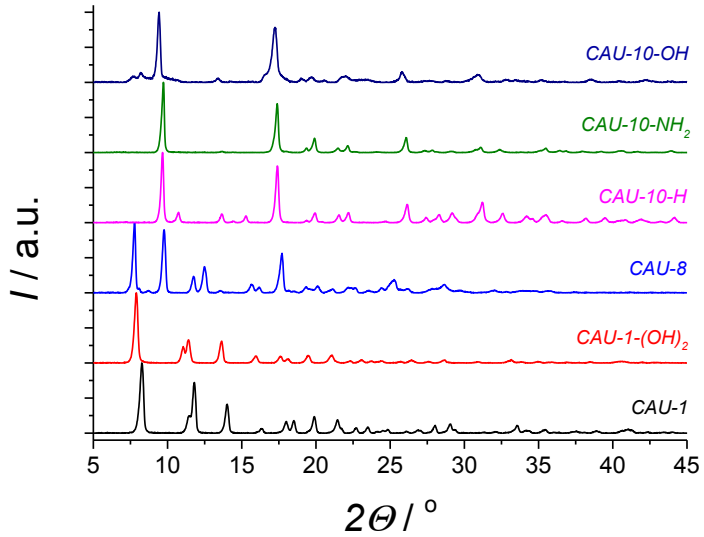


**Figure S 1:** X-ray diffraction patterns of CAU-1, CAU-1-$(OH)_2$, CAU-8, CAU-10-H, CAU-10-$NH_2$ and CAU-10-OH. Measured with Co-*Kα* radiation.

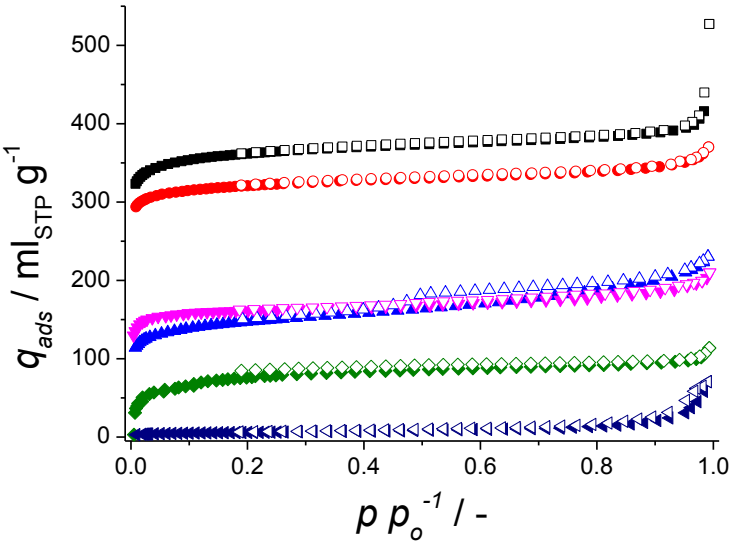


**Figure S 2**: Nitrogen adsorption isotherms at 77 K for CAU-1 (■), CAU-1-$(OH)_2$ (●), CAU-8 (▲), CAU-10-H (▼), CAU-10-$NH_2$ (◆) and CAU-10-OH (◀).

**Table S 1:** Reported and measured pore volumes of materials under investigation, all determined for $p/p_o = 0.5$.

| Material | $V_p$ lit. / ml $g^{-1}$ | $V_p$ this work / ml $g^{-1}$ |
|---|---|---|
| CAU-1 | 0.64 [1] | 0.61 |
| CAU-1-$(OH)_2$ | - | 0.50 |
| CAU-8 | 0.23 [3] | 0.25 |
| CAU-10-H | 0.25 [4] | 0.25 |
| CAU-10-$NH_2$ | - | 0.13 |
| CAU-10-OH | - | - |

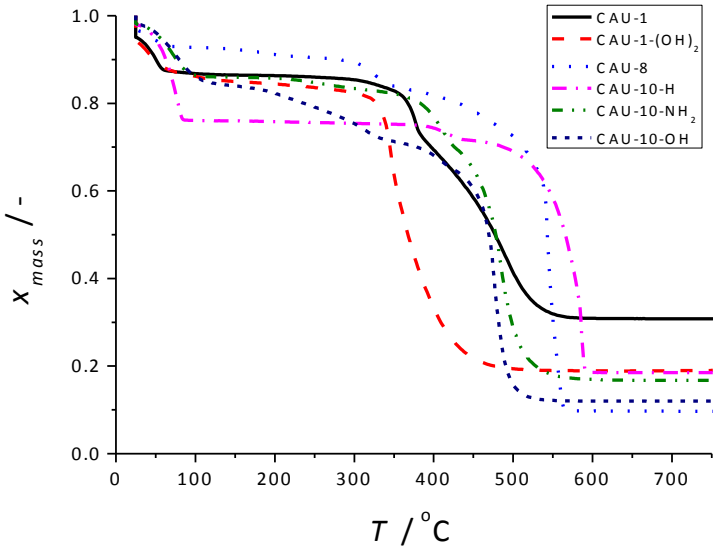


**Figure S 3:** TGA-profiles of CAU-1 (*black solid*), CAU-1-$(OH)_2$ (*red dashed*), CAU-8 (*blue dotted*), CAU-10-H (*pink dot-dash*), CAU-10-$NH_2$ (*olive dot-dash*) and CAU-10-OH (*dark blue dashed*). Measured in a flow of 100 ml $min^{-1}$ air with a heating rate of 5 °C $min^{-1}$.

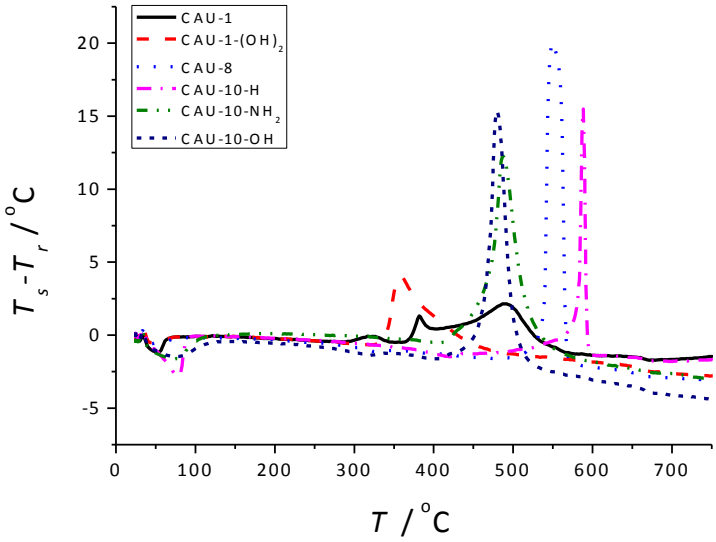


**Figure S 4:** SDTA-profiles of CAU-1 (*black solid*), CAU-1-$(OH)_2$ (*red dashed*), CAU-8 (*blue dotted*), CAU-10-H (*pink dot-dash*), CAU-10-$NH_2$ (*green dash-dot-dot*) and CAU-10-OH (*dark blue short dashes*). Measured in a flow of 100 ml $min^{-1}$ air with a heating rate of 5 °C $min^{-1}$. $T_s$ sample temperature and $T_r$ reference temperature.

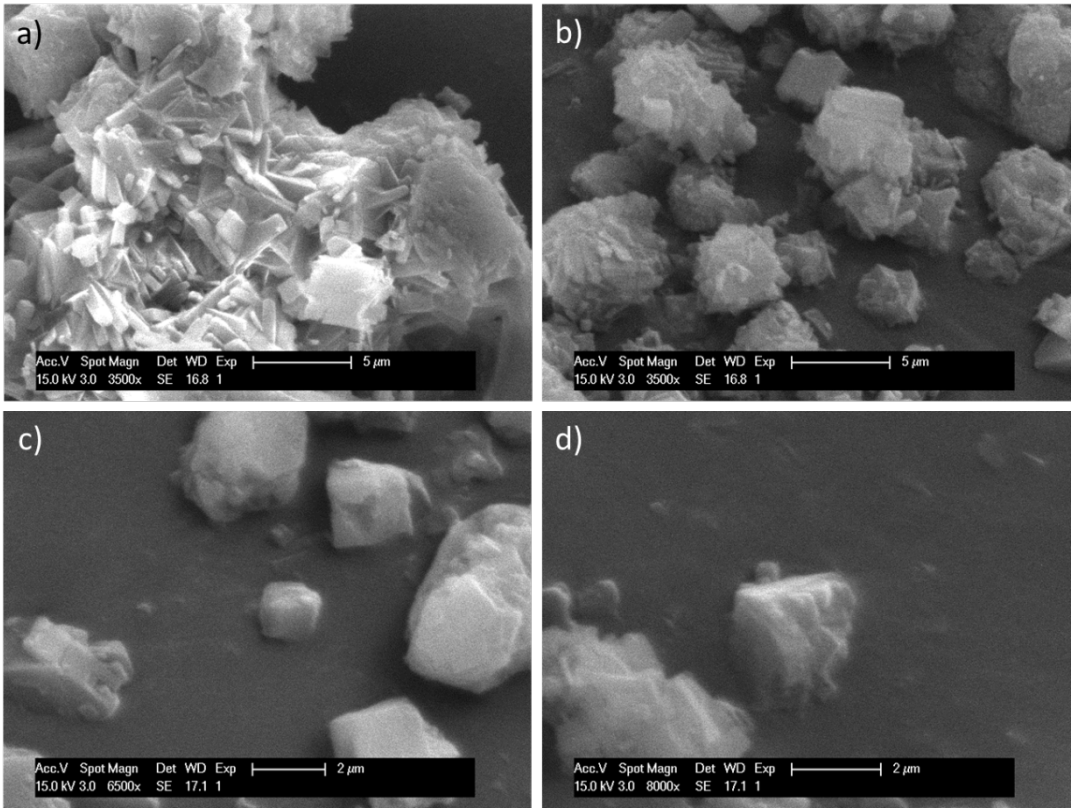


**Figure S 5:** Various SEM images of synthesized CAU-10-H powder.

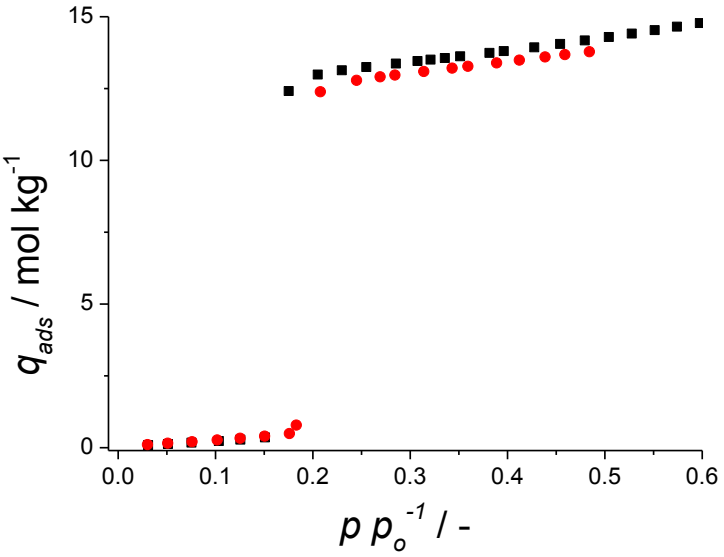


**Figure S 6:** $H_2O$ adsorption isotherms of CAU-10-H at 298 K (■) and 308 K (●). Estimated Isosteric heat of adsorption, on average is about -54 kJ mol$^{-1}$ from the step in uptake onwards.

## S.3 - Characterization of CAU-10-H on alumina supports

This section contains TGA- (Figure S 7) and SDTA-profiles (Figure S 8) of syntheses of CAU-10-H on α-alumina, TGA- (Figure S 9) and SDTA-profiles (Figure S 10) of CAU-10-H on γ-alumina, and XRD patterns (Figure S 11), $N_2$ adsorption isotherms (Figure S 12) and water adsorption measurements of CAU-10-H on γ-alumina (Figure S 13). Low magnification SEM pictures of these beads (Figure S 14) and of the interior of a purposely cracked open bead (Figure S 15) are presented as well. Furthermore, it can be seen that there are two crystal shapes present on the surface, as depicted in Figure S 16. Both rhombic crystals, roughly 5-15 µm diameter, and larger spherical crystals, about 40-60 µm in size, appear on the surface. Without acid the latter seems predominant, with acetic acid and even more with HCl, rhombic crystals become more present. Crystals obtained from bulk synthesis of CAU-10-H resemble rhombic crystals (Figure S 5), though the average size is slightly lower (2- 5 µm).

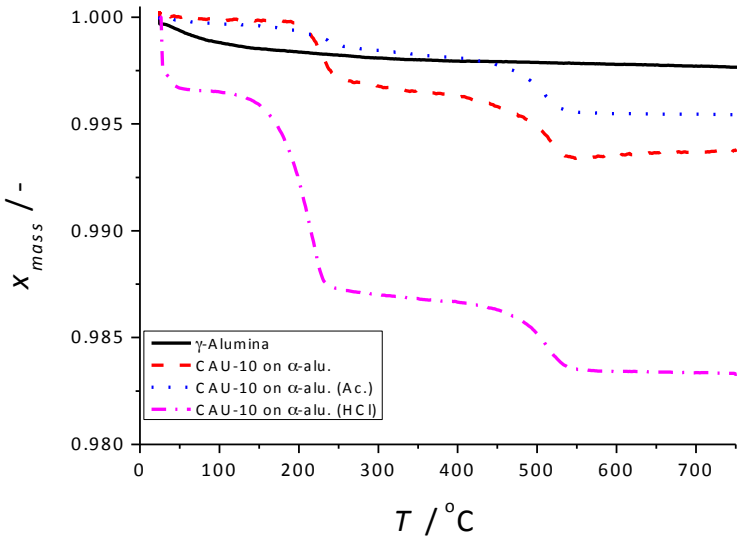


**Figure S 7:** TGA-profiles of α-alumina and CAU-10-H synthesized on α-alumina (*black solid*), either using no acid (*red dashed*), acetic acid (*blue dotted*) or hydrochloric acid (*pink dot-dash*). Measured in a flow of 100 ml $min^{-1}$ air with a heating rate of 5 $^{o}C$ $min^{-1}$.

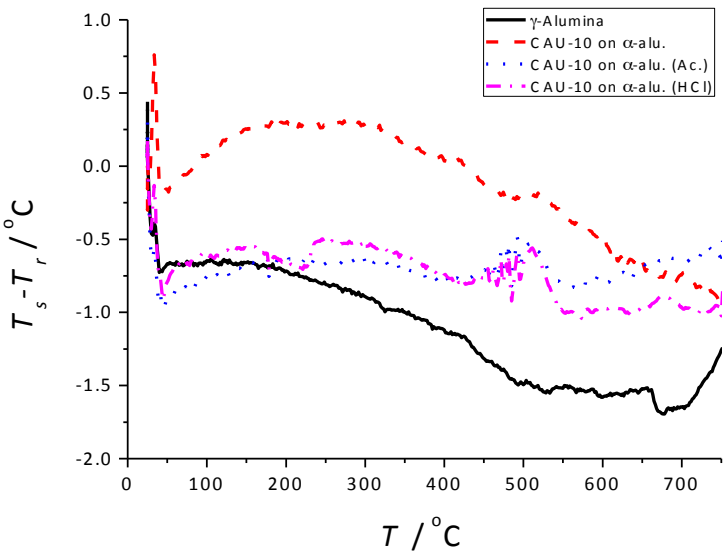


**Figure S 8:** SDTA-profiles of α-alumina and CAU-10-H synthesized on α-alumina (*black solid*), either using no acid (*red dashed*), acetic acid (*blue dotted*) or hydrochloric acid (*pink dot-dash*). Measured in a flow of 100 ml $min^{-1}$ air with a heating rate of 5 °C $min^{-1}$. $T_s$ sample temperature and $T_r$ reference temperature.

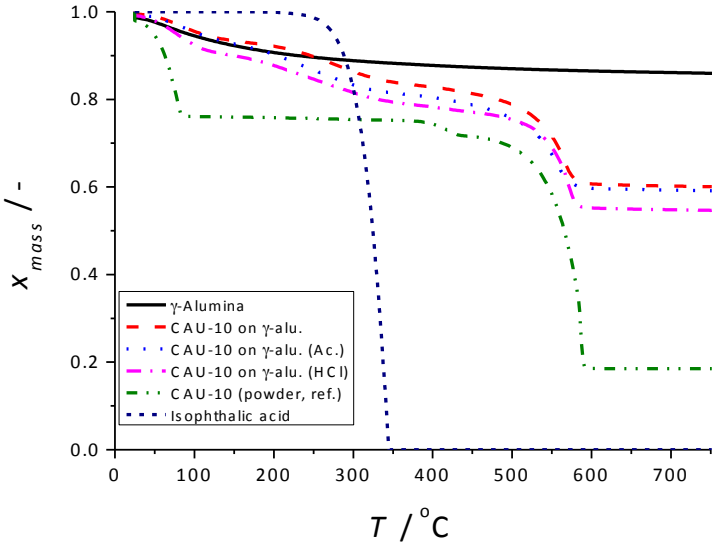


**Figure S 9:** TGA-profiles of γ-alumina (*black solid*), CAU-10-H synthesized on γ-alumina either using no acid (*red dashed*), acetic acid (*blue dotted*) or hydrochloric acid (*pink dash-dot*), CAU-10 reference powder (*green dash-dot-dot*) and of isophthalic acid (*dark blue short dashes*). Measured in a flow of 100 ml $min^{-1}$ air with a heating rate of 5 °C $min^{-1}$.

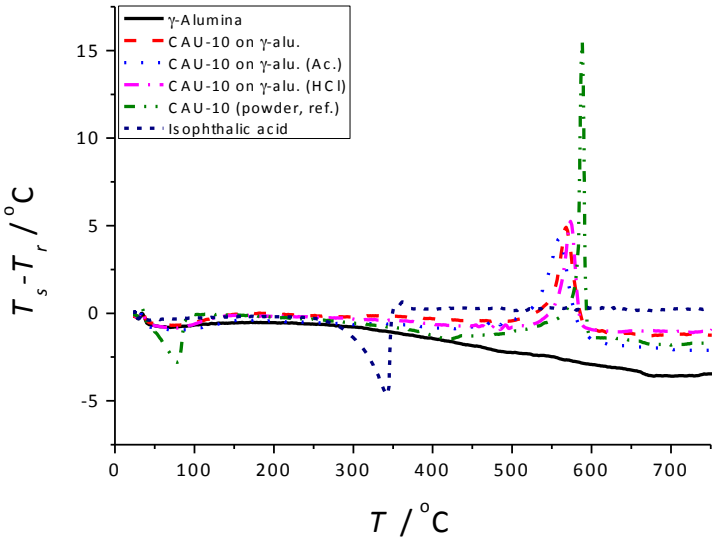


**Figure S 10:** SDTA-profiles of of γ-alumina (*black solid*), CAU-10-H synthesized on γ-alumina either using no acid (*red dashed*), acetic acid (*blue dotted*) or hydrochloric acid (*pink dash-dot*), CAU-10 reference powder (*green dash-dot-dot*) and of isophthalic acid (*dark blue short dashes*). Measured in a flow of 100 ml $min^{-1}$ air with a heating rate of 5 $^{o}C$ $min^{-1}$. $T_s$ sample temperature and $T_r$ reference temperature.

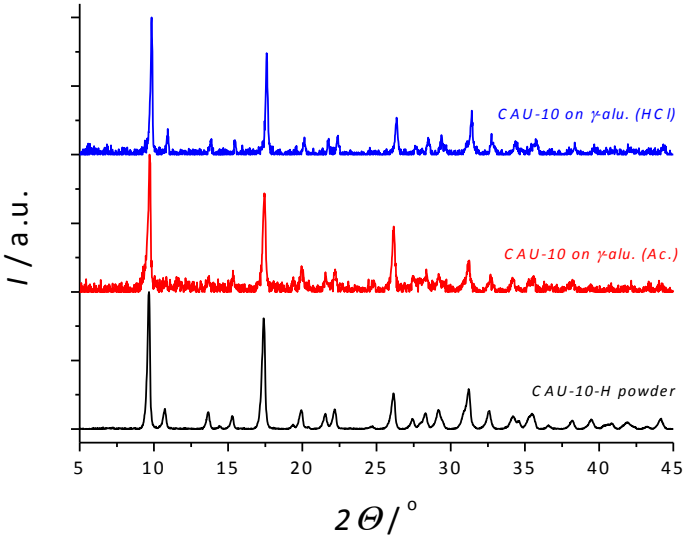


**Figure S 11:** X-ray diffraction patterns of synthesized CAU-10-H (powder, *bottom*) and CAU-10-H synthesized on γ-alumina either with acetic acid (*middle*) or hydrochloric acid (*top*). Measured with Co-*Kα* radiation. No clear pattern could be collected from a bead after synthesis without any acid addition.

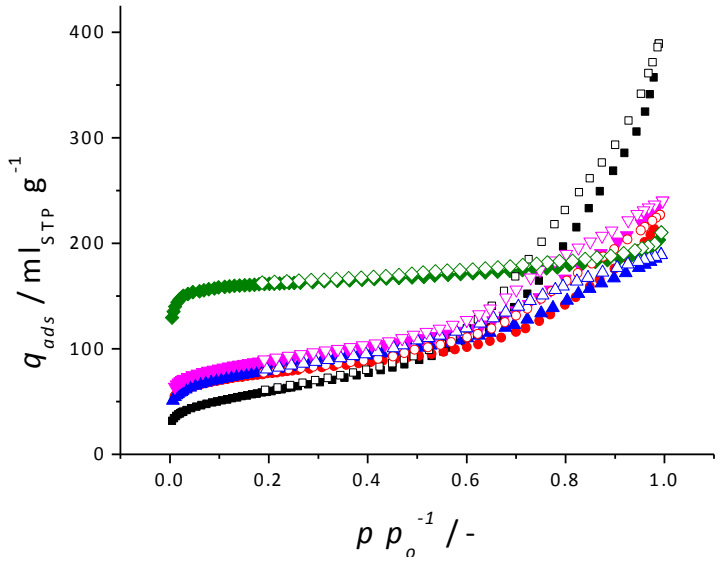


**Figure S 12:** Nitrogen adsorption isotherms at 77 K for γ-alumina (■), CAU-10-H on γ-alumina w/o addition of acid (●), CAU-10-H on γ-alumina with acetic acid (▲), CAU-10-H on γ-alumina with HCl (▼) and for comparison CAU-10-H of the pure powder sample (◆). Solid symbols adsorption, open symbols desorption branch.

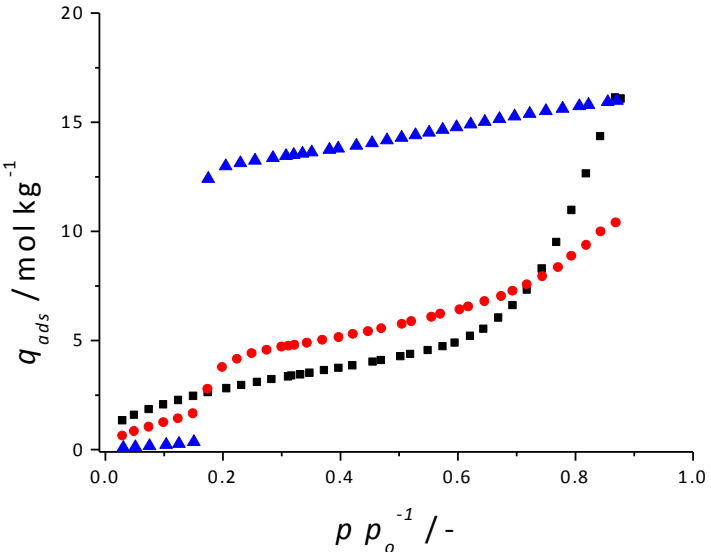


**Figure S 13:** $H_2O$ adsorption isotherms at 298 K of γ-alumina (■), CAU-10-H on γ-alumina with HCl (●) and for comparison CAU-10-H of the pure powder sample (▲).

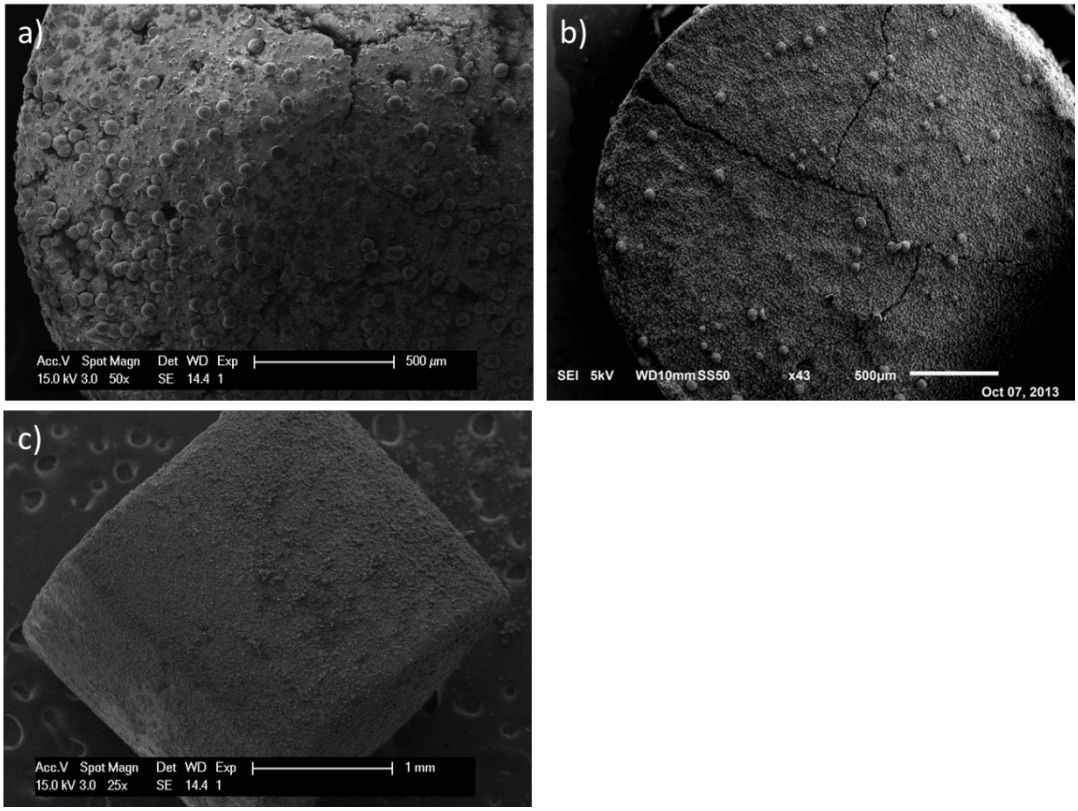


**Figure S 14:** SEM images (low magnification) of CAU-10-H synthesized on γ-alumina beads without any acid (*a*), with addition of acetic acid (*b*) and with addition of hydrochloric acid (*c*).

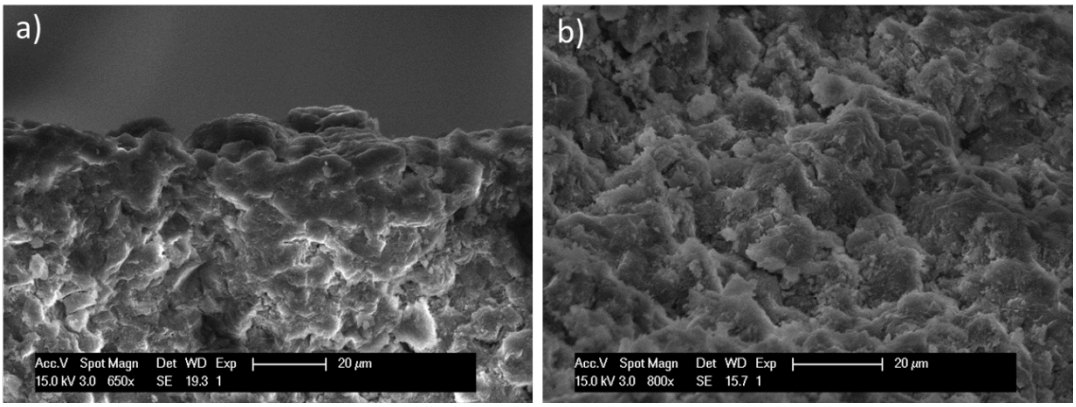


**Figure S 15:** SEM images of exterior surface layer (*a*) and interior (*b*) of a cracked open bead of CAU-10-H containing γ-alumina (HCl synthesis).

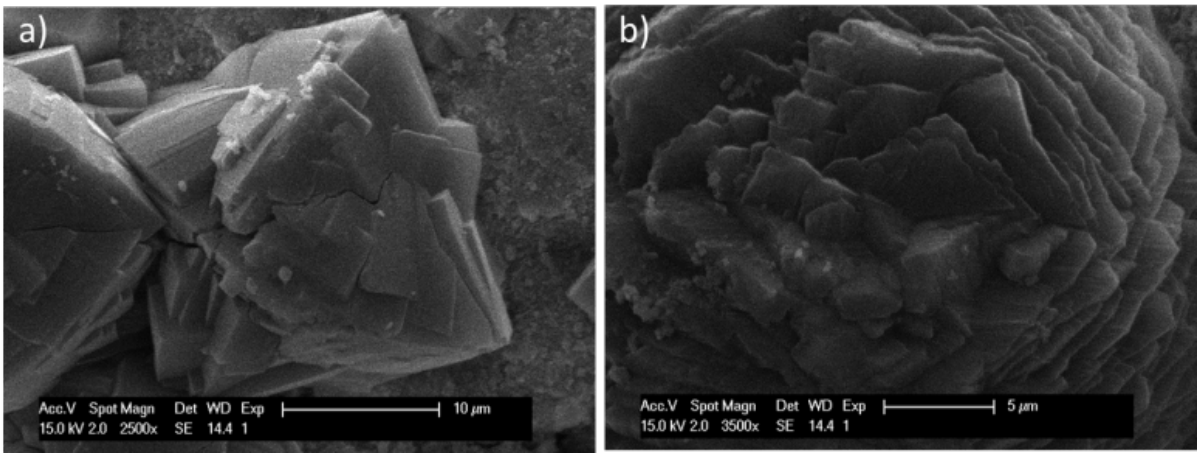


**Figure S 16:** SEM images of the two different crystal shapes present; rhombic (*a*) and spherical (*b*). Taken from synthesis without added acid.

### S.4 - Characterization of CAU-10-H on metallic aluminium

This section contains XRD-patterns of CAU-10-H synthesized on metallic aluminium (Figure S 17). For comparison, the effect on the addition of HCl to powder synthesis of CAU-10-H is depicted as well (Figure S 18).

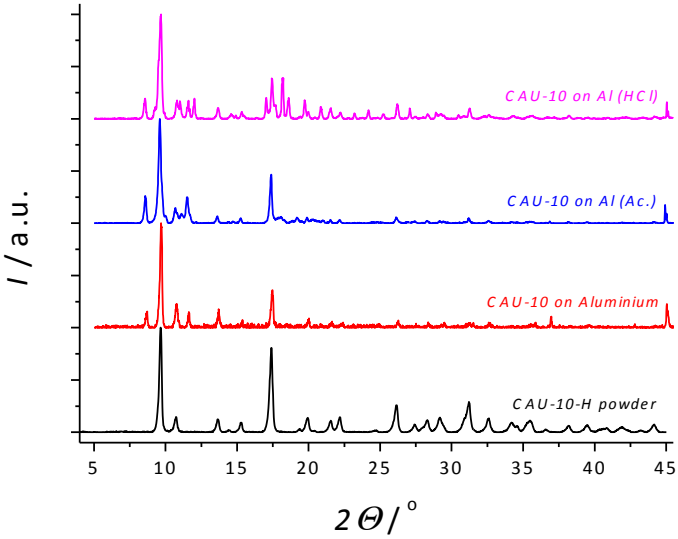


**Figure S 17:** XRD diffraction patterns of synthesized CAU-10-H (powder, *bottom*) and CAU-10-H synthesized on metallic aluminium, using either no acid (*middle bottom*), acetic acid (*middle top*) or hydrochloric acid (*top*). Measured with Co-*Kα* radiation.

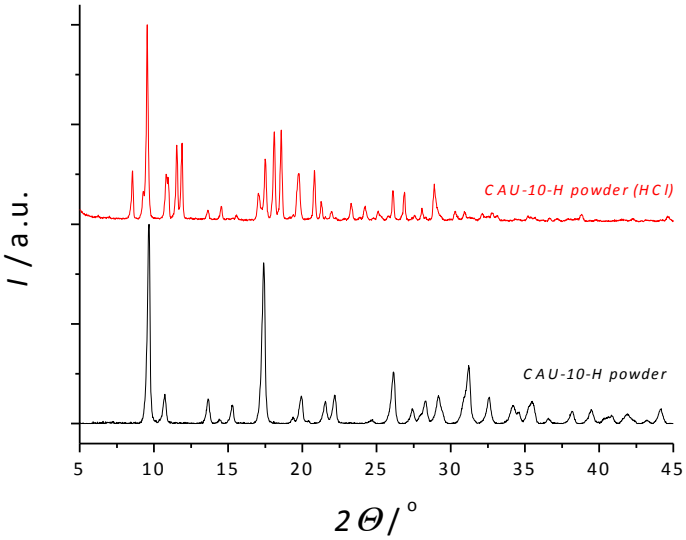


**Figure S 18:** XRD diffraction patterns of synthesized CAU-10-H (powder) both with (*top*) and without addition of hydrochloric acid (*bottom*). Measured with Co-*Kα* radiation.

References


1. T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margiolaki, T. Loiseau, G. Férey, J. Senker and N. Stock, *Angewandte Chemie International Edition*, 2009, **48**, 5163-5166.
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