- Supplementary Information -

Manufacture of dense CAU-10-H coatings for application in adsorption driven heat pumps:

Optimization and characterization

Martijn F. de Lange^{a,b}, Thomas Zeng^{a,c}, Thijs J.H. Vlugt^b, Jorge Gascon^a, Freek Kapteijn^a*

^a Catalysis Engineering, Chemical Engineering Department, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.

^b Engineering Thermodynamics, Process & Energy laboratory, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands

^c Department Thermo-chemical Conversion, Deutsches Biomasseforschungszentrum gemeinnützige GmbH, Torgauer Straße 116, 04347 Leipzig, Germany

SUPPLEMENTARY MATERIAL

Additional information on the following items can be found in this file:

S-1: Pretreatment protocols	
S-2: Characterization methods	3
S-3: Bare support characterisation	
S-4: Direct synthesis	
S-5: Reactive seeding	
S-6: Thermal seeding	
S-7: Comparison	
References	

S-1: Pretreatment protocols

Pretreatment of as-received substrates might be necessary to remove surface impurities, and furthermore to enhance reactivity of the substrate before synthesis. To this end, two different substrate pretreatment methods have been applied, based on previously reported procedures of Arnold *et al.*¹ and Bux *et al.*²

- <u>Method A</u>: The substrates were placed in a flask and submerged in 25 ml of acetone for at least 30 min at room temperature. The substrates were rinsed with deionized water and subsequently submerged in 25 ml deionized water for at least 30 min at room temperature. Afterwards, the substrates were rinsed again with deionized water and dried in a muffle oven at 100 °C for 1 h and stored in sample bottles.
- <u>Method B</u>: The substrates were placed in a flask and submerged in 25 ml of acetone for at least 30 min at room temperature. The substrates were rinsed with deionized water and subsequently submerged in 25 ml diluted HCl solution (6 % in water) for 30 min at room temperature. The substrates were rinsed with deionized water and subsequently submerged in 25 ml deionized water for at least 30 min at room temperature. Afterwards, the substrates were rinsed again with deionized water and dried in a muffle oven at 100 °C for 1 h and stored in sample bottles.

S-2: Characterization methods

X-ray diffraction (XRD). XRD patterns were collected with a PANalytical X'pert PRO diffractometer using a Co-*K* α X-ray source with a Ni-filter, operating at 45 kV and 40 mA in Bragg-Brentano geometry. Measurements were carried out at angles $5 \le 2\theta \le 90^{\circ}$. A divergence slit of 0.3, a scan speed of 0.4 s per step and an increment of 0.02 were defined. Sample rotation was used for MOF powders. Diffraction patterns of

coated substrates have been normalized employing the maximum peak height observed for $2\theta \le 40^{\circ}$, disregarding reflections from the aluminium substrate in the normalization, to better envisage the formed structure(s). Especially for substrates with a low coverage, reflections of CAU-10-H and possible by-product(s) would be hardly visible otherwise. For selected powder sample(s), a special sample holder has been employed that can be sealed with an X-ray transparent, leak-tight dome (type A100 B33, Bruker), to be able to measure dehydrated samples, dried and loaded onto the holder in a glove box.

Scanning electron microscopy (SEM). Scanning electron micrographs were obtained with a Jeol JSM 6010AL. For (coated) substrates, backscattered electron imaging (shadowed images) was applied at low vacuum mode (pressure of 30 Pa) operating with a high voltage of 20 kV, working distance (WD) 9 - 12 mm and spot size typically adjusted to 50. With this set of parameters, the yield of back-scattered electrons could be increased and charging effects could be minimized, and highest resolution for the images were obtained. For powder samples, secondary electron imaging was applied with a voltage of 5-10 kV, with a fixed working distance of 10 mm and a spot size of 50. Samples were sputtered with gold before analysis to minimize charging effects.

Infrared spectroscopy (IR). IR spectra were recorded with a Thermo Fisher Scientific, type Nicolet 8700 FT-IR in reflectance mode. The measurements were performed in a spectral range of 400 to 4000 cm⁻¹ using a mid-IR source. 124 scans were recorded for each spectrum. IR spectra for loaded substrates were obtained without further additional drying. Both the background and the spectrum of the bare substrates (measured once per substrate) were subtracted from the spectra of CAU-10-H synthesized on supports. For CAU-10-H powder, the background was recorded 4 every measurement using KBr powder. Again measurements were performed in reflectance mode.

Thermo-gravimetric analysis (TGA). Thermo-gravimetric analyses were performed using a Mettler Toledo TGA/SDTA 851e / SF / 1100°C with a resolution of 1 μ g. The substrates were cut into small pieces (30 - 80 mg) and inserted into alumina crucibles with a capacity of 30 μ l (for powders roughly 30 mg was used). The samples were heated from 25 to 800 °C in a flow of air (100 ml/min). A heating rate of 5 °C/min was applied. Simultaneous differential thermal analysis (SDTA) provides information on the endo- or exothermic processes associated with the recorded mass change during TGA experiments.

Nitrogen physisorption. Nitrogen physisorption measurements (at 77 K) were performed with a Micromeritics TriStar III. The loaded substrates were cut into rectangles of 20 x 5 mm and inserted into a sample tube with a diameter of 12 mm. MOF powders were inserted, without further modification, in a sample tube with a diameter of 9 mm. In both cases, pretreatment consisted of evacuation for 16 h at 150 °C using a Micromeritics VacPrep 061 with a heating rate of 10 °C/min.

Volumetric water adsorption. Water adsorption isotherms were measured on a Micromeritics 3Flex, routinely at 298 K. Pretreatment consisted of evacuation for 16 h at 150 °C using a Quantachrome MasterPrep with a heating rate of 5 °C/min. A second isotherm was measured at 288 K, for the calculation of the isosteric enthalpy of adsorption. The isosteric enthalpy of adsorption, $\Delta_{ads}H$, for a given amount adsorbed, q, can be calculated from adsorption isotherms at two or more different temperatures, using:³

$$\Delta_{\text{ads}} H_{q} = R \left(\frac{\partial \ln p}{\partial \left(\frac{1}{T} \right)} \right)_{q}$$
(S.1)

Here R is the universal gas constant, p is the absolute pressure and T is the temperature. Using this equation, it is (tacitly) assumed that adsorption is fully reversible (no chemisorption occurs), that both the internal energy of the adsorbent surface and the adsorbent structure don't change during adsorption, and equilibrium is reached between adsorbent and adsorbate.

Gravimetric water adsorption. Cyclic ad- and desorption measurements were performed with a Rubotherm magnetic suspension balance (resolution 0.01 mg), equipped with a vapour dosing unit. The evaporator temperature (vapour dosing unit) was fixed at 22 °C, whilst the measurement temperature (sample chamber) was alternated between 45 and 75 °C. Both the vapour dosing and the measurement temperature were controlled with thermostat baths (Julabo FP25-Me and FP 50-Me, respectively). Pretreatment was performed and monitored in situ. Evacuation was applied at 150 °C until no further decrease in mass could be observed (< 4 h, generally).

S-3: Powder synthesis

CAU-10-H has been synthesized employing either conventional or microwave heating. For comparison, XRD patterns (Fig. S1), TGA and SDTA profiles (Fig. S2) and adsorption isotherms of water and nitrogen (Fig. S3) are shown. SEM images of both powders are shown in Fig. S4.



Figure S1: XRD patterns for hydrated CAU-10-H powder synthesized using conventional and microwave heating.



Figure S2: TGA (*left*) and SDTA (*right*) profiles of CAU-10-H powder synthesized by conventional and microwave synthesis. Measurements were performed using a flow of air (100 ml/min) and a heating rate of 5 °C/min. Here T_s is the sample temperature and T_r the reference temperature.



Figure S3: Nitrogen adsorption (*left*, 77 K) and water adsorption (*right*, 298 K) isotherms of CAU-10-H synthesized by conventional heating (\blacksquare) and by microwave heating (\bigcirc). Closed symbols depict adsorption, open desorption.



Figure S4: SEM images of CAU-10-H synthesized with microwave synthesis (*a*, scale bar represents 10 μ m) and with conventional synthesis (*b*, scale bar represents 10 μ m, *c*, scale bar represents 5 μ m).

S-3: Bare support characterisation

Characterization of the pristine supports by XRD and SEM images is presented in Fig. S5. Comparing the XRD patterns of both m-Al and a-Al to that of a simulated aluminium pattern reveals that preferential orientation exists for the aluminium in both substrates. SEM microscopy unveils a difference in physical appearance of the substrates. Where m-Al shows unidirectional grooves across the surface, the surface of a-Al contains spherical blisters, as result of the anodization process. Nitrogen and water isotherms have been measured on pristine m-Al and a-Al substrates (Fig. S6).



Figure S5: XRD patterns of bare *m*-*Al* and *a*-*Al* supports and a simulated metallic aluminium pattern (*left*) and SEM images of the same bare supports (*right*, scale bar represents 100 μm).



Figure S6: Nitrogen adsorption (*left*, 77 K) and water adsorption (*right*, 298 K) isotherms of a-Al (\blacksquare) and *m*-Al (\bullet , only H₂O). Closed symbols depict adsorption, open desorption.

For *a-Al*, nitrogen adsorption reveals mesoporosity, not surprisingly as the anodization layer is supposed to be porous. Interestingly, even though the amount adsorbed is not that high, based on the total mass of the whole sample, the desorption hysteresis closes completely. The adsorbed amount is small, because compared to the mass of the non-porous, non-adsorbing bulk aluminium layer, the mass of the anodized oxidic layer is significantly smaller. The adsorption hysteresis that is displayed by *a-Al* substrates when water is adsorbed does not fully close. This might well be due to the stronger interactions of water with the support.

S-4: Direct synthesis

Initial experiments to increase coverage of CAU-10-H on aluminium utilized the supports as received, *i.e.* without pretreatment. As pretreatment has a more profound effect on anodized aluminium (*vide infra*), focus is on metallic aluminium for these experiments.

Addition of aluminium sulphate

As all Al-ions are extracted from the support in case of the standard synthesis protocol (SSP), it might well be that the availability of these ions is a limiting factor for crystal growth. Hence it might make sense to add additional aluminium. Syntheses of CAU-10-H on m-Al (without pretreatment) with various amounts of added aluminium sulphate are performed. XRD patterns of both the coated substrates and filtration residues are shown in Fig. S7.



Figure S7: XRD patterns for CAU-10-H synthesis directly on *m*-Al substrates (without pretreatment) with varying amounts of $Al_2(SO_4)_3$ 18H₂O, both for obtained substrates (*left*) and filtration residues (*right*), when possible. No added salt represents results obtained for the standard synthesis protocol (SSP).

With increasing amount of added aluminium, less CAU-10-H can be found on the surface of the support, and more in the solution (Fig. S7). The more Al-ions are added, the less CAU-10-H can be found on the surface of the support as the inflections of

CAU-10-H diminish with respect to those of the support. Additionally, at higher Alcontent in the synthesis solution, the undesired secondary crystalline phase is more dominantly observed. In fact, already at 2 g aluminium sulfate, the visible layer already detaches from the support during post-processing (Fig. S8). This apparent layer consists of crystals formed in solution that agglomerated on the surface and are not attached to the support.



Figure S8: Photographs of CAU-10-H synthesized directly on *m*-*Al* (without pretreatment) using standard conditions (SSP) (*left*) and with addition of 2 g Al₂(SO₄)₃^{-18H₂O (*right*).}

Influence of hydrochloric acid

Another method of influencing crystal growth is by varying the amount of hydrochloric acid added. HCl induces stronger dissolution of Al-ions from a given support⁴ and has been found to influence the crystallization kinetics of certain MOFs.^{5, 6} SEM images of CAU-10-H synthesized on *m*-*Al* with 50, 100 and 200% HCl, with respect to the standard synthesis protocol, are presented in Fig. S9. Halving the amount of added HCl results in a slightly lower coverage. For both syntheses (50 and 100%), an undesired broad crystal size distribution is observed. Interestingly, when the amount of HCl is doubled (Fig. S9), coverage is greatly reduced and crystals seemingly appear only along grooves, likely created by the preferential dissolution of Al³⁺ ions from

local aluminium crystal boundaries in the metallic support, as was observed in a previous study.⁷



Figure S9: SEM images of directly synthesized CAU-10-H on *m*-*Al* (without pretreatment) using 50% HCl (*a*), 100% HCl (*b*, SSP) and 200% HCl (*c*) (*top* scale bar represents 500 μ m, *bottom* scale bar represents 100 μ m).

In Fig. S10 the XRD patterns of syntheses on both *m*-*Al* and *a*-*Al* with different concentrations of HCl are shown.



Figure S10: XRD patterns for CAU-10-H synthesized directly on *m*-*Al* (left) and *a*-*Al* (*right*), both without pretreatment, varying the amount of HCl solution (37% in aq. solution, in all cases) added to the synthesis mixture, compared to standard synthesis conditions (denoted as 100% HCl).

X-ray diffraction does not only indicate a reduced crystal coverage when 200% HCl is employed, but also a large fraction of the crystals belong to the unidentified secondary phase, also observed previously.⁷ As lower pH results in a faster release of Al³⁺-ions, the added HCl will lead to promotion of the secondary phase, similar as in experiments with high concentrations of aluminium sulfate.

For *a-Al*, even without HCl, significant by-product formation is observed. When HCl is used, a poorly crystalline product is observed. The first trial applying standard reaction conditions (SSP) to *a-Al* substrates led to the deterioration of the substrate (Fig. S11).





Figure S11: Photographs of CAU-10-H directly synthesized on *a-Al* (without pretreatment) at standard conditions. First (*left*) and second (*right*) attempt.

Upon replication of this initial trial, the substrate could be recovered, indicating the poor reproducibility under acidic conditions for untreated *a*-*Al*, but this did not yield satisfactory results, as very broad reflections of CAU-10-H were observed (Fig. S10), indicating that the excess of Al due to dissolution of the anodized layer leads to mostly amorphous material. In Fig. S12 the SEM images of CAU-10-H synthesized on *a*-*Al* are shown, both with and without added hydrochloric acid, revealing indeed a foam-like morphology of the product with very inhomogeneous substrate coverage.



Figure S12: SEM images of directly synthesized CAU-10-H on *a-Al* (without pretreatment) using no HCl (*a*) and 100% HCl (*b*, second attempt) (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Without the use of any HCl this is not observed, though the *a-Al* substrate is not fully covered and significant amounts of crystalline by-products are observed (Figs. S10, S12). Clearly, the anodized layer makes the substrate surface more reactive. The added isophthalic acid linker is thus more than sufficient to extract Al^{3+} -ions from the support. The utilization of additional acids thus is not a necessity and actually has an adverse effect on the formation of MOF crystals on *a-Al* substrates. Hence, the standard synthesis protocol is adjusted for all further experiments employing anodized aluminium, excluding the addition of any additional acid (SSPa).

DMF concentration

the DMF:H₂O ratio can be adjusted to regulate kinetics of growth. The reduction of DMF leads to increased crystal growth and nucleation in the synthesis of MIL-53(Al)-NH₂, a MOF that also contains aluminium-hydroxide chains.⁸ In addition, a water-based synthesis would be more environmentally benign. SEM images of experiments with reduced amounts of DMF, employing *m*-*Al* are presented in Fig. S13. In Fig. S14 XRD patterns are displayed for the

samples of these experiments for both m-Al and a-Al. When the amount of DMF is slightly reduced (for syntheses on m-Al) crystal size distribution becomes more homogeneous but more by-product(s) are formed (Fig. S13-14) and for DMF contents below 25% (with respect to standard synthesis) apparently no crystals are formed (Figs. S13-S14).



Figure S13: SEM images for CAU-10-H synthesized directly on *m*-*Al* (without pretreatment), employing 75% (*a*), 50% (*b*), 25% (*c*) or 0% (*d*) of DMF (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).



Figure S14: XRD patterns for CAU-10-H synthesized directly on *m*-Al (*left*) and *a*-Al (*right*), both without pretreatment, varying the amount of DMF in the synthesis mixture, compared to standard synthesis conditions (\equiv 100% DMF).

TGA and SDTA profiles, shown in Fig. S15 for *m*-*Al*, indicate that a large fraction of the crystals belong to recrystallized isophthalic acid.



Figure S15: TGA (*left*) and SDTA (*right*) profiles for filtration residues for the direct synthesis of CAU-10-H on *m-Al* (without pretreatment) for 75, 50 and 25 % DMF (*solid lines*). For comparison, the TGA-profiles of isophthalic acid (*dot-dashed lines*) are included. Measured using a flow of air (100 ml/min) and a heating rate of 5 °C/min.

for syntheses with varying amounts of DMF on *a-Al*, SEM images are shown in Fig. S16.



Figure S16: SEM images for CAU-10-H synthesized directly on *a-Al* (without pretreatment), employing 75% (*a*), 50% (*b*), 25% (*c*) or 0% (*d*) of DMF (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Influence of temperature and reaction time (untreated)

In Fig. S17, the XRD pattern and a SEM image of CAU-10-H synthesized on *m*-Al at 115 $^{\circ}$ C are shown. The effect of reaction time on syntheses at 135 $^{\circ}$ C is shown in Fig. S18 for metallic aluminium substrates.



Figure S17: XRD patterns for CAU-10-H on 115 °C and 135 °C (SSP) on *m*-Al, without pretreatment (*left*) and SEM image after synthesis at 115 °C (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).



Figure S18: SEM images for CAU-10-H synthesized directly on *m*-*Al* (without pretreatment), for 6 (*a*), 12 (*b*, SSP), 18 (*c*) and 24 (*d*) h of reaction time (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

In Fig. S19 XRD patterns of CAU-10-H on *m-Al* substrates without pretreatment are presented to show the effect of synthesis reaction time.



Figure S19: XRD patterns for CAU-10-H synthesized directly on *m*-*Al* without pretreatment, for 6, 12 (SSP), 18 and 24 h of reaction time.

Pretreatment

Previous experiments, especially those employing *a*-*Al* and HCl (Figs. S10-S12), might indicate that differences exist between substrate samples from the same batch, driven perhaps by varying levels of impurities present. This issue might be mitigated by proper pretreatment of the substrate. Pretreatment, in the context of this work, can have two possible effects. Firstly, it removes likely pollutants present on the substrate surface that might have an adverse effect on synthesis.^{1, 9-11} Secondly, it can be employed to create additional OH-groups, in order to improve reactivity.^{1, 2, 12, 13} To this end, substrate pretreatment methods A and B (Experimental) are employed systematically on both metallic and anodized aluminium. For *m*-*Al* substrates, surface

coverage and crystal size distributions seem hardly altered when either of the pretreatment methods is applied (SEM images, Fig. S20).



Figure S20: SEM images for CAU-10-H synthesized directly on *m*-*Al*, depicting the effect of pretreatment. Results for untreated (*a*), method A (*b*) and method B (*c*) (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

This is notably different for anodized aluminium substrates, as SEM pictures reveal that coverage is systematically increased from untreated to samples pretreated with method A and further with method B (Fig. S21).



Figure S21: SEM images for CAU-10-H synthesized directly on *a*-*Al*, indicating the effect of pretreatment. Results for untreated (*a*), method A (*b*) and method B (*c*) (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

The difference might well be attributed to the fact that the metallic aluminium substrate of *a-Al*, has a very high quality and introduction of impurities by the anodization process is highly likely. In addition, XRD patterns (Fig. S22) indicate that, as pretreatment becomes more severe, the formed CAU-10-H layer increases in purity and by-product formation is hampered. For metallic aluminium, especially pretreatment method B induces by-product formation (Fig. S22), and thus should be avoided when these substrates are utilized.



Figure S22: XRD patterns for CAU-10-H synthesized directly on *m*-*Al* (*left*) and *a*-*Al* (*right*), indicating the effect of pretreatment. Results for untreated samples and after treatment with method A or method B.

Reproducibility

The XRD patterns in Fig. S23 show the influence of pretreatment of synthesis reproducibility for both *m*-*Al* and *a*-*Al* supports. SEM images of three individual experiments under identical conditions are shown for the synthesis of CAU-10-H on untreated *m*-*Al* (Fig. S24), pretreated *m*-*Al* (method A, Fig. S25), untreated *a*-*Al* (Fig. S26) and pretreated *a*-*Al* (method B, Fig. S27).



Figure S23: XRD patterns for CAU-10-H synthesized directly on *m*-*Al* (*left*, SSP) and *a*-*Al* (*right*, SSPa) for three separate synthesis trials, without substrate pretreatment (*top*) and after pretreatment (*bottom*, method A for *m*-*Al*, B for *a*-*Al*).

The effect of pretreatment method A for *m-Al* and especially method B for *a-Al*, has a beneficial effect on reproducibility, as indicated by the XRD patterns of three repeated syntheses under identical conditions (Fig. S23). Clearly, for untreated *a-Al* several differences between the XRD patterns of the samples of the three trials can be observed, whereas the XRD patterns for the three trials employing pretreated (method B) supports are much more identical. For sample *m-Al* this can also be observed, but both without and with treatment more impurities can be observed. SEM images confirm these trends (Figs. S24-S27).

Figure S24: SEM images for trial 1 (*a*), 2 (*b*), and 3 (*c*) for the direct synthesis of CAU-10-H on *m*-*Al* without pretreatment (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S25: SEM images for trial 1 (*a*), 2 (*b*), and 3 (*c*) for the direct synthesis of CAU-10-H on *m*-*Al* employing pretreatment method A (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S26: SEM images for trial 1 (*a*), 2 (*b*), and 3 (*c*) for the direct synthesis of CAU-10-H on *a*-*Al* without pretreatment (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S27: SEM images for trial 1 (*a*), 2 (*b*), and 3 (*c*) for the direct synthesis of CAU-10-H on *a*-*Al* employing pretreatment method B (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Influence of reaction time (after pretreatment)

For untreated *m*-Al supports it was found that extending the reaction time by 18 h or longer results in severe Ostwald ripening and formation of unwanted by-products (Figs. S18, S19). SEM images for *m*-Al pretreated with method A (Fig. S28) or B (Fig. S29) and *a*-Al,

pretreated with method A (Fig. S30) or B (Fig. S31) for 12, 14 and 16 h reaction time, as well as the accompanying XRD patterns (Fig. S32) indicate that the observed trends do not vary when the support is changed or pretreatment is applied. This as longer reaction timesusing pretreated samples also lead to unwanted Ostwald-ripening behaviour and to a higher population of additional crystalline phase(s) (Figs. S28-S32), as found for untreated *m-Al* (Figs. S18-S19).

Figure S28: SEM images for CAU-10-H synthesized directly on *m*-*Al*, employing pretreatment method A, for 12 (*a*, SSP), 14 (*b*) and 16 (*c*) h of reaction time (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S29: SEM images for CAU-10-H synthesized directly on *m*-*Al*, employing pretreatment method B, for 12 (*a*, SSP), 14 (*b*) and 16 (*c*) h of reaction time (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S30: SEM images for CAU-10-H synthesized directly on *a-Al*, employing pretreatment method A, for 12 (*a*, SSPa), 14 (*b*) and 16 (*c*) h of reaction time (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S31: SEM images for CAU-10-H synthesized directly on *a-Al*, employing pretreatment method B, for 12 (*a*, SSPa), 14 (*b*) and 16 (*c*) h of reaction time (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S32: XRD patterns for CAU-10-H synthesized directly on *m-Al* (*left*) and *a-Al* (*right*), employing pretreatment method A (M.A., *top*) and method B (M.B., *bottom*), for 12, 14 and 16 h of reaction time.

S-5: Reactive seeding

The SEM images of pretreated *m*-*Al* (method A) and *a*-*Al* (method B) after reactive seeding for either 1 or 2 h are shown in Fig. S33. XRD patterns of both substrates after the seeding step are shown in Fig. S34. SEM images after secondary growth on substrates submitted to reactive seeding for either 3 or 4 h, employing a reactant dilution factor of 2 are shown in Fig. S35. Accompanying XRD patterns of both the substrates and filtration residue obtained after secondary growth are shown in Fig. S36.

Figure S33: SEM images after reactive seeding of CAU-10-H on pretreated *m*-*Al* (method A) for 1 h (*a*) and 2 h (*b*) reaction time and on pretreated *a*-*Al* (method B) for 1 h (*c*) and 2 h (d) reaction time (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S34: XRD patterns of substrates after reactive seeding for pretreated *m*-Al (method A) and pretreated *a*-Al (method B), employing a reactive seeding time of 3 or 4 h.

Figure S35: SEM images of CAU-10-H synthesized by reactive seeding and secondary growth with precursor solution diluted by a factor 2, for pretreated *m*-*Al* (method A) employing a reaction time for the seeding step of 3 (*a*) and 4 (*b*) h and for pretreated *a*-*Al* (method B), employing a reaction time for the seeding step of 3 (*c*) and 4 (*d*) h (*top*, scale bar represents 500 μ m, *bottom*, scale bar represents 100 μ m).

Figure S36: XRD patterns of substrates (*left*) and filtration residue (*right*) after reactive seeding and secondary growth with a precursor solution diluted by a factor of 2, for pretreated m-Al (method A) and pretreated a-Al (method B), employing a reactive seeding time of 3 or 4 h.

S-6: Thermal seeding

In Fig. S37, SEM images after thermal seeding with solution 1 on both pretreated *m*-*Al* (method A) and *a*-*Al* (method B) are presented.

Figure S37: SEM images after thermal seeding with solution 1, for pretreated *m*-*Al* (method A) (*a*) and pretreated *a*-*Al* (method B) (*b*).

S-7: Comparison

In Fig. S38 the XRD pattern of CAU-10-H synthesized directly on untreated *a-Al*, conditions under which significant amount of by-product(s) are formed, is compared to possible Al(OH)₃ phases, γ -AlO(OH) and synthesis reactants isophthalic acid and aluminium sulfate. Clearly, none of the patterns match with any of the observed by-product reflections.

Figure S38: XRD patterns of CAU-10-H obtained from direct synthesis (DS.) on untreated (UT.) *a-Al*, compared to selected Al(OH)₃ phases (*left*) and to boehmite (γ -AlO(OH)) and synthesis reactants (*right*).

In Fig. S39, IR spectra of bulk CAU-10-H and pristine *m-Al* and *a-Al* are shown. The spectrum of CAU-10-H contains a sharp absorbance at 3685 cm⁻¹, attributed to the OH-vibrations of the hydroxide groups on the aluminium oxide-hydroxide chains.¹⁴ Furthermore, the CH-vibration at the aromatic ring at 3075 cm⁻¹ is clearly observed.¹⁴ Lastly, the bands at 755 cm⁻¹ and 724 cm⁻¹ are characteristic for 1,3-substituted benzene-rings (out-of-plane-deformation of C-H bonds) and the band at around 1685 cm⁻¹ indicates that DMF might be present inside the pores.¹⁴ For anodized aluminium, the observed broad band between 3660 and 2940 cm⁻¹ corresponds to the OH-vibrations of the aluminium hydroxide, and further indicates hydrogen bonding from water present inside the porous layer,¹⁵ despite the drying process applied. The band around 1600 cm⁻¹ corresponds to the Al=O stretch vibrations of double-bonded oxygen.¹⁵ The two bands at roughly 1230 and 980 cm⁻¹ correspond to Al-OH bending vibrations, of which the latter is likely to be from the surface layer.¹⁵

Figure S39: IR spectra of bulk CAU-10-H (conventional) and pristine *m*-Al and *a*-Al.

Figure S40: IR spectra of CAU-10-H obtained by direct synthesis (DS.) on untreated (UT.) *a*-*Al* and *m*-*Al* and on pretreated *a*-*Al* (M.B.) and *m*-*Al* (M.A.), and by reactive seeding (RS.) on both pretreated *a*-*Al* and *m*-*Al* (*a*-*Al* with *black lines*, *m*-*Al* with *grey lines*).

IR spectra of CAU-10-H coated substrates after secondary synthesis (Fig. S40) show similarity with the recorded spectrum for pure CAU-10-H (Fig. S39). However, there are notable differences as well. Specially, a shoulder is observed at slightly lower wavenumber than the sharp absorbance at 3685 cm⁻¹, which is attributed to the OH-stretch vibrations of the MOF. This shoulder is more predominantly perceived for substrates coated by direct synthesis (DS.) method, for which it is known that a significant amount of by-product is formed. Hence, it is plausible that the by-product contains OH-groups as well. Furthermore, the CH-vibration of the aromatic ring at 3075 cm⁻¹ is generally less strongly observed when more by-product is formed, an indication that the formed by-product might contain no, or at least less, isophthalic acid. The peaks belonging to Al=O (stretch) and Al-OH (bend) of the anodized support at 1600, 1230 and 980 cm⁻¹ are no longer distinguishable. At this point it should be

noted that in addition to the background spectrum, the spectrum of the bare substrate (Fig. S40) is subtracted as well, which is the reason for this. Between the absorbances at 3685 cm⁻¹ and 3075 cm⁻¹, the spectrum is convex for metallic aluminium substrates. This is because the synthesis reaction creates a significant amount of additional Al-OH groups on the surface itself due to leaching. These are clearly not present in the pristine *m*-*Al* support and are thus not subtracted. This phenomenon is not present for the *a*-*Al* supports. In fact, for untreated (UT.) *a*-*Al* after direct synthesis (DS.) this part of the spectrum is concave. Seemingly, compared to the pristine anodized support, Al-OH groups have diminished, due to leaching of this reactive substrate, even without the presence of HCl.

Figure S41: SDTA profiles for *a*-*Al* (*black lines*) and *m*-*Al* (*grey lines*) for untreated (*solid lines*) and pretreated (*dashed lines*) substrates obtained after direct synthesis and after reactive seeding (*dot-dashed lines*) employing pretreated substrates only.

SDTA profiles of selected substrates are shown in Fig. S41 (corresponding TGA profiles in Fig. 7). Both TGA and SDTA clearly indicate the presence of CAU-10-H on the selected substrates. The SDTA profile further indicates some solvent loss at low temperatures (< 150

^oC). Notable exception is the profile for the direct synthesis on pretreated *a-Al*, which shows a broad endothermic peak between 300 and 500 ^oC, followed by a low signal for the exothermic oxidation. The onset of this curve at 300 ^oC might indicate the evaporation of isophthalic acid (Fig. S15), although compared to the pure linker, this process is severely diffusion limited and therefore spread out over a wide temperature range. XRD (Fig. 5) does not indicate the presence of crystalline isophthalic acid, in agreement with a dispersed phase.

Figure S42: N₂ adsorption isotherms (77 K) for direct synthesis on untreated m-Al (\blacksquare) and a-Al (\bullet) and on pretreated m-Al (method A) (\blacktriangle) and a-Al (method B) (\triangledown) and for reactive seeded on pretreated m-Al (method A) (\blacktriangleleft) and a-Al (method B) (\triangleright). Open symbols represent the desorption branch.

In Fig. S42 nitrogen physisorption isotherms are shown for selected samples. In contrast to adsorption on bare *a*-*Al* (Fig. S6), isotherms in Fig. S42 indicate diffusional limitations, as no nitrogen seems to desorb upon pressure decrease, resulting in a hysteresis loop that clearly does not close. This is likely due to the micropores of CAU-10-H, as limitations were also observed for powder obtained from conventional synthesis (Fig. S3). For the samples containing only a small amount of porous material the apparent amount adsorbed becomes

negative, and during pressure decrease an apparent increase in adsorbed amount is observed, because of the wrongly assessed cell volume in these measurements. This effect is strongly magnified when compared to powder measurements.

In Table S1 indicative amounts of CAU-10-H present on selected substrates, based on weighing the substrates before and after coating (both dry), is shown.

Table S1: Indicative amounts of CAU-10-H present on selected substrates, estimated from substrate weighing before and after the synthesis of coatings.

Synthesis method	substrate	Loading based on weighing / mg cm ⁻²
Direct, no pretreatment	m-Al	4.8
	a - $Al^{[a]}$	2.3
Direct, with pretreatment	$m-Al^{[b]}$	7.2
	$a-Al^{[c]}$	4.0
Reactive seeding ^[d]	$m-Al^{[b]}$	3.4
	$a-Al^{[c]}$	1.0

[a] Without HCl. [b] Method A. [c] Method B. [d] With pretreatment, seed reaction time 4 h. *n.d.* means not determinable.

The difference in weight before and after synthesis could be attributed to the deposition of (crystalline) material on the surface. This method likely underestimates loading as during synthesis and/or pretreatment aluminium may have leached from the surface and subsequently dissolved in the synthesis liquid. Furthermore, comparing first the observed loading of CAU-10-H on the two different substrates for the same synthesis method, the amount of MOF is systematically significantly lower for *a-Al*. This can easily be rationalized, as leaching from the reactive anodized amorphous aluminium oxide occurs more readily than from metallic aluminium. Indeed, by weighing no clear indication can be obtained on the amount of CAU-10-H present on a substrate.

References

- 1. M. Arnold, P. Kortunov, D. J. Jones, Y. Nedellec, J. Kärger and J. Caro, *Eur. J. Inorg. Chem.*, 2007, 2007, 60-64.
- 2. H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y.-S. Li and J. Caro, *Chem. Mater.*, 2011, 23, 2262-2269.
- 3. F. Rouquerol, J. Rouquerol and K. Sing, *Adsorption by powders & porous solids*, Academic Press, London, 1999.
- 4. W. Stumm and R. Wollast, *Reviews of Geophysics*, 1990, 28, 53-69.
- 5. M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, 49, 9449-9451.
- 6. M. G. Goesten, P. C. Magusin, E. A. Pidko, B. Mezari, E. J. Hensen, F. Kapteijn and J. Gascon, *Inorg. Chem.*, 2014, 53, 882-887.
- 7. M. De Lange, C. Ottevanger, M. Wiegman, T. Vlugt, J. Gascon and F. Kapteijn, *CrystEngComm*, 2015, 17, 281-285.
- 8. E. Stavitski, M. Goesten, J. Juan-Alcañiz, A. Martinez-Joaristi, P. Serra-Crespo, A. V. Petukhov, J. Gascon and F. Kapteijn, *Angew. Chem. Int. Ed.*, 2011, 50, 9624-9628.
- 9. H. Guo, G. Zhu, I. J. Hewitt and S. Qiu, J. Am. Chem. Soc., 2009, 131, 1646-1647.
- 10. R. Makiura, S. Motoyama, Y. Umemura, H. Yamanaka, O. Sakata and H. Kitagawa, *Nature Mater.*, 2010, 9, 565-571.
- 11. K. Yusenko, M. Meilikhov, D. Zacher, F. Wieland, C. Sternemann, X. Stammer, T. Ladnorg, C. Wöll and R. A. Fischer, *CrystEngComm*, 2010, 12, 2086-2090.
- 12. F. Jeremias, D. Frohlich, C. Janiak and S. K. Henninger, *RSC Adv.*, 2014, 4, 24073-24082.
- 13. S. Hermes, D. Zacher, A. Baunemann, C. Wöll and R. A. Fischer, *Chem. Mater.*, 2007, 19, 2168-2173.
- 14. H. Reinsch, M. A. van der Veen, B. Gil, B. Marszalek, T. Verbiest, D. de Vos and N. Stock, *Chem. Mater.*, 2012, 25, 17-26.
- 15. G. Dorsey, J. Electrochem. Soc., 1966, 113, 169-172.