

ELECTRONIC SUPPORTING INFORMATION

Instant MOFs: continuous synthesis of metal organic frameworks by rapid solvent mixing

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S1: Powder X-ray diffraction

For sample identification, PXRD studies were carried out using a Bruker AXS D8 Advance X-Ray diffractometer operating with Cu-K α 1/2 radiation (λ average = 1.5418 Å); data were measured at room temperature in flat-plate geometry from powders pressed into a Macor ceramic holder.

For the CPO-27 samples, a Panalytical X-Pert Pro MPD diffractometer was used operating with Cu-K α 1 (λ = 1.54056 Å) samples were measured at room temperature in flat-plate geometry from polycrystalline samples pressed in steel sample holders.

Profile refinement was performed using the GSAS suite of software [1].

[1] A. C. Larson and R. B. V. Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 1994

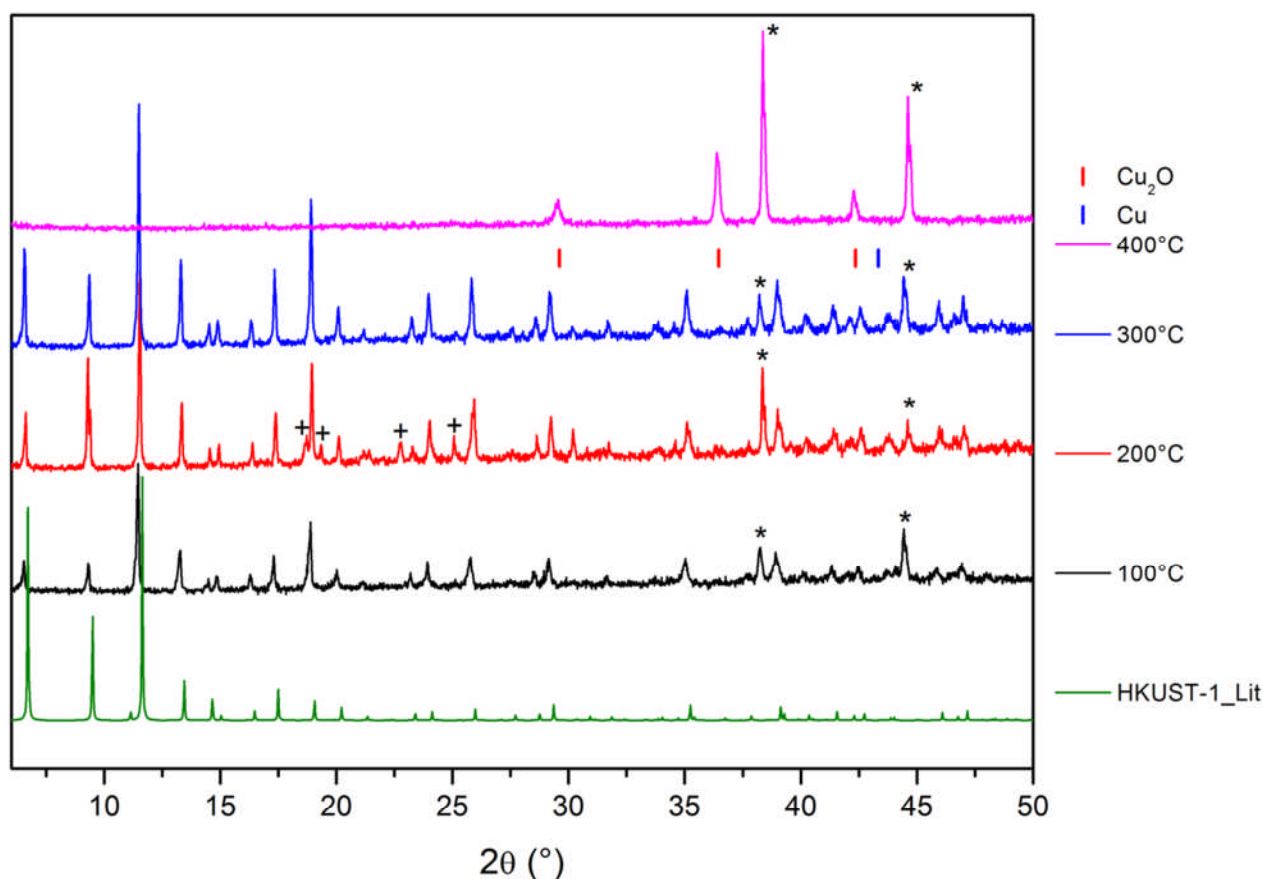


Figure S1.1: Powder XRD patterns of HKUST-1 prepared at various temperatures (concentration of Cu²⁺ = 0.03 M) along with the simulated pattern expected from the published single crystal structure. Note that relative peak intensities are affected by preferred orientation effects, as expected for the anisotropic crystal morphology (Figure 2 of paper). * indicates peaks due to the aluminium sample holder, and + indicates a minor unidentified impurity in the sample prepared at 200 °C. Tick marks of the expected peaks positions for Cu and for Cu₂O are shown.

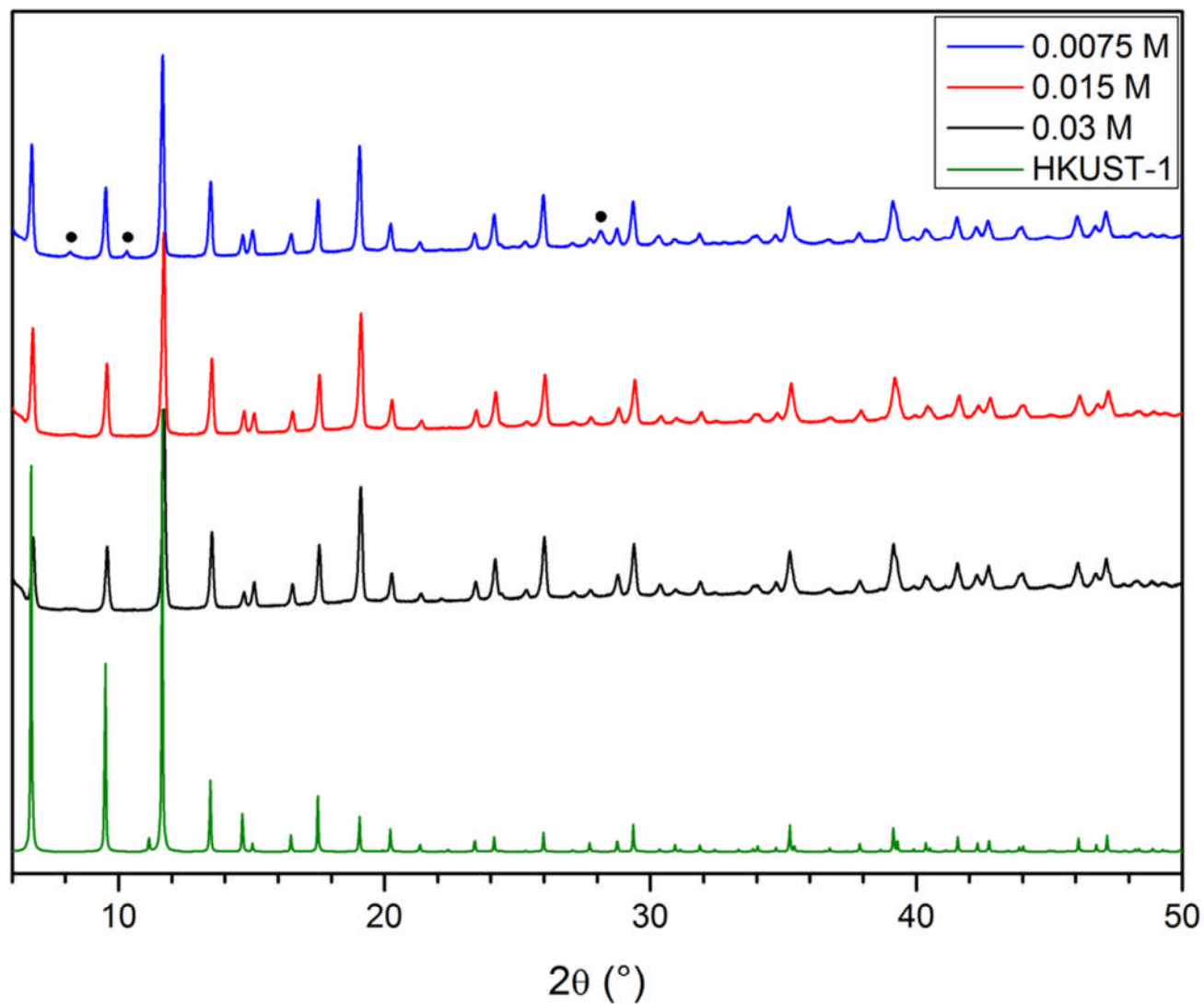


Figure S1.2: Powder XRD patterns of HKUST-1 prepared at 300 °C at different reagent dilutions. Note that relative peak intensities are affected by preferred orientation effects, as expected for the anisotropic crystal morphology (Figure 2 of paper). • indicates peaks due to a minor unidentified impurity in the sample prepared at 0.0075 M concentration.

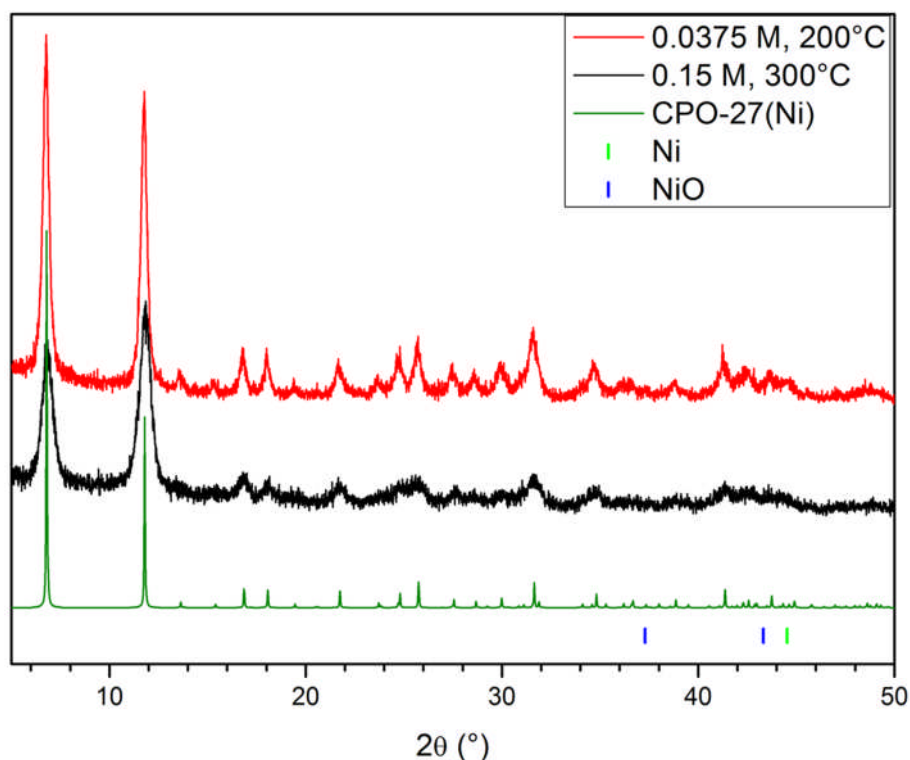


Figure S1.3: Powder XRD patterns of CPO-27 prepared using different conditions. Note that relative peak intensities are affected by preferred orientation effects, as expected for the anisotropic crystal morphology (Figure 3 of paper). The tick marks of expected peak positions of NiO and Ni are included, along with the simulated pattern from the published crystal structure.

S2: Electron Microscopy

Scanning electron microscopy was performed using a Zeiss Supra 55-VP SEM operated at 20 kV under high vacuum was used for imaging. The powdered product was suspended in methanol and sonicated with an ultrasonic bath for 5 minutes and placed onto a piece of clean silicon wafer. After evaporation, samples were placed onto an aluminium stud and gold coated prior to analysis.

HR-TEM images of nanocrystalline CPO-27 were acquired using a JEM-2100 LaB₆ transmission electron microscope operating at 200 kV. The sample was dispersed on a lacy carbon film from a methanol suspension which was reinforced on a copper grid. The suspension was sonicated with an ultrasonic bath for 5 minutes before dispersion.

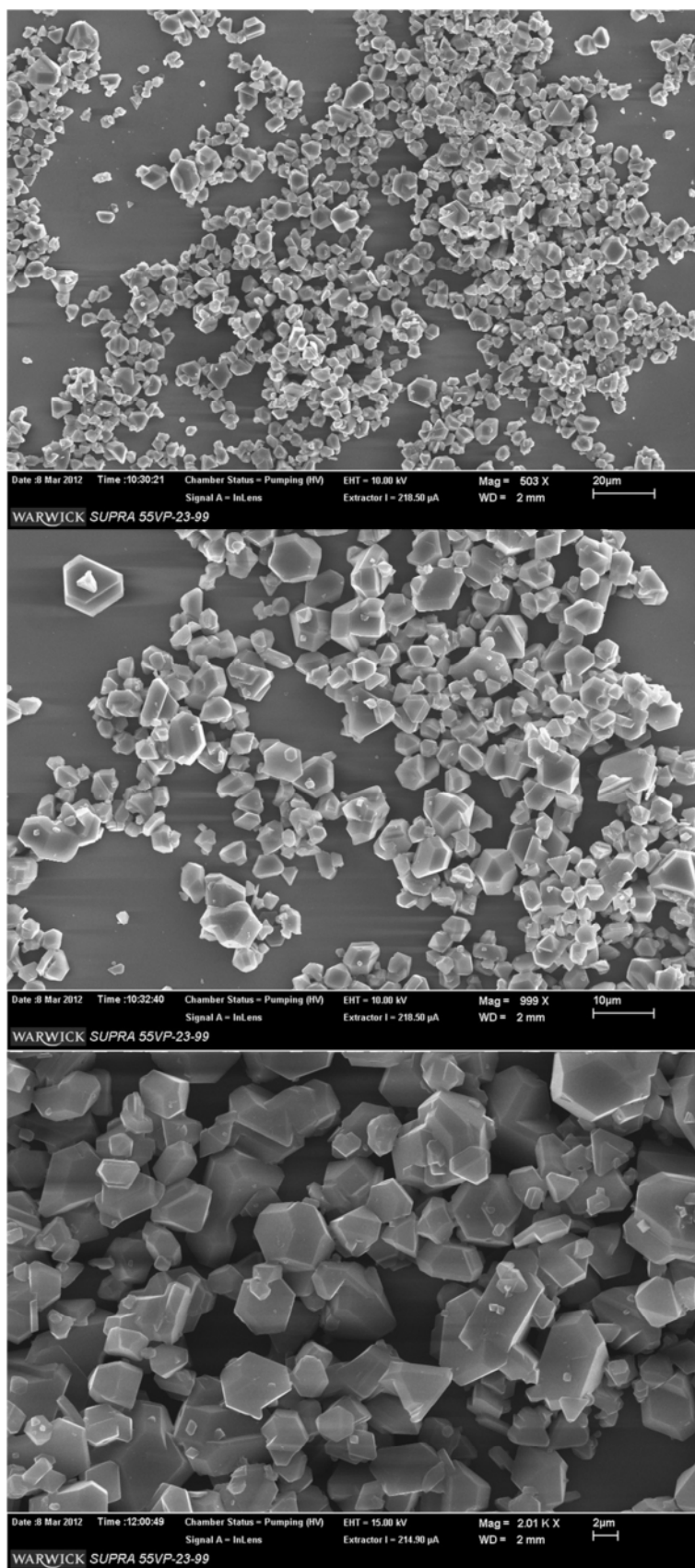


Figure S2.1: SEM Images of HKUST-1 sample prepared at 300 °C with 0.03 M reagent solution (based on Cu^{2+}). Views of the sample with magnification x500 (top), x 1k (middle) and x 2k (bottom)

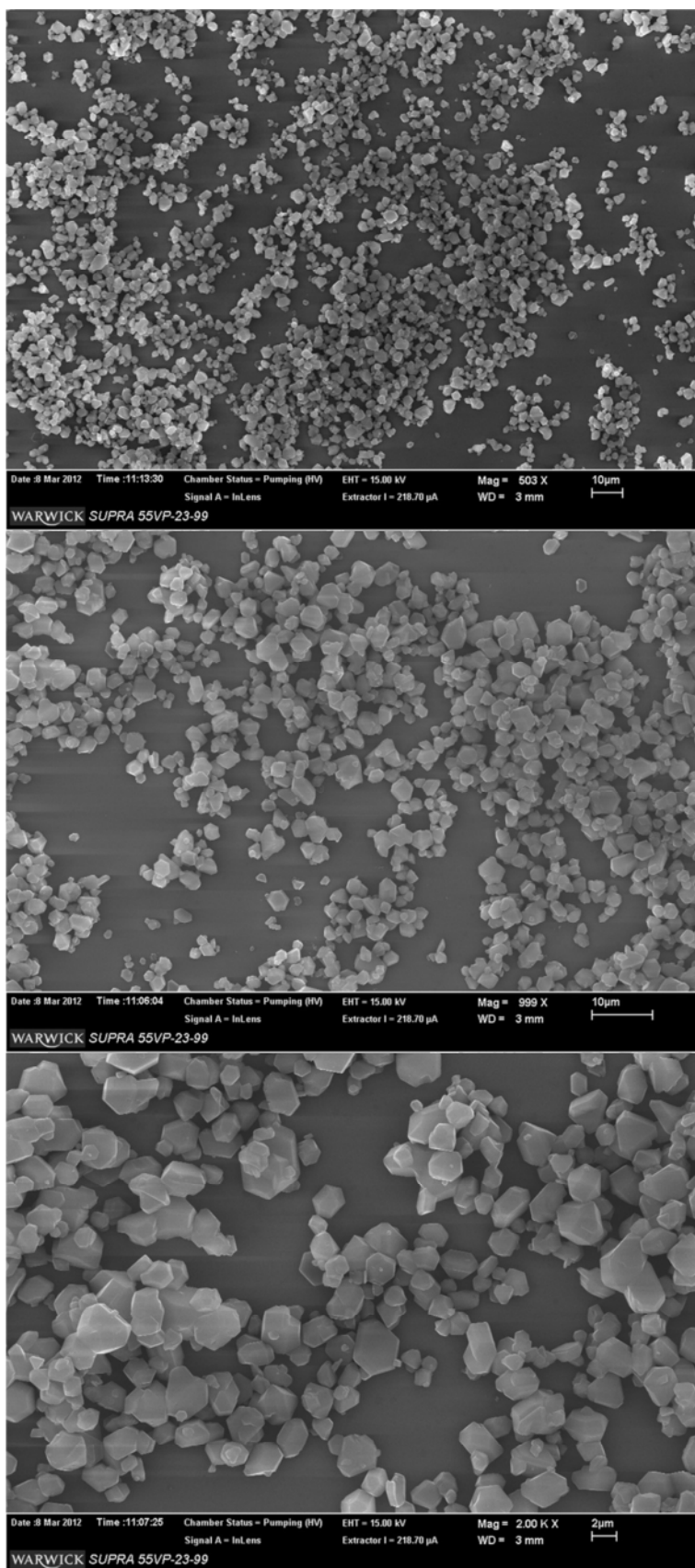


Figure S2.2: SEM Images of HKUST-1 sample prepared at 300 °C with 0.015 M reagent solution (based on Cu^{2+}). Views of the sample with magnification x500 (top), x 1k (middle) and x 2k (bottom)

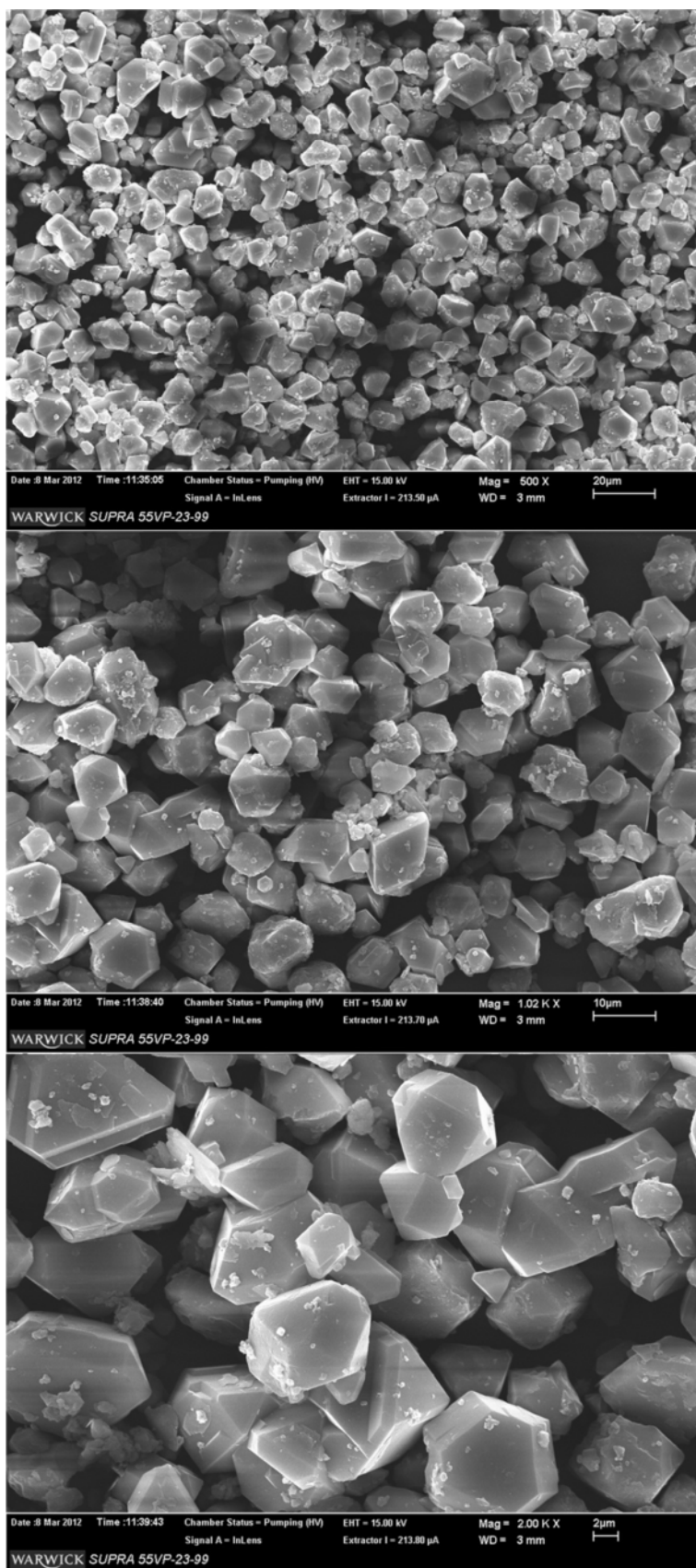


Figure S2.3: SEM Images of HKUST-1 sample prepared at 300 °C with 0.0075 M reagent solution (based on Cu^{2+}). Views of the sample with magnification x500 (top), x 1k (middle) and x 2k (bottom).

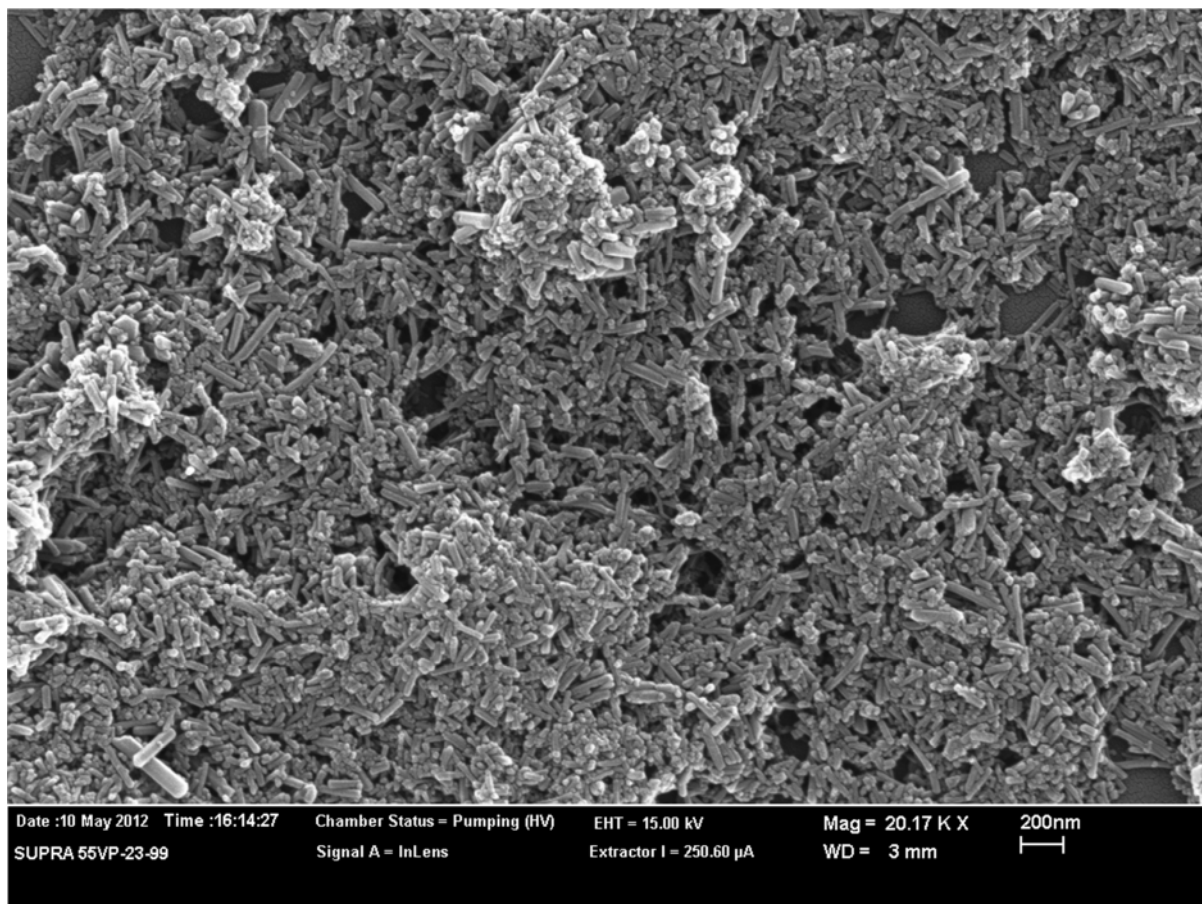


Figure S2.4: SEM Image of CPO-27 sample prepared at 200 °C with 0.015 M reagent solution (based on Ni²⁺).

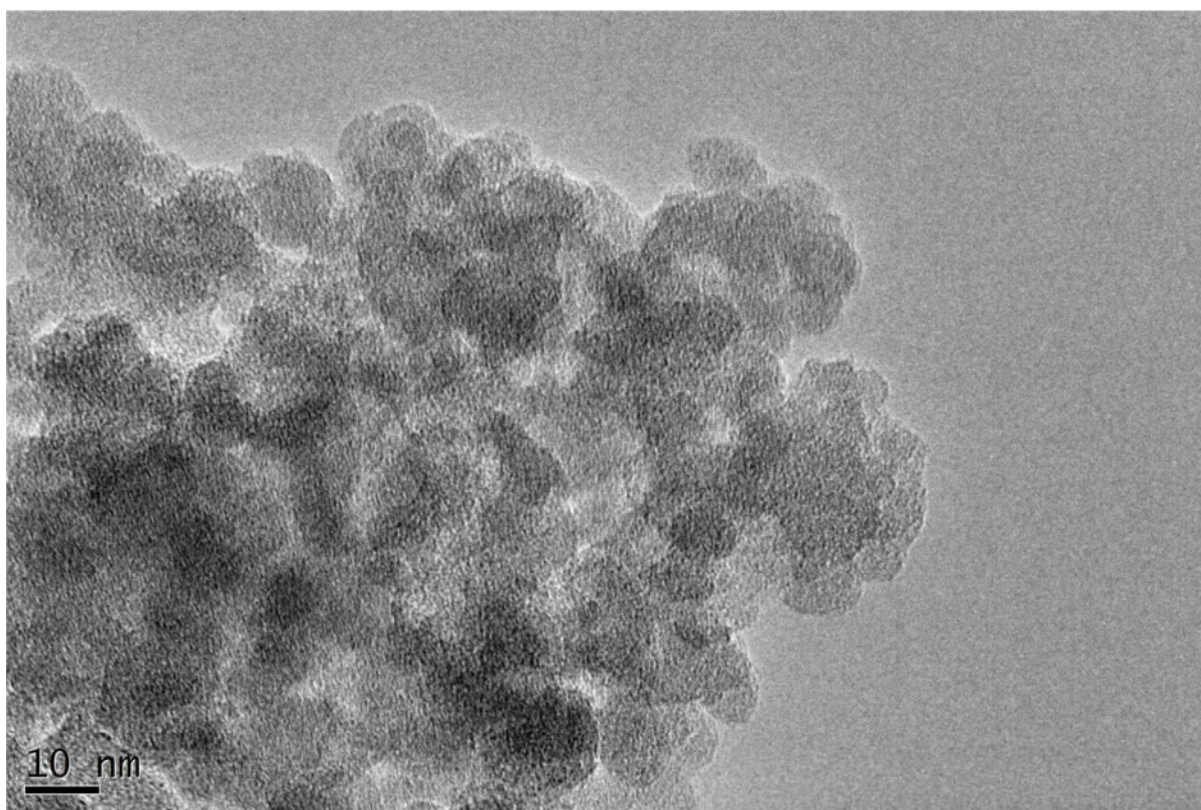


Figure S2.5: TEM image of CPO-27: overview of sample prepared at 300 °C and 0.15 M Ni²⁺ solution.

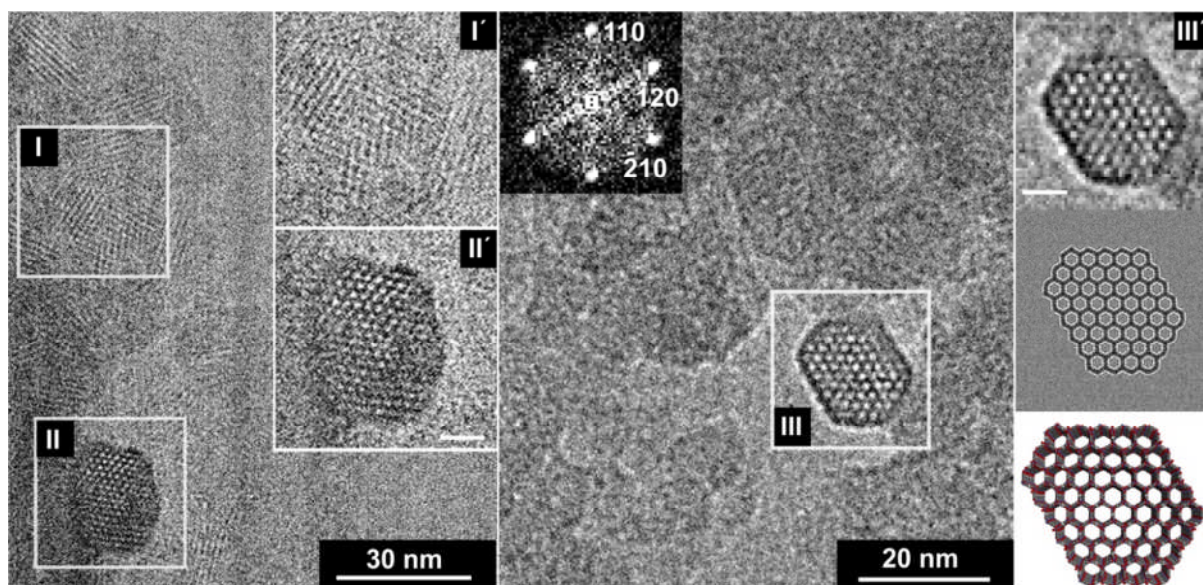


Figure S2.5: HR-TEM images of CPO-27: expanded version of Figure 5 in main paper showing various orientations of nanocrystals for sample prepared at 300 °C and 0.15 M Ni²⁺ solution.

S3: Textural Properties (N₂ Isotherms)

Textural characterisation was carried out with a Micromeritics ASAP 2420 (Norcross, GA, USA) using N₂ as the adsorbate. Approximately 0.20 g of sample was degassed under vacuum at 110 °C for 24 hours. N₂ isotherms were acquired from 1.00 x 10⁻⁷ to 0.99 P/P₀. Helium was used to calculate the free space

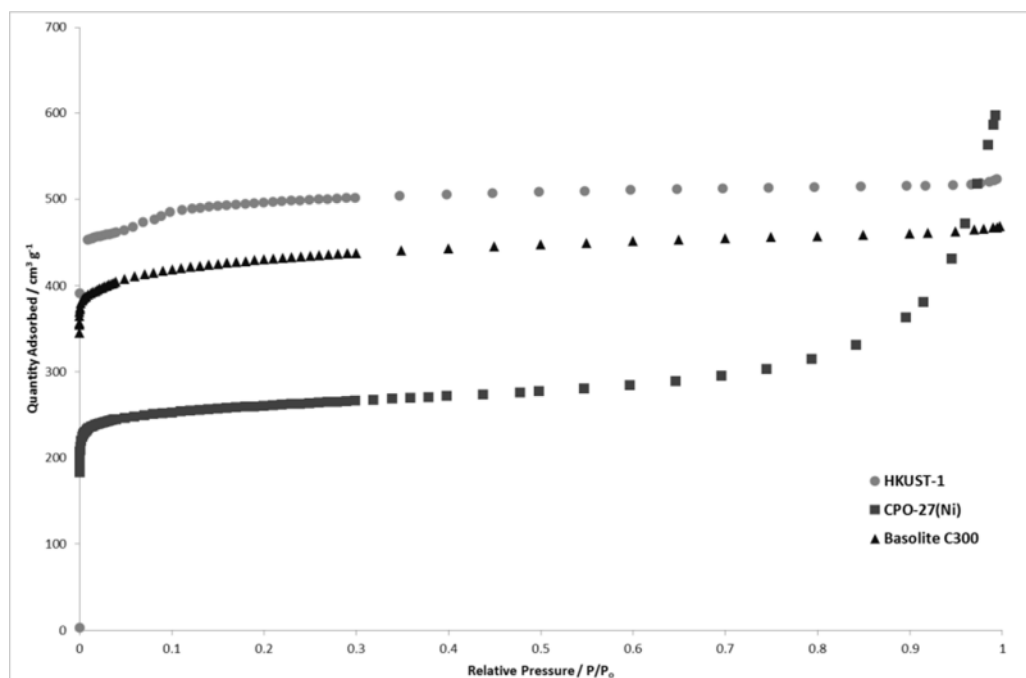


Figure S3.1: N₂ isotherms for the HKUST-1, CPO-27(Ni) and commercial Basolite C300. Samples were washed in excess methanol and dried at 70 °C before study.

Table S3.1 Comparison with surface area data for HKUST-1 and CPO-27 from the literature.

Sample	BET _{SA} / m ² g ⁻¹	Lang _{SA} / m ² g ⁻¹	V _m / cm ³ g ⁻¹	Reference
HKUST-1	1950	1998	0.77	Our sample (prepared at 300 °C, 0.03 M Cu ²⁺)
	1694	1750	0.70	Commercial Basolite, our data
	1800	2257	0.37	J. Vitillo <i>et al. JACS</i> , 2008, 130, 8386
	692.2	917.6	-	S. Chui <i>et al. Science</i> , 199, 283, 1148
	1482	2302	0.828 (0.995 atm)	J. Liu <i>et al. J. Phys. Chem. C</i> , 2007, 111, 9305
CPO-27	1030	1065	0.40	Our sample (prepared at 200 °C, 0.015 M Ni ²⁺)
	1200	1315	0.47	J. Vitillo <i>et al. JACS</i> , 2008, 130, 8386
	1200	1315	-	F. Bonino <i>et al. Chem Mater.</i> 2008, 20, 4957
	1218	1312	0.47 (V _p)	P. D.C. Dietzel <i>et al. Chem Commun</i> , 2010, 46, 4962
	1242	1316	-	S. Chavan <i>et al. Phys. Chem. Chem. Phys.</i> , 2009, 11, 9811–9822

S4: Thermal stability studies

Thermal stability studies were carried using a TA Instruments Q500 TGA (New Castle, DE, USA). Approximately 10 mg of sample (HKUST-1) were placed on to platinum sample pan, and thermal stability was monitored over a temperature range of 25 – 900 °C at a heating rate of 5 °Cmin⁻¹ under the flow of nitrogen (N₂) gas (1 bar, 100 ml min⁻¹). The synthesized sample was compared to Basolite C300 (purchased from Sigma-Aldrich, St. Louis, Missouri, USA) under identical conditions as above. A blank correction was carried out prior to analysis.

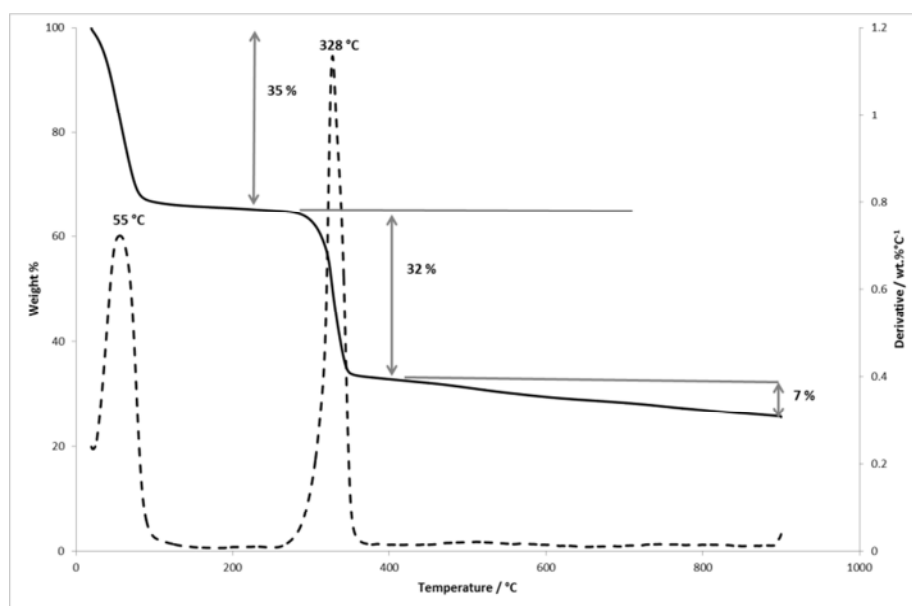


Figure S4.1: Thermal stability profile of our HKUST-1.

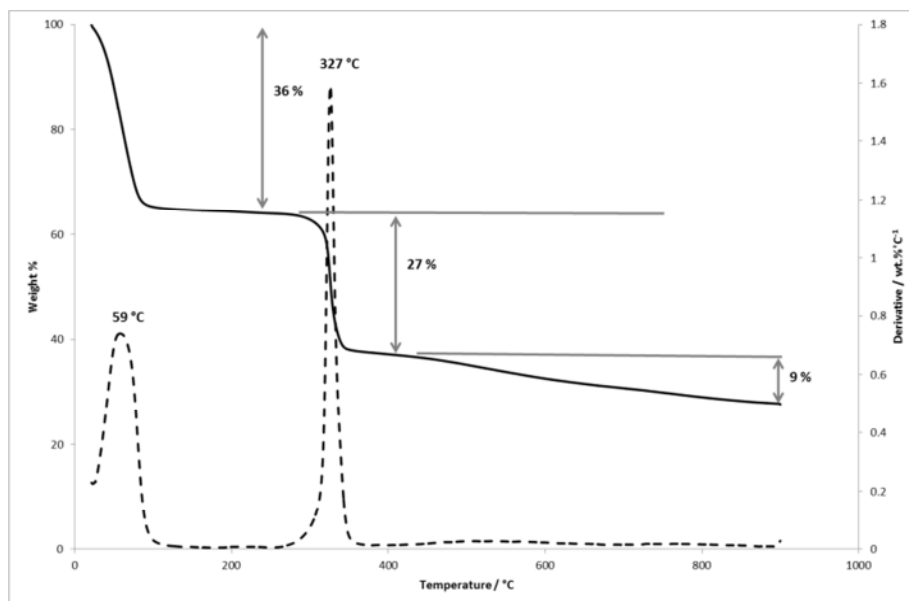


Figure S4.2: Thermal stability profile of commercial Basolite C300.

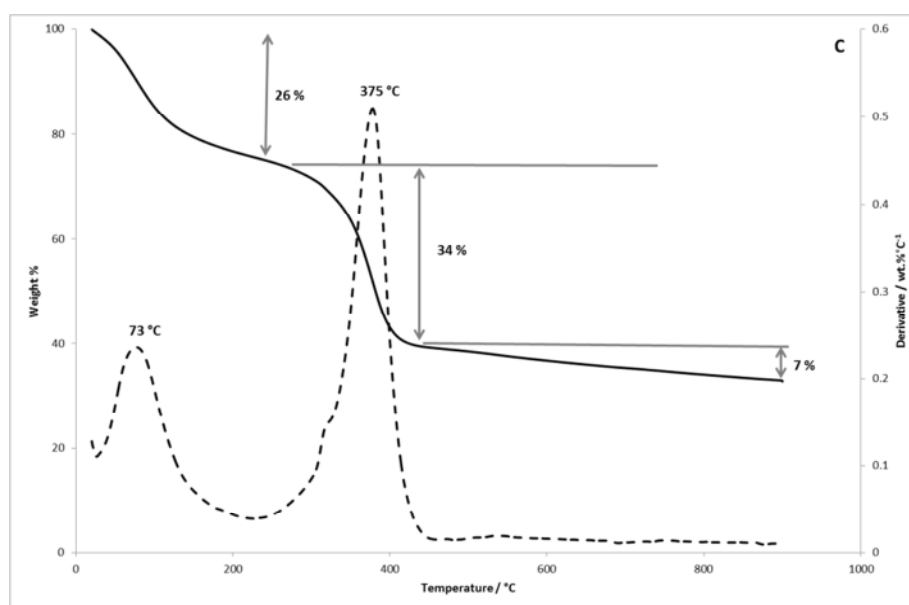


Figure S4.3: Thermal stability profile of CPO-27 (sample prepared at low reagent concentration).

S5: Gas Adsorption

Adsorption experiments were carried out using a TA instruments Q500 TGA. Moisture was removed from approximately 10 mg of sample (see moisture removal step in CO₂ adsorption isotherm section above) and cooled to 25 °C for adsorption. Adsorption capacity was measured at 25 °C in either pure CO₂, oxygen (O₂) or N₂ (1 bar, 100 mlmin⁻¹). It should be noted that helium was used as the moisture removal gas when measuring N₂ adsorption. Identical experiments were carried out for Basolite C300 for comparison. Blank corrections were carried out prior to analysis to correct for changes in gas density and gas viscosities.

Measured CO₂ uptake at 298 K, 1 bar:

HKUST-1 25.5 wt %

CPO-27(Ni) 19.57 wt%

Literature data for CO₂ uptake by HKUST-1:

1 bar, 4.1 mmol/g = 2.5 molec/f.u.¹ (18.0 wt%)

0.9 bar and 295 K, 4.5 mol/kg² (19.9 wt)

0.8 bar and 298 K, 2.68 mol/kg = 0.11 CO₂/Cu = 5.3 CO₂/unit cell (pellets)³ (11.7 wt %)

Literature data for CO₂ uptake by CPO-27(Ni):

CO₂ uptake of 25.6 wt% at 1 atm at 296 K⁴

(5: 1) N₂/CO₂ flow- CO₂ uptake at 1 atm at 298 K = 12.6 wt%⁵

298 K and 1 atm, static – 5.61 mol/kg, dynamic – 5.37 mol/kg⁶ (24.6 wt%)

1 bar and 298 K, 6.68 mol/kg = 0.63 CO₂/Ni = 11.3 CO₂/unit cell (pellets)³ (29.9 wt%)

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