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A new class of Cu/ZnO catalysts derived from zincian georgeite precursors prepared by co-precipitation

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Experimental

Materials. Copper (II) acetate monohydrate (puriss. p. a., ≥ 99.0%), copper (II) nitrate hydrate (99.999%), zinc (II) acetate dihydrate (puriss. p. a., ≥ 99.0%), zinc (II) nitrate hydrate (99.999%), ammonium acetate (for molecular biology, ≥ 98%), sodium acetate trihydrate (reagent plus, ≥ 99.0%), potassium bromide (FT-IR grade), nitric acid (≥ 99.999% trace metals basis) and high purity atomic emission standards for copper, zinc and sodium (TraceCERT, 1000 mg/L in 2% nitric acid) were all purchased from Sigma-Aldrich. Ammonium carbonate (ACS grade), ammonium bicarbonate (99%) and sodium carbonate (99+%) were all purchased from Acros Organics. Ethanol (absolute 99.8%, Certified AR) was purchased from Fischer Scientific and CO_2 (CP grade) was provided by BOC. All purchased materials were used as received. Deionised water was provided in-house (determined sodium concentration < 1 ppm).

Zincian georgeite preparation by supercritical CO_2 anti-solvent (SAS) precipitation. A mixed solution of $Cu(OAc)_2.H_2O$ (4 mg/ml) and $Zn(OAc)_2.2H_2O$ (2.13 mg/ml) was prepared in a 10 *vol*. % H_2O/ethanol mixture (500 ml) to give a nominal Cu:Zn molar ratio of 2:1. SAS experiments were performed using apparatus manufactured by Separex. Liquefied CO_2 was pumped to give a flow rate of 6.5 kg/h and the whole system was pressurised up to 110 bar and held at 40 °C. Initially pure solvent (10 *vol*. % H_2O/ethanol) was pumped through the fine capillary into the precipitation vessel, with a flow rate of 6.5 ml/min for 15 minutes, in co-current mode with $scCO_2$ in order to obtain steady state conditions inside the vessel. After this initial period the flow of liquid solvent was stopped and the mixed acetate solution was delivered at a flow rate of 6.5 ml/min. This gave a $scCO_2$/metal solution molar ratio of 22:1. The system pressure and temperature were maintained and the preparation conditions were carefully controlled. Leak checks were also periodically carried out throughout the procedure using snoop solution. As the solution exited the capillary the droplet and $scCO_2$ rapidly diffused into each other, causing expansion and reducing the solvent power. The zincian georgeite precipitated rapidly and when all the solution had been processed a drying step was carried out. This was achieved by pumping pure ethanol at 6.5 ml/min co-currently with $scCO_2$ for 30 min, before leaving with just $scCO_2$ to pump for a further 60 min. This was to wash the vessel in case residual solvent condensed during depressurisation and partly solubilised the prepared zincian georgeite, modifying its morphology. Furthermore, it was essential to completely dry georgeite phases to prevent subsequent ageing into malachite. When the drying step was completed the $scCO_2$ flow rate was stopped, the vessel was depressurised to atmospheric pressure and the precipitate was collected. Experiments were conducted for approximately 3.5 hours which resulted in the synthesis of *ca*. 1.1-1.3 g of solid.

Catalyst characterisation. FT-IR spectroscopy was performed on a Jasco 660 plus spectrometer in transmission mode over the range 400-4000 cm^{-1}. Samples were first pressed with KBr to generate a thin optically transparent disk with *ca.* 1 *wt*. % of the investigated sample. A background scan using just KBr was always performed before each scan and subtracted from the spectra.

XRD analysis was performed on a (θ-θ) PANalytical X'pert Pro powder diffractometer with a Ni filtered CuK_α radiation source operating at 40 keV and 40 mA. Patterns were recorded over the 2θ angular range 10-80 ° using a step size of 0.016 °. Analysis was performed using a back filled sample holder or with the sample dispersed on a silicon wafer when limited sample was available. Phase patterns were identified using the ICDD database and crystallite sizes were determined using the Scherrer equation.

Synchrotron PDF data were derived from XRD data as collected on the 11-ID-B beamline at the Advanced Photon Source at Argonn National Laboratory, USA. Powder samples were packed into Kapton capillaries having an internal diameter of 1 mm. Room temperature powder XRD data were collected at a wavelength of 0.2114 Å using the Rapid Acquisition PDF method. The scattering data ($0.5 \leq Q \leq 22$ Å^{-1}) was processed into a PDF using the program GudrunX.

Raman spectroscopy was performed using a Renishaw inVia microscope with a green argon ion laser (λ = 514 nm). Samples were prepared by pressing the powder onto a Raman inactive aluminium plate. Before samples could be analysed, the laser was first calibrated using an internal Si reference, and then the samples were brought into focus by adjusting the sample holder height. Typically, 10 s of exposure and 10 accumulations were used in each scan. Only 5% laser power was used in order to prevent modification of the hydroxycarbonates, which are heat sensitive materials. Cosmic rays were also removed from each analysis.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray (EDX) analysis was performed using a Carl Zeiss Evo 40 microscope, operated at 5-20 kV and 50-2000 pA. Analysis was performed by dispersing catalysts on adhesive carbon discs, mounted on 12.5 mm aluminium stubs. 20 x 20 µm scan areas were carried out for quantification on more than 20 particles, with the standard deviation ± 1 *at*. %. Materials for examination by scanning transmission electron microscopy (STEM) were dry dispersed onto a holey carbon TEM grid. These supported fragments were examined using BF- and HAADF-STEM imaging mode in an aberration corrected JEOL ARM-200CF scanning transmission electron microscope (STEM) operating at 200 kV. 55 HAADF- and BF- pairs were collected for each sample analysed. This microscope was also equipped with a Centurio silicon drift detector (SDD) system for energy dispersive X-ray spectroscopy analysis.

Microwave plasma atomic emission spectroscopy (MP-AES) was performed using a 4100 MP-AES system manufactured by Agilent Technologies in order to quantify specific elements to parts-per-million (ppm) concentrations in various solid samples and effluents. For analysis of solid samples, materials of known mass were digested in HNO_3. Residual solid was removed using PTFE filter membranes. Sample solutions were then accurately produced using an acid matrix solution (20 *vol*. % HNO_3/H_2O). Blanks and calibration standards were also accurately prepared using the same matrix solution. Three emitted wavelengths were analysed for each element with an average taken of the findings. Data produced for the sample solutions was only accepted if the determined concentration was within the calibration range. In some instances, this required diluting the sample solutions further, whereby the true concentration could be calculated from the determined dilution factor. Analysis of co-precipitation effluents followed a similar protocol, but with the exclusion of the digestion step.

TGA in conjunction with DTA was performed using a Setaram Labsys 1600. Samples (20-50 mg) were loaded into alumina crucibles, heated to 600 °C (at 1 or 5 °C/min) in a flow of synthetic air (50 ml/min) and held for 10 minutes before cooling. In addition, hyphenated TGA and mass spectrometry was also run on a Pyris 1 TGA, linked to a Perkin Elmer Frontier followed by a Clarus 580 GC-MS, using a TL-9000 interface. The TL-9000 was set to continuously sample 70 ml/min of effluent gas. TGA was performed under helium, from 30-600 °C (at 5 °C/min) using *ca.* 25 mg of sample. The GC-MS was set up, to negate the GC column, with the effluent gas analysed by MS. For all specified TGA runs, a blank run was first carried out with these results subtracted from the relevant data to remove buoyancy effects.

BET surface area and porosity analysis was performed using a Quantachrome Autosorb-1. Samples (200 mg) were degassed under vacuum at 40 °C. The vacuum enabled utilisation of the low degas temperature, which was required for the heat sensitive hydroxycarbonates. In each case an 80 point (40 adsorption and 40 desorption points) isotherm was obtained using N_2 at -196.15 °C. Surface area analysis was carried out using an 8 point BET plot in the P/P_0 range 0.06-0.35. The pore volume and size distribution were calculated from the entire adsorption isotherm using the DFT Monte-Carlo model. The N_2-silica adsorption branch at -196.15 °C was the kernel file chosen.

Copper surface area analysis was carried out on a Quantachrome ChemBET chemisorption analyser. Calcined samples (100 mg) were packed into a quartz glass U-tube using quartz wool and purged with high purity He for 5 min to remove any adsorbed surface species. Reduction to final state catalysts was performed using 10% H_2/Ar (30 ml/min) with heating to 140 °C at 10 °C/min, and then to 225 °C at 1 °C/min. The ramp rate was reduced to 1 °C/min in order to minimise the extent of Cu nanoparticle sintering. Samples were held at 225 °C for 20 min to ensure complete reduction took place. Residual H_2 was flushed from the system by switching the gas line back over to He (80 ml/min), whilst holding the sample at 220 °C for another 10 min. The temperature was then reduced down to 65 °C for N_2O pulsing. A programme of 12 N_2O pulses (113 µl each), with a 5 min stabilisation time between each pulse was used, followed by 3 pulses of N_2 for calibration. The mass of each sample after reduction was used for determination of Cu surface area values. The amount of N_2 emitted was assumed to amount to half a monolayer coverage of oxygen and the surface density of Cu was taken as 1.47×10^{19} atoms/m^2.

CO_2-TPD analysis was carried out using a Quantachrome ChemBET chemisorption analyser equipped with a thermos-conductivity detector. Calcined samples (100 mg) were reduced under 10% H_2/Ar (30 ml/min) to 140 °C at 10 °C/min, and then to 225 °C at 1 °C/min. The materials were held at this temperature for 20 min to ensure complete reduction to the final state active catalyst has occurred, before cooling back down to ambient temperature under flowing He (80 ml/min). The catalysts were then exposed to an excess quantity of CO_2 (80 ml/min) for 30 min before desorption was performed. The temperature was increased from 25 to 600 °C at a ramp rate of 10 °C/min and held at 600 °C for 20 min under the flow of helium.

Catalyst testing. Catalyst testing for methanol synthesis and the LTS reaction was performed using 0.5 g of each catalyst precursor, which had been calcined (300 °C, 1 °C/min, 4 h in static air), pelleted and ground to a sieve fraction of 0.6-1.0 mm diameter. After charging the reactors, the final state catalysts were produced *via in- situ* reduction by heating to 225 °C (ramp rate of 1 °C/min) using a 2% H_2/N_2 gas mixture (60 ml/min).

Methanol synthesis testing was performed in a single stream six-fixed bed reactor with an additional by-pass line. After reduction, catalysts were subjected to synthetic syngas (CO : CO_2 : H_2 : N_2 composition = 6 : 9.2 : 67 : 17.8 *mol*. %) at 3.5 L/h, 25 bar pressure and reaction temperatures of either 190 or 205 °C. In-line gas analysis was performed using an FT-IR spectrometer, which detected CO, CO_2, H_2O and MeOH. The total system flow was maintained using the by-pass line. Carbon moles balances were ≥ 98%.

LTS testing was performed in six parallel fixed bed reactors with a single stream feed and an additional by-pass line. After reduction, catalysts were subjected to synthetic syngas (CO : CO_2 : H_2 : N_2 composition = 4 : 16 : 55 : 25 *mol*. %) at 27.5 bar pressure and a reaction temperature of 220 °C. The reactant gas stream was passed through vaporised water to give a water composition of 50 *vol*. % (or a steam ratio of 0.5). This gives a total reactant gas composition of H_2O : CO : CO_2 : H_2 : N_2 = 50 : 2 : 8 : 27.5 : 12.5 *mol*. %. In-line IR gas analysis was performed to measure CO conversion. Space and mass velocity variation tests were performed at 65 h time-on-line by altering the flow for each catalyst bed. Relative activities were calculated by altering the flow for each catalyst bed in order to achieve 75% CO conversion after 75 h time-on-line. The total system flow was maintained using the by-pass line. Commercial catalysts for methanol synthesis and the LTS reaction were used as standards and have been described elsewhere (see main manuscript).

Results

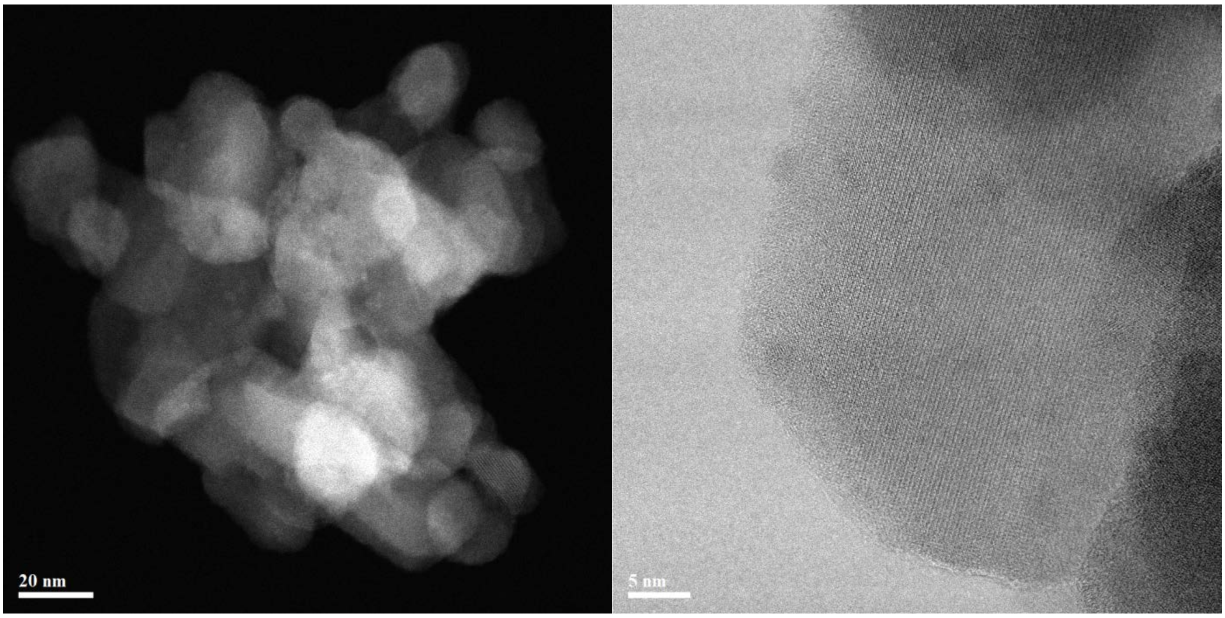

Figure S1. Representative (A) DF-STEM and (B) BF-STEM micrographs of the 2:1 zincian malachite precursor.

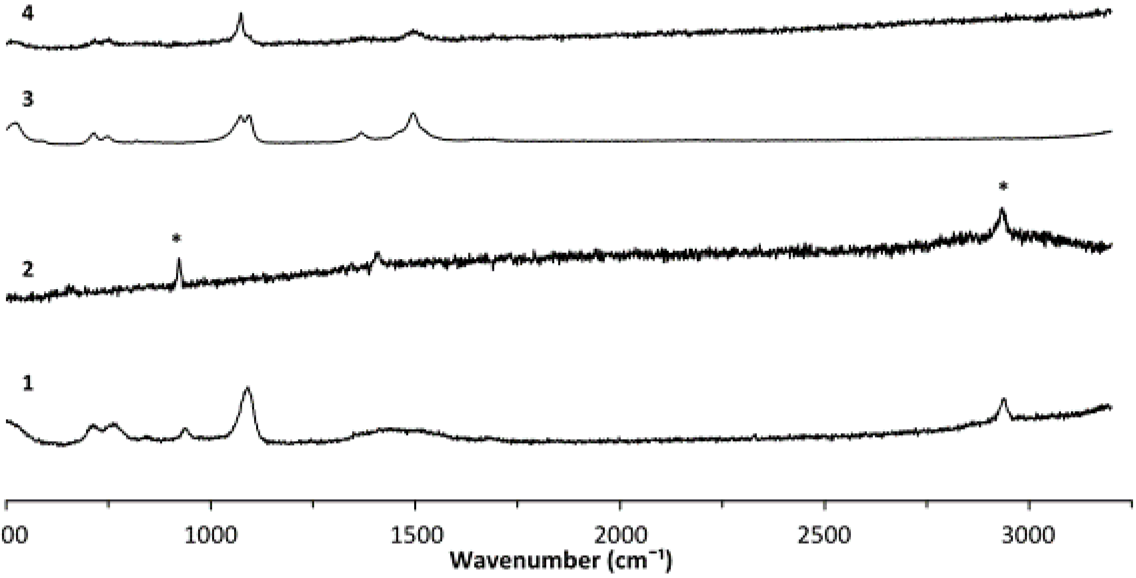

Figure S2. Raman spectroscopy of (1) Cu:Zn 2:1 hydroxycarbonate prepared using acetates and $(NH_4)_2CO_3$. For reference: (2) as received ammonium acetate. Cu:Zn hydroxycarbonates were also prepared using nitrates and Na_2CO_3 with Cu:Zn molar ratios of (3) 2:1 and (4) 1:1. For clarity, acetate reflections (*) are marked.

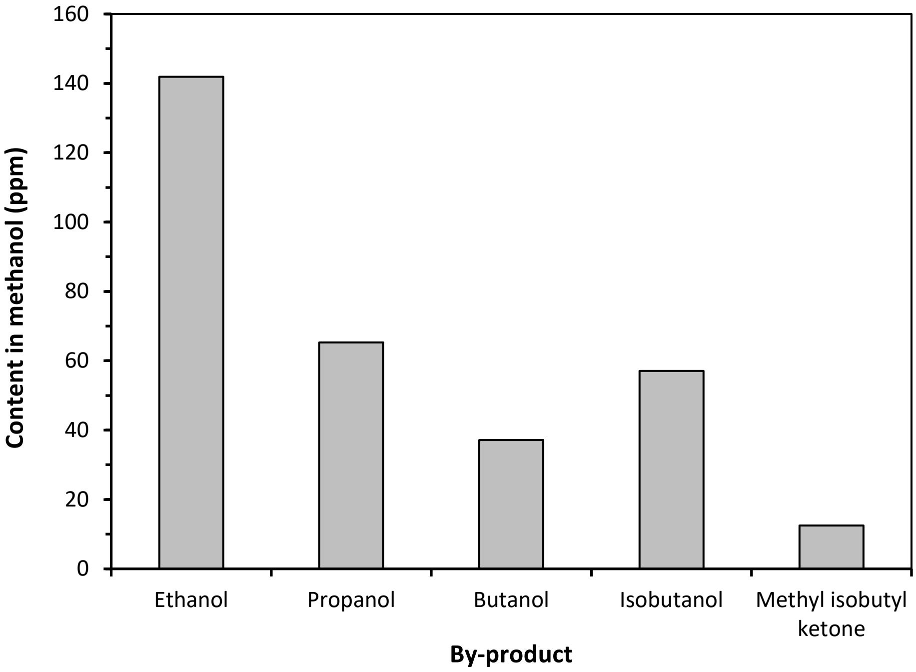

Figure S3. By-product distribution from methanol synthesis reaction for the commercial catalyst.

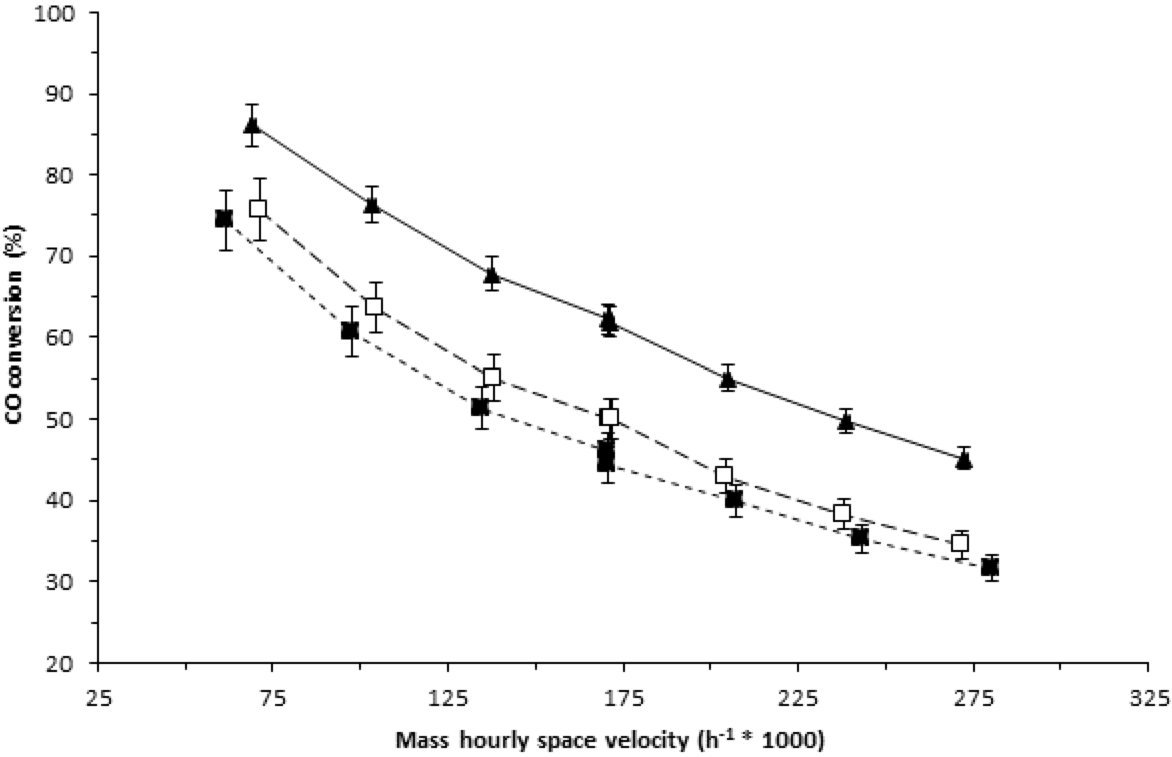

Figure S4. LTS activity at selected mass hourly space velocities. Key: (▲) zincian georgeite derived catalyst, (■) zincian malachite derived catalyst and (□) industrial standard. Compositions of catalysts by *wt*. % were 64:36 CuO/ZnO, 67:33 CuO/ZnO and 50:33:17 CuO/ZnO/Al$_2$O$_3$ respectively.

Table S1. Methanol formation rates during LTS testing.

Catalyst	Time on line (h)	MeOH (ppm)	MeOH rate (mmol/h)	CO conv. (mmol/h)	MeOH rate (%)
zincian georgeite derived	67.5	461	0.0997	30.234	0.33
	91.5	480	0.1036	30.096	0.34
zincian malachite derived	67.5	140	0.0302	24.409	0.12
	91.5	108	0.0235	22.547	0.1
LTS standard	67.5	236	0.0514	27.364	0.19
	91.5	227	0.0495	26.899	0.18

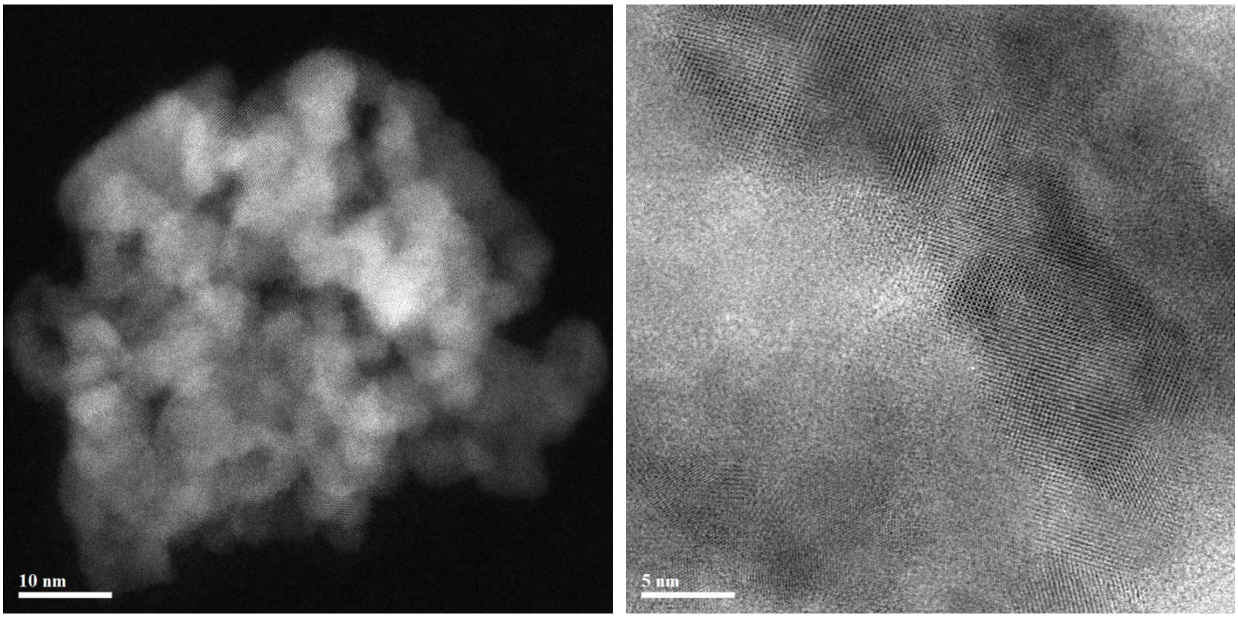

Figure S5. Representative (A) DF-STEM and (B) BF-STEM micrographs of the 2:1 zincian malachite precursor after calcination at 300 °C for 2 h.

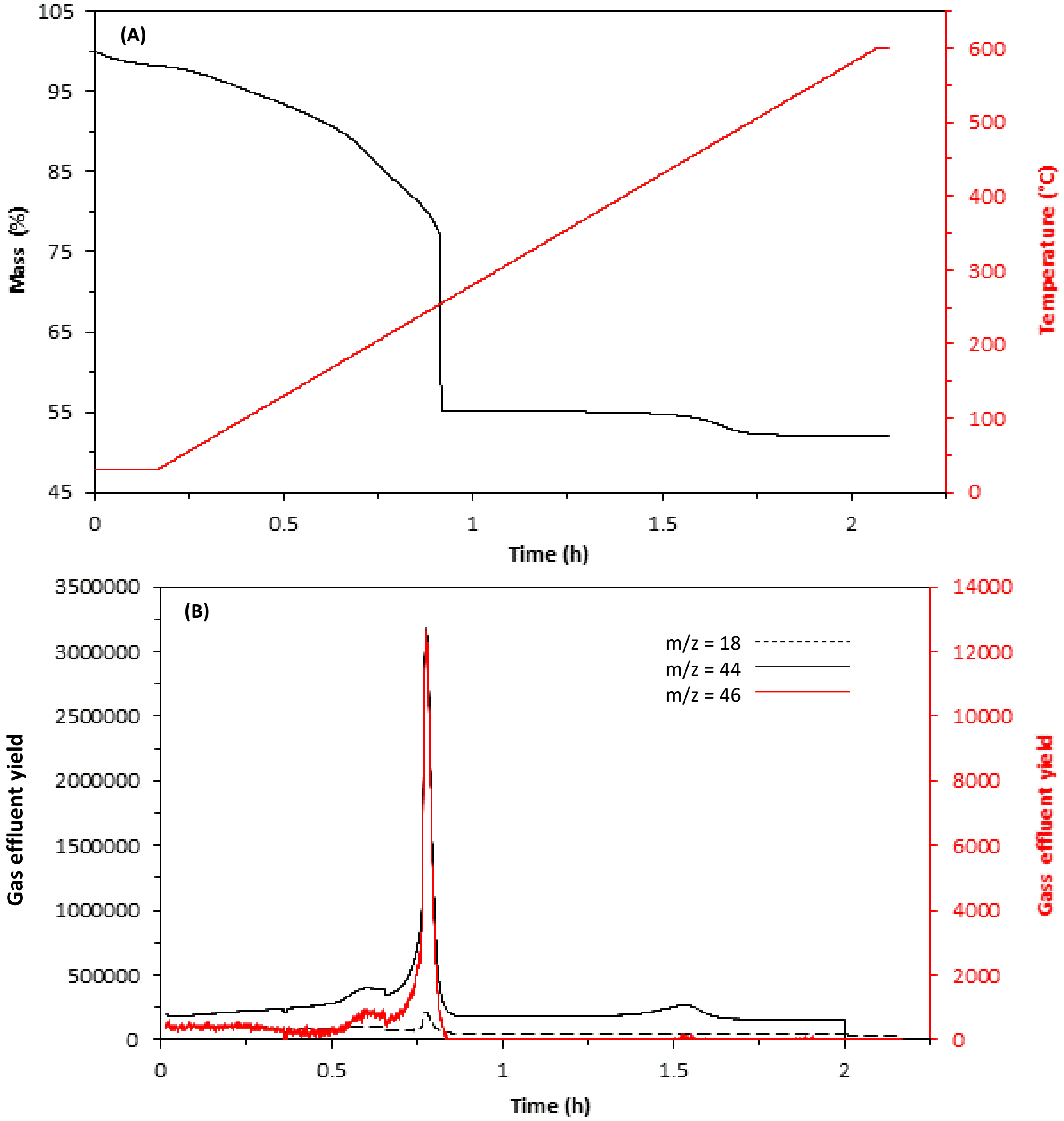

Figure S6. (A) TGA and (B) EGA of zincian georgeite prepared using $(NH_4)_2CO_3$. The hydroxycarbonate had not been washed after filtration and a ramp rate of 5 °C/min was used in order to maximise m/z values observed for evolved gases.

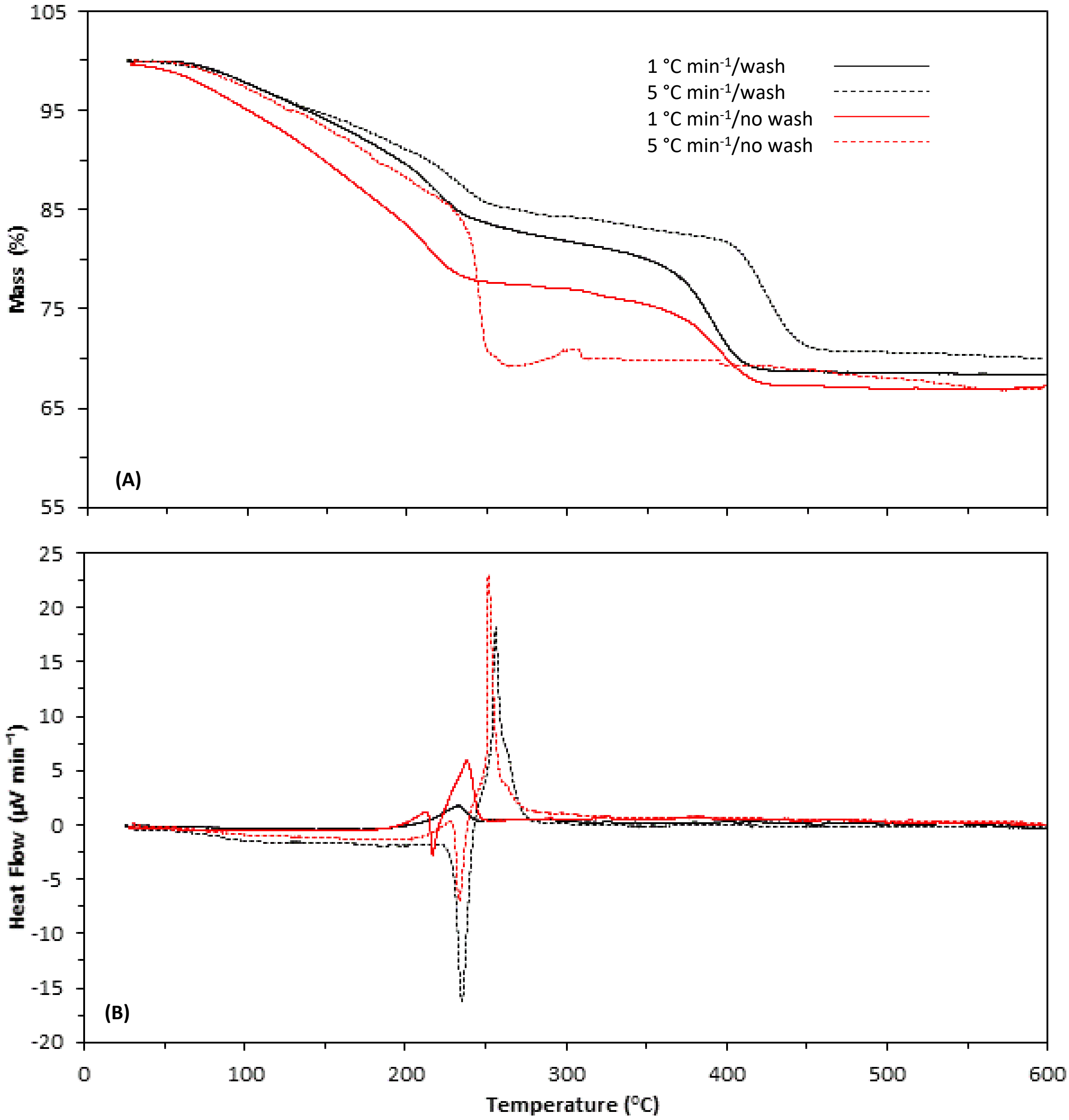

Figure S7. (A) TGA and (B) DTA illustrating the effect of heating ramp rate and washing treatment on the thermal decomposition of zincian georgeite prepared using $(NH_4)HCO_3$.

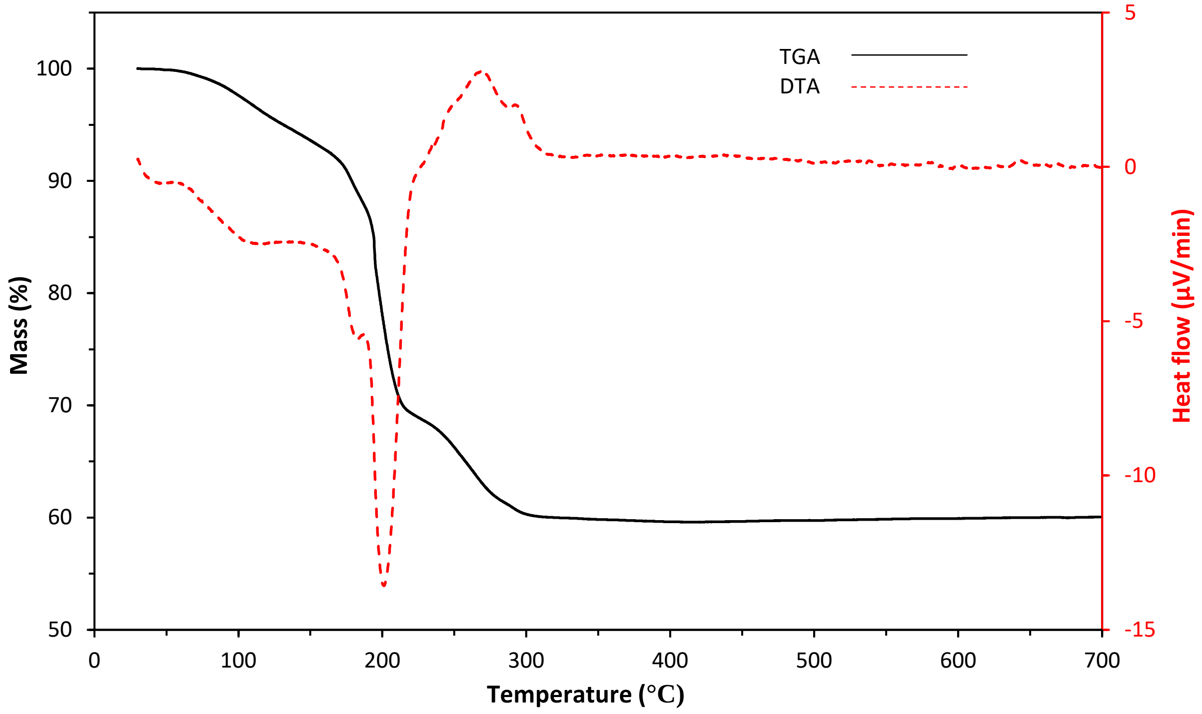

Figure S8. TGA and DTA carried out under nitrogen for zincian georgeite prepared without washing using $(NH_4)_2CO_3$. The highly exothermic decomposition associated with ammonium carbonate is removed from the absence of oxygen.