Electronic Supporting Information For:

Phosphinate Stabilised ZnO and Cu Colloidal Nanocatalysts for CO_2 Hydrogenation to Methanol

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Experimental Section

Materials

Solvents were distilled from either sodium or CaH_2 and stored under nitrogen. Unless otherwise stated, solvents were freshly degassed prior to use by performing at least three freeze−pump thaw cycles. Squalane, zinc bis(stearate) and diethylzinc were purchased from Aldrich. Diethyl zinc, in common with many other organometallic compounds, is pyrophoric and must be handled with appropriate precautions. Copper(II) bis(stearate),[1] copper bis(di octyl phosphinate),[2] zinc bis(di octyl phosphinate),[3] and di-octyl phosphinic acid[4] were synthesised according to a methods reported in the literature. The ternary reference catalyst was purchased from Alfa Aesar (45776, "Copper based methanol synthesis catalyst" composition CuO; 63.5 %, ZnO; 24.7 %, Al_2O_3; 10.1 %, MgO; 1.3 %) and ground from pellet form to a fine powder using a pestle and mortar.

Methods

Spectroscopic Methods: NMR spectra were collected on a Bruker AV-400 instrument; $^{31}P\{^1H\}$ NMR were determined at 162 Hz. Infrared (IR) spectroscopy was carried out using a Perkin-Elmer Spectrum 100 Fourier Transform IR spectrometer. Powder samples were analyzed using the Attenuated Total Reflection (ATR) accessory. Optical absorption spectra (UV-Vis) were collected on a Perkin-Elmer Lambda 950 spectrophotometer, from toluene solutions.

Thermogravimetric analysis (TGA): were carried out using a Perkin-Elmer Pyris 1 TGA instrument, under a flow of artificial air (20 % air, 80 % nitrogen), from 323 to 1073 K, at a heating rate of 10 K/min or under nitrogen (flow rate of 60 $mLmin^{-1}$) at a heating rate of 10 K min.

X-ray diffraction (XRD): was performed using an X'Pert Pro diffractometer (PANalytical B. V., The Netherlands) and X'Pert Data Collector software, version 2.2b. The instrument was used in the theta/theta reflection mode, fitted with a nickel filter, 0.04 rad Soller slit, 10 mm mask, 1/4° fixed divergence slit, and 1/2° fixed antiscatter slit. Samples were analyzed with a step size of 0.0042°, at a scanning speed of $0.028°s^{-1}$. The diffraction patterns were analysed using Fityk (version 0.9.0; Marcin Wojdyr, 2010): the peaks were fitted to a Pseudo-Voigt function using the Levenberg−Marquardt algorithm, and the particle size was calculated using the fitted full-width half-maximum.

Transmission electron microscopy (TEM): Nanoparticle samples were drop-cast (toluene solution) onto 300-mesh, holey carbon-coated copper or gold films (Agar Scientific) and imaged at an operating voltage of 200 kV on a JEOL 2010 microscope. The HR-TEM images were recorded by an FEI 80–300 kV Titan operated at 300 kV. It is equipped with a monochromator. The spatial resolution of the microscope is 0.3nm/0.12eV Digital images were analysed for particle sizing using the software ImageJ, version 1.40 g (W. Rasband, National Institutes of Health).

Synthesis Section

ZnO nanoparticles with stearate ligands

Under an inert atmosphere, ZnEt2 (247 mg, 2.0 mmol) and zinc stearate (140 mg, 0.22 mmol) were added to dry toluene (8.6 mL) to make a suspension (0.15 M). This fluid was left to stir for 16 h, then heated gently until it turned colourless. A solution of water (72 mg, 4.0 mmol) in acetone (4.7 mL, 0.87 M solution of water) was added to the solution, slowly, over 5 minutes. The solution changed to a yellow colour, then formed a gel and finally a cloudy suspension was evolved. This suspension was stirred for 1 h before being transferred to a centrifuge tube, and further precipitated with acetone. The product was separated by centrifugation (20 min 3900 rpm) and washed twice with toluene (4 mL) and acetone (15 mL). The white powder was air-dried in the centrifuge tubes. Yield 293 mg (96 %).

ZnO nanoparticles with di(octyl phosphinate) ligands

Di(octyl) phosphinic acid (500 mg, 1.72 mmol) was dried under vacuum for 1 h, dry toluene (57.5 mL) and ZnEt2 (882 µL, 8.61 mmol) was added to make a 0.15 M solution. This fluid was left to stir for 20 h, before a solution of water (310 mg, 17.22 mmol) in acetone (0.4 M, 43 mL) was added, slowly, over 10-15 minutes. The solution turned a pale yellow colour, then formed a translucent gel and finally evolved a cloudy suspension. This suspension was stirred for a further 2 h, before being transferred to a centrifuge tube, and further solid precipitated by the addition of acetone. The product was separated by centrifugation (20 min, 3900 rpm) and washed twice with toluene (4 mL) and acetone (15 mL). The product was air-dried in the centrifuge tubes for 20 h, forming a translucent pellet which was ground with a mortar and pestle to yield a white powder. Yield 1.10 g (93 %).

Copper(0) nanoparticles with stearate ligands

A suspension of copper(II) stearate (2.65 g, 4.20 mmol) in squalane (80 mL) was heated until completely dissolved, then N2H4 (0.269 g, 8.40 mmol, as a 1 M solution in THF) was added slowly over 5 minutes. The mixture was then heated, under nitrogen, at 60°C for 16 h, after which the dark red solution was placed under vacuum for 3 hours to remove any excess hydrazine and THF.

Copper(0) nanoparticles with di octyl phosphinate ligands

A suspension of copper(II) bis(di octyl phosphinate) (0.17 g, 0.27 mmol) in squalane (80 mL) was heated until completely dissolved, then N2H4 (0.5 mL, 0.58 mmol, as a 1 M solution in THF) was added slowly over 5 minutes. The mixture was then heated, under nitrogen, at 333 K for 16 h, after which the dark red /brown solution was placed under vacuum for 3 hours to remove any excess hydrazine and THF.

Carbon Dioxide Hydrogenation Catalytic Testing

A 300 mL stainless steel Parr reactor was filled with squalane (100 mL) and the appropriate mass of ZnO particles was added, the mixture was then stirred at 298 K, under a flow of N_2 (350 mLmin^{-1}), for 30 minutes. Whilst under the flow of N_2, an aliquot of the Cu(0) solution in squalane (4 mL) was added and the mixture stirred at 298 K for a further 10 minutes. The reactor was then charged with the reaction gas mixture and the vessel heated to the reaction temperature.

Catalytic runs were conducted in a CSTR reactor using gas mixtures H_2:CO_2 (75:25 combined flow rate 166 mLmin^{-1}), pressurised to 50 bar and heated to 523 K. Squalane was selected as the solvent as it has a high boiling point and possesses good gas solubility of the feed gases, in addition it has been shown that the use of non-polar solvents promotes methanol production.[5] The product flow and unreacted material was continuously monitored by online GC (Varian 450-GC Gas

Chromatograph, using a PACKED SS COL 1/8"x 2m Porus Polymer (Haysap C) 80/100. A heated (523 K) transfer line of 1/8” 316 steel was used to connect to the autoclave.

Activation and Pre-Reduction of the Ternary Catalyst (Alfa Aesar: 45776)

The ternary catalyst (0.3 g) was suspended in squalane (100 mL) and pre-reduced using a flow of H_2 gas at 30 bar and 75 mLmin^{-1}, the temperature was 473 K, for 2 h.

Sample Preparation Methods for Analytical Techniques

UV-Vis Spectra of Cu nanoparticles

The squalane suspension of stereate capped copper nanoparticles was centrifuged, at 3900 rpm for 20 minutes, and the excess squalane decanted. The process was repeated using dry, de-gassed hexane (twice) and the sample dried under high vacuum. The red powder was then suspended in dry, degassed toluene (approximately 4 mg in 3 mL toluene) and the spectra collected using an air-tight cuvette.

TEM

ZnO and Cu Nanoparticles with stearate ligands

The TEM image of the post-reaction ZnO/Cu mixtures with stearate ligands was obtained by cooling the reactor solution (squalane), and exposing the sample to air. The solution was centrifuged (3900 rpm, 20 minutes) and the precipitate was washed with toluene (twice) to remove the excess squalane. It was then re-suspended in toluene and the sample drop cast onto the TEM grid.

ZnO with di(octyl)phosphinate ligands and Cu with stearate ligands

The TEM image of the ZnO/Cu mixture with DOPA post-reaction mixture was obtained via a different method, owing to the increased solubility of the particles. The solution was washed numerous times with acetone, in order to precipitate the particles from the solution. The particles were then dissolved in toluene and drop cast onto the TEM grids

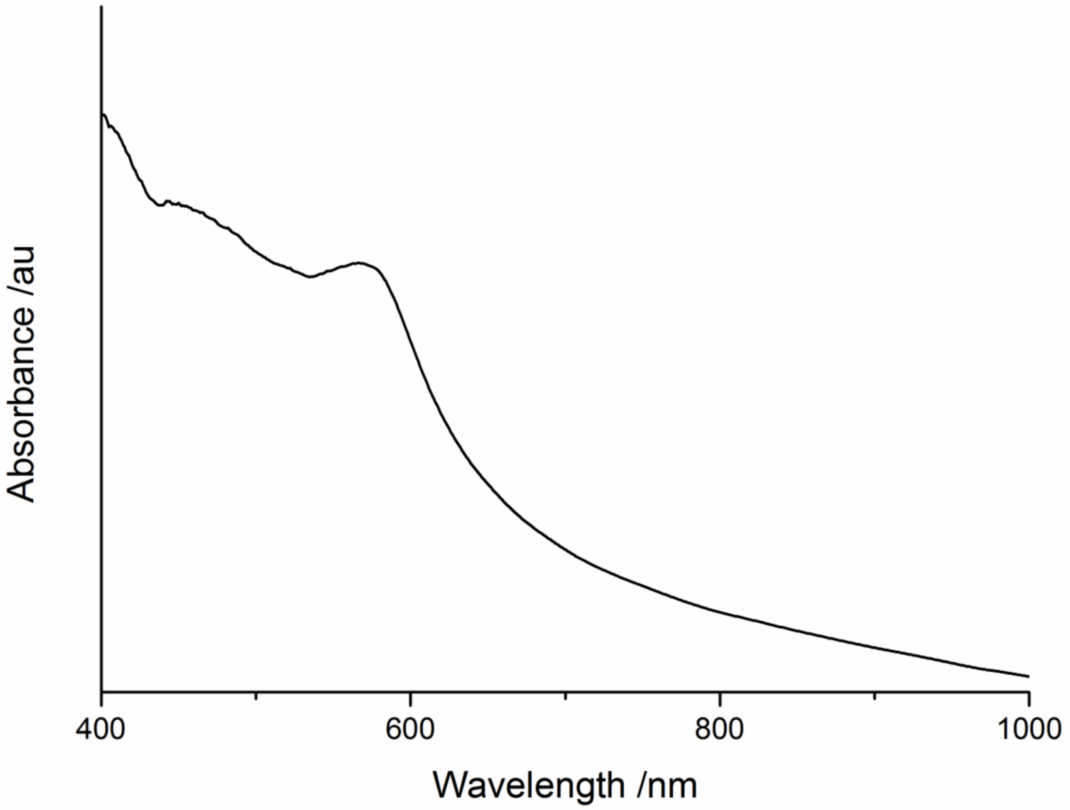

Figure S1: Copper nanoparticles formed by reduction of Cu(stearate)$_2$ with N_2H_4; UV-vis spectrum in toluene of the nanoparticles.

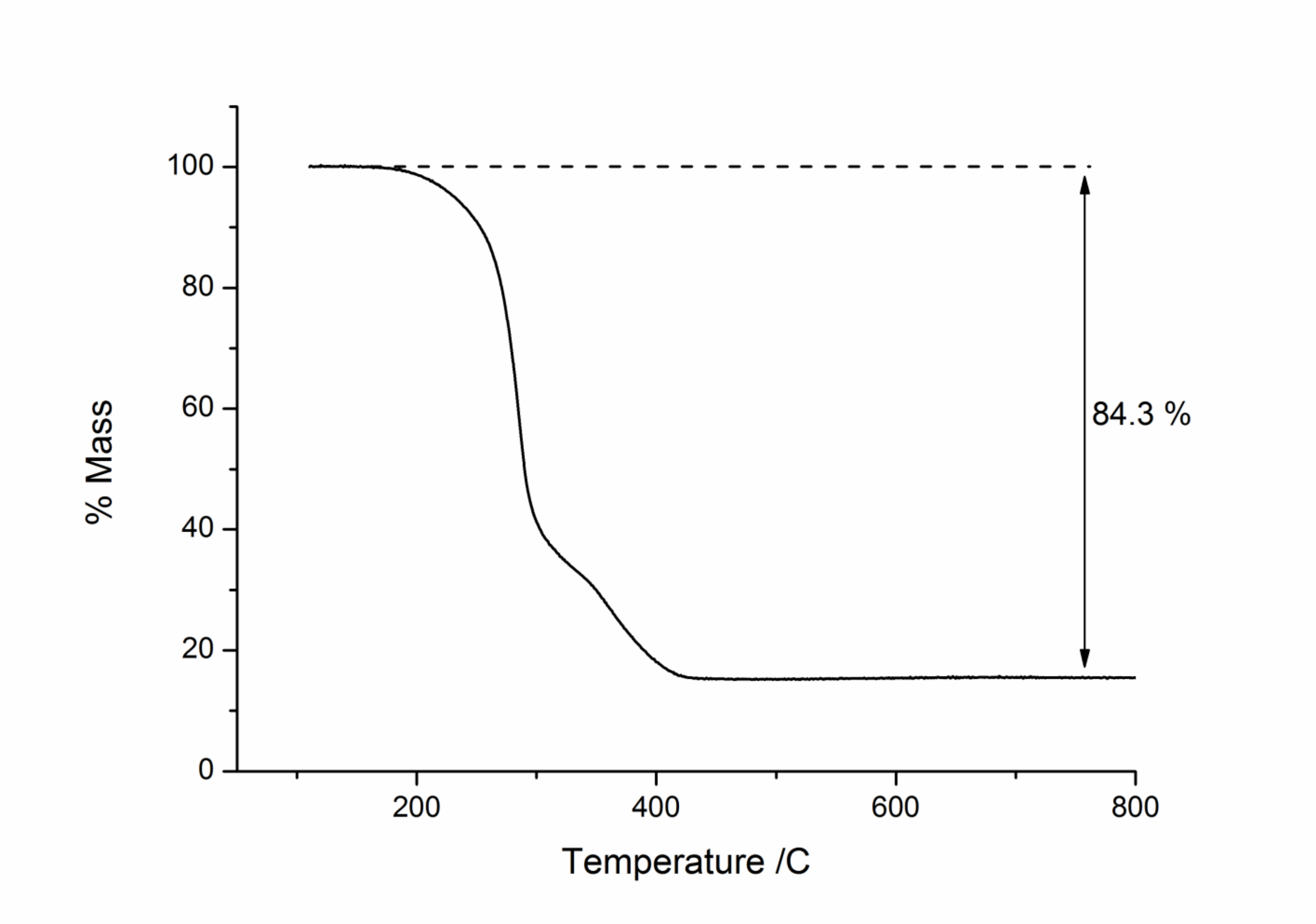

Figure S2: Thermal Gravimetric Analysis, in air, of copper nanoparticles formed by reduction of Cu(stearate)$_2$ with N_2H_4.

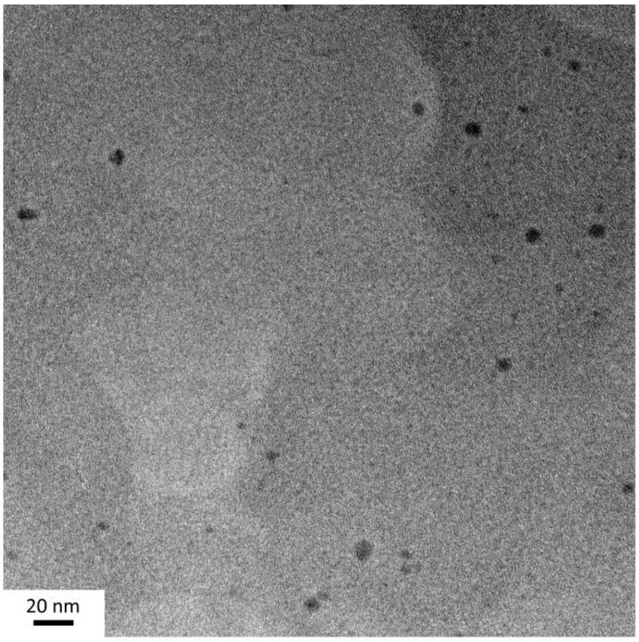

Figure S3: TEM image of copper nanoparticles formed by reduction of Cu(stearate)$_2$ with N_2H_4.

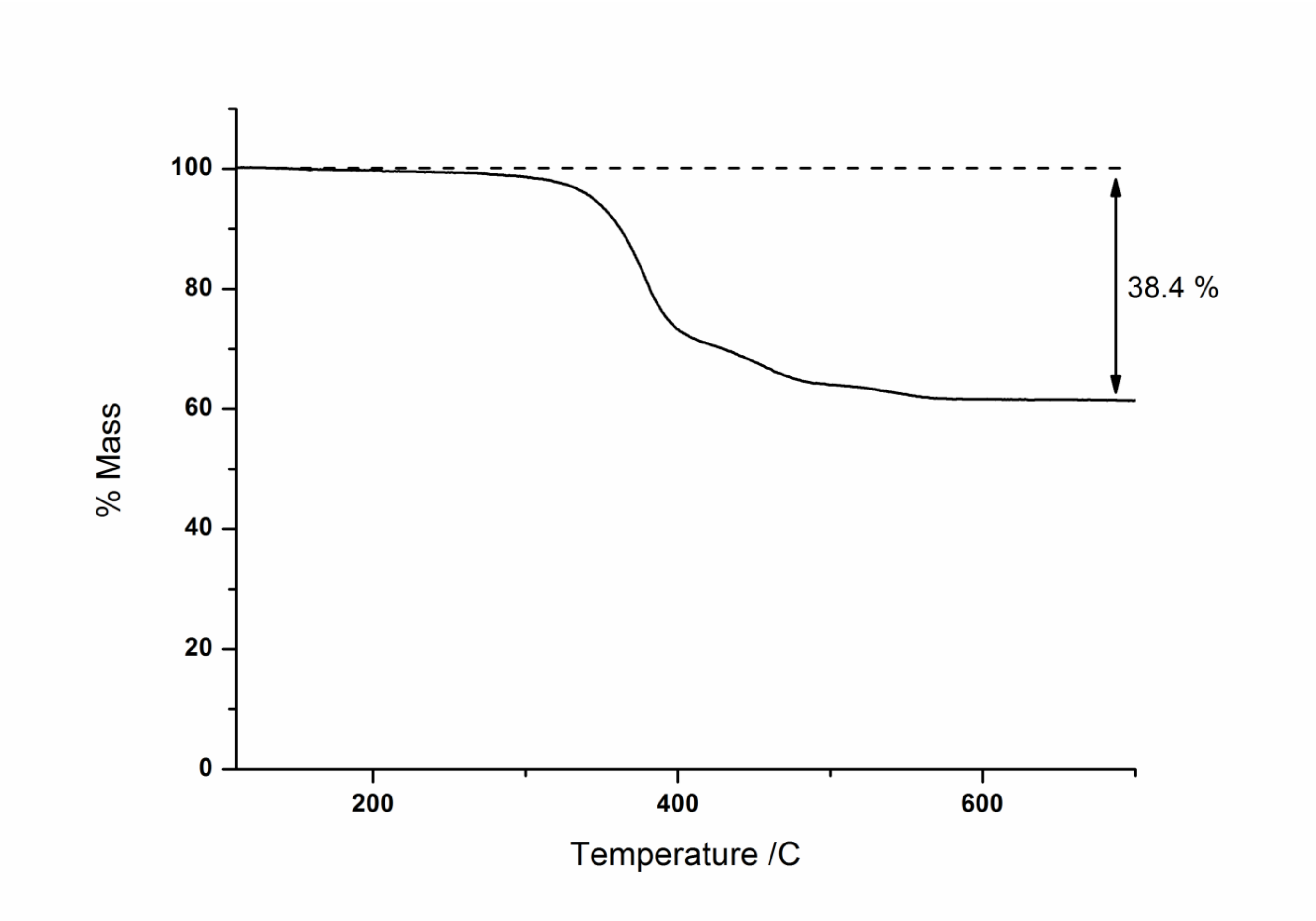

Figure S4: Thermal Gravitmetric Analysis, in air, of ZnO nanoparticles with stearate capping ligands.

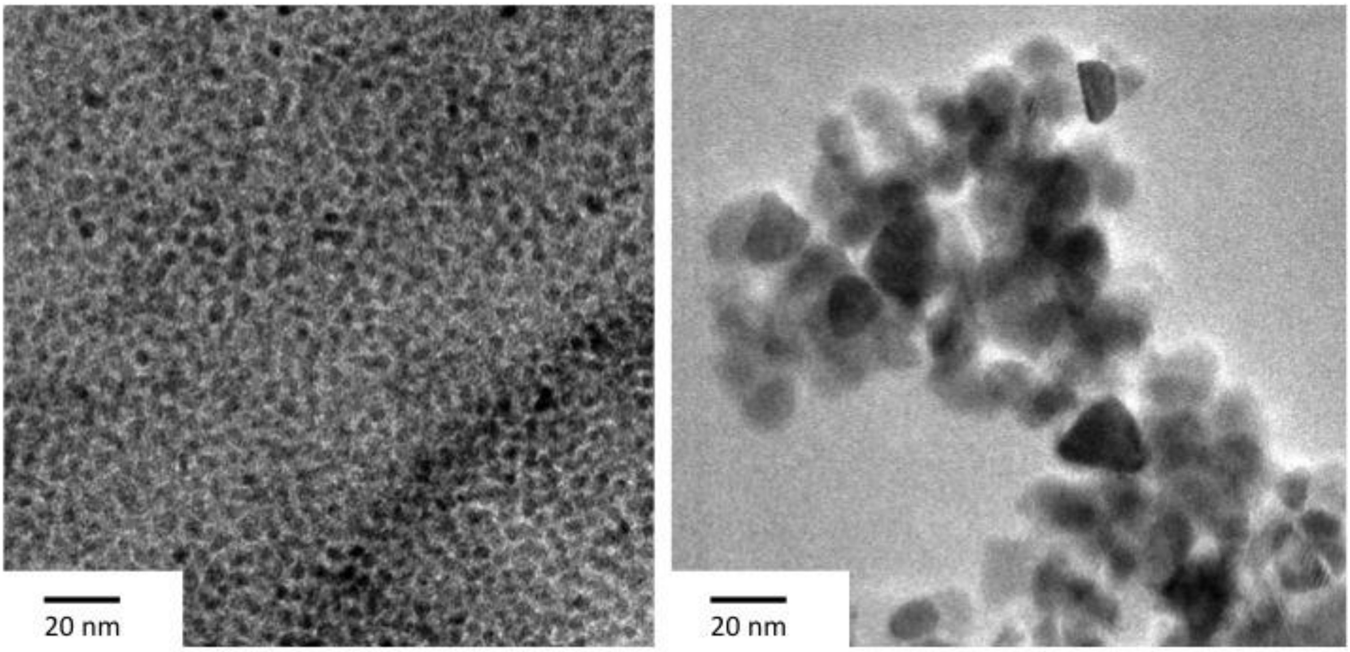

Figure. S5: TEM images showing the stearate capped nanoparticles before (LHS) and after (RHS) reaction with carbon dioxide and hydrogen (ZnO:Cu 50:50, 50 bar, 3:1 H_2:CO_2, 523 K, 166 mLmin^{-1}, 16 h). Note: resolution of RHS limited due to presence of organics and trace amounts of squalane solvent.

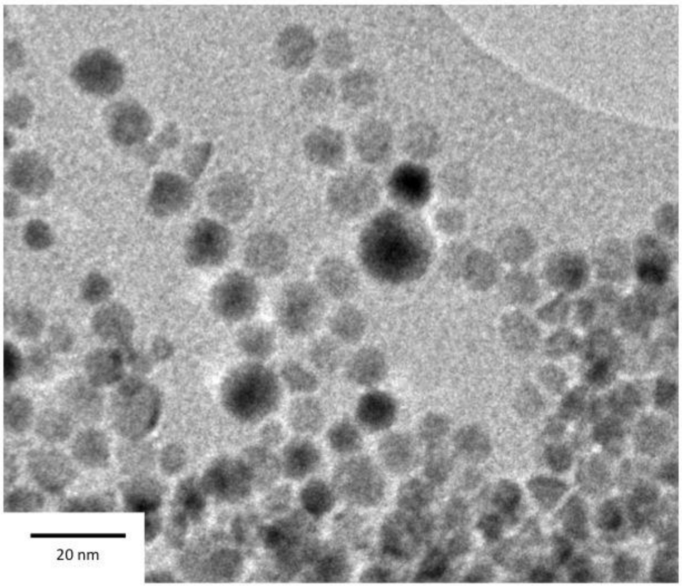

Figure. S6: TEM image of zinc oxide nanoparticles with stearate capping ligands, after being subjected to reducing conditions (30 bar H_2, 488 K, 2 h). Note: resolution islimited due to presence of organics and trace amounts of squalane solvent.

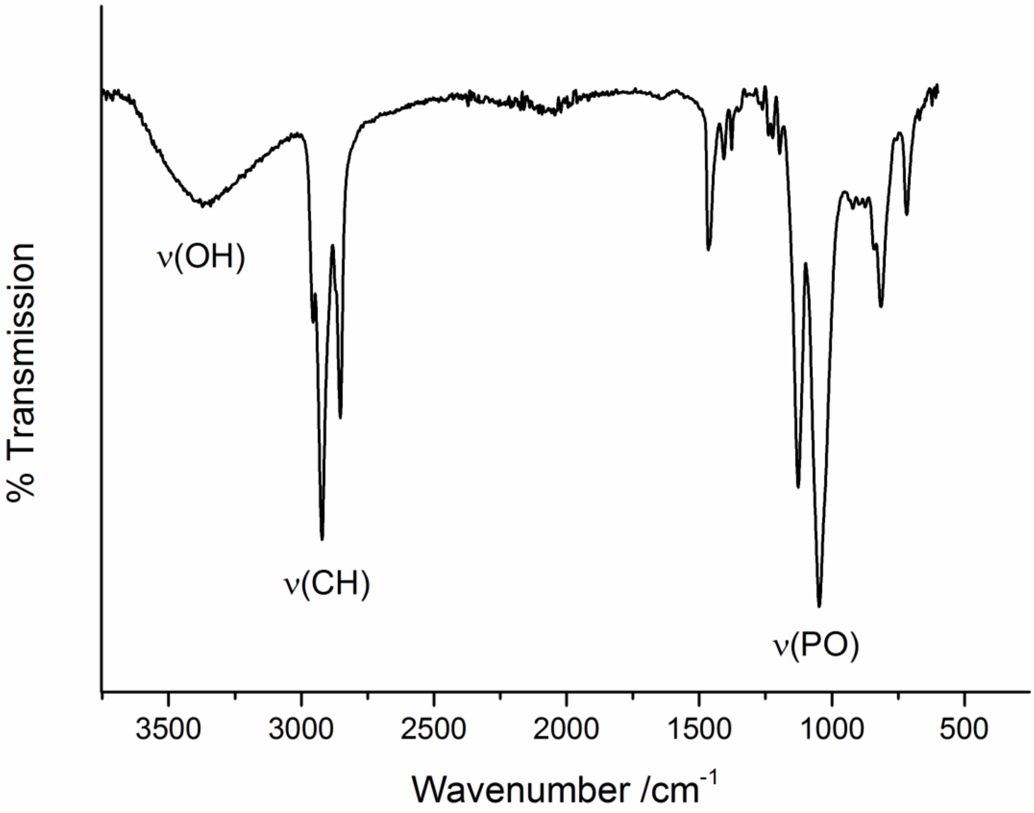

Figure S7: ATR-IR of zinc oxide nanoparticles with di(octyl)phosphinate capping ligands.

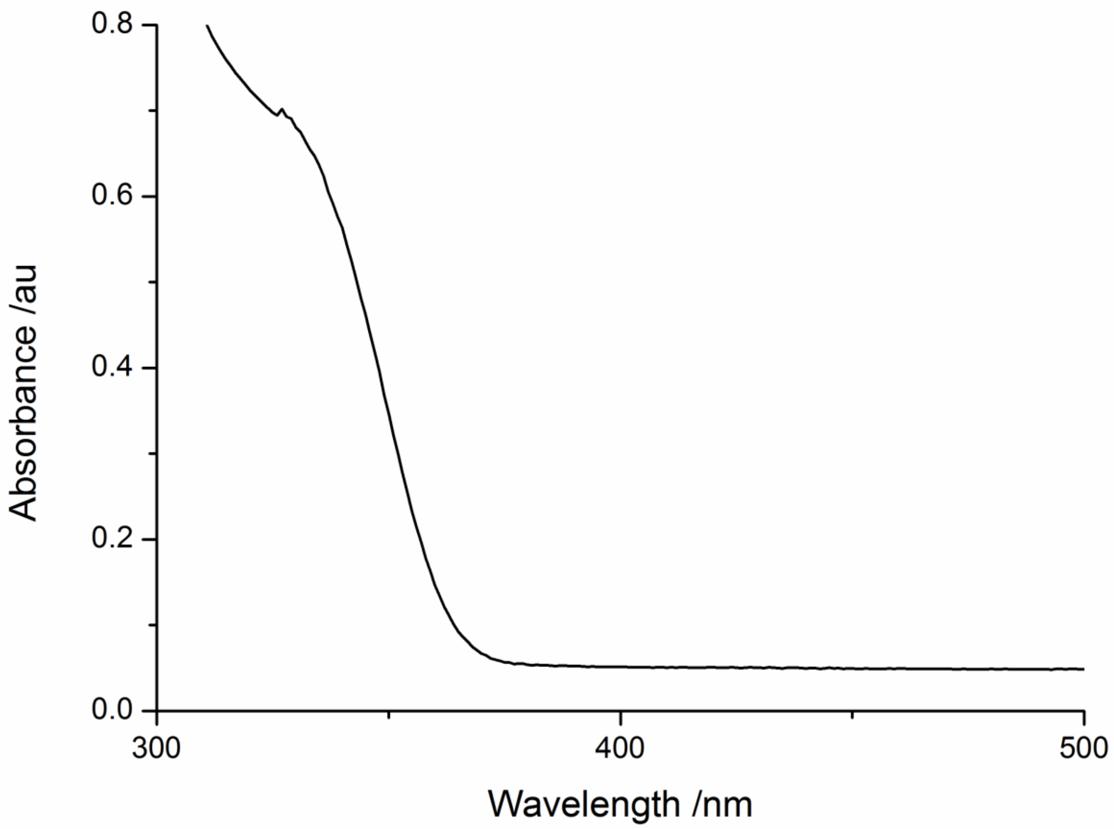

Figure S8: UV-Vis spectrum, in toluene, of zinc oxide nanoparticles with di(octyl)phosphinate capping ligands.

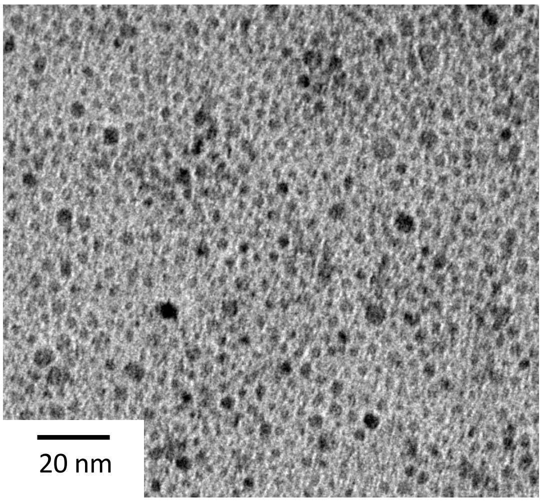

Figure S9: TEM image of zinc oxide nanoparticles with di(octyl)phosphinate capping ligands.

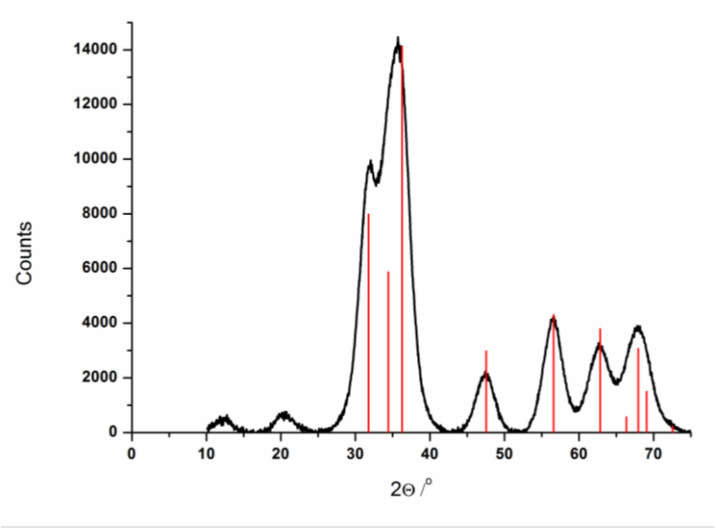

Figure S10: XRD of zinc oxide nanoparticles with di(octyl)phosphinate capping ligands. The red lines reference the ZnO peaks against the wurtzite structure (reference lines from PDF 036-1451, ICDD PDF4+ database).

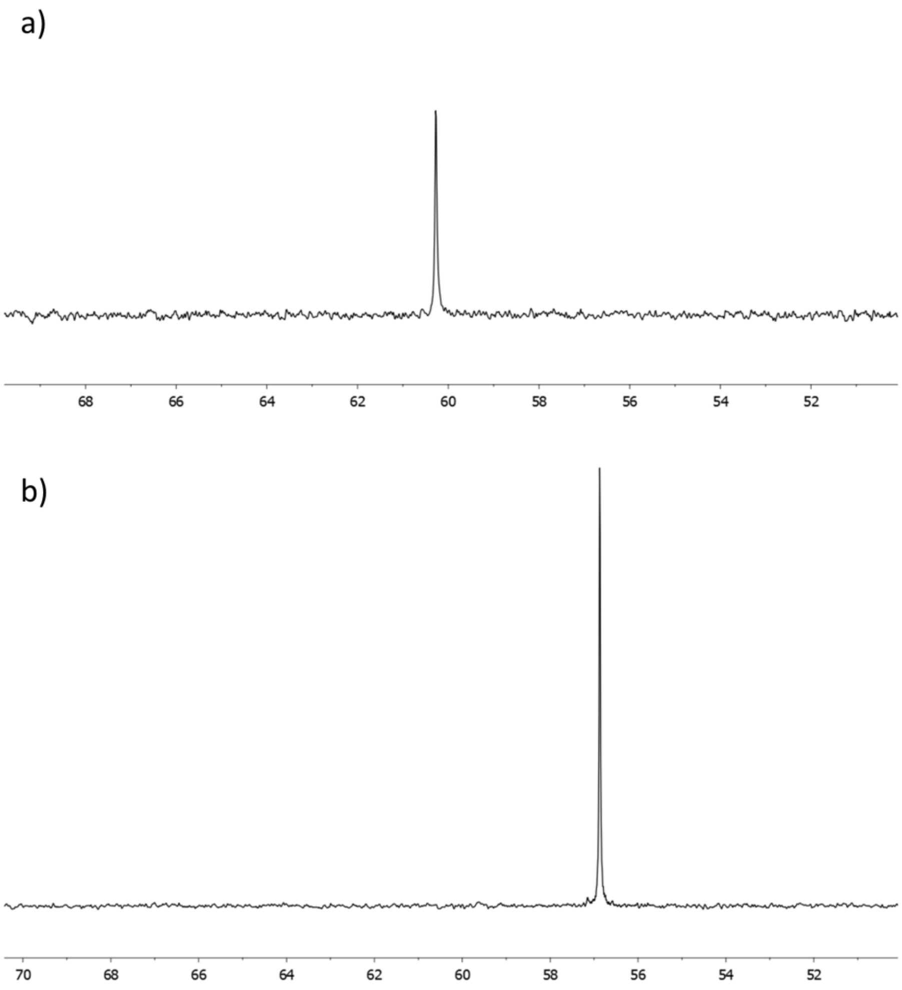

Figure S11: $^{31}P\{^{1}H\}$ NMR in CD_2Cl_2 of a) di(octyl)phosphinic acid amd b) zinc oxide nanoparticles with di(octyl)phosphinate capping ligands.

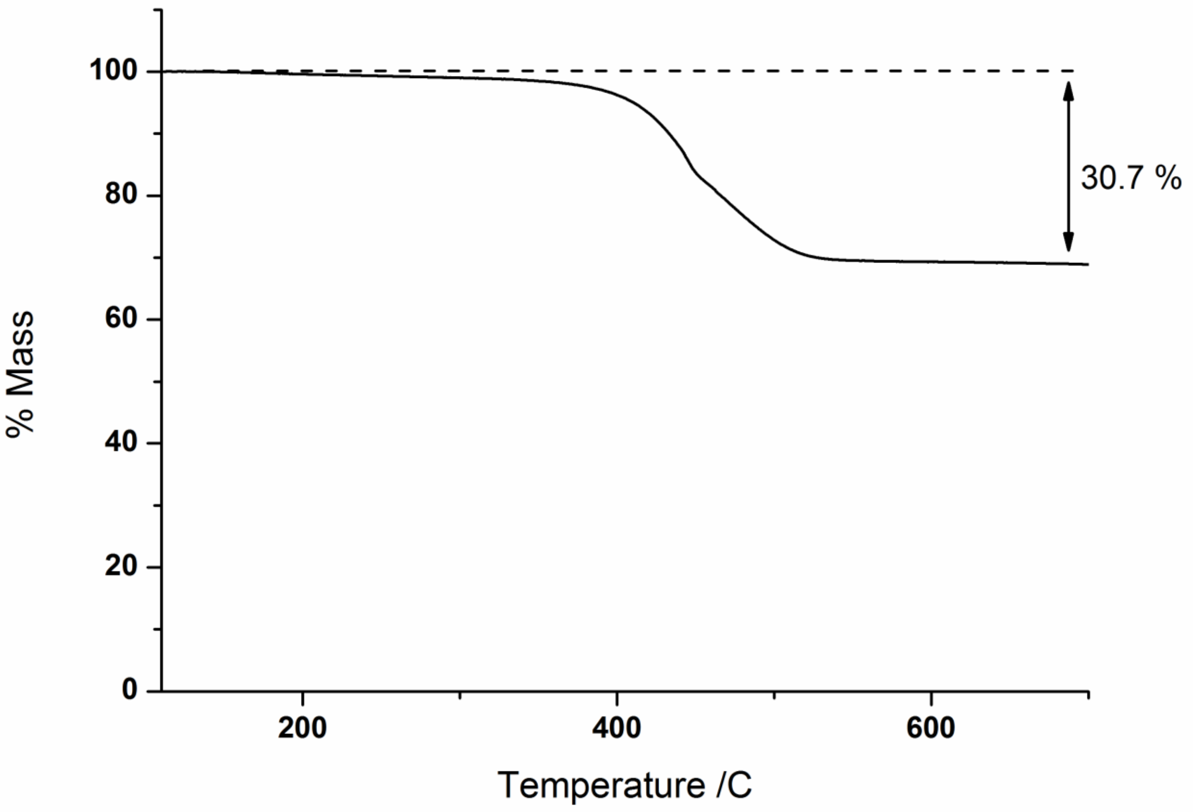

Figure S12: TGA of the zinc oxide nanoparticles with di(octyl)phosphinate capping ligands, under N_2 flow.

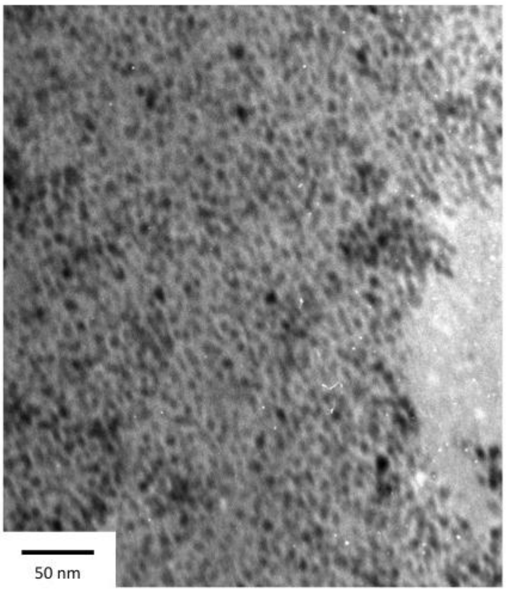

Fig. S13: TEM image of the di(octyl)phosphinate capped ZnO nanoparticles after being exposed to reducing conditions (30 bar H_2, 488 K, 2 h). Note: resolution is limited due to presence of organics and trace amounts of squalane solvent.

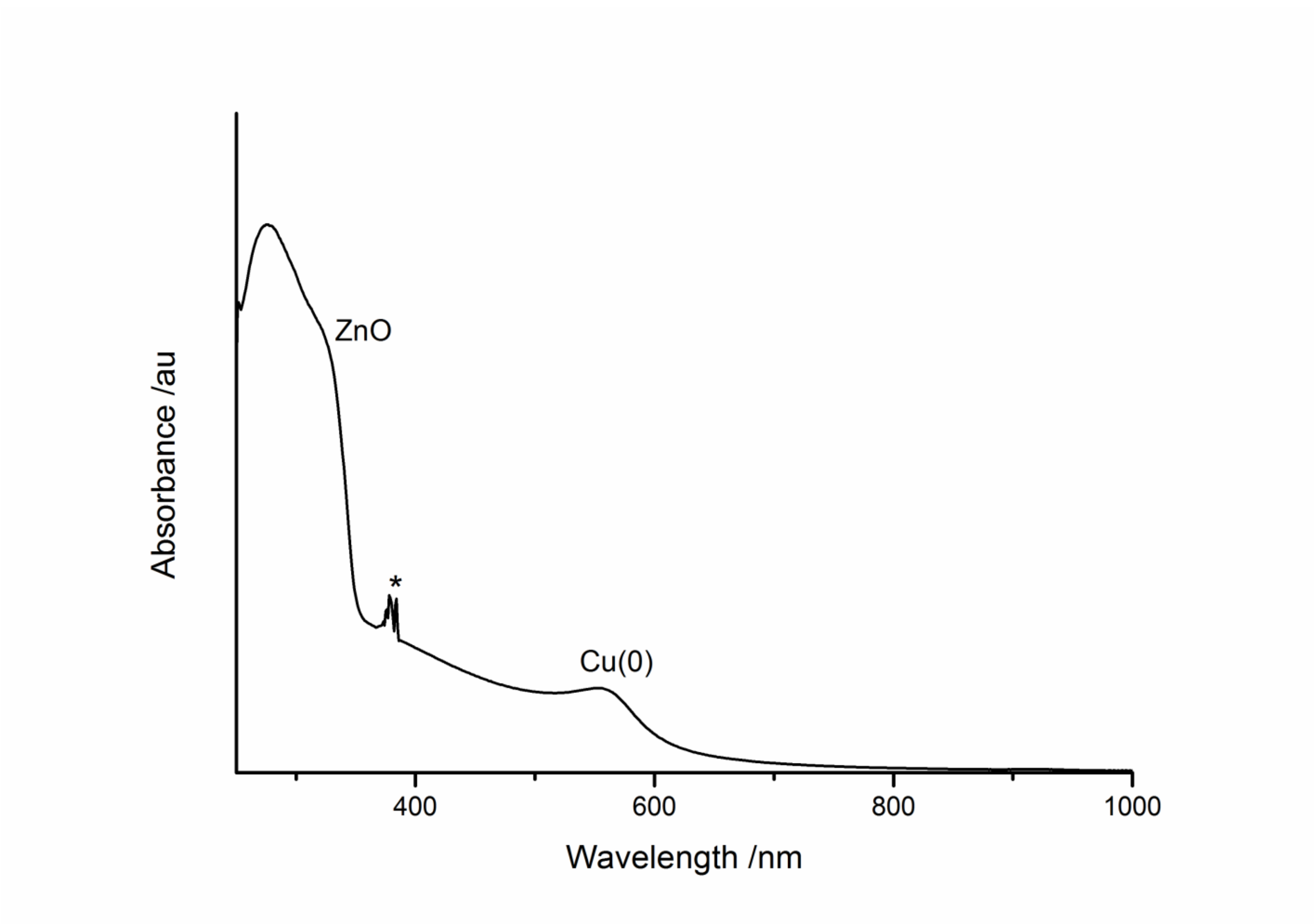

Figure S14: UV-Vis spectrum, in toluene, of the post-reaction solution from a catalytic run using ZnO:Cu (63:35), with di(octyl)phosphinate capped zinc oxide and stearate capped Cu nanoparticles (* is an artefact from the spectrometer bulb change) (Table 2, entry 3).

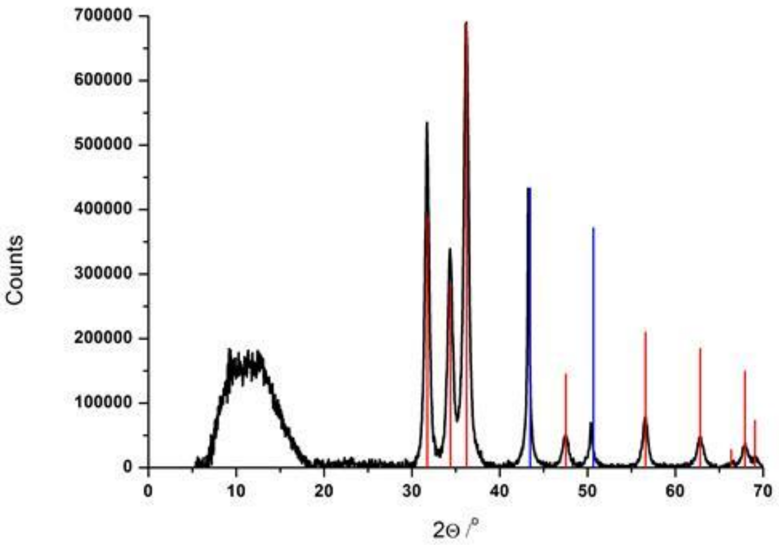

Figure S15: XRD pattern of red powder isolated from the post-reaction solution from a catalytic run using ZnO:Cu (63:35), with di(octyl)phosphinate capped zinc oxide and stearate capped Cu nanoparticles (Table 2, entry 3). The solid sample was isolated by precipitation from squalane using excess acetone, centrifugation and drying (in vacuo). The sample isolation and characterisation were maintained in an anaerobic environment to limit oxidation, where possible. The red lines reference the ZnO peaks against the wurtzite structure (reference lines from PDF 036-1451, ICDD PDF4+ database) and blue lines reference peaks against metallic copper.[6] The peaks at low angles are assigned to the surface capping ligands (di(octyl)phosphinate and stearate) and/or to residual (excess) squalane.

ZnO with DOPA Particles Theoretical Determination:

The theoretical total surface area (S_T) of the samples is given as:

$$S_T = S_P \times N_P \quad (1)$$

where S_P is the surface area per particle and N_P is the total number of particles, given by:

$$N_P = \frac{nV_m}{V_P} \quad (2)$$

where n is the number of moles of ZnO, V_m is the molar volume of ZnO (1.4353×10^{25} Å^{3}mol^{-1}) and V_P is the volume per particle. Assuming that the particles are perfect spheres, rearranging equations 1 and 2 gives:

$$\frac{S_T}{S_P} = \frac{nV_m}{V_P} \rightarrow \frac{S_T}{4\pi r^2} = \frac{nV_m}{\left(\frac{4}{3}\pi r^3\right)} \rightarrow S_T = \frac{3nV_m}{r} \quad (3)$$

where r is the radius of the particles (average of measurements by HR-TEM, UV-vis, and XRD analysis).
The number of moles of carboxylate per mole of ZnO, n_c, for each sample was calculated from the organic content measured by TGA:

$$n_c = \frac{\left({}^{W_O}/_{M_O}\right)}{\left({}^{W_i}/_{M_i}\right)} \quad (3)$$

where W_O, W_i are the weight percent (wt%) of organic and inorganic components, respectively, and M_O and M_i are the molecular weight of the organic and that of ZnO respectively.

The surface area per phosphinate molecule was estimated as 24.4 Å^2 using a similar method to Cooper et al.[7] based on the calculated head group surface area of a phosphinate based on the literature bond lengths and bond angles of P-O and O-P-O respectively. The sterate molecule was estimated to have an area of 20 Å^2.

Assuming that all the phosphinates are bound to the surface and form a close packed monolayer, the theoretical surface area that could be occupied by phosphinate groups, S_S was then calculated as:

$$S_S = Z \times n_C \times 24.4\text{Å}^2 \quad (4)$$

where Z is Avogadro's number, and n_C is the number of moles of phosphinate (calculated from the total organic content). The ratio of S_S to S_T gives the percentage coverage.

Example calculation:
For a ZnO nanoparticle with an initial loading of 5 equivalents of DOPA. The nanoparticles were found to have a diameter of 3.5 nm by TEM, UV-Vis and XRD calculations. Thus, based on equation 3 the surface area of the particles is estimated to be $2.46\text{x}10^{24}$ Å^2/mol (304 m^2/g).

Based on equation 4, the number of moles of DOPA is given as

$$n_c = \frac{\left({}^{31.7}/_{226.2}\right)}{\left({}^{68.3}/_{81.39}\right)} = 0.167 mol$$

These DOPA molecules will form a monolayer over a surface of:

$$S_S = Z \times 0.167 \times 24.4\text{Å}^2 = 2.4526 \text{ x } 10^{24} \text{ Å}^2$$

Which divided the by the surface area of the ZnO gives a percent coverage of:

$$\frac{S_S}{S_T} = \frac{2.4526 \times 10^{24}}{2.46051 \times 10^{24}} = 99.6\%$$

Catalytic Activity Calculations and Plots

The mass of the colloidal nanoparticle catalysts were determined as the sum of the Cu and ZnO contents, as determined by TGA.

1)ZnO Stearate capped particles:

The mass of ZnO present was determined according to:

m(ZnO) = m(nanoparticles) x 0.616

where 0.616 is determined from the 38.4% mass loss observed in the TGA, in air, due to the pyrolysis of the stearate group (Fig. S4).

2)Copper stearate particles:

The mass of Cu present was determined according to:

m(Cu) = m(solution) x 0.0.125,

Where the multiplier 0.125 corresponds to the copper content of the residual mass of CuO (where the Cu mass fraction of CuO is 0.799). The residual mass (15.7%) of CuO results from the 84.3% mass loss observed in the TGA, in air, due to the pyrolysis of the stearate group (Fig. S2).

3)ZnO Phosphinate capped particles:

The mass of ZnO present was determined according to:

m(ZnO) = m(nanoparticles) x 0.703,

where 0.703 is determined from the 30.7% mass loss observed in the TGA (under N_2) due to the pyrolysis of the phosphinate group (Fig. S12).

The ratio of ZnO:Cu (w/w) was determined from these values. The mass of the ternary catalyst was determined as the sum of the weight fractions of Cu and ZnO present in the sample.

The GC detector was calibrated using a range of methanol concentrations so as to enable interpolation of the methanol concentrations obtained using the nanocatalysts. The concentration of methanol (Eq. 1) was determined according to the method previously published by Torkelson et al.[8] Eqs. 2-4 outline how the activity, F_{MeOH} (μmol.g^{-1}.h^{-1}) was determined

$$C_{MeOH}\ (\mu mol.\mu L^{-1}) = \left\{\left[\frac{GC\ Counts}{RF}\right].\frac{1}{loop\ size}\right\}.\left[\frac{loop\ temp.}{vapour\ temp.}\right] \qquad (Eq.\ 1)$$

$$F_{MeOH}\ (\mu molmin^{-1}) = C_{MeOH}\ (\mu mol.\mu L^{-1}).V\ (\mu L.min^{-1}) \qquad (Eq.\ 2)$$

$$F_{MeOH}\ (\mu molh^{-1}) = C_{MeOH}\ (\mu mol.min^{-1}).60 \qquad (Eq.\ 3)$$

$$F_{MeOH}\ (\mu molg^{-1}h^{-1}) = \frac{C_{MeOH}\ (\mu mol.h^{-1})}{mass\ of\ ZnO\ and\ Cu\ (g)} \qquad (Eq.\ 4)$$

C_{MeOH} (µmol.µL^{-1}) = the vapour concentration of methanol, GC Counts = the peak area (GC), RF = calibration constant (2000000), loop size = 250 µL, loop temperature = vapour temperature = 523 K, V = volumetric flow rate of the gases (166 µL.min^{-1}).

The methanol activity was monitored vs time, peak activity is reached after ~ 2 h. A representative plot is illustrated in Fig. S16

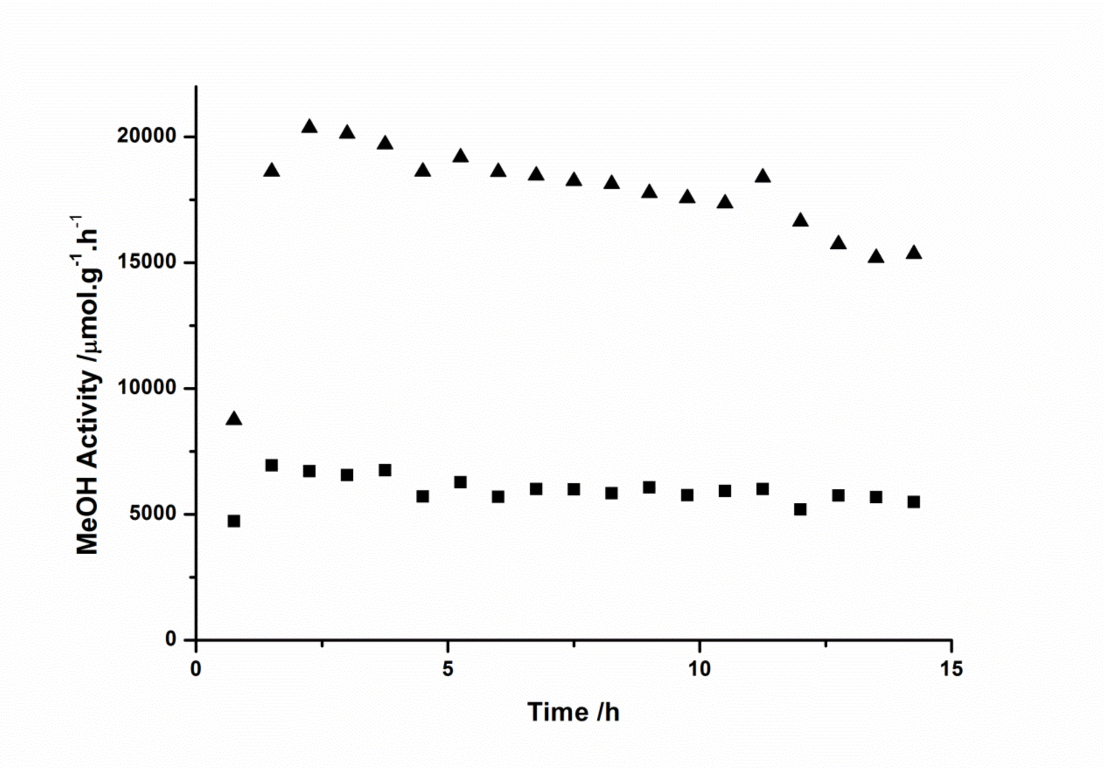

Figure S16: Plot illustrating the methanol activities versus time for a representative colloidal nanocatalyst (triangles) and the ternary reference (squares). The colloidal nanocatalyst refers to Table 2, entry 3: 65:35 (w/w) ZnO with di(octyl)phosphinate ligands: Cu with stearate ligands). Peak activity is reached 1-2 hours and is a combination of both the colloidal catalyst re-structuring to form the active species and the saturation of the head-space and liquid medium with the reactants and products.

Cu(0) Particle Size Distribution

Size analysis (using ImageJ) of the TEM image (Fig. S3) gave the mean particle size to be 5.3 nm ±0.5 nm and the particles in a range of 1 – 10 nm. EDX analysis of the TEM micographs collected (on gold grids) show copper pesence throughout the area, indicating that copper is present on the grid as resolved particles (1 – 10 nm) and as un-resovled particles (sub 1 nm).

In addition, dynamic light scattering (DLS) experiments were conducted which gave a paticle size range of 7.1 – 11.3 nm. DLS measurements iclude the particle as a whole, including the organic corona around the copper particles, a simple substraction of the length of a stearate chain (2.8 nm) gave a size range of 1.1 – 5.7 nm.

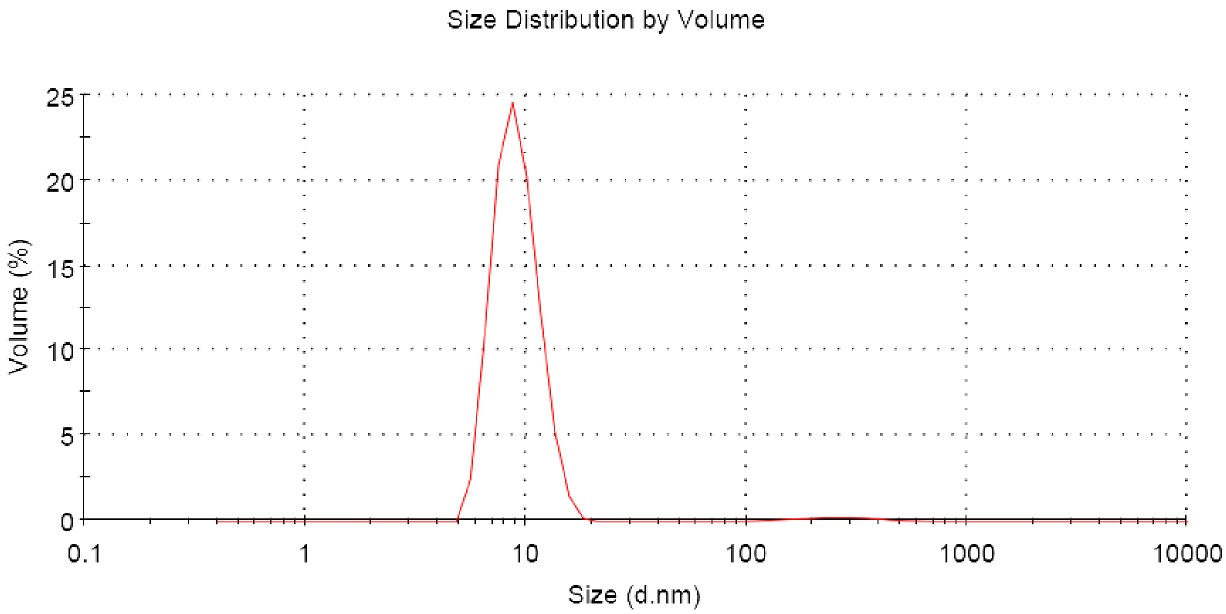

Figure S17: DLS plot of Cu(0) nanoparticles in toluene in a sealed cuvette (solution filtered before through a 1 micron filter to remove any dust particles)

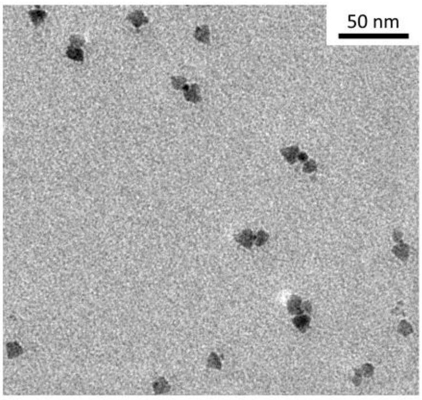

Figure S18: Additional TEM image of particles isolated from catalyst **2** to accompany the image shown in the main manuscipt.

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