A colloidal ZnO/Cu nanocatalyst for methanol synthesis†

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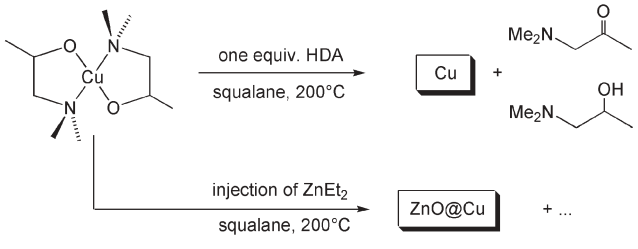
Free-standing, ZnO surface decorated Cu nanoparticles of 1–3 nm size were obtained by sequential co-pyrolysis of $[Cu(OCHMeCH_2NMe_2)_2]$ and $ZnEt_2$ in squalane in the absence of additional surfactants and proved to be highly active quasi homogeneous catalysts for methanol synthesis from CO and H_2.

Colloidal catalysts, composed of free-standing metal nanoparticles, which are specifically surface modified or decorated in order to tune their stability, solubility and functionality, represent a growing branch of nanochemistry.[1,2] The preparation of such colloids typically involves metal salt reduction in the presence of surfactants[2] *e.g.* the polyol-process[3] or electrochemical methods.[4] Alternative approaches include the Bönnemann concept, namely metal precursor reduction and particle stabilisation with alkylaluminium compounds[5] and the hydrogenolysis of labile all-hydrocarbon metal complexes developed by Chaudret.[6] Most recently, Schüth *et al.* have demonstrated a novel quasi homogeneous methanol synthesis from CO and H_2 over highly active Cu particles (3–5 nm), obtained by reducing $[Cu(acac)_2]$ with AlR_3 (R = *n*-octyl, *n*-butyl) in THF.[7] This report prompted us to present here our parallel results on comparably active *binary* Cu/ZnO colloids derived by metalorganic precursor pyrolysis in hydrocarbon media.

With a capacity of about 30 million tons per year worldwide, the methanol synthesis over ternary $Cu/ZnO/Al_2O_3$ solid-state catalysts is a very important industrial process and is regarded as a proto-typical case of the so-called strong metal support interaction (SMSI) in heterogeneous catalysis.[8] Liquid-phase processes using the same type of $Cu/ZnO/Al_2O_3$ catalysts prepared by classical aqueous co-precipitation/calcination techniques and supplied as a slurry in non-aqueous media have been studied as alternatives to the heterogeneous gas-phase process.[9] The characterisation of the catalytic properties of free-standing, ZnO and/or Al_2O_3 surface decorated Cu nanoparticles as a function of composition, surface to volume ratio and the particular surface structure is suggested to offer novel options for process development[1,2] as well as for investigating the SMSI and related effects.[7,8]



Scheme 1 Reaction pathways towards HDA/Cu and ZnO/Cu colloids (squalane: 2,6,10,15,19,23-hexamethyltetracosane).

We have been active in setting up such a tuneable colloidal system of Cu/ZnO composite nanoparticles over the last few years, and $[Cu(OCHMeCH_2NMe_2)_2]$ (**1**) was found to be a very suitable precursor for clean Cu nanoparticle formation upon pyrolysis at 473 K (200 °C) in non-aqueous inert solvents (Scheme 1, Fig. 1a).[10] The reversible redox-chemistry, which involves Cu_2O/Cu core-shell particles stabilised by hexadecylamine (HDA), was probed by FT-IR CO-adsorption studies.[11] Photo decoration of ZnO particles with Cu using **1** was described.[12] We also reported on α/β–Cu/M (M = Al, Zn) colloids, *i.e.* nanobrass, obtained by co-pyrolysis of **1** and $ZnEt_2$[13] or by co-hydrogenolysis of $[CpCu(PMe_3)]$ with $[ZnCp^*_2]$[14] as well. But none of these colloids, even after oxidation/reduction cycles, proved catalytically active, so far. However, when $ZnEt_2$ was added just 1–2 min *after* the injection of **1** into pure hot squalane (Scheme 1), rather than in parallel, and *without* the addition of HDA as done before,[10,13] unusually small and uniform *free-standing* ZnO/Cu particles of 1–3 nm in size were formed (Fig. 1b). These surprisingly stable, red-brown colloids proved to be very active methanol catalysts (Table 1).

Neither (nano-) crystalline Cu nor Zn or ZnO were detected by selected area electron diffraction (not uncommon for very small particles), but energy dispersive X-ray spectroscopy (EDS) of the precipitated, washed and re-dispersed particles revealed both Cu and Zn in the expected molar ratios. According to extended X-ray absorption fine structure analysis (EXAFS) the as-synthesised

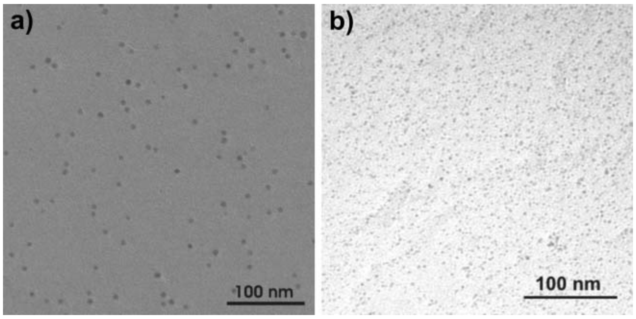


Fig. 1 Transmission electron microscopy (TEM) images of (a) HDA/Cu colloids of 3–6 nm particle size and (b) ZnO/Cu (50 : 50) colloids of 1–3 nm particle size.

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Table 1 Catalytic activity of HDA/Cu and ZnO/Cu colloids referenced to an industrial catalyst (slurry) at the same conditions.

Sample	Productivity/ μmol g_{cat}^{-1} h^{-1}	Activity (%)
HDA/Cu	9	0.4
ZnO/Cu (25 : 75)	1371	58.5
ZnO/Cu (50 : 50)	1971	84.1
Ternary reference catalyst 50 CuO/35 ZnO/15 Al_2O_3	2342	100

samples can be described as being composed of ∼1.8 nm Cu particles (from the coordination number of the first Cu–Cu shell, which is related to the particle size,[15] matching the TEM data), together with a non-aggregated oxygen deficient ZnO-phase (Fig. 2). The Cu–Cu distance of 2.511(±0.003) Å is shortened by about 1.5% compared to a Cu reference colloid of 2.542(±0.004) Å (Cu foil: 2.543 ± 0.002 Å), the shrinkage being a bit more pronounced than the 0.8% reduction of Schüth's organoaluminium stabilised, slightly larger Cu particles.[7] This observation is attributed to a particle-size effect[16] and the influence of the ZnO surface species.[17]

Upon a few minutes contact with air at 25 °C some copper oxide is formed (EXAFS), as shown in the traces in Fig. 2 denoted as Air(1 ×) and Air(2 ×). The Cu–O distance of 1.88 Å indicates a mixture of predominantly Cu^+ and probably some Cu^{2+}. The ZnO-like phase simultaneously incorporates O-atoms and develops into a phase more akin to the ZnO bulk structure (Fig. 2c and 2d, XANES, and supplementary information†) without exhibiting distinct long-range order (EXAFS). Correspondingly, the 564 nm UV-vis absorption of the as-synthesised material only gradually red-shifts (595 nm) over 30 min of oxidation (Fig. 3), while pure, *i.e.* ZnO-free, Cu-colloids instantaneously change colour from red to blue-green.[11] This significant deceleration of the Cu-oxidation together with the EXAFS data suggests small Cu particles which are only *partly* surface covered with ZnO species, denoted as ZnO/Cu.

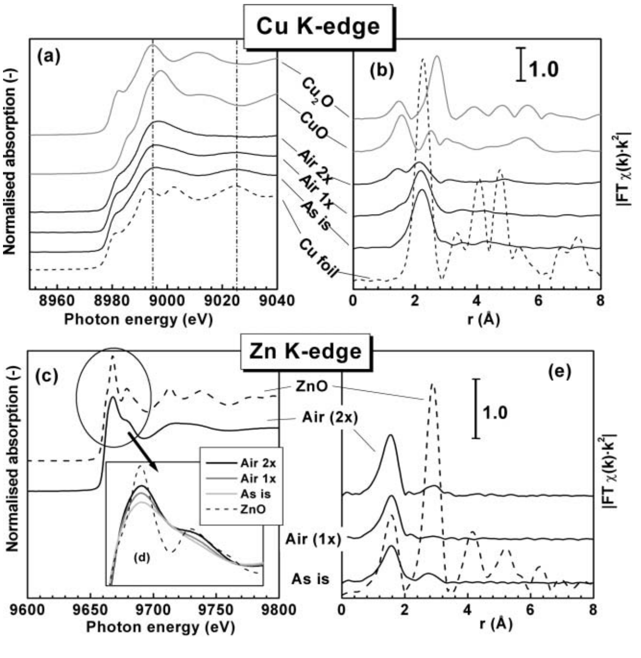

Fig. 2 XAFS of ZnO/Cu (50 : 50) colloid samples. Shown are CuK and ZnK XANES (a,c,d) and EXAFS (b,e). Graph d is an enlargement and overlay of a part of the ZnK XANES. Coordination number of first (Cu) shell in "as is" sample (b): 8.6 ± 0.6.

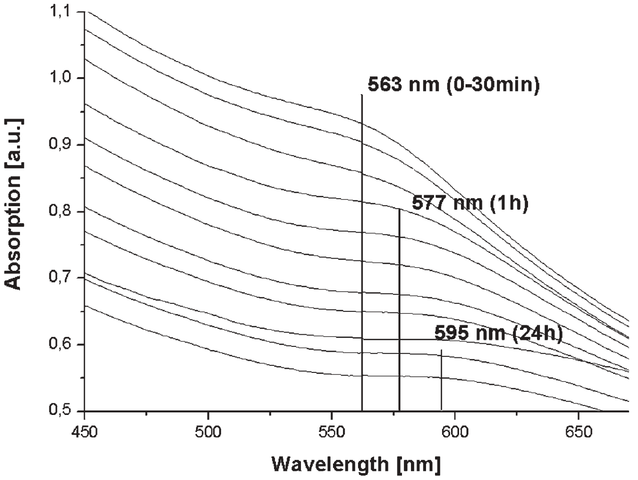

Fig. 3 UV-vis spectra of the *in situ* oxidation of ZnO/Cu colloids.

The synthesis principle can thus be described as kinetic trapping of growing Cu particles by surface deposition of ZnO. The intrinsic formation of ZnO species under inert conditions (Ar) is explained by the fast ligand metathesis reaction of **1** and/or its decomposition products (Scheme 1) with $ZnEt_2$ to yield Cu, *n*-butane and $[Zn(OCHMeCH_2NMe_2)_2]$ which then releases ZnO adsorbing to the Cu particle surface.[18] Interestingly, the particle size distribution remained unaffected by the ZnO content.† The idea proved extendable to other ZnO/M (M = Ni, Pd) composite particles, so far. The use of $[MeZnOR]_4$ (R = CH_2CH_2OMe) as direct ZnO precursor[19] instead of $ZnEt_2$ gave similar results.

Catalytic tests were conducted in a continuously operated high pressure liquid reactor in squalane solution with freshly synthesised colloids of c(Cu) = 0.1…0.5 mol L^{-1} at 2.6 MPa with a feed gas mixture of 72% H_2, 10% CO, 4% CO_2 and 14% N_2. Squalane was selected as solvent because of very good gas solubility of the gases. The methanol productivity was continuously monitored by online GC every 22 min during *several days* of testing at 493 K (220 °C). Afterwards the colloids were checked again by TEM revealing no significant changes. Methyl formate was not detected as product or (trace) intermediate contrasting the Bönnemann-type Cu colloids.[7] The data were referenced to a commercially available ternary catalyst, which was crushed, sieved (<63 μm), suspended in squalane and pre-reduced at 493 K using diluted hydrogen (0.5 MPa) to yield the active $Cu/ZnO/Al_2O_3$ state.[17] The steady-state results are compiled in Table 1.

The HDA/Cu colloid exhibited a negligible activity of 9 μmol g_{Cu}^{-1} h^{-1}. Despite this we found that H_2, CO, CO_2 and O_2 penetrate through the surfactant shell and reversibly adsorb at the particle surface,[11] we cannot rule out the inhibition by HDA as the reason for the observed low activity. However, it should be noted here, that the catalytically active Cu particles (also ZnO-free) reported by Schüth *et al.* are likely to contain (organo-) aluminium surface species.[5,7] From that comparison it appears, that the intrinsic activity of unsupported, very small Cu nanoparticles without any promoting surface decoration is still an open question.

Our composite particles ZnO/Cu (25 : 75) exhibited 58.5% relative activity and by raising the ZnO content to ZnO/Cu (50 : 50) a remarkable level of 84.1% of the *ternary* reference catalyst was reached (Table 1). This dependence of the catalyst activity from the Cu/ZnO molar ratio is well known from the detailed micro-structure/activity analysis of industrial catalysts and closely related to binary Cu/ZnO systems. The effect was correlated to the strain in the Cu nanoparticles enhanced by ZnO surface species due to interfacial interactions.[17] The HDA/Cu particles agglomerate and precipitate under the conditions of catalytic testing within two days, while the ZnO/Cu colloids most surprisingly remained unchanged over two weeks. The supposed *partial* surface decoration with ZnO species apparently stabilises the Cu particles against agglomeration quite effectively, probably by electrostatic forces. In contrast, the alloy nanoparticles $Cu_{1-x}M_x$ (M = Al, Zn; $0.1 \leqslant x \leqslant 0.5$), which were synthesised by co-hydrogenolysis of suitable precursors, and their surface oxidised core–shell type congeners $(ZnO)_\delta/Cu_{1-x}Zn_{x-\delta}$ and $(Al_2O_3)_\delta/Cu_{1-x}Al_{x-\delta}$ ($\delta \leqslant x$), need to be stabilised by the addition of surfactants like poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO).[14]

In summary, we suggest our ZnO/Cu nanoparticles as an alternative quasi homogeneous system for catalytic methanol synthesis from CO and H_2, allowing a detailed kinetic analysis. Comparing the productivities of Table 1 with the industrial process is not straightforward. However, using reported kinetic data at 50 bar being suitable for screening heterogenous methanol catalysts (linear extrapolation), the methanol synthesis rate of the colloids is on the same order of magnitude.[20] A more detailed study of these issues is underway. The colloid synthesis described and discussed above offers the option of rational variation of the particle composition by free adjustment of the molar ratios of the precursors without simultaneously changing the particle size distribution. An extension of the preparation concept to the ternary Cu/ZnO/Al_2O_3 and similar surface oxide decorated colloidal nanocatalysts,[1,2] seems possible and attractive.‡

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Notes and references

‡ All manipulations were carried out in anhydrous solvents under an argon atmosphere. *Colloid Synthesis and Catalytic Testing.* Injection of a mesitylene solution (5 ml) of [Cu(OCHMeCH$_2$NMe$_2$)$_2$] (**1**, 0.486 g, 1.8 mmol) into 20 ml dried and degassed squalane charged with an equimolar amount of HDA at 200 °C and 20 min annealing afforded a deep red solution of colloidal copper. If samples of $ZnEt_2$ (0.077 g, 0.6 mmol and 0.22 g, 1.8 mmol respectively) dissolved in 2 ml mesitylene were injected about 60 s after injection of **1** into pure hot squalane, the ZnO/Cu colloids were obtained. The catalytic test reactor was charged with the colloids (300 mg) and 200 ml of pure squalane, pressurised with the feed gas mixture and set to 443 K (Table 1).[21] The composition of gas phase was monitored by GC (Porapak and a molecular sieve column). The methanol concentrations were in the range up to 1%. *Transmission Electron Microscopy*. Samples were prepared under Ar (glove box) by placing a droplet of the colloid onto a carbon-coated Au grid (*Hitachi* H-8100, 200 kV, LaB_6-filament). *X-ray Absorption Spectroscopy (XANES, EXAFS).* The absorption edges of Cu and Zn at 8979.0 and 9659.0 eV, respectively were measured at the E4 beamline of Hasylab (Hamburg, Germany) using a Si(111) double-crystal monochromator detuned to give 50% of maximum intensity for exclusion of higher harmonics. Samples were prepared in their native colloidal form using a custom-made EXAFS cell, in which the liquid was entrapped between two sheets of Kapton foil, excluding any contact to the ambient atmosphere. The spectra $\mu(k)$ were recorded at room temperature (transmission mode, a metal foil measured in parallel for energy calibration). Data treatment was carried out using the software package VIPER.[22] For background subtraction a Victoreen polynomial was fitted to the pre-edge region. A smooth atomic background $\mu_0(k)$, was evaluated using smoothed cubic splines. The radial distribution function FT[$k^2\chi(k)$] was obtained by Fourier transformation of the k^2-weighted experimental function $\chi(k) = (\mu(k)–\mu_0(k))/\mu_0(k)$ multiplied by a Bessel window. Duplicate spectra were recorded to ensure data reproducibility.

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