Preparation, microstructure characterization and catalytic performance of Cu/ZnO and ZnO/Cu composite nanoparticles for liquid phase methanol synthesis

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Received 16th February 2012, Accepted 16th April 2012
DOI: 10.1039/c2cp40482f

Stearate@Cu/ZnO nanocomposite particles with molar ratios of ZnO : Cu = 2 and 5 are synthesized by reduction of the metal–organic Cu precursor [Cu{(OCH(CH3)CH2N(CH3)2)}2] in the presence of stearate@ZnO nanoparticles. In the case of ZnO : Cu = 5, high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) combined with electron-energy-loss-spectroscopy (EELS) as well as attenuated total reflection infrared (ATR-IR) spectroscopy are used to localize the small amount of Cu deposited on the surface of 3–5 nm sized stearate@ZnO particles. For ZnO : Cu = 2, the microstructure of the nanocomposites after catalytic activity testing is characterized by HAADF-STEM techniques. This reveals the construction of large Cu nanoparticles (20–50 nm) decorated by small ZnO nanoparticles (3–5 nm). The catalytic activity of both composites for the synthesis of methanol from syn gas is evaluated.

1. Introduction

Binary Cu/ZnO and ternary Cu/ZnO/Al2O3 solid state nano-composites, which are usually fabricated by co-precipitation/calcination/reduction processes, are considered as typical examples of supported heterogeneous copper catalysts in two-phase gas/solid systems and have been utilized and optimized for industrial production of methanol from synthesis gas (CO, CO2 and H2O) for a long time. These systems show the so-called strong metal support interaction (SMSI) that depends upon the interface between the Cu and the ZnO phase, which is also important for related catalytic reactions such as methanol oxidation and methanol steam reforming.1–4 The same type of catalyst for methanol synthesis can also be used in a three-phase system. An example is the use of finely ground solid catalyst powder, dispersed in a liquid slurry phase, in a pressurized batch or continuously operated reactor.5 Quasi homogeneous, colloidal catalysts in non-aqueous media featuring Cu and ZnO nanoparticles in interfacial contact have also been developed by Fischer et al.,6 and Schüth et al.7 Sophisticated organometallic precursor chemistry was employed in order to take advantage of both colloidal and nanoparticle chemistry in terms of control of composition, size and shape of the dispersed catalyst particles and modulation of the Cu/ZnO interface. Kimura et al.,8 and Muhler et al.,9 reported on related colloidal systems which were prepared by the reduction of low-cost and easily available air-stable metal stearates, with H2. In particular, highly active and selective colloidal Cu/ZnO catalysts for liquid phase methanol synthesis were obtained by this stearate precursor route and the mechanism and dynamic properties of Cu and ZnO particle formation and aggregation were studied.8

Microstructure–activity relationships for ZnO supported Cu catalysts have been studied extensively and conclusions were drawn about the specific copper surface area10 and the microstrain in the copper particles11 as important parameters affecting the activity of this type of catalyst. Industrial Cu/ZnO/Al2O3 catalysts are commonly prepared by precipitating copper–zinc hydroxycarbonates from metal nitrate solutions, and it is established that this precipitation process greatly influences the activity of the resulting Cu/ZnO catalysts for methanol synthesis through precipitate ageing and reduction, i.e. the kinetics of the nanocomposite formation.12–14 Schlögl et al. showed that the activity of Cu/ZnO catalysts obtained from precipitates aged for more than 30 min correlates with an...
increase in microstrain in the copper NPs.\textsuperscript{13} The same authors reported high resolution transmission electron microscopy (HRTEM) investigations of the microstructure of (reduced) Cu/ZnO catalysts obtained from hydroxycarbonate precipitates with different aging periods. It was found that the activity towards methanol steam reforming correlates with the distinct change in the microstructure of the catalysts at Cu/ZnO interfaces.\textsuperscript{14} On the other hand, Poul L. Hansen et al. used in situ transmission electron microscopy to obtain atomic resolution images of copper NPs on zinc oxide and silica support materials.\textsuperscript{15} It was found that copper NPs supported on ZnO undergo dynamic reversible shape changes in response to the redox-potential of the gaseous environment. This clearly establishes the dynamic nature of the catalyst during the catalytic reaction and underlines the importance of understanding the interfaces present in a Cu/ZnO sample. Recently, the catalytic activity of a physical mixture of copper and ZnO nanoparticles of controlled morphologies has been studied by Tsang et al.,\textsuperscript{16} and commented upon by F. C. Meunier.\textsuperscript{17} Tsang and co-workers showed that the interaction between Cu NPs and the (002) polar planes of platelet-like ZnO crystals is stronger than that detected between Cu NPs and rod-like ZnO crystals in which the apolar faces (100) and (101) were exposed. This resulted in higher selectivity to methanol of about 70\% in the case of ZnO platelets compared to about 40\% in the case of ZnO nanorods.\textsuperscript{16,17}

Interestingly, all reports on ZnO/Cu (ZnO surface species decorated Cu NPs) or on the reverse case of Cu/ZnO (Cu surface species supported by ZnO NPs) exhibit the common feature of preparation of the composite nanoparticles with a large amount of Cu, which is more or less equimolar to the ZnO content or even exceeds this level (matching with the molar ratio in the industrial catalyst).\textsuperscript{8} In all of these reported microstructure characterization studies, the typical particle sizes of the Cu and ZnO phases with interfacial contact were large enough to be characterized using common microscopic techniques, \textit{i.e.} bright field and HRTEM. However, Cu/ZnO interfaces with surface Cu layers of only a few atomic-layers thick of Cu are rarely studied in the literature due to the limitation of materials and specimen preparation and ordinary microscopic techniques. Therefore, we undertook a study aiming to prepare colloidal Cu/ZnO nanoparticles with a comparably small amount of Cu; only a few atomic layers dispersed on the surface of small ZnO nanoparticles (≤ 5 nm). These Cu/ZnO NPs were obtained by selective photo-reduction of a controlled amount of copper precursor [Cu[[O(CH(CH₃)CH₂N(CH₃)₂)]₂] and Cu deposition at the surface of preformed stearate stabilized ZnO NPs in colloidal solution.\textsuperscript{6c} A molar ratio of ZnO : Cu = 5 was selected and we used a combination of advanced electron microscopic techniques (HAADF-STEM and spatially resolved EELS) for microstructure characterization. Standard bright field and HRTEM techniques gave only a preliminary understanding of the structure of the Cu/ZnO composite. Further, we used ATR-IR spectroscopy to establish the interface unambiguously. The catalytic performance of these Cu decorated ZnO particles was compared to a system of a more or less reverse microstructure, namely a ZnO/Cu composite with small ZnO NPs decorating the surface of larger Cu NPs. This latter reference system was prepared by H₂ reduction of copper stearate in the presence of preformed stearate@ZnO NPs in squalane under conditions matching for subsequent \textit{in situ} catalyst testing and comparison of both the Cu/ZnO and the ZnO/Cu system with our previous data on colloidal methanol catalysts obtained from co-reduction of copper and zinc stearate precursors.\textsuperscript{5}

\section{Experimental section}

\subsection{Materials and preparation of the stearate@ZnO nanoparticles}

All operations were performed under an inert atmosphere, using standard Schlenk techniques and an MBraun glovebox unless stated otherwise. All solvents were of analytical grade, degassed and dried (<5 ppm H₂O) using MBraun SPS. [Cu[[O(CH(CH₃)CH₂N(CH₃)₂)]₂] was synthesized according to a known literature procedure published by Buhro et al., by reacting copper methanolate with the corresponding amino alcohol in an alcohol exchange procedure.\textsuperscript{18} Copper(ii) stearate was synthesized according to the method reported in the literature,\textsuperscript{19} as commercial Cu stearate contains Ni impurities. HDA-stabilized ZnO nanoparticles (HDA@ZnO NPs) were prepared according to the method described in our previous publication.\textsuperscript{20} In brief, [CH₃ZnOPr₄] was injected into wet HDA at 250 °C and the mixture was kept under stirring at this temperature over a period of 30 min. In order to fully oxidize the precursor a stream of Ar, passed through a bubbler filled with water (wet Ar), was bubbled through the reaction vessel. Product isolation was performed by repeated washing with alcohol and subsequent re-dispersion of the particles in toluene. The final material could be well dispersed in non-polar solvents like toluene and n-hexane. The replacement of HDA with stearic acid as a surfactant was achieved by addition of a few drops of melted stearic acid to a hot solution of HDA@ZnO NPs suspended in toluene. The mixture was refluxed for 30 min and then cooled down to room temperature followed by repeated washing with methanol and subsequent re-dispersion of the particles in toluene for isolation of stearate@ZnO NPs. The quantitative exchange of the surfactants and the formation of stearate@ZnO NPs were easily confirmed by FTIR measurements.

\subsection{Preparation of stearate@Cu/ZnO NPs (ZnO : Cu = 5), sample 1}

The preparation concept of surfactant stabilized Cu/ZnO NPs (sample 1) was described in our recent publication (where HDA was used as a surfactant instead of stearate).\textsuperscript{6c} In brief, a sample of 0.8 g of 3–5 nm in diameter stearate@ZnO NPs (the real wt. of pure ZnO NPs without stabilizer is 0.58 g) was placed in a quartz Schlenk tube and dried at 140 °C under vacuum over a period of 4 h in order to remove moisture and air. A volume of 80 mL of toluene was added and the suspension was left to stir for 30 min, resulting in a light yellow transparent dispersion. A sample of 0.316 g of [Cu[[O(CH(CH₃)CH₂N(CH₃)₂)]₂] dissolved in 20 mL of toluene and a volume of 15 mL of freshly dried methanol was added under argon protection to the mixture thus forming a transparent violet dispersion. The suspension was left to stir for 30 min at room temperature and a cooling finger, connected to a cryostat, was attached to the reaction vessel in order to keep the temperature of...
the reaction at 24 °C during the photoreduction. The mixture was then irradiated with UV light (Hg high-pressure lamp, Original Hanau GmbH, Heraeus AG, TQ 718/N 9380, operating at 254 nm (62% relative intensity) and 365 nm (100% relative intensity) at 500 W) over a period of 2 h. The initially deep violet suspension gradually turned to light reddish color mixed with some violet color as the reaction proceeded as a result of partial reduction of the Cu precursor. The only partial photoreduction of the Cu precursor, i.e. the presence of some free Cu precursor in the reaction medium, was confirmed by ATR-IR and HRTEM measurements. The product, i.e. stearate@Cu/ZnO NPs (<15 wt% Cu with respect to the weight of ZnO), was obtained by removal of all volatiles in vacuum at 50 °C overnight, to obtain a reddish sticky solid material. This material was readily dispersed in non-polar solvents like toluene, n-hexane or squalane (for catalysis testing and transfer to the continuously operated stirred tank reactor (CSTR)) and showed high stability for a long time. Purification through washing away of the low molecular weight Cu-precursor was excluded in order to avoid the removal of the stabilizer and oxidation of the copper content (which is always followed by instability of the nanocolloid).

2.3. Preparation of stearate@ZnO/Cu NPs (ZnO : Cu = 2), sample 2

The Cu-based colloidal nanocomposite ZnO/Cu was prepared from Cu(n) stearate and preformed 3–5 nm sized-stearate@ZnO NPs (see above). Cu(n) stearate ([Cu(CH2(CH3)5COO])2; 0.75 g, 1.2 mmol) and stearate@ZnO NPs (0.2 g ZnO NPs or 0.28 g stearate@ZnO NPs with 28% organic contribution, 2.4 mmol) were suspended in 75 mL of squalane. Squalane can be considered as the best solvent for the catalytic activity testing because of the high boiling point, inertness, the low viscosity and the high gas solubility of the synthesis gas. The colloidal particles preparation and the subsequent catalytic reaction were performed in a continuously operated high-pressure reactor (CSTR). The suspension was stirred at 200 rpm and purged until air-free. The reduction procedure was performed as follows: for the optimized reduction procedure, the reaction mixture at 110 °C was purged with nitrogen for 1 h to remove residual water and air. Then, the reduction was started by switching to pure H2, increasing the pressure to 5 bar and heating to 220 °C (5 K min−1, hold time = 16 h) at a flow rate of 100 mL min−1. The reduction procedure resulted in a red colloidal solution of stearate@ZnO/Cu NPs [Cu/ZnO = 1 : 2 molar ratio]. In order to examine the catalytic activity of the colloidal catalyst in methanol synthesis, the pressure was increased with hydrogen to 26 bars and then switched fully to synthesis gas.

2.4. Catalytic test experiments

Catalytic testing of sample 1 and sample 2 was conducted in the CSTR reactor with freshly prepared nanocolloids by switching from reduction gas to synthesis gas (64% H2, 32% CO, 2% CO2, 2% N2), pressurized to 26 bar at 220 °C. The product flow containing the evaporated methanol and water as well as the non-converted gas components was continuously monitored by an online GC (Porapak® and a molecular sieved packed column) every 20 min. The catalytic activity of the nanocolloids was referenced to a ternary catalyst (50% CuO/35% ZnO/15% Al2O3), which was crushed, sieved (<63 nm), suspended in squalane and pre-reduced by increasing the temperature and the hydrogen content step-by-step from 100 °C to 220 °C and from 5 to 20 vol% to yield the active Cu/ZnO, respectively, Cu/ZnO/Al2O3 state.

2.5. Characterization

Transmission Electron Microscopy and Spectroscopy, High Resolution Transmission Electron Microscopy (HRTEM), High Resolution High Angle Annular Dark Field (HR-HAADF-STEM and spatially resolved Electron Energy-Loss Spectroscopy (STEM-EELS) experiments were carried out at EMAT on a FEI Titan 80–300 “cubed” microscope fitted with an aberration-corrector for the imaging lens and another for the probe forming lens as well as a monochromator, operated at 300 kV. For HAADF-STEM imaging, an inner collection semi-angle β of 50 mrad was used. EEL spectroscopy experiments were performed on a GIF-QUANTUM spectrometer. The STEM convergence semi-angle used was ~21.5 mrad, providing a probe size of ~1 Å at 300 kV. The collection semi-angle β was ~100 mrad. Where plotted, the data were background subtracted using a common power-law background model.21 To generate the elemental maps, the data were treated using principle component analysis and mapped by plotting the integrated intensity under the power-law background subtracted EELS edges using an integration window. Powder X-ray diffraction (PXRD). XRD diffractograms were taken on a D8-Advance Bruker AXS diffractometer with Cu Kα radiation (λ = 1.54178; 0–20 scan; 2θ = 20–80°). The sample was placed into standard capillaries (0.7 mm diameter) under inert gas and measured in Debye–Scherer geometry with a position-sensitive detector. The reference data for the hexagonal wurtzite structure of ZnO and fcc-Cu were taken from the International Centre for Diffraction Data (ICDD, PDF-2 Release 2004) database.

In situ ATR-IR spectroscopy. ATR (attenuated total reflection) IR spectra were recorded using a SensIR DuraSamplIR II flow-through cell equipped with a single reflection diamond internal reflection element (IRE). The cells were mounted in a Nicolet Nexus Fourier transform infrared spectrometer (FTIR) equipped with a mercury cadmium telluride (MCT-A) detector. Spectra were acquired at 4 cm−1 resolution, accumulating 150–300 scans. The ATR cell was operated at temperatures up to 200 °C and pressures up to 1.0 MPa. The colloidal dispersion (stearate@Cu/ZnO colloids in hexadecane) was saturated with gases in a home-made steel reactor equipped with a glass liner and was continuously circulated through the cell with a gear pump (ISMATEC Reglo-ZS). The gases and gas mixtures were supplied with the following purities: H2 (99.9999%), CO (99.997%), CO2 (99.995%), Ar (99.9999%) and synthetic air (20% O2/N2) (99.999%, hydrocarbon free). A trap with zeolite Y was operated at 300 °C, to decompose metal carbonyls from the CO line.

3. Results and discussion

3.1. Preparation and characterization of small stearate@ZnO NPs decorated with a few atomic layers of Cu, sample 1 (Cu/ZnO)

The colloidal HDA@ZnO NPs with 3–5 nm ZnO particle size distribution were derived from [CH2ZnO(PO)4 in toluene as described previously.20a For catalytic testing of the Cu/ZnO
composite NPs in a liquid phase the exchange of HDA for stearate as a surfactant is necessary in order for the results to be compatible with our previous work on Cu/ZnO colloids in squalane, derived by the metal stearate precursor route (see the Experimental part). Replacement of HDA with stearic acid resulted in a quenching of the surface trap green emission (at 535 nm) and an enhancement of the narrow UV yellow emission (at 365 nm) of the ZnO NPs upon excitation at 325 nm (see Fig. S1, ESI†). Actually, this reflects the contribution of the stearate as a surface capping group (surfactant) for ZnO NPs and may explain the less efficient photo-reduction of copper precursors at the modified surface of ZnO, as compared to its quantitative decomposition in the case of HDA as a surface capping group (see Discussion below). The surface modification of ZnO NPs with stearate was confirmed by FTIR measurements. The FTIR spectrum of the stearate@ZnO NPs shows the absence of N–H vibration peaks at 3000–3500 cm⁻¹ and the appearance of two peaks at 1584 and 1480 cm⁻¹ which are assigned to asymmetric and symmetric stretchings of the COO⁻ group of the stearate stabilizer in contact with the ZnO surface (see Fig. S2, ESI†).

For the preparation of Cu/ZnO sample 1, the copper alkoxide precursor [Cu{(OCH(CH3)2CH2N(CH3)2)}2] was added to the dry toluene stearate@ZnO NPs dispersion and finally the sacrificial electron donor methanol was added to the mixture. The initial toluene dispersion of stearate@ZnO NPs remained stable even if a reasonable amount of alcohol (5–20 mL) was added to it. This procedure was done in order to achieve a maximum deposition of 15 wt% of Cu at the surface of stearate@ZnO NPs. Thus, the initial solution containing all reagents was transparent, violet in color and without any signs of undesired precipitation. The solution was irradiated with UV light at 365 nm (Hg mercury lamp, 500 W) over a period of 2 h at 24 °C. A gradual color change from violet to light reddish color occurred but mixed with violet color as the reaction proceeded as a result of only partial reduction of the Cu precursor. This only partial reduction of the Cu precursor is assigned to the effect of the stearate stabilizer that prevents some copper precursors from reaching the surface of ZnO NPs and to the modification of surface states as discussed above. The fact that some traces of copper precursor were observed on the wall of the Schlenk tube during removal of the volatiles under vacuum at 50 °C can be seen as an indication of the presence of free precursor material. Note that we tried to avoid the presence of untreated Cu precursor residues by using a sample of HDA@Cu/ZnO particles and exchanging the HDA for stearate. However, we could not obtain a stable colloid in that case because of the many steps of washing, precipitation and resuspension in toluene during the exchange process.

Interestingly, the presence of photodeposited Cu in combination with a stearate stabilizer on the surface of ZnO NPs leads to a very efficient saturation of surface traps of the ZnO NPs, meaning sample 1 only emits at the band gap as a result of exciton recombination (see Fig. S3, ESI†).

The microstructural characterization of sample 1 was very demanding, as the low amount of Cu at the surface of the stearate@ZnO NPs was not detectable by high resolution transmission electron microscopy (HRTEM) in our related, previous work on Cu deposition on HDA@ZnO NPs.⁶c To confirm the suggested composition and microstructure of sample 1 as stearate@Cu/ZnO NPs with a Cu/Zn molar ratio of 1 : 5 (see Fig. S4, ESI†), HAADF-STEM in combination with spatially resolved electron-EELS as well as attenuated total reflection Fourier transform infrared (ATR-IR) spectroscopy were applied to localize the small amount of Cu forming an interfacial contact with the surface of the stearate@ZnO NPs. An overview of HAADF-STEM of the stearate@Cu/ZnO colloids with a corresponding Fourier transform (FFT) pattern is displayed in Fig. 1a.

All colloidal particles of sample 1 in the HAADF-STEM image have sizes ranging from 3 to 5 nm in diameter, and the Fourier transform only shows d-spacings corresponding to wurtzite hexagonal ZnO. A typical high resolution image of a stearate@ZnO NP imaged along the [111] zone axis orientation is displayed as an inset. No Cu or CuO structure shell is visible from the image, and no d-spacings corresponding to another phase are detected. The fact that all particles are wurtzite ZnO is confirmed by the uniform image contrast; as the image contrast in HAADF-STEM images is known to be mass-thickness sensitive, a dense Cu shell or metallic Cu NPs would light up in this imaging mode.

To confirm the presence of Cu at the surface of these stearate@Cu/ZnO NPs, we adopted spatially resolved electron energy-loss spectroscopy. First, an EELS spectrum was taken from several particles simultaneously (Fig. 1b, spectrum 2). The spectrum clearly shows the presence of a Zn peak at 1020 eV and a Cu peak at 930 eV (see reference peaks for the Zn L2,3 and Cu L2,3 edges respectively), confirming the sample contains Cu. To map the Cu at the surface of individual stearate@Cu/ZnO nanoparticles, we adopted the spectrum imaging (SI) technique. In this technique, the electron probe is scanned over the sample in small steps, acquiring an EELS spectrum at each point. The scanned region is displayed in the HAADF-STEM image in Fig. 1c. From the acquired EELS data Cu (Fig. 1d), O (Fig. 1e) and Zn (Fig. 1f) maps were generated. A color map is displayed in Fig. 1g. It is clear that the nanoparticles are ZnO with a small amount of Cu at the ZnO surface. The EELS spectrum (Fig. 1b, spectrum 3) from a single nanoparticle (signal averaged over the region indicated in the Cu map in Fig 1d) is displayed together with the other EELS spectra for reference.

This single-particle spectrum also shows the presence of Cu—assuring us that the Cu must be present in a few atomic layers at the surface or as single atoms at the ZnO surface, as all scanned particles only showed the presence of wurtzite ZnO in HAADF-STEM imaging.

As a confirmation for the adsorption of Cu at the surface of stearate@ZnO NPs of sample 1, the colloid was probed by in situ ATR-IR CO adsorption studies. Previously we reported on the redox chemistry of Cu nanocolloids in toluene stabilized by HDA⁶d and Cu/TiO₂ stabilized by oleic acid.⁶e In these cases, CO penetrates the shell of organic capping ligands and adsorbs at the Cu surface and the reported data can be taken as a reference for our study herein. Also, HDA@CuO₄/Cu core shell particles were formed by oxidation and were reduced by dosing CO. Re-oxidation by dosing O₂ was also possible without changing the particle size distribution.⁶f ATR-FTIR spectroscopy is a powerful technique to validate not only the presence of Cu colloids but also the location of Zn adspecies on the Cu colloids.⁶g It is very well established in the literature that...
The stretching vibrations of linearly adsorbed CO bound to Cu in different electronic states are pronounced in three spectral regions. The spectral range of 2220–2150 cm\(^{-1}\) is assigned to CO molecules bound to Cu\(^{2+}\) and that from 2160–2080 cm\(^{-1}\) is assigned to CO molecules bound to Cu\(^{+}\). Vibration bands lower than 2130 cm\(^{-1}\) are assigned to CO molecules bound to Cu\(^{0}\). Strong shifts to lower frequencies were acquired for co-adsorbed Zn atoms.

For related Cu/ZnO colloids, the differences in the CO vibration frequencies during CO adsorption on Cu were explained as an indication for the migration of Zn species onto the Cu surface forming new surface structures.\(^8\),\(^2^5\)

In order to study the properties of the particles in sample I in more detail, adsorption studies were carried out under conditions similar to those of catalytic methanol synthesis in a liquid phase (180 °C, 1 bar, in squalane; see the catalysis testing section below). Pure CO gas (99.997%) was bubbled through a concentrated solution of the stearate@Cu/ZnO nanocomposite material (content of Cu was 75 mg) in squalane as a solvent. Fig. 2a represents the results of the CO adsorption studies on sample I dissolved in dry squalane as monitored by \textit{in situ} ATR-IR spectroscopy. Spectrum 1 of Fig. 2a constitutes the start of the experiment, that is, it corresponds to a background measurement before CO flow. In spectrum 2 obtained after 20 min of CO gas flow at 1 bar and 180 °C (Fig. 2a), two bands originating from CO adsorption on Cu were observed at 2160 and 1940 cm\(^{-1}\). After 200 min (Fig. 2a, spectrum 3), the intensity of the band at 1940 cm\(^{-1}\) maximized and shifted to 1950 cm\(^{-1}\), and the
band at 2160 cm\(^{-1}\) reduced to a greater extent. Furthermore, a new band appeared at 2100 cm\(^{-1}\). In spectrum 4 obtained after 3 min in CO gas at 8 bar and 180 °C (Fig. 2a), the intensities of the two bands at 2100 and 1950 cm\(^{-1}\) increased and reached their maximum after 45 min in CO gas at 8 bar and 180 °C (Fig. 2a, spectrum 5). The band at 1940 cm\(^{-1}\), that shifted to 1950 cm\(^{-1}\), is assigned to CO adsorbed on Cu sites with Zn adatoms (Cu–Zn alloys) and applies to areas with different amounts of Zn adatoms on the Cu surface. The band at 2160 cm\(^{-1}\) is assigned to CO adsorbed on Cu\(^{2+}\). The Cu\(^{2+}\) species, probably arising from the remaining free (not decomposed) Cu alkoxide precursor in the reaction medium, were reduced under the action of CO gas at 8 bar and 180 °C, which leads to formation of some amount of separate Cu nanoparticles (as shown clearly in the TEM image of Fig. 2b) that were eventually in contact with ZnO particles, too. This resulted in the appearance of a band at 2100 cm\(^{-1}\) that was assigned to adsorption of CO on Cu\(^{3+}\). Thus, the ATR-IR measurements provide strong indication that, under reducing conditions of CO at high pressure and temperature, ZnO\(_x\) species from ZnO supported Cu NPs migrate onto the Cu surface (as pronounced by appearance of bands at 1940–1950 cm\(^{-1}\)) and partially oxidize the Cu surface atoms (bands at 2160 cm\(^{-1}\)).

This interfacial contact of Cu and stearate@ZnO particles that was predicted in our recent publication\(^8\) is evidently important to achieve a high interface area between Cu and ZnO. The adsorption sites near Zn adatoms seem to be more favorable than the adsorption sites on partially oxidized Cu, which are only populated at higher CO partial pressure.\(^8,24\)

These results support the importance of Zn adspecies for the creation of catalytically active areas under reducing methanol synthesis conditions. The TEM image of sample 1 after ATR-IR measurements (Fig. 2b) shows the presence of large separated Cu NPs in the size range of 30–40 nm (as also evidenced by an energy dispersive X-ray (EDX) spectrum taken from a group of larger particles, Fig. S5, ESI\(^+\)) together with the original, unchanged 3–5 nm sized Cu/ZnO particles with a small amount of Cu. Comparing this image with the HAADF-STEM image that was taken for Cu/ZnO particles before ATR measurements (Fig. 1), we can clearly attribute the presence of Cu NPs to the free Cu precursors in the reaction medium that were reduced under the action of CO gas at 8 bar and 180 °C leading to formation of separate Cu nanoparticles.

### 3.2. Preparation and characterization of stearate@ZnO/Cu NPs with a high content of Cu (with a ratio of ZnO : Cu = 2), sample 2

Sample 2, stearate@ZnO/Cu nanocomposites with the Cu : ZnO = 1 : 2 molar ratio were prepared by thermal reduction of Cu stearates under hydrogen in the presence of preformed stearate@ZnO NPs at 220 °C, as described in detail in the Experimental section. The obtained colloid was characterized by X-ray diffraction after reduction and after catalytic activity testing. Fig. 3a illustrates the powder XRD pattern of the stearate-stabilized hexagonal, wurtzite ZnO phase. The peaks appear to be very broad with a relatively low signal to background ratio. Such behavior is to be expected from a sample containing nanocrystalline material with coherence lengths (crystalline domains) well below 10 nm. Fig. 3b represents the corresponding pattern of sample 1 after reductive treatment for characterization (Fig. 2), namely Cu/ZnO NPs (with the Cu : ZnO 1 : 5 molar ratio) after photodeposition of Cu on the surface of stearate@ZnO NPs and after ATR measurements under CO pressure. It shows weak reflections of nanocrystalline Cu due to the small amount of Cu in sample 1 and the formation of further amorphous Cu can also not be excluded. In sample 2, the pattern is substantially different and shows strong reflections, compared to that of sample 1, corresponding to Cu\(^0\) as shown...
zone axis (as evidenced by the inset Fourier transform) and demonstrating extensive twinning, and ZnO nanoparticles connected to the Cu NP surface. The ZnO particles are wurtzite hexagonal ZnO, and the particle indicated by the white square in Fig. 4c is imaged along the [211] zone axis orientation, as evidenced by the inset Fourier transform.

This close interfacial contact between the Cu and ZnO phases has previously been confirmed spectroscopically through UV-Vis, photoluminescence and Raman measurements.6c

By comparing the microscopic characterization data, we deduce separate nucleation and growth of Cu NPs under thermal H2 reduction for sample 2 in contrast to the photo-decoration in the case of sample 1. The Cu NP formation is apparently not affected by the presence of stearate@ZnO particles in the case of sample 2. However, the continuous heating of the reaction medium at 220 °C during the reduction procedures allows the attachment of the present, small ZnO NPs to the surface of the individually formed large Cu NPs. The composite microstructure consisting of small ZnO NPs attached to the surface of each Cu particle contributes to the activation of the current nanocomposite as a catalyst for methanol synthesis (ZnO-free, pure Cu NPs are catalytically inactive).

3.3. Catalytic testing of samples 1 and 2

The colloidal samples 1 and 2 were tested for liquid phase methanol synthesis under the same conditions (see Experimental part) as previously reported for stearate stabilized Cu/ZnO nanocomposite particles dispersed in squalane and fabricated by a co-reduction protocol.8 The obtained methanol production rates over sample 2 (stearate@ZnO/Cu colloid with 1 : 2 Cu : ZnO molar ratio) in comparison to a slurry of a commercial Cu/ZnO/Al2O3 powder catalyst are presented in Fig. 5 as a function of time on stream. The catalytic activity of the Cu/ZnO/Al2O3 reference catalyst after 50 h heating of the reaction medium at 220 °C was 6222 molCH3OH g−1Cu h−1. The corresponding rate of methanol formation of colloid sample 2 versus time on stream was lower by 35% (4000 instead of 6222 molCH3OH g−1Cu h−1) at the state of highest activity and lower by 50% (3000 instead of 6222 molCH3OH g−1Cu h−1) after 50 h time on stream. Nevertheless, sample 2 clearly revealed quite significant activity toward methanol formation even though the Cu particles were quite large and the Cu/ZnO particle size presented a mismatch. However, the best performance data of related colloidal Cu/ZnO catalysts obtained by co-reduction of metal stearate precursors were in the range of 6408 molCH3OH g−1Cu h−1 and the microstructure characterization of these colloids revealed a better size match between the Cu and the ZnO component.8 Sample 1, the stearate@Cu/ZnO nanocomposite with the Cu : ZnO 1 : 5 molar ratio, was also examined as a colloidal catalyst for methanol synthesis under the same conditions as for sample 2. Interestingly, the observed methanol productivity was very poor and too small for a reliable quantification and to address the activity of this catalyst against the commercial reference. The observed strong activity of sample 2 is probably due to the migration of some ZnO species onto the surface of the Cu particles, as was the case for the industrial methanol synthesis catalyst.11c,16,26

From our results, we can conclude that not only (1) the existence of interfacial contact between the metal (Cu) and...
the support (ZnO) but also (2) the relative amounts of Cu and ZnO, (3) the type of microstructure of the interface between Cu and ZnO phases and (4) the size and morphology of the supported metal and the support strongly affect the activity of colloidal ZnO/Cu composite nanoparticles in liquid phase methanol synthesis.\textsuperscript{16,17} Interestingly, a few layers of Cu on crystalline ZnO nanoparticles (3–5 nm) are clearly not sufficient to switch on the synergetic SMSI effect. However decoration or contact of comparably large Cu nanoparticles (20–50 nm) with small ZnO particles works quite well. That is, the absence of the microstrain in the Cu phase of sample \textit{1} due to the tiny amount of Cu at the surface of ZnO probably the reason for the poor productivity of methanol. However, in the case of sample \textit{2} and due to the presence of large Cu particles at the vicinity of ZnO (like mixing Cu and ZnO nanoparticles) the interaction between the Cu nanoparticles and polar planes of ZnO particles probably increase the activity of the catalyst.\textsuperscript{17}

4. Conclusion

Two samples of colloidal methanol catalysts exhibiting distinctly different microstructures were prepared. Sample \textit{1} features a few atomic layers of Cu on the surface of stearate@ZnO nanoparticles as characterized by ATR-IR and HAADF-STEM in combination with EELS spectroscopy. The preparation of sample \textit{1} was performed by a photo deposition technique and characterization of sample \textit{1} supports the assignment as Cu/ZnO, \textit{i.e.} Cu decorated small ZnO nanoparticles stabilized by stearate as a surfactant. Additionally, ZnO/Cu nanocomposites with a high amount of Cu (Cu : ZnO 1 : 2 molar ratio) were prepared by thermal H\textsubscript{2} reduction of Cu stearate in the presence of the original stearate@ZnO nanoparticles at 5 bar and heating to 220 °C for 16 h. After H\textsubscript{2} reduction this nanocomposite, denoted as ZnO:Cu, consisted of well-separated Cu particles within the range of 20–50 nm in contact with small ZnO nanoparticles in their original size regime as clearly shown by HAADF-STEM imaging after ATR measurement.
metal-oxide nanoparticles appears to be of similar complexity in high performance colloidal catalysts featuring composite metal/oxide microstructures with matching Cu and ZnO particle sizes. From our data and the discussion above we conclude that preparation of high performance colloidal catalysts featuring composite metal/oxide nanoparticles appears to be of similar complexity in terms of kinetic (memory) effects on the catalyst activity as it is known from established coprecipitation/calcination protocols for solid state catalysts.

Acknowledgements

The authors gratefully acknowledge financial support by the Research Center on Metal-Support Interaction in Heterogeneous Catalysis (SFB-558, TP B10) and the Research Department Interfacial Systems Chemistry (IFSC) established at Ruhr University Bochum. M. A. S. is grateful for a fellowship of the Egypt Government and membership of the Graduate College Chemical Processes at Oxide Surfaces associated with SFB 558. S.T. gratefully acknowledges the financial support from the Fund for Scientific Research Flanders (FWO). The microscope used for this work was partially funded by the Hercules foundation. G.V.T. acknowledges the financial support from the Fund for Scientific Research Flanders (FWO). The microscope used for this work was partially funded by the Hercules foundation.

Notes and references