Catalyst Research

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Quasi-Homogeneous Methanol Synthesis Over Highly Active Copper Nanoparticles**

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Heterogeneously catalyzed methanol synthesis from synthesis gas over Cu/ZnO/Al_2O_3 is one of the most important processes in the chemical industry, with a world production capacity of more than 28 million tons per year.[1] Despite the enormous number of publications on methanol synthesis over copper-based catalysts, however, the nature of the active site(s), the reaction mechanism, the role of Cu and ZnO in the solid catalyst,[2] and further issues remain highly controversial. This is partly due to the problems associated with the analysis of a complex solid catalyst. However, a homogeneous model system for the methanol synthesis catalyst, which would help to address these questions, is lacking so far.[3] We have now succeeded in the development of a quasi-homogeneous version of the process which uses aluminum-stabilized copper colloids with a size of about 5 nm. This catalyst, rather surprisingly, has a productivity that is very high in spite of the absence of ZnO. Consequently, the intrinsic activity of copper in this reaction is much higher than previously thought. Mechanistic studies suggest that the reaction proceeds in a similar manner as on the solid catalyst, which opens new roads for a detailed understanding of one of the most important commercial catalytic systems.

There are several reports in the literature on homogeneously catalyzed methanol synthesis;[4] they typically use catalysts based on transition metals such as Ru,[5,6] Ni,[7,8] or Re.[7] However, these catalysts bear no resemblance to the technically used Cu/ZnO/Al_2O_3 system. The homogeneous analog of this process—methanol synthesis over copper-based catalysts—has not been described up to now. Indeed, our attempts with simple copper complexes in solution did not result in the formation of methanol from synthesis gas. However, copper nanoparticles synthesized by reduction of copper acetylacetonate with trialkylaluminum were found to be highly active in this reaction. This shows that copper can have a very high intrinsic activity for methanol synthesis, and opens the door to mechanistic studies of the process with techniques known from homogeneous catalysis.

In the present study colloidal copper nanoparticles were obtained by reduction of copper acetylacetonate in THF with a triorganoaluminum reagent.[9] The organoaluminum compounds also stabilizes the colloid by forming an organometallic protecting shell around the nanoparticles.[10] The resulting copper nanoparticle solutions were deep-red and stable for months in the absence of air. The copper particle size can be tuned in the 3–5 nm range, with a narrow size distribution, by varying the alkyl groups of the aluminum reagent. Figure 1a shows a TEM image of roughly spherical, isolated copper nanoparticles with sizes of (4.5 ± 1.5) nm. The nano-

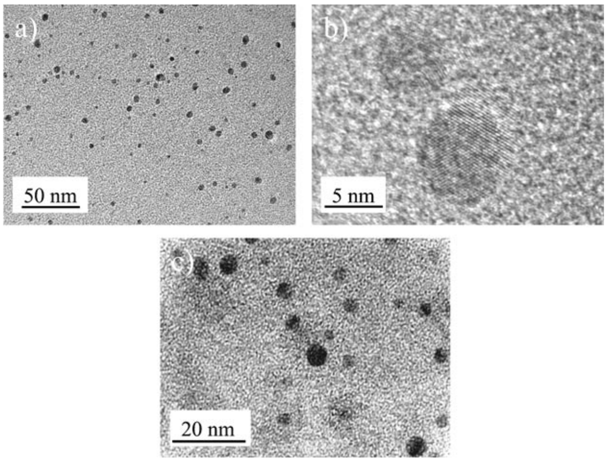

Figure 1. TEM images of trioctylaluminum-stabilized copper nanoparticles: a) freshly prepared (multiple nanoparticles), b) high-resolution TEM, c) after catalysis at 150 °C.

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particles are protected against aggregation by a layer of condensed triorganoaluminum molecules. High-resolution TEM images (Figure 1 b) revealed that the nanoparticles are crystalline, and upon closer inspection some of the particles were found to consist of one single-crystal domain, while others seemed to be composed of several domains. Lattice fringes with a lattice spacing of about 2.17 Å, which corresponds to the Cu (111) plane, can be resolved in the HRTEM images of Cu nanocrystals (Figure 1 b).

The Cu nanoparticles were also subjected to a Cu K-edge EXAFS analysis to obtain complementary insight into the structure of the Cu nanoparticles in solution, especially the oxidation state and the Cu–Cu distance. Figure 2 displays the extracted EXAFS functions at the Cu K-edge and the corresponding radial distribution functions of trioctylaluminum-stabilized copper colloids compared with that of copper foil.

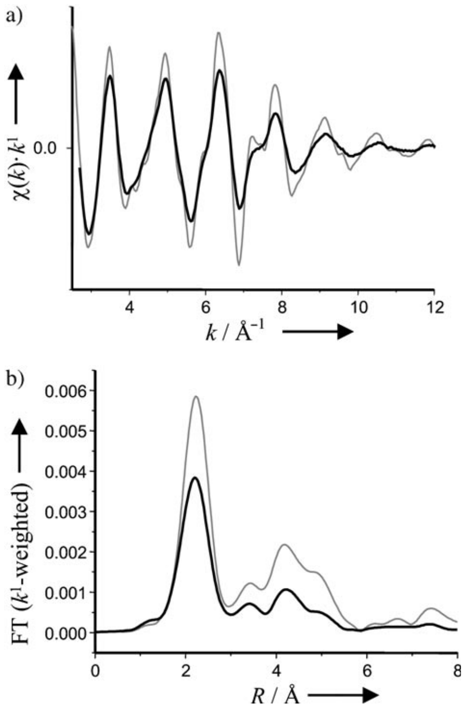

Figure 2. EXAFS function at the Cu K-edge in terms of a) the k^1-weighted $\chi(k)$-function and b) the corresponding radial distribution functions (Fourier-transformed k^1-weighted EXAFS spectra, not corrected for the phase shift) of trioctylaluminum-stabilized copper colloids (black line) in comparison to copper foil as reference (gray line).

The EXAFS experiment confirmed the zero-valent state of copper in the colloids. In the $\chi(k)$-extracted EXAFS functions the same frequency was observed for Cu foil, as reference, and the Cu colloids. The relatively lower amplitude of the function representing the Cu colloids is due to the small size of the Cu nanoparticles (Figure 2 a). The Fourier-transformed EXAFS spectra show mainly the first Cu–Cu shell (Figure 2 b). Fitting of the EXAFS spectra resulted in a Cu–Cu distance of 2.53 Å, compared to 2.55 Å in bulk copper, which is shorter because of the small size of the Cu nanoparticles.[11,12] This is also supported by the fact that the next nearest neighbors ($R > 4$ Å) give a smaller contribution in the Fourier-transformed EXAFS spectrum. No oxygen shells were detected. The coordination number is significantly lower than in bulk copper (10.9 for trioctylaluminum-stabilized copper colloids and 12 for copper foil) and corresponds to a particle size of about 3 nm.

Freshly synthesized copper colloids dissolved in THF were tested for methanol formation in a laboratory-made, high-pressure, stainless-steel autoclave in a quasi-homogeneous phase. Quantitative online analysis of the reaction mixture was performed with a gas chromatograph coupled directly to the high-pressure autoclave. The ratio of gases in the reaction gas mixture was adjusted to correspond to the typical gas-phase composition ($H_2/CO/CO_2 = 74:20:6$), although the different solubility of the reaction gases in THF resulted in a gas-phase composition with a different molar ratio ($H_2/CO/CO_2 = 86:10:4$). In a typical procedure, the high-pressure autoclave was charged with copper colloid solution (40 mL, 9.8 mM Cu) followed by sequential pressurization with synthesis gas (H_2/CO) and CO_2 at room temperature. The reaction mixture was heated with a ramp of 0.5 K min^{-1} to the desired reaction temperature. Surprisingly, methanol formation started already at 130 °C. The results of the methanol formation under these reaction conditions at temperatures with trioctylaluminum-stabilized copper colloids as catalyst are summarized in Figure 3.

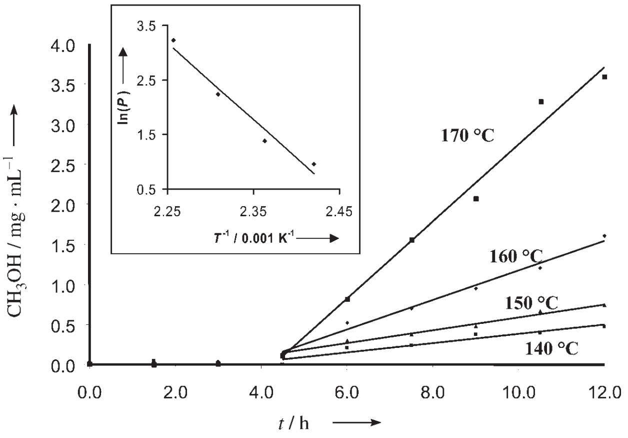

Figure 3. Formation of methanol at temperatures between 140 and 170 °C. Inset: Arrhenius plot for the determination of the apparent activation energy.

The productivity of the methanol formation ($mol_{methanol}/(kg_{Cu}\,h)$) was obtained from the slope of the linear regression of these data points (the first three data points show the methanol formation during the heating period and were not considered in the linear regression). Productivities, P, as high as 25.2 $mol_{methanol}/(kg_{Cu}\,h)$ were observed at elevated reaction-gas pressure and temperature. The results of the temperature-dependent catalytic experiments over trioctylaluminum-stabilized copper colloids are summarized in Table 1 and show an increase in productivity with increasing reaction temperature. From these, turnover

Table 1: Catalytic performance of trioctylaluminum-stabilized copper colloids at different temperatures.

T [°C]	P [$\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$]	TOF [10^{-4} s^{-1}]
140.0	2.6	3.2
150.0	4.0	4.9
160.0	9.3	11.3
170.0	25.2	30.7

frequencies (TOF) were calculated assuming spherical Cu particles with a diameter of 5 nm and approximately 800 Cu surface atoms per particle. From the temperature-dependent experiments an apparent activation energy of 116 kJ mol^{-1} was calculated from the slope of an Arrhenius plot (see inset in Figure 3).

An isotope-labeling experiment with deuterium instead of hydrogen was performed to confirm methanol formation from the reaction gases and to gain further information on the catalytic process. At 150 °C and a gas-phase composition of $D_2/CO/CO_2 = 86{:}9{:}5$ at an initial pressure of 11.2 MPa a productivity of 6.8 $\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$ was determined. GC-MS analysis revealed the formation of deuterated methanol (CD_3OH; -OD to -OH exchange occured during the separation process) and perdeuterated methyl formate. Methyl formate is often observed as a by-product in the heterogeneously catalyzed synthesis of methanol. It has to be noted, though, that after an initial increase the concentration of methyl formate remained constant throughout the entire run in all experiments. This indicates that methyl formate reaches a steady-state concentration and may therefore not be a by-product but rather an intermediate. To elucidate the role of the methyl formate, the following experiments were conducted: 1) catalysis was performed with synthesis gas only, excluding CO_2. In this experiment, only negligible formation of methanol was observed ($P = 0.4$ $\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$); 2) the reaction was carried out with H_2 and CO_2 only, which gave initial methanol formation with the production dropping to zero after 10 h. The initial productivity was determined to be 1.7 $\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$ at 140 °C; 3) the reaction was performed with synthesis gas and a trace amount of methyl formate (50 μL in 40 mL of Cu colloid solution), which gave fast initial formation of methanol ($P = 4.2$ $\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$). The concentration of methyl formate reaches a steady state due to hydrogenolysis of methyl formate and simultaneous conversion of synthesis gas into methanol via methyl formate. It should be noted that the stability of the Cu colloids in experiment 3 was greater than in experiments where CO_2 was present in the gas phase. Productivity differences were within a margin of error of ± 1.6 $\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$.

These experiments with our model Cu catalyst suggest that the reduction of CO_2 to methyl formate is the initial step for methanol formation. However, more detailed studies are necessary to distinguish between different mechanistic pathways.

To exclude the remote possibility that methanol is formed from the acetylacetonate ligands of the copper precursor some of the experiments were repeated with copper colloids synthesized from copper bis(hexafluoroacetylacetonate) by reduction with trioctylaluminum. The resulting Cu colloids were less stable than those synthesized from the non-fluorinated Cu precursor, but were also active in methanol production, although with a reduced productivity $P =$ 2.0 $\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$ at 150 °C. No fluorinated by-products or fragments beside hexafluoroacetylacetonate were detected, which, together with the results of the experiments with deuterium as a synthesis gas component, proves that methanol is indeed formed from the synthesis gas.

In an effort to compare these data with the results for a commercially available methanol synthesis catalyst (ICI Katalco 51-8, powder, < 125 μm, same copper amount as in colloidal solution), this catalyst was reduced under H_2 at 250 °C, following the prescribed protocol, and suspended in THF solution. Catalytic testing was performed in a stainless-steel reactor in batch mode at 150 °C with the same reaction conditions as described above. A methanol productivity of 5.5 $\text{mol}_{\text{methanol}}/(\text{kg}_{\text{Cu}}\,\text{h})$ was determined after a reaction time of 20 h. This is higher than with the Cu colloids described here. However, it should be kept in mind that the Cu colloids do not contain any Zn species, which are thought to improve the catalytic activity.[2b] Studies of the catalytic activity of commercial catalysts cannot be compared directly to the value measured here for the $Cu/ZnO/Al_2O_3$ system (ICI Katalco 51-8) since these investigations are typically performed at appreciably lower pressures at different temperatures and in the gas phase.

Our study shows that copper nanoparticles are remarkably active catalysts in the quasi-homogeneous phase for methanol synthesis from synthesis gas without any solid support. Similar results have been obtained in independent studies on colloidal Cu/ZnO particles by Fischer.[13] Our results show, in particular, that the ZnO component of the technical catalyst is not absolutely necessary to induce high activity for methanol synthesis, since the colloids without a Zn compound display similar activities as the commercial catalyst, which is in agreement with surface science studies on polycrystalline or single-crystal copper surfaces.[14–16]

Experimental Section

All preparations were carried out in anhydrous THF as solvent under an argon atmosphere.

Organoaluminum-stabilized Cu colloids were synthesized by the dropwise addition of $Al(n\text{-octyl})_3$ (7.3 mL, 16.5 mmol) or $Al(n\text{-butyl})_3$ (6.7 mL, 27.5 mmol) in THF (30 mL) to a solution of $[Cu(acac)_2]$ (1.45 g, 5.5 mmol) in THF (400 mL) at room temperature with mechanical stirring. After 2–3 h the deep-red solution was filtered through a glass frit and stored under argon.

To determine the effective copper concentration an aliquot of the copper colloid solution was dissolved in hydrochloric acid and titrated with ethylenediaminetetraacetic acid solution (0.1 M) using murexide as indicator at pH 8.0.

Safety warning: Experiments using large amounts of compressed gases, especially CO, are potentially hazardous and must only be carried out with the appropriate equipment and safety precautions.

The catalytic experiments were carried out in a laboratory-built, stainless-steel, high-pressure autoclave connected to a microvolume high-pressure valve system (0.2 μL) and an online GC analysis setup equipped with a fused-silica column coated with poly(dimethylsiloxane) SE30 (ID 250 μm, film thickness 500 nm). Typically, the Cu colloid solution (40 mL) was placed under argon in the 225-mL, window-equipped autoclave together with *n*-heptane (50 µL) as internal standard. A preformed H_2/CO gas mixture (molar ratio 9:1) was prepared in a 5-L autoclave at 25.0 MPa and used throughout the experiments. The reactor was pressurized to the desired starting pressure (10.0–14.0 MPa) whilst stirring vigorously and CO_2 gas (0.6 MPa) was added. The pressurized system was heated to the reaction temperature with a ramp of 0.5 $K\,min^{-1}$ (pressure at reaction temperature was 17.5–21.5 MPa). Samples were automatically analyzed every 90 min. After the reaction, the reactor was vented to ambient pressure and the collected samples were analyzed by GC, GC-MS, and TEM.

XAS data were collected at the European Synchrotron Radiation Facility (ESRF, Grenoble, France, beamlines SNBL and DUBBLE) using a specially designed cell for liquid samples. The XAS data were obtained in transmission geometry using a Si(111) channel-cut monochromator. For XAS measurements at the Cu K-edge (8.980 keV) the incident and transmitted X-rays were recorded with ionization chambers. Three ionization chambers, located before and after the spectroscopic cell as well as after a Cu foil for energy calibration, were used to measure the incident and output X-ray intensities. The colloidal solution, prepared as above, was introduced into the liquid cell under argon. Kapton windows allowed transmission of the X-rays, and due to appropriate sealing the cell could be dried and evacuated before filling with exclusion of air (for details see ref. [17]). The EXAFS spectra were extracted after background correction, normalization, and energy correction with the WINAXS 3.1 software.[18] Fourier transformation was applied in the region 3 to 12.5 $Å^{-1}$ (the distance scale in the Fourier-transformed EXAFS spectra was not phase-shift corrected) and data fitting was performed in R-space using theoretical phase and amplitude functions calculated with the FEFF 6.0 code.[19]

TEM studies were performed with a Hitachi 7500 and Hitachi HF2000 microscope. Samples were prepared by placing a drop of the dispersed colloidal solution onto a carbon-coated Ni grid. The samples were prepared in a glove box to prevent exposure to air.

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