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Knowledge-based development of a nitrate-free synthesis route for Cu/ZnO methanol synthesis catalysts *via* formate precursors†Malte Behrens,^{*a} Stefan Kißner,^a Frank Girsgdies,^a Igor Kasatkin,^a Felix Hermerschmidt,^a Katharina Mette,^a Holger Ruland,^b Martin Muhler^b and Robert Schlögl^a

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High-performance Cu/ZnO/(Al₂O₃) methanol synthesis catalysts are conventionally prepared by co-precipitation from nitrate solutions and subsequent thermal treatment. A new synthesis route is presented, which is based on similar preparation steps and leads to active catalysts, but avoids nitrate contaminated waste water.

High concentrations of nitrate in aqueous solutions are environmentally harmful, require extensive waste water treatment, and—according to the principles of green chemistry—should be avoided during chemical synthesis processes. Industrial preparation of Cu/ZnO/(Al₂O₃) catalyst precursors by co-precipitation creates large amounts of concentrated nitrate waste water due to the application of nitrate salts as soluble metal sources. It is therefore highly desirable to find new synthesis routes for high-performance methanol synthesis catalysts. A variety of alternative methods, like citrate² or cyanide³ precursor decomposition, sol-gel⁴ or colloidal methods,⁵ or mechano-chemical synthesis⁶ have been reported in the literature. The big success, however, of the industrially applied conventional catalyst synthesis, which was introduced already in 1966 by ICI company, has so far prevented its substitution by usually less feasible or less successful alternative approaches.

This success is based on a sequential meso- and nano-structuring of the catalyst precursor,⁷ allowing a high dispersion of the active Cu phase as well as an intimate contact between Cu and ZnO, which is beneficial for the methanol synthesis activity of the resulting catalyst,^{8–11} and on the highly optimized synthesis conditions.¹² In more detail, a mixed basic carbonate precursor, zincian malachite (Cu_{1-x}Zn_x)₂(OH)₂CO₃, is prepared by co-precipitation and ageing in form of needles. These needles decompose into

nano-particulate CuO/ZnO mixtures upon calcination, in which the CuO component can be reduced to Cu(0) during the activation step. The precursor plays a key role for preparation of a good catalyst and one critical property is a low thickness of the crystallite needles on the order of the final Cu particle size (few nanometres), allowing high porosity of the resulting catalyst aggregates (mesostructure). In addition, a high Zn content *x* is desired, which, depending on the exact synthesis conditions, is around 0.3 in zincian malachite, allowing an effective nano-structuring and homogeneous

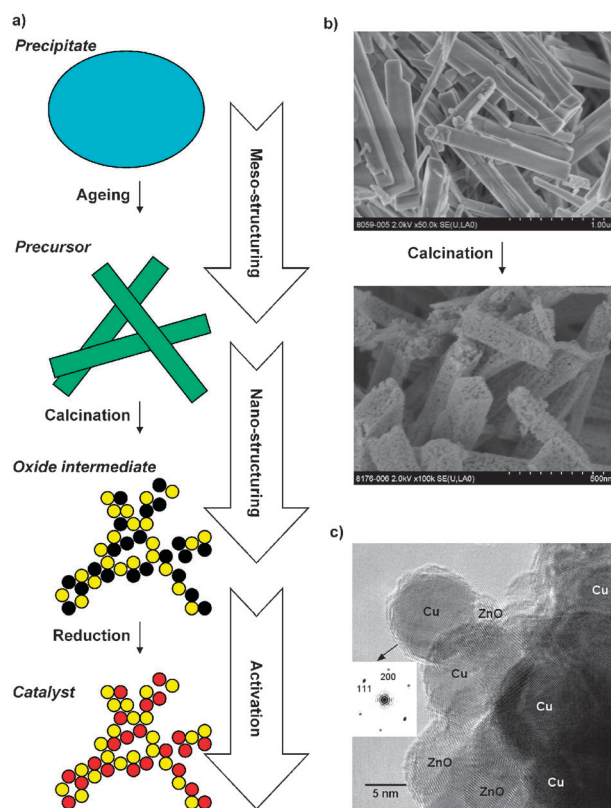


Fig. 1 Cartoon of the industrially applied preparation of Cu/ZnO catalysts *via* needle-like zincian malachite precursors (a), SEM of the (Cu_{0.78}Zn_{0.22})₂(OH)₂HCO₂ precursor before and after calcination (b) and TEM of an ex-formate Cu/ZnO catalyst (Cu : Zn = 81 : 19); inset shows a power spectrum of the Cu particle (c).

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distribution of Cu and ZnO. This preparation scheme of Cu/ZnO is shown schematically in Fig. 1a.

It was our goal not to completely change this appealing and proven concept of Cu/ZnO catalyst preparation, but rather to extend it to new precursor systems by substituting zincian malachite with alternative phases, which are not prepared from nitrate solutions. In our recent work,¹³ we identified mixed basic formates, $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_3\text{HCO}_2$, as promising candidates.¹⁴ These compounds can be prepared by co-precipitation from Cu,Zn formate solutions leading to a nitrate-free mother liquor containing less harmful and bio-degradable formate anions instead.

First, we will discuss the crystal structure of the $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_3\text{HCO}_2$ precursor to identify the limit of Zn incorporation. Due to the similarity of the diffraction patterns with that of the monoclinic polymorph of the layered basic nitrate $\text{Cu}_2(\text{OH})_3\text{NO}_3$, a similar crystal structure was assumed for Rietveld refinements on the XRD patterns of the $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_3\text{HCO}_2$ series. Recently, the single crystal structure of the pure Cu compound has been reported.¹⁵ Details of the chosen structural model, selected results and graphical representations of the fitted XRD patterns are presented in the ESI.† The crystal structure can be conceptually derived from that of the mineral brucite, $\text{Mg}(\text{OH})_2$, and consists of stacked layers of edge-sharing CuO_6 octahedra. In contrast to brucite, every fourth hydroxide anion is substituted by a formate group, which points to the interlayer space. For the purpose of structure refinement, highly crystalline precursors were prepared by controlled co-precipitation at pH 5.5 and $T = 65^\circ\text{C}$ using Na_2CO_3 as a precipitating agent. It is noted that when following this procedure, no complete precipitation of the metals in solution was obtained and the Zn-contents x in the precipitates determined by XRF were always lower than expected from the concentration of the starting solutions. However, highly crystalline solids were obtained and used as model precursors to study the effect of Cu–Zn substitution on the crystal structure of the $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_3\text{HCO}_2$ phase. It can be seen in Fig. 2 that the lattice parameters evolve—similarly to the zincian malchite case¹⁶—anisotropically in a linear Vegard-type fashion in the range $0 \leq x \leq 0.21$. For $x > 0.21$, the crystallinity decreased

rapidly resulting in broad and asymmetric peak profiles and no reliable refinement was possible. Furthermore, an additional unidentified phase was detected in the XRD patterns indicating formation of low amounts of a second, poorly crystalline Zn-rich phase in addition to highly substituted $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_3\text{HCO}_2$ (see ESI†). It can be estimated on the basis of the trend in the peak positions, however, that higher substitution levels $x > 0.21$ might be possible in the two-phase regime. For the sake of studying the properties of the formate precursor system, only homogeneous single phase precursors are considered here.

From these crystal chemical considerations the maximum Zn content x yielding phase pure precursors under the given conditions can be identified as 0.21 for the $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_3\text{HCO}_2$ precursor system. According to the preparation scheme shown in Fig. 1a, this composition should lead to the highest dispersion of the oxides after calcination. The nano-structuring step of the precursor crystals upon thermal treatment can be seen in SEM micrographs (Fig. 1b) showing the crystalline $(\text{Cu}_{0.79}\text{Zn}_{0.21})_2(\text{OH})_3\text{HCO}_2$ precursor before and after calcination in oxygen at 200°C . The single phase precursor material is decomposed and porosity develops due to H_2O and CO_2 emission and phase segregation of CuO and ZnO evidenced by XRD (see ESI†).

Having seen the successful nano-structuring of our crystalline model precursors (Fig. 1b), further room for optimization lies in the proper meso-structuring, *i.e.* in the attempt to prepare the precursor crystallites as small as possible with a Zn content near $x = 0.2$. Such material was synthesized at modified conditions (pH = 7.0, $T = 25^\circ\text{C}$, precipitation agent: NaOH, almost complete precipitation of Cu and Zn, for details see ESI†) and exhibited a Zn content of $x = 0.19$ and a specific surface area of $43\text{ m}^2\text{ g}^{-1}$, compared to $20\text{ m}^2\text{ g}^{-1}$ for the model precursor shown in Fig. 1b. Nano-structuring upon calcination leads to an increase in surface area to $51\text{ m}^2\text{ g}^{-1}$, which is in the range of conventionally prepared binary ex-zincian malachite materials. Reduction of the calcined intermediate at 240°C in diluted H_2 yields a Cu/ZnO catalyst of a Cu surface area of $18\text{ m}^2\text{ g}^{-1}$. TEM confirms the arrangement of Cu and ZnO nanoparticles in form of porous aggregates in the reduced catalysts (Fig. 1c, see ESI† for more TEM results). The volume weighted average Cu particle size was determined to be 11.7 nm. This microstructure is similar to that observed in industrial methanol synthesis catalysts.¹⁷ In the tough comparison with such an optimized and promoted Cu/ZnO/ Al_2O_3 sample (provided by Süd-Chemie company), our novel catalyst showed a relative methanol synthesis activity of 66% (10 bar, 220°C , for details see ESI†). The reason for the lower performance is most probably the lack of the Al_2O_3 promoter, known to stabilize the Cu particles against sintering,¹¹ and the larger size of the particles due to the higher Cu:Zn ratio. Optimized catalysts typically show average particle sizes below 8 nm.¹⁸ To check for this hypothesis, the ex-formate sample was compared to an unpromoted binary ex-zincian malachite catalyst of the same Cu:Zn ratio prepared in our laboratory, which despite a higher Cu surface area of $27\text{ m}^2\text{ g}^{-1}$, only reached an activity of 49% relative to the Cu/ZnO/ Al_2O_3 reference. Attempts to

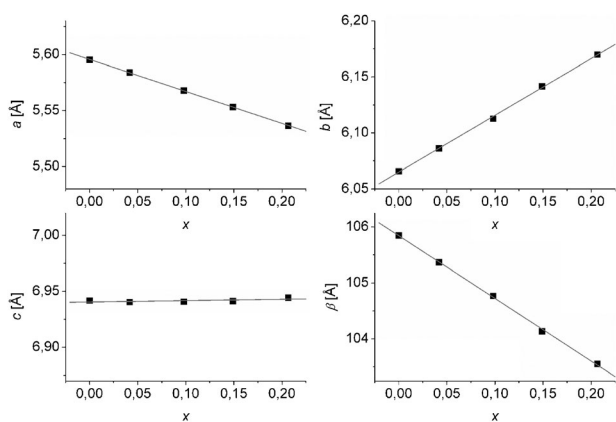


Fig. 2 Evolution of the lattice parameters of $(\text{Cu}_{1-x}\text{Zn}_x)_2(\text{OH})_3\text{HCO}_2$ as a function of Zn content x . Estimated error bars are smaller than the size of the symbols.

incorporate the Al₂O₃ promoter in the formate precursor by coprecipitation are currently under investigation.

In summary, it was shown that a scalable nitrate-free synthesis route for high-performance methanol synthesis catalysts was developed by adopting the established synthesis concept of industrial Cu/ZnO catalyst preparation for a novel basic formate precursor system.

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