

# The Role of the Oxide Component in the Development of Copper Composite Catalysts for Methanol Synthesis\*\*

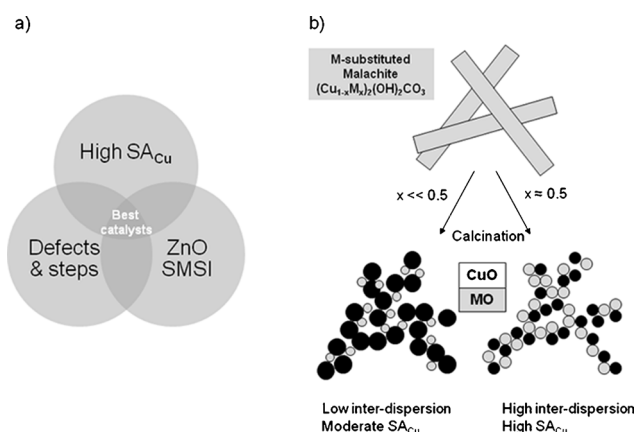
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The development and optimization of industrially applied high-performance catalysts is usually a continuous process that is to a large extent based on the experience of the manufacturer. The accumulated knowledge from the combination of empirical trial-and-error experimentation and a subsequent structure–function-relationship-guided optimization approach within the boundary conditions of a feasible and scalable synthesis often leads to very complex recipes, which are sometimes generalized as the “black magic” of catalyst preparation. In the last few years, we have worked on better understanding of the synthesis and functionality of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst using the well-documented industrially applied preparation route<sup>[1]</sup> as starting point. As a result of this effort, we have elaborated a model of the so-called “chemical memory”<sup>[2]</sup> of catalyst preparation and of the active site in this catalyst system.<sup>[3]</sup> Herein, we show how this knowledge can be applied to develop a new family of copper-based catalysts.

With the help of structure–performance relationships observed within a series of functional powder catalysts and DFT calculations, the active site of industrial methanol synthesis could be identified as a combination of a surface defect of Cu and the presence of partially reduced Zn species at this defect,<sup>[3]</sup> explaining the widely studied Cu–ZnO synergy.<sup>[4]</sup> In the industrial synthesis, high concentrations of these sites can be realized by preparation of defective Cu nanoparticles and migration of ZnO<sub>x</sub> species onto the Cu surface as a result of a strong metal–support interaction (SMSI)<sup>[3,5]</sup> and an intimate interface contact of both catalyst components. At the same time, the total accessible Cu surface area (SA<sub>Cu</sub>) is large, because the bulk catalyst is prepared with

a porous microstructure<sup>[2a,6]</sup> from a co-precipitated precursor compound. In this context, ZnO acts as a geometrical spacer between the Cu nanoparticles and helps to increase and stabilize the Cu dispersion.<sup>[4b,7]</sup> Thus, ZnO has two functions in the final catalyst: 1) As nanoparticles it acts as a physical spacer between the Cu particles, stabilizing the porous microstructure; and 2) as a thin layer at the surface of the Cu particles it is an essential ingredient for the active site, and its presence has been shown to affect the adsorption properties.<sup>[8]</sup> The work presented herein was guided by the idea of separating these two effects.

A simplified scheme of the relevant properties of Cu/ZnO methanol synthesis catalysts is shown in Figure 1a. Three



**Figure 1.** a) Schematic representations of the necessary ingredients for a high-performance methanol synthesis catalyst. b) The role of precursor composition for the Cu dispersion in the final catalyst.

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prerequisites have to be fulfilled to generate a high-performance catalyst. The material should have a high SA<sub>Cu</sub> to expose a large number of active sites; the Cu phase must be defective to achieve a high density of active sites at the surface; and SMSI-induced synergetic effect of ZnO must be present to activate the defect sites for methanol synthesis. Only if all three factors come together (in the darkest shaded region of Figure 1a) will the catalyst be highly active for methanol synthesis. The defects are generated by the careful and delicate preparation method yielding distorted Cu nanoparticles<sup>[9]</sup> in close contact to the oxide phase, while the other two properties are governed by function (1) and (2) of the ZnO component.

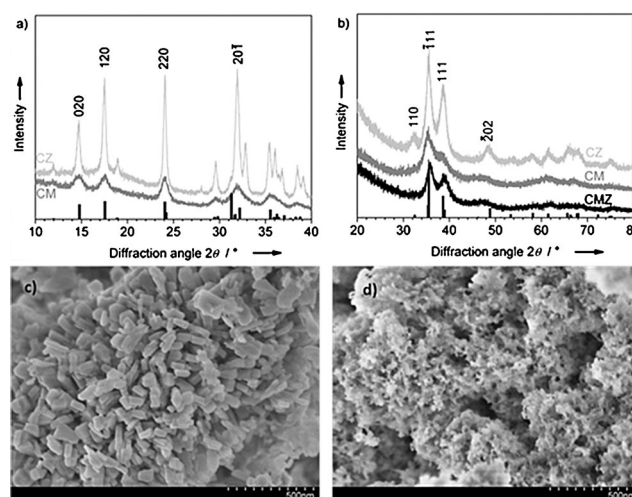
The synthesis route for preparing Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>) catalysts follows a multistep procedure including temperature- and pH-controlled co-precipitation<sup>[2b]</sup> of aqueous Cu, Zn, Al

nitrate solution with sodium carbonate solution followed by aging,<sup>[10]</sup> washing, and drying to yield a hydroxide–carbonate precursor. This material is calcined and finally activated by reduction of CuO to Cu metal. Low amounts of Al<sub>2</sub>O<sub>3</sub> acts as a structural promoter in the industrial catalyst.<sup>[11]</sup>

The relevant precursor material has been identified as thin needles of zincian malachite, (Cu,Zn)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>.<sup>[2a]</sup> The incorporation of Zn<sup>2+</sup> into the cationic lattice of malachite favors the nanostructuring of the CuO/ZnO aggregates formed upon calcination owing to the perfect distribution of both species in the joint crystal lattice of the precursor compound. This can be understood as a purely geometric effect, which is shown in Figure 1 b and is the basis for the first functionality of ZnO. Zn<sup>2+</sup> is well-suited for this purpose because it exhibits the same charge and an ionic radius similar to Cu<sup>2+</sup> favoring substitution in the precursor. However, incorporation into the malachite lattice is limited to less than 30 % owing to solid-state chemical constraints<sup>[12]</sup> that are most likely due to the differences in the coordination environment between the Jahn–Teller-ion Cu<sup>2+</sup> (d<sup>9</sup>) and Zn<sup>2+</sup> (d<sup>10</sup>). Mg<sup>2+</sup> is an interesting replacement for Zn<sup>2+</sup>, because its charge matches and its ionic radius differs, alike Zn<sup>2+</sup>, by less than 2 % from that of Cu<sup>2+</sup>. Furthermore, (Cu,Mg)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> crystallizes in the rosasite crystal structure, which is closely related to that of malachite and therefore provides an opportunity for a comparable precursor chemistry between Cu,Zn and Cu,Mg compounds. Moreover, (Cu,Mg)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> is naturally occurring as the mineral McGuinnessite<sup>[13]</sup> that can incorporate even more Mg<sup>2+</sup> than Cu<sup>2+</sup>, which to date could not be achieved for synthetic zincian malachite. Thus, an even more efficient dilution of the Cu<sup>2+</sup> ions might be possible with Mg<sup>2+</sup> compared to Zn<sup>2+</sup> by application of lower amounts of Cu to further promote the nanostructuring and increase the Cu dispersion.

In this work we compare the classical zinc-containing malachite-derived Cu/ZnO with a new Cu/MgO catalyst at a fixed molar ratio of Cu to Zn and Mg, respectively, of 80:20. At this ratio, Zn incorporation into malachite does not exceed the critical Zn concentration in zinc-containing malachite to assure synthesis of phase-pure precursor compounds, resulting in high comparability of the Cu,Zn and Cu,Mg systems and in uniform catalysts whose properties can be easily traced back to the phase-pure precursor compounds. Both precursors were prepared from mixed nitrate solutions by controlled co-precipitation with sodium carbonate solution and subsequent ageing in the mother liquor. They are denoted CZ and CM in the following. Impregnation of the calcined CM with 5 wt % ZnO yielded a catalyst labeled CMZ that is discussed later.

X-Ray diffraction (XRD) of the precursors confirmed the formation of single-phase materials with a crystal structure similar to malachite (Figure 2a). In comparison to the literature pattern of malachite, a pronounced shift of the 20 $\bar{1}$  peak is seen in both compounds. This is an indication for the incorporation of non-Jahn–Teller cations in the lattice of malachite, and from the similar angular position of the reflections in both patterns a similar degree of substitution can be estimated (Table 1), suggesting that the non-Jahn–Teller ions have been completely incorporated into the



**Figure 2.** a) XRD patterns of the precursor materials of CZ (light gray) and CM (dark gray). The reference pattern is malachite (black bar graph; ICSD: 72-75). b) XRD patterns of the calcined samples CZ (light gray), CM (dark gray), and CMZ (black). The reference pattern is CuO (black bar graph; ICSD: 80-76). c) SEM images of CZ and d) of CM.

**Table 1:** Properties of the CZ, CM, and CMZ catalysts.<sup>[a]</sup>

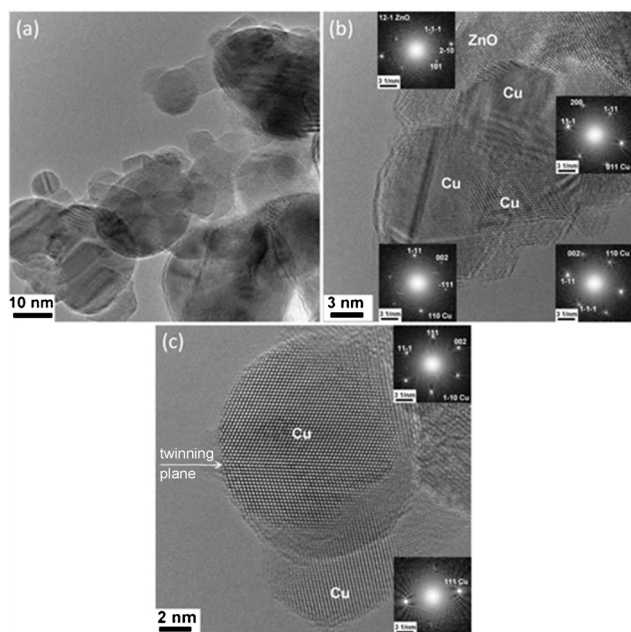
| Sample | Cu:M ratio             | D <sup>[d]</sup> [nm] prec./cal. | SA <sub>BET</sub> [m <sup>2</sup> g <sup>-1</sup> ] prec./cal. | SA <sub>Cu</sub> <sup>[e]</sup> [m <sup>2</sup> g <sub>cat</sub> <sup>-1</sup> ] |
|--------|------------------------|----------------------------------|----------------------------------------------------------------|----------------------------------------------------------------------------------|
| CZ     | 80:20 <sup>[b]</sup>   | 26.6/5.8                         | 36/83                                                          | 16.0                                                                             |
| CM     | 83:17 <sup>[b]</sup>   | 8.0/2.8                          | 81/73                                                          | 20.3                                                                             |
| CMZ    | 79:16:5 <sup>[c]</sup> | 8.0/3.9                          | 81/80                                                          | 24.2                                                                             |

[a] prec. = precursor material, cal. = calcined material. [b] molar, determined by XRF, ± 1 mol %. [c] molar, estimated. [d] Crystallite domain size of (Cu,M)<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (precursor) and CuO/MO (calcined), ± 0.2 nm derived from XRD peak profiles. [e] Specific Cu surface area of the reduced catalyst determined by N<sub>2</sub>O chemisorption, ± 1 m<sup>2</sup> g<sup>-1</sup>.

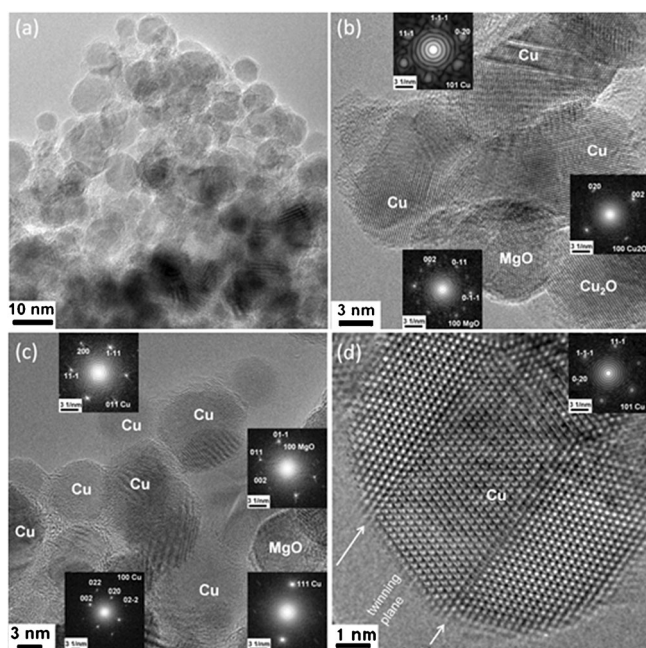
malachite structure in both samples. It is noted that CM exhibits significantly broader XRD peaks indicative of smaller crystallites. Also the particle morphology of CM (Figure 2d) looks rather spongy compared to CZ, which exhibits larger and well-separated particles (Figure 2c). Accordingly, a larger BET surface area of the CM precursor has been observed (Table 1).

Upon calcination at 603 K, poorly crystalline CuO is formed in both samples, as evidenced by XRD (Figure 2b), while the ZnO and MgO components are mostly X-ray amorphous. Again CM exhibits a significantly smaller crystallite size according to the XRD peak width, but a slightly smaller specific surface area (Table 1). Furthermore, CM yields a by more than 20 % higher SA<sub>Cu</sub> than CZ after reduction.

TEM investigation of the reduced catalysts showed that the general microstructure of CZ (Figure 3a,b) and CM (Figure 4a–c) is similar in both catalysts and characterized by arrangements of round shaped Cu particles separated by differently sized crystallites of ZnO or MgO, respectively. The presence of larger Cu particles in CZ compared to CM is consistent with the difference in Cu surface areas (Table 1).



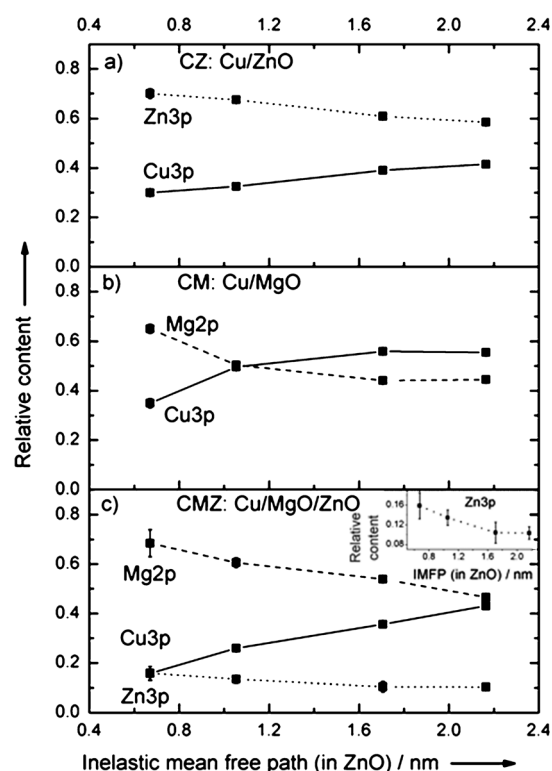
**Figure 3.** (HR-)TEM images of the reduced CZ catalyst. The insets show power spectra of the neighboring particles and are used for phase identification.



**Figure 4.** (HR-)TEM images of the reduced CM catalyst.

This result indicates that MgO is an intrinsically better geometrical spacer compared to ZnO as even at the non-ideal 80:20 ratio, Cu particles can be obtained that with an average size below 10 nm are similarly small as found in state-of-the-art Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>[6]</sup> Thus, the structurally promoting role (1) of ZnO has been successfully replaced with MgO.

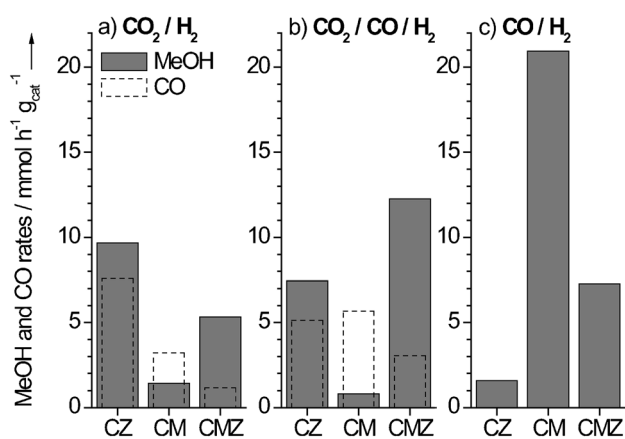
The formation of a thin ZnO<sub>x</sub> overlayer<sup>[3,5b]</sup> upon reduction of CZ was not directly observed by HRTEM, but the surface coverage of the Cu particles was clearly probed by



**Figure 5.** Surface and near-surface composition of the reduced catalysts recorded with synchrotron XPS at a function of information depth. a) CZ; b) CM; c) CMZ. Error bars represent estimated uncertainty based on several fits with random variation of background fitting parameters.

depth-sensitive XPS measurements (Figure 5a; Supporting Information, Figure S2); a pronounced Zn enrichment at the surface of the catalysts was observed. This deviation from the nominal 80:20 ratio is slowly and continuously lowered if the information depth is increased to 2 nm and beyond exceeding the first surface layers. This trend is in agreement with previous results obtained on Cu/ZnO-based catalysts<sup>[3,14]</sup> and indicates the presence of (some of) the Zn species at the surface in form of a thin overlayer. The situation is different for CM, where beyond 1 nm Cu is already the most abundant near-surface species, as expected from the nominal composition of CM. The measurements indicate Mg enrichment only at the very outermost surface and a lower tendency of overlayer formation, which is in agreement with the expected weaker metal–oxide interaction in CM compared to CZ, owing to the less reducible nature of MgO.

High-resolution TEM showed that the Cu particles in both samples contain planar defects, which have been shown to contribute to the methanol synthesis activity in Cu/ZnO catalysts<sup>[3]</sup> (CZ: Figure 3c; CM: Figure 4d and Supporting Information, Figure S1). Thus, the important defectiveness of Cu is present in both catalysts CZ and CM and is probably a result of the precursor decomposition approach common to both catalysts, which leads to crystallization of distorted Cu crystallites.



**Figure 6.** Results for the methanol synthesis with the CZ, CM, and CMZ catalysts in different feed gas compositions at 30 bar and 503 K.

Both catalysts CZ and CM have been tested in methanol synthesis with various feed gas compositions, that is, hydrogenation of pure CO<sub>2</sub>, a CO<sub>2</sub>/CO mixture and pure CO (Figure 6, Supporting Information, Table S1). In the hydrogenation of pure CO<sub>2</sub>, CZ showed a much higher activity than CM, showing clearly that the methanol synthesis rate is not only a function of the exposed Cu surface area alone (Figure 6a). Following the scheme in Figure 1a and in accordance with the XPS results (Figure 5), the low activity of CM can be explained with the absence of the synergetic SMSI-effect as MgO is an irreducible oxide that does not show the necessary SMSI in the relevant temperature regime. The situation is similar if methanol is produced from a typical synthesis gas mixture with CO<sub>2</sub> and CO in the feed (Figure 6b). CZ shows a slightly lower rate of methanol production compared to the CO<sub>2</sub>/H<sub>2</sub> feed, while CM catalyzes the reverse water gas shift reaction (rWGS), but remains essentially inactive for methanol synthesis despite the large exposed Cu surface area. These results strikingly confirm the crucial synergetic role of the ZnO-promoter that has been subject of many previous reports.

With the idea of “switching on” the lacking Cu-ZnO synergy by addition of Zn (similar to that reported earlier for model catalysts<sup>[11b,15]</sup> and physical mixtures),<sup>[4a,c]</sup> the catalyst CMZ was prepared by impregnation of the calcined CM with 5 wt% ZnO. The procedure resulted in a catalyst that was indeed able to convert CO<sub>2</sub> and the synthesis gas mixture much better than CM (Figure 6a,b). The weight-based methanol production rate from synthesis gas of CMZ was even higher than that of CZ, which is probably a result of the higher Cu dispersion, as the intrinsic rates per SA<sub>Cu</sub> were similar for CZ and CMZ in this experiment (Supporting Information, Figure S4). Interestingly, only the formation of methanol was promoted by the addition of ZnO not the rWGS (Figure 6b,c), rendering the CMZ catalysts a very promising material for selective CO<sub>2</sub> hydrogenation.

(HR-)TEM images of CMZ are reported as supporting information (Supporting Information, Figure S3a,b) and show a similar general microstructure and particle morphology like CM, but additionally confirmed the presence of ZnO at the

Cu/MgO aggregates (Supporting Information, Figure S3c). Interestingly, the XPS results obtained on CMZ showed that the concentration profile of Mg was hardly changed by the impregnation and subsequent reduction (Figure 5c). However, the surface abundance of Cu was significantly lowered at the expense of Zn, with a clear surface enrichment of the latter as shown by the trends of the Cu and Zn depth profiles (Figure 5c, inset). Thus, the dramatic change in the catalytic performance appears to be associated with the formation of a ZnO<sub>x</sub> overlayer in CMZ that has been absent in CM.

These results show that the functions of the oxide component can be successfully separated in Cu-based methanol synthesis catalysts. It was shown for a given catalyst composition as a proof-of-principle that this approach enables preparation of high-performance catalysts and leaves additional degrees of freedom for future optimization. In particular, Cu dispersion can be optimized within the proven malachite-precursor method by increasing the Cu substitution without being bound to the constraints of the Cu,Zn system. Furthermore, the method of addition and optimal amount of the synergistic promoter can be varied for a given highly dispersed Cu/oxide system to switch on the production of methanol from CO<sub>2</sub> or synthesis gas.

Interestingly, the catalytic performance of the samples is completely changed when a CO/H<sub>2</sub> feed is used for methanol synthesis. Here CM shows a very high methanol production rate, which clearly exceeds that of CZ or CMZ in the other feed gases (Figure 6c). This result is in line with previous studies,<sup>[16]</sup> that have shown that MgO-supported Cu is a powerful CO hydrogenation catalyst. Interestingly, while it was a prerequisite for methanol production in CO<sub>2</sub>-containing feeds, the addition of Zn to CM was detrimental in this reaction possibly by partially covering of the active surface. Thus, along with being a very powerful CO hydrogenation catalyst, the CM and derived CMZ also represent a suitable material basis for basic studies on the roles of synergy, dispersion, and structural dynamics for methanol synthesis in different feed gases. In particular, an investigation of the carbon source for methanol on the ZnO-free Cu/MgO in CO/CO<sub>2</sub>/H<sub>2</sub> mixtures, which was found to be CO<sub>2</sub> for an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst,<sup>[17]</sup> seems interesting and will be addressed in our future work.

In summary, the high comparability of the three concept-catalysts, which is due to the similar general morphology found by TEM investigation, allows the differences in activity of the samples to be traced back to the influence of the oxide phase(s) ZnO and/or MgO. These two oxides do not only act as structural promoters, but also determine the preferred pathway of methanol synthesis from CO<sub>2</sub> or CO as carbon source. We propose that the synthetic approach presented here opens the door to exploit new forms of the traditional Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst system that are based upon a solid functional understanding of the respective components. Furthermore, the presented materials show potential to fertilize new progress in studies of the mechanism of methanol synthesis by providing fundamental insight into the role of different material components. Finally, with respect to nonconventional feed compositions available for methanol as an energy carrier molecule, new possibilities for

catalyst development occur through the present modular approach composing the relevant functions of the catalyst according to the chemical potential of the intended gas feed.

### Experimental Section

Hydroxide-carbonate precursors of CZ and CM were synthesized by coprecipitation ( $T=338\text{ K}$ ) from Cu,Zn and Cu,Mg (80:20) nitrate solutions and  $\text{Na}_2\text{CO}_3$  solution as precipitating agent in an automated lab reactor (LabMax, Mettler Toledo). The pH was set to 6.5 for CZ and 9.0 for CM. The precipitates were aged ( $>60\text{ min}$ ), filtered, washed, and dried. Calcination was carried out in air at  $603\text{ K}$  ( $2\text{ K min}^{-1}$ ) for 3 h. One part of the calcined CM was impregnated with Zn citrate solution, dried, and calcined again at the same  $T$ . Catalytic tests were carried out in a fixed-bed flow reactor with a feed of 72%  $\text{H}_2$ , 24%  $\text{CO}_2$ , 4% Ar (internal standard) for  $\text{CO}_2$  hydrogenation, 59%  $\text{H}_2$ , 6%  $\text{CO}$ , 8%  $\text{CO}_2$ , for syngas conversion and 14%  $\text{CO}$ , 59%  $\text{H}_2$ , 4% Ar for  $\text{CO}$  hydrogenation; balance was He. Online analysis of products was performed with a gas chromatograph (Agilent 7890A). After the start of the reaction, the catalysts were allowed to stabilize for 6 h at  $523\text{ K}$ . Measurements were done at  $503\text{ K}$  and 30 bar. More details on the characterization and testing methods used can be found in the Supporting Information.

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