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Copper/Zinc L-Tartrates: Mixed Crystals and Thermolysis to a Mixture of Copper Oxide and Zinc Oxide That Is Catalytically Active in Methanol Synthesis

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The system consisting of copper/zinc L-tartrate mixed crystals has been systematically explored in the whole range from pure copper tartrate to pure zinc tartrate. Mixed crystal L-tartrates were prepared and their thermochemical behaviour under oxygen was investigated. Oxidic precatalysts (CuO/ZnO) for catalytic tests in methanol synthesis were prepared by mild thermolysis of the mixed tartrates in air at 300 °C. Catalytic tests were performed with a multi-channel parallel reactor. The catalytic activity shows a maximum at about equal amounts of copper and zinc whereas the specific surface area (BET surface) increases strongly when going from CuO to ZnO. This system offers a convenient, inexpensive route to CuO/ZnO precatalysts with adjustable compositions that avoids all other metals during preparation.

Introduction

Methanol is the most important chemical base material due to its use as a solvent or as a parent compound for the industrial synthesis of higher organic compounds.[1] The industrial synthesis of methanol is typically carried out with synthesis gas containing H_2, CO and CO_2 with Cu/ZnO/Al_2O_3 as catalyst, which is prepared by reduction of a CuO/ZnO/Al_2O_3 precatalyst.[2–8] These oxide composites are usually prepared by thermolysis of co-precipitated hydroxycarbonate precatalysts in which all three metals are present.[9] Despite numerous experimental and theoretical studies, the catalytic processes on the surface of the bulk catalysts are not yet fully understood.[9–15] The activities of the obtained catalysts depend on many factors. To reduce the number of factors that influence the performance of the catalyst, the catalytic system is often limited to the system Cu/ZnO. Even then, the thermolysis temperature and pressure, the reduction temperature and the composition remain important external factors.[3–5,7,9,11,12,16] In the case of dinuclear complexes that contain both copper and zinc, the thermolysis is always complex due to the decomposition of the corresponding anions.[17,18] It was our goal to find a precursor that contains both metals in one solid phase (to achieve a good interaction in the final catalyst) and which can be decomposed at moderate temperature (to avoid sintering to larger crystals). Mixed copper/zinc L-tartrates turned out to be well suited for this purpose because their synthesis is straightforward and also because inorganic counterions like alkali metals or carbonate can be avoided.

Results and Discussion

Preparation

Metal L-tartrates (MTTs) with different ratios of Cu/Zn were prepared in aqueous solution by precipitation from copper acetate and zinc acetate with L-tartaric acid (H_2TT) [Equation (1)].

$$x\,Cu(OAc)_2 + y\,Zn(OAc)_2 + H_2TT \rightarrow Cu_xZn_yTT\cdot n\,H_2O + 2\,HOAc;\ x + y = 1 \text{ and } n \leq 3 \quad (1)$$

Note that the only counterion is acetate, which remains quantitatively in solution. At a final tartrate concentration of 0.05 M large single crystals were obtained after slow crystallisation. Unfortunately, these were always twinned and not suitable for single-crystal X-ray structure analysis. At a higher final tartrate concentration of 0.2 M a fast precipitation occurred and the product was obtained as a microcrystalline powder. These microcrystalline samples were used for all experiments described below. In all cases we obtained hydrates of the mixed tartrates in which the water

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Table 1. Elemental analysis results of the anhydrous copper/zinc tartrates after removal of water of crystallisation at 130 °C. The molar fractions of Cu and Zn can be derived from the formulae in the last column. They correspond well to the expected molar fraction (first three columns).

Sample	Expected [mol-%] Cu	Zn	Found [wt.-%] Cu	Zn	C	H	Calcd. [wt.-%] O	Calculated formulae from elemental analysis (normalised to C_4) $C_4H_4O_6Cu_xZn_y$
CuTT	100	0	29.25	0.00	22.28	2.22	46.26	$C_4H_{4.75}O_{6.24}Cu_1Zn_0$
$Cu_{0.9}Zn_{0.1}$TT	90	10	26.86	2.62	22.06	2.20	46.28	$C_4H_{4.75}O_{6.30}Cu_{0.92}Zn_{0.09}$
$Cu_{0.8}Zn_{0.2}$TT	80	20	24.29	4.95	22.33	2.21	46.23	$C_4H_{4.71}O_{6.22}Cu_{0.82}Zn_{0.18}$
$Cu_{0.7}Zn_{0.3}$TT	70	30	22.11	7.47	22.46	2.16	45.81	$C_4H_{4.59}O_{6.12}Cu_{0.75}Zn_{0.25}$
$Cu_{0.6}Zn_{0.4}$TT	60	40	18.88	10.79	22.51	2.03	45.80	$C_4H_{4.30}O_{6.11}Cu_{0.64}Zn_{0.35}$
$Cu_{0.5}Zn_{0.5}$TT	50	50	15.21	14.96	22.28	2.00	45.55	$C_4H_{4.28}O_{6.14}Cu_{0.51}Zn_{0.49}$
$Cu_{0.4}Zn_{0.6}$TT	40	60	11.22	19.24	22.29	2.03	45.23	$C_4H_{4.33}O_{6.10}Cu_{0.38}Zn_{0.63}$
$Cu_{0.3}Zn_{0.7}$TT	30	70	8.42	22.18	22.20	2.00	45.21	$C_4H_{4.30}O_{6.12}Cu_{0.29}Zn_{0.73}$
$Cu_{0.2}Zn_{0.8}$TT	20	80	5.71	25.44	22.29	1.98	44.59	$C_4H_{4.28}O_{6.01}Cu_{0.19}Zn_{0.84}$
$Cu_{0.1}Zn_{0.9}$TT	10	90	2.95	28.47	22.30	2.01	44.28	$C_4H_{4.30}O_{5.97}Cu_{0.10}Zn_{0.94}$
ZnTT	0	100	0.00	31.10	22.21	2.03	44.67	$C_4H_{4.36}O_{6.04}Cu_0Zn_1$

loss starts at room temperature. In order to obtain anhydrous samples with a defined stoichiometry the products were fully dehydrated at 130 °C in air. Elemental analysis (Table 1) showed that the compositions of the samples were in good accordance with the intended composition, i.e. that all metal ions present in solution were also present in the same ratio in the precipitate. The Cu/Zn ratio was thereby easily controlled by variation of the ratio of copper/zinc in solution. Unfortunately, it was not possible to synthesise a ternary precursor that also contains aluminium by precipitation or crystallisation due to the high solubility of Al_2TT_3.

Crystal Structures, Powder Diffraction Patterns and Precursor Morphology

The structures of the hydrates $ZnTT\cdot 2.5\,H_2O$[19] and $CuTT\cdot 3\,H_2O$[20] are both known. These compounds are not isostructural. No structural data are available in the literature for Cu/Zn tartrate mixed crystals. The crystal structures of anhydrous copper L-tartrate and zinc L-tartrate are also unknown. However, after the removal of water of crystallisation all precursor samples were still crystalline according to X-ray diffractometry. The diffraction patterns of copper and zinc L-tartrate are similar, but still distinguishable (Figure 1). The change between the two structures occurs around an equimolar ratio of copper/zinc. Because the single-crystal structures are not known, it is not possible to draw safe conclusions about the phases that are present. However, the powder diffractograms clearly indicate that two structurally different phases of dimetallic tartrate precursors are present, both of which contain copper and zinc in the same phase.

The morphology of the Cu/Zn dimetallic tartrates was studied by SEM (Figure 2). The particle shape depended on the ratio of the two metals, but all samples were microcrystalline, as also supported by the narrow X-ray diffraction peaks in Figure 1.

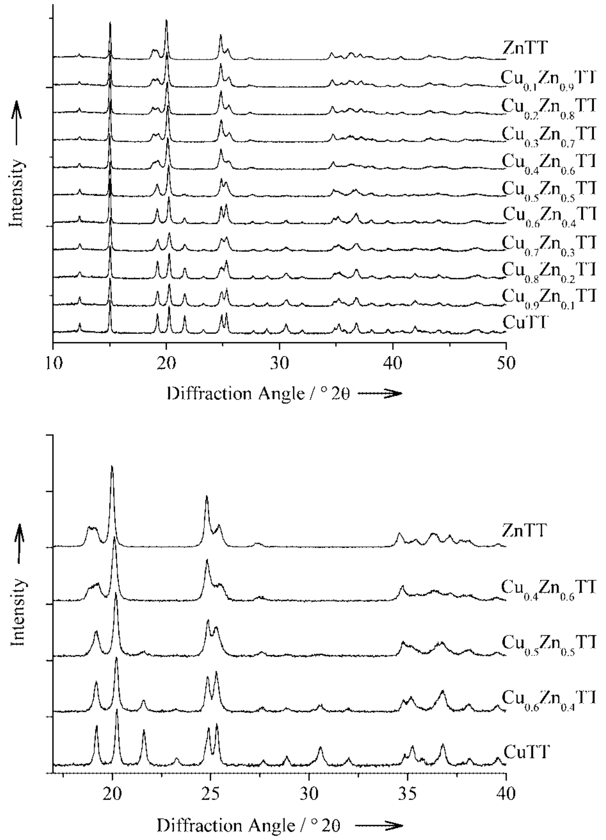

Figure 1. Powder diffraction patterns of the mixed Cu/Zn tartrates. Top: overview; bottom: magnification of selected samples.

Thermogravimetric Analysis

Three MTT samples were heated to 500 °C under pure oxygen (50 mL min^{-1}) at 5 K min^{-1}. The thermolysis occurs in one step and is accompanied by sharp exothermic DTA peaks (Figure 3). Incidentally, the exothermic nature of the thermolysis (combustion) was clear from the observation that the sample glowed red in the furnace, even at 300 °C (autocatalytic oxidation by oxygen). The onset temperature

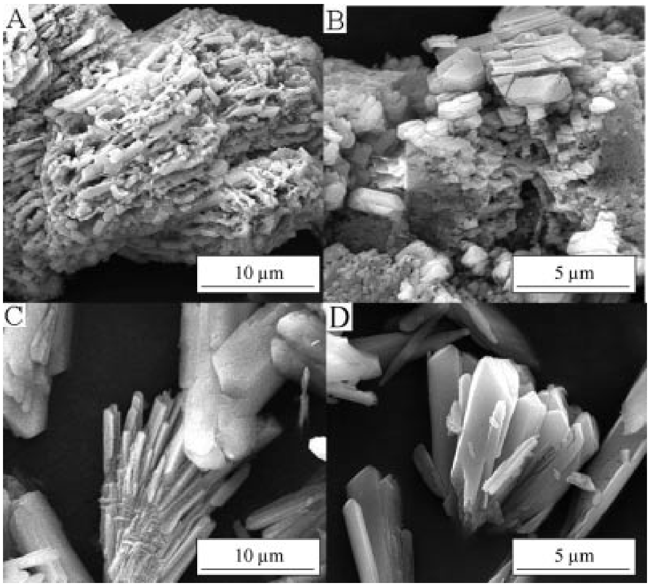

Figure 2. Scanning electron micrographs of the tartrates CuTT (A), $Cu_{0.7}Zn_{0.3}$TT (B), $Cu_{0.3}Zn_{0.7}$TT (C) and ZnTT (D).

of thermolysis increases with increasing zinc content. The mass increase above 250 °C for CuTT can be ascribed to an oxidation of the initially formed Cu_2O to CuO. Interestingly, such a mass increase was not observed for $Cu_{0.5}Zn_{0.5}$TT, which means that this sample is directly converted into CuO/ZnO during the combustion step. The obtained final masses at 500 °C (CuTT: 36.7 wt.-%; $Cu_{0.5}Zn_{0.5}$TT: 38.4 wt.-%; ZnTT: 37.3 wt.-%) correspond well to the calculated masses (CuO from CuTT: 37.5 wt.-%; CuO/ZnO from $Cu_{0.5}Zn_{0.5}$TT: 37.8 wt.-%: ZnO from ZnTT: 38.1 wt.-%). The final products contained neither carbon nor hydrogen (by elemental analysis). The external morphology of the tartrate crystals is preserved in the assembly of the product crystals (Figure 4). Note that Schmid and Felsche have reported that the thermolysis of copper tartrate under inert gas (argon) leads to copper metal.[21]

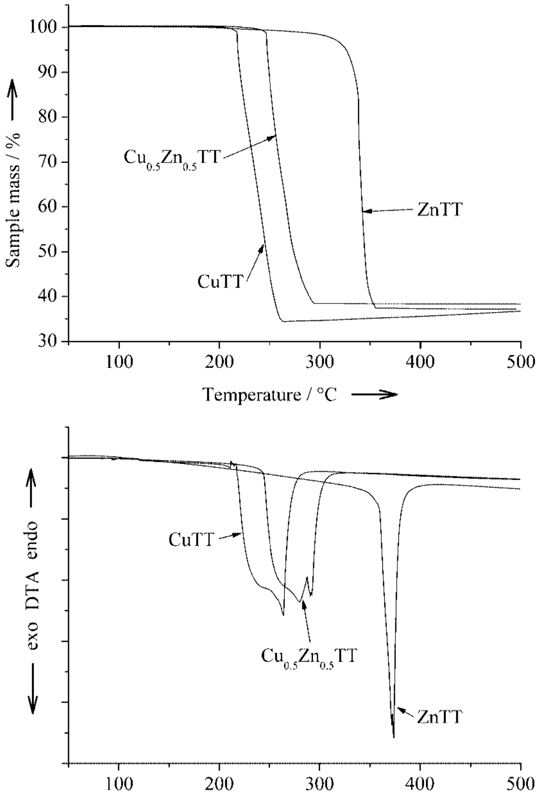

Figure 3. Top: Thermogravimetric measurements of CuTT, $Cu_{0.5}Zn_{0.5}$TT and ZnTT under a dynamic oxygen atmosphere. Bottom: The mass loss is accompanied by sharp exothermic DTA peaks in all three cases, indicating local combustion processes.

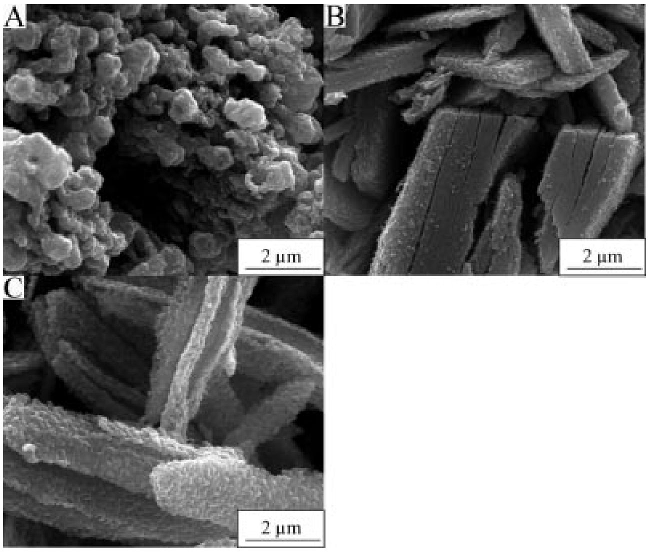

Figure 4. Scanning electron micrographs of the oxide samples obtained after thermogravimetry of CuTT (A), $Cu_{0.5}Zn_{0.5}$TT (B) and ZnTT (C) under oxygen (500 °C). Note the preservation of the morphology of the original large crystals.

Thermolysis in Air and Morphologic Studies

Larger amounts of the oxide samples for catalytic studies were prepared by thermolysis in air at 300 °C for 24 h, followed by slight mechanical grinding. Note that a thermolysis at 250 °C for 48 h gave very similar results. The lowermost temperature necessary for complete thermolysis was chosen in order to avoid sintering of the reaction products to larger crystals. Note that a small crystallite size is important for the catalytic performance.[22] A high specific copper surface area is also important for a good catalytic performance.[2,23] The diffraction pattern of the product from CuTT shows the presence of Cu_2O and CuO. In contrast, all mixed oxide samples that contain copper contain only CuO and ZnO. ZnTT leads to ZnO after thermolysis (Figure 5). Under these conditions, the precursor morphology is better conserved and the surface of the former tartrate crystals is smoother (Figure 6).

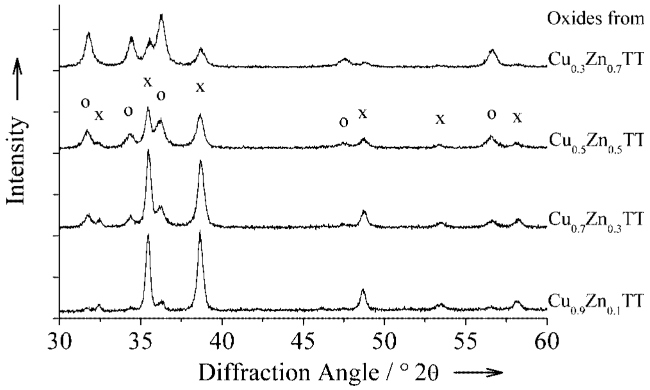

Figure 5. Powder diffraction patterns of oxide mixtures obtained by thermolysis in air at 300 °C (24 h) and containing CuO (x; tenorite; JCPDS no. 481548) and ZnO (o; wurtzite; JCDPS no. 361451).

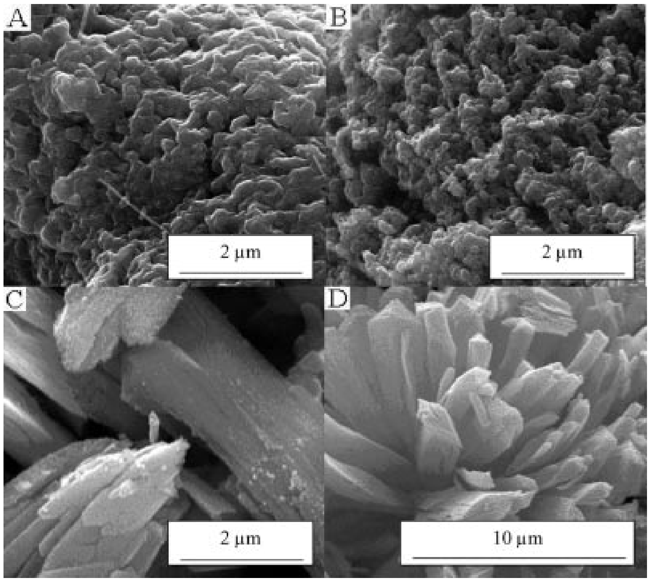

Figure 6. Scanning electron micrographs of the oxide samples obtained by thermolysis of CuTT (A), $Cu_{0.7}Zn_{0.3}$TT (B), $Cu_{0.3}Zn_{0.7}$TT (C) and ZnTT (D) in air at 300 °C (24 h).

Catalytic Activity

The oxide samples were tested regarding their ability to catalyze the formation of methanol from synthesis gas (CO, CO_2 and H_2). The CuO/ZnO mixture was reduced directly in the catalytic reactor to Cu/ZnO with H_2. The Cu/Zn ratio had a remarkable influence on the catalytic activity, showing a clear maximum for an approximately equimolar ratio of Cu and Zn (Figure 7). Although the thermolysis was performed at moderate temperatures, the catalytic activities are low in comparison to an industrial benchmark catalyst (set to 100%). However, the maximum activity (17%) was of the order of a Cu/ZnO catalyst prepared from co-precipitated hydroxycarbonate (about 25%).[18] The specific surface area of the oxide precatalysts shows an almost linear increase, starting from almost zero (0.46 $m^2 g^{-1}$) for pure CuO up to 30–40 $m^2 g^{-1}$ for samples with high zinc content. The sample $Cu_{0.5}Zn_{0.5}$TT was also subjected to temperature-programmed reduction (TPR) and to reactive frontal chromatography (RFC). The content of 50 mol-% Cu was confirmed by TPR. However, the specific copper surface area (by RFC) was only 0.34 $m^2 g^{-1}$ (note that the accuracy of values below 1 $m^2 g^{-1}$ is limited), which is surprisingly small given the considerable catalytic activity of this sample. For comparison, the specific copper surface area is 17.0 $m^2 g^{-1}$ for the aforementioned hydroxycarbonate-based catalyst and 23.4 $m^2 g^{-1}$ for the industrial reference catalyst.[18]

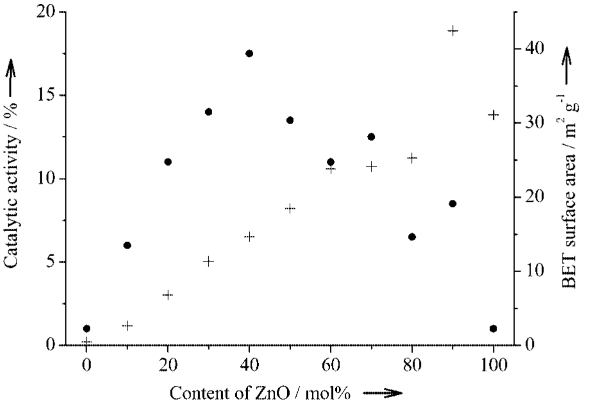

Figure 7. Catalytic activity of CuO/ZnO samples after thermolysis of mixed tartrates (300 °C; air; 24 h) after reduction to Cu/ZnO in situ in a multireactor with H_2, measured at 245 °C and 4.5 MPa (●; left scale). The activity of a technical methanol catalyst was set to 100%. The BET surface area of the oxide precatalysts (i.e. before reduction) is shown on the right (+).

A possible explanation for the lower activity compared to hydroxycarbonate-derived catalysts could be the fact that the thermolysis of the tartrates is associated with an exothermic effect, in contrast to the endothermic decomposition of hydroxycarbonates. This exothermic effect may lead to microscopic self-heating and thereby to a growth of oxide crystals. This is supported by the X-ray diffraction data (Figure 5), which show narrow peaks for the oxides, i.e. no nanocrystalline particles that would give rise to diffraction peak broadening. These CuO particles form the active centres of the final reduced catalyst (Cu on ZnO), and it is known that larger copper crystals are catalytically less active than smaller copper crystals.[2,22,23] This is corroborated by the small observed specific copper surface area for the 50:50 sample.

Conclusions

Metal L-tartrates that contain both copper and zinc as a mixed crystal are well-suited precursors to prepare CuO/ZnO precatalysts that can then be reduced to Cu/ZnO, i.e. an active methanol catalyst. The maximum activity is found at about equimolar amounts of copper and zinc, although the specific surface area increases strongly with increasing zinc content. The presence of this activity maximum reflects the interplay between metal (Cu) and support (ZnO) and the necessity for a sufficiently high specific surface area. The preparation by precipitation easily allows control of the ratio of Cu/Zn in the precursor, and thereby of the catalytic activity. Except for carbonate, other ions are avoided during the synthesis. This synthetic method presents an alternative to classical hydroxycarbonate precursors.

Experimental Section

General: Deionised water was used for all preparations.

Preparation of the Precursor Samples: A solution of 50 mmol of copper acetate and/or zinc acetate in the appropriate ratio in 200 mL of water (55 °C) and a solution of 50 mmol of L-tartaric acid in 50 mL of water (room temperature) were prepared. The solution of the acid was rapidly poured into the solution of the metal acetates with vigorous stirring. Approximately 30 s after the addition, the precursor began to precipitate. The mixture was stirred at about 50 °C for another 15 min. After sedimentation of the precipitate, the precipitate was filtered and washed three times with water and then once with ethanol. The tartrates were first dried at 70 °C for 2 h and then at 130 °C for 12 h. With the exception of ZnTT, all products were obtained as fine powders. CuTT was slightly blue, ZnTT was white, and the mixed crystals showed a continuous row of intermediate colours.

Catalytic Measurements: Measurements were performed in a high-throughput 49-parallel channel reactor.[5] The samples (100 mg diluted with 200 mg of quartz per well) were placed in a sample holder consisting of a stainless-steel cartridge closed at the bottom by a stainless-steel sinter metal frit. Prior to the catalytic measurements, the catalysts were reduced with H_2 at 245 °C according to the procedure for the commercial benchmark catalyst ICI Katalco 51-8. Before measuring the catalytic activity, all samples were equilibrated for 3 h (reaction pressure: 4.5 MPa; reaction temperature: 245 °C; analytic flow: 20 $\mathrm{mL\,min^{-1}}$). The reaction gas consisted of 70 vol% H_2, 24 vol% CO and 6 vol% CO_2. A double GC system (HP GC 6890) equipped with a methanizer FID was used for online gas analysis. Oxo product separation (H_3COH, $HCOOCH_3$, $H_3CCOOCH_3$, H_3CCH_2OH) was carried out on a SuppelcoWAX 0.53 mm column and CO, CO_2 and CH_4 were separated on a Carboxen 1006 column. Methanol productivities for all measured samples were compared to the productivity of the industrial benchmark catalyst ICI Katalco 51-8 [P_{ICI} = 40 mol MeOH$(\mathrm{kg_{cat}\,h})^{-1}$ at 245 °C and 4.5 MPa].

Analytical Techniques: Combined thermogravimetry-IR spectroscopy (TG-IR) was carried out with a Netzsch STA 209 TG-DTA/DSC instrument. Samples were heated from 30 to 500 °C at a rate of 5 $\mathrm{K\,min^{-1}}$ under dynamic O_2 atmosphere (50 $\mathrm{mL\,min^{-1}}$). Scanning electron microscopy images were recorded with an ESEM Quanta 400 instrument (FEI) on Au/Pd-sputtered samples. X-ray powder diffractometry was carried out in Bragg–Brentano mode with a Bruker AXS D8 Advance instrument with Cu-K_{α} radiation. Atomic absorption spectroscopy (AAS) was performed with a Thermo Electron Corporation instrument (M series) to determine the contents of copper and zinc in the samples. The contents of carbon and hydrogen were determined by standard combustion analysis with an EA 1110 (CE Instruments) instrument. The specific surface area was determined by nitrogen physisorption at 77 K (BET method) on the oxide precatalysts (i.e. CuO/ZnO). Temperature-programmed reduction (TPR) was carried out on the oxide product from the sample $Cu_{0.5}Zn_{0.5}$TT. About 0.1 g of this sample was placed in a quartz reactor. The reduction was performed under flowing diluted H_2 (4.2 vol% H_2 in He) by increasing the temperature to 240 °C at a rate of 1 $\mathrm{K\,min^{-1}}$ and maintaining that temperature for 1 h. The active surface area of Cu was determined by N_2O reactive frontal chromatography at 300 K on the same sample of $Cu_{0.5}Zn_{0.5}$TT.[24]

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