DOI: 10.1002/ejic.200600005

Catalytic Activity of Copper Oxide/Zinc Oxide Composites Prepared by Thermolysis of Crystallographically Defined Bimetallic Coordination Compounds

Rainer Weiss,[a] Yanzhi Guo,[a] Sascha Vukojević,[b] Lamma Khodeir,[c] Roland Boese,[a] Ferdi Schüth,[b] Martin Muhler,[c] and Matthias Epple*[a]

Keywords: Heterogeneous catalysis / Copper / Zinc / Thermochemistry / Structural chemistry

The suitability of bimetallic coordination compounds in the systems Cu/Zn/CN and Cu/Zn/CN/ethylenediamine as precursors for CuO/ZnO was explored. The kinetic and thermodynamic equilibria in these systems are discussed. The introduction of ethylenediamine led to crystalline precursor compounds, and the bimetallic coordination compounds $[Zn(en)]_2[Cu_2(CN)_6]$ and $[Zn(en)_3]_6[Cu_2(CN)_7]_2[Cu(CN)_3]\cdot 8.4H_2O$ were structurally characterised. The oxide mixtures of CuO/ZnO, prepared by mild thermolysis of the precursor compounds, were tested for their catalytic activity in the formation of methanol from synthesis gas, i.e. $CO/CO_2/H_2$. While the oxide mixtures from $Zn[Cu(CN)_3]$ were not catalytically active, the oxide mixtures derived from the crystalline compounds with ethylenediamine as the ligand had about 20–30 % of the activity of an industrial methanol catalyst. This underscores the importance of the origin of the catalyst, i.e. the dependence of its activity from the structure of its precursor.

Introduction

Cu/ZnO is a widely used system in heterogeneous catalysis for methanol synthesis and steam reforming.[1–3] Although $Cu/ZnO/Al_2O_3$ is a more efficient catalyst, Cu/ZnO is often examined as an easier model to understand the catalytic process (note that even ZnO alone is an active catalyst in methanol synthesis[4]). Conventionally, such catalysts are prepared by thermolysis of coprecipitated carbonates or oxalates.[5] Here we report on the preparation, structural characterisation, thermolysis and catalytic activity of two bimetallic coordination compounds that contain copper and zinc within the same crystal. We showed earlier that it is possible to prepare $Zn[Cu(CN)_3]$ with two metals in the same crystal.[6] It is reasonable to assume that the oxides prepared by oxidative thermolysis occur in an intimately dispersed state, thereby enhancing the catalytic activity. Two well-defined bimetallic coordination compounds can be decomposed to intimate mixtures of CuO and ZnO. The catalytic activity of the oxides derived from these precursor compounds containing Cu–Zn–CN and Cu–Zn–CN–ethylenediamine in methanol synthesis was investigated. Therefore, a comprehensive picture ranging from the single crystal structure, through to thermolysis and on to the catalytic performance is presented here.

Results and Discussion

Some General Remarks about the Thermodynamic and Kinetic Equilibria in the Cu/Zn/CN Precursor System

All syntheses were typically performed by mixing aqueous solutions of the first metal with aqueous solutions of a cyanide complex of the second metal. It turned out that a number of different species are present in solution, e.g. $[Cu^{II}(H_2O)_6]^{2+}$, $[Zn^{II}(H_2O)_6]^{2+}$, $[Zn^{II}(CN)_4]^{2-}$, "$[Cu^{II}(CN)_4]^{2-}$", $[Cu^{I}(CN)_4]^{3-}$ and $[Cu^{I}(CN)_3]^{2-}$.[7] Note that "$[Cu(CN)_4]^{2-}$" is just a formal description because Cu^{II} cyanide complexes are subject to an internal redox reaction resulting in Cu^{I} and $(CN)_2$. In the case of the reaction of Cu^{2+} with $[Zn^{II}(CN)_4]^{2-}$, the kinetic lability of the cyanocomplexes of copper and zinc had a strong influence on the products that formed. Starting with solutions of $[Zn^{II}(CN)_4]^{2-}$ and Cu^{2+}, the main product was $Zn^{II}[Cu^{I}(CN)_3]$, whereas $Cu^{II}[Zn^{II}(CN)_4]$ and $Zn^{II}[Zn^{II}(CN)_4]$ were only found as side products.[6]

Furthermore, in the system Cu/CN there are not only different species in solution, but also many different types of structural elements consisting of Cu^{I} coordinated by CN^- exist in the solid state. For instance, the unit "$[Cu(CN)_3]^{2-}$" can be either a mononuclear trigonal-planar complex, or a dinuclear complex $[Cu_2(CN)_6]^{4-}$, as in

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[a] Inorganic Chemistry, University of Duisburg-Essen,
Universitätsstrasse 5–7, 45117 Essen, Germany
Fax: +49-201-183-2621
E-mail: matthias.epple@uni-due.de
[b] Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany
[c] Industrial Chemistry, Ruhr University of Bochum,
Universitätsstrasse 150, 44801 Bochum, Germany

$[Cu^{II}(en)_2]_4[Cu^{I}(CN)_3]_2[Cu^{I}_2(CN)_6]\cdot 2H_2O$ (ref.[8]) or a part of an infinite three-dimensional network as in $[Zn(en)]_2[Cu_2(CN)_6]$ (**1**; see the structure below). It is essential to have the crystal structures of the precursors in this system because the crystal structure of the precursor determines the structure and morphology of the reaction products if the thermolysis is carried out at moderate temperature, i.e. not under thermodynamic equilibrium conditions.[1,9] This is of particular interest in heterogeneous catalysis where surface effects are often more important than the composition.[10,11]

The different kinetic stabilities of cyanometallate complexes are important for the preparation: In a bimetallic system which contains a kinetically stable complex, e.g. $[Fe(CN)_6]^{3-}$, and a counterion which does not form a cyanide complex itself, e.g. Gd^{3+}, the preparation of a bimetallic coordination compound like $Gd[Fe(CN)_6]$ is straightforward and easy.

In the pair $Cu^{I/II}$ and Zn^{II}, two metals are present which form kinetically unstable cyanocomplexes with comparable stability constants. The stability constant of $[Zn^{II}(CN)_4]^{2-}$ is 4×10^{19} M^{-4} (ref.[12]) and much smaller than that of $[Cu^{II}(CN)_4]^{2-}$ with 1×10^{27} M^{-4} (ref.[13]), therefore the latter compound is preferred in equilibrium. However, Cu^{II} is reduced by CN^- to Cu^{I} upon mixing $[Zn^{II}(CN)_4]^{2-}$ and Cu^{II}, and the anion $[Cu^{I}(CN)_3]^{2-}$ is formed as the main copper species in solution.[6] This may serve as an example as to how the constitution of the complexes found in the solid state often cannot be predicted from the formulae of the dissolved precursor molecules, making a rational synthesis difficult.

Bimetallic Cyanides as Precursors for CuO/ZnO for Methanol Catalysis

Mixtures of CuO and ZnO were prepared from $Zn[Cu(CN)_3]$ by oxidative thermolysis under different conditions (temperature from 200 to 500 °C). In addition, the grain size of $Zn[Cu(CN)_3]$ was adjusted by variation of the precipitation conditions as reported earlier (continuous overflow method).[6] Although the oxide mixtures (CuO and ZnO) were analytically pure (no residual cyanide compound was left after thermolysis, which was checked by IR spectroscopy and elemental analysis), the catalytic activities for methanol synthesis were practically zero in all cases. The reason for this behaviour is not known, but it is possible that the decomposition temperature was too high to preserve a sufficiently high specific surface (the BET surface area was around 5 to 10 $m^2 g^{-1}$ for these samples) and possibly some sintering had occurred.[14] On the other hand, the surface of the active copper and zinc oxide particles may have been poisoned by small amounts of cyanide that were still adsorbed under these conditions, but no longer detectable by bulk-phase techniques.

The Precursor System Cu/Zn/CN/Ethylenediamine (en)

A better control over the precursor is possible if its crystal structure is known, yielding the coordination environment of both metals and also the unequivocal evidence that both metals are present within the same crystal. To obtain such single crystalline precursors, the solubility of the coordination compounds in the system Cu/Zn/CN had to be increased. The chelating ligand ethylenediamine, $H_2N–CH_2–CH_2–NH_2$, can substitute cyanide as a ligand.[15] It also prevents the formation of metal–cyanide–metal bonds, which lead to rapid precipitation of polymeric compounds, like the well-known Prussian Blue that contains a three-dimensional network of Fe–CN–Fe bridges or like $Zn(CN)_2$ that contains an adamantane-like network.

In the system Cu/Zn/CN/en, the formation of compounds does not only depend on the composition of the solutions. It also depends on the pH and the content of K^+. This was found by experiments with solutions of the formal composition "$[Cu^{II}(en)_2][Zn^{II}(CN)_4]$". From this solution, two different bimetallic compounds were obtained, just by simple modification of the conditions:

(1) From KCN and in the presence of $(NH_4)_2SO_4$ buffer (pH about 8), the compound $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**) (pale green crystals) was obtained.

(2) From NaCN (not buffered; pH about 10), the compound $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (**2**) (bluish or colourless crystals) was obtained.

These structures indicate that in these systems Zn^{2+} has a close affinity to ethylenediamine and that Cu^+ has a close affinity to cyanide. The coordination geometry around zinc and copper depends on the synthesis conditions. Chi and Fedkiw reported that $[Cu(CN)_3]^{2-}$ is the main species in the system Cu^+/CN^-, even if cyanide is present in excess.[16] The formation of the dinuclear anion $[Cu_2(CN)_7]^{5-}$ can be derived from joining a $[Cu(CN)_3]^{2-}$ unit with a $[Cu(CN)_4]^{3-}$ unit. The fact that both compounds are slightly coloured suggests that small amounts of Cu^{2+} are also present in the crystal, possibly as substitution for Zn^{2+} (Cu^{I} and Zn^{II} are both colourless).

Here, the structure of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**) was determined for the first time (see Figure 1, Table 1 and Table 2). Crystalline $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ contains units of $[Cu^{I}_2(CN)_6]^{4-}$ and $[Zn^{II}(en)]^{2+}$, which together form a three-dimensional network. Each zinc atom is connected to three $[Cu_2(CN)_6]^{4-}$ units by one cyanide ligand. This leads to an unusual square-pyramidal coordination of zinc where two nitrogen atoms from ethylenediamine and two nitrogen atoms from cyanide form the base of the pyramid. Copper and zinc atoms are in close vicinity in the crystal structure. The structure of $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (**2**) was reported earlier by Kappenstein et al.[17,18] and confirmed here by single-crystal structure analysis.

The infrared spectra (Figure 2) show strong similarities between the two compounds. Especially the N–H bands ($[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**): 3367/3352/3292 cm^{-1}; $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (**2**): 3342/3293 cm^{-1}) and the C–H bands ($[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**): 2962/2924/2899 cm^{-1}; $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (**2**): 2962/2934/2883 cm^{-1}) are almost identical whereas the C–N bands ($[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**): 2116 cm^{-1};

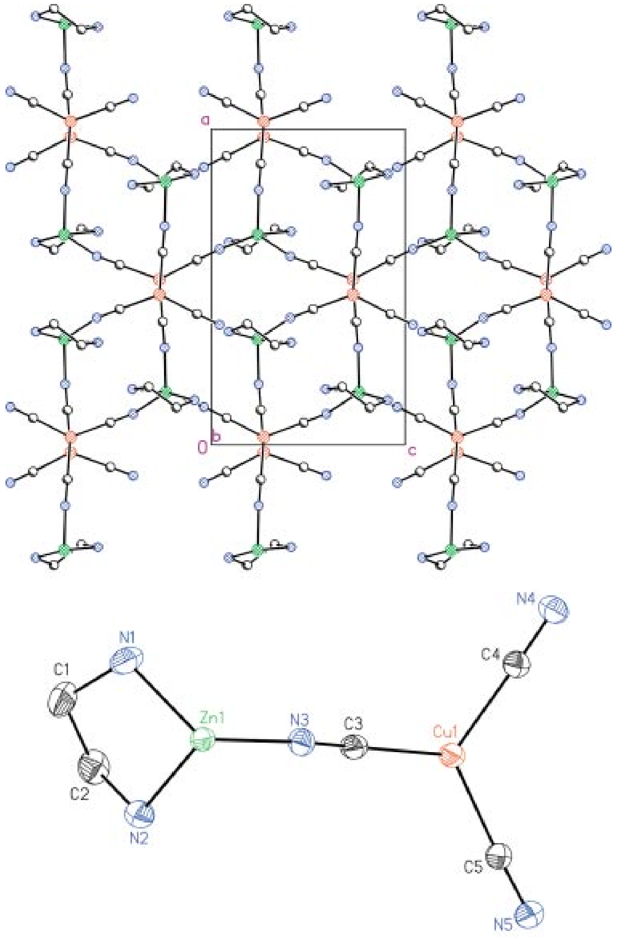

Figure 1. Structure of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**): Top: Packing of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ in the crystal; bottom: Asymmetric unit of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$. Hydrogen atoms from ethylenediamine were omitted for clarity.

Table 1. Crystallographic data of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**).

Empirical formula	$C_5H_8CuN_5Zn$
$\rho_{calcd.}$ [g cm^{-3}]	2.000
Wavelength [Å]	0.71073
Space group	$P2_12_12$ (orthorhombic)
$F(000)$	528
Temperature [K]	203(2)
Crystal size [mm^3]	0.14 × 0.11 × 0.03
Crystal colour	cyan
Crystal description	plate
a [Å]	13.7514(4)
b [Å]	7.6762(3)
c [Å]	8.4007(3)
α [°]	90.000(2)
β [°]	90.000(2)
γ [°]	90.000(2)
Volume [Å^3]	886.77(5)
Z	4
Reflections collected	82644
Independent reflections	5459 [R(int) = 0.0619]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0320, wR_2 = 0.0693
R indices (all data)	R_1 = 0.0477, wR_2 = 0.0755
Diffractometer	Siemens SMART three axis goniometer with an APEX II area detector system
Computing structure solution	Bruker AXS SHELXTL 6.12

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$. U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	–3338(1)	5234(1)	12376(1)	20(1)
Cu(1)	243(1)	6874(1)	12703(1)	25(1)
C(1)	–3817(2)	1502(3)	11828(3)	35(1)
C(2)	–3166(2)	1440(3)	13263(3)	33(1)
C(3)	–1100(1)	6111(2)	12540(2)	24(1)
C(4)	854(1)	7735(3)	10761(2)	24(1)
C(5)	706(1)	7709(3)	14757(2)	25(1)
N(1)	–3583(2)	3089(3)	10899(2)	32(1)
N(2)	–3239(2)	3125(3)	14110(2)	31(1)
N(3)	–1928(1)	5896(2)	12430(2)	24(1)
N(4)	1198(1)	8227(3)	9595(2)	29(1)
N(5)	980(1)	8297(3)	15935(2)	28(1)

$[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4\ H_2O$ (**2**): 2081 cm^{-1}) can clearly be distinguished and may be used to distinguish both compounds.

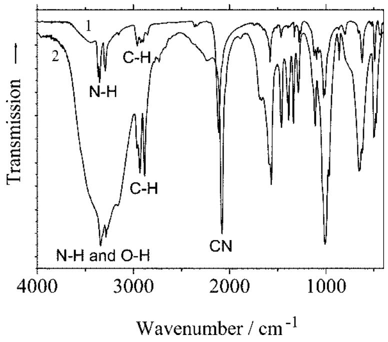

Figure 2. Infrared spectra of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**) and $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (**2**).

Thermolysis of 1 and 2

The thermolysis of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**) and $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (**2**) under oxygen to CuO/ZnO was followed in situ by thermogravimetry combined with infrared spectroscopic gas analysis (Figure 3 and Figure 4).

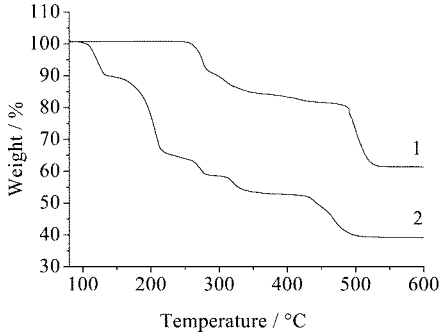

Figure 3.Thermogravimetry of **1** and $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (**2**) to CuO/ZnO under a dynamic oxygen atmosphere.

The thermolysis of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**) can be divided into three parts. In a first step from 250 °C to about

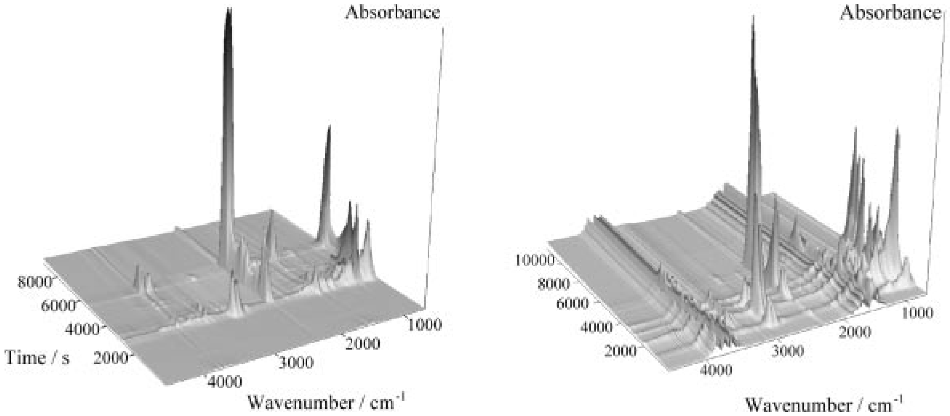

Figure 4. Time-resolved IR spectra of gases evolved from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) (left) and $[Zn^{II}(en)_3]_6[Cu^I_2(CN)_7]_2[Cu^I(CN)_3]\cdot 8.4H_2O$ (**2**) (right) during thermolysis to CuO/ZnO.

295 °C, ethylenediamine is released without oxidation, as is visible from the C–H bands in the infrared spectrum at around 3000 cm^{-1}. From 295 to 490 °C the remainder of the ethylenediamine and a part of the cyanide undergo combustion as indicated by the evolution of CO_2 (four bands from 3740 to 3590 cm^{-1} and several bands from 2560 to 2310 cm^{-1}) and H_2O. Finally, the combustion of cyanide to carbon dioxide and nitrous oxide (NO) occurs above 490 °C. The residual mass of 61.43 wt.-% corresponds well to the theoretical value of 60.25 wt.-% for a 1:1 mixture of ZnO and CuO.

The thermolysis of $[Zn^{II}(en)_3]_6[Cu^I_2(CN)_7]_2[Cu^I(CN)_3]\cdot 8.4H_2O$ occurs in five well-separated steps. In the first step, from 90 to 145 °C first water and then also ethylenediamine are released. Up to 240 °C, about 10 of the 18 molecules of ethylenediamine and all the crystal waters are lost. Starting around 240 °C, the reaction turns to oxidative combustion with the release of CO_2, first of ethylenediamine and then of cyanide. The final mass of 38.9 wt.-% corresponds well to the calculated value of 37.1 wt.-% for a 6:5 mixture of ZnO and CuO.

The morphology of the oxide mixtures, prepared by mild thermolysis of $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) and $[Zn^{II}(en)_3]_6[Cu^I_2(CN)_7]_2[Cu^I(CN)_3]\cdot 8.4H_2O$ (**2**) in air at 300 °C for 48 h was investigated by scanning electron microscopy (Figure 5). The crystallites have a size of a few 100 nm up to a micrometer, comparable to those obtained earlier by thermolysis of $Zn[Cu(CN)_3]$.[6] High-resolution X-ray powder diffraction (synchrotron) confirmed the absence of precursors or other crystalline impurities.

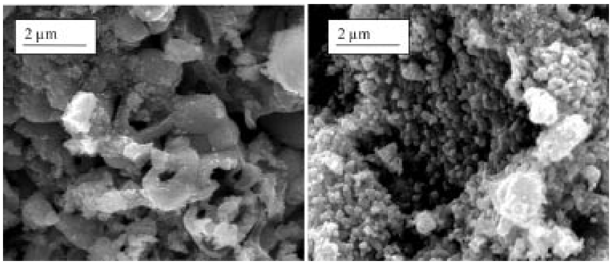

Figure 5. Scanning electron micrographs of the resulting CuO/ZnO mixtures from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) (left) and $[Zn^{II}(en)_3]_6[Cu^I_2(CN)_7]_2[Cu^I(CN)_3]\cdot 8.4H_2O$ (**2**) (right) after annealing for 48 h at 300 °C.

Catalytic Activity of Cu/ZnO from the Precursor System Cu/Zn/CN/Ethylenediamine (en)

The oxide samples were tested for their catalytic activity in the formation reaction of methanol from $CO/CO_2/H_2$ by two different methods. First, a 49-channel parallel flow multitubular reactor was used for rapid scanning of many samples (Table 3).[19] Note that CuO/ZnO was always reduced prior to the catalytic test in order to obtain the active catalyst Cu/ZnO. This was done in situ in the catalytic reactor. Because the absolute catalytic performance strongly depends on the specific conditions, all activities were related to an industrial benchmark catalyst (ICI Katalco 51–8) whose activity was set to 100%. This multitubular reactor permitted highly efficient parallel testing of numerous samples, including control experiments with the same sample. The oxides derived from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) and $[Zn^{II}(en)_3]_6[Cu^I_2(CN)_7]_2[Cu^I(CN)_3]\cdot 8.4H_2O$ (**2**) showed similar activities that were much higher than the activities of the oxide mixtures from $Zn[Cu(CN)_3]$, which contained only cyanide as a ligand (see above; almost no activity). In a second experiment, both precursors were mixed with finely dispersed Al_2O_3 (for chromatography) as a support before the thermal decomposition to increase the specific surface. However, with this support, the catalytic activity (related to the content of CuO/ZnO in the catalyst) decreased considerably, i.e. the active surface of the catalyst could not be increased by this method.

In a single-tube reactor, the oxide mixture derived from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) was studied more closely with regard to its reduction to Cu/ZnO, the specific copper surface area and the catalytic activity. Again, it was compared to the industrial benchmark catalyst (ICI) and also to another oxide sample derived by the conventional coprecipitation method of carbonates.[20] The content of CuO was approxi-

Table 3. Catalytic activity of CuO/ZnO samples after in situ reduction to Cu/ZnO in the multitubular reactor.

Sample	Activity
Cu/ZnO from $Zn[Cu(CN)_3]$	≈ 0%
Cu/ZnO from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**)	30%
5 Cu/6 ZnO from $[Zn^{II}(en)_3]_6[Cu^I_2(CN)_7]_2[Cu^I(CN)_3]\cdot 8.4\ H_2O$ (**2**)	29%
Cu/ZnO from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) + Al_2O_3	13%
5 Cu/6 ZnO from $[Zn^{II}(en)_3]_6[Cu^I_2(CN)_7]_2[Cu^I(CN)_3]\cdot 8.4\ H_2O$ (**2**) + Al_2O_3	9%
Industrial reference catalyst (ICI)	100%

mately 50 mol-% for these three samples. The content of CuO in the oxide derived from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) was confirmed by the quantitative reduction (Figure 6). After reduction, the sample had a copper surface area of 2.42 $m^2\,g^{-1}$ (Figure 7). Compared with the catalyst based on coprecipitated carbonate and the industrial catalyst, the sample had a smaller copper surface area, but the activity related to the copper surface area was surprisingly high (see Table 4). Note that an adsorption of nonvolatile fragments of the organic ligands on the copper surface that leads to a decrease in activity is unlikely but cannot be excluded with this compound. It was shown earlier that the Cu surface generally decreases during the catalytic process because of sintering of the Cu particles.[14]

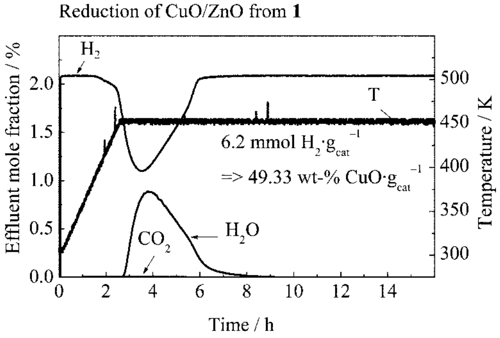

Figure 6. Reduction of CuO/ZnO from thermolysis of $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) to Cu/ZnO in the single-tube reactor.

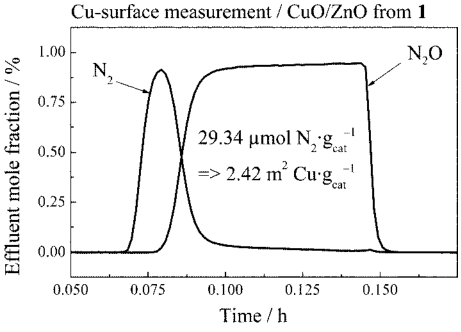

Figure 7. Measurement of the specific copper surface of Cu/ZnO prepared from the oxide derived from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) by reaction with N_2O in the single-tube reactor.

Table 4. Catalytic activity of CuO/ZnO prepared from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) in the single-tube reactor (reduced to Cu/ZnO) and of two reference catalysts.

Sample	Cu surface $[m^2 g^{-1}]$	Production rate $[\mu mol\, g^{-1}_{cat}\, h^{-1}]$
Cu/ZnO from **1**	2.42	92
Cu/ZnO from coprecipitated carbonate	17.0	115
Industrial $Cu/ZnO/Al_2O_3$ catalyst (ICI)	23.4	410

Note that the catalytic activity results obtained with the multitubular reactor cannot be directly compared with data from the single channel flow system. This is a result of the different set-ups as well as differences in the reduction process, different pressures (4.5 MPa for the parallel set-up vs. atmospheric pressure in the single-tube reactor) and slightly different feed compositions. Thus the catalytic activity of Cu/ZnO prepared from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) measured in the single-tube reactor corresponds to 23% of the activity of the commercial ICI catalyst, which is in satisfactory agreement to the data obtained from the parallel set-up (30% of ICI). In general, the efficiency of the Cu/ZnO mixture derived from the cyanide/ethylenediamine coordination compounds is between 20 and 30% of the industrial reference catalyst.

Kurtz et al. gave a linear relationship between the specific copper surface and the catalytic activity.[14] For our CuO/ZnO catalyst from $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**), only 40% of the actually observed activity would have been expected, i.e. about 40 $\mu mol\, g^{-1}_{cat}\, h^{-1}$. An optimised thermolysis of $[Zn^{II}(en)]_2[Cu^I_2(CN)_6]$ (**1**) with regard to a high surface area of copper oxide may lead to an even higher catalytic activity. Unfortunately, the “easy route” to increase the specific surface area by adding Al_2O_3, as further support, was not successful (see Table 3).

Conclusions

By the preparation and thermolysis of bimetallic coordination compounds, which contain copper and zinc in the same crystal, it is possible to prepare active Cu/ZnO catalysts for methanol synthesis. However, if only cyanide is present as the ligand, the activity of the resulting oxide mixture is almost zero, possibly because of poisoning of the surface. The introduction of ethylenediamine as an additional ligand leads to Cu/ZnO with a catalytic activity of 20 to 30% of the industrial reference catalyst. It is important to note that the morphology (by scanning electron microscopy) and the chemical composition (CuO and ZnO) of the thermolysis products from both kinds of precursors are practically indistinguishable. This underscores the strong influence of the precursor structure on the catalytic activity of the resulting oxide,[1,2] which, despite sophisticated in situ studies,[21,22] is not yet fully understood.

Experimental Section

For all preparations, deionised water was used.

Preparation of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (1): KCN (2.6 g, 40 mmol) and $(NH_4)_2SO_4$ (2.64 g, 20 mmol) were dissolved in water (50 mL). $ZnSO_4\cdot 7H_2O$ (2.91 g, 10 mmol) was added to this solution whilst stirring until complete dissolution occurred. A second solution of $CuSO_4\cdot 5H_2O$ (2.53 g, 10 mmol) and ethylenediamine (1.1 mL, 20 mmol) was prepared in water (25 mL). The solutions were poured together whilst stirring and a slightly blue precipitate was obtained. Water was added to a volume of 100 mL, and the unfiltered mixture of precipitate and solution was stored in a closed flask for three days. Pale green crystals were obtained, filtered, washed with water and dried for several days at room temperature in air. Yield: 43%. $C_{10}H_{16}Cu_2N_{10}Zn_2$ (534.16) (average of four independent preparations with standard deviations): calcd. C 22.49, H 3.02, Cu 23.79, N 26.22, Zn 24.48; found C 22.16 ± 0.64, H 2.76 ± 0.34, Cu 25.06 ± 1.38, N 25.64 ± 0.86, Zn 23.70 ± 1.47. The powder diffraction pattern of $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (**1**) was simulated using the single-crystal structure data. It showed an excellent agreement with the experimental powder diffraction pattern, therefore the bulk phase has the same structure as the single crystal.

Preparation of $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (2): NaCN (1.96 g, 40 mmol) was dissolved in water (40 mL). CuCl (0.99 g, 10 mmol) was added to this solution whilst stirring until complete dissolution occurred. A second solution of $Zn(OAc)_2\cdot 2H_2O$ (3.29 g, 15 mmol) and ethylenediamine (3 mL, 45 mmol) was prepared in water (35 mL). The solutions were mixed and then stored in a sealed flask for a week. Slightly bluish crystals were obtained. After addition of a small amount of ethanol, more crystals were obtained from the mother liquor. Yield: 51%. $C_{53}H_{160.8}Cu_5N_5Zn_6$ (2385.41) (average of four independent preparations with standard deviations): calcd. C 26.69, H 6.79, Cu 13.32, N 31.12, Zn 16.44; found C 26.50 ± 0.54, H 6.83 ± 0.15, Cu 12.71 ± 0.46, N 30.60 ± 0.39, Zn 16.37 ± 0.39; traces of Na were also detected (0.58 ± 0.28 from three preparations). The powder diffraction pattern of **2** was simulated using the single-crystal structure data. It showed an excellent agreement with the experimental powder diffraction pattern, therefore the bulk phase has the same structure as the single crystal.

Preparation of CuO/ZnO from $[Zn^{II}(en)]_2[Cu^{I}_2(CN)_6]$ (1) and $[Zn^{II}(en)_3]_6[Cu^{I}_2(CN)_7]_2[Cu^{I}(CN)_3]\cdot 8.4H_2O$ (2): The compounds were heated in an open crucible in air at 300 °C for 24 h. The product was then ground and heated again for 24 h at 300 °C. For the carrier experiment the precursor (100 mg) was intimately ground with Al_2O_3 (400 mg). The thermolysis was carried out as before.

Catalytic Measurements: (a) High-throughput screening in the multitubular reactor: Measurements were performed with a high-throughput 49-parallel channel reactor.[19] The catalyst (100 mg diluted by 200 mg quartz per well) was 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 518 K following 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 518 K, analytic flow 20 mL min^{-1}). The reaction gas consisted of 70% H_2, 24% CO and 6% CO_2. A double GC system (HP GC 6890) equipped with a methaniser 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 mmol MeOH/($g^{-1}_{cat}\,h^{-1}$) at 518 K and 4.5 MPa].

(b) Single-tube reactor: 100 mg of the sample (sieves fraction 250–355 μm) were placed in a fixed-bed glass-lined U-tube reactor. The reduction was performed under flowing diluted H_2 (2% H_2 in He) by increasing the temperature up to 448 K by 1 K min^{-1} and maintaining it there for 14 h. To ensure complete reduction, the temperature was then increased to 513 K and the sample was treated with pure H_2. The active surface area of Cu was determined by N_2O reactive frontal chromatography at 300 K as described earlier.[23] The methanol formation activity was measured at 493 K under atmospheric pressure. The feed gas consisted of 72% H_2, 10% CO, 4% CO_2 and 14% He. Gases of the highest available purity (>99.9995%) were used. The online analysis of the products was performed by a previously calibrated quadrupole mass spectrometer (Balzers GAM 422).

Analytical Techniques: Combined thermogravimetry-infrared spectroscopy (TG-IR) was carried out with a Netzsch STA 209 TG-DTA/DSC instrument connected to a Bruker Vertex 70 infrared system with a TGA-IR measurement cell for gas analysis. Samples were heated from 30 °C to 800 °C at a rate of 5 K min^{-1} under a dynamic O_2 atmosphere at a flow rate of 50 mL min^{-1}. Infrared spectroscopy was carried out with a Bruker Vertex 70 (KBr pellets), scanning electron microscopy with an ESEM Quanta 400 instrument (FEI) on nonsputtered samples. High-resolution X-ray powder diffractometry was carried out in transmission geometry at beamline B2 at HASYLAB/DESY, Hamburg, Germany.[24]

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft within the scope of the Collaborative Research Center SFB 558: Metal–substrate interactions in heterogeneous catalysis. We thank HASYLAB at DESY, Hamburg, for the generous allocation of X-ray diffraction beam time.

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Received: January 4, 2006