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


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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)2Cu2(CN)6] and [Zn(en)3Cu2(CN)7]2[Cu(CN)3]·8.4H2O 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/CO2/H2. 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/Al2O3 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. [CuII(H2O)6]2+, [Zn II(H2O)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 CuII cyanide complexes are subject to an internal redox reaction resulting in CuI and (CN)2. In the case of the reaction of Cu2+ with [Zn II(CN)4]2–, the kinetic lability of the cyanide complexes of copper and zinc had a strong influence on the products that formed. Starting with solutions of [ZnII(CN)4]2– and Cu2+, the main product was ZnII[CuI(CN)3]2–, whereas CuII[ZnII(CN)4] and ZnII[ZnII(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 CuI 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 [Cu2(CN)6]3−, as in

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