New heterometallic copper zinc alkoxides: synthesis, structure properties and pyrolysis to Cu/ZnO composites

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Abstract

The copper compound \([(\text{THF})KCu(OtBu)_3]\) 1 was obtained by interaction of a 1:1 mixture of ZnCl₂/CuCl₂ with KOtBu. Bi- and trifunctional aminoalcohols were used to synthesize the intramolecularly donor stabilized Cu(II) alkoxides \(\text{Cu(OCH(R)CH}_2\text{NMe}_2)\) where 4 was structurally characterized. Lewis acid–base adduct formation with (Me₃Si)₃CZnCl gave the heterodinuclear compounds \((\text{Me}_3\text{Si})_3\text{CZnCl} \cdot \text{Cu(OCH(R)CH}_2\text{NMe}_2)\) 5: R = Me, 6: R = CH₂NMe₂), which were characterized by X-ray single-crystal structure analysis. The two metal centers Cu and Zn of 5 and 6 are bridged by two oxygen atoms to form a Cu–O–Zn core. Pyrolysis of compounds 5 and 6 in dry argon or a \(\text{H}_2/\text{N}_2\) mixture at atmospheric pressure forms metallic copper and zinc oxide, whereas pyrolysis under \(\text{O}_2/\text{Ar}\) forms additionally oxidized copper species. Elemental analysis of the pyrolysis products showed carbon and nitrogen contamination. Scanning electron microscopy and energy dispersive X-ray analysis were performed to get information on the morphology and the chemical composition of the pyrolysis products. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mixed-metal oxides represent an important class of materials for advanced applications, including catalysts, structural ceramics, sensors and actuators as well as ferroelectric and dielectric materials for microelectronic data processing devices [1–6]. The investigation and the use of heterometallic alkoxides as single molecule precursors (SMPs) for the synthesis of mixed-metal oxides have continuously increasing over the past decade. This is particularly connected with the elucidation of the complex sol–gel chemistry of oxide materials processing in general [7] as well as with the related precursor chemistry for the growth of metal oxide thin film materials by chemical vapor deposition techniques [1,2,4,8]. However, virtually all of these examples refer to single-phased metal oxide materials. Only recently it was shown, mainly by the work of Veith et al. [9], that SMPs can be designed to produce unusual multiphased composite materials directly in one single step depending on both the metal composition and the particular precursor design. Within the context of heterogeneous catalysis the most noteworthy examples are thin films or powders of nanostructured metals homogeneously dispersed in a metal oxide matrix derived from SMPs. Many catalysts are composed of finely dispersed, i.e. nanoscale metal particles bound to a metal oxide support (metal@metal-oxide) [10]. Tailored SMPs may thus represent an interesting alternative approach for catalyst preparation.

We were attracted by this idea and selected the Cu@ZnO system as a study object. The Cu@ZnO system is of eminent importance in large-scale industrial methanol synthesis (10⁷ tonnes per year) from CO/CO₂/\(\text{H}_2\) [11]. The industrial Cu@ZnO-based catalysts for methanol synthesis are generally prepared by a well developed and empirically optimized coprecipitation technique. An aqueous solution of alkali carbonates is