Nano-Brass: Bimetallic Copper/Zinc Colloids by a Nonaqueous Organometallic Route Using [Cu(OCH(Me)CH₂NMe₂)] and Et₂Zn as Precursors

Julia Hambrock, Marie K. Schröter, Alexander Birkner, Christoph Wöll, and Roland A. Fischer*

Lehrstuhl für Anorganische Chemie II, Organometallics & Materials Chemistry, Ruhr-University Bochum, D-44780 Bochum, Germany

Received March 10, 2003. Revised Manuscript Received July 31, 2003

We present a synthetic approach toward alloyed Cu/Zn nanoparticles using [Cu(OCH(Me)CH₂NMe₂)] and Et₂Zn as precursors. The thermolysis in the hot coordinating solvent hexadecylamine, HDA, leads to the formation of nanoscale, colloidal Cu/Zn systems with zinc contents (by EDX) of 5, 30, and 65%, respectively. All systems have been analyzed using UV/Vis spectroscopy, transmission electron microscopy, EDX, and selected area electron diffraction (SAED). These analytical data suggest that alloying between zinc and copper takes place, revealing crystalline phases of CuZn and CuZn₂ besides Cu as components of the particles in the case of higher zinc concentrations. The characteristic surface plasmon resonance (UV) for pure HDA-capped copper colloids at 558 nm, still observed for copper-rich alloy particles, disappears for zinc-rich particles.

Introduction

Many heterogeneous catalysts can be regarded as nanocomposites of high surface area metal nanoparticles dispersed on suitable support materials, and the catalyst is promoted by various additives. Among those systems, the Cu/ZnO nanocomposite is prototypical for the so-called strong metal-support interaction (SMI) and of particular importance for the large-scale industrial methanol production from syngas at moderate temperatures and pressures.¹⁻³ Such copper-based methanol catalysts can be grouped into three classes: the binary systems Cu/ZnO and CuAl₂O₃ and the ternary system Cu/ZnO/Al₂O₃. These catalysts are prepared along precisely controlled aequous coprecipitation/calcination/reduction procedures using cheap copper and zinc salts (nitrates, carbonates, and acetates) as precursors. The catalytically active systems show a linear correlation of the methanol productivity with the specific copper surface.⁴⁻⁵ It is known that the Al₂O₃ component stabilizes the system against sintering (structural promoters) and the ZnO component further increases the activity at a given copper dispersion. Much research has been directed to elucidate the special nature of the synergetic effect between the Cu and the ZnO component. Most recent studies revealed that the structure of local sites at the Cu/ZnO interface seem to be most important and relate to the segregation of Zn species to the Cu surfaces, forming a Cu/Zn surface alloy as well as surface Zn atoms and ZnO ad-species as a function of the redox potential of the ambient (composition of the gas and temperature/pressure). Consequently, the state of the catalyst appears to be dynamic, and different types of structures may only be dominant features under limited sets of reaction conditions as some leading authors in that field have pointed out.⁶⁻⁷

We were attracted by the relevance and complexity of the Cu/ZnO nanocomposite in the solid state and started out to establish a colloid chemistry of the Cu/ZnO system with the long-term goal of deriving some type of soluble model catalyst to enter the above cited discussion from a new side. There exists a plethora of work on copper colloids and ZnO colloids for many reasons referring to fundamental interests, for example, effects of particle size, shape, and surface structure on physical properties, “size quantization”, along the transition from the bulk to molecular dimensions and thus addressing many interesting applications.⁸⁻¹⁶ However,