Copper–zinc nanocomposites were prepared by thermolysis of copper–zinc cyanides under mild conditions. Two different routes were used for the preparation of the cyanide complex: A batch precipitation method and the continuous overflow precipitation method. The thermolysis of the cyanides was studied in situ by thermogravimetry coupled with infrared spectroscopy (TG-IR) and by thermogravimetry coupled with mass spectroscopy (TG-MS). The structure of the nanocomposites was investigated by X-ray powder diffraction (XRD) and extended X-ray absorption fine structure (EXAFS). Geometric models were suggested on the atomic scale based on EXAFS results for the precursor, the mixed oxides (CuO/ZnO), and the reduced copper–zinc samples (Cu/ZnO, i.e. catalyst for methanol synthesis). In the batch precipitation method, the influence of temperature on the morphology of the thermolysis products was explored. In the continuous overflow method, the morphology of the Cu–Zn cyanide complex was investigated as a function of concentration and residence time. A high solution concentration and a short residence time (equivalent to a high flow rate) led to smaller particles.

Introduction

Copper–zinc oxide nanocomposites can be obtained in a variety of morphologies, including thin films,[1] nanowires[2] and nanoparticles.[3] High surface area copper/zinc oxide is an active catalyst for methanol synthesis, for water-gas shift reactions, and for various hydrogenations.[4] It is widely accepted that zinc oxide can improve the dispersion of copper and thereby the catalytic activities.[5] Copper–zinc oxide nanocomposites are usually prepared by co-precipitation from aqueous solutions. Typically, a mixed solution of copper and zinc salts (usually nitrates or acetates) is prepared and the precipitation of both carbonates is induced by addition of sodium or ammonium carbonate whilst stirring, followed by drying and calcination.[6–9] The particle size and crystallinity of the products can be adjusted by the pH, the concentration, the stirring rate, the duration of precipitation and aging, and the calcination conditions.[10] Pollard et al.[4] used the minerals georgeite \([\text{Cu}_5(\text{CO}_3)_3(\text{OH})_4 \cdot 6\text{H}_2\text{O})]\) and azurite \([\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]\) as precursors for copper–zinc mixed oxides. Recently, a nonaqueous organometallic route was developed by Hambrock et al.[11] and uniform copper–zinc nanoparticles were obtained. They used Cu-[OCH(Me)CH_2NMe_2] and Et_2Zn as precursors. The thermolysis was carried out in the coordinating solvent hexadecylamine at elevated temperatures and nano-scale colloidal copper–zinc systems with different zinc contents were obtained. Zhou et al.[2] prepared copper–zinc nanowires by heating CuI_2 and ZnI_2 in a dynamic oxygen atmosphere. A self-catalysed vapour-liquid-solid growth mechanism was suggested.

Polymeric metal cyanides represent a homogeneous mixture of the individual metals on the atomic length scale. The heterogeneous mixing of individual compounds is therefore avoided. The controlled thermolysis of these compounds can be carried out at comparatively low temperature due to the presence of a suitable organic leaving group, i.e. the cyanide in the precursors. A higher temperature is usually required in conventional syntheses to achieve a sufficiently fast diffusion. We have shown that the composition as well as the crystal structure of the bimetallic Fe–Sn and Ru–Sn composites can be fine-tuned by the thermolysis conditions such as time, temperature and the atmosphere.[12–14] Such systems are suitable precursors for the preparation of bimetallic nanocomposites that incorporate the initially blended metals.

Recently we adopted the continuous overflow method for the preparation of calcium phosphate nanoparticles from solution.[15] The particle size, morphology and crystallinity can be adjusted by the process parameters, mainly the residence time (the flow rate of the solutions), and the concentration of the solutions. It was therefore the aim of this work to prepare a suitable cyanide precursor for the Cu/ZnO system and to control its morphology by different crystallisation methods. Thereby, the properties of the final product should be adjustable.[16–18]