CuO/ZnO Nanoparticles in a Matrix of Amorphous Silica as High-Surface Precursors for Methanol Synthesis


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An intimate mixture of CuO/ZnO nanocrystals was prepared by an easy sol-gel synthesis (precipitation in methanol by hydroxide in the presence of a silane). The organic substituents of the silane were almost completely removed by a subsequent photochemical oxidation. The resulting amorphous SiO₂ prevented the growth of the catalytically active particles to larger crystals. The coating layer of silica can easily be penetrated by gaseous reactants, as shown by the high specific surface area of about 110–130 m² g⁻¹ (probably due to both silica and nanocrystalline CuO/ZnO) and the good catalytic activity in methanol synthesis from CO/CO₂/H₂ synthesis gas (7 to 37 %, compared to an industrial standard methanol catalyst). The ratio of CuO to ZnO can be easily varied by the used preparation method.

Introduction

Cu/ZnO is a widely used model catalyst system for investigations in heterogeneous catalysis.[1] In most cases, the methanol synthesis and the steam reforming reaction are studied. The industrial catalyst is based on Cu/ZnO/Al₂O₃,[1,2] but often Cu/ZnO is examined as simplified binary model system.[3–15] Although copper is the more important catalytically active component,[16,17] pure ZnO is itself active in methanol synthesis.[18–20] The most common preparation methods for the catalyst precursor CuO/ZnO are based on the co-precipitation of carbonates or oxalates, followed by thermolysis to the corresponding oxides.[6,8,11,14,21–23] We have recently shown that active catalysts can also be prepared by thermal dissolution of bimetallic coordination compounds,[24] xerogels and aerogels,[25] and tartrate mixed crystals.[26] Copper nanoparticles in liquid dispersion were recently shown to be active as methanol catalysts,[27] as well as metal-loaded mesoporous silicates[28] and metal-oxide frameworks (MOFs).[29]

Here we report on the preparation, characterization and catalytic activity of ZnO and CuO/ZnO nanocomposites which were obtained by a combination of sol-gel synthesis and photochemical oxidation which was applied earlier to prepare nanoscale ZnO.[30] By precipitating the oxides in the presence of a silane in alcohol, a highly dispersed mixture of the oxides with a high specific surface area[31] is obtained because the silane prevents the growth and agglomeration of the oxide crystals.[32] Subsequently, the organic substituents of the silane are photochemically oxidized and almost completely removed.[30] The ratio of copper to zinc can be easily varied by this method, opening a way to nanocrystalline systems of CuO/ZnO in amorphous silica with a high overall specific surface area. Copper oxide can then be reduced to Cu, resulting in Cu/ZnO/SiO₂, i.e. the active methanol catalyst, preserving a high specific surface area which is advantageous for a high catalytic activity. This approach to co-precipitate the nanoparticles with a porous inorganic matrix is different from the often applied approach to fill an already existing porous template.

Result and Discussion

Four samples with different ratios of CuO/ZnO (A: 0.76 wt.% Cu; B: 4.37 wt.% Cu; C: 15.6 wt.% Cu; D: 34.4 wt.% Cu) were prepared by a combination of sol-gel synthesis and photochemical oxidation and compared to a sample of pure ZnO (Z), prepared by the same method.[30] The coating with silane prevented crystal growth and agglomeration of the primary oxides. The subsequent photochemical treatment almost completely destroyed the organic fragments of the silica and led to the formation of X-ray amorphous silica ("SiO₂").

Scanning electron microscopy (SEM) showed an agglomerated material with particle sizes of a few hundred nano-