Cu/ZnO aggregates in siliceous mesoporous matrices: Development of a new model methanol synthesis catalyst

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Dedicated to Prof. Volker Staemmler at the occasion of his 65th birthday

Abstract

Copper and zinc were introduced into mesoporous siliceous matrices with the goal of obtaining model methanol synthesis catalysts with intense interaction between copper and the ZnO promoter. The preparation methods included various aqueous routes starting from acetate solutions (into MCM-48) and a route involving an organometallic step—thermolysis of a liquid heterocubane of Zn₄O₄ type ([CH₃ZnOCH₂CH₂OCH₃]₄) in a wormhole-type silica of 5 nm average pore size—followed by aqueous Cu (nitrate) impregnation. The materials were characterized by XRD, nitrogen physisorption, N₂O frontal chromatography, TPR, and EXAFS, and their methanol synthesis activity was measured at 493 K and normal pressure. In the aqueous preparations with acetate solutions, excessive formation of silicates (particularly zinc silicate) led to damage of the pore system. A significant delay in Cu reduction was assigned to the influence of micropores formed, together with some copper silicate formation. These samples exhibited poorly accessible Cu surface areas despite small Cu particle sizes indicated by EXAFS and disappointing methanol synthesis activity. In contrast to this, a highly active catalyst was obtained via the heterocubane route that meets industrial standards in terms of reaction rate per Cu surface area. Orientation studies (EXAFS at the Cu K and Zn K edges) reflecting a redox behavior of the ZnO x component illustrate the potential of this catalyst type for use in basic studies of the Cu–ZnO x interaction in methanol synthesis catalysts.

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1. Introduction

Today it is widely accepted that in the Cu/ZnO/Al₂O₃ methanol synthesis catalyst, the interaction between Cu and ZnO plays a vital role in the development of high catalytic activity. The mechanism of this interaction remains under discussion. The most relevant models agree in assuming that defective ZnO created in a strongly reductive atmosphere exerts a dramatic influence on the copper, but they differ in the interpretation of the consequences on the active copper site, which is considered a metallic site by most, but not all, groups.

It has been found that the defective ZnO causes changes in the particle morphology of the copper (wetting/nonwetting effect) [1–3], which leads to different exposures of copper facets, particularly of the most active (111) facet. Based on this finding, attempts have been made to fit real kinetic data of methanol synthesis with a microkinetic model, in which kinetic data for the steps of the underlying reaction mechanism are taken from stud-