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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 Zn_4O_4 type ($[CH_3ZnOCH_2CH_2OCH_3]_4$) 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, N_2O 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 CuK and ZnK 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.

Keywords: Methanol synthesis; Copper; Zinc oxide; Metal–support interaction; Model catalyst; Mesoporous silica; MCM-48; XAFS; TPR

1. Introduction

Today it is widely accepted that in the $Cu/ZnO/Al_2O_3$ 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-

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ies on Cu single-crystal surfaces. The fact that this model has been successful when complemented with a routine describing the exposure of these surfaces with varying oxidation potentials of the mixture [4] suggests that the morphology change alone explains the promoting influence of the zinc.

An alternative view has been advocated by Günter et al., according to which the intrinsic activity of copper is enhanced by strain imposed on it by the interaction with ZnO (misfit at the contact surface, bulk inclusion of ZnO_x entities [5,6]). This mode of activation, which might be a general feature of metal–support relations, was observed for methanol synthesis and methanol steam reforming.

It is, however, also known that under strongly reducing conditions, ZnO_x species migrate onto the copper surface [2,7,8], which has a favorable effect on methanol synthesis activity. This suggests that sites of particular reactivity may exist at the Cu–ZnO_x interface, the extension of which increases when ZnO_x species migrate onto the Cu surface. This view has been supported by groups that adhere to Cu metal as the active site for methanol synthesis [2,8,9], as well as by those that advocate a deciding role for Cu^+ [10–13]. However, with a traditional $Cu/ZnO/Al_2O_3$ catalyst, the comparison of TPD experiments (H_2 TPD vs. N_2O titration) after methanol synthesis and after CO treatment implies that the actual coverage of the Cu surface by ZnO_x may be quite low under actual reaction conditions [8]. But because a moderately active Cu/Al_2O_3 catalyst can be dramatically boosted by gas-phase interaction with diethyl zinc [9], it has been concluded that the Cu–ZnO interface plays a vital role in methanol synthesis.

There are several reasons why obtaining reliable insight into the nature of the Cu–ZnO interaction from experiments with catalysts of technical interest is very difficult. Although prepared by seemingly simple methods (co-precipitation, calcinations), the actual microstructures of the catalyst precursors and the resulting catalytic materials after activation are very complex and depend on many parameters that are difficult to control. In addition, studying the interface between Cu particles and ZnO aggregates is very complicated, because at particle sizes of several nm (and well above 10 nm for ZnO), only a very small percentage of the Cu atoms (or Zn ions) are engaged in the mutual interaction. This percentage can be increased by imposing a high dispersion on *both* Cu and ZnO, which should be beneficial to the catalyst's general performance as well [9].

The approach adopted by our groups to force the catalyst components into high dispersion and intense interaction with one another simultaneously provides an opportunity to apply more well-defined preparation steps. By embedding the catalytically active component into a well-defined superstructure (e.g., a hierarchically structured mesoporous matrix), it should be possible to simultaneously simplify and miniaturize the supported catalyst [14–20] and to utilize in the preparation the favorable effects of the spatially confined reaction conditions on the chemistry occurring in the porous solid [21]. However, this approach carries the risk of interference by the pore walls of the matrix. Indeed, a strong interaction was previously observed between the silicate wall and zinc species introduced by aqueous techniques or by interaction with dimethyl zinc, which was stable during calcination and rendered the zinc in a completely disordered state, probably as a zinc silicate layer covering the wall instead of nanoparticulate ZnO [22,23]. In redox experiments in which the response of the IR reflectivity on changes in the gas atmosphere was followed, these zinc species turned out to be redox-inactive [23], unlike bulk ZnO.

The activation of copper particles previously produced in the mesoporous matrix by treatment with diethyl zinc seems an obvious approach for the creation of a large Cu–ZnO_x interface, and it has been realized in a companion work in which copper was introduced from a volatile organometallic source as well [24]. But although this preparation demonstrates that active methanol synthesis catalysts can be obtained by the miniaturization approach described above, most of the zinc ends up deactivated at the pore walls in this case as well, impeding the goal of studying those zinc species engaged in the Cu–ZnO interaction.

The goal of our research was to create a matrix-encapsulated methanol synthesis catalyst that combines high activity with high potential for investigation of the metal–support interaction. After considerable effort aimed at achieving this goal with seemingly simple preparations starting from aqueous copper and zinc acetate solutions [22,23], a promising catalyst was obtained via a route involving the deposition of zinc into a mesoporous silicate via thermolysis of a liquid organometallic precursor [16]. Conventional impregnation of such ZnO-modified mesoporous silicate with copper nitrate resulted in a methanol synthesis catalyst with an activity of the same order of magnitude as a catalyst of technical relevance and clear indications of zinc redox activity as demonstrated by XAFS. In this paper, structural and catalytic data for the new model catalyst are compared with results from a typical material obtained via the aqueous route to illustrate the critical points in the synthesis. We show that the new material, which is a simplified but competitive catalyst obtained via a complicated route, opens up an interesting approach for both further optimization and model studies on the nature of the Cu–ZnO interaction.

2. Experimental

2.1. Materials

The matrix used in the present study is a mesoporous silica with a wormhole-type pore structure. The preparation of silica monoliths with tunable mesopore size via the true liquid-crystal templating route has been described elsewhere [16,25,26]. These materials have a bicontinuous pore system, with micropores connecting the mesopores. In this study, we concentrate on a material with an average pore size of 50 Å prepared with Pluronic P123 as a template, labeled as wh(50)-SiO_2. For comparison, a preparation with an MCM-48 matrix is reported as well. The synthesis of this matrix has been described previously [23] where characterization data are given as well [XRD—*d* spacing of (211) reflection—3.272 nm].

The organometallic precursor of "Zn_4O_4" heterocubane type ($[CH_3ZnOCH_2CH_2OCH_3]_4$ (**I**)),