Preparation of Cu/ZnO and Cu/ZnO/Al$_2$O$_3$ Methanol Catalysts by Gas-Phase Loading of Mesoporous Silica: Aiming at Superior Catalytic Activity by Molecular Control of their Microstructure

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Abstract

Copper-based catalysts (Cu/ZnO and Cu/ZnO/Al$_2$O$_3$) are the basis of the industrial methanol synthesis and methanol oxidation and are important components of fuel cell technology. For the preparation of these catalysts, metal–organic chemical vapor deposition (MOCVD) technique has proven its potential. Furthermore, studying synergistic metal–support interactions, strategies can be developed to gain molecular control over the interfaces that would provide the basis for the knowledge-driven improvement of heterogeneous catalysts. Since there is in principle no limit in respect to the simultaneous maximization of the specific copper surface area and the Cu/ZnO interface area, there is no limit to the increase of the catalytic activity beyond that which is currently possible. In order to maximize the specific copper surface area and the Cu/ZnO interface area, the loading of copper in the matrices can be increased by the repetition of the loading cycles. Furthermore, the combination of different Cu precursors with different zinc- and aluminium-oxide precursors opens up a certain degree of freedom to optimize the loading process. Current findings of this work include successful deposition of Cu/ZnO catalysts by the MOCVD using templated silica as a support. The molecular control of the Cu/ZnO interface is achieved by variation of dimension and framework of the pores and by exploration of the precursor chemistry. After the first loading cycle, the specific copper surface area of the obtained Cu/ZnO@PMS samples was in the range of 5-6 m^2_{Cu}/g$_{cat}$, while the XRD and EXAFS studies revealed exceptionally low copper crystallite size and degree of aggregation. The methanol synthesis performance is found to be 19-130 μmol/g$_{cat}$h, using a special catalytic test set-up referenced to the industrial ternary catalyst having a value of about 450 μmol/g$_{cat}$h.

Introduction

Copper-based catalysts (especially Cu/ZnO and Cu/ZnO/Al$_2$O$_3$) make the basis of the industrial methanol synthesis and methanol oxidation and they are important component of fuel cell technology [1]. From the scientific point of view, the binary Cu/ZnO catalyst is also a prototype for the exploration of synergistic metal–support interactions for the understanding of catalytic reactions on the molecular level [2] - the so-called strong metal support interactions (SMSI). Eventually, strategies can be developed to gain molecular control over the Cu/ZnO interface that would provide the basis for the knowledge-driven improvement of heterogeneous catalysts. However, a need emerges for model systems representing Cu/ZnO/Al$_2$O$_3$ heterogeneous catalysts, which would enable studies of the synergetic effect between the components. There are numerous reports that suggest that the properties of the active sites are strongly influenced by the presence of alumina species [3]. Moreover, the stability of the Cu/ZnO catalyst is improved by the addition of alumina. It is also believed that aluminium oxide has the ability to keep the copper particles apart and stabilise them against sintering, i.e. to behave as a so-called structural promoter in that catalyst system. Therefore, synthesis strategies

should be developed that enable strict control over the properties of this material, which would lead to the establishment of the model system for the $Cu/ZnO/Al_2O_3$ system.

There is in principle no direct limit in respect to the simultaneous maximization of the specific copper surface area and the Cu/ZnO interface area, and thus to increase of the catalytic activity beyond that which is currently possible as long as low density and high surface area mesoporous host matrices are used to anchor the catalytically active species [4,5]. For further enhancement of the catalytic performance of these systems, but also for further scientific understanding of the mechanisms, chemical vapor deposition of the components is studied in more detail and the introduction of Al_2O_3 as the third component is considered. Since the activity of these catalysts depends on the numerous (structural) factors such as chemical composition, crystallite size, copper surface area, as well as bulk structural parameters like microstrain in the copper particles, further research in this area is needed in order to establish clear structure-activity relationships. Considering state-of-the-art research and current challenges, the objectives of the work are:

- Increasing the Cu loading (wt %) and keeping the Cu dispersion as high as possible at the same time.

- Introduction of the Al_2O_3 component and establishment of a model system for the $Cu/ZnO/Al_2O_3$ heterogeneous catalyst. Free adjustment of the loading parameters of all the three components.

- Determination of the activity of the synthesised catalysts and establishment of the structure-activity relationship. With respect to the catalytic activity, the aim is to achieve comparable or to exceed specific activities (activity per total mass) of the industrial co-precipitated bench-mark catalyst.
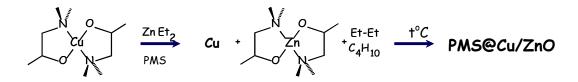
Approach and techniques

Support

Nanochemistry in the pores and cavities can be tuned depending on the type of supporting mesoporous material i.e. its pore size, available surface area, surface properties, etc. The influence of the mesoporous matrix properties on the catalyst properties can be studied by using various periodic mesoporous silicate supports with different pore size, pore size distributions, pore shapes, etc. Owing to their high specific surface area and precisely controllable pore structures in the lower nanometer range, periodic mesoporous silica (PMS), such as MCM-41, MCM-48, SBA-15, MCF and related materials including inorganic-organic hybrid derivatives and similar, have been proven to be excellent supports for numerous catalytically active species, but also suitable matrix materials for the research of the in-pore chemistry [6].

Synthesis technique

In addition to conventional aqueous impregnation/calcination procedures, metal–organic chemical vapor deposition (MOCVD) techniques has proven its potential for the preparation of the highly active catalysts [4,7]. The clear advantage of this technique comparing with the typical solution-phase method that uses salt type precursor is that unwanted effects of the solvent can be completely avoided in the gas phase. Moreover, the molecular organo-metallic (MOCVD) precursors tend to cleanly generate the desired materials with controlled growth rate at relatively low growth temperature [8]. $[Cu(OCHCH_3CH_2N(CH_3)_2)_2]$ and $Zn(CH_2CH_3)_2$ are used as the MOCVD precursors. $ZnEt_2$ acts as elegant reducing agent for the copper alkoxide and in parallel covers the silica surface with ZnEt-species which in turn are converted into the ZnO promoter component upon calcination/reduction cycles (Scheme 1). The ternary $Cu/ZnO/Al_2O_3$ system can be made by the MOCVD loading of the

PMS support using an appropriate Al_2O_3 precursors, for example aluminum alkoxides such as $Al(O^iPr)_3$ or aluminum alkyls and hydrides such as $Al(CH_3)_3$ and $H_3Al(N(CH_3)_3)$, all being typical choices and commercially available MOCVD precursors of aluminium oxide and aluminium, respectively. The combination of different Cu precursors known from classical Cu MOCVD with different zinc- and aluminium-oxide precursors opens up a certain degree of freedom to optimize the loading process.

Scheme 1: Reaction of $Cu(OCHMeCH_2NMe_2)_2$ and $ZnEt_2$ in the pores of PMS-support

In order to maximize the specific copper surface area and the Cu/ZnO interface area, the loading of copper in the matrices can be increased by the repetition of the loading cycles. During the process, copper particle size and agglomeration should be kept as low as possible, while accessible surface area of the loaded porous matrix stays as high as possible. Simultaneously, the particle size and porosity as a function of the loading cycle number and the conditions are determined.

Furthermore, fluidized bed chemical vapour deposition (FB-CVD) type reactors are investigated, since that is an industrially relevant catalyst preparation technique.

Characterization techniques

PXRD is the main technique used to determine the degree of crystallisation and particle size of copper. In principle, the copper XRD peak should be kept as broad as possible even under the conditions of repeated loading cycles. The influence of the Al_2O_3 component is also studied in this way. Additional information about particle aggregation and species can be obtained using XANES and EXAFS. Further, FTIR is applied to reveal the surface properties of the materials under consideration. For the determination of the pore size and internal surface area standard nitrogen absorption (BET/BJH methods) is used. As additional routine methods temperature-programmed reduction and copper area determination by N_2O frontal chromatography is applied. Visual examination and the chemical composition of the final materials is carried out using TEM-EDX. Finally, detailed catalysis tests of selected and promising samples (those with high copper loading, broad PXRD copper peaks and high specific surface area) is carried out. Microstructure of the samples that show respectably high or superior activity would be again investigated in some more detail to elucidate the particular properties aiming to contribute to the understanding of the SMSI effect and related metal support interactions in the particular system.

Results

Between 8 and 12% of copper and 21-25% of zinc were successfully deposited by MOCVD using MCM48 and MCF materials as a matrix. The specific copper surface area of the obtained Cu/ZnO@PMS samples was in the range of 5-6 m^2_{Cu}/g_{cat}, while the XRD and EXAFS studies revealed exceptionally low copper crystallite size and degree of aggregation. When the MCM48 was used as a matrix, the absence of characteristic copper peaks suggests particle size lower than 2 nm, while in the case of MCF average particle size of 5 nm was estimated using the Scherrer formula. However, repeated loading led to a significant decrease of the material internal surface area, This is assigned to

the low pore size of this material, and for further studies of the repeated loading, silica based porous materials with the average pore size of 10 nm and above were used. The methanol synthesis performance is found to be 19-130 µmol/g$_{cat}$h, using a special catalytic test set-up referenced to the industrial ternary catalyst having a value of about 450 µmol/g$_{cat}$h. Catalysts of the type Cu/ZnO/A$_2$O$_3$@Matrix have also been prepared and their catalytic activity as well as synergetic effect between the components is under investigation.

Conclusions

MOCVD technique, both fixed and fluidized bed, has been demonstrated as a successful method for the synthesis of Cu/ZnO and Cu/ZnO/Al$_2$O$_3$ and catalysts using templated silica and porous alumina particles as a support. The molecular control of the Cu/ZnO interface is achieved by variation of dimension and framework of the support pores and by exploration of the precursor chemistry. Catalytic activity of the studied materials is higher then expected for the catalysts with the corresponding copper surface area, which proves their potential for the exceeding activity of industrially co-precipitated bench-mark catalyst.

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