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Correlations between synthesis, precursor, and catalyst structure and activity of a large set of $CuO/ZnO/Al_2O_3$ catalysts for methanol synthesis

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ABSTRACT

Ternary $Cu/ZnO/Al_2O_3$ catalysts were systematically prepared via the coprecipitation route under strict control of parameters such as pH, precipitation temperature, and calcination temperature. All catalysts were tested with respect to their methanol synthesis activity in a 49-fold multitubular high-throughput experimentation setup under conditions similar to the commercial methanol production route, using a syngas mixture of CO, CO_2, and H_2. Representative samples were chosen for a more detailed structure and morphology analysis to reveal correlations between the catalyst's "preparation history" and the methanol productivity. The best catalytic performance was observed for catalysts obtained from precursors precipitated in the pH range of 6–8 at 70 °C. XRD measurements allowed the "grouping" of catalysts based on their phases. It was found that a group of best-performing catalysts exhibited the characteristic XRD pattern of nondecomposed Cu/Zn hydroxy carbonate residues in the calcined precursors, leading to the assumption that carbonate species in this state may enhance productivity. Further investigations of these hydroxy carbonate-containing catalysts provided more detailed insight into the dynamic aging process and its affect on catalytic performance. The greatest methanol synthesis activity was observed for catalysts aged for 20–60 min after an initial phase formation time. The optimum calcination temperature was found to be in 250–300 °C. Under these conditions, the resulting Cu/Zn/Al hydroxy carbonates remained stable. In addition, the syngas feed composition was varied under reaction conditions and correlated to catalytic activities. The greatest methanol productivity over $Cu/ZnO/Al_2O_3$ catalysts was observed for the following gas concentrations: 50–60% for H_2, 30–40% for CO, and 5–10% for CO_2, at 4.5 MPa and 245 °C.

1. Introduction

$Cu/ZnO/Al_2O_3$ catalysts are used predominantly in the industrial low-pressure methanol synthesis process starting from synthesis gas, a mixture of H_2, CO, and CO_2. To date, the best catalytic performance has been achieved over $Cu/ZnO/Al_2O_3$ catalysts prepared by the coprecipitation method using nitrates of Cu, Zn, and Al and alkali bicarbonates or alkali carbonates as basic precipitating agents. The resulting hydroxy carbonates are converted to metal oxides by subsequent calcination at ca. 300–500 °C. The final active catalyst is obtained by reduction of CuO to metallic Cu under a diluted H_2 flow before feeding the synthesis gas mixture [1–3]. Each step in the synthetic procedure may influence the activity of the final catalyst under reaction conditions, the structure of which may be different from that of a sample recovered after the reaction and analyzed ex situ. Numerous studies have evaluated sample sets covering a limited part of the parameter space or parts of the full catalyst synthesis sequence. Several of these studies focused on the binary Cu/ZnO system. Due to the somewhat fragmented data in the literature, it seemed worthwhile to undertake a more comprehensive study of the whole sequence from hydroxy carbonate precursor over oxide precursor to the reduced catalyst in the $Cu/ZnO/Al_2O_3$ system, and to attempt to elucidate the influence of the conditions and the structure of the solid after each step on the final activity of the catalyst.

The role of metallic copper in the reaction mechanism has been widely discussed in the literature over the past 20 years and remains a matter of debate. Today, it is widely accepted that metallic copper clusters are the active sites for the methanol synthesis reaction over Cu/ZnO-based catalysts [4,5]. The main function attributed to the ZnO is to increase Cu dispersion in the calcined sample, thus providing a high number of active sites exposed to the reaction gases [1]. In addition, however, ZnO may contribute to the high activity through some other effects, as discussed below.

Studies on the phases in the precipitate of Cu/Zn hydroxy carbonates in combination with aging effects have revealed that some precipitate phases seem to favor the dispersion of copper. For instance, in aurichalcite $(Cu,Zn)_5(CO_3)_2(OH)_6$, Cu is atomically dispersed in a zinc hydroxy carbonate matrix, whereas in zincian-

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malachite $(Cu,Zn)_2(OH)_2CO_3$, Cu is atomically substituted by Zn in the typical malachite structure. Subsequent calcination leads to the formation of small CuO crystallites believed to be the ideal intermediates for obtaining the final reduced catalyst. In addition, dissolution of small amounts of Cu^{2+} ions in the ZnO framework has been suggested to contribute to the high degree of copper dispersion [6]. The addition of M^{3+} ions (e.g., Al^{3+}) has been reported to increase the BET surface area and copper dispersion while inhibiting the sintering of Cu particles under on-stream conditions [7,8]. The nature and arrangement of carbonate residues in the calcined ternary $Cu/ZnO/Al_2O_3$ catalyst structure and their contribution to catalyst performance has not been studied in detail to date.

Schlögl et al. [9] investigated another possible function of the ZnO in the catalyst (or rather in the hydroxy carbonate precursor). They found that for Cu/ZnO catalysts derived from hydroxy carbonates (the industrial catalyst synthetic route), the copper lattice is strained compared with bulk copper, and that this strain correlates with high methanol synthesis activity [9]. Therefore, strained copper particles, brought about by the close interaction with the ZnO, may have a greater intrinsic activity for methanol synthesis than bulk-structured copper.

As mentioned above, the classical hydroxy carbonate route leads to the formation of several mixed-metal hydroxy carbonates, including aurichalcite $[(Cu,Zn)_5(CO_3)_2(OH)_6]$, zincian-malachite $[(Cu,Zn)_2(OH)_2CO_3]$, and a Cu–Zn hydrotalcite-like phase $[(Cu,Zn)_6Al_2(OH)_{16}CO_3\cdot 4H_2O]$. All of these phases decompose to give well-dispersed oxidic phases [10,11]. It is known from studies on Cu/ZnO hydroxy carbonate systems that the presence of residual carbonate in the calcined sample plays an important role, supposedly due to subsequent formation of a copper suboxide species, increasing the chemical activity of catalysts [12]. One motivation for the ongoing research into the chemical and structural nature of these precursors is the presumed conjunction with the activity of the final catalyst. The final catalyst is created in a multistep procedure, with each preparation step contributing separately to the catalyst properties. So far, few comparative studies on the effects of various synthesis procedures on the catalyst activity exist. These studies often lack detailed information on reaction parameters and reveal contradictory findings [8,13,14]. Most studies of coprecipitated systems have dealt with the zinc–copper catalyst, assuming that effective investigation of the industrial catalyst system can be done successfully only with a firm knowledge of the binary system.

Over the past 10 years, high-throughput experimentation (HTE) has proven to be a reliable technology for the evaluation and development of solid catalysts [15–17]. Methanol synthesis is an interesting example reaction for applying high-throughput techniques, because it is a very time-consuming reaction due to the need for high-pressure conditions for satisfactorily high conversions and the carefully conducted catalyst activation and reduction processes. Taking into account the industrial reduction and reactor startup period, even superficial catalyst testing by conventional means may take several days. Our HTE parallel reaction setup allows us to operate as closely as possible to single-channel conventional catalyst testing while saving time through an initial *collective* catalyst pretreatment [18]. The conditions applied during the activation and reaction periods are very close to the industrial standard.

The objective of the present study was to systematically investigate the synthesis/structure/activity relationships of the ternary Cu/Zn/Al methanol synthesis catalyst at different steps in catalyst preparation by high-throughput methods. The main focus is the study of different preparation parameters during the precursor formation process and their influence on methanol productivity. Numerous catalysts were tested for their methanol synthesis activity by high-throughput screening, and interesting samples were analyzed in more-detailed studies. In particular, selected catalysts and precursor materials were investigated with regard to phase and morphology changes induced by aging effects and calcination procedures.

2. Experimental

2.1. Catalyst preparation

Ternary $CuO/ZnO/Al_2O_3$ catalysts were prepared by coprecipitation analogous to the coprecipitation procedure described by Kiener et al. [18]. A solution of metal nitrates $[(Cu(NO_3)_2$ (0.6 mol/L), $Zn(NO_3)_2$ (0.3 mol/L), $Al(NO_3)_3$ (0.1 mol/L))] and a solution of Na_2CO_3 (1 mol/L) as a precipitant were pumped (at constant flow rate of 5 ml/min) into a stirred and heated glass reactor with a starting volume of 200 ml of demineralized water. During the precipitation process, pH, temperature and aging time were controlled. While the metal nitrate solution was being pumped continuously, the sodium carbonate solution was added to maintain a constant pH (±0.1 unit), controlled by a WTW 296 pH meter. The coprecipitation was stopped when 40 mL of metal nitrate solution had been added. The pH was kept constant also during the aging process through the controlled addition of metal nitrate or sodium carbonate solution except in the studies of the aging process, where some batches were aged without pH control ("free aging"). After aging for 1 h, the precipitates were filtered and washed three times with 150 mL of demineralized water each, and then dried overnight at 80 °C. After grinding, 200–500 mg of the dried hydroxy carbonate precursor was calcined at 300 °C under air for 3 h (heating ramp 2 °C/min), resulting in the oxide precursor.

2.2. Characterization

Transmission electron microscopy (TEM) was done with a Hitachi HF 2000 operated at 200 kV, equipped with a cold-field emission gun at a beam energy of 200 kV and NORAN Instruments Si (Li) EDX spectrometer for point resolved elemental analysis. Solid samples were dry-prepared on lacey carbon-coated nickel grids.

The metal contents of the precursors and catalysts were determined by energy-dispersive X-ray (EDX) analysis, performed on a Hitachi S-3500N scanning electron microscope equipped with an Oxford EDX system.

X-ray diffraction (XRD) measurements were performed on a STOE STADI P transmission X-ray powder diffractometer equipped with a linear position sensitive detector using $CuK\alpha_1$ radiation. XRD patterns were recorded in the range of 5–80° (2θ).

Temperature-programmed reduction (TPR) was performed in a special flow reactor, using a gas mixture of 5 vol% H_2 in nitrogen at a flow of 90 ml/min. The reactor was heated up to 300 °C at a ramp rate of 6 °C/min. Typically, 50 mg of catalyst powder was used as a sample. Before measurement, the sample was heated in nitrogen atmosphere to 120 °C (10 °C/min). To study the Cu amount of the catalysts, the time-resolved H_2 consumption peak was integrated. For determination of copper content via this method, reduction from CuO to Cu was assumed.

Nitrogen adsorption was done using a NOVA Quantachrome 3200e Multi-Station High-Speed Gas Sorption Analyzer, version 7.30. Before analysis, samples were activated under vacuum at 150 °C for 2 h. Isotherms were recorded at 77.3 K. N_2-physisorption was used to characterize the surface area. The BET surface area was calculated from the adsorption data in the relative pressure interval from 0.04 to 0.2.