New synthetic routes to more active Cu/ZnO catalysts used for methanol synthesis

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New preparation routes are applied to synthesize novel Cu/ZnO catalysts exhibiting high catalytic activity in methanol synthesis. In particular, the deposition–precipitation of copper onto high specific surface area (SSA) zinc oxide particles and the chemical vapor deposition of diethyl zinc turned out to be effective techniques, leading to promising methanol synthesis catalysts due to the enlargement of the Cu-ZnO interface.

KEY WORDS: Cu-based catalysts; methanol synthesis; coprecipitation; deposition–precipitation; chemical vapor deposition (CVD); area-activity relationship; Cu-ZnO interface.

1. Introduction

The synthesis of methanol from $CO_2/CO/H_2$ using Cu/ZnO-based catalysts is an important industrial process [1]. Although extensive research has been carried out applying classical methods to supported Cu catalysts as well as surface science techniques to Cu-model catalysts, the debate is still continuing concerning the role of ZnO and the nature of the active sites [2]. Commercially applied ternary $Cu/ZnO/Al_2O_3$ catalysts are prepared in large quantities by coprecipitation. Technical advances toward a more precise control of the precipitation process were achieved by the application of the flow cavitation reactor technology [3] and by the use of micromixers [4]. More advanced approaches to generate nanocrystalline oxides from solutions employ the controlled hydrolysis of metal alkoxides or halides. Particles obtained from such preparation techniques have fully hydroxylated surfaces unless extreme heat treatment or chemical dehydroxylation reactions are applied. It is known that residual hydroxyl groups influence the material properties significantly. Obviously, there is a need for other preparation techniques than the classical ones to extract more detailed information on the synergy between Cu and ZnO.

In this work, we describe two novel preparation routes for Cu-based catalysts employed in methanol synthesis. The synthesis routes were inspired by two recent experimental studies. Günter *et al.* [5] observed a positive correlation of the catalytic activity expressed as methanol turnover frequency (TOF) with the microstrain of the Cu particles detected by X-ray powder diffraction (XRD). Thus, we attempted to maximize the Cu–ZnO interface by using size-defined ZnO nanocrystals formed by a nonhydrolytic route followed by deposition–precipitation of Cu, resulting in a highly active binary Cu/ZnO catalyst. Fujitani and Nakamura [6] were able to promote a Cu(111) single-crystal surface efficiently by depositing Zn. They identified a Cu–Zn surface alloy as the catalytically active site on this model catalyst for methanol synthesis from CO [6]. Thus, in a second novel approach, a ternary catalyst was prepared from a coprecipitated reduced Cu/Al_2O_3 catalyst via the chemical vapor deposition (CVD) of diethyl zinc (Et_2Zn), resulting in a large increase in methanol TOF.

2. Experimental

Coprecipitation was applied to prepare reference Cu catalysts with different Cu content. Metal nitrates were used as precursors, and an aqueous solution of Na_2CO_3 was added as precipitation agent. Good reproducibility was attained by controlling the preparation conditions (purity of the chemicals, concentrations, temperature, stirring velocity, pH value, aging time, and washing treatment) carefully [7]. The calcination treatment was conducted in flowing air at 600 K for 3 h. The reduction was carried out in a catalytic test equipment [8] with a mixture of 2.1% H_2 in He raising the temperature from 300 to 513 K.

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The precursor $[Zn(OSiMe_3)_2]_n$ for the high specific surface area (SSA) ZnO is accessible by Brønsted acid/base reaction of triorganosilanols Me_3SiOH with the zinc base $ZnMe_2$ [9–13]. The thermolysis of the compound forms nanocrystalline ZnO as a sublimation product [14].

BET (Brunauer–Emmett–Teller) surface areas were obtained from isotherms measured in a Quantachrome Autosorb using N_2 as adsorbant at 77 K. X-ray powder patterns were recorded in a Bruker AXS D8 Advance diffractometer utilizing Cu $K\alpha$ radiation and a position sensitive detector (PSD). Catalytic activity was measured in a standardized test at ambient pressure and at temperatures of 473 and 493 K, respectively [15]. The inlet synthesis gas contained 14% He, 72% H_2, 4% CO_2, and 10% CO. A modified space velocity of 500 mL $(\mathrm{min}\, g_{cat})^{-1}$ (STP) was chosen. The Cu surface area was derived from frontal chromatography experiments with N_2O at 300 K in the same setup [16,17].

3. Results and discussion

As previously reported [14], a large BET surface area of 110 $m^2\,g^{-1}$ was obtained for the pure SSA ZnO. The value even increased to 153 $m^2\,g^{-1}$ when a lower pretreatment temperature of 573 K compared to 373 K was chosen. Methanol synthesis was carried out over the ZnO powder, indicating a structure sensitivity for this test reaction [18]. Copper was introduced by deposition–precipitation onto the SSA ZnO in order to achieve highly dispersed Cu particles in close contact with ZnO. First, the ZnO powder was slurried in water. Then, the aqueous solution of $Cu(NO_3)_2$ was added dropwise followed by the precipitating solution of Na_2CO_3 at a constant pH value of 7. Subsequently, the filtered and washed sample was calcined and reduced. Figure 1 shows the *ex situ* XRD pattern of the resulting Cu/ZnO catalyst after carrying out methanol synthesis. In addition to the broad ZnO (□) reflections, the reflections of metallic Cu (○) can be detected as minority phase.

The second synthesis route for obtaining a pair of ZnO-free and ZnO-containing Cu/Al_2O_3 catalysts is based on a combination of coprecipitation and CVD. A Cu/Al_2O_3 catalyst was prepared by standard coprecipitation, reduced in flowing H_2, and characterized with respect to Cu surface area and catalytic activity. Then, 600 mg of the passivated Cu/Al_2O_3 sample were removed from the reactor under Ar in a glove box. This sample and 0.2 g of Et_2Zn were filled into separate test tubes and placed in a Schlenk tube inside a dry box. The catalyst was treated with Et_2Zn vapor for 2 h at room temperature under static vacuum (10^{-2} mbar). Figure 2 shows the XRD pattern of the $Cu/ZnO/Al_2O_3$ catalyst after reaction. It consists exclusively of the XRD reflections of metallic Cu, i.e., both the Al_2O_3 and the ZnO components are X-ray amorphous.

Figure 3 displays the methanol production rate as a function of the specific Cu surface area for the catalysts synthesized via the novel preparation routes (Cu/ZnO (●), Cu/Al_2O_3 (★), and $Cu/ZnO/Al_2O_3$ (★)). Various coprecipitated binary (■) and ternary (▲) Cu catalysts are included for direct comparison regarding catalytic activity. A linear relationship between the methanol synthesis activity and the specific Cu surface area is found in our study. Nevertheless, deviations from the linear correlation are observed within the class of binary and ternary Cu catalysts. Ternary Cu catalysts are more active than the binary catalysts with the same Cu surface area. In addition, the catalysts prepared by the novel synthesis routes show significant differences in their catalytic behavior. The Cu/ZnO catalyst obtained from deposition–precipitation displays a catalytic activity, which clearly exceeds that of conventionally prepared binary catalysts with the same Cu surface area. Despite a loss in Cu metal surface area, adding Zn to the Cu/Al_2O_3 catalyst resulted in a large increase in catalytic activity beyond the expected value based on the linear correlation curve for the ternary catalysts.

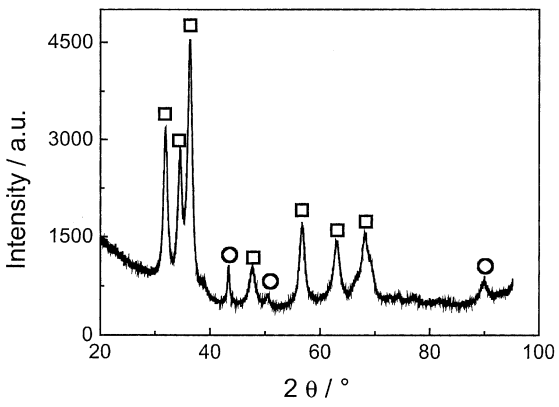

Figure 1. XRD pattern of Cu/ZnO after reaction. (□) and (○) represent the reflections of ZnO and of metallic Cu respectively.

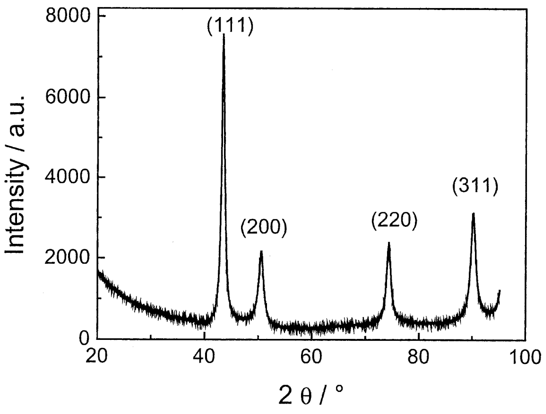

Figure 2. XRD pattern of $Cu/ZnO/Al_2O_3$ after reaction.

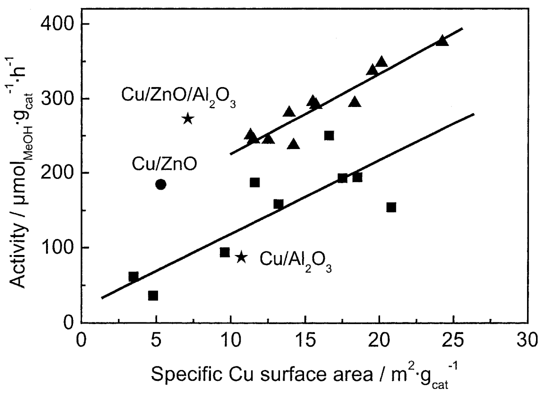

Figure 3. Area–activity relationship for various Cu-based catalysts. Binary (■) and ternary (▲) catalysts synthesized by coprecipitation; Cu/ZnO (●) by deposition–precipitation; Cu/Al_2O_3 (★) by coprecipitation; $Cu/ZnO/Al_2O_3$ (★) by coprecipitation + CVD.

It is generally accepted that Cu is present in the catalyst in the metallic state during methanol synthesis reaction conditions, and that the critical reaction steps take place on the Cu metal surfaces with methanol being formed predominantly from adsorbed CO_2. On the other hand, there are no doubts about the importance of ZnO for these catalysts to achieve high activity, but the origin of this synergy is still unclear. Recent theoretical results suggest that Zn and/or ZnO species may be present in the vicinity of the active Cu sites [19]. The observed deviations in the area–activity relationship clearly demonstrate that in addition to the Cu surface area other factors influence the catalytic activity under the highly reducing conditions of methanol synthesis. These related phenomena are assumed to be the induced microstructural strain [5] and the presence of promoting Zn + O adspecies on the metallic Cu surface ($CuZnO_x$ sites) [19–21]. Alternating pretreatment of a coprecipitated ternary catalyst with CO and methanol synthesis gas (CO_2, CO, H_2) demonstrated the reversibility of the structural changes under reaction conditions [20]. These phenomena are attributed in accordance with the results of the Topsøe group [22,23] to a change of the morphology of the metallic Cu particles and to strong metal–support interactions (SMSI), leading to highly active $CuZnO_x$ sites when severe reducing conditions are applied [20]. Furthermore, steady state kinetic measurements revealed that the methanol synthesis activity strongly depends on the number of $CuZnO_x$ sites induced by the pretreatment gas applied [20]; the higher the reduction potential in the pretreatment, the more active the catalyst. Thus, the SMSI state of the $Cu/ZnO/Al_2O_3$ catalyst caused by the strongly reducing methanol synthesis reaction conditions is correlated with high catalytic activity. Obviously, the CVD synthetic route in our current study enhances the synergy between Cu and ZnO, leading to catalysts with an unprecedented methanol TOF.

4. Concluding remarks

The results of the present work show that novel preparation routes such as the combination of coprecipitation and chemical vapor deposition have indeed the potential to achieve highly active Cu-based catalysts in methanol synthesis. Moreover, the adding of Zn to a coprecipitated Cu/Al_2O_3 sample and the deposition–precipitation onto zinc oxide with a high specific surface area clearly underlines the importance of metal-substrate interactions, leading to highly active $CuZnO_x$ species under industrially relevant reaction conditions. Moreover, the preparation conditions can be further improved, leading to catalysts with a high total Cu surface area and optimized Cu–ZnO interface. A detailed characterization study is still missing, which is the subject of an ongoing study in the research groups within the scope of our Collaborative Research Center (SFB 558) [24].

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References

[1] M.V. Twigg, *Catalyst Handbook* (Wolfe, 1989).
[2] J.B. Hansen, in *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knözinger and J. Weitkamp (eds), Vol. 4 (VCH Verlagsgesellschaft, Weinheim, 1997) p. 1856.
[3] J. Find and W.R. Moser, J. Mater. Sci. 38 (2003) 1917.
[4] M. Schur, B. Bems, A. Dassenoy, I. Kassatkine, J. Urban, H. Wilmer, O. Hinrichsen, M. Muhler and R. Schlögl, Angew. Chem. Int. Ed. 42 (2003) 3815; Angew. Chem. 115 (2003) 3945.
[5] M.M. Günter, T. Ressler, B. Bems, C. Büscher, T. Genger, O. Hinrichsen, M. Muhler and R. Schlögl, Catal. Lett. 71 (2001) 37.
[6] T. Fujitani and J. Nakamura, Appl. Catal. A: General 191 (2000) 111.
[7] B. Bems, M. Schur, A. Dassenoy, H. Junkes, D. Herein and R. Schlögl, Chem.—Eur. J. 9 (2003) 2039.
[8] T. Genger, O. Hinrichsen and M. Muhler, Catal. Lett. 59 (1999) 137.
[9] F. Schindler, H. Schmidbaur and U. Krüger, Angew. Chem. 77 (1965) 865.
[10] F. Schindler and H. Schmidbaur, Angew. Chem. 79 (1967) 697.
[11] M. Driess, K. Merz and S. Rell, Eur. J. Inorg. Chem. (2000) 2517.
[12] R. Schoenen, K. Merz, S. Rell and M. Driess, J. Phys. IV France 11 (2001) Pr3-547.
[13] K. Merz, R. Schoenen and M. Driess, J. Phys. IV France 11 (2001) Pr3-467.
[14] J. Hambrock, S. Rabe, K. Merz, A. Birkner, A. Wohlfahrt, R.A. Fischer and M. Driess, J. Mater. Chem. 13 (2003) 1731.
[15] H. Bielawa, M. Kurtz, T. Genger and O. Hinrichsen, Ind. Eng. Chem. Res. 40 (2001) 2793.
[16] G.C. Chinchen, C.M. Hay, H.D. Vanderwell and K.C. Waugh, J. Catal. 103 (1987) 79.

[17] O. Hinrichsen, T. Genger and M. Muhler, Chem. Eng. Technol. 11 (2000) 956.

[18] H. Wilmer, M. Kurtz, K.V. Klementiev, O.P. Tkachenko, W. Grünert, O. Hinrichsen, A. Birkner, S. Rabe, K. Merz, M. Driess, C. Wöll and M. Muhler, PCCP 5 (2003) 4736.

[19] J. Greeley, A.A. Gokhale, J. Kreuser, J.A. Dumesic, H. Topsøe, N.-Y. Topsøe and M. Mavrikakis, J. Catal. 213 (2003) 63.

[20] H. Wilmer and O. Hinrichsen, Catal. Lett. 82 (2002) 117.

[21] J.B. Wagner, P.L. Hansen, A.M. Molenbroek, H. Topsøe, B.S. Clausen and S. Helveg, J. Phys. Chem. B 107 (2003) 7753.

[22] J.-D. Grunwaldt, A.M. Molenbroek, N.-Y. Topsøe, H. Topsøe and B.S. Clausen, J. Catal. 194 (2000) 452.

[23] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen and H. Topsøe, Science 295 (2002) 2053.

[24] http://www.sfb558.de.