Cu/ZnO Catalyst Preparation via Formate Precursors

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Poster Introduction

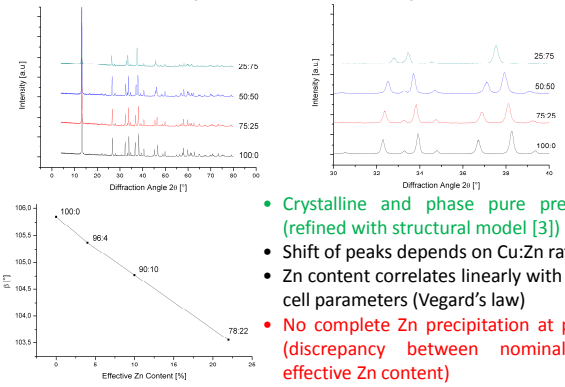
Cu/ZnO/(Al_2O_3) catalysts are of major industrial interest as they have been successfully applied in methanol synthesis for over 40 years. Highly productive catalysts exhibit a homogeneous microstructure and an optimal dispersion of the active copper phase. During synthesis of the catalyst, the relevant precursor phase is a mixed metal hydroxy *carbonate*, zincian malachite [1], which is typically co-precipitated from nitrate solutions. As an alternative approach, we synthesized metal hydroxy *formates* with different Cu:Zn ratios and used them as precursors for Cu/ZnO catalysts, the major advantage being a nitrate-free "green" catalyst synthesis. In this work we present precursor preparation and characterization as well as first catalytic results and discuss the potential of this novel preparation route for methanol synthesis catalysts.

Preparation

CuZn hydroxy formate precursors were synthesized from acidic Cu/Zn formate solution and Na_2CO_3 or NaOH solution as basic precipitating agent [2]. The precipitations were performed in an automated lab reactor (LabMax, Mettler Toledo) under controlled conditions: dosing (20 g/min), stirring (300 rpm), temperature (25–65 °C) and pH value (5.5–7.0). After aging (30 min) the slurry was filtrated, the precipitate washed with water and dried at 60 °C overnight.

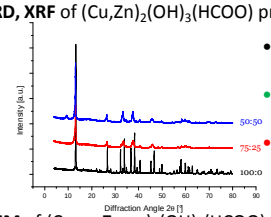
Precursor Characterization

XRD, XRF of $(Cu,Zn)_2(OH)_3(HCOO)$ precursor (Na_2CO_3, pH 5.5; T = 65 °C)



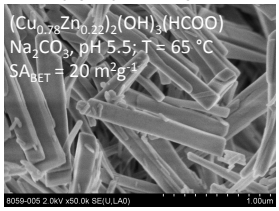
- Crystalline and phase pure precursor (refined with structural model [3])
- Shift of peaks depends on Cu:Zn ratio
- Zn content correlates linearly with lattice cell parameters (Vegard's law)
- No complete Zn precipitation at pH 5.5 (discrepancy between nominal and effective Zn content)

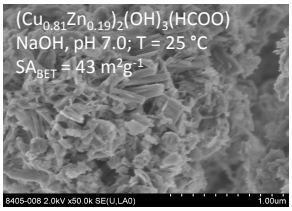
XRD, XRF of $(Cu,Zn)_2(OH)_3(HCOO)$ precursor (NaOH, pH 7.0; T = 25 °C)



- Crystallinity is low for Zn-containing precursor (small domain size)
- Nearly complete Zn precipitation at pH 7.0
- No more phase purity for nominal Zn content of 50 mol% (limit near 19 mol%)

SEM of $(Cu_{0.78}Zn_{0.22})_2(OH)_3(HCOO)$ precursor

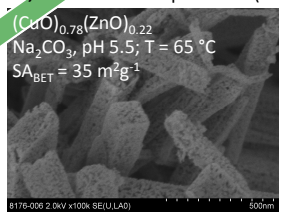


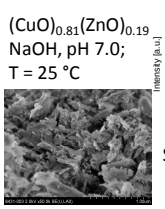


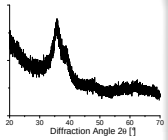
- Needle-like structure with quadrangular shape
- Homogeneous element distribution (not shown)

Calcined Sample Characterization

XRD, SEM of calcined precursor (200 °C, 3 h)



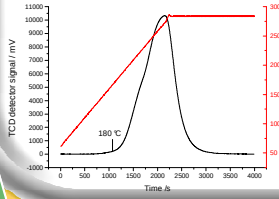




SA$_{BET}$ =83 m^{2}g^{-1}

- Calcination was performed at 200 °C in 100 % O_2 to avoid partial reduction of Cu(II) to Cu(I) (leading to large Cu_2O crystals and segregation)
- Broad peaks in XRD suggest small domain size of crystalline CuO (ZnO is amorphous)
- Nano-structuring leads to finely dispersed CuO and ZnO particles (homogeneous distribution in elemental mapping in SEM; not shown)

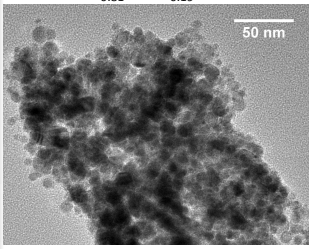
TPR of $(CuO)_{0.81}(ZnO)_{0.19}$ (NaOH, pH 7.0; T = 25 °C)



- One main peak indicates homogeneity of sample
- Small shoulder on the left characteristic for intermediate existence of Cu(I)
- Low onset temperature of 180 °C related to good reducibility

Reduced Sample Characterization

TEM of $(Cu)_{0.81}(ZnO)_{0.19}$ (NaOH, pH 7.0; T = 25 °C)



- Reduction was performed with 5 % H_2 in Ar up to 200 °C
- Nano-particulate microstructure
- Dispersion and homogeneity maintained after reduction (elemental mapping in TEM; not shown)
- Needle-like pseudo-morphology

Methanol synthesis **test (10 bar, 220 °C), N_2O-RFC** of $(CuO)_{0.81}(ZnO)_{0.19}$ (performed at Ruhr-University Bochum, group of M. Muhler)

Catalyst	Cu surface area [m²/g]	Activity [mmol/h*g$_{cat}$ MeOH]
$(Cu)_{0.81}(ZnO)_{0.19}$ (from formate route)	18 (55 %)	0.30 (66 %)
Conventionally prepared Catalyst	33 (100 %)	0.45 (100 %)

Summary

- Hydroxy formate precursor of the formula $(Cu,Zn)_2(OH)_3(HCOO)$
- Easy thermal decomposition generates nano-structured metal oxides
- Reduction preserves nano-particulate microstructure and homogeneous distribution of Cu and Zn
- Promising methanol synthesis activity of formate derived Cu/ZnO
- Formate route possibly competitive with conventional synthesis

References: [1] M. Behrens; *J. Catal.* *267* **(2009)**; 24-29
[2] S. Polier, M. Hieke, D. Hinze; *Patent* **(2006)** WO2006117190 A1
[3] Behrens et al. *in preparation*

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