



Preparation of Cu/ZnO/Al₂O₃ catalysts applying continuous precipitation



Stefan Kießner, Malte Behrens, Robert Schlögl
Fritz-Haber-Institute of the Max-Planck-Society,
Department of Inorganic Chemistry, Faradayweg 4-6, D - 14195 Berlin

Introduction - Methanol

Consumption: Methanol is one of the most important basic components in the chemical industry with an annually worldwide production volume of about 40 million tons. It is used in organic chemistry and also to obtain precursors for polymerization (Fig. 1). Aside a steadily increasing amount is applied as fuel additive due to its high energy content of 173,6 kcal/mol and good transport and storing properties. Furthermore, methanol is a promising candidate for chemical hydrogen storage and may play a key role in a future hydrogen economy leading to more independence from fossil sources.

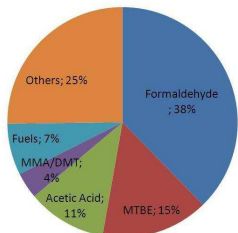


Fig. 1: Consumption of Methanol, 2007

Synthesis: In industrial scale methanol is produced from synthesis gas (H₂, CO, CO₂) in presence of Cu/ZnO/Al₂O₃ catalytic systems (Fig. 2). Modern plants produce more than 5000 tons every day. The mechanism of the synthesis has not been fully understood at present but it is reported that the activity of the catalyst depends on the Cu surface area and additional intrinsic effects which are determined by the parameters during catalysts preparation like composition, pH, T, c, etc.

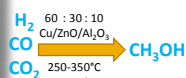


Fig. 2: Methanol synthesis

Catalysts: Preparation of Cu/ZnO/Al₂O₃ catalysts has been optimized in the last 40 years of industrial application and currently follows a multi-step synthesis route. Mixed metal hydroxy carbonate precursors are formed by controlled coprecipitation (e.g. pH 6.5, T = 65°C) from aqueous Cu/Zn/Al nitrate solutions and soda solution as precipitating agent. Subsequently the precipitate is aged in the mother liquor, filtrated, washed, dried, calcined to yield a dark powder (Fig. 3) and finally reduced.

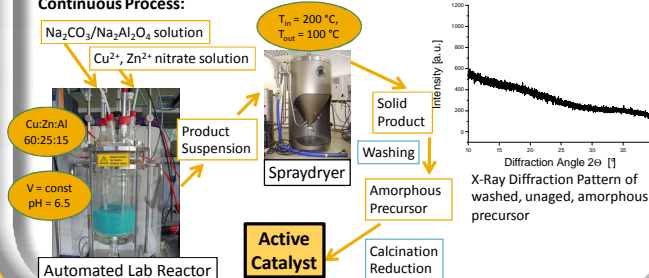


Fig. 3: CuO/ZnO/Al₂O₃

Experimental

	Modified Synthesis Route	Conventional
Metal solution	Acidic Cu,Zn nitrate solution	Acidic Cu,Zn,Al nitrate solution
Precipitation agent	Na ₂ CO ₃ / Na ₂ Al ₂ O ₄ solution	Na ₂ CO ₃ solution
Process Mode	Continuous	Batch
Aging	Aging suppressed by immediate spraydrying	Aging in slurry
Product	Amorphous	Crystalline

Continuous Process:



Results

Aim: To optimize parameters of the continuous precipitation, we modified the overall metal concentration and the temperature of the precipitation step with the aim of obtaining higher specific surface areas of the products while simultaneously maintaining the high intrinsic activity.

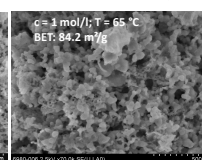
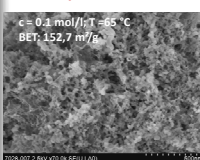
Table 1: BET surface area; T = const = 65 °C

Overall metal concentration	Precursor BET surface area
1.0 mol / l	84.2 m ² / g
0.3 mol / l	96.3 m ² / g
0.1 mol / l	152.7 m ² / g

Table 2: BET surface area; c_{Metal} = const = 1 mol/l

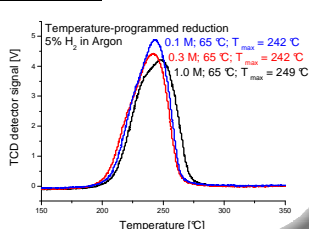
Temperature	Precursor BET surface area
65 °C	84.2 m ² / g
45 °C	52.5 m ² / g
25 °C	65.9 m ² / g

BET: Within the range of the investigated overall metal concentrations the BET surface area increased with decreasing concentration (Table 1). The dependance on the temperature revealed no obvious correlation (Table 2).



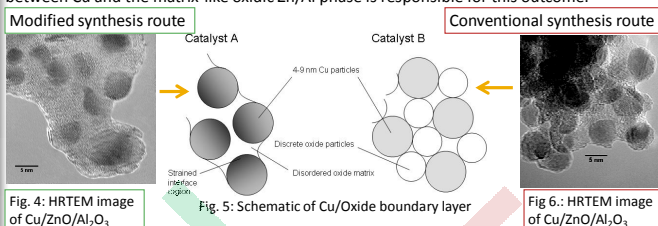
SEM: The comparison of two samples of the concentration series showed in both cases roundish particles and some platelets. The higher BET surface area corresponded with a smaller particle size.

TPR: The reduction curves of the calcined (330°C for 3 h) samples correspond to the reduction of CuO to metallic Cu. Similar reducibilities were found for all three samples of the concentration series suggesting comparable intrinsic properties of the Cu phases. Close inspection reveals slightly narrower and more symmetric profiles for CuO prepared from smaller precursor particles.



Catalyst Preparation – Effect of Modifications

In a previous work we could show the effect of some modifications during precursor preparation (see Experimental) which yielded very active catalysts with good homogeneity [1]. Probably the special microstructure (Fig. 4, 5) with its intensive boundary layer contact between Cu and the matrix-like oxidic Zn/Al phase is responsible for this outcome.



The Cu surface area of catalyst A (modified synthesis route) was smaller than that of catalyst B (Fig. 7). Nevertheless, the higher intrinsic activity (activity related to the Cu surface area) compensated this drawback and even led to higher productivity. Because of the similarity of elemental composition and Cu particle size and shape in both samples, this differences can be related to the microstructure of the oxide phase.

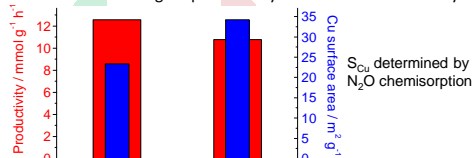


Fig. 7: Comparison of Productivity and Cu surface area

[1] M. Behrens, A. Furche, I. Kasatkin, A. Trunschke, W. Busser, M. Muhler, B. Knierp, R. Fischer, R. Schlögl, in preparation

Conclusions: continuous precipitation technique can lead to precursors with high surface areas

- BET:** → correlation between surface area and metal concentration
- no obvious correlation between surface area and precipitation temperature
- SEM:** → surface area corresponds with particle size
- TPR:** → similar reducibilities indicate similar intrinsic properties of the Cu phase