**Developing industrial Methanol catalysts: Using lab-scale understanding to optimize a well-known process**

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**Introduction**

In industry a ternary Cu/ZnO/Al2O3 catalyst is used for the large-scale production of methanol. The synthesis of the catalyst is carried out in the following steps along the process chain: precipitation of metal salts using sodium carbonate, aging in a stirred vessel, washing, drying, calcination and subsequent pelletizing [1]. For this seemingly simple process, large gains in catalyst performance are achievable by optimizing preparation conditions, which has been demonstrated on small scales.[2] For an optimal industrial catalyst production process additional knowledge on all scales is needed in order to generate an high performance material. This contribution tries to illustrate the whole work-flow from models of precipitation [3], advanced characterization [4], kinetic/mechanistic considerations [5], high-throughput material screening towards simulation & optimization of catalyst application in industrial processes.

**Materials and Methods**

For the validation of theoretical modelling precipitation reaction is carried out in a T-mixer which offers well-defined mixing conditions in experiments and simulations [3]. Prepared samples are analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), inductively coupled plasma mass spectrometry (ICP) and x-ray powder diffraction (XRD) measurements. The used multi-component precipitation model takes the following model parts into regard population balance system, mixing, particle formation kinetics, hydrochemistry of metal salts, activity modelling and mass balances.

Catalytic screening measurements are taken out in a 16-fold powder μ-reactor high-throughput unit at 60 bar(g) synthesis gas, 235°C under industrially relevant conditions to measure MeOH yields. Selected materials are characterized using HR-TEM and advanced chemisorption measurements[4]. Subsequently full-particle (tablet) tests are carried out in a bench-scale reactor to determine selectivities and long-term stability under extreme conditions.

Kinetic measurements are taken out in a gradient-free internal-recycle reactor (Berty-type) at varying temperatures, pressures and gas compositions. Based on these measurements, parameters of a kinetic model [6] are estimated using a log-likelihood based optimizer in gProms. Considering mass and heat transfer processes the model is suitable to describe the performance of catalysts in the industrial methanol synthesis process.

**Results and Discussion**

In the first part of this contribution the development of a precipitation model based on a numerical population balance is illustrated. The acquired model shows a good agreement in modelling temporal evolutions of super-saturation and mean particle size for the seven-component system. pH obtained by the simulation can be compared to measured values in the experiments. From the results of the population balance the solid dry weight of the prepared catalyst can be estimated which is an important factor in scaling-up precipitations.

In the second part, advanced characterization techniques such as N2O reactive frontanal chromatography to determine active copper surface area are discussed. Together with HR-TEM investigations these serve as descriptors for optimizing catalyst textures by improved drying and calcination procedures. Also, powdered materials are evaluated in a high-throughput setup to evaluate catalytic performance.

The third part illustrates kinetic measurements of these catalysts to provide a model basis for simulation of industrial processes. Using quasi-stationary measurements taken in a Berty-reactor, a rigorous estimation of 10 parameters involving rate factors of MeOH synthesis and the rWGS, adsorption constants and respective activation energies based on a microkinetic model is carried out, which is able to predict catalyst performance with a high accuracy (cf. Fig 1). The acquired model is then used to simulate overall plant performance and identify catalyst parameters that would increase the overall performance under industrial conditions.

**Significance**

Most scientific publications are based on the experimental investigations of the Cu/ZnO-systems with a focus on material performance under lab scale conditions. This contribution tries to show, how a detailed understanding of individual steps in preparation and application of a catalyst are used together to yield an industrial, high performance methanol catalyst for different industrial reactor set-ups.

**References**


**Figure 1.**

a) Quasi-stationary determination of activity in a Berty-type internal recycle reactor.  
b) Parity plot of measured and calculated WTY based on the microkinetic model.