# Metal-support interactions in methanol synthesis catalysts

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**Abstract:** Metal support interactions between Cu and a series of common catalyst carriers were studied using surface titration techniques. The industrially used Cu/ZnO system were examined in greater detail by extending the titration measurements and combining these results with an environmental electron microscopy study, activity measurements, thermodynamic data and density functional theory calculations. The results demonstrate that metal support interactions can be studied by commonly used surface titration techniques. A quantitative model is presented for the metal support interactions in the Cu/ZnO system.

**Keywords:** Methanol catalysts, metal support interactions, Cu-Zn synergy.

## 1. Introduction

Cu based catalysts are of great global importance as they are commonly used in the processes of converting natural gas to ammonia (water gas shift reaction) and to methanol (conversion of synthesis gas into methanol), which are essential products for the agriculture and chemical industry. In 2016, close to 70 million tons of methanol was produced from synthesis gas over $Cu/ZnO/Al_2O_3$ catalysts worldwide. The production and importance of methanol is increasing, and methanol is considered to play an important role in realizing the vision of a new green economy[1]. Methanol can be produced from renewable resources such as organic waste or from $CO_2$ waste streams after addition of hydrogen produced by electrolysis. In the latter case, methanol could make use of excess electricity from wind mills or solar panels.

With the aim of improving methanol synthesis catalysts, metal support interactions between Cu and ZnO in industrial type catalysts were studied in detail using a combination of surface area titration, electron microscopy, activity measurements and density functional theory calculations[2-3]. These studies were accompanied with studies of the metal support interaction between Cu and a series of reducible and non-reducible carriers using surface area titration techniques[4].

## 2. Experimental

A fully automated fixed-bed flow setup was used to study a large series of catalysts by $H_2$-TPD, $N_2O$-RFC (reactive frontal chromatography) and *in situ* BET measurements, as previously described in detail by Kuld et al.[2,3]. The interaction of Cu and ZnO in industrial type methanol catalysts were both studied after treatment in hydrogen and reactive gases. $Cu/ZnO/Al_2O_3$ samples were also examined in a combined HPC (high pressure cell) and UHV (ultra-high vacuum) setup equipped with XPS (X-ray photoelectron spectroscopy)[3] to determine the chemical state of Cu and Zn after the gas treatments. Environmental transmission electron microscopy (ETEM) as well as density functional theory were also applied for the Cu/ZnO system.

## 3. Results and discussion

Cu-support interactions were studied by means of the $N_2O$-RFC and $H_2$-TPD methods. A reference correlation between $N_2O$ and $H_2$ titrations of pure unsupported Cu samples was established as an interaction-free baseline and surface stoichiometries for O:Cu ($N_2O$-RFC) and $H_2$:Cu ($H_2$-TPD) were determined by

comparison with independent BET measurements. A wide range of different support materials was investigated and compared to the interaction-free baseline[4]. In general, Cu on reducible oxides provide increased oxygen adsorption from $N_2O$ and decreased H adsorption, while Cu on irreducible oxides generally show a weakly reverse trend. These examples demonstrate that one can use $N_2O$-RFC and $H_2$-TPD measurements to get insight into the metal support interaction between Cu and various carriers.

A special focus was directed towards understanding how methanol synthesis over copper nanoparticles is boosted by zinc oxide in the industrial type methanol catalyst. It was shown that ZnO can reduce and form a Cu/Zn surface alloy in the presence of hydrogen and that the coverage of Zn ($\theta_{Zn}$) in the Cu surface increase with the $H_2$ partial pressure during pretreatment[2]. $\theta_{Zn}$ was measured directly by three independent techniques; X-ray photoelectron spectroscopy (XPS), $H_2$ temperature programmed desorption (TPD) and $N_2O$ reactive frontal chromatography (RFC). At steady state, $\theta_{Zn}$ is controlled by the methanol synthesis conditions (reduction potential of the synthesis gas) and $\theta_{Zn}$ was identified as a key descriptor for the activity[4].

Fig. 1A shows the steady state $\theta_{Zn}$ directly measured after treatments of an industrial type methanol catalyst in $CO/CO_2/H_2$(2%), $CO/CO_2$, $H_2O/H_2$ and in synthesis gas together with a theoretically predicted $\theta_{Zn}$ derived from thermodynamics and Density Functional Theory (DFT) calculations. The good correspondence between measured and modeled data indicates that the physical principles in the model are sufficient to describe the dynamic dependency of $\theta_{Zn}$ on the reduction potential of the methanol synthesis gas (represented by the $CO/CO_2$ ratio). Fig. 1B depicts that the methanol synthesis activity is strongly dependent on $\theta_{Zn}$ and illustrates that $\theta_{Zn}$ is a key parameter for understanding the activity of the industrial-type $Cu/ZnO/Al_2O_3$ methanol catalyst, where Zn-covered Cu sites most likely constitute the active site for methanol synthesis. The complete model provides a design basis for tuning the activity of the catalyst system[4]. Interestingly, we predict that catalysts prepared using small ZnO particles will promote the Zn/Cu alloy formation hence the intrinsic activity of the catalyst system.

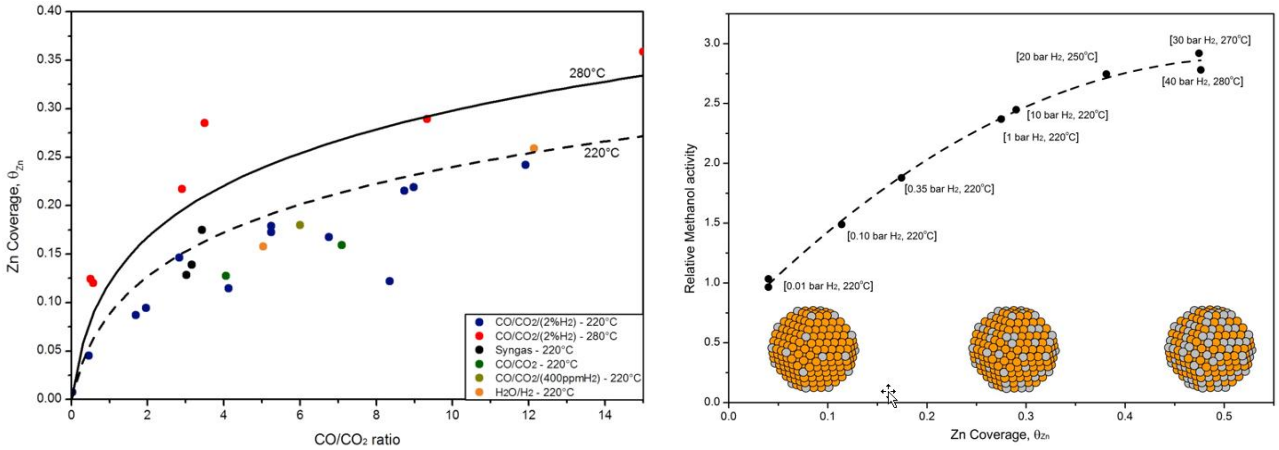


**Figure 1.** Description of graph A) steady state Zn coverages measured by $H_2$-TPD compared to those predicted theoretically at 220°C (dashed line) and 280°C (solid line) vs. the reduction potential of the synthesis gas B) Relative measured methanol exit concentrations as a function of the measured post-reaction values of $\theta_{Zn}$. The different initial values of $\theta_{Zn}$ are obtained by pretreatments in $H_2$ at different pressures. The dashed line is a fit to the data and a guide to the eye.

## 4. Conclusions

Metal support interactions between Cu and a series of common catalyst carriers were studied using surface area titration methods. A quantitative model predicting the effect on activity of metal support interactions in the Cu/ZnO system was developed based on theoretical and thermodynamic data. The analysis framework may advantageously be applied for other supported metal catalyst systems.

## References

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