

Counting of Oxygen Defects versus Metal Surface Sites in Methanol Synthesis Catalysts by Different Probe Molecules**

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Abstract: Different surface sites of solid catalysts are usually quantified by dedicated chemisorption techniques from the adsorption capacity of probe molecules, assuming they specifically react with unique sites. In case of methanol synthesis catalysts, the Cu surface area is one of the crucial parameters in catalyst design and was for over 25 years commonly determined using diluted N_2O . To disentangle the influence of the catalyst components, different model catalysts were prepared and characterized using N_2O , temperature programmed desorption of H_2 , and kinetic experiments. The presence of ZnO dramatically influences the N_2O measurements. This effect can be explained by the presence of oxygen defect sites that are generated at the Cu-ZnO interface and can be used to easily quantify the intensity of Cu-Zn interaction. N_2O in fact probes the Cu surface plus the oxygen vacancies, whereas the exposed Cu surface area can be accurately determined by H_2 .

Methanol counts among the most important basic chemicals and is an important C1 building block for industrial chemicals. It is commonly produced by hydrogenation of carbon monoxide or carbon dioxide. In the typically used low-pressure process over Cu/ZnO/Al₂O₃ catalysts pressures ranging from 50 to 100 bar and temperatures of 483 to 563 K are employed.^[1] As methanol is a platform molecule

and can in general be generated from sustainable hydrogen and CO₂ sources, it gathers rising attention as a renewable energy storage and carrier.^[2]

Even today, 50 years after the commercial introduction of the Cu/ZnO/Al₂O₃ system, the nature of the active site(s) of methanol synthesis is still under heavy investigation, and a vast number of techniques are employed to elaborate the reaction mechanism and active center of the methanol synthesis on copper.^[3–6] This lack of understanding can be partially contributed to the strong interaction of the different catalyst components. Especially the role of zinc oxide is still under debate. The well-known ZnO promotion of copper has been described by various mechanisms, such as alloy material and structural support or a hydrogen reservoir providing adsorbed hydrogen to copper by spill-over.^[7–10] Many promotional effects or the activity of pure ZnO in methanol synthesis have in some way been attributed to the reducibility of ZnO and the formation of oxygen vacancy sites, and it was shown that the presence of oxygen defects is also a crucial factor for the methanol synthesis activity of pure ZnO.^[5,11,12] In situ TEM and EXAFS studies have confirmed the formation of oxygen vacancy sites in ZnO depending on the reactive conditions over the catalyst. This behavior is specifically attributed to the Cu-ZnO interaction (SMSI effect), and the defect concentration is high enough to influence the copper particle morphology in model systems.^[13–16] Recently Schott et al. reported about the aplanar distortion of thin ZnO layers on copper, leading to a systematically less strongly oxidized Zn^{δ+}.^[17] In real catalysts, an amorphous overlayer of partially reduced ZnO_x influencing the adsorption properties of copper is found covering the copper particles after the activation procedure, and the resulting catalyst characteristics have been extensively studied.^[14,18] This can be seen as a precursor state to the partial formation of Cu-Zn surface alloys, which in fact might be the driving force for the strong interaction.

The complexity of the typical surface termination of Cu nanoparticles in common Cu/ZnO/Al₂O₃ catalysts as formed after reduction is shown in the high-resolution TEM image in Figure 1. At the surface, a disordered 1–2 nm thick termination layer indicates the overgrowth of the Cu particle with disordered ZnO_x owing to Cu-ZnO interaction under reducing conditions. It can be seen that the metal termination underneath this layer is very rough with many steps and missing atoms at the Cu-ZnO_x interface. These structural details suggest that the reactivity of such dynamic SMSI state in Cu/ZnO catalysts toward reactive probe molecules such as N₂O might be more complex than simple monolayer chemisorption observed at well-defined pure Cu facets.^[19]

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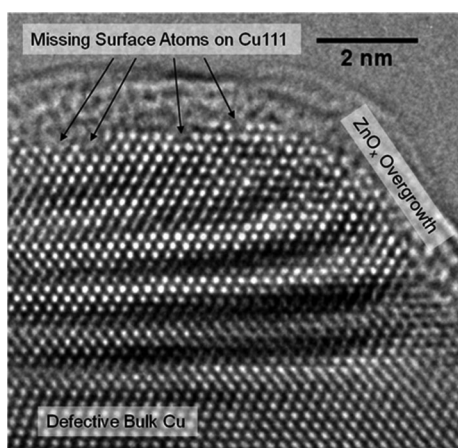


Figure 1. HRTEM image of the surface termination of the ZnO_x-overgrown Cu nanoparticles in the catalyst CMZ1. The contrast fluctuations seen in the bulk of the Cu particle are moiré fringes that arise owing to partial overlapping with other particles.

From a structural point of view, it is not easy to decide if under working conditions the extent of ZnO reduction in such arrangement exceeds the observed Zn^{δ+}O_x-covered Cu state and dynamically reaches a true surface alloy state. However, from a functional point of view, the difference of both models seems rather small as they have in common the existence of partially reduced and thus oxophilic Zn^{δ+} atoms in a close neighborhood to metallic Cu sites. These Zn^{δ+} sites are thought to act as adsorption sites for CO₂ and reaction intermediates such as formate, while the hydrogen is likely supplied from the metallic Cu sites. A similar bifunctional mechanism was also proposed for methanol synthesis on Cu/ZrO₂ catalysts with CO₂ being activated on the surface of the zirconia promoter.^[20] These CO₂ adsorption centers in Cu/ZrO₂ were modeled at the Cu-oxide interface, where in case of Cu/ZnO oxophilic Zn^{δ+} sites can be expected.^[21] It has been shown that the contact to Cu can promote the formation of oxygen vacancies in ZnO.^[22] Alternatively, functionally similar oxophilic Zn sites can be modeled by inserting metallic surface Zn atoms on Cu defect sites.^[5]

The existence of such oxophilic sites owing to ZnO reduction creates an inherent problem when looking at the “classic” characterization of methanol synthesis catalysts by reactive nitrous oxide frontal (N₂O-RFC) or pulse chromatography, which has been performed for over 25 years to quantify the copper surface area.^[23] Especially the assumption that N₂O specifically oxidizes the copper surface and ignores the partially reduced ZnO_x is questionable. This study investigates the influence of ZnO on the copper surface area measured by N₂O-RFC and hydrogen temperature-programmed desorption (H₂-TPD) on different Cu/ZnO/Al₂O₃, Cu/ZnO, Cu/MgO, and Cu/ZnO/MgO catalysts. It unravels the significant bias which is introduced by the oxidation of ZnO_x sites using H₂-TPD as a complementary characterization method, which provides a very selective, sensitive, and accurate way of describing the exposed copper surface area, that is, the copper surface area not covered by ZnO_x species.^[13]

To shed light on the interplay of exposed copper surface area, partially reduced zinc oxide and apparent N₂O-RFC area, different model catalysts are prepared and characterized (Supporting Information I). With the purpose to elucidate the influence of the reducible ZnO component, Al₂O₃ and MgO were also studied as alternative, irreducible structural promoters. Table 1 gives an overview of the systems employed and their composition and BET surface areas. To study the effect of ZnO, a ZnO-impregnation was applied to the Cu/MgO system using different synthetic procedures.

Table 1: Compositions and BET surface areas of the catalysts used.

Sample	C/X ^[a,b]	S _{BET} ^[c]	Sample	C:X ^[a,b]	S _{BET} ^[c]
C	100/–	15	CMZ1	79/16/5 ^[d]	94
CA1	20:80	100	CMZ2	79/16/5 ^[d]	90
CA2	87/13	70	CMZ3	67/29/4 ^[d]	121
CM1	83/17	100	CZA1	43/49/8	78
CM2	70/30 ^[d]	99	CZA2	58/26/16	74
ZA	–/84/16	78	CZA3	70/28/2	118

[a] Cu, Zn, Al, Mg = C, Z, A, M. [b] Molar, determined by ICP and XRF. [c] Calcined precursor, [m² g_{cat}^{–1}]. [d] Nominal composition.

After activation of the catalysts in a glass-lined single-pass fixed-bed reactor (Supporting Information II), multiple H₂-TPD spectra are gathered at heating ramps of 4, 6, and 10 K min^{–1} (Supporting Information III). Next, the N₂O copper surface area is determined using the same catalyst at 308 K, 1 bar pressure using N₂O (1%) in He (Supporting Information IV). A mean copper surface density of 1.47 × 10¹⁹ atoms per m² is used for converting the measured amount of copper into specific surface area. Activity measurements of the Zn-containing catalysts are performed after the H₂-TPD and N₂O-RFC measurements (Supporting Information II).

Correlating the hydrogen adsorption capacity and N₂-evolution during the N₂O-RFC, which should be proportional to the copper surface area according to both methods, reveals the heavy bias which is introduced by ZnO. This is shown in Figure 2.

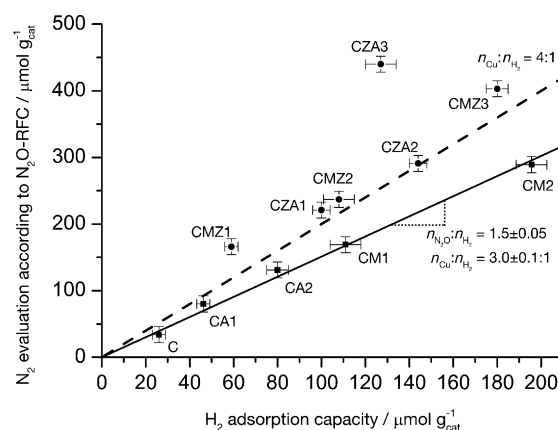


Figure 2. Correlation of the H₂-TPD and N₂O-RFC results.

The N_2O surface area of polycrystalline Cu agrees well with published data, and the H_2 -TPD area of the CA-systems matches with data published by Muhler et al. reasonably well.^[5,24] Assuming the formal oxidation of the exposed copper surface on Zn-free samples by N_2O to Cu_2O , the $\text{Cu}:\text{H}_2$ ratio can be determined using Equation (1) and the

$$\frac{\text{Cu}}{\text{H}_2} = 2 \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2}} \quad (1)$$

value of the decomposed N_2O per adsorbed H_2 . This ratio $n_{\text{N}_2\text{O}}:n_{\text{H}_2}$ is given by the slope of the solid line in Figure 2.

A $\text{Cu}:\text{H}_2$ ratio of $3.0 \pm 0.1:1$ is obtained for the Zn-free materials. This experimental value mismatches the classically assumed 4:1 ratio, which is commonly deduced from UHV studies and described with a 0.5 monolayer (ML) coverage of copper.^[25] However, the formation of a $\frac{2}{3}$ ML coverage, which corresponds with the measured $\text{Cu}:\text{H}_2$ ratio, has been observed at higher H_2 exposure and theoretically studied in detail.^[26–28] These findings are also in line with the formation of ordered $\frac{1}{3}$ ML and $\frac{2}{3}$ ML adsorption structures during dissociative hydrogen adsorption on other fcc-type metals.^[29]

The Cu/H_2 ratio is independent of the irreducible structural promoter and copper particle size. It also is in very good agreement with the BET surface area ($3.1 \text{ m}^2 \text{ g}_{\text{cat}}^{-1}$) of the activated sample C. The fact that even the low-surface area polycrystalline copper sample C matches well the H_2 - N_2O correlation underlines the high sensitivity and precision which is obtained using H_2 -TPD. The Zn-containing catalysts show a non-linear behavior where the majority roughly follow a Cu/H_2 ratio of 4:1 (dashed line in Figure 2). Generally, all Zn-containing systems yield a significant higher N_2O -copper surface area than would be expected from the corresponding H_2 -TPD experiments. According to the concept of reduced ZnO_x on top of the particles, this can be explained by the overconsumption of N_2O by oxidizing partially reduced ZnO_x . Furthermore, the ZnO_x layer is not necessarily of a monolayer type, and de-wetting of previously covered copper upon oxidation of ZnO_x has to be considered.

In the case of H_2 -TPD measurements, it is reasonable to say that hydrogen desorption from ZnO_x species is not observed within the experimental window that is supported by the impregnation experiments (see below). In general, the position of the H_2 -TPD signal is sensitive to the adsorption enthalpy, and in case of the examined copper catalysts is well aligned with the desorption signal of metallic copper. The difference in measured N_2O surface area and corresponding theoretical N_2O surface area according to the H_2 -TPD quantifies the amount of over-oxidation and thus oxophilic $\text{Zn}^{\delta+}$ sites in ZnO_x .

Although the ZA sample exhibits a comparable BET surface area, the H_2 -TPD and N_2O -RFC measurements do not show any significant signals in the specified experimental window after activation. This supports the assumption that the high amount of measurable defect sites stems from the copper zinc interaction and is not introduced by the sheer presence of ZnO. The extent of this interaction will be promoted by an initially high interdispersion of both phases, which is a function of the catalyst preparation. Thus, a strict

linear behavior in case of the Zn-containing catalysts is not expected a priori.

Recently Behrens et al. presented a systematic study about the homogeneous incorporation of the different metals in the methanol synthesis catalysts and presented a highly active system with an optimized incorporation of Al^{3+} in the ZnO phase, leading to a strong defect structure in ZnO_x .^[30] The sample CZA3 prepared analogously to this publication confirms this behavior well, as the determined defect concentration is more than 100% higher than in the other conventional CZA and CMZ systems. Furthermore, the impregnation experiments of the CM samples support these findings. Normally a drop in metal surface area of the activated impregnated samples should be expected, as a ZnO_x overlayer is formed over the copper particles blocking them from chemisorption.^[10] In case of the presented CMZ samples this is only true for the H_2 -TPD measurements, whereas the N_2O -surface area even increases in comparison with the corresponding CM precursors. The results highlight the critical role of catalyst synthesis for the intensity of Cu-Zn interaction. The ZnO -impregnation of the calcined pre-catalyst ($\text{CM1} \rightarrow \text{CMZ1}$) leads to heavy blocking of half of the Cu surface area detected by the decrease in H_2 capacity and only a low degree of Cu-Zn interaction indicated by the little increase in N_2O capacity. In contrast, if impregnation is done already on the co-precipitated catalyst precursor ($\text{CM1} \rightarrow \text{CMZ2}$ and $\text{CM2} \rightarrow \text{CMZ3}$), a much lower loss in Cu surface area and a substantial increase in N_2O capacity indicative for an intimate Cu-Zn interaction is observed.

The microstructure of the CZA catalysts was additionally characterized by TEM. As observed previously, the Cu particle shape can be described by a pseudosphere with an oxide matrix that spatially separates the individual nanoparticles. Based on a statistical Cu particle size evaluation, a theoretical maximal exposed Cu surface area can be calculated assuming that the particles were round and completely unsupported (Table 2). This value exceeds the

Table 2: Specific copper surface areas (SSA) and defect concentrations in SSA equivalents.

Sample	max. $\text{SSA}_{\text{TEM}}^{\text{[a]}}$	$\text{SSA}_{\text{H}_2\text{-TPD}}^{\text{[b]}}$	$\text{SSA}_{\text{N}_2\text{O-RFC}}^{\text{[b]}}$	O defects ^[b]
CZA1	21.7	12.3	18.1	5.8
CZA2	27.9	17.7	23.8	6.1
CZA3	49.3	15.6	36.1	20.5
CMZ1	n.d.	7.1	13.6	6.5
CMZ2	n.d.	12.9	19.4	6.5
CMZ3	n.d.	22.1	33.0	10.9

[a] Determined as described in the Supporting Information (n.d. = not determined). [b] Mass based on calcined precursor, $[\text{m}^2 \text{ g}_{\text{cat}}^{-1}]$.

probe gas derived surface areas in all cases, which is reasonable considering that a fraction of this hypothetical surface area must be present as interface to the stabilizing oxide matrix. A microstructural model of the catalyst in relation to the probe gas chemisorption capacities including the insensitivity of hydrogen toward Cu-ZnO interaction is discussed in the Supporting Information.

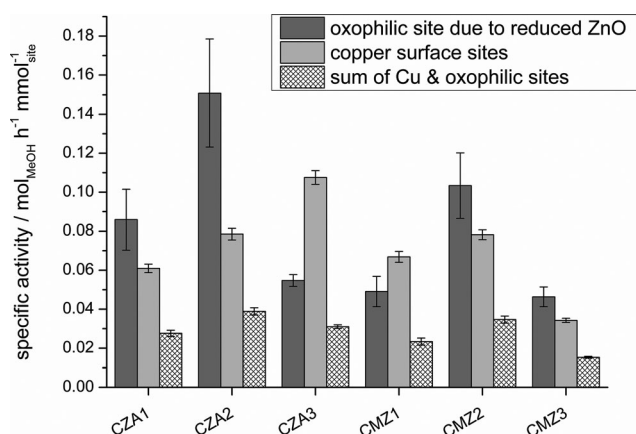


Figure 3. Specific activity of the different catalysts depending on the site type.

The specific activity evaluation of the Zn-promoted catalysts in Figure 3 reveals that there is neither a direct correlation between the H_2 - or N_2O -copper surface area and the catalyst activity nor between the catalyst activity and amount of oxophilic sites generated by ZnO. The latter one is estimated from the difference of the N_2O -RFC surface area and real copper surface which is calculated using the H_2 -TPD data (see Supporting Information IV). According to the data, without optimization of the irreducible structural support (CZA3) this amount is almost constant independent of the preparation technique and Zn content. This implies again the Cu-Zn interaction as origin. Table 2 gives an overview of the determined specific surface areas.

The missing direct correlation between surface area and activity is not surprising and has been reported before, as the active site of the methanol synthesis is not considered to be metallic copper or the vacancy sites themselves, but a combination of multiple factors.^[5,10,31] Interestingly, with exception of CMZ3, there is a relationship between the N_2O -RFC surface area and the activity data, which suggests that the N_2O -RFC (despite the conceptual problem) can be used to characterize and evaluate many methanol synthesis catalysts. This trend has been reported often, but was often misinterpreted as linear relationship between Cu surface area and activity to conclude structure-insensitivity of methanol synthesis on Cu/ZnO-based catalysts. In case of the highly active catalyst CZA3, it was shown that oxygen vacancies can in fact account for more than 50% of the N_2O -RFC capacity. This result shows that recent progress in catalyst development is not necessarily related to further increase in Cu surface area, but that great potential lies in the design of the Cu-Zn interaction. It furthermore strongly suggests that N_2O -derived surface areas should not be used to calculate TOFs of Cu/ZnO-based catalysts. While the N_2O capacity is an intrinsic and catalytically important property, it does not (only) represent the amount of metal surface sites, which can be better quantified by H_2 chemisorption.

In summary, we are able to show that the presence of ZnO introduces a heavy bias in the determination of copper surface area using N_2O -RFC whereas both the N_2O -RFC and H_2 -TPD characterization methods lead to well-matching results

in absence of ZnO. Based on these measurements and recent findings about the nature of the Cu-ZnO interaction, we propose that a method established over 25 years for the characterization of the surface area of methanol synthesis catalysts does in fact not only describe the copper surface area, but also the oxygen defects which are present at the copper zinc interface. Although, the N_2O -RFC has often proved to be characteristic for the description of activity-structure relationships, it draws a misleading picture in terms of functional relationships in the catalysts and might lead to false assumptions for the mechanistic description and understanding. We are able to show that quantitative measurement of ZnO_x oxygen vacancies in methanol synthesis catalysts is possible by combining H_2 -TPD and N_2O -RFC measurements. As both measurements can easily be done in situ in a fixed-bed reactor setup, this greatly enhances the possibility of systematic studies on methanol synthesis catalysts. With little adaption, these measurements can be extended to other important catalytic systems with a pronounced SMSI effect like many Group 8–10 metals supported on reducible transition metal oxides.

Experimental Section

The catalysts C, CA1-2, CZA1-3, ZA, CM1-2, and CMZ1-3 were produced by co-precipitation following literature recipes (see the Supporting Information I). The catalyst activity and the copper surface area according to H_2 -TPD and nitrous oxide reactive frontal chromatography (N_2O -RFC) are determined in a glass-lined single-pass fixed-bed reactor described in the Supporting Information II. A detailed description of the procedures for the activity tests, N_2O -RFC and H_2 -TPD measurements is given in the Supporting Information II, III, and IV.

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