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

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Supporting Information

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I) Catalyst preparation and characterization

The catalysts C, CA2, ZA, CZA1 and CZA2 are produced by coprecipitation of the metal nitrates at a constant pH of 7 and temperature of 333 K following the recipe presented in ref. [1]. CZA3 is a reproduction of the catalyst described in previous work and detailed characterization data can be found therein and in a forthcoming publication.\textsuperscript{[2,3]} The synthesis procedure is also based on co-precipitation using the concept of the industrial catalyst, which has been recently reviewed in detail elsewhere.\textsuperscript{[1,3]} In brief, aqueous nitrate solutions of the metals in a Cu:Zn = 70:30 ratio with additional 3 mol% of Al were co-precipitated at a constant pH of 6.5 using sodium carbonate as precipitating agent. The co-precipitate was aged in the mother liquor at 338 K to crystallize a substituted malachite precursor phase, \( \text{(Cu,Zn)}_2\text{(OH)}_2\text{CO}_3 \) (M = Zn). The precursor was calcined in air at 603 K to yield a CuO/ZnO:Al pre-catalyst with an intimate mixture of the oxides.

The Cu/MgO catalysts labeled CM were produced accordingly, but at a constant pH of 9 to completely precipitate the Mg\textsuperscript{2+} ions. The Cu-to-Mg ratio was 80:20 (CM1) or 70:30 (CM2), allowing co-precipitation of a phase-pure Mg-substituted malachite precursor, \( \text{(CuMg)}\text{(OH)}_2\text{CO}_3 \), and subsequent transformation into a uniform material upon calcination and reduction. The follow-up impregnation of the CM catalysts with Zn-citrate to yield CMZ catalyst with a ZnO loading of 5 wt.% was done either on the malachite-like precursors of CM1 and CM2 (CMZ2 and CMZ3) or on the calcined CuO/MgO pre-catalyst of CM1 (CMZ1). In the latter case the catalyst was recalcined at 563 K. The resulting nominal molar ratios of the catalysts are given in Table S1. The catalysts CM1 and CMZ1 are identical or reproductions of the catalysts already described in previous work.\textsuperscript{[4]} The Cu/Al\textsubscript{2}O\textsubscript{3} catalyst CA1 was co-precipitated from a Cu:Al = 20:80 solution at pH8, washed and calcined at 603 K.

Table S1 provides an overview of selected samples used in this study and reports the internal FHI sample database numbers that should be used in future correspondence to facilitate communication.

<table>
<thead>
<tr>
<th>Label</th>
<th>Metal composition (nominal, molar)</th>
<th>Precursor</th>
<th>Calcined</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA3</td>
<td>Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} (70/28/2)</td>
<td>14328</td>
<td>15018</td>
<td>Reproduction of ref. [2]</td>
</tr>
<tr>
<td>CM1</td>
<td>Cu/MgO (80:20)</td>
<td>9278</td>
<td>15882</td>
<td>Precursor identical to ref. [4], calcination reproduced</td>
</tr>
<tr>
<td>CM2</td>
<td>Cu/MgO (70:30)</td>
<td>15316</td>
<td>15883</td>
<td>Analogous to CM1 besides composition</td>
</tr>
<tr>
<td>CMZ1</td>
<td>Cu/MgO/ZnO (79:16:5)</td>
<td>9278</td>
<td>13537</td>
<td>Precursor identical to ref. [4], impregnation reproduced on calcined catalyst</td>
</tr>
<tr>
<td>CMZ2</td>
<td>Cu/MgO/ZnO (79:16:5)</td>
<td>9278</td>
<td>13192</td>
<td>Precursor identical to ref. [4], impregnation was done on co-precipitated precursor</td>
</tr>
<tr>
<td>CMZ3</td>
<td>Cu/MgO/ZnO (67:29:4)</td>
<td>15316</td>
<td>16180</td>
<td>Precursor identical to CM2, impregnation was done on co-precipitated precursor</td>
</tr>
<tr>
<td>CA1</td>
<td>Cu/Al\textsubscript{2}O\textsubscript{3} (20:80)</td>
<td>13560</td>
<td>16090</td>
<td>-</td>
</tr>
</tbody>
</table>

The metal content of the calcined C, CA2, ZA and CZA1-2 precursors is analyzed by ICP-OES (SpectroFlame FTMOA81A, Spectro Analytical Instruments). Using this method, the samples are also checked for the absence of sodium and potassium impurities. Prior to the analysis, the samples are dissolved in boiling aqua regia, inspissated and diluted with 1M HNO\textsubscript{3}. Those samples listed in Tab. S1 have been investigated by X-ray fluorescence (XRF) using a Bruker S4 Pioneer X-ray spectrometer.

Nitrogen physisorption of the calcined precursors is measured at 78 K in a NOVA 4000e Surface Area & Pore Size Analyzer (Quantachrome Instruments). Prior to analysis, all samples are outgassed under vacuum at 523 K for 3 h. For analysis of the BET surface area ten evenly spaced points in the pressure region from 0.05 to 0.3 bar are used.

For high resolution TEM investigation shown in Figure 1 of the main article and Figure S6c,d, a FEI Titan Cs 80-300 microscope operated at 300 kV, equipped with a FEG, Gatan Tridiem Filter was used. Spherical aberrations were corrected by use of the CEOS C\textsubscript{x}-corrector reaching an information limit of 0.8 Å. The particle size evaluation leading to the TEM-based Cu surface area estimations given in Table 2 of the main article was based on images such as shown in Figure S1, which were taken on a Philips CM200FEG microscope operated at 200 kV. The high-resolution image shown in Figure S6a was taken on the same machine and processed to obtain the power spectra which were used to measure inter-planar distances and angles for phase identification. For all measurements the reduced samples (at 250°C for 30 min in 5% H\textsubscript{2}/Ar) were transferred via a glovebox to the microscope using a vacuum transfer holder to exclude the contact to air.
**II) Experimental setup and activation procedure**

The catalyst activity and the copper surface area according to H₂-TPD and nitrous oxide reactive frontal chromatography (N₂O-RFC) are determined in a glass lined single-pass fixed-bed reactor (internal diameter 4.5 mm) with internal thermocouple, an upstream gas mixing unit and a prior to every experiment calibrated mass spectrometer (Pfeiffer Vacuum OmniStar GSD 301 O) for time resolved in-situ analysis, as well as an Agilent 7820A gas chromatograph equipped with two thermal conductivity detectors, a packed Porapack-N column (Sigma Aldrich) for the quantification of CH₄, CO₂, H₂O, CH₃OH and a packed Molsieve 5 Å column (Sigma Aldrich) for the quantification of Ar, N₂, CH₄ and CO. The setup can be pressurized up to 28 bar and operated in a temperature range from 77 K up to 773 K. During the catalyst activation, N₂O-RFC and activity measurements each catalyst is treated with the same premixed gases of the following compositions and purities: 2% H₂ (99.9999%)/He (99.9999%), 1% N₂O (99.9990%)/He(99.9999%), 13.5% CO (99.997%)/3.5% CO₂ (99.9995%)/9.5% N₂ (99.9999%/73.5% H₂ (99.9999%). All other measurements are conducted using single high purity gases: H₂, He, N₂ 99.9999%. In order to remove traces of sulfur and carbonyls from the synthesis gas stream, a guard reactor is employed.

In a typical measurement 75 mg up to 150 mg catalyst (according to the expected amount of surface area) of the 250-355 μm sieve fraction and 500 mg purified silicon carbide of the same sieve fraction are heated up at atmospheric pressure for 15 hours in 2.0% H₂ in He raising the temperature from 300 to 448 K at 1 K min⁻¹, then in pure H₂ raising the temperature from 448 K to 513 K at 1 K min⁻¹ and holding for 30 minutes. Under these conditions no brass formation in the catalyst bulk phase takes place.[5] In all cases a specific flow rate of 0.2 sccm g⁻¹cat⁻¹ is used.

The activity studies are performed after the H₂-TPD and N₂O-RFC measurements at 24 bar in synthesis gas (13.5% CO, 3.5% CO₂, 9.5% N₂, 3.5% H₂). The temperature ranges from 453 K to 523 K. Prior to the study, the catalysts are reactivated for 60 minutes at 448 K in 2% H₂/He. All conversions were checked to be lower than 10% of the corresponding equilibrium conversion, the selectivity is in all cases beyond 99% and the mass balances are within 3% relative accuracy. In case of the most active sample CZA3, the formation of hotspots has
been thoroughly checked to be absent by varying the dilution with SiC. Here, also the absence of intraparticle diffusion limitation was checked using different particle sieve fractions. The results are given in figure S4.

**III) Hydrogen Temperature Programmed Desorption (H\textsubscript{2}-TPD)**

After the activation procedure, the catalyst is cooled down in helium to 235 K and pressurized for 30 minutes with 24 bar H\textsubscript{2}. Variation of the adsorption pressure and adsorption time showed, that a full hydrogen coverage of copper can be achieved using these conditions. After the adsorption period the catalyst is rapidly cooled down to 77 K, depressurized to 1 bar and flushed with He for another 30 minutes until the H\textsubscript{2} baseline in the mass spectrometer is stable. The H\textsubscript{2}-TPD experiment is conducted at 1 bar using a He flow rate of 100 sccm and heating rates $\beta$ of 4, 6 and 10 K min\textsuperscript{-1}. It has been shown that under these conditions transport limitations are absent.\[6\] The amount of hydrogen is calculated using the full area under the desorption peak. In this context, signals above 375 K are ignored.

Exemplary results of the N\textsubscript{2}O-RFC and H\textsubscript{2}-TPD measurements are given in figure S2 and give an impression of the high data quality available for the detailed description of the catalyst surface. Even for the - compared to the other catalysts - low dispersion of pure copper a clean and distinct H\textsubscript{2}-TPD signal is visible. To our knowledge, this is the first time that a clean and fully covered H\textsubscript{2}-TPD of polycrystalline copper is presented under atmospheric conditions. The obtained H\textsubscript{2}-TPD peak temperatures (heating rate $\beta = 6$ K min\textsuperscript{-1}: C & CA systems 283±2 K, CZA systems 300±2 K) are in good agreement with published data.\[7,8\] Whereas in the C, CA and CM samples the desorption curve is perfectly symmetric, in the case of all CZA and CMZ catalysts a typical asymmetric curve is visible, which has been attributed to the morphologic structure of the copper particles.\[9,10\] However, it should be noted that the MgO supported samples show no shift of the H\textsubscript{2}-desorption maximum after impregnation with ZnO but resemble the same shape and peak values as CZA samples. Careful reproduction of the experiments with fresh catalyst were performed with C, CA2 and CZA3, resulting in a maximum error margin of 5% for the H\textsubscript{2} area and ±2 K for the peak temperature. Temperature effects due to the position of the catalyst bed in the reactor have not been observed. With exception of the pure copper sample C no sintering tendencies are observed. The H\textsubscript{2} amount is also independent from the heating rate $\beta$. For every catalyst, the reported error bars are a result of at least three measurements, in case of the copper sample C three measurements each with fresh catalyst are employed. In all cases, the activated samples show no or very small traces of water contamination (signals at $T > 375$ K)\[11\] or other desorption signals within the given temperature range. Also no signal can be found in the given temperature range reproducing the experiments with pure SiC.

![Figure S2. Exemplary H\textsubscript{2}-TPD study on activated methanol synthesis catalysts. Measurement conditions: $Q = 100$ sccm, $m_{\text{cat}} = 100$ mg (based on calcined precursor), $\beta = 6$ K min\textsuperscript{-1}](image-url)
IV) Nitrous Oxide-Reactive Frontal Chromatography

The \( \text{N}_2\text{O} \) copper surface area is determined using the activated catalyst sample after the \( \text{H}_2\)-TPD treatment at 308 K, 1 bar pressure and a flow rate setpoint of 7.5 sccm \( \text{N}_2\text{O} \) (1%) in He. The actual flow rate is determined prior and after the measurement with an automatic flow meter (BIOS Definer 220). At the chosen temperature, no significant bulk oxidation of copper is present and the \( \text{N}_2\text{O} \) decomposes according to theory quantitatively on the copper surface following the reaction:[12]

\[
\text{N}_2\text{O} + 2 \frac{\text{Cu}_{\text{surface}}}{\text{Cu}_2\text{O} + \text{N}_2}
\]

Holding the reactor under helium, the remaining setup is flushed with \( \text{N}_2\text{O}/\text{He} \) and after switching the reactor to 1% \( \text{N}_2\text{O}/\text{He} \) a breakthrough curve in the reactor effluent stream is measured using the calibrated mass spectrometer. The amount of copper surface atoms is calculated from the catalyst mass, exact flow rate and nitrogen area until the \( \text{N}_2\text{O} \) breakthrough. The specific \( \text{Cu} \) metal surface area is determined by using a value of \( 1.47 \cdot 10^{19} \) atoms per \( \text{m}^2 \) for the mean \( \text{Cu} \) surface atom density. The latter one is the arithmetic mean value of the low index planes \( \text{Cu} \) (111), \( \text{Cu} \) (110), \( \text{Cu}(100) \). As the subsurface oxidation cannot be completely avoided, the intersection between the falling \( \text{N}_2 \) signal and rising \( \text{N}_2\text{O} \) signal at the breakthrough point is used as a limit for the integration of the \( \text{N}_2 \) signal and a conservative error margin of \( 1 \text{ m}^2 \text{ g}_{\text{cat}}^{-1} (12 \mu \text{mol N}_2 \text{O g}_{\text{cat}}^{-1}) \) is assumed, which is higher than the actual measured error when reproducing the experiments. An exemplary \( \text{N}_2\text{O}-\text{RFC} \) curve is given in figure S3 and the results are given in figure S4. The amount of oxophilic sites generated by the presence of \( \text{ZnO} \) is calculated from the difference of theoretical \( \text{N}_2\text{O} \)-adsorption capacity according to the copper surface determined via \( \text{H}_2\)-TPD and experimentally measured \( \text{N}_2\text{O} \)-adsorption capacity:

\[
\frac{1}{2} n_{\text{Cu,surface}} = \frac{3}{2} n_{\text{H}_2\text{-TPD}} - n_{\text{N}_2\text{O,experiment}}
\]

\( n_{\text{defects}} = n_{\text{N}_2\text{O,experiment}} \)

**Figure S3.** Exemplary \( \text{N}_2\text{O}-\text{RFC} \) curves of two catalysts. In case of \( \text{CA}2 \), the area used to determine the amount of produced \( \text{N}_2 \) is shaded gray. Experimental conditions: \( T = 308 \text{ K}, p = 1 \text{ bar}, Q = 7.5 \text{ sccm} \).
V) Model For The Microstructure of Common Cu/ZnO/(Al2O3) Methanol Synthesis Catalysts

Figure S5 shows a comparison of the expected “specific Cu surface areas” of the CZA catalysts in m²g⁻¹, that is obtained if the N₂O chemisorption capacity is conventionally evaluated as probing the metallic surface only. The values are compared to the hypothetical maximal Cu surface area as determined by TEM and to the real Cu surface area as determined by H₂ chemisorption. As described in the main text in detail, the discrepancy of N₂O and H₂ Cu surface areas in all ZnO-containing catalysts can be explained with the contribution of SMSI-induced defect sites of ZnO. While it seems clear that the “extra N₂O” is consumed on (partially) reduced Zn sites, we here make an attempt to relate these surface area differences with the microstructure of the Cu/ZnO/Al₂O₃ catalyst as shown in the TEM images in Figures 1, S1 and S6.

![Graphical representation of activity measurements and determined adsorption capacities](image)

**Figure S4.** Graphical representation of the activity measurements and determined adsorption capacities according to N₂O-RFC, H₂-TPD and corresponding amount of oxophilic sites generated by the presence of ZnO.

**Figure S5.** Comparison of the probe gas capacities of the CZA catalysts in this study if interpreted as specific Cu surface areas with the hypothetical maximal Cu surface area determined by TEM investigations shown in Figure S1.

Images of the microstructure of methanol synthesis catalysts are shown in Figures 1 (main text) and S6a-c as HRTEM and schematic representation. Typically, a disordered ZnO₅ layer of 1-2 nm is found at the surface of the Cu particles after reduction. In rare cases, the
ZnO\textsubscript{x} overgrowth shows atomic ordering like in Figure S6c or stabilizes the atomically flat low-energy (111) facets of Cu and show a smaller down to the monolayer thickness, like the one in Figure S6d on the left side of the particle.

We assume that three types of Cu surfaces/interfaces exist: (i) a fraction present as interface to Wurzite-type ZnO particles that act as physical support of the Cu particles, (ii) a fraction that is covered by ZnO\textsubscript{x}-overgrowth as shown in Figure 1 of the main article and thus involved in Cu-ZnO interaction; and (iii) a fraction that is uncovered and directly exposed to the gas phase. A suggestion of the microstructural arrangement of these types of surfaces in the catalysts is indicated in Figure S6b using pink color for type (i), light blue to type (ii) and dark blue for type (iii).

According to this simplified interpretation, the difference between TEM and N\textsubscript{2}O surface areas can be seen as an estimate of the contact area between Cu and Wurzite-type ZnO, which are inaccessible for probe molecules and guarantees structural integrity to the catalysts (type (i)). The N\textsubscript{2}O surface area would be the sum of type (ii) and type (iii), i.e. the difference between N\textsubscript{2}O and H\textsubscript{2} surface areas is a measure for the...
degree of Cu-ZnO interaction, leading to partial reduction of ZnO and formation of ZnO$_x$-overgrowth. Finally type (iii) is directly measured by H$_2$ chemisorption. According to the quantification shown in Figure S5, this interpretation seems reasonable. However, other models involving, e.g., surface alloy formation or dynamic de-wetting of Cu are possible as well. In particular, the reactivity of the ZnO$_x$-overlayer toward O and H atoms is not clear and needs further investigation. Independent of these structural details, the better correlation of the N$_2$O-derived chemisorption capacity with the methanol synthesis activity within this catalyst series (sum of metallic Cu and oxophilic Zn$^{2+}$ sites) compared to the H$_2$-derived capacity (only Cu sites) or the difference of both (only Zn$^{2+}$ sites) supports the idea of a bi-functional active site for methanol synthesis.

References