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Published in:
Catalysis Letters

Link to article, DOI:
[10.1007/s10562-020-03162-7](https://doi.org/10.1007/s10562-020-03162-7)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Nielsen, N. D., Jensen, A. D., & Christensen, J. M. (2020). Quantification of Formate and Oxygen Coverages on Cu Under Industrial Methanol Synthesis Conditions. *Catalysis Letters*, 150(9), 2447-2456.
<https://doi.org/10.1007/s10562-020-03162-7>

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Quantification of formate and oxygen coverages on Cu under industrial methanol synthesis conditions

Niels D. Nielsen, Anker D. Jensen and Jakob M. Christensen*

Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søtofts Plads B229, 2800 Kgs. Lyngby (Denmark).

*Correspondence to: jmc@kt.dtu.dk

Abstract:

A method for quantifying the surface coverage of adsorbate species for reactions at high pressure and high temperature is presented. Methanol was synthesized from CO₂/CO/H₂ (3/29/68) at 523 K and 50 bar on Raney Cu, which yielded a turnover frequency (TOF) per Cu surface atom of $(6.22 \pm 1.04) \cdot 10^{-3} \text{ s}^{-1}$. Rapid quenching by submerging the catalytic reactor in ice water during operation allowed the formate surface coverage on Cu ($\theta_{\text{Cu-HCOO}}$) at reaction conditions to be determined in a subsequent temperature programmed desorption experiment. This yielded $\theta_{\text{Cu-HCOO}} = 0.071 \pm 0.012 \text{ ML}$ and a corresponding TOF per adsorbed HCOO of $0.088 \pm 0.021 \text{ s}^{-1}$. CO₂ was essentially observed to be the exclusive source of methanol formation over Raney Cu, as the CO in the syngas could be replaced by N₂ without impact on the methanol formation rate. Based on this observation and the considerable support in the literature for a CO₂-pathway via surface formate on Cu the TOF per surface formate species should represent the true rate of the catalytic cycle in Cu-catalyzed methanol synthesis. Temperature programmed hydrogenation of Raney Cu and unsupported Cu after quenching during high-pressure operation did not indicate a presence of oxygen species (O or OH) on the working Cu surface.

1. Introduction

The surface coverage of adsorbate species under reaction conditions is an important parameter for catalytic reactions. This also applies for the Cu-catalyzed hydrogenation of CO₂ to methanol. Methanol synthesis from CO₂ is a major industrial process from coal or natural gas derived syngas (CO/CO₂/H₂) and could have applications for storage of renewable energy in the form of methanol [1]. In methanol synthesis formate (HCOO) is an important adsorbate to quantify on the metallic Cu surface. Formate is an important reaction intermediate as indicated by the correspondence between disappearance of formate on Cu and the appearance of methoxide/methanol [2] and by the similar response of methanol production and formate IR bands to variations in the CO₂ pressure [3, 4]. In situ infrared spectroscopy [3] and sum frequency generation [5] studies on supported and unsupported Cu have unambiguously identified HCOO on the copper surface under methanol synthesis conditions, but no quantification of $\theta_{\text{Cu-HCOO}}$ was provided. Gravimetric analyses [6] show that the industrial Cu/ZnO/Al₂O₃ catalyst is highly covered by surface adsorbates in a syngas atmosphere at high pressure, but this technique cannot distinguish between adsorbates on the metal and oxide components of the catalyst. Experimental approaches to quantification of $\theta_{\text{Cu-HCOO}}$ include X-ray Photoelectron Spectroscopy (XPS) post methanol synthesis (523 K, 18 bar) on Cu single crystals yielding $\theta_{\text{Cu-HCOO}} \cong 0.005\text{-}0.024 \text{ ML}$ [7] and temperature programmed desorption (TPD) after methanol synthesis (1 atm, 438 K) on Cu/ZnO catalysts resulting in $\theta_{\text{Cu-HCOO}} = 0.083$ [2]. However, these studies provide no details regarding the post reaction cooling procedure, which ideally should be infinitely fast to quench the working state of the catalyst. Micro-kinetic models

[8–13] based on Cu surface science data or DFT calculations report formate coverages in the entire range from sub-percentage levels to full coverage under industrial methanol synthesis conditions and thus offer no unified estimate of $\theta_{\text{Cu-HCOO}}$. Quantitative estimates of the formate coverage on Cu at industrially relevant conditions ($T = 523 \text{ K}$, $P = 50 \text{ bar}$ [14]) are therefore necessary to improve the fundamental understanding of the Cu-catalyzed methanol synthesis and guide kinetic modelling studies.

This study presents a quantitative method for determination of $\theta_{\text{Cu-HCOO}}$ on Cu during methanol synthesis by integrating the desorbed amount of CO_2 in a TPD experiment after rapid quenching of the working catalyst by submerging the reactor in a cooling medium. Coverages are reported as the number of adsorbates relative to the total number of Cu surface atoms. For adsorbates such as HCOO that tend to adopt a bidentate configuration with bonding to two copper atoms full coverage should thus correspond to 0.5 ML. Raney Cu was used to approximate the intrinsic properties of Cu because it was observed to have superior thermal stability compared to unsupported Cu, and studies on Raney Cu thus improve the reliability of the analyses. Comparisons of the TOF for CO_2 hydrogenation for Raney Cu to measurements on unsupported Cu and to single crystal values from the literature are used to support that Raney Cu is a reasonable model for the intrinsic properties of Cu.

2. Experimental

2.1 Catalysts

Raney Cu from Strem Chemicals (The producer reports: 98.9 wt% Cu, 0.81 wt% Al, 0.1 wt% Fe, 0.05 wt% Ni) was received as an aqueous slurry, from which small portions were pre-dried in air at room temperature in a fume hood before loading it into the reactor. This method proved more convenient and no difference in catalytic activity was observed between loading in a wet or dried state. Unsupported Cu was obtained from pure CuO. The CuO used to produce unsupported Cu for activity tests was prepared by precipitation from the nitrate and calcination to CuO in flowing air as described in detail elsewhere [15]. The CuO used to generate unsupported Cu for the TPH experiment identifying adsorbed oxygen on the working copper surface was CuO nanopowder (<50 nm) from Sigma Aldrich.

2.2 Experimental setup

Methanol synthesis experiments and subsequent TPD or temperature programmed hydrogenation (TPH) experiments to quantify adsorbate coverages were conducted in a high pressure flow reactor setup described in more detail elsewhere [15]. In brief, the catalyst was placed in a U-tube reactor (SGE Analytical Science borosilicate glass lined steel). The U-tube reactor was placed within an Entech tubular oven that can be opened rapidly to access the reactor. Thereby the U-tube reactor containing the catalyst can be cooled rapidly by raising a liquid (ice water, boiling water or liquid N_2) filled dewar to submerge the U-tube in the cooling liquid. The effluent from the reactor during catalytic reaction and temperature programmed experiments was analyzed using a Thermo Fisher Trace 1300 GC and a Hiden HPR-20 EGA mass spectrometer.

2.3 Activation of catalyst by H₂ reduction

Raney Cu is partly oxidized during storage or during the pre-drying of the sample. Thus before any use, Raney Cu was reduced in situ in 5% H₂/N₂ by ramping with 1 K/min to first 448 K and secondly to 523 K with a 2 hour dwell time at both temperatures. A similar activation procedure was initially employed for unsupported Cu, but water evolution terminated at the 448 K step indicating complete reduction already at 448 K. Because unsupported Cu was less thermally stable and fully reduced already at 448 K all results reported for unsupported Cu are obtained with pre-reduction at 448 K (1 K/min, 2 h holding time).

2.4 Surface area measurement

The specific Cu surface area was evaluated based on the N₂O Reactive Frontal Chromatography (RFC) method [16]. The pre-reduced/activated catalyst was exposed to 19 Nml/min of 1% N₂O/He at 333 K and ambient pressure. The N₂O consumption was converted into a Cu surface area assuming a Cu:O stoichiometry of 2:1 [17] and an average Cu surface atom density of $1.47 \cdot 10^{19}$ atoms/(m² Cu) [18] based on the arithmetic mean of the low index Cu facets (Cu(111), Cu(100) and Cu(110)). N₂O-RFC was conducted both in a Quantachrome IQ₂ setup and in the high pressure setup also applied for the quenching and methanol activity experiments.

The Raney Cu sample contained residual Al in the form of Al₂O₃. Because of the low surface free energies of oxides compared to metals [19] the oxide components in Raney Cu may represent a larger concentration on the surface. The extent of the Al₂O₃ covered surface was determined from the difference between a BET measurement of the total surface area and an N₂O-RFC measurement of the metallic Cu surface area. A Quantachrome NOVAtouch Gas sorption analyzer was applied to perform the BET analysis. Pre-dried Raney Cu was reduced ex-situ (see section 3.2) with fixed temperature for 4 hours (due to use of a larger amount of sample) at 448 K and 2 hours at 523 K before He flush and cooling to room temperature. The ex-situ activated Raney Cu was then loaded into the NOVAtouch analyzer and vacuum degassed with 10 K/min heating to 423 K and holding for 16 hours. Degassed Raney Cu was weighed before performing a standard 6-point BET surface area measurement.

2.5 Measurement of catalytic activity and activation energy

After catalyst pre-reduction the reactor was pressurized to 50 bar in He (99.999%) and the catalyst was then subjected to the reaction gas, which was mixed from pure H₂ (99.999%) and pre-mixed 9.00 mol% CO₂ in CO or 9.00 mol% CO₂ in N₂ (all gasses from Air Liquide Denmark). The methanol concentration in the effluent was measured by gas chromatography, and the effluent flow was measured by a soap film flowmeter. For determining the activation energy pre-reduced Raney Cu was cooled to 423 K and pressurized in He before feeding with 280 Nml/min of CO₂/CO/H₂ (3/29/68). The reaction temperature was raised in steps of 20 K from 423 K to 523 K each time with a fixed temperature for 1-2 hours to reach a stable methanol effluent concentration, which was quantified by online gas chromatography.

2.6 Procedure to estimate the surface coverage of formate on Cu

Fig. 1 illustrates the experimental procedure for quantifying $\theta_{\text{Cu-HCOO}}$. After pre-reduction of Raney Cu, the reactor was at 523 K pressurized in He to 50 bar before feeding 280 Nml/min of $\text{CO}_2/\text{CO}/\text{H}_2 = 3/29/68$ at constant temperature and pressure. All measurements were conducted at differential conditions with a maximum of 0.10 mol% methanol in the effluent gas stream. Once the methanol signal (evaluated by the MS using $m/z = 31$) reached its peak level, the methanol production was quantified by a GC measurement, before the catalyst was rapidly cooled in the reaction gas by different cooling methods described below. At room temperature or below, the syngas pressure was released, and the reactor was thoroughly purged with He before conducting a TPD in flowing He with a 2 K/min heating ramp.

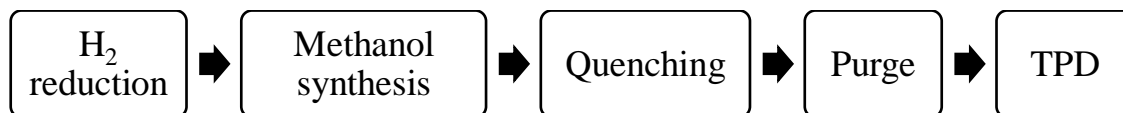


Fig. 1 Block diagram of the protocol for quantifying the surface adsorbate coverage at reaction conditions on Raney Cu.

Fig. 2 shows the cooling profile measured by two thermocouples (TCs) – one placed inside the reactor tube at the top of the catalyst bed (red) and one on the external surface of the reactor tube at the bottom of the catalyst bed (blue). The cooling was set to start at $t = 0$ in Fig. 2 by swiftly opening the oven and moving a dewar filled with the cooling liquid (ice water was used in Fig. 2) vertically upwards to cool the U-shaped reactor (see Fig. 2), and after a few seconds both TCs were at (or below) room temperature. The cooling profile experienced by the catalyst bed is an average of the temperature profiles measured by the two TCs, and this average is plotted as T_{ave} in Fig. 2. In the case of cooling with boiling water, the dewar was removed after cooling to 383 K and further cooling was due to ambient air circulation around the U-shaped reactor. Cooling by static air occurred by opening the oven and allowing the reactor to cool by the ambient room temperature air. Two additional repetition experiments confirmed the reproducibility of quenching profiles with ice water (see supplementary information Fig. S1). After cooling to room temperature or below, the pressure was released, and the syngas was thoroughly flushed out with He before removing the dewar with the cooling liquid (except for boiling water where the dewar was removed at 383 K) under continuous He flush and allowing the reactor to heat naturally to room temperature, if the temperature during He purging was below room temperature. Starting from room temperature, a TPD was carried out with 2 K/min heating to 673 K in a He flow. The He flow was calibrated for each experiment using a soap film bubble flow meter and was within the interval from 42 to 45 Nml/min. A Hiden EGA mass spectrometer continuously measured desorbing CO_2 ($m/z = 44$), CO ($m/z = 28$), H_2O ($m/z = 18$) and H_2 ($m/z = 2$).

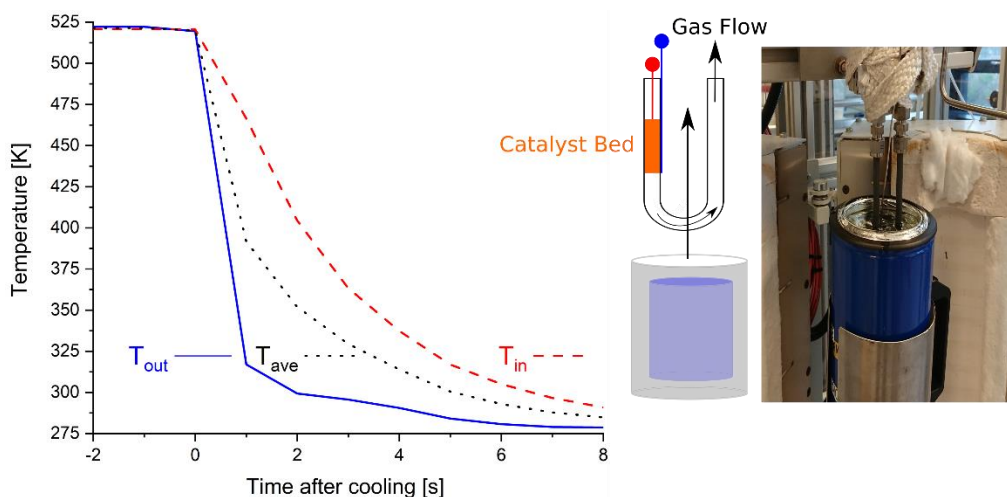


Fig. 2 Left: Cooling of the catalyst in the reaction mixture started at $t = 0$, while two thermocouples (TCs) positioned inside at the top (red, dashed) of the catalyst bed (orange) and outside at the bottom of the catalyst bed (blue, solid) monitored the cooling process. Right: Schematic view of cooling process by raising the filled dewar to submerge and cool the U-tube including positions of the thermocouples (red and blue). Far right: Image of the U-tube submerged in ice water.

The CO_2 MS signal was calibrated using a certified 500 ppm CO_2 in He gas mixture from Air Liquide Denmark. This allowed determination of $\theta_{\text{Cu-HCOO}}$ from integration of the calibrated CO_2 signal. Desorbed H_2 could in principle also be used to quantify $\theta_{\text{Cu-HCOO}}$, since HCOO on Cu decomposes to CO_2 and H_2 , but the hydrogen desorption was observed to be very complex with multiple peaks - most likely from decomposition of species on both the metal and Al_2O_3 parts of the surface yielding H_2 . It was therefore concluded that it was too complex to quantify $\theta_{\text{Cu-HCOO}}$ based on desorbed H_2 .

2.7 Evaluation of the coverage of adsorbed oxygen by temperature programmed hydrogenation

Two TPH experiments were designed to evaluate the coverage of adsorbed oxygen species (O or OH) on the Cu surface under reaction conditions. Both TPHs were performed in 60 Nml/min flow of 5% H_2/N_2 with 2 K/min heating ramp from 300 K to 673 K. In one experiment pre-reduced Cu was oxidized by 1 mol% N_2O in He at 333 K, which yields half a monolayer of oxygen on Cu as verified by studies [16, 17] benchmarking N_2O -RFC against BET surface area measurements. Next, the half monolayer of oxygen was hydrogenated in a TPH and formed H_2O was quantified to calibrate the H_2O ($m/z=18$) MS signal by equating the integral H_2O signal to 0.5 ML of O. In a second experiment the working catalyst was quenched using ice water (see section 2.5) and then subjected to a TPH instead of TPD. The oxygen coverage on the working catalyst was estimated from integration of the H_2O MS signal acquired during TPH of the quenched catalyst. A blank TPH experiment without catalyst (but similar to the procedure for the second experiment) showed no gas desorption thus verifying that products formed in the two TPH experiments were associated with the catalyst.

2.8 X-ray photo-electron spectroscopy on Raney Cu and unsupported CuO

XPS analyses were performed on Raney Cu and unsupported CuO to qualitatively assess the surface composition of Raney Cu. The XPS source was a monochromatic and micro-focused Al K-Alpha source (1486.6 eV) with a 180° double focusing hemispherical analyzer and a 128-channel detector from Thermo Scientific with an optimal base pressure of $6 \cdot 10^{-9}$ mbar. XPS experiments were performed with a chamber pressure of $4 \cdot 10^{-8}$ mbar and analysed using the Avantage software. Survey spectra were acquired for fresh unsupported CuO, predried Raney Cu and predried and then reduced Raney Cu. Survey spectra were recorded for all three samples and extra spectra were recorded to detect Al in Raney Cu.

3. Results & Discussion

3.1 Surface composition of Raney Cu

In agreement with previous XPS studies [20] on Raney Cu ex situ XPS measurements (see supplementary material Fig. S14- Fig. S17) on the pre-reduced Raney Cu sample showed that there were two peaks in the 70-80 eV range, namely a Cu3p peak at ca. 78 eV and an Al2p peak at 75 eV (see Fig. S16). The binding energy of the Al2p peak suggests that the Al was in an oxidized Al₂O₃ form [20–23]. This shows that the surface of Raney Cu is partly covered by Al₂O₃. N₂O-RFC yielded a Cu metal area of 5.18 m²/g for Raney Cu, whereas the BET area of the pre-reduced catalyst, which includes both the metallic Cu surface and the Al₂O₃ covered surface, yielded 13.94 m²/g. Consequently, the Al₂O₃ covered the major part of the surface (by difference between BET and N₂O-RFC around 8.8 m²/g) despite Al constituting less than 1 wt% of Raney Cu.

3.2 Benchmarking against the intrinsic properties of Cu

The present work seeks to evaluate the intrinsic properties of Cu at a realistic methanol synthesis temperature of 523 K, and Raney Cu was used because it has a reasonable thermal stability at these conditions. However, as discussed above the Raney Cu sample also had an extensive oxide surface and thus sites such as the Cu/oxide interface that are not present in pure Cu. To evaluate, if Raney Cu is a reasonable approximation of the intrinsic properties of Cu concerning methanol synthesis, the rate of CO₂ hydrogenation to methanol was compared to unsupported Cu (0.494 m² Cu/g_{cat}). Both Raney Cu and unsupported Cu were tested at 498 K in CO₂/N₂/H₂ = 3/29/68 at 50 bar of pressure and showed very similar TOFs of $3.65 \cdot 10^{-3}$ s⁻¹ and $2.78 \cdot 10^{-3}$ s⁻¹, respectively (Table 1). The evaluation was performed at 498 K rather than 523 K, as measurements of unsupported Cu were unreliable at 523 K, where it transitioned from powder to a massive pellet. Rapid activity loss for unsupported Cu at 523 K is also known in the literature [24]. Unsupported Cu is prone to sintering due to a low Hüttig temperature (408 K) above which surface mobility becomes significant [25], and copper particles are known to agglomerate above 473 K [26]. Given the propensity of unsupported Cu towards sintering the TOF agreement within ca. 25% between unsupported and Raney Cu is taken as evidence that Raney Cu is a good approximation of the

intrinsic properties of Cu. By assuming a linear hydrogen pressure dependence, as also employed by others [11], and utilizing reported activation energies under the assumption of an Arrhenius-type temperature dependence, previously reported [27, 28] TOF-values for CO₂ hydrogenation on Cu(111) and polycrystalline Cu were extrapolated to the present conditions (498 K, p_{H₂} = 34 bar). Table 1 compares these extrapolated TOF-values [27, 28] to the ones for Raney Cu and unsupported Cu obtained in this study, and the results generally show a good agreement. Based on the correspondence in TOF between Raney Cu and both unsupported Cu and previous single crystal studies it is concluded that Raney Cu is a reasonably good approximation to the intrinsic properties of copper.

Table 1 TOF values for Raney Cu and unsupported Cu at 498 K, 50 bar, CO₂/N₂/H₂ = 3/29/68 and TOF-values from single crystal studies extrapolated to the conditions of this study (T = 498 K, p_{H₂} = 34 bar) using their reported activation energies.

Catalyst	T [K]	p _{H₂} [bar]	E _{act} reported [kJ/mol]	TOF reported [s ⁻¹]	TOF extrapolated [s ⁻¹]	Reference
Cu(111)	523	13.5	73.6	2.06·10 ⁻³	2.07·10 ⁻³	[27]
Polycrystal. Cu	510	4.67	77	1.2·10 ⁻³	5.7·10 ⁻³	[28]
Unsupported Cu	498	34		2.78·10 ⁻³	2.78·10 ⁻³	This study
Raney Cu	498	34	55.3	3.65·10 ⁻³	3.65·10 ⁻³	This study

The methanol synthesis rate in CO/CO₂/H₂ was measured at 50 bar and temperatures ranging from 423 K to 523 K to determine the activation energy for the methanol synthesis on Raney Cu. Fig. 3 shows an Arrhenius plot determined from these measurements, which yields an apparent activation energy of 55.3 kJ/mol. Previous measurements [15] in the same setup on unsupported Cu at 50 bar and a CO₂/H₂ feed suggest an activation energy of 60 kJ/mol for unsupported Cu, which within the uncertainty also indicates a reasonable agreement between Raney Cu and unsupported Cu in terms of the activation energy.

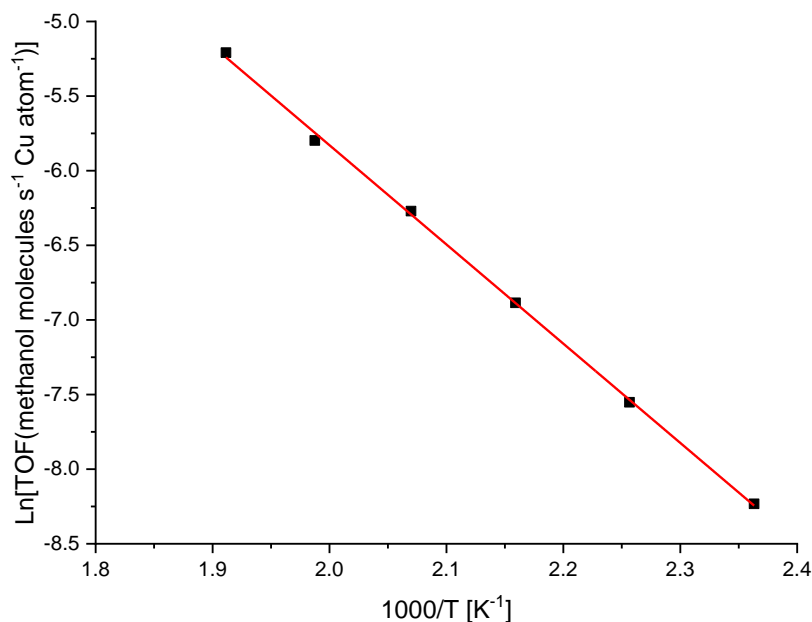


Fig. 3 Arrhenius plot for methanol synthesis over Raney Cu exposed to reaction conditions (50 bar, CO₂/CO/H₂ = 3/29/68, GHSV = 6.7·10⁴ Nml/g_{cat}/h).

3.3 Formate quantification by a TPD method

Raney Cu was allowed to reach steady state in CO₂/CO/H₂ at 50 bar and 523 K. At that point the activity was measured by gas chromatography, and the catalyst was rapidly quenched by submerging the U-tube reactor in ice water. The ice water cooling yielded reproducible and rapid cooling profiles (see Fig. S1). The quenched sample was then subjected to a TPD, and Fig. 4 shows the evolution of CO, CO₂, H₂ and H₂O during the TPD. The reproducibility of the obtained TPD profiles was verified by three repeated experiments (see also Fig. S2 and Fig. S3). Fig. 5 shows the CO₂ desorption deconvoluted into three Gaussian peaks termed α , β , and γ . The main CO₂ desorption (the β -peak) occurred at 410 K. In a Redhead analysis [29, 30] with the commonly applied pre-factor of 10¹³ s⁻¹ this temperature corresponds to an activation energy for desorption of 122 kJ/mol, which is consistent with formate desorption from Cu [31–34]. Fujita et al. [2] also observed that the CO₂ TPD peak corresponding to the β -peak in Fig. 4 scaled with the Cu surface area for a range of formate covered Cu/ZnO samples. This further supports that the CO₂ β -peak arises from a species on the Cu surface. Although the hydrogen desorption was too diffuse to be used in quantification, the CO₂ β -peak also coincided with a shoulder in the H₂ desorption, which is consistent with formate on Cu yielding desorption of both CO₂ and H₂. On this basis the CO₂ β -peak was unambiguously assigned to formate on Cu. The β -peak was therefore used to determine $\theta_{\text{Cu-HCOO}}$, and the orange area in Fig. 5 marks the area integrated to calculate the formate coverage.

The main CO desorption peak at 464 K was assigned to methoxide on the Al₂O₃ part of the surface. The main argument for this assignment is that Tamm et al. [35] observed concurrent desorption of CO and H₂ and to a lesser extent CO₂ at a similar temperature during TPD after methanol adsorption on γ -Al₂O₃. The CO₂ γ -peak coincided with the CO desorption at 464 K and

was therefore most likely also related to desorption from the oxide surface similar to the one also observed by Tamm et al. [35].

Desorption above 550 K must originate from highly stable adsorbed species most likely on the oxide and therefore not likely to influence the methanol synthesis reaction at 523 K. It was reported that formate on Al_2O_3 may desorb as CO and H_2O [36] at higher temperatures, and Cu might also facilitate water-gas shift [37, 38] of these species to CO_2 and H_2 . The higher temperature desorption was therefore assigned to the oxide surface. As discussed in section 3.1 the oxide surface presents a major fraction of the total surface area, which supports that species on the oxide contributes significantly to desorbed gas species during post reaction TPD.

The lower temperature desorption below approximately 383 K was attributed to chemisorbed H_2O and reactants on the sample. This includes the small, low temperature α - CO_2 peak in Fig. 5. As the α -peak is centered at ca. 370 K, where CO_2 chemisorbed on Al_2O_3 is reported [39] to desorb, the α -peak is attributed to chemisorbed CO_2 on the alumina part of the surface and not included in the formate quantification. However, given the small size of the α -peak this does not change the conclusions markedly.

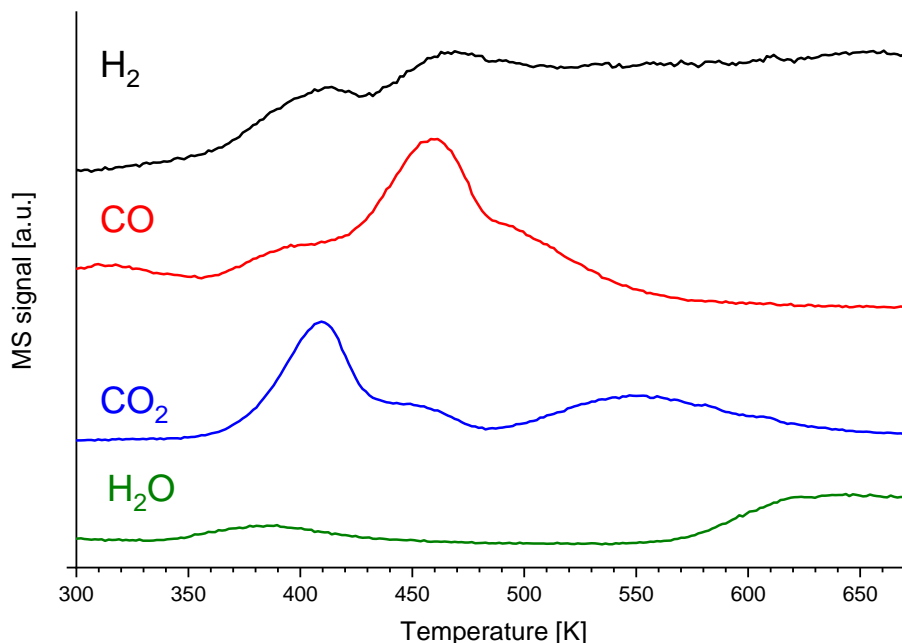


Fig. 4 Measured gas profiles during the TPD with 2 K/min as heating ramp after methanol synthesis at 523 K, 50 bar pressure in $\text{CO}_2/\text{CO}/\text{H}_2 = 3/29/68$ and subsequent quenching. MS signals are vertically offset on the linear y-axis for clarity.

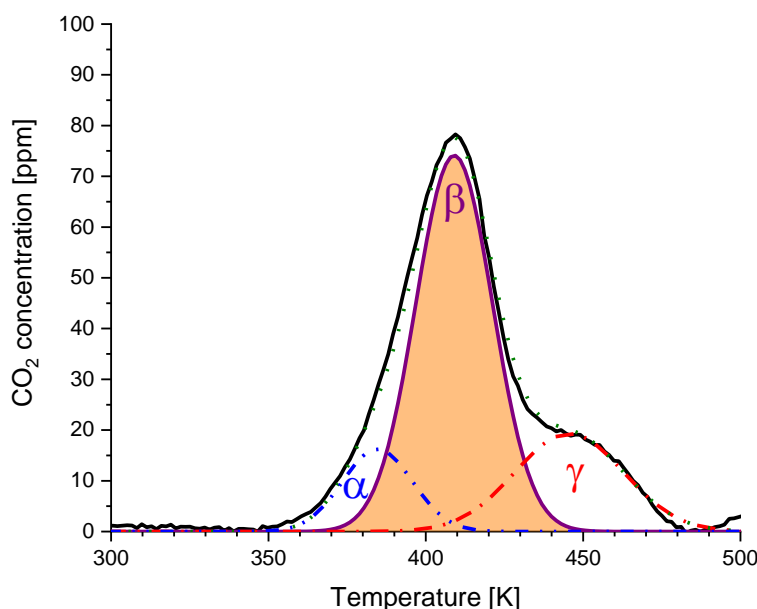


Fig. 5 Peak fitting to the measured black solid CO₂ desorption line using three Gaussian peaks (α , β , and γ), which sum up to dotted green profile. HCOO was quantified by the integrated area (orange) under the CO₂ β -peak. Heat ramp: 2 K/min. He flow: 42.5 Nml/min.

3.4 Evaluation of cooling methods

We have previously [15] compared the rates of methanol formation from CO and CO₂ on Cu with the same Cu-based materials investigated here, and found that the rate from CO₂ is approximately an order of magnitude faster than the rate from CO. Additionally, an experiment was performed, where the CO in the syngas was exchanged with N₂, and this had essentially no influence on the methanol formation rate (see Fig. S12). Consequently, there should be little uncertainty in attributing the entire methanol production to the pathway from CO₂. There is considerable experimental data to support that the pathway from CO₂ is via formate [2–4], and the formation and hydrogenation of formate can be expressed in a simplified manner by reactions R1 and R2 (with HCOO* denoting adsorbed formate and * denoting an active site) [8, 40]:



To provide the true working coverage of the catalyst the quenching must therefore be rapid enough to avoid that neither R1 nor R2 change the coverage during cooling. To evaluate this the quenching rate was varied using different cooling media, and the measured formate coverages was compared after cooling with ice water, boiling water, liquid N₂, and static air. Table 2 summarizes the

measured TOF and $\theta_{\text{Cu-HCOO}}$ in 3 tests quenching the reaction in ice water, and Fig. 6 illustrates the relation between the measured formate surface coverage and the time it took to reach 383 K during quenching with the various cooling media (showing that ice water was most efficient). Table 2 shows that the TOF at 523 K is $(6.22 \pm 1.04) \cdot 10^{-3} \text{ s}^{-1}$. Extrapolation of previously measured [40] rates for R1 on Cu to 523 K suggests that R1 should be 1-2 orders of magnitude faster than the TOF. Consequently, R1 should be quasi equilibrated under reaction conditions, and R2 is the rate limiting step in the reaction.

Table 2 Experimental parameters for each experiment with methanol synthesis over Raney Cu at 523 K, 50 bar in $\text{CO}_2/\text{CO}/\text{H}_2 = 3/29/68$ followed by quenching and TPD. Uncertainties correspond to two standard deviations, and the specific Cu surface area of Raney Cu was $5.2 \text{ m}^2/\text{g}_{\text{cat}}$.

	Cooling method	Ave. time to 383 K [s]	m_{cat} [mg_{cat}]	TOF [CH_3OH molecules (Cu surface atom) $^{-1} \text{ s}^{-1}$]	θ_{HCOO} [ML]
Test 1	Ice water	1.1	258.43	$5.63 \cdot 10^{-3}$	0.0640
Test 2	Ice water	0.5	254.36	$6.46 \cdot 10^{-3}$	0.0748
Test 3	Ice water	1.4	259.54	$6.59 \cdot 10^{-3}$	0.0730
Average		1		$(6.22 \pm 1.04) \cdot 10^{-3}$	0.071 ± 0.012

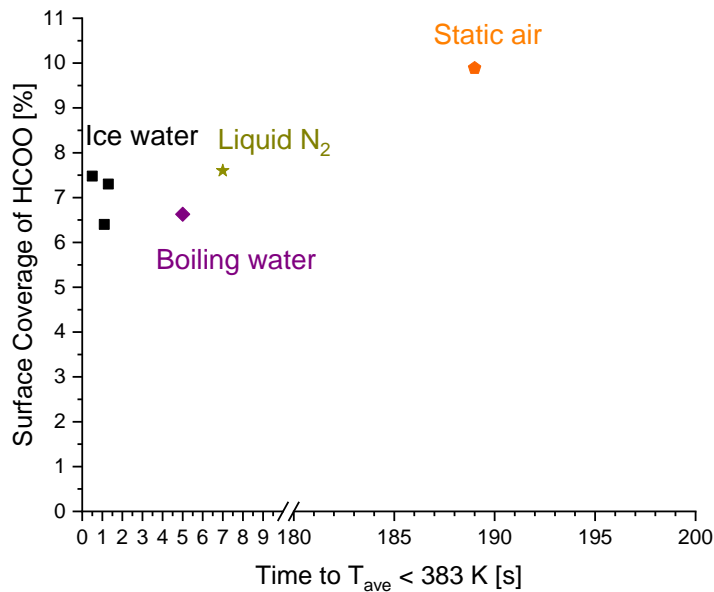


Fig. 6 Formate surface coverage as function of the time it takes the average temperature of the two thermocouples to reach 383 K using different cooling methods.

Adsorption reactions are by necessity exothermic to compensate for the loss of entropy, and this is also the case for R1 [40]. This means that during cooling the reverse reaction of R1 will stop

before the forward reaction. Consequently, if the cooling is too slow, R1 will raise the HCOO coverage during cooling. Previous measurements [40] suggest that at 383 K the forward rate of R1 is 0.0013 formate molecules/Cu atom/second, which means that it would take several hundred seconds to cover the surface. This is so slow compared to the cooling that R1 can be regarded as terminated at 383 K. Fig. 6 therefore evaluates the measured coverage as a function of time required to reach 383 K with various cooling methods. Fig. 6 shows that water based cooling methods yield a measured coverages that within uncertainty is independent of cooling rate, and this is taken as evidence that the cooling speed has reached the point, where the quenching is sufficiently fast to avoid that R1 modifies the coverage during cooling. Using liquid N₂ as a cooling medium gives a slightly slower cooling. This is rationalized from a poor heat transfer in the gas film created when N₂ boils around the hot reactor tube. However, the coverage obtained with the slower liquid N₂ cooling seems, within the uncertainty, to be identical to the coverage obtained with ice water cooling. By contrast, cooling in static air is considerably slower, and Fig. 6 shows that this slower cooling does result in an increased coverage as expected from the exothermic nature of R1. Table 2 shows that quenching using ice water, which is concluded to be fast enough to avoid being influenced by R1 yields $\theta_{\text{Cu-HCOO}} = 0.071 \pm 0.012$ ML (two standard deviations) and a corresponding TOF per adsorbed HCOO of $(6.22 \pm 1.04) \cdot 10^{-3} \text{ s}^{-1} / (0.071 \pm 0.012 \text{ ML}) = 0.088 \pm 0.021 \text{ s}^{-1}$. This suggests that each surface formate species on average is converted to methanol every $1/(0.088 \text{ s}^{-1}) \cong 11.4$ seconds at 523 K. This represents the time it would take R2 to remove all formate on the surface, if no new formate is generated. As quenching to below 383 K occurred rapidly compared to this lifetime, which increases exponentially with decreasing temperature, the reported formate coverage after ice water quenching was not significantly affected by R2. Since the quenching using ice water was concluded to be sufficiently fast to avoid major alterations of the coverage by both R1 and R2 during quenching the three ice water quenching tests (see Fig. 2, Fig. 6, and Fig. S1) were used to obtain the best estimate of the formate coverage on the working Cu surface, which as summarized in Table 2 is $\theta_{\text{Cu-HCOO}} = 0.071$ ML. Among existing micro-kinetic models the best agreement is with the model by Askgaard et al. [8] using Cu surface science data and the model by Grabow and Mavrikakis [9] using DFT calculations on Cu(111) both suggesting HCOO coverages of several percent at conditions similar to those used in the present study.

With the strong indications of a mechanism via formate [2–4], and assuming that all the detected formate on Cu participates in the reaction, the determined TOF per adsorbed HCOO of $0.088 \pm 0.021 \text{ s}^{-1}$ should represent the best estimate of the true rate of the catalytic cycle for methanol synthesis on Cu at industrially relevant conditions.

3.5 Oxygen coverage on Cu during methanol synthesis

Previous studies [14, 33, 41, 42], which during methanol synthesis have flushed the reactor with inert gas before cooling and then quantified the free Cu surface with N₂O-RFC, have observed the existence of oxygen species on the Cu surface of the working catalyst. However, the existence of adsorbed oxygen has caused debate [43–46], as it is surprising that any noteworthy oxygen buildup should occur in a reducing gas mixture at high pressure. Nevertheless, recent in situ ambient

pressure XPS studies [47] also observed oxygen on the Cu surface during CO₂ hydrogenation and thus call for further quantification of the oxygen coverage on Cu under industrially relevant methanol synthesis conditions. To verify that adsorbed oxygen is present on Cu during reaction conditions, unsupported Cu (from reduction of Sigma-Aldrich CuO nanopowder) was exposed to syngas (CO₂/CO/H₂ = 3/29/68) at 50 bar and 448 K, quenched in syngas by ice water cooling and after He flush subjected to a TPH in a flow of 5 mol% H₂ in N₂. As shown in Fig. S13, water was evolved in the 293-393 K range during the TPH, which supports that there are oxygen species (O or OH) on the Cu surface that can form water by reaction with H₂. Quantification of the oxygen coverage on the working Cu surface was based on the evolution of H₂O during two TPH experiments on Raney Cu pre-covered by either (1) 0.5 ML of oxygen after oxidation by 1 mol% N₂O at 333 K or (2) reaction intermediates after quenching during methanol synthesis. Figure 7 displays H₂O formation profiles after the N₂O oxidation (post N₂O) and the methanol synthesis and ice water quenching (post quenching). A minor water evolution was observed during TPH of the quenched sample, but such water evolution also occurred in TPH of a freshly reduced sample (see Fig. S13). The water evolution was therefore attributed to water impurities in the TPH feed that adsorb on the sample prior to the start of the TPH and then desorb in the initial stages of the TPH instead of being due to reduction of oxygen species on the Cu surface. Consequently, the oxygen coverage on the working Cu surface was concluded to be below the detection limit of our TPH method.

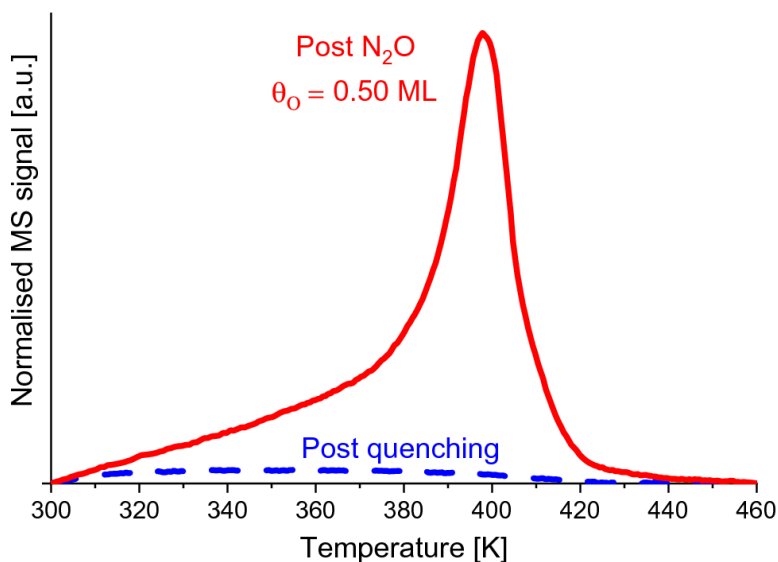


Fig. 7 The H₂O signal in TPH as a function of temperature with Raney Cu after quenching during methanol synthesis at 523 K, 50 bar of pressure in CO₂/CO/H₂=3/29/68 (Post quenching) or after N₂O-RFC on pre-reduced Raney Cu (Post N₂O). TPH conditions are 2 K/min in 60 Nml/min of 5% H₂/N₂. Both signals are individually and linearly baseline corrected using the specific data points at T = 300 K and T = 460 K for each experiment.

Conclusion

A reproducible and quantitative method for estimating the surface coverage of adsorbate species under high temperature and high-pressure reactions conditions was outlined. Ice water provided the fastest cooling rate and fixated the surface coverages obtained at reaction conditions. Activity measurements in CO₂/CO/H₂ at 523 K and 50 bar of pressure yielded a TOF per Cu surface atom of $(6.22 \pm 1.04) \cdot 10^{-3} \text{ s}^{-1}$ for Raney Cu (all uncertainties are here two std. deviations). Based on the quenching method with ice water, the surface coverage of formate was determined to be $\theta_{\text{Cu-HCOO}} = 0.071 \pm 0.012 \text{ ML}$ for Raney Cu yielding a corresponding TOF per adsorbed HCOO of $0.088 \pm 0.021 \text{ s}^{-1}$. Given the strong indications that the methanol synthesis proceeds via formate this TOF per adsorbed HCOO should represent the best estimate of the true rate of the catalytic cycle. Such estimations are vital for improving the understanding of kinetic reactions and guide kinetic modelling studies. Comparisons of Raney Cu to unsupported Cu and reports from single crystal studies suggested that Raney Cu, at least in terms of methanol synthesis activity and CO₂ hydrogenation properties, was a good approximation to pure Cu. TPH of the Raney Cu surface post methanol synthesis suggested that the oxygen coverage on the working Cu surface was below the detection limit of our TPH method.

Acknowledgements

This work was supported by the Villum Foundation Center for Science of Sustainable Fuels and Chemicals, Villum Foundation V-SUSTAIN grant 9455.

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