

In Situ Quantification of Reaction Adsorbates in Low-Temperature Methanol Synthesis on a High-Performance Cu/ZnO:Al Catalyst

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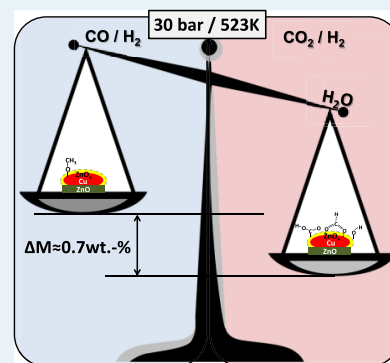
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Supporting Information

ABSTRACT: The industrial low-temperature process has been applied for 50 years; however, in situ data under relevant conditions are rare. We report on the in situ quantification of the surface adsorbates present under industrially relevant conditions by high-pressure thermogravimetry. In addition, high-pressure IR spectroscopy is applied for the identification of carbon-based adsorbates. On a high-performance Cu/ZnO:Al catalyst it has been shown that during CO₂ hydrogenation adsorbates of up to 1.9 wt % of the catalyst are reversibly accumulated, and 70% of the ad-layer consists of H₂O-derived species. Under CO-hydrogenation conditions, the weight accumulation on the surface is limited to an increase of 1.2 wt % mainly due to the absence of H₂O. The stable adsorbate layers from different feeds are qualitatively assigned by surface titration experiments and spectroscopic insights. In accordance with the literature, it is clearly illustrated that, on the basis of the feed-dependent coverage of the surface, different reaction mechanisms for the methanol formation are involved. These investigations under realistic conditions finally show the importance of Zn–OH groups, likely located at the Cu/ZnO interface, as being crucial for activation and hydrogenation of CO₂-derived intermediates to CH₃OH. The accumulation of H₂O- and carbon-derived species on the surface of the catalyst might explain the poor activity in CH₃OH formation at low temperatures and consequently limits the application of Cu/ZnO-based catalysts under mild, thermodynamically preferred conditions.

KEYWORDS: methanol synthesis, surface adsorbates, Cu/ZnO:Al catalyst, high-pressure infrared spectroscopy, high-pressure thermogravimetry



INTRODUCTION

The conversion of synthesis gas (CO/CO₂/H₂) to CH₃OH is one of the most important industrial processes, in particular with respect to the CO₂ emissions as the main cause of climate change. For decades, a Cu/ZnO-based catalyst has been applied and is still controversially discussed.¹ The interfacial contact of Cu/ZnO is generally accepted as an important site where the synergistic effects (structural and electronic) are focused.² To gain information on relevant intermediates of the CH₃OH formation, the adsorption of CO and CO₂ on Cu- and Cu/ZnO-based catalysts has been intensely studied.³ In addition, the experimental reports and numerous theoretical calculations agreed on the presence of carbon- and water-derived surface species. The most abundant species observed are formates,⁴ methoxy,^{4d,5} carboxyl,^{3b,6} formyl,^{4b,7} carbonates,⁸ hydroxyl,⁸ and H₂O (Scheme S1). These studies, however, are often performed under low surface coverages and conditions far from industrial relevance. In an attempt to bridge the pressure gap, several IR-reactivity studies were performed under elevated pressure up to 6 bar. The results of a transient kinetic analysis^{6a,9} made evident the formation of a formate layer, which was found to be unreactive toward methanol and suggested the reaction pathway through an elusive carboxyl intermediate.⁶ Investigations on Cu/ZnO

model catalysts, in contrast, identified formates as reaction intermediates.^{2f}

Another intriguing phenomenon observed^{6a,b} is the ambiguous effect of H₂O upon CO/CO₂ hydrogenation on the CH₃OH formation rate. The promotional effect of H₂O at finite conversions in 1–4% CO₂ has been reported previously.¹⁰ On the other hand, at integral conditions, product inhibition by water decreases the CH₃OH rate as shown by Sahibzada et al.^{10a} Beyond mechanistic considerations, the accumulation and influence of reaction products and intermediates on Cu/ZnO-based catalysts are of high relevance, since lower reaction temperatures are needed due to the thermodynamic limitations within the CO₂-utilization concept.¹

Herein, we report on probing a Cu/ZnO:Al industrial-like catalyst under CH₃OH synthesis conditions in CO- and CO₂-containing feeds. High-pressure in situ thermogravimetry investigations provide quantitative insights into the composition of adsorbed layers. The observed results are qualitatively compared with in situ IR experiments at 30 bar and transient

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surface reaction/titration experiments. Special attention is given to the role of water-derived species as part of the catalytically formed ad-layer and on possible carbon-based reaction adsorbates stable under reaction conditions. The complementary applied characterization techniques give new insights into the surface composition under industrially relevant conditions, clearly emphasizing the complexity of catalytic surface processes.

■ QUANTIFICATION OF THE REACTION ADSORBATES

The in situ thermogravimetric measurement in different feed compositions at 30 bar and 523 K is shown in Figure 1. The

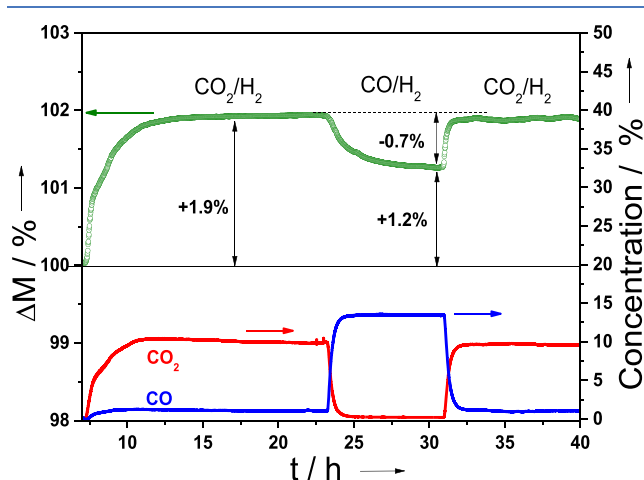


Figure 1. In situ thermogravimetry in different feed gases at 523 K. $\text{CO}_2/\text{H}_2/\text{He}$ (12/59/29), $\text{CO}/\text{H}_2/\text{Ar}/\text{He}$ (14/59/4/23), 120 mL min^{-1} at 30 bar, with online analysis of the gas phase.

correction for the buoyancy force for various gas mixtures is described in the Supporting Information (SI, see also Table S1). After activating the catalyst (20% H_2 in Ar), the gas mixture is switched to a CO_2 -containing feed. A direct weight increase makes evident the formation of an adsorbate layer on the catalyst surface, reaching a steady-state situation after ≈ 10 h under H_2/CO_2 feed and a mass gain of 1.9 wt % of the initial mass. Changing the feed composition to H_2/CO causes a reversible loss of 0.7 wt % within a period of ≈ 8 h (Figure 1). One has to consider that the pure support also shows a reversible mass uptake of 0.1–0.2 wt % when substituting H_2/CO by H_2/CO_2 (Figures S1 and S2). This deviation defines the accepted level of tolerance for the mass at steady state.

Based on transient H_2 adsorption and N_2O reactive frontal chromatography techniques, the Cu sites are given as $400 \mu\text{mol g}_{\text{cat}}^{-1}$ and ZnO_x sites as $273 \mu\text{mol g}_{\text{cat}}^{-1}$ (see also Table 1 and Table S2). The experimental values of the available redox active surface sites are used to calculate a possible mass increase based on the available surface sites. The good agreement between the calculated and experimentally quantified mass gain in the thermobalance also serves as validation of the applied surface and reaction model. To clarify the possible role of H_2O and H_2O -derived species (e.g., OH groups), the catalyst was saturated in the thermobalance with a H_2/Ar stream enriched with 1.5 vol % H_2O (Figure 2A). After

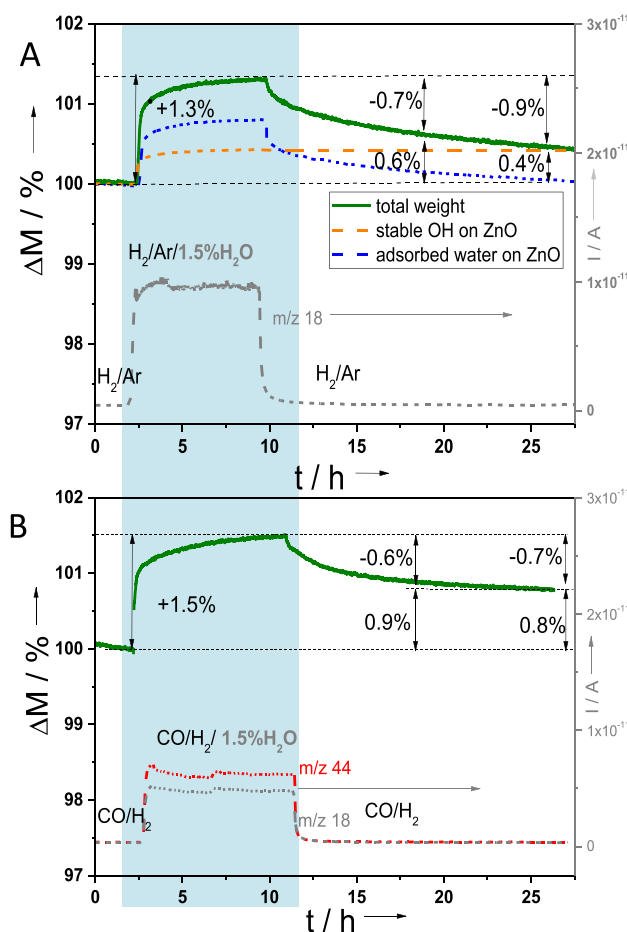


Figure 2. In situ TG of Cu/ZnO:Al at 1 bar, 523 K. Introduction of 1.5 vol % H_2O vapor to (A) 85% H_2/Ar feed (dotted lines visualize the adsorbed H_2O -derived species on ZnO_x) and (B) 14% $\text{CO}/59\%$ $\text{H}_2/27\%$ inert.

Table 1. Theoretical Mass Increase of the Catalyst under the Assumption of a Surface Fully Covered with One Type of Species^a

group/ $M, \text{g mol}^{-1}$	surface stoichiometry	$\Delta M, \text{g \% (Cu sites)}$	$\Delta M, \text{g \% (ZnO sites)}$	full $\Delta M, \text{g \% (Cu/ZnO}_x \text{ sites)}$
$\text{H}_2\text{O}/18$ water	1	0.72	0.49	1.21
$\text{OH}/17$ hydroxy	1	0.68	0.46	1.14
$\text{OCH}_3/31$ methoxy	1	1.24	0.85	2.09
$\text{CHO}/29$ formyl	1	1.16	0.79	1.95
$\text{CHOO}/45$ formate	2/1	1.8/0.9	1.2/0.6	3/1.5

^aPercent of the initial catalyst loading indicated. ^bProposed stable surface species present on the surface.¹³ ^cCalculation performed using the number of Cu sites of $400 \mu\text{mol}(\text{Cu}) \text{g}_{\text{cat}}^{-1}$ as determined by the H_2 transient adsorption technique.¹⁴ ^dThe amount of oxygen vacancies of layered ZnO_x ¹⁵ was measured as the difference of the values obtained from N_2O RFC and H_2 TA as suggested by Schumann et al.,^{14a} and assessed as $273 \mu\text{mol}(\text{ZnO}_x) \text{g}_{\text{cat}}^{-1}$. Calculations are shown in the SI.

ca. 10 h time-on-stream (TOS), a stable mass increase of 1.3 wt % was reached. Switching to H_2/Ar leads to a mass decrease of 0.7 wt % within ≈ 8 h which continued to decrease slowly. An identical experiment was conducted with H_2/CO enriched using 1.5 vol % H_2O . After stabilizing at a mass increase of 1.5 wt %, a mass loss of 0.6 wt % is observed upon switching to H_2/CO again (Figure 2B). The experiments of switching the gas feed (H_2/CO_2 and H_2/CO) and H_2/Ar enriched with 1.5% H_2O were repeated with a Cu/MgO reference catalyst (Figure S3A,B). This catalyst exposes an almost identical Cu nanostructure (compared to $\text{Cu}/\text{ZnO}:\text{Al}$, see Table S2), but the mass uptake in the H_2O -containing feed seems to be negligible (Figure S3B). This makes evident that the mass increase under H_2O atmosphere directly correlates with the presence of ZnO . These findings are already incorporated into Figure 2A, where the mass increase is separated into two contributions from ZnO , adsorbed H_2O and strongly bound OH groups. The weight increase due to the stable OH groups (0.4–0.6 wt %) correlates very well with the calculated values based on oxygen vacancies in ZnO_x (Table 1 and Table S2, 0.5 wt %) and supports our findings. To investigate the possible impact of $p(\text{H}_2\text{O})$ on the mass gain, a series of experiments with different H_2O concentrations in H_2/Ar (up to 2.0 vol %) were conducted (Figure S4). Already at comparably low H_2O concentrations (0.5 vol %), the mass uptake levels off, and a saturation regime is reached. This implies that the experiments described in Figure 2 already reached steady state. In addition, the gained information from the TG curves in Figure 2A,B makes evident that, in Figure 1, when switching between H_2/CO_2 and H_2/CO , the mass loss is also due to the removal of H_2O -derived species. As a consequence, the maximum amount of strongly bound OH groups still present on the ZnO_x surface ranges from 0.4 to 0.8 wt % of the catalyst, again in agreement with our reference experiments (Figure 2A,B, Figure S3, and Table 1). Further, it is very likely that, depending on the gas feed used, carbon-based reaction intermediates are also present. This is supported by the residual mass after switching from H_2/CO_2 to H_2/CO (Figure 1A, stable ad-layer of 1.2 wt %); at least 0.4–0.8 wt % consists of non- H_2O -related adsorbates, namely, carbon-based derivatives (dependent on the stable OH group concentration). The majority of the carbon-derived adsorbates might be placed on the Cu moieties, also in agreement with Cu/MgO reference experiments (Figure S3A).

Figure 3 illustrates the deconvolution of experimental mass changes in different reaction feeds (H_2/CO_2 or CO) to H_2O -derived and carbon-derived.¹¹ Approximately 70% of the ad-layer consists of H_2O -derived species. The amount of carbon-based intermediates is interpreted as stable upon switching to the H_2/CO feed. This 0.6 wt % (or $\sim 30\%$ of the ad-layer) does, very likely, not consist of similar adsorbates, since different mechanisms (and intermediates) are discussed for the hydrogenation of CO and CO_2 .^{3a,6a,b,12} However, it is expected that the CO_2 -related ad-layer is very stable, which hinders its activation in the CO/H_2 feed after consecutive switching, and the exchange might be slow.^{3a} Consistent with a previous spectroscopic analysis,¹³ the remaining layer may comprise –methoxy ($-\text{OCH}_3$), –formyl ($-\text{CHO}$), and/or –formate ($-\text{O}_2\text{CH}$) species balanced with OH groups, in very good agreement with the mass changes and resulting quantitative assessments from our thermogravimetric experiments (Table 1).

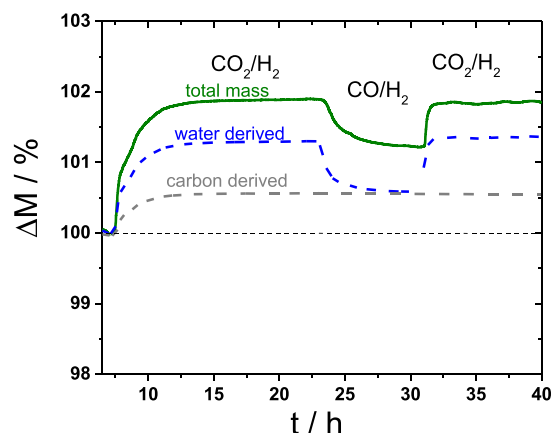


Figure 3. In situ thermogravimetry with different gas feeds [$\text{CO}_2/\text{H}_2/\text{He}$ (12/59/29) and $\text{CO}/\text{H}_2/\text{Ar}/\text{He}$ (14/59/4/23), 120 mL min^{-1}] at 523 K and 30 bar. Dotted lines visualize the possible mass change associated with H_2O - and carbon-derived species.

■ NATURE OF THE CARBON-BASED ADSORBATES

To further clarify the nature of the intermediates adsorbed during catalysis, high-pressure IR experiments were conducted under reaction conditions (30 bar, 523 K) in a cell as already described.¹⁶ To overcome the high noise level caused by the low IR transparency of the catalyst, four spectra with 2048 scans each were averaged for the data evaluation.

The spectra are dominated by the gas phase signals of the applied feeds, namely, CO and/or CO_2 and the corresponding overtones (Figure 4A). With the onset of the reaction, bands due to the reaction product CH_3OH (2960 and 1033 cm^{-1}) become visible and directly make evident the active state of the catalyst within the spectrometer. In addition to this, in the H_2/CO_2 feed, the rotovibrational bands of the rWGS reaction products H_2O (centered at 3780 and 1600 cm^{-1}) and CO (centered at 2143 cm^{-1}) occur. The H_2O signals are strongly decreased under H_2/CO conditions, since CO reacts instantly with traces of H_2O under the formation of CO_2 (Figure 4A, WGS reaction).

Only after correcting for the gas phase products, a meaningful interpretation of surface adsorbates is possible (Figure 4B). In the H_2/CO_2 feed, a broad feature with a maximum at 2890 cm^{-1} and a weaker one at ~ 2600 cm^{-1} are assigned to C–H stretching vibrations and are distinctly different from the CH_3OH band at 2950 cm^{-1} . The clearly visible bands around 1520 and 1390 cm^{-1} are similar to assignments of formate species.¹⁷ The mode around 1520 cm^{-1} corresponds either to formate on the $\text{ZnO}:\text{Al}$ support (or at the interface to Cu) or to its asymmetric stretch vibration on Cu .^{17a} The band at 1390 cm^{-1} is assigned to the symmetric vibration of bidentate formate on Cu . These findings agree well with the bidentate formate C–H modes at 2890 cm^{-1} . The signal at the 2600 cm^{-1} band is typical for C–H stretching modes of formyl species, which is supported by the $\text{C}=\text{O}$ stretching vibration at 1760 cm^{-1} .¹⁸ The shoulder to higher wavenumbers at 2950 cm^{-1} might be related to methoxy groups.¹³ Since the IR bands are rather broad, other carbon-based intermediates like carboxylates cannot be ruled out. The presence of surface O–H groups is evident from IR absorption features around 3500–3700 cm^{-1} partly obscured by the CO_2 overtones and supported by thermogravimetric measurements.

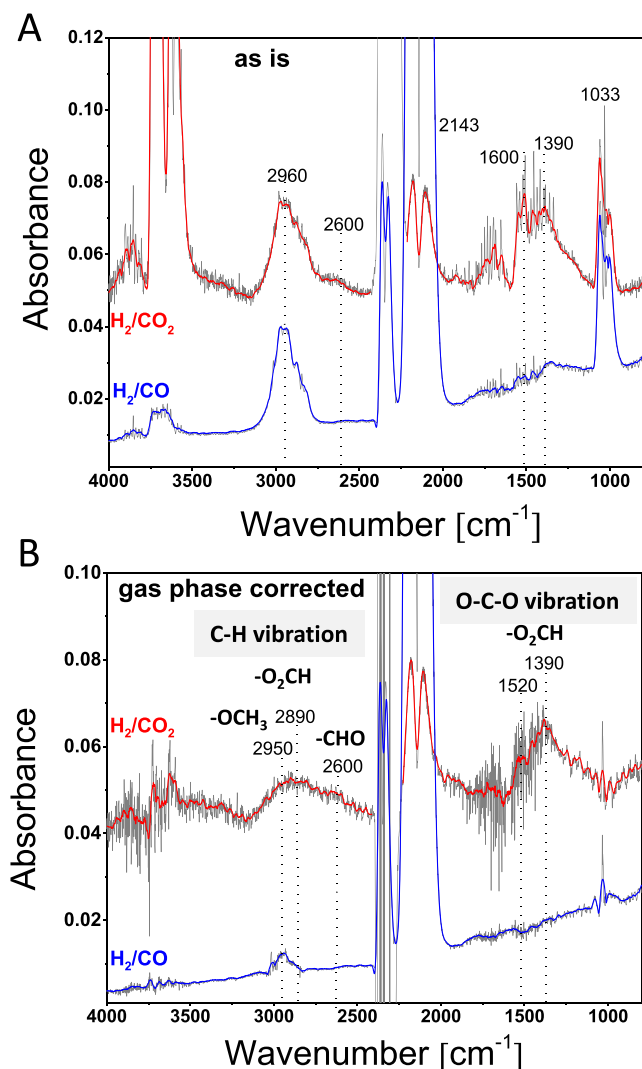


Figure 4. In situ IR spectroscopy at 30 bar and 523 K: (A) H_2/CO_2 feed and H_2/CO feed and (B) with gas phase correction. The colored lines represent the smoothed spectra.

Thus, the results of high-pressure in situ IR spectroscopy in the H_2/CO_2 feed confirm the presence of surface formate groups on Cu (bands at 2890 and 1390 cm^{-1}), possibly on $\text{ZnO}:\text{Al}$ or the interface to Cu (1520 cm^{-1}), methoxy groups (2950 cm^{-1}), and surface hydroxyl groups (~ 3500 cm^{-1}). Carbonates are ruled out since CO_2 does not adsorb at 483 K/523 K and 30 bar pressure (Figure S5B). These findings agree well with the interpretation of the thermogravimetry experiments discussed above, identifying H_2O - and carbon-derived adsorbates on the surface (Figures 1 and 3 and Table 1). The presence of methoxy groups is further supported by the gas phase corrected spectra from the H_2/CO feed (Figure 4B). The pronounced signal at 2950 cm^{-1} is clearly identified as the C–H stretch vibration of the methoxy group, with small contributions of the C–O stretching or bending modes at 1020 cm^{-1} and not part of the gas phase CH_3OH signals. In addition, no formate contributions are detected. Changes in the range of 3500 cm^{-1} due to additional OH groups (i.e., $\text{Zn}-\text{OH}$ groups, in comparison to the H_2/Ar reduction mix) are also absent. This means that, under different feed gas compositions (H_2/CO versus H_2/CO_2), the nature of the adsorbates is differently pronounced. The intermediate

concentration increases with higher temperatures and reaction rates (Figure S6, 523 versus 483 K), which is an indication for a surface accumulation. To mimic the switch of the gas feed applied in Figure 1 ($\text{H}_2/\text{CO}_2 \rightarrow \text{H}_2/\text{CO} \rightarrow \text{H}_2/\text{CO}_2$), an adapted transient experiment was conducted in the IR spectrometer (Figure 5A,B). Starting from a H_2/CO feed

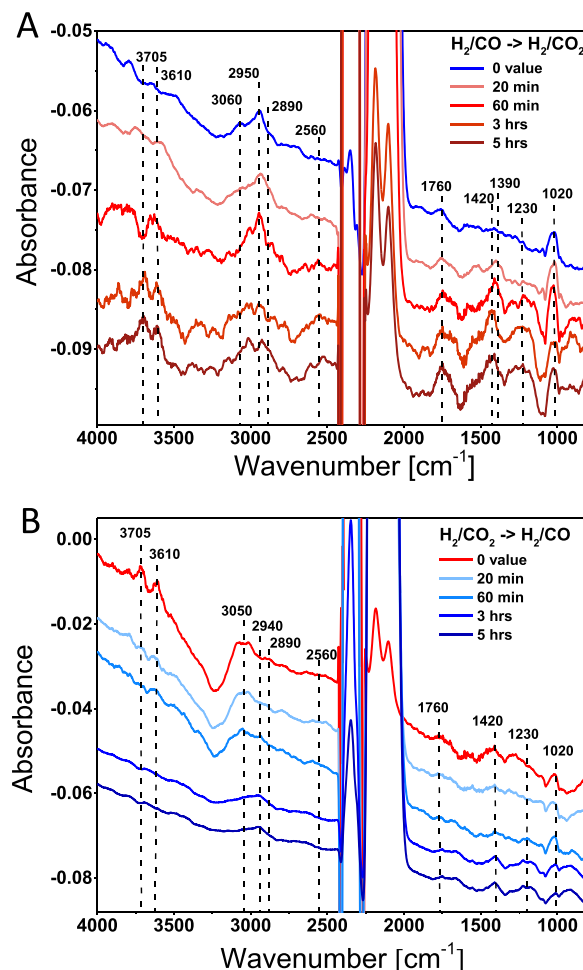


Figure 5. In situ IR spectroscopy at 523 K and 30 bar, upon switching the gas phase from (A) H_2/CO (blue) to H_2/CO_2 (red) and (B) from H_2/CO_2 (red) to H_2/CO (blue). The curves represent smoothed spectra.

(Figure 5A, blue curve), a change to H_2/CO_2 leads also to a change of the adsorbed species (Figure 5A, red curves). From a methoxy dominated surface (2950 cm^{-1} , 1020 cm^{-1}) with contributions from a carboxylate species (3040 cm^{-1} , 1760 cm^{-1} , 1230 cm^{-1}),^{3b} formate (2890 cm^{-1} , 1390 cm^{-1}) and formyl (2600 cm^{-1} , around 1760 cm^{-1}) species start to grow. As a function of time, the latter become more intense, and the OH/ H_2O influence is clearly visible between 3500 and 3750 cm^{-1} (O–H stretching modes) and 1500–1750 cm^{-1} (O–H bending modes). Likely, the asymmetric modes of formate intermediates contribute to the shoulder at 1520 cm^{-1} and shift the maximum at 1390 cm^{-1} (symmetric formate vibration) to higher wavenumbers (1420 cm^{-1}).⁹ The inverse experiment (Figure 5B) clearly shows that a gas switch from the H_2/CO_2 to H_2/CO feed does not lead to a complete exchange of the carbon-derived species toward methoxy groups but to a removal of the H_2O -derived species (e.g., above 3500

cm^{-1}). Still, after hours, absorption features of other oxygenates are present. The exchange of surface intermediates triggered by a change of the gas phase seems to be rather a process of hours,¹⁹ which is in line with the thermogravimetric kinetics and, e.g., the recovering of a Cu/MgO catalyst after poisoning with CO_2 .^{3a} The formation of, e.g., the H_2/CO_2 -induced surface intermediates directly after activation seems to be a rather fast process and not resolvable on the minute scale (Figure S5A).

Figure 6 shows additional experiments in the thermobalance, where from the H_2/CO feed (green curve) the same mass gain

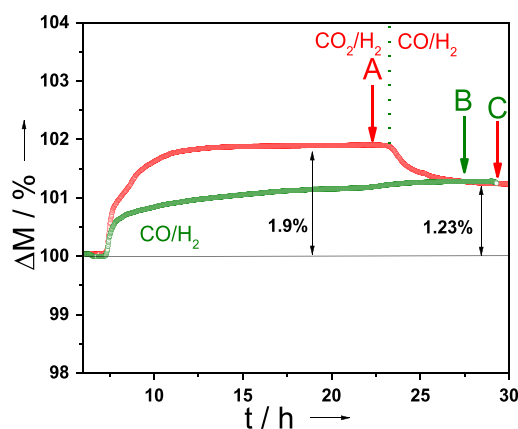


Figure 6. In situ TG experiments at 30 bar and 523 K, exposures starting from H_2/CO (green) and H_2/CO_2 (red). Letters indicate the points where the titration experiments in a fixed bed reactor were performed.

is reached as upon switching to H_2/CO after introducing H_2/CO_2 (red curve). With respect to the assignments made by high-pressure in situ IR experiments, the mass gain in H_2/CO is interpreted as mainly caused by methoxy groups on Cu sites, which would allow for a mass increase in the range of 1.24% according to Table 1. It is very likely that also OH groups contribute as a minor fraction to the mass increase and that the Cu surface is not completely covered since H_2 activation has to be possible.²⁰ Further, we propose different surface adsorbates in H_2/CO after H_2/CO_2 treatment (Figure 6, state C) compared to only the H_2/CO feed (Figure 6, state B). This means that the accumulated adsorbates, e.g., formyl- and formate groups (Figure 6, state A), are in part substituted by methoxy groups during H_2/CO treatment at 30 bar, also made evident by IR spectroscopy (Figure S5B).

■ REACTIVITY OF THE SURFACE AD-LAYER

To probe the stability and difference in origin of the carbon-related species formed in H_2/CO_2 and H_2/CO feeds, a transient surface titration technique analogous to that reported by Yang et al.^{6a,21} was applied. In addition, as shown previously in our purging experiments,^{3a} a sustained methanol production for several hours was observed when switching from the CO_x/H_2 feed gas to H_2/Ar .

Herein, after reaching steady state at 30 bar, the catalysts were purged with Ar gas until reaching a zero signal (baseline, monitored by online GC). Subsequently, H_2/Ar mixtures were introduced to mobilize possible surface intermediates. Figure 6 shows the different steady-state points A, B, and C for which the investigations were performed. The experimental results are shown in Figure 7, also named as A, B, and C. In Figure 7A

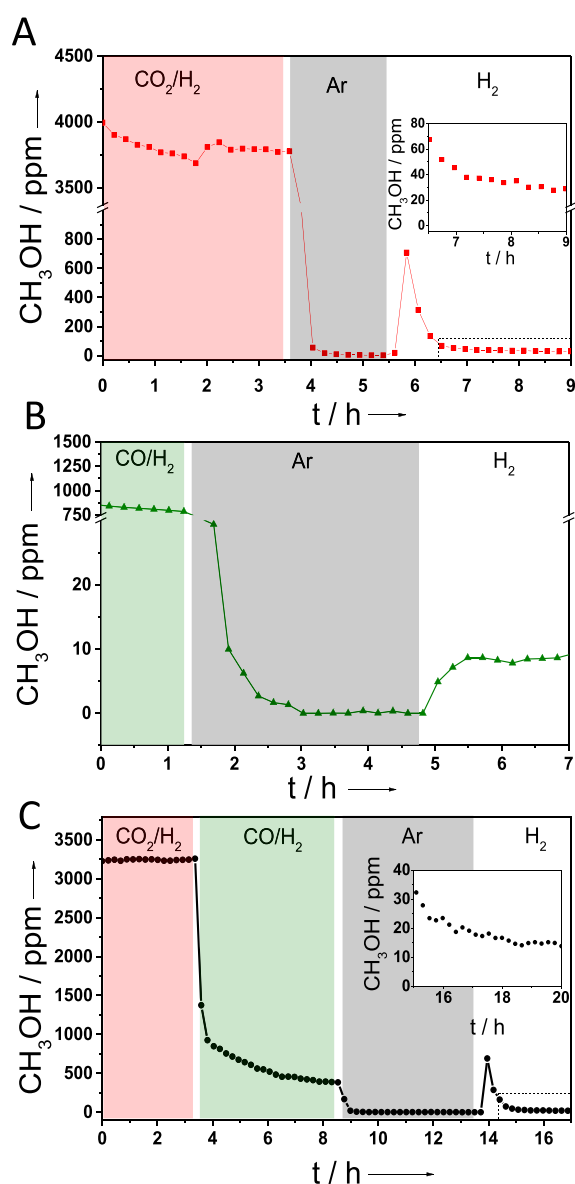


Figure 7. H_2 surface titration experiments after purging with Ar from steady state at 523 K and 30 bar. Starting in the (A) H_2/CO_2 feed, (B) H_2/CO feed, (C) H_2/CO_2 feed, and followed by the H_2/CO feed.

a steady-state CH_3OH concentration of ~ 3800 ppm is reached, and upon switching to Ar within 0.5 h, no traces of CH_3OH are detected anymore. Introducing H_2 finally leads to an increase of the CH_3OH concentration up to several hundred ppm. Still, after hours, low CH_3OH concentrations are detected (see the inset in Figure 7A). Besides the CH_3OH evolution also H_2O formation is observed (Figure S7B), which is in accordance with the interpretation of the in situ thermogravimetric results (Figures 1 and 2B). Performing the identical experiment starting from a H_2/CO feed (Figure 7B), a steady-state concentration of ~ 800 ppm is measured. After purging with Ar and switching to H_2/Ar , a relatively lasting increase of the CH_3OH concentration to ~ 10 ppm is detected, and no additional H_2O is detected (Figure S7B). With respect to the surface titration from the H_2/CO_2 feed, a different kinetic behavior is clearly visible (see also MS traces in Figure S7A,C). Interestingly, the carbon-derived adsorbates

formed under H_2/CO_2 conditions stay on the surface even after introducing H_2/CO for hours, made evident by an identical profile and concentration of CH_3OH while titrating with H_2/Ar after purging in Ar (Figure 7C, Figure S7A MS signals). This is additionally supported by a lower catalytic activity in the H_2/CO feed if H_2/CO_2 was applied before (Figure S9, CO_2 -derived intermediates block active sites). A similar purging experiment was conducted in the thermobalance (Figure S8) by switching from a H_2/CO_2 feed to H_2/CO and finally purging with H_2 (see also Figure 1). According to the results discussed above (Figure 2A), the surface is still covered with strongly bound OH groups and carbon-derived species. The introduction of H_2 leads to a fast mass decrease within the first 30 min followed by a slow one (lasting for hours). This interpretation is in very good agreement with the results in Figure 7A,C and Figure 7A,B, where a fast $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ evolution occurs followed by a slow and lasting decrease. Generally, the quantity of adsorbed carbon-derived intermediates (Table 1) and the amount of CH_3OH formed upon surface titration are in an acceptable agreement.

The conversion of, e.g., the methoxy groups (see also Figures 7B and 4B) formed likely on the Cu sites ($400 \mu\text{mol g}_{\text{cat}}^{-1}$) would lead to a calculated constant formation of 10 ppm of CH_3OH lasting for 20 h. Another selected example is the CH_3OH formation of H_2/CO_2 -derived adsorbates (Figure 7C). Surface titration with H_2/Ar leads to a calculated constant CH_3OH concentration of 65 ppm for 5 h (based on the available Cu sites of $400 \mu\text{mol g}_{\text{cat}}^{-1}$). Again, a reasonable agreement between the surface titration experiments (Figure 7) and the quantitative assessment from the thermobalance (Figures 1 and 3) is obtained.

■ GENERAL DISCUSSION AND CONCLUSION

On the basis of the results gained from high-pressure in situ thermogravimetric experiments (Figures 1–3, Table 1), the quantitative assessment of the adsorbates is in the range ~ 1 –2 ML (monolayers) with respect to the surface titration experiments. The carbon-based ad-layer (~ 0.25 ML) is in fair agreement with the findings interpreted by Yang et al. and also very likely located on the Cu moieties.^{6b} As we discussed the activated state of the catalyst under steady-state conditions, a significant amount of the surface adsorbates consist of water-derived species (at least when a CO_2 -containing feed is applied). Consequently, for any fundamental discussion, the role of OH groups and H_2O has to be considered. This interpretation is confirmed by in situ high-pressure IR spectroscopy, where under realistic conditions the presence of carbon- and $\text{H}_2\text{O}/\text{OH}$ -derived intermediates was identified. In addition, surface titration experiments showed that the carbon-based intermediates are convertible into CH_3OH upon titration with H_2/Ar . The oxygenates formed under the CO_2 -containing atmosphere seem to be quite stable, since they are still present after changing the feed gas to H_2/CO . Solely under H_2/CO atmosphere methoxy groups are highly populated. The titration of methoxy to CH_3OH is a very slow process (high reaction barriers),^{2f,12} which would explain the poor reaction rate of CH_3OH in H_2/CO (800 ppm versus 4000 ppm for H_2/CO_2) and the lasting CH_3OH decrease upon titration (Figures 4B and 7). The surface titration experiments from the CO_2 -based feed (Figure 7A,C, Figure S8A,B) show that the carbon-based adsorbates are convertible into CH_3OH and H_2O . The different kinetics upon titration with respect to the CH_3OH formation under the H_2/CO feed suggest that

another carbon intermediate is involved and that $\text{H}_2\text{O}/\text{OH}$ groups are needed for its conversion (see Figure S7B, no H_2O evolution since CO_2 free). The importance of $\text{H}_2\text{O}/\text{OH}$ for the CH_3OH formation was already indicated for Cu systems.^{6b,c} Since we investigate a high-performance Cu/ZnO:Al, the residual strongly bound OH groups are located on the ZnO moieties of the catalyst (Figures 1 and 2). Kattel et al.^{2f} already suggested the relevance of OH groups located on ZnO at the interface to Cu. Our findings from high-pressure in situ IR, thermogravimetry, and surface titration experiments support this interpretation. In this context, the promoting role (electronic and structure)^{14a,22} of ZnO has to be extended to a mechanistic one, where $\text{H}_2\text{O}/\text{OH}$ groups are crucial for the activation of, e.g., formates, formyl, or carboxylates (CO_2 -derived oxygenates). To what extent the detected intermediates are part of the rate-determining step and reaction mechanism is beyond the scope of this article. The apparent activation energy of this catalyst for CH_3OH ($E_{\text{A}} = 53 \text{ kJ mol}^{-1}$, determined under differential conditions, Figure S10A,B) matches perfectly with the literature values.²³ For H_2O a comparably high value of $E_{\text{A}} = 75 \text{ kJ mol}^{-1}$ is measured, which is interpreted as a proxy of the rWGS contribution,^{2d} resulting from the CO_2 hydrogenation to CO and/or CH_3OH (Figure S10B). However, as the importance of H_2O for the CH_3OH formation was already made evident, we tentatively interpret the adsorption–desorption processes of accumulated H_2O -derived species as strongly rate influencing (activation barrier $\sim 1 \text{ eV}$)^{6c} and possibly defining for the lowest temperature of operation.

In summary, our results make evident the formation of a reactive ad-layer with considerable lifetimes on the surface of a high-performance Cu/ZnO:Al catalyst during and after CO_2 hydrogenation. The present observations demonstrate for the first time a quantitative assessment of the catalytically formed intermediates under realistic conditions (1.9 wt % or 1–2 ML). An exchange of accumulated intermediates is a process lasting for hours. This is in agreement with surface titration experiments, where, e.g., a fraction of a ML of carbon-derived intermediates is converted with H_2 within hours. H_2O -derived species play a crucial role within the reaction network as intermediates, reaction participants, and possibly rate-determining reactants. Further, the accumulation of H_2O on Cu/ZnO catalysts might also be one reason for its limited applicability at milder temperatures (thermodynamically more favored conditions). The combined approach of in situ thermogravimetry (quantitative), in situ IR spectroscopy (qualitative), and surface titration experiments enabled the identification of another promoting effect of ZnO, since the CO_2 -derived reaction intermediates are only activated when Zn–OH is present. Our experimental data and their corresponding interpretation are in very good agreement with the literature and further clarify some ambiguities since investigations were performed on a real Cu/ZnO:Al catalyst under meaningful conditions. The current work may be considered as an example of the development and implementation of a new diagnostic tool based on a well-established method, providing highly relevant in situ data for a reliable mechanistic/kinetic discussion and modeling in the future.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b01241.

Experimental section and additional data and figures including reference measurements, thermobalance experiments, impact of the $p(\text{H}_2\text{O})$, IR reference experiments, surface titration experiments, and catalytic data (PDF)

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Notes

The authors declare no competing financial interest.

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