Following the structure of copper-zinc-alumina across the pressure gap in carbon dioxide hydrogenation

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Copper-zinc-alumina catalysts are used industrially for methanol synthesis from feedstock containing carbon monoxide and carbon dioxide. The high performance of the catalyst stems from synergies that develop between its components. This important catalytic system has been investigated with a myriad of approaches, however, no comprehensive agreement on the fundamental source of its high activity has been reached. One potential source of disagreement is the considerable variation in pressure used in studies to understand a process that is performed industrially at pressures above 20 bar. Here, by systematically studying the catalyst state during temperature-programmed reduction and under carbon dioxide hydrogenation with in situ and operando X-ray absorption spectroscopy over four orders of magnitude in pressure, we show how the state and evolution of the catalyst is defined by its environment. The structure of the catalyst shows a strong pressure dependence, especially below 1 bar. As pressure gaps are a general problem in catalysis, these observations have wide-ranging ramifications.

he improvement of heterogeneous catalysts is central to sustainable development of energy conversion and the production of chemicals. Historically, such development relied heavily on trial-and-error-based research. More recently, advances in characterization methods allowed the study of catalysts under pretreatment and catalytic conditions, thus in situ and operando. This permitted fundamental insights into the state of the catalyst whilst it is actually working¹. Ideally, a detailed understanding of the mechanisms of the desired catalytic reaction emerge. Many of these methods, such as electron microscopy and X-ray photoelectron spectroscopy, remain limited in their routine application to pressure regimes in the millibar range²⁻⁵; others, however, such as X-ray absorption spectroscopy (XAS) and X-ray diffraction, suffer no restrictions in this sense and can be applied at pressures well above ambient⁶⁻⁹. On the industrial scale, key chemical processes are operated far from millibar and ambient pressure ranges: for instance, the Fischer-Tropsch synthesis (10-25 bar)¹⁰, the Haber-Bosch process (150-300 bar)¹¹, the (high temperature) water-gas shift reaction (60-80 bar)¹² and methanol synthesis (50-150 bar)¹³. These high pressures are required to shift thermodynamic equilibria and reaction kinetics towards the desired products, thereby increasing efficiency and productivity, and reducing cost. This results in a considerable discrepancy between the technologically realizable pressure range of many in situ and operando studies, and the actual pressures applied in the industrial process: the long-recognized issue of the pressure gap (Fig. 1a)¹⁴. There have been many attempts to relate the kinetic and structural information obtained on model surfaces, often single crystals at low pressures, to real catalysts under actual operation conditions, sometimes with remarkable success¹⁴⁻¹⁸. However, extrapolation of results to much higher pressures is only possible if the reaction is structure-insensitive and if the catalyst structure and reaction mechanism are preserved across the pressure range¹⁹. Although it is widely accepted that the structure of

a catalyst is different in ultra-high vacuum (UHV) than under much higher pressures²⁰, surprisingly few studies have systematically bridged the pressure gap²¹⁻²³, especially for non-model systems.

The copper-zinc-alumina (CZA) catalyst is an archetypal multicomponent catalyst that is heavily employed in some of the above-mentioned processes, most notably methanol synthesis from feeds containing carbon monoxide, carbon dioxide and hydrogen. Copper and zinc exhibit synergies that results in a catalytic performance that far exceeds that of the single components. Understanding the origin of this synergism can provide a foundation for its greater exploitation²⁴. However, after decades of intensive research, no consensus exists regarding the active structures present within this catalyst. This lack of understanding severely hampers advancement through rational design. Several models have been proposed to explain the origin of the components' synergism, which have yet to be satisfactorily resolved²⁵⁻²⁸. Disagreements exist with regard to: the reduction temperature of the copper(II) oxide and zinc oxide phases;^{29,30} the nature of the active site for carbon dioxide hydrogenation;^{2,25,31,32} and the catalytically relevant structure of the resulting copper-zinc composite^{31,33-35}. Either the presence of a copper-zinc alloy phase^{29,31,36,37}, or interfacial sites between metallic copper and zinc oxide nanoparticles^{2,25,33,34,38-41} are seen to be responsible for the superior carbon dioxide hydrogenation behaviour of this system (Fig. 1b). Sources of these diverse opinions may be differences in experimental procedures used to study the catalyst, in the structure of the (model) catalyst and in the applied measurement conditions. From studies that have focused on the temperature-dependent CZA structure^{30,42}, we do know that CZA is sensitive to the conditions under which it is studied. However, while this temperature dependence does not represent a technical problem for in situ and operando methods, the application of catalytically relevant pressure regimes remains challenging. Conditions of characterization range from in situ studies in the millibar^{2,31,43}, ambient³¹ and 10-bar to

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Fig. 1 Pressure dependence as the source of differing opinions on CZA catalysts. a, Schematic depictions of the pressure gap existing between in situ characterization methods and conditions applied in industrial processes. **b**, Two competing models regarding the fundamental mechanisms at work, and the nature of the active sites, in CZA catalysts for methanol synthesis. **c**,**d**, Cu (**c**) and Zn (**d**) K-edge XANES obtained during temperature-programmed reduction (heating rate 5 °C min⁻¹) using partial pressures of H₂ from 1 mbar to 10 bar. The rainbow colour scale represents increasing temperature from 25 °C (purple) to 500 °C (dark red) in steps of 5 °C.

20-bar^{37,44} pressure ranges. Many examples of ex situ analyses also exist based on high-pressure treatment with subsequent inert transfer of the sample to a UHV set-up^{25,29,33,34,45}.

Herein, we present a study on an industrial CZA catalyst, based on in situ and operando X-ray absorption spectroscopy (XAS)³⁰ at both Cu and Zn K-edges. We reveal the changes in composition and electronic structure in the copper and zinc components of the catalyst during reduction in hydrogen and carbon dioxide hydrogenation over four orders of magnitude of pressure (from 1 mbar to 10 bar). Within the studied pressure range, it is apparent that the phases present, the kinetics of their interconversion and the morphology of the CZA catalyst are extremely sensitive to the applied pressure and temperature. As a result, experiments carried out in very different pressure regimes are likely to capture the state of the working catalyst in rather different ways and lead to different conclusions as to how the material functions.

Results

Dynamic reduction behaviour of CZA at different pressures. We first focused our attention on the initial reduction of CZA, which is required to activate the catalyst³¹. A commercially available industrial catalyst precursor composed of 64% copper(II) oxide, 25% zinc(II) oxide and 10% alumina and 1% magnesium(II) oxide was reduced in situ under variable pressures of hydrogen (1 mbar $\le p \le 10$ bar) to 500 °C (heating rate 5 °C min⁻¹). This temperature range includes the temperatures relevant for catalysis (200–300 °C) and those that have been used in the literature to induce CuZn alloy formation (up to 500 °C)^{30,46}. The evolution of the structure of copper and zinc was followed by the rapid collection (1 Hz) of both Cu and Zn K-edge XAS⁴⁷ in a single scan. The overall evolution of the sample, from the

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perspective of the Cu and Zn K-edge X-ray absorption near-edge structure (XANES), is shown in Fig. 1c,d. The XANES regions enable us to specify and quantify the oxidation states in both elements: 0, +1 and +2 in the case of copper, and 0 and +2 in the case of zinc. The starting point in the temperature-programmed reduction (TPR) shows that, independently of the pressure of hydrogen, both copper and zinc are present in the +2 state. At each pressure, by the time the TPR is concluded, the copper has been reduced and exists as metallic copper(0). In the case of the Zn K-edge, however, the end-point is a distinct function of the hydrogen pressure. Under 1 mbar of hydrogen pressure, although there are changes in the Zn K-edge XANES, no significant change in the zinc (+2) oxidation state is observed even at 500 °C. In this case, close inspection of the edge indicates a very small, lower energy shoulder, which develops at higher temperature. However, by 100 mbar of hydrogen pressure, this lower energy feature to the XANES has become far more pronounced by the end of the experiment. This spectral feature continues to increase as the experiment is repeated at increasing hydrogen pressures of 1, 5 and, finally, 10 bar. Moreover, from 100 mbar these changes are accompanied by distinct changes in the first EXAFS feature at around 9,700 eV (Supplementary Fig. 7). Both of these observations, made as a function of temperature and pressure, indicate that substantial changes in both the oxidation state of zinc and the overall structures occur above 100 mbar.

The speciation of both copper and zinc (Fig. 2) was quantified as a function of temperature and hydrogen pressure using a principal component analysis coupled with iterative target testing (PCA-ITT, Supplementary Fig. 8)⁴⁸. This analysis permits the XANES of both elements to be semiquantitatively deconvolved into their probable components on the basis of spectra derived from a number of bulk

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Fig. 2 | Composition of the copper and zinc phases during reduction in hydrogen. a,**b**, Relative fractions of copper (**a**) and zinc (**b**) components as a function of temperature during TPR performed under hydrogen partial pressures from 1 mbar to 10 bar, as derived from PCA-ITT analysis. Panel **b** contains the normalized peak area of the Zn-Cu(/Zn) first shell for a CuZn alloy structure as an indicator for CuZn alloy formation. **c**, The first derivative of the copper(\square) oxide reduction with temperature, with varying the partial hydrogen pressure. The onset of reduction decreases by about 50 °C per hydrogen pressure decade. **d**, Plot of the relationship between the temperature of maximum copper(\square) oxide reduction rate and hydrogen pressure. (The *y* axis error bar is the estimated impression of \pm 10 °C in the temperature measurements due to displacement of the thermocouple in between different experiments).

standards, namely copper(II) oxide, copper(I) oxide, metallic copper, Cu_{0.66}Zn_{0.33} alloy, zinc hydroxide carbonate and zinc oxide. This approach reveals how the development of the system is linked to the pressure of hydrogen. From the perspective of copper (Fig. 2a), within this analysis three components were resolved. They correspond to the three oxidation states of copper (0, +1 and +2). The reduction of copper(II) oxide follows a sigmoidal shape at all pressures. The +1 oxidation state is observed as an intermediate in the reduction process at hydrogen pressures of ≤ 100 mbar. At pressures above 100 mbar, the intermediate becomes progressively more transient and the degree to which it can be observed is greatly reduced. The strong effect of the partial pressure of hydrogen on the kinetics of reduction is reflected in this temperature-programmed experiment by the temperatures at which the various components appear or are consumed. Figure 2c illustrates this dependence, using the derivative of the copper(II) oxide component. At a hydrogen

pressure up to 1 bar, the derivative resolves the reduction of the copper phase into two events, which eventually merge (at 5 and 10 bar) into a single event. At 1 mbar, the maximum rate of reduction, and concurrent formation of copper(0), occurs at \sim 300 °C. At 10 mbar pressure this point is shifted down by \sim 50 °C. This pattern of behaviour continues as the pressure of hydrogen is increased. At 10 bar, this temperature has dropped by over 250 °C relative to the 1-mbar case, to \sim 150 °C. The extreme nature of the pressure dependence of the reduction of the catalyst is displayed in Fig. 2d, which reveals that the maximum in the copper(II) oxide reduction rate roughly follows a power law in the pressure range between 1 mbar and 5 bar.

The Zn K-edge XANES (Fig. 2b) reveals a more complex reduction behaviour. Three components can be identified, only one of which is indicative of reduced zinc (labelled as $Zn_{reduced}$ and modelled using the Zn K-edge XANES derived from a $Cu_{0.67}Zn_{0.33}$ foil). The other two components are due to zinc in a +2 oxidation

state, and correspond to zinc oxide and zinc that is hydroxylated and carbonated (modelled using respective powder standards). Complementary diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) confirms the presence and subsequent removal of absorbed water and carbonates during the TPR (Supplementary Figs. 10 and 11). The detection of metallic zinc by the PCA-ITT analysis is based on a CuZn alloy standard (Zn_{reduced}). It is mainly the coupled and inverse behaviour of two features in the Zn K-edge XANES region at 9,656 and 9,660 eV that is responsible for identification of this component. Similar features have, however, also been found in oxygen-vacancy-rich zinc(II) oxide structures in the absence of copper^{49,50} and for other structural rearrangements in the zinc oxide phase⁵¹. We consider the generation of oxygen vacancies to be the most likely explanation. Thus, mere analysis of the XANES is insufficient to differentiate between the formation of oxygen vacancies/structural rearrangements and the formation of a CuZn alloy phase. An examination of the EXAFS region provides more definitive insight into the formation of the alloy phase. The k³-weighted Fourier transform (FT) of the Zn K-edge EXAFS region (Fig. 3a) of the samples studied in situ at room temperature after the TPR experiment, identifies a Zn/Cu shell at around 2.5 Å, which is indicative of the formation of a $Cu_{r}Zn_{1-r}$ alloy phase. From the EXAFS, the CuZn allov is only definitively observed at or above 100 mbar. However, even after reduction in 10 bar at 500 °C, some residual oxygen coordination is still observed from the perspective of the Zn K-edge. Thus, not all of the zinc(II) oxide is reduced at any of the pressures investigated. Inspection of the Cu-Cu/Zn distance of the samples at room temperature after TPR (Fig. 3b), determined from the Cu and Zn K-edge EXAFS, is therefore a reliable means to estimate the fraction of zinc present as CuZn after reduction at 500 °C (0% below 100 mbar, 45% at 100 mbar, 78% at 1, 5 and 10 bar). Consequently, the shell integral of the Zn/Cu shell is also depicted in Fig. 2b. The formation of reduced zinc is always found to be much slower than reduction of copper for any given pressure, and is consistently preceded by desorption of water and release of carbon dioxide from the carbonates (Supplementary Figs. 10 and 11). The formation of reduced zinc appears at pressures above 100 mbar shortly after the initial formation of copper(0). However, the detection of a CuZn alloy (from EXAFS analysis) occurs at higher temperatures than the detection of reduced zinc oxide; at 430°C in 100 mbar and at 300 °C above 1 bar (Supplementary Fig. 12). We estimate that the EXAFS analysis can detect fractions of Zn in the alloy phase above 5%, which corresponds to an alloy stoichiometry of Cu₆₀Zn (Supplementary Note 3), and that surface alloy formation may also be sensitively identified as a result of the nanosized nature of the CZA catalyst (copper and zinc oxide crystal size ≈ 5 nm). Whilst for experiments above 1 bar, from the point of view of speciation, only minor differences can be seen for the transformation of copper and zinc in the system, the analysis of the EXAFS region of both the Cu and Zn K-edge (Supplementary Figs. 2-6) reveals structural differences in the sample throughout the whole pressure range studied. Figure 3c depicts the coordination number (CN) derived through analysis of the EXAFS for Cu-Cu(Zn) scattering. The exact values of the CN should not be considered as absolute, since there is a strong correlation between the Debye-Waller factor and the CN obtained by EXAFS fitting (Supplementary Note 1). However, the trends observed in the evolution of the CN do have a real physical meaning. From 1 mbar to 10 mbar, the CN increases from below 6 to above 9. This discontinuity occurs without any alloy formation at either pressure, as indicated by the bond distances, which are related to the scattering phase and which may be determined in a precise manner (Supplementary Note 1). Therefore, this discontinuity is indicative of a radical change in the nature of the reduced copper, probably as a result of a change in average particle size and/ or morphology, which takes place in the absence of any alloy formation (Supplementary Note 5). From 10 mbar and above, the CN is

seen to gradually decrease with increasing pressure. This probably originates from increases in both static and thermal disorder within the copper phase and the migration of reduced zinc into the copper towards alloy formation. Such gradual changes in CN might also be partially related to a decrease in particle size and/or morphology. Longer reduction times than those applied in the TPR experiments could lead to further reduction of the catalyst. This is especially interesting for reduction at 260 °C, which is the typical temperature applied for catalyst pretreatment and industrial operation. The catalyst was treated in a laboratory-based reactor at three different hydrogen pressures at 260 °C: at 10 bar for 24 h, at 1 bar for 24 h and at 1 mbar for 72h. Subsequently, the catalysts were transferred in an inert atmosphere to the synchrotron for XAS measurements. XANES and EXAFS analyses (Fig. 3d and Supplementary Fig. 21) show that the increased reduction time led to CuZn alloy formation at 1 and 10 bar. The structure and speciation obtained from these two pressures are similar. The CuZn alloy formed contains around 40% of the Zn species, which corresponds to a Cu_{6.4}Zn alloy. In contrast, after 72-h reduction under 1 mbar hydrogen pressure, the copper is present as metallic copper, and no zinc reduction, and thus no alloy formation, was detected. Zinc is exclusively present as cationic zinc, leading to a fundamentally different structure. Therefore, at pressures below 1 bar we observe structural differences as a function of pressure that cannot be bridged by any experimentally reasonable timescale. Overall, the TPR experiments revealed that the evolution and final structural composition of the CZA catalyst during reduction are strongly pressure dependent over the whole pressure range studied (Fig. 3d).

Isothermal reduction behaviour. Thus far our analyses have revealed that the use of different pressure regimes results in fundamentally different structures, which arise to a large extent as a result of the pressure dependence of the transformation kinetics. Isothermal reduction experiments, which provide a deeper insight into the kinetic character of reduction processes, were performed at 1 and 10 bar (Fig. 4). The temperature was chosen to be 150 °C for two reasons. First, 150 °C is a temperature at which CZA catalysts have been evaluated for methanol productivity at 1 bar (ref. ³¹) and, second, our TPR experiments revealed that, for 1 and 10 bar, the onset of all major transformations is 150 °C. In the copper reduction, two kinetic regimes (Fig. 4a,c) are visible at both pressures. However, the timescales on which they operate are very different. Initially, there is a phase of accelerating reduction, which indicates an autocatalytic process^{52,53}, although dependence of the reduction process on particle size may also contribute to the observed behaviour. In this regime, the formation of copper(I) oxide, as a short-lived intermediate, occurs at both pressures. The reduction of the copper and transformations of the zinc appear to be related. From these measurements, we can further assess the rates of the reduction process in terms of how they relate to the pressure of hydrogen (Supplementary Fig. 19). The highest rates at each pressure differ by a factor ~14.5, suggesting a rate dependence of $r(CuO) \propto C(H_2)^{-1.4}$ (with r(CuO) as the rate of copper(II) oxide reduction and C(H₂) as the hydrogen concentration). This matches the dependence on hydrogen pressure derived from the TPR experiments (Fig. 2d). The two-step reduction can be interpreted as the result of a nucleation-controlled initial autocatalytic phase⁵², which is followed by a second slower phase where the whole copper(II) oxide surface is reduced to metallic copper and the reduction follows a contracting sphere model⁵⁴ (Fig. 4d). Both the autocatalytic and the contracting sphere phase can have orders of reaction of 1 and above. However, alternative explanations may exist. A similar trend can be observed for consumption of the zinc(II) hydroxide carbonate species and the formation of zinc(II) oxide and reduced zinc species (Fig. 4b). In this case, the rates change by a factor of ~10 between 1 and 10 bar, suggesting a first-order dependence on



Fig. 3 | Structure of the CZA catalyst as a function of hydrogen pressure. a, Fourier-transforms of the k³-weighted Zn K-edge EXAFS after reduction to 500 °C (measured, as a function of hydrogen pressure, post-reduction at room temperature). In EXAFS, CuZn alloy formation becomes apparent at 100 mbar. b, The M-M (M=Cu, Zn) distance derived from the Cu and Zn K-edge measured for the samples at room temperature after the H₂-TPR experiment. **c**, The M-M (M=Cu, Zn) CN, derived from the Cu and Zn K-edge (measured, as a function of hydrogen pressure, post-reduction at room temperature). **d**, Scheme of the evolving structures at different pressures during our H₂-TPR experiment (heating rate 5 °C min⁻¹) and after long-time treatment at 260 °C. Error bars in **b** and **c** represent the fitting error based on EXAFS fitting.

hydrogen pressure. The removal of water and carbon dioxide is found to be incomplete at this temperature and timescale. Subsequent to this experiment the gas atmosphere was changed again to argon and the sample was heated to 260 °C, the temperature of the industrial process. The gas atmosphere was then switched back to hydrogen. The copper speciation did not change, since the copper was already in a metallic state. However, the zinc phase was further transformed (Fig. 4e). At both pressures the zinc(II) hydroxide carbonate is immediately consumed. At 1 bar, this rapid transformation occurs via the formation of both zinc(II) oxide and reduced zinc species. After the initial increase, the formation of reduced zinc proceeds at the expense of zinc(II) oxide at a slower rate. At 10 bar, the transformation occurs directly by the formation of reduced zinc. These findings show that the associated rates of transformation remain strongly pressure dependent above 1 bar.

Methanol synthesis from hydrogen and carbon dioxide. Finally, we studied the effect of pressure on the catalyst structure under

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Fig. 4 | Reduction kinetics of the CZA catalyst. Reduction kinetics studied after a switch from argon gas atmosphere to pure hydrogen at 1 and 10 bar. **a,b**, The evolution of copper (**a**) and zinc (**b**) species at 150 °C. **c**, The magnified version of the evolution of the copper species at 10 bar. The formation of copper(1) oxide occurs at both pressures. **d**, The two regions of different reduction rates suggest a change in reduction regime from a nucleation-controlled autocatalytic regime to a diffusion-limited shrinking core model. Subsequent to this experiment the gas atmosphere was changed again to argon and the sample was heated to 260 °C. At 260 °C the gas atmosphere was switched to hydrogen. **e**, Showing the evolution of the zinc species at 260 °C.

carbon dioxide hydrogenation conditions (H₂:CO₂ of 3:1). The catalysts were pretreated in hydrogen at the respective pressure (1 mbar-10 bar) at 260 °C for one hour. Then, while maintaining the total pressure, the gas composition was switched to the hydrogen and carbon dioxide mixture (Fig. 5). Mass spectrometry (MS) measured online (Fig. 5e) shows that methanol is produced under all conditions. At 1 mbar and 10 mbar, methanol formation is restricted to the initial phase of the experiment and diminishes rapidly after 10 min. Such behaviour suggests that, at these pressures, methanol is produced in a non-catalytic manner. Potentially, the reduction for 1 h in hydrogen results in the formation of a limited amount of, for example, oxygen vacancies in the zinc(II) oxide phase. These sites are consequently consumed by the formation of methanol. At 1 and 10bar, however, methanol is produced in a continuous catalytic process. The rate of the methanol production is 16.2 times higher at 10bar than at 1 bar. The Cu K-edge XAS spectra did not reveal any change on switching to the reaction mixture, at any pressure.

From the EXAFS analysis of the Zn K-edge (Fig. 5a), no CuZn alloy was observable during the pretreatment under hydrogen at any of the applied pressures. Thus, no changes in the EXAFS are observed during the transient gas switch. However, at 1 and 10 bar, the Zn K-edge shows subtle changes in the XANES region. These changes are best seen in the first derivatives of the XANES (Fig. 5b) at 9,656 eV and 9,660 eV. These changes, as described earlier, can be attributed to the formation of oxygen vacancies or other structural distortions in the zinc(II) oxide^{49,50}. In Fig. 5c the temporal evolution of this reduced zinc component is tracked during the switch to reaction conditions. When carbon dioxide is introduced, the evolution of the component concentration suggests that the oxygen vacancies or geometric distortions initially present within the zinc oxide phase are removed to a greater degree for the 10-bar case relative to the 1-bar case, and that these changes go hand in hand with the increasing MS signal for methanol (Fig. 5e). The oxidation potential of carbon dioxide increases with

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Fig. 5 | Structure under catalytic conditions. a, Fourier-transforms of the Zn K-edge at 260 °C in hydrogen and 30 min after the switch to reaction mixture $(H_2:CO_2 \text{ of } 3:1)$. The FTs do not show any significant differences (see Supplementary Fig. 13 for the k³-weighted EXAFS). **b**, The derivatives of the Zn K-edge XANES at 1 and 10 bar revealing subtle changes at 9,656.6 and 9,660.1 eV. These features can be related to the removal of oxygen vacancies from the zinc(II) oxide phase^{49,50} Curve colours from purple to dark red correspond to hydrogen pressure 30 min after the switch to reaction mixture (time step 1 min). **c,d**, Evolution of the Zn_{reduced} **(c)** and Zn-HCOO **(d)** component derived by PCA-ITT analysis during the switch from hydrogen to the reaction mixture reveals a pressure dependence. At 1 and 10 mbar no appreciable changes occur. For 1 and 10 bar, the oxidation increases with applied pressure. **e**, MS trace of methanol (31 atomic mass units) during the switch from hydrogen to the reaction mixture (H₂:CO₂ of 3:1). **g**, The corresponding methanol and CO production quantified by gas chromatography.

partial pressure, irrespective of the simultaneous increase in hydrogen partial pressure. Recently, zinc formate was identified as a crucial reaction intermediate⁴⁶. Here, at 10 bar the concentration of zinc formate (Fig. 5d) shows an increase from 0% to 1% under reaction conditions. At 1 bar, the detection of zinc formate under reaction conditions is much lower. Further experiments were conducted to evaluate whether the observations made over the course of the 30-min exposure to the reaction mixture also hold true for much longer timescales. The catalysts were reduced for 24h at 260 °C at 1 bar and 10 bar, after which catalytic conditions ($H_2:CO_2 = 3:1$ at 260 °C) were applied for 44 h. The catalytic performance (Fig. 5g and Supplementary Fig. 17) is found to be strongly pressure dependent. Methanol productivity reaches a stable value within the first hour at both pressures (Fig. 5e). The rate of methanol production is found to be 17 times higher at 10 bar, whereas the production of carbon monoxide rises by only a factor of 1.2. Thus, the methanol selectivity is much higher at 10 bar. This shows the effect of the thermodynamics that govern the selectivity of the process. After the catalytic test the samples were characterized without exposure to air using XAS (Supplementary Fig. 21). Figure 5f reports the Fourier transforms of the k³-weighted Zn K-edge EXAFS obtained after 24 h in hydrogen and after 44 h of catalysis. In contrast to the 30-min reduction of the in situ experiment, after 24 h in hydrogen both samples at 1 and 10 bar contain a extended fraction of CuZn. However, after the extended catalysis the CuZn phase is no longer observed, in both cases. Since the ratio of methanol production rate between 1 bar and 10 bar during our in situ laboratory experiment is the same, and in both cases the CuZn alloy phase is removed, we suggest that the presence of an alloy in the starting material has

no pronounced influence on the chemical structure of the catalyst present during catalysis. Carbon dioxide is oxidizing the zinc with a pressure-dependent rate.

Discussion

This collection of data allows us to reassess controversies that exist regarding the CZA catalyst. First, we will consider the formation of a zinc oxide overlayer on the copper surface. Most prominently, such an overlayer was described by transmission electron microscopy (TEM) studies^{33,34}. These studies investigated the catalyst with TEM after catalytic testing. After catalysis at 30 and 60 bar, the sample was transferred to the TEM without exposure to air. In both studies, a pronounced overlayer of zinc oxide was found to encapsulate the copper nanoparticles. These data are in contrast to in situ TEM measurements, where no formation of such an overlayer was seen during various catalyst treatments^{31,35,55}. In these studies, the pressures applied were much lower, between 1 mbar (ref. ³¹) and 10 mbar (ref. 55). In the present work, it is established that the chemical state of the materials is substantially different across these pressure ranges. For the migration of an oxide overlayer on top of a metal particle, reduction of the metal oxide is often required⁵⁶. Our H₂-TPR data show that under the conditions of the in situ TEM experiments (≤ 10 mbar), no reduction of zinc oxide occurs, while under the high-pressure conditions (\geq 30 bar) of the postcatalysis characterization studies^{33,34} a substantial amount of reduced zinc species is present, which would allow material transport of the reduced zinc oxide onto the copper surface. Therefore, these observations do not exist in contradiction to each other, but are the outcome of the difference in the pressure regimes used in these studies. Second, we examine the most prominent discussion of the CZA catalyst, which is the role of the CuZn alloy in the catalytic process. Density functional theory has identified CuZn alloy sites as a potential candidate for a highly active carbon dioxide hydrogenation site². Yet, experimental findings seem to disagree on whether such sites are present under reaction conditions. In one of the most compelling examples, which identified CuZn surface alloy sites as active centres³¹, hydrogen treatments at varying hydrogen pressure and temperature were employed, leading to different amounts of CuZn alloy sites on the copper surface³⁶. These catalysts were then tested for methanol synthesis and a strong correlation between the activity for methanol production and the amounts of CuZn alloy sites was found. This study stands in apparent opposition to studies that have concluded that CuZn alloy formation does not influence the catalytic performance in any sense, since the alloyed zinc is extracted from the metallic phase under conditions of catalysis and the enhanced activity for the copper-zinc oxide system stems from the sites at the copper-zinc oxide interface^{25,32,46,57,58}. The data in our study (Fig. 5) show that if any CuZn alloying occurs, or is enforced before catalysis, it is removed with an efficiency that is related to the pressure and carbon dioxide content of the reaction mixture. A comparison of pressure and temperature used in the studies discussed above can resolve the discrepancies that exist with respect to the nature of the active phases. In the case where the CuZn alloy was identified as an active phase³¹, the catalytic activity was measured at 150 °C and 1 bar, conditions under which the alloy phase is considerably more stable than at higher pressures, since the kinetics for zinc oxidation by carbon dioxide are expected to be very slow. By contrast, high pressures of 15-60 bar have been studied in cases where the oxidized zinc with a copper interface was found to be the active site^{32,46,57,58}. Therefore, careful assessment of past studies with respect to their experimental conditions (Supplementary Table 1) will reveal essential insights in light of this systematic evaluation.

In summary, the evolution of the CZA precursor to the activated state is highly sensitive to the applied pressures of hydrogen and carbon dioxide within the studied pressure range. CuZn alloy formation is only observed when applying hydrogen pressures of at least 100 mbar. The transformation rates of the initial copper and zinc phases into other, potentially active states depends on the hydrogen pressure by a reaction order greater than 1. Under conditions of carbon dioxide hydrogenation, operando spectroscopy yields no evidence for the presence of a stable CuZn alloy phase at any pressure up to 10 bar, the highest pressure recorded here. Instead, the Zn K-edge XANES provides evidence for the formation of oxygen vacancies in the zinc oxide phase, which are then consumed to greater degrees with increasing pressure as the catalyst progresses to steady-state operation. Thus, working in different pressure regimes leads to very different catalyst structures. Deviation from conditions close to those applied in the actual industrial process will therefore result in observations that may only give limited insights into the industrially relevant state of the catalyst. The complex structuresensitivity relationship that we have observed in the case of the CZA system as a function of pressure makes extrapolation across these pressure regimes fraught with pitfalls. The structure-function relationships derived can only be seen to be valid within the particular pressure regimes in which they were observed. The pressure gap remains a relevant and general problem for the in situ and operando characterization of functional materials and should be systematically assessed before pursuing detailed studies on the role of constituents that might eventually prove to be irrelevant. Our systematic investigation shows that the pressure and materials gaps are strongly related and cannot be treated separately. As such, a verifiable structure insensitivity must be shown to exist before any extrapolation of structural or kinetic data from low pressure regimes can be made with any confidence¹⁵.

Methods

Materials. A commercially available copper-zinc-alumina catalyst was used with an elemental composition of 63.5% CuO, 24.7% ZnO, 10.1% Al_2O_3 and 1.3% MgO (Alfa Aesar, catalogue no. 45776, lot no. I06Z036).

In situ XAS. Time-resolved in situ XAS was performed at the SuperXAS beamline, Swiss Light Source of the Paul Scherrer Institute, Villingen, Switzerland. XAS data were collected in transmission geometry using fast, gridded ion chambers and a quick scanning channel-cut Si(111) monochromator (1 Hz oscillation frequency)47. The Cu K-edge and Zn K-edge were collected within one experiment using the scanning energy range of 8,719-10,800 eV. A zinc foil standard was collected simultaneously for energy calibration. X-ray-induced sample transformation can strongly influence experimental findings⁵⁹. Therefore, before the main study, experiments were performed varying the X-ray beam size from 500 µm x 500 µm to 2,500 µm x 500 µm. No alteration of the reduction behaviour of the sample was observed for both beam sizes. The presented experiments were then performed with the stronger defocus and with the beam size of 2,500 um x 500 um. The catalyst sample was diluted with five time the mass of boron nitride (Alfa Aesar) and was placed inside a 0.8-mm (wall thickness 0.01 mm) quartz capillary reactor and positioned by two quartz wool plugs. Around 5 mg of the diluted samples was used per experiment. A modified version of the plug-flow reactor developed for X-ray scattering methods was used⁶⁰. The temperature during the experiments was monitored by a 0.3-mm K-type thermocouple placed inside the sample bed. Gas flows (2-10 ml min⁻¹) were controlled using Bronkhorst mass flow controllers. The total pressure in the reactor was controlled by a Bronkhorst EL-Press back-pressure regulator. Gas switches between different gas mixture compositions were performed with a remote-controlled 6-port 2-position valve (VICI, Valco Instruments). The gas mixtures where allowed to equilibrate in the exhaust line for 1 h before any switch. To obtain the different partial pressures various gas mixtures where produced. The partial pressure of 1 mbar was reached with premixed 0.1 vol% H₂ (99.999% purity) in He (99.999% purity) and 0.1 vol% CO₂ (99.995% purity) in He (99.999% purity) purchased from Pangas. For 10 mbar partial pressure the same gas mixture was used at a total pressure of 10 bar. A 100-mbar partial pressure was obtained by mixing 9 ml min⁻¹ of Ar (99.999% purity) flow with 1 ml min⁻¹ of H₂ (99.999% purity) or respectively a mix of H₂ (99.999% purity) and CO2 (99.995% purity). A 1-bar partial pressure was obtained by using pure H2 or a respective gas mixture containing 24 vol% of CO2, 72 vol% of H2 and 4 vol% of Ar (Messer). Experiments at 5 and 10 bar partial pressure were obtained by pressurizing the reactor with the same gases to the respective pressures. For the catalyst experiments with reaction gas mixture $(H_2 + CO_2)$ a similar procedure was used. For the temperature-programmed reduction experiments in H2 the samples were exposed to the gas mixture at room temperature for 30 min before being heated to 500 °C with a heating ramp of 5 °C min-1. For the kinetic experiments the samples were heated (5 °C min⁻¹) in Ar to 150 °C, then a switch to H₂ was performed. After the reduction process the gas atmosphere was switched to Ar and the sample was further heated to 260 °C. At 260 °C the flow was switched to H₂. For the catalytic experiments the samples were heated in the respective H2 mixture at 5 °C min-1 to 260 °C and were kept there for 1 h. Then, the gas mixture was switched to a H₂:CO₂ mixture with a ratio of 3:1.

XANES analysis. Initial analysis and energy calibration were performed using ProXAS v.2.34 software⁶¹. In the TPR experiments 60 spectra were averaged, while for all other experiments 200 spectra were averaged. XANES data analysis was performed using the PrestoPronto data suite48,62. Verification of the results obtained using PrestoPronto was obtained through use of the ProXAS multicomponent analysis (MCA) algorithm based on multivariate curve resolution. The PCA coupled with iterative target factor analysis of the data in each experiment was combined with references (Supplementary Fig. 8). Standards for the Cu K-edge were: copper(11) oxide, copper(1) oxide, copper(0) and copper-zinc alloy, as well as the CZA catalysts pretreated in oxygen at 500 °C for 1 h for a fully oxidized standard and the CZA catalyst reduced at 600 °C in 15 bar of H₂ for a fully alloved reference. Standards for the Zn K-edge were: zinc oxide, zinc(0), zinc hydroxide carbonate (Zn(OH)₂·ZnCO₃), zinc formate Zn(CHOO)₂ and a copper-zinc (Cu_{0.67}Zn_{0.33}) alloy, as well as the treated CZA catalyst mentioned for the Cu K-edge. Additionally, we performed a linear combination analysis (LCA) (PrestoPronto). The LCA (Supplementary Fig. 18) showed the same trend. However, there is a difference between LCA and PCA, as PCA pertains to the original data. It considers the various features that are present in the edge structure of the catalyst. The catalyst is a nanometric object and the standards are bulk samples. As such, there is a natural difference in the electronic structure of the samples. This discrepancy becomes visible in the difference of the reconstructed spectra to the original bulk standard. The observed peak broadenings and changes in peak intensity are such size effects. The advantage of a PCA-ITT method is that it picks up minor changes much more sensitively than would be the case for LCA because the components are based on the original data.

EXAFS analysis. Data analysis of the EXAFS region was carried out using the EXCURV software package^{63,64} (2006 update). The fitting range was $2 \le k$ (Å⁻¹) ≤ 11.5 unless stated otherwise.

DRIFTS. DRIFTS measurements where performed using a Fourier transform infrared (FTIR) spectrometer (Varian Excalibur, MCT detector) and in situ cell based on the commercially available Harrick Praying Mantis set-up. For the experiment, around 20 mg of sample (50–125 µm grain size) was placed on a bed of silicon carbide powder. The cell was then purged with 10 vol.% of H_2 in He (5.0) with a total flow of 100 ml min⁻¹. After 1 h the background spectrum was collected. Subsequently, the catalyst bed was heated up (manually controlled) and every 20 °C a spectrum was collected. In parallel, the outlet gas flow was analysed using a mass spectrometer (Hiden Analytical).

Carbon dioxide hydrogenation activity. Catalytic CO₂ hydrogenation over the catalyst was tested in a fixed-bed stainless-steel reactor using 25 mg of catalyst (fraction 50-100 µm). The catalyst was positioned inside a stainless-steel tube (internal diameter, 4 mm; outer diameter, 6 mm) and fixed between two quartz wool beads. The reactor tube was mounted inside a single-zone furnace. Temperature was controlled using a K-type thermocouple positioned inside the catalyst bed. The total pressure was either 1 bar or 10 bar. First, catalysts were pretreated in situ in a flow of H₂ (50 ml min⁻¹) at 260 °C and ambient pressure for 24 h (heating rate 5 °C min⁻¹). Total pressure was controlled by a back-pressure regulator (Bronkhorst, EL-press series). Catalytic CO2 hydrogenation was performed at 260 °C. The feed-gas mixture during the catalytic experiment contained 24 vol% of CO₂, 72 vol% of H₂ and 4 vol% of Ar (tracer and internal standard), while the gas flow rate was equal to 50 ml min⁻¹ (controlled by a Bronkhorst mass flow controller). The conversion of CO₂ was in the range 2-5%. Analysis of outlet gases was performed by gas chromatography using a 3000 Micro GC gas analyzer (Inficon) equipped with 10-m Molsieve and 8-m PlotU columns and thermal conductivity detectors.

Hydrogen treatment of the catalysts. In addition to the synchrotron experiments, long-time reduction treatments were tested. The catalyst was mounted in the same set-up as described for the catalytic activity. Treatments were carried out at 1 mbar, 1 bar and 10 bar of partial H₂ pressure. In the cases of 1 and 10 bar, pure H₂ was used to perform the treatment. In the case of 1 mbar H₂ pressure, a premixed gas (0.1 vol% of H₂ (5.0) in He (5.0)) was used. For the 10 bar case the set-up was pressurized to 10 bar, otherwise it was operated at ambient pressure. The samples where heated in H₂ to 260 °C (5 °C min⁻¹) and then kept at 260 °C for 24 h (1 bar and 10 bar) and 64 h (1 mbar).

Ex situ X-ray absorption of the postcatalysis and hydrogen-treated samples.

After the catalytic test and the H_2 treatment the reactor inlet and outlet were closed and the reactor was transferred into a N_2 glovebox, and the samples were filled into quartz capillaries (internal diameter, 0.5 mm) and sealed. Subsequently, the samples were transferred to the SuperXAS beamline at Swiss Light Source and XAS at the Cu and Zn K-edge were measured.

Data availability

All data generated or analysed during this study are included in this published article (and its Supplementary Information files) or can be obtained from the authors on reasonable request.

Received: 4 October 2020; Accepted: 28 April 2021; Published online: 17 June 2021

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Acknowledgements

We thank H. Frey, D. Cartagenova, I. Sadykov and M. Ghosalya for support during the beamtime experiments; Z. Jovanovic for discussion on the kinetics; F. Krumeich for the provided electron microscopy. The authors also thank A. Clark for providing access to the ProXAS program for qXAS spectra calibration, normalization and SIMPLISIMA-LCF analysis. Part of this work was performed at the Swiss Light Source, Paul Scherrer Institute, Switzerland. We acknowledge the Swiss Light Source for providing synchrotron radiation beamtime at the SuperXAS beamline. A.B. and J.A.v.B. acknowledge the SNSF project 200021_178943. M.W. acknowledges funding from the SNSF project 200021_181053. M.A.N. acknowledges Shell Global Solutions for the part funding of his position.

Author contributions

A.B. wrote the manuscript. A.B., M.Z. and O.S. conducted the experiments and performed the data analysis. M.A.N. contributed the EXAFS analysis. A.B., M.W. and J.A.v.B. designed the study. All authors participated in discussions and writing the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41929-021-00625-x.

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Peer review information *Nature Catalysis* thanks Janis Timoshenko and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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