Insight into the Nature of the ZnO\textsubscript{x} Promoter during Methanol Synthesis

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ABSTRACT: Despite the great commercial relevance of zinc-promoted copper catalysts for methanol synthesis, the nature of the Cu−ZnO\textsubscript{x} synergy and the nature of the active Zn-based promoter species under industrially relevant conditions are still a topic of vivid debate. Detailed characterization of the chemical speciation of any promoter under high-pressure working conditions is challenging but specifically hampered by the large fraction of Zn spectator species bound to the oxidic catalyst support. We present the use of weakly interacting graphitic carbon supports as a tool to study the active speciation of the Zn promoter phase that is in close contact with the Cu nanoparticles using time-resolved X-ray absorption spectroscopy under working conditions. Without an oxidic support, much fewer Zn species need to be added for maximum catalyst activity. A 5−15 min exposure to 1 bar H\textsubscript{2} at 543 K only slightly reduces the Zn(II), but exposure for several hours to 20 bar H\textsubscript{2}/CO and/or H\textsubscript{2}/CO/CO\textsubscript{2} leads to an average Zn oxidation number of +0.5−0.6, only slightly increasing to +0.8 in a 20 bar H\textsubscript{2}/CO\textsubscript{2} feed. This means that most of the added Zn is in a zerovalent oxidation state during methanol synthesis conditions. The Zn average coordination number is 8, showing that this phase is not at the surface but surrounded by other metal atoms (whether Zn or Cu), and indicating that the Zn diffuses into the Cu nanoparticles under reaction conditions. The time scale of this process corresponds to that of the generally observed activation period for these catalysts. These results reveal the speciation of the relevant Zn promoter species under methanol synthesis conditions and, more generally, present the use of weakly interacting graphitic supports as an important strategy to avoid excessive spectator species, thereby allowing us to study the nature of relevant promoter species.

KEYWORDS: methanol synthesis, CO hydrogenation, CO\textsubscript{2}, zinc oxide promotion, carbon support, silica, X-ray absorption spectroscopy, copper nanoparticles

1. INTRODUCTION

Methanol synthesis is an important, decades-old industrial process. Nowadays, a coprecipitated Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst is used to hydrogenate CO\textsubscript{2} to methanol in a CO-rich environment. It has been well established that the methanol is predominantly formed from CO\textsubscript{2} rather than from CO. The role of the CO is to supply CO\textsubscript{2} via the reaction with water, which also keeps the water level low.\textsuperscript{1−6} Generally accepted is that Cu is the main active component where ZnO\textsubscript{x} plays a crucial role in promoting the catalyst activity with about an order of magnitude.\textsuperscript{5,7−11} Yet, the exact role of the ZnO\textsubscript{x} promoter is still under debate,\textsuperscript{12−14} especially due to a lack of detailed knowledge on the ZnO\textsubscript{x} speciation, structure, and its interaction with Cu under the typical methanol synthesis conditions at 473−573 K and 20−100 bar.\textsuperscript{15,16}

Various hypotheses exist to explain the role of the ZnO\textsubscript{x} promoter. It has been suggested that ZnO\textsubscript{x} increases the Cu dispersion and thereby the active Cu surface area\textsuperscript{17,18} and that the promoter supplies hydrogen to the Cu surface by spillover.\textsuperscript{19,20} The oxidation state of ZnO\textsubscript{x} can also play a role in the morphological change of small Cu particles due to a varying degree of the Cu−ZnO\textsubscript{x} interaction, thereby varying the exposed Cu surface planes.\textsuperscript{21} However, by now it is broadly accepted that the coverage of Cu nanoparticles with partially reduced ZnO is essential for the enhanced methanol production. An open question is still whether the promotion is due to the formation of a ZnO\textsubscript{x} layer on the Cu particles,\textsuperscript{19,22−24} to the formation and migration of Zn atoms on (or into) the Cu surface,\textsuperscript{10,13,25,26} or to the creation of active defects upon Cu−ZnO\textsubscript{x} interaction.\textsuperscript{19,23,27} Research is typically performed on catalysts supported on metal oxides, which may obscure the
active ZnO phase by the formation of mixed metal oxides and hence may significantly differ from the relevant speciation and distribution of the active fraction of the ZnO promoter.

It is generally accepted that ZnO (partially) covers the Cu nanoparticles in reducing conditions. The fractional coverage of Cu with ZnO during reaction conditions is mainly influenced by three factors: the feed composition, governing the degree of ZnO reduction; the ZnO loading; and the Cu particle size. For example, Kuld et al.\textsuperscript{13} showed that by applying various feeds during catalyst activation an optimal Zn coverage over a Cu surface of 0.47 was achieved using a Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst of constant composition during CO/CO\textsubscript{2} hydrogenation at ambient pressure. Yet, contradictory results for the optimal Zn coverage were reported by varying the ZnO loading under different reaction conditions.\textsuperscript{28,29} Also in a pure H\textsubscript{2}/CO feed, an optimal Zn coverage of 0.20, or an atomic Zn/Cu ratio of 1.2—1.6, was reported for Cu/ZnO catalysts.\textsuperscript{19,22,23,30,31} The question remains what the actual state of the ZnO is during working conditions in different feeds at high pressure (e.g., H\textsubscript{2}/CO feed), syngas enriched with a relevant amount of CO\textsubscript{2} (2—6 vol %), or an H\textsubscript{2}/CO feed.

Much effort has been devoted to studying the interaction and oxidation state of ZnO species in CuZn-based catalysts in the calcined state\textsuperscript{39,40,35} and before/after\textsuperscript{29,33,35} or during\textsuperscript{14,32,40—43} exposure to reducing atmospheres at (near)-ambient pressures (up to 8 bar). On the basis of those results, it is still inconclusive whether the oxidation state of ZnO slightly changes\textsuperscript{35,36,40} or whether Cu—Zn alloys are formed\textsuperscript{43,38,44} or not.\textsuperscript{33,35,41,42} For example, recent studies reported the formation of a Cu—Zn alloy in a Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst during a (CO\textsubscript{2}/H\textsubscript{2}) treatment at 15 bar and 533 K,\textsuperscript{45} but this alloy formation was absent for a Cu/ZnO/faujasite catalyst with almost a 1-to-1 ratio of Cu and Zn.\textsuperscript{46} A recently developed, unique tool that allows us to gain insight into the Zn oxidation state and speciation under realistic high-pressure conditions and in the working state is X-ray absorption spectroscopy (XAS). Very recently, Divins et al.\textsuperscript{24} published an interesting operando study at 20—40 bar in a CO\textsubscript{2}-enriched syngas feed using silica and alumina supports, ascribing the active ZnO speciation to a distorted ZnO\textsubscript{2} phase with a maximum content of 9 at% Zn\textsuperscript{8} atoms but most of the Zn species present as metal oxides.

A major obstacle to study the nature of the active site of the ZnO promoter is the strong interaction of the promoter with the oxidic spectator support, which leads to the formation of a large fraction of Zn spectator species present as formates, oxides, or mixed metal phases.\textsuperscript{24,37,45—49} Hence, the active promoter species represents only a fraction of the Zn species present in the system, and averaged information, such as the Zn oxidation state and coordination number, are not representative for the active ZnO promoter species.

We present graphitic carbon as a support with very limited interaction with Cu and ZnO.\textsuperscript{47,48} In combination with a relatively low ZnO\textsubscript{2} loading, it allows us to study specifically the ZnO in contact with the Cu nanoparticles during methanol synthesis and its speciation and interaction with the Cu, based on time-resolved XAS experiments under working conditions, also as a function of different feed compositions.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. A series of CuZnO\textsubscript{x}/C catalysts, with similar Cu weight loadings (8.0 ± 0.4 wt %) but varying Zn/Cu molar ratios, were prepared via incipient wetness impregnation following a published method.\textsuperscript{1} In brief, powdered high-surface-area graphite (TIMREX E-HSAG500, TIMCAL Graphite & Carbon) was dried at ca. 443 K under dynamic vacuum for 1.5 h. The support was impregnated at room temperature under static vacuum to 95% of the total pore volume with an acidified aqueous solution containing 1.8 M copper nitrate (Acros Organics, 99%) and 0—1.8 M zinc nitrate (Sigma-Aldrich, ≥99%). Subsequently, the impregnated support was dried overnight at room temperature under dynamic vacuum and further reduced at 503 K (ramp 2 K min\textsuperscript{−1}) in a 100 mL min\textsuperscript{−1} flow of 20 vol % H\textsubscript{2}/N\textsubscript{2} for 2.5 h. After cooling to room temperature, the sample was exposed to a flow of 100 mL min\textsuperscript{−1} flow of 5 vol % O\textsubscript{2}/N\textsubscript{2} for 1 h, heated to 473 K with a ramp of 1 K min\textsuperscript{−1} and oxidized at 473 K in 15 vol % O\textsubscript{2}/N\textsubscript{2} for 1 h.

The Cu/C (8.1 wt % Cu), ZnO\textsubscript{x}/C (9.9 wt % ZnO), and CuZnO\textsubscript{x}/SiO\textsubscript{2} catalysts were synthesized following the same procedure as for the CuZnO\textsubscript{x}/C catalysts using the respective metal nitrate(s). A different heat treatment was applied only for the ZnO/SiO\textsubscript{2} catalyst (10.0 wt % ZnO): the dried impregnate was heated to 723 K (ramp 2 K min\textsuperscript{−1}) in a 200 mL min\textsuperscript{−1} flow of 2 vol % NO/inert for 1 h.\textsuperscript{50} Both SiO\textsubscript{2}-based catalysts were supported on silica gel (25—75 μm, Davissil, grade 643, Sigma-Aldrich, ≥99%). All catalysts are named CuZn-X/C or CuZn-X/SiO\textsubscript{2}, in which X represents the molar Zn/(Cu + Zn) ratio expressed as percentage and is based on the nominal loading. A commercial Cu/ZnO/Al\textsubscript{2}O\textsubscript{3}/MgO catalyst from Alfa Aesar, containing a Cu/Zn/Al/Mg ratio of 63.8/24.8/10.1/1.3 wt %, served as a reference.

2.2. Catalyst Characterization. N\textsubscript{2} physisorption isotherms were recorded on a Micromeritics TriStar II Plus apparatus at 77 K. The samples were first dried at 443 K (or at 573 K for the SiO\textsubscript{2} support) under an N\textsubscript{2} flow overnight. The BET surface area was determined according to the IUPAC procedure.\textsuperscript{51} A Barrett–Joyner–Halenda (BJH) analysis was applied to obtain pore size distributions, using either a carbon black or Harkins-Jura statistical thickness curve. The single total pore volume \(V_{\text{tr}}\) was determined at \(p/p_0 = 0.995\). Integration of the differential pore size distribution (derived from the adsorption branch) between 2 and 50 nm yielded the mesoporosity. The micropore volume \(V_{\text{micro}}\) was calculated using the t-plot method.

Transmission electron microscopy (TEM) imaging was performed on an FEI Tecnai 20 apparatus, operating at 200 kV. High-angle, annular, dark-field scanning transmission electron microscopy (HAAADF-STEM) images were obtained on a Thermo Fisher Scientific Talos F200X apparatus, operating at 200 kV. With the same apparatus, chemical maps were recorded using energy-dispersive X-ray (EDX) detectors. The EM samples for the carbon-supported catalysts were prepared by deposition of an ethanolic dispersion of the catalyst onto holey carbon film-coated Cu or Au grids (Agar, 300 mesh). As adequate TEM measurements on the silica-supported catalysts as such were not possible, they were ultramicrotomed. The catalysts were embedded in a two-component epoxy resin (Struers, EpoFix), which was heated overnight at 333 K and cut in 60—70 nm slices on a Leica Urtacract E. The slices were deposited on the aforementioned Au grids, which were made hydrophilic by glow discharge in a Cressington 208 carbon coater. At least 350 individual particles at various locations within the sample were measured to determine the number-averaged Cu(Zn)O\textsubscript{x} particle sizes \(d_{\text{N}}\) with the standard deviation \(\sigma_{d}\) representing the width of the size distribution. These mean sizes were translated into surface-averaged particle sizes \(\bar{d}_{\text{S}}\) via
\[ d_i \pm s_i = \sqrt{\frac{1}{N} \sum_{i=1}^{N} d_i^2} \pm \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (d_i - d)_{\text{avg}}^2}, \]

with \( d_i \) the i-th particle size and \( N \) the total number of measured particles. Only the relevant part of the log-normal distribution (>1% of maximum) was considered for the calculation of the average particle sizes.

Powder X-ray diffractograms were recorded on a Bruker AXS D2 Phaser diffractometer at room temperature with a fixed divergence slit. Samples were irradiated by Cu Kα radiation (\( \lambda = 1.790 \text{ Å} \)) at 30 kV and 10 mA. Not only fresh catalysts, but also used catalysts were analyzed. These were exposed to ambient conditions, separated from the SiC in the reactors, finely ground, and characterized without any further pretreatment.

Temperature-programmed reduction (TPR) profiles were obtained on a Micromeritics AutoChem II 2920 apparatus. The sample (50 mg, <75 \( \mu \text{m} \) granulites) was first dried in situ under an Ar flow at 1 \( \text{L min}^{-1} \ \text{g}_{\text{sam}}^{-1} \) at 393 K for 30 min. The cooled sample was then exposed to 5 vol % \( \text{H}_2/\text{Ar} \) at the same flow and heated to 873 K with a ramp of 2 K min \(^{-1} \). The formed \( \text{H}_2\text{O} \) was captured with a dry ice/isopropanol cold trap, and the reduction profiles were recorded with a thermal conductivity detector (TCD). The \( H_2 \) reduction profiles of the CuZn-15/C and CuZn-15/SiO\(_2\) catalysts (25−75 \( \mu \text{m} \)) were also obtained at a temperature ramp of 5 K min \(^{-1} \) in a 0.5 \( \text{L min}^{-1} \ \text{g}_{\text{sam}}^{-1} \) flow without prior drying to directly compare with the \( \text{H}_2 \) treatment during XAS.

Time-resolved, operando X-ray absorption spectroscopy (XAS) measurements on simultaneously the Cu (8979 eV) and Zn K-edges (9659 eV) were performed at the SOLEIL synchrotron (ROCK beamline). Typically, ca. 3.5 mg of catalyst (25−75 \( \mu \text{m} \) sieve fraction) was loaded in a quartz capillary (ID 1.5 mm, 50 \( \mu \text{m} \) thickness), which was tightly glued into a frame connected to gas feed lines. Heating of the capillary was ensured by a hot gas blower (FMD Oxford). After the capillary was leak-checked at 20 bar, XAS data was obtained in He at room temperature. The catalyst was exposed to a 15 \( \text{mL min}^{-1} \) flow of 20 vol % \( \text{H}_2/\text{He} \) and heated to 543 K (ramp 5 K min \(^{-1} \)) with a hold time of 5−15 min at ambient pressure. After the \( \text{H}_2 \) treatment, the capillary was cooled to 453 K prior to introducing CO\(_2\)-free syngas (\( \text{H}_2/\text{CO/He} = 60/30/10 \) vol %), leading to a flow of 0.2−2.1 L min \(^{-1} \ \text{g}_{\text{sam}}^{-1} \) and a gas-hourly space velocity (GHSV) of 400−53 200 h \(^{-1} \). The reactors were pressurized to 40 bar (g), heated to 533 K (ramp 2 K min \(^{-1} \)), and the reaction was run for at least 100 h. Alternatively, the ZnO/C and ZnO/SiO\(_2\) catalysts were alternately exposed to the predefined \( \text{H}_2/\text{CO/He} \) and \( \text{H}_2/\text{CO/CO}_2/\text{He} \) feeds. A triphase carbonyl trap (activated carbon, γ-Al\(_2\)O\(_3\), ZnO) was located upstream of the CO feed to remove metal carbonyls and sulfur species. Products were periodically analyzed by online gas chromatography every 15 min. After catalysis, the samples were slowly exposed to air at 393 K. Details on the calculations of activity, selectivity, and stability are given in section S5.

**3. RESULTS AND DISCUSSION**

**3.1. Structural Properties of the Catalysts.** Figure 1 shows representative electron micrographs, including elemental maps, of CuZn-15/SiO\(_2\) (frames A−C) and CuZn-15/C (frames D−F) catalysts both with 8.1 wt % Cu and 1.8 wt % ZnO (see Figures S2−S5 for other catalysts and zoomed-out micrographs). Note that the number in the catalyst names refers to the Zn/(Cu + Zn) fraction of 15 at%. The silica as support consists of aggregated spheres of ca. 8 nm, whereas the graphitic carbon has a sheet-like morphology of a few nanometers thick. Both materials have a high specific surface area (>260 m\(^2\) g\(^{-1}\)) and a 50−60% of the total pore volume consists of mesopores (Figure S1, Table S1), making these materials suitable supports for model catalyst studies. Frame A shows no clear Cu(Zn)O\(_x\) nanoparticles on the silica support, demonstrating that it was challenging to distinguish metal particles on the silica support because of the limited phase contrast. Only by imaging ultramicrotomed slices were we able to obtain a representative HAADF-STEM micrograph with an elemental map (frame B). Cu(Zn)O\(_x\) particles of ca. 3−4 nm (bright spots) were observed for the CuZn-15/SiO\(_2\) catalyst, corresponding to mainly Cu species (blue dots) and ZnO\(_x\) species (red dots). The distribution of Cu and ZnO\(_x\) looked similar after 150 h of catalysis (frame C), which is probably more representative for the catalyst during catalysis.
When using a graphitic support (frame D) CuO nanoparticles of ca. 4 nm were clearly discernible by TEM and well-distributed (dark spots indicated with white arrows) on the carbon surface (light gray).

The distribution was confirmed by the elemental maps of Cu and Zn species, projected on a HAADF-STEM image (frame E). There was a strong correlation between the location of the Cu nanoparticles and the distribution of the ZnO species, both in the fresh CuZn-15/C catalyst and after catalysis (frames E and F). The characteristics of the full series carbon-supported CuZnO/C catalysts both in the fresh and used state can be found in the Supporting Information (Table S2) and shows similar Cu(Zn)O particle sizes (d_N = 5−9 nm) with varying ZnO loadings. Additional structural information includes N2 physisorption (Figure S1), additional electron microscopy imaging (Figures S2−S5), X-ray diffraction (XRD) analysis (Figure S8), and H2 reduction profiling (Figure S9). Overall, we showed that in both catalysts well-distributed Cu(Zn)O particles of similar size were present and that the relatively thin sheets of graphitic carbon as a model support facilitated the determination of the particle sizes by electron microscopy.

3.2. Influence of the Support and Feed Composition.

In this section, we compare the catalytic performance of CuZn-15/SiO2 and CuZn-15/C catalysts, which were prepared and tested in the same way and have similar Cu(Zn)O particle sizes and ZnO loadings but only have a different support. Figure 2 shows the methanol formation rate under industrially relevant temperature and pressure as a function of time in an H2/CO feed as well as in an H2/CO/CO2 feed (mimicking industrially relevant conditions1−5). Figure S10 gives the CO (+ CO2) conversion and total activity, and Table S4 provides additional information on the conversion levels, turnover frequencies (TOFs), and Cu(Zn)O particle growth during catalysis.

The TOF for the carbon-supported catalyst (3.9−15.3 × 10−3 s−1) was always higher than for the silica-supported catalyst (1.6−3.0 × 10−3 s−1) (Table S4). Strikingly, the beneficial effect of CO2 enrichment of the syngas feed on the methanol formation rate was much larger for the CuZn-15/C catalyst (factor 3.5) than for the CuZn-15/SiO2 catalyst (factor 1.7) (Figure 2). Upon CO2 enrichment the methanol selectivity increased from 83 to 99% and from 85 to 98% after 100 h on stream for, respectively, the CuZn-15/SiO2 and CuZn-15/C catalysts, in line with earlier published results5 and significantly higher than recently reported for CuZnOx/Al2O3.24
are reported for Cu/ZnO/Al2O3 catalysts depending on the reaction conditions,2,3,47 and differences were also observed between silica- and alumina-supported CuZnOx particles.24 However, our results, obtained in the same reaction conditions and with similar Cu particle sizes, unequivocally proves that promotion with a given amount of ZnOx is much more efficient using a carbon than using an oxide support. Under all conditions, the ZnOx promotion is more effective in the CuZn-15/C catalyst than in the CuZn-15/SiO2 catalyst, but the effect is especially pronounced with CO2 enrichment of the feed.

It is known that ZnOx itself can also act as a methanol synthesis catalyst, albeit with a lower activity than in combination with Cu.16,54,65 Supported ZnOx species without Cu were investigated under similar reaction conditions to check if the catalysis by ZnOx on graphitic carbon contributed significantly. The ZnOx/SiO2 and ZnOx/C catalysts have the same ZnO loading (both 10 wt %) with ZnOx particle sizes of 7.7 and ca. 4.5 nm, respectively. Figure 3 shows the CO (+ CO2) conversion versus time on stream in the presence and absence of CO2 and for both an oxidic and a carbon support.

Irrespective of the syngas composition, carbon-supported ZnOx species were much more active than silica-supported ZnOx species, even when taking the slightly different Zn surface areas into account (Figure S12). EM analysis showed no Zn-based nanoparticles (Figure S4) in the fresh ZnOx/SiO2 catalyst (frame B), whereas they were present in the ZnOx/C catalyst (frame A). During pure CO hydrogenation, the ZnOx/C catalyst had a significant conversion of ca. 2% (of which ca. 1.3% was methanol (Figure S12)). The activity of both supported ZnOx species clearly decreased in the presence of CO2. The conversion level was restored when switching back to an H2/CO feed. This demonstrates that the negative CO2 effect on the conversion is not related to, for example, irreversible changes in the catalyst morphology but probably can be attributed to the significant reduction of ZnO in a CO2-free feed, making it a more efficient methanol synthesis catalyst. Yet, the activity of the supported ZnOx was too small to explain the overall effects of CO2-enrichment in methanol synthesis of CuZnOx-based catalysts. Nevertheless, these results clearly show that an oxide support has a strong interaction with the ZnOx and leads to a different speciation than for the weaker interacting carbon supports.

3.3. Influence of the ZnOx Loading on Activity and Stability. For the carbon-supported catalysts, we investigated in more detail the effect of the ZnOx loading on the activity and stability of supported Cu nanoparticles. Figure 4 shows the specific activity (see Figures S13–S14 for the total activity) as a function of the ZnOx loading in a syngas atmosphere with and without CO2 (please note the logarithmic scale) for ca. 5.1 nm Cu nanoparticles supported on either a carbon support (black lines) or an oxide support (red markers). The activity increased when CO2 was in the feed for all studied ZnOx-promoted catalysts. After the initiation period, all catalysts had a methanol selectivity of >97% in CO2-enriched syngas. The highest TOFMeOH values were obtained for carbon-supported catalysts with Zn/(Cu + Zn) molar fractions between 0.15 and 0.25, irrespective of the presence of CO2 in the feed. These ZnOx loadings are lower than the well-established optimal loading for the commercially used Cu/ZnO/Al2O3/MgO methanol synthesis catalyst as well as for other oxide-based Cu catalysts in literature (Zn/(Cu + Zn) content of 29–47 at %).10,13,15,19,22,23,28–31,56

Another important factor in catalysis is the stability. In Figure S15, this stability is defined as the ratio between the activity after 100 h and after 50 h on stream. The addition of only 5 at% ZnOx was sufficient to increase the catalyst stability from 74 ± 8% to 84 ± 3% upon syngas conversion. Further increasing the ZnOx content to 15–35 at% maximized the stability to 91 ± 2% and 83 ± 3% in an H2/CO and H2/CO/CO2 feed, respectively. In the most heavily promoted CuZn-50/C catalyst, the stability was somewhat lower. The presence of 15–35 at% ZnOx, apparently limited the CuZnOx particle growth during catalysis as evident from TEM and XRD analysis (Figures S3, S7, and S8) and is in line with the stability improvement for intermediate amounts of ZnOx. Hence, ZnOx is not only an activity promoter but also a stability promoter for carbon-supported Cu catalysts.

3.4. Catalyst Evolution during Reduction in H2. From the literature, it is known that the coverage of the Cu surface with ZnOx species13 and the reduction degree of these ZnOx species15,35 are parameters that determine the effectiveness of ZnOx as a promoter. However, mostly metal oxides are employed to support CuZnOx particles, which can result in the formation of spectator species such as zinc silicates and aluminates,11,17,48–50 hampering the study of the active fraction of the ZnOx promoter. The presence of the mixed Zn metal oxides may hence obscure the results also of, for example, electron energy loss spectroscopy (EELS) and operando X-ray absorption spectroscopy (XAS) measurements. While EELS is a valuable technique to study the local oxidation state of metals,56,57 we chose to assess the chemical state of our supported catalysts by XAS because of the small particle sizes and relatively low metal
loadings. Hence, our hypothesis was that our use of a carbon support would allow us to much better study the formation, oxidation state, and structure of the relevant ZnO_x promoter by time-resolved, operando XAS at simultaneously the Cu and Zn K-edges at 20 bar and up to 533 K.

A first piece of information about the interaction between CuO_x and ZnO_x species can be derived from the reduction profiles. Figure 5 shows the ex situ H_2 reduction profiles of the CuZn-15/SiO_2 and CuZn-15/C catalysts. The theoretically maximum Cu surface coverage by a monolayer of Zn atoms is 75–95% for these catalysts with 15 at% ZnO_x. The maximum CuO reduction temperature (T_max) as well as the offset temperature for reduction (T_offset) were clearly lower for the CuZn-15/C catalyst than for the CuZn-15/SiO_2 catalyst (T_max of 465 vs 475 K, T_offset of 421 vs 434 K, respectively). Hence, the CuO is more easily reduced on a carbon support than on a silica support. We ascribe this to a stronger interaction of CuO_x with silica.

The reducibility of the CuZn-15/SiO_2 and CuZn-15/C catalysts was also investigated with in situ XAS under similar conditions as for the ex situ H_2 treatments. Time-resolved X-ray absorption spectra (Figure S16) were analyzed by fitting linear combinations of the macrocrystalline references to extract the Cu oxidation state evolutions (Figure S17), showing that the CuO species in both catalysts were fully reduced to Cu^0 via the formation of Cu^+ upon an H_2 treatment up to 543 K for 5–15 min. This was confirmed by a more in-depth study using multivariate analysis in which no prior information on the component spectra was imposed but which yielded eigenspectra that corresponded well to the macrocrystalline Cu references (Figure S18). This full reduction of CuO in ZnO_x-promoted CuO nanoparticles has also been reported in the literature.14,24,42,58

During the H_2 treatment we also studied changes in the ZnO_x oxidation state by in situ XAS. Figure 6 presents the time-resolved, normalized X-ray absorption near edge structures (XANES) and first derivatives at the Zn K-edge before and upon the H_2 treatment. We start with ZnO_x species in the Zn(II) oxidation state for both CuZn-15/SiO_2 (frames A and C) and CuZn-15/C (frames B and D) catalysts, as clear from the comparison to the first derivative of the ZnO reference. Upon heating in an H_2 atmosphere the Zn K-edge shifted to a lower energy (indicated by the arrows), showing that partially reduced ZnO_x was formed in both catalysts. The dominant features were still due to the presence of Zn^2+, as clear from the peak at 9.6626 keV on the first derivatives, although its intensity had slightly decreased. Interestingly, the CuZn-15/SiO_2 catalyst (frame A) displayed two distinct peaks in the normalized XANES spectra (indicated with α and β). This peak combination has been reported before and is ascribed to the presence of zinc silicates in a single phase such as Zn_2SiO_4.37,59–62 Yet, the CuZn-15/C catalyst (frame B)
only had one single, broad peak (indicated with γ), in line with a ZnO phase which was also observed in electron microscopy (Figure 1, frame E). The estimated, average Zn oxidation number (ON) was slightly lower for the CuZn-15/C catalyst than for the CuZn-15/SiO2 catalyst (+1.3 vs +1.6, see also Table S5). Multivariate analysis on the Zn K-edge is more challenging than for the Cu K-edge, as the XAS signal is lower. Extraction of the components (Figure S20) suggests the presence of three distinct phases for the CuZn-15/SiO2 catalyst. The eigenspectrum of one of the components resembles that of Zn2SiO4 and its contribution is relatively stable throughout the experiment, indicating the presence of a substantial amount of Zn spectator species in the CuZn-15/SiO2 catalyst. It has to be noted that because of the relatively low Zn loading, these spectator species of low crystallinity and/or not very well-defined phases. This conclusion is supported by multivariate analysis (Figure S20). The fact that only a slight reduction of the Zn species was observed in the CuZn-15/SiO2 catalyst down to room temperature to obtain sharper features (average Zn ON of +1.1) was confirmed by a measurement after cooling the catalyst to 77 K. This was confirmed by a measurement after cooling the catalyst to 77 K. The overall results, including CO2 hydrogenation, are shown in Figures S19 and S21−S24. Note that because of the XAS setup restrictions, the amount of catalyst and hence the conversion was limited (Figure S25). For the CuZn-15/SiO2 catalyst, the ZnO phase was only slightly further reduced during methanol synthesis (frames A and C) with an estimated Zn ON of +1.1. This was confirmed by a measurement after cooling the catalyst down to room temperature to obtain sharper features (average Zn ON of +1.2, Figure S19). Features that were attributed to zinc silicates were dominant at all stages in the XAS spectra for the CuZn-15/SiO2 catalyst, as confirmed by multivariate analysis (Figure S20). The fact that only a slight reduction of the Zn(II) is observed when using oxidic supports and that the Zn species strongly interact with the support is in line with earlier reports using oxidic supports.37,45

Remarkably, in the CuZn-15/C catalyst, a large fraction of metallic Zn was formed during methanol synthesis at 20 bar (Figure 7, frames B and D). This observation was confirmed by multivariate analysis, which showed a resemblance of the independently extracted eigenspectrum of the Zn species to the XAS spectrum of metallic Zn (Figure S20). The average Zn ON was only ca. 0.6. Assuming that the Zn species are either in the Zn(II) or Zn(0) oxidation state, this means that about 70% of the Zn species was completely reduced. With the addition of 3 vol % CO2 in the feed, a slightly less-reducing gas atmosphere was created. Nevertheless, the Zn ON decreased further with time to ca. +0.5 after nearly 3 h in the H2/CO/CO2 feed, which is probably rather an effect of time than feed composition. Upon switching to a pure H2/CO feed, the average Zn ON slightly increased to + (0.6−0.8). An increase is expected in a more oxidizing gas feed, as it is also predicted computationally that

Figure 7. (A,B) Normalized absorption and (C,D) corresponding first derivatives of operando, normalized XANES spectra at the Zn K-edge of the (A,C) CuZn-15/SiO2 and (B,D) CuZn-15/C catalysts (solid lines). Depicted during H2/CO (and subsequent H2/CO/CO2) conversion at 20 bar and 533 K, each after 160 min. Gas compositions: H2/CO/He = 60/30/10 vol % and H2/CO/CO2/He = 60/27/3/10 vol %. Dashed lines show the initial catalyst state (ZnO), macrocrystalline Zn2SiO4 and Zn30Cu70, and Zn foil at 298 K.
there will be a slight dependence of the ON (and hence probably the Zn coverage) on the exact feed composition. However, even under these conditions, most of the Zn species remain in the fully reduced state under operando conditions. This means that the relatively high Zn ONs in methanol synthesis systems reported until now (in the presence of an oxidic support) can probably be explained by a strong promoter–support interaction, and hence, a large fraction of the Zn promoter species is being chemically bound to the oxidic support (and hence inactive). In contrast, our use of a weakly interacting carbon support allows us to assess an average Zn oxidation state and coordination number that are much more representative of the true nature of the active ZnO promoter phase during methanol synthesis.

Several hypotheses have been postulated for the ZnOx speciation during Cu-catalyzed methanol synthesis. First, the beneficial effect of the ZnOx promoter was ascribed to the so-called strong metal-support interaction (SMSI) with slightly reduced ZnO having a high affinity for the Cu0 metal and partially covering the Cu nanoparticle surface. Alternative explanations involve the influence of ZnOx on the structure of the Cu nanoparticles. For instance, it was proposed that specific steps sites were exceptionally active sites on the Cu surface and that these step sites were stabilized by Zn0 atoms. Metallic Cu and Zn are quite miscible; up to 33 at% Zn can dissolve in Cu (solid solution) at temperatures between 473 K and the melting point (>1175 K). Some groups proposed that the active site was related to the decoration of Cu0 nanoparticles with Zn0 atoms and shallow diffusion of Zn0 atoms into the Cu surface. However, results from ex situ and low-pressure studies have limited value, as it is known that the catalytically active phase dynamically adjusts to the working conditions. A recent high-pressure operando study, based on oxidic supports, concluded that a distorted ZnOx layer was the majority phase under working conditions with at most 9% of the Zn being present as Zn0 atoms. Our experiments clearly show that, if a strong interaction of the Zn species with an oxide support is avoided, a much more truthful picture of the active fraction of the Zn promoter species under high-pressure methanol synthesis conditions is obtained, and that this fraction is clearly reduced to zerovalent Zn upon prolonged methanol synthesis conditions.

Zooming in on the local coordination of the Cu and Zn atoms during high-pressure methanol synthesis, we analyzed the extended X-ray absorption fine structure (EXAFS) region of the XAS data. Figure 8 shows the EXAFS data on the Zn K-edge in R-space for the CuZn-15/SiO2 (frame A) and CuZn-15/C (frame B) catalysts in the initial state and upon heating in an H2 atmosphere. The EXAFS-derived R-spaces at the Cu K-edge and the EXAFS fitting parameters are available in Figure S24 and Tables S6–S9, respectively. The initial spectra of both catalysts have a main peak at 1.50 Å in the Fourier transform, which corresponds to first-shell Zn–O bonds such as in ZnO with a bond length of 1.97 Å. The R-space of the CuZn-15/SiO2 (frame A) closely resembles that of the Zn3SiO4 reference, showing that a majority of the Zn atoms is bound to the oxide support, as reported before. No contribution of second-shell Zn–Zn bonds was observed (frames A and B) (which could be expected in crystalline ZnO at 2.91 Å in the nonphase corrected Fourier transform, corresponding to a real bond length of 3.2 Å), indicating the absence of larger ZnO crystallites in both samples and in line with the high ZnO dispersion observed by TEM (Figure 1). During in situ H2 reduction, the Zn–O bond intensity at 1.50 Å apparently decreased for both catalysts, but this was simply due to the increasing measurement temperature as the overall peak intensities significantly increased in the spectra taken at room temperature after catalysis (purple lines in frames C and D).
compared with the spectra taken during the last stage of catalysis at high temperature. It is important to note that in neither of the catalysts was Zn$^0$ formation observed during reduction in atmospheric-pressure H$_2$ (the Zn–Zn or Zn–Cu bond fingerprint is expected at 2.30 Å in the nonphase corrected Fourier transform, its position is indicated with an unlabeled arrow in the frames). After the in situ H$_2$ reduction, the first-shell Cu–Cu coordination number (CN) in metallic Cu was ca. 11 (for bulk Cu$^0$ this CN is 12), and it remained unchanged for both catalysts, independent of the exact feed. This means that no change in the Cu nanoparticles was observed upon exposure to working conditions: neither a significant fraction of oxidized copper nor the presence of highly dispersed copper. This is in agreement with the fully reduced Cu observed in the spectra at the XANES region.

We continue the EXAFS analysis under operando methanol synthesis conditions by focusing on the Zn local surrounding. Figure 8 (frames C,D) shows selected R-spaces from the EXAFS data on the Zn K-edge for both catalysts (for the complete set, please see Figure S23). For the CuZn-15/SiO$_2$ catalyst during CO hydrogenation, only a very minor fraction of metallic Zn was observed (signal around 2.30 Å indicated with the arrow in frame C), in line with earlier reports on oxide-supported catalysts. Nevertheless, a change was observed, as the first-shell Zn–O CN decreased from 4 (as in bulk ZnO and Zn$_2$SiO$_4$) to 2.6 ± 0.5 and a very low second-shell Zn–Zn or Zn–Cu (from here onward denoted as Zn–M) CN of 2.2 ± 1.4 was obtained (for bulk Zn$^0$ this CN is 12). This indicates a very slight change in the average Zn surroundings, but because of the small changes and the very similar Zn–Zn and Zn–Cu bonding distances, it is not possible to analyze this in detail. Overall, the signal remains dominated by features that are attributed to Zn silicate species, and there is very little difference between the reduced fresh catalyst and that under working conditions.

Interestingly, the CuZn-15/C catalyst (frame D) displayed large changes when switching to working conditions, which was already expected from the zerovalent Zn as evidenced by the XANES analysis (Figure 7, frame B). An average Zn–M bond length of 2.54 Å (close to that of 2.66 Å of the Zn$^0$ foil reference) and a quite high Zn–M CN of 6.1 ± 1.3 were obtained. This is a clear supporting evidence for the large fraction of zerovalent Zn species in the active catalysts. Upon prolonged exposure (while slightly enriching the feed with CO$_2$), the increase in coordination number continues to a Zn$^0$ CN of ca. 8. This means that the majority of the Zn promoter species is present in metal nanoparticles. The very similar Zn–Zn and Zn–Cu bonding distances do not allow us to unequivocally derive the nature of these metal nanoparticles. However, the zerovalent Zn is very likely located in Cu–Zn nanoparticles. The high Zn–M coordination number suggests that the Zn does not remain as adatoms or a monolayer on the outside of the Cu particle. The diffusion coefficient of Zn$^0$ in Cu$^0$ strongly depends on the Cu particle size and temperature (see also Table S10) but is high enough to support a full distribution of the Zn$^0$ throughout the relatively small Cu$^0$ particles at the time scale of hours, in line with the XRD pattern of the used CuZn-15/C catalyst showing a small downshift of the Cu$^0$ diffraction line and hence suggests CuZn alloy formation (Figure S8, frame D).

Interestingly, the time scale of the formation of highly coordinated zerovalent Zn is quite in line with the generally observed activation period for Cu methanol synthesis catalysts exposed to high-pressure working conditions. To our knowledge, no clear explanation for this activation period has so far been reported in academic literature, but our results suggest that the gradual reduction of Zn(II) to active Zn(0) promoter species might be an important factor in this activation.

Figure 9 summarizes the results of our study by depicting the ZnO$^2$ speciation in silica- and carbon-supported Cu catalysts containing 15 at% Zn/(Cu + Zn) after reduction as well as during high-pressure methanol synthesis. On both supports, the Cu$^{2+}$ nanoparticles (depicted in dark blue) were fully reduced to Cu$^0$ nanoparticles in 5–15 min exposure to 1 bar H$_2$ at 543 K. Even during high-pressure methanol synthesis with a H$_2$/CO$_2$ feed, no significant subsequent change in the oxidation state of the Cu was observed. Using an oxidative support, which is standard in commercial catalysts and most academic studies, it was difficult to derive detailed information about the speciation of the Zn component (depicted in red) that was active as a
promoter. Only slight changes in the average Zn speciation were observed (in line with earlier literature), as the signal was dominated by Zn species that had a strong interaction with the oxidic support (depicted as a layer of ZnSiO₃), and these species remained dominant under all (also methanol synthesis) conditions. In contrast, using a much less strongly interacting carbon support, allowed us to follow the fraction of the Zn species that was closely affiliated with the Cu nanoparticles and hence most likely represents the active Zn promoter species during catalysis. Under methanol synthesis conditions, the relevant ZnO₂ phase is in a deeply reduced state with an average Zn oxidation number of only +0.6. Assuming that only Zn²⁺ and Zn⁰ species exist, this means that ca. 70% of the ZnO is fully reduced to Zn⁰. The Zn−M coordination number was as high as 8 during methanol synthesis working conditions, showing that the Zn⁰ is almost fully coordinated with other metal atoms and has likely mostly diffused into the Cu nanoparticles. It is likely that this Zn speciation for the active promoter species is also relevant for the more conventional oxide-supported catalysts, to which much more Zn must be added to reach an optimum promoter effect, which is probably explained by the fact that a large fraction of the added Zn is not active as promoter.

4. CONCLUSIONS

Cu nanoparticulate catalysts on graphitic carbon were prepared, and compared to SiO₂-supported catalysts, to better understand the interaction between the Cu and the Zn-based promoter species and the speciation of Zn acting as a promoter during high pressure methanol synthesis. With a modest amount of ZnO₂ promoter, the methanol formation for the CuZnO₃/C catalyst was significantly faster than for a CuZnO₂/SiO₂ catalyst with similar Cu particle size in a pure H₂/CO feed. This difference was even much more pronounced in a CO₂-enriched syngas feed. Importantly, the use of graphitic carbon model supports allowed us to reveal the true speciation of the active fraction of the Zn-based promoter under commercially relevant methanol synthesis conditions. The vast majority of the Zn(II) is reduced all the way to Zn(0) during methanol synthesis at 20 bar. Also the Zn coordination number was high, making it likely that the Zn(0) diffused into the Cu nanoparticles. The characteristic time for this diffusion corresponds to the activation time that is generally observed with this type of catalysts. For the first time this gives direct insight into the nature of the active fraction of the Zn-based promoter in high pressure methanol synthesis, not obscured by the commonly large fraction of Zn species that strongly interacts with an oxidic support, and hence dominates the structural characterization results.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c05101.

Brief descriptions of electron imaging, crystallinity, reducibility, and the porosity of the catalysts; additional information on the catalyst activity and stability; complete set of XAS data; and details on the calculation of catalyst performance (PDF)

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Note

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