Copper-Zinc Alloy-Free Synthesis of Methanol from Carbon Dioxide over Cu/ZnO/Faujasite

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ABSTRACT: *The mechanism of carbon dioxide hydrogenation to methanol over Cu/ZnO materials has been explored for decades, however, the question of the active site still remains open to discussion. We used operando time resolved XAS and time-resolved isotope labeling experiments coupled with FTIR spectroscopy and MS analysis to elucidate the reaction mechanism and study the active sites and intermediates over a Cu/ZnO catalyst in the course of carbon dioxide conversion to methanol. No reduction of the zinc oxide, or formation of copper-zinc alloy were observed even under highly reducing conditions (15 bar of hydrogen, 260 °C), which leads to the conclusion that a copper zinc alloy phase is not required for high methanol yields and selectivity to be obtained. We attribute the reactive superiority of copper-zinc based system to the interplay between copper and zinc oxide phases. Our synthesis protocol provides a way to produce this copper zinc oxide interface, without having to go through an alloy phase.*

KEYWORDS: CO₂ hydrogenation, methanol, CuZn alloy, operando XAS, Cu/ZnO catalyst, isotope-labelling experiment.

The valorization of carbon dioxide through conversion into methanol has long been considered as a promising process.¹ Not only might such a process help to decrease anthropogenic greenhouse effects of carbon dioxide upon the environment, but methanol itself is a valuable product which can be used either as a liquid fuel additive, or as a precursor to value-added chemicals.²⁻⁴ In spite of extensive efforts from both industry and academia, however, industrial application of this process has yet to become a reality.⁵⁻⁷

Cu/ZnO based catalysts currently possess the highest activity for catalytic carbon dioxide hydrogenation to methanol.⁸ To further improve this catalytic system an understanding of the reaction mechanism and the structure of the active sites is vital for achieving the highest carbon dioxide conversion and methanol selectivity. Despite numerous extensive studies over past decades, however, the nature of active sites and reaction pathways of this process over Cu/ZnO systems remains the subject of intense debate.⁹⁻¹⁷

The mechanistic concept, which attributes activity in this reaction to the formation of a surface copper-zinc alloy, has dominated this discussion for some time. Numerous works have claimed that surface copper-zinc alloys at low zinc coverages ($\theta_{\text{Zn}} \leq 0.15$ monolayers) are stable under reaction conditions and responsible for methanol synthesis. Recently, however, Kattel et al.¹⁵ have shown by X-ray

photoemission spectroscopy (XPS) that copper-zinc alloy, even at low zinc coverage, undergoes oxidation and that copper-zinc oxide interfacial sites are the active species for methanol synthesis from carbon dioxide. This observation has caused a new round of debate.^{16,17} We believe that, at least in part, the reasons for such discrepancies originate from carrying out experiments under widely varying experimental conditions that deviate significantly from those required ($240 \leq T \leq 280$ °C and $P \geq 15$ bar) in the catalytic process. Our recent operando study of the Cu/ZnO/Al₂O₃ industrial catalyst at 15 bars and 220 - 280 °C has shown that the copper-zinc alloy does indeed undergo oxidation in the presence of carbon dioxide and as such can be considered only as possible precursor to the genuine active sites.¹⁸

In this study, we perform a mechanistic investigation of carbon dioxide hydrogenation to methanol over a copper-zinc alloy-free catalyst comprised of metallic copper and zinc oxide phases supported on zeolite faujasite (Cu/ZnO/FAU) under process-relevant catalytic conditions. By using operando time-resolved X-ray absorption spectroscopy (XAS), and high-pressure steady-state isotope labeling experiments coupled with infrared spectroscopy, we have found no spectroscopic evidence of the existence of copper-zinc alloy or its participation in the reaction mechanism.

Cu/ZnO/FAU, containing 2.6 wt. % of copper and 2.4 wt. % of zinc, was prepared through ion-exchange of commercial zeolite faujasite ($\text{SiO}_2/\text{Al}_2\text{O}_3=12$) followed by the precipitation of basic copper and zinc carbonates in the zeolite pores using 0.1 M sodium carbonate. By using this method, separate copper and zinc oxide phases with high dispersions are initially formed inside the zeolite pores (Figures S1-S3). Figure 1 shows the results of catalytic carbon dioxide hydrogenation over this material in a continuous flow fixed bed reactor between 240 °C and 260 °C and 30 bar. TEM investigation of the spent catalyst (Figures S4-S5) revealed partial extrusion of copper- and zinc-containing phases to the external surface of the zeolite.

Figure 1. Results of catalytic carbon dioxide hydrogenation over Cu/ZnO/FAU catalyst in the temperature range of 240 – 260 °C and pressure 30 bar.

Operando IR spectroscopy was used to identify the nature of the surface species formed during carbon dioxide hydrogenation. Introduction of the reaction feed leads to the appearance of several bands at 1661, 1608 and 1383 cm^{-1} (Figure S6). The first two bands are ascribed to asymmetric stretching vibrations of adsorbed formate species, whilst that at 1383 cm^{-1} arise from symmetric stretches of this species.^{19–23} The presence of the two higher frequency bands points to the presence of at least two types of formate species, with the band at 1661 cm^{-1} assigned to the asymmetric bending of monodentate formate, while the band at 1608 cm^{-1} corresponds to the same vibration arising from a bidentate formate species.^{24,25} With increasing pressure, a new band at 1470 cm^{-1} , attributed to bending vibrations of methoxy species, develops. Notably, no spectroscopic signatures of carbonate species were observed.

To access the structure and kinetic behavior of the intermediates formed during the hydrogenation of carbon dioxide, a steady-state transient $^{12}\text{CO}_2/^{13}\text{CO}_2$ isotope switch monitored by FTIR and mass-spectrometry (MS) was performed (Figure 2a). Figure 2b shows the normalized responses of the main reaction products and reagents, following a switch from a mixture of $^{12}\text{CO}_2/\text{H}_2$ to one of $^{13}\text{CO}_2/\text{H}_2$, with respect to inert tracer (argon). Immediately after switching, the signal due to $^{12}\text{CO}_2$ decreases together with the tracer signal, indicating a residence time of close to zero. This strongly suggests that the first step in carbon

dioxide activation is irreversible and, does not proceed through the formation of strongly bound species such as carbonates; a proposition confirmed by FTIR (Figure S6). In contrast, the MS responses of two main products, carbon monoxide and methanol, show significant delay with respect to argon. This indicates that methanol formation occurs via several steps subsequent to the initial activation of carbon dioxide (Figure S7), as well as possible re-adsorption effects for methanol as it travels through the catalyst bed.

Figure 2. a) *in situ* FTIR difference spectra collected during transient isotope switch from $^{12}\text{CO}_2/\text{H}_2$ to $^{13}\text{CO}_2/\text{H}_2$ mixture over Cu/ZnO/FAU catalyst at 260 °C and 15 bar; b) Normalized MS and IR transient responses following $^{12}\text{CO}_2/\text{H}_2$ to $^{13}\text{CO}_2/\text{H}_2$ isotope switch over Cu/ZnO/FAU catalyst at 260 °C and 15 bar.

To access the reactivity of formate and methoxy intermediates, we followed the dynamics of these surface species during the isotope switch. Figure 2a shows difference time-resolved infrared spectra acquired after the switch from the mixture of $^{12}\text{CO}_2/\text{H}_2$ to one of $^{13}\text{CO}_2/\text{H}_2$. After the switch, the intensity of all bands corresponding to unlabeled formate species decreases, as they are simultaneously replaced by the bands at 1558 and 1298 cm^{-1} (see Figure 2a, Figure S8 and supplementary discussion). These bands are due to the ^{13}C -labeled formate species formed from the $^{13}\text{CO}_2$ now present in the reaction feed. Importantly, after ~15 mins of reaction, full and reversible interconversion of unlabeled formate species into ^{13}C -labeled ones is observed. This behavior confirms the participation of both monodentate and bidentate formate species in the reaction mechanism. Notably, no isotope exchange was observed for the methoxy species (Figure 2a and Figure

S8). This points to the high stability of methoxy species on the catalyst surface and that, once formed, they do not participate in any consecutive reaction. Integration of the relative intensity of the IR bands corresponding to formates allows a comparison of their kinetic behavior with that observed for reaction products concurrently detected by mass spectrometry (Figure 2b). The normalized and zero-time corrected formate response follows precisely that due to the evolution of methanol, and therefore confirms that formate species are the reactive intermediates that lead directly to methanol.

Cu K-edge XANES and EXAFS spectra (Figures S9-S10, Table S1), show that the copper(II) cations initially present in the zeolite undergo complete reduction to yield metallic copper nanoparticles on the surface of the catalyst during activation in hydrogen (Figure S9 and associated discussion). Data from transient experiments, analogous to those already presented for time-resolved isotope labeling experiment and based on cycling of the feed gas composition between CO₂/H₂ mixture and hydrogen, show that copper remains predominantly present as a nanoparticulate metallic copper phase and does not undergo any significant change (Figure S11).

In contrast, the Zn K-edge XANES of the catalyst activated in hydrogen undergoes changes at 9662.8, 9666.3 and 9672.1 eV during these transient experiments (Figure 3a). Importantly, no evidence for the presence of reduced zinc in the form of copper zinc alloy (pre-edge at 9659 eV, Figure S12), either in the activated sample, or during *operando* carbon dioxide hydrogenation, was observed.

The difference XANES spectra (Figure 3a and Figure S13) indicate that the main changes after the switch from hydrogen to CO₂/H₂ mixture occurs in the region with maximum at 9666.3 eV. At the same time, the main peak of zinc formate is located at ~9666.8 eV (Figure S12). The active intermediate formate species observed during time-resolved isotope labeling experiment (Figure 2a) are therefore associated with the zinc during methanol synthesis. To make unambiguous assignment of the different zinc phases that are responsible for the observed changes in Zn K-edge XANES spectra, analysis of the EXAFS, and Principal Component Analysis (PCA) of the XANES, were undertaken (Figures S14-S16 and Table S2). PCA of Zn K-edge XANES spectra of Cu/ZnO/FAU upon cycling feed gas composition at 260 °C and 15 bar reveals the presence of three principal components. The major zinc component, a highly dispersed Zn²⁺ phase (Figure S14a), shows a nearly constant ~96 mol. % fraction and no significant response to cycling of the feed gas composition (Figure 3b). Besides this phase, a minority wurtzite-like zinc oxide phase is detected after the catalyst pretreatment in hydrogen. If any other minority phases are present during catalytic carbon dioxide hydrogenation, their concentrations are below detection limit and we cannot determine their role in this process. After switching the feed gas from hydrogen to the CO₂/H₂ reactive mixture, this phase undergoes conversion to a zinc formate type phase; a process that is found to be completely reversible upon returning the feed to hydrogen

from the reaction mixture. This is in line with work of Kattel et al.,¹⁷ who also observed decomposition of formates once the CO₂/H₂ reaction mixture was removed.

Figure 3. a) Zn K-edge XANES spectra evolution as well as difference spectrum between final and initial spectra for Cu/ZnO/FAU sample during *operando* switch from hydrogen to CO₂/H₂ gas reaction mixture at 15 bar and 260 °C; b) The relative fractions of zinc formate, zinc oxide-wurtzite and highly dispersed Zn²⁺ phases determined from PCA analysis as function of time upon cycling feed gas composition at 260 °C and 15 bar.

This experiment clarifies the controversial question concerning the participation of copper-zinc alloy in the catalytic cycle of methanol synthesis from carbon dioxide. Gotti and Prins²⁶ had, in the late 90s, questioned the finding of Nakamura et al.,²⁷ making the point that the presence of carbon dioxide and water could prevent the formation of a copper-zinc alloy. Moreover, recent publications have shown that copper-zinc alloy is unstable under carbon dioxide hydrogenation conditions and undergoes oxidation to zinc oxide or/and zinc formate.^{15,17,18} In the present work, the alloy phase was never observed to any measurable degree, even after the highly reductive pretreatment. Yet, the catalyst achieves significant activity and selectivity for carbon dioxide hydrogenation to methanol: the activity, normalized per mol of copper, obtained from this sample is comparable to that observed over the

commercial Cu/ZnO/Al₂O₃ catalyst, which does form a copper-zinc alloy during pretreatment (Table S3 and Figure S17). The fact that, under hydrogen, no observable amount of alloy phase forms, suggests that under reaction conditions, and therefore in the presence of carbon dioxide and water, the formation of such a phase, even in the form of short-lived intermediates, is highly unlikely. Instead, our results suggest that activation of carbon dioxide and formation of zinc formate species occur at zinc oxide surfaces in close proximity to metallic copper nanoparticles. Furthermore, purely oxide-based systems, like ZnO, In₂O₃, ZnO-Cr₂O₃, and ZnO-ZrO₂, also convert carbon dioxide to methanol.^{9,28–32} This indicates that the presence of alloyed phases are not necessary to perform this reaction. However, bi-functional catalysts that contain both an oxide component, which is responsible for activation of carbon dioxide, and a metallic counterpart, which can activate and split hydrogen efficiently, show much higher catalyst activity than these oxide-only systems.

Figure 3b shows that only a small fraction of zinc, in this case zinc oxide in a wurtzite-like form, in Cu/ZnO/FAU is active in carbon dioxide hydrogenation to methanol. The zeolite acts as a reservoir that permits the extrusion of both copper and zinc to the surface of the catalyst during reduction, where these components can achieve the intimacy of interaction required to generate the active sites required for the selective conversion of carbon dioxide. In this material copper is extruded, reduced, and then sintered to yield sizeable copper nanoparticles (see TEM and Cu K-edge EXAFS fitting in supplementary) on the outer zeolite surface. At the same time, according to Zn K-edge EXAFS fitting (Figure S16 and Table S2 and associated discussion), as well as PCA XANES analysis of activated Cu/ZnO/FAU sample (Figure 3 and Figures S14–S15), zinc oxide is more resistant to extrusion and/or sintering, and only a small fraction of zinc is transformed into a wurtzite-like zinc oxide located at the external zeolite surface. And only this phase, which is in intimate contact with the metallic copper (Figures S4–S5), is responsible for activation of carbon dioxide, yielding zinc formate species that can be hydrogenated to yield methanol (Figures 2 and 3b). At the same time, a highly dispersed Zn²⁺ phase located in zeolite cavities remains inactive, indicating the importance of Cu/ZnO interplay in this catalyst.

To summarize, we have used a combination of *operando* time resolved XAS and steady-state ¹²CO₂/¹³CO₂ isotope transient experiment coupled with infrared spectroscopy and MS analysis to monitor the reactive behavior of a Cu/ZnO/FAU catalyst under realistic reaction conditions (260 °C and 15 bar). Even in a pure hydrogen environment, no zinc phase is reduced and a copper zinc alloy phase does not form over Cu/ZnO/FAU: the presence of this phase is, therefore, not a prerequisite for the bifunctional Cu/ZnO system to be an active and selective catalyst for methanol synthesis from carbon dioxide and hydrogen. Only the wurtzite-like zinc oxide, present at the surface of the zeolite crystals and in intimate contact with metallic copper nanoparticles, forms the reactive zinc formates. Our re-

sults constitute a significant step in understanding the reaction mechanism and structure of active sites in copper-zinc based catalysts for hydrogenation of carbon dioxide. From the methodological point of view, a combination of powerful techniques such as time-resolved X-ray and infrared spectroscopies, with isotope tracing and switch experiments provides molecular-level insight into reaction mechanisms under harsh and industrially relevant conditions.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Preparation and characterization of Cu/ZnO/FAU material, description of *operando* XAS and IR experiments, TEM micrographs, additional FTIR and XAS results.

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Author Contributions

M.Z. and J.A.v.B conceived the idea for the study. V.L.S. and M.Z. designed, performed and analyzed FTIR experiments. M.Z., V.L.S. and M.A.N. designed, performed and interpreted *operando* XAS experiments. M.A.N. performed the EXAFS data analysis. M.Z. wrote the draft with contributions from all the other authors.

Notes

The authors declare no competing financial interest

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In this operando study, we show that methanol synthesis over Cu/ZnO/FAU catalyst occurs via formate species associated with zinc. Meantime, we came to the conclusion that copper zinc alloy phase is not required to result in the desired reactivity. We attribute the reactive superiority of this catalytic system to the unique interplay between copper and zinc oxide phases.