CO₂ hydrogenation on Cu-catalysts generated from Zn II single-sites: Enhanced CH₃OH selectivity compared to Cu/ZnO/Al₂O₃

Erwin Lam a, Gina Noh a, Kim Larmier a, Olga V. Safonova b, Christophe Copéret a,⇑

a Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir Prelog Weg 2, CH-8093 Zurich, Switzerland
b Paul Scherrer Institute, CH-5232 Villigen, Switzerland

1. Introduction

The conversion of carbon dioxide (CO₂) to value added products would allow the mitigation of CO₂ emissions that are recognized as a major contributor to climate change [1,2]. One strategy to mitigate the deleterious effect of CO₂ emissions would be to convert it by hydrogenation to methanol (CH₃OH), an important bulk chemical that can also be used for the generation of energy, thereby forming a closed carbon-fuel-cycle, referred to as the “methanol economy” [3–6]. This entails the sustainable production of H₂, the efficient capture of CO₂ as well as the use of highly active and selective hydrogenation catalysts. Currently, copper-based catalysts are among the most common hydrogenation catalysts used for the production of CH₃OH from CO, a mixture of CO/CO₂ as well as CO₂ [7]. The most studied and industrially used catalyst is Cu/ZnO/Al₂O₃, where the role of the different components is still under debate. The role of ZnO has been particularly discussed and has mainly assigned to the formation of highly active Cu-ZnO interfacial sites or a CuZn surface alloy [8–15]. However, these catalysts still suffer from low activity, selectivity and stability in CO₂ rich streams [16]. Alternatively, Cu/ZrO₂ has also been reported to be an efficient catalyst for the formation of CH₃OH [17–20]. We recently showed that the role of ZrO₂ is to act as a Lewis acidic surface site at the periphery of Cu nanoparticles to stabilize reaction intermediates (formate and methoxy) [21]. Furthermore, by using a surface organometallic chemistry approach, we could show that Cu nanoparticles supported on silica decorated with isolated Zr IV surface sites (Cu-Zr/SiO₂) [22] display the same performance as Cu/ZrO₂ by also providing Lewis acidic Zr IV sites at the interface with Cu thereby increasing CH₃OH selectivity. The same effect is observed with Lewis acidic isolated Ti IV surface sites on SiO₂ as a support [23,24]. However, all these catalysts suffer from fast erosion of selectivity with increasing conversion due to competitive adsorption of methanol/water on the Lewis acid sites needed for CO₂ activation and conversion to methanol (competitive adsorption).

More recently, we have shown that this approach could be used to improve the CH₃OH selectivity when starting from a silica support consisting of well-defined Ga III sites. In this case, grafting of the Cu precursor followed by a hydrogen treatment yields CuGa₆ alloy nanoparticles (Cu-Ga/SiO₂) along with remaining isolated Ga III sites [25]. This catalyst shows high activity and excellent CH₃OH selectivity, especially at higher conversion, in sharp contrast to Cu-M/SiO₂ with M = Ti or Zr. In situ X-ray absorption spectroscopy (XAS) showed that, under reaction conditions, such catalysts...
evolve to generates Cu⁰ and fully oxidized gallium sites. Compared to other catalysts prepared by surface organometallic chemistry (SOMC), no formate but only methoxy surface species are observed in the case of Cu-Ga/SiO₂, which correlates with and can explain the increase in selectivity at higher conversion [26].

We thus decided to investigate the formation of the corresponding Cu/Zn systems starting from the silica-supported isolated Zn²⁺ surface sites [27] using an SOMC approach to explore its catalytic performance and to compare it with Cu/ZnO/Al₂O₃ and other SOMC CO₂ hydrogenation catalysts.

2. Materials and methods

2.1. General

SiC (FisherEU), ZnO (AlfaAesar), and CuZn (AlfaAesar) were used as received. Toluene was purified over two solvent purification alumina columns (MBraun) and degassed prior to use. Pyridine (Acros Organics) was dried over CaH₂, distilled under argon and degassed. H₂ for catalyst preparation and CO for adsorption experiments were purified over activated R3-11 BASF catalyst and activated 4 Å molecular sieves. Unless otherwise specified all preparations of catalysts were carried out under argon using standard Schlenk techniques and gloveboxes. [Cu(OtBu)]₄ [28], Zn₁⁰@SiO₂ [27], Cu/SiO₂ [22], Cu-Zr/SiO₂ [22] and Cu-Ga/SiO₂ [25] and were synthesized according to literature procedures and stored in an argon filled glovebox. Two Cu/ZnO/Al₂O₃ catalysts were used as benchmark provided by Prof. Malte Behrens (denoted as Cu/ZnO/Al₂O₃) and Alfa Aesar (KATALCO 51–9 s, denoted as Cu/ZnO/Al₂O₃ Katalco) [29,30].

2.2. Synthesis of Cu-Zn/SiO₂

A solution of [Cu(OtBu)]₄ (110 mg, 0.20 mmol) in 20 mL of toluene was added to 1 g of Zn₁⁰@SiO₂ wetted with toluene. The suspension was stirred for 4 h, washed three times with toluene (5 mL) and dried at 10⁻³ mbar for 1 h. The solid was then reduced under H₂ at 500 °C for 5 h (100 °C h⁻¹) cooled down to room temperature under H₂, evacuated under high vacuum (10⁻⁵ mbar) and stored in an argon filled glovebox.

2.3. Material characterization

Elemental analyses of all materials were performed by the Mikroanalytisches Labor Pascher, Remagen, Germany. Powder X-ray diffraction (pXRD) patterns were recorded on a PANalytical X’Pert PRO-MPD diffractometer at a voltage of 40 kV and a current of 40 mA by applying Cu-Kα radiation (γ = 1.54060 Å). Catalyst morphology was obtained by transmission electron microscopy (TEM) on a Hitachi HT7700 microscope within the facilities of ScopeM at ETH Zurich. For the determination of the particle size distribution, >100 individual particles were considered, and the mean particle size and standard deviation are given according to a log-normal distribution function. Fourier-Transform Infrared (FTIR) spectroscopy experiments were performed on self-supporting wafers using a Bruker Alpha FT-IR spectrometer in transmission mode (24 scans, 4 cm⁻¹ resolution) under exclusion of air. The specific surface area of the catalysts was measured from a N₂ physisorption isotherm recorded at 77 K on a BEL JAPAN BELSORP-mini II apparatus. The samples were degassed at 300 °C under vacuum (10⁻³ mbar) for 3 h prior to measurement. The data was analyzed by the BET method with a p/p° range between 0.1 and 0.3. H₂ chemisorption isotherms were obtained using a BELSORP-max apparatus on the reduced samples at 40 °C and fitted according to a Langmuir isotherm (Eq. (1)),

\[
Q_{H₂} = \frac{\sqrt{K_{H₂} P_{H₂,eq}}}{1 + \sqrt{K_{H₂} P_{H₂,eq}}} Q_{H₂, max}
\]

where \(P_{H₂,eq}\) is the equilibrium hydrogen pressure, \(Q_{H₂}\), the hydrogen uptake (μmol g⁻¹cat), \(Q_{H₂, max}\) the saturation uptake of H₂ and \(K_{H₂}\), the thermodynamic constant for the dissociative hydrogen chemisorption.

Metal surface area was determined by N₂O titration. In a typical experiment 30–50 mg of sample were weight into a U-shape quartz tube and connected to the instrument (BEL Japan, INC, BELCAT-B). Prior to analysis, the samples were pretreated under a flow of 50% H₂/He at 300 °C for 2 h, after which 25–30 successive pulses of the titration gas mixture (1% N₂O in He) were introduced by a calibrated injection valve (2.77 μLₙ₂₀ (STP) per pulse). The amount of N₂O consumed was determined by monitoring the amounts of N₂O and N₂ in the exhaust with a thermal conductivity detector. The quantity of surface metal sites are then determined considering the titration equation [31]:

\[
2 \text{M}_\text{S} + \text{N}_2 \text{O} = \text{M}_{\text{S}}/\text{Z}_2 \text{O} + \text{N}_2 \text{N}_2 \text{O}_2 = 2 \text{N}_2 \text{O}_2\]

Pyridine adsorption experiments were performed on a self-supporting pellet of the Cu-based catalysts and monitored by infrared spectroscopy (Nicolet NEXUS 6700) in transmission mode with a 4 cm⁻¹ spectral resolution. After exposure of pyridine in the gas phase, the pellet was subsequently placed under high vacuum (10⁻⁵ mbar) at room temperature (rt), 100 °C, 200 °C, 300 °C, 400 °C and 500 °C (300 °C/min) for 15 min prior to measurement of the IR spectrum. Similar to pyridine adsorption, CO adsorption was performed on a self-supporting pellet of the Cu-based catalyst by exposure of ca. 90 mbar of CO at room temperature followed by recording the infrared spectrum in transmission mode.

2.4. X-ray absorption spectroscopy (XAS)

X-ray absorption spectra at the Cu and Zn K-edge were measured at the SuperXAS beamline at the Swiss Light Source (SLS). The SLS was operating in top-up mode at a 2.4 GeV electron energy and a current of 400 mA. The incident photon beam provided by a 2.9 T super bend magnet source was selected by a Si(1 1 1) quick-EXAFS monochromator [32] and the rejection of higher harmonics and focusing were achieved by a silicon collimating mirror at 2.5 mrad. During the measurements the monochromator was rotating with 10 Hz frequency and X-ray absorption spectra were collected in transmission mode using ionization chambers specially developed for quick data collection with 1 MHz frequency [32]. The resulting spectra were averaged over 5 min. Calibration of the monochromator energy position was performed by setting the inflection point of a Cu or Zn foil spectrum recorded simultaneously with the sample to 8979 or 9662 eV for Cu or Zn K-edges, respectively.

In a typical in situ experiment, about 10–20 mg of the powder sample was packed into a 3 mm thick quartz capillary (0.1 mm wall thickness), which was connected with a pressurizable gas flow system. The catalysts were reduced under a H₂/N₂ mixture (15%, 1 bar) at 300 °C for 60 min, and then cooled down to reaction temperature (230 °C). The reduction gas was flushed with N₂ for 15 min and then changed to the reaction gas mixture (CO₂:H₂: N₂ = 1:3:1, 5 mL min⁻¹). Under reaction gas, the setup was purged to 5 bar using a back-pressure regulator and the spectra was recorded every 15 min for one hour or until no changes in the spectra occurred. The spectra were background-corrected and normalized using the Demeter software package. Ex situ samples were pressed in pellets with optimized thickness for transmission detection and placed in aluminumized plastic bags (Polyaniline...
Solid-state NMR experiments on $^{1}$H and $^{13}$C were recorded on a Bruker 400 MHz AVANCE III HD spectrometer with a 4 mm MAS triple resonance probe operating in double resonance mode with a magic angle spinning frequency of 10 kHz. The chemical shift scale was calibrated using adamantane as an external secondary reference. Ramped cross polarization ($^{1}$H–$^{13}$C) was used for experiments with a magic angle spinning frequency of 10 kHz. The contact time was 2 ms for 1D experiments and for $^{1}$H–$^{13}$C HETCOR experiments. Additionally, for $^{1}$H–$^{13}$C HETCOR experiment, DUMBO homonuclear ($^{1}$H–$^{1}$H) decoupling was used during $t_{1}$. The static magnetic field was externally referenced by setting the $^{13}$C higher frequency to 38.4 ppm. The $^{1}$H excitation and decoupling radiofrequency ($r_{f}$) fields were set at 100 kHz. CP conditions were optimized to fulfill the Hartmann-Hahn condition under magic-angle spinning with minor adjustments to reach optimal experimental CP efficiency. All samples were packed in an argon filled glovebox. For preparing the ex situ sample, to 100 mg of Cu-Zn/SiO$_2$ (reduced at 300 °C under H$_2$ after exposure to air) in a thick-walled glass reactor was introduced 1 bar of CO$_2$, which was then condensed under liquid nitrogen cooling. Then 1 bar of H$_2$ was introduced while still maintaining cooling of liquid nitrogen at −196 °C. The reactor was then heated up to 230 °C which leads to a pressure increase to 5 bar. After 12 h, the reaction vessel was cooled down to room temperature and evacuated under high vacuum (10$^{-5}$ mbar) and the resulting solid was stored in an argon filled glovebox.

2.6. Catalytic testing in CO$_2$ hydrogenation

CO$_2$ hydrogenation reactions were conducted in a fixed-bed tubular reactor (9.1 mm ID) in down-flow configuration (PID Eng&Tech). In a typical experiment 250 mg of catalyst powder oxidized in air was mixed with 5.0 g of SiC and loaded in the reactor under ambient conditions (20 and 30 mg was used for Cu/ZnO/Al$_2$O$_3$ and Cu/ZnO/Al$_2$O$_3$ Katalco, respectively). First, the catalytic reactor was reduced for 1 h under a flow of 15% H$_2$/N$_2$ (50 mL min$^{-1}$) at 300 °C and atmospheric pressure. After cooling down to 230 °C, the reactor was pressurized to 25 bar with a flow of CO$_2$:H$_2$:N$_2$ (1:3:1; 50 mL min$^{-1}$) for 30 min. The reactor was then set to measurement conditions (230 °C, 25 bar) and the gas phase was analyzed via online gas chromatography (Agilent 7890B) equipped with an FID for CH$_3$OH and TCD for N$_2$, CO, and CH$_4$. Different contact times were probed by changing the gas flow rate from 100 mL (STP) min$^{-1}$ to as low as 6 mL (STP) min$^{-1}$. Finally, activity data was collected at the initial flow rate of 100 mL min$^{-1}$ to check for potential deactivation of the catalyst. The reaction rates, conversions and selectivities were calculated using the following set of equations (Eqs. (2)–(5)):

$$X_{CO_2} = \frac{\sum_{i=1}^{n} F_{i, out}}{F_{CO_2, in}}$$  \hspace{1cm} (5)

where $F_{i, out}$ is the total gas inlet flowrate [mol h$^{-1}$], $F_{CO_2, in}$ is the total gas outlet flow rate [mol h$^{-1}$], $C_{in}$ and $C_{out}$ are the inlet and outlet gas fraction of species $x$, $r_{Cu}$ is the formation rates of species $x$ per gram copper [$g^{-1}$ h$^{-1}$], $m_{cat}$ is the mass of catalyst in the reactor [$g$], $w_{Cu}$ is the weight loading of copper [$wt\%_{Cu}$], $S_{x}$ is the product based selectivity of product $x$, $F_{i, out}$ the flowrates of the products, and $X_{CO_2}$ the conversion of CO$_2$. Intrinsic formation rates (with respect to the contact time) are obtained by using a second/third order polynomial fit on the experimental data at conversions below 7%.

3. Results and discussion

3.1. Catalyst synthesis and characterization

A silica support having well-defined isolated Zn$^{2+}$ sites was prepared by grafting [Zn(OiPr)$_2$OSi(OtBu)$_3$]$_2$ [33] followed by a thermolytic step at 500 °C to generate Zn$^{2+}$@SiO$_2$ [27] according to a combined SOMC and thermolytic precursor (TMP) approach [34,35]. This material was further used to graft [Cu(OtBu)$_4$] on surface silanols present in Zn$^{2+}$@SiO$_2$. Infrared (IR) spectroscopy (Fig. S1) shows the consumption of Si-OH groups (3747 cm$^{-1}$) and appearance of C-H stretching (2700–3000 cm$^{-1}$) and bending (1300–1500 cm$^{-1}$) bands, consistent with grafting of [Cu(OtBu)$_4$] on Si-OH groups via protonolysis (Fig. S1). Subsequent, treatment under H$_2$ at 500 °C yields supported nanoparticles (vide infra) in Cu-Zn/SiO$_2$ while regenerating the Si-OH groups; it also helps removing all organic groups, as evidenced by IR spectroscopy (Fig. S1). The reduction temperature of 500 °C was chosen to allow the full removal of the chemisorbed organic functionalities, such as -OttBu. Analysis of this material – Cu-Zn/SiO$_2$ – by inductively coupled plasma optical emission spectroscopy (ICP-OES) shows metal loadings of 4.16 wt% copper and 1.62 wt% zinc (5:2 Cu/Zn atomic ratio).

The specific surface area of this material is 187 m$^2$ g$^{-1}$ as determined by N$_2$ physisorption isotherms and Brunauer-Emmet-Teller (BET) analysis (Table S1), which is close to the initial SiO$_2$ material (ca. 200 m$^2$ g$^{-1}$). Transmission electron microscopy (TEM) studies show the presence of small and narrowly distributed CuZn$_x$ alloy (vide infra) nanoparticles of Cu-Zn/SiO$_2$ (3.9 ± 1.0 nm) (Fig. 1b). The particle size is slightly larger than for the corresponding Cu/SiO$_2$ (2.9 ± 1.3 nm) prepared via a similar approach and more similar to corresponding gallium based materials (Cu/Ga/SiO$_2$) (4.6 ± 1.4 nm) [22]. A surface metal nanoparticle concentration of 52 μmol g$^{-1}$ was determined by N$_2$O titration for Cu-Zn/SiO$_2$ (assuming a 1:2 stoichiometry between N$_2$O and the surface sites) (Table S1), which is similar to what is obtained for Cu/SiO$_2$ [22] considering the larger particle sizes for Cu-Zn/SiO$_2$. This increased N$_2$O consumption for Cu-Zn/SiO$_2$ is likely due to the reaction of N$_2$O with reduced zinc sites arising from CuZn$_x$ (surface)alloy (vide infra) [37]. Chemisorption experiments using H$_2$ at 40 °C was performed since it was shown to be a reliable method to obtain metal dispersions for Cu-based systems with similar physicochemical properties [31]. A metal surface site concentration of 64 μmol g$^{-1}$ for Cu-Zn/SiO$_2$ (assuming a 1:2 stoichiometry between H$_2$ and the metal surface site) was obtained, consistent with the number obtained from N$_2$O titration (Table S1 and Fig. S2). Powder X-ray diffraction show no crystalline phases, due to the amorphous nature of the SiO$_2$ support and the presence of small metal nanoparticles (Fig. S3). IR spectroscopy of Cu-Zn/SiO$_2$ in the presence of 90 mbar CO at room temperature shows stretching bands at 2092 cm$^{-1}$ which is red-shifted with respect to what is observed for pure Cu/SiO$_2$ at 2106 cm$^{-1}$ indicating a different
copper morphology/structure (Fig. S4). Furthermore, the presence of Lewis acidic zinc sites is shown by pyridine adsorption and IR spectroscopy [38], where the ring vibrational band of pyridine at 1611 cm⁻¹ for Cu-Zn/SiO₂ is observed, likely associated with its adsorption on Zn II sites (Fig. S5). Pyridine on Cu-Zn/SiO₂ is fully desorbed at 500 °C under high vacuum (10⁻⁵ mbar) (Fig. S5).

In order to obtain further information regarding the oxidation states and structural environments of zinc and copper in Cu-Zn/ SiO₂, the XAS spectra at the zinc and copper K-edges are recorded for the as-prepared material ex situ under inert conditions (Fig. 1c). The zinc K-edge for Cu-Zn/SiO₂ shows an edge energy at 9658 eV while for ZnII@SiO₂ and ZnO the edge energy is higher at 9662 eV (Fig. S6). This decrease in edge energy for Cu-Zn/SiO₂ corresponds to reduced Zn species [39]. A feature at 9662 eV shown by the first derivative of the Zn K-edge XANES spectrum of Cu-Zn/SiO₂ also evidences that a fraction of the zinc sites remain as ZnII (Fig. 1c). The XANES spectrum of the Cu K-edge has an edge energy at 8979 eV indicative of reduced copper (Fig. S7). Linear combination fits using ZnII@SiO₂ and α-brass shows that 51% of the sites can be fitted as ZnII and 49% as α-brass (Fig. S8). Overall, the XAS spectra show that reduction of the samples after Cu grafting (500 °C under H₂) leads to a partial reduction of Zn IV with the formation of CuZnₓ alloys along with remaining Zn II sites. These findings are similar to what was found for corresponding Cu-Ga/SiO₂ system where the formation of a CuGaₓ alloy is also observed [25], but contrasts with what was observed for Cu-Ti/SiO₂ [23] and Cu-Zr/SiO₂ [22] systems that remained as isolated Ti IV and Zr IV sites upon Cu nanoparticle formation.

3.2. Catalytic performance in CO₂ hydrogenation

Cu-Zn/SiO₂ was tested in CO₂ hydrogenation at 230 °C and 25 bar (Fig. S9). Following exposure to air, the material was first reduced at 300 °C under H₂. The catalyst was then tested by varying the gas flow rate to examine the effect of contact time (Fig. S10) on the catalytic activity/selectivity at conversions below 10% (ca. 15% conversion for thermodynamic equilibrium).

The intrinsic formation rates obtained from extrapolating to zero contact time are evaluated and compared with Cu/SiO₂, Cu-Zr/SiO₂ and Cu-Ga/SiO₂. These materials have similar Cu loadings, particle size distribution as well as metal (M) site densities in Cu-M/SiO₂ (M = Ga, Zn and Zr), albeit slightly lower for Zr (Table S2), thus allowing a direct comparison between these catalysts and Cu-Zn/SiO₂. Two Cu/ZnO/Al₂O₃ catalysts, one commercially available and one prepared from a malachite precursor were used as benchmark materials [30]. The intrinsic CH₃OH formation rate is 1.6 g h⁻¹ g⁻¹ Cu for Cu-Zn/SiO₂ which is 5 times higher than Cu/SiO₂ and also slightly higher than Cu-Zr/SiO₂ or Cu-Ga/SiO₂ (Fig. 2a). Note that the catalytic activity of the support by itself (ZnII@SiO₂) is below detection limits. The intrinsic CO formation rates for Cu-SiO₂ and Cu-Zr/SiO₂ (0.3 g h⁻¹ g⁻¹ Cu) are similar to Cu-Zn/SiO₂. This leads overall to a CH₃OH selectivity of 86% for Cu-Zn/SiO₂, with CO being the only byproduct. Thus, Cu-Zn/SiO₂ has a higher CH₃OH selectivity than unpromoted Cu/SiO₂ (48%) or even Cu-Zr/SiO₂ (77%), and is similar to, albeit slightly lower than Cu-Ga/SiO₂ (90%) [22]. Both the CH₃OH and CO formation rates decrease at longer contact times (Fig. S11), indicating product inhibition involved in both pathways for Cu-Zn/SiO₂, similar to Cu-Zr/SiO₂ [25]. It is particularly noteworthy that for the corresponding Cu-Ti/SiO₂ and Cu-Zr/SiO₂ catalysts, only CH₃OH formation rates decrease with longer contact times [22,23]. Since both CH₃OH and CO formation rates decrease with increasing contact time, a high selectivity toward CH₃OH is maintained for Cu-Zn/SiO₂ (>70%) at conversions up to 5% (Figs. 2b and S12). The high CH₃OH selectivity at higher conversions is not observed for similar type of catalysts that are more affected by conversion: Cu/SiO₂ and Cu-Zr/SiO₂ only reaches 30% and ca. 40% CH₃OH selectivity at a conversion of 5% (Fig. 3b).

In comparison to Cu-Zn/SiO₂ and Cu/ZnO/Al₂O₃ [29] (Figs. S13–S18) shows higher formation rates for CH₃OH (3.9 g h⁻¹ g⁻¹ Cu) under the
And thus a higher partial pressure of H2O. However, this experiment is fully oxidized under air and fully reduced under H2. The temperature was then decreased to 230 °C and the reaction gas mixture consisting of CO2:H2:N2 (1:3:1) was introduced and the pressure was increased to 5 bar (see materials and methods section). The zinc K-edge after exposure to air shows an edge energy at 9662 eV consistent with the complete oxidation of zinc. Upon reduction of the oxidized catalyst at 300 °C under H2, the white line intensity decreases and a feature towards lower energy (9658 eV) appears, which is indicative of reduced zinc sites (Fig. 3). A similar feature is observed for the as-prepared catalyst but with a higher intensity of the signal at lower energy (9658 eV), indicating that the reduction of the catalyst exposed to air results in a lower fraction of reduced zinc than in the as-prepared catalyst. Under reaction conditions – at 230 °C and at 5 bar under a mixture of CO2: H2:N2 (1:3:1) – the intensity of the white line is intermediate between these of the material after exposure to air vs. after reduction. The feature at lower energy (9658 eV) persists, indicating the presence of remaining reduced zinc sites for the Cu-Zn system. In comparison, the XAS spectrum of ZnII@SiO2 has a higher white line intensity and lacks the feature at 9658 eV characteristic of reduced zinc sites under H2 at 300 °C (Fig. S20). This shows that in order to have reduced zinc sites, the presence of copper is necessary. In order to obtain a more quantitative ratio of the reduced zinc sites, linear combination fits using isolated Zn II surface sites (Fig. S21) are performed; this analysis shows that after H2 treatment at 300 °C, 71% of the zinc sites are fitted as Zn II and the remaining sites can be fitted as α-brass (Fig. S22). Linear combination fits of the XANES spectrum under the reaction gas mixture show that 84% of zinc are present as ZnII sites, with the remaining sites being fitted as α-brass (Fig. S22). This contrasts with what was found for Cu-Ga/SiO2 where all the gallium sites are oxidized under the same reaction conditions (25). Since the in situ XAS measurements were only carried out at 5 bar in contrast to 25 bar for the catalytic test due to instrumental limitation, one may expect that increasing the total pressure (e.g. to 25 bar) could further favor the oxide form of zinc and CuO due to a higher CO2 conversion and thus a higher partial pressure of H2O. However, this experiment at low pressure already indicates the subtle differences between Cu-Zn/SiO2 and Cu-Ga/SiO2. At the Cu K-edge, copper in Cu-Zn/SiO2 is fully oxidized under air and fully reduced under H2 and remains so under reaction conditions (Fig. S23). In summary, in situ XAS shows that the oxidation state of zinc in Cu-Zn/SiO2 is highly dependent on the reaction conditions, where ZnII and Zn0 sites are coexisting under reaction conditions.

The common features between all the Cu-based CO2 hydrogenation catalysts prepared via SOMC is that they contain well-defined Lewis acidic surface metal sites on SiO2 (ZnII, TiIV, GaIII and ZnII). They likely play an important role in driving CH3OH selectivity for group 4 metals as demonstrated previously (22,23,25). Note same reaction conditions, but it also favors the formation of CO (0.9 g mol-1 gcat-1), hence the overall lower intrinsic CH3OH selectivity (71% vs. 86%) (Fig. 2b). The CH3OH selectivity of Cu/ZnO/Al2O3 drops more drastically with conversion (50% CH3OH selectivity at around 5% conversion) compared to Cu-Zn/SiO2. It shows that the Cu-Zn based catalyst generated via SOMC can maintain a higher CH3OH selectivity at higher conversion (Fig. 2b). The main difference is that the CO formation rate is less affected by contact time for Cu/ZnO/Al2O3 compared to Cu-Zn/SiO2 suggesting different reaction mechanisms for CO formation between the two materials.

A similar particle size distribution by TEM is obtained for the spent Cu-Zn/SiO2 catalyst (4.2 ± 1.3 nm (Fig. S19)) compared to the fresh catalyst (3.9 ± 1.0 nm). This is further confirmed by absence of any crystalline phases by powder X-ray diffraction (Fig. S3).

### 3.3. In situ X-ray absorption spectroscopy

In order to obtain further insights of the structure of zinc and copper in Cu-Zn/SiO2, the material was further investigated by in situ XAS at the Zn and Cu K-edges (Fig. 3). The X-ray absorption spectra of Cu-Zn/SiO2 were measured after oxidation of the catalyst in air, followed by reduction at 300 °C under H2. The temperature was then decreased to 230 °C and the reaction gas mixture consisting of CO2:H2:N2 (1:3:1) was introduced and the pressure was increased to 5 bar (see materials and methods section).

Fig. 3. In situ XANES spectrum (top) and its first derivative (bottom) at the zinc K-edge for Cu-Zn/SiO2 under air at room temperature, reduced at 300 °C under H2 and under reaction conditions at 5 bar with CO2:H2:N2 (1:3:1) at 230 °C.

The common features between all the Cu-based CO2 hydrogenation catalysts prepared via SOMC is that they contain well-defined Lewis acidic surface metal sites on SiO2 (ZnII, TiIV, GaIII and ZnII). They likely play an important role in driving CH3OH selectivity for group 4 metals as demonstrated previously (22,23,25). Note
that having too highly Lewis acidic surface sites such as with Al2O3 can also have a detrimental effect on the CH3OH formation rate and selectivity [26]. However, in case of Cu-Zn/SiO2, it is more difficult to pinpoint the origin of the improved CH3OH synthesis performance, that can be due to the presence of Lewis acidic surface sites and/or reduced zinc sites. In the case of metal dopant like GaIII and ZnIII, their reducibility helps the formation of a CuMx (M = Ga or Zn) alloy, that likely play an important role in driving CH3OH selectivity. One can speculate that the reversible formation of alloy, evidenced by the evolution of CuMx as a function of reaction conditions (H2/CO2 vs. pure H2), can help maximizing the amount of interfacial sites between metallic copper and MOx thus increasing CH3OH formation rate and selectivity.

3.4. Ex situ solid state NMR spectroscopy

In order to detect surface species, especially on the ZnII sites, the 1H–13C HETCOR spectrum of Cu-Zn/SiO2 was recorded. Cu-Zn/SiO2 (reduced after exposure to air) was contacted with 5 bar of \( \text{H}_2/\text{CO}_2 \) (3:1) for 12 h at 230 °C followed by evacuating the gas phase under high vacuum (10⁻⁵ mbar) at room temperature. This allows the determination of possible surface species on Cu/Zn/SiO2. The NMR spectra of Cu-Zn/SiO2 shows a cross-peak at 3/50 ppm (1H/13C), corresponding to methoxy species (Fig. S24). Formate species (present in the case of Cu/ZrO2, Cu-Zr/SiO2, Cu-Ti/SiO2 or Cu/Al2O3) [21–23,26] on Lewis acidic zinc sites are absent. The IR spectrum of the ex situ Cu-Zn/SiO2 samples (Fig. S25) also shows the absence of formate and the presence of only methoxy species by the 13C stretches at around 2955 and 2855 cm⁻¹. It is noteworthy that Cu-Zn/SiO2 and Cu-Ga/SiO2 [25], which only show the presence of methoxy surface species, are also both highly selective for CH3OH at higher conversions. This likely indicates that the absence of stable formate surface species could play a major role in improving the CH3OH selectivity over CO. In fact, we have recently shown that highly stabilized formate species as in the case of Cu/Al2O3 leads to the preferential formation of CO likely via formation of methyl formate at higher conversion that can readily decompose in CO and methanol [26].

4. Conclusion

A Cu-Zn based catalyst was generated by surface organometallic chemistry forming Cu/Zn alloy nanoparticles along with residual ZnII sites on SiO2. This material contrasts with the previously prepared Cu-Zr or Cu-Ti based systems were no reduction of ZrIV and TiIV occurred but display similar feature to reported Cu-Ga based systems, which also consist of CuGa alloy in the as-synthesized material. The Cu-Zn based catalyst also shows high activity in CO₂ hydrogenation, mainly forming CH₃OH as the main product, even at relatively high conversion. Comparing to Cu/ZnO/Al2O3, the Cu-Zn based catalyst generated via SOMC shows higher CH₃OH selectivity especially at higher conversions. Under reaction conditions, zinc is present in both its reduced state and as ZnIII sites according to in situ XAS, which contrast with what is observed with CuGa₃, where only GaII sites are present. Noteworthy, no formate species are intercepted and only methoxy surface species are observed according to ex situ solid state NMR and IR spectroscopy; this observation is consistent with the higher CH₃OH selectivity at higher conversion. The Cu-Zn based catalyst shows structural and catalytic similarities to the previously reported Cu-Ga based system, and thus indicates important features required for highly active and selective catalysts for the hydrogenation of CO₂ to CH₃OH. We are currently working on transposing these findings to develop improved industrial catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.04.028.

References

[1] D. Lüthi, M. Le Floch, B. Bereiter, T. Blunier, J.-M. Barnola, U. Siegenthaler, D. Thouveny, Formation of the climate impact on policy-relevant limits to global warming: the case of 1.5 °C and 2 °C, Earth Syst. Dyn. 7 (2016) 327–351.
[2] J. Arzt, T.E. Müller, K. Thunert, J. Klenkner, R. Meys, A. Sternberg, A. Baradow, W. Leitner, Sustainable conversion of carbon dioxide: an integrated review of catalysis and life cycle assessment, Chem. Rev. 118 (2018) 434–504.
[3] G.A. Olah, A. Goepert, A. Surya Prakash, G.K. Surya Prakash, M.C. Olah, Recycling of carbon dioxide to methanol and derived products - closing the loop, Chem. Soc. Rev. 43 (2014) 7995–8048.
[4] A. Álvarez, A. Bansode, A. Urajawi, A.V. Bavykina, T.A. Wezenendonk, M. Makkee, J. Gascon, F. Kapteijn, Challenges in the greener production of formates/formic acid, methanol, and DME by heterogeneous catalyzed CO₂ hydrogenation processes, Chem. Rev. 117 (2017) 9804–9838.
[5] S. Kuld, M. Thorhauge, H. Falsig, C.F. Elskjær, S. Helveg, I. Chorkendorff, J. Sehested, Quantiﬁcation of the promotion of Cu catalysts by ZnO for methanol synthesis, Science 352 (2016) 969.
[6] M. Behrens, F. Studt, I. Kasatkin, S. Kühn, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Gergsdes, P. Kurr, B.-L. Kniep, M. Tovar, R.W. Fischer, J.K. Nerskov, R. Schögl, The active site of methanol synthesis over Cu/ZnO/Al2O3 industrial catalysts, Science 336 (2012) 893.
[7] T. Lunkenbein, J. Schumann, M. Behrens, R. Schögl, M.G. Willinger, Formation of a ZnO overlayer in industrial Cu/ZnO/Al2O3 catalysts induced by strong metal-support interactions, Angew. Chem. Int. Ed. 54 (2015) 4544–4548.
[8] J. Nakamura, Y. Choi, T. Fujitani, On the issue of the active site and the role of ZnO in Cu/ZnO methanol synthesis catalysts, Top. Catal. 22 (2003) 277–285.
[9] S. Kattel, P.J. Ramirez, J.G. Chen, J.A. Rodriguez, P. Liu, Active sites for CO₂ hydrogenation to methanol on Cu/ZnO catalysts, Science 355 (2017) 1296.
[10] A. Le Valant, C. Comminges, C. Tisseraud, C. Canalf, L. Pinard, Y. Pouilloux, The Cu–ZnO synergy in methanol synthesis from CO₂, Part 1: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu/ZnO mixed catalysts, J. Catal. 324 (2015) 41–49.
[11] C. Tisseraud, C. Comminges, T. Belin, H. Abouari, A. Souilah, Y. Pouilloux, A. Le Valant, The Cu–ZnO synergy in methanol synthesis from CO₂, Part 2: Origin of the methanol and CO selectivities explained by experimental studies and a sphere contact quantation model in randomly packed binary mixtures on CO₂–ZnO coprecipitate catalysts, J. Catal. 330 (2015) 533–544.
[12] F. Studt, M. Behrens, E.L. Kunkes, N. Thomas, S. Zander, A. Tarasov, J. Schumann, E. Frei, J.B. Varley, F. Abild-Pedersen, J.K. Nerskov, R. Schögl, The mechanism of CO and CO₂ hydrogenation reaction on zirconia-supported catalysts: a diffuse reflectance FTIR study, Part II: Surface species on copper/zirconia catalysts: implications for methanol synthesis selectivity, J. Mol. Catal. A 63 (1999) 243–254.
[18] K.-D. Jung, A.T. Bell, Role of hydrogen spillover in methanol synthesis over Cu/ZrO2, J. Catal. 193 (2000) 207–223.
[19] K.T. Jung, A.T. Bell, Effects of zirconia phase on the synthesis of methanol over zirconia-supported copper, Catal. Lett. 80 (2002) 63–68.
[20] K. Li, J.G. Chen, CO2 hydrogenation to methanol over ZrO2-containing catalysts: insights into ZrO2 induced synergy, ACS Catal. 9 (2019) 7840–7861.
[21] K. Larmier, W.C. Liao, S. Tada, E. Lam, R. Verel, A. Bansode, A. Urakawa, A. Comas-Vives, C. Copéret, CO2-to-methanol hydrogenation on zirconia-supported copper nanoparticles: reaction intermediates and the role of the metal-support interface, Angew. Chem., Int. Ed., 56 (2017) 2318–2323.
[22] E. Lam, K. Larmier, P. Wolf, S. Tada, O.V. Safonova, C. Copéret, Isolated Zr surface sites on silica promote hydrogenation of CO2 to CH3OH in supported Cu catalysts, J. Am. Chem. Soc. 140 (2018) 10530–10535.
[23] G. Noh, E. Lam, J.L. Allen, K. Larmier, K. Searles, P. Wolf, C. Copéret, Selective hydrogenation of CO2 to CH3OH on supported Cu nanoparticles promoted by isolated TiIV surface sites on SiO2, ChemSusChem 12 (2019) 968–972.
[24] G. Noh, S.R. Docherty, E. Lam, X. Huang, D. Mance, J.L. Allen, C. Copéret, CO2 hydrogenation to CH3OH on supported Cu nanoparticles: nature and role of Ti in bulk oxides vs isolated surface sites, J. Phys. Chem. C 121 (2019) 31082–31093.
[25] E. Lam, G. Noh, K.W. Chan, K. Larmier, D. Lebedev, K. Searles, P. Wolf, O.V. Safonova, C. Copéret, Enhanced CH3OH selectivity in CO2Hydrogenation using Cu-based catalysts generated via SOMC from GaIII-Single-sites, Chem. Sci. (2020). https://doi.org/10.1039/d0cs00465k.
[26] E. Lam, J.J. Corral-Pérez, K. Larmier, G. Noh, P. Wolf, A. Comas-Vives, A. Urakawa, C. Copéret, CO2 Hydrogenation on Cu/Al2O3: Role of the Metal/Support Interface in Driving Activity and Selectivity of a Bifunctional Catalyst, Angew. Chem., Int. Ed., 58 (2019) 13989–13996.
[27] A.K. Cook, C. Copéret, Alkyne hydroamination catalyzed by silica-supported isolated Zn(II) sites, Organometallics 37 (2018) 1342–1345.
[28] A. Roussey, P. Gentile, B. Lafond, E. Martinez, J.L. Alfke, C. Thieuleux, C. Copéret, Cu nanoparticles on 2D and 3D silica substrates: controlled size and density, and critical size in catalytic silicon nanowire growth, J. Mater. Chem. C 1 (2013) 1583–1587.
[29] M. Behrens, R. Schlogl, How to prepare a good Cu/ZnO catalyst or the role of solid state chemistry for the synthesis of nanostructured catalysts, Z. Anorg. Allg. Chem. 639 (2013) 2683–2695.
[30] J. Schumann, T. Lunkenhein, A. Tarasov, N. Thomas, R. Schlogl, M. Behrens, Synthesis and characterisation of a highly active Cu/ZnO: Al catalyst, ChemCatChem 6 (2014) 2889–2897.
[31] K. Larmier, S. Tada, A. Comas-Vives, C. Copéret, Surface sites in Cu-nanoparticles: chemical reactivity or microscopy?, J. Phys. Chem. Lett. 7 (2016) 3259–3263.
[32] O. Muller, M. Nachtsgaual, J. Just, D. Lutzenkirchen-Hecht, R. Frahm, Quick-EXAFS setup at the SuperXAS beamline for in situ X-ray absorption spectroscopy with 10 ms time resolution, J. Synchrotron Radiation 23 (2016) 260–266.
[33] K. Su, T.D. Tilley, M.J. Sailor, Molecular and polymer precursor routes to manganese-doped zinc orthosilicate phosphors, J. Am. Chem. Soc. 118 (1996) 3459–3468.
[34] C. Copéret, Fuels and energy carriers from single-site catalysts prepared via surface organometallic chemistry, Nat. Energy 4 (2019) 1018–1024.
[35] C. Copéret, Single-sites and nanoparticles at tailored interfaces prepared via surface organometallic chemistry from thermolytic molecular precursors, Acc. Chem. Res. 52 (2019) 1697–1708.
[36] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–319.
[37] S. Kuld, C. Conradsen, P.G. Moses, I. Chorkendorff, J. Sehested, Quantification of zinc atoms in a surface alloy on copper in an industrial-type methanol synthesis catalyst, Angew. Chem., Int. Ed. 54 (2015) 5941–5945.
[38] E.P. Parry, An infrared study of pyridine adsorbed on acidic solids. Characterization of surface acidity, J. Catal., 2 (1963) 371–379.
[39] D. Grandjean, V. Pelipenko, E.D. Batyrev, J.C. van den Heuvel, A.A. Khassin, T.M. Yurieva, B.M. Weckhuysen, Dynamic Cu/Zn interaction in SiO2 supported methanol synthesis catalysts unraveled by in situ XAFS, J. Phys. Chem. C 115 (2011) 20175–20191.