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# The roles of CO and CO<sub>2</sub> in high pressure methanol synthesis over Cu-based catalysts

Niels D. Nielsen, Anker D. Jensen and Jakob M. Christensen\*

Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søtofts Plads Building 229, 2800 Kgs. Lyngby, Denmark.

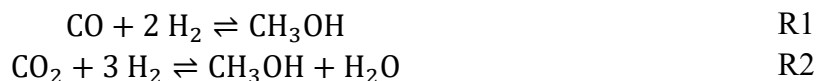
\*Correspondence to: jmc@kt.dtu.dk

## Abstract

The roles of CO and CO<sub>2</sub> in Cu-catalyzed methanol synthesis from syngas were evaluated in experiments with gas switching between CO/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> feeds and between a CO<sub>2</sub>/CO/H<sub>2</sub> feed and a corresponding CO-free CO<sub>2</sub>/inert/H<sub>2</sub> feed. Switching between CO/Ar/H<sub>2</sub> (3/29/68) and CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> (3/29/68) for Cu/Al<sub>2</sub>O<sub>3</sub> showed that the rate of methanol synthesis on Cu is more than an order of magnitude higher from CO<sub>2</sub> compared to CO. Experiments switching between CO<sub>2</sub>/CO/H<sub>2</sub> and CO<sub>2</sub>/inert/H<sub>2</sub> showed that at low conversion conditions with negligible product formation, CO is purely inhibiting for Raney Cu and for a range of supported (on SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO) Cu-catalysts including the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. Given the generality across Cu-based samples the mechanism of this inhibition is most likely competitive adsorption of CO on the Cu surface. However, as conversion is increased by lowering the gas space velocity there is a sharp transition from an inhibiting to a beneficial role of CO relative to a CO-free feed. With increasing conversion more water is formed, and as water is a far stronger inhibitor to Cu-based catalysts than CO, the beneficial effect of CO arises from the removal of water through the water-gas shift reaction. At low conversion the methanol synthesis rate is thus highest for a CO-free feed that minimizes CO inhibition, whereas the rate at high conversion is optimal with a CO-rich syngas that minimizes water inhibition. The transition between these two types of behavior occurs around the conversion range leading to 1 mol% of methanol in the effluent gas. Hence CO has a beneficial role at commercial high conversion conditions. The ZnO support exerts a strong, beneficial support effect at low conversion conditions, where the strong reductant CO has a purely negative effect. This could suggest that reduced Zn-sites (oxygen vacancies in ZnO or Cu-Zn surface alloy sites), whose concentration are expected to depend on the reductive potential of the atmosphere, are not critical to the support effect from ZnO. At both industrial conditions (523 K, 50 bar), mild conditions (448 K, atm. pressure) and in a nominally oxidizing gas (498 K, 20 bar with CO<sub>2</sub> > H<sub>2</sub>) the addition of CO to the feed was detrimental to the activity of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at low conversion conditions. This supports that CO plays no beneficial role by facilitating ZnO-reduction and possibly that Zn alloyed into the Cu surface is unimportant for catalytic activity.

## Introduction

Conventional methanol synthesis proceeds from syngas, a CO<sub>2</sub>/CO/H<sub>2</sub> mixture, over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst operating at 473-573 K and 50-100 bar [1–3]. Hydrogenation of CO (R1) and CO<sub>2</sub> (R2) constitute two potential reaction pathways for methanol synthesis on supported Cu catalysts.



For Cu itself and for the current industrial Cu/ZnO-based catalysts there is a strong preference for the reaction pathway from CO<sub>2</sub> (R2). Isotope labeling studies [4–7] in the 1970s/80s unambiguously established CO<sub>2</sub> as the primary carbon source for methanol formation with industrial Cu/ZnO-catalysts. Experimental studies of a Cu single crystal [8] and of polycrystalline Cu [9,10] support that for Cu itself the CO<sub>2</sub> pathway (R2) is also intrinsically 1-2 orders of magnitude faster than the CO pathway (R1). Although many supported systems such as Cu/ZnO(/Al<sub>2</sub>O<sub>3</sub>) and Cu/Al<sub>2</sub>O<sub>3</sub> qualitatively share the intrinsic properties of Cu in terms of exhibiting a far greater rate from CO<sub>2</sub> compared to CO [9], there is also a strong support effect, whereby the turnover frequency (TOF) can vary by orders of magnitude depending on the support [11–13]. For certain Cu-based catalysts, such as Cu/MgO, R1 is faster than R2. However, this is not related to the intrinsic properties of Cu, but is instead the result of a Cu-MgO synergy that strongly accelerates R1 [9]. This synergistic pathway is most likely relying on basic support sites in the vicinity of the metal particle which is inhibited by the acidic gas CO<sub>2</sub> [9]. From a CO/CO<sub>2</sub>/H<sub>2</sub> feed this CO<sub>2</sub>-inhibition of the synergistic pathway from CO entails that even Cu/MgO primarily produces methanol from CO<sub>2</sub> [14], as only the CO<sub>2</sub>-pathway on the metallic Cu surface of Cu/MgO prevails when the CO pathway is interrupted [9].

Whereas the role of CO<sub>2</sub> as the primary reactant is relatively unambiguous in most cases, the role of CO in the syngas feed for the industrial process is less clear. Some studies [14–18] observe that the methanol synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is faster in CO<sub>2</sub>/H<sub>2</sub> than in CO/CO<sub>2</sub>/H<sub>2</sub>, and correspondingly kinetic studies [19] have observed a negative reaction order in CO. By contrast other studies [16,20–22] observe a faster methanol formation from a CO-rich CO/CO<sub>2</sub>/H<sub>2</sub> mixture. As methanol synthesis from sustainably generated H<sub>2</sub> and locally available CO<sub>2</sub> point sources is envisioned to become an important energy storage solution in a sustainable future society [23], it is important to clarify the exact role of CO in the current industrial process from syngas.

There are several potential roles of CO that need to be unraveled. One of these roles is in removal of water through the water-gas shift (WGS) reaction (R3), as water is observed [11,19,24] to be a strong kinetic inhibitor of the methanol synthesis. However, this role will be limited to higher conversions, where significant water concentrations build up.



It has also been proposed that the strong promoting support effect of ZnO in the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is due to the creation of strongly reduced Zn-sites featuring high activity, such as oxygen vacancies in the ZnO phase [25] or Cu-Zn surface alloy sites [26,27] in the metal surface. With CO being the most reducing component in the syngas [28–30] the CO concentration regulates the concentration of such sites [25,27] and hence the activity, if these reduced Zn-sites are the primary active centers. Thirdly, CO may govern the oxygen coverage on the Cu surface. Ambient pressure X-ray Photoelectron Spectroscopy (XPS) studies [31,32] have shown that oxygen can deposit on the Cu surface in CO<sub>2</sub> or H<sub>2</sub>/CO<sub>2</sub> atmospheres, but the oxygen coverage is found to be low on the Cu surface in CO-rich syngas [24], which suggests that CO may play a role in removing oxygen from the Cu surface.

Here we investigate the roles of CO and CO<sub>2</sub> in Cu-catalyzed methanol synthesis using Raney Cu and a variety of supported Cu catalysts. This work is based on methanol synthesis experiments

switching between CO/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> feeds and by switching between a CO/CO<sub>2</sub>/H<sub>2</sub> feed and a corresponding CO-free N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub> feed.

## 2. Experimental

Gas flows are reported at normal conditions referring to a temperature of 273.15 K and a pressure of 1 atmosphere (denoted by “N” e.g. NmL/min).

### 2.1 Catalysts

The catalysts were synthesized from Cu(II) nitrate hemi(pentahydrate) (98.6%, Alfa Aesar) using co-precipitation (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> with 56 wt% Cu, Cu/ZnO with 10 wt% Cu and Cu/Al<sub>2</sub>O<sub>3</sub> with 67 wt% Cu), incipient wetness impregnation (Cu/SiO<sub>2</sub> with 36 wt% Cu) or deposition precipitation (Cu/TiO<sub>2</sub>(20) with 20 wt% Cu and Cu/TiO<sub>2</sub>(60) with 60 wt% Cu). Raney Cu (98.9 wt% Cu, 0.81 wt% Al, 0.1 wt% Fe, 0.05 wt% Ni) from Strem Chemicals was received as an aqueous slurry and was pre-dried in air at room temperature before use. XPS and surface area analyses of the Raney Cu presented elsewhere [24] have shown that an Al<sub>2</sub>O<sub>3</sub> film covers ca. 60% of the surface, whereas the metallic Cu constitutes the remaining surface. The preparation of the co-precipitated samples is described elsewhere [33]. For the deposition-precipitation the TiO<sub>2</sub> support material (anatase nanopowder, 21 nm particle size from Sigma Aldrich) was dispersed in 500 mL of H<sub>2</sub>O before the precipitation. The Cu was then added by dripping aqueous solutions of Cu(II) nitrate and Na<sub>2</sub>CO<sub>3</sub> (Sigma Aldrich, ≥99.8%) into this TiO<sub>2</sub>-containing slurry at 338 K and a pH of 6.5 followed by 1 h ageing at 338 K with unrestricted pH (same procedure as in co-precipitations). After precipitation the samples were washed in demineralized H<sub>2</sub>O and dried at 313 K overnight.

Cu/SiO<sub>2</sub> was prepared by incipient wetness impregnation of crushed and sieve fractionated (150-300 μm) silica (Saint Gobain, SS61138) with an aqueous solution of Cu(II) nitrate hemi(pentahydrate). All catalyst precursors were calcined in 1 NL/min air flow with a 2 K/min ramp to 573 K, which was maintained for 3 hours. Further characterization of some of these samples using various techniques can be found elsewhere [9,24,33].

### 2.2 Catalyst pre-reduction/activation

All catalysts were pre-reduced in a 60 NmL/min flow of 5% H<sub>2</sub>/N<sub>2</sub> (Air Liquide Denmark) using a heating ramp of 1 K/min and a holding period of 1-4 hours at 448 K before further heating with 1 K/min to 523 K for 2 hours. At both temperatures, water generation terminated as verified by the MS within the allocated holding times. For Cu/Al<sub>2</sub>O<sub>3</sub> the standard reduction was followed by an additional step using 50 NmL/min of 100% H<sub>2</sub> (Air Liquide Denmark) at 523 K for 1 h. After reduction all samples were flushed with He at the final reduction temperature. In selected cases the pre-reduction of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> sample was stopped after the holding period at 448 K and then flushed with He at 448 K in order to probe the effect of CO in the reaction gas after a milder pre-reduction treatment.

### 2.3 Measurements of Cu surface area and total surface area

N<sub>2</sub>O-reactive frontal chromatography (N<sub>2</sub>O-RFC) [34,35] was used to evaluate the Cu surface area at 333 K using a 19 NmL/min flow of 1% N<sub>2</sub>O/He on pre-reduced catalysts. This was done

in an Autosorb iQ<sub>2</sub> setup according to the procedure described elsewhere [9]. The Cu surface area was determined using a Cu:O = 2:1 stoichiometry and a Cu surface atom density of  $1.47 \cdot 10^{19}$  surface Cu atoms/(m<sup>2</sup> Cu) [35,36]. Previous studies [11] using the same setup have revealed a known uncertainty of 6% on the measurement. For ZnO-supported Cu it is known that ZnO-reduction can distort the Cu area measured by N<sub>2</sub>O-RFC. To ensure that the surface area measurements were not impacted by ZnO-reduction the Cu/ZnO(/Al<sub>2</sub>O<sub>3</sub>) samples were subjected to N<sub>2</sub>O-RFC after varying pre-reduction conditions. The sample was either subjected to the standard pre-reduction in 5% H<sub>2</sub> with holding at 448 K and 523 K, to a milder reduction that was terminated after the holding period at 448 K or to a harsher reduction where the standard procedure was followed by exposure to 100% H<sub>2</sub> at 523 K until the water evolution stopped. The results from these 3 pre-reduction tests are shown in Fig. S1a and S1b. For the present Cu-rich Cu/Al<sub>2</sub>O<sub>3</sub> sample similar tests (Fig. S1c) showed that Cu reduction was completed with 5 % H<sub>2</sub> at 523 K. However, previous work [11] on a Cu/Al<sub>2</sub>O<sub>3</sub> sample with lower Cu-content required the use of 100% H<sub>2</sub> at 523 K for complete reduction. Consequently the present Cu/Al<sub>2</sub>O<sub>3</sub> sample was also, as a precaution to ensure complete reduction, treated with 100 % H<sub>2</sub> at 523 K after the standard 5 % H<sub>2</sub> pre-reduction.

The total surface area of the samples was measured on samples that had been pre-reduced (see section 2.2) in an Autosorb iQ<sub>2</sub> setup. The pre-reduced samples were then rapidly transferred through the air to a Quantachrome NOVAtouch Gas sorption analyzer and dried/degassed under vacuum at 423 K for 16 h. After drying the total surface area was determined by a 6-point BET surface area measurement in the NOVAtouch Gas sorption analyzer.

## 2.4 Catalytic tests

Methanol synthesis experiments were conducted in a high pressure flow reactor setup with the catalyst placed in a U-shaped, glass lined, stainless steel reactor. The setup and calibration procedures are described in detail elsewhere [9]. Transient developments in product concentrations were monitored by a Hiden HPR-20 EGA mass spectrometer (MS). Quantitative analyses of product concentration were conducted using a Thermo Fisher Trace 1300 GC equipped with one channel composed of a TG5 column guiding the gas to an FID detector and one channel composed of an OV-1 column followed by a Shincarbon column guiding the gas to a TCD detector.

### 2.4.1 Syngas switching experiments

After catalyst pre-reduction the reactor was pressurized in He to 50 bar at 523 K before switching to one of three syngas mixtures (CO<sub>2</sub>/CO/H<sub>2</sub> = 3/29/68, CO/inert/H<sub>2</sub> = 3/29/68 or CO<sub>2</sub>/inert/H<sub>2</sub> = 3/29/68 mol%) dosed from pure H<sub>2</sub> (99.9999%), pure He (99.9999%), and pre-mixed 9.50% CO/Ar, 9.00% CO<sub>2</sub>/N<sub>2</sub> and 9.00% CO<sub>2</sub>/CO all from Air Liquide Denmark. Time resolved monitoring of the methanol synthesis activity was based on mass spectrometry (MS) measurements ( $m/z = 31$ ), while reported activities were based on the methanol production quantified by online gas chromatography (GC). After obtaining a steady state or quasi-steady state in one gas mixture the feed was switched to another mixture. Catalyst loadings in the reactor were adapted for each catalyst to yield low conversion conditions with <0.3 mol% methanol in the effluent gas.

### 2.4.2 Impact of CO at varying conversion levels

Methanol synthesis was conducted over Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at 523 K and 50 bar at varying conversion levels in the presence (CO<sub>2</sub>/CO/H<sub>2</sub> = 3/29/68) and absence of CO (CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> = 3/29/68). The feed flow and catalyst loading were adjusted to regulate the conversion level. Reported effluent water concentrations for the CO-free feed were based on an oxygen balance assuming that only methanol synthesis (R2) and WGS (R3) occur, whereby the H<sub>2</sub>O production is equal to the sum of the produced CH<sub>3</sub>OH and CO, which are quantified by the calibrated GC.

### 2.4.3 Mild syngas switching experiment over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was mildly reduced in 60 NmL/min of 5% H<sub>2</sub>/N<sub>2</sub> by heating with 1 K/min to 448 K for 1 h to activate Cu but prevent any ZnO reduction. Next, a syngas experiment at 448 K and atmospheric pressure was conducted by starting with CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> (3/29/68) and monitoring the catalytic activity. Once activity had stabilized the feed was switched to CO<sub>2</sub>/CO/H<sub>2</sub> (3/29/68) at a constant gas flow of 280 NmL/min.

### 2.4.4 Methanol synthesis in oxidizing atmosphere over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was mildly reduced in 60 NmL/min of 5% H<sub>2</sub>/N<sub>2</sub> by heating with 1 K/min to 448 K to activate Cu but prevent ZnO reduction, which according to [37] initiates above 0.05 bar H<sub>2</sub> at 493 K. Next, the catalyst was flushed with He and heated to 498 K, where it was pressurized to 20 bar in He before switching to CO<sub>2</sub>/H<sub>2</sub>/He (40/30/30) and monitoring the catalytic activity. The feed was then replaced by a feed of CO<sub>2</sub>/H<sub>2</sub>/CO (40/30/30) with the same flow rate at 498 K and 20 bar of pressure.

## 2.5 Equilibrium calculations

Equilibrium constants for the WGS and methanol formation from Graaf and Winkelman [38] and an assumption of ideality in the gas phase were used to determine the equilibrium product composition for the present experiments.

## 3 Results and Discussion

### 3.1 Sample properties

Nielsen et al. [33] have previously reported Cu surface areas for some of the presently applied samples. Here the Cu surface areas of all the presently applied samples are summarized in Table 1. It is well-established [37,39,40] that partial ZnO reduction can distort the Cu surface area measured from the N<sub>2</sub>O uptake in Cu/ZnO systems. To ensure that the obtained Cu surface areas were free of this effect, the Cu surface area of the Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>) samples was measured after varying pre-reduction treatments to identify the onset of ZnO reduction. Here the standard pre-reduction in 5% H<sub>2</sub> with holding at 448 K and 523 K was compared to a milder pre-reduction terminated after the holding period at 448 K or to a harsher pre-reduction with exposure to 100% H<sub>2</sub> at 523 K after the standard pre-reduction. The results from these experiments are shown in Fig. S1 in the Supporting Information. It is concluded from the results of Kuld et al. [37] that no ZnO reduction will take place with the pre-reduction in 5% H<sub>2</sub> at 448 K, and Fig. S1 shows that with 5% H<sub>2</sub> pre-reduction the Cu area is the same (within the known uncertainty) after reduction at both

448 K and 523 K. From this it is concluded that ZnO-reduction is negligible in the present standard reduction program using 5% H<sub>2</sub>, and consequently the Cu areas in Table 1 should also be accurate for the Cu/ZnO(/Al<sub>2</sub>O<sub>3</sub>) samples.

Table 1: Cu surface areas from N<sub>2</sub>O-RFC determined in this study and by Nielsen et al. [33]. The known uncertainty on the Cu area is 6% [11].

Sample	BET area [m <sup>2</sup> /g <sub>cat.</sub> ]	Cu area [m <sup>2</sup> /g <sub>cat.</sub> ]
Cu/SiO <sub>2</sub>	143.13	1.40
Cu/Al <sub>2</sub> O <sub>3</sub>	82.13	7.16
Cu/TiO <sub>2</sub> (60)	23.20	1.82
Raney Cu	13.94 <sup>†</sup>	5.18 <sup>*</sup>
Cu/ZnO	48.18	5.00 <sup>*</sup>
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	76.92	20.25 <sup>*</sup>
Cu/TiO <sub>2</sub> (20)	42.94	1.19 <sup>*</sup>

<sup>†</sup> Previously reported by Nielsen et al. [24].

<sup>\*</sup> Values reported by Nielsen et al. [33].

### 3.2 The carbon source in methanol synthesis over Cu

Theoretical models [14,41–43] have predicted that the rate of methanol formation on pure Cu should be far higher from CO than from CO<sub>2</sub>. However experimental studies [8–10] unanimously show the opposite – that the rate is far higher from CO<sub>2</sub>. A proposed [14] explanation for this contradiction has been that stable CO<sub>2</sub>-derived intermediates may obscure the fast pathway from CO identified by theoretical studies. To test this Cu-rich Cu/Al<sub>2</sub>O<sub>3</sub> was used, as it possesses good thermal stability and has previously [9] been shown to qualitatively reflect the behavior of unsupported Cu. Cu/Al<sub>2</sub>O<sub>3</sub> was subjected to experiments with gas switching between CO/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> feeds to evaluate, if the reaction rate in CO/H<sub>2</sub> is affected by prior exposure to CO<sub>2</sub>/H<sub>2</sub>. If very stable CO<sub>2</sub>-derived intermediates affect the pathway from CO the order of the gas mixtures should be of great importance. Fig. 1a shows the result of this switching experiment starting from CO<sub>2</sub>/H<sub>2</sub>, whereas Fig. 1b shows the result when starting in CO/H<sub>2</sub>. Fig. 1 illustrates that the rate of methanol synthesis from CO<sub>2</sub> is more than an order of magnitude faster than the rate from CO regardless of the order of the gas mixtures. At these conditions the equilibrium methanol concentration is 1.09 mol% from CO<sub>2</sub>/inert/H<sub>2</sub> and 2.31 mol% from CO/inert/H<sub>2</sub>. Hence the greater reaction rate from CO<sub>2</sub> occurs despite a considerably closer proximity to the equilibrium. These results show that even in the absence of CO<sub>2</sub>-derived intermediates occupying the surface, the route from CO is still far inferior to the route from CO<sub>2</sub>. The results help to substantiate that CO<sub>2</sub> is the primary carbon source in methanol synthesis over Cu. Our previous work [9] and additional tests for the Cu/TiO<sub>2</sub> catalysts (see Supporting Information Fig. S2) show that this conclusion applies to all the Cu-based catalysts investigated here. Here we thus focus on materials that share the intrinsic properties of Cu, where the rate from CO<sub>2</sub> is far higher and where CO<sub>2</sub> consequently is the primary reactant for methanol synthesis. It may be added that the alternative synergistic pathway for CO-hydrogenation, which is particularly strong in materials such as Cu/MgO, most likely relies on basic support sites in the vicinity of the metal particle [9]. Consequently this

pathway is strongly inhibited by the acidic gas  $\text{CO}_2$  [9], but relatively uninhibited by a basic gas such as  $\text{NH}_3$  [44].

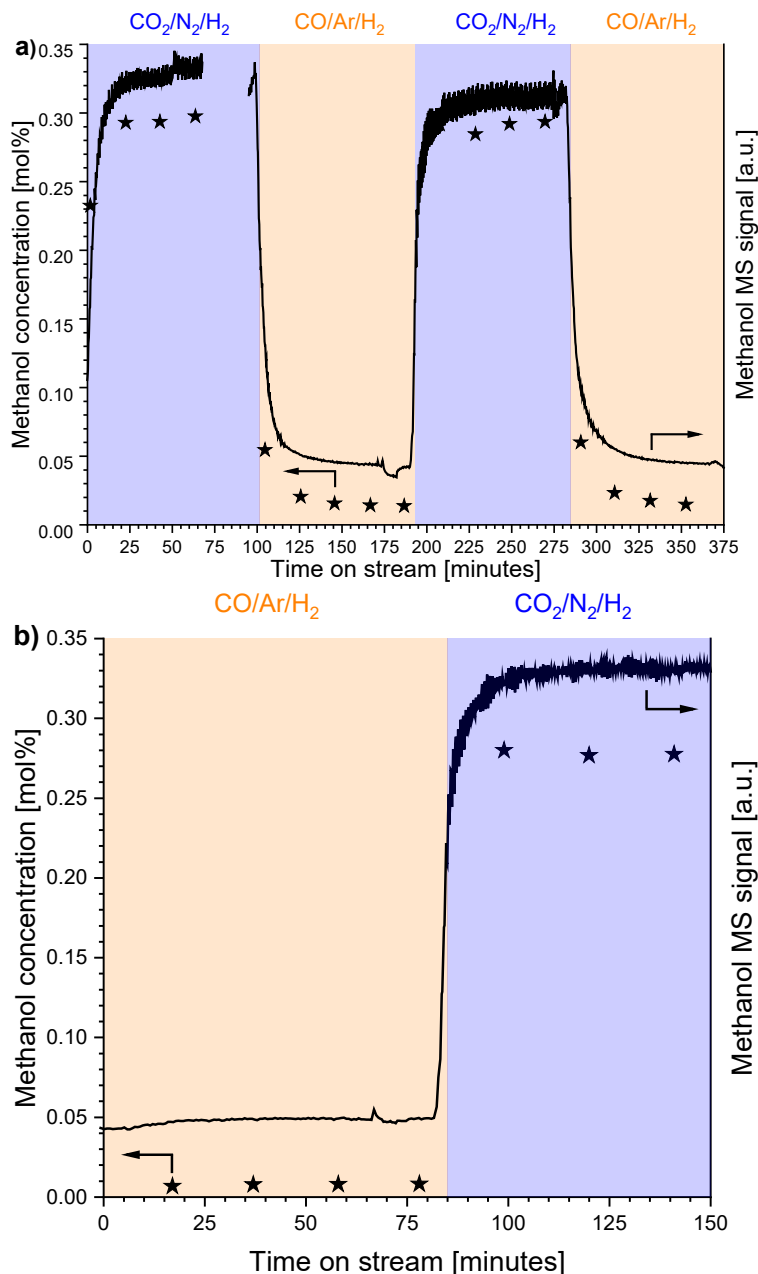


Fig. 1: The effluent methanol concentration (stars) achieved over  $\text{Cu}/\text{Al}_2\text{O}_3$  as function of time on stream when switching between  $\text{CO}_2/\text{H}_2$  and  $\text{CO}/\text{H}_2$  feeds (both balanced with inert gas) starting from a)  $\text{CO}_2/\text{H}_2$  or b)  $\text{CO}/\text{H}_2$ . The MS signal (solid line) for methanol ( $m/z = 31$ ) is also shown to better illustrate the transient development. Flow measurement required bypass of the MS resulting in a data gap in the MS signal in a). Reaction conditions:  $T = 523 \text{ K}$ ,  $P = 50 \text{ bar}$ , feed flow =  $275 \pm 3 \text{ NmL/min}$ ,  $\text{CO}_x/\text{inert}/\text{H}_2 = 3/29/68$ ,  $\text{Cu}/\text{Al}_2\text{O}_3$  loading =  $180.2 \text{ mg}$  in a)  $148.4 \text{ mg}$  in b). Fig. 1b is reproduced with permission from Nielsen et al. [9].



### 3.3 The role of CO in methanol synthesis from syngas

Since CO<sub>2</sub> is the primary reactant for methanol synthesis on the investigated catalysts it is relevant to elucidate the role of CO in a ternary CO/CO<sub>2</sub>/H<sub>2</sub> atmosphere. To do this both Raney Cu and supported Cu catalysts were allowed to stabilize in a CO<sub>2</sub>/CO/H<sub>2</sub> feed, and the CO in the feed was then replaced with an identical concentration of N<sub>2</sub>, while all other conditions were maintained. In these experiments flows and catalyst loadings were adjusted to preserve low conversion conditions (< 0.3 mol% CH<sub>3</sub>OH produced) in order to minimize the effects of the reaction products, H<sub>2</sub>O and CH<sub>3</sub>OH. At these conditions the equilibrium methanol concentration is 1.09 mol% for the CO-free feed and 23 mol% from CO<sub>2</sub>/CO/H<sub>2</sub>, so the present experiments are generally also far from equilibrium. Fig. 2 shows the development in methanol productivity during such an experiment for Cu/TiO<sub>2</sub>(20) and illustrates that the methanol production actually increases, once CO is removed from the feed. Fig. 3 summarizes the stabilized productivity levels with and without CO for all samples. To facilitate comparison the stabilized level in CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> is assigned as a relative productivity of 1.00 for each sample, and the final productivity in CO<sub>2</sub>/CO/H<sub>2</sub> prior to the shift to CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> is shown relative to this level. The figure clearly illustrates that at these low conversion conditions all samples exhibit a faster rate in CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>. Hence, CO is an inhibitor for all the investigated Cu-catalysts.

This qualitative generality suggests that the inhibiting effect of CO comes from an interaction with the metallic Cu surface, which is the only common feature of these samples. It follows from this argument that if all the catalysts are impacted by CO interacting with the Cu surface, then the reaction must also be located on the Cu surface for all the samples. While there have been previous reports [19,45] of CO-inhibition for Cu/ZnO-systems the generality of this effect has not previously been identified. These results thus clearly point to the metallic Cu surface as the location of the active centers in methanol synthesis with supported Cu in agreement with previous studies supporting the same conclusion. Yoshihara and Campbell [46] observed that the TOF for methanol synthesis on an open Cu(110) single crystal surface was higher than the TOF of a supported Cu/ZnO-system and thereby illustrated that the high rates achievable with ZnO-supported industrial catalysts are possible on a Cu surface. Furthermore, there are numerous linear correlations [11,47–53] between the metallic Cu surface area and the methanol synthesis rate (from CO<sub>2</sub>) for supported catalysts. There is thus strong evidence that the reaction occurs on the metallic surface. However, since the reaction also has a strong support effect (note the support dependent TOF in Fig. 3), this support effect must arise from a support-induced modification to the properties of the metallic Cu surface.

From repeated cycling between a feed with and without CO for thermally stable systems, such as Cu/TiO<sub>2</sub>(60), it is evident that the inhibiting effect of CO is fully reversible over the time scale of a few minutes (see Fig. S3). This suggests that the effect of CO is on the kinetics of the surface reactions. The most likely cause for the inhibiting effect of CO is competitive adsorption. The CO adsorbed on the Cu surface is only converted to methanol with a very low rate (Fig. 1), and blockage of the surface with adsorbed CO will inhibit the rate by preventing the much faster pathway from CO<sub>2</sub>. However, there could be a secondary inhibiting effect of CO. There are indications from ambient pressure XPS studies [31] that oxygen deposits on the Cu surface in H<sub>2</sub>/CO<sub>2</sub> atmospheres, and it has been proposed [10] that this oxygen exerts a promotional role on

the methanol synthesis. In a previous study [24] we found that the oxygen coverage on Cu was insignificant (below our detection limit of 0.04 ML) in a CO-rich syngas. The CO may therefore also inhibit the methanol formation by scavenging away oxygen from the metal surface.

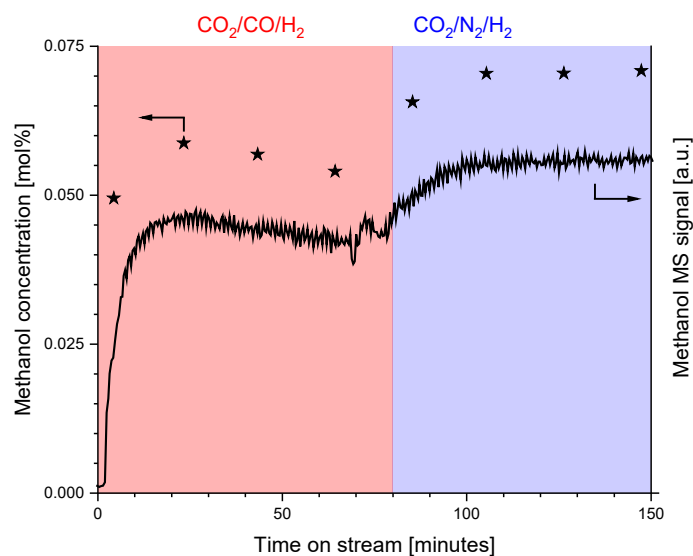


Fig. 2: The methanol concentration (stars) as a function time on stream for Cu/TiO<sub>2</sub>(20), when switching from a CO<sub>2</sub>/CO/H<sub>2</sub> feed to a CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> feed. The MS signal (solid line) for methanol (m/z = 31) is also included. Reaction Conditions: T = 523 K, P = 50 bar, feed flow = 280 ± 5 NmL/min, CO<sub>2</sub>/X/H<sub>2</sub> = 3/29/68 with X = CO or N<sub>2</sub>, Cu/TiO<sub>2</sub>(20) loading = 261.5 mg. Here the final measurement in each gas is used to construct Fig. 3.

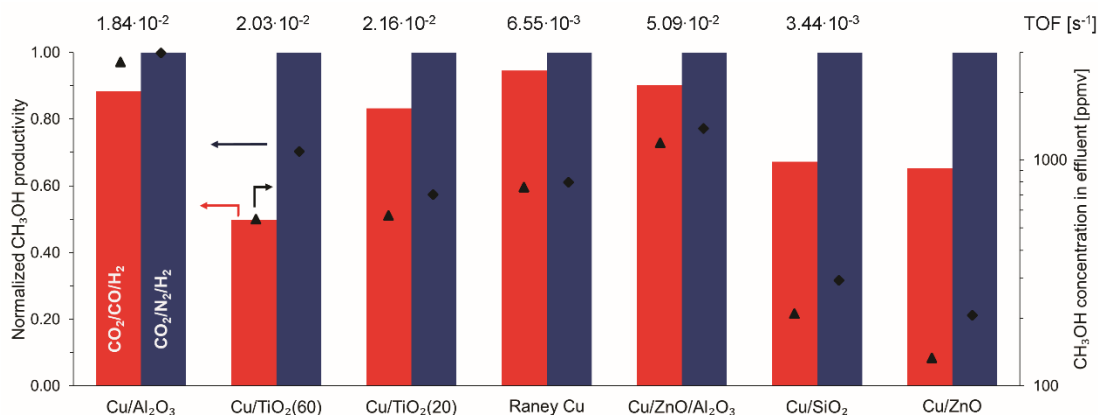


Fig. 3: The normalized methanol productivity (left vertical axis) in CO/CO<sub>2</sub>/H<sub>2</sub> (red bars) and CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> (blue bars) for Raney Cu and various supported Cu-samples. Each catalyst is allowed to stabilize in CO/CO<sub>2</sub>/H<sub>2</sub> before replacing CO with an identical concentration of N<sub>2</sub> as illustrated in Fig. 2. The black data points (triangle and diamond) show the effluent methanol concentration in each experiment on the right vertical axis. The TOF for methanol formation (per Cu surface atom) in the CO-free feed is also shown above each set of bars. Cu/ZnO was allowed to stabilize for a prolonged period prior to the gas switch, and as sintering may have occurred no TOF is reported for this sample. Reaction conditions: T = 523 K, P = 50 bar, CO<sub>2</sub>/X/H<sub>2</sub> = 3/29/68 with X = CO or N<sub>2</sub>. Space velocity was varied (between 3.1 · 10<sup>4</sup> and 145 · 10<sup>4</sup> NmL/g<sub>cat</sub>/h) to ensure low conversion conditions.

Fig. 3 shows that stronger CO inhibition generally occurs in the experiments with the lowest conversions and hence the lowest product concentration in the effluent. This indicates that the impact of CO is dependent on the conversion level. It is well known that the water produced in the methanol synthesis reaction (R1) is strongly inhibiting to Cu-catalyzed methanol synthesis. Thrane et al. [11] found that adding 1500 ppmv H<sub>2</sub>O to the syngas feed caused the methanol synthesis rate over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> to drop by 60-70% when operating in the 493-523 K range at 41 bar. Sahibzada et al. [18] also found that such a catalyst lost 90% of its methanol synthesis activity, when 2 vol% H<sub>2</sub>O was added to the feed at 523 K and 50 bar of pressure. The occurrence of water inhibition for Cu-catalysts is not support specific, as Yang et al. [54] found that adding 0.2 mol% H<sub>2</sub>O to the feed caused Cu/SiO<sub>2</sub> to lose approximately 40% of its methanol synthesis activity at 413 K and 6 bar. Hence, the water inhibition is general for Cu catalysts, although the available data do not rule out that the strength of the effect could be support dependent. Saito et al. [45] also conducted direct comparisons of inhibition from CO and H<sub>2</sub>O for Cu/ZnO/ZrO<sub>2</sub> and found that H<sub>2</sub>O is a far stronger inhibitor than CO. Hence, at higher conversion CO can exert a relative positive effect by removing a worse inhibitor, water, through the WGS reaction (R3).

To investigate the water scavenging effect at higher conversion, switching experiments between CO<sub>2</sub>/CO/H<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> were conducted for Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at varying conversion levels. The conversion was varied by adjusting the catalyst loading and feed flow to change the space velocity/residence time. Fig. 4 shows the results from such experiments with Cu/Al<sub>2</sub>O<sub>3</sub>, where the gas switch is conducted at different space velocities. Fig. 4a shows that at the

highest space velocity (lowest conversion and water concentration) there is a slight negative effect of CO. Fig. 4b shows that for lower space velocities, where conversion and water concentration are higher, there is oppositely a significant positive effect of CO relative to a CO-free gas. Here it is important to emphasize that both CO and H<sub>2</sub>O are inhibitors, and the highest productivity occurs with high space velocity and no CO in the feed (Fig. 4a), whereby the total presence of the inhibitors is minimized. The benefit of CO is a relative benefit due to the exchange of a stronger inhibitor (H<sub>2</sub>O) with a weaker one (CO).

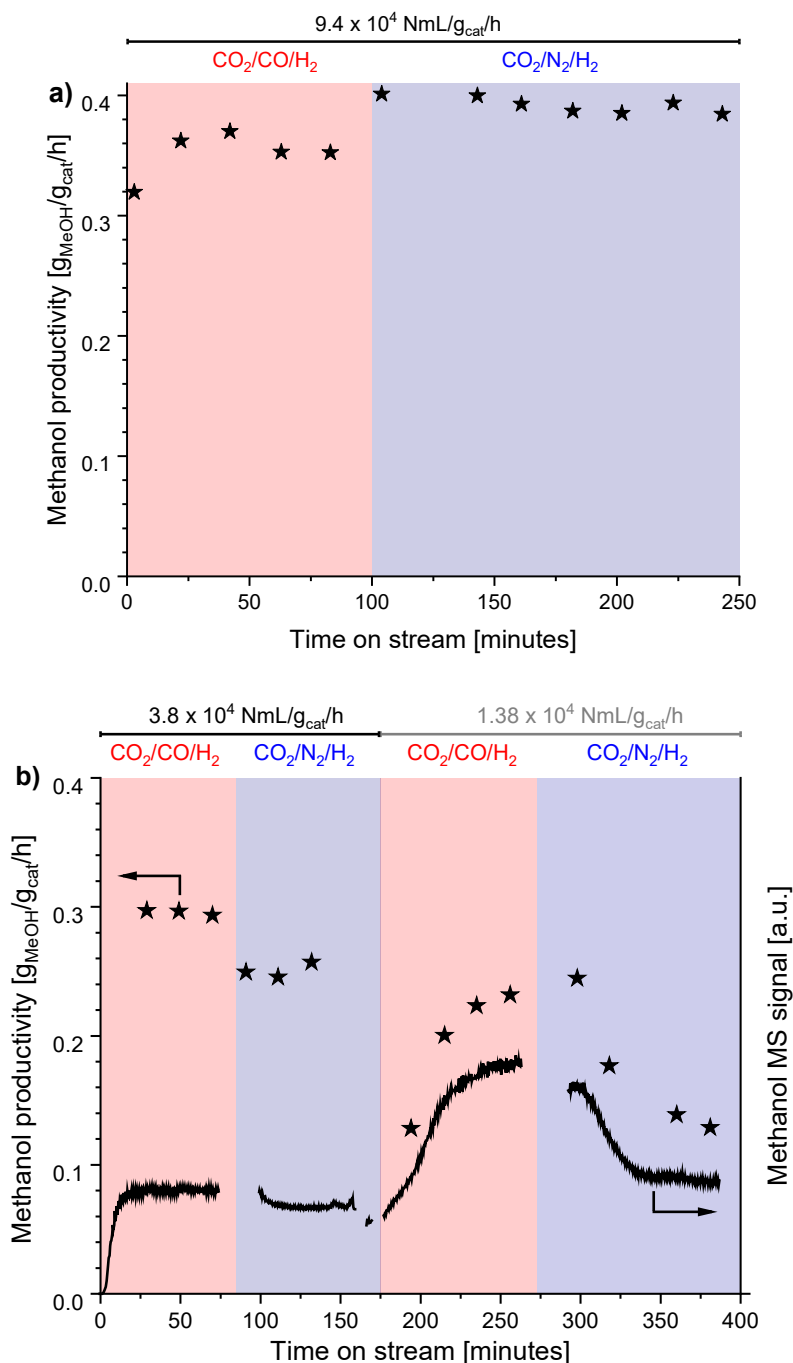


Fig. 4: The methanol production rate as a function of time on stream with Cu/Al<sub>2</sub>O<sub>3</sub> and a gas space velocity of a)  $(9.42 \pm 0.07) \cdot 10^4 \text{ NmL/g}_{\text{cat}}/\text{h}$  and b) both  $(3.80 \pm 0.06) \cdot 10^4 \text{ NmL/g}_{\text{cat}}/\text{h}$  and  $(1.38 \pm 0.04) \cdot 10^4 \text{ NmL/g}_{\text{cat}}/\text{h}$ . In b) the methanol MS signal ( $m/z = 31$ ) is also shown to illustrate that the product concentration as expected is higher for the lower space velocity. Gaps in the methanol MS signal are due to bypass for flow measurements. Reaction conditions:  $T = 523 \text{ K}$ ,  $P = 50 \text{ bar}$ ,  $\text{CO}_2/\text{X}/\text{H}_2 = 3/29/68$  with  $\text{X} = \text{CO}$  or  $\text{N}_2$ , Cu/Al<sub>2</sub>O<sub>3</sub> loading = 178.6 mg in a) and 433.7 mg in b).

Fig. 5 shows the ratio between the rates with and without CO as a function of the water concentration in the effluent for the CO-free feed. The water concentration is estimated from an oxygen balance as the sum of the production of methanol and CO assuming that only reactions R1 and R3 occur. Since negligible formation of DME or other products were detected by the GC, this is expected to be a good assumption. Fig. 8 shows that at low conversion the H<sub>2</sub>O formation is low, and CO only impacts the activity negatively for both Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>. By increasing the conversion level the H<sub>2</sub>O concentrations rises, and for both Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> there is a sharp transition, where CO becomes beneficial compared to a CO-free gas. As described above this benefit can be attributed to the role of CO as a scavenger of water by the WGS reaction. The transition to a positive effect of CO occurs at a lower water concentration for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. This can be rationalized from the known support effect of ZnO upon the heat of adsorption of water on the catalyst. In the limit of zero water coverage the heat of adsorption of water on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is 65 kJ/mol [55], whereas the heat of adsorption on pure Cu is around 45 kJ/mol [56–58]. It would be consistent with the stronger bonding of water on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> that the inhibiting effect of water, and hence the need for water removal by reaction with CO, becomes important at a lower water concentration for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. However, the beneficial effect of CO also emerges for Cu/Al<sub>2</sub>O<sub>3</sub> although at a higher water concentration. This is in agreement with the results of Yang et al. [54] showing that water inhibition is also important for ZnO-free supports.

For the experiments in Fig. 5 with a CO-free feed, where the water content can be accurately estimated through the oxygen balance, the approach to equilibrium for WGS and methanol synthesis were evaluated, and the results are summarized in Table S1 in the supporting information. The highest approach to equilibrium among these tests were 59.1% for the WGS and 20.8% for methanol synthesis. Hence, both reactions are in the kinetically controlled regime although with the faster (reverse) WGS generally closer to an equilibration.

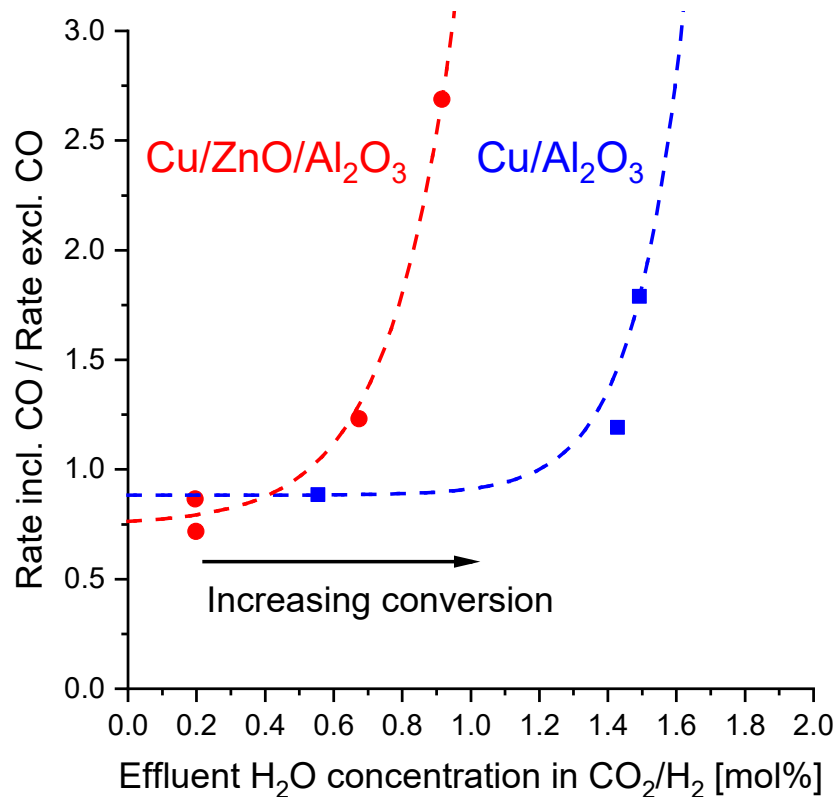


Fig. 5: The ratio between the methanol formation rates in  $\text{CO}_2/\text{CO}/\text{H}_2$  and  $\text{CO}_2/\text{N}_2/\text{H}_2$  as a function of the estimated effluent concentration of water in the  $\text{CO}_2/\text{N}_2/\text{H}_2$  atmosphere for  $\text{Cu}/\text{Al}_2\text{O}_3$  and  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ . Reaction conditions:  $T = 523 \text{ K}$ ,  $P = 50 \text{ bar}$ ,  $\text{GHSV} = (2.4\text{-}14.5) \cdot 10^5 \text{ NmL/g}_{\text{cat}}/\text{h}$  for  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  and  $(1.4\text{-}94.1) \cdot 10^4 \text{ NmL/g}_{\text{cat}}/\text{h}$  for  $\text{Cu}/\text{Al}_2\text{O}_3$ .

### 3.4 Optimal $\text{CO}/\text{CO}_2$ ratio for methanol synthesis over $\text{Cu}/\text{ZnO}$ -based catalysts

As the hydrogenation of  $\text{CO}_2$  provides a faster pathway (Fig. 1) the concentration of  $\text{CO}_2$  in the syngas feed is obviously important. Fig 6 summarizes the literature [59–61] on the effect of the  $\text{CO}_2$  partial pressure in the feed, when only the  $\text{CO}_2$  concentration is varied. Fig. 6 shows that the methanol synthesis is approximately 1<sup>st</sup> order in  $\text{CO}_2$  to around 1 bar of pressure and then becomes 0<sup>th</sup> order in  $\text{CO}_2$  for higher partial pressures. IR studies [59,61] suggest that the stagnation occurs because the concentration of formate intermediates on the Cu surface saturates.

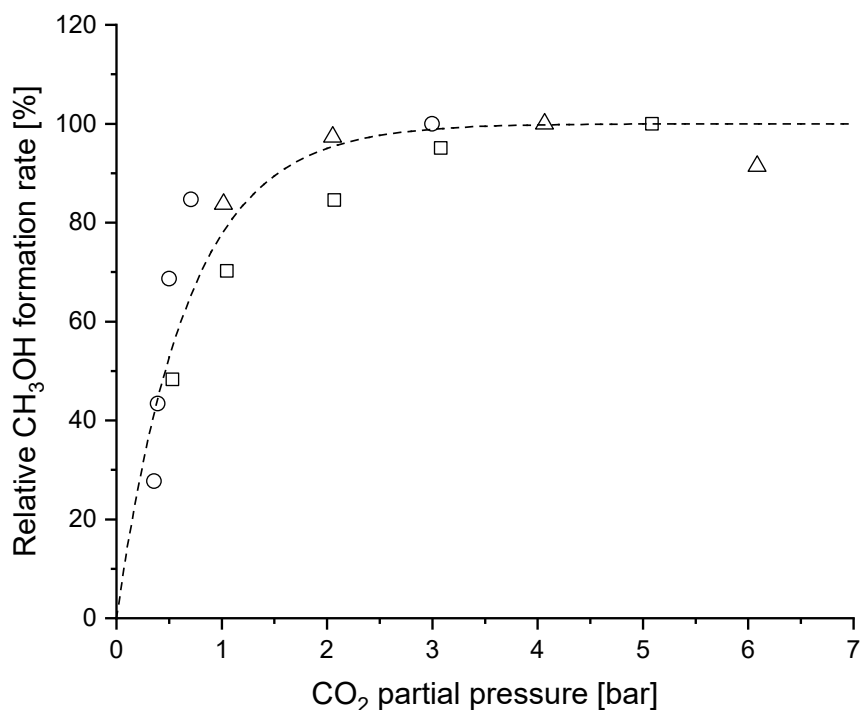


Fig. 6: The relative methanol production rate of Cu/ZnO-based catalysts as a function of the CO<sub>2</sub> partial pressure in the feed. Data (in the 496-523 K range) from: Amenomiya and Tagawa [61] (□), Le Peltier et al. [59] (○), and Nomura et al. [60] (△). The data are normalized by setting the highest productivity in each study to 100%.

Studies that instead vary the CO/CO<sub>2</sub> ratio in the CO<sub>x</sub> part of the syngas have yielded seemingly contradictory observations, as optimal activity has been reported for both CO-free and CO-rich atmospheres. The observation of a transition from a detrimental to a beneficial effect of CO on the activity, when varying the conversion level (Figs. 4 and 5), can help to rationalize these observations. At low conversion the inhibiting effect of CO means that the CO concentration should be as low as possible, but at high conversion a high concentration of CO is needed to remove water. Fig. 7 summarizes literature results for Cu/ZnO/(Al<sub>2</sub>O<sub>3</sub>) catalysts by showing the normalized methanol productivity as a function of the fraction of CO<sub>2</sub> in the CO<sub>x</sub> part of syngas feed with a fixed CO<sub>x</sub>/H<sub>2</sub> ratio. These results are obtained at industrially relevant high pressure conditions. The literature results are separated into low conversion conditions with negligible product formation (Fig. 7a) and high conversion conditions with non-negligible product formation (Fig. 7b). An analysis (see Table S4) of the product concentrations in the experiments in Fig. 7 shows that this low conversion behavior in Fig. 7a occurs for methanol effluent concentrations below ca. 1 mol%, whereas the high conversion behavior in Fig. 7b occurs above ca. 1 mol% methanol in the effluent. Hence, the transition between the two types of behavior occurs around the conversion region leading to 1 mol% methanol in the effluent gas.



Fig. 7a shows that at low conversion conditions the methanol formation rate rises strongly until CO<sub>2</sub> constitutes 10-20% of the CO<sub>x</sub> whereafter the increase continues albeit less profoundly until CO<sub>2</sub> is the only CO<sub>x</sub> component. The sharper initial rise in Fig. 7a until 10-20% CO<sub>2</sub> in the CO<sub>x</sub> can be attributed to the regime, where the reaction has a positive dependence on CO<sub>2</sub> (see Fig. 6) and where CO<sub>2</sub> thus brings an advantage of its own. Above this level additional CO<sub>2</sub> may not bring strong beneficial effects of its own, since the reaction becomes 0<sup>th</sup> order in CO<sub>2</sub>. However, as CO is inhibiting it is nevertheless still beneficial to replace CO with CO<sub>2</sub>, and maximal activity occurs in a completely CO-free gas.

Fig. 7b shows that at high conversion conditions with higher product concentrations the methanol production is optimal for a syngas with a CO<sub>x</sub> fraction of ca. 10% CO<sub>2</sub> and 90% CO. At high conversion it is beneficial to include sufficient CO<sub>2</sub> to reach the 1-2 bar CO<sub>2</sub> partial pressure that saturates the beneficial effect of CO<sub>2</sub> (see Fig. 6). However, once this CO<sub>2</sub>-concentration is reached, the CO<sub>2</sub> offers no additional benefit, and it is instead preferable that the remaining part of the CO<sub>x</sub> is CO in order to optimize the removal of water by the WGS reaction. The optimal CO<sub>x</sub> composition is thus a CO-rich mixture at higher conversions. The composition dependencies in Fig. 7 can thus be described in terms of the beneficial effect of CO<sub>2</sub> (Nielsen et al. [9] and Figs. 1 and 6), the inhibiting effect of CO (Fig. 3), and the inhibiting effect of water (e.g. Thrane et al. [11] and Yang et al. [54]) that all are general among Cu catalysts regardless of the support. This implies that it is the kinetics of the surface reactions on Cu and not support-dependent effects that cause the dependencies on the CO<sub>x</sub> composition. However, Fig. 5 clearly shows that the transition between the two regimes in Fig. 7 will depend upon the support, and any support-dependencies in the formate coverage could also cause factors such as the location of the optimum in Fig. 7b to vary with the support.

It should be added that at high conversion with significant methanol concentrations, the water scavenging effect of CO operates in parallel to a methanol-assisted autocatalytic mechanism, whereby methanol facilitates the generation of additional methanol [11]. For catalysts such as Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> the combined effect of the autocatalytic acceleration and the water scavenging means that the absolute rate increases with increasing conversion for CO-rich feeds [11]. The alcohol-assisted mechanism that causes the autocatalytic effect does not seem to require CO [62–64]. The increase in absolute activity of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> with increasing conversion in the presence of CO is therefore not likely to be the result of CO participating directly in the autocatalytic pathway, but rather the result of CO removing water and thus providing optimal conditions for the autocatalytic pathway.

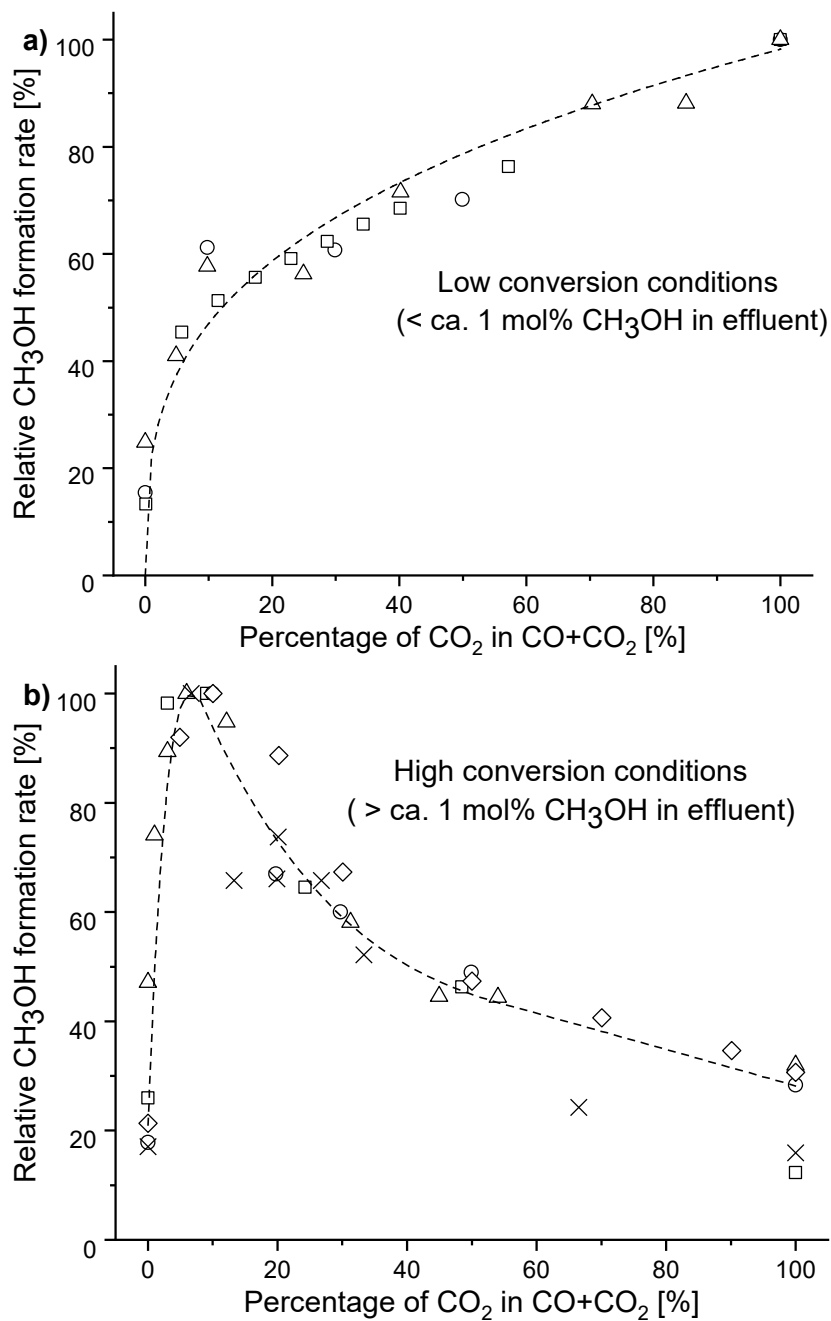


Fig. 7: The relative methanol synthesis activity for Cu/ZnO(Al<sub>2</sub>O<sub>3</sub>) catalysts as a function of the CO<sub>2</sub> fraction in the CO<sub>x</sub> part of the syngas for: a) low conversion conditions with negligible product concentrations and b) high conversion conditions with non-negligible product concentrations. Here the CO<sub>x</sub> composition is varied at a fixed CO<sub>x</sub>/H<sub>2</sub> ratio and all studies are normalized to the highest activity achieved in the study. Data in a) from: Studt et al. [14] (□), Chanchlani et al. [15] (△) and Lee et al. [16] (○). Data in b) from: Martin and Perez-Ramirez [20] (△), Barbier et al. [21] (□), Sahibzada et al. [18] (◇), Lee et al. [16] (○) and Klier et al. [22] (×). The exact data used from the literature studies are specified in Tables S2-S4 in the Supporting Information.

### 3.5 Role of CO-induced rise in reductive potential for Cu/ZnO-catalysts

It is well established that ZnO exerts a strong support effect on the Cu-catalyzed methanol synthesis (see Fig. 3 and refs. [11–13,65,66]), although the exact mechanism by which this support effect operates remains imperfectly understood. One proposal is that reduced Zn-sites, such as oxygen vacancies in the ZnO [25] or Zn alloyed into the metallic surface [27,37,67–70], are sites of particularly high activity. The reductive potential of the syngas, which is governed by especially the CO/CO<sub>2</sub> ratio, will have a major impact on the concentration of such reduced Zn-sites [25,27], which should be reflected in a major impact on the catalytic activity.

Fig. 8 shows the turnover frequency (TOF) in methanol synthesis per Cu surface atom for Raney Cu and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at the low conversion conditions of Fig. 3 both with and without CO in the feed.

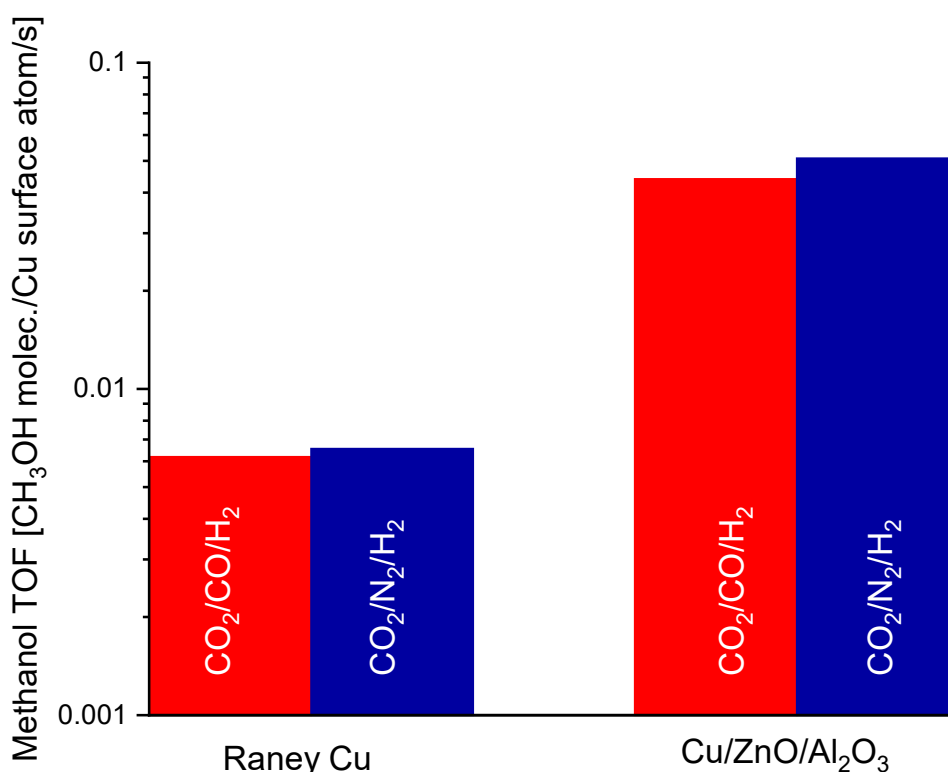


Fig. 8: The turnover frequency for methanol synthesis (per Cu surface atom) for Raney Cu and Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> in both CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> (red) and CO<sub>2</sub>/CO/H<sub>2</sub> (blue). These results are at low conversion conditions (see effluent concentrations in Fig. 3). Reaction conditions: T = 523 K, P = 50 bar, CO<sub>2</sub>/X/H<sub>2</sub> = 3/29/68 with X being CO or N<sub>2</sub>, GHSV = (8.3-8.4)·10<sup>4</sup> NmL/g<sub>cat</sub>/h (Raney Cu) and (1.4-1.5)·10<sup>6</sup> NmL/g<sub>cat</sub>/h (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>).

We have previously [24] confirmed that the Raney Cu sample is a good quantitative approximation to the intrinsic properties of Cu, and Fig. 8 shows that at these low conversion conditions the TOF for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is 7-8 times higher than the TOF for Raney Cu. Fig. 8 also illustrates that at these conditions a strong support effect is present, but the most reducing component in the gas, CO, nevertheless has a negative effect on the performance of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> system. This could suggest that reduced Zn-sites, whose concentration rises with increasing CO/CO<sub>2</sub> ratio [25,27], are

not important for the catalytic activity. However, it cannot be fully excluded that the high hydrogen pressure at the conditions of Fig. 8 is sufficient to saturate the concentration of such reduced Zn-sites. Switching experiments were therefore conducted at two sets of model conditions, where the presence of CO should be essential for the creation of reduced Zn-sites, such as Cu-Zn surface alloy sites.

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was subjected to mild (5% H<sub>2</sub> at 448 K and atm. pressure) pre-reduction to ensure minimal reduction of the ZnO component. The methanol synthesis activity was then investigated at 448 K and atmospheric pressure starting from a less reducing CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> mixture and then switched to a more reducing CO<sub>2</sub>/CO/H<sub>2</sub> gas mixture. The N<sub>2</sub> and CO concentrations were identical to ensure that all other parameters remained constant. Fig. 9 shows the methanol formation during the switching experiment and illustrates that also at these conditions CO exerts an exclusively negative effect and causes a 34% drop in the methanol formation rate. Equilibrium methanol concentrations at these conditions are 9136 ppm for CO<sub>2</sub>/CO/H<sub>2</sub> and 201 ppm for CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>. Hence, the rate in the absence of CO is higher despite a considerably closer proximity to the equilibrium, which emphasizes the role of CO as a kinetic inhibitor. The negative role of CO at these conditions is in good agreement with the results of Cherifi et al. [19], who studied the reaction kinetics with a similar catalyst and conditions and also observed an exclusively negative effect of CO.

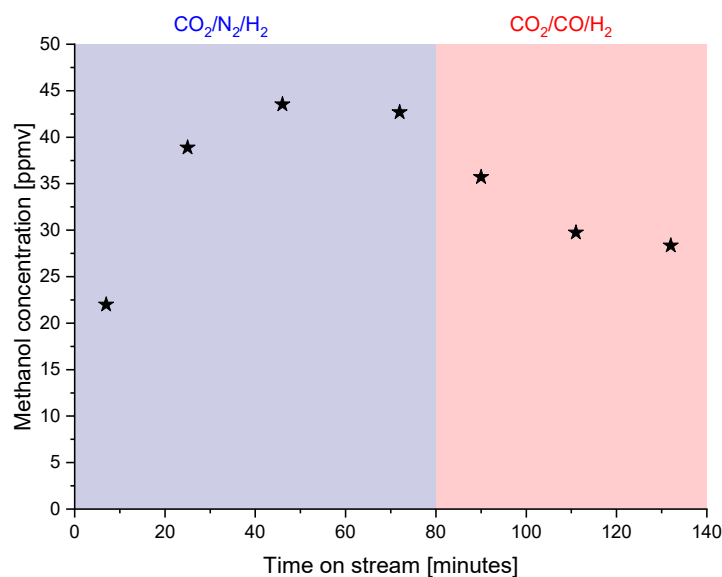


Fig. 9: The methanol production as a function of time on stream when mildly pre-reduced (5% H<sub>2</sub>/N<sub>2</sub> at 448 K) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is exposed to first CO<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub> followed by replacement of the N<sub>2</sub> with CO. Reaction conditions: T = 448 K, atmospheric pressure feed flow = 281 ± 4 NmL/min, CO<sub>2</sub>/X/H<sub>2</sub> = 3/29/68 with X = N<sub>2</sub> or CO, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> loading = 25.3 mg.

In a second model study Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was mildly (5% H<sub>2</sub> at 448 K) pre-reduced before being heated in He to 498 K and pressurized to 20 bar. The sample was then subjected to a CO<sub>2</sub>/He/H<sub>2</sub> (40/30/30) feed i.e. a nominally oxidizing gas (CO<sub>2</sub> > H<sub>2</sub>). The methanol formation was allowed to stabilize before the He was replaced with CO, which changed the atmosphere to a nominally

reducing gas ( $\text{CO} + \text{H}_2 > \text{CO}_2$ ). Fig. 10 shows the methanol formation during the stabilization and gas switch and illustrates that CO is also inhibiting at these conditions, as the activity drops by 40-50% upon introduction of CO.

These results clearly illustrate that CO plays no beneficial role in facilitating the reduction of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>. Additionally, the fact that CO has a negative effect at these model conditions, where the reductive power of CO should be critical to the formation of reduced Zn-sites, suggests that e.g. Cu-Zn surface alloy sites are not the source of the beneficial support effect from ZnO. The present results showing that a CO-induced rise in the reductive potential to be detrimental for the catalytic activity are in conceptual agreement with the results of Frei et al. [71], who observed that raising the reductive potential during pre-reduction through increasing temperature was detrimental for a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst in terms of TOF and activation energy.

In conclusion the present results have two primary implications for the support effect in Cu-catalyzed methanol synthesis. The generality in how reaction conditions, such as the CO concentration, impacts a wide variety of Cu-based catalysts (Figs. 3 and 5) implies that the active sites are located on the metallic Cu surface, which is the only common feature of these samples. This suggests that support effects, such as the beneficial effect of ZnO, arise from a modification of the metallic Cu surface. However, the detrimental effect of CO even under model conditions (Figs. 9 and 10), where an increased reductive potential should influence the alloying of Zn into the metallic surface makes it unlikely that such CuZn surface alloying is the source of the support induced modifications to the properties of the metallic Cu surface.

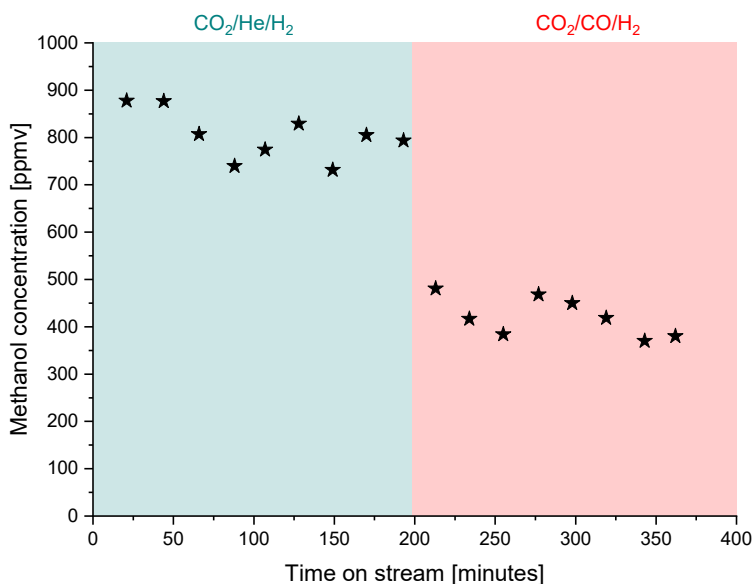


Fig. 10: The methanol concentration as a function of time on stream when mildly pre-reduced (5% H<sub>2</sub>/N<sub>2</sub> at 448 K) Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is exposed to first a formally oxidizing CO<sub>2</sub>/He/H<sub>2</sub> atmosphere followed by replacement of He with CO to create a formally reducing atmosphere. Reaction conditions: T = 498 K, P = 20 bar, feed flow = 280 ± 3 NmL/min, X/H<sub>2</sub>/CO<sub>2</sub> = 30/30/40, GHSV = 1.23 · 10<sup>6</sup> NmL/g<sub>cat</sub>/h. The equilibrium methanol concentrations at these conditions are 3.62 mol% with CO in the feed and 0.37 mol% without CO in the feed. Hence, the results are in the kinetically controlled regime.

#### 4. Conclusion

Catalytic methanol synthesis is currently a major industrial process operating from CO/CO<sub>2</sub>/H<sub>2</sub> with a Cu-based catalyst. However, future uses of the process could involve the conversion of CO<sub>2</sub>/H<sub>2</sub> feeds from sustainably derived hydrogen and CO<sub>2</sub> captured at locally available point sources. It is therefore relevant to evaluate the roles of CO and CO<sub>2</sub> for the Cu-catalyzed reaction. Here we have conducted switching experiments between feeds with and without CO over Cu based catalysts to elucidate the roles of CO and CO<sub>2</sub> at varying conversion levels. Switching between CO/H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> feeds for Cu/Al<sub>2</sub>O<sub>3</sub> clearly showed that the methanol synthesis rate from CO<sub>2</sub> is more than an order of magnitude faster than the rate from CO, which helps to substantiate that CO<sub>2</sub> is the immediate carbon source for methanol on Cu. Low conversion experiments switching between CO/CO<sub>2</sub>/H<sub>2</sub> and N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub> feeds, where the presence or absence of CO is the only change, showed that CO is inhibiting to Raney Cu and to Cu supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO and ZnO/Al<sub>2</sub>O<sub>3</sub>. Competitive adsorption on the Cu surface may explain the observations, although the removal of promotional oxygen species from the Cu surface by CO cannot be fully excluded as a reason for the inhibiting effect of CO. At higher conversion the presence of CO was found to be beneficial compared to conditions without CO in the feed. This can be explained by the ability of CO to remove a worse inhibitor, water, through the WGS reaction. As a result the optimal feed is a CO-free gas at low conversion, but at higher conversion a CO-rich syngas that efficiently removes produced water is preferable. The transition between these two types of behavior occurs around the conversion range leading to 1 mol% of methanol in the effluent gas.

Comparisons of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and Raney Cu showed that a strong, beneficial support effect from ZnO was present at low conversion conditions, where the effect of CO is observed to be purely detrimental for both samples. One proposed mechanism for the ZnO-support effect has been that reduced Zn species are alloyed into the metal surface, and the CO concentration has previously been found to be important for the creation of the reduced Zn-species. The fact that the support effect is strong at conditions where the carbon monoxide-induced rise in the reductive potential of the atmosphere was detrimental for the activity is a clear indication that such reduced Zn-species are not critical to the support effect from ZnO. In a further experiment Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> was at high space velocity (low conversion) exposed to a H<sub>2</sub>/He/CO<sub>2</sub> gas mixture with an excess of CO<sub>2</sub> compared to H<sub>2</sub> i.e. a nominally oxidizing atmosphere. Once activity had stabilized, the He was replaced with an equal concentration of CO, which changed the atmosphere into a nominally reducing gas. Again the effect of CO was purely inhibiting. The fact that CO is also detrimental at such oxidizing conditions is a further indication that reduced Zn-sites may not be involved in creating the beneficial synergy between Cu and ZnO.

#### Acknowledgements

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## References

- [1] J.B. Hansen, P.E.H. Nielsen, Methanol Synthesis, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handb. Heterog. Catal.*, 2nd ed., Wiley-VCH Verlag GmbH, 2008: pp. 2920–2949. <https://doi.org/10.1002/9783527610044.hetc0148>.
- [2] J. Sehested, Industrial and scientific directions of methanol catalyst development, *J. Catal.* 371 (2019) 368–375. <https://doi.org/10.1016/j.jcat.2019.02.002>.
- [3] H.H. Kung, *Methanol production and use*, CRC Press, 1994. <https://doi.org/10.5860/choice.32-3898>.
- [4] Y.B. Kagan, A.Y. Rozovskij, L.G. Liberov, E. V. Slivinskij, G.I. Lin, S.M. Loktev, A.N. Bashkirov, Study of mechanism of methanol synthesis from carbon monoxide and hydrogen using radioactive carbon isotope C<sup>14</sup>, *Dokl. Akad. Nauk SSSR*. 224 (1975) 1081–1084.
- [5] G.C. Chinchin, P.J. Denny, D.G. Parker, M.S. Spencer, D.A. Whan, Mechanism of methanol synthesis from CO<sub>2</sub>/CO/H<sub>2</sub> mixtures over copper/zinc oxide/alumina catalysts: use of <sup>14</sup>C-labelled reactants, *Appl. Catal.* 30 (1987) 333–338. [https://doi.org/10.1016/S0166-9834\(00\)84123-8](https://doi.org/10.1016/S0166-9834(00)84123-8).
- [6] A.Y. Rozovskii, New data on the mechanism of catalytic reactions with the participation of carbon oxides, *Kinet. Catal.* 21 (1980) 78-87 (in Engl. translation).
- [7] G.C. Chinchin, P.J. Denny, D.G. Parker, G.D. Short, M.S. Spencer, K.C. Waugh, D.A. Whan, The activity of Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalysts, *Prepr. Amer. Chem. Soc., Divn. Fuel Chem.* 29 (1984) 178–188.
- [8] J. Nerlov, I. Chorkendorff, Methanol synthesis from CO<sub>2</sub>, CO, and H<sub>2</sub> over Cu(100) and Ni/Cu(100), *J. Catal.* 181 (1999) 271–279. <https://doi.org/10.1006/jcat.1998.2301>.
- [9] N.D. Nielsen, J. Thrane, A.D. Jensen, J.M. Christensen, Bifunctional Synergy in CO Hydrogenation to Methanol with Supported Cu, *Catal. Lett.* 150 (2020) 1427–1433. <https://doi.org/https://doi.org/10.1007/s10562-019-03036-7>.
- [10] G.C. Chinchin, M.S. Spencer, K.C. Waugh, D.A. Whan, Promotion of methanol synthesis and the water-gas shift reactions by adsorbed oxygen on supported copper catalysts, *J. Chem. Soc. Faraday Trans. 1*. 83 (1987) 2193–2212. <https://doi.org/10.1039/f19878302193>.
- [11] J. Thrane, S. Kuld, N.D. Nielsen, A.D. Jensen, J. Sehested, J.M. Christensen, Methanol-assisted autocatalysis in catalytic methanol synthesis, *Angew. Chemie - Int. Ed.* 59 (2020) 18189–18193. <https://doi.org/10.1002/anie.202006921>.
- [12] T. Fujitani, M. Saito, Y. Kanai, T. Kakumoto, T. Watanabe, J. Nakamura, T. Uchijima, The role of metal oxides in promoting a copper catalyst for methanol synthesis, *Catal. Lett.* 25 (1994) 271–276. <https://doi.org/10.1007/BF00816307>.
- [13] K.M. M. Saito, Development of high performance Cu/ZnO-based catalysts for methanol synthesis and the water-gas shift reaction, *Catal. Surv. Asia*. 8 (4) (2004) 285–294. <https://doi.org/10.1007/s10563-004-9119-y>.
- [14] F. Studt, M. Behrens, R. Schlögl, E.L. Kunkes, N. Thomas, S. Zander, A. Tarasov, J. Schumann, E. Frei, J.B. Varley, F. Abild-Pedersen, J.K. Nørskov, The Mechanism of CO and CO<sub>2</sub> Hydrogenation to Methanol over Cu-Based Catalysts, *ChemCatChem*. 7 (2015) 1105–1111. <https://doi.org/10.1002/cctc.201500123>.
- [15] K.G. Chanclani, R.R. Hudgins, P.L. Silveston, Methanol synthesis from H<sub>2</sub>, CO, and CO<sub>2</sub> over Cu/ZnO catalysts, *J. Catal.* 136 (1992) 59–75. [https://doi.org/10.1016/0021-9517\(92\)90106-R](https://doi.org/10.1016/0021-9517(92)90106-R).

- [16] J.S. Lee, S.H. Han, H.G. Kim, K.H. Lee, Y.G. Kim, Effects of space velocity on methanol synthesis from CO<sub>2</sub>/CO/H<sub>2</sub> over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, *Korean J. Chem. Eng.* 17 (2000) 332–336. <https://doi.org/10.1007/Bf02699049>.
- [17] S. Zander, E.L. Kunkes, M.E. Schuster, J. Schumann, G. Weinberg, D. Teschner, N. Jacobsen, R. Schlögl, M. Behrens, The role of the oxide component in the development of copper composite catalysts for methanol synthesis, *Angew. Chemie - Int. Ed.* 52 (2013) 6536–6540. <https://doi.org/10.1002/anie.201301419>.
- [18] M. Sahibzada, I.S. Metcalfe, D. Chadwick, Methanol Synthesis from CO/CO<sub>2</sub>/H<sub>2</sub> over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at Differential and Finite Conversions, *J. Catal.* 174 (1998) 111–118. <https://doi.org/10.1006/jcat.1998.1964>.
- [19] O. Cherefi, S. Monteverdi, M.M. Bettahar, M. Forissier, V. Perrichon, O. Cherifi, S. Monteverdi, M.M. Bettahar, M. Foorissier, V. Perrichon, Kinetics of CO<sub>2</sub> hydrogenation into methanol on a Cu-Zn-Al oxide catalyst, *Bull. Soc. Chim. Fr.* (1985) 405–409.
- [20] O. Martin, J. Pérez-Ramírez, New and revisited insights into the promotion of methanol synthesis catalysts by CO<sub>2</sub>, *Catal. Sci. Technol.* 3 (2013) 3343–3352. <https://doi.org/10.1039/c3cy00573a>.
- [21] J. Barbier, J. Fortin, P. Courty, P. Chaumette, Rôle du dioxyde de carbone lors de la synthèse du méthanol sur catalyseurs à base de cuivre, *Bull. La Société Chimique Fr.* 6 (1987) 925–929.
- [22] K. Klier, V. Chatikavanij, R.G. Herman, G.W. Simmons, Catalytic Synthesis of Methanol from CO/H<sub>2</sub>, *J. Catal.* 74 (1982) 343–360. [https://doi.org/10.1016/0021-9517\(82\)90040-9](https://doi.org/10.1016/0021-9517(82)90040-9).
- [23] G.A. Olah, A. Goepfert, G.K.S. Prakash, Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons, *J. Org. Chem.* 74 (2009) 487–498. <https://doi.org/10.1021/jo801260f>.
- [24] N.D. Nielsen, A.D. Jensen, J.M. Christensen, Quantification of Formate and Oxygen Coverages on Cu Under Industrial Methanol Synthesis Conditions, *Catal. Lett.* 150 (2020) 2447–2456. <https://doi.org/10.1007/s10562-020-03162-7>.
- [25] J.C. Frost, Junction effect interactions in methanol synthesis catalysts, *Nature.* 334 (1988) 577–580. <https://doi.org/10.1038/332141a0>.
- [26] J. Nakamura, I. Nakamura, T. Uchijima, T. Watanabe, T. Fujitani, Model Studies of Methanol Synthesis on Copper Catalysts, *Stud. Surf. Sci. Cat.* 101 (1996) 1389–1399. [https://doi.org/10.1016/s0167-2991\(96\)80351-x](https://doi.org/10.1016/s0167-2991(96)80351-x).
- [27] S. Kuld, M. Thorhauge, H. Falsig, C.F. Elkjaer, S. Helveg, I. Chorkendorff, J. Sehested, Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis, *Science.* 352 (2016) 969–974. <https://doi.org/10.1126/science.aaf0718>.
- [28] P.C.K. Vesborg, I. Chorkendorff, I. Knudsen, O. Balmes, J. Nerlov, A.M. Molenbroek, B.S. Clausen, S. Helveg, Transient behavior of Cu/ZnO-based methanol synthesis catalysts, *J. Catal.* 262 (2009) 65–72. <https://doi.org/10.1016/j.jcat.2008.11.028>.
- [29] C. V. Ovesen, B.S. Clausen, J. Schiøtz, P. Stoltze, H. Topsøe, J.K. Nørskov, Kinetic Implications of Dynamical Changes in Catalyst Morphology during Methanol Synthesis over Cu/ZnO Catalysts, *J. Catal.* 168 (1997) 133–142. <https://doi.org/10.1006/jcat.1997.1629>.
- [30] K.-D. Jung, O.-S. Joo, S.-H. Han, Structural change of Cu/ZnO by reduction of ZnO in Cu/ZnO with methanol, *Catal. Lett.* 68 (2000) 49–54. <https://doi.org/10.1023/A:1019027302428>.



- [31] Y. Ren, K. Yuan, X. Zhou, H. Sun, K. Wu, S.L. Bernasek, W. Chen, G.Q. Xu, Catalytic Intermediates of CO<sub>2</sub> Hydrogenation on Cu(111) Probed by In Operando Near-Ambient Pressure Technique, *Chem. - A Eur. J.* 24 (2018) 16097–16103. <https://doi.org/10.1002/chem.201802931>.
- [32] B. Eren, R.S. Weatherup, N. Liakakos, G.A. Somorjai, M. Salmeron, Dissociative Carbon Dioxide Adsorption and Morphological Changes on Cu(100) and Cu(111) at Ambient Pressures, *J. Am. Chem. Soc.* 138 (2016) 8207–8211. <https://doi.org/10.1021/jacs.6b04039>.
- [33] N.D. Nielsen, T.E.L. Smitshuysen, C.D. Damsgaard, A.D. Jensen, J.M. Christensen, Characterization of oxide-supported Cu by infrared measurements on adsorbed CO, *Surf. Sci.* 703 (2021) 121725. <https://doi.org/10.1016/j.susc.2020.121725>.
- [34] G.C. Chinchin, C.M. Hay, H.D. Vandervell, K.C. Waugh, The measurement of copper surface areas by reactive frontal chromatography, *J. Catal.* 103 (1987) 79–86. [https://doi.org/10.1016/0021-9517\(87\)90094-7](https://doi.org/10.1016/0021-9517(87)90094-7).
- [35] O. Hinrichsen, T. Genger, M. Muhler, Chemisorption of N<sub>2</sub>O and H<sub>2</sub> for the Surface Determination of Copper Catalysts, *Chem. Eng. Technol.* 23 (2000) 956–959. [https://doi.org/10.1002/1521-4125\(200011\)23:11<956::AID-CEAT956>3.0.CO;2-L](https://doi.org/10.1002/1521-4125(200011)23:11<956::AID-CEAT956>3.0.CO;2-L).
- [36] R. Chatterjee, S. Kuld, R. Van Den Berg, A. Chen, W. Shen, Mapping Support Interactions in Copper Catalysts, *Top. Catal.* 62 (2019) 649–659. <https://doi.org/10.1007/s11244-019-01150-9>.
- [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. Chemie - Int. Ed.* 53 (2014) 5941–5945. <https://doi.org/10.1002/anie.201311073>.
- [38] G.H. Graaf, J.G.M. Winkelman, Chemical Equilibria in Methanol Synthesis Including the Water-Gas Shift Reaction: A Critical Reassessment, *Ind. Eng. Chem. Res.* 55 (2016) 5854–5864. <https://doi.org/10.1021/acs.iecr.6b00815>.
- [39] D.S. King, R.M. Nix, Thermal stability and reducibility of ZnO and Cu/ZnO catalysts, *J. Catal.* 160 (1996) 76–83. <https://doi.org/10.1006/jcat.1996.0125>.
- [40] M.B. Fichtl, J. Schumann, I. Kasatkin, N. Jacobsen, M. Behrens, R. Schlögl, M. Muhler, O. Hinrichsen, Counting of oxygen defects versus metal surface sites in methanol synthesis catalysts by different probe molecules, *Angew. Chemie - Int. Ed.* 53 (2014) 7043–7047. <https://doi.org/10.1002/anie.201400575>.
- [41] W.J. Van Rensburg, J.A. Van Den Berg, M.A. Petersen, M.S. Datt, P. Van Helden, On the Kinetic Interpretation of DFT-Derived Energy Profiles: Cu-Catalyzed Methanol Synthesis, *Catal. Lett.* 145 (2015) 559–568. <https://doi.org/10.1007/s10562-014-1407-1>.
- [42] M.S. Tameh, A.K. Dearden, C. Huang, Accuracy of Density Functional Theory for Predicting Kinetics of Methanol Synthesis from CO and CO<sub>2</sub> Hydrogenation on Copper, *J. Phys. Chem. C.* 122 (2018) 17942–17953. <https://doi.org/10.1021/acs.jpcc.8b06498>.
- [43] M. Behrens, F. Studt, I. Kasatkin, S. Köhl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. Knief, M. Tovar, R.W. Fischer, J.K. Nørskov, R. Schlögl, The Active Site of Methanol Synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Industrial Catalysts, *Science.* 336 (2012) 893–898. <https://doi.org/10.1126/science.1219831>.
- [44] D. Laudenschleger, H. Ruland, M. Muhler, Identifying the nature of the active sites in methanol synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts, *Nat. Commun.* 11 (2020) 3898. <https://doi.org/10.1038/s41467-020-17631-5>.
- [45] M. Saito, T. Fujitani, M. Takeuchi, T. Watanabe, Development of copper/zinc oxide-

- based multicomponent catalysts for methanol synthesis from carbon dioxide and hydrogen, *Appl. Catal. A Gen.* 138 (1996) 311–318. [https://doi.org/10.1016/0926-860X\(95\)00305-3](https://doi.org/10.1016/0926-860X(95)00305-3).
- [46] J. Yoshihara, C.T. Campbell, Methanol synthesis and reverse water-gas shift kinetics over Cu(110) model catalysts: Structural sensitivity, *J. Catal.* 161 (1996) 776–782. <https://doi.org/10.1006/jcat.1996.0240>.
- [47] J.L. Robbins, E. Iglesia, C.P. Kelkar, B. DeRites, Methanol synthesis over Cu/SiO<sub>2</sub> catalysts, *Catal. Lett.* 10 (1991) 1–10. <https://doi.org/10.1007/BF00764730>.
- [48] C. Baltés, S. Vukojević, F. Schüth, Correlations between synthesis, precursor, and catalyst structure and activity of a large set of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts for methanol synthesis, *J. Catal.* 258 (2008) 334–344. <https://doi.org/10.1016/j.jcat.2008.07.004>.
- [49] S. Natesakhawat, J.W. Lekse, J.P. Baltrus, R. Paul, B.H. Howard, X. Deng, C. Matranga, Active Sites and Structure-activity Relationships of Copper-based Catalysts for Carbon Dioxide Hydrogenation to Methanol, *ACS Catal.* 2 (2012) 1667–1676. <https://doi.org/10.1021/cs300008g>.
- [50] W.X. Pan, R. Cao, D.L. Roberts, G.L. Griffin, Methanol synthesis activity of Cu/ZnO catalysts, *J. Catal.* 114 (1988) 440–446. [https://doi.org/http://dx.doi.org/10.1016/0021-9517\(88\)90047-4](https://doi.org/http://dx.doi.org/10.1016/0021-9517(88)90047-4).
- [51] G.C. Chinchén, M.S. Spencer, Sensitive and Insensitive Reactions on Copper Catalysts: The Water-Gas Shift Reaction and Methanol Synthesis from Carbon Dioxide, *Catal. Today.* 10 (1991) 293. [https://doi.org/10.1016/0920-5861\(91\)80009-X](https://doi.org/10.1016/0920-5861(91)80009-X).
- [52] M. Kurtz, H. Wilmer, T. Genger, O. Hinrichsen, M. Muhler, Deactivation of Supported Copper Catalysts for Methanol Synthesis, *Catal. Letters.* 86 (2003) 77–80. <https://doi.org/10.1023/A:1022663125977>.
- [53] G.J.J. Bartley, R. Burch, Support and morphological effects in the synthesis of methanol over Cu/ZnO, Cu/ZrO<sub>2</sub> and Cu/SiO<sub>2</sub> catalysts, *Appl. Catal.* 43 (1988) 141–153. [https://doi.org/10.1016/S0166-9834\(00\)80907-0](https://doi.org/10.1016/S0166-9834(00)80907-0).
- [54] Y. Yang, C.A. Mims, D.H. Mei, C.H.F. Peden, C.T. Campbell, Mechanistic studies of methanol synthesis over Cu from CO/CO<sub>2</sub>/H<sub>2</sub>/H<sub>2</sub>O mixtures: The source of C in methanol and the role of water, *J. Catal.* 298 (2013) 10–17. <https://doi.org/10.1016/j.jcat.2012.10.028>.
- [55] J. Słoczyński, R. Grabowski, J. Janas, J. Skrzypek, Adsorption model of methanol synthesis reactants on CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst-I. Adsorption on the catalyst, *Chem. Eng. Sci.* 46 (1991) 2599–2610. [https://doi.org/10.1016/0009-2509\(91\)80053-2](https://doi.org/10.1016/0009-2509(91)80053-2).
- [56] J. Słoczyński, R. Grabowski, J. Janas, Adsorption Model of Methanol Synthesis Reactants on CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> Catalyst - II Adsorption on the individual components of the catalyst, *Chem. Eng. Sci.* 46 (1991) 2611–2623. [https://doi.org/10.1016/0009-2509\(91\)80054-3](https://doi.org/10.1016/0009-2509(91)80054-3).
- [57] E. Colbourn, R.A. Hadden, H.D. Vandervell, K.C. Waugh, G. Webb, Adsorption of water on polycrystalline copper: relevance to the water gas shift reaction, *J. Catal.* 130 (1991) 514–527. [https://doi.org/10.1016/0021-9517\(91\)90132-N](https://doi.org/10.1016/0021-9517(91)90132-N).
- [58] J. Nakamura, J.M. Campbell, C.T. Campbell, Kinetics and mechanism of the water-gas shift reaction catalysed by the clean and Cs-promoted Cu(110) surface: A comparison with Cu(111), *J. Chem. Soc. Faraday Trans.* 86 (1990) 2725–2734. <https://doi.org/10.1039/FT9908602725>.
- [59] F. Le Peltier, P. Chaumette, J. Saussey, M.M. Bettahar, J.C. Lavalley, In situ FT-IR and kinetic study of methanol synthesis from CO<sub>2</sub>/H<sub>2</sub> over ZnAl<sub>2</sub>O<sub>4</sub> and Cu-ZnAl<sub>2</sub>O<sub>4</sub>

- catalysts, *J. Mol. Catal. A Chem.* 132 (1998) 91–100. [https://doi.org/10.1016/S1381-1169\(97\)00235-5](https://doi.org/10.1016/S1381-1169(97)00235-5).
- [60] N. Nomura, T. Tagawa, S. Goto, Titania supported copper catalysts for methanol synthesis from carbon dioxide, *React. Kinet. Catal. Lett.* 63 (1998) 9–13. <https://doi.org/10.1007/BF02475423>.
- [61] Y. Amenomiya, T. Tagawa, Infrared study of methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> on supported copper-zinc oxide catalysts, Ertl. G. (Ed.), *Proc. 8th Int. Congr. Catal.*, 2 Verlag Chemie. (1984) 557–567.
- [62] L. Fan, Y. Sakaiya, K. Fujimoto, Low-temperature methanol synthesis from carbon dioxide and hydrogen via formic ester, *Appl. Catal. A Gen.* 180 (1999) 13–15. [https://doi.org/10.1016/S0926-860X\(98\)00345-7](https://doi.org/10.1016/S0926-860X(98)00345-7).
- [63] N. Tsubaki, M. Ito, K. Fujimoto, A new method of low-temperature methanol synthesis, *J. Catal.* 197 (2001) 224–227. <https://doi.org/10.1006/jcat.2000.3077>.
- [64] P. Reubroycharoen, T. Yamagami, T. Vitidsant, Y. Yoneyama, M. Ito, N. Tsubaki, Continuous low-temperature methanol synthesis from syngas using alcohol promoters, *Energy and Fuels.* 17 (2003) 817–821. <https://doi.org/10.1021/ef020240v>.
- [65] M. Kurtz, N. Bauer, H. Wilmer, O. Hinrichsen, M. Muhler, Rational Catalyst Design of Methanol Synthesis Catalysts, *Chem. Eng. Technol.* 27 (2004) 1146–1150. <https://doi.org/10.1002/ceat.200407032>.
- [66] R. Burch, S.E. Golunski, M.S. Spencer, The role of copper and zinc oxide in methanol synthesis catalysts, *J. Chem. Soc. Faraday Trans.* 86 (1990) 2683–2691. <https://doi.org/10.1039/ft9908602683>.
- [67] T. Fujitani, I. Nakamura, T. Uchijima, The kinetics and mechanism of methanol synthesis by hydrogenation of CO<sub>2</sub> over a Zn-deposited Cu (111) surface, *Surf. Sci.* 383 (1997) 285–298. [https://doi.org/10.1016/S0039-6028\(97\)00192-1](https://doi.org/10.1016/S0039-6028(97)00192-1).
- [68] Y. Kanai, T. Watanabe, T. Fujitani, M. Saito, J. Nakamura, T. Uchijima, Evidence for the migration of ZnO<sub>x</sub> in a Cu/ZnO methanol synthesis catalyst, *Catal. Letters.* 27 (1994) 67–78. <https://doi.org/10.1007/BF00806979>.
- [69] M. Sano, T. Adaniya, T. Fujitani, J. Nakamura, Oxidation of a Zn-deposited Cu(111) surface studied by XPS and STM, *Surf. Sci.* 514 (2002) 261–266. [https://doi.org/10.1016/S0039-6028\(02\)01639-4](https://doi.org/10.1016/S0039-6028(02)01639-4).
- [70] M. Sano, T. Adaniya, T. Fujitani, J. Nakamura, Formation Process of a Cu-Zn Surface Alloy on Cu (111) Investigated by Scanning Tunneling Microscopy, *J. Phys. Chem.* 106 (2002) 7627–7633. <https://doi.org/10.1021/jp012810i>.
- [71] E. Frei, A. Gaur, H. Lichtenberg, L. Zwiener, M. Scherzer, F. Girgsdies, T. Lunkenbein, R. Schlögl, Cu–Zn Alloy Formation as Unfavored State for Efficient Methanol Catalysts, *ChemCatChem.* 12 (2020) 4029–4033. <https://doi.org/10.1002/cctc.202000777>.