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The synthesis of hydrocarbons and oxygenates during CO hydrogenation on CoCuZnO catalysts: Analysis at the site level using multiproduct SSITKA

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ABSTRACT

This paper addresses the effect of component interaction in CoCuZnO catalysts on oxygenate synthesis during CO hydrogenation. Formation of the various products was investigated for the first time using in-situ multiproduct SSITKA. CO hydrogenation was carried out in a fixed-bed differential reactor at 250 °C and 1.8 atm. Reaction results indicate that the activities for all products decrease with the combination of Co with Cu, possibly, based on SSITKA results, due to partial blockage of the Co surface by Cu. ZnO alone, on the other hand, seems to serve primarily as a support for Co but may increase slightly the intrinsic activities for higher oxygenates. The effects of Cu and ZnO on Co, however, were not additive. The Co–Cu–ZnO combination resulted in a synergy that greatly increased selectivities for higher oxygenates by significantly decreasing the ability for hydrocarbon formation. Interestingly, the rate of synthesis for C_2 oxygenates on Co/CuZnO was identical to that on Co/Al_2O_3 (considered by most to be only a hydrocarbon synthesis catalyst)—but without the high production rate of hydrocarbons.

1. Introduction

Higher oxygenates, especially alcohols, synthesized from syngas have been widely touted as an attractive alternative source of liquid transportation fuels. Also, because of environmental reasons, use of low molecular weight alcohols as octane enhancers for automotive fuels is now widespread [1,2]. The use of ethanol (EtOH) as an alternative fuel in automobiles has been proposed since it exhibits the same quantity of chemical energy as that of regular gasoline but with less emission of greenhouse gases as well as other pollutants [3]. In addition to the environment benefits as an alternative fuel to gasoline, EtOH has also the potential to be considered as a transportation fuel and the source of hydrogen for fuel cell applications [4,5]. The research and development of EtOH synthesis from syngas, therefore, has received much attention [6].

There are five typical classes of catalysts offering ways to prepare alcohols from syngas: (1) Rh-based catalysts [7–9]; (2) Mo-based catalysts [10–13]; (3) modified Fischer–Tropsch synthesis catalysts [14,15]; (4) modified methanol (MeOH) synthesis catalysts (by doping with alkali species) [16–20] and (5) Co–Cu catalysts, which is a combination of (3) and (4) [21–28]. Rh-based catalysts have been found to be the most efficient catalysts for the synthesis of C_{2+} oxygenates at mild conditions of low temperature and pressure [7,8]. However, the industrial application of Rh-based catalysts is limited due to Rh's low activity and high cost. CuZnO-based catalysts and supported Co catalysts (especially Co/Al_2O_3) are typical choices for MeOH synthesis and Fischer–Tropsch synthesis (FTS), respectively. Co–Cu catalysts were heavily researched by *Institute Français du Petrole* (IFP) in the 1980s and were considered to be potentially high-performance catalysts due to their high selectivity, ca. 70–80%, for higher oxygenate synthesis [27–29]. The elemental composition of choice for IFP Co–Cu catalysts included Cu, Co, Zn, Al and alkali promoters. Proposed reaction conditions varied but the total pressure and reaction temperature were usually between 20–250 bar and 150–400 °C, respectively (preferably between 50–150 bar and 220–350 °C) [27]. For fixed operating conditions, the higher alcohol ($C_{2+}OH$) yield increased with the Co/Cu ratio [21]. A mechanism for the synthesis of alcohols on CoCu-based catalysts was proposed by Kiennemann et al. [30], involving the interaction of formyl and formate intermediates for the synthesis of MeOH and carbene intermediates for chain growth and formation of higher alcohols.

Unfortunately, the preparation of IFP catalysts does not appear to be easily scaled up for industrial application because of a high tendency to uncontrolled decomposition of the glassy intermediate [21] and/or the difficulty of reproducible preparations because of the complexity of the preparation process. Research on Co–Cu

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catalysts has not been pursued significantly, and knowledge about the mechanism and the effect of the different elemental components in the catalyst on catalytic performance is still limited, even though no suitable commercial higher oxygenate catalyst has yet been found.

This study is a follow-up investigation to that reported in Ref. [31] by our group. The objective for Ref. [31] was to probe the interactions of different components in model Co/CuZnO catalysts deduced from the IFP patents. CuZnO is a commercial MeOH synthesis catalyst, while Co is a well-known and active FTS catalyst. Cu and ZnO as catalyst components in a higher oxygenate synthesis catalyst have received a great deal of attention [1,32–37]. The reaction results given in Ref. [31] confirm that only the combination of all three components (Co, Cu and ZnO) leads to a relatively high selectivity for C_{2+} oxygenates. Steady-state isotopic transient kinetic analysis (SSITKA) was also carried out at methanation conditions to investigate the effects of the various catalyst components on CO hydrogenation activity. SSITKA is a powerful technique that provides in-situ surface kinetic information for a reaction on a heterogeneous catalyst under actual reaction conditions. SSITKA permits the estimation of the surface reaction residence times, concentrations of active intermediates and intrinsic site activities and can help in the delineation of the surface reaction mechanism. This technique was first developed by Happel [38], Bennett [39], Biloen [40] and Bell et al. [41] in late 1970s and 1980s. In the previous study [31], the presence of ZnO and/or Cu in Co/CuZnO were found to apparently cover/block significant numbers of active sites on Co for CO hydrogenation resulting in the significantly lower activity of the Co/CuZnO combination. The main focus of this study was to better understand the relationships between different products at the site level. In this study, multiproduct SSITKA was utilized to further investigate the catalysts studied in Ref. [31] by measuring the surface reaction parameters leading to various hydrocarbon and oxygenate products.

2. Experimental

2.1. Catalyst preparation

The catalysts used in this study were the same as used in Ref. [31]. Their preparations are summarized here. Cobalt nitrate hexahydrate (Aldrich, synthetic), Copper nitrate trihydrate (Alfa Aesar, 99.5%) and Zinc nitrate hexahydrate (Alfa Aesar, 99.998%) were used without further purification. CuZnO, CoCu and CoZnO were prepared by a precipitation method. The metal loading ratios used, as shown in Table 1, were determined based on the optimum ratios for alcohol synthesis proposed by Arena et al. [42] and Slaa et al. [36]. Taking CuZnO as an example, the desired amount of copper and zinc nitrate solution (0.06 and 0.15 mol of zinc nitrate hexahydrate and copper nitrate trihydrate, respectively, dissolved in 180 g deionized water) was constituted sufficient to produce 6 g of CuZnO catalyst. The mixture was precipitated using a Na_2CO_3 solution (Na_2CO_3:H_2O = 1:3 in volume) added drop-by-drop into the Cu/Zn nitrate solution with a burette at room temperature. The resulting mixture was then stirred for 2 h and left in a fume hood overnight. The mixture was then filtered, washed six times with 1 L of hot (ca. 100 °C) deionized water, dried at 120 °C for 12 h and then calcined in air at 350 °C for 4 h. CoCu and CoZnO were prepared by a similar procedure with appropriate amounts of the metal salts to give the final elemental ratios. The resulting catalysts were confirmed to have minimal residual sodium (<0.2 wt) based on elemental analysis. Co/CuZnO was prepared by impregnation to incipient wetness of the prepared CuZnO using an aqueous solution of cobalt nitrate hexahydrate (1.5 mL cobalt nitrate solution/1 g CuZnO). The incipient wetness impregnation method was used for the combination of Co with CuZnO rather than precipitation based on a preliminary comparison of catalysts prepared by the two different methods. The results showed that Co/CuZnO prepared by impregnation exhibited higher alcohol selectivities comparing to the catalyst with the same composition but prepared by the co-precipitation method. After impregnation, the catalyst precursor was dried at 120 °C for 12 h before being calcined in air at 350 °C for 4 h (ramp rate to 350 °C of 10 °C/min). Co/γ-Al_2O_3 (Alfa Aesar, γ-phase, 99.98%) with 10 wt.% Co was also prepared by the incipient wetness impregnation method for comparison purposes. The preparation procedure is described in detail elsewhere [43]. The reproducibility of catalyst preparation was within ±10% based on elemental analysis and activity tests.

2.2. Catalyst characterization

Although XRD was carried out in our previous study for the investigation of structure and crystallite size for the calcined catalysts, the actual oxidation state and crystallinity for Cu-containing Co catalysts after reduction were not clear. XRD was performed in this study to identify the phases and crystallinity of Cu-containing Co catalysts (CoCu and Co/CuZnO) after reduction. The reduced form of Co is well known to give the active sites for Fischer–Tropsch synthesis [44]; thus, it is necessary to activate Co catalysts by reduction prior to reaction. However, the oxidation potential of highly dispersed reduced cobalt metal exposed to air and the high exothermicity of this oxidation would cause the degradation of reduced Co catalysts exposed to air by sintering and would be a potential fire hazard [45]. Therefore, passivation of the reduced Co surface is necessary to prevent rapid oxidation upon exposure to air prior to XRD measurements. The catalysts were reduced in-situ in a differential fixed-bed reactor at 300 °C in H_2 (30 mL/min) for 1 h using a ramp rate of 5 °C/min. Following the reduction, the catalysts were flushed by inert gas (He, 30 mL/min) as the temperature decreased to room temperature and then passivated with 2% O_2/Ar (4 mL/min) for 1 h at room temperature. X-ray diffraction

Table 1
Composition, preparation method, BET surface area, pore volume and average pore size of the catalysts studied (from [31]).

Catalyst	Co[a] (wt.%)	Molar ratio[a]	Preparation method[b]	BET surface area[d] (m^2/g)	Pore volume[e] (cm^3/g)	Average pore size[e] (nm)
Co/Al_2O_3	10	–	Impregnation	102.0	0.60	25.8
CuZnO	–	Cu:Zn = 2.5:1	Co-precipitation	29.8	0.13	30.5
CoZnO	30.4	Co:Zn = 1.1:1	Co-precipitation	96.4	0.57	29.7
CoCu	18.8	Co:Cu = 1.0:2.5	Co-precipitation	12.6	0.33	31.8
Co/CuZnO	16.5	Co:Cu:Zn = 1.1:2.5:1	Impregnation and co-precipitation [c]	21.1	0.12	22.1

[a] Based on elemental analysis.
[b] All catalysts were calcined at 350 °C in static air after preparation.
[c] CuZnO was first prepared by co-precipitation followed by calcination at 350 °C. Then, Co was added to CuZnO by the impregnation method, followed by calcination at 350 °C.
[d] Max error = ±5%.
[e] Max error = ±10%.

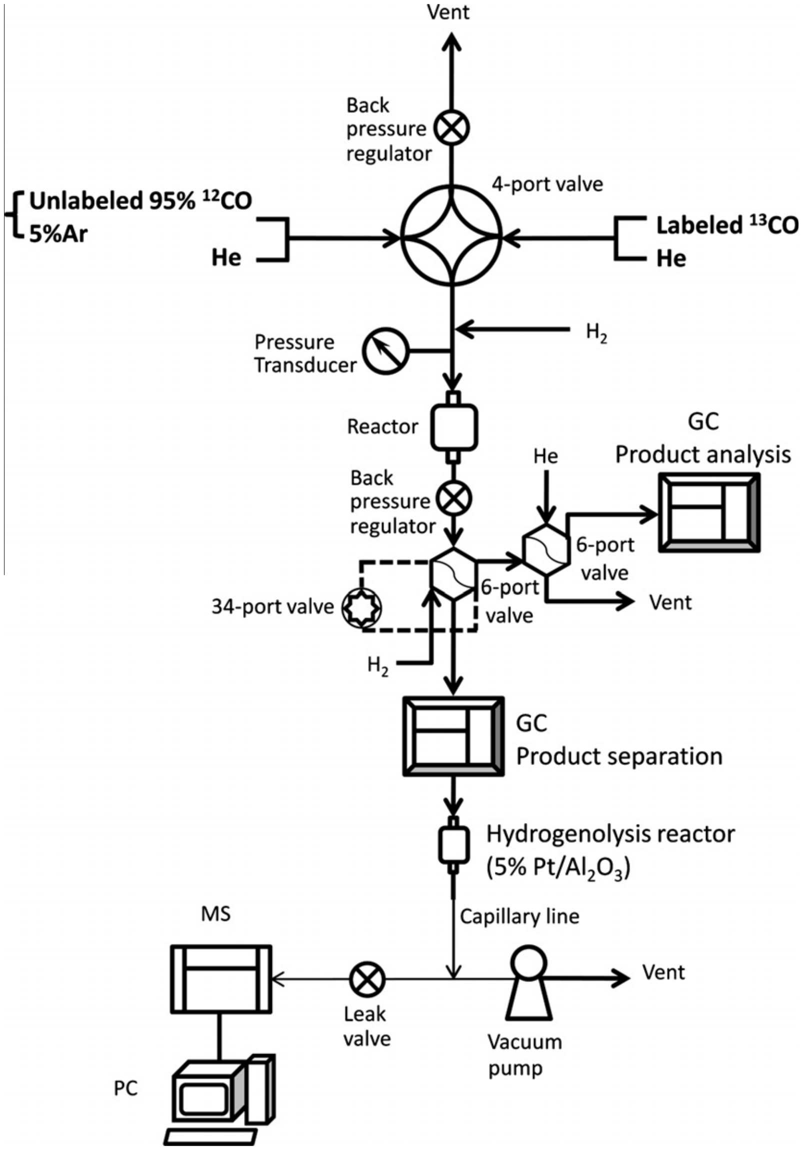

Fig. 1. The reaction system for multiproduct SSITKA.

patterns for the catalysts after pretreatment were collected in a Scintag XDS 2000 θ/θ powder X-ray diffractometer (XRD) using Cu Kα1/Kα2 ($\lambda = 1.540592$ Å and 1.544390 Å, respectively) radiation and a step size of 0.03° in the 2θ range of 5–70°.

2.3. CO hydrogenation

The reaction system setup is shown in Fig. 1. CO hydrogenation was carried out in a differential fixed-bed reactor with a maximum conversion below 10% in order to minimize concentration and temperature gradients. A catalyst sample (0.05 g for CoZnO and Co/Al_2O_3; 0.3 g for other catalysts) with 3 g of an inert powder (α-alumina) were mixed and used to avoid channeling effects and hot spots. The samples were then loaded between quartz wool plugs in the middle of the reactor and the temperature was observed by a thermocouple positioned close to the catalyst bed. The reaction lines and the sampling valves were kept at ca. 200 °C by wrapping with heating tape to avoid condensation of oxygenate and higher hydrocarbon products. A Varian 3380 GC equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was used to analyze the effluent samples online. A Restek RT-QPLOT column (I.D. 0.53 mm and length 30 m) connected to an FID was capable of separating and detecting C_1–C_7 hydrocarbons and oxygenates, while a Restek HayeSep® Q column (I.D. 3.18 mm and length 1.83 m) connected to a TCD was used for the separation and detection of CO and other inorganic gases.

Prior to the reaction, the catalyst was reduced in-situ at 300 °C with a ramp rate of 5 °C/min under 30 mL/min of H_2 for 1 h at 1 atm and then cooled down to the reaction temperature of 250 °C. After reduction, the reaction started as the gas flow was switched to a CO–H_2–He mixture (95%CO + 5%Ar: 9 mL/min; H_2: 18 mL/min; He: 3 mL/min) at a constant pressure of 1.8 atm. A H_2/CO ratio of 2:1 was used to ensure preferable conditions for EtOH production [7,46]. Although the selectivities of oxygenates may be greater at other conditions (e.g., lower reaction temperature and higher pressure), the reaction conditions used here were chosen in order to maximize the formation of C_1–C_2 products, especially C_{2+} oxygenates, for the purpose of more accurate kinetic and isotopic analyses [7]. The conditions of reaction used for the catalysts in this study were also found (data not shown) to result in no mass or heat transfer effects on the reaction kinetics measured. The reaction reached a pseudo-steady state after 15 h TOS (time-on-stream). The identification and calibration of the products were achieved using standard gases [alkanes (C_1–C_7), alkenes (C_2–C_7) and oxygenates (MeOH, EtOH, 1-propanol, 1-butanol, acetaldehyde and acetone) obtained from Scott Specialty Gases]. The selectivity (C atom%) for a specific product was calculated based on carbon efficiency using the formula $n_iC_i/\sum n_iC_i$, where n_i and C_i represent the carbon number and molar concentration of the ith product, respectively.

2.4. SSITKA

Surface reaction measurements were carried out after reaction steady-state was reached. During SSITKA measurements (Fig. 1), a switch between 95% $^{12}CO + 5\%$ Ar (National Specialty Gases) and ^{13}CO (Isotec, 99%) was made using a Valco 2-position valve with an electric actuator without disturbing any other reaction conditions. That is, the reaction total flow rate and the total pressure for the two gas feed streams were maintained at constant values during the switch. Two back pressure regulators in the reaction system were used to minimize any pressure disturbance during the switch. The gas-phase holdup time was determined by using 5% Ar in the unlabeled ^{12}CO stream as an inert tracer.

Direct isotopic analysis by mass spectroscopy (MS, Pfeiffer Vacuum) was difficult due to fragmentation and overlapping of the heavier hydrocarbons/oxygenates. To avoid this, products heavier than CH_4 were converted to CH_4 prior to MS analysis. Thus, a Valco 34-port auto-sampling valve was employed to collect 16 effluent samples during the 5-min period of the isotopic transients after a switch. The collected effluent samples were injected into and separated by a GC equipped with an RT-QPLOT column. Thirty cc/min of H_2 was used as the carrier gas and as a source of H_2 for the subsequent hydrogenolysis. After separation, the products were fed into a hydrogenolysis/hydrogenation reactor containing 5 g of Pt/Al_2O_3 held at 400 °C to convert hydrocarbons and oxygenates to CH_4. The resulting CH_4 was subsequently injected into the MS equipped with a high-speed data acquisition system for analysis. The isotopic concentrations detected by MS were able to be applied for further interpretation to the specific products collected in the sample loops of the 34-port valve.

Fig. 2 shows a typical set of normalized isotopic transients of CH_4, C_2H_n, MeOH, AcH and EtOH obtained by switching from ^{12}CO to ^{13}CO for Co/CuZnO at steady-state. Surface reaction parameters for the intermediates of CH_4, C_2H_n, MeOH, AcH and EtOH were determined from the isotopic transient curves for the specific species by SSITKA data analysis software. The areas between the normalized transients of the corresponding species and the inert tracer Ar are equal to the average surface residence times (τ_i) of the reactive species. The concentration of active surface intermediates for a specific product can be determined by $N_i = \text{Rate}_i * \tau_i$ [47,48]. A major improvement of this methodology (multiproduct SSITKA) is that surface reaction parameters can be determined for the various products, without the common MS analysis problem caused by fragmentation or overlapping of different products.

3. Results

3.1. Catalyst Characterization

The basic characterizations such as BET surface area, pore volume, average pore size and elemental analysis were carried out and performed earlier [31] but the results are given here in Table 1 for completeness. Table 1 also shows the preparation method and composition for the various catalysts. CoZnO showed a significantly higher BET surface area than the copper-containing catalysts since Cu/CuO provides very limited surface area [49]. Co/Al_2O_3 exhibited a similar BET surface area and pore volume to that of CoZnO. The average pore sizes, however, were similar for all catalysts.

Fig. 3 shows XRD patterns for the reduced and passivated catalysts contained Co and Cu (CoCu and Co/CuZnO). XRD characterization for the as-prepared calcined catalysts is given in our previous study [31]. However, the structure and crystallite sizes for Co and Cu after reduction may be more meaningful for understanding these catalysts. As can be seen, the peaks corresponding to metallic Cu (ICDD 040836) were prominent for both catalysts. The metallic Cu peaks presented for both catalysts could be attributed to face-centered cubic Cu [50,51]. Cu oxide structures, in both Cu_2O (ICDD 030892) and CuO (ICDD 741021) forms, could be identified for Co/CuZnO, but the peak intensity was much stronger for CuO than for Cu_2O. No discernable Co-related peaks could be observed for CoCu, which may indicate that Co is X-ray amorphous (i.e., highly dispersed) for this catalyst. It is known that Co and Cu metals do not alloy [50–52]. Co/CuZnO, however, exhibited distinguishable diffraction peaks for Co_3O_4 (ICDD 421467). It should be noted that the species of Cu_2O, CoO and Co_3O_4 all display a diffraction peak at about 36.5°, resulting in difficulty in identifying the XRD patterns for these individual compounds at this location [53]. The possibility of the presence of a Cu–Co oxide spinel structure could not be ruled out due to a distinct shoulder peak at about 44° [54]. How-

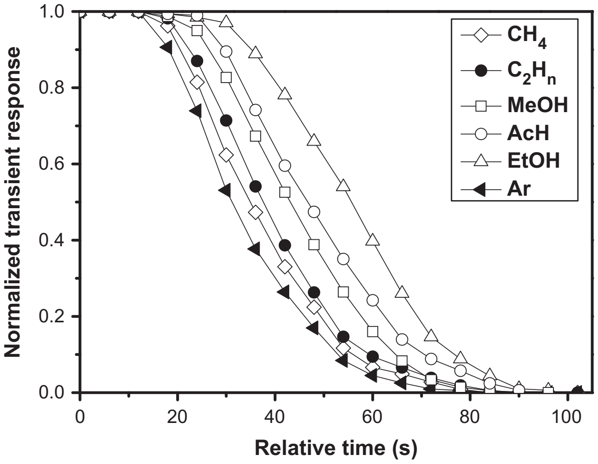

Fig. 2. Typical normalized SSITKA transient responses for ^{12}C in CH_4, C_2H_n, MeOH, AcH, EtOH and for Ar, following a $^{12}CO/^{13}CO$ switch during steady state for CO hydrogenation on Co/CuZnO.

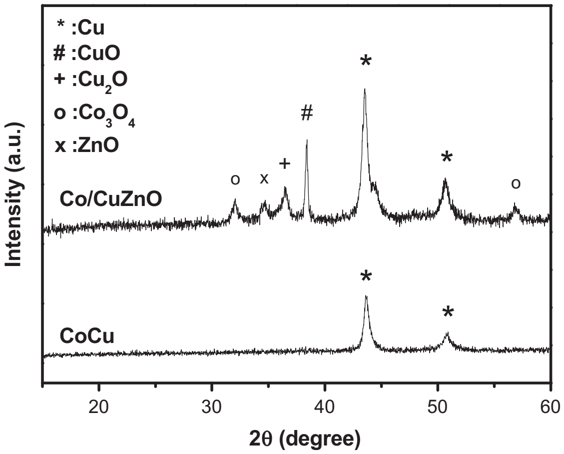

Fig. 3. Powder XRD patterns for the reduced and passivated CoCu and Co/CuZnO catalysts.

ever, it is difficult to identify Cu–Co oxide spinel by other diffraction peaks due to the overlap of these diffraction peaks with Cu_2O, CoO and Co_3O_4 at about 32° and 37°. A weak peak, which can be attributed to ZnO (ICDD 890511), could be observed for Co/CuZnO. A significant difference for the XRD results of as-prepared and reduced passivated Co–Cu-containing catalysts is the presence of metallic Cu, which is consistent with what has been reported by Llorca et al. [52], that is, that metallic copper aggregates exist with highly dispersed cobalt as inferred from their XRD, TEM and XPS results. The results are also in line with our previous TPR results that reduction of Cu oxide occurs at a relatively low temperature (<250 °C) [31]. The average crystallite size can be estimated by applying the Scherrer equation. Reduced Co/CuZnO had an average crystallite size of 13.2 nm for Co_3O_4. This value is pretty much the same as the value (14.6 nm) obtained for the calcined Co/CuZnO [31].

3.2. CO hydrogenation

Table 2 summarizes the results for CO hydrogenation at 250 °C and 1.8 atm. The steady-state rates were measured after 15 h TOS. Activities are compared on both a per catalyst weight basis and a per cobalt weight basis. It can be seen that CoZnO exhibited the highest reaction rate among all the catalysts on a "per catalyst weight" basis. However, Co/Al_2O_3 showed a higher activity than CoZnO on a "per Co weight" basis. All Cu-containing catalysts exhibited significantly lower reaction rates (1–2 orders of magnitude) than Co/Al_2O_3 and CoZnO. The catalytic activity for all catalysts in this study followed the same trend (CoZnO > Co/Al_2O_3 > CoCu > CuZnO ~ Co/CuZnO) as found in our previous study [31].

With respect to the oxygenate product selectivity, it can be seen from Table 2 that Co/Al_2O_3, CoZnO and CoCu exhibited similar results. Most products for the three catalysts were hydrocarbons but with somewhat different distributions. The total oxygenate selectivities for the three catalysts were all <5%. CuZnO produced mainly MeOH (99.3%) as expected. The low activity and high MeOH selectivity is typical for CuZnO. Co/CuZnO exhibited a product distribution completely different from the other catalysts. The selectivity for oxygenates was nearly 60%, including 30.1% C_2 oxygenates (EtOH and ACH). The results are similar to what has been found previously for alkali promoted or unpromoted Co/CuZnO catalysts (selectivities of 30–70% for alcohols and 30–50% for EtOH) [2,55,56]. Thus, only the combination of Co, Cu and ZnO resulted in a high selectivity for C_{2+} oxygenates.

3.3. SSITKA

Multiproduct SSITKA measurements permitted the determination of how different combinations of Co, Cu and ZnO species affect the surface reaction parameters, including the surface reaction residence times (τ_i) and surface concentrations of intermediates (N_i) for the different products. The methods used to estimate the surface reaction parameters have been reported in detail elsewhere [7,48,57]. Table 3 shows the surface reaction residence times (τ_i) for different products on the various catalysts studied. Space time had little or no effect on the τ_i's for the hydrocarbons. However, the average surface reaction residence times of MeOH, AcH (acetaldehyde) and EtOH changed with different space times (not shown). This is due to the significant readsorption of these products in the catalyst bed and the resulting chromatographic effect, as reported in previous papers from our group [7,58,59]. Fig. 4 shows how the average residence times of MeOH, AcH and EtOH for Co/CuZnO linearly increased with increasing space time. Similar phenomena were observed for all catalysts in this study which produced these oxygenates. Readsorption effects, therefore, have to be taken into consideration before any further interpretation of SSITKA data. More accurate estimation of τ_i (τ_i^0) can be obtained by correcting for readsorption by extrapolating the value of τ_i to 0 space time. The corrected values of τ_i (τ_i^0), N_i (N_i^0) and TOF_{ITK} (TOF_{ITK}^0) are shown in Table 3 (see footnotes to Table 3 for how N_i^0 and $TOF_{ITK,I}^0$ were calculated). The corrected values for reversibly adsorbing CO and hydrocarbons were identical with the values measured due to minimal readsorption. Later discussion will focus only on the corrected surface reaction parameters rather than the uncorrected ones because the former reflect the synthesis and are not complicated by readsorption effects.

TOF_{ITK}^0, which is the reciprocal of τ_i^0, is a reasonable estimate of site turnover frequency. It is equal to R_i/N_i^0 with units of s^{-1} [48]. It can be seen from Table 3 that the intrinsic activities for each individual product for all catalysts followed the same trend: $TOF_{CH_4}^0 > TOF_{C_2H_n}^0 > TOF_{MeOH}^0 > TOF_{AcH}^0 > TOF_{EtOH}^0$. However, the differences between the TOF_i^0's were significant, both among products and among catalysts. CH_4 and C_2H_n had relatively larger values of TOF_{ITK}^0, which is not surprising for catalysts producing mostly hydrocarbons, such as Co/Al_2O_3, CoZnO and CoCu. However, CuZnO and Co/CuZnO, which produced primarily oxygenates, showed similar values for $TOF_{CH_4}^0$ and $TOF_{C_2H_n}^0$ as found for the catalysts producing mainly hydrocarbons. The TOF_i^0's for CH_4 and C_2H_n measured for the catalysts in this study were relatively greater than those reported for Rh-based catalysts [7], which indicates, not surprisingly, a better capability for hydrocarbon production on Co catalysts than on Rh catalysts. As to the intrinsic activities for oxygenates, the TOF_i^0 for MeOH was slightly larger for CuZnO ($0.24\ s^{-1}$) than for the other catalysts. The TOF_{AcH}^0's were very similar for CoZnO and Co/CuZnO, while CoCu exhibited a smaller one. TOF_{EtOH}^0's were much lower than those of other products, which was ca. $0.05\ s^{-1}$ for all catalysts except CoZnO ($0.12\ s^{-1}$).

Table 2
Catalytic properties of the various catalysts for CO hydrogenation at steady state.[a]

Catalyst	Rate[b] (μmol C/g-cat/s)	Rate (Co basis)[b] (μmol C/g-Co/s)	Selectivity[c] (C-atom%)					
			CH_4	C_2+HC[d]	MeOH	AcH[e]	EtOH	Other C_{2+} oxy.[f]
Co/Al_2O_3	6.90	69.0	47.1	51.3	1.0	–	0.4	0.2
CuZnO	0.08	–	0.7	–	99.3	–	–	–
CoZnO	8.97	29.5	37.4	59.6	0.7	0.6	1.0	0.7
CoCu	0.20	1.06	25.4	70	1.2	0.7	2.0	0.7
Co/CuZnO	0.10	0.61	16.4	23	18.2	4.2	25.9	12.3

[a] Catalyst: 0.3 g (0.05 g for Co/Al_2O_3 and CoZnO); Inert: 3 g α-alumina; reduction at 300 °C; reaction conditions: $T = 250$ °C, $P = 1.8$ atm; flow rate = 30 mL/min (H_2:CO:He = 18:9:3); data were taken at TOS = 15 h.

[b] Max. error = ±5% of all the values measured.

[c] Molar selectivity = carbon efficiency = $n_iC_i/\sum n_iC_i$.

[d] Hydrocarbons with 2 or more carbons.

[e] AcH refers to acetaldehyde.

[f] Oxygenates with 2 or more carbons.

Table 3
Uncorrected and corrected surface reaction parameters for CO hydrogenation on the various catalysts measured by SSITKA[a].

Product (or reactant)	Rate[b] (μmol C/g/s)	Selectivity[c] (C-atom%)	$\tau_i^{d,i}$ (s)	$\tau_i^{0e,i}$ (s)	TOF^{0}_{ITK} [f] (s^{-1})	N_i^{0g} (μmol/g-cat)
Co/Al$_2$O$_3$						
CO	–	–	1.5	1.5	–	67.0
CH_4	3.25	47.1	2.1	2.1	0.48	6.82
C_2H_n[h]	3.54	51.3	3.3	3.3	0.30	11.7
MeOH	0.07	1.0	6.2	4.6	0.21	0.32
AcH	–	–	–	–	–	–
EtOH	0.03	0.4	19.7	17.4	0.06	0.48
CuZnO						
CO	–	–	2.2	2.2	–	16.4
CH_4	0.0005	0.7	3.6	3.6	0.28	0.001
C_2H_n[h]	–	–	–	–	–	–
MeOH	0.076	99.3	6.4	4.1	0.24	0.31
AcH	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
CoZnO						
CO	–	–	1.2	1.2	–	53.6
CH_4	3.35	37.4	1.5	1.5	0.67	5.03
C_2H_n[h]	5.35	59.6	3.6	3.6	0.28	19.1
MeOH	0.06	0.7	6.2	4.9	0.20	0.31
AcH	0.05	0.6	7.2	6.1	0.16	0.33
EtOH	0.09	1.0	9.4	8.0	0.12	0.72
CoCu						
CO	–	–	1.6	1.6	–	11.9
CH_4	0.051	25.4	2.0	2.0	0.50	0.10
C_2H_n[h]	0.140	70.0	3.4	3.4	0.29	0.48
MeOH	0.002	1.2	9.6	6.9	0.14	0.02
AcH	0.001	0.7	12.3	9.9	0.10	0.01
EtOH	0.004	2.0	23.6	20.2	0.05	0.08
Co/CuZnO						
CO	–	–	2.4	2.4	–	17.9
CH_4	0.016	16.4	3.5	3.5	0.29	0.06
C_2H_n[h]	0.023	23.0	5.0	5.0	0.20	0.12
MeOH	0.018	18.2	8.7	6.0	0.17	0.11
AcH	0.004	4.2	10.2	7.7	0.13	0.03
EtOH	0.026	25.9	19.3	16.6	0.06	0.42

[a] Co/Al$_2$O$_3$ and Co/ZnO: 0.05 g, other catalysts: 0.3 g; Inert: 3 g α-alumina; reduction at 300 °C; reaction conditions: T = 250 °C, P = 1.8 atm; flow rate = 30 mL/min (H_2:CO:He = 18:9:3); data were taken at TOS = 15 h. All reactions were carried out at differential conversions with% CO conversion <5%.

[b] At steady-state rate.

[c] Molar selectivity = carbon efficiency = $n_iC_i/\sum n_iC_i$. For Co/CuZnO, the selectivity of C_{2+} hydrocarbons (about 13%) was not shown in this table.

[d] Uncorrected surface residence time of intermediates.

[e] Corrected surface residence time of intermediates.

[f] $TOF^0_{ITK,i} = 1/\tau_i^0 = \mathrm{Rate}_i/N_i^0 = (\text{rate of } i \text{ formation})/(\text{concentration of } i \text{ surface intermediates})$.

[g] $N_i^0 = \mathrm{Rate}_i * \tau_i^0$. For N_{CO}, Rate = flow rate of nonreacted CO.

[h] Hydrocarbons with 2 carbons.

[i] Experimental errors of all the results for CH_4 and C_2H_n are ±0.3 s; experimental errors of all the results for MeOH, AcH and EtOH are ±0.8 s.

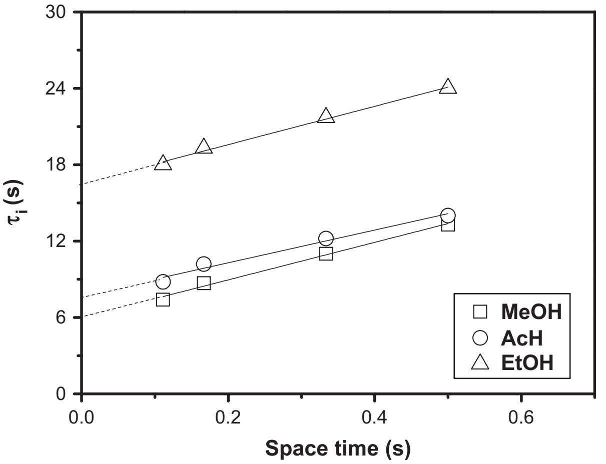

Fig. 4. τ_{MeOH}, τ_{AcH} and τ_{EtOH} vs. space time during steady state for CO hydrogenation on Co/CuZnO.

The corrected surface concentrations of intermediates (N_i^0) are also shown in Table 3. This is the concentration of active intermediates for product "i" on the surface and can be regarded as an approximation of the number of active sites producing a particular product i. Although τ_i^0's for a specific product were similar to a large degree, N_i^0's changed dramatically from catalyst to catalyst.

With respect to the formation of C_1-products (CH_4 and MeOH), $N^0_{CH_4}$ for Co/Al$_2$O$_3$ and CoZnO were about two orders of magnitude greater than those for other catalysts, not surprising since they were also the most active in making hydrocarbons. N^0_{MeOH} for the different catalysts followed the trend of Co/Al$_2$O$_3$ ~ CoZnO ~ CuZnO > Co/CuZnO > CoCu. It should be noted that, although Co/Al$_2$O$_3$ and CoZnO had very small selectivities for MeOH, the surface concentrations of MeOH intermediates were comparable to that for CuZnO, which primarily produced only MeOH. This seeming contradiction is a function of the high activities of Co/Al$_2$O$_3$ and CoZnO but low MeOH selectivities, compared to the low activity of CuZnO but very high (>99%) selectivity for MeOH.

C_{2+} products in this study included mainly C_2H_n, AcH and EtOH. Similar to $N^0_{CH_4}$, $N^0_{C_2H_n}$ for Co/Al$_2$O$_3$ and CoZnO exhibited values two orders of magnitude higher than for other catalysts. It should be noted that $N^0_{CH_4}$ was less than $N^0_{C_2H_n}$ for all catalysts except CuZnO. The difference between $N^0_{CH_4}$ and $N^0_{C_2H_n}$ was larger for CoZnO than for Co/Al_2O_3, demonstrating the higher potential of chain growth for hydrocarbons on CoZnO (see selectivities in Table 2). N^0_{AcH} and N^0_{EtOH} followed the same order for catalysts that could produce both AcH and EtOH: CoZnO > Co/CuZnO > CoCu. N^0_{AcH} for CoZnO was more than one order of magnitude greater than for the other two catalysts. Although N^0_{EtOH} had the same trend as N^0_{AcH} for the three catalysts, the differences between the values were not identical to those for N^0_{AcH}. The value of N^0_{EtOH} for CoZnO was almost 2× and 10× larger than those for Co/CuZnO and CoCu, respectively.

4. Discussion

There have been very few studies focusing on the mechanism of chain growth and formation of higher oxygenates on CoCuZnO-based catalysts, due in part to the complexities associated with multicomponent catalysts and higher oxygenate synthesis. More insight into reaction at the site level, however, was obtained by this study using CO hydrogenation on different systematic combinations of the Co, Cu and ZnO components (CoCu, CoZnO and Co/CuZnO). The reaction conditions used were chosen for the purpose of maximizing the formation of C_1–C_2 products (hydrocarbons and oxygenates) for easier analysis. Therefore, the results are not at the conditions necessary to maximize the production of higher alcohols. However, previous results show that the trend in activities for the different catalysts was similar even for different H_2/CO ratios [31].

The results for Co/Al_2O_3 and CuZnO will first be addressed in order to clarify the catalyst performances of these two reference catalysts. CoCu and CoZnO will then be discussed to explore the effects on Co of Cu and of ZnO. Finally, the results of Co/CuZnO will be introduced and compared with the results for the other catalysts.

In a preliminary study, CuZnO was found to exhibit a higher intrinsic activity and a higher concentration of active surface intermediates for MeOH synthesis when compared to Cu or ZnO catalysts, or even to catalysts with Cu or ZnO supported on Al_2O_3 and expected to have much better active catalyst dispersions [60]. These results are indicative of a synergy between Cu and ZnO species to form active sites for MeOH synthesis. As seen in Table 3, a low activity of CuZnO for CH_4 was observed and was reflected in a low surface concentration of active CH_4 intermediates ($N^0_{CH_4}$), or CH_4 formation sites. However, TOF^0_{ITK}'s for CH_4 and MeOH were similar. CuZnO had a three orders of magnitude higher concentration of MeOH intermediates than CH_4 ones—the source of its high MeOH selectivity and its CO hydrogenation activity. However, the activity of CuZnO was still two orders of magnitude lower than the overall activity of Co/Al_2O_3.

Most products of CO hydrogenation on Co/Al_2O_3 at the reaction conditions used in this study were hydrocarbons, as expected (Tables 2 and 3). The total selectivity for oxygenates was less than 2%. TOF^0_{ITK} for MeOH and EtOH were approximately 50% and 10%, respectively, of that for CH_4, indicating that the rates of formation of MeOH and EtOH on the sites were slower than for CH_4. Because of that and more importantly the greater (order of magnitude) concentration of CH_4 active intermediates, the selectivity for CH_4 was ca. 50× and 100× greater than for MeOH and EtOH, respectively. Similar results were also found for higher hydrocarbons. Even though most products made by Co/Al_2O_3 were hydrocarbons, it is noteworthy that its ability to produce MeOH, based on site activity (TOF^0_{ITK}) for MeOH and concentration of active MeOH intermediates (N^0_{MeOH}), was comparable to that of CuZnO. Thus, Co/Al_2O_3 was technically as good a MeOH synthesis catalyst in terms of rate as CuZnO under these reaction conditions. This ability is just not usually noted due to the greater activity of Co/Al_2O_3 for the synthesis of hydrocarbons which results in a low selectivity for MeOH.

Table 2 shows that the combinations of CoCu and Co/CuZnO (the Cu-containing Co catalysts) exhibited very low activities relative to Co/Al_2O_3; however, the combination of CoZnO led to a very high activity for CO hydrogenation. The combinations of Co with Cu or ZnO alone exhibited less than 5% selectivities for the formation of oxygenates. Co/CuZnO, on the other hand, produced about 60% oxygenates with 30.1% C_{2+} oxygenates (EtOH and ACH).

By comparing the multiproduct SSITKA results for Co/Al_2O_3 and CoCu, it can be seen that the intrinsic activities (TOF^0_{ITK}) for making hydrocarbons and higher oxygenates were very close (within experimental error) for the two catalysts, except that CoCu had a better ability to produce AcH. The tremendous difference in reaction rates for the two catalysts (Co/Al_2O_3 ≫ CoCu) was due to the large difference in the concentration of active surface intermediates (N^0_i) for both hydrocarbons and higher oxygenates.

The results for CoZnO suggest that the presence of ZnO (in CoZnO) may have somewhat enhanced the site activities (TOF^0_{ITK}) for making CH_4 and higher oxygenates (compared to Co/Al_2O_3). The increased rate for higher oxygenate formation (relative to Co/Al_2O_3) was due to both higher intrinsic activity (TOF^0_{ITK}) and greater surface concentration of active sites (N^0_i). CO and intermediates coverage of Co during CO hydrogenation as determined by SSITKA has been shown to be very representative and similar to typical chemisorption measurements for Co catalysts used to determine Co dispersion [62]. Based on the similarity in concentrations of adsorbed species (CO + product precursors) during reaction on CoZnO and Co/Al_2O_3 (79 and 86 μmoles/g, respectively), it would appear that ZnO acted as a support for Co, permitting a reasonable Co dispersion and leading to the presence of high concentrations of product producing sites. Similar observations about ZnO have also been made previously for Cu-based catalysts [60,61]. Contrast this with the results for CoCu where total adsorbed species during reaction was only 12.6 μmoles/g.

Co/CuZnO exhibited a very low activity for CO hydrogenation, similar to CoCu. Comparing Co/Al_2O_3 and Co/CuZnO, while the concentrations of intermediates/sites (N^0_i) for C_{2+} oxygenates were essentially the same for both catalysts, the concentrations of intermediates/sites for hydrocarbons were reduced by two orders of magnitude. It was this loss of sites for hydrocarbons, not a loss of activity by the sites, that appears to have caused the shift in selectivity toward higher oxygenates (and also MeOH) when CuZnO was combined with Co. Intriguingly, the rate of oxygenate synthesis on Co/CuZnO is similar to that on Co/Al_2O_3. However, this fact is not usually noticed since the rates are so low relative to that for hydrocarbons on Co/Al_2O_3. The synergy of Co, Cu and ZnO appears to decrease hydrocarbon formation relative to oxygenate formation.

The dramatic decrease in surface concentration of hydrocarbons was probably not just due to blockage of Co by Cu since it is hard to argue that somehow Cu or CuZnO would only block hydrocarbon formation without also blocking sites for oxygenate formation. It should be noted that N^0_{CO}, the coverage of reversibly adsorbing CO during reaction as determined by SSITKA, was about four times greater for Co/Al_2O_3 than Co/CuZnO, indicating further the lower dispersion of Co (less exposed Co surface atoms) for the latter catalyst.

The low activities for the Cu-containing catalysts are perhaps somewhat surprising on the one hand since Cu has been widely suggested to provide the main active sites for MeOH synthesis [65,66] and important ones for higher oxygenate synthesis [67,68]. Cu is also a well-known reduction promoter for Fe-based FTS catalysts [69] and also decreases the temperature required for Co reduction [31]. Several studies have found that the activity for CO hydrogenation does not change much with the addition of Cu to Co while the selectivity alters significantly [21,70]. Our

XRD profiles showed that Co-species were X-ray amorphous and likely highly dispersed in the CoCu catalyst even without a refractory oxide support. Therefore, the low activity of CoCu must be due to factors other than Co dispersion (in the sense of Co particle size). Several factors have been proposed [31,68,71] that may explain this seeming contradiction between the present study and some of the others. The most probable would be the effective blockage of potentially FTS active sites on the Co surface by Cu as well as Cu aggregation due to high loadings of Cu (>20% in the Cu-containing catalysts in this study). Other factors, such as different preparation methods or different compositions, especially the presence of alkali species [21,70], may also play a role.

The XRD results (see Fig. 3) for the reduced/passivated CoCu and Co/CuZnO catalysts show that CoCu had essentially no (detectable by XRD) crystalline Co (Co structures <3–4 nm) whereas the results for Co/CuZnO show evidence of somewhat larger Co structures. In an excellent recent paper, den Breejen et al. [63] were able to show that Co particle size can have an effect on Co catalyst activity and TOF for methanation. The TOFs based on SSITKA reported in the present study for methane are remarkably similar to those calculable from Fig. 3 in Ref. [63], given the difference in reaction temperature (250° here vs. 220 °C there) and H_2/CO ratio (2 here vs. 10 there). All of our TOF results (based on SSITKA) for methane synthesis were similar for the catalysts containing Co, except for Co/CuZnO catalyst that was about 50% smaller. Our results do not show evidence for particle size effects; however, multiple formulations of catalysts such as studied here for the objectives of this study are not suitable for attempting to determine effects just due to particle size. Based on the results given in [63], one would hypothesize that particle size effects may play some role in the variation in TOF for catalysts such as studied here, along with the effects of the presence of Cu and ZnO. However, any effects of Co particle size in this study may have been complicated by the effects due to the other catalyst components in the Co–Cu–ZnO series of catalysts. Several recent studies also suggest that particle size effect of Co on the activities or intrinsic activities for various products may be complicated by other effects [43,64].

5. Conclusions

The relationships between the hydrocarbon and oxygenate products during CO hydrogenation on CoCuZnO-based catalysts were investigated for the first time at a site level using multiproduct SSITKA. By comparing the SSITKA results for the various catalysts, several conclusions can be made about the combination of Co with Cu and/or ZnO:

(1) Cu alone acts to decrease activity of Co for all products, probably in part by blockage of the Co surface since. Based on XRD results, Co was highly dispersed (small crystallites) in the Cu-containing Co catalysts. Cu does not affect the intrinsic activities for either hydrocarbon or oxygenate formation based on the $\mathrm{TOF}_{\mathrm{ITK}}^{0}$ results.

(2) ZnO alone seems to act as a support (dispersion agent), keeping Co highly dispersed and very active for hydrocarbon synthesis. It appears to also increase the site activities for C_{2+} oxygenates somewhat.

(3) The combination of Cu and ZnO with Co appears to maintain the oxygenate synthesis ability of highly dispersed Co (such as for Co/Al_2O_3) while simultaneously decreasing its ability to make hydrocarbons by loss of hydrocarbon synthesis sites.

Previous studies [21,30] proposed that the combination of Co with CuZnO could effectively increase the selectivities for higher oxygenates due to the C_1-oxygenate sites (–CH_xO) contributed by CuZnO. Higher alcohols were hypothesized to be formed through the reaction of a hydrocarbon species and a C_1-oxygenate entity. The results from this study, however, indicate that Co (in the form of Co/Al_2O_3) already makes oxygenates including higher oxygenates. This fact tends to be overlooked due to the high hydrocarbon activity of Co/Al_2O_3. In combination with CuZnO, the hydrocarbon activity of Co is so diminished that this oxygenate formation ability become significant not in terms of high activity but rather in terms of high selectivity. In absolute terms, the rate of formation of C_{2+} oxygenates was identical on Co/Al_2O_3 and Co/CuZnO. It is hard to argue, however, that the partial blockage by Cu of the Co surface alone causes the two orders of magnitude decrease in the hydrocarbon formation rate without affecting C_{2+} oxygenate synthesis. Thus, synergy between Co–Cu–ZnO cannot be ruled out and perhaps takes a form that in essence decreases/blocks those sites solely able to make hydrocarbons. Clearly, the effects of Cu and ZnO on Co catalysis are not simply additive. It is interesting that the formation of C_{2+} oxygenates on Co/Al_2O_3 is as good in terms of rate as on Co/CuZnO—just not as selective. The results of this study do not support the hypothesis that the addition of CuZnO to Co primarily has the effect of somehow placing CO-insertion sites next to hydrocarbon chain growth sites to produce higher oxygenates.

Finally, and as mentioned earlier, the conditions of reaction chosen were to maximize the formation of C_1–C_2 oxygenates and hydrocarbons to make isotopic tracing more exact. If, as would be the more applied case, one would want to maximize the yield of higher alcohols, higher pressures and lower temperatures would be used. Given that H_2/CO ratio does not seem to affect the catalyst trends [31], it is quite possible that the conclusions reached here for 1.8 atm and 250 °C would largely be in play in the temperature range of 220–280 °C. However, it is hard to say at this time if the conclusions would still apply at very high pressures >25 atm due in part to the effect of CO at higher pressures on catalyst structures. Unfortunately, isotopic tracing would be difficult and prohibitively expensive at such high pressures.

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