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Effect of component interaction on the activity of Co/CuZnO for CO hydrogenation

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ABSTRACT

Co/CuZnO is known as a base metal catalyst active for C_{2+} oxygenate synthesis. This study probed the interactions of the different components of Co/CuZnO catalysts on CO hydrogenation using Fischer–Tropsch synthesis (250 °C, $H_2/CO = 2$) and SSITKA. Only combination of all three metal components produced a catalyst with relatively high C_{2+} oxygenate selectivity, but with much lower activity compared to that for Co/Al_2O_3. In situ reaction characterizations, albeit at somewhat different conditions than alcohol synthesis, helped explain interaction of the components. SSITKA, under methanation conditions, indicated that the most striking feature for the combination of Co with ZnO and/or Cu was a much decreased amount of reaction intermediates. Ethane hydrogenolysis results suggested that the different components for these catalysts were in close contact and few or no large ensembles ($n \geqslant 12$) of Co atoms existed, confirming that ZnO and/or Cu covered/blocked a substantial number of active sites on Co for CO hydrogenation.

1. Introduction

In order to alleviate the demand for fuel from imported crude oil and reduce the harmful impact on the environment, there is a renewed interest in the direct synthesis of oxygenates, especially higher alcohols via syngas derived from coal, natural gas, or biomass [1–3]. As summarized in several reviews [3–14], four types of catalysts have been studied to carry out CO hydrogenation for the formation of higher oxygenates: Rh-based catalysts, Mo-based catalysts, modified methanol synthesis catalysts, and modified Fischer–Tropsch synthesis (FTS) catalysts. Rh-based catalysts have been studied extensively, in part due to unique CO adsorption behavior [15], and have been found to have relatively high selectivities for the synthesis of C_{2+} oxygenates. However, they have low overall activities, and the high cost of Rh makes Rh-based catalysts less competitive for industrial application. The latest progress in Rh-based catalysts can be found in recent publications and references herein [16–21].

Among the base metal–based catalysts for higher oxygenate synthesis from syngas, modified FTS catalysts developed at *Institut Francais du Petrole* (IFP) in the 1980s based on a combination of Co (a hydrocarbon synthesis catalyst) and CuZnO (a methanol synthesis catalyst) have been reported to have the best overall performance with selectivities for C_{2+} oxygenates as high as 80% at 220–350 °C and 50–150 atm [22–26]. The fourth-generation IFP catalysts were claimed to retain excellent activities after 1000 h TOS, and the main components included Cu, Co, Al, Zn, A (an alkali or alkaline-earth metal), and M (a group VIII noble metal). Zn may be replaced by Cd or Mn; Al by Cr, Mn, or Ti. Preferred wt.% (with respect to total metal) for each metal component except for A has been given as: Cu (15–45%); Co (9–20%); Al (7–25%), Zn (15–50%); and M (0.02–0.8%) [13]. These IFP catalysts can be prepared either by co-precipitation (followed by alkalinization using impregnation) or by decomposition of a homogeneous precursor mixture. It has been reported that preparation procedure has a determining effect on the final selectivity for alcohols, with the decomposition method leading to a better catalytic performance [23]. Unfortunately, scaling up the decomposition procedure for industrial application is not straight forward due to the difficulty in controlling the decomposition of the glassy intermediate generated during the process [23].

To the best of our knowledge, the excellent pioneering work of IFP has not been commercialized, probably due to the fluctuation of oil prices and the complexities of the catalysts (i.e., multiple components and difficulty in preparation), and the catalytic process for the direct synthesis of alcohols from syngas. In addition, mechanistic studies to understand the correlation between the physicochemical properties of the IFP catalysts and their catalytic performance have also been surprisingly limited. This lack of fun-

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damental and systematic studies of Co/CuZnO-based catalysts has certainly not helped in the development of catalytic processes to convert syngas to higher oxygenates with high selectivity.

The objective of this study was to probe the interaction of different components in model Co/CuZnO catalysts deduced from industrial formulations patented by IFP. Besides ex situ characterization techniques, including BET surface area, porosity analysis, XRD, and TPR, the intrinsic natures of the different catalysts were also probed by SSITKA (steady-state isotopic transient kinetic analysis) and ethane hydrogenolysis. SSITKA has been suggested to be the most powerful *in situ* technique to provide definitive information about the amount of active intermediates and their activities under typical reaction conditions [27,28]. Ethane hydrogenolysis is a structure-sensitive reaction that can be used to characterize the decoration of metal surfaces due to the fact that blocking of just one surface metal atom in a multi-atom site renders that catalytic site inactive [29–35]. Thus, these two methodologies can provide more insight into the interaction of different components in the model Co/CuZnO catalysts. In order to better understand the effect of the various components on the catalyst activity, especially as relates to Co, SSITKA measurements of CO hydrogenation were carried out under methanation conditions.

2. Experimental

2.1. Catalyst preparation

$Zn(NO_3)_2·6H_2O$ (99.998%, Alfa Aesar), $Cu(NO_3)_2·3H_2O$ (99.5%, Alfa Aesar), and $Co(NO_3)_2·6H_2O$ (synthetic, Aldrich) were used without further purification. CuZnO, CoCu, and CoZnO were prepared by co-precipitation. In general, the desired amounts of aqueous nitrate solutions were mixed and then precipitated using Na_2CO_3 aqueous solution at room temperature. The resulting mixture was left in a fume hood overnight, and then the precipitate was filtered, washed six times using boiled water, and dried for 12 h at 120 °C, followed by calcination in static air 350 °C for 4 h. Co/CuZnO was prepared by the impregnation to incipient wetness of as-prepared CuZnO with an aqueous solution of $Co(NO_3)_2·6H_2O$ (1.5 mL solution / 1 g CuZnO), followed by drying for 12 h at 120 °C and calcination in static air at 350 °C for 4 h. The final compositions of all the catalysts in this study were determined by elemental analysis, and some variance in molar ratio can be seen among the catalysts due to the difficulty in obtaining the exact metal compositions of the catalysts using the precipitation method. It was also found from elemental analysis that each catalyst contained ~0.2 wt.% Na. For comparison purposes, a Co (10 wt.%) catalyst supported on Al_2O_3 (Alfa-Aesar, γ-phase/α-phase, 99.98%) was also prepared using the incipient wetness impregnation method. The experimental error of catalyst preparation was <10% based on elemental analysis and activity tests.

2.2. Catalyst characterization

The metal compositions of the catalysts were determined by the Galbraith Laboratory in Knoxville, Tennessee (USA).

A Micromeritics ASAP 2020 was used to obtain BET surface area, pore volume, and average pore size at −196 °C using N_2 adsorption. Prior to N_2 adsorption, the catalyst samples were degassed under vacuum at 150 °C for 4 h.

Powder X-ray diffraction patterns were collected in a Scintag XDS 2000 θ/θ powder X-ray diffractometer (XRD) equipped with Cu Kα1/Kα2 (λ = 1.540592 Å and 1.544390 Å, respectively) radiation with a step size of 0.03° in the 2θ range of 5–65°. In this study, XRD work was carried out on as-prepared samples, and the effect of reduction on the structure of the catalysts will be probed in a follow-up study.

TPR was carried out using a quartz reactor. The effluent gas was analyzed by a Pfeiffer mass spectrometer, and an Omega temperature logger was used to monitor the temperature of the sample. The as-prepared sample (0.3 g) was pretreated at 300 °C in He for 1 h prior to a TPR measurement. During a TPR experiment, 5 v/v % H_2/Ar was used at 30 mL/min and the temperature was ramped from room temperature (RT) to 750 °C at 10 °C/min, while the effluent gas was analyzed.

2.3. Reaction

CO hydrogenation (under FTS conditions) and ethane hydrogenolysis were performed in a fixed-bed differential reactor as described elsewhere [36]. The catalyst was loaded between quartz wool plugs in the middle of the reactor. A thermocouple close to the catalyst bed was used to monitor and control the bed temperature. Molecular sieve traps (Alltech) were used to remove H_2O in He, H_2, and CO (99.999%, National Welders). CO was further purified by a CO purifier (Swagelok). Prior to reaction, the catalyst was reduced *in situ* in hydrogen (flow rate = 30 mL/min) at 1 atm by ramping the temperature from RT to 300 °C at a ramp rate of 5 °C/min and then holding at 300 °C for 1 h, followed by cooling down to reaction temperature. Preliminary analysis suggested that varying reduction temperature (300–500 °C) or reduction duration time (1–15 h) did not result in noticeable changes in catalytic behavior of the catalysts in this work. Thus, 300 °C and 1 h were used for the catalyst reduction procedure for all the reactions.

For CO hydrogenation (FTS), a catalyst sample (0.05 g for CoZnO and Co/Al_2O_3, and 0.3 g for the other catalysts) was diluted with 3 g of an inert (α-alumina). The reaction was carried out at 250 °C, as the gas flow was switched to H_2 (30 mL/min) + CO (15 mL/min) and a total pressure of 1.8 atm. The choice of the pressure (1.8 atm) was based on our previous experience with SSITKA, since operating at 1.8 atm leads to a smooth switch of feeds without disturbing reaction. It is well known that reaction conditions play a significant role in governing the catalytic performance. However, the main focus of this study was not to provide direct data for industrial application, but, instead, to probe the nature of active sites using *in situ* techniques under the reaction conditions as close to commercial application as reasonably possible.

For ethane hydrogenolysis, 0.6 g (0.1 g for CoZnO and Co/Al_2O_3) of the catalyst was diluted with 3 g of an inert α-alumina. After reduction, the catalyst bed was cooled to 260 °C and the reaction started by flowing a gas mixture containing 30 mL/min H_2, 40 mL/min He, and 1.5 mL/min C_2H_6.

A Varian 3380 GC was used to analyze the effluent gas on line. Hydrocarbons and oxygenates were separated by a Restek RT-QPLOT column of I.D. 0.53 mm and length 30 m and were analyzed by an FID. CO and other inorganic gases were analyzed by a TCD after separation with a Restek HayeSep® Q column of I.D. 3.18 mm and length 1.83 m. The identification and calibration of gas products were accomplished using standard gases and liquids. The selectivity of a certain product was calculated based on carbon efficiency using the formula $n_iC_i/\sum n_iC_i$, where n_i and C_i are the carbon number and molar concentration of the ith product, respectively. CO conversion in CO hydrogenation and ethane conversion in ethane hydrogenolysis were all kept below ca. 5%. No mass or heat transport limitations were observed for the gas-phase reactions carried out under the specified reaction conditions.

2.4. SSITKA

A steady-state isotopic transient kinetic analysis (SSITKA) system as described elsewhere [37,38] was used to carry out isotopic analysis in order to examine how activity for hydrocarbon synthesis changed due to interaction of Co with the other components.

The reaction conditions were the same as the standard FTS reaction, except that the ratio of H_2:CO (containing 5% Ar) was 20:1 (total flow rate = 45 mL/min, CO:H_2:He = 1.5:30:13.5) and the reaction conditions were 280 °C and 1.8 atm. The purpose of adding a small amount of Ar to ^{12}CO was to use Ar as an inert tracer to determine gas-phase hold-up time. The use of a higher temperature and a higher H_2 partial pressure shifts the product distribution in CO hydrogenation to have CH_4 as the primary product, which simplifies the mass spectrometric (MS) analysis of the isotopic transients. It has been, in general, accepted that the formation of CH_x species is the first step for the formation of CH_4 and any C_{2+} products (hydrocarbons or oxygenates), although the pathway for CO dissociation is still not very clear. Therefore, the formation of C_{2+} oxygenates share first step with CH_4, and exploring the active sites under the methanation conditions also provides useful information. Isotopic transient measurements started as ^{12}CO (5% Ar)/He was switched to ^{13}CO/He after reaction reached steady state. The same pressure for both ^{12}CO and ^{13}CO-feed streams was maintained by the back-pressure regulators in order to minimize perturbation of surface reaction during switching of the isotopically labeled feed streams. The effluent gas was analyzed online by GC for reaction rate and product distribution, and by a Pfeiffer mass spectrometer (MS) with a high-speed acquisition system for isotopic transients.

Note that this study is part of a more extended investigation using a variety of techniques under different conditions to gain clues of the function of each component. The focus of this manuscript is the effect of different components on the activity of Co/CuZnO at the catalytic site level. The effect on the selectivity will be addressed in detail in a follow-up study (manuscript is accepted) using multi-product SSITKA.

3. Results and discussion

3.1. Catalyst characterization

Table 1 lists the catalyst composition, preparation method, BET surface area, and average pore volume and size for each catalyst used for comparison in this study. It is well known that different preparation methods can affect metal dispersion, reducibility, and activity for CO hydrogenation catalysts [39–45]. The IFP catalysts showing the best performance were prepared using a decomposition method [23]; however, as discussed in the introduction, this method has been reported to have problems with uncontrolled decomposition of precursors [23], making the procedure not easily adopted on an industrial scale. Thus, in this study, co-precipitation was used to prepare CuZnO, CoCu, and CoZnO. Co/CuZnO was prepared in this work by the addition of Co to CuZnO using the impregnation method, since our preliminary study found that Co/CuZnO prepared this way resulted in similar activity, but higher alcohol selectivity compared to a catalyst having the same composition but prepared using co-precipitation of all three metal components. The loading ratios of the different metals were based on the optimum ratios for the synthesis of alcohols reported in the literature [46,47], and no effort using statistical experimental design/analysis was made to investigate catalyst synthesis in this study. Due to the difficulty in obtaining the same ratio of metals as in the starting materials using the precipitation method, some variance in molar ratio based on elemental analysis can be seen among the catalysts. In addition, it was found from elemental analysis that each catalyst contained ~0.2 wt.% Na, which was residue from the precipitation agent Na_2CO_3. It has been reported that alkali metals can have a large impact on the catalytic activity and selectivity of Co-based and Cu-based catalysts for CO hydrogenation [48–52]. However, since all the catalysts in this study had similar amounts of residual Na and the Na content was relatively low (it has been reported that Na content $\leqslant$0.2 wt% does not lead to any significant effects on the physicochemical properties of Co/CuZnO type catalysts [51]), the effect of Na was not probed in detail in this study.

From Table 1, the BET surface area and pore volume of the catalysts studied in this work followed the same trends with Co/Al_2O_3 ~ CoZnO > CuZnO ~ Co/CuZnO > CoCu. Although Co/Al_2O_3 and CoZnO had at least 2X higher BET surface areas and pore volumes than those for the other catalysts, the average pore sizes for all the catalysts were around 22–30 nm. Since the BET surface area measurements were carried out on as-prepared samples, the surface areas of the catalysts under the reaction conditions after *in situ* reduction may no longer follow exactly the trend as observed for the as-prepared catalysts.

The structure and crystallite size of each calcined catalyst were examined using powder XRD. It is worth pointing out that XRD can only identify crystalline phases and cannot detect any X-ray amorphous phases that may also exist side by side with the detected crystalline phases in these catalysts. As shown in Fig. 1, CuO (ICDD card No. 74-1021) and ZnO (ICDD card No. 89-0511) structures could be identified for CuZnO, but the peak intensities for CuO were much stronger than those for ZnO. This observation is consistent with the TEM results of Kasatkin et al. [53] in that ZnO and Al_2O_3 tend to show a lower degree of crystallinity than Cu. For CoCu, only the diffraction peaks corresponding to CuO could be observed, and for CoZnO, only the diffraction peaks corresponding to Co_3O_4 (ICDD card No. 42-1467) were distinguishable. The XRD profile of Co/CuZnO indicated the existence of CuO with relatively high intensity and relatively weak peaks belonging to Co_3O_4. The average Co_3O_4 crystallite sizes calculated using the Scherrer equation for CoZnO and Co/CuZnO were 3.8 nm and 9.8 nm, respectively. As indicated in our previous study [54], 10 wt.% Co loaded on γ-

Table 1
Composition, preparation method, BET surface area, pore volume, and average pore size of the catalysts studied.

Catalyst	Co wt.% [a]	Molar ratio [a]	Metal loading method [b]	BET surface area (m^2/g)[d]	Pore volume (cm^3/g)[e]	Average pore size (nm)[e]
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
CoCu	18.8	Co:Cu = 1.0:2.5	Co-precipitation	12.6	0.33	31.8
CoZnO	30.4	Co:Zn = 1.1:1	Co-precipitation	96.4	0.57	29.7
Co/CuZnO	16.5	Co:Cu:Zn = 1.1:2.5:1	Impregnation/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.
[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 again at 350 °C.
[d] Max error = ±5%.
[e] Max error = ±10%.

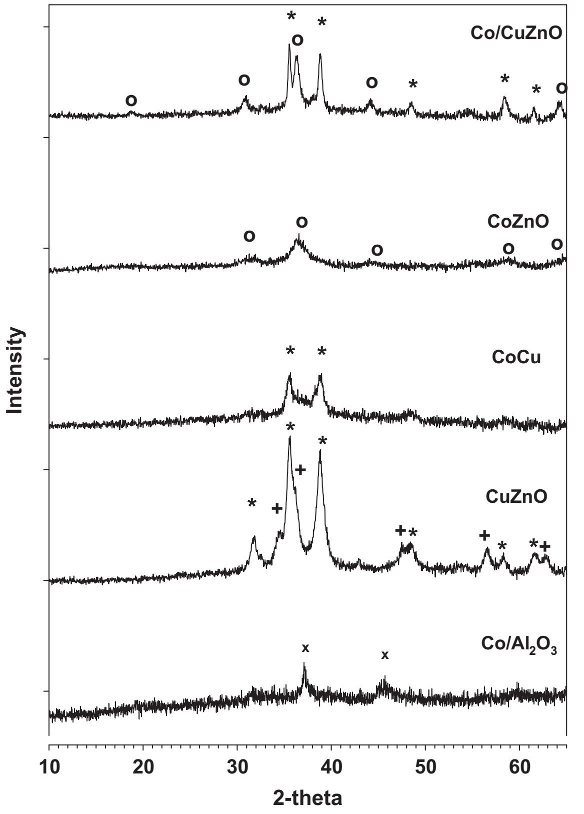

Fig. 1. Powder XRD profiles for the different calcined catalysts. (o: Co_3O_4; $*$: CuO; +: ZnO; x: γ-Al_2O_3).

Al_2O_3 did not lead to any discernable diffraction peaks ascribed to Co-related phases, suggesting high dispersion of Co. The weak diffraction peaks around 37° and 46° for Co/Al_2O_3 correspond to the γ-Al_2O_3 phase. The average CuO crystallite sizes were relatively larger with Co/CuZnO having the largest particle size of 14.6 nm for CuO. Apparently, the addition of Co to CuZnO in this study resulted in the growth of CuO crystallites, most likely due to the sequential preparation method used.

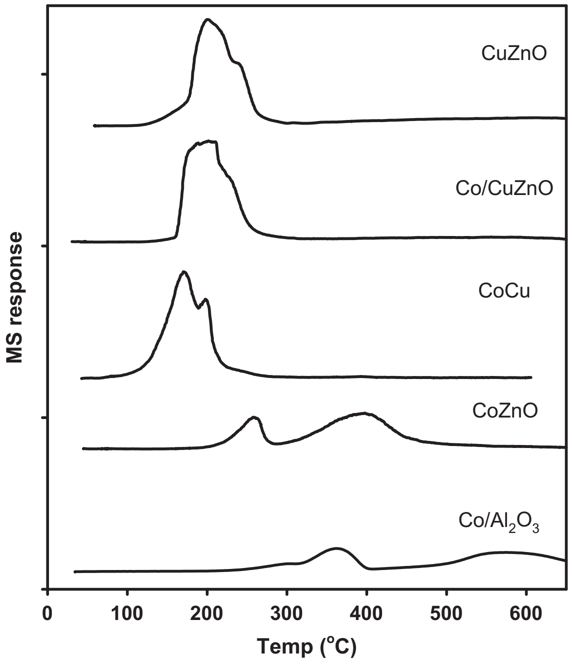

Fig. 2. TPR profiles for the different catalysts.

Fig. 2 presents the TPR profiles of the calcined catalysts. Since the reduction of ZnO below 700 °C is negligible [55], all the reduction peaks observed in this study in the temperature range of 30–750 °C can be ascribed to the reduction of CuO and/or Co_3O_4. As shown in Fig. 2, several features are worth noting:

(1) A major peak at 200 °C along with a shoulder peak at 220 °C can be observed in the TPR profile of CuZnO. These peaks correspond to the reduction of CuO to metallic Cu with the major peak corresponding to the one-step reduction of CuO to Cu^0 and the shoulder peak corresponding to the Cu^+ to Cu^0 reduction of a small fraction of Cu species [56–58]. It can also be seen that the reduction temperatures for CuZnO were much lower than that for bulk CuO, which is around 400 °C [59]. This observation is consistent with the literature [57] that ZnO promotes the reduction of CuO by enhancing the dispersion of CuO.

(2) The TPR profile of CoZnO consists of two peaks in the temperature range of 200–300 °C and 300–450 °C, corresponding to the reduction of Co_3O_4 to CoO and CoO to Co, respectively [60,61]. Compared to the TPR profile of Co/Al_2O_3, it is apparent that Zn also promoted the reduction of Co_3O_4 by shifting reduction peaks to lower temperatures, in agreement with the literature [62]. In addition, the formation of hard-to-reduce species due to the strong interaction of Co and the support, such as Co–Al_xO_y in the case of Al_2O_3-supported Co, was not observed for CoZnO. This is evidenced by the full reduction of Co by 500 °C.

(3) For the TPR profiles for CoCu and Co/CuZnO, only one major peak and one shoulder peak can be observed, indicating that the reduction peak(s) of CuO overlap with those of Co_3O_4 for these two catalysts. It has been reported by Dalmon et al. [51] that Cu can enhance the reducibility of Co more significantly than Zn, which is in agreement with this work, as evidenced by the much lower reduction temperature compared to that of CoZnO. The higher mean reduction temperature for Co/CuZnO compared to that for CoCu may be an indication that ZnO interferes with the reduction of Cu and the reduction promotion of Co caused by Cu.

(4) The lower reduction temperature required for all the catalysts containing Cu indicates that Cu acts as a strong reduction promoter for Co. There is no evidence, however, that it affects the reducibility of ZnO, at least up to 600 °C.

3.2. Catalytic activities for CO hydrogenation (FTS)

Table 2 lists the activities and selectivities of the catalysts for CO hydrogenation (FTS: $H_2/CO = 2$) at 250 °C and 1.8 atm. The data were collected at 15 h TOS after steady state had been reached. The catalytic activity under similar reaction conditions for an Rh-based catalyst from a previous study in our laboratory has also been listed for comparison purposes. In this study, CoZnO exhibited the highest CO hydrogenation rate (8.75 μmol/gcat/s) based on the bulk weight of catalyst. However, the activity of CoZnO based on Co content alone (see column 3 in Table 2) was lower than that of Co/Al_2O_3. The combination of Cu and Co led to a much decreased activity, which is surprising since Courty et al. [23] reported that the addition of Cu to Co altered the selectivity but had little effect on the activity. Three facts probably account for these seemingly contradictory results. First, and probably most importantly, the presence of large amounts of Cu (as in the CoCu catalyst in this study) leading to lower activities for Co catalysts is due to the fact that Cu and Co do not alloy. Because of their thermodynamic prop-

Table 2
Steady-state catalytic properties of catalysts for CO hydrogenation.[a]

Catalyst	CO conv. (%)	Rate[b] (μmol/gcat/s)	Rate[b] (μmol/gCo/s)	Selectivity[c] (C atom%)						α Values	
				CH_4	$C_{2+}HC$[d]	MeOH	Acetaldehyde	EtOH	Other C_{2+} oxy.[e]	HC	Oxy*
Co/Al_2O_3	2.84	6.35	63.5	49.1	48.5	1.2	0.2	0.8	0.4	0.52	0.20
CuZnO	0.10	0.038	–	1.8	–	98.2	–	–	–	0	0
CoZnO	3.92	8.75	28.8	38.0	60.1	0.3	0.3	0.8	0.5	0.65	0.17
CoCu	0.30	0.11	0.59	27.1	67.7	1.3	0.5	2.4	1.0	0.52	0.21
Co/CuZnO	0.10	0.038	0.23	16.9	21.9	14.8	4.3	26.9	15.2	0.35	0.22
Rh–La–Fe/V [f] [17]	0.53	0.20	–	18.7	33.2	5.7	4.4	34.6	3.4	–	–

[a] Catalyst: 0.3 g (0.05 g for Co/Al_2O_3 and CoCu); Inert : 3 g α-alumina; Reduction at 300 °C; Reaction conditions: $T = 250$ °C, P = 1.8 atm; Flow rate = 45 mL/min ($H_2/CO = 2$); Data taken at TOS = 15 h.

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

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

[d] Hydrocarbons with 2 or more carbons.

[e] Oxygenates with 2 or more carbons.

[f] Reduction at 500 °C and reaction at 230 °C. Other pretreatment/reaction conditions were the same as those for Co/Cu-based catalysts.

[*] The α value for oxygenates purposely excludes MeOH, which is made by a very different mechanism and is not related to chain growth.

erties, Cu atoms when present in the vicinity of Co particles may sit on the Co surface, blocking active FTS sites of Co as observed by other researchers [24,63]. This effect will be addressed in more detail later using SSITKA. Second, reaction conditions used in the different studies were quite different, and it has been reported that reaction conditions can have a significant effect on the activity of Co/CuZnO-type catalysts [51,64,65]. Third, the existence of other components, especially alkali species, can significantly affect the catalytic behavior. With regard to selectivity, similar hydrocarbon distributions were observed for CoCu, CoZnO, and Co/Al_2O_3, showing mostly hydrocarbons. The selectivities for oxygenates for these three catalysts were all <5%.

As expected, the main product for CuZnO was MeOH with a selectivity of 98.2%. The activity of this catalyst was the lowest among the catalysts in this study, which is consistent with our previous studies showing low activities for Cu and ZnO catalysts supported on SiO_2 and Al_2O_3 (<0.001 μmol/gcat/s for 0.5 wt.% Cu(ZnO)/SiO_2 [66], ~0.01 μmol/gcat/s for 10 wt.% Cu(ZnO)/Al_2O_3).

The Co/CuZnO catalyst exhibited the same activity (on a per g catalyst basis) as that for CuZnO, but a quite different selectivity. Much less hydrocarbons (than CoZnO and CoCu) and MeOH (than CuZnO) but a significant increase in the selectivity for higher oxygenates were observed for Co/CuZnO. The overall performance of this catalyst is close to the Rh-based catalysts from our precious studies [17,36], except that the activity is much lower. It is obvious that modifying Co with just Cu or ZnO only impacted Co activity. Only the incorporation of all these three components led to a much higher selectivity for C_{2+} oxygenates.

In order to further understand the possible difference in reaction pathways, chain growth probability factors for both hydrocarbons and oxygenates were also calculated based on an Anderson–Schulz–Flory (ASF) product distribution. Since CO hydrogenation on CuZnO only produced MeOH and CH_4, chain growth probabilities were zero. As shown in Table 2, it is obvious that α values for hydrocarbons for Co-containing catalysts were reasonably similar with the exception of Co/CuZnO. Similar α values for C_{2+} oxygenates were also obtained for all the Co-containing catalysts, suggesting that the use of these different components with Co does not affect the higher oxygenate formation mechanism. However, α values for hydrocarbons and oxygenates differed significantly, as might be expected, given their related but slightly different mechanisms and active sites. This observation is in agreement with those for a $Cu/Co/ZnO/Al_2O_3/K$ catalyst [67] and Rh-based catalysts [16,21]. The HC α was significantly lower for Co/CuZnO than for the other Co-containing catalysts, although still greater than that for oxygenates. It appears that the effect of the combination of CuZnO with Co was to shift some hydrocarbon synthesis to C_{2+} oxygenate synthesis.

3.3. SSITKA

3.3.1. CO hydrogenation under methanation conditions

Table 3 summarizes the results of the SSITKA study under methanation ($H_2/CO = 20$) conditions. As mentioned earlier, since the current focus of our study is to investigate the effect of catalyst components on activity and in particular Co activity, carrying out SSITKA under methanation conditions presents the most direct way. It can be seen that the steady-state rate for methanation was significantly larger for Co/Al_2O_3 and significantly smaller for CuZnO than the rest of the catalysts. The steady-state rates for methanation, however, followed the same trend as that for FTS with $H_2/CO = 2$ on a Co basis (see Table 2): Co/Al_2O_3 > CoZnO > CoCu > Co/CuZnO ≫ CuZnO.

One obvious observation is that the relative activities for CoZnO and CuZnO were much decreased compared to their relative activities under FTS conditions using Co/Al_2O_3 as a "standard." Since it is well known that the activation energy for CO hydrogenation should not differ significantly (observed activation energy is usually between 70 and 105 kJ mol^{-1} [68,69]) for different catalysts, the dramatic change in relative catalytic activity for CoZnO and CuZnO should not be caused just by the change in reaction temperature (250 °C for FTS and 280 °C for methanation). Thus, the significantly decreased relative catalytic activity for these two catalysts under methanation conditions must mainly be due to effects of the different partial pressures of reactants. It is well known that the rate of CO hydrogenation is also a strong function of the partial pressures of H_2 and CO [20,21,70,71]. Different catalysts can have different partial pressure dependence depending on variations in the rate-limiting step, even when the same mechanism is operable. Obviously, adding the complexity of producing hydrocarbons, MeOH, and higher oxygenates increases the mechanistic complexity and consequently the partial pressure variations. Apparently, the combination of ZnO with Co was not as effective at higher partial pressures of H_2 (methanation conditions) compared to at lower partial pressures of H_2 (FTS conditions). This observation supports the claim in the literature that one possible promoting function of Zn is to supply atomic H to Cu metal through H spillover [65,72]. In other words, the promoting effect of ZnO is not obvious under methanation conditions, since the availability of H_2 on catalyst surface is no longer a limiting fact due to the much higher partial pressure of H_2. Despite the much decreased relative activity compared to regular CO hydrogenation for the ZnO-containing catalysts, the

Table 3
SSITKA results for CO hydrogenation on the catalysts studied.[a]

Catalyst	CO conv. (%)	SS Rate [b] (μmol C/gcat/s)	CH_4 selectivity (%)	τ_{CH4} (s)	TOF_{ITK} [c] (s^{-1})	N_{CH4} [d] (μmol/gcat)
Co/Al_2O_3	6.9	10.47	98.1	3.7	0.27	39.8
CuZnO	0.003	0.001	67.2	7.9	0.13	0.005
CoCu	3.38	0.13	93.7	4.2	0.24	0.50
CoZnO	2.66	0.30	99.6	2.7	0.37	0.80
Co/CuZnO	2.16	0.08	92.9	8.3	0.12	0.62

[a] Catalyst: 0.3 g (0.1 g for CoZnO), Inert : α-alumina 3 g; Reaction at 280 °C; P = 1.8 atm; Flow rate = 45 mL/min ($H_2/CO/He = 30/1.5/13.5$).
[b] Reaction conversion was less than 5% in all cases. Experimental error: ±10%.
[c] TOF based on SSITKA, calculated as $TOF_{ITK} = 1/\tau_{CH4}$.
[d] $N_i = Rate_i * \tau_i$.

use of methanation conditions still permitted the determination of the effect of different components on the surface reaction kinetic parameters for CO hydrogenation, as will be discussed in more detail in the following section.

3.3.2. Surface reaction kinetic parameters for CO hydrogenation on different catalysts

Fig. 3 shows typical normalized transients after a switch from ^{12}CO (5% Ar) to ^{13}CO during CO hydrogenation under methanation conditions. SSITKA allows the determination of how different combinations of Co, Cu, and ZnO affect the average surface reaction residence time of methane (τ_{CH4}, which is inversely related to the site TOF_{ITK} [28]) and the concentration of active surface reaction intermediates of methane (N_{CH4}). The methods used to calculate the average surface residence time and the concentration of active surface intermediates have been described in detail elsewhere [28].

The TOF_{ITK} calculated based on the residence time of CH_4 precursors for different catalysts followed the trend of CoZnO > Co/Al_2O_3 ~ CoCu > CuZnO ~ Co/CuZnO, but the values were within a factor of 3. The combination of ZnO with Co boosted the site activity of Co/Al_2O_3 by ca. 1/3; however, the combination of Co and Cu seemed to have little effect on the activity of the Co sites (not surprising, since Cu has essentially no activity for CO hydrogenation). It can also be seen that the reaction sites on CuZnO and Co/CuZnO were much less active. CuZnO is well known to be primarily a MeOH synthesis catalyst.

It is noteworthy that the turnover rate for Co/Al_2O_3 obtained from SSITKA in this study after temperature, pressure, and reducibility correction was about one order of magnitude higher than TOF data reported in the literature [73,74] for supported and bulk Co. TOF for Co/Al_2O_3 based on hydrogen chemisorption results from our previous study [54] is 0.11 s^{1}, also much smaller than the TOF obtained from SSITKA (0.27 s^{-1}). This difference can be mainly explained by the different methods used in determining active sites. As demonstrated in previous findings of our research group [37,75], TOF commonly calculated using H_2 or CO chemisorption is often an order of magnitude lower than that obtained using SSITKA, due to an overestimation of the number of active reaction sites by both H_2 and CO chemisorption. The results obtained in this work once again suggest that the number of active sites based on chemisorption is not reliable in an absolute sense.

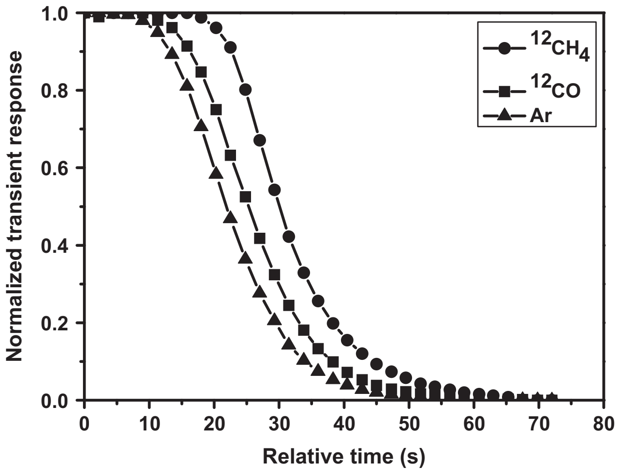

Fig. 3. Normalized isotopic transients for Co/Al_2O_3 during CO hydrogenation under methanation conditions.

With respect to the concentration of surface reaction intermediates leading to CH_4 (and an approximation for the number of active CH_4 synthesis sites), Co/Al_2O_3 had about 50 times more CH_4 intermediates than CoZnO. CoZnO had slightly more CH_4 intermediates than CoCu and Co/CuZnO, but the difference was not significant (<50%). CuZnO had the lowest concentration of CH_4 intermediates, about two orders of magnitude less than that for Co/CuZnO. This observation also implies that there may be two completely different sites for the formation of hydrocarbons and methanol, respectively. Since under FTS conditions, the main product for CuZnO is MeOH, it can be suggested that the formation of MeOH is diminished on CuZnO under methanation conditions, and these sites are not active for the formation of CHx species. Once the reaction conditions shifted to favor the formation of CH_4, the limitation in reaction sites for the formation of CH_4 was more obvious. Interestingly, some earlier studies carried out by other research groups found that the addition of Co to CuZnO led to much decreased MeOH synthesis activity without significantly altering the formation of rates for other products (include hydrocarbons and oxygenates) [45,76]. It was proposed by these authors that only a small fraction of the measured Cu surface area is active for methanol formation, and the role of Co was to block the pathway for methanol formation. Another conclusion can be drawn here is that the addition of Co to CuZnO led to a larger number of active CH_4 synthesis sites based on the comparison of N_{CH4} for CuZnO and Co/CuZnO. However, the increased amount of active methanation sites with the addition of Co to CuZnO was still not comparable to that for Co on Al_2O_3, with even a smaller weight percentage of Co. This is why Co/CuZnO had a much smaller methanation activity than Co/Al_2O_3.

3.4. Ethane hydrogenolysis

Ethane hydrogenolysis was chosen as a characterization reaction to investigate the Co surface in the catalysts, since this reaction has been reported to be very structure sensitive on Co and to require site ensembles of ca. 12 metal atoms [29–31]. The main purpose of using ethane hydrogenolysis in this study was to determine whether large Co ensembles exist after the addition of other components; therefore, no extensive study, including theoretical

Table 4
Ethane hydrogenolysis results.[a]

Catalyst	Ethane conv. (%)	CH_4 formation rate (μmol/gcat/s)[b]
Co/Al_2O_3	1.41	0.16
Cu/Al_2O_3	<0.01	0.0
ZnO/Al_2O_3	<0.01	0.0
CuZnO	<0.01	0.0
CoCu	0.46	0.009
CoZnO	0.04	0.004
Co/CuZnO	<0.01	0.0

[a] Catalyst: 0.6 g (0.1 g for Co/Al_2O_3 and CoZnO); Inert : 3 g α-alumina; Reduction at 300 °C; Reaction conditions: T = 260 °C, P = 1.8 atm; Flow rate = 71.5 mL/min ($H_2/C_2H_6/He$ = 30/1.5/40); Data taken at TOS = 10 min. CH_4 is the only product under the reaction conditions.

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

analysis for ethane hydrogenolysis, was carried out in this work. Table 4 lists the activities of the different catalysts for ethane hydrogenation at TOS = 10 min. Cu (20 wt.%) and ZnO (20 wt.%) supported on Al_2O_3 were also tested for comparison purposes. As shown in Table 4, Cu/Al_2O_3 and ZnO/Al_2O_3 as well as CuZnO had no activity for ethane hydrogenolysis. For Co-containing catalysts, only Co/Al_2O_3 showed comparable activity to other traditionally supported Co catalysts [77]. All the other catalysts had very small or negligible activity for ethane hydrogenolysis. These results suggest that there were no or few relatively large ensembles ($n \geqslant 12$) of Co surface atoms on Co/CuZnO, CoCu, or CoZnO. Thus, it is likely that the different metal components in these Co/CuZnO-related catalysts were in intimate contact with each other, and most of the Co particles were decorated by ZnO or Cu or both.

3.5. Summary of the effect/interaction of the different components

Based on the results from physicochemical characterization, reaction activities, and isotopic tracing, it is obvious that the significant differences in activity and selectivity cannot be simply ascribed to surface area, structure, crystallite size, or reducibility. Higher surface area may contribute to the higher activity observed for Co/Al_2O_3 and CoZnO under FTS conditions, but cannot explain the activity difference under methanation conditions. The same rationale can be applied to reducibility. Co/Al_2O_3 had the lowest reducibility at 300 °C, the reduction temperature used in this study, but its catalytic activities were the highest per unit weight of Co under both FTS and methanation conditions. Combining the SSITKA and ethane hydrogenolysis results, the following suggestions can be made:

(1) Cu helps in reduction of Co, but Cu does not improve Co activity because it decorates the Co surface, blocking surface reaction sites.
(2) Neither ZnO nor Cu by itself causes Co-containing catalysts to produce a significant fraction of C_{2+} oxygenates.
(3) ZnO also appears to decorate the Co surface, leading to fewer surface reaction sites (both for methanation and ethane hydrogenolysis).
(4) Although the presence of both Cu and ZnO leads Co to selectively make significantly more C_{2+} oxygenates, they also appear to block significantly a large fraction of Co sites, resulting in a diminished overall activity.

It is worth noting that the surface morphology in this study was elucidated mostly from SSITKA and ethane hydrogenolysis. Unfortunately, electron microscopy is very limited for catalysts having such loadings of metals as these, is an ex-situ method, and cannot really distinguish active sites in any case. Thus, the information obtained by *in situ* techniques, including SSIKA and ethane hydrogenolysis, is more meaningful.

4. Conclusions

Despite the fact that the Co/CuZnO-based catalysts have received a great deal of attention in the past for the synthesis of higher alcohols, this study has explored for the first time at the site level the effect of individual components on activity. Based on BET analysis, XRD, and TPR for Co/Al_2O_3, CuZnO, CoCu, CoZnO, and Co/CuZnO, it was found that the different combinations of Cu, Zn, and/or Co resulted in significant differences in surface area, structure, crystallite size, and reducibility for the catalysts. These catalysts also exhibited significantly different catalytic activities and selectivities for CO hydrogenation under FTS conditions. ZnO improved the dispersion of Co to some extent and might also enhance hydrogenation. Cu greatly enhanced reducibility of Co. Only the combination of all these three metal components, however, led to the formation of higher oxygenates with substantially higher selectivity. There appears to be no correlation of surface area, particle size, and reducibility with activity and selectivity of the catalysts.

In situ reaction characterizations using SSITKA at methanation conditions and ethane hydrogenolysis were employed to develop a better understanding of the possible interactions of the various components. Although probably similar to what exists under CO hydrogenation at alcohol synthesis conditions, some interactions/catalyst structures may be affected somewhat at the different reaction conditions. It was found from SSITKA under methanation conditions that compared to Cu, the addition of ZnO to Co boosted the site activity to some extent, while Cu seemed to have little effect on the activity of Co. The most pronounced differences for these catalysts were observed for the amounts of the reaction intermediates on the surface. The combination of Co with ZnO and/or Cu led to much decreased surface concentrations of reaction intermediates for CH_4. The results for ethane hydrogenolysis indicated that the different components for these multi-component catalysts were in close contact, and few or no relatively large ensembles ($n \geqslant 12$) of Co atoms existed on the surface in these catalysts. Thus, it can be suggested that Co/CuZnO achieves its high selectivity for oxygenates by blockage of a significant portion of the hydrocarbon synthesis sites while retaining oxygenate synthesis sites, but at the cost of the high activity normally expected for Co catalysts.

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