Preparation and Characterization of lanthanum-promoted cobalt-copper catalysts for the conversion of syngas to higher oxygenates: Formation of cobalt carbide

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Abstract

A series of La-promoted cobalt-copper catalysts with various Co:Cu ratios have been used to study the conversion of syngas to oxygenates and hydrocarbons. In particular, the effect of the Co:Cu composition on the selectivity to oxygenates versus hydrocarbons has been examined.

Three bulk catalysts were synthesized by coprecipitation, reduced in H₂/He flow, then cobalt carbide was formed during CO hydrogenation. The composition of the catalysts were: Co:Cu = 12:9, 7:13, and 0:21 (cobalt only). CO hydrogenation tests were performed at differential conversions and 30 bar, H₂/CO=2/1 and 250°C.

The C₁ selectivity (methane + methanol + CO₂) was ~64% for the two catalysts containing Co and Cu, and slightly less for the Co-only catalyst (52%). These products are formed by three mechanisms: (1) CH₄: hydrogenation of dissociatively adsorbed CO at metallic cobalt sites, (2) CH₃OH: hydrogenation of associatively adsorbed of CO at copper sites, and (3) CO₂: water gas shift, also at the copper sites. C₂₊ alcohol selectivity for the two Cu-containing catalysts is greater than for the Co-only catalyst, while the Co-only catalyst has the highest selectivity to acetaldehyde. The formation of

C₂₊ oxygenates is consistent with the CO insertion mechanism, in which associatively adsorbed CO is inserted into the CH_x species and forms the first C-C bond, producing a CH_xCO intermediate that can be hydrogenated into ethanol or acetaldehyde.

Key words:

Higher alcohol synthesis; Syngas; Cobalt; Copper; Cobalt carbide; Modified Fischer-Tropsch catalysts; Turnover frequency.

1. Introduction

Catalytic conversion of syngas is a complex step-wise mechanism in which both C₁ and higher carbon-number products are produced. The final product mixture is the net result of interactions between CO and hydrogen and the surface sites, forming both simple and more complex intermediates. Cobalt-copper catalysts are one class of materials that have been studied for syngas conversion. These catalysts contain sites that activate CO both dissociatively and associatively. While cobalt is thought to be the site at which CO is dissociated, the interaction of copper with CO in the formation of higher oxygenates is not fully understood [1-3].

It is well-known that in Fischer-Tropsch synthesis, cobalt dissociates carbon monoxide, but there is a lack of consensus of the mechanism leading to higher oxygenates. In principle, the formation of higher oxygenates must involve (i) an activated but associatively adsorbed CO, (ii) activated but dissociatively adsorbed CO, and (iii) atomic proximity of these two activated CO molecules so that the initial C-C bond can be formed.

The role of both cobalt and copper has been studied. CO adsorbed on copper is thermally unstable at 200 °C, while the CO hydrogenation reaction is usually carried out

above this temperature [4-6]. This implies that associatively adsorbed CO on copper has little relationship with CO insertion and higher oxygenate formation. Some authors claim that the active sites are cobalt-copper alloy nanocrystals and the selectivity of higher alcohols varies with the cobalt-copper ratio.[7, 8] However, bulk Co-Cu bimetallic alloys are not likely to exist because both metals show low solubility (a maximum of 9 atom % from phase diagrams) [9, 10]. Other researchers believe cobalt cations [4] or cobalt carbide serve as the CO insertion site. Baker et al.[11] claim that the role of copper promoters in cobalt-based catalyst is to control hydrogenation activity, not participating in the CO insertion mechanism, while Xiang et al.[9, 12, 13] synthesized a series of cobalt core/ copper shell catalysts promoted by Mn or Mo. Major physical and chemical reconstruction was observed during activation and reaction, and the surface cobalt is in a Co_2C phase with higher oxidation state. Volkova et al.[14] proposed that copper promotes the formation of cobalt carbide by alloying with cobalt.

In the Fischer Tropsch synthesis, the formation of cobalt carbide is usually a cause of deactivation because Co_2C particles are considered inactive for CO dissociation [15, 16]. In higher alcohol synthesis, however, Co_2C has been identified as the active species in the formation of higher alcohols by both experimental and computational studies [14, 17-19]. Lebarbier et al.[18] presented a combined theoretical and experimental study of the mixed higher alcohol synthesis from syngas using La_2O_3 -promoted cobalt catalysts. According to the characterization results, Co exists in both metallic form and carbide phase, and the amount of Co_2C greatly depends on the presence of La. In the CO hydrogenation experimental studies, the alcohol selectivity increased slightly for the sample with the highest $\text{Co}_2\text{C}/\text{Co}^0$ ratio. Theoretical studies

indicate that the hydrocarbon chain growth on Co^0 is more energetically favorable than on Co_2C , and the growth of oxygenates is more favorable on Co_2C by coupling CO_{ads} and $(\text{CH}_x)_{\text{ads}}$ to form a C-C bond ($\text{CH}_x + \text{CO} \rightarrow \text{CH}_x\text{CO}$).

The effect of lanthanum on promoting cobalt carbide formation is also reported in other works [3, 20, 21]. Liu et al.[3] prepared and characterized a $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$ perovskite-type catalyst for higher alcohol synthesis from syngas. After the reduction of the catalyst, La_2O_3 is homogeneously mixed with bimetal Cu-Co particles. La_2O_3 promotes metallic cobalt and carbon monoxide to form Co_2C . Therefore, the ratio of Co^{2+} to cobalt metal is optimized to favor the synthesis of ethanol and higher oxygenates. Jiao et al.[20] observed the existence of Co_2C species on the activated carbon-supported La-promoted cobalt catalysts with different La concentrations (denoted as 15Co-xLa/AC). The highest alcohol selectivity (38.9 wt.%) was found on a catalyst with 0.5 wt.% La doping.

Cobalt and copper composition in the catalyst also significantly affects the product selectivity. Dong et al.[22] investigated a series of CoCu catalyst supported on carbon nanotubes with the same support content but different Co/Cu molar ratio. The catalyst with the Co/Cu molar ratio of 3/1 showed the highest yield to alcohols. Prieto et al.[2] used DFT calculations and microkinetic models to identify the optimum composition to selectively produce higher alcohols. The results show that hydrocarbons were favored on the metallic Co sites, and methanol was favored on the metallic Cu sites. The maximum selectivity to ethanol was postulated to be on an atomically adjacent cobalt-copper surface with slightly Co-enriched compositions. The experimental study showed that the highest yield to ethanol was achieved on a catalyst

with Cu/Co $\approx 1/2$. Therefore, the higher alcohols production is favored on a Co-rich surface. Considering the fact that cobalt carbide could form during the reaction, therefore, a Co-rich catalyst surface could produce more cobalt carbide on the surface, leading to higher selectivity to higher alcohols.

In this study here, a series of La-promoted cobalt-copper catalysts are synthesized and tested for CO hydrogenation. The goal is to investigate the formation of cobalt carbide and the role of copper and cobalt carbide for higher oxygenates. The ratio of cobalt/copper is varied to determine the highest selectivity to these products. Characterizations of the catalysts in this study include TPR, TEM and DRIFTS study.

2. Materials and Methods

2.1 Catalyst Preparation

Catalysts were prepared by coprecipitation in ammonia carbonate solution. A typical synthesis method has been reported elsewhere[21]. Copper nitrate, cobalt nitrate and lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were dissolved in water. The concentrations of cobalt and copper nitrate were adjusted to synthesize catalysts with different cobalt/copper ratios, as shown in Table 1. The solution is heated to 80°C and an ammonia carbonate solution was titrated to keep the pH at 7.00 ± 0.2 . The solution was then aged for six hours at room temperature. The precipitate was filtered and washed with deionized water, and dried at 90°C for 24 hours. The dried precursor was calcined in air flow at 500°C for 3 h with a ramp rate of 2°C /min.

2.2 Catalyst characterization

H₂-TPR was done on 50mg of calcined catalyst in an Altamira AMI-200 system. The catalysts were pretreated in Helium flow at 150°C for 30 min first. The samples were cooled down to room temperature, and a flow of 10% H₂/Ar passed through the

reactor while the temperature was ramped to 700°C. The consumption of hydrogen was monitored by a thermal conductivity detector. A calibration on 20, 35 and 50 mg Ag₂O with the same TPR procedures allowed quantitative analysis of catalyst hydrogen uptake.

Catalyst dispersion and crystallite size was determined by CO pulse chemisorption on the Altamira AMI-200 system. 100mg of calcined catalyst was reduced at 400°C for 1h followed by 30 mins helium flush at 50°C and atmospheric pressure. A total of 15 CO pulses were injected into the helium flow. The composition of the stream exiting the sample cell is monitored quantitatively by the TCD. CO pulse calibration was conducted to calculate the amount of CO adsorbed on the surface. The stoichiometric adsorption ratio for CO on active cobalt metal sites(CO/Co_s) is 1.2/1, which is appropriate for catalysts prepared by coprecipitation [23].

The morphology and the particle sizes of the reacted catalysts were characterized by a JEOL 2011 High-Resolution TEM at an accelerating voltage of 200kV. After the reaction process, the catalysts were cooled to room temperature, then passivated in 1% O₂/He gas for 30 mins. The powders were grounded and suspended in ethanol, then a drop of the solution was deposited on a lacey carbon coated 300 mesh copper grid. A STEM-EDX map of Co and La was collected on a FEI Titan Themis 3 STEM with Super-X quad EDS detector at 80 kV.

2.3 In-situ DRIFTS Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy of adsorbed CO was performed on a Thermo Scientific Nicolet 6700 spectrometer with a Harrick Praying Mantis

accessory. Diffuse reflectance spectra were collected with a liquid-nitrogen cooled MCT detector.

In the FTIR measurements, The sample was maintained in helium flow at 400°C for 30 minutes for the reduction, then the chamber was cooled down to 25°C in helium atmosphere. During this stage background spectra were collected from 400°C to room temperature with 50°C intervals. In-situ surface reactions were performed after background spectra collection. The sample was kept in a syngas flow ($H_2/CO=2$) at ambient pressure. The spectra were taken from 100°C to 300°C with 50°C intervals. Sample spectra (64 averaged scans, with resolution 4 cm^{-1}) were collected every minute.

2.4 Reactions

An Altamira AMI-200R-HP system was used to carry out the reactions at differential conditions. During each run, 50 mg of freshly-calcined samples were loaded into a 1/4 inch glass-lined stainless steel reactor tube. The catalyst was reduced by 10% H_2 /He gas at 400°C. After the reduction, the temperature was set to 250°C, and the reactor was pressurized to 30 bar. At this point, a mixed flow of hydrogen and CO flowed through the reactor to carry out the CO hydrogenation reaction. Products were analyzed by a Shimadzu GC-2014 gas chromatograph with one flame ionization detector (FID) and two thermal conductivity detectors (TCDs). Reaction data was collected every $\frac{3}{4}$ hour until steady state was reached.

3. Results

3.1 Catalyst composition

Table 1 Catalyst Composition by ICP-OES test

Catalyst	Composition			Co/Cu molar ratio
	Cu wt. %	Co wt. %	La wt. %	

$\text{Cu}_1\text{Co}_1\text{La}$	11.7	9.4	12.7	0.87
$\text{Cu}_1\text{Co}_2\text{La}$	7.11	13	11.8	1.98
Co_1La	0	20.8	11.8	-

The composition of the catalysts are shown in Table 1. During the synthesis, the concentration of cobalt nitrate and copper nitrate were adjusted to yield three catalysts with different cobalt-copper ratios, whereas the lanthanum nitrate concentration was consistent to maintain the same lanthanum composition for all the catalysts. In Table 1, $\text{Cu}_1\text{Co}_1\text{La}$ has a copper:cobalt mole ratio of 1:1, while the $\text{Cu}_1\text{Co}_2\text{La}$ sample has a 1:2 copper to cobalt mole ratio. There no copper added in Co_1La .

3.2 H₂-TPR

Figure 1 TPR results for $\text{Cu}_1\text{Co}_1\text{La}$, $\text{Cu}_1\text{Co}_2\text{La}$ and Co_1La from 70°C to 700°C. 50 mg of samples were reduced in 10% H_2/Ar . Ramp rate=20°C/min

Temperature programmed reduction profiles of all the catalysts are shown in Figure 1. The reduction of the cobalt-copper catalysts includes both the reduction of CuO to Cu and the two-step reduction of Co₃O₄ to CoO and CoO to Co metal. The reduction of cobalt is promoted by copper in close proximity [24], and the choice of promoters such as copper significantly affects the reduction behavior of cobalt oxides[2, 9, 17]. The TPR profiles in Figure 1 are consistent with this expected behavior. Taking Cu₁Co₁La as an example, the first shoulder at ~190°C corresponds to the reduction of CuO to Cu. The other feature at 215°C is a combination of both Co₃O₄ to CoO and CoO to metallic cobalt^[24]. The lack of copper in Co₁La requires higher temperature for complete reduction---the reduction of Co₁La started at ~290°C, and ends at 550°C.

Table 2 shows the H₂ consumption of the three catalysts during the TPR. The expected role of copper to promote the reduction of the two copper-containing catalysts (Cu₁Co₁La and Cu₁Co₂La) is apparent. The H₂ consumption was calculated from two temperature regions: 50°C-400°C and 50°C-700°C. Below 400°C, 86% of the total metal (copper plus cobalt) in both Cu₁Co₁La and Cu₁Co₂La is reduced, while only 72% of the metal in Co₁La is reduced in this same region.

Table 2 Quantitative H₂ Consumption during TPR* and Dispersion from CO pulse chemisorption

Catalyst	Expected consumption (μmol/g)	50°C to 400°C		50°C to 700°C		Dispersion (%) [†]
		H ₂ consumed (μmol/g) [*]	Metal reduced %	H ₂ consumed (μmol/g) [*]	Metal reduced %	
Cu ₁ Co ₁ La	395	343±8	86.8 ± 2.0	362±8	91.5±2.0	10.6
Cu ₁ Co ₂ La	405	350 ± 8	86.3 ± 2.0	370±8	91.2±2.0	9.6
Co ₁ La	470	336 ± 5	71.6 ± 1.1	435±6	92.5±1.1	9.0

* H₂ consumption is based on the area under the curve in Figure 1 from 50°C to 400°C and from 50°C to 700°C region. The consumption is calibrated using Ag₂O as standard.

* Errors in the H₂ consumption values are within 95% confidence interval.

192 † Dispersion is based on CO pulse chemisorption at 50°C. Error of measurement was ±5%

193 3.3 TEM

194 Figure 2 (a-c) shows the TEM image of $\text{Cu}_1\text{Co}_1\text{La}$, $\text{Cu}_1\text{Co}_2\text{La}$ and Co_1La after 3
195 hours of reduction followed by 15 hours of CO hydrogenation reaction at 250°C. The
196 magnified image of Co_1La is shown in Figure 2 (d). The catalysts show particles with the
197 size ranging from 20 nm to 50 nm. All three catalysts are bulk materials so that most of
198 the particles tend to overlap and form assorted crystal structures. $\text{Cu}_1\text{Co}_2\text{La}$ showed

Figure 2 TEM image of (a) $\text{Cu}_1\text{Co}_1\text{La}$, (b) $\text{Cu}_1\text{Co}_2\text{La}$ and (c) Co_1La after H_2 reduction and syngas exposure at 250°C for 15 h. (d) TEM image of Co_1La at higher resolution.

less overlap than the other two catalysts. The lattice parameters for each smaller particles ($\text{size} \leq 10 \text{ nm}$) are shown in Figure 2 (b). The particles with a lattice spacing of $\sim 0.210 \text{ nm}$ corresponds to the (111) plane of Co or Cu metal. On the peripheral areas, another type of nanoparticles with larger lattice spacing (0.241 nm to 0.257 nm) is shown, which matches the lattice spacing of Co_2C (101) and (200) plane. Therefore, during the 15 hours of CO hydrogenation reaction, the metallic cobalt particles on the surface have partially transformed to cobalt carbide, and the surface contains three types of particles: metallic Co, metallic Cu and Co_2C .

Co_1La also shows graphitic layers on the outer surface of the catalyst particles, as shown in Figure 2 (c) and zoomed in Figure 2 (d). The graphitic carbon covers the surface of the catalysts and forms a graphitic shell that covers the catalyst, which must have formed on Co_1La during the 15 hours of CO hydrogenation reaction.

Figure 3 HAADF image of $\text{Cu}_1\text{Co}_2\text{La}$, with Cobalt (Co-K) map, and Lanthanum (La-L) map of the particle in the white box.

Figure 3 shows a STEM analysis with EDX map on Co and La on the spent $\text{Cu}_1\text{Co}_2\text{La}$ catalyst. La is homogeneously distributed in the particle, with no existence of large lanthanum oxide islands. Cobalt and lanthanum are in close proximity after the calcination→reduction→reaction process, which indicates the extraordinary mixing of cobalt and lanthanum is preserved during CO hydrogenation.

3.4 DRIFTS

Figure 4 shows the in-situ DRIFTS spectra of $\text{Cu}_1\text{Co}_2\text{La}$ during a temperature programmed surface reaction experiment. The spectra taken at 100°C under syngas atmosphere show the peaks of gas phase CO (2124cm^{-1} and 2175cm^{-1}) and CO linearly adsorbed on copper (2113cm^{-1}). Once the temperature reaches 200°C, the 2113cm^{-1}

Figure 3 DRIFTS spectra of $\text{Cu}_1\text{Co}_2\text{La}$ in CO/H_2 flow at 100°C, 200°C, 250°C and 300°C. Spectra are labeled as Temperature and time sequence. E.g. 300°C 10 min is taken when temperature is kept at 300°C after 10 minutes.

222 peak disappeared, indicating the desorption of CO from the copper surface[4, 25].

223 Meanwhile, an absorption peak appeared at 1995 cm^{-1} . This peak grows in intensity and

224 became stable after 10 minutes at 200°C . At 250°C this peak slightly shifted to 1998 cm^{-1}

225 $^{-1}$ with the same intensity. However, the intensity of this peak at 1998 cm^{-1} reduces and

226 shifted to 1986 cm^{-1} at 300°C . The new band corresponds to CO adsorbed on a new

227 type of site generated in the presence of syngas at elevated temperatures. This site

228 adsorbs CO above 200°C , and desorbs at $\sim 300^{\circ}\text{C}$.

229 To confirm that the peak at 1998 cm^{-1} corresponds to CO adsorption on the new

230 site, a new experiment is performed on reduced $\text{Cu}_1\text{Co}_2\text{La}$ catalyst. The spectra are

Figure 4 DRIFTS spectra of $\text{Cu}_1\text{Co}_2\text{La}$ when CO/H_2 flow is switched to He at 200°C . Spectra are labeled as Temperature and Gas sequence. E.g. 200°C He is taken in Helium flow at 200°C . The sequence of the spectra is: 200°C Syngas $\rightarrow$ 200°C He $\rightarrow$ 250°C He $\rightarrow$ 200°C Syngas again.

shown in Figure 5. In this test, the catalyst is kept at 250°C in CO/H₂ flow for one hour first, and 1995 cm⁻¹ is clearly shown in yellow color “200°C syngas”. Then the flow is switched to helium to flush all gaseous CO. Gaseous CO peaks at 2174 cm⁻¹ and 2112 cm⁻¹ diminish in size as CO is flushed out of the reaction chamber but the feature at 1995 cm⁻¹ persists, which is shown in “200°C He”. Once the temperature is ramped to 250°C, however, the peak at 1995 cm⁻¹ decreases in intensity and changes to a lower frequency at 1986cm⁻¹(shown in “250°C He”). Even when the temperature is reduced to 200°C and syngas flow is flowed again, the spectra (“200°C syngas again”) still shows the feature at 1995 cm⁻¹, but the intensity is much smaller comparing with the spectra taken before increasing the temperature.

This result confirms that the peak at 1995 cm⁻¹ corresponds to CO adsorption on new sites. This new site is formed under syngas exposure at 200°C, and is stable at 250°C but disappears at 300°C. In helium flow, the site attributed to associatively adsorbed CO is still present at 200°C. However, at 250°C the peak loses intensity and shifts to lower wavenumbers (1986 cm⁻¹). This is because of the decreased CO coverage on the sites. The intensity of 1995 cm⁻¹ peak decreased in the CO re-adsorption at 200°C, suggesting the decomposition of the sites at high temperatures.

The bands in the region of 2040-1800 cm⁻¹ are due to CO adsorption on Co^{δ+} species[26-28]. Based on the literature [29-31], the peak at 1998 cm⁻¹ can be attributed to linear CO adsorption on cobalt carbide sites. A similar conclusion was reached by Bian et al[29], who performed syngas adsorptions at high pressures and elevated temperatures on a reduced cobalt catalyst. From DRIFTS, they observed the band at 1999 cm⁻¹ after syngas adsorption at 1.2MPa and 240°C for 6h. Combining with the

results from XPS and XRD, they conclude that after syngas adsorption, the cobalt on the surface transformed to Co_2C , while bulk metallic cobalt phase is maintained.

The results on $\text{Cu}_1\text{Co}_2\text{La}$ indicate that cobalt carbide species are formed under syngas exposure at 200°C . These cobalt carbide species are able to linearly adsorb CO from 200°C to 250°C . The cobalt carbide phase decomposes to cobalt metal and polymeric carbon at 300°C in syngas. Once the carbide species decomposes and transforms to metallic cobalt and polymeric carbon [26, 32], the associatively adsorbed CO began to desorb from the Co_2C site.

3.5 Reactions

Table 3 summarizes the activity and carbon selectivity for the $\text{Cu}_1\text{Co}_1\text{La}$, $\text{Cu}_1\text{Co}_2\text{La}$ and Co_1La catalysts. For all the three catalysts, the reaction undergo a transition state for the first 10 hours with continuously loss of CO conversion and inconsistent selectivity, then the catalysts performance is stable up to 15 hours of reaction. Table 3 shows the results at steady state, between 10 and 15 hours of reaction.

Table 3 Activity & Products Selectivity 250°C and 30 bar*

	Catalyst		
	$\text{Cu}_1\text{Co}_1\text{La}$	$\text{Cu}_1\text{Co}_2\text{La}$	Co_1La
Carbon Selectivity			
Methane	38.84	38.76	37.55
Methanol	17.59	16.16	11.89
Ethanol	8.28	10.78	6.12
Acetaldehyde	1.23	2.22	10.39
C_{2+} oxygenates	2.81	4.64	2.75
$\text{C}_2\text{-C}_8$ Hydrocarbons	22.99	22.22	29.2
CO_2	8.26	5.22	2.1

Conversion %	0.44	0.85	2.05
TOF [†] sec ⁻¹	1.25E-02	2.13E-02	3.09E-02

*reaction condition: Pressure=30 bar, Temperature=250 °C, H₂/CO=2:1. GHSV=36000 scc/g_{cat}/h;

[†]TOF from dispersion measured in CO pulse chemisorption.

The initial decrease in the activity in the first 10 hrs is caused by surface reconstruction [9, 33] and the formation of cobalt carbide and other carbon species [4, 18]. The reconstruction of the catalyst surface results in greater higher oxygenate selectivities. At steady state, all the catalysts showed high methane selectivity around 38%. This agrees with the studies that methane selectivity is significant when cobalt carbide is formed in unmodified and modified Fischer-Tropsch catalysts [16, 34, 35].

Cobalt/copper composition considerably affected the CO conversion and the selectivity to higher oxygenates, as seen in Table 3. The CO conversion increased from 0.44% to 0.85% when cobalt to copper ratio was increased from 1:1 to 2:1, while the highest conversion was at 2.05% on Co₁La, which is the cobalt-only catalyst. Table 3 shows that the TOF for the three catalysts studied here are between 0.01 and 0.03 s⁻¹, which are in the range for most Co-Cu based catalysts[36-38]. The TOF increases with cobalt content: Co₁La>Cu₁Co₂>Cu₁Co₁, consistent with the results reported by Wang et al[36]. All three catalysts had similar selectivity for methane and higher hydrocarbons. Cu₁Co₂La showed the highest selectivity to ethanol and C₃₋₆ oxygenates (propanol and butanol). Methanol selectivity was higher for Cu₁Co₁La, which has a higher Cu loading than Cu₁Co₂La and Co₁La. The selectivity to acetaldehyde is greater for Co₁La than Cu₁Co₁La or Cu₁Co₂La.

4. Discussion

4.1 Higher oxygenate synthesis on cobalt carbide

Based on the results from DRIFTS and TEM, at above 200°C and under CO/H₂ flow, the reduced cobalt on the surface is partially transformed into Co₂C. The surface Co₂C can adsorb CO associatively at reaction temperature (250°C), which is shown in the in-situ DRIFTS study. The associatively adsorbed CO can then form a C-C bond with an atomically adjacent surface hydrocarbon group (CH_x), and form an “enol” intermediate[39]. Further hydrogenation of these intermediates leads to the formation of higher oxygenates. The postulated reaction mechanism is given in Figure 6.

Figure 5 Associatively adsorption of CO on Co₂C phase and coupling of CO and CH_x to form oxygenates. Further hydrogenation yields to ethanol or acetaldehyde.

In this mechanism, cobalt metal reacts with CO to form Co₂C under Fischer Tropsch reaction conditions[32]. Co₂C that is formed during the reaction is not as stable

as other carbides such as iron or nickel carbide. It can decompose to Co metal and polymeric carbon at 300°C [26].

The in-situ DRIFTS results show a band around 1995 cm⁻¹ that can be assigned to CO stretching on Co₂C site. This band forms once the temperature increases to 200°C, which is the temperature for metallic cobalt and CO to form cobalt carbide[19]. At 300°C the linearly adsorbed CO desorbed as the band decreased considerably in intensity. This is due to the decomposition of cobalt carbide to cobalt metal and polymeric carbon[29]. When the temperature was adjusted to 250°C again, the band intensity is much smaller comparing to the previous spectra at the same temperature before heated to 300°C. Therefore, the cobalt carbide site cannot be restored once the catalyst reaches 300°C. The behavior of the unstable cobalt carbide site is in agreement with the results from the literature [26, 32].

4.2 The function of copper in higher alcohol synthesis catalysts

The addition of copper greatly changes the reduction behavior of the catalysts. The two copper-promoted catalysts (Cu₁Co₁La and Cu₁Co₂La) are much easier to reduce than the non-promoted catalyst (Co₁La), as shown in Fig. 1. After the reduction, the cobalt on Cu₁Co₁La and Cu₁Co₂La is metallic, while the cobalt on Co₁La remains in the form of CoO. However, in the CO hydrogenation reaction tests, both CO conversion and TOF are greater for the cobalt-only Co₁La catalyst than for the two copper-cobalt materials (Table 3). The literature suggests that the cobalt on Co₁La may be completely reduced to metallic form, which is active at the conditions tested here [40].

The CO hydrogenation tests showed that Co₁La had much higher acetaldehyde selectivity than the two copper-containing catalysts. Based on the CO insertion

mechanism, the oxygenates are synthesized by the hydrogenation of the “enol” intermediates. Hydrogenation of both carbon and oxygen on the acyl group yields to alcohols [41-43]. Meanwhile, acetaldehyde can be a byproduct in the “CO insertion” mechanism, formed by mono-hydrogenation of the two carbon atoms without the formation of the hydroxyl group. For $\text{Cu}_1\text{Co}_1\text{La}$ and $\text{Cu}_1\text{Co}_2\text{La}$, copper in close proximity with cobalt could provide more hydrogen via H_2 spillover to promote the hydrogenation of the intermediates. Thus, on these two catalysts, the selectivity to acetaldehyde is lower but the selectivity to alcohols are higher than Co_1La . For Co_1La , however, surface H^* is not as abundant as for the copper- promoted catalysts. The CH_xCO intermediate formed following the CO insertion mechanism can only be partially hydrogenated to form acetaldehyde, therefore, the acetaldehyde selectivity on Co_1La is higher than the other two catalysts. The reaction mechanism is shown in the right part of Figure 6. Isotropic tracer studies have shown that ethanol is not produced via the direct hydrogenation of acetaldehyde.[44].

The function of copper is clear: Copper serves as a reducing promoter for cobalt. During the reaction, copper also provides hydrogen via H_2 spillover to hydrogenate the intermediates formed on the $\text{Co}/\text{Co}_2\text{C}$ surface to produce ethanol and higher alcohols. At the reaction temperature of this study (250°C), copper is unable to adsorb CO associatively. Therefore, copper site is not involved in the CO insertion step. Lanthanum oxide promotes the formation of cobalt carbide, which agrees with the literature [18, 20]. In the presence of CO and H_2 , metallic cobalt can be partially converted to Co_2C , which then adsorbs CO and bonds with CH_x to form the precursor to higher oxygenates, such as ethanol and acetaldehyde.

4.3 Increasing the carbon selectivity to higher oxygenates

The selectivity to higher oxygenates was the highest on cobalt-rich $\text{Cu}_1\text{Co}_2\text{La}$, which has a Co/Cu ratio of 2/1. This agrees with the results previously reported by Prieto[2] and Dong[22]. Both of these studies claim the selectivity to higher alcohols is the highest on the catalyst that has a higher cobalt concentration than copper. Copper has been used for methanol synthesis [25, 45]. Comparing with Co_1La which has no copper, the presence of copper in $\text{Cu}_1\text{Co}_1\text{La}$ and $\text{Cu}_1\text{Co}_2\text{La}$ resulted in greater methanol selectivity (Table 3), since methanol is produced by the direct hydrogenation on CO.

Ethanol is formed via the CO insertion and subsequent C-C bond formation. $\text{Cu}_1\text{Co}_2\text{La}$ has higher cobalt concentration than $\text{Cu}_1\text{Co}_1\text{La}$, therefore, the Co_2C phase that was formed on the surface of $\text{Cu}_1\text{Co}_2\text{La}$ is more abundant, leading to higher CO_{ads} linearly adsorption and a greater degree of CO_{ads} insertion probability and greater ethanol and higher oxygenate selectivity.

Table 4 compares the conversion and carbon selectivity of $\text{Cu}_1\text{Co}_1\text{La}$ with other cobalt-copper catalyst for higher oxygenates synthesis. However, a direct comparison at industrial operation conditions [46], or with other literature is not possible because of the different reaction conditions in these papers, such as reaction temperature, pressure, space velocity. In addition, some literature has excluded CO_2 from the total carbon selectivity, which results in higher selectivity to alcohols and hydrocarbons. Comparing with these catalysts, the $\text{Cu}_1\text{Co}_2\text{La}$ has intermediate selectivity to higher alcohols in the present study.

Table 4 Comparison of CO conversion and carbon selectivity with Co-Cu catalysts in the references

Catalyst	Temperature / °C	Pressure / bar	H ₂ /CO	GHSV/ml·gcat-1·h-1	X _{CO} [#] (%)	Carbon Selectivity (mol %)			
						CO ₂	RH*	ROH*	C ₂₊ ROH*
Co ₂ Cu ₁ [9]	240	40	1.5	7200	5.7	1.4	50.5	37.9	—
4Cu-8Co/(Mo/Al)[47]	280	60	1	—	3.4	9.2	73.4	17.4	12.2
Cu _{1.1} /Co/Zn/Al[48]	280	60	1	9600	10.0	7.5	69.7	22.8	17.0
Co/CuZnO[49]	250	18	2	54000	0.3	—	38.8	46.0	31.2
Cu ₁ Co ₂ La [†]	250	30	2	36000	0.85	5.2	60.98	33.8	17.6

[†]Catalyst in this study. [#]X_{CO}: Conversion of CO.

*RH: carbon selectivity for C₂₋₈ hydrocarbons. ROH: selectivity for C₁₋₆ oxygenates. C₂₊ROH: selectivity for C₂₋₆ oxygenates.

The results here suggest additional areas of study. For example, the H₂/CO ratio of the inlet gas flow can be lowered to 1/1 to decrease the methane selectivity. Temperature and pressure can be altered to favor oxygenate selectivity. Other promoters, such as alkali metals and noble metals, can be added to modify the catalyst. A systematic study of the formation of cobalt/Co₂C composition and its effect on product selectivity would be of interest. Finally, computational work can determine the effects of the degree and atomic-level intimacy of copper and cobalt, and the net result of Co₂C and C-C bond formation.

5. Conclusion

Three lanthanum promoted cobalt-copper catalysts with different Co:Cu ratio were synthesized using coprecipitation. Under the CO hydrogenation reaction conditions, cobalt carbide is formed on the surface of the catalyst. The new formed Co₂C phase can associatively adsorb CO and insert the CO into adjacent CH_x species, which are formed on the Co⁰ sites. The CH_xCO intermediate formed via CO insertion is subsequently converted to higher oxygenates, such as ethanol and acetaldehyde.

Copper promotes the reduction of cobalt oxide in the H₂ reduction pretreatment. During the reaction, copper also promotes the complete hydrogenation of the CH_xCO intermediates to form ethanol. For the cobalt-only catalyst, the CH_xCO intermediate tends to form acetaldehyde, but which is not fully hydrogenated to form ethanol due to the lack of adsorbed hydrogen on the surface. The highest selectivity to ethanol and other higher oxygenates is at a cobalt to copper molar ratio of 2:1.

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GRAPHICAL ABSTRACT