



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



Zi Wang, Nitin Kumar, James J. Spivey*

Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

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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, and then cobalt carbide was formed during CO hydrogenation. The composition of the catalysts was as follows: Cu:Co = 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 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.

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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 on 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 serving 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,

* Corresponding author at: Department of Chemical Engineering, Louisiana State University, S. Stadium Drive, Baton Rouge, LA 70803, USA. Fax: +1 225 578 1476.

E-mail address: jjspivey@lsu.edu (J.J. Spivey).

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 $15\text{Co}-x\text{La}/\text{AC}$). 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 catalysts 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 alcohol 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 was 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 6 h at room temperature. The precipitate was filtered and washed with deionized water, and dried at 90 °C for 24 h. 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

H_2 -TPR was done on 50 mg 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% H_2/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 Ag_2O with the same TPR procedures allowed quantitative analysis of catalyst hydrogen uptake.

Catalyst dispersion and crystallite size were determined by CO pulse chemisorption on the Altamira AMI-200 system. 100 mg of calcined catalyst was reduced at 400 °C for 1 h followed by 30 min 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 200 kV. After the reaction process, the catalysts were cooled to room temperature, and then passivated in 1% O_2/He gas for 30 min. 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 min 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 ($\text{H}_2/\text{CO} = 2$) 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.

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	–

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