Effect of ZrO_2 , Al_2O_3 and La_2O_3 on cobalt-copper catalysts for higher alcohols synthesis

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Graphical Abstract to

Abstract

Three cobalt-copper catalysts singly promoted with La, Zr, or Al were studied for catalytic conversion of syngas to higher alcohols. The properties of the promoted catalysts have been characterized by TPR, XRD, XPS and BET. CO hydrogenation was carried out in a plug-flow reactor under 30 bar, GHSV=36000 scc/g_{cat}/h, H₂/CO=2, and 250°C at differential conversions. The catalyst activity and selectivity to higher alcohols are greatest on CuCoLa₂O₃: ethanol selectivity 10.5% at a conversion of 0.76%. During 9 hours of time-on-stream, CO conversion decreased on CuCoLa₂O₃ while methanol and higher alcohol selectivity increased. The behavior on CuCoZrO₂ and CuCoAl₂O₃ were different. On these two catalysts, CO conversion and selectivity reached a near-steady state much more quickly than CuCoLa₂O₃. These results suggest changes on CuCoLa₂O₃ that increase the selectivity for oxygenates continue with time, at least over the time scale investigated here.

Key words: Higher alcohols synthesis; Syngas; Cobalt; Copper; Metal oxide promoters; Modified Fischer-Tropsch catalysts

1. Introduction

Increasing demand has focused on renewable and environmentally benign energy sources for the catalytic conversion of biomass-, natural gas-, and coal-derived syngas to liquid fuel. An alternative to producing long-chain hydrocarbon products via Fischer-Tropsch (FT) synthesis is the conversion of syngas into more valuable higher alcohols. These higher carbon-number alcohols can be used as hydrogen carriers for fuel cells, or as additives directly blended into gasoline [1, 2]. However, additional research is required before extrapolating lab-scale studies to industry-level application. Currently, it is difficult to commercialize this process due to relatively low activity, yield and stability of the catalysts. Rh-based catalysts have shown high yield to higher alcohols in CO hydrogenation, with net yields typically ranging from 10-20% [3-6]. However, the relatively high price of these catalysts has limited the development of more practical processes [7]. Among all the non-noble metal based catalysts, cobalt-copper modified Fischer Tropsch catalysts are promising substitutes for noble metal-based catalysts [8-11].

Recent studies have shown that promoters can increase the selectivity of Co-Cu catalysts to oxygenates. The Institut Francais du Petrole (IFP) filed a number of patents on the development of cobalt-copper based modified Fischer Tropsch catalysts for higher alcohols synthesis [8, 12-16]. Under moderate operating conditions, the selectivity to higher alcohols ranged from 20% to 70%. The ethanol yield over Cu-Co-based catalysts ranged from 100 to 300 mg/(g·cat·h), suggesting commercial interest in these catalysts. Following the IFP work, a wide range of studies on Co-Cu bimetallic catalysts are reported to further increase the selectivity to higher alcohols [10, 17, 18]. Researchers correlate the activity and selectivity of the catalysts with the type of synthesis method, the alkali promoters used, and physicochemical properties of

the catalysts such as metal particle sizes, dispersions, and the atomic proximity of cobalt and copper.

Specifically, metal oxide promoters such as ZrO_2 , La_2O_3 and Al_2O_3 greatly affect the reduction and product selectivity of cobalt-copper-based catalysts. For instance, ZrO_2 assists the reduction of Co^{2+} species to metallic cobalt for CO hydrogenation, and ZrO_2 promoted catalysts show increased selectivity to ethanol[19]. According to Lebarbier et al.[20] , La_2O_3 -supported cobalt catalyst reached almost complete cobalt reduction after H_2 treatment, and cobalt dispersion on La_2O_3 supported catalyst was higher than those on activated carbon and Al_2O_3 . Alumina-supported cobalt FT catalysts show greater stability, high activity and strong metal-support interactions comparing with TiO_2 and MgO [21, 22]. A study of alumina-supported copper-cobalt bimetallic catalysts for CO hydrogenation by Wang et al.[23] reported increased interaction between cobalt and copper particles on a $\gamma\text{-Al}_2\text{O}_3$ supported catalyst compared with unpromoted catalysts, which improved the selectivity of the catalysts to higher alcohols. Past work shows that the choice of the metal oxide promoters greatly influences catalyst morphology, cobalt-copper interaction, and reduction or reaction performance. These metal oxides also promote cobalt copper catalysts in activity and selectivity to ethanol and other oxygenates.

Therefore, the purpose of this work is to study zirconia, alumina and lanthana as metal oxide promoters for cobalt-copper higher alcohols synthesis catalysts. In the present study, cobalt and copper salts are coprecipitated with the third metal salt (Zr, Al or La) to synthesize three promoted catalysts, denoted as CuCoZrO_2 , $\text{CuCoAl}_2\text{O}_3$, and $\text{CuCoLa}_2\text{O}_3$. Coprecipitated metal oxides serve as supports to maintain highly dispersed metal clusters that contain both cobalt and copper particles. The promoting effects of these metal oxides are measured by H_2 Temperature-Programmed Reduction, X-Ray Diffraction, X-Ray Photoelectron Spectroscopy, BET surface

area, and CO hydrogenation activity studies. The aim of this study is to directly compare the promoting effects of the metal oxides on the activity, selectivity, and stability of these catalysts for higher alcohols synthesis.

2. Experimental

2.1 Catalyst Preparation

Catalysts were prepared by pH-coprecipitation method. In the coprecipitation method, cobalt nitrate, copper nitrate and corresponding metal salts ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2$, or $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were dissolved together in deionized water. The molar ratio of Cu nitrate to Co nitrate to metal salts was kept at 2:2:1. The solution were titrated to 100ml water under magnetic stirring at 80°C. Meanwhile, a solution of ammonia carbonate was titrated in order to maintain the pH at 7.00 ± 0.2 . After the titration, the solution was aged at room temperature for 6 hours, then the solid was recovered by washing and filtration. Collected precipitates were dried at 90 °C for 24 hours, then calcined at 500°C for 3h under air flow. The samples are denoted as $\text{CuCoAl}_2\text{O}_3$, $\text{CuCoLa}_2\text{O}_3$ and CuCoZrO_2 to demonstrate the promoters used in the catalysts.

2.2 Composition and Surface Area

The compositions of the calcined catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) method using a Perkin Elmer 2000 DV ICP-optical emission spectrometer.

BET surface area of freshly calcined catalyst were determined by N_2 adsorption at -196°C. Prior to analysis, the samples were treated in helium flow at 150°C for 30 minutes to remove the moisture. A flow BET procedure using N_2 concentrations of 10%, 20%, and 30% in a He carrier was used in an Altamira AMI-200 system.

2.3 Hydrogen Temperature Programmed Reduction (H₂-TPR)

H₂-TPR was done on 50mg of calcined catalyst in an Altamira AMI-200 system. 50mg of calcined catalysts were pretreated in Helium flow at 150°C for 30 min to remove moisture. Reducing gas of 50 sccm 10% H₂/Ar flowed through the reactor as the temperature increased at 5°C/min to 550°C. A thermal conductivity detector (TCD) monitored the consumption of H₂. A calibration using TPRs of 20, 35 and 50 mg Ag₂O allowed quantitative analysis of hydrogen uptake by the catalysts.

2.4 In situ X-Ray Diffraction (XRD)

XRD measurements of the catalysts were done at the Center for Nanophase Materials Science at Oak Ridge National Laboratory. Catalyst Samples were loaded into an Anton Paar XRK900 reactor chamber. A 4% H₂/He gas was flowed through the chamber to conduct the reduction process, and a PANalytical X'Pert Pro MPD diffractometer with Cu K α radiation ($\lambda=0.15406$ nm) was used to record XRD patterns at different temperatures. The spectra were collected from 15° to 70° with a step size of 0.0167°. X'pert HighScore Plus were used to identify phases by the Search & Match feature.

2.5 X-Ray Photoelectron Spectroscopy (XPS)

XPS experiments on calcined catalysts were performed on a Kratos AXIS 165 X-Ray Photoelectron Spectrometer using monochromatic Al K α_1 radiation ($h\nu = 1486.6$ eV, intrinsic linewidth 0.3 eV). The pressure in the analysis chamber was kept between 10⁻⁸ and 10⁻⁹ Torr during the experiments. Survey spectra with a pass energy of 160 eV were taken on each sample prior to the measurement to check correct sample alignment. High resolution scans of Co 2p, Cu 2p, C 1s, O 1s, Al 2p, La 3d and Zr 3d were recorded with a pass energy of 40 eV. C 1s peak at 284.8 eV were used as known standard to calibrate binding energy scale.

2.6 Reaction Studies

Reactions were carried out in an Altamira AMI-200R-HP system equipped with a 1/4-in. glass-lined stainless steel reactor tube. 50 mg of calcined sample was reduced in a mixture of H₂ and He for 3 hours at a standard temperature 400°C. After reduction, the reactor was cooled to room temperature in He, then pressurized to 30 bar and heated to 250°C. At this point, He is switched by a simulated-syngas flow (space velocity=36000 scc/g_{cat}/h, H₂/CO=2). Products were analyzed in a Shimadzu GC2014 gas chromatograph with flame ionization and thermal conductivity detectors (FID and TCD). Reaction data was measured continuously until the results are steady.

The reactions were carried out at differential conversion (CO conversion<3%). This minimizes deactivation as well as temperature and concentration gradients in the reactor. This also eliminates the need to capture and analyze a liquid, integral sample over extended periods of time, which does not measure any changes in the product composition with time.

2.7 Temperature Programmed Oxidation (TPO) Coupled With Mass Spectroscopic Measurements on Used Catalysts

After the reaction, the samples were purged in He for 30 minutes at 25°C. The reactor was then heated to 750°C at 15°C/min in 30 sccm 10% O₂/He flow. The profiles of CO₂ evolution (m/z=44) were collected by an Ametek Quadrupole MS.

3. Results and Discussion

3.1 Composition and Surface Area

ICP-OES Sample composition and BET surface area results are listed in Table 1.

CuCoAl₂O₃ showed the highest surface area (94.1 m²/g), while CuCoLa₂O₃ had the lowest surface area (49.7 m²/g). Bulk Co and Cu composition by ICP-OES are shown in Table 1. Note that the molar ratios of Co:Cu:Metal Oxides are intentionally kept as 2:2:1 for all three catalysts.

3.2 TPR

Temperature programmed reduction profiles obtained for the three catalysts are shown in Figure 1.

All three catalysts displayed similar reduction behavior between 185°C to 250°C. For CuCoZrO₂, the first shoulder at ~190°C is attributed to reduction of CuO to Cu⁰. The peak at around 200°C and the shoulder at 230°C correspond to the two-step reduction of Co₃O₄ to CoO and CoO to Co⁰. CuCoAl₂O₃ has a similar reduction behavior. The broad shoulder from 250°C to 350°C in both CuCoZrO₂ and CuCoAl₂O₃ are due to the reduction of residual CoO to metallic cobalt.

The CuCoLa₂O₃ reduction profile is somewhat different. Although the same reduction of copper at ~190°C is seen, the feature at 215°C shows an asymmetric peak for CuCoLa₂O₃, which can be assigned as the combination of Co₃O₄ to CoO and CoO to Co⁰ reduction. The broad shoulder above 250°C, associated with the extended reduction of cobalt due to less easily reduced cobalt for the Zr- and Al-promoted catalysts, is not seen on CuCoLa₂O₃. This is probably because of higher dispersion of Cu-Co particles and stronger interaction between cobalt and copper in La-promoted catalysts, consistent with the literature. The promoting effect of H₂ reduction by hydrogen spillover mechanism associated with La₂O₃ has been reported on lanthanum promoted cobalt catalysts before[20], therefore, the possibility that La₂O₃ promoted the reduction of cobalt in CuCoLa₂O₃ catalyst cannot be ruled out.

Table 2 shows the experimental and expected hydrogen consumption during the TPR. Reduction of cobalt and copper is essentially complete up to 250°C on all three promoted catalysts, with CuCoAl₂O₃ being slightly less reduced (92.7 ± 2.0) than for the other two (97.5 ± 1.2 and 96.4 ± 1.6). This is consistent with literature that ZrO₂ and La₂O₃ facilitate H₂ reduction

of cobalt and copper oxides, leading to more complete reduction of the CuCoZrO₂ and the CuCoLa₂O₃ than the CuCoAl₂O₃ catalyst [9, 19].

3.3 *In situ* X-ray Diffraction

XRD patterns of the three catalysts during H₂- reduction are shown in Figure 2. For CuCoAl₂O₃, the fresh, calcined catalyst include Co₃O₄ and CuO (Figure. 2 (a)). At 200°C, the intensity of the peaks for Co₃O₄ and CuO had decreased, and metallic phases at 43.2° and 50.3° begin to appear. Meanwhile, a peak at 61.8° emerged, which indicates the existence of a CoO phase was apparent at 300°C, but disappeared at 400°C. Only metallic phases are present at 400°C.

The results of the in-situ XRD combined with the TPR patterns clearly show that reduction of CuO starts at ~185°C. The expected reduction sequence of copper and cobalt oxides to reduced metals is apparent in the loss of the crystalline oxides and appearance of the reduced metals. The long shoulders from 250°C to 350°C in the CuCoZrO₂ and CuCoAl₂O₃ that are seen in the TPR are not easily distinguished in the XRDs from the CuCoLa₂O₃. At 400°C, all three catalysts are fully reduced. Based on the width of the peaks of all three catalysts, copper clusters are more crystalline than cobalt clusters, which are quite amorphous.

CuCoLa₂O₃ and CuCoZrO₂ had reduction patterns similar to CuCoAl₂O₃. CuCoLa₂O₃ had a tilted background due to a higher dispersion of Co₃O₄ and CuO clusters (Figure 2 (b)). This is consistent with the TPR results, which did not show a broad shoulder above ~250°C. CuCoZrO₂ displayed minor CuO features below 200°C, which indicates the existence of both crystalline and amorphous copper oxide in the calcined catalyst. Significantly, there is no peak that could be directly attributed to cobalt aluminate or lanthanum cobalt oxides, but the possibility of forming cobalt-metal oxides in the catalysts cannot be ruled out.

3.4 XPS

XPS studies of calcined samples were carried out in order to study the chemical state of the elements at catalyst surface, and determine surface metal compositions. The XPS spectra of the three fresh, calcined catalysts for Co ($2p_{3/2}$) and Cu($2p_{3/2}$) are shown in Figure 2 (d) and (e) respectively. Co $2p_{3/2}$ peak located at 779.3 eV for all three samples, which shows that cobalt is in the form of Co_3O_4 on the surface [18, 19]. The Cu $2p_{3/2}$ main peak is positioned at 933.6 eV with a shake-up satellite peak accompanied at 942 eV, thus copper ions on the surface for all three catalysts are in the form of CuO [24], as expected.

Table 3 summarizes copper and cobalt binding energies of the samples surfaces. Surface and bulk Cu/Co atomic ratios calculated by XPS and ICP respectively are also shown in Table 3. Although $\text{CuCoAl}_2\text{O}_3$ and $\text{CuCoLa}_2\text{O}_3$ show slightly higher Cu/Co atomic ratio on the surface than in the bulk, these results indicate that all three samples are composed of relatively uniform particles with a constant atomic ratio of cobalt and copper.

3.5 Catalyst Activity Test

Figure 3 shows the CO conversion as a function of time-on-stream at 250°C and 30 bar. Note that all CO conversions are intentionally kept at differential CO conversion (<3%) to avoid condensation (section 2.6).

$\text{CuCoAl}_2\text{O}_3$ had highest activity under reaction condition. While CuCoZrO_2 and $\text{CuCoLa}_2\text{O}_3$ had much lower activity. $\text{CuCoAl}_2\text{O}_3$ and CuCoZrO_2 slightly lost activity in the first two hours of reaction, then reaching near steady-state after 2~3 hours of operation. For $\text{CuCoLa}_2\text{O}_3$ catalyst, however, CO conversion decreased with time over the 9 hours of operation.

Figure 4 shows the changes of product selectivity with time. For CuCoZrO₂ and CuCoAl₂O₃, the selectivity to alcohols and C₂₊ products were relatively stable through 9 hours of reaction, whereas methane selectivity slightly increased with time. Nevertheless, CuCoLa₂O₃ displays more significant changes of the selectivity to C₂₊ products. The most striking fact is the increase of methanol and ethanol selectivity at 250°C with time. At this temperature, the selectivity to ethanol increased from 6.5 % to 10.5 % and the selectivity to methanol had increased from 5% to 16.9% after 9 hours on stream. The increased alcohols selectivity is associated with a small decrease of ethane and propane selectivity.

CuCoLa₂O₃ shows increased selectivity of methanol and decreased selectivity of methane with time. Methane is synthesized from dissociated CO while methanol is formed from associatively adsorbed CO [25]. Therefore, the increase of methane and the decrease of methanol selectivity indicate the increase of associatively adsorbed CO and the decrease of dissociatively adsorbed CO with time.

The product selectivity distribution for the three catalysts over 9 hr time-on-stream is shown in Table 4. At 250°C, CuCoLa₂O₃ catalyst showed highest selectivity to ethanol among the three catalysts, CuCoZrO₂ and CuCoAl₂O₃ had similar selectivity toward ethanol, C₂₊ oxygenates and C₂₊ hydrocarbons. Table 4 shows that CuCoLa₂O₃ is less selective to C₂₊ hydrocarbons, which means Fischer Tropsch synthesis in the reaction is inhibited on CuCoLa₂O₃, leading to higher methanol and ethanol selectivity of CuCoLa₂O₃ catalyst. In general, CuCoAl₂O₃ has properties very similar to traditional Fischer-Tropsch catalysts, with a high selectivity to methane and C₂₊ hydrocarbons. CuCoZrO₂ also favors C₂₊ hydrocarbons, but produces more C₂₊ oxygenates than CuCoAl₂O₃. This could be due to the reason that ZrO₂

provide more basic sites than Al_2O_3 , which suppress hydrocarbon selectivity and favor oxygenates formation[26].

$\text{CuCoLa}_2\text{O}_3$ shows significantly greater selectivity to methanol and C_{2+} oxygenates than CuCoZrO_2 or $\text{CuCoAl}_2\text{O}_3$. There is a difference between the formation of methanol and C_{2+} oxygenates. Methanol is formed by the hydrogenation of associatively adsorbed CO, while C_{2+} oxygenates are formed by the hydrogenation of atomically adjacent sites, one of which is a CH_x moiety produced from dissociatively adsorbed CO and one of which is formed by associatively adsorbed CO. These two moieties then form the first C-C bond, from which C_{2+} oxygenates are produced[2, 27]. The relative rates of the formation of these two moieties produces the observed product selectivities---e.g. C_{2+} oxygenates. The relatively high methane selectivity is consistent with the mechanism in which hydrogenation of dissociatively adsorbed CO on cobalt sites is faster than C-C bond formation to C_{2+} oxygenates.

From characterization results, there are no major differences in reduction behavior and surface distribution among the three catalysts. This suggests that change of selectivity with time is due to reconstruction of the surface on the $\text{CuCoLa}_2\text{O}_3$ catalyst that produces sites favorable to alcohols—both methanol and C_{2+} oxygenates. Such surface reconstruction of cobalt-copper particles in the presence of syngas has been reported by Yizhi et al. [28], who showed major Co surface segregation of the Co-Cu particles took place during syngas exposure, and an “onion-like” graphitic carbon shell was observed on the particle surface. Lebarbier et al.[20] reported the effect of La_2O_3 on cobalt catalysts, claiming that exposure to CO leads to the formation of Co_2C on the surface, thus Co exists in both metallic Co and Co_2C phase. Reaction studies showed slightly increase in the alcohol selectivity was observed for the sample with highest $\text{Co}_2\text{C}/\text{Co}^0$ ratio on the surface. Furthermore, Volkova et al.[29] proposed that Co_2C is able to activate CO

associatively and insert CO into $(\text{CH}_x)_{\text{ads}}$ species that lead to higher alcohols. On $\text{CuCoLa}_2\text{O}_3$ here (Figure 4), the selectivity to C_{2+} hydrocarbons decreases while methanation rate increases, which could be caused by the formation of surface carbon or Co_2C [30]. The formation of carbon or cobalt carbide will decrease catalyst activity and increase methane selectivity [31, 32].

Figure 5 shows the TPO results to measure any carbon deposition on used $\text{CuCoLa}_2\text{O}_3$, CuCoZrO_2 and $\text{CuCoAl}_2\text{O}_3$ catalysts after 9 hours of reaction. The amount of carbon on the used CuCoZrO_2 was much more than $\text{CuCoLa}_2\text{O}_3$ or $\text{CuCoAl}_2\text{O}_3$. This clearly suggests that the relative low activity of the CuCoZrO_2 is due to carbon deposition.

CuCoZrO_2 and $\text{CuCoAl}_2\text{O}_3$ shows similar TPO peaks between 200°C and 295°C , but with much more of this carbon on CuCoZrO_2 , as measured by the area under the TPO peaks. $\text{CuCoLa}_2\text{O}_3$ shows a shoulder at 230°C , a larger peak at 320°C and another peak at 565°C . Literature attributes the peaks in the $200\text{--}300^\circ\text{C}$ region to the oxidation of polymeric carbon species for all three catalysts [33–35]. Cobalt carbide decomposes above 300°C [36], therefore, the peak around 320°C on the $\text{CuCoLa}_2\text{O}_3$ catalyst can be assigned to the decomposition and oxidation of cobalt carbide. The $\text{CuCoLa}_2\text{O}_3$ peak at 565°C corresponds to the decomposition of graphitic carbon on the surface [37, 38].

Lanthanum promoter in $\text{CuCoLa}_2\text{O}_3$ seems to play a vital role in promoting the surface reconstruction and changing the product selectivity to favor alcohols. More in-situ characterizations are required to study the mechanism of surface reconstruction and formation of intermediates during syngas exposure, which will help us to further increase higher alcohols selectivity in CO hydrogenation reaction. The selectivity to ethanol and higher alcohols can also be further increased by adjusting reaction conditions. For instance, changing the H_2/CO ratio to

1/1 will decrease the methane and the methanol selectivity and favor the higher alcohols synthesis [1, 25].

4. Conclusion

No major difference in the catalyst reduction behavior is observed for these promoted catalysts during the TPR. The reduction of cobalt and copper are completed for all the catalysts by 300°C, which is consistent with literature. XRD results show CuO and Co₃O₄ phases in the fresh, calcined catalysts. The samples show uniform particles which have the same Cu/Co ratios on the surface and in the bulk. In the activity tests, CuCoAl₂O₃ displayed highest CO conversion, while CuCoLa₂O₃ yielded much higher carbon selectivity to methanol (16.9%) ethanol (10.5%) than the other two tests. All three catalysts showed changes with time-on-stream, with more significant increases in methanation and methanol formation compared to other products. Increases in selectivity were particularly significant for CuCoLa₂O₃, suggesting the existence of surface reconstruction and intermediate formation on the surface during the exposure of syngas. Post-reaction TPO detected polymeric carbon on all used catalysts, while CuCoZrO₂ showed highest polymeric carbon accumulation. TPO also showed the existence of cobalt carbide on spent CuCoLa₂O₃.

The addition of the three metal promoter oxides leads to significant differences. Specifically, the C₁-C₆ alcohol selectivity for the CuCoLa₂O₃ (34.9%) is far greater than either CuCoAl₂O₃ (13.1%) or CuCoZr₂O₄ (17.8%). This suggests fundamental reasons for CuCoLa₂O₃, Perhaps the surface basicity is increased by Lanthanum oxide to favor alcohols formation [39]. Another difference for CuCoLa₂O₃ is the hydrocarbon selectivity. The difference in C₂-C₆ hydrocarbon selectivity between the CuCoAl₂O₃ (26.0%) and CuCoZrO₂ (29.6%) on one hand, and CuCoLa₂O₃ on the other hand (14.4%) appears to reflect that on

CuCoLa₂O₃ the relative rates of the hydrogenation of surface CH_x to hydrocarbons is lower than the relatively rates of the hydrogenation of the CO_{ads}-CH_x bond to C₂⁺ alcohols [2, 17, 25]. The metal promoter oxides studied here clearly affect the formation of the final products on the associative and dissociative adsorption sites, and La in particular promotes the selectivity to oxygenates versus hydrocarbons.

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Figure 1 TPR results for CuCOZrO_2 , $\text{CuCoAl}_2\text{O}_3$ and $\text{CuCoLa}_2\text{O}_3$ from 70°C to 550°C

Figure 2 Characterization on calcined CuCoAl2O3, CuCoLa2O3 and CuCoZrO2 samples by XRD and XPS. (a) XRD patterns during reduction in 4% H₂/He at indicated temperatures for CuCoAl2O3; (b) XRD patterns during reduction in 4% H₂/He at indicated temperatures for CuCoLa2O3; (c) XRD patterns during reduction in 4% H₂/He at indicated temperatures for CuCoZrO2; (d) XPS spectra of Co 2p region for CuCoAl2O3, CuCoLa2O3 and CuCoZrO2 sample (e) XPS spectra of Cu 2p region for CuCoAl2O3, CuCoLa2O3 and CuCoZrO2 sample.

Figure 3. CO conversion as a function of time on stream of CuCoLa2O3, CuCoZrO2 & CuCoAl2O3 at 250 °C , 30 bar, and GHSV=36000 scc/g_{cat}/h.

Figure 4 Selectivity changes as a function of time on stream on CuCoLa2O3, CuCoZrO2 and CuCoAl2O3 during reaction at 250°C.

Figure 5 TPO of CuCoLa2O3 and CuCoAl2O3 after CO hydrogenation Reaction at 250 °C for 9 hours.

Table 1 Catalyst composition by ICP-OES and BET surface area ^a

Catalyst	Composition (wt%)		Cu/Co molar ratio	Surface Area m ² /g
	Co	Cu		
CuCoAl ₂ O ₃	26.6	32.0	1.11	94.1
CuCoLa ₂ O ₃	18.8	23.3	1.14	49.7
CuCoZrO ₂	25.7	30.4	1.09	88.8

a. The molar ratio of Cu:Co:Metal oxide(Al₂O₃, La₂O₃ and ZrO₂)=2:2:1.

Table 2 Quantitative H₂ Consumption During TPR ^a

Catalyst	H ₂ consumed (μmol/g)	Expected consumption (μmol/g)	Metal reduced %
CuCoAl ₂ O ₃	291±6	314	92.7 ± 2.0
CuCoLa ₂ O ₃	235 ± 3	241	97.5 ± 1.2
CuCoZrO ₂	294 ± 5	305	96.4 ± 1.6

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

Table 3 XPS Binding Energies and Surface Composition Analysis

Catalyst	Binding Energies		Cu/Co atomic ratio by XPS	Cu/Co atomic ratio by ICP
	Cu 2p _{3/2}	Co 2p _{3/2}		
CuCoAl ₂ O ₃	933.8	779.7	1.17	1.11
CuCoLa ₂ O ₃	933.6	779.5	1.23	1.14
CuCoZrO ₂	933.6	779.8	1.09	1.09

Table 4 Activity & Products Selectivity for CuCoAl₂O₃, CuCoLa₂O₃ and CuCoZrO₂ at 250 °C and 30 bar ^a

Catalyst	Carbon Selectivity					CO ₂	CO Conversion (%)
	Methane	Methanol	Ethanol	C ₃₋₆ Oxygenates	C ₂₋₆ Hydrocarbons		
CuCoAl ₂ O ₃	35.63	5.02	5.66	2.38	26.06	23.25	1.93
CuCoLa ₂ O ₃	31.37	16.92	10.46	7.47	14.45	18.03	0.76
CuCoZrO ₂	28.14	4.35	7.32	6.09	29.63	22.67	0.58

a. Selectivity and CO conversion were taken at near steady state after 9 hours of reaction.