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REACTION ENGINEERING, KINETICS, AND CATALYSIS

Effect of Reaction Conditions on Supercritical Hexanes Mediated Higher Alcohol Synthesis over a Cu—Co—Zn Catalyst

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Higher alcohol synthesis (HAS) from syngas over a Cu—Co based catalyst was investigated under supercritical hexanes conditions. The effects of hexanes/syngas molar ratio, H_2/CO molar ratio, and gas hourly space velocity (GHSV) on gas-phase HAS and supercritical hexanes-phase HAS (SC-HAS) were investigated. The CO conversion remained relatively constant with increases in the hexanes/syngas molar ratio, whereas the CH_4 selectivity decreased. Higher alcohol productivity was found to increase monotonically with an increase in the hexanes/syngas molar ratio. Productivity of higher alcohols increased with an increase in the H_2/CO ratio under the gas-phase conditions. An opposite trend in higher alcohol productivity with H_2/CO was observed in SC-HAS. Further experiments were performed using argon as the reaction medium for comparison with the supercritical hexanes medium results. The enhanced higher alcohol productivity observed in this system can be attributed to improved extraction of alcohol products from the catalyst pores under the supercritical conditions. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 1786–1796, 2014
Keywords: copper-cobalt catalyst, higher alcohol synthesis, supercritical fluid, supercritical reaction media

Introduction

The synthesis of higher alcohols represents a promising pathway for the utilization of synthesis gas (a mixture of CO and H_2, referred to as syngas) to create liquid fuels and/or fuel additives.[1–7] The driving force behind the research that focuses on the use of syngas as a fuel production platform is that syngas can be derived from various carbonaceous sources, such as coal and biomass, which are either abundant or renewable.[5,6,8–10] Although, the process of converting syngas to alcohols has been under development for nearly a century,[2,5,11,12] from a practical point of view, it still suffers from low selectivity toward higher alcohols.[1,5,13,14] To meet the practical requirements of industry, numerous studies have been devoted to the investigation of higher alcohols synthesis (HAS) over the past 30 years,[2,3,15–26] including the development of modified catalysts,[20,22,27–29] the utilization of double bed reactors[25,30] and so forth.

The first use of a Cu—Co based catalyst was reported by IFP (Institute Français du Pétrole), who then further claimed a number of patents on Cu—Co based catalysts.[31–33] It is believed that Co dissociates CO and hydrogenates those resulting surface carbon species into hydrocarbons, and Cu assists in nondissociative activation of CO.[26,34] The idea of combining Co and Cu is intended to promote adsorption of molecular CO on the Cu, which terminates the carbon chain growth that occurs on the Co, thereby leading to higher alcohols. Cu—Co catalysts have been reported to suffer from deactivation caused by coke deposition, separation of Co from the originally homogeneously distributed Co and Cu phases, loss of cobalt as carbonyls, and formation of surface carbides.[33] It has also been found on $CuO/CoO/ZnO/Al_2O_3$ catalysts that the tendency for methanation was high when the reaction temperature was over 290°C.[33] Difficulties were also found in thermally controlling start-up of the reactions.[33] Furthermore, the selectivity toward alcohols has been found to be highly dependent upon the preparation and temperature-dependent activation procedures.[35] As discussed below, supercritical reaction media can provide certain advantages relative to gas-phase operation in terms of maintaining thermal uniformity. Therefore, better temperature control during start-up and continuous operation of these Cu—Co catalyst systems can be achieved and it has been shown that the supercritical fluid (SCF) media can improve the performance of similar exothermic catalytic reactions.[36–38]

SCF have been recognized as a unique medium for heterogeneous reactions, offering single phase operation, a tunable density between typical liquid-like and gas-like densities, as well as gas-like diffusivity. These properties can provide enhanced mass transfer and heat transfer, help to eliminate mass transport limitations, integrate reaction and product separation processes, and enhance *in situ* extraction of low volatility products from porous catalysts.[39–43] The utilization of supercritical media in Fischer–Tropsch synthesis (FTS) has been developed for more than 20 years.[36,41,44,45] It has been shown that the presence of supercritical media provides several advantages in FTS as listed below:

1. SCF media provide improved heat transfer relative to gas-phase operation, thereby better managing the large exotherm of FTS.[36,41]
2. SCFs can increase the *in situ* extraction of heavy products in supercritical FTS.[41,43,46]

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3. The catalyst effectiveness factor and pore accessibility increase with pressure in SCF media.[43–45]
4. The selectivity toward α-olefins is enhanced under SCF operation.[47,48]
5. Optimal operating conditions exist when there is a fine balance between the effects of SCF bulk diffusion versus pore diffusivity within the SCF depending on the temperature and pressure used.[40]

HAS represents another highly exothermic reaction that could benefit from the advantages provided by supercritical reaction media. Jiang et al.[49] investigated the influence of a mixture of C_{10}—C_{13} alkanes as SC reaction media in HAS over a Zn—Cr—K catalyst and found that the selectivity toward ethanol, *n*-propanol and isobutanol was raised and that the selectivity toward methanol was decreased. To the authors' knowledge, there is no literature to date that reports the performance of Cu—Co catalysts under the influence of supercritical reaction media for HAS. Herein, we investigate HAS under a series of reaction conditions that span the supercritical regime and compare these results with those obtained from analogous gas-phase operation. The purpose of this study is to investigate the effect of reaction conditions on the supercritical hexanes phase HAS, including the specific reaction performance parameters of carbon chain growth, productivity, and selectivity toward higher alcohols.

Experimental Section

Catalyst preparation

The preparation of the Cu—Co based catalysts used in this study consists of continuous coprecipitation of nitrate solutions of respective metals under controlled conditions. A Cu/Co/Zn/Al mixed nitrate salt solution was first prepared at a mass ratio of 43.5:14.5:24:18. The precursor was prepared by coprecipitating this mixed nitrate salt solution with a 1.0 mol/L K_2CO_3 solution in a 1-L flask, which was initially filled with 200-mL deionized water at 80°C. The pH value was strictly kept at 7 to achieve a homogeneous dispersion. After aging for an hour, the precipitate was decanted and then washed with sufficient deionized water at 80°C to eliminate the excess K introduced with the carbonate. The wet precursors were dried at 80°C and at ambient pressure for 24 h. The dried precipitate was then ground and calcined at 350°C under continuous air flow to give the corresponding mixed oxides. The promotion of K was carried out through the incipient wetness method using aqueous potassium carbonate solution. The slurry paste was then dried at 80°C overnight and calcined at 350°C for 4 h.

Catalyst characterization

The composition of this catalyst was determined by inductively coupled plasma emission spectrometry (ICP-OES) on a Spectro Ciros ICP (SPECTRO Analytical Instruments, Kleve, Deutschland) after the sample was completely dissolved with diluted nitric acid. ICP results demonstrated that for every 1 g of catalyst there are 4.1 mg K, 101 mg Co, 386 mg Cu, 186 mg Zn, and 84 mg Al.

The properties of the porous structures were determined from N_2-sorption measurements at -196°C using Quantachrome autosorb iQ gas sorption system. The total surface area and pore volume of the catalysts were listed in Table 1.

Table 1. BET Results of Catalysts

	BET Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Fresh catalyst	248.34	0.76	12.27
Used catalyst	94.71	0.21	8.94

The activity and selectivity of the Cu—Co catalyst for the synthesis of higher alcohols from syngas were determined using a stainless steel fixed-bed reactor, reported in Xu et al.[50] Hexanes solvent (a mixture of hexane isomers) was purchased from VWR and syngas (64% H_2, 32% CO, and 4% N_2) was purchased from and certified by Airgas. The flow rate of syngas and argon balancing gas was controlled by a mass flow controller (Brooks 5850 E), whereas the volumetric flow rate of hexanes was controlled by an HPLC pump (Acuflow Series III). Hexanes and syngas were heated separately and mixed together before entering the reactor. Reaction pressure was controlled by a back pressure regulator (Straval-BPH) installed between the hot trap and the cold trap. One gram of catalyst (45–70 mesh) was loaded into our high pressure reactor and fixed into position by packing with glass wool. Effluent from the reactor passed through a hot trap (240°C), a heat exchanger, and a cold trap (5°C) and was then separated into gas-phase and liquid-phase products. Reactants and products were analyzed by two gas chromatographs. The analyses of gas-phase products were performed on a Varian CP-3380 gas chromatograph equipped with a Haysep-DB column and a thermal conductivity detector (TCD). The analyses of liquid phase products were performed on a Varian CP-3300 Gas Chromatograph equipped with a capillary DB-wax column and a flame ionization detector (FID).

Results and Discussion

The effect of hexanes/syngas molar ratio on the catalytic performance

To perform the synthesis of higher alcohols from syngas under the supercritical reaction media conditions, hexanes solvent was continuously injected with the reactant gases into the fixed-bed reactor. A hexanes/syngas molar ratio was determined by the molar flow rate of hexanes and the molar flow rate of syngas. The higher the hexanes/syngas molar ratio, the closer the properties of the mixture are to that of the pure solvent, therefore, more readily achieving single phase supercritical operation.[51] Hexanes/syngas molar ratios in the range of 3.0–3.5 have been previously used in the studies of FTS under supercritical solvent conditions.[36,52,53] Xu et al.[50] have investigated supercritical mixed alcohol synthesis over a Cu-based catalyst at a series of hexanes/syngas molar ratios and found that the productivity of higher alcohols increased with the increase in the hexanes/syngas molar ratio. In the current work (this article), cobalt was added to the Cu-based catalyst to enhance the carbon chain growth of alcohol products. This article presents a similar hexanes/syngas molar ratio study on this Cu—Co based catalyst under supercritical hexanes reaction conditions so as to determine the suitable hexanes/syngas molar ratio for the optimal formation of higher alcohols with additional interests on the fact that hydrocarbons can also form at the Co active sites. The syngas flow rate was kept constant at 3000 L/Kg_{cat}/h, the flow rate of hexanes was then adjusted to provide the required hexanes/syngas molar ratio. The reaction pressure was controlled as a function of the hexanes/syngas molar ratio, whereas the partial pressure of syngas was kept

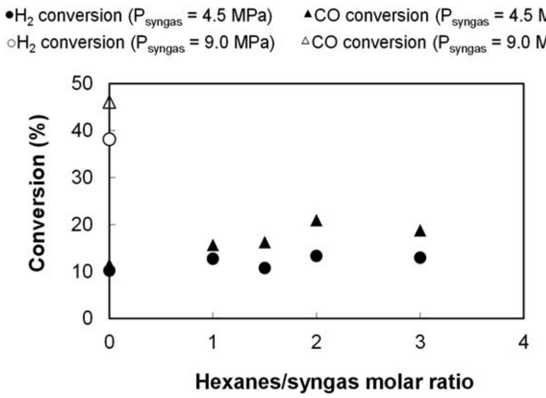

Figure 1. CO and H_2 conversion as a function of hexanes/syngas molar ratio.

Reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, syngas flow rate: 3000 $L/Kg_{cat}/h$, $H_2/CO = 2.0$, temperature 300°C, pressure 4.5–18 MPa.

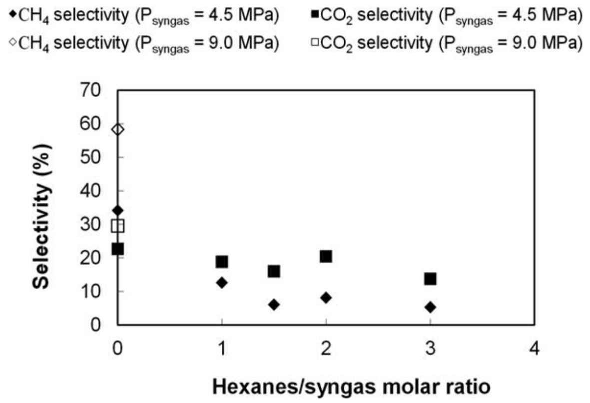

Figure 2. CO_2 and CH_4 selectivity as a function of hexanes/syngas molar ratio.

Reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, syngas flow rate: 3000 $L/Kg_{cat}/h$, $H_2/CO = 2.0$, temperature 300°C, pressure 4.5–18 MPa.

constant. It must be noted that the conversion, selectivity, and productivity results are the average values of at least 20 data points obtained once the reaction had reached steady state (as evidenced by stable CO conversion). It should also be noted that each experiment was replicated at least once to determine the reproducibility of the results, where the deviation in conversion was less than 5% between runs.

Figure 1 presents the conversion of CO and H_2 as a function of the hexanes/syngas molar ratio over the 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$ catalyst under gas-phase (hexanes/syngas molar ratio of zero) and supercritical hexanes phase conditions (hexanes/syngas molar ratios of 1, 2, and 3). Under gas-phase conditions (hexanes/syngas molar ratio = 0) the conversions of H_2 and CO are around 10%. In increasing the gas-phase reaction pressure from 4.5 to 9.0 MPa, the conversions increased rapidly to 38% in the case of H_2 conversion and 46% in the case of CO conversion. A slight increase in CO and H_2 conversion was observed when the reaction conditions were changed from gas-phase to supercritical hexanes phase. While the syngas partial pressure was kept at 4.5 MPa, the conversion of CO and H_2 remained stable with an increase in the hexanes/syngas molar ratio as shown in Figure 1.

Figure 2 presents the selectivity toward CH_4 as a function of hexanes/syngas molar ratio over the same catalyst under both gas-phase and supercritical-phase conditions. When the HAS was conducted under gas-phase conditions (at hexanes/syngas molar ratio = 0), the selectivity toward CH_4 was close to 35%. Increasing the pressure from 4.5 to 9.0 MPa under the gas-phase reaction conditions (at hexanes/syngas molar ratio = 0) increased the CH_4 selectivity from 35 to 59%, as shown in Figure 2. This observation is consistent with that of Courty el al.,[33] Aquino and Cobo,[54] and Subramanian et al.,[55] who observed high methane selectivity over Cu—Co—Al catalysts at elevated pressure. Subramanian et al.[55] reported that the thermodynamically favored methane formation must be kinetically limited in order to increase the ethanol yield and selectivity. Figure 2 also shows that CH_4 selectivity decreased significantly when the reaction conditions were switched from gas-phase (ca. 34.1%) to supercritical hexanes phase conditions. Furthermore, CH_4 selectivity decreased from 12.6% at hexanes/syngas molar ratio of 1 to 5.2% at hexanes/syngas molar ratio of 3, due in part to the improved ability of the supercritical medium to manage the reaction heat effectively.[36,38]

Figure 2 also presents the selectivity toward CO_2 as a function of hexanes/syngas molar ratio. Under gas-phase reaction conditions (Hexanes/syngas molar ratio = 0), the increase in pressure had a slight positive effect on the CO_2 selectivity, which increased from 22 to 30% when pressure increased from 4.5 to 9 MPa. As also shown in Figure 2, CO_2 selectivity was almost stable with or without the presence of supercritical hexanes, where the CO_2 selectivity remained about 20% at each of the hexanes/syngas ratios studied, whereas the partial pressure of syngas was held constant at 4.5 MPa. This indicates that the water-gas-shift reaction over this Cu—Co catalyst reaches equilibrium and is slightly affected by the presence of supercritical hexanes.

Figure 3 shows the distribution of higher alcohols as a function of hexanes/syngas molar ratio. Linear alcohols, such as 1-propanol and 1-butanol, were observed as the main products in the gas-phase reaction (hexanes/syngas molar ratio = 0) over this Cu—Co based catalyst. This observation is consistent with those previously reported in the literature.[20,56,57] Conducting the reaction under supercritical hexanes phase conditions again yielded linear alcohols, although the enhancement in productivity of higher alcohols was quite significant. For example, the productivity of 1-butanol increased from 0.5 to 1.4 $g/kg_{cat.}/h$ as the hexanes/syngas molar ratio was increased from 0 to 3, and the productivity

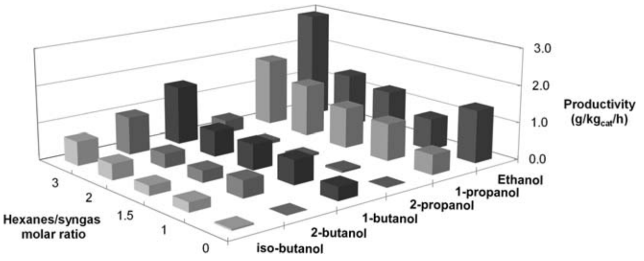

Figure 3. Higher alcohol productivity as a function of hexanes/syngas molar ratio.

Reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, syngas flow rate: 3000 $L/Kg_{cat}/h$, $H_2/CO = 2.0$, temperature 300°C, pressure 4.5–18 MPa.

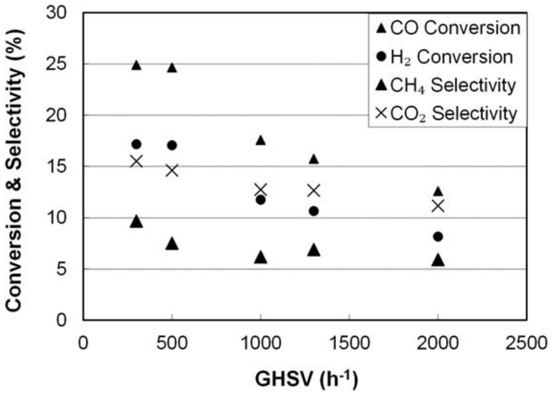

Figure 4. CO conversion, H_2 conversion, CH_4 selectivity, and CO_2 selectivity as a function of GHSV.

The reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, H_2/CO ratio = 2.0, temperature = 300°C, pressure = 18 MPa, hexanes/syngas molar ratio = 3. GHSV was calculated based on the volumetric flow rate of syngas and the volume of catalyst bed.

of 1-propanol increased from 0.6 to 1.7 g/$kg_{cat.}$/h. It is important to note that the productivity of each higher alcohol increased monotonically with the increase in the hexanes/syngas molar ratio. The hexanes/syngas molar ratio of 3 appears to be the most suitable reaction condition for HAS among the conditions studied. Note that to maintain the syngas partial pressure at the value of 4.5 MPa a total pressure of 18 MPa was required in the case of the hexanes/syngas molar ratio of 3 (supercritical hexanes phase conditions). Unfortunately, higher hexanes/syngas molar ratios could not be examined due to pressure limitations in this particular reactor system. The hexanes/syngas molar ratio of 2 also showed appreciable increases in the production of higher alcohols compared to gas-phase operation.

The effect of GHSV on SC-HAS

It is a common observation that the selectivity to higher alcohols over a modified methanol synthesis catalyst can be enhanced by lowering the space velocity under typical methanol synthesis conditions.[1] The effect of GHSV on HAS over this catalyst has been investigated under supercritical hexanes phase conditions in this study. The use of supercritical hexanes allows for much smaller values of GHSV to be applied. Specifically, the GHSV values under the supercritical conditions used in this study range from 300 to 2000 h^{-1}, which are much smaller than most of the values previously reported in the literature.

Figure 4 presents the CO conversion, the H_2 conversion, and the selectivity toward CH_4 and CO_2 when the GHSV was increased from 300 to 2000 h^{-1} under supercritical hexanes phase conditions. The CO conversion decreased from 24.9% at GHSV = 300 h^{-1} to 12.6% at GHSV = 2000 h^{-1}. H_2 conversion follows a similar trend, but decreased more slowly from 17.1 to 8.1% with the same increase in GHSV, as shown in Figure 4. The CH_4 and CO_2 selectivity is favored by the lower GHSV values (i.e., longer contact times) under the supercritical hexanes phase conditions.

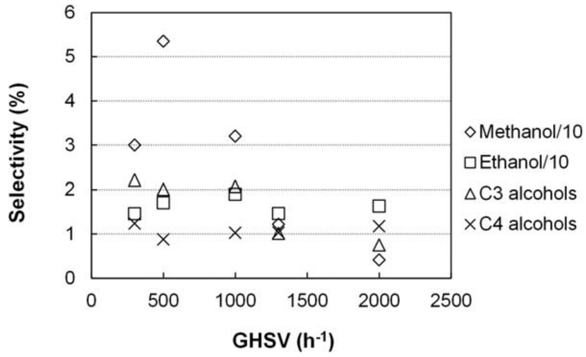

Figure 5. Selectivity of methanol, ethanol, propanol, and butanol isomers as a function of GHSV.

Reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, H_2/CO ratio = 2.0, temperature = 300°C, pressure = 18 MPa, hexanes/syngas molar ratio = 3.

In Figure 5, the effect of GHSV on the selectivity toward methanol and higher alcohols is presented. It was found that the selectivity toward methanol reached a maximum at the GHSV of 500 h^{-1} when holding the total pressure at 18 MPa and the hexanes/syngas molar ratio at a value of 3. Ethanol selectivity reached its highest value somewhere around 1000 h^{-1} GHSV. The selectivity toward the C_3 and C_4 alcohols was consistently in the range of 1–2% over the range of GHSV values studied under these supercritical hexanes phase conditions. These results suggest that moderate residence time (ca. 1000 h^{-1}) favors higher alcohol formation, whereas additional contact time with the catalyst results in a significant increase in the formation of methanol and CH_4 at the expense of higher alcohol selectivity. Table 2 shows the effect of GHSV on the CO conversion and alcohol selectivity under gas-phase conditions. When the GHSV was increased from 500 to 2000 h^{-1} under gas-phase conditions, the CO conversion decreased from 29.2 to 18.9%, as shown in Table 2. It was also observed that the CO_2 selectivity decreased from 20.7 to 13.3% as the GHSV increased from 500 to 2000 h^{-1}. CH_4 selectivity was at the level of 60%, when the GHSV was within the range of 500–2000 h^{-1} under these gas-phase conditions. The low space velocity values that were used in this study (compared to higher values that have been used in the literature[1,5,29,35,58,59]) have

Table 2. The Effect of GHSV on CO Conversion and Product Selectivities under Gas Phase Conditions

			Selectivity (%)		
GHSV (h^{-1})	CO Conversion (%)	Activity (g/kg_{cat}/h)	$C_{2+}OH$	CO_2	CH_4
500	29.17	0.0659	NA	20.7	60.5
1000	27.76	0.0603	10.1	17.8	57.7
2000	18.92	0.1385	7.2	13.3	69.6

Reaction conditions: $T = 300°C$, catalyst: 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, $H_2/CO = 2$.
Alcohols: C_1—C_6 alcohols.
S_{c2+OH}: weight percentage of C_{2+} alcohols/(methanol + C_{2+} alcohols).

Table 3. The Effect of Argon and Supercritical Hexanes Reaction Media on the Conversion and Selectivity

Reaction Medium	Total Pressure (MPa)	P_{syngas} (MPa)	CO Conversion (%)	Selectivity (%)			
				CO_2	S_A	S_H	S_{c2+OH}
Argon	13.5	4.5	55.5	42.7	4.5	25.5	96.2
SC Hexanes	13.5	4.5	33.9	43.5	16.0	18.9	73.7

Reaction conditions: $T = 300°C$, catalyst: 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, $H_2/CO = 2$, syngas flow rate: 3000 $L/Kg_{cat}/h$.
S_A: selectivity towards $C_1—C_6$ alcohols.
S_H: selectivity towards $C_2—C_5$ hydrocarbons.
$S_{c2+OH:}$ weight percentage of C_{2+} alcohols/(methanol+ C_{2+} alcohols).

resulted in very high methanation activity under these gas-phase conditions, resulting from poor heat management within the catalyst. Table 2 also shows the C_{2+}OH selectivity, which is the weight of C_{2+} alcohols over the total alcohol product. Under these gas-phase conditions, the low GHSV (500–2000 h^{-1}) resulted in a liquid product that was composed of 90% methanol. Overall, the low space velocity under gas-phase conditions favors the formation of methanol and CH_4, and a GHSV value greater than 2000 h^{-1} would be suggested for the formation of higher alcohols over this Cu—Co catalyst under gas-phase conditions.

Using argon as balance gas

Investigations were also conducted to determine the impact of the presence of the supercritical hexanes on the activity and productivity by varying the partial pressure of the SCF and by maintaining constant space velocity by using argon as the balance gas. The addition of argon as an inert balance gas allowed GP-HAS experiments to be performed with comparable total flow rate (i.e., contact time) and syngas concentration to those used in supercritical-phase HAS (SC-HAS). In the studies involving the effect of hexanes/syngas molar ratio (section: The effect of hexanes/syngas molar ratio on the catalytic performance above), it was observed that CH_4 selectivity decreased rapidly and higher alcohols productivity increased monotonically with an increase in the hexanes/syngas ratio under supercritical conditions. However, no definitive conclusion could be drawn on this effect due to the fact that both the total pressure and partial pressure of SCF were varied simultaneously. In this current experiment, a constant total pressure of 13.5 MPa and a partial pressure of syngas of 4.5 MPa were maintained, whereas argon was used to offset the change in the partial pressure of hexanes. Due to limitations in the pressure that could be supplied by the argon tank used in this set of experiments (as limited by the manufacturer), the total system pressure was maintained at 13.5 MPa instead of 18 MPa. Therefore, a hexanes/syngas molar ratio of 2 was used in this experiment instead of 3, as used in the sections above.

Table 3 presents the effect of both argon and supercritical hexanes reaction media on the CO conversion as well as the selectivity toward $CO_{2,}$ alcohols and hydrocarbons. These data represent the average values obtained at each reaction condition operated for at least 50 h. CO conversion was 55.5% under the argon gas-phase conditions, which was higher than the average value under supercritical hexanes phase conditions (ca. 33.9%). CO_2 selectivity was found to be quite stable as the reaction medium was changed from argon gas-phase to supercritical hexanes phase. The selectivity toward alcohols was observed to be 16.0% under supercritical hexanes phase reaction conditions and 4.5% under the argon gas-phase conditions, whereas the partial pressure and the flow rate of syngas were kept constant. However, the light hydrocarbon selectivity (the S_H shown in Table 3) was found to be much higher under argon gas-phase conditions than under the supercritical hexanes phase conditions. The $C_8—C_{20}$ hydrocarbon selectivity under both reaction conditions was found to have a value of 6.0% (not included in Table 3.)

Figure 6 presents a comparison of the alcohols productivity obtained from argon gas-phase conditions and supercritical hexanes phase conditions. This data clearly demonstrated that the presence of the supercritical hexanes medium enhanced the productivity of alcohols significantly. An interesting observation is that the productivity of $C_1—C_6$ linear alcohols decreased monotonically with the increase in carbon number under the supercritical hexanes phase conditions; however, a maximum productivity was found at 1-butanol under argon gas-phase reaction conditions. Figure 7 shows a comparison of the $C_8—C_{18}$ paraffin productivity obtained under both GP- and SC-HAS conditions. A nearly doubled $C_8—C_{11}$ paraffin productivity was observed in argon GP-HAS compared with SC-HAS. The higher productivity of $C_8—C_{11}$ paraffins observed in the liquid product analysis corresponds well with the higher light hydrocarbon selectivity obtained from the vapor phase product analysis as shown in Table 3.

There are several proposed mechanisms for the formation of alcohols and hydrocarbons over Cu—Co catalyst

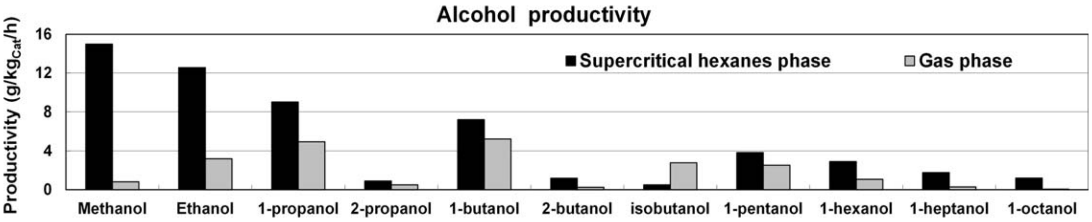

Figure 6. Productivity of $C_1—C_8$ alcohols in gas-phase and supercritical-phase HAS.

The reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, H_2/CO ratio = 2.0, temperature = 300°C, pressure = 13.5 MPa, hexanes/syngas molar ratio = 2 for the supercritical hexanes phase operation, Argon/syngas molar ratio = 2 for the argon phase operation.

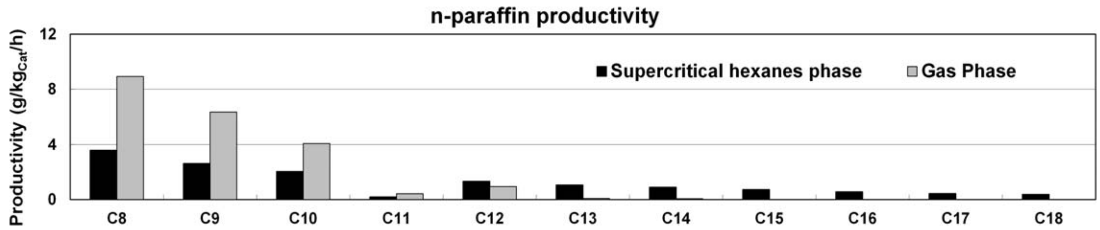

Figure 7. Productivity of C_8—C_{18} n-paraffin in GP-HAS and SC-HAS.

Reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, H_2/CO ratio = 2.0, temperature = 300°C, pressure = 13.5 MPa, hexanes/syngas molar ratio = 2 for the supercritical hexanes phase operation, Argon/syngas molar ratio = 2 for the argon phase operation.

systems.[1,18,19,60] Although, many intermediates have been proposed regarding the carbon chain growth in HAS, such as alkyl[61] or acyl entities,[19] it is has been suggested that alcohols and hydrocarbons are formed from the same intermediates.[13] Moreover, the linear alcohol products have been reported to follow the Anderson-Schulz-Flory (ASF) distribution,[1,29,57] as described by

$$\log(w_n/n) = n\log\alpha + \log((1-\alpha)^2/\alpha)$$

where w_n is the weight percentage of C_n alcohols and n is the number of carbon atoms. The probability of chain growth α can be determined from the slope of the log (w_n/n) vs. n plot. Figure 8 shows the variation of log (w_n/n) vs. n for the alcohol synthesis and hydrocarbon synthesis, respectively. It can be observed that under supercritical hexanes phase conditions the formation of the alcohols obeys the ASF distribution with a carbon chain growth number, α, of 0.52. As expected, the hydrocarbons also follow the ASF distribution and the carbon chain growth number was found to be $\alpha = 0.76$. As shown in Figure 6, the productivity of C_1—C_3 linear alcohols is significantly lower in the argon phase than in the supercritical hexanes phase. Combined with the observation that the light hydrocarbon selectivity was much higher under the argon gas-phase conditions, as shown in Table 3, it is reasonable to speculate that the termination step of converting lower carbon number surface intermediates to paraffin was promoted under the argon phase conditions. Therefore, a deviation from the linear ASF type distribution was observed for the alcohol products in argon as illustrated in Figure 9.

The productivity results in Figures 6 and 7 show that the termination step toward alcohols is preferred over the termination step toward hydrocarbons under the supercritical conditions. As a result, the productivity of alcohols is enhanced significantly. Because of the unique properties of SCF, the presence of the supercritical hexanes provided enhanced heat capacity and solubility compared to gas-phase operation. As such, the heat removal and the mass transport will be enhanced in the presence of supercritical hexanes. As a result of the enhanced heat removal, localized hotspots in the reactor were avoided and the selectivity toward C_1—C_4 n-paraffins was significantly reduced.[13,62] Moreover, the improved extraction capacity of the SCF solvent can allow for more efficient removal of FTS products from the catalyst resulting in higher C_{13}—C_{20} hydrocarbons productivity under the SC-HAS conditions.

Effect of H_2/CO ratio on GP-HAS and SC-HAS

The effect of H_2/CO ratio on HAS was investigated under gas-phase conditions where the H_2/CO ratio was maintained at the different values of 2.0, 1.75, 1.35, and 1.0, respectively. Figure 10 shows the CO conversion, H_2 conversion, CO_2 selectivity, and CH_4 selectivity in this GP-HAS experiment under these four H_2/CO molar ratio conditions. As shown in Figure 10, the CO conversion increased considerably from 22.4% at H_2/CO ratio = 1 to 47.6% at H_2/CO ratio = 2. H_2 conversion shows a similar trend but changed less dramatically from 10.8 to 17.1% when the H_2/CO ratio was changed from the value of 1 to 2. CO_2 selectivity was stable with the change in H_2/CO ratio. It is interesting to note that under gas-phase conditions the CH_4 selectivity exhibited a maximum at an intermediate H_2/CO ratio, approximately between the values of 1.35 and 1.75.

The effect of H_2/CO ratio on the reaction performance of HAS under SC-HAS is shown in Figure 11. It can be seen that the CO conversion remained stable in the range of 30.0 to 35.0% under supercritical conditions when changing the

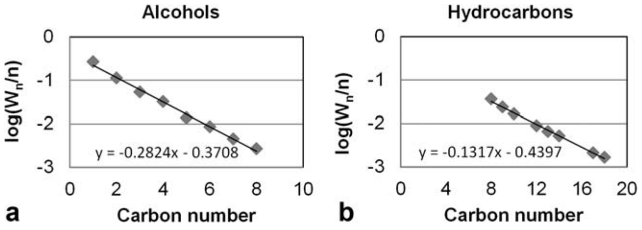

Figure 8. The variation of log (w_n/n) with respect to n (the number of carbon atoms) of alcohols (left) and hydrocarbons (right) obtained in SC-HAS.

Reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, H_2/CO ratio = 2.0, temperature = 300°C, pressure = 13.5 MPa, hexanes/syngas molar ratio = 2.

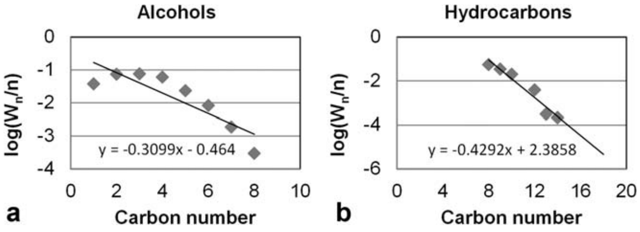

Figure 9. The variation of log (w_n/n) with respect to n (the number of carbon atoms) of alcohols (left) and hydrocarbons (right) obtained in GP-HAS.

Reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, H_2/CO ratio = 2.0, temperature = 300°C, pressure = 13.5 MPa, Argon/syngas molar ratio = 2.

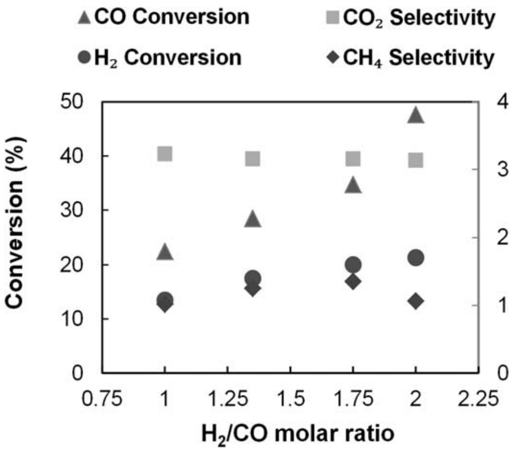

Figure 10. Effect of H_2/CO ratio on conversion and gas product selectivity in GP-HAS.

The reaction conditions were as follows: catalyst = 0.5 wt % K promoted Cu/Co/ZnO/Al_2O_3, syngas flow rate = 3000 L/Kg_{cat}/h, temperature = 290°C, pressure = 4.5 MPa.

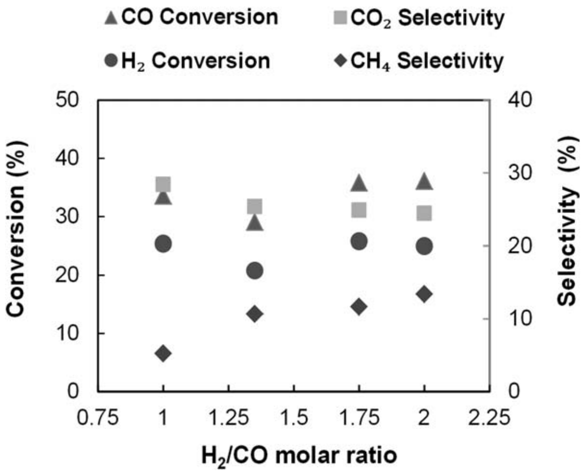

Figure 11. Effect of H_2/CO ratio on conversion and gas product selectivity in SC-HAS.

The reaction conditions were as follows: catalyst = 0.5 wt % K promoted Cu/Co/ZnO/Al_2O_3, syngas flow rate = 3000 L/Kg_{cat}/h, temperature = 290°C, pressure = 13.5 MPa, syngas partial pressure = 4.5 MPa, hexanes/syngas molar ratio = 2.

H_2/CO ratio from 1 to 2, whereas the CO conversion under gas-phase conditions increased monotonically from a value that was lower than supercritical phase at $H_2/CO = 1$ to a value considerably higher than supercritical phase at $H_2/CO = 2$. Fan et al.[63] observed a lower CO conversion in the supercritical-phase FTS reaction compared to the gas-phase FTS reaction and attributed this to the fact that the diffusion of synthesis gas in the supercritical phase was slower than in the gas-phase. A similar trend was observed in this HAS experiment when the H_2/CO ratio was maintained at 1.75 or 2.0. However, at the H_2/CO ratio of 1.0 or 1.35, the opposite trend was observed where the CO conversion in SC-HAS was actually higher than that obtained in GP-HAS, illustrating that this cannot be the effect of differences in diffusion alone. The H_2 conversion also follows a similar trend when the H_2/CO ratio was changed from 1 to 2 in SC-HAS, where the H_2 conversion was relatively steady across all of the H_2/CO ratios employed. In addition, CO_2 selectivity decreased slightly as the H_2/CO ratio increased from 1 to 2 in the SC-HAS experiment. However, the CH_4 selectivity was found to increase remarkably in SC-HAS from 5.3% at H_2/CO ratio = 1 to a value of 13.4% at H_2/CO ratio = 2.

Table 4 demonstrates the selectivity toward alcohol products and hydrocarbon products as a function of the H_2/CO ratio in GP-HAS. Under gas-phase operation, alcohol products were comprised of C_1—C_8 linear mixed alcohols, and hydrocarbons were collected up to C_{20} *n*-paraffin. It can be seen that selectivity toward alcohol products increased from 2.98 to 5.71% when the H_2/CO ratio increased from 1 to 2 in GP-HAS. Selectivity toward C_8—C_{20} *n*-paraffin did not demonstrate a clear trend as the H_2/CO ratio was increased from 1 to 2, and was in the range of 2.5 to 6.5%. In addition, Table 4 also presents the alcohol product distribution in terms of alcohol weight percentage (ROH wt %), which is defined as the weight of alcohols having a certain carbon number over the weight of total alcohol products. It has been found that this Cu—Co based catalyst has a good selectivity toward higher alcohols, with methanol selectivity lower than 6% for the conditions studied in the gas phase.

In contrast, Table 5 shows the catalytic performance in SC-HAS as a function of H_2/CO ratio. It can be seen that selectivity toward alcohol products slightly decreased from 15.09% when H_2/CO ratio = 1 to a value of 12.61% when H_2/CO ratio = 2. Table 5 also lists the alcohol products distribution as a function of H_2/CO ratio. Increasing the H_2/CO ratio under supercritical hexanes phase conditions favors the formation of methanol and ethanol. Little to no change was observed in the formation of C_3 and C_4 alcohols when H_2/CO ratio increased from 1 to 2. However, C_{5+} alcohol decreased significantly with the increase in H_2/CO ratio. Table 5 also presents the selectivity toward hydrocarbon products in SC-HAS. Under supercritical hexanes phase conditions, up to C_{24} linear paraffin was observed in the FID chromatogram, suggesting that the presence of supercritical hexanes facilitates the extraction of longer carbon chain hydrocarbons (C_{20} to C_{24}) from the catalytic sites.

Table 4. Catalytic Performance as a Function of H_2/CO Ratio in Gas Phase HAS

		Selectivity (%)		ROH (wt %)					α	
H_2/CO Molar Ratio	CO Conversion (%)	ROH	HC	C_1	C_2	C_3	C_4	C_{5+}	ROH	HC
1.00	22.5	2.98	2.59	3.93	25.52	32.38	27.28	10.90	0.35	0.62
1.35	28.4	3.51	6.37	3.12	25.65	30.50	25.68	15.05	0.42	0.60
1.75	24.7	3.91	2.55	5.63	32.21	33.78	19.38	8.99	0.36	0.61
2.00	47.6	5.71	5.69	3.06	23.72	30.63	23.68	18.91	0.49	0.59

Reaction conditions: catalyst = 0.5 wt % K promoted Cu/Co/ZnO/Al_2O_3, $T = 290°C$, $P = 4.5$ MPa, syngas flow rate = 3000 L/Kg_{cat}/h.
ROH: C_1—C_8 alcohols.
HC: C_8—C_{20} hydrocarbons.

Table 5. Catalytic Performance as a Function of H_2/CO Ratio in SC-HAS

		Selectivity (%)		ROH (wt.%)					α	
H_2/CO Molar Ratio	CO Conversion (%)	ROH	HC	C_1	C_2	C_3	C_4	C_{5+}	ROH	HC
1.00	33.6	15.09	16.20	2.11	12.97	22.53	22.37	40.01	0.70	0.81
1.35	29.1	13.44	7.11	4.23	17.21	25.53	23.03	30.00	0.62	0.78
1.75	35.8	12.65	7.70	8.30	21.12	23.13	20.91	26.55	0.59	0.80
2.00	36.1	12.61	7.87	9.39	21.86	21.89	21.46	25.40	0.58	0.78

Reaction conditions: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, $T = 290°C$, $P = 13.5$ MPa, $P_{syngas} = 4.5$ MPa, syngas flow rate = 3000 L/Kg_{cat}/h, hexanes/syngas molar ratio = 2.
ROH: C_1—C_8 alcohols.
HC: C_8—C_{24} hydrocarbons.

The observation that the production of higher alcohols can be enhanced by the presence of supercritical solvent in the HAS process has been reported by our group and others previously.[13,50,64] A comparison of the data in Tables 4 and 5 illustrates that the ROH selectivity in SC-HAS was significantly higher (average of 13.5%) than the ROH selectivity observed in GP-HAS (average of 4.0%), confirming these prior observations. It is also worth pointing out that under supercritical hexanes phase conditions the lower H_2/CO ratios actually promoted the formation of higher alcohols significantly. The difference in the effect that changes in the H_2/CO ratio can have on the formation of higher alcohols in GP-HAS compared to SC-HAS can also be seen in the different trends that are observed for the higher alcohol productivity, as shown in Figures 12 and 13. Figure 12 demonstrates that with the decrease in the H_2/CO ratio from 2 to 1, the productivity of higher alcohols decreased almost monotonically in GP-HAS. The stoichiometry of alcohol synthesis from syngas reveals that two moles of H_2 and one mole of CO are required for the synthesis of methanol and higher alcohols. However, due to a multitude of side reactions that occur in parallel to the HAS process, such as the water-gas-shift reaction, the optimum H_2/CO ratio in actual practice may be different from the theoretical value of 2. It has been reported by several investigators that the optimum H_2/CO ratio for HAS is below the stoichiometric value of 2.[1,35] In general, decreasing the H_2/CO ratio while maintaining the same reaction pressure will result in an increase in the CO partial pressure. Higher CO partial pressure would favor the CO insertion and promote the C—C chain growth in the HAS process, thereby resulting in an increased production of higher alcohols and/or hydrocarbons.[26] However, higher H_2 partial pressure (higher H_2/CO ratio) could diminish coke formation, thereby sustaining catalytic activity. From Figure 12, it can be observed that of the four reaction conditions applied in this study, the H_2/CO ratio of 2 seems to be the optimum value in GP-HAS for the production of each of the C_2 to C_8 higher alcohols. This can primarily be attributed to the higher CO conversion (ca. 47.6%) at the H_2/CO ratio of 2, compared to the much lower CO conversion (ca. 22.5%) at the H_2/CO ratio of 1. An opposite trend in the productivity of each higher alcohol is observed in SC-HAS as a function of the H_2/CO ratio, as shown in Figure 13. Among the H_2/CO ratios studied, the productivity of higher alcohols was much higher in SC-HAS than in GP-HAS. When the H_2/CO ratio decreased from 2 to 1, a monotonic increase in the formation of higher alcohols was observed, as demonstrated in Figure 13. Combined with the fact that the CO conversion was relatively stable with respect to the change in H_2/CO ratios in SC-HAS, it can be inferred that the presence of the supercritical solvent as a reaction medium further enhanced the carbon chain growth process at low H_2/CO ratios. Further evidence of this can be found in the fact that the C_{5+} alcohol weight percentage under SC-HAS conditions was significantly higher than that observed in GP-HAS conditions (e.g., 40.01% in SC-HAS vs. 10.90% in GP-HAS when the H_2/CO ratio = 1). Increased higher alcohol formation under supercritical conditions and at low H_2/CO ratios is also demonstrated by the differences between the carbon chain growth probability factors for both GP-HAS and SC-HAS, as discussed below.

The alcohol products produced over Cu—Co catalysts have been reported to obey the Schulz-Flory distribution.[1,2,26] Bailliard et al.[65] reported a same α value (ca. 0.45)

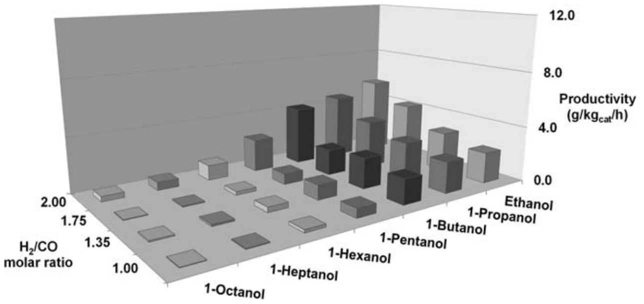

Figure 12. Effect of H2/CO ratios on the productivity of higher alcohols under gas-phase conditions.

The reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, syngas flow rate = 3000 L/Kg_{cat}/h, temperature = 290°C, pressure = 4.5 MPa.

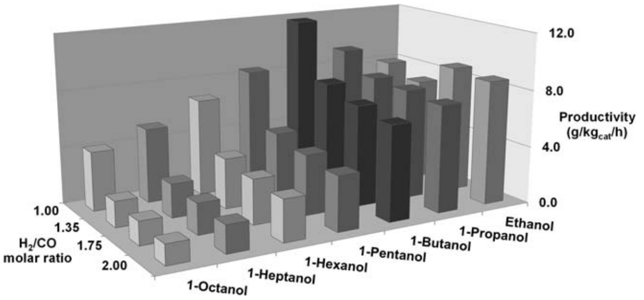

Figure 13. Effect of H_2/CO ratios on the productivity of higher alcohols under supercritical hexanes phase conditions.

The reaction conditions were as follows: catalyst = 0.5 wt % K promoted $Cu/Co/ZnO/Al_2O_3$, syngas flow rate = 3000 L/Kg_{cat}/h, temperature = 290°C, pressure = 13.5 MPa, syngas partial pressure = 4.5 MPa, hexanes/syngas molar ratio = 2.

for both the alcohol and hydrocarbon products, indicating that the formation of alcohols and hydrocarbons occurs in parallel. In the current study, as shown in Table 4, an α value of alcohol formation was found to be 0.49 at the standard reaction conditions (H_2/CO ratio of 2 in GP-HAS), whereas the α value of hydrocarbon formation was slightly higher (ca. 0.59). As the H_2/CO ratio decreased from 2 to 1, little to no difference was observed in the α values for both the alcohol and hydrocarbon products in GP-HAS. However, very different values and trends for the carbon chain growth probability factor were observed in SC-HAS with respect to changes in the H_2/CO ratio, as shown in Table 5. Compared to $\alpha = 0.49$ for higher alcohols in GP-HAS, an α value of 0.58 was found in SC-HAS for the same H_2/CO ratio of 2, illustrating a higher probability for carbon chain growth. This difference is even more obvious in the α values for the formation of hydrocarbons, where an $\alpha = 0.78$ was obtained in SC-HAS vs. an $\alpha = 0.59$ in GP-HAS at the same H_2/CO ratio of 2. Furthermore, the decrease in the H_2/CO ratio from 2 to 1 under supercritical hexanes phase conditions resulted in a further increase in the α value for the formation of alcohols (from 0.58 to 0.70), as shown in Table 5. Elbashir et al.[51] found that availability of active sites increased in supercritical FTS relative to gas-phase operation, and that the supercritical media may promote both the adsorption of the reactant molecules (CO and H_2) and possible incorporation of primary products (α olefins) into the chain growth process. Based on the results presented above, the presence of supercritical hexanes may similarly improve the accessibility of catalyst active sites in the SC-HAS process thereby resulting in improved production of higher alcohols. As a result, when the partial pressure of CO increased (H_2/CO ratio decreased from 2 to 1), the CO insertion reaction pathway was promoted. As such, the α value of alcohol products increased from 0.58 to 0.70. Hydrocarbon formation, however, was not affected by the change in H_2/CO ratio under both gas-phase and the supercritical hexanes phase conditions, although it should be noted that the value was significantly higher under supercritical phase conditions in all instances.

Conclusions

In summary, we have described the preparation of a K_2O promoted $Cu/Co/ZnO/Al_2O_3$ catalyst and investigated the effect of supercritical hexanes on its catalytic performance as well as alcohol productivities. We also investigated the effect of GHSV and H_2/CO molar ratio on the synthesis of higher alcohols under both gas-phase and supercritical hexanes phase conditions.

The presence of supercritical hexanes has been shown to enhance the heat-transfer rate and significantly reduce the selectivity toward CH_4. With increases in the hexanes/syngas molar ratio, the productivity toward higher alcohols increased monotonically among the conditions studied and reached its highest value at a hexanes/syngas molar ratio of 3.

When the hexanes/syngas molar ratio was set at 3 and the reaction pressure was set at 18 MPa, it was found that decreasing the GHSV from 2000 to 500 h^{-1} had a positive effect on the formation of methanol and CH_4. The use of a GHSV higher than 1000 h^{-1} would be suggested for subsequent studies of SCF-HAS to further improve the formation of higher alcohols.

The benefits of using supercritical hexanes as a reaction medium was confirmed when SC-HAS was compared with argon GP-HAS under the same operating conditions. The type of alcohol products obtained in SCF-HAS was the same as that obtained in the gas-phase studies. In addition, the formation of alcohols under the supercritical hexanes conditions was found to obey the Schulz-Flory distribution. The introduction of the SCF medium improved the heat removal from the active sites, resulting in a remarkably lower selectivity toward C_1—C_4 paraffins. The significantly enhanced alcohols productivity, especially that of C_1—C_5 linear alcohols, was likely due to improved extraction of these alcohols from catalyst pores by the supercritical hexanes.

Under gas-phase conditions, the CO conversion decreased with decreases in the H_2/CO ratio from 2 to 1. However, under supercritical hexanes phase conditions, the CO conversion remained quite stable with changes in H_2/CO ratio. Changes in H_2/CO ratio had little effect on CO_2 selectivity in GP-HAS and slightly influenced CO_2 selectivity in SC-HAS, indicating that the water-gas-shift reaction approached equilibrium at the conditions studied. CH_4 selectivity exhibited a maximum at moderate H_2/CO ratios in GP-HAS, but decreased significantly with decreasing H_2/CO in SC-HAS.

Under gas-phase conditions, higher H_2/CO ratios favor the productivity and selectivity of higher alcohols by promoting CO hydrogenation. Under supercritical hexanes phase conditions, however, a lower H_2/CO ratio resulted in much higher alcohol productivity and enhanced carbon chain growth probability factor. Much higher carbon chain growth probability factors for both the alcohol and the hydrocarbon formation were observed in SC-HAS compared to the GP-HAS at the same reaction conditions. An increase in the carbon chain growth probability factor for alcohol formation was also found as the H_2/CO ratio decreased from 2 to 1 under supercritical hexanes phase conditions. This change can be attributed to improved CO insertion resulting from enhanced CO partial pressure in SC-HAS.

Acknowledgments

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