

Synthesis of Methanol and Higher Alcohols from Syngas over K Promoted Cu Based Catalysts in Supercritical Solvent

by

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Abstract

With today's increasing crude oil prices and a desire to reduce our dependence on imported oil, the synthesis of methanol and higher alcohol represents a promising pathway for utilizing synthesis gas (a mixture of CO and H₂, and usually called syngas) in order to create liquid fuels or fuel additives. The driving force behind the research that focuses on 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. Although the process of converting syngas to alcohols has been under development for nearly a century, from a practical point of view, it still suffers from low selectivity towards higher alcohols. In order to meet the practical requirements of industry, numerous studies have been devoted to the investigation of the higher alcohols synthesis (HAS) over the past thirty years, including the development of modified catalysts, the utilization of double bed reactors, etc.

The objective of this work is to identify and demonstrate the benefits of introducing supercritical solvent into alcohol synthesis from syngas. In chapter 3, we have prepared a traditional low temperature methanol synthesis Cu based catalyst and evaluated its catalytic performance under gas phase conditions. Supercritical hexanes was introduced into the system as a reaction medium in order to evaluate the effect of the supercritical solvent on methanol and higher alcohol synthesis. The results illustrate a notable reduction in the CH₄ selectivity due to the enhanced heat transfer in the supercritical hexanes medium while this solvent medium also

facilitated the extraction of alcohols, especially methanol, from the catalyst pores. As such, the formation of mixed alcohols is promoted by the presence of the supercritical hexanes medium.

In chapter 4, this Cu-based methanol synthesis catalyst was promoted by cobalt, which is widely recognized to provide active sites for carbon chain growth reactions. The interaction between Cu and Co was assumed to enhance the formation of higher alcohols. We investigated higher alcohol synthesis under a series of reaction conditions that span the supercritical regime and compare these results with those obtained from gas phase operation. The results from experiments performed when using supercritical hexanes as the reaction media for this catalytic system illustrate that the presence of the SCF medium improves the heat transfer from the catalyst bed as evidenced by a significant reduction in the formation of CH_4 . In addition, the results of these catalytic investigations demonstrate that the presence of the supercritical medium has a significant effect on the selectivity and the productivity towards higher alcohols.

In chapter 5, the effect of syngas composition on the formation of higher alcohols over the Cu-Co based catalyst has been evaluated under both gas phase and supercritical hexanes phase reaction conditions. Four different values of H_2/CO ratio, 2.0, 1.75, 1.35, and 1.0, were utilized in order to represent the common syngas composition derived from various carbonaceous resources. The results demonstrate that under the presence of supercritical hexanes CO conversion was maintained at a stable value while decreasing the H_2/CO ratio from 2 to 1. Additionally, lower H_2/CO ratio effectively enhanced the carbon chain growth in supercritical higher alcohol synthesis.

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Chapter 1 A Review of Mixed Alcohol Synthesis

1.1 Introduction

Extensive research efforts in the past eight decades have been devoted to the utilization of C₁-chemistry as a possible pathway for fuels and chemicals. C₁-chemistry refers to the utilization of single-carbon molecules; such as carbon monoxide, syngas (a mixture of CO and H₂), carbon dioxide, methane etc.

The main resources of C₁ molecules are natural gas, coal, biomass, and organic wastes. The driving force behind the increasing demand of alternative fuels is that the supplies of crude oil are expected to be less available, more expensive and that there will be more environmental concern in the coming century (Dresselhaus & Thomas, 2001). One pathway for converting syngas into fuels is the synthesis of mixed alcohols, which has been researched and utilized for nearly a century. Methanol and higher alcohols, together referred as mixed alcohols, can be used as transportation fuels or as fuel additives. Although the production of methanol from syngas has been industrialized, the production of higher alcohols suffers from low selectivity and has not advanced beyond the pilot scale. Research into higher alcohol synthesis includes the development of new catalysts as well as the utilization of innovative processes or technologies with the goal of achieving the criteria of selectivity and productivity in order to justify this process industrially.

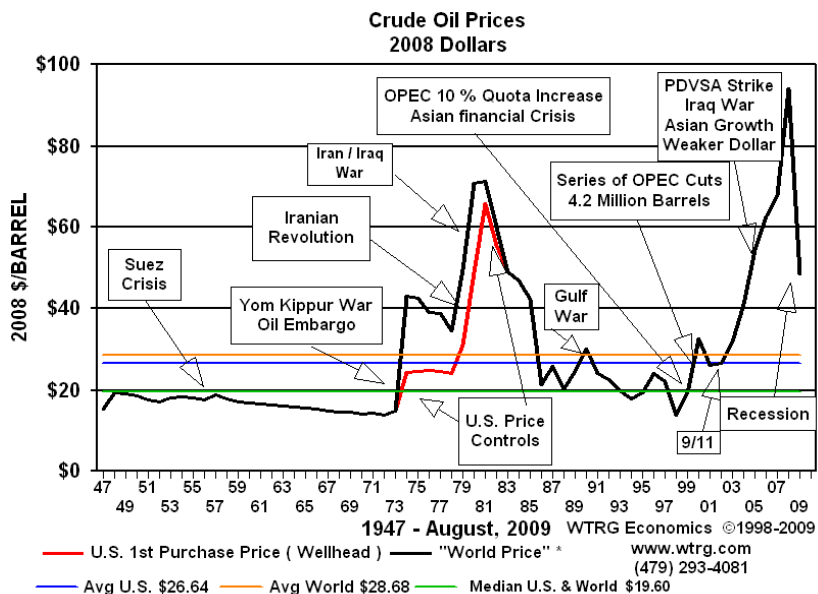


Figure 1.1 Crude oil prices history: 1947-2008 (www.wtrg.com)

With the crude oil price floating up and down, the investigation of higher alcohol synthesis developed rapidly at times while experiencing plateaus at other times. Figure 1.1 demonstrates that crude oil prices changed significantly over the years, where it depended not only on the demand but was also affected by political happenings around the world. Sharp increases in the price of crude oil called for the use of alternative fuels and produced a sudden driving force to this field of research, as evidenced by a summit in the number of papers published. Fig.1.2 shows a plot of the number of articles reported by “*Engineering Village*” as a function of year, as indexed with keywords “alcohol synthesis” and “synthesis gas”. It can be observed that two summits in the number of papers produced were experienced in the year 1986 and 2009, which occurred a few years after the peaks in the global crude oil prices shown in Fig.1.1.

As the reserves of crude oil are depleted and concerns over their environmental impacts continue to escalate, it could be expected that the conversion of syngas, as derived from various

carbonaceous resources, into alternative fuels would receive significant attention. Although, replacing gasoline or diesel fuel with alternative fuels of equivalent energy densities is going to take much more effort and greater control over chemical reactivity.

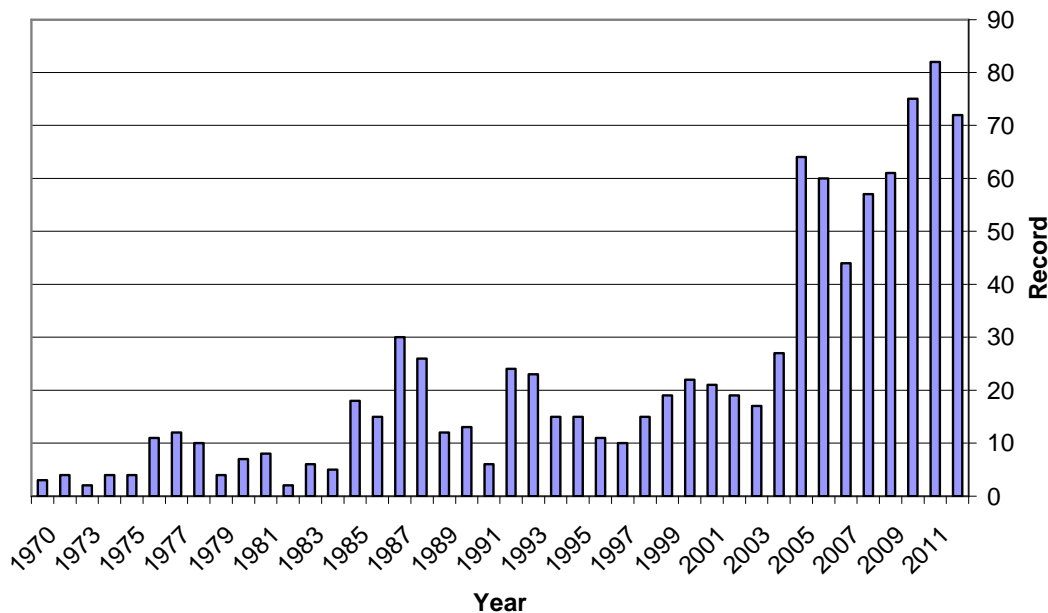


Figure 1.2 Histogram from the indexing site Engineering Village of papers including both “alcohol synthesis” and “synthesis gas” by year

1.1.1 Background

Synthesis gas (syngas) is a gas mixture that consists of varying amounts of carbon monoxide (CO) and hydrogen (H₂). Syngas can be derived from steam reforming or partial oxidation of natural gas (CH₄), the gasification of coal or biomass and in some cases waste-to-energy gasification facilities. Syngas is combustible and is often used as a fuel source or as an intermediate for the production of fuels and other chemicals. These conversion processes include ammonia production, methanol synthesis, and Fischer-Tropsch synthesis (Beychok, 1974).

The utilization of syngas started at the beginning of the 20th century by the production of methane via the hydrogenation of carbon monoxide in 1902. In the 1920s, the discovery of the

Fischer-Tropsch synthesis and its subsequent use in manufacturing methanol and higher alcohols made the utilization of syngas a more popular research topic (Wender, 1996). Various processes for converting syngas to generate fuels, fuel additives and chemicals are shown in Fig. 1.3. Depending on reaction conditions and the catalysts used, different chemicals can be produced on a large industrial scale using these synthesis routes. These conversion processes from syngas provide alternative pathways to produce fuels, fuel additives, and chemicals with lower sulfur concentration compared to conventional petroleum fuels.

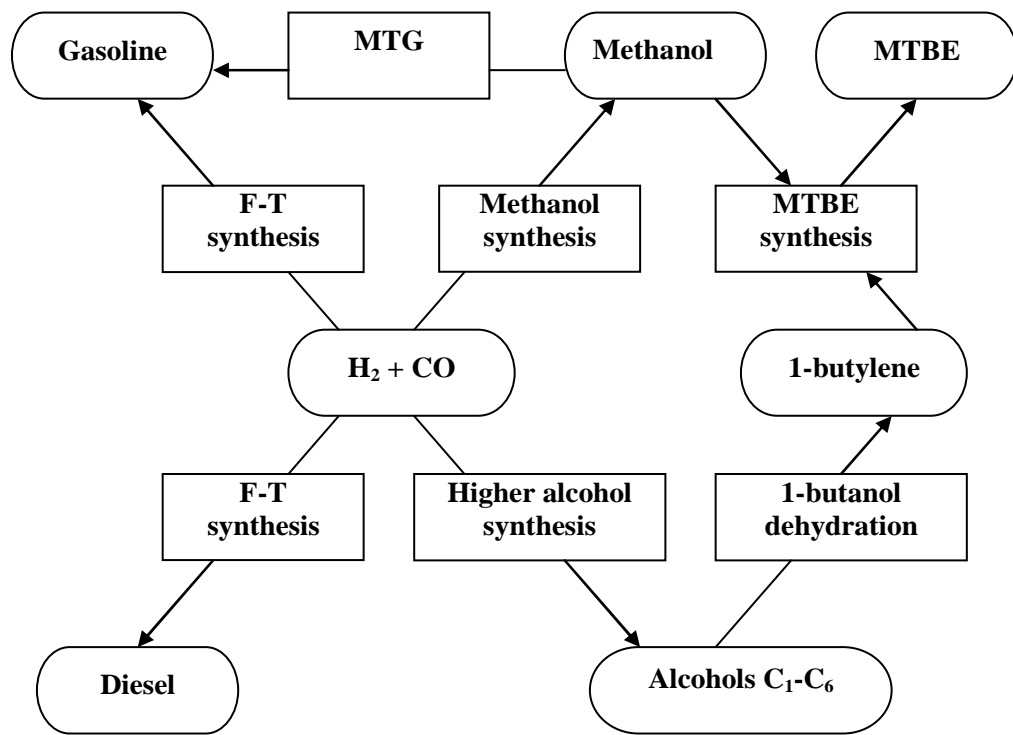


Figure 1.3 Pathways for syngas conversion to fuels, additives and chemicals (Stelmachowski & Nowicki 2003)

One of the pathways in Figure 1.3 involves the synthesis of methanol and mixtures of higher alcohols (i.e. C₂ to C₆ alcohols). Our study is and will be mainly focused on this pathway of syngas conversion.

1.2 Alcohol Synthesis from Syngas

1.2.1 Methanol Synthesis

1.2.1.1. Background

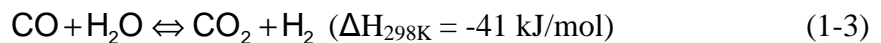
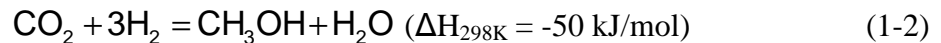
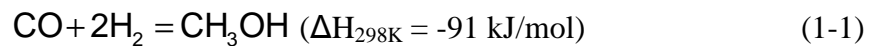
Methanol is a basic chemical, a transportation fuel, and an energetic material for fuel cells. 11 billion gallons of methanol are produced annually worldwide (Herman, 2000). According to a report from the Methanol Institute, the methanol industry generates \$12 billion in economic activity each year around the world, while creating nearly 100,000 jobs (Dolan, 2010).

The utilization of methanol as an alternative fuel began in 1965, when pure methanol was widely used in a USAC Indy car competition (Reed & Lerner, 1973). During the OPEC 1973 oil crisis, Reed and Lerner (1973) advocated methanol from coal as a proven fuel with well established manufacturing technology and sufficient resources to replace gasoline. Using methanol as a fuel in spark ignition engines can offer increased thermal efficiency and increased power output (as compared to gasoline) due to its high octane rating and high heat of vaporization. However, due to its high hygroscopic properties, it may absorb water directly from the atmosphere, causing a phase separation of methanol-gasoline blends (Reed & Lerner, 1973). Methanol also presents some disadvantages, including low volatility, difficulty in ignition, and difficulty in blending with gasoline. Despite these disadvantages, methanol has been considered as a replacement for gasoline-based fuel and a number of attempts have been made towards switching from gasoline to methanol. In response to the oil price shocks, the state of California ran an experimental program from 1978 to 1990 which subsidize the conversion of gasoline fueled vehicle to 85% methanol (with 15% additives of choice) fueled vehicle (Bromberg & Cheng, 2010). Although the methanol transition program successfully reduced the emissions of smog, NO_x, CO and particulate matter, the development of methanol vehicles faced considerable difficulties (Dolan, 2010). In 2005, California's Governor, Arnold Schwarzenegger, stopped the

methanol conversion program after 25 years and 200,000,000 miles, to join the expanding use of ethanol (driven by producers of corn) (Dolan, 2010). In spite of this, 2006 Noble prize winner George A. Olah and colleagues proposed an entire methanol economy based on energy storage in synthetically produced methanol.

China is currently the largest user of methanol for transportation fuels in the world. Interest in China on the use of methanol as a transportation fuel is high (but local) as there is an abundance of readily available feedstocks, with coal being the main choice (Li et al., 2009). Presently, M5 (5% methanol in gasoline), M10, M15, M85 and M100 methanol gasoline are sold on the market. The estimated volume of methanol consumption in the Chinese transportation sector is around 1.5–2 billion gallons (Bromberg & Cheng, 2010).

The production of methanol is typically from syngas via steam reforming of natural gas, although some is from coal (Bromberg & Cheng, 2010). Other feed stocks include wood, municipal solid wastes and sewage. Catalytic synthesis of methanol from syngas is one of the most active and selective industrial processes carried out on a commodity scale today (Herman, 2000). Three conversions are involved in the process, which are given by the following stoichiometric relationships:



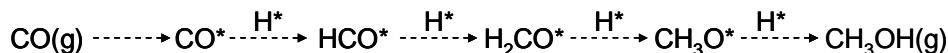
Equation 1-1 suggests an ideal molar ratio of $\text{H}_2/\text{CO} = 2$ for a single pass conversion, and these reactions are highly exothermic. Water-gas-shift and reverse water-gas-shift reactions (Eqs. 1-3) co-exist, resulting in a change of the ideal syngas stoichiometric ratio. Accounting for both CO and CO₂ hydrogenation, Lange (2001) adjusted the ideal stoichiometric ratio to (H₂-

$\text{CO}_2)/(\text{CO}+\text{CO}_2) = 2$. The effect of syngas molar ratio on the production of alcohols will be further discussed in 1.2.2.4.4.

1.2.1.2. Mechanism for methanol synthesis

Various mechanisms have been proposed for the synthesis of methanol from syngas. Four mechanisms are discussed as below:

a) Xu et al.(1987) regarded the following mechanism proposed by Ellgen et al. (1979) as the most plausible one.



The * denotes the adsorbed surface species and (g) denotes gaseous species. This mechanism has been supported by kinetic studies with isotopic labeling and spectroscopic observation of the reaction intermediates (Chinchen, Waugh, & Whan, 1986). It has been proven that copper is present in the catalyst both in the metallic and ionic form (Mehta, Simmons, Klier, & Herman, 1979). The formation of methanol and the dissociation of hydrogen occur at the metallic copper part of the catalyst surface, whereas the adsorption of CO takes place on the Cu ion site (Xu et al. 1987). Consequently, an active and selective methanol catalyst requires the homogenous distribution of both metallic and ionic Cu.

b) Nakamura et al. (1990) have proposed the “surface-redox” mechanism and “formate mechanism” for the water-gas shift reaction. Strong evidence for the surface-redox mechanism has been found in Cu single-crystal studies (Campbell and Daube 1987). Based on the redox mechanism, Askgaard (1995) proposed a kinetic model for methanol synthesis, elementary steps of which are listed in Table 1.1. From steps 1 to 8 in table1.1, $\text{H}_2\text{O(g)}$ is completely dissociated to O^* and $\text{H}_2(\text{g})$, and the surface oxide O^* is removed by CO^* to produce $\text{CO}_2(\text{g})$. Elementary steps 9-13 constitute the simplest reaction mechanism of the methanol synthesis reaction. The

apparent rate determining step in this mechanism has been found to be the hydrogenation of H_2COO^* to methoxide and oxide (step 14) (Askgaard et al., 1995).

c) Dissimilarly, the “formate mechanism” suggested that H_2O^* dissociates into OH^* and H^* , followed by the formation of the formate HCOO^* converting from CO^* and OH^* . HCOO^* reacted with H^* and eventually converted to methanol (Nakamura et al. 1990).

d) It is worthy to note that alternative to the pathways above, carbonylation of methanol and hydrogenation of methyl formate were also considered as a pathway for the reaction (Palekar et al., 1993).

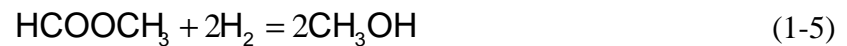
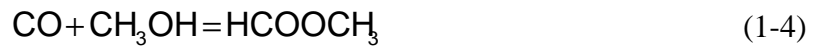


Table 1.1 Elementary steps proposed in the “redox” mechanism of methanol synthesis (Askgaard et al. 1995)

Steps	Surface reactions
1	$\text{H}_2\text{O}(\text{g}) + * \rightleftharpoons \text{H}_2\text{O}^*$
2	$\text{H}_2\text{O}^* + * \rightleftharpoons \text{OH}^* + \text{H}^*$
3	$2\text{OH}^* \rightleftharpoons \text{H}_2\text{O}^* + \text{O}^*$
4	$\text{OH}^* + * \rightleftharpoons \text{O}^* + \text{H}^*$
5	$2\text{H}^* \rightleftharpoons \text{H}_2 + 2^*$
6	$\text{CO}(\text{g}) + * \rightleftharpoons \text{CO}^*$
7	$\text{CO}^* + \text{O}^* \rightleftharpoons \text{CO}_2^* + *$
8	$\text{CO}_2^* \rightleftharpoons \text{CO}_2(\text{g}) + *$
9	$\text{CO}_2^* + \text{H}^* \rightleftharpoons \text{HCOO}^* + *$
10	$\text{HCOO}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{COO}^* + *$
11	$\text{H}_2\text{COO}^* + \text{H}^* \rightleftharpoons \text{H}_3\text{CO}^* + \text{O}^*$
12	$\text{H}_3\text{CO}^* + \text{H}^* \rightleftharpoons \text{CH}_3\text{OH}^* + *$
13	$\text{CH}_3\text{OH}^* \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) + *$
14	$\text{H}_2\text{COO}^* + * \rightleftharpoons \text{HCHO}^* + \text{O}^*$
15	$\text{HCHO}^* \rightleftharpoons \text{HCHO}(\text{g}) + *$
16	$\text{H}_2\text{COO}^* + \text{H}^* \rightleftharpoons \text{HCHO}^* + \text{OH}^*$

1.2.1.3. Catalysts for methanol synthesis

The catalytic synthesis of methanol is typically carried out over two types of catalysts,

a) The first type of methanol synthesis catalyst is copper-free zinc chromite ($\text{ZnO}/\text{Cr}_2\text{O}_3$) catalysts operating under high temperature ($400\text{ }^\circ\text{C}$) and pressure reaction conditions (10-20 MPa) (Herman, 2000). The liquid product synthesized by this type of catalyst is essentially pure methanol with a small amount of water and higher alcohols. The maximum volume percentage of methanol in the liquid product is about 90%. A certain $\text{ZnO}-\text{Cr}_2\text{O}_3$ based catalyst that could hydrogenate CO to methanol at 24-30 MPa and $350-400\text{ }^\circ\text{C}$ was commercially adopted by BASF in 1923 (Satterfield, 1991). However, the high selectivity and formation rate toward methanol for this catalyst is restricted to these rigorous reaction conditions. Bradford et al. (2003) found that when operating a $\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst at only $320\text{ }^\circ\text{C}$ and 3.41 MPa, the maximum allowable conversion of CO to CH_3OH was restricted to 4.2%.

b) The second type of methanol synthesis catalyst is copper-based catalysts that contain ZnO and oxide support and operate at a low temperature ($250\text{ }^\circ\text{C}$) and low pressure (5-10 MPa), e.g. $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ or $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ (Herman, 2000). The low-temperature methanol synthesis process using these catalysts has entirely replaced the older high-temperature process that operated at 15 MPa and $400\text{ }^\circ\text{C}$ using a Cu-free “zinc-chromite-type” ($\text{ZnO}/\text{Cr}_2\text{O}_3$) catalyst (Subramani & Gangwal, 2008). The high selectivity, long term performance, and resistance to oxidizing gases have resulted in this kind catalyst being widely used in the methanol synthesis industry (Xu et al. 1987). For example, a $\text{Cu}/\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst was shown to have a $200\text{g}/\text{kg}_{\text{cat}}\cdot\text{h}$ methanol formation rate at the reaction conditions of $P = 7.6\text{ MPa}$, $T = 275\text{ }^\circ\text{C}$, $\text{H}_2/\text{CO} = 0.45$, and a space velocity of $3200\text{ l}/\text{g}_{\text{cat}}\cdot\text{h}$ (Campos-Martín, 1996). An interesting characteristic of these catalysts is that the mixed catalysts are at least three orders of magnitude more active than each of the separate catalyst components (Herman et al. 1979). Mehta et al.

(1979) proved that copper is indeed soluble in the zinc oxide, and that the electron transfer between copper metal and ZnO may play a contributory, but not an essential, role in promoting the synthesis of methanol. The disadvantages of these copper-based catalyst are few but significant: low resistance to thermal shocks, which does not allow the catalyst to be operated above 300 °C and extreme sensitivity to sulfur and chlorine poisoning that requires a careful and expensive purification of the syngas (Herman et al. 1979).

Overall, the Cu/ZnO/Al₂O₃ catalyst has been the preferred catalyst for methanol synthesis industry for many years, producing billions of gallons of methanol every year worldwide.

1.2.2 Mixed Alcohols Synthesis (MAS)

1.2.2.1. Background

The phrase “mixed alcohol” refers to the mixture of methanol and higher alcohols, which are usually C₂-C₄ alcohols (ethanol, propanol, butanol and isomers). The general chemical formula for higher alcohols is C_nH_{2n+1}OH (n ≥ 2). They can be synthesized chemically or biologically, and they have characteristics allowing them to be used in current engines (Forzatti et al. 1991).

The direct catalytic synthesis of higher alcohols from carbon monoxide and hydrogen was first reported in the 1920's (Mahdavi et al. 2005). Synthesis of higher alcohols, isobutanol in particular, from coal, biomass or natural gas via syngas has been attracting research interest due to the potential for producing clean and high octane-value fuels.

Higher alcohols can be used directly as fuels, as fuel additives, and can be further converted into valuable chemicals. The advantages and disadvantages are as follows.

a) It has been confirmed that higher alcohols are clean burning fuels when used directly. Higher alcohols have comparable and some even have higher octane ratings, with ethanol at 130 RON (Research Octane Number), 96 MON (Motor Octane Number), (which equates to 113 AKI)

and n-butanol at 96 RON, 78 MON (which equates to 87 AKI), as shown in Table 1.2. Note that AKI refers to “Anti-Knock Index” which averages the RON and MON ratings and is reported on U.S. gas station pumps. It has been shown that a fuel with a higher octane rating is less prone to knocking (extremely rapid and spontaneous combustion by compression) and possesses improved energy efficiency, leading to a better fuel economy than the conventional gasoline. In spark ignition engines, alcohols can run at much higher exhaust gas recirculation rates and with higher compression ratios (Klier et al. 1997). Moreover, alcohols have been shown to reduce the emission of CO, hydrocarbons, ozone, and particulates, and may reduce the emission of NO_x. A test with E85 (ethanol 85%) fueled Chevrolet Lumina showed that NMHC (non-methane hydrocarbons) went down by 20-22%, NO_x by 25-32% and CO by 12-24% compared to reformulated gasoline (Kelly, Bailey, Coburn, Clark, & Lissiuk, 1996). It is important to note that using alcohols directly as fuels in current vehicle systems requires modifications to some components in the engine system.

b) Higher alcohols, ethanol in particular, are often used as fuel additives. In order to reduce pollution, many states in the U.S. have mandated that all gasoline fuels be blended with 10 percent alcohol (usually ethanol) during some or all of the year. Butanol has a higher energy density than ethanol and has been demonstrated to work in vehicles designed for use with gasoline without modification. The current butanol supply mainly comes from the fermentation of biomass and the refining of fossil fuels. With the development of bacteria modification, the number of commercial butanol plants has been growing, supplying increasing amounts of butanol to the fuel additive market. Characteristics of using the mixtures of alcohols as fuel additives include:

1. Loss of energy density. As shown in Table 1.2, one liter of ethanol contains 21.1 MJ, a liter of methanol 15.8 MJ and a liter of gasoline approximately 32.6 MJ. Consequently, for the same energy content as one liter of gasoline, one needs 1.6 liters of ethanol and 2.1 liters of methanol. However, actual fuel consumption doesn't increase as much as energy content numbers indicate, because the alcohol fuels are more energy efficient (Li et al. 2004).

2. Enhancement of octane number. Octane number parameters such as RON and MON are important properties of fuel that reflect their propensity to resist “knock” in spark-ignited engines. In general, RON and MON values of pure hydrocarbons decrease in the following order: aromatics, iso-paraffins, olefins and naphthenes, and n-paraffins (Anderson et al. 2010). Higher alcohols have smaller molecular weight and directly provide oxygen to gasoline, therefore a range of higher octane numbers could be achieved by changing the composition of alcohol additives. The properties of different types of fuels with or without alcohol additives are summarized in Table 1.2. Higher AKI could be observed from the Gasohol and E85, when comparing to the value of traditional gasoline.

3. Improved combustion efficiency. As a fuel additive, mixed alcohols have been shown to exhibit a reduction in CO, HCs, and NO_x emissions (Hohlein, Von Oer Decken, Holtje, & Mausbeck, 1991). Table 1.3 compares the emissions from combusting different types of fuels in terms of the amount of CO, HC, and in the exhaust gas. It is clear that adding methanol or DME into gasoline can reduce the emission of hydrocarbon and NO_x. A study of the influence of ethanol on emissions and fuel consumption of automobiles showed that with increasing the percentage of ethanol in gasoline (from 5% to 25%) the emission of CO and NO_x decreased continuously (Gautam et al. 2000)

4. Integration of use within the existing gasoline infrastructure and vehicles. Higher alcohols are preferred over methanol in this respect because of their lower water solubility, reducing the possibility of damaging current vehicles systems.

Table 1.2 Properties of different types of fuels (Methanol institute, 2010)

Fuels	Energy density (MJ/L)	Air-fuel ratio	Specific energy (MJ/kg air)	Heat of vaporization (MJ/kg)	RON	MON	AKI
Gasoline and biogasoline	32	14.6	2.9	0.36	91-99	81-89	86-94
Butanol fuel	29.2	11.1	3.2	0.43	96	78	87
Ethanol fuel	19.6	9.0	3.0	0.92	130	96	113
Methanol	16	6.4	3.1	1.2	136	104	120
Gasohol (10% ethanol)	28.06	n/a	n/a	n/a	96-101	83-92	89-97
E85 (85% ethanol)	25.65	n/a	n/a	n/a	113	94	104

Table 1.3 Emission comparisons for different fuel types (Methanol institute, 2010)

Emission (g/km)	H ₂	DME	Methanol	CNG ^a	LPG ^b	Diesel	Gasoline with carburetor	Gasoline without carburetor
CO	0	0.12	0.34	0.4	0.89	0.24	1.47	8.96
HC	0	0.04	0.043	0.41	0.115	0.095	0.09	1.27
NO _x	0.037	0.034	0.102	0.125	0.155	0.67	0.315	2.64

a Compressed natural gas (CNG)

b Liquefied petroleum gas (LPG)

c) Higher alcohols could be used as feed stock in the chemical process industry. First, ethanol is an important industrial ingredient and has widespread use as a base chemical for other organic compounds. These include ethyl halides, ethyl esters, diethyl ether, acetic acid, ethyl amines and to a lesser extent butadiene. Second, water-soluble alcohols (low-molecular weight products) are used as solvents for the manufacture of coatings, dyes and inks, plastics, flavorings, personal-care products, pharmaceuticals, and cleaners. Higher molecular weight alcohols (C₆-C₉

and C₁₀-C₁₆) and their derivatives are used as intermediates of plasticizers, detergents and lubricants (Mertzweiller, Rouge, Cull, & McCracken, 1958).

Overall, higher alcohols present good energy efficiency and provide options for sustainable renewable transportation fuels. With the increasing demand for fuels, higher alcohols could potentially reduce the dependence on imported crude oil. In 2007, U.S government established a new Renewable Fuel Standard (RFS2) in the Energy Independence and Security act, as a result of which greater biofuel production and consumption is expected through 2022.

1.2.2.2. Catalysts for Mixed Alcohols Synthesis (MAS)

The synthesis of higher alcohols suffers from low selectivity, impeding the industrialization. Modification of catalysts as an effective means to enhance higher alcohols' selectivity has been widely developed and reviewed (Nunan et al. 1989; Majocchi et al. 1998; Hilmen et al. 1998; Herman 2000; Spath and Dayton 2003; Fang et al. 2009; Subramani and Gangwal 2008). For approximately the last 25 years, there has been intensive research centered on the development of active and selective catalysts for shifting alcohol synthesis away from methanol and toward higher alcohols (Herman 2000). These catalysts can be divided into four categories, with examples of each shown in Table 1.4. Spath & Dayton (2003) believed that the modified methanol and modified FT catalysts have been the most effective in the production of mixed alcohols. Other catalyst types that have been researched for higher alcohol synthesis include sulfide-based, oxide-based, and rhodium based.

a) Modified methanol catalysts. The modification of methanol catalysts for higher alcohol formation is usually accomplished by the addition of alkali promoters, which leads to the formation of higher alcohols from H₂/CO mixtures (Hilmen et al., 1998). Aldol condensation of alcohols occurs within the coordination sphere of the heavy alkali cation, which enhance the

basicity of the catalyst (Klier et al., 1993). Among the alkali-metal dopants, it has been shown that the order of promotion is Cs > Rb > K > Na using formate salt (Nunan et al. 1989) or hydroxide (Vedage, Himelfarb, Simmons, & Klier, 1985). Cs appears to be the best promoter, but K is often used because of its availability and low cost.

b) Fischer Tropsch Synthesis (FTS) elements (Fe, Co, Ni, etc.) modified copper catalysts and group VI-VIII metal-based catalysts, e.g. Mg and Fe supported catalysts. Copper is known to be the major element for methanol synthesis, enabling the dissociative chemisorption of hydrogen and the associative adsorption of CO (Xu et al., 1987). FTS elements such as Co and Ni have been found to be effective promoters to enhance the alcohol and hydrocarbon yields. Sibillia et al. (1984) found that the addition of Fe to Cu/ZnO methanol synthesis catalysts led to a significant increase in hydrocarbons yields. The use of Co-Cu based catalysts has been reported to give high catalytic activity and good selectivity towards higher alcohols (Courty, Durand, Freund, & Sugier, 1982). In addition, the carbon number distribution of products over the Co-Cu catalysts follows the Anderson-Schulz-Flory (ASF) distribution (Smith and Anderson, 1984).

Table 1.4 Catalytic performances over different types of alcohol synthesis catalysts (Thao, 2007)

No.	Catalysts	Conditions				CO Conversion (%)	Selectivity (carbon atom,%)		Productivity (g/kgcat•h)	
		T(K)	P(MPa)	H ₂ /CO	GHSV		MeOH	C ₂₊ OH	MeOH	C ₂₊ OH
1	Cs/Zn/Cr	678	6.9	1	Not found	9.0	72.2	0.8	116	1
2	Pd/Cu/Me/Ce	583	4.5	1	6000 l/kgcat/h	10.6	74.4	11.6	23.6	7.8
3	Cs/Cu/Zn/Al	583	7.6	0.45	5330 l/kgcat/h	13.8	85.1	5.9	436.5	16.9
4	Cs/Cu/Zn/Cr	583	7.6	0.45	5530 l/kgcat/h	21.1	48.7	29.8	202.0	51.9
5	K/Cu/Co/Zn/Al	563	6.0	0.5-2	4000 h-1	21-24	20-27	30-50	60-100	NA
6	Cu/Co/Zn/Al	573	6.0	1	3000 h-1	Not reported	44.0	30	85.0	NA
7	Na/Cu/Co/Zn/Al	573	6.0	1	3000 h-1	Not reported	37.0	33.0	85.0	NA
8	Cs/Co/Mo/Clay	573	13.8	1.1	4000 h-1	4.7	61.8	26.11	60-64	35-40
9	LaRhO ₃	573	0.6	1	Not found	Not reported	12.2	5.6	16	15

c) Sulfide-based catalyst. Alkali-promoted transition metal sulfide catalysts, particularly MoS₂ require the similar reaction conditions as those employed with the low temperature copper-based oxide catalysts (Fang et al., 2009). In contrast to the alkali-promoted Cu-based catalysts, it has been shown that the higher alcohols formed over the sulfide catalysts were linear and that C-C bond formation proceeded via a CO-insertion into an α -carbon mechanism (Smith et al. 1991). The products formed over MoS₂ catalysts contained 15%-20% hydrocarbons, principally consisting of methane. The carbon number distribution of both the alcohols and the hydrocarbons followed an ASF distribution (Spath & Dayton, 2003). Because of the ASF distribution, selectivity to higher alcohols is limited. Additionally, the sulfide-based catalysts are less active than oxide-based catalysts, especially the Cu/ZnO-based catalysts.

It is important to note that alkali-doped molybdenum sulfide catalysts possess an excellent sulfur tolerance and high activity for the water-gas-shift reaction, making them promising catalysts for mixed alcohol synthesis. These catalysts can be operated at a relatively high reaction temperatures (270-330 °C) and operation pressure 10-28 MPa with H₂/CO ratio of 1-2. The product mixture usually comprises 70%-80% alcohols and 15%-30% hydrocarbons on CO₂-free basis. The total alcohol yield can reach 0.3 g/ml_{cat}/h, but with more than 50% products as methanol (Forzatti et al. 1991).

d) Rh based complexes. Rhodium-based catalysts are very selective toward methane (Nirula 1994) and C₂ oxygenated products, such as ethanol, acetaldehyde and acetic acid (Fukushima, Arakawa, & Ichikawa, 1985; Ichikawa, 1982). Li, Fu, and Jiang (1999) argued that a strong interaction occurs between the rhodium modifiers and the K-Mo-O support. They further concluded that the coexistence of cationic and metallic Rh stabilized by this interaction may be responsible for the increased selectivity toward higher alcohols. Foley et al. (1990) suggested

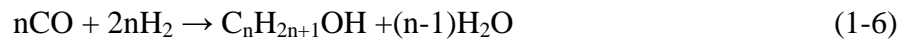
that the interaction between Rh and Mo leads to the formation of electron-poor sites where the formation of higher alcohols occurs. Decanio et al. (1991) believed that, depending on the status of the rhodium species, properties of alkali promoter, nature of the support, and the reaction conditions, the rhodium species are capable of catalyzing dissociation, insertion, and CO hydrogenation. The Rh-based catalysts, which are especially selective for C₂ oxygenates, are interesting from both a theoretical and practical point of view. However, Rh is scarce and its price is very high compared to other elements used in the synthesis of higher alcohols. The availability of Rh is limited to about 20 ton/y at present and over 70% of the available Rh is already being consumed by the automobile industry for making three-way auto-exhaust catalysts (Subramani & Gangwal, 2008). The high cost and limited availability of rhodium for higher alcohol synthesis catalysts will impact any commercialization of these synthetic processes for converting syngas to higher alcohols (Xu et al. 1987).

1.2.2.3. Chemistry and Reaction Mechanism of Mixed Alcohol Synthesis

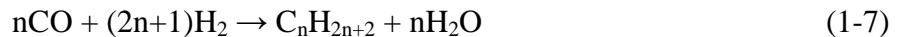
1.2.2.3.1 Chemistry

Mixed alcohol synthesis (MAS) is similar to methanol synthesis and Fisher-Tropsch synthesis, preferring to be operated at high pressure and relatively low temperature. Views both from the reaction stoichiometry and exothermic nature of the reaction lend evidence to these reaction conditions (Minahan, Epling, & Hoflund, 1998). In the MAS process, the major reaction is the alcohol formation, while hydrocarbon formation and the water-gas-shift reaction constitute side reactions:

Alcohol formation



Hydrocarbon formation



Water-gas-shift reaction



Meanwhile, the hydrogenation of CO over alkali-doped catalysts also leads to the formation of a small amount of other reaction products: aldehyde, ester, ketones etc. (Forzatti et al. 1991). This complexity of the product mixture is consequent to the wide variety of catalytic functions that are active under synthesis conditions. A discussion of different mechanism that has been proposed for MAS is presented below:

The reaction pathways that link these products are then specific to each catalyst type. CO-insertion mechanisms are believed to be dominant mechanism for modified Fischer Tropsch synthesis catalysts (Hindermann et al. 1993). Aldol-type condensation mechanisms of C_n with C_1 species are believed to prevail on the low temperature Cu-based catalysts (Nunan et al., 1988). $\text{C}_n + \text{C}_1$ and $\text{C}_n + \text{C}_m$ condensations and ketonizations are active over high-temperature alkali-

modified methanol catalysts (Forzatti et al. 1991; Tronconi et al. 1992). It is not always clear whether a proposed mechanism on one type of catalyst is necessarily applicable to other catalysts. Furthermore, the effects of catalyst supports and promoters make the mechanism more complicated.

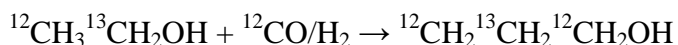
1.2.2.3.2 Mechanism for the low temperature Cu-based catalysts

In order to probe the mechanisms of the C-C bond formation process, various experimental methods have been used, including ^{13}C NMR (Nunan et al., 1988; Nunan, Bogdan, Herman, et al., 1989), in situ FTIR (Yang et al. 2005), and cofeeding probe molecules in pairs (Beretta, Tronconi, et al., 1996).

Figure 1.4 shows a general reaction network that has been proposed for the synthesis of higher oxygenates over the modified methanol synthesis catalysts (Cu based) (Hilmen et al., 1998). This mechanism is consistent with the ones proposed by Smith & Anderson (1983), Smith et al (1991) and (Breman et al. 1994; Breman et al. 1995). The individual steps of the mechanistic network can be grouped into several distinct reaction types illustrated as below, including linear and aldol condensation chain growth mechanisms.

a) α addition (linear chain growth):

α addition occurs at the alcohol end of the growing chain to give linear primary alcohols such as ethanol, 1- propanol, 1-butanol. For example,



The alpha addition is a slow step with a large activation energy (140 kJ/mol) while beta addition is faster and has a smaller activation energy (66 kJ/mol) (Smith & Anderson, 1984). Based on the hydrogenation-base bifunctionality of the catalyst, a probable reaction mechanism utilized a nucleophilic attack at the α carbon of an absorbed aldehydic intermediate by a formyl

species (HCO^\ominus) yields a deoxygenated species (Nunan et al. 1988, 1989a). This species subsequently undergoes hydrogenation/dehydration to yield the C_{n+1} alcohol (Fox, Pesa, & Curatolo, 1984). The nature of the C_1 reactive species has not been conclusively identified. Lietti et al.(1992) investigated different oxidation states with C_1 probe molecules, indicating formaldehydes at catalyst surface as the most probable reactant.

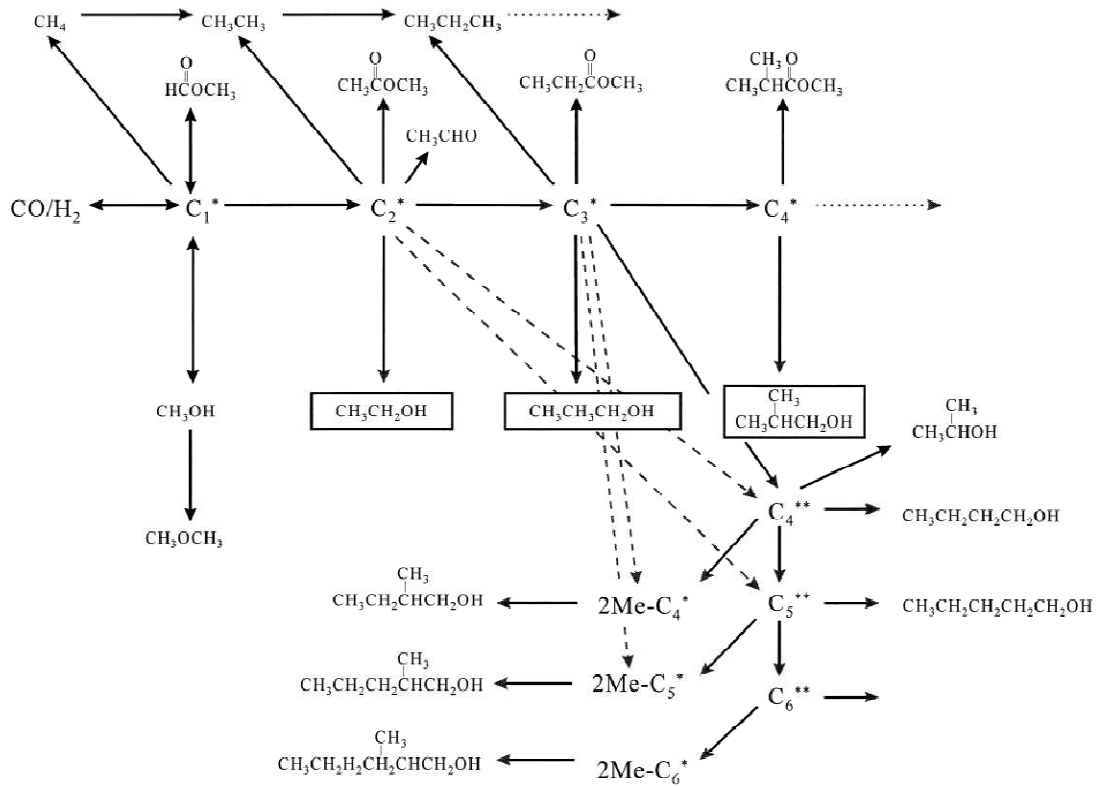
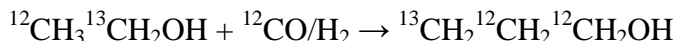


Figure 1.4 Proposed reaction network for methanol and higher alcohol synthesis (Hilmen et al. 1998)

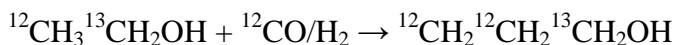
b) β -addition

β -additions include the major β addition between C_1 and C_n ($n \geq 2$) surface species and the minor β addition between C_m ($m = 2,3$) and C_n ($n \geq 2$) surface species. The former results in 1-propanol and branched primary alcohols such as 2-methyl-1-propanol, the latter gives rise to a variety of alcohols such as 1-butanol, 2-butanol, 1-pentanol (Nunan et al., 1988, 1989a). The mechanism of β addition involves two paths, aldol coupling with oxygen retention reversal $\beta(R)$ and aldol condensation $\beta(N)$. Aldol-type coupling reactions of alcohols require both Cu and basic sites (Hilmen et al., 1998).

Aldol coupling with oxygen retention reversal $\beta(R)$: this step involves the retention of oxygen associated with the C_1 fragment and the rejection of oxygen associated with the C_n fragment. In this step, carbon chain growth is dominated by $\beta(R)$ addition wherein the adding C_1 intermediate retains its oxygen. A stoichiometric relationship is presented as below,



Aldol condensation $\beta(N)$: this step involves the retention of oxygen associated with the C_n fragment and the rejection of oxygen associated with the C_1 fragment:



Due to the high C_1 concentration (the methanol concentration is roughly one order of magnitude higher than the concentration of the other alcohols (Majocchi et al., 1998)), it is likely that the $C_n + C_1 \rightarrow C_{n+1}$ processes dominate over the $C_n + C_m \rightarrow C_{n+m}$ steps in the chain growth mechanisms, resulting in isobutanol as a terminal species due to no β carbon in its precursor (Lietti et al., 1992). This has also been observed by Nunan et al. (1988), who claims that of the two types of β additions $\beta(N)$ and $\beta(R)$, oxygen retention reversal $\beta(R)$ dominates the C_2 to C_3 step over the Cs/Cu/ZnO catalyst at high temperature.

1-propanol can be formed both by aldol coupling and by linear chain growth (carbonylation) pathways. 1-butanol is predominately formed by ethanol aldol self-condensation instead of linear chain growth pathways. Isobutanol is formed only by C₁ addition to 1-propanol or propionaldehyde (Nunan et al., 1989a, 1988). Aldol condensation pathways are about eight times faster than linear chain growth on 2.9 wt% Cs-Cu/ZnO/Al₂O₃ catalysts (Hilmen et al., 1998).

Hydrocarbon formation may involve dehydration from the corresponding alcohol (with the corresponding alkyl group as intermediates) and/or a parallel Fisher-Tropsch pathway (Majocchi et al., 1998). A significant increase in ethane formation that has been observed upon ethanol injection in the feed stream confirms that the formation of hydrocarbons via alcohol dehydration is active over the Cu-based catalyst (Majocchi et al., 1998).

It should be noted that before the aldol C-C bond formation can be utilized in the chain growth of higher alcohols from lower alcohols, the single carbon species must be converted to a C₊ oxygenate. This can occur by various chemical mechanisms but one usually dominates over another when different catalysts are used (Klier et al., 1997).

1.2.2.4. Aspects affecting higher alcohols' selectivity

1.2.2.4.1 Temperature

It is well known that the exothermic alcohol synthesis reaction is thermodynamically limited by high temperature. The increase of reaction temperature shift the methanol equilibrium backwards towards the reactants and increase temperature also tends to favor the formation of various side-products that include dimethyl ether (DME) and CH₄ (Li et al. 2004). A strong effect of temperature on the product distribution has been widely observed, an example for a Cu-based catalyst being shown in Figure 1.5.

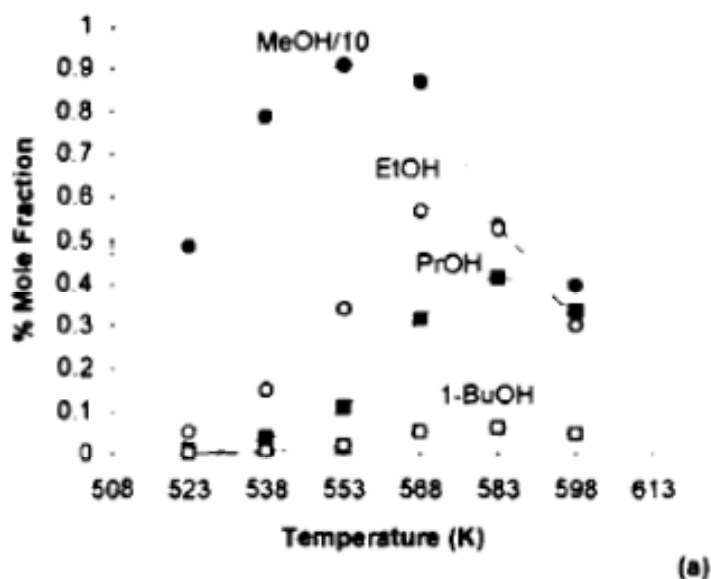


Figure 1.5 Effect of reaction temperature on the alcohol distribution for MAS on Cu-based catalyst (Majocchi et al. 1998).

Within the studied temperature range (225 °C-325 °C) the methanol and C₂₊ linear alcohols selectivities show maxima on increasing the reaction temperature. The formation of branched alcohols and methane (not listed in figure 1.5) also increase with increasing temperature but level off at high temperature. Methanol formation is believed to approach chemical equilibrium with increasing the reaction temperature. Because of the exothermic nature of the reaction, further increasing the reaction temperature can decrease the methanol formation.

The effect of temperature on MAS is similar for different type of catalyst. Mahdavi et al.(2005) investigated the effect of temperature (270 °C-355 °C) on Co containing Cu-based catalyst's activity at constant pressure (4.05 MPa). It was found that increasing temperature from 270 °C to 325 °C significantly increased the activity. CH₄ and C₂₊OH selectivity decreased with temperature slightly, and a maximum in the total alcohol selectivity was observed at 325 °C.

285 °C -300 °C was regarded as a proper range of operation, because the values of the alcohols' selectivity remained constant.

Temperature plays an important role in the selectivity of higher alcohols. It is believed that higher reaction temperature will shorten the catalysts' lifetime and diminish the active surface areas due to bulking of the catalyst. Meanwhile, some oxygenates are not be stable enough and will decompose at temperature as low as 450 °C, which sets an upper temperature limit to the synthesis of alcohols (Xu et al. 1987).

Additionally, when HAS is operated at lower temperatures smaller contents of ketones relative to primary alcohols are expected. Smaller quantities of aldehydes are typically reported among the products of HAS over modified low temperature methanol catalysts than over high temperature methanol catalysts (Forzatti et al. 1991). Majocchi et al.(1998) showed that for Cu based ZnO doped catalysts the lowest viable reaction temperature is 250 °C corresponding to the temperature threshold for the formation of C₂₊ oxygenates.

1.2.2.4.2 Pressure

Generally, the selectivity to mixed alcohols increases with increasing operating pressure. In the normal operating ranges, the higher the pressure at a given temperature, the more selective the process will be to alcohols. For example, Burcham et al. (1998) studied the effect of reaction pressure (varied in the range of 7.6 MPa – 12.4 MPa) on the synthesis rate of isobutanol for a Cs/Cu/ZnO/Cr₂O₃ catalyst. An Increase in reaction rate was found, but the effect was most pronounced for the formation of methanol. Mahdavi et al. (2005) concluded that an increase in pressure had a strong effect on the conversion rate, and therefore, led to an increased total liquid production rate. Additionally, with increasing pressure, the selectivity to higher alcohols increased and selectivity towards methane decreased. However, while high operating pressures

may be desirable, the pressure is often limited primarily by the cost of high pressure vessels, compressors and the energy costs needed to carry out the higher pressure reactions (Stevens and Conway, 1988).

1.2.2.4.3 Syngas flow rate

The syngas flow rate, represented by gas hourly space velocity (GHSV), is a measure of the volume of syngas at standard temperature and pressure passing a given volume of catalyst in an hour's time. Higher space velocity means a shorter contact time. It is commonly observed that the selectivity towards higher alcohols can be enhanced by decreasing the GHSV (longer residence time, higher conversion) (Boz et al. 1994; Majocchi et al. 1998; Forzatti et al. 1991), indicating that the formation of higher alcohols takes place consecutively to the formation of methanol.

Hilmen et al.(1998) compared the effects of space velocity on alcohol synthesis rates and selectivities for 1.2 wt% Cs-Cu/ZnO/Al₂O₃ and 1.0 wt% K-Cu_{0.5}Mg₅CeO_x catalysts. CO conversions were found to increase linearly with decreasing syngas flow rate at low CO conversions, except for when the predominant methanol synthesis approaches thermodynamic equilibrium. C₂-C₃ alcohols' selectivity reached maximum values at intermediate residence times, indicating they are intermediate products that undergo further chain growth. The selectivity towards isobutanol increases monotonically with decreasing syngas space velocity, indicating they are formed in secondary chain growth reactions.

Another example is illustrated by Mahdavi et al.(2005). Increasing the syngas flow rate was shown to have a negative effect on both the catalytic activity and the C₂₊OH selectivity. Majocchi et al.(1998) observed that with increasing GHSV the branched/linear alcohol ratio

slightly decreased. For the short contact times, C₂-C₃ production is favored with respect to the higher oxygenates.

However, (Xu et al. 1987) believed that when the reaction is partially or totally mass transfer controlled, an increase in space velocity will be favorable for the mass transfer of reactants to the core of the catalyst particles and unfavorable for secondary reactions. Since the influence of mass transfer on various reactions is different (more severe for higher alcohols and higher hydrocarbons), an increase of space velocity may be favorable for the synthesis of higher alcohols. This phenomenon was observed with the MoS₂-based catalyst (Xu et al. 1987), where at a high space velocity the selectivity for higher alcohols was higher.

Hence, in order to achieve the optimum higher alcohol to methanol ratios, the optimal GHSV/conversion level will vary with the catalyst type.

1.2.2.4.4 H₂/CO ratio

Overall, the formation of alcohols:



Consequently, the ideal stoichiometrical consumption ratio (H₂/CO) is 2.0. Additionally, formation of other products such as water-gas shift reactions, alkenes or alkanes formations can occur, making the actual ratio of H₂/CO change along the reactor and differ from the one at the inlet value (Xu et al. 1987). Several investigators have reported that the optimum H₂/CO ratio for HAS over various catalysts is below 2 (Forzatti et al. 1991; Smith and Anderson 1983; Herman 2000; Boz et al. 1994). Forzatti et al. (1991) found that for a ZnCrO + 15% Cs₂O catalyst a maximum in the yields of methanol occurs at the molar ratio of 2 and the maximum of higher alcohols is at the molar ratio of 1.

The H₂/CO ratio plays an important role in the formation of higher alcohols. Under constant total pressure, a change in the H₂/CO ratio will change the partial pressure of both H₂ and CO. It is expected that an increase in the hydrogen partial pressure will favor the hydrogenation of the aldehydic intermediates to the corresponding alcohols, thus inhibiting the chain growth to higher oxygenates (Xu et al. 1987). As a result, the gradual enrichment of hydrogen in the reactant mixture causes a progressive increase in the formation of methanol and a decrease in the amounts of both linear and branched higher alcohols. The average carbon atom number of the C₂₊ oxygenates slightly decreases on increasing the H₂/CO ratio. The rate of formation of methane and higher paraffins (for example: ethane) is largely unaffected by the feed composition in the investigated range (Majocchi et al., 1998).

Moreover, it has been found that lower H₂/CO ratio has a negative effect over the conversion of CO and a positive effect over the selectivity to C₂₊ alcohols. In addition, coke formation is unfavorable at higher H₂ partial pressure, resulting in good activity maintenance (Xu et al. 1987). A H₂/CO = 1 has usually been adopted as a reasonable ratio for the investigation of HAS (Mahdavi et al., 2005).

1.2.2.4.5 Addition of alkali metal oxide

It is well known that the catalytic activity of HAS can be promoted by adding an alkali metal oxide, such as Na, K, Cs, Sr, Ba, etc, into a methanol synthesis catalyst (Herman 2000; Forzatti et al. 1991; Fang et al. 2009; Subramani and Gangwal 2008). Vedage et al. (1985) and Sheffer & King (1989) found that catalytic activity upon the addition of group 1A elements increased in the order of Li to Cs. Potassium is regarded as the most cost effective additive, and most research has concentrated on its effect.

The addition of alkali promoters titrate the surface acidity of the catalyst and increase the density of basic sites (Hilmen et al., 1998), thereby facilitates various C-C and C-O bond-forming reactions (Nunan et al., 1988) and suppressing unwanted side reactions such as isomerization, dehydration, coke deposition etc (Subramani & Gangwal, 2008). In CO hydrogenation reactions, it is generally believed that the CO molecules adsorbed dissociatively are responsible for hydrocarbon formation while those adsorbed associatively favor the formation of alcohols (Subramani & Gangwal, 2008). The addition of an alkali promoter can reduce the active sites for dissociative adsorption of CO, thereby decreasing the formation of hydrocarbons.

An optimum amount of alkali doping has been observed, depending on the kind of catalyst used. Methanol and higher alcohol synthesis rates were previously shown to reach a maximum with increasing alkali loading (Nunan et al. 1989; Smith & Anderson 1983; Vedage et al. 1985). Smith & Anderson (1983) and Calverley and Smith (1991) found that the activity for both methanol and higher alcohol production is promoted by the addition of alkali metal oxides up to around 1 wt% while further addition has an inhibiting effect. Smith & Anderson (1983) found that the selectivity to higher alcohols, in particular isobutanol, goes through a maximum as the K loading is increased. Furthermore, (Boz et al., 1994) observed that methanol selectivity increased continuously with increasing K loading from 0 to 5 wt%, mostly at the expense of hydrocarbons, and the selectivity of both higher alcohols and aldehydes reached maxima at a loading of 0.5 wt% K₂O.

Excess amount of alkali may block active sites on the catalyst surface and decrease the BET surface area, leading to activity loss (Smith & Anderson, 1983). At very high Cs concentrations,

alcohol synthesis rates may ultimately decrease, because Cu-metal sites, required for carbon chain growth, can also be titrated by Cs (Hilmen et al., 1998).

To sum up, the amount of alkali required for optimum higher alcohol synthesis depends on the identity of the alkali and on the density of acid sites that require titration on a given catalyst (Nunan et al. 1989).

1.2.2.4.6 Heat transfer rate

As was discussed in section 1.2, reactions which produce alcohols, hydrocarbons and methane are highly exothermic. Excessive heat release from the active pore sites requires a rapid heat transfer rate to prevent temperature runaway, catalyst deactivation and other problems.

Methanol formation is less exothermic than the formation of higher alcohols. Consequently, the equilibrium constant for methanol formation does not decrease as rapidly with increasing temperature as the equilibrium constants for higher alcohol formation. It was demonstrated in section 1.3.3.1 that high temperature is not favorable for the formation of higher alcohols. Thermodynamics constraints may affect the selectivity of the synthesis for many products, such as methanol, water, aldehydes, secondary alcohols, ketones, esters, as well as the overall production of CO₂ (Forzatti et al. 1991). The low heat transfer capacity provided by vapor phase reaction medium may not effectively remove the reaction heat, resulting in decrease of selectivity towards higher alcohols.

Methanol synthesis is frequently done by using a fixed bed reactor design. Most of the researches of HAS are also investigated by using this kind of reactor. An alternative reactor design to improve upon heat management includes slurry phase and bubble column reactors; these have been utilized in methanol synthesis and the HAS researches (Brown et al. 1991;

Roberts et al.1997; Tijm et al. 2001). The advantages of slurry phase reactor applying for higher alcohol synthesis are summarized in the section 1.4.4.

Overall, thermodynamic constraints limit the possible yield of HAS. As in other syngas-to-liquids processes one of the most important issues to HAS is the removal of the considerable heat of reaction. The relationship between heat transfer rate and the synthesis of mixed alcohols has not been examined, although it is well known that these exothermic reactions could benefit from high heat transfer rate.

1.2.3 Advances in the synthesis of higher alcohols

As was discussed in the mechanism section above, there is no β -carbon to assist in converting the C_1 intermediates in order to form ethanol, so C_1 to C_2 step is the slow and rate determining step in the formation of the higher alcohols from synthesis gas (Tronconi et al. 1990). In order to realize a commercial HAS process, substantial research efforts have been applied into developing catalysts and defining operating conditions that produce greater selectivity toward higher alcohols (Fierro, 1993). Approaches to achieve necessary higher space time yields of higher alcohols include developing modified catalysts, injection of lower alcohols into the reactant stream, using catalyst beds in series, and using a slurry phase reactor.

1.2.3.1. Modified Catalysts

The activating character of alkali metal promoters is a function of their basicity. Alkali metals provide a basic site to catalyze the aldol condensation reaction by activating surface adsorbed CO and enhancing the formation of the formate intermediate (Spath & Dayton, 2003).

Cu is known to be the major element for alcohol synthesis, serving as the site for dissociative chemisorption of hydrogen and the associative adsorption of CO (Xu et al. 1987). Fe or Co element is the active site for Fischer-Tropsch (F-T) function of dissociative CO adsorption (C-C

chain growth) and hydrogenation. Fang et al. (2009) believed that the production of higher alcohols requires the synergetic functioning of both Fe (or Co) and Cu, which means that a metallic copper atom should be adjacent to an iron atom. Thus, the modification of this kind catalyst requires precise preparation conditions to achieve a homogeneous distribution of the metals.

Another approach made to increase the productivity of isobutanol formation from synthesis gas is to combine ZnO with an “isosynthesis” component, i.e. ZrO₂, and promote the catalyst with a redox oxide and a strong base. Isosynthesis is a high pressure process directed toward converting synthesis gas to aliphatic branched hydrocarbons, especially C₄ hydrocarbons. High productivities and selectivities for isobutanol were observed with these catalysts at a high reaction temperature and high pressure. For example, W. Falter (1994) achieved an isobutanol productivity of 630 g/L_{cat}/h over a K/Pd promoted Zr/Zn/Mn catalyst at a temperature of 427 °C and 25 MPa (Herman 2000). A disadvantage of these catalysts is that the high reaction temperature increases the productivity of hydrocarbons along with that of the alcohols, decreasing the alcohol selectivity.

The 3d transition metals, in particular F-T elements such as Co and Ni, have also been found to be effective promoters for MoS₂ catalysts in enhancing the alcohol yields and C₂₊OH selectivity. A Ni promoted MoS₂-based catalyst showed very high yield of total alcohols (0.40 g/ml cat/h), high yield of C₂₊ alcohols (0.16 g/ml cat/h) as well as a up to 2000 hours of stable performance (Fang et al., 2009).

Based on the fact that molybdenum carbide exhibits some properties similar to MoS₂, and the fact that the addition of 3-d transition metals (such as Co, Ni, Rh, Pd) is able to improve the catalytic activity and selectivity of C₂₊ alcohols over MoS₂-based catalysts, (Xiang et al. 2007)

developed a series K/Co/ β -Mo₂C catalysts and investigated their catalytic performance. Their results showed that the activity and selectivity of higher alcohols is significantly influenced by the Co/Mo molar ratio, and that the cobalt promoter exerted strong promotion for carbon chain growth, especially for the C₁OH to C₂OH step. Mo₂C catalysts promoted with K₂CO₃ have been found to greatly enhance the selectivity to linear C₁-C₇ alcohols. Compared to Cu-based methanol synthesis catalysts, molybdenum Carbide catalysts possess much higher catalytic activity, higher selectivity towards hydrocarbons (consisting of 80-100% olefins), higher selectivity towards CO₂ (around 50%), as well as a high yield of higher alcohols (Fang et al., 2009).

Hilmen et al. (1998) used a number of K-Cu_yMg₅CeO_x catalysts for CO hydrogenation reactions to form higher alcohols. K promoted Cu_{0.5}Mg₅CeO_x catalysts are active for isobutanol synthesis and give products with a high alcohol-to-hydrocarbon ratio at a relatively low temperature (583K) and pressures (4.5MPa). The addition of small amounts of Pd to K-Cu_{0.5}Mg₅CeO_x demonstrated that Pd promoted isobutanol synthesis selectivity and rates only at high CO₂ concentrations, suggesting that Pd resisted oxidation, retained its hydrogenation activity and weakened the inhibitory effects of CO₂.

1.2.3.2. Addition of Lower Alcohols

Since the C₁ to C₂ step that leads the conversion from methanol to ethanol is the bottleneck to forming isobutanol in high space time yields, injection of ethanol or n-propanol into the synthesis gas stream entering a fixed-bed continuous flow reactor has been studied in order to react directly with the C₁ intermediate, leading to the formation of the higher alcohols (Herman 2000). In principle, the addition of lower alcohols should increase the probability of the intermediates which further go through carbon chain growth thus eventually enhancing the

formation of higher alcohols (isobutanol) kinetically. The net formation of methanol may be reduced to zero by recycling a sufficient amount of methanol to satisfy the equilibrium relationship for its synthesis (Mawson, McCutchen, Lim, & Roberts, 1993). It has been shown through isotope labeling that at 280 °C with the injection of ethanol nearly all of the 1-butanol, 2-butanol, and 2-methyl-1-propanol observed in the product were formed. Additionally, it increased the yields of 1- propanol by a factor of 18.6 and of methyl acetate by a factor of 47 (Nunan et al., 1988). These results clearly support the conclusion that the pathway for the formation of C₃₊ oxygenates includes ethanol. Similar research was conducted by Hilmen et al.(1998). Adding ethanol or 1-propanol was shown to significantly enhance the selectivity towards higher alcohols. Similarly, Majocchi et al.(1998) also found a general increase in the productivity of the various reaction products after adding ethanol into the feed gas mixture, indicating that ethanol plays a key-role in the chain growth process to higher oxygenates. An increase in the amount of ethane has also been observed during ethanol addition, indicating that ethanol may go through dehydration step leading to ethylene followed by a rapid hydrogenation of the olefinic intermediate.

Additionally, Nunan et al.(1988) used ¹³C-NMR characterization method to investigate the reaction mechanism on a Cs doped Cu-based catalyst by injecting methanol and ethanol with abundance of ¹³C in specific positions respectively. They found that lower alcohols were incorporated into the synthesis of higher alcohols and proposed the “aldol coupling with oxygen retention reversal” reaction pathway. Details of this pathway are discussed in the section 1.2.2.3.2.

The addition of alcohols to the MAS process is a promising pathway, although industrially it would require an external source or extensive recycling.

1.2.3.3. Dual-bed reactor

In addition to catalyst development, reactor design also have potentials for increasing the HAS yield and enhanced selectivity towards higher alcohols. Methanol synthesis is an extremely exothermic reaction and the productivity of methanol is severely limited by increasing the reaction temperature. Herman (2000) argued that methanol has an unfavorable equilibrium constant for high temperature operation, and increasingly decomposes back to synthesis gas as temperature is increased. However, the productivity of $C_{2+}OH$ increases with increasing the reaction temperature. Based on these thermodynamic features, the concept of a dual-bed reactor has been proposed and has been investigated for different catalyst combinations and reaction conditions (Beretta et al. 1995). The most common scenario to date is to maximize the formation of methanol in the first bed by using Cu-based catalyst at lower temperature, followed by a second catalyst bed equipped with high temperature catalyst promoting the subsequent carbon chain growth step.

Sequential beds of Cs-Cu/ZnO/Cr₂O₃ catalysts with the top bed at 325 °C and lower bed at 340 °C were tested in a single down flow reactor under higher alcohol synthesis conditions (Burcham et al., 1998). The upper, low-temperature, bed provided oxygenates (i.e. methanol, ethanol, 1-propanol) to the second, higher temperature, bed where they were converted by a chain growth mechanisms to higher alcohols. This configuration produced a greater yield isobutanol (202 g/kg_{cat}/h) than either catalyst in a single bed configuration. Beretta et al. (1995) also reported a doubled productivity of isobutanol by using the dual bed reactor configuration as compared with using the same Cs/Cu/ZnO/Cr₂O₃ catalyst in a single configuration. A kinetic model for methanol synthesis from H₂/CO mixtures over Cu/Zn oxide-based catalysts was developed and was shown to be a useful predictive tool for optimizing the relative amounts of the catalyst in each bed to maximize $C_{2+}OH$ formation (Smith et al. 1990; 1991). They also argue

that kinetic models can be used to optimize the reaction conditions, such as the size of each bed, pressure and space velocity of syngas.

1.2.3.4. Slurry Phase Reactor

Fang et al. (2009) believed that the highly exothermic nature of mixed alcohol synthesis result in the generation of hotspots, facilitating the carbon deposition and the sintering of active materials. Therefore, rapid removal of the reaction heat is a major consideration for the design of HAS reactors. It has been shown that carrying out the synthesis of higher alcohols in a slurry phase reactor rather than a fixed bed configuration has several advantages:

1. A high heat transfer rate can be achieved in a slurry phase reactor (Herman 2000). Syngas conversion and selectivity towards higher alcohols could be enhanced theoretically by using slurry phase reactor.
2. Slurry phase reactor has good temperature control and greater thermal uniformity. This aspect effectively prevents hot spots that induce sintering and deactivation of catalysts (Herman, 2000).
3. It is possible to add more catalysts into the slurry phase reactor on-line and withdraw portions of used catalyst, which can increase plant on-stream days and decrease downtime (Herman, 2000).
4. Slurry phase reactor has a smaller pressure drop, compared to fixed bed reactor.
5. Fine powder catalysts used in slurry phase reactor can enhance the diffusion and the reaction rate.

The synthesis of higher alcohols using slurry phase reactor has been investigated at the pilot scale (Air Products and Chemicals, LaPorte, TX). A 0.45 m diameter and 12.2 height stainless-steel reactor was designed to operate at up to 12.5 MPa and 350 °C. The charge to the reactor

consisted of 502 kg of Cs-promoted Cu/ZnO/Al₂O₃ catalyst in a 40 wt% oil slurry was utilized. The productivity to isobutanol was found in the range of 17-26 g/kg_{cat}/h. Moreover, the slurry phase reactor can also be utilized in combination of the injection of lower alcohols in order to further enhance the higher alcohol selectivity.

1.2.3.5. Supercritical Phase Reaction

A supercritical fluid (SCF) is any substance whose temperature and pressure is higher than its critical point. At the critical point, the two fluid phases (liquid and vapor) become indistinguishable. Above the critical point no phase change is possible. SCFs are widely accepted as a unique and sometimes superior medium for chemical reactions, facilitating single phase operation while possessing a high diffusivity and low viscosity. Utilizing SCFs as reaction media was considered shortly after their discovery. Interest in utilization of SCFs flourished in the 1980s, spreading in industries like food, chemicals, oils, pharmaceuticals, etc (Johnston, 1994).

The unique properties of SCFs offer enhancement in heat transfer and mass transfer for reactions, especially for heterogeneous reactions. By facilitating single phase operation and possessing gas-like viscosity and liquid-like diffusivity SCF can enhance the in situ extraction of non-volatility/low volatility products from catalysts pores, diminish the limitation of transport in reactions, and integrate desorption and separation processes (Baiker, 1999; Subramaniam, 2001; Elbashir et al., 2010). The advantage of being able to easily change the chemical reaction media properties (e.g. density) near the critical point by slightly tuning the operation temperature and/or pressure makes SCFs favorable.

Supercritical fluids have been used in many heterogeneous catalysis reactions, including alkylation, amination, cracking, disproportionation, esterification and Fischer-Tropsch synthesis. Baiker (1999) summarized the benefits brought by proper use of supercritical fluids in

heterogeneous catalysis, including a) enhancing the reaction rate, b) enhancing mass and heat transfer, c) increasing catalyst lifetime and regeneration, d) tunability of solvent properties by pressure and co-solvent, e) facilitating easier separation, f) offering unique opportunities in catalyst preparation.

In hydrocarbon synthesis with heterogeneous catalysis, Subramaniam (2001) demonstrated the ability of SCF as reaction medium to extract and dissolve the low-volatile hydrocarbons (heavy hydrocarbons) from catalysts pore surface. This property of SCFs gives rise to higher pore active site accessibility, better coking resistance, and increased primary product selectivity. Additionally, results in the hydrocarbon synthesis study with SCF media demonstrated that the selectivity to methane was significantly suppressed (Fan and Fujimoto, 1999; Huang et al., 2004). It is recognized that hot spots in the catalyst bed can result in enhancement of methane selectivity, and the dense supercritical media can offer better axial thermal uniformity than FTS in gas phase, which can help reduce hot spots (Van Der Laan and Beenackers, 1999; Huang, 2003; Fan and Fujimoto, 1999; Huang et al., 2004).

Considerable and intensive effort has been expended in exploring the application of supercritical fluids in Fischer-Tropsch synthesis (Yokota and Fujimoto, 1989; 1991(a); 1991(b); Jacobs et al., 2003; Huang, 2003; Huang et al., 2004; Elbashir et al., 2005). Yokota and Fujimoto (1989) have reported that the F-T synthesis reaction in a supercritical fluid has unique characteristics for either the reaction rate or the product distribution. Heat transfer in the supercritical phase was also found more effective than in the gas phase and close to that in the liquid phase. The enhanced in situ extraction of primary products when using SCF as reaction media has also been shown by a number of studies (Huang, 2003; Bukur et al., 1997; Lang et al., 1995; Yokota and Fujimoto, 1991; Fan et al., 1999). Figure 1.6 shows the olefin and paraffin

yields for each carbon number varies with different carbon number in SC-FTS, liquid phase FTS (LP-FTS) and GP-FTS (Fan et al., 1999). The decrease in the olefin content with increasing carbon number in SCF-FTS is attributed to the well balanced desorption and the diffusion of products, resulting in suppression of the hydrogenation of primary olefins. However, the chain growth probabilities were similar for gas phase, supercritical hexane phase and liquid phase's operation, which suggest that the supercritical n-hexane had little effect on the reaction itself (Yokota and Fujimoto 1991).

Similar to Fischer-Tropsch synthesis, both higher alcohol formation and methanation are all exothermic. Fang et al. (2009) believed that the use of supercritical synthesis fluid medium could solve most the problems for both methanol and higher alcohol synthesis, such as alleviating the “hotspot” phenomena. By using a suitable supercritical solvent, the equilibrium for methanol synthesis could shift beyond the thermodynamic limitation under traditional reaction conditions, and the selectivity for higher alcohol synthesis could also be improved.

Higher selectivity toward $C_{2+}OH$ can be expected when applying a properly selected SCF medium into the process. Liu, Qin, and Wang (2001) calculated the effects of several solvents on the equilibrium alcohol yield in alcohol synthesis using the SRK equation of state. These calculated results showed that n-hexane and n-heptane enhanced the conversion to methanol at a temperature of 200 °C to 210 °C (lower than their critical points) and the pressure above 8 MPa. C_{10} to C_{16} alkanes as supercritical media promoted higher alcohols formation at higher temperatures. A experimental exploration was made by Jiang, Niu, and Zhong (2001); they utilized a mixture of C_{10} to C_{13} normal alkanes as their supercritical media and investigated the synthesis of higher alcohols over a Zn-Cr-K catalyst at 400 °C, syngas pressure 7.5 MPa, and GHSV 1700 h^{-1} . They claimed that the introduction of SCF increased the selectivity of ethanol

and n-propanol from 1-3% to 6-12%, and that methanol selectivity was decreased by 30%. However, in this study the partial pressure of reaction media was much lower than the critical point, and the molar ratio of the medium to the reaction is very low making the phase behavior of the reaction mixture very different from the reaction media.

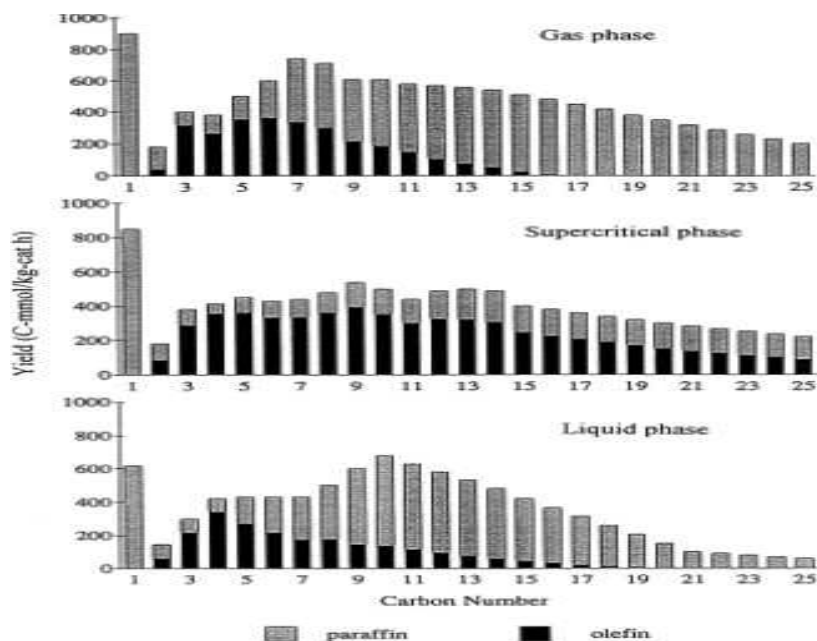


Figure 1.6 Olefin and paraffin yields versus carbon number for FTS reactions in various phases over Ru/Al₂O₃ catalyst (Fan and Fujimoto, 1999).

1.3 Summary

Generally, as one of the alternative routes to the petroleum pathway, the mixed alcohol synthesis offers a compelling alternative to petroleum based fuels and chemicals. However, the process suffers from the low selectivity to higher alcohol. The current focus of the higher alcohol synthesis is on the enhancement of higher alcohols' selectivity and productivity. Typically,

higher alcohol/methanol weight ratios in the range 30:70 – 50:50 represent the industrial target (Forzatti et al. 1991).

Our group has extensive experience in SC-FTS. Previous investigations into SCF-FTS have suggested the following advantages: (1) in situ extraction of heavy hydrocarbons from the catalyst due to high solubility in the supercritical phase (Elbashir et al., 2010); (2) elimination of interphase transport limitations, thus promoting reaction pathways toward the desired products (Elbashir et al., 2005); (3) enhanced desorption of primary products prior to their undergoing secondary reactions promotes a high α -olefin selectivity (Huang and Roberts, 2003); (4) superior heat transfer compared to gas-phase reaction, resulting in more long chain products (Huang and Roberts, 2003). Studies conducted by other group (Ginosar & Subramaniam, 1994; Yokota & Fujimoto, 1989, 1991; Yokota et al., 1991) have consistently shown that supercritical reaction media enhance catalyst lifetime, promote heat and mass transfer and improve the selectivity to desired products.

The purpose of this study is to investigate the effect of supercritical media phase on the synthesis of methanol and higher alcohols, and to develop novel reaction operating strategies for the catalytic conversion of syngas to higher alcohols. The project objectives are to investigate the effect of temperature, operating pressure, reaction media, and syngas ratio on the CO conversion, product distribution, selectivity to CH_4 and higher alcohols as well as productivity to mixed alcohols in a fixed bed reactor.

Chapter 2 **Supercritical Fluids and its Application in Heterogeneous Catalytic Reactions**

In 1869, Thomas Andrews first recognized the presence of the critical point of CO₂, which gave birth to a new world of critical phenomena and supercritical fluid science (Huang, 2003). Later in 1879, Hannay and Hogarth found that supercritical ethanol was able to dissolve inorganic salts which are insoluble in liquid ethanol (Huang, 2003). More interestingly, they found that they were able to manipulate the solubility of the solutes by changing the pressure. By the mid 1980s, research on new applications of SCFs shifted towards more complex and valuable substances that undergo a much broader range of physical and chemical transformations (Elbashir, 2004). Since then, the tunable solvent characteristics of supercritical fluids has been widely recognized and utilized in various areas, including extraction, dry cleaning, gas chromatography and chemical reactions, etc.

2.1 Background on the application of supercritical fluids in heterogeneous reactions

Figure 2.1 presents a pressure versus temperature phase diagram of a pure substance, which illustrates the existence of a supercritical fluid region. The areas where the substance exists as a single solid, liquid or gas phase are labeled, as is the triple point where the three phases coexist. At the critical point, the densities of the two phases become identical and the distinction between the gas and the liquid disappears. The critical point has pressure and temperature co-ordinates on the phase diagram, which are referred to as the critical temperature, T_{cr} , and the critical pressure, P_{cr} . The region, in which temperature and pressure are both above the critical point, is called the supercritical region and the fluid located in this supercritical region is called a supercritical fluid (Huang, 2003).

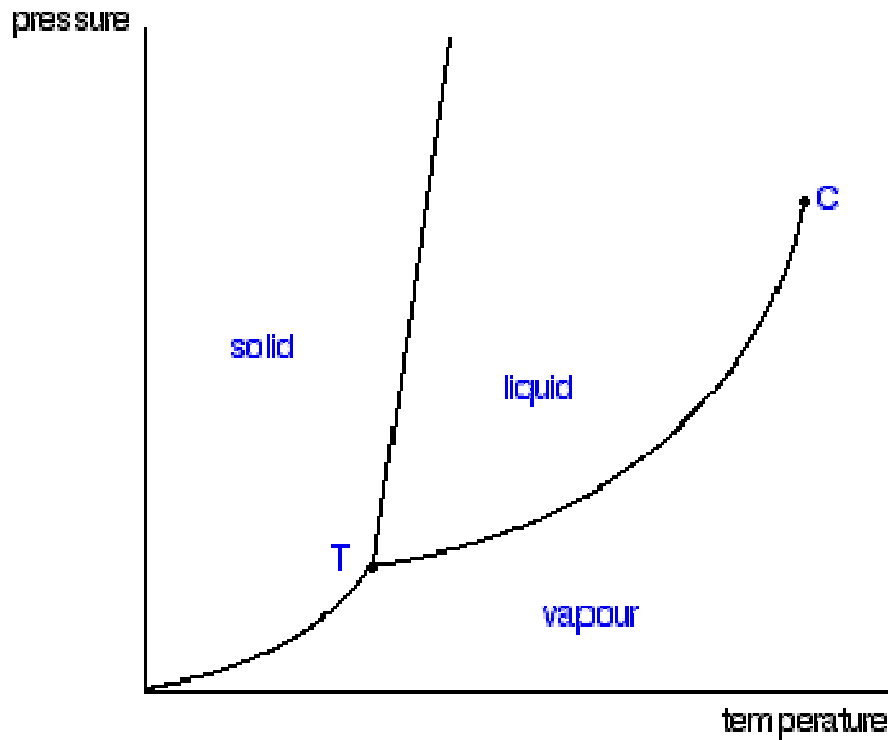


Figure 2.1 Pressure-temperature schematic diagram for a pure fluid showing the supercritical region path

Table 2.1 Comparison of density and transport properties of CO₂ in gas, liquid and supercritical phases (Taylor, 1996)

Property	Gas	Liquid	Supercritical
Density (kg m ⁻³ *10 ⁻³)	10 ⁻³	1.0	0.7
Viscosity (kg m ⁻¹ s ⁻¹ *10 ⁵)	10 ⁻¹	10	5
Diffusion coefficient (m ² s ⁻¹)	10 ⁻⁵	10 ⁻⁹	10 ⁻⁷

Many physical properties of a supercritical fluid are intermediate between those of a liquid and a gas (Schmitt and Reid 1988; Sengers 1991; Huang 2003). This is particularly true for density dependent properties of fluids, which influence mass and heat transfer (diffusivity, viscosity, thermal conductivity, heat capacity). Table 1.1 provides a rough comparison of the magnitude of

some of these properties for liquids, gases, and supercritical fluids in the near critical region. The unique property of an SCF is its pressure-dependent density, which can be continuously adjusted from that of a vapor to that of a liquid (Baiker, 1999; Huang, 2003). In the Vicinity of the critical point (1.05-1.2 T_c and 0.9-2.0 P_c), fluids are highly compressible, and their density and transport properties can be continuously varied from gas-like to liquid-like values via relatively small variations in pressure (Subramaniam, 2001). These unique properties of supercritical fluids can cause that compounds which are insoluble in a fluid at ambient conditions become soluble in the fluid at supercritical conditions (McHugh & Paulaitis, 1980), or conversely, compounds which are soluble at ambient conditions can become less soluble at supercritical conditions (Armellini & Tester, 1993).

The utilization of supercritical fluids (SCF) have been thoroughly reviewed, including the use of SCF extraction technology in chemical separation processes (Subramaniam and McHugh 1986; Penninger et al. 1985), and the use of a SCF solvent as a reaction medium (Baiker, 1999; Elbashir et al., 2010; Subramaniam & McHugh, 1986; Subramaniam, 2001). Supercritical fluids have been increasingly used as solvents for separations and reaction in the chemical, food, pharmaceutical and biochemical industries. They offer many advantages over traditional solvents: (1) the solvent power of SCFs for dissolving nonvolatile substances approach that of conventional solvents due to liquid-like densities; (2) the low viscosity and high diffusivity of SCFs result in superior mass transfer characteristics compared to liquids; (3) the surface tension of the SCFs is low enabling easy penetration into the pores of a solid matrix (catalyst) for extraction of nonvolatile materials from the pores; (4) gases are completely miscible with SCFs resulting in high concentrations compared to that in liquid solvents; (5) the high compressibility of SCFs near the critical point induces large changes in density with very small changes in

pressure and temperature enabling separation of dissolved material from the SCF easily and completely (Sengers 1991; Huang 2003).

2.2 Application of SCFs in heterogeneous catalytic reactions

As briefly mentioned in Chapter 1, SCFs possess great potential as reaction media in heterogeneous catalytic reactions. Several opportunities present themselves in SCFs including: the ability to dissolve gases and liquids in one phase; the elimination of external film resistances; the minimization of internal pore-diffusion limitations; enhanced heat transfer from the catalyst surface and in-situ extraction of coke precursors. As a result, proper use of supercritical fluids in heterogeneous catalysis can enhance the catalyst activity, control selectivity and increase catalyst lifetime (Baiker, 1999).

2.2.1 Activity Enhancement

A significant part of the effect of pressure on the reaction rate in the supercritical region is attributed to the thermodynamic pressure effect on the reaction rate. Other reasons such as enhanced mass transfer or higher reactant solubility, can also contribute to the increase in the reaction rate (Baiker, 1999). Another promoting factors of SCFs may be attributed to the fact that reactions can be performed homogeneously in the mixture critical regime and, thus, better promote intimate contact between the reactants and the catalyst (Subramaniam & McHugh, 1986).

An example coming from Fischer-Tropsch synthesis showed that SCFs help to balance the rate of coke formation and the rate of heavy product deposition, thereby stabilizing the catalyst activity (Huang, 2003). In conventional reaction media, the coke and heavy products accumulation results in progressively increasing diffusion limitations by pore-mouth plugging. Because the coke precursor compounds and heavy products have low volatilities in gas phase

reaction environment, very little of these oligomers is desorbed from the catalyst, thereby causing the oligomers to accumulate in the catalyst pores (Huang and Roberts 2003). The adsorbed oligomers can undergo further transformation to consolidated coke, leading to catalyst deactivation. When the reaction occurs in a liquid phase, the oligomers may be dissolved by the reaction medium. However, pore diffusion limitations hinder the transport of the extracted oligomers out of the catalyst pores. Hence, the optimal reaction medium would be one that has liquid-like densities to solubilize (i.e. desorb) the coke precursors and gas like transport properties to effectively transport these coke species out of the catalyst pores. Supercritical fluids media may be pressure-tuned to possess such an optimum combination of fluid properties. The effective in situ removal of the coke precursors by SCFs media would mitigate coke buildup and pore diffusion limitations, therefore improving the catalyst activity (Huang, 2003).

2.2.2 Control of Selectivity

For a network of parallel or competing reactions, the thermodynamic pressure effect on each of the individual rate constants may be different due to different activation volumes (Baiker, 1999). Thus, increased pressure may favor one of the reactions over the others. This offers some potential to enhance the selectivity to the desired product by operating at the appropriate pressure and temperature, where the desired reaction is favored compared to the unwanted side reactions (Baiker, 1999; Huang, 2003). Under supercritical conditions the reaction mixture can be a single phase, which allows an independent control of the reaction parameters, such as temperature, pressure, and concentrations. Further possibilities for selectivity control are linked with tunable solubility, tuning of solute-solvent interactions (change of local density, clustering) and the use of cosolvents which through specific interactions with a transition state or a product can alter rates and product distributions (Baiker, 1999; Dillow et al., 1997).

2.2.3 Enhanced Mass and Heat Transfer

In heterogeneous catalysis, transport properties such as diffusivity, viscosity, and thermal conductivity are crucial for a reaction system. A well-known advantage of supercritical fluids compared to ordinary liquids is that overall diffusion coefficients in supercritical fluids are higher than that in liquids by the elimination of multiple phases, which may exist in multicomponent systems under ordinary conditions (Huang, 2003). This results in significantly enhanced mass transfer under supercritical conditions. The viscosity of a supercritical fluid is comparable to that of the gas at the same temperature, but the density is at least 2 orders of magnitude higher. Because of the greater diffusivities and lower viscosities than liquid, mass transfer controlled liquid reaction may be accelerated by working under supercritical conditions. Supercritical fluids possess significantly higher thermal conductivity than corresponding gases and consequently heat transfer is enhanced in these media. This effect can be utilized for better heat removal in highly exothermic gas-phase reactions, where careful temperature control is essential for selectivity and product stability (Baiker, 1999).

2.2.4 Catalyst Lifetime and Regeneration

As mentioned in section 2.2.2, supercritical fluids exhibit considerably higher solubility than corresponding gases for heavy products which may act as catalyst blocking agents and thereby deactivate catalyst. This deactivation may be suppressed by changing reaction conditions from gas phase to dense supercritical media (Ginosar & Subramaniam, 1994). Furthermore, enhanced diffusivity can accelerate the transfer of poisons from the internal and external catalyst surface (Baiker, 1999). Regeneration of catalyst deactivated by coking can be accomplished by extracting the carbonaceous deposits from the catalyst surface.

As emerges from the discussion above, the potential of supercritical fluids can be realized in various ways for heterogeneous catalytic reactions. Many heterogeneous catalytic reactions have been investigated under supercritical fluid medium conditions, including alkylation, amination, cracking, hydrogenation and Fischer-Tropsch synthesis etc (Baiker, 1999).

Chapter 3 **Supercritical Hexanes as a Reaction Medium for Mixed Alcohol Synthesis in a Continuous Fixed Bed Reactor**

Abstract

Mixed alcohol synthesis (MAS) from syngas involves an overall reduction in the number of moles (i.e. volume reduction) and is highly exothermic. As such, the high-pressure, dense-phase solvent conditions of a supercritical reaction medium affords opportunities to enhance the reactions via Le Chatelier's principle and to improve heat transfer relative to gas phase operation due to the improved heat transfer capacity of the supercritical fluid (SCF). The effect of solvent on the reaction performance of mixed alcohol synthesis under supercritical conditions was studied in a fixed bed reactor. Hexanes was chosen as the solvent due to the fact that its critical temperature and pressure are close to the reaction conditions for mixed alcohol synthesis. The catalyst used was a 0.5 wt% K promoted Cu based mixed metal oxide catalyst. Investigations were performed in order to study the effect of the supercritical reaction medium on the production of C₁ to C₄ alcohols in the liquid product. The results illustrated a notable reduction in the CH₄ selectivity due to the enhanced heat transfer in the supercritical hexanes medium while this solvent medium also facilitated the extraction of alcohols, especially methanol, from the catalyst pores. As such, the formation of mixed alcohols is promoted by the presence of the supercritical hexanes medium.

Keywords: *Mixed alcohol synthesis; supercritical fluid; supercritical reaction media; copper catalyst*

3.1 Introduction

There remains considerable interest in the synthesis of methanol and higher alcohols (referred to mixed alcohols) from syngas, particularly give their potential in view of its applicability as an alternative fuel, fuel additives and especially as a raw material for various chemicals.

The synthesis of methanol and higher alcohols from mixtures of hydrogen and carbon oxides using mixed metals and metal oxides has been investigated since 1923(Tijm et al., 2001). Cu based catalysts, such as Cu/ZnO/Al₂O₃ or Cu/ZnO/Cr₂O₃, have been widely used in the methanol synthesis industry(Fang et al., 2009; Gerber, White, & Stevens, 2007; Herman, 2000; Stelmachowski & Nowicki, 2003; Wender, 1996). When promoted with alkali, such as Li, K and

Cs, the Cu based catalysts demonstrate a certain ability to produce higher alcohols. Compared to pure methanol, mixtures of methanol and higher alcohols exhibit several advantages as fuel additives, including 1) low tendency towards phase separation in the presence of water (Bromberg & Cheng, 2010; Forzatti et al., 1991); 2) higher octane blending characteristics (Gautam et al., 2000; Gautam & Martin II, 2000); 3) good compatibility with the materials employed in the existing automobile fuel system (Bromberg & Cheng, 2010), etc. Given the Open Fuel Standard Act of 2011 which advocated the use of flexible fuel vehicles, mixed alcohols are receiving renewed attentions as a promising alternative fuel to gasoline, thereby bringing broader research interests to the synthesis and utilization of mixed alcohols.

Similar to Fischer-Tropsch synthesis (FTS), which is another means of converting syngas to transportation fuels and other chemicals, mixed alcohol synthesis is highly exothermic and its performance is promoted by high pressure. Fujimoto's group pioneered the study of FTS under supercritical fluid conditions and elucidated several characteristic features of this type of operation, including effective heat management, and mass transfer, and improved accessibility of the catalytic sites due to extraction of high boiling products (Fan & Fujimoto, 1999; Fan, Yokota, & Fujimoto, 1992; Yokota & Fujimoto, 1989, 1991; Yokota et al., 1991). These benefits have been attributed to the unique properties of the supercritical reaction media which are intermediate to those of a liquid or a gas. The density, while is less than that of a liquid, is remarkably higher than that of a gas. The diffusivity, while lower than that of a gas, is significantly higher than that of a liquid. These unique-characteristics of supercritical fluids provide several motivating reasons for considering SCF reaction media in fixed bed mixed alcohol synthesis.

Supercritical fluids have been previously employed in some early studies for methanol and mixed alcohols synthesis. Liu et al.(Liu et al., 2001) calculated the equilibrium conversions of methanol synthesis under different supercritical fluid reaction media conditions by using Soave-Redlich-Kwong equation of state. Their results showed that the addition of proper solvents, such as n-hexane and n-heptane, could provide a solvent effect on the reaction beyond the simple dilution effect, therefore improving the CO conversion. Jiang et al.(Jiang et al., 2001) have tested a mixture of C₁₀ – C₁₃ alkanes as a reaction medium for the mixed alcohol synthesis over a Zn-Cr-K catalyst in a fixed bed reactor. The partial pressure of reaction medium was kept at 1.78 MPa and a syngas partial pressure at 7.5 MPa. Although the partial pressure of reaction solvent is much lower than the critical points of reaction media, the effect of having added this solvent was observable despite the fact that the operation conditions are well below the critical point of the overall reaction medium. An enhancement in CO conversion was related to the pressure dependence of the reaction rate coefficient. The introduction of the reaction medium was believed to promote the carbon chain growth and change the product distribution. Reubroycharoen et al.(Reubroycharoen, Yoneyama, Vitidsant, & Tsubaki, 2003) utilized 2-butanol as a reaction medium to improve the methanol synthesis. They found that the use of 2-butanol as reaction medium improved the CO conversion and the product distribution. These improvements were attributed to not only the better heat and mass transfer but also the catalytic solvent effect that 2-butanol played in the formation of methanol as an intermediate. Zhang et al.(Zhang, Li, & Zhu, 2006) have investigated supercritical phase methanol synthesis in a three-phase slurry reactor using n-hexane as a reaction medium. They believed that the use of n-hexane as a supercritical medium enhanced the rapid removal of products out of the reaction system, thereby overcoming the inherent reaction equilibrium and enhancing the conversion of reactants.

This paper presents the results of a series of investigations in which supercritical hexanes was employed as a reaction medium for MAS in a continuous, high pressure fixed-bed reactor using a K promoted Cu-based catalyst (0.5 wt% K doped Cu/ZnO/Al₂O₃). The reaction pressures (4.5-20 Mpa) employed in this study provided the ability to ensure that the partial pressure of solvent was sufficiently high to provide liquid like densities in the supercritical reaction medium. The effect of supercritical hexanes on the CO conversion, CO₂ and CH₄ selectivity, and especially mixed alcohols productivity and distribution are discussed in detail. In addition, the effect of temperature (200 °C to 300 °C) on this MAS system was examined under both supercritical phase and gas phase conditions.

3.2 Experimental Section

3.2.1 Catalyst preparation

The catalyst used in this study is a potassium promoted copper based zinc oxide and alumina catalyst (0.5 wt% K promoted Cu/ZnO/Al₂O₃). A Cu/Zn/Al mixed nitrate salt solution was first prepared at a mass ratio of 58:24:18. The single phase precursor was prepared by the simultaneous addition of the nitrate salt solution and a 1.0 M K₂CO₃ solution dropwise to a 1L flask, which was initially filled with 200 ml of deionized water at 80 °C. Continuous stirring and a pH of 7 were maintained during the addition of the mixed metal salt solution. After subsequent aging for an hour, the precipitate was decanted, and then washed three times with deionized water at 80 °C. The filter mass was dried at ambient pressure at 80 °C for 24 hours. The dried precipitate was then ground, followed by stepwise calcinations to 350 °C to give the corresponding mixed oxides. Before doping with potassium, the total pore volume was determined by adding deionized water into the mixed oxides until it formed a slurry paste, followed by drying. Equal amounts of 0.025 M K₂CO₃ solution was added into the dried mixed

oxides in order to disperse potassium uniformly within of the pore structure. The paste was then dried at ambient pressure at 80 °C overnight. This process may be repeated several times in order to reach the required loading of K₂O. Finally, the dried powder was recalcined in air by heating at a rate of 5 °C/min up to 350 °C and then held for 4 hours.

3.2.2 Catalyst characterization

BET surface area of catalysts were determined by N₂ adsorption at -196 °C using a Quantachrome NOVA 2200e surface area analyzer, and powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 advanced diffractometer using Cu K α radiation.

A summary of the BET measurement of the catalyst is shown in Table 3.1. The BET surface area of the used catalyst is lower than that of the unreduced catalyst (19.7 m²/g versus 26.0 m²/g). However, the pore volumes of the catalysts are nearly identical before reduction and after reaction. A decrease in pore radius has been observed after the reaction (40.0 Å versus 30.2 Å). The diffraction peaks in XRD patterns demonstrate the primary phase of the copper in the unused catalyst is CuO while the primary phase after reaction is Cu, as shown in Figure 3.1.

Table 3.1 Physical-chemical properties of catalysts

	0.5 wt% K promoted Cu/ZnO/Al ₂ O ₃ catalyst	
	Before reduction	After reaction
BET area (m ² /g)	26.0	19.7
Pore volume (cm ³ /g)	0.1	0.1
Pore radius (Å)	40.0	30.2
Phase of copper detected by XRD	CuO	Cu

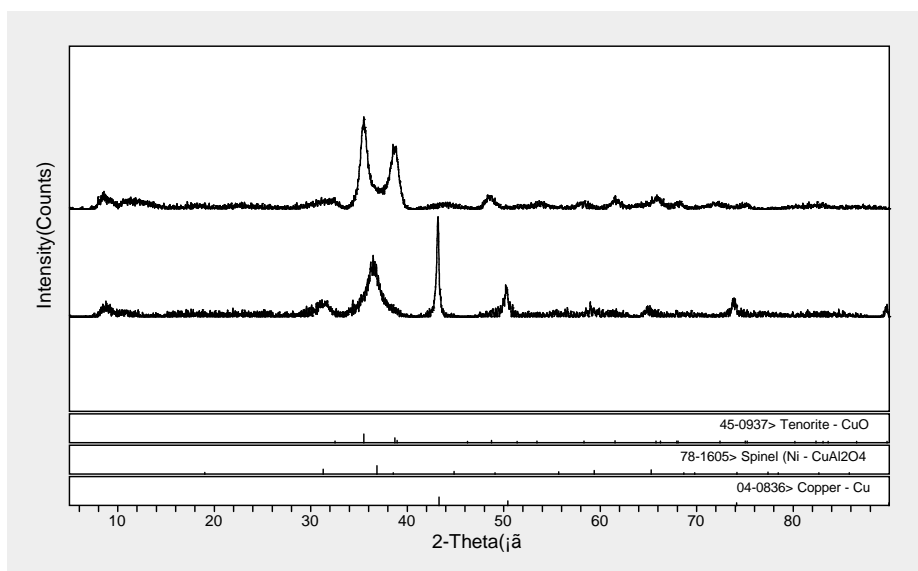


Figure 3.1 XRD patterns of the catalysts before reduction and after reaction

3.2.3 Reaction procedure and product analysis

The schematic diagram of the high pressure MAS reaction system is shown in Figure 3.2. This reactor design allows H_2 , syngas and helium to be delivered individually into the reaction zone at desired flow rates controlled by mass flow controllers (Brooks 5850E). A liquid solvent is delivered via an HPLC pump (Acuflow series III, Fisher) and is introduced into a pre-heater where it is heated under pressure in order to be converted to the desired supercritical state prior to the reactor. Before being mixed with the supercritical solvent, the syngas is passed through a 5 inch long, $\frac{1}{4}$ inch diameter tubing that is packed with glass wool and heated to $250\text{ }^\circ\text{C}$ in order to remove iron carbonyls contained in the premixed syngas. The solvent and syngas are combined just prior to entering the reactor, where the high temperature results in a supercritical phase mixture. The reactor is situated in a furnace with a programmed temperature controller system. The reaction pressure is controlled by a back pressure regulator (Straval-BPH) located between the hot trap and the cold trap. Two pressure indicators are located at the inlet of reactor and the outlet of the hot trap, respectively, to monitor the reaction pressure. After leaving the reactor, the

effluent passes through a hot trap that is maintained at 200 °C to condense heavy components (heavy hydrocarbons, if any), which might cause blockage of the delivery lines. The effluent is then delivered into heat exchanger that is cooled externally with cold water before entering the cold trap (maintained at 5 °C) where the effluent stream is then separated into two phases. The liquid phase products are collected and manually injected into a Varian 3380 gas chromatograph (GC) with a capillary column (DB-wax) equipped with a FID detector. The gas phase exiting the cold trap is analyzed by an online Varian GC with a packed column (Hayesep-DB 100/120) equipped with a TCD detector.

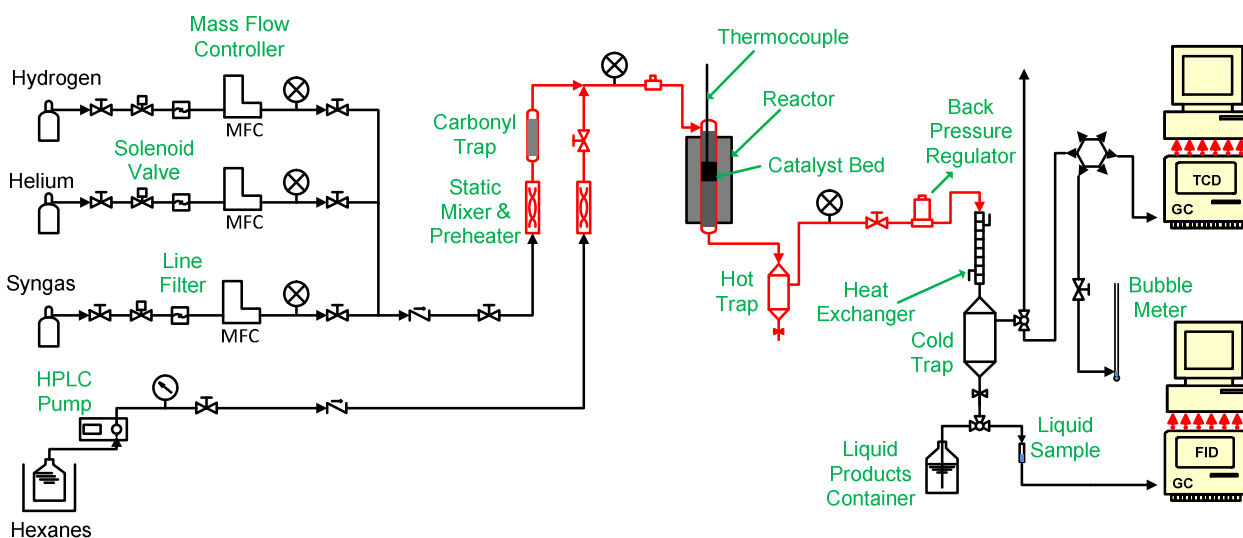


Figure 3.2 Schematic diagram of the high-pressure MAS reactor and analysis system

In a typical gas phase experiment, one gram of the catalyst mixed with 1.5 ml glass beads (45–70 mesh) was loaded into the reactor, and held in place in the middle of the reactor by glass wool packed on both sides of the catalyst bed. Before initiating the reaction, the catalyst was pretreated using a flow of 5% H₂ in 95% N₂ at a flow rate of 50 sccm (standard cubic centimeter per min) at 300 °C and ambient pressure for 12 hours. Helium was then delivered into the system until the desired reaction pressure was reached. After the temperature and pressure were stabilized, a predetermined syngas flow rate was initiated and controlled by a mass flow

controller. The reactions were allowed to run continuously until a steady state was achieved with respect to both the conversion and selectivity. The gas phase products were analyzed approximately every two hours and the liquid phase product was collected every 12 hours and injected into the GC-FID for analysis.

Studies involving supercritical hexanes were performed with identical loadings of the catalyst as described in the paragraph above. The pretreatment of the catalyst was also performed as described above. Hexanes was preheated (250 °C), delivered at flow rates controlled by a HPLC pump, and then mixed with the preheated syngas prior to entering the reactor. Under supercritical hexanes phase conditions, reaction temperatures and pressure ranged from 200 °C to 300 °C and 4.5 MPa to 20 MPa, respectively. The supercritical solvent used in this study is a mixture of hexane isomers (ACS grade), and as such is referred to as “hexanes”. The syngas concentration used in this study is 64.0% H₂, 32.0% CO, and 4.0% N₂ (internal standard).

CO or H₂ conversion was defined as the molar ratio of the consumed carbon monoxide or hydrogen to that which was fed to the reactor. Taking CO as an example, the CO conversion is defined as:

$$X_{CO} = 1 - \frac{n'_{CO}}{n_{CO}}$$

where n'_{CO} is the molar flow rate of the outlet CO and n_{CO} is the initial molar flowrate of CO in the syngas inlet. In addition, the selectivity of any species in the outlet stream is defined as:

$$S_i = \frac{n_i \times N_i}{n_{CO} - n'_{CO}} \times 100\%$$

Where n_i is the molar flow rate of species i in the outlet stream, and N_i is carbon number of that species (e.g. N_i for methane is 1). Similarly, the selectivity towards each alcohol product can be calculated by using the equation above.

3.3 Results and Discussion

The results of the MAS studies over a Cu/Zn/Al catalyst under both the gas phase and supercritical hexanes phase conditions at different hexanes/syngas ratios are presented in Table 3.2. The molar ratio of the supercritical solvent to the reactants (i.e. hexanes/syngas molar ratio) is considered to be an important factor affecting catalytic performance (Elbashir et al., 2005). Elbashir et al. (2005) demonstrated that higher hexanes/syngas ratios in their SCF-FT studies resulted in phase behavior and mixture physical properties more closely resembled that of the pure solvent thereby making it easier to maintain single phase operation. However, in order to maintain the same syngas partial pressure and therefore similar reactivity at elevated hexanes/syngas molar ratios, higher pressures and higher solvent throughput will be needed (Elbashir et al., 2010). Increasing the solvent/syngas molar ratio affects the overall concentration of CO and H₂ due to a simple solvent dilution effect thereby decreasing the mole fraction of the reactant gases in the feed mixture. In addition, if the solvent/syngas molar ratio is too low, the addition of this modest amount of solvent cannot provide enough density to enhance the heat transfer properties, as desired under SCF conditions. Ratios in the range of 3.0 to 3.5 have been commonly employed in the studies of FTS under supercritical solvent conditions (Bochniak & Subramaniam, 1998; Elbashir et al., 2010; Jacobs et al., 2003; Linghu, Li, Asami, & Fujimoto, 2006). In the current MAS study, the syngas flow rate was kept constant at 50 sccm/g_{cat}. The flow rate of hexanes was then adjusted to provide the required hexanes/syngas molar ratio. In order to keep the syngas partial pressure consistent and to focus on the effect of the supercritical

hexanes on the MAS, the reaction pressure was controlled as a function of hexane/syngas molar ratio.

Table 3.2 Conversion, selectivity and yields of supercritical MAS obtained with a $H_2/CO = 2.0$ synthesis gas at 300 °C and at various hexanes/syngas molar ratios with GHSV = 3000 L/kg cat/hr

	Hexanes/syngas molar ratio				
	0	1	1.5	2	3
Partial pressure of syngas (MPa)	4.5	4.5	4.5	4.5	4.5
Reaction pressure (MPa)	4.5	9.0	11.2	13.5	18
CO Conversion (%)	27.7	31.0	49.1	52.1	60.2
H ₂ Conversion (%)	17.8	18.5	35.7	40.3	48.7
Selectivity (%)					
CO ₂	25.1	20.8	15.8	12.7	10.2
CH ₄	6.4	4.4	3.5	2.8	2.4
Alcohols	37.5	45.0	56.3	66.7	65.5
Alcohol yields (g/kgcat/h)					
Methanol	139.6	163.1	321.9	434.1	506.5
Ethanol	11.1	15.7	32.0	12.1	10.8
1-propanol	0.1	1.3	2.7	6.0	4.7
1-butanol	0.1	0.8	1.5	3.01	2.24
α value (C ₁ -C ₄ linear alcohol)	0.05	0.10	0.10	0.13	0.11

3.3.1 Effects of hexanes/syngas molar ratio on CO and H₂ conversions

Figure 3.3a illustrates the influence of the hexanes/syngas molar ratio on the activity of the catalyst as measured by CO and H₂ conversion at 300 °C and syngas partial pressure of 4.5 MPa. When the hexanes/syngas ratio = 0 ($P_{total} = P_{syngas} = 4.5$ MPa), the data represents the catalytic behavior under gas phase conditions. A CO conversion of 27.7% and a H₂ conversion of 17.8% have been observed, as shown in Fig. 3.3a. A modest increase in CO conversion was obtained when shifting the process from gas-phase operation (hexanes/syngas = 0) to the operating condition where the molar ratio of hexanes/syngas = 1 (e.g. the CO conversion was changed from 27.7% to 31.0%) while holding the syngas partial pressure constant. As the hexanes/syngas molar ratio was further increased to the value of 2, the conversion of CO and H₂ increased

sharply to values of 52.1% and 40.3%, respectively. The CO and H₂ conversions continued to increase when the molar ratio was further elevated to the value of 3, where the CO conversion was 60.2% and the H₂ conversion was 48.7%.

Huang & Roberts (2003) have shown that activity in SCF-FTS can be higher than in the gas-phase FTS over a cobalt catalyst. They attributed an observed increase in activity to higher solubility of FTS products and in situ extractability of the SCF solvent medium which resulted in more active sites being available for reaction. Bukur, Lang, & Nowicki (2005) studied FTS on an iron catalyst where they attributed an increase in activity under supercritical fluid conditions to higher diffusivities relative to the conventional mode of operation (stirred tank slurry phase). In the case of SCF methanol synthesis, Liu et al. (2001) described that the addition of a supercritical solvent into a system at a certain temperature and pressure could influence the CO conversion in two ways, namely a dilution effect and a solvent effect. In the current study, the experiments were well designed such that the partial pressure of syngas was maintained at a consistent value of 4.5 MPa at each total pressure studied, in order to be able to separate the inherent reaction rate (which is proportional to the reactant gas partial pressure) from the effect of the SCF solvent on reactivity. Figure 3a demonstrates that the addition of supercritical hexanes at a molar ratio from 1 to 3 has a significant effect on the CO and H₂ conversion. The increase in reactivity may come either from a thermodynamic pressure effect (total pressure) on the activity of alcohol synthesis (X. Xu et al., 1987) or from a solvent effect on the reaction due to the elevated amount of hexane present (Wu, Klein, & Sandler, 1991).

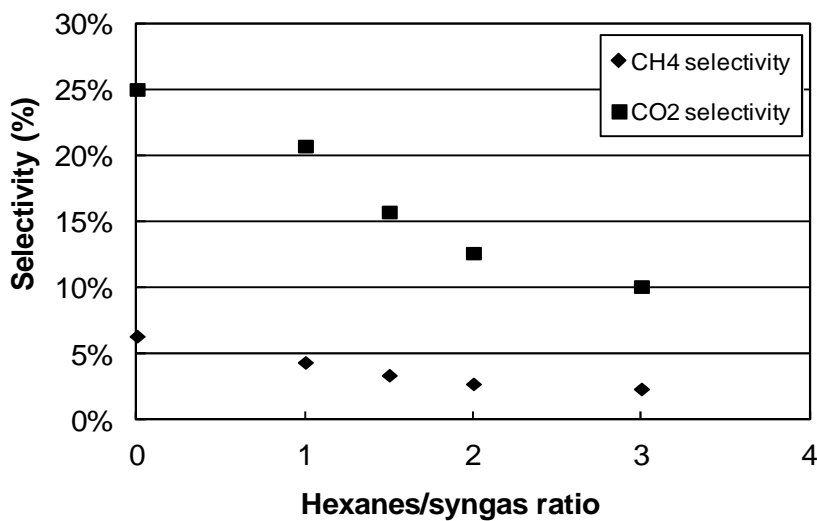
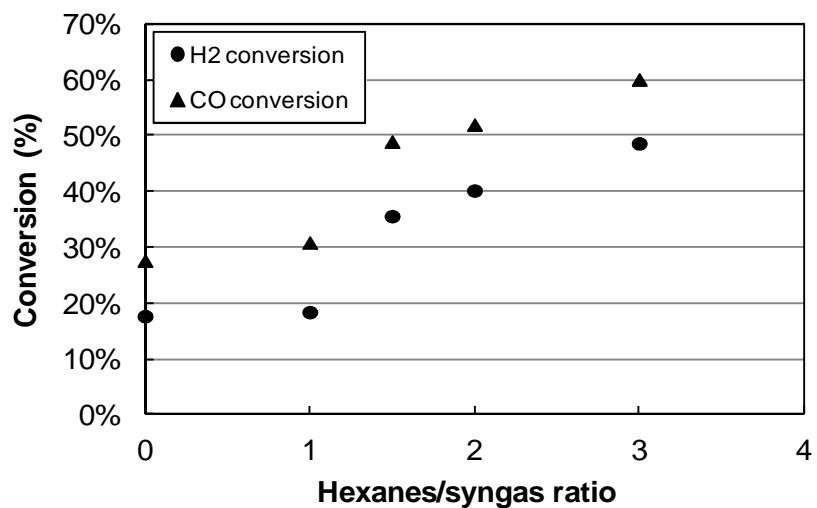


Figure 3.3 Syngas conversion and selectivity to CO₂ and CH₄ as a function of hexane/syngas molar ratio. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature 300 °C, pressure 4.5 MPa-20 MPa

3.3.2 Effects of hexanes/syngas molar ratio on CO₂ and CH₄ selectivity

Figure 3.3b shows that upon switching the reaction from gas phase operation to SCF phase operations, the selectivity to CO₂ decreased from 25.1% to 10.2%. CH₄ selectivity was also reduced from 6.4% under gas phase conditions to around 2% under supercritical phase conditions (Hexane/syngas = 3). Due to the fact that two variables are changing at the same time, i.e. the total pressure and the hexane flow rate, more evidence is needed to prove that this is the result of a supercritical solvent effect. Study of MAS under gas phase conditions has shown that selectivity to CO₂ and CH₄ is relatively stable with increasing pressure, as shown in Figure 3.5. Therefore, the decrease in CO₂ and CH₄ selectivity in this case can be attributed to the elevated presence of the supercritical hexanes. This observation is consistent with previous research findings on SCF-FTS (Fan et al., 1992; Huang & Roberts, 2003; Yokota & Fujimoto, 1991; Yokota et al., 1991). They further attributed the lower selectivity towards methane to the more effective removal of reaction heat from the catalyst surface than in the gas-phase reaction. Huang and Roberts (2003) also reported a significant decrease in methane selectivity in SCF-FTS compared to gas phase FTS. The large amount of heat generated in the FTS reaction was believed to be resulting in the cracking of long chain hydrocarbons into smaller ones if this heat is not efficiently removed from the catalyst pores. In the supercritical phase, however, the heat transfer rate was believed to be improved due to the higher heat capacity and thermal conductivity as compared to gas phase. As in the process of FTS the rapid removal of reaction heat is also considered as an important issue in the mixed alcohol synthesis. The high heat transfer capacity provided by supercritical hexanes has significantly reduced the selectivity towards to CH₄ and CO₂. Combining with the fact that remarkable increase in CO conversion has been found under supercritical hexanes phase conditions (hexanes/syngas molar ratio >1), it is

reasonable to speculate that more carbon has been converted into liquid product under supercritical hexanes phase conditions.

In order to examine the influence of pressure on this reaction, an experiment was performed where the overall pressure was increased at constant syngas and hexanes flow rate as shown in Figure 3.4 (both syngas and hexanes partial pressure were increased). This figure demonstrates that an increase in total pressure and syngas partial pressure results in an increase in the CO and H₂ conversion to values that are roughly doubled that at lower pressure operation. It should be noted that the CO₂ selectivity decreased with this increase in total pressure and the CH₄ selectivity remained relatively low and fairly constant at a value of around 4%. Unfortunately, this experiment does not allow determination as to whether the increase in activity with the increased addition of solvent (observed as in Figure 3.3a) is from a pressure effect or from the presence of the supercritical medium.

To further examine the effect of pressure on this reaction, a set of experiments were performed in the absence of supercritical hexanes under gas phase conditions at a series of elevated pressures. This was done in order to determine the inherent effect of elevated pressure on the reactivity and selectivity of this particular catalyst. Figure 3.5 presents the effect of pressure on syngas conversion and selectivity at pressures ranging from the initial syngas partial pressure of 4.5 MPa to 20 MPa. It demonstrates that there is a significant pressure effect on the CO and H₂ conversion where the CO conversion increased rapidly from 27.7% all the way to 75.3% over this pressure range, consistent with pressure effects observed previously in the synthesis of mixed alcohol (Burcham et al., 1998; Mahdavi et al., 2005), this figure also illustrates that there is little to no effect on both the CO₂ and CH₄ selectivity over the pressure range of 4.5 to 12 MPa. When pressure further increased from 12 MPa to 20 MPa under gas phase conditions, CH₄

selectivity increased from 8.7% to 18.9%. Recall that Figure 3.3b demonstrated that the presence of supercritical solvent affected a decrease in both the CO₂ and CH₄ selectivity to a significant degree, when the hexanes/syngas molar ratio was increased from 0 (gas phase condition, syngas partial pressure at 4.5 MPa) to 3 (total pressure at 18.5 MPa, syngas partial pressure at 4.5 MPa). These results demonstrate that the presence of supercritical solvent allows the activity to be positively affected by pressure while also providing suppression of undesired side reactions to CO₂ and CH₄.

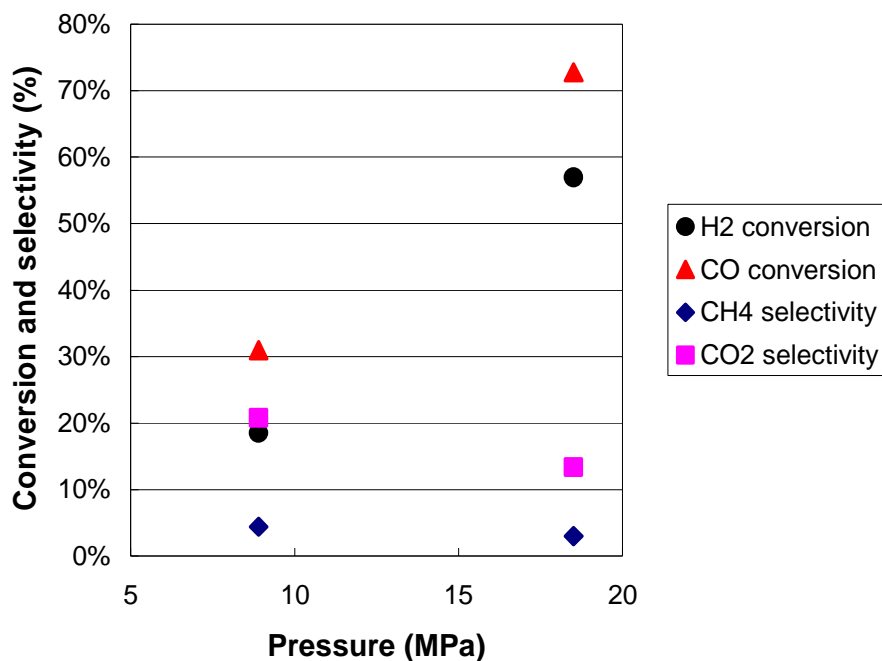


Figure 3.4 Pressure effect on the conversion and selectivity. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature 300 °C, hexanes/syngas molar ratio = 1

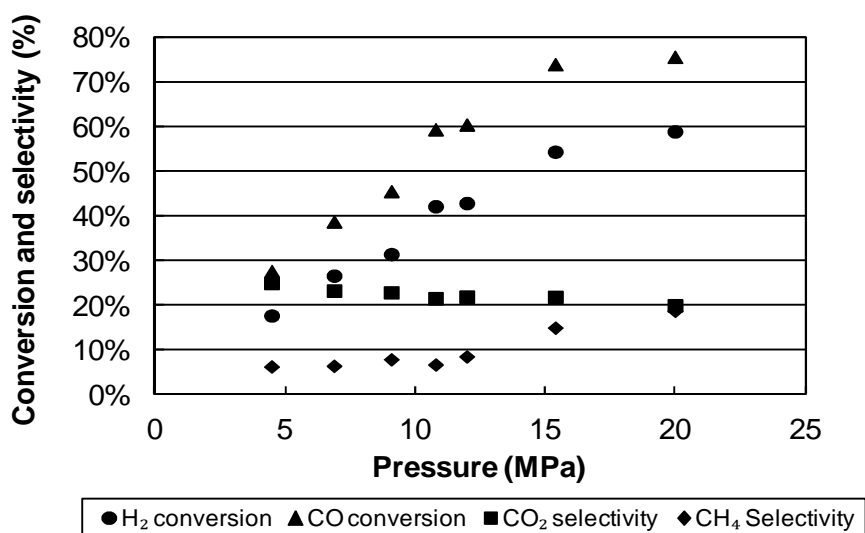


Figure 3.5 Pressure effect on syngas conversion and selectivity to CO₂ and CH₄ under gas phase conditions. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature 300 °C, pressure 4.5 MPa-20 MPa

3.3.3 Effects of hexanes/syngas molar ratio on alcohols' productivity and selectivity

Figure 3.6 presents the effect of hexanes/syngas molar ratio on the productivity towards methanol and ethanol. It shows that methanol formation is significantly enhanced by the introduction of the supercritical fluid solvent. Of the conditions studied, the methanol formation rate reaches a maximum at a molar ratio equal to 3. The increase in productivity can be attributed to both the presence of supercritical hexanes and the enhanced reaction pressure. As shown in Figure 3.6b, the ethanol productivity increased first from 1.3 g/kg cat/h to 32.0 g/kg cat/h with the increase in hexanes/syngas molar ratio from 0 to 1.5 and then decreased to 10.8 g/kg cat/h with a further increase in hexanes/syngas molar ratio to 3. It suggested that a maximum in the formation of ethanol would appear somewhere between the hexanes/syngas molar ratio of 1 and 2. The productivities of higher alcohol species observed over this particular catalyst were two orders of magnitudes less than the value for ethanol under gas phase conditions and were

positively affected by the presence of the SC hexanes. The productivities of the C₁ to C₄ linear alcohols under this set of elevated hexanes/syngas molar ratios are presented in Table 3.2, as well as the carbon chain growth factors for each of the hexanes/syngas molar ratios studied. The enhancement in the productivity towards higher alcohols by the introduction of supercritical hexanes into the system is apparent. For instance, a productivity of 6.03 g/kg cat/h towards 1-propanol has been obtained under hexanes/syngas molar ratio of 2 reaction conditions, compared to that of 0.1 g/kg cat/h under gas phase conditions. An interesting observation has been found in terms of the α values. The presence of supercritical hexanes seems to have a positive effect on the α value, i.e. it doubled from 0.05 under gas phase condition to a value of 0.1 under hexanes/syngas molar ratio of 1 reaction conditions. However, further elevation in the amount of supercritical hexanes introduced into the system appears to have little to no effect on the carbon chain growth factor, indicating that the mechanism of alcohol formation may not be dependent on the reaction media.

Furthermore, in order to better understand the impact of the SCF on the formation of mixed alcohols, the carbon selectivity was plotted as a function of hexane/syngas molar ratio. Figure 3.7 shows that the selectivity towards methanol has been remarkably enhanced by the presence of supercritical hexanes, though it is only slightly increased at a molar ratio equal to one. Based on the combined results of productivity and selectivity, it is expected that a hexanes/syngas molar in the range of 1.5 to 2 would allow for maximal impact of the SCF on the formation of ethanol and other higher alcohols. Figure 3.7 also shows that the presence of SC hexanes did improve the carbon selectivity towards each higher alcohol compared to the results under gas phase conditions (where the molar ratio equals zero). Of the conditions studied, a maximum value for each higher alcohol was found at a hexanes/syngas molar ratio of 2. The results of the

liquid product analysis indicates that there is an optimum amount of hexanes needed to be added in order to get a maximum productivity towards different higher alcohol products over this 0.5 wt% K promoted Cu/ZnO/Al₂O₃ catalyst.

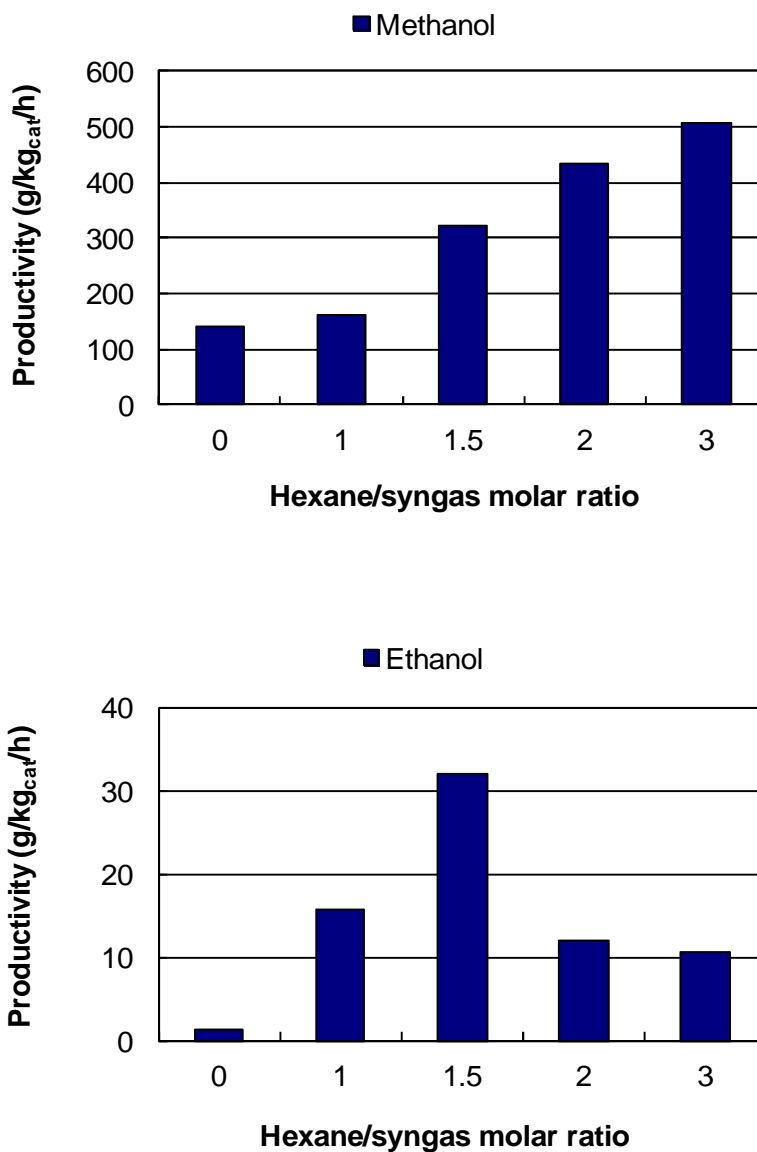


Figure 3.6 Effect of hexane/syngas molar ratio on the productivity of methanol (a) and ethanol (b). Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature 300 °C, pressure 4.5 MPa-18 MPa

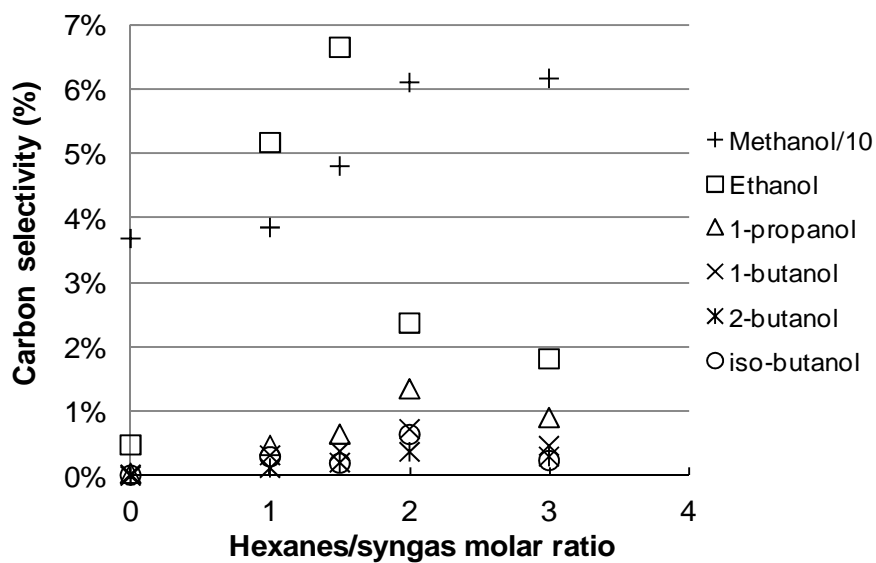


Figure 3.7 Effect of hexane/syngas molar ratio on the carbon selectivity towards C₁-C₄ alcohols. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃; syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature 300 °C, pressure 4.5 MPa-18 MPa

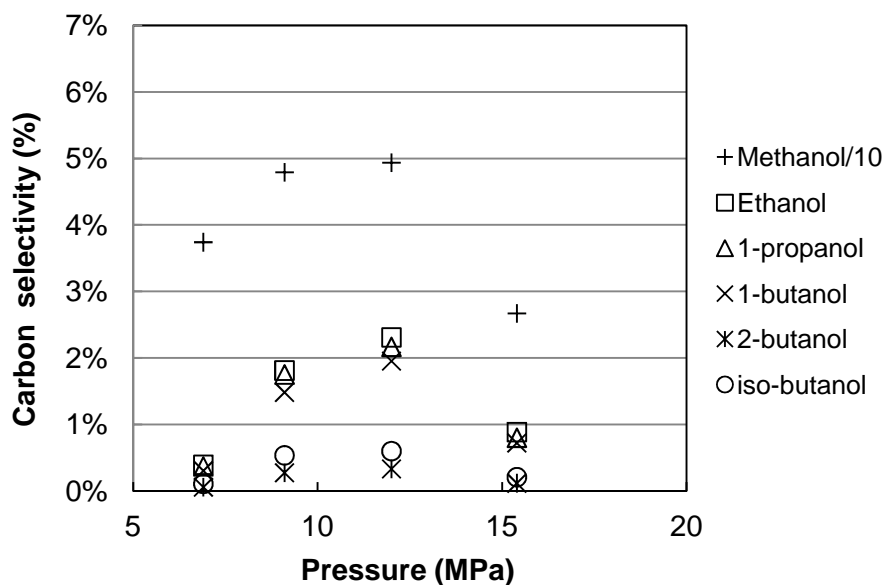


Figure 3.8 Pressure effect on alcohol selectivity under gas phase conditions. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature 300 °C, pressure 6.9 MPa-15.4 MPa

Figure 3.8 presents the effect of pressure on the selectivity towards each of the C₁ to C₄ alcohols under gas phase conditions. It can be observed that selectivity of methanol initially increased from 37.4% to 49.3%, when pressure was increased from 6.9 to 12 Mpa. A decrease in methanol selectivity was found when the pressure was further increased to 15.4 MPa. Similar trends have been observed for the selectivity towards ethanol and higher alcohols over the same pressure range but at much lower values. It should be noted that an increase in CH₄ selectivity has been detected when the pressure was increased from 12 MPa to 15.4 MPa in gas phase, as shown in Figure 3.5. Recall that pressure has a positive effect on the CO and H₂ conversion over the whole 4.5 MPa to 20 MPa range. The decrease in selectivity towards mixed alcohols, and the corresponding increase in CH₄ selectivity might indicate that when the reaction pressure is higher than 12 MPa in gas phase operation the excessive pressure favors the formation of hydrocarbons over the formation of alcohols.

When the effect of pressure on the selectivity towards mixed alcohols under gas phase conditions (Figure 3.8) is compared with this effect under supercritical hexanes phase conditions (Figure 3.7), it can be found that instead of exhibiting a maximum at 12 MPa under gas phase, the methanol selectivity continued to increase when the total pressure increased from 11.25 MPa (hexanes/syngas molar ratio of 1.5) to 18.5 MPa (hexanes/syngas molar ratio of 3). The highest value of ethanol selectivity was achieved at ca. 6.7% when the MAS was operated under hexanes/syngas molar of 1.5, much higher than the value of 2.3% achieved under gas phase. The increase in the C₃ and C₄ alcohols selectivity under supercritical hexanes phase conditions can be mainly attributed to the beneficial effect of increased system pressure.

Overall, the results presented above suggest that the presence of the supercritical hexanes facilitates heat and product removal thereby resulting in a significant increase in the production

of methanol and ethanol and a remarkable reduction in the methane formation, while also sustaining the beneficial effects of the elevated pressure on the CO and H₂ conversion and on the selectivity towards C₃ and C₄ alcohols. A value of hexanes/syngas molar ratio in the range of 1 to 2 would be suggested for the subsequent studies in order to optimize the effect of supercritical hexanes on the MAS process.

3.3.4 Effect of temperature on conversion and selectivity under both gas and SCF phase conditions

The kinetics of MAS (the rate of the various reactions that occur on the catalyst surface) is strongly influenced by the reaction temperature (Park, 1997; X. Xu et al., 1987). The reaction temperature also affects the phase behavior of the reaction media, as well as the thermo-physical properties of the mixture (reactants, solvent, and products) (Subramaniam & McHugh, 1986). The effect of reaction temperature at 200-300 °C on supercritical hexanes phase mixed alcohol synthesis was investigated, while maintaining the syngas partial pressure at 6.2 MPa and a mass space velocity of 3000 L(STP) kg⁻¹ h⁻¹ under reaction conditions both with and without hexanes as reaction media.

Figure 3.9 presents the effect of temperature on the syngas conversion (Figure 3.9 a&b) and selectivity towards CO₂ (Fig. 3.9c) and CH₄ (Fig. 3.9d). In increasing the temperature from 200 °C to 300 °C under gas phase reaction conditions, the CO conversion increased rapidly from 5% to about 35%. A more rapid increase in CO conversion was observed when the temperature was increased under supercritical hexane phase conditions. At temperature of 300 °C under supercritical hexanes phase conditions, a CO conversion of 66% was achieved. The effect of temperature on the H₂ conversion follows a similar trend as on the CO conversion. Under gas phase conditions, the H₂ conversion initially increased with an increase in temperature from 200 °C to 240 °C, and then increased even more rapidly as the temperature was raised beyond

260 °C. Under supercritical phase reaction conditions, the H₂ conversion increased with the increase in temperature from 200 °C to 240 °C, and the highest value of 55% (among all the temperatures studied) was obtained at 290 °C.

Fig. 3.9c demonstrated that selectivity to CO₂ was favored with the increase in reaction temperature for both gas phase and supercritical phase conditions. However, the presence of the supercritical hexane fluid media maintained the CO₂ selectivity at a relatively low value. For instance, at the reaction temperature of 300 °C, the CO₂ selectivity was 11.5% under supercritical hexanes phase conditions, much lower than the CO₂ selectivity of 23.5% that was obtained under gas phase conditions. Fig. 3.9d shows that the selectivity towards CH₄ was remarkably reduced when the temperature was increased from 200 °C to 240 °C under gas phase conditions. It should be noted that the CO and H₂ conversions were less than 10% in the temperature range of 200 °C to 290 °C in the gas phase. It should also be noted that no liquid product was detected in the gas phase in this same temperature range. Therefore, the high methane selectivity in this instance is the result of the negative effect of temperature on the conversion of CO to alcohols and not an increase in methanation since methanation is thermodynamically favored at higher temperatures. At these low temperatures in the gas phase, the conversions are low, the productivities of alcohols are low, and the CO that does react is converted to methane in high percentage. Fig. 3.9d also shows that the selectivity to CH₄ was maintained at a relatively low value (around 2%) as temperature increased from 200 °C to 300 °C in the presence of the solvent. These significantly lower values of CO₂ and CH₄ selectivity are attributed to the improved thermal uniformity afforded by the SCF solvent, consisted with similar observations in supercritical phase Fischer-Tropsch synthesis(Abbaslou,

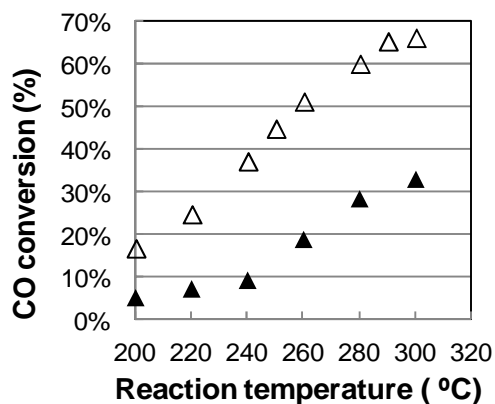
Mohammadzadeh, & Dalai, 2009; Durham, Zhang, & Roberts, 2010; Elbashir et al., 2005; Huang & Roberts, 2003).

Figure 3.10 shows the carbon selectivity towards C₁-C₄ alcohols as a function of temperature under gas phase reaction conditions. It can be observed that the selectivity towards methanol and ethanol went through a maximum at ea. 260 °C as the temperature was increased from 240 °C to 300 °C. At temperatures higher than 260 °C, the selectivity towards C₁-C₄ alcohols decreased rapidly, especially methanol. Majocchi et al. (1998) studied the temperature effect on the mixed alcohol synthesis over a Cs-promoted Cu/ZnO/Cr₂O₃ catalyst. They found that within a certain temperature range (225 °C to 325 °C) the methanol and C₂₊ linear alcohols productivity show maxima upon increasing the reaction temperature, which is quite similar to what has found in this current study. Methanol formation is believed to approach chemical equilibrium with increasing the reaction temperature. Similarly, Boz et al. (1994) showed that the formation of methanol is less favored thermodynamically at higher temperatures when investigating MAS over a similar Cu/ZnO/Al₂O₃ catalyst under gas phase condition.

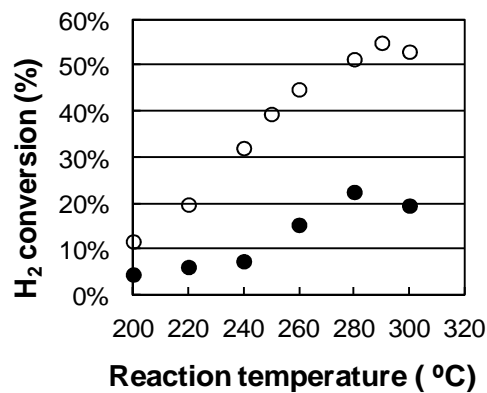
The changes observed in the selectivity towards each of the C₁ to C₄ alcohols upon increasing the reaction temperature in the range of 240-300 °C under supercritical hexanes phase conditions are shown in Figure 3.11. At 240 °C, methanol accounts for almost all of the overall liquid productivity. Only minor amounts of higher alcohols are formed, along with CO₂ and CH₄ (shown in Fig. 3.9 c&d). Increasing the temperature has a positive effect on the formation of alcohols in the presence of supercritical hexanes. The selectivity towards methanol and higher alcohols exhibits maximum around 290 °C, which is higher than that obtained under gas phase conditions where the maximum selectivity occurred around a temperature of 260 °C. The presence of a maximum in the productivity of methanol under gas phase conditions is related to

kinetic and thermodynamic reasons (Majocchi et al., 1998). As the temperature is increased, the methanol synthesis reaction approaches chemical equilibrium such that a further increase in temperature results in a decrease in the methanol concentration since this is an exothermic reaction. The presence of supercritical hexanes will enhance the removal of the reaction heat and can therefore mitigate thermodynamic restriction. As such, the productivity of methanol is monotonically increased with the increase in temperature under supercritical hexanes conditions, as shown in Table 3.3.

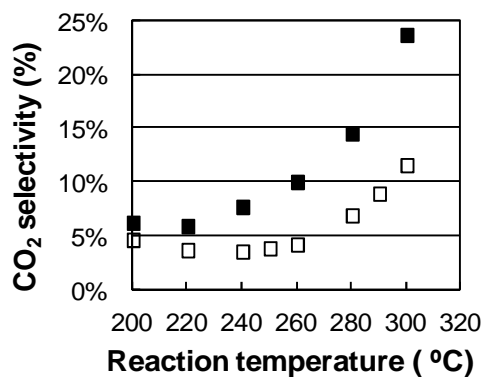
The carbon chain growth probability factor for alcohol as a function of temperature for gas phase and supercritical phase condition are summarized in Figure 3.11. It can be observed that alcohols have one constant chain growth factor (0.35 ± 0.05) over the temperature range investigated in this study. The rate of methanol formation falls on the Schulz-Flory line used in chain growth probability factor calculations. This correspond well with the observations reported by Boz(Boz, 2003), in which only one mechanism for methanol and higher alcohols' formation was believed. Slightly changes have been observed when the chain growth factor in supercritical phase conditions was compared with the one obtained in gas phase. It indicates that the mechanism of alcohol formation may not be dependent on the reaction media.



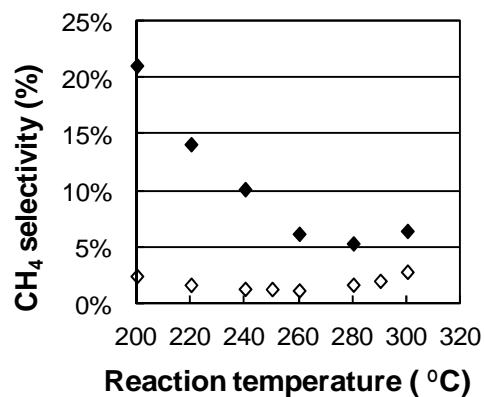
(a)



(b)



(c)



(d)

Figure 3.9 Effect of temperature on the syngas conversion and selectivity to CH₄ and CO₂ (filled icons represent the data obtained under gas phase conditions and the open icons represent the data obtained under SCF phase conditions) Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, syngas partial pressure 6.2 MPa

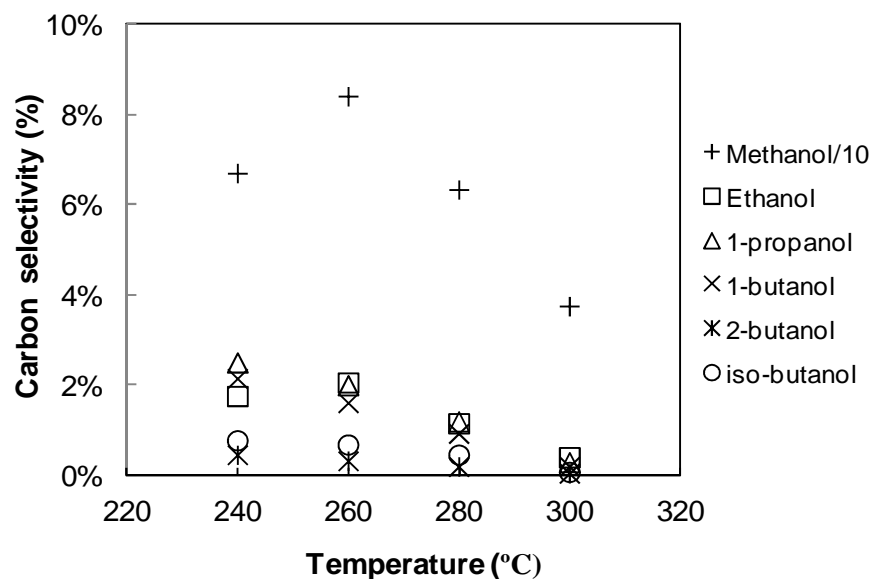


Figure 3.10 The effect of temperature on the carbon selectivity to alcohol products under gas phase condition. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, pressure 6.2 MPa

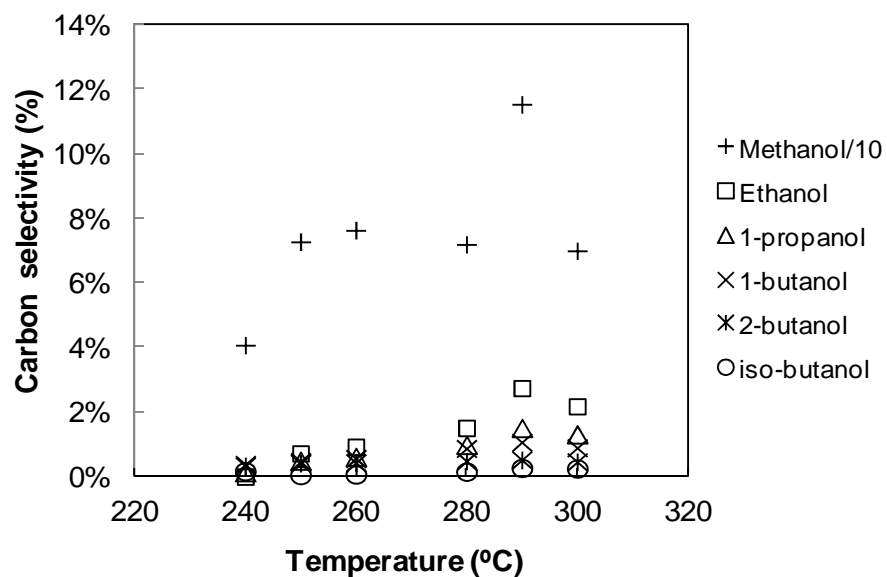


Figure 3.11 The effect of temperature on the carbon selectivity to alcohol products under SCF condition. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, hexanes/syngas molar ratio 2, syngas partial pressure 6.2 MPa

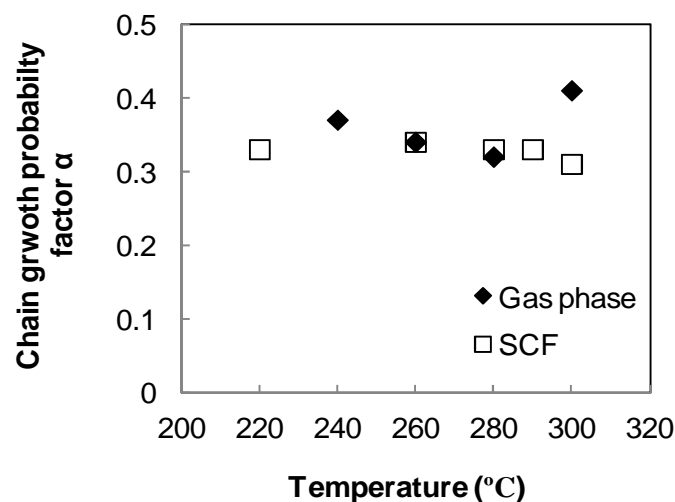


Figure 3.12 Changes in chain growth probability factor α with reaction temperature under gas phase and supercritical hexanes phase conditions. Reaction conditions were as follows: catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, syngas partial pressure 6.2 MPa

Table 3.3 Effect of reaction temperature on CO conversion, CO₂ and CH₄ selectivity, and alcohol productivity obtaining under both gas phase and SCF phase conditions.

T (°C)	CO %	Selectivity (%)		Productivity (g/kg cat/h)				
		CO ₂	CH ₄	Methanol	Ethanol	C ₃ alcohols	C ₄ alcohols	
Gas phase	220	7.2	5.9	14.1	57.6	Na	Na	Na
	240	9.2	7.7	10.1	84.1	1.6	2.1	2.4
	260	18.8	10.0	6.2	214.7	3.8	3.4	3.8
	280	28.3	14.5	5.3	244.0	3.2	3.0	3.5
	300	32.9	23.6	6.4	198.0	1.5	1.0	0.89
SCF Phase	240	37.2	3.5	1.3	247.0	Na	0.4	2.5
	260	51.1	4.2	1.2	533.1	4.6	3.5	4.3
	280	60.0	6.9	1.7	589.1	8.9	6.2	7.1
	300	66.0	11.6	2.8	630.8	14.1	8.6	8.3

Reaction conditions were as follows:

catalyst = 0.5 wt% K doped Cu/ZnO/Al₂O₃

syngas flow rate = 50 sccm/g_{cat}

H₂/CO = 2.0

pressure 6.2 MPa for gas phase condition, 18.6 MPa for SCF condition.

3.4 Conclusion

The 0.5 wt% K promoted Cu/ZnO/Al₂O₃ catalyst prepared in this study demonstrated stable catalytic activity for mixed alcohol synthesis. It was observed that syngas conversion, methanol productivity, and higher alcohol selectivity can be enhanced by introducing supercritical hexanes as a reaction medium. A set of hexanes/syngas molar ratios were investigated in order to determine suitable reaction conditions, while maintaining a partial pressure of syngas of 4.5 MPa in all cases. The introduction of supercritical hexanes into the reaction mixture results in a rapid increase in both CO and H₂ conversion and has been attributed to the increase in reaction pressure that corresponds to the amount of hexanes introduced. A significant decrease in the selectivity towards CH₄ has been observed under supercritical reaction conditions compared to gas phase and this has been attributed to the enhanced heat transfer provided by the supercritical hexanes. The presence of the supercritical hexanes allows the activity to be positively affected by pressure while also providing suppression of undesired side reactions to CO₂ and CH₄, thereby achieving an increase in the productivity of alcohols, especially methanol and ethanol. Of the conditions studied, a hexanes/syngas molar ratio in the range of 1 to 2 would be suggested for optimizing the effect of the supercritical solvent on the MAS studies. The effect of temperature has also been investigated on conversion, selectivity and alcohol productivities for operation under both gas phase and supercritical phase conditions. An optimum temperature was found to be ca. 290°C under supercritical hexanes phase conditions. In general, this work has shown that the use of supercritical hexanes as a reaction medium provides opportunities to enhance the performance of mixed alcohol synthesis and similar results would be expected on other related catalyst systems.

Chapter 4 Investigation of Supercritical Fluids as Reaction Media for Higher Alcohol Synthesis from Syngas over a K Promoted Cu-Co-Zn Catalyst

Abstract

Due to the unique properties of supercritical fluid, the use of it as reaction media has been demonstrated a lot benefits in Fischer-Tropsch synthesis and methanol synthesis from syngas. In this study, a Cu-Co based catalyst (0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃) has been investigated in a fixed bed reactor under supercritical hexanes phase conditions. A series of hexanes/syngas molar ratio has been studied, while the syngas partial pressure was maintained at 4.5 MPa. It has been found that the CO conversion was remained stable as increasing the hexanes/syngas molar ratio, while the CH₄ selectivity decreased continuously. Higher alcohol productivity was found increased monotonically with the increase in hexanes/syngas molar ratio. A molar ratio higher than 2 was suggested for the subsequent higher alcohol synthesis study. Comparison of results in the gas phase with those in the supercritical phase demonstrated that CH₄ selectivity has been reduced significantly under the supercritical hexanes conditions. At the same CO conversion of 12.6%, switching reaction conditions from gas phase to supercritical hexanes phase resulted in enhanced ethanol selectivity at the expense of methanol selectivity. In addition, the effect of GHSV in the range of 500 to 2000 h⁻¹ has also been investigated. The introduction of supercritical hexanes provides a clear thought about the effect of GHSV in this low flow rate range on the higher alcohol synthesis. At last, argon was used as a reaction media to compare with supercritical hexanes. It has been found that the enhanced higher alcohol productivity in line with the improved extraction of alcohol products from the pores. The introduction of the supercritical media improved the heat removal from the active sites, resulting in a remarkably lower selectivity towards C₁-C₄ paraffin.

Keywords: *Supercritical fluid; Higher alcohol synthesis; Supercritical reaction media; Copper-Cobalt catalyst*

4.1 Introduction

The synthesis of higher alcohol represents a promising pathway for the utilization of synthesis gas (a mixture of CO and H₂, referred to as syngas) in order to create liquid fuels and/or fuel additives. 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. Although the process of converting

syngas to alcohols has been under development for nearly a century, from a practical point of view, it still suffers from low selectivity towards higher alcohols (Fang et al., 2009; Feng, Wang, Jiang, & Ji, 2011; Forzatti et al., 1991; Subramani & Gangwal, 2008). In order to meet the practical requirements of industry, numerous studies have been devoted to the investigation of the higher alcohols synthesis (HAS) over the past thirty years (Boz, 2003; Burcham et al., 1998; Chaumette, Courty, Kiennemann, & Ernst, 1995; Dalmon, Chaumette, & Mirodatos, 1992; Herman, 2000; Kiennemann, Diagne, Hindermann, Chaumette, & Courty, 1989; Klier et al., 1997; Ma, Li, Lin, & Zhang, 2010; Mawson et al., 1993; Nunan, Bogdan, Klier, et al., 1989; Smith & Anderson, 1983; Tronconi et al., 1990; Xiang et al., 2008; X. Xu et al., 1987), including the development of modified catalysts (Boz, 2003; Dong et al., 2009; D. Li et al., 2007; Nguyen Tien-Thao, Zahedi-Niaki, Alamdari, & Kaliaguine, 2007; Xiang et al., 2008), the utilization of double bed reactors (Beretta, Sun, Herman, & Klier, 1996; Burcham et al., 1998), etc.

Various catalysts that have been used in HAS studies have been thoroughly discussed in the literature (Dalmon et al., 1992; Fang et al., 2009; Forzatti et al., 1991; Gerber et al., 2007; Herman, 2000; Spivey & Egbebi, 2007; Subramani & Gangwal, 2008; Vannice, 1976). These HAS catalysts are commonly divided into four types: i) modified low temperature methanol synthesis catalysts (Cu-based catalysts), ii) molybdenum sulfide catalysts, iii) Rh containing catalysts, and iv) modified Fischer-Tropsch catalysts (Ni, Fe or Co containing catalysts). 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 (Courty et al., 1982; Sugier, Freund, & Page, 1982; Sugier & Freund, 1981). Typically, a suitable Cu-Co based catalyst contains Cu, Co, other trivalent metals (Al or Cr), Zn or Mg and an alkali metal (Chaumette et al., 1995; Courty, Chaumette, Durand, & Verdon, 1988). It is believed that Co dissociates CO and

hydrogenates those resulting surface carbon species into hydrocarbons, and Cu assists in non-dissociative activation of CO (Courty et al., 1988; X. Xu et al., 1987). 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 based catalysts require similar reaction conditions to the modified low temperature methanol synthesis catalyst. The IFP process operates at 6-10 MPa, 260 °C – 320 °C, and GHSV 3000 – 6000 with H₂/CO ratios of 1.0 - 2.0 (Courty et al., 1982). It has been shown that Cu-Co based catalysts have high activity and selectivity towards higher alcohols (Chaumette et al., 1995). With the CuO/CoO/ZnO/Al₂O₃ catalysts, productivity up to 0.2g/g cat/h was reached at moderate temperature (below 310 °C). Straight chain alcohols have been observed as the main products on this type of catalyst, following an Anderson-Schulz-Flory (ASF) type distribution. A 60%-80% selectivity towards C₁-C₆ alcohols and a C₂₊OH/(C₂₊OH + C₁OH) ratio higher than 60% has been observed (Kiennemann et al., 1989).

Cu-Co based catalysts contain at least four components. The composition of each element plays an important part in the catalytic activity and the product selectivity. Dalmon et al.(1992) discuss that the complex and successful combination of Co and Cu ions in spinel-like structures is considered to be the key step leading to the tight interaction observed between the two elements in the activated catalyst, which provides selectivity towards alcohol synthesis (Dalmon et al., 1992).

In the case of ternary Cu-Co-Cr oxide catalysts, the diagram in Figure 1 shows the composition of these catalysts that promote methanol synthesis, hydrocarbon synthesis or higher alcohol synthesis. For intermediate compositions, especially in the area defined by $1 \leq \text{Cu}/\text{Co} \leq 3$, $\text{Co}/\text{Cr} \geq 0.5$, a mixture of C₁-C₆ light alcohols is obtained with C₁-C₆ hydrocarbons as byproducts.

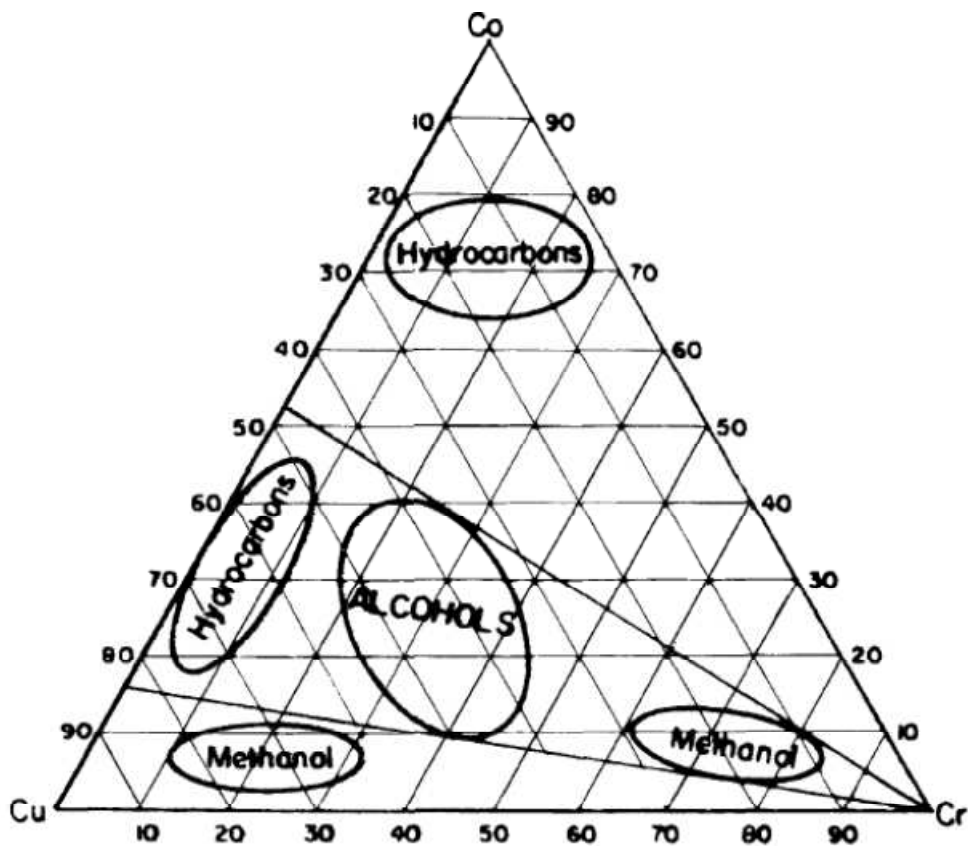


Figure 4.1 Selectivity as function of composition in the ternary system CuO-CoO-Cr₂O₃ (Courty et al., 1982)

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 (Courty et al., 1982). To further improve the catalytic performance of Cu-Co catalysts, nonconventional catalysts, such as Co/Cu based perovskites (Thao, 2007), Co/Cu supported on multiwall carbon nanotubes (Dong et al., 2009), and Co/Cu nanoparticles (Subramanian, Balaji, Kumar, & Spivey, 2009a) have been investigated. In general, these studies aimed to develop a catalyst that would have a good Cu and Co structural homogeneity in order to enhance the selectivity towards higher alcohols.

It has been found on CuO/CoO/ZnO/Al₂O₃ catalysts that the tendency for methanation was high when the reaction temperature was over 290 °C (Courty et al., 1982). Difficulties were also found in thermally controlling start-up of the reactions (Courty et al., 1982). Furthermore, the selectivity towards alcohols has been found to be highly dependent upon the preparation and temperature-dependant activation procedures (Mahdavi et al., 2005). As discussed below, supercritical fluid reaction media can provide certain advantages in maintaining thermal uniformity, and therefore better temperature control during start-up and continuous operation of these Cu-Co catalysts systems, where they have been shown to improve the performance of similar exothermic catalytic reactions (Durham et al., 2010; Elbashir et al., 2010; Huang et al., 2004).

Supercritical fluids have been recognized as an 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 (Abbaslou et al., 2009; Fan & Fujimoto, 1999; Huang & Roberts, 2003; Subramaniam & McHugh, 1986; Wu et al., 1991). The utilization of supercritical media in Fischer-Tropsch Synthesis (FTS) has been developed for more than twenty years. It has been shown that the presence of supercritical media provides several advantages into FTS as listed below;

- 1) SCFs increase the in situ extraction of heavy products in supercritical FTS (Fan & Fujimoto, 1999).
- 2) The catalyst effectiveness factor and pore accessibility increases with pressure in SCF media (Bochniak & Subramaniam, 1998).

- 3) The selectivity towards α -olefins is enhanced under SCF operation (Lang et al., 1995).
- 4) Optimal operating conditions exist when there is a fine balance between the effects of SCF bulk diffusion vs. pore diffusivity within the SCF depending on the temperature and pressure employed (Huang & Roberts, 2003).

Higher alcohol synthesis represents another highly exothermic reaction that could benefit from the advantages provided by supercritical reaction media. Jiang et al. (2001) investigated the influence of a mixture of C₁₀-C₁₃ alkanes as SC reaction media in higher alcohol synthesis over a Zn-Cr-K catalyst and found that the selectivity towards ethanol, n-propanol and isobutanol were raised and that of methanol was decreased. To the author's knowledge, there is no literature to date that reports on the performance of Cu-Co catalysts under the influence of supercritical reaction media for higher alcohol synthesis. 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 supercritical hexanes on the formation of higher alcohols, including the specific reaction performance parameters of carbon chain growth, productivity and selectivity towards higher alcohols.

4.2 Experimental Section

4.2.1 Catalyst preparation

The preparation of the Cu-Co based catalysts employed 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 co-precipitating this mixed nitrate salt solution with a 1.0 M K₂CO₃ solution in a 1L flask, which was initially filled with 200 ml deionized water at 80 °C.

The pH value was strictly kept at 7 in order to get a homogeneous dispersion. After aging for an hour, the precipitate was decanted and then washed with sufficient deionized water at 80 °C in order to eliminate the excess K introduced with the carbonate. The moisturized precursors were dried at 80 °C and at ambient pressure for 24 hours. The dried precipitate was then ground, calcined at 350 °C under continuous air flow to give the corresponding mixed oxides. The promotion of K was carried out through 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 hours.

4.2.2 Catalyst testing

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. Hexanes solvent was purchased from VWR and syngas (64% H₂, 32% CO and 4% N₂) was purchased and certified by Airgas. The flow rate of syngas and balancing gas argon was controlled by a mass flow controller (Brooks 5850 E), while 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 fixed into position by packing with glass wool. Effluent from the reactor passes through the hot trap (240 °C), a heat exchanger, and 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 TCD detector. The analyses of

liquid phase product were performed on a Varian CP-3300 Gas Chromatograph equipped with a capillary DB-wax column and a FID detector.

4.3 Results and Discussion

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

In order 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 is 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 (Elbashir et al., 2005). Hexanes/syngas molar ratios in the range of 3.0 to 3.5 have been previously employed in the studies of FTS under supercritical solvent conditions (Bochniak & Subramaniam, 1998; Elbashir et al., 2010; Linghu et al., 2006). Xu et al (2012) has 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 paper), cobalt was added into the Cu based catalyst in order to enhance the carbon chain growth of alcohol products. This paper 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 50 sccm, 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, while the partial pressure of syngas was kept constant.

Figure 4.2 presents the conversion of CO and H₂ as a function of the hexanes/syngas molar ratio over the 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃ catalyst under gas phase (hexanes/syngas molar ratio at 0) and supercritical hexane phase conditions (hexanes/syngas molar ratios of 1, 2, and 3). Under gas phase conditions (hexanes/syngas molar ratio = 0) the conversion of H₂ and CO are around 10%. In increasing the gas phase reaction pressure from 4.5 MPa to 9.0 MPa, the conversions increased rapidly to 38% in the case of H₂ conversion and 46% in the case of CO conversion. A slight increase in CO and H₂ conversion has been observed when the reaction condition was changed from gas phase to supercritical hexanes phase. While the syngas partial pressure was kept at 4.5 MPa, the conversion of CO and H₂ remains stable with an increase in the hexanes/syngas molar ratio as shown in Figure 4.2.

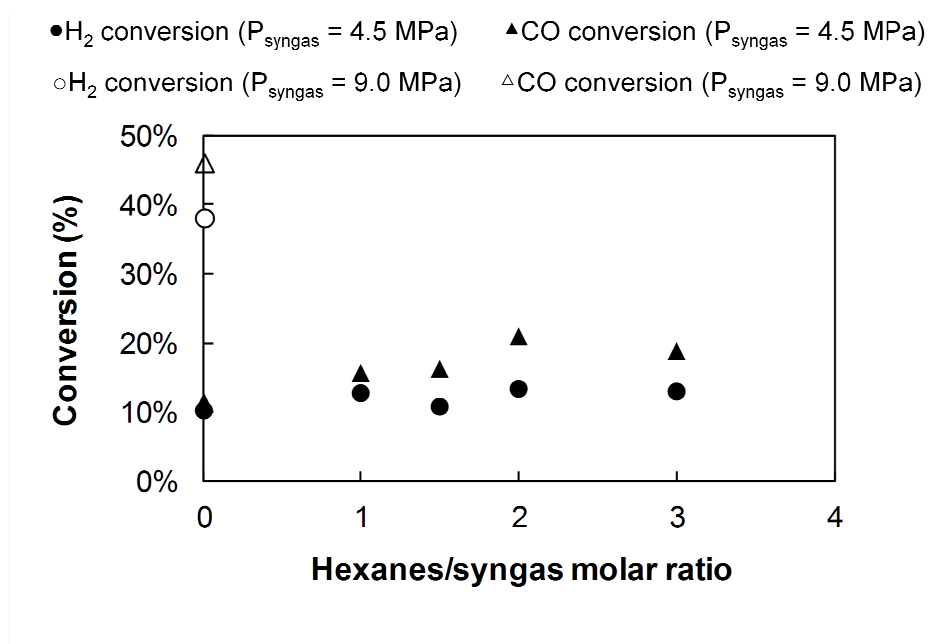


Figure 4.2 CO and H₂ conversion as a function of hexanes/syngas molar ratio. Reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 50 sccm, H₂/CO = 2.0, temperature = 300 °C, pressure = 4.5 MPa-18MPa

Figure 4.3 presents the selectivity towards CH₄ 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 towards CH₄ was close to 35%. Increasing the pressure from 4.5 MPa to 9.0 MPa under the gas phase reaction conditions (at hexanes/syngas molar ratio = 0) increased the CH₄ selectivity from 35% to 59%, as shown in Figure 4.3. This observation is consistent with that of Courty et al. (1982), De Aquino & Gomez Cobo (2001) and Subramanian et al. (2009a), who observed high methane selectivity over Cu-Co-Al catalysts at elevated pressure. Subramanian et al. (2009a) reported that the thermodynamically favored methane formation must be kinetically limited in order to increase the ethanol yield and selectivity. Figure 4.3 also shows that CH₄ selectivity decreased significantly when the reaction conditions were switched from gas phase (ca. 34.1%) to supercritical hexanes phase conditions. Furthermore, CH₄ 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 (Durham et al., 2010; Elbashir et al., 2010).

Figure 4.3 also presents the selectivity towards CO₂ 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 CO₂ selectivity, which increased from 22% to 30% when pressure increased from 4.5 MPa to 9 MPa. As also shown in Figure 4.3, CO₂ selectivity was very stable with or without the presence of supercritical hexanes, where the CO₂ selectivity remained ca. 20% at each of the hexanes/syngas ratios studied while the partial pressure of syngas was held constant at 4.5 MPa.

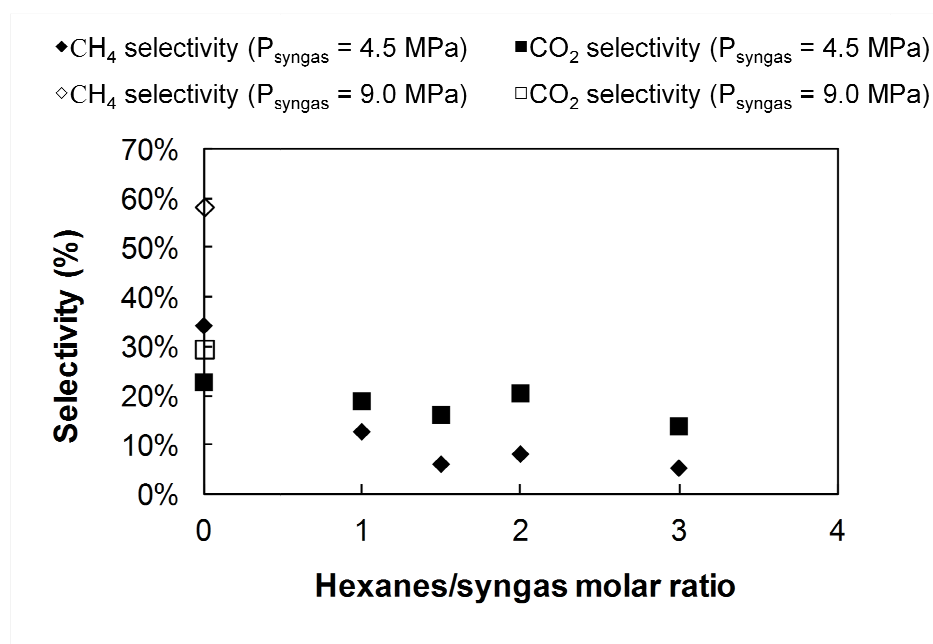


Figure 4.3 CO₂ and CH₄ selectivity as a function of hexane/syngas molar ratio. Reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature = 300 °C, pressure = 4.5 MPa-18MPa

Figure 4.4 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 corresponds with previously reported literature (Boz, 2003; Gerber et al., 2007; N Tien-Thao, Hassanzahediniaki, Alamdari, & Kaliaguine, 2007). Conducting the reaction under supercritical hexanes phase conditions again yielded linear alcohols, though the enhancement in productivity of higher alcohols was quite significant. For example, the productivity of 1-butanol increased from 0.5 g/kg_{cat}/h to 1.4 g/kg_{cat}/h as the hexanes/syngas molar ratio was increased from 0 to 3, and the productivity of 1-propanol increased from 0.6 g/kg_{cat}/h to 1.7 g/kg_{cat}/h. It is important to note that the productivity of each higher alcohol increase 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 of all of the conditions studied. Note that in order 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.

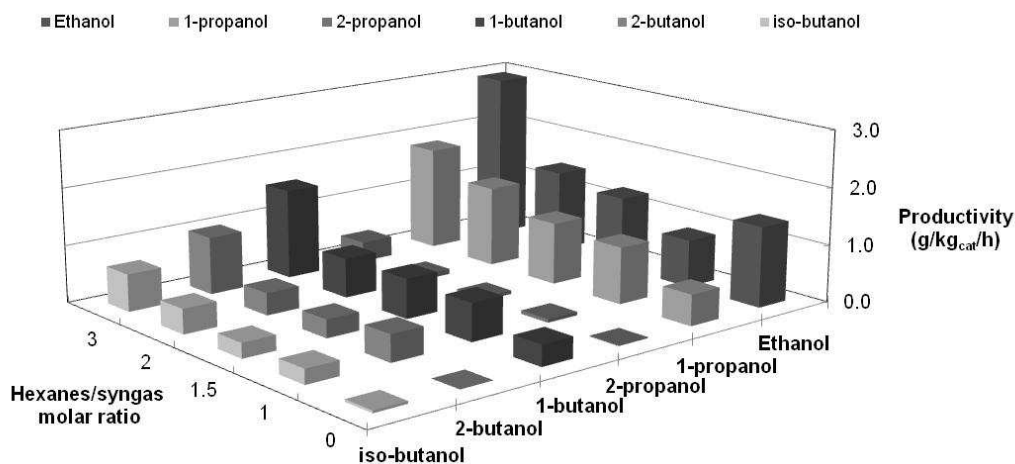


Figure 4.4 Higher alcohol productivity as a function of hexanes/syngas molar ratio. Reaction Conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 50 sccm, H₂/CO = 2.0, temperature = 300 °C, pressure = 4.5 MPa-18MPa

In order to better understand the impact of the SCF solvent on the formation of higher alcohols, the C_nOH wt% was plotted as a function of hexane/syngas molar ratio, as shown in Figure 4.5. The C_nOH wt% was defined as the weight of a certain alcohol divided by the total weight of all the alcohol products collected in the liquid product stream. Figure 4.5 demonstrated that the selectivity of methanol has been remarkably enhanced by the presence of supercritical hexanes when the molar ratio is higher than 1. Interestingly, the productivity towards methanol was the lowest at a molar ratio of 1. Moreover, the selectivity towards ethanol is optimal at a

molar ratio of 1 among the conditions studied. Further studies on this topic are required before firm conclusions should be drawn about optimal molar ratio for ethanol.

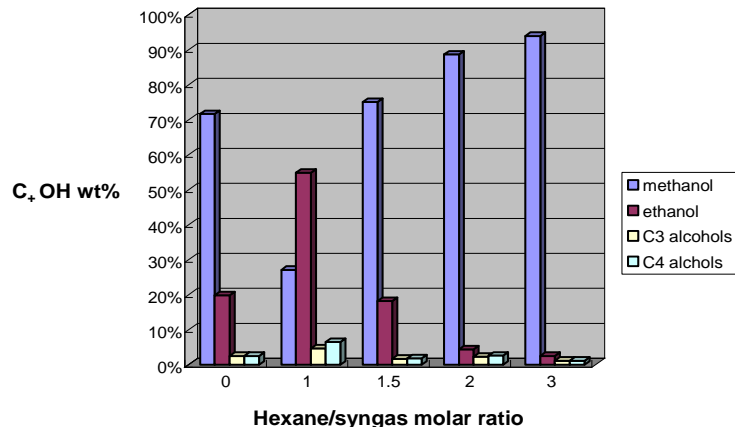


Figure 4.5 C_nOH wt% as a function of hexane/syngas molar ratio (C_nOH wt% defined as the weight of C_nOH divided by the total weight of alcohol products). Reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 50 sccm/g_{cat}, H₂/CO = 2.0, temperature = 300 °C, pressure = 4.5 MPa-18MPa

4.3.2 Selectivity comparison for same conversion under gas phase and SCF phase conditions

In order to better evaluate the effect of the supercritical hexanes solvent on the reaction performance, CO₂ and CH₄ selectivities obtained under both gas phase and supercritical hexanes phase conditions were compared at the same CO conversions, as shown in Figure 4.6. The SC-HAS reaction conditions were maintained at a hexanes/syngas molar ratio of 3, and the reaction pressure was held constant at 18 MPa. The CO conversion was varied by changing the gas hourly space velocity (GHSV) of syngas under gas phase conditions, while both the GHSV of syngas and the flow rate of hexanes were simultaneously adjusted under the supercritical phase conditions in order to make direct comparisons between the gas phase operation and the supercritical phase operation at the same levels of CO conversion. It can be observed from Figure 4.6 that the presence of the supercritical hexanes reaction medium significantly decreased

the selectivity towards CH₄ and had a negligible effect on the selectivity of CO₂ at each of the conversions studied. In comparison, for a conversion of 24.9% under supercritical hexanes phase conditions, the CH₄ selectivity was maintained at 9.7% which was significantly lower than the CH₄ selectivity of 64.9% that was obtained at the same conversion in gas phase. The CH₄ selectivities at each of the three conversion levels in the gas phase were in the range of 60%, in good keeping with prior observations that methanation was high over this Co containing catalyst at similar reaction conditions (Forzatti et al., 1991; Subramanian, Balaji, Kumar, & Spivey, 2009b). Previous studies have suggested that the high CH₄ selectivity could be associated with the sintering of the active sites at high temperature which leads to higher selectivity towards hydrocarbons (Chaumette et al., 1995). In addition, the gas phase CO conversion steadily increased as a function of time on stream over the 250 hours period of experimentation in this study, which can be mainly attributed to the enhanced methanation activity.

Under gas phase reaction conditions, the reaction heat removal is insufficient and local overheating of the catalyst can thereby result in a slow segregation of Co from the Cu-Co interactive structure (Chaumette et al., 1995; Courty et al., 1988, 1982). This inhomogeneity is believed to convert the catalyst from an alcohol synthesis catalyst to a Fischer-Tropsch synthesis catalyst thereby enhancing the selectivity towards CH₄ and hydrocarbons as has been observed previously (Courty et al., 1982; Spath & Dayton, 2003). This potential segregation of the Co from the Cu-Co catalyst under gas phase conditions, as opposed to the supercritical phase conditions, is further revealed from a comparison of the respective alcohol productivity levels shown in Figure 4.7. At the same CO conversion (ca. 12.6%), ethanol accounts for 69% of the total alcohols produced under supercritical hexanes phase conditions while it constitutes only 7% of the total alcohols obtained in the gas phase. Methanol, in contrast, predominates under gas

phase conditions (ca. 90% of the total alcohol produced). Tien-Thao et al (2006) reported that copper located outside the supporting materials (perovskite in their case) leads to the formation of methanol and methane. In the current study, switching from supercritical phase to gas phase conditions reduces the ability to remove heat from the active sites, thereby resulting in gradual catalyst segregation. Therefore, methanol and methane were found to be the predominate products under gas phase conditions.

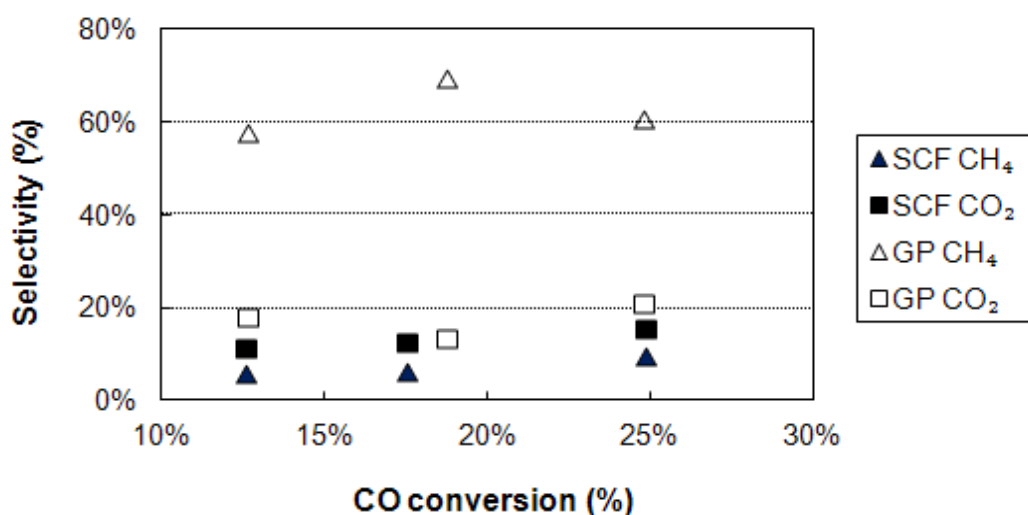


Figure 4.6 Comparison of CH₄ and CO₂ selectivities as a function of CO conversion under both gas phase and supercritical phase conditions. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 15-100 sccm/g_{cat}, H₂/CO ratio = 2.0, temperature = 300 °C; pressure = 4.5 MPa under gas phase conditions and pressure =18 MPa under supercritical phase conditions (where hexanes/syngas molar ratio = 3)

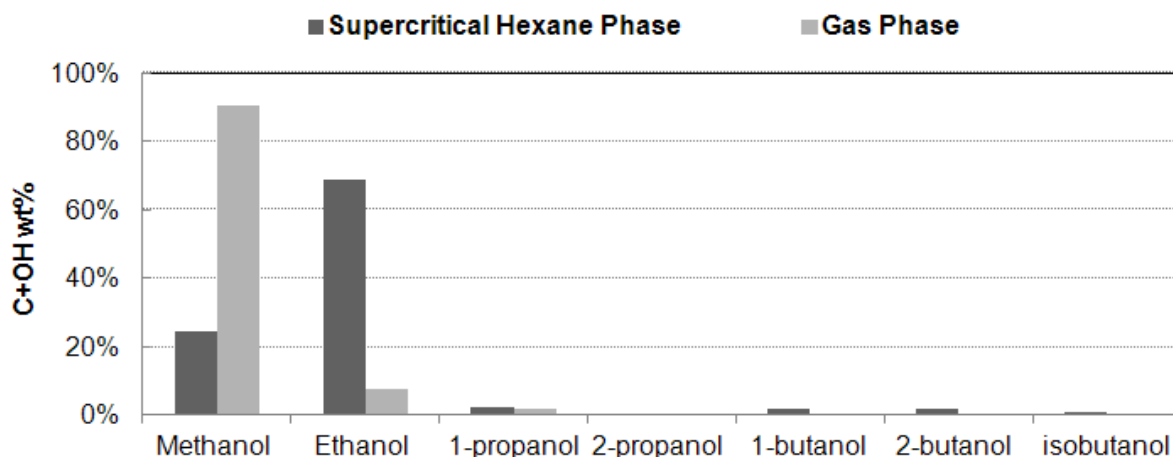


Figure 4.7 Comparison of alcohol selectivities at the same CO conversion under both gas phase and supercritical phase conditions. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 15-100 sccm/gcat, H₂/CO ratio = 2.0, temperature = 300 °C; pressure = 4.5 MPa under gas phase conditions and pressure = 18 MPa under supercritical phase conditions (where hexane/syngas molar ratio = 3), CO conversion = 12.6%.

4.3.3 The effect of GHSV

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 (Forzatti et al., 1991). 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 employed 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 4.8 presents the CO conversion, the H₂ conversion, and the selectivity towards CH₄ and CO₂ 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. H₂ 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 4.8. The CH₄ and CO₂ selectivity is favored by the lower GHSV values (i.e. longer contact times) under the supercritical hexanes phase conditions.

In Figure 4.9, the effect of GHSV on the selectivity towards methanol and higher alcohols is presented. It was found that the selectivity towards 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 towards the C₃ and C₄ 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, while additional contact time with the catalyst results in a significant increase in the formation of methanol and CH₄ at the expense of higher alcohol selectivity. Table 4.1 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 4.1. It was also observed that the CO₂ selectivity decreased from 20.7% to 13.3% as the GHSV increased from 500 h⁻¹ to 2000 h⁻¹. CH₄ selectivity was at the level of 60%, when the GHSV was within the range of 500 h⁻¹ to 2000 h⁻¹ under these gas phase conditions. The low space velocity values that were employed in this study (compared to higher values that have been used in the literature (Forzatti et al., 1991; Mahdavi et al., 2005; Mahdavi & Peyrovi, 2006; Majocchi et al., 1998; Subramani & Gangwal, 2008; Nguyen Tien-Thao et al., 2007)) have resulted in very high methanation activity under these gas phase conditions, resulting from poor heat management within the catalyst. Table 4.1 also shows the C₂₊OH selectivity, which is the weight of C₂₊ alcohols over the total alcohol product. Under

these gas phase conditions, the low GHSV (500 h^{-1} - 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 in the gas phase.

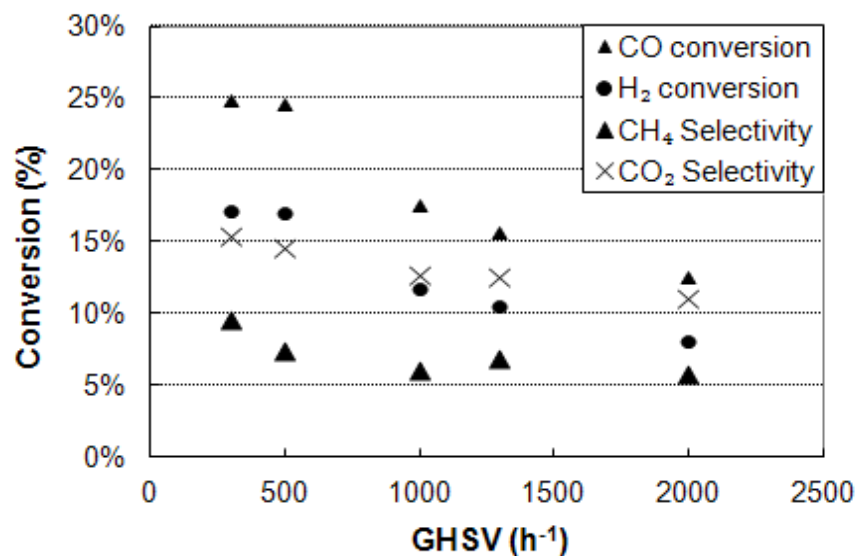


Figure 4.8 CO conversion, H_2 conversion, CH_4 selectivity, and CO_2 selectivity as a function of GHSV in SC-HAS. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/ Al_2O_3 , H_2/CO ration = 2.0, temperature = $300 \text{ }^\circ\text{C}$, pressure = 18 MPa, hexanes/syngas molar ratio = 3. GHSV was calculated based on the volumetric flow rate of syngas and the volume of catalyst bed.

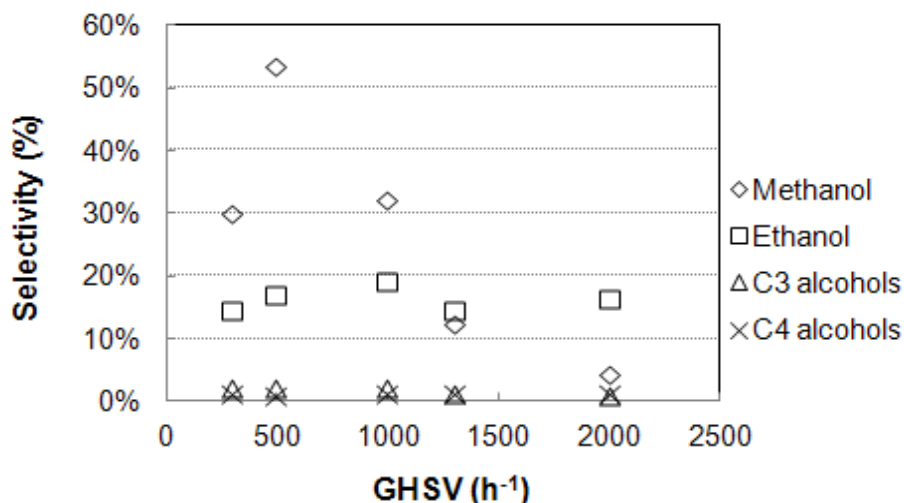


Figure 4.9 Selectivity of methanol, ethanol, propanol and butanol isomers as a function of syngas flow rate in SC-HAS. Reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, H₂/CO ratio = 2.0, temperature = 300 °C, pressure = 18 MPa, hexanes/syngas molar ratio = 3.

Table 4.1 The effect of GHSV on the conversion and selectivities under gas phase conditions

GHSV (h ⁻¹)	CO Conversion (%)	Activity (g/kg _{cat} /h)	Selectivity (%)		
			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/Al₂O₃, H₂/CO = 2

Alcohols: C₁-C₆ alcohols

Sc₂₊OH: weight percentage of C₂₊ alcohols / (methanol + C₂₊ alcohols)

4.3.4 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 supercritical fluid and by maintaining constant space velocity by using argon as the balance gas. The addition of argon as an inert balance gas allowed gas phase HAS experiments to be performed with comparable total flow rate (i.e. contact time) and syngas concentration to those used in

supercritical phase higher alcohol synthesis (SC-HAS). In the studies involving the effect of hexanes/syngas molar ratio (section 4.3.1 above), it was observed that CH₄ 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 supercritical fluids 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, while 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 employed 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 employed in this experiment instead of 3, as used in the sections above.

Table 4.2 presents the effect of both argon and supercritical hexanes reaction media on the CO conversion as well as the selectivity towards CO₂, alcohols and hydrocarbons. 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%). CO₂ selectivity was found to be quite stable as the reaction medium was changed from argon gas phase to supercritical hexanes phase. The selectivity towards alcohols was observed to be 16.0% under supercritical hexanes phase reaction conditions and 4.5% under the argon gas phase conditions, while the partial pressure and flow rate of syngas was kept constant. However, the light hydrocarbon selectivity (the S_H shown in Table 4.2) was found to be much higher under argon gas phase conditions than under the supercritical hexanes phase conditions. The C₈-C₂₀ hydrocarbon selectivity under both reaction conditions was found to have a value of 6.0% (not included in Table 2.).

Table 4.2 The effect of reaction medium 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/Al₂O₃, H₂/CO = 2, syngas flow rate = 50 sccm/g_{cat}.

S_A: selectivity towards C₁-C₆ alcohols

S_H: selectivity towards C₂-C₅ hydrocarbons

S_{c2+OH}: weight percentage of C₂₊ alcohols / (methanol+ C₂₊ alcohols)

Figure 4.10 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 C₁-C₆ 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 4.11 shows a comparison of the C₈-C₁₈ paraffin productivity obtained under both gas phase and supercritical phase HAS conditions. A nearly doubled C₈-C₁₁ paraffin productivity was observed in argon gas phase HAS compared with supercritical phase HAS. The higher productivity of C₈-C₁₁ paraffin 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 4.2.

There are several proposed mechanisms for the formation of alcohols and hydrocarbons over Cu-Co catalyst systems (Chaumette et al., 1995; Forzatti et al., 1991; Kiennemann et al., 1989; M. Xu & Iglesia, 1999). Although many intermediates have been proposed regarding the carbon chain growth in higher alcohol synthesis, such as alkyl (Pan, Cao, & Griffin, 1988) or acyl entities (Chaumette et al., 1995), it has been suggested that alcohols and hydrocarbons are formed from the same intermediates (Fang et al., 2009; Spivey, Egbebi, & Kumar, n.d.).

Moreover, the linear alcohol products have been reported to follow the Schulz-Flory distribution (REF), 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 $\log(w_n/n)$ versus n plot. Figure 4.12 shows the variation of $\log(w_n/n)$ versus 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 Schulz-Flory 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 4.10, the productivity of C_1 - C_3 linear alcohols is significantly lower in the argon phase than under the supercritical hexanes phase conditions. Combined with the observation that the light hydrocarbon selectivity was much higher under the argon gas phase conditions, as shown in Table 4.2, 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 4.13.

The productivity results in Figures 4.11 and 4.12 show that the termination step towards alcohols is preferred over the termination step towards hydrocarbons under the supercritical conditions. As a result, the productivity of alcohols is enhanced significantly. Because of the unique properties of supercritical fluids, 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 were 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 towards C₁-C₄ n-paraffin was significantly reduced. Moreover, the improved extraction capacity of the supercritical fluid solvent can allow for more efficient removal of FTS products from the catalyst resulting in higher C₁₃-C₂₀ hydrocarbons productivity under the SC-HAS conditions.

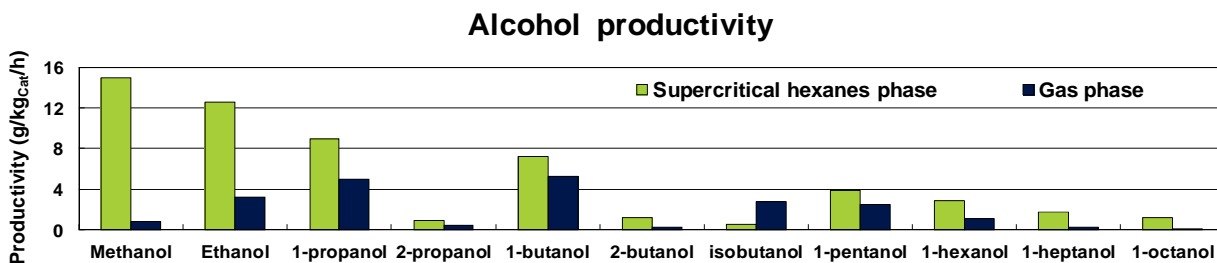


Figure 4.10 Productivity of C₁-C₈ alcohols in gas-phase and supercritical-phase HAS. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, H₂/CO ratio = 2.0, temperature = 300 °C, pressure = 13.5 MPa, hexanes/syngas molar ratio = 2 for the supercritical hexanes phase operation, argon/syngas molar ratio = 2 for the argon phase operation.

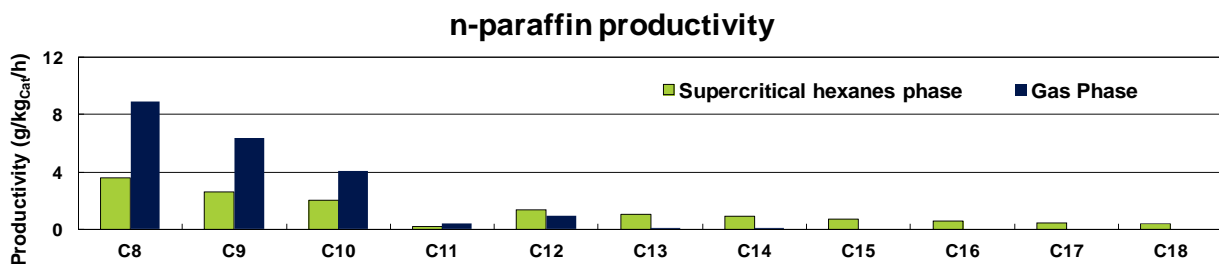


Figure 4.11 Productivity of C₈-C₁₈ n-paraffin in gas phase and supercritical phase HAS. Reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, H₂/CO ratio = 2.0, temperature = 300 °C, pressure = 13.5 MPa, hexanes/syngas molar ratio = 2 for the supercritical hexanes phase operation, argon/syngas molar ratio = 2 for the argon phase operation.

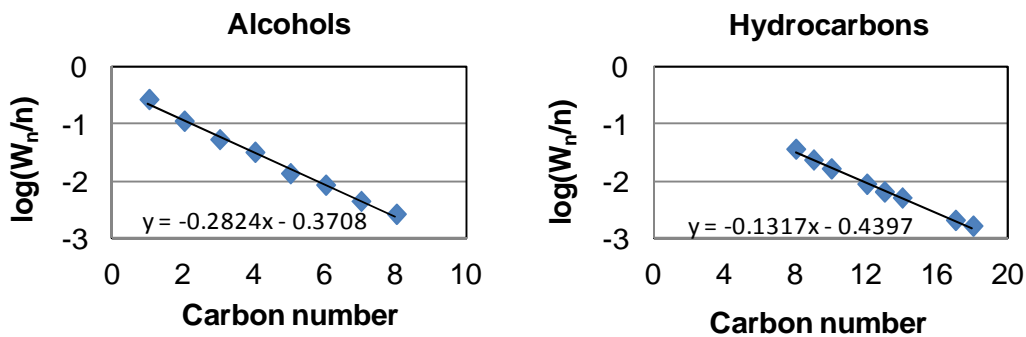


Figure 4.12 The variation of $\log(w_n/n)$ with respect to n (the number of carbon atoms) of alcohols (left) and hydrocarbons (right) obtained in SC-HAS. Reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, H₂/CO ratio = 2.0, temperature = 300 °C, pressure = 13.5 MPa, hexanes/syngas molar ratio = 2.

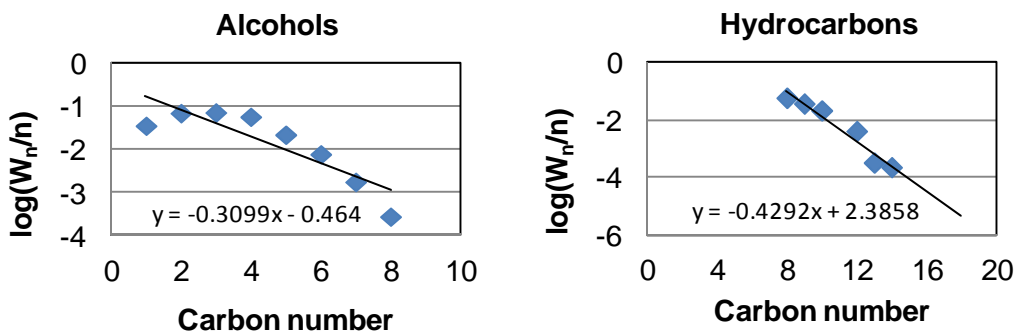


Figure 4.13 The variation of $\log(w_n/n)$ with respect to n (the number of carbon atoms) of alcohols (left) and hydrocarbons (right) obtained in gas phase HAS. Reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, H₂/CO ratio = 2.0, temperature = 300 °C, pressure = 13.5 MPa, argon/syngas molar ratio = 2.

4.4 Conclusion

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. The presence of supercritical hexanes has been shown to enhance the heat transfer rate and significantly reduce the selectivity towards CH_4 . Additionally, the effect of hexanes/syngas molar ratio on the productivity of methanol and higher alcohols has been investigated. With increases in the hexanes/syngas molar ratio, the productivity towards 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 h^{-1} 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 SC-HAS in order 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 gas phase HAS under the same operating conditions. The type of alcohol products obtained in SC-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 supercritical fluid medium improved the heat removal from the active sites, resulting in a remarkably lower selectivity towards 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.

Chapter 5 **Effect of H₂/CO ratio on higher alcohol synthesis over a Cu-Co catalyst under supercritical hexanes conditions**

Abstract

The effect of H₂/CO ratio on higher alcohol synthesis was studied over a K promoted Cu/Co/ZnO/Al₂O₃ catalyst using supercritical hexanes as a reaction medium. A series of syngas mixtures with H₂/CO ratios of 2, 1.75, 1.35 and 1 were employed in order to simulate the syngas compositions which can be derived from various carbonaceous resources. The catalytic performance of this Cu-Co based catalyst was investigated under both gas phase and supercritical hexanes phase conditions. As the H₂/CO ratio decreased from 2 to 1, the CO conversion decreased considerably under gas phase conditions, while the CO conversion remained relatively stable under supercritical hexanes phase conditions. Methane selectivity was found to decrease as the H₂/CO ratio decreased from 2 to 1 under supercritical hexanes phase conditions. The alcohol and hydrocarbon products formed over this Cu-Co catalyst follow the Schulz-Flory distribution. Productivity of higher alcohols was found to increase as a function with the H₂/CO ratio under the gas phase conditions applied in this study. However, an opposite trend in higher alcohol productivity with H₂/CO was observed under the supercritical hexanes phase conditions. Among all the conditions studied, the presence of the supercritical hexanes reaction medium combined with a syngas H₂/CO ratio of 1 resulted in maximum higher alcohol productivity.

Keywords: *Copper-Cobalt catalyst; Higher alcohol synthesis; H₂/CO ratio; Supercritical fluid; Supercritical reaction media*

5.1 Introduction

Higher alcohol synthesis (HAS) has long been developed as one of the primary pathways for converting syngas (a mixture of CO and H₂) in to valuable fuels and fuel additives. As the demand for alternative fuels increases, the higher alcohol synthesis (HAS) process is becoming increasingly more important and is receiving attention from both academic and industrial sectors. Syngas can be derived from a variety of carbonaceous resources, such as coal, natural gas and biomass, via gasification or partial oxidation. The H₂/CO ratio of a certain syngas is determined by the type of the carbonaceous resource used and the processing technology and conditions

employed. For instance, depending on the gasification method employed, syngas produced from biomass can have a broad range of H_2/CO ratios that vary from 0.45 to 2 (Faaij, Hamelinck, & Hardeveld, 2002). As another example, the H_2/CO ratio of syngas produced from certain coal species is correlated to the H/C ratio of the coal, with the H_2/CO ratio regularly close to 1 (Cao, Gao, Jin, Zhou, & Cohron, 2008). In addition, syngas can also be derived from natural gas via steam reforming or partial oxidation. The H_2/CO ratio of the syngas produced from the steam reforming process is typically rich in hydrogen (e.g. it can be as high as $H_2/CO = 3$); however, the H_2/CO ratio of syngas formed in the partial oxidation process commonly varies from 1.5 to 2 (Fong & Wilson, 1996).

The H_2/CO ratio is one of the operating variables that can significantly affect the catalytic behavior and the selectivity towards higher alcohols in the HAS process. As such, it is expected that the use of syngas that is derived directly from various carbonaceous resources would lead to different alcohol and other product distributions and yields in the HAS process. Boz et al. (1994) investigated the effect of varying the H_2/CO ratio over a 0.5 wt% K promoted Cu/ZnO/Al₂O₃ catalyst under the reaction conditions of 4 MPa, 290 °C and 3000 h⁻¹. The CO conversion was found to increase with an increase in the H_2/CO ratio from 0.5 to 3.3. Lower CO content was found to favor the formation of higher alcohols while also favoring the formation of hydrocarbons. Higher H_2/CO ratios produced more methanol instead. Additionally, at a H_2/CO ratio as low as 0.5, the overall activity was quite low, such that the productivity of alcohols was actually lower than the value obtained at an intermediate H_2/CO ratio. Two possible reasons were given a) low H_2/CO ratio results in a limiting H_2 availability, b) Cu is more likely to be reduced to Cu⁰ in the presence of excess CO. Forzatti et al. (1991) studied the effect of H_2/CO feed ratio on the product distribution using a ZnCrCsO catalyst and found that a H_2/CO ratio of 2 was the

optimal condition for the production of methanol. For the selectivity towards higher alcohols, however, the maximum was reported when the H₂/CO ratio was ca. 1. Moreover, due to different side reactions involved in the HAS processes, especially the parallel water-gas shift reaction, the H₂/CO ratio within the reactor changed as the reaction process goes on. Mahdavi et al. (2005) examined three H₂/CO ratios over a Cu-Co catalyst at 285 °C, 4 MPa and GHSV = 3410 h⁻¹. They reported that the activity and selectivity towards alcohols were stable when the H₂/CO ratio was changed from 2 to 1. A further decrease in H₂/CO ratio to 0.5 decreased the activity rapidly. Methane selectivity increased significantly as H₂/CO ratio decreased from 1 to 0.5.

It has been shown that higher alcohol synthesis from syngas can benefit from the utilization of a supercritical fluid solvent as the reaction medium given that the HAS process is a highly exothermic polymerization reaction (Jiang et al., 2001; Qin, Liu, & Wang, 2004; Zhang et al., 2006). Supercritical fluids have unique characteristics in terms of their thermodynamic and transport properties which are intermediate to those of a liquid and those of a gas (Baiker, 1999; Fan, Yokota, & Fujimoto, 1995; McHugh & Krukoni, 1994; Subramaniam & McHugh, 1986). For example, the density, which is typically less than that of a normal liquid, is remarkably higher than that of a gas. As such, density dependent properties can be tuned in a supercritical fluid reaction medium in order to affect desired changes on catalytic reaction performance through improved heat transfer, mass transfer, as well as product and reactant solubilities, just to name a few. For instance, the presence of a supercritical fluid can significantly enhance the heat transfer rate in an exothermic heterogeneous catalytic process compared to gas phase operation. Accordingly, it has been shown that the use of supercritical hexanes as reaction media in HAS has significantly reduced the formation of CH₄, which is thermodynamically favored (as shown in Chapter 3 and 4). As another example, the diffusivity of a supercritical fluid, while lower than

that of a gas, is significantly higher than that of a liquid and can provide improved transport properties in heterogeneous catalysis applications (Baiker, 1999; Elbashir et al., 2010; Subramaniam & McHugh, 1986). A supercritical fluid reaction medium can also offer enhanced solubility of certain reactants and products. Compounds that are largely insoluble in a fluid at ambient conditions can be made more soluble in the solvent medium at supercritical conditions and vice versa (Savage, Gopalan, Mizan, Martino, & Brock, 1995). These differences in the solubilities and diffusivities of H₂ and CO can give rise to a consequence that the actual H₂/CO ratios within the reactor differ substantially from that of the gas that is fed to the reactor.

Since it is well known that the H₂/CO ratio at the catalyst surface affects liquid product distribution, as well as the formation of free carbon (Stern, T. Bell, & Heinemann, 1983), it becomes quite important to establish the extent to which the presence of a supercritical fluid solvent influences the H₂/CO ratio in the reaction media. In this work, higher alcohol synthesis was examined using syngas of different H₂/CO ratios over a K promoted Cu-Co based catalyst. These studies were performed both with and without the presence of supercritical solvent. In particular, the effect of H₂/CO ratio on the distribution of higher alcohol products and the conversion of CO has been studied.

5.2 Experimental Section

5.2.1 Catalyst preparation

The preparation of the Cu-Co based catalysts employed in this study involves the 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 co-precipitating this mixed nitrate salt solution with a 1.0 M K₂CO₃ solution in a 1L flask, which was initially filled with 200 ml of deionized water at 80 °C.

The pH value was strictly kept at 7 in order to achieve a homogeneous dispersion. After aging for an hour, the precipitate was decanted and then washed with sufficient deionized water at 80 °C in order to eliminate the excess K introduced with the carbonate. The moisturized precursor (filter cake) was dried at 80 °C and ambient pressure for 24 hours. 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 an aqueous potassium carbonate solution. The slurry paste was then dried at 80 °C overnight and calcined in air at 350 °C for 4 hours.

5.2.2 HAS Catalytic Testing

H₂/CO ratio studies of higher alcohol synthesis from syngas over the Cu-Co catalyst were carried out using a stainless steel fixed-bed reactor. Four syngas mixtures of varying compositions were prepared by Airgas, with the H₂/CO ratios ranging from 1 to 2, as shown in Table 5.1. N₂, with a consistent concentration of 4.0%, was used as an internal standard in order to calculate the molar flow rate of the effluent.

Table 5.1 Syngas inlet compositions with respect to different H₂/CO ratio

H ₂ /CO ratio	H ₂ (mol%)	CO (mol%)	N ₂ (mol%)
1.00	48.0	48.0	4.0
1.35	55.2	40.8	4.0
1.75	61.1	34.9	4.0
2.00	64.0	32.0	4.0

One gram of catalyst (45-70 mesh) diluted with 2.5 ml of the same sized glass beads was loaded into the high pressure reactor. A mixture of hexane isomers (refer to as hexanes, purchased from VWR) was selected as the inert supercritical reaction medium. The standard conditions were as follows: total pressure = 4.5 MPa in gas phase operation, total pressure = 13.5

MPa in SCF phase operation, partial pressure of syngas = 4.5 MPa in both gas phase and SCF phase operation, T = 290 °C, syngas flow rate = 50 sccm, hexanes pumping rate = 0.51 ml/min (only in SCF phase operation), H₂/CO ratio = 2, hexanes/syngas molar ratio = 2 (only in SCF phase operation).

The effluent from the reactor was passed through a hot trap, a heat exchanger, and a cold trap, in which it was separated into gas phase and liquid phase product streams. The gas phase products were analyzed using a Varian CP-3380 Gas Chromatograph equipped with a Haysep-DB column and a TCD detector. The liquid phase products were analyzed using a Bruker 430 Gas Chromatograph equipped with a capillary DB-wax column and a FID detector.

In the gas phase HAS experiments, 200 ml hexanes were injected into the cold trap in order to facilitate collection of the volatile alcohol products. This process was repeated after each liquid sample collection. When switching from one H₂/CO ratio to another in the gas phase operation, the residual products inside the catalyst and/or reactor were extracted with hexanes at reaction temperature and pressure for 1 hour. These recovered products were also analyzed by GC-FID in order to determine whether heavy products were retained in the catalyst bed during gas phase operation.

5.3 Results and Discussion

The effect of H₂/CO ratio on higher alcohol synthesis was investigated under gas phase conditions where the H₂/CO ratio was maintained at the different values of 2.0, 1.75, 1.35 and 1.0, respectively. Figure 5.1 shows the CO conversion, H₂ conversion, CO₂ selectivity and CH₄ selectivity in this gas phase higher alcohol synthesis (GP-HAS) experiment under these four H₂/CO molar reaction conditions. It must be noted that the conversion and selectivity are the average values of the data obtained once the reaction had reached steady state (as evidenced by

stable CO conversion). As shown in Figure 5.1, 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.

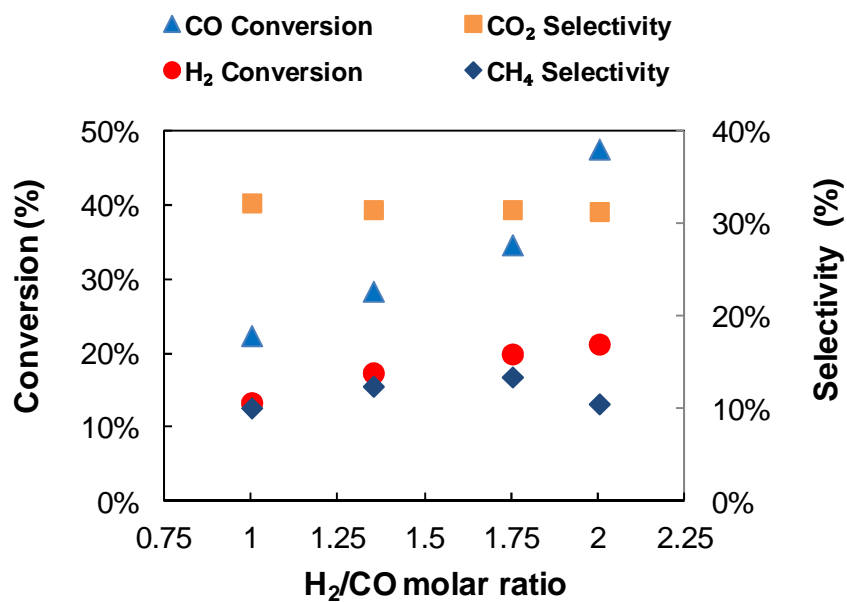


Figure 5.1 Effect of H_2/CO ratio on conversion and gas product selectivity in GP-HAS. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/ Al_2O_3 , syngas flow rate = 50 sccm, temperature = 290 °C, pressure = 4.5 MPa

The effect of H_2/CO ratio on the reaction performance of higher alcohol synthesis under supercritical hexanes phase conditions (SC-HAS) is shown in Figure 5.2. 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 H_2/CO ratio from 1 to 2, while 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 and coworkers (Fan et al.,

1995) 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 H₂/CO ratio was maintained at 1.75 or 2.0. However, at the H₂/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 H₂ conversion also follows a similar trend when the H₂/CO ratio was changed from 1 to 2 in SC-HAS, where the H₂ conversion was relatively steady across all of the H₂/CO ratios employed. In addition, CO₂ selectivity decreased slightly as the H₂/CO ratio increased from 1 to 2 in the SC-HAS experiment. However, the CH₄ selectivity was found to increase remarkably in SC-HAS from 5.3% at H₂/CO ratio = 1 to a value of 13.4% at H₂/CO ratio = 2.

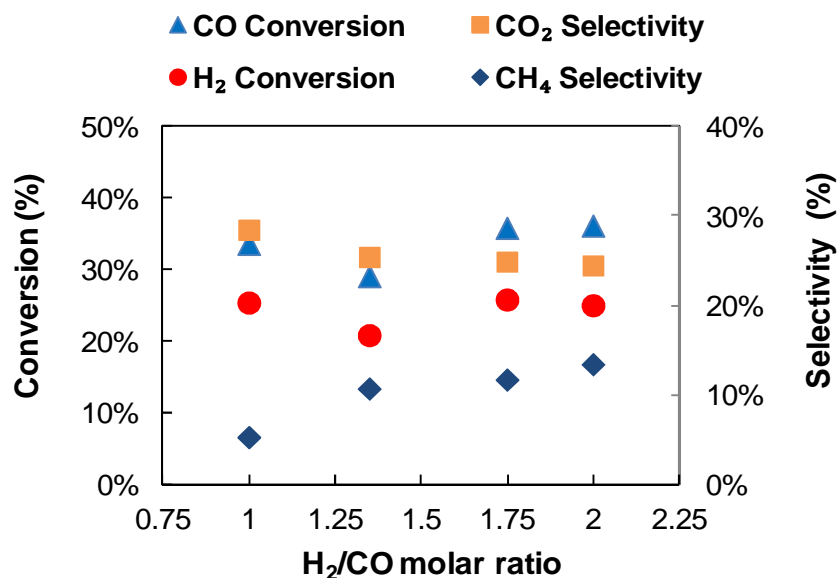


Figure 5.2 Effect of H₂/CO ratio on conversion and gas product selectivity in SC-HAS. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 50 sccm, temperature = 290 °C, pressure = 13.5 MPa, syngas partial pressure = 4.5 MPa, Hexanes/syngas molar ratio = 2

Table 5.2 demonstrates the selectivity towards alcohol products and hydrocarbon products as a function of the H₂/CO ratio in GP-HAS. Under gas phase operation, alcohol products were comprised of C₁-C₈ linear mixed alcohols, and hydrocarbons were collected up to C₂₀ n-paraffin. It can be seen that selectivity towards alcohol products increased from 2.98% to 5.71% when the H₂/CO ratio increased from 1 to 2 in gas phase HAS. Selectivity towards C₈-C₂₀ n-paraffin did not demonstrate a clear trend as the H₂/CO ratio was increased from 1 to 2, and was in the range of 2.5% to 6.5%. In addition, Table 5.2 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 towards higher alcohols, with methanol selectivity lower than 6% for the conditions studied in the gas phase.

Table 5.2 Catalytic performance as a function of H₂/CO ratio in gas phase HAS

H ₂ /CO Molar Ratio	CO Conversion (%)	Selectivity (%)		ROH (wt.%)					α	
		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/Al₂O₃, T = 290 °C, P = 4.5 MPa, syngas flow rate = 50 sccm/g_{cat}.

ROH: C₁-C₈ alcohols

HC: C₈-C₂₀ hydrocarbons

In contrast, Table 5.3 shows the catalytic performance in SC-HAS as a function of H₂/CO ratio. It can be seen that selectivity towards alcohol products slightly decreased from 15.09% when H₂/CO ratio =1 to a value of 12.61% when H₂/CO ratio = 2. Table 5.3 also lists the alcohol products distribution as a function of H₂/CO ratio. Increasing the H₂/CO ratio under supercritical hexanes phase conditions favors the formation of methanol and ethanol. Little to no change was observed in the formation of C₃ and C₄ alcohols when H₂/CO ratio increased from 1 to 2.

However, C₅₊ alcohol decreased significantly with the increase in H₂/CO ratio. Table 5.3 also presents the selectivity towards hydrocarbon products in SC-HAS. Under supercritical hexanes phase conditions, up to C₂₄ linear paraffin was observed in the FID chromatogram, suggesting that the presence of supercritical hexanes facilitates the extraction of longer carbon chain hydrocarbons (C₂₀ to C₂₄) from the catalytic sites.

Table 5.3 Catalytic performance as a function of H₂/CO ratio in SC-HAS

H ₂ /CO Molar Ratio	CO Conversion (%)	Selectivity (%)		ROH (wt.%)					α	
		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/Al₂O₃, T = 290 °C, P = 13.5 MPa, P_{syngas} = 4.5 MPa, syngas flow rate = 50 sccm/g_{cat}, hexanes/syngas molar ratio = 2.

ROH: C₁-C₈ alcohols

HC: C₈-C₂₄ 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 (Fang et al., 2009; Qin et al., 2004). A comparison of the data in Table 2 and Table 3 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 H₂/CO ratios actually promoted the formation of higher alcohols significantly. The difference in the effect that changes in the H₂/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 3 and 4. Figure 3 demonstrates that with the decrease in the H₂/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 H₂ and

one mole of CO are required for the synthesis of alcohols heavier than methanol. 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 (Forzatti et al., 1991; Mahdavi et al., 2005). 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 (X. Xu et al., 1987). However, higher H_2 partial pressure (higher H_2/CO ratio) could diminish coke formation, thereby sustaining catalytic activity. From Figure 5.3, 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 5.4. 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 5.4. 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 versus 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.

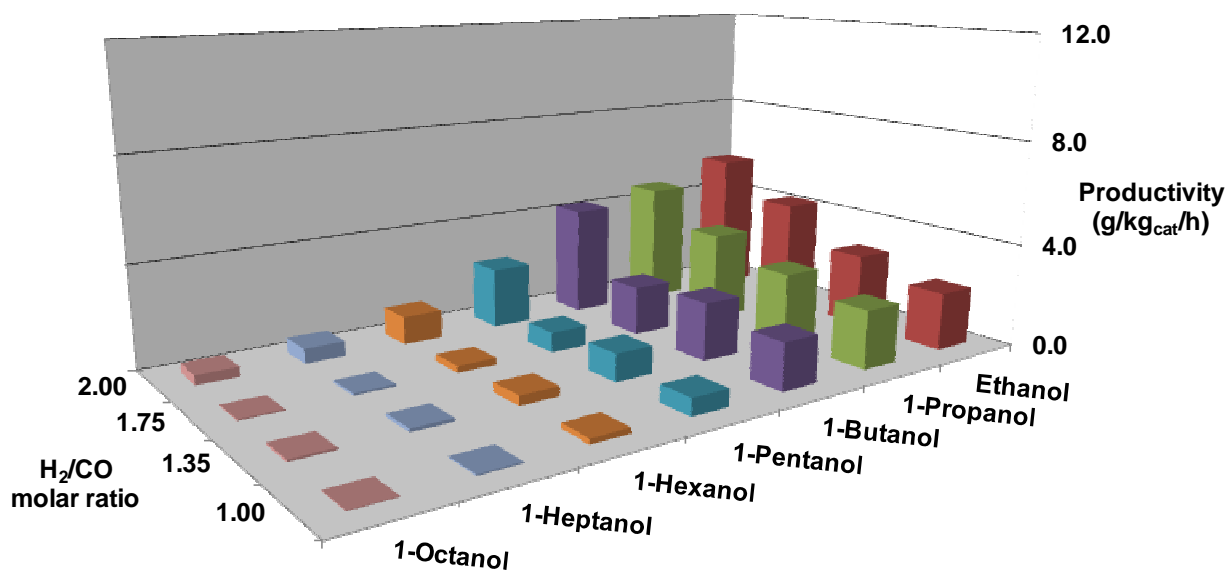


Figure 5.3 Effect of H_2/CO ratios on the productivity of higher alcohols under gas phase conditions. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/ Al_2O_3 , syngas flow rate = 50 sccm, temperature = 290 °C, pressure = 4.5 MPa

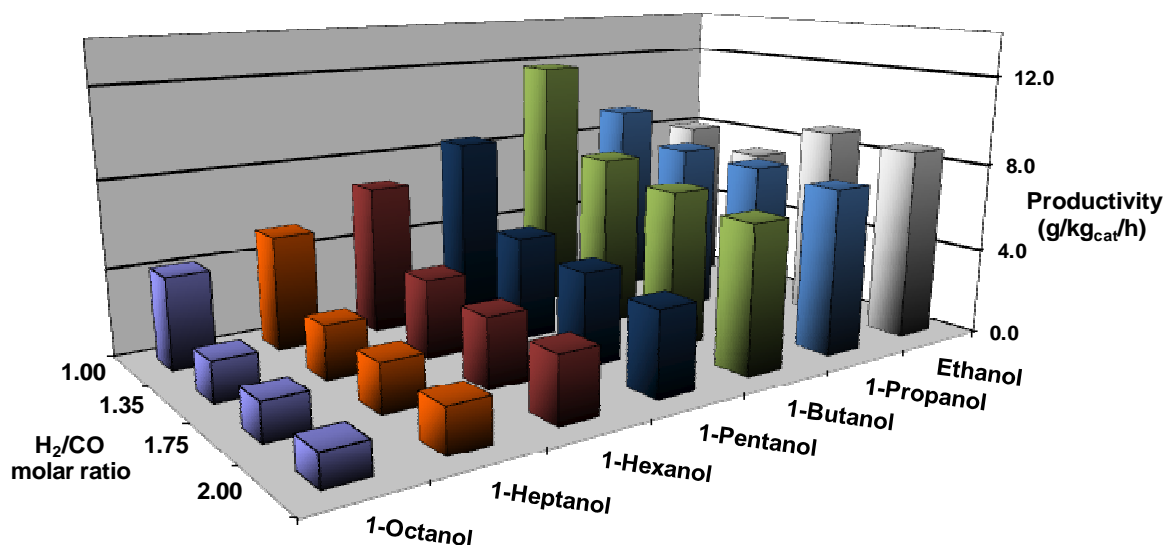


Figure 5.4 Effect of H₂/CO ratios on the productivity of higher alcohols under supercritical hexanes phase conditions. The reaction conditions were as follows: catalyst = 0.5 wt% K promoted Cu/Co/ZnO/Al₂O₃, syngas flow rate = 50 sccm, temperature = 290 °C, pressure = 13.5 MPa, syngas partial pressure = 4.5 MPa, Hexanes/syngas molar ratio = 2

The alcohol products produced over Cu-Co catalysts have been reported to obey the Schulz-Flory distribution (Forzatti et al., 1991; Herman, 2000; X. Xu et al., 1987). The carbon chain growth probability factor (α value) is commonly derived from the slope of a plot of $\ln(W_i/n)$ vs. n , where W_i is the weight percentage of a certain alcohol product and n is the carbon number of this product. Bailliard et al. (1989) reported a same α value (ca. 0.45) 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 2, an α value of alcohol formation was found to be 0.49 at the standard reaction conditions (H₂/CO ratio of 2 in GP-HAS), while the α value of hydrocarbon formation was slightly higher (ca. 0.59). As the H₂/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 H₂/CO ratio, as shown in Table 3.

Compared to $\alpha = 0.49$ for higher alcohols in GP-HAS, an alpha 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 versus 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 5.3. Elbashir and Roberts (Elbashir et al., 2005) found that availability of active sites increased in supercritical Fischer-Tropsch synthesis 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, though it should be noted that the value was significantly higher under supercritical phase conditions in all instances.

5.4 Conclusion

In the present study we investigated the effect of H₂/CO ratio on the synthesis of higher alcohols under both gas phase and supercritical hexanes phase conditions. From our study, four conclusions have been drawn as listed below:

1. Under gas phase conditions, the CO conversion decreased with decreases in the H₂/CO ratio from 2 to 1. However, under supercritical hexanes phase conditions, the CO conversion remained quite stable with changes in H₂/CO ratio.
2. Changes in H₂/CO ratio had little effect on CO₂ selectivity in GP-HAS and slightly influenced CO₂ selectivity in SC-HAS, indicating that the water gas shift reaction approached equilibrium at the conditions studied. CH₄ selectivity exhibited a maximum at moderate H₂/CO ratios in GP-HAS, but decreased significantly with decreasing H₂/CO in SC-HAS.
3. Under gas phase conditions, higher H₂/CO ratios favor the productivity and selectivity of higher alcohols by promoting CO hydrogenation. Under supercritical hexanes phase conditions, however, a lower H₂/CO ratio resulted in much higher alcohol productivity and enhanced carbon chain growth probability factor.
4. Linear alcohols and hydrocarbon products followed the Schulz-Flory distribution. 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 found as the H₂/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.

The benefits of using supercritical hexanes as a reaction medium was confirmed by comparing SC-HAS with GP-HAS under the same operating conditions and H₂/CO ratios. The total alcohol selectivity in SC-HAS is remarkably higher than that obtained in GP-HAS, indicating that the supercritical hexanes facilitated the removal of alcohol products from the active sites of the catalyst and therefore promoted the conversion of syngas into alcohols.

Chapter 6 Future work

6.1 Catalyst characterization of the fresh and spent catalysts

In chapter 4&5, we have shown that the presence of supercritical hexanes as a reaction medium can promote the carbon chain growth probability factors over this Cu-Co based catalyst, and significantly reduce the CH₄ formation. However, it has been reported that the activity of Cu-Co based catalysts (usually referred to as IFP type catalysts) highly depends on the homogeneity of the dispersion of Cu and Co, which can be affected by various step in preparation and reduction process (Courty et al., 1988, 1982). The use of STEM-EDS would allow us to be able to determine the extent of interaction between Cu and Co. The comparison of the EDS results of catalysts used for SC-HAS and GP-HAS might provide more evidence from a characterization perspective that the supercritical solvent improves the catalyst maintenance. Moreover, TEM, XPS and ICP would also be interesting to utilize to garner further fundamental understanding of the catalyst characteristics under these operating conditions.

6.2 Modified catalyst for supercritical higher alcohol synthesis from syngas

As discussed in chapter 1, there are four types of catalysts that have been under development for the synthesis of higher alcohols. This works has focused on the modified low temperature methanol synthesis catalyst (Cu-based) and the Cu-base catalyst modified with Fischer-Tropsch synthesis element (Cu-Co based). The Rh modified catalyst has also been shown to provide a high selectivity towards both higher alcohols while also generating significantly more CH₄ under gas phase conditions. Since it has been proven that the presence of supercritical hexanes would result in a significant reduction in the CH₄ formation over both the Cu based and Cu-Co based catalyst in this study, it would be valuable to investigate the application of a supercritical solvent when using a Rh modified catalyst system in HAS.

6.3 Comparison of supercritical phase and slurry phase higher alcohol synthesis

Besides the exploration of the catalysts, the innovation of different reactor and process technology is also important in order to further improve yields and selectivity. In the current work, the catalytic performance in supercritical phase higher alcohol synthesis (SC-HAS) has been compared with the performance in gas phase higher alcohol synthesis (GP-HAS). Benefits of introducing supercritical hexanes in to HAS as a reaction medium has been partially attributed to the enhance heat transfer provided by the supercritical solvent. Similarly, because of the highly exothermic nature of the HAS process, slurry phase reactor systems, which also provide improved heat transfer capability, would be interesting to investigate and to further compare with SC-HAS over a same catalyst.

By operating the same catalyst in each reaction media (gas-phase, supercritical, and slurry phase) at the same CO conversion levels, the function of the supercritical solvent would be more distinguishable and therefore better understand.

6.4 Dual catalyst bed reactor design

In chapter 3, it has been demonstrated that the formation of methanol was enhanced significantly by the presence of supercritical hexanes over the traditional low temperature methanol synthesis catalyst, namely 0.5 wt% promoted Cu/ZnO/Al₂O₃ catalyst. Additionally, in chapter 4, it has been shown that by adding cobalt into the Cu based methanol synthesis catalyst and applying the supercritical hexanes as a reaction medium, the formation of higher alcohols has been enhanced. Combining these two observations with previously reported dual reactor bed configuration concept (Herman, 2000), it would be interesting to develop a set of experiments on a supercritical hexanes phase higher alcohol synthesis using a dual catalyst bed reactor system.

The idea of this configuration is to maximize the formation of methanol from syngas in the first bed, and convert methanol into the higher alcohols as much as possible at the second bed. Beretta et al. (1995) investigated a dual bed system using Cs/Cu/ZnO/Cr₂O₃ catalyst in the first bed and Cs/ZnO/Cr₂O₃ catalyst in the second bed. They found the isobutanol productivity was more than doubled compared with only using the Cs/Cu/ZnO/Cr₂O₃ catalyst in a single bed operation. In their reaction scheme, methanol reacted with ethanol or propanol in the second catalyst bed via aldol condensation over the Cs/ZnO/Cr₂O₃ catalyst.

By using Cu-Co based catalyst (the same catalyst in Chapter 4&5) in the second catalyst bed and introducing the supercritical hexanes as a reaction medium, methanol whose productivity has been maximized in the first bed, would be expected to readsorb onto the Cu-Co active sites and be converted into higher alcohols via CO insertion. If this assumption proved true, then the formation of a certain higher alcohol (i.e. certain carbon number) could be maximized by adjusting the bed sizes and other reaction conditions, such as GHSV, temperature, and H₂/CO molar ratio, etc.

6.5 Mechanistic study of higher alcohol synthesis over the Cu-Co catalysts

In chapter 5, the formation of higher alcohols in SC-HAS is enhanced by the presence of supercritical hexanes. The carbon chain growth probability factors of alcohol was found distinct from the values of hydrocarbon in both SC-HAS and GP-HAS. A clear understanding of the carbon chain growth intermediate and fundamental mechanism would be extraordinarily meaningful for elucidating the beneficial effect of the supercritical solvent on formation of higher alcohols.

6.6 Phase behavior study of the reaction mixtures in HAS

The composition of the reaction mixture varies along the length of the reactor due to conversion of the syngas to various products thereby causing the critical properties of the mixture to continually change as the reaction proceeds. As such these reaction studies need to be complemented with investigations of the phase-behavior of the reaction mixture at various conversions and conditions in order to gain an understanding of the fundamentals of the thermodynamics and kinetics of the HAS chemical reactions in solution. The SCF-HAS mixture consists of a solvent (e.g. hexane), reactant gases (CO, H₂), light hydrocarbons (CH₄, CO₂), and light alcohols (C₁-C₄ alcohols). As a result, near-critical and supercritical phase HAS operations are governed not only by the properties of the supercritical fluid solvent, but also by the properties of the HAS mixture obtained when the process reaches steady state. Gao et al. (2001) reported critical points for hexane (> 94 mol %) and reactants (CO and H₂) mixtures at different moles ratios. They observed that the critical temperature and critical density of the solvent-reactant mixture decreased as the concentration of CO and H₂ increased, whereby the critical pressure increased with CO and H₂ concentration. In future studies, a series of mixtures that contain different compositions of CO, H₂, CO₂, CH₄, hexanes(or other supercritical media) and C₁-C₄ alcohols should be investigated in order to better understand the phase behavior of the reaction mixtures along the length of the reactor.

Reference

- Abbaslou, R. M. M., Mohammadzadeh, J. S. S., & Dalai, A. K. (2009). Review on Fischer–Tropsch synthesis in supercritical media. *Fuel Processing Technology*, *90*(7-8), 849–856.
- Anderson, J. E., Kramer, U., Mueller, S. a., & Wallington, T. J. (2010). Octane Numbers of Ethanol– and Methanol–Gasoline Blends Estimated from Molar Concentrations. *Energy & Fuels*, *24*(12), 6576–6585.
- Armellini, F. J., & Tester, J. W. (1993). Solubility of sodium chloride and sulfate in sub- and supercritical water vapor from 450-550 °C and 100-250 bar. *Fluid Phase Equilibria*, *84*, 123–142.
- Askgaard, T. S., Norskov, J. K., Ovesen, C. V., & Stoltze, P. (1995). A Kinetic Model of Methanol Synthesis. *Journal of Catalysis*, *156*(2), 229–242.
- Baiker, A. (1999). Supercritical Fluids in Heterogeneous Catalysis. *Chemical Reviews*, *99*(2), 453–474.
- Bailliard Letournel, R. M., Gomez Cobo, A. J., Mirodatos, C., Primet, M., & Dalmon, J. A. (1989). About the nature of the Co-Cu interaction in Co-based catalysts for higher alcohols synthesis. *Catalysis Letters*, *2*(3), 149–156.
- Beretta, A., Sun, Q., Herman, R. G., & Klier, K. (1995). Synthesis of 2-methylpropan-1-ol?methanol mixtures from H₂?CO synthesis gas over double-bed Cs/Cu/ZnO/Cr₂O₃ and Cs/ZnO/Cr₂O₃ catalysts. *Journal of the Chemical Society, Chemical Communications*, *203*(24), 2525.

- Beretta, A., Sun, Q., Herman, R. G., & Klier, K. (1996). Production of Methanol and Isobutyl Alcohol Mixtures over Double-Bed Cesium-Promoted Cu / ZnO / Cr₂O₃ and ZnO / Cr₂O₃ Catalysts, 2, 1534–1542.
- Beretta, A., Tronconi, E., Forzatti, P., Pasquon, I., Micheli, E., Tagliabue, L., & Antonelli, G. B. (1996). Development of a Mechanistic Kinetic Model of the Higher Alcohol Synthesis over a Cs-Doped Zn/Cr/O Catalyst. 1. Model Derivation and Data Fitting. *Industrial & Engineering Chemistry Research*, 35(7), 2144–2153.
- Beychok, M. R. (1974). Coal gasification and the Phenosolvan process. *American Chemical Society 168th National Meeting* (Vol. 51).
- Bochniak, D. J., & Subramaniam, B. (1998). Fischer-tropsch synthesis in near-critical n-hexane: Pressure-tuning effects. *AIChE Journal*, 44(8), 1889–1896.
- Boz, I. (2003). Higher alcohol synthesis over a K-promoted Co₂O₃/CuO/ZnO/Al₂O₃ catalyst. *Catalyst letters*, 87(3), 187–194.
- Boz, I., Sahibzada, M., & Metcalfe, I. S. (1994). Kinetics of the higher alcohol synthesis over a K-promoted CuO/ZnO/Al₂O₃ catalyst. *Ind. Eng. Chem. Res.*, 33(9), 2021–2028.
- Bradford, M. C. J., Konduru, M. V., & Fuentes, D. X. (2003). Preparation, characterization and application of Cr₂O₃/ZnO catalysts for methanol synthesis. *Fuel Processing Technology*, 83(1-3), 11–25.
- Breman, B. B., Beenackers, A. A. C. M., Schuurman, H. A., & Oesterholt, E. (1995). Kinetics of the gas-slurry methanol-higher alcohol synthesis from CO/CO₂/H₂ over a Cs---

- Cu/ZnO/Al₂O₃ catalyst, including simultaneous formation of methyl esters and hydrocarbons. *Catalysis Today*, 24(1-2), 5–14.
- Breman, B. B., Beenackers, A. C. C. M., & Oesterholt, E. (1994). A kinetic model for the methanol-higher alcohol synthesis from CO/CO₂/H₂ over Cu/ZnO-based catalysts including simultaneous formation of methyl esters and hydrocarbons. *Chemical Engineering Science*, 49(24, Part 1), 4409–4428.
- Bromberg, L., & Cheng, W. K. (2010). *Options for sustainable and / or energy-secure transportation. Perception.*
- Brown, D. M., Bhatt, B. L., Hsiung, T. H., Lewnard, J. J., & Waller, F. J. (1991). Novel technology for the synthesis of dimethyl ether from syngas. *Catalysis Today*, 8(3), 279–304.
- Bukur, D. B., Lang, X., Akgerman, A., & Feng, Z. (1997). Effect of Process Conditions on Olefin Selectivity during Conventional and Supercritical Fischer–Tropsch Synthesis. *Industrial & Engineering Chemistry Research*, 36(7), 2580–2587.
- Bukur, D. B., Lang, X., & Nowicki, L. (2005). Comparative study of an iron Fischer–Tropsch catalyst performance in stirred tank slurry and Fixed-Bed reactors. *Ind. Eng. Chem. Res*, 44(16), 6038–6044.
- Burcham, M. M., Herman, R. G., & Klier, K. (1998). Higher alcohol synthesis over double bed Cs–Cu/ZnO/Cr₂O₃ catalysts: optimizing the yields of 2-methyl-1-propanol (Isobutanol). *Ind. Eng. Chem. Res*, 37(12), 4657–4668.

- Calverley, E. M., & Smith, K. T. (1991). The effects of carbon dioxide, methanol, and alkali promoter concentration on the higher alcohol synthesis over a Cu/ZnO/Cr₂O₃ catalyst. *Journal of Catalysis*, *130*(2), 616–626.
- Campbell, C. T., & Daube, K. A. (1987). A surface science investigation of the water-gas shift reaction on Cu(111). *Journal of Catalysis*, *104*(1), 109–119.
- Campos-Martín, J. (1996). Promoter Effect of Cesium on C–C Bond Formation during Alcohol Synthesis from CO/H₂ over Cu/ZnO/Cr₂O₃ Catalysts. *Journal of Catalysis*, *163*(2), 418–428.
- Cao, Y., Gao, Z., Jin, J., Zhou, H., & Cohron, M. (2008). Synthesis Gas Production with an Adjustable H₂ / CO Ratio through the Coal Gasification Process: Effects of Coal Ranks And Methane Addition, *100*(7), 1720–1730.
- Chaumette, P., Courty, P., Kiennemann, A., & Ernst, B. (1995). Higher alcohol and paraffin synthesis on cobalt based catalysts: Comparison of mechanistic aspects. *Topics in Catalysis*, *2*(1), 117–126.
- Chinchen, G. C., Waugh, K. C., & Whan, D. A. (1986). The activity and state of the copper surface in methanol synthesis catalysts. *Applied Catalysis*, *25*(1-2), 101–107.
- Courty, P., Chaumette, P., Durand, D., & Verdon, C. (1988, October 25). Process for manufacturing a mixture of primary alcohols from a synthesis gas, in the presence of a catalyst containing copper, cobalt, zinc and at least one alkali and/or alkaline earth metal. *US Patent 4,780,481*.

- Courty, P., Durand, D., Freund, E., & Sugier, A. (1982). C1-C6 alcohols from synthesis gas on copper-cobalt catalysts. *Journal of Molecular Catalysis*, *17*(2-3), 241–254.
- Dalmon, J. A., Chaumette, P., & Mirodatos, C. (1992). Higher alcohols synthesis on cobalt based model catalysts. *Catalysis Today*, *15*(1), 101–127.
- De Aquino, A. D., & Gomez Cobo, A. J. (2001). Synthesis of higher alcohols with cobalt and copper based model catalysts: effect of the alkaline metals. *Catalysis Today*, *65*(2-4), 209–216.
- Decanio, E. C., Edwards, J. C., Scalzo, T. R., Storm, D. A., & Bruno, J. W. (1991). FT-IR and solid-state NMR investigation of phosphorus promoted hydrotreating catalyst precursors. *Journal of Catalysis*, *132*(2), 498–511.
- Dillow, A. K., Hafner, K. P., Yun, S. L. J., Deng, F., Kazarian, S. G., Liotta, C. L., & Eckert, C. a. (1997). Cosolvent tuning of tautomeric equilibrium in supercritical fluids. *AIChE Journal*, *43*(2), 515–524.
- Dolan, G. A. (2010). Methanol Production and Utilization. In A. A. Vertès, N. Qureshi, H. P. Blaschek, & H. Yukawa (Eds.), *Biomass To Biofuels*.
- Dong, X., Liang, X., Li, H., Lin, G., Zhang, P., & Zhang, H. (2009). Preparation and characterization of carbon nanotube-promoted Co-Cu catalyst for higher alcohol synthesis from syngas. *Catalysis Today*, *147*(2), 158–165.
- Dresselhaus, M. S., & Thomas, I. L. (2001). Alternative energy technologies. *Nature*, *414*(6861), 332–7.

- Durham, E., Zhang, S., & Roberts, C. B. (2010). Diesel-length aldehydes and ketones via supercritical Fischer Tropsch Synthesis on an iron catalyst. *Applied Catalysis A: General*, 386(1-2), 65–73.
- Elbashir, N. O. (2004). *Utilization of Supercritical Fluids in the Fischer-Tropsch Synthesis Over Cobalt-based Catalytic Systems. Annals of Physics.*
- Elbashir, N. O., Bukur, D. B., Durham, E., & Roberts, C. B. (2010). Advancement of Fischer-Tropsch synthesis via utilization of supercritical fluid reaction media. *AIChE Journal*, 56(4), 997–1015.
- Elbashir, N. O., Dutta, P., Manivannan, A., Seehra, M. S., & Roberts, C. B. (2005). Impact of cobalt-based catalyst characteristics on the performance of conventional gas-phase and supercritical-phase Fischer–Tropsch synthesis. *Applied Catalysis A: General*, 285(1-2), 169–180.
- Ellgen, P. C., Bartley, W. J., Bhasin, M. M., & Wilson, T. P. (1979). Rhodium-Based Catalysts for the Conversion of Synthesis Gas to Two-Carbon Chemicals. *Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen* (Vol. 178 SV - 1, pp. 147–157). AMERICAN CHEMICAL SOCIETY.
- Faaij, P. C., Hamelinck, C. N., & Hardeveld, M. R. M. Van. (2002). Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification, 23, 129–152.

- Fan, L., & Fujimoto, K. (1999). Fischer–Tropsch synthesis in supercritical fluid: characteristics and application. *Applied Catalysis A: General*, 186(1-2), 343–354.
- Fan, L., Yokota, K., & Fujimoto, K. (1992). Supercritical phase Fischer-Tropsch synthesis: Catalyst pore-size effect. *AIChE Journal*, 38(10), 1639–1648.
- Fan, L., Yokota, K., & Fujimoto, K. (1995). Characterization of mass transfer in supercritical-phase Fischer-Tropsch synthesis reaction. *Topics in Catalysis*, 2(1-4), 267–283.
- Fang, K., Li, D., Lin, M., Xiang, M., Wei, W., & Sun, Y. (2009). A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas. *Catalysis Today*, 147(2), 133–138.
- Feng, W., Wang, Q., Jiang, B., & Ji, P. (2011). Carbon Nanotubes Coated on Silica Gels as a Support of CuÀCo Catalyst for the Synthesis of Higher Alcohols from Syngas, 11067–11072.
- Fierro, J. L. G. (1993). Catalysis in C1 chemistry: Future and prospect. *Catalysis Letters*, 22(1), 67–91.
- Foley, H. C., Hong, A. J., Brinen, J. S., Allard, L. F., & Garratt-Reed, A. J. (1990). Bimetallic catalysts comprised of dissimilar metals for the reduction of carbon monoxide with hydrogen. *Applied Catalysis*, 61(1), 351–375.
- Fong, wing-C. F., & Wilson, R. F. (1996). Gasification process combined with steam methane reforming to produce syngas suitable for methanol production.pdf.

- Forzatti, P., Tronconi, E., & Pasquon, I. (1991). Higher alcohol synthesis. *Catalysis Reviews*, 33(1-2), 109–168.
- Fox, J. R., Pesa, F. A., & Curatolo, B. S. (1984). Formation of higher alcohols from methanol in the presence of metal acetylides. *Journal of Catalysis*, 90(1), 127–138.
- Fukushima, T., Arakawa, H., & Ichikawa, M. (1985). In Situ High-pressure FT-IR Studies on the Surface Species Formed in CO Hydrogenation on SiO₂-Supported Rh-Fe Catalysts. *J. Phys. Chem.*, 89, 4440–4443.
- Gao, L., Hou, Z., Zhang, H., He, J., Liu, Z., Zhang, X., & Han, B. (2001). Critical Parameters of Hexane + Carbon Monoxide + Hydrogen and Hexane + Methanol + Carbon Monoxide + Hydrogen Mixtures in the Hexane-Rich Region. *Journal of Chemical & Engineering Data*, 46(6), 1635–1637.
- Gautam, M., & Martin II, D. W. (2000). Combustion characteristics of higher-alcohol/gasoline blends. *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 214(5), 497–511.
- Gautam, M., Martin II, D. W., & Carder, D. (2000). Emissions characteristics of higher alcohol/gasoline blends. *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 214(2), 165–182.
- Gerber, M. A., White, J. F., & Stevens, D. J. (2007). *Mixed alcohol synthesis catalyst screening. Contract.*

- Ginosar, D. M., & Subramaniam, B. (1994). Coking and activity of a reforming catalyst in near-critical and dense supercritical reaction mixtures. *Studies in Surface Science and Catalysis*, 88, 327–334.
- Herman, R. G. (2000). Advances in catalytic synthesis and utilization of higher alcohols. *Catalysis Today*, 55, 233–245.
- Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., & Kobylinski, T. P. (1979). Catalytic synthesis of methanol from CO/H₂: I. Phase composition, electronic properties, and activities of the Cu/ZnO/M₂O₃ catalysts. *Journal of Catalysis*, 56(3), 407–429.
- Hilmen, A.-M., Xu, M., Gines, M. J. L., & Iglesia, E. (1998). Synthesis of higher alcohols on copper catalysts supported on alkali-promoted basic oxides. *Applied Catalysis A: General*, 169(2), 355–372.
- Hindermann, J. P., Hutchings, G. J., & Kiennemann, A. (1993). Mechanistic Aspects of the Formation of Hydrocarbons and Alcohols from CO Hydrogenation. *Catalysis Reviews*, 35(1), 1–127.
- Hohlein, B., Von Oer Decken, C. B., Holtje, J., & Mausbeck, D. (1991). Production of Energy Alcohols. In K.-J. J. and S. K. B. T.-S. in S. S. and C. A. Holmen (Ed.), *Natural Gas Conversion* (Vol. Volume 61, pp. 549–555). Elsevier.
- Huang, X. (2003). *Supercritical fluids as alternative reaction media for Fischer-Tropsch synthesis*.

- Huang, X., Elbashir, N. O., & Roberts, C. B. (2004). Supercritical Solvent Effects on Hydrocarbon Product Distributions from Fischer–Tropsch Synthesis over an Alumina-Supported Cobalt Catalyst. *Industrial & Engineering Chemistry Research*, 43(20), 6369–6381.
- Huang, X., & Roberts, C. B. (2003). Selective Fischer–Tropsch synthesis over an Al₂O₃ supported cobalt catalyst in supercritical hexane. *Fuel Processing Technology*, 83(1-3), 81–99.
- Ichikawa, M. (1982). Cluster-derived supported catalysts and their use. *Chemtech*, 12, 674.
- Jacobs, G., Chaudhari, K., Sparks, D., Zhang, Y., Shi, B., Spicer, R., Das, T. K., et al. (2003). Fischer–Tropsch synthesis: supercritical conversion using a Co/Al₂O₃ catalyst in a fixed bed reactor. *Fuel*, 82(10), 1251–1260.
- Jiang, T., Niu, Y., & Zhong, B. (2001). Synthesis of higher alcohols from syngas over Zn–Cr–K catalyst in supercritical fluids. *Fuel Processing Technology*, 73(3), 175–183.
- Kelly, K. J., Bailey, B. K., Coburn, T. C., Clark, W., & Lissiuk, P. (1996). *Federal Test Procedure Emissions Test Results from Ethanol Variable-Fuel Vehicle Chevrolet Lumina*. *Federal Test Procedure Emissions Test Results from Ethanol Variable-Fuel Vehicle Chevrolet Lumina. Test.*
- Kiennemann, A., Diagne, C., Hindermann, J. P., Chaumette, P., & Courty, P. (1989). Higher alcohols synthesis from CO+2H₂ on cobalt–copper catalyst: Use of probe molecules and

- chemical trapping in the study of the reaction mechanism. *Applied Catalysis*, 53(2-3), 197–216.
- Klier, K., Beretta, A., Sun, Q., Feeley, O. C., & Herman, R. G. (1997). Catalytic synthesis of methanol, higher alcohols and ethers. *Catalysis Today*, 36(1), 3–14.
- Klier, K., Herman, R. G., Himelfarb, P. B., Young, C.-W., Hou, S., & Marcos, J. A. (1993). C-C Bond Formation Via [beta]-Addition with Oxygen Retention Reversal in Oxygenate Synthesis. In F. S. L. GUCZI (Ed.), *Studies in Surface Science and Catalysis* (Vol. Volume 75, pp. 1441–1452). Elsevier.
- Lang, X., Akgerman, A., & Bukur, D. B. (1995). Steady State Fischer-Tropsch Synthesis in Supercritical Propane. *Ind. Eng. Chem. Res.*, 34(1), 72–77.
- Lange, J.-P. (2001). Methanol synthesis: a short review of technology improvements. *Catalysis Today*, 64(1-2), 3–8.
- Li, D., Ma, Y., Qi, H., Li, W., Sun, Y., & Zhong, B. (2004). Progress in Synthesis of Mixed Alcohols from CO Hydrogenation. *Progress in Chemistry*, 16(4), 584–592.
- Li, D., Yang, C., Zhao, N., Qi, H., Li, W., Sun, Y., & Zhong, B. (2007). The performances of higher alcohol synthesis over nickel modified K₂CO₃/MoS₂ catalyst. *Fuel Processing Technology*, 88(2), 125–127.
- Li, W., Li, Z., & Xie, K. (2009). The Development of Methanol Industry and Methanol Fuel in China. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 31(18), 1673–1679.

- Li, Z., Fu, Y., & Jiang, M. (1999). Structures and performance of Rh–Mo–K/Al₂O₃ catalysts used for mixed alcohol synthesis from synthesis gas. *Applied Catalysis A: General*, 187(2), 187–198.
- Lietti, L., Tronconi, E., & Forzatti, P. (1992). Mechanistic aspects of the higher alcohol synthesis over K₂O-promoted ZnCr oxide: Temperature-programmed reaction and flow experiments of C₃, C₄, and C₅ oxygenates. *Journal of Catalysis*, 135(2), 400–419.
- Linghu, W., Li, X., Asami, K., & Fujimoto, K. (2006). Process design and solvent recycle for the supercritical Fischer–Tropsch synthesis. *Energy & Fuels*, 20(1), 7–10.
- Liu, J., Qin, Z., & Wang, J. (2001). Methanol synthesis under supercritical conditions: calculations of equilibrium conversions by using the Soave–Redlich–Kwong equation of state. *Ind. Eng. Chem. Res.*, 40(17), 3801–3805.
- Ma, C.-H., Li, H.-Y., Lin, G.-D., & Zhang, H.-B. (2010). MWCNT-Supported Ni–Mo–K Catalyst for Higher Alcohol Synthesis from Syngas. *Catalysis Letters*, 137(3-4), 171–179.
- Mahdavi, V., & Peyrovi, M. H. (2006). Synthesis of C₁–C₆ alcohols over copper/cobalt catalysts. *Catalysis Communications*, 7(8), 542–549.
- Mahdavi, V., Peyrovi, M. H. H., Islami, M., & Mehr, J. Y. (2005). Synthesis of higher alcohols from syngas over Cu-Co₂ O₃/ZnO, Al₂O₃ catalyst. *Applied Catalysis A: General*, 281(1-2), 259–265.

- Majocchi, L., Lietti, L., Beretta, A., Forzatti, P., Micheli, E., & Tagliabue, L. (1998). Synthesis of short chain alcohols over a Cs-promoted Cu/ZnO/Cr₂O₃ catalyst. *Applied Catalysis A: General*, 166(2), 393–405.
- Mawson, S., McCutchen, M. S., Lim, P. K., & Roberts, G. W. (1993). Thermodynamics of higher alcohol synthesis. *Energy & Fuels*, 7(2), 257–267.
- McHugh, M. A., & Krukonis, V. J. (1994). *Supercritical Fluid Extraction* (2nd Edition). Elsevier.
- McHugh, M. A., & Paulaitis, M. E. (1980). Solid solubilities of naphthalene and biphenyl in supercritical carbon dioxide. *Journal of Chemical & Engineering Data*, 25(4), 326–329.
- Mehta, S., Simmons, G. W., Klier, K., & Herman, R. G. (1979). Catalytic synthesis of methanol from CO/H₂: II. Electron microscopy (TEM, STEM, microdiffraction, and energy dispersive analysis) of the Cu/ZnO and Cu/ZnO/Cr₂O₃ catalysts. *Journal of Catalysis*, 57(3), 339–360.
- Mertzweiler, Joseph K., Rouge, B., Cull, N. L., & McCracken, E. A. (1958). Preparation of high molecular weight alcohols.
- Minahan, D. M., Epling, W. S., & Hoflund, G. B. (1998). Higher-alcohol synthesis reaction study V. Effect of excess ZnO on catalyst performance. *Applied Catalysis A: General*, 166(2), 375–385.
- Nakamura, J., Campbell, J. M., & Campbell, C. T. (1990). Kinetics and mechanism of the water-gas shift reaction catalysed by the clean and Cs-promoted Cu(110) surface: a comparison with Cu(111). *Journal of the Chemical Society, Faraday Transactions*, 86(15), 2725–2734.

- Nirula, S. (1994). *Dow/Union Carbide Process for Mixed Alcohols from Syngas; PEP Review No. 85-1-4* (Vol. 46). Menlo Park, CA: American Chemical Society.
- Nunan, J. G., Bogdan, C. E., Herman, R. G., & Klier, K. (1989). Efficient carbon-carbon bond formation in ethanol homologation by CO/H₂ with specific C1 oxygen retention over Cs/Cu/ZnO catalysts. *Catalysis Letters*, 2(1), 49–55.
- Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C.-W., & Herman, R. G. (1988). Methanol and C₂ oxygenate synthesis over cesium doped Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts: A study of selectivity and ¹³C incorporation patterns. *Journal of Catalysis*, 113(2), 410–433.
- Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C.-W., & Herman, R. G. (1989). Higher alcohol and oxygenate synthesis over cesium-doped Cu/ZnO catalysts. *Journal of Catalysis*, 116(1), 195–221.
- P., J. K. (1994). *J. Phys. Chem.*, 98, 441.
- Palekar, V. M., Jung, H., Tiemey, J. W., & Wender, I. (1993). Slurry phase synthesis of methanol with a potassium methoxide/copper chromite catalytic system. *Applied Catalysis A: General*, 102(1), 13–34.
- Pan, W. X., Cao, R., & Griffin, G. L. (1988). Direct alcohol synthesis using copper/cobalt catalysts. *Journal of Catalysis*, 114(2), 447–456.
- Park, T. (1997). Kinetic analysis of mixed alcohol synthesis from syngas over K/MoS₂ catalyst. *Industrial & engineering chemistry*, 36(12), 5246–5257.

- Penninger, J. M. L., McHugh, M. A., Radosz, M., & Krukonis, V. J. (1985). *Supercritical fluid technology. BioTechniques* (Vol. 50). Elsevier Science Pub. Co., Inc., New York, NY.
- Qin, Z., Liu, J., & Wang, J. (2004). Solvent effects on higher alcohols synthesis under supercritical conditions: a thermodynamic consideration. *Fuel Processing Technology*, 85(8-10), 1175–1192.
- Reed, T. B., & Lerner, R. M. (1973). Methanol: A Versatile Fuel for Immediate Use. *Science*, 182(4119), 1299–1304.
- Reubroycharoen, P., Yoneyama, Y., Vitidsant, T., & Tsubaki, N. (2003). Catalytically active supercritical fluid to accelerate methanol synthesis. *Fuel*, 82(18), 2255–2257.
- Roberts, G. W., Márquez, M. a., & McCutchen, M. S. (1997). Alcohol synthesis in a high-temperature slurry reactor. *Catalysis Today*, 36(3), 255–263.
- Satterfield, C. N. (1991). Heterogeneous catalysis in industrial practice. *2nd edition ed.* (Vol. 51, p. 447). McGraw-Hill.
- Savage, P. E., Gopalan, S., Mizan, T. I., Martino, C. J., & Brock, E. E. (1995). Reactions at supercritical conditions: Applications and fundamentals. *AIChE Journal*, 41(7), 1723–1778.
- Schmitt, W. J., & Reid, R. C. (1988). The solubility of paraffinic hydrocarbons and their derivatives in supercritical carbon dioxide. *Chemical engineering communications*, 64, 155–176.

- Sengers, J. M. H. L. (1991). *Supercritical Fluids—Fundamentals and Applications. Physical Chemistry Chemical Physics* (Vol. 13). Kluwer Academic Publishers.
- Sheffer, G. R., & King, T. S. (1989). Differences in the promotional effect of the group IA elements on unsupported copper catalysts for carbon monoxide hydrogenation. *Journal of Catalysis*, *116*(2), 488–497.
- Sibillia, J. A., Dominguez, J. M., Herman, R. G., & Klier, K. (1984). *Alcohol synthesis over Fe/Cu/ZnO catalysts*.
- Smith, K. J., & Anderson, R. B. (1983). The higher alcohol synthesis over promoted Cu/ZnO catalysts. *The Canadian Journal of Chemical Engineering*, *61*(1), 40–45.
- Smith, K. J., & Anderson, R. B. (1984). A chain growth scheme for the higher alcohols synthesis. *Journal of Catalysis*, *85*(2), 428–436.
- Smith, K. J., Herman, R. G., & Klier, K. (1990). Kinetic modelling of higher alcohol synthesis over alkali-promoted Cu/ZnO and MoS₂ catalysts. *Chemical Engineering Science*, *45*(8), 2639–2646.
- Smith, K. J., Young, C.-W., Herman, R. G., & Klier, K. (1991). Development of a kinetic model for alcohol synthesis over a cesium-promoted copper/zinc oxide catalyst. *Industrial & Engineering Chemistry Research*, *30*(1), 61–71.
- Spath, P. L., & Dayton, D. C. (2003). Preliminary Screening — Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for

Biomass-Derived Syngas Preliminary Screening — Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals w. *Contract*, (December).

Spivey, J. J., & Egbebi, A. (2007). Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas. *Chemical Society reviews*, 36(9), 1514–28.

Spivey, J. J., Egbebi, A., & Kumar, N. (n.d.). CO hydrogenation to higher oxygenates : mechanistic studies at CNMS.

Stelmachowski, M., & Nowicki, L. (2003). Fuel from the synthesis gas—the role of process engineering. *Applied Energy*, 74(1-2), 85–93.

Stern, D., T. Bell, A., & Heinemann, H. (1983). Effects of mass transfer on the performance of slurry reactors used for fischer-tropsch synthesis. *Chemical Engineering Science*, 38(4), 597–605.

Stevens, R. R., & Conway, M. M. (1988). Mixed alcohols production from syngas.

Subramani, V., & Gangwal, S. K. (2008). A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol. *Energy & Fuels*, 22(2), 814–839.

Subramaniam, B. (2001). Enhancing the stability of porous catalysts with supercritical reaction media. *Applied Catalysis A: General*, 212(1-2), 199–213.

Subramaniam, B., & McHugh, M. A. (1986). Reactions in supercritical fluids - a review. *Industrial & Engineering Chemistry Process Design and Development*, 25(1), 1–12.

- Subramanian, N. D., Balaji, G., Kumar, C. S. S. R., & Spivey, J. J. (2009a). Development of cobalt-copper nanoparticles as catalysts for higher alcohol synthesis from syngas. *Catalysis Today*, *147*(2), 100–106.
- Subramanian, N. D., Balaji, G., Kumar, C. S. S. R., & Spivey, J. J. (2009b). Development of cobalt–copper nanoparticles as catalysts for higher alcohol synthesis from syngas. *Catalysis Today*, *147*(2), 100–106.
- Sugier, A., & Freund, E. (1981). Process for manufacturing alcohols and more particularly saturated linear primary alcohols from synthesis gas. *US Patent 4,291,126*.
- Sugier, A., Freund, E., & Page, J.-F. Le. (1982). Production of alcohols from synthesis gas. *US Patent App. 20,070/004,588*.
- Taylor, L. T. (1996). *Supercritical fluid extraction*. New York: Wiley.
- Thao, N. T. (2007). *DEVELOPMENT OF PEROVSKITE CATALYSTS FOR THE SYNTHESIS OF HIGHER ALCOHOLS*.
- Tien-Thao, N, Alamdari, H., Zahedi-Niaki, M. H., & Kaliaguine, S. (2006). LaCo_{1-x}Cu_xO_{3-δ} perovskite catalysts for higher alcohol synthesis. *Applied Catalysis A: General*, *311*(0), 204–212.
- Tien-Thao, N, Hassanzahediniaki, M., Alamdari, H., & Kaliaguine, S. (2007). Effect of alkali additives over nanocrystalline Co–Cu-based perovskites as catalysts for higher-alcohol synthesis. *Journal of Catalysis*, *245*(2), 348–357.

- Tien-Thao, Nguyen, Zahedi-Niaki, M. H., Alamdari, H., & Kaliaguine, S. (2007). Conversion of syngas to higher alcohols over nanosized LaCo_{0.7}Cu_{0.3}O₃ perovskite precursors. *Applied Catalysis A: General*, 326(2), 152–163.
- Tijm, P. J. A., Waller, F. J., & Brown, D. M. (2001). Methanol technology developments for the new millennium. *Applied Catalysis A: General*, 221(1-2), 275–282.
- Tronconi, E., Forzatti, P., & Pasquon, I. (1990). An investigation of the thermodynamic constraints in higher alcohol synthesis over Cs-Promoted ZnCr-oxide catalyst. *Journal of Catalysis*, 124(2), 376–390.
- Tronconi, E., Lietti, L., Groppi, G., Forzatti, P., & Pasquon, I. (1992). Mechanistic kinetic treatment of the chain growth process in higher alcohol synthesis over a Cs-promoted Zn-Cr-O catalyst. *Journal of Catalysis*, 135(1), 99–114.
- Van Der Laan, G., & Beenackers, A. (1999). Kinetics and Selectivity of the Fischer–Tropsch Synthesis: A Literature Review. *Catalysis Reviews*, 41(3&4), 255–318.
- Vannice, M. A. (1976). The Catalytic Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen. *Catalysis Reviews*, 14(1), 153–191.
- Vedage, G. A., Himelfarb, P. B., Simmons, G. W., & Klier, K. (1985). Alkali-Promoted Copper-Zinc Oxide Catalysts for Low Alcohol Synthesis. *Solid State Chemistry in Catalysis* (Vol. 279 SV - 2, pp. 18–295). American Chemical Society.
- Wender, I. (1996). Reactions of synthesis gas. *Fuel Processing Technology*, 48(3), 189–297.

- Wu, B. C., Klein, M. T., & Sandler, S. I. (1991). Solvent effects on reactions in supercritical fluids. *Ind. Eng. Chem. Res*, 30(5), 822–828.
- Xiang, M., Li, D., Li, W., Zhong, B., & Sun, Y. (2007). Synthesis of higher alcohols from syngas over K/Co/ β -Mo₂C catalysts. *Catalysis Communications*, 8, 503–507.
- Xiang, M., Li, D., Xiao, H., Zhang, J., Qi, H., Li, W., Zhong, B., et al. (2008). Synthesis of higher alcohols from syngas over Fischer–Tropsch elements modified K/ β -Mo₂C catalysts. *Fuel*, 87(4-5), 599–603.
- Xu, M., & Iglesia, E. (1999). Carbon–Carbon Bond Formation Pathways in CO Hydrogenation to Higher Alcohols. *Journal of Catalysis*, 188(1), 125–131.
- Xu, X., Doesburg, E. B. M., & Scholten, J. J. F. (1987). Synthesis of higher alcohols from syngas - recently patented catalysts and tentative ideas on the mechanism. *Catalysis Today*, 2(1), 125–170.
- Yang, R., Zhang, Y., & Tsubaki, N. (2005). Dual catalysis mechanism of alcohol solvent and Cu catalyst for a new methanol synthesis method. *Catalysis Communications*, 6(4), 275–279.
- Yokota, K., & Fujimoto, K. (1989). Supercritical phase Fischer-Tropsch synthesis reaction. *Fuel*, 68(2), 255–256.
- Yokota, K., & Fujimoto, K. (1991). Supercritical-phase Fischer-Tropsch synthesis reaction. 2. The effective diffusion of reactant and products in the supercritical-phase reaction. *Ind. Eng. Chem. Res*, 30(1), 95–100.

Yokota, K., Hanakata, Y., & Fujimoto, K. (1991). Supercritical phase Fischer–Tropsch synthesis reaction: 3. Extraction capability of supercritical fluids. *Fuel*, 70(8), 989–994.

Zhang, S., Li, T., & Zhu, B. (2006). Study of supercritical three-phase methanol synthesis with n-hexane at supercritical state. *Chemical Engineering Science*, 61(4), 1167–1173.