Direct Alcohol Synthesis Using Modified Cobalt Catalysts

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ABSTRACT

We have investigated factors affecting methanol and higher alcohol synthesis using mixed copper/cobalt based catalysts. We studied coprecipitated Cu/Co/Zn/Al/K catalysts in our preliminary studies. We prepared mixed oxide precursors and Cu/Co/Cr/K catalysts by the complexation method. We studied the effects of CO_2/CO and H_2/CO ratios and catalyst composition on the activities and the alcohol selectivities of Cu/Co/Cr/K catalysts. CO_2 in the feed gas inhibited activity and alcohol selectivity of unpromoted Cu/Cr and Cu/Co/Cr catalysts but did not affect the hydrocarbon yield. Decreasing H_2/CO ratio decreased the activity of unpromoted Cu/Cr and Cu/Co/Cr catalysts but increased the alcohol yield of Cu/Co/Cr catalysts. Feed gas composition had little effect on the activity and selectivity of Cu/Cr/K catalyst. Increasing the Co content in the catalyst resulted in a decrease in catalyst activity and alcohol selectivity and an increase in hydrocarbon selectivity. K inhibited the activity and alcohol selectivity of Cu/Cr catalysts in the presence of a CO_2-free feed gas whereas K promoted the alcohol selectivity of Cu/Co/Cr catalysts. We developed an oxide coverage model to account for the effect of K and CO_2 on the methanol synthesis rate. We proposed a unified model for active sites in Cu/Co/Cr/K catalysts.

EXECUTIVE SUMMARY

We prepared Cu/Co/Cr/K catalysts by citric acid complexation method. We studied the effects of feed gas composition, catalyst composition and the role of alkali promoter on the activity and selectivity of complexed Cu/Co/Cr/K catalysts. As a result of this work, we offer the following conclusions:

1. Increasing the CO_2/CO ratio in the feed gas from 0.0 to 0.25 decreased the overall activity of unpromoted Cu(2)/Cr(1) and Cu(1.5)/Co(0.5)/Cr(1.0) catalysts by 29% and 17% respectively. CO_2/CO ratio had little effect on the activity of K promoted Cu(2)/Cr(1)/K(0.045) catalyst. The alcohol yield of Cu/Cr and Cu/Co/Cr catalysts decreased by 35% and 45% respectively. Hydrocarbon yield of Cu/Co/Cr catalyst decreased by 10%.

2. Increasing the CO/H_2 ratio in the feed gas from 0.4 to 1.0 decreased the overall activity of unpromoted Cu(2)/Cr(1) and Cu(1.5)/Co(0.5)/Cr(1.0) catalysts by 43% and 84% respectively. H_2/CO ratio had little effect on the activity of K promoted Cu(2)/Cr(1)/K(0.045) catalyst. The alcohol yield of Cu/Cr catalyst decreased by 12% while the alcohol yield of Cu/Co/Cr catalyst increased by 22%. The hydrocarbon yields of Cu/Cr and Cu/Co/Cr catalysts decreased by 98% with decrease in H_2/CO ratio.

3. Increasing the Co/Cu ratio from 0.0 to 0.33 resulted in a decrease in the catalyst activity by 35-45% for CO_2-free and CO_2 containing feed gas mixtures. The overall alcohol yield decreased by 89% for CO_2-free feed gas and 76% for CO_2-containing feed gas. The methanol yields decreased by 92% for both feed gas compositions with increase in Co/Cu ratio. The hydrocarbon yield increased by 30% for both feed gases.

4. The effect of K loading in Cu/Cr catalysts was found to be dependent on feed gas composition. For a CO_2-free feed gas, K reduced the catalyst activity by 57%. The alcohol and hydrocarbon yields decreased by about 95% with increase in K content from 0 to 1.5%. For a feed gas containing CO_2, K had a small effect on the catalyst activity which increased by 5%. The overall alcohol yield increased by 17% while the hydrocarbon yield decreased by 15%.

5. For a CO_2-free feed gas, K promoted catalyst activity by 200%. The overall alcohol yield increased by 118% while the overall hydrocarbon yield increased by 25% on the K promoted Cu/Co/Cr/K catalyst. For a CO_2 containing feed gas, K did not have any effect on the overall activity of the K promoted Cu/Co/Cr catalyst. The overall alcohol yield increased by 73% while the hydrocarbon yield decreased by 14%.

6. The maximum higher alcohol yield of 0.024 g/g/hr was obtained on the Cu(1.5)/Co(0.5)/Cr(1.0)/K(0.045) catalyst using a feed gas containing $CO_2/CO/H_2$ = 0/30/70 vol%. Selectivity to alcohols was 97% with higher alcohol selectivity being 66%. Methanol yield of 0.104 g/g/hr and higher alcohol yield of 0.019 g/g/hr were obtained for Cu(2)/Cr(1) catalyst and the overall alcohol selectivity was 77%.

7. We propose a theoretical model showing the effect of oxygen coverage on the methanol yield in order to explain experimentally observed effects of CO_2 and alkali promoter on Cu/ZnO and Cu/Cr methanol synthesis catalysts. The methanol synthesis rate was found to be dependent on the number of perimeter or alkali sites and CO_2 content in feed gas.

8. We propose a unified model for active sites for alcohol synthesis. We propose that Cu sites are active for methanol synthesis and aldehyde hydrogenation. Co sites promote CO dissociation and chain growth. Hydrogenation of alkyl intermediates results in hydrocarbon formation. Co sites modified by neighbouring alkali promoter (viz.K) sites promote chain termination by CO insertion, resulting in increase in oxygenate yield and a concomitant decrease in the hydrocarbon yield.

CONTENTS

1.1 INTRODUCTION

Hydrocarbon mixtures, manufactured from petroleum feedstocks, are used as motor fuels for transportation purposes. Until recently, manufacture and use of hydrocarbon fuels was determined solely by economic considerations. However, the following factors have influenced new public concern for alternate fuels (Eugene and Mills, 1989):

Environmental Protection: Desire for improved air quality has resulted in government regulations on key vehicle exhaust gases (viz. CO, unreacted hydrocarbons, and oxides of N_2). Anti-knock compounds containing tetraethyl lead have been phased out. Carbon monoxide causes drowsiness and respiratory problems. Hydrocarbons react with oxides of N_2 in presence of sunlight to create smog, which subsequent results in formation of ozone. Ozone causes respiratory problems. NO_x is an irritant to lungs and eyes and is a precursor to formation of acid rain which corrodes buildings and monuments.

Political Considerations: Alternate fuels can be made easily using country's own abundant natural resources (viz. coal, natural gas, petroleum fractions, residua and agricultural products). Alternate fuels help in reducing international trade deficit, national budget deficit and dependence on foreign fuel supply.

Oxygenate fuels (viz., alcohols and ethers), have emerged as feasible alternatives to hydrocarbon mixtures. Factors favoring oxygenates are as follows:

- High octane characteristics required for high compression ratio automobile engines.

- Oxygenates can be manufactured easily from coal, natural gas, agricultural products like corn and sugarcane and petroleum fractions.

- Lesser environmental damage by oxygenates such as ethers, which have low volatility.

Most oxygenate fuels are manufactured by a two-step process. In the first stage, natural gas (methane), coal, or petroleum fractions are used for production of synthesis gas containing a mixture of H_2 and oxides of carbon. The syngas is then converted catalytically to desired product. Ethanol can be made by fermentation of corn or sugar cane. Methanol can be converted to gasoline using Mobil's methanol to gasoline process. Ethers, especially methyl tert-butyl ether (MTBE), are used in gasoline blends because they are non-polar and easily miscible with gasoline, boost octane rating, and have low evaporative emissions.

1.2 METHANOL SYNTHESIS

Copper-based catalysts are presently used commercially for methanol synthesis from syngas (i.e., $CO/CO_2/H_2$ mixtures derived from coal or natural gas). The hallmark of these catalysts is their great selectivity for methanol (e.g., greater than 98%). This is attributed to copper's ability to activate CO and/or CO_2 for hydrogenation, without simultaneously activating these molecules for complete dissociation and subsequent Fischer-Tropsch condensation to produce hydrocarbon products.

1.2.1 Comparison of catalysts The commercial methanol catalysts currently in use are multicomponent mixtures of Cu, ZnO, and Cr_2O_3 or Al_2O_3 (Wainwright, 1988; Bowker, 1988; Klier, 1982). For example, ICI recently announced a new formulation based on an active Cu phase

supported on a "specifically designed" $ZnAl_2O_4$ compound (C&EN, April 16, 1990; p. 27). Activities on the order of 1 g/g/hr are obtained at reaction conditions of 500-525K and 50-100 atm. These temperatures are about 100 degrees lower than those required by the previous generation of catalysts, which were based on ZnO-Cr_2O_3 mixtures. Thus it is generally accepted that activity of current catalyst resides primarily with the Cu component.

Herman et al. (1979) studied a coprecipitated CuO(30wt%)/ZnO(70wt%) catalyst and obtained methanol yields of 1.35 g/g/hr. The BET surface area of the used catalyst was 37.1 m^2/g. Feed gas containing $CO_2/CO/H_2$ = 6/24/70 vol% was passed through a 1.27 cm i.d. tubular reactor at reaction conditions of 250 deg C, 75 atm, and GHSV of 5000/hr. The authors proposed that a compound containing Cu(I) cations dissolved in ZnO was the active component of the catalysts.

Chinchen et al. (1986) used a CuO(60wt%)/ZnO(30%)/Al_2O_3(10%) catalyst and obtained a methanol yield of 1.1 g/g/hr. The Cu surface area of the catalyst was 33.1 m^2/g using the N_2O chemisorption technique. Feed gas containing CO(14%)/CO_2(14%)/H_2(46%)/He(26%) was passed through the reactor at reaction conditions of 50 atm and 250°C. They obtained a linear relationship between methanol activity and Cu surface area of Cu/ZnO/Al_2O_3 catalysts. Cu supported on other materials (viz. MgO, SiO_2) had the same turnover number as Cu/ZnO/Al_2O_3 catalysts.

Pan et al. (1988a) studied methanol synthesis in a tubular reactor using coprecipitated Cu/ZnO catalysts at reaction conditions of 250°C and 50 atm for feed gas composition of $CO_2/CO/H_2$ = 6/24/70 (vol%). Using Cu(30%)/ZnO(70%) catalyst, the yield was 1.9 g/g/hr. The BET and Cu surface areas were 65 and 60 m^2/g, respectively. The specific activity of the catalyst was 0.03 g $CH_3OH/m^2/hr$. Methanol synthesis rate varied linearly with Cu surface area. Activity was found to be dependent on catalyst preparation method and composition.

Sheffer and King (1989) obtained a maximum selectivity to methanol of 93 wt% for an unsupported Cu catalyst promoted with 1.2 mol% K. Feed gas containing $H_2/CO/Ar$ = 2/1/0.5 (molar) was admitted into a tubular reactor at a GHSV of 4000/hr at 275 C and 50 atm. Conversions to methanol were less than 5%. The BET surface area of the used catalyst was 0.71 m^2/g and the rate of synthesis was 0.06 g/g/hr. The specific activity of the catalyst was 0.08 $g/m^2/hr$. They found that both activity and selectivity for methanol synthesis increased with increasing K concentration. Pure Cu metal was found to be inactive for CO hydrogenation. Using x-ray diffraction they concluded that potassium was in either a microcrystalline or an amorphous phase as K_2CO_3. Using x-ray photo electron spectroscopy (XPS), they concluded that the calcined catalyst containing only Cu(II) species was reduced to Cu(I) and Cu metal.

1.2.2 Effect of alkali promoter Vedage et al. (1985) studied a series of alkali promoted Cu/ZnO catalysts for methanol synthesis at reaction conditions of 250°C and 75 atm and for a feed gas of H_2/CO = 70/30. Promoter levels of 0.4 mol% of LiOH, NaOH, KOH, RbOH, CsOH and $Ba(OH)_2$ were added to 30/70 mol% Cu/ZnO catalysts respectively. They obtained maximum methanol selectivity of 0.45 g/g/hr for Cs promoted catalyst. They observed an increase of ZnO and Cu particle sizes using x-ray powder diffraction analysis. Increase in activity for methanol production and catalyst selectivity for C_2-C_4 alcohols and methyl formate, acetate and propionate were observed.

Nunan et al. (1989a) studied Cs doped 30mol%Cu/70%ZnO catalysts at reaction conditions of 310°C and 75 atm pressure and for a feed gas of H_2/CO = 0.45. A maximum methanol yield of 0.21 g/g/hr was obtained for 0.5 mol% Cs. Addition of Cs decreased selectivity to methanol and increased selectivity to C_{2+} oxygenates.

Nunan et al. (1989b) investigated the effect of alkali (Cs) on $Cu/ZnO/M_2O_3$ (M = Al,Cr) catalysts under the reaction conditions given above. Maximum methanol yields of 0.24 g/g/hr and 0.44 g/g/hr were obtained for 30 mol% Cu/45% Zn/25% Cr/5% Cs and 30 mol% Cu/45% Zn/25% Al/0.73% Cs catalysts respectively. The Cs/Cu/Zn/Al catalysts were highly selective to methanol and overall alcohol yields were high but CO conversion was lower.

Smith and Anderson (1983) studied the promotional effect of potassium on Cu/ZnO methanol synthesis catalysts under reaction conditions of 285°C and 130 atm. pressure and for a feed gas containing H_2/CO of 0.5. Maximum methanol selectivity was 82.4% for catalyst containing 3 wt% K_2CO_3. They observed that addition of potassium carbonate to Cu/ZnO catalysts increased higher alcohol selectivity.

1.2.3 Discussion of active sites Chinchen et al. (1986), Hoppener et al. (1986), Bridgewater et al. (1986) and Andrew (1980) found that the rate of methanol synthesis was directly proportional to the Cu surface area of Cu/ZnO catalysts. Pan et al. (1988) found that methanol synthesis rate was linearly correlated to Cu surface area of coprecipitated Cu/ZnO catalysts. Based on IR studies and CO and H_2 TPD experiments, they postulated that methanol was synthesized on segregated Cu clusters on the catalyst surface.

Herman et al. (1979) proposed that methanol was synthesized from active Cu(I) sites present in the ZnO phase in coprecipitated $Cu/ZnO/M_2O_3$ (M = Al,Cr) catalysts. They proposed that the role of CO_2 was to maintain Cu in Cu(I) state in the ZnO phase. Active Cu(I) sites were believed to chemisorb and activate CO nondissociatively while the ZnO surface was believed to activate hydrogen. This proposition is in contrast to the proposition by Chinchen et al. and other workers that methanol synthesis rate was linearly proportional to the Cu surface area.

Monnier et al. (1984) studied effect of CO_2 on Cu/Cr_2O_3 catalysts. Using X-ray photoelectron spectroscopy (XPS), they found that stability of Cu(I) species in $Cu\text{-}Cr_2O_3$ catalysts was independent of CO_2. Using temperature programmed desorption (TPD), they concluded that non-catalytic, competitive adsorption of CO_2 on Cu(I) sites inhibited methanol synthesis.

Vedage et al. (1985) studied alkali promoted Cu/ZnO catalysts and suggested that at low CO_2 concentrations, Cs formate, obtained by reaction of CsOH with CO, was hydrogenated to methanol by hydrogen activated on the active Cu(I)/ZnO surface in the intimate neighborhood CsOH sites. At higher CO_2 concentrations, whole active surface of Cu(I)/ZnO components was believed to be responsible for methanol production while some Cs sites were lost due to probable formation of surface carbonate. They found that alkali hydroxides were more effectively dispersed on the catalyst surface than alkaline earth metal hydroxides.

In contrast to the proposition by Vedage et al. (1985), Sheffer and King (1989) studied the effect of K on unsupported Cu catalysts and proposed that upon reduction, active Cu(I) sites were stabilized by phase formation of K with Cu in the form of $KCuCO_3$.

In summary, it appears that active Cu(I) sites are produced by oxidation of Cu by support oxides (viz. ZnO, Al_2O_3 and Cr_2O_3). Alkali promoters also produce oxidized Cu(I) sites. The presence of small amounts of CO_2 in the feed gas oxidizes Cu in Cu/ZnO catalysts. However, at higher concentrations, CO_2 can poison alkali promoted catalysts by forming carbonates which block active Cu(I) sites. In the case of Cu/Cr_2O_3 catalysts, CO_2 in the feed gas blocks active Cu(I) sites.

1.3 HIGHER ALCOHOL SYNTHESIS

1.3.1 Alkali promoted Cu/ZnO catalysts. Smith and Anderson (1983) studied the promotional effect of potassium on 46wt%CuO/46%ZnO/8%Al_2O_3 methanol synthesis catalysts under reaction conditions of 285°C and 130 atm pressure and for a feed gas containing H_2/CO of 0.5. For 0.5wt% K_2CO_3, they obtained alcohol selectivities of 61.3wt% methanol, 4.3wt% ethanol, 5.9wt% propanol, 13.7wt% 2-methyl-1-propanol and 10.3wt% pentanol. They observed that potassium-promoted Cu/ZnO catalysts had increased higher alcohol selectivity, especially for 2-methyl-1-propanol. Maximum butanol selectivity was obtained at 0.5wt% K_2CO_3. Maximum reactant consumption was obtained at 1.0 wt% K_2CO_3. Decreasing the H_2/CO ratio from 2.0 to 0.5 led to a two-fold increase in the selectivity to isobutanol.

Hofstadt et al. (1983) studied the effect of preparation method and promoter on the activity of $Cu/Zn/Al_2O_3$ catalysts. They found that most active and thermoresistant catalysts were prepared by the coprecipitation method. The reaction conditions used were 250°C, 100 atm and feed gas composition was $CO/CO_2/H_2/N_2$ = 29.5/1.5/62.5/6.5. They obtained maximum yield of 0.47 g/g/hr and 79% conversion to methanol using a CuO(44wt%)/ZnO(33wt%)/Al_2O_3(18wt%) catalyst. MnO, Cr_2O_3 and ThO_2 promoted ethanol, n-propanol and n-butanol production, respectively.

Nunan et al. (1989a) studied Cs-promoted Cu/ZnO catalysts at reaction conditions of 310°C and 75 atm pressure and for a feed gas of H_2/CO = 0.45. Methanol was obtained as the main product. However the combined yield of C_{2+} oxygenates sometimes exceeded the methanol yield. Maximum product yields of 0.16 g/g/hr of methanol and 0.22 g/g/hr of C_{2+} oxygenates were obtained for 0.3-0.5 mol% Cs. They observed an increase in yields of 1-propanol, 1-butanol, 2-methyl-1-propanol and 2-methyl-1-butanol using alkali promoted catalyst.

Nunan et al. (1989b) investigated the effect of alkali (Cs) on $Cu/ZnO/M_2O_3$ (M = Al,Cr) catalysts under reaction conditions given above. Maximum overall alcohol yield was 0.31 g/g/hr for 3 mol%Cs/Cu/ZnO/Cr_2O_3 catalysts. 2.5mol%Cs/Cu/ZnO/Al_2O_3 catalysts were highly selective to methanol and overall alcohol yields of 0.44 g/g/hr were obtained, but CO conversion was lower.

Discussion of active sites. From their studies of coprecipitated $Cu/ZnO/K_2CO_3$ catalysts, Smith and Anderson (1983) believed that CO decreased the relative rate of hydrogenation of methanol precursor. Their results agreed with Graves' (1931) mechanism, which proposes chain growth by condensation of two lower alcohols. Secondary alcohols were believed to react only by the loss of the hydroxyl group.

Vedage et al. (1985) studied unpromoted and Cs promoted Cu/ZnO catalysts and observed the initial agglomeration and susequent dispersion of alkali hydroxides on the surface during activity tests. They proposed methanol formation by hydrogenation of intermediate formate species on Cs promoted catalyst at low CO_2 concentrations. Higher alcohols were then proposed to be obtained by stepwise attachment of either the C or the O atom of an intact C-O bond of a C_1 intermediate to a growing alcohol chain. Based on their product compositions, at a lower H_2/CO ratio of 0.45, they proposed that aldol condensation reaction at β-carbon sites was more efficient than CO insertion reaction for unpromoted and Cs promoted Cu/ZnO catalysts. At a higher H_2/CO ratio of 0.89, CO insertion reaction was proposed to be more efficient than aldol condensation reaction for unpromoted Cu/ZnO catalysts. Straight chain higher alcohols were believed to be formed by CO insertion reaction while branched chain alcohols were believed to be obtained by aldol condensation at the β-carbon sites.

Hoftstadt et al. (1983) studied $Cu/ZnO/M_2O_3/K$ catalysts and proposed that oxygenates were obtained on active Cu(I)/ZnO phase while species with methylene structure were obtained on active metallic Cu sites promoted by K. Cr was believed to affect Cu(I)/Cu(0) ratio and concentration of surface species resulting in formation of alcohols with C-chains of different lengths. Potassium was believed to accelerate interaction of surface species. They believed that methanol was synthesized by hydrogenation of CO on active Cu(I) sites in Cu/ZnO catalysts. They proposed that methanol was formed partially by hydrogenolytic splitting of surface formate obtained from intermediate species with methylene structure using Cu/ZnO/K catalyst.

1.3.2 Cu/Co catalysts Courty et al. (1983) used Cu-Co based catalysts at 260-320°C, 60-100 atm pressure, and 3000-6000/hr GHSV. The composition ratio of Cu/Co was 4-5 in $CuO/CoO/Al_2O_3$ catalysts. The composition ratio of Cu/Cr was 2-3 in $CuO/CoO/Cr_2O_3$ catalysts. The productivity was 0.2 g/g cat/hr when selectivity of C_1-C_6 alcohols was 60-80%. The product contained MeOH 50-70%, EtOH 16-23%, PrOH 8-14% and the rest C_{4+} alcohols.

Courty et al. (1982) studied the effect of Cu-Co based catalysts on alcohol synthesis and found that small concentrations of Co promoted methanol synthesis. When $1 < Cu/Co < 3$, a mixture of straight chain alcohols was obtained with hydrocarbons as side products. Large Co concentrations resulted in a Fischer-Tropsch catalyst. Increasing Cr/Co ratio decreased overall activity and increases selectivity to methanol. Alkali was found to reduce methanantion and increase selectivity.

Pan et al. (1988a) used a Cu(20)/Co(20)/Zn(20)/Al(40)/K(0.5) catalyst in a reactor maintained at 290°C, 50 atm, and $H_2/CO = 1.0$. The rate of conversion of CO was 0.168 gCO/gcat/hr and the overall conversion of CO was 25% at a space time of 40 gcat-hr/gmol. The product contained MeOH 6-8%, C_2-C_6 alcohols 42-50%, C_1-C_6 hydrocarbons 15-20%, and CO_2 25%.

Sheffer and King (1988) studied the effect of feed gas composition on complexed Cu/Co/Cr/K =1/1/0.8/0.09 catalysts. They found that decreasing the H_2/CO ratio from 2 to 1 decreased the alcohol selectivity but the aldehyde selectivity increased. The overall catalyst activity increased by 19%. Upon further decreasing the H_2/CO ratio from 1 to 0.5, they found that the overall activity decreased by 67%. Selectivity to alcohols decreased from 46wt% to 28wt%. Increasing the CO_2/CO ratio from 0.0 to 0.6 resulted in decrease in catalyst activity by 17% and increased selectivity to hydrocarbons.

Discussion of active sites Spencer (1986) used ESCA and SIMS on $Cu/Co/ZnO/Al_2O_3$ catalysts and found that surface Co concentrations were much higher than the bulk Co concentrations. They proposed that surface of Cu crystallites was covered by an oxidic layer containing Co and support oxides which would prevent CO chemisorption by Cu-Co bonding.

In contrast, Cao et al. (1988) studied adsorption behaviour of coprecipitated $Cu/Co/ZnO/Al_2O_3$ catalysts using IR and TPD techniques and found that the surface of the reduced catalyst consisted of metallic Cu clusters containing isolated Co atoms. These Co atoms were believed to block active Cu sites for methanol synthesis but were capable of accomplishing elementary steps associated with Fischer Tropsch reactions. Co atoms were found to adsorb multiple CO molecules and dissociate C-O bonds.

Pan et al. (1988b) studied coprecipitated Cu/Co/Zn/Al catalysts and proposed chain growth of a common surface alkyl intermediate on Co sites followed by chain termination on Cu sites resulted in alcohol formation. They found that secondary reactions of alcohol products i.e., homologation did not constitute a major part of chain growth mechanism. They observed

condensation reactions at higher alcohol concentrations and proposed that bimolecular reaction occurs at acid-base sites on the oxide component of the catalyst. Since they did not observe any chain growth due to gas phase methanol, they discounted the theory that higher alcohols are formed from methanol produced on Cu sites followed by homologation on Co sites.

Courty et al. (1982) studied coprecipitated Cu/Co/Cr catalysts and proposed that Co must be partly combined in a spinel type structure in the precursor. In the activated catalyst Co was believed to be present either in the pure form or was alloyed with Cu. They believe that alkali cation first suppressed acidity by suppressing alcohol dehydration and then modified electronic properties of Co. They believe that CO was at least partly chemisorbed and incorporated non-dissociatively since alcohols were obtained by Fischer-Tropsch mechanism along with hydrocarbons. Courty et al. proposed that Cu(I) was stabilized as Cu(I) chromite and was responsible for CO adsorption leading to higher alcohol synthesis.

Sheffer et al. (1989) studied complexed Cu/Co/Cr/K catalysts and did not find any evidence of Cu(I) ions or Co metal on the activated catalyst surface. Therefore, they disagree with the proposition by previous workers that alkyl chain growth on Co metal sites followed by alcohol termination on molecularly adsorbed CO was responsible for higher alcohol formation. Instead they proposed that Cu may be electronically modified on a K promoted Co/Cr spinel. They went on to propose that K reduced the activity of Cu/Co/Cr catalysts due to probable electronic effect resulting from electron donation to Co by K. Since they did not observe any higher alcohol formation on Cu/Cr/K catalyst, they discounted the theory that Cu(I)-Cr_2O_3 methanol sites were modified by K. Instead they proposed that Co was a necessary component for higher oxygenate formation in the Cu/Co/Cr/K catalysts.

1.4 COBALT CATALYSIS

1.4.1 Fischer-Tropsch synthesis. Storch et al. (1951) reviewed Fischer-Tropsch synthesis extensively. According to Storch et al., Franz Fischer and Hans Tropsch used alkalized iron turnings in 1923 and obtained an oily liquid containing oxygenates from H_2 and CO under reaction conditions of 100-150 atm and 400-450°C. However, the German goal in 1930's was synthesis of hydrocarbons to be used as gasoline, diesel, paraffins etc. In 1930, Fischer passed a feed gas containing H_2/CO = 2 over a Co/Cu/Th = 9/1/2 catalyst in a double pass tubular reactor and obtained hydrocarbons under reaction conditions of 1 atm and 220 deg C. The hydrocarbon composition was CH_4 (27wt%), C_2H_6 (6.6wt%), C_3+C_4 (10.2wt%), gasoline (37.6wt%), diesel oil (17.5wt%) and paraffin (1.6wt%).

Initially, only Co catalysts were found to be commercially feasible and were used by Ruhrchemie in 1937. The compositions of commercial Co catalysts were Co/ThO_2/Kieselguhr = 100/18/200 (wt) and Co/ThO_2/MgO/Kieselguhr = 100/5/8/200 (wt) respectively. The major products were wax, oil, H_2O, gaseous hydrocarbons containing mostly straight chain paraffins and small amounts of CO. Alcohols were produced in small amounts by Co catalysts at moderate to high pressures.

Anderson et al. (1947) studied Co/ThO_2/MgO/Kieselguhr = 100/6/12/200 by weight. Under reaction conditions of 1 atm, 181°C and for a feed gas containing H_2/CO = 2, they obtained products containing CO_2 (1.8wt%), H_2O (57.3wt%), C_1 (5.5wt%), C_2 (0.7wt%), C_3+C_4 (3.3wt%) and liquid hydrocarbons (C_{5+} = 31.4wt%). The liquid hydrocarbons were 77wt% of the total hydrocarbons.

Anderson (1984) also reviewed Fischer-Tropsch synthesis and concluded that Co metals are active Fischer-Tropsch catalysts but readily form carbonyls. At 1 atm, catalyst pores were filled with wax which could be removed by H_2/solvent treatment. At 7-12 atm, catalyst pores were permanently filled with liquid hydrocarbons. The Fischer-Tropsch synthesis is known to occur even in the liquid phase. In 1940's, Co catalysts were replaced by active Fe catalysts commercially. Fe catalysts were easily available and thus were more economically attractive. Fe catalysts were also active for oxygenate synthesis and thus imparted flexiblity to the Fischer-Tropsch synthesis process.

Olefin synthesis catalysts According to Anderson (1984), Pichler et al. (1967) found that olefins, particularly alpha-olefins, were the major products on Co catalysts. The olefin composition passed through a maximum at C_3-C_4 (80% of C number) and then diminished. Dent and Lin (1979) studied impregnated, supported Co catalysts in a Berty reactor under reaction conditions of 7.8 atm and feed gas containing $CO/H_2/He$ = 1/3/6. They found that $Co/Mn/Al_2O_3/K_2O$ catalysts had the greatest selectivity to C_2-C_4 olefins (ca. 50%) in the temperature range of 177-350 deg C. K_2O was found to increase the olefin yield.

McMahon et al. (1987) used microwave discharge method to prepare highly dispersed Co clusters in zeolites. Catalysts were prepared by sublimation of $Co_2(CO)_8$ into dehydrated NaX zeolite. The resulting plasma was then ignited, resulting in decomposition of $Co_2(CO)_8$. Under reaction conditions of 1 atm, 239-271°C and 1-3% conversion, they obtained 26 wt% C_2-C_4 olefins in the product. The particle size of Co clusters was detemined by ferromagnetic resonance, electron microscopy and H_2 chemisorption. Co zeolites had lower activity than Co/Al_2O_3 but were found to be highly selective to low molecular weight olefin formation. They obtained shape selective catalysts with a cutoff at C_6 chain length. Selectivity was found to be affected by Si/Al ratio, pore size of zeolite and/or acidity of the support.

Methanation catalysts Vannice (1975) studied $2\%Co/Al_2O_3$ at 1 atm and 240-280 deg C. Using CO chemisorption, they obtained methanation activity of 0.02 mol CH_4/metal site/sec and and CO reactivity of 0.028 mol CO/site/sec. Ru was found to be the most active FTS catalyst for methanation. For the Co catalyst, they proposed that rate of methanation was first order in H_2 and inverse half order in CO.

Vannice (1977) studied a $4\%Co/SiO_2$ catalyst in a differential glass reactor maintained at 1 atm. Under reaction temperature of 203°C and for a feed gas containing H_2/CO = 3, they obtained CO conversion of 4%. The molar composition of hydrocarbons was C_1 (67%), C_2= (0.7%), C_2 (7.1%), C_3= (5.6%), C_3 (2.5%), C_4= (2.3%), C_4 (5.4%) and C_5+ (9.2%). The methanation activity and average molecular weight of hydrocarbon chain was greater for Co/SiO_2 catalyst than for Co/Al_2O_3 catalyst.

Dent and Lin (1979) studied impregnated, supported Co catalysts in a Berty reactor under reaction conditions of 7.8 atm and feed gas containing $CO/H_2/He$ = 1/3/6 and found that Co/Cr_2O_3/ Kieselguhr and Co/ZrO_2/Kieselguhr catalysts had the highest overall activity. The selectivity to methane was 70%.

Borghard and Bennett (1979) studied a commercial $CoO(34\%)/SiO_2$ catalyst under reaction conditions of 20 atm and 250°C in a tubular reactor. For a feed gas containing H_2/CO = 2 at pressure of 20 atm, products comprised of gaseous hydrocarbons (34.9wt%), liquid hydrocarbons (3.8wt%), C_3+ (29.8wt%), H_2O and alcohols (23.8wt%) and CO_2 (7.7wt%). The gaseous composition was H_2 (79%), CO (0.02%), CO_2 (3%), CH_4 (9%), H_2O (2%), C_2 (1%), C_3 (1%), C_4 (1%) and C_{5+} (4%). Water was found to be the major product (99.8wt%) in the aqueous stream with trace amounts

of ethanol and propanol. They found that Co favored methanation but did not favor alcohol formation. The olefin/paraffin ratio was found to be greater for Fe catalyst than for Co catalyst.

Amelse et al. (1981) studied pure Co metal under reaction conditions of 250°C and 1 atm. The CO conversion was 3.1%. The molar composition of the hydrocarbon product was found to be C_1 (79.3%), C_2 (4.7%), C_2= (1.8%), C_3 (1.5%), C_3= (7.1%), C_4 (3.9%) and C_5 (1.8%).

Oxygenate synthesis Takeuchi et al. (1989) studied Co/SiO_2 catalysts obtained from $Co_2(CO)_8$ and found that alcohols and hydrocarbons were generated via acyl-Co complexes which are common intermediates. They obtained hydrocarbon selectivity of 80-90% for unpromoted Co catalysts and up to 48 wt% oxygenate selectivity on Ba-promoted Co/SiO_2 catalysts. For heterogeneous Co catalysts, they proposed that growth of hydroxymethyl intermediate formed on surface of Co metal particles lead to $C_{2+}OH$ generation.

Effect of metal dispersion Nijs and Jacobs (1980) believed that hydrocarbon formation by Fischer-Tropsch mechanism was limited by metal crystallite size. Therefore they incorporated effect of metal crystallite size in Anderson-Schulz-Flory equation and were able to explain observed deviation from classical Anderson-Schulz-Flory kinetics.

Ruel and Bartholomew (1984b) studied the effect of support on activity of Co catalysts and found that specific activity based on H_2 adsorption decreased with increase in dispersion. They obtained a twenty-fold increase in specific activity upon increasing the Co loading from 3% to 15% by weight on Al_2O_3. The gasoline range hydrocarbon fraction C_5-C_{12} also increased from 18 wt% to 86 wt% with increase in Co loading. The extent of reduction increased with increase in temperature and the dispersion decreased resulting in increase in average C number presumably due to more Co-support interaction. They proposed that high CO_2 selectivity of poorly reduced Co catalysts was due to abundance of stable surface oxides, e.g., Co aluminate spinels, which were found to be inactive for CO hydrogenation but active for water gas shift reaction. Higher H_2/CO at surface promoted formation of lighter hydrocarbons viz. methane. Moderately dispersed Co promoted higher hydrocarbon formation.

Fu and Bartholomew (1985) found that specific activity based on H_2 adsorption and average carbon number of the hydrocarbon product varied significantly with metal loading, reduction temperature and preparation method. These changes were linearly correlated with change in dispersion and indicated that CO hydrogenation on Co/Al_2O_3 was structure sensitive. High specific activity favored strongly bound CO sites. They obtained ten-fold increase in specific activity upon increasing the metal loading from 3wt% to 25wt% while metal dispersion was found to decrease from 15% to 6.7%. They proposed that variation in carbon number was due to change in rate of termination relative to rate of propagation. They believed that subcarbonyl CO species adsorbed on well dispersed Co sites were less active than linear CO species adsorbed on poorly dispersed Co sites. In contrast to proposition by Nijs and Jacobs (1980), they propose that deviation from Fischer-Tropsch synthesis mechanism was due to partial adsorption and condensation of C_{10+} hydrocarbon in pores of support and heated lines of the sampling/analysis system.

1.4.2 Methanol Carbonylation Methanol carbonylation is defined as the chemical reaction of methanol with CO resulting in formation of oxygenates (viz. higher alcohols and acids) using cobalt and rhodium based homogeneous catalysts. Methanol carbonylation is of interest here because previous workers (Wender et al., 1950, Orchin, 1981) on higher alcohol synthesis found that light alcohols are produced with good selectivity starting from methanol via a molecular mechanism using cobalt-based homogeneous catalysts.

In 1913, BASF obtained a patent for manufacture of acetic acid by methanol carbonylation reaction (Hohenschutz et al., 1966). Phosphoric acid in conjunction with metal salts and boron fluoride were used as catalysts at 210-250°C and 7000-10000 psig. Corrosion was a severe problem under these extreme conditions. Acrylic acid, propionic acid and acetic acid are produced on large scale by carbonylation reactions.

Reppe et al. (1949) found that Fe, Ni and Co catalysts were effective for methanol carbonylation between 250-270°C and 3000-5000 psi if halogens or halogen containing promoters were present. Activity of catalysts varied as Ni > Co > Fe. Iodine was the best halogen promoter.

Later Paulik and Roth (1968) found that a new iodide promoted Rh catalyst gave yields of 99% on methanol and 90% on CO at 1 atm. Commercial carbonylation chemistry has subsequently involved primary the Rh catalyst. However, Roth et al. (1971) found that the Co catalyzed reaction rate was second order in P_{CO} and first order in methanol, unlike Rh catalyzed reaction which was zero order in both CO and CH_3OH concentrations. Therefore, they believe that different rate controlling steps exist for Co and Rh catalysts based on possibly different mechanisms. For our present purposes, therefore, we shall review the cobalt chemistry.

According to Hohenschutz et al. (1966), BASF found that Co carbonyl hydride and iodine catalysts were most active. Reversible side products like methyl acetate, dimethyl ether and formic acid were recycled. Irreversible byproducts like methane and acetaldehyde were obtained by consumption of H_2 evolved from the water gas shift reaction. Propionic acid was the main byproduct. They proposed the following reaction mechanism for Co catalysts:

$$CH_3OH + HI = CH_3I + H_2O$$

$$CH_3I + HCo(CO)_4 = CH_3Co(CO)_4 + HI$$

$$CH_3Co(CO)_4 = CH_3COCo(CO)_3$$

$$CH_3COCo(CO)_3 + CO = CH_3COCo(CO)_4$$

$$CH_3COCo(CO)_4 + H_2 = CH_3CHO + HCo(CO)_4$$

$$RCHO + HCo(CO)_4 = RCH_2OCo(CO)_4$$

$$RCH_2OCo(CO)_4 + HCo(CO)_4 = RCH_2OH + Co_2(CO)_8$$

Wender et al. (1950) found that unsaturated aldehydes were hydrogenated to higher alcohols under reaction conditions of 180-185°C, 200-300 atm using synthesis gas containing H_2/CO = 1. They found that alcohols could be obtained directly from olefins at 185 deg C, but aldehydes were the major product at lower temperatures.

2. EXPERIMENTAL

2.1 ACTIVITY MEASUREMENTS

2.1 Reactor system. The activity measurements are performed using a laboratory scale, high pressure, plug flow tubular reactor, generally operated at integral conversion levels. A Brooks mass flow controller (Model 5850E) is used to control and measure the inlet feed gas flow rate. The reactor pressure is maintained at 50 atm using two needle valves which serve as a pressure regulator. The reactor is heated to the reaction temperature using insulated electrical heating tapes. Products exiting the reactor system are analyzed online using a Hewlett-Packard (HP) 5890A gas chromatograph and a HP 3393A integrator. Products exiting the gas chromatograph are passed through a cold trap to remove condensable products and high molecular weight compounds. A soap bubble flowmeter is used to measure the exit gas flow rate. The gas stream is then vented off.

The reactor itself consists of a stainless steel cylindrical block measuring 10 cm in diameter and 20.7 cm in length. It contains a preheater section and a stainless steel tubular reactor. A stainless steel U-tube measuring 0.4 cm in diameter is used to connect the preheater section to the tubular reactor section. The preheater is a stainless steel tube measuring 0.7 cm in diameter and 26.7 cm in length. The preheater is packed with 1 mm diameter glass beads to ensure proper mixing of feed gases. In the preheater, feed gas is preheated to the reaction temperature before it enters the tubular reactor. The tubular reactor is a stainless tube measuring 0.7 cm in diameter and 26.7 cm in length. The reactor is packed with the desired catalyst for activity tests and 1 mm diameter glass beads. The ends of the reactor are plugged with glass wool to prevent entrainment of the catalyst particles into the gaseous stream exiting the reactor.

Reactor pressure is measured and indicated on a 2.5" dial gauge having a range of 0-1000 psig. The tubular reactor system is heated by a jacket-type furnace. The furnace is wrapped with electrical heating tape (Thermolyne Corp.). The reactor system is insulated from the surroundings by a 3.81 cm thick annulus of insulation containing aluminum silicate. The insulated reactor system is enclosed in a 0.75 cm thick aluminum metal jacket. The reactor temperature is measured by a K-type thermocouple inserted in a thermowell in the cylindrical block.

2.1.2 Catalyst activation The reactor was loaded with the required catalyst sample for activity measurements. Both ends of the tubular reactor were plugged with glass wool to prevent entrainment of fine catalyst particles into the gaseous stream. The reactor was packed with glass beads measuring 1.0 mm in diameter to ensure proper mixing of the gases and for uniform dispersion of the catalyst in the packed bed which would lead to an increase in the surface area.

We reduced the catalysts by passing a gaseous mixture containing $5\%H_2/95\%N_2$ through the reactor at atmospheric pressure with GHSV of 2000 hr^{-1}. The gas flow rate was measured by a Matheson flowmeter. The reactor was heated to 100°C and maintained at that temperature until dehydration of the catalyst was complete. The water content in the gaseous stream, obtained by reduction of the catalyst, was monitored online using the Hewlett-Packard 5890A gas chromatograph attached to a HP 3393A integrator. Dehydration is considered to be complete at each temperature step when there is no detection of a water peak in the chart recorder attached to the HP 3393A integrator. The reactor temperature was raised at the rate of 15-20°C/hr. The oven temperature of the HP 5890A GC was maintained at 140°C. Catalyst reduction was stopped at a temperature of 250°C, which is the reactor temperature used for activity tests.

For the activity measurements, a feed gas mixture containing $CO_2/CO/H_2$ in the desired molar ratio was passed through the experimental setup. The mass flow rate of the gaseous stream was monitored and controlled using a Brooks mass flow controller (Model Nos. 5850E and 5876). The feed gas was preheated in the preheater section of the reactor system. Then the feed gas passed over the activated catalyst at typical reactor conditions of 50 atm pressure and a temperature of 250°C. The gaseous stream exiting the reactor comprised of products of chemical reactions and unreacted reactants. The gaseous stream was analyzed online using a Hewlett Packard 5890A gas chromatograph attached to a HP 3393A integrator. The gaseous stream leaving the gas chromatograph was passed through a trap to remove condensable products. The gaseous stream exiting the trap is passed through a bubblemeter and then vented off.

2.1.3 Product analysis The components observed in the product stream included unreacted CO and H_2, CO_2, C_{1-6} hydrocarbons, C_{1-6} alcohols and H_2O. Using online vapor sampling to a Hewlett Packard (HP) 5890A gas chromatograph (GC) and from peak areas determined by a HP 3393A integrator, we obtained the molar composition of the gaseous stream exiting our reactor system. Ultra high purity (UHP) He was used as the carrier gas. Grade A He was used as the reference gas. The carrier and reference gas flow rates were 20 and 25 cm^3/min respectively at room temperature. The Porapak T column pressure was maintained at 40 psig. Sampling interval was one hour. The products were separated using a Porapak T column and quantified using a thermal conductivity detector (TCD) maintained at 140°C. The column injection temperature was 140°C. The oven temperature in the GC was programmed to increase from 30°C to 188°C as shown in Fig.2.3.2.1 to ensure separation and detection of compounds exiting the reactor.

The HP 3393A integrator contained a chart recorder. Peak areas were obtained every hour (sampling interval) for the products exiting the reactor. After maintaining the reactor conditions constant for about 12-24 hours, we obtained steady state peak areas. We multiplied the average steady state peak areas by the appropriate calibration factors in order to determine the molar concentration of the products.

We computed the molar composition of products in the 1 cm^3 sample loop in the gas chromatograph by multiplying average peak areas obtained in the HP 3393A integrator with appropriate calibration factors. We estimated the inlet volumetric flow rate using a Brooks mass flow controller (Model 5850E). Then we computed the inlet molar flow rate assuming ideal gas behaviour. Then the space time "W/F" (g cat-hr/gmol C) was determined from knowing the weight of the catalyst and the inlet molar composition of the feed gas. We obtained the rates of formation of products using the following expression:

$$R_i = (n_i/n_C) * (F_{Cin}/W) * MW_i \text{ g/(gcat-hr)}$$

where

n_C = Total moles of C/cm^3 gas in the sample loop
= Sum (n_i * C_i)

n_i = Moles of product 'i'/cm^3 gas in the sample loop
C_i = Number of carbon atoms in n_i
F_{Cin} = Moles C entering/hr

2.2 CATALYST PREPARATION

2.2.1 Coprecipitation method We originally prepared 30%CuO/70%ZnO catalysts for methanol synthesis using the coprecipitation method (Pan et al. (1988a)). A solution of 1.0 M $Zn(NO_3)_2$ is mixed with 1.0 M $Cu(NO_3)_2$ to give the desired Cu/Zn molar ratio. This mixed solution was added simultaneously with 1.0 M Na_2CO_3 solution into a glass container at carefully controlled flow rate to ensure mixing at neutral pH conditions using an electric stirrer. The precipitates obtained were then filtered, washed, dried and calcined in air at 250°C for 16 hours.

We also prepared $Cu/Co/ZnO/Al_2O_3$ catalysts for higher alcohol synthesis using the same method. In this case 1.0 M $Cu(NO_3)_2$ solution is mixed with molar solutions of $Co(NO_3)_2$, $Zn(NO_3)_2$ and $Al(NO_3)_3$ in the desired molar ratio. This solution is added simultaneously with 1.0 M Na_2CO_3 solution into a glass container at carefully controlled flow rates to maintain neutral pH and the resulting solution is mixed thorougly using an electric stirrer. The resulting precipitates are then filtered, dried and calcined in air at 250°C for 16 hours.

2.2.2 Complexation method We were also interested in non-traditional preparation methods for these multi-component catalysts. Courty et al. (1973,1983), Di Cosimo and Apesteguia (1989), Gherardi et al. (1983) and Marcilly et al. (1970) obtained bulk mixed oxide catalysts by citric acid complexation method. Citric acid was added to a concentrated aqueous solution containing all the required ions as metal nitrates so as to obtain 1 g.eq. of acid/g.eq. of metals. The solution was first boiled for 20-30 min and then dehydrated under vacuum in a revolving flask at 75°C until viscosity was sufficiently high (500 cP at 20°C). The dehydration was completed in a vacuum oven at 80°C for 13 hours. The mixed oxide precursor was obtained by thermal decomposition of homogeneous precursor upon calcination at 500°C for 4 hrs.

In the Pechini method (Lessing (1989)), a chelate was formed between mixed cations with a hydrocarboxy acid viz. citric acid. The solution mixture containing nitrate and citric acid was mixed with polyhydroxyl alcohol viz. ethylene or diethylene glycol and stirred while heating in the temperature range of 80-110°C until a clear solution was obtained. Heating to moderate temperatures of 150-250°C caused a polyesterification reaction resulting in formation of a solid polymeric "resin". The resin structure was found to be dependent on stoichiometric ratios of reactants. Calcination of resin in air caused a breakdown of polymer and "charring" at 400°C. Subsequently cations were oxidized to form crystallites of mixed cation oxides at 500-900°C.

Sheffer and King (1988,1989) obtained complexed Cu based catalysts by addition of citric acid to an aqueous solution of cupric nitrate and potassium nitrate to yield 1 g.-eq. of acid per g.-eq. of metal. The resulting solution was evaporated under vacuum at room temperature to form a thick slurry which was dried overnight at 80°C. The solid obtained was then calcined at 350°C in air for 4 hrs. At 200°C, catalyst precursor rapidly decomposed with evolution of large amounts of heat and gas. Catalysts made from cupric acetate precursors were more stable but had significantly lower activity.

For this work we used the citric acid complexation method to prepare $ZnAl_2O_4$, $ZnCr_2O_4$, $CoAl_2O_4$, $CoCr_2O_4$ and $CoZn(Cr_2O_4)_2$ spinels to use as catalysts or catalyst supports. Citric acid was added to an aqueous solution mixture containing the metal nitrates in the desired molar ratio to yield 1 g.eq. acid/g.eq metals. The solution mixture was then dried at 130°C for 15 hrs (overnight). A spongy substance thus obtained was ground to fine powder using a mortar and a pestle. The finely ground powder was loaded into two glass boats and calcined in an electric furnace at a temperature range of 650-700 deg C for about 7 hrs. The structure of the calcined

material was determined using powder x-ray diffraction method using a Scintag Diffractometer. The x-ray diffraction experiments confirmed the formation of spinel phases for the above mentioned compounds.

We prepared Cu(2)/Cr(1) catalysts by adding 1.0 M $Cu(NO_3)_2$ to 1.0 M $Cr(NO_3)_3$ in the desired Cu/Cr ratio of 2/1 in a 600 ml glass beaker. Baker analyzed anhydrous citric acid powder was added to this solution mixture to yield 1 g.eq. acid/g.eq. metals. A purple solution was obtained upon stirring with a glass rod at room temperature. The solution is then heated to 120°C in an oven until a dry, spongy substance is obtained. The dried substance was then ground to fine powder using a mortar and a pestle. The powdered substance was calcined in an electric furnace at 350°C for 12 hrs to yield a black catalyst of the desired composition.

For comparison, 30%CuO/70%ZnO catalysts were also prepared by the same procedure using starting solutions of 1.0 M $Cu(NO_3)_2$ and 1.0 M $Zn(NO_3)_2$. A blue solution was obtained upon mixing the solutions with anhydrous citric acid. Upon drying and calcining at 350 deg C, a brown catalyst containing CuO(30%)/ ZnO(70%) was obtained.

We prepared Cu/Co/Cr/K catalysts for higher alcohols synthesis using Sheffer's complexation method (1988). Molar solutions of $Cu(NO_3)_2$, $Co(NO_3)_2$, $Cr(NO_3)_3$ and KOH are added in the desired molar ratio in a 600 ml glass beaker. Baker analyzed anhydrous citric acid powder is added to the solution mixture. Upon stirring with a glass rod at room temperature, a clear solution is obtained. The solution is then dried at 120°C in an oven until a dry, spongy gray substance is obtained. The substance obtained is finely ground using a mortar and a pestle. The powdered substance thus obtained is calcined to 350°C in an electric furnace for 12 hrs to give a black catalyst containing Cu/Co/Cr/K in the desired molar ratio.

2.3 METAL SURFACE AREA

The surface area of pure and supported copper catalysts can be determined using N_2O chemisorption technique (Chinchen et al.(1986), Pan et al. (1988a)). Decomposition of N_2O molecules on Cu surface resulting in production of adsorbed oxygen atoms and gas phase nitrogen molecules is the basis for this technique. The reaction taking place is

$$N_2O\ (g)\ +\ 2\ Cu\ (s)\ \longrightarrow\ N_2\ (g)\ +\ (Cu\text{-}O\text{-}Cu)\ (s)$$

We observe that moles of N_2 in the gaseous stream are equivalent to number of adsorbed oxygen atoms on the Cu surface. Chinchen et al. (1986) obtained 5.0×10^{14} oxygen atoms/cm^2 Cu.

The pulse chemisorption experiment is conducted using a Micrometrics PulsChemisorb 2700 instrument. The gas pulse size is monitored using a thermal conductivity detector. A known amount of catalyst sample is placed in a glass sample holder. Initially all the metal tubing in the experimental setup is purged with He to remove all air in the tubing. The catalyst is then reduced by feed gas containing 5%H_2/95%N_2 at GHSV of 2000/hr. The temperature of the sample holder is increased from room temperature to 250°C at known intervals of time from previously known catalyst reduction behaviour.

After reduction is completed, He carrier gas is passed through the sample at room temperature for 30 min to remove adsorbed hydrogen molecules. Then N_2O which is the analysis gas is injected into the catalyst sample from a sample loop measuring 0.495 cm^3 in volume. After 5 min, the reading displayed is noted (S_1). Injection of N_2O gas is continued and the reading

displayed is noted (S_2,S_3,..) until the steady state value (S_{max}) is obtained. The Cu surface area of the catlayst is then determined by the following expression:

$$A = A^{o}(n/W)\ m^2/g$$

where

W = weight of catalyst in g
A^o = Cu surface area/oxygen atom
= 1.2×10^5 m^2 Cu/mol N_2O chemisorbed
n = mol N_2O chemisorbed

2.4 X-RAY DIFFRACTION

The crystalline structure of catalysts has been determined using the powder X-ray diffraction method. We were interested in using XRD for determining the spinel phases and separated oxide phases of catalysts and catalyst supports. The catalyst sample is ground to fine powder using a mortar and a pestle. Then the sample holder measuring 1 cm^3 in volume (1" x 1" x 1/16") is filled with the powdered sample. A glass plate is used to hand press the powder in the sample holder so that the powder does not fall out when the sample holder is inclined to an angle of 60 degrees to the horizontal. The amount of sample that can be loaded in the sample holder is dependent on the sample density.

The sample holder is then placed in the department's Scintag Diffractometer. We used Cu-K alpha1 source which produces x-rays of wavelength 1.54059 angstroms. Initially the voltage of the diffractometer is increased manually from 0 kV to 10 kV. Then the current of the diffractometer is increased manually from 0 mA to 1 mA. A computer software program "XDS5" is then used to run the diffractometer. Table 2.5.1 gives the normal operating parameters for the obtaining the x-ray diffraction patterns.

After giving the required information for running the diffractometer using XDS5, the power setting of the Scintag Diffractometer is increased manually to 45 kV and 35 mA in succession before beginning the x-ray analysis. The time required to obtain the x-ray diffraction pattern using a step scan for each sample is 4.5 hrs. A continuous scan can be done on crystalline samples and takes about 10 min.

After completing the step scan, a graphics software package called "TC9" is used to view the X-ray diffraction pattern of the sample and compare it with standard patterns in the literature. The reference numbers for the standard patterns in the literature are obtained from "Powder Diffraction file (Inorganic Phases), 1987" containing the crystalline phases of the compound and the corresponding reference numbers. The standard patterns thus obtained can be overlapped onto the sample x-ray diffraction pattern to identify the phases on the screen. The standard patterns are plotted underneath the sample pattern.

3. RESULTS

3.1 OXIDE PRECURSORS

We were interested in the preparation of oxide precursors to be used as catalyst support materials. In this case the copper and cobalt components will be added by conventional impregnation method. The preparation procedure for and characterization of different mixed oxide precursors is described in the remainder of this section.

3.1.1 Chromium Oxide Spinels Courty et al. (1982) and Sheffer et al. (1989) have obtained high oxygenate yields using Cu/Co/Cr/K catalysts. They have also observed the formation of a mixed oxide spinel phase along with the CuO phase. Courty et al. (1982) have proposed that Cu(I) was stabilized in the spinel phase or as copper chromite. Therefore, we were interested in preparation of spinels containing chromium oxide and subsequently impregnating copper in order to determine the effect of spinel on the catalyst activity and selectivity.

$ZnCr_2O_4$ spinel phase was obtained using the citric acid complexation method. 60 cm^3 of 1.0 M $Zn(NO_3)_2$ solution was added to 120 cm^3 of 1.0 M $Cr(NO_3)_3$ solution in a 600 cm^3 beaker. Anhydrous citric acid was added to the aqueous solution mixture to yield 1 g.eq.acid/g.eq.metal. Upon stirring, a violet solution is obtained at room temperature which is then dehydrated at 130°C for 15 hours. A green substance was obtained upon complete drying after gelation. This material was then ground to fine powder and calcined at a temperature of 705°C in an electric furnace for at least 7 hours. This resulted in the formation of a gray substance.

The crystalline structure of the calcined material was determined using powder x-ray diffraction method using a Scintag diffractometer. After completing a step scan on the powdered sample, we used a software program "TC9" in order to determine the diffraction pattern of the sample. We found that the sample diffraction pattern matched the diffraction pattern of standard zinc chromium oxide (File No. 22-1107). (File numbers refer to the Powder Diffraction File - Inorganic Phases - Alphabetical Index, JCPDS international centre for diffraction data, 1987). The BET surface area of the $ZnCr_2O_4$ sample was found to be 32.2 m^2/g.

$CoCr_2O_4$ spinel phase was obtained by using the citric acid complexation method outlined above. 60 cm^3 of 1.0 M $Co(NO_3)_2$ solution was added to 120 cm^3 of 1.0 M $Cr(NO_3)_3$ solution in a 600 cm^3 beaker. A green substance was obtained upon calcining at 705 deg C in an electric furnace for 7 hours.

The crystalline structure of the calcined material was determined using powder x-ray diffraction method previously described. We found that the sample diffraction pattern matched the diffraction pattern of standard cobalt chromium oxide (File No. 22-1084). The BET surface area of the $CoCr_2O_4$ sample was found to be 20.75 m^2/g. The Co surface area was found to be 3.884 m^2/g using N_2O chemisorption technique after reduction of the sample at 350°C.

$CoCr_2O_4$ and $ZnCr_2O_4$ spinel phases were obtained by using the citric acid complexation method. 30 cm^3 of 1.0 M $Co(NO_3)_2$ solution and 30 cm^3 of 1.0 M $Zn(NO_3)_3$ were added to 120 cm^3 of 1.0 M $Cr(NO_3)_3$solution in a 600 cm^3 beaker. A dark green substance was obtained upon calcination of dried homogeneous precursor to 700°C for 7 hrs.

The crystalline structure of the calcined material was determined using powder x-ray diffraction method outlined before. We found that the sample diffraction pattern matched the diffraction patterns of standard cobalt chromium oxide (File No. 22-1084) and zinc chromium oxide

(File No. 22-1107). Since the diffraction patterns of cobalt and zinc chromium oxides are identical suggesting a similar crystal lattice for both spinels, it is difficult to determine whether a single phase or both phases were present. The three strongest lines in the diffraction pattern with relative intensities in parentheses for $CoCr_2O_4$ are 2.51(100), 1.47(5) and 2.95(4) while the three strongest lines for $ZnCr_2O_4$ are 2.51(100), 2.95(5) and 1.47(4). Sheffer et al. (1989) have also observed that it is not possible to determine phase composition of a spinel by comparison of unit cell sizes.

3.1.2 Aluminum oxide spinels. Herman et al. (1979) and Nunan et al. (1989a) have obtained higher activity and alcohol selectivity on unpromoted and Cs promoted $Cu/ZnO/Al_2O_3$ catalysts than $Cu/ZnO/Cr_2O_3$ catalysts. Therefore, we were interested in the preparation of alumina spinels in order to determine the effect of alumina spinels impregnated with Cu on the catalyst surface area and the activity.

$ZnAl_2O_4$ spinel phase was obtained by using the citric acid complexation method. 60 cm^3 of 1.0 M $Zn(NO_3)_2$ solution was added to 120 cm^3 of 1.0 M $Al(NO_3)_3$ solution in a 600 cm^3 beaker. Anhydrous citric acid was added to the aqueous solution mixture to yield 1 g.eq.acid/g.eq.Zn+Al metal. Upon stirring, a clear solution is obtained at room temperature which is then dehydrated at 130°C for 15 hours. A brown substance, obtained upon complete drying, was ground to fine powder and calcined in the temperature range of 630-660°C in an electric furnace for at least 7 hours. We observed the formation of a white substance.

The crystalline structure of the calcined material was determined using powder x-ray diffraction method using a Scintag diffractometer. We found that the sample diffraction pattern matched the diffraction pattern of standard zinc aluminum oxide (Gahnite) (File No. 5-669). The BET surface area of the $ZnAl_2O_4$ sample was found to be 25.9 m^2/g.

$CoAl_2O_4$ spinel phase was obtained by using the citric acid complexation method. 60 cm^3 of 1.0 M $Co(NO_3)_2$ solution was added to 120 cm^3 of 1.0 M $Al(NO_3)_3$ solution in a 600 cm^3 beaker. Upon stirring, a violet solution is obtained at room temperature which is then dehydrated at 130°C for 15 hours. A blue substance was obtained upon calcination at 660°C in an electric furnace for about 7 hrs.

The crystalline structure of the calcined material was determined using powder x-ray diffraction method using a Scintag diffractometer. We found that the sample diffraction pattern matched the diffraction pattern of standard cobalt aluminum oxide (File No. 10-458). The BET surface area of the $CoAl_2O_4$ sample was found to be 46.7 m^2/g.

3.1.3 Copper Oxide Precursors Courty et al. (1982) and Sheffer et al. (1989) have reported that calcined Cu/Co/Cr/K catalysts consisted of CuO and a mixed oxide spinel. Therefore we were interested in determining the phase compositions of our Cu/Co/Cr catalysts using the powder x-ray diffraction method.

Cu/Co/Cr = 2/0/1 We prepared a catalyst having molar composition of Cu/Cr = 2 because we were interested in obtaining CuO and $CuCr_2O_4$ phases in equimolar ratio. We were also interested in determining the effect of the CuO phase and the spinel phase on catalyst activity and surface area. 50 cm^3 of 1.0 M $Cr(NO_3)_3$ solution was added to 100 cm^3 of 1.0 M $Cu(NO_3)_2$ solution in a 600 cm^3 glass beaker. Anhydrous citric acid powder was added to this solution mixture to yield 1 g-eq.acid/g.eq.metals. The solution thus obtained was dried and calcined at 350°C using the complexation procedure described earlier.

The crystalline structure of the calcined material was determined using powder x-ray diffraction method using a Scintag diffractometer. We found that the sample diffraction pattern matched the diffraction pattern of standard copper oxide (File No.5-661). We found that there was no change in the diffraction pattern for the Cu(2)/ Cr(1) calcined at a temperature of 663°C. We did not obtain any $CuCr_2O_4$ spinel as obtained by Sheffer et al. for $CuCrK_{0.064}$ catalyst. We believe that spinel structure is not obtained for a catalyst composition of Cu/Cr = 2 due to excess Cu present in the catalyst which appears to favor CuO formation over the spinel formation. The BET surface area of the catalyst was found to be 28.58 m^2/g. The Cu surface area of fresh catalyst was 4.696 m^2/g using N_2O chemisorption technique.

Cu/Co/Cr = 1.5/0.5/1 Courty et al.(1982) proposed that methanol was obtained on the CuO sites while higher alcohols were obtained on the Co-Cr spinel phase in Cu/Co/Cr/K catalysts. We prepared a catalyst having molar composition of Cu/Co/Cr = 1.5/0.5/1.0 because we were interested in obtaining CuO and $CoCr_2O_4$ phases in order to determine their effect on the activity, selectivity and surface area of the catalyst. 37 cm^3 of 1.0 M $Cr(NO_3)_3$ solution was added to 18.5 cm^3 of 1.0 M $Co(NO_3)_2$ solution and 55.5 cm^3 of 1.0 M $Cu(NO_3)_2$ solution in a 600 cm^3 glass beaker. Anhydrous citric acid powder was added to this solution mixture to yield 1 g-eq.acid/g.eq.metals. The solution thus obtained was dried and calcined at 350°C using the complexation procedure described earlier.

The crystalline structure of the calcined material was determined using powder x-ray diffraction method using a Scintag diffractometer. We found that the sample diffraction pattern matched the diffraction patterns of standard copper oxide (File No.5-661) and standard cobalt chromium oxide (File No.22-1084) as observed by Courty et al. (1982) and Sheffer et al. (1989). Addition of Co to Cu/Cr catalysts lead to an increase in the metal and BET surface areas by a factor of 2.3. The BET surface area of the catalyst was found to be 68.37 m^2/g. The metal surface area of fresh catalyst was 11.091 m^2/g using N_2O chemisorption technique. We did not observe any chemisorption on $CoCr_2O_4$ after reduction at 250 deg C. However, Courty et al. (1982) and Sheffer et al. (1989) have observed that Cu promotes reduction of Co^{3+} to Co^{2+}. Therefore we believe that the metal surface area of 11.091 m^2/g is the Cu-Co surface area. Addition of Co increases total surface area due to formation of a $CoCr_2O_4$ spinel. We also observe that the ratio of metal/BET surface area for both Cu(2)/Cr(1) and Cu(1.5)/ Co(0.5)/ Cr(1.0) catalyst is 0.17. Therefore addition of Co had no effect on the ratio of BET to metal surface area.

3.2 REDUCTION BEHAVIOR

In this section we describe the reduction behaviour of the different Cu-containing catalyst precursors prepared by the complexation method. Catalysts were heated in stages from 25°C to the final reaction temperature of 250°C using a feed gas containing $5\%H_2/95\%N_2$. At each heating step, the catalyst was maintained at a fixed temperature until dehydration was complete, as determined by absence of a water peak in the exit gas stream (monitoring using the HP 5890A gas chromatograph).

We observed that maximum reduction for Cu(2)/Cr(1) and Cu(1.5)/Co(0.5)/Cr(1.0) catalysts occurred at 150°C. In the temperature range of 150-200°C, we observed further reduction of Cu(2)/Cr(1) catalyst but we did not observe any reduction of the Cu(1.5)/Co(0.5)/Cr(1.0) catalyst. The Cu(2)/Cr(1) catalyst was mostly reduced by 200°C, while further reduction of the Cu(1.5)/Co(0.5)/Cr(1) catalyst occurred at a temperature of 225°C.

Based on the temperatures at which the maximum rate of reduction takes place for different Cu/Co catalysts, we make the following observations:

1. For the coprecipitated Cu/ZnO and Cu/Co/Zn/Al/K catalysts, maximum reduction takes place at a lower temperature, around 125-130°C.

2. For the unpromoted Cu/Cr and Cu/Co/Cr catalysts, maximum reduction takes place at 150°C. Thus the spinel forming tendency of the Cr component inhibits reduction.

3. For K promoted Cu/Cr and Cu/Co/Cr catalysts, maximum reduction takes place at 125°C. Therefore K in the catalyst appears to promote catalyst reduction.

4. For the Cu(2)/Cr(1) and Cu(1.5)/Co(0.5)/Cr(1) catalysts, we observe that maximum reduction takes place at a temperature of about 150°C, presumably due to reduction of essentially pure CuO phase. The Cu/Cr catalyst is mostly reduced when the reactor temperature reaches 200°C. However, we observed some reduction of the Cu/Co/Cr catalyst at about 225°C. Therefore, we believe that Cu promotes reduction of some of the Co cations in the Cu/Co/Cr catalyst. We have observed a similar effect of Co upon reduction of coprecipitated Cu/ZnO and $Cu/Co/ZnO/Al_2O_3/K$ catalysts.

Surface area measurements. The metal surface area was obtained by the N_2O chemisorption technique. The BET surface area of the mixed oxide precursors was determined using a flow adsorption apparatus. From the BET and metal surface area measurements we make the following observations:

1. We failed to obtain high Cu surface area and activity on impregnated Cu/chromium oxide spinel catalysts. Our results are in contradiction to observation by Sheffer et al. (1989) that impregnating $Cu(NO_3)_2$ onto a Co-Cr spinel resulted in increase in catalyst activity with oxygenate selectivity of 60 wt%.

2. Impregnated Cu/chromium oxide spinel catalysts had a larger metal surface area than impregnated Cu/aluminum oxide spinel catalysts.

3. CuO had the least BET surface area of 9 m^2/g while Cu(1.5)/Co(0.5)/Cr(1.0) catalyst had the maximum BET surface area of 68 m^2/g.

4. Co in the Cu/Co/Cr catalyst had little effect on the ratio of metal/BET surface area.

5. Coprecipitated CuO(30%)/ZnO(70%) catalysts had larger Cu surface area compared to complexed CuO(30%)/ZnO(70%) catalysts. Therefore, the complexation method of preparation does not appear to yield catalysts with high Cu surface area.

6. Coprecipitated CuO(30%)/ZnO(70%) had the largest Cu surface area of 19.041 m^2/g.

3.3 ACTIVITY MEASUREMENTS

3.3.1 Cu(2)/Co(0)/Cr(1)/K(0) Catalysts were prepared by complexation method described above. The first catalyst in this series had molar composition of Cu(2)/Cr(1). This composition was chosen in order to determine the effect of Cr on the activity and selectivity of Cu/Cr catalysts.

Using the N_2O chemisorption technique, the fresh and used Cu surface areas were found to be 4.7 and 4.0 m_2/g respectively. The BET surface area of the fresh catalyst was 28.6 m^2/g.

Experiments were conducted to determine the effect of changing the H_2/CO ratio and CO_2/CO ratio at fixed reaction conditions of 250°C and 50 atm pressure. Increasing the CO_2/CO ratio from a mixture containing $CO_2/CO/H_2$ = 0/30/70 vol% to one containing $CO_2/CO/H_2$ = 6/24/70 vol% decreased the rate of CO conversion by 29%. The change in CO_2/CO ratio also resulted in a decrease in catalyst selectivity to alcohols. The rate of formation of methanol decreased by 24%. No higher alcohol formation was observed at the higher CO_2/CO ratio. Increasing CO_2/CO ratio did not have any significant effect on the CH_4 yield. The rate of formation of higher hydrocarbons, produced in trace quantities, decreased by 36%.

We studied the effect of CO/H_2 ratio using reactant mixtures having molar compositions of $CO_2/CO/H_2$ = 0/30/70 vol% and $CO_2/CO/H_2$ = 0/50/50 vol%. Increasing the CO/H_2 ratio resulted in a significant decrease in the catalyst activity. The rate of CO conversion decreased by 43%. The CO/H_2 increase also resulted in a significant decrease in overall selectivity to alcohol formation. The rates of formation of methanol and ethanol decreased by 8% and 38% respectively. The rates of formation of i-butanol and n-butanol decreased by 8% and 50% respectively. The isopentanol yield was not affected while no n-pentanol was obtained at the lower H_2/CO ratio. Increasing the CO/H_2 also resulted in a marked decrease in selectivity to hydrocarbon formation. Methane and ethane were not obtained at the higher CO/H_2 ratio. The rate of formation of propane decreased by 29%.

3.3.2 Cu(2)/Co(0)/Cr(1)/K(0.045) This catalyst was prepared by the complexation method as described above, but with the addition of K at the final step. The Cu surface of the fresh catalyst was determined using N_2O chemisorption technique and was found to be 6.5 m^2/g; i.e., slightly higher than that achieved without the addition of K.

Using the same feed gas compositions described above, we observed that increasing the CO_2/CO ratio from 0/30 to 6/24 had little effect on the rate of CO conversion; e.g., the methanol formation rate increased by 7%. No higher alcohol formation was observed at the higher CO_2/CO ratio. There was a small decrease in the hydrocarbon yield.

We observed that increasing the CO/H_2 ratio from 30/70 to 50/50 also had little effect on the rate of CO conversion or the overall rate of alcohol formation (e.g., methanol formation increased by 8%). There was also a decrease in the amount of hydrocarbon formation.

We also studied the effect of space time on the activity and selectivity of the catalyst sample using a feed gas containing $CO_2/CO/H_2$ = 6/24/70 vol%. Increasing space time (W/F_C) from 67.65 to 103.15 g-hr/gmol C increased the average rate of CO conversion by 75%. The methanol formation rate was not affected by the increase in space time, the formation rate of higher alcohols increased. The higher space time also promoted the rate of methanation, but did not affect the formation of higher hydrocarbons.

3.3.3 Cu(1.5)/Co(0.5)/Cr(1.0) The BET area of the fresh catalyst was 68 m^2/g. Using the N_2O chemisorption technique, the metal surface areas of the fresh and used catalyst were found to be 11.1 and 3.5 m^2/g respectively. This catalyst undergoes a significant reduction in metal area during exposure to reaction conditions.

Using feed gas compositions of $CO_2/CO/H_2$ = 0/30/70 vol% and $CO_2/CO/H_2$ = 6/24/70 vol%, we showed that increasing the CO_2/CO ratio resulted in a decrease in the rate of CO conversion

by 17%. The rate of formation of methanol decreased by 17%, while ethanol formation decreased by 27%. No alcohols above ethanol were observed at the higher CO_2/CO ratio. Increasing the CO_2/CO ratio caused a small increase in the overall rate of hydrocarbon formation. The rate of methane formation decreased by 18%, while the rate of formation of ethane, propane and butane formation increased by 4%, 30% and 10% respectively.

We studied the effect of CO/H_2 ratio using feed compositions of $CO_2/CO/H_2$ = 0/30/70 vol% and $CO_2/CO/H_2$ = 0/50/50 vol%. Increasing the CO/H_2 ratio decreased the rate of CO conversion by 84%. However, the rate of formation of methanol and ethanol increased by 96% and 11%, respectively, and alcohols greater than ethanol were observed.

3.2.4 Cu(1.5)/Co(0.5)/Cr(1)/K(0.045). Limited results were obtained for this catalyst, using feed gas compositions of $CO_2/CO/H_2$ = 6/24/70 vol% and $CO_2/CO/H_2$ = 0/50/50 vol%. Thus we could not study the effect of CO_2/CO and CO/H_2 ratios independently. The effect of catalyst composition at each reactant composition is discussed below.

4. DISCUSSION

4.1 OBSERVED TRENDS

4.1.1 Effect of CO_2/CO ratio. We studied the effect of CO_2/CO ratio on the activity of a series of complexed Cu/Co/Cr/K catalysts. The catalysts studied had molar compositions of Cu/Co/Cr/K = 2/0/1/0, 2/0/1/0.045 and 1.5/0.5/1/0, respectively. From a comparison of the results obtained for the different catalyst compositions, we make the following observations:

1. Increasing the CO_2/CO ratio from 0.0 to 0.25 had a significant effect on the activity of unpromoted Cu/Cr and Cu/Co/Cr catalysts. The rate of CO conversion decreased by 29% for Cu(2)/Cr(1) catalysts, while it decreased by 17% for Cu(1.5)/Co(0.5)/Cr(1) catalysts. Increasing CO_2/CO ratio had little effect on the activity of Cu(2)/ Cr(1)/ K(0.045) catalysts.

2. Increasing the CO_2/CO ratio from 0.0 to 0.25 had a pronounced effect on the overall alcohol formation rate for unpromoted Cu/Cr and Cu/Co/Cr catalysts. The overall alcohol yield for the Cu(2)/Cr(1) catalyst decreased by 35%. The methanol formation rate decreased by 24% and no higher alcohols were formed at the higher CO_2/CO ratio. For the Cu(1.5)/Co(0.5)/Cr(1) catalyst, the overall alcohol yield decreased by 45%. The rates of formation of methanol and ethanol decreased by 17% and 27% respectively. No C_{2+} alcohol formation was observed at the higher CO_2/CO ratio. The rate of formation of methanol increased by 7% for Cu(2)/Cr(1)/K(0.045) catalysts while no higher alcohol formation was observed at the higher CO_2/CO ratio.

3. Increasing the CO_2/CO ratio from 0.0 to 0.25 resulted in a 10% decrease in the overall hydrocarbon yield for Cu(1.5)/Co(0.5)/Cr(1) and Cu(2)/Cr(1)/K(0.045) catalysts. The overall hydrocarbon and methane yields of Cu(2)/Cr(1) catalyst were not affected. For the Cu(1.5)/ Co(0.5)/ Cr(1) catalyst, the methanation rate decreased by 18% while the rates of formation of propane and butane increased to a small extent. For the Cu(2)/Cr(1)/K(0.045) catalyst, no methanation was observed at either CO_2/CO ratio. The rate of formation of trace quantities of propane decreased by 8%.

The presence of CO_2 in the feed gas has been known to have a marked effect on the methanol synthesis rate for coprecipitated Cu/ZnO catalysts. Chinchen et al. (1984) and Rozovskii et al. (1977) believe that CO_2 is the principal reactant for methanol synthesis and all CO in the

feed gas is converted to CO_2. In contrast, Herman et al. (1979) and Klier et al. (1982) propose that the principal role of CO_2 is to maintain sufficient oxidation potential to prevent reduction of active Cu(I) sites in the ZnO phase rather than undergo direct hydrogenation to methanol. Vedage et al. (1985) found that there was a maximum on the dependence of methanol synthesis rate on the CO_2 content in the feed gas for both unpromoted and Cs promoted Cu/ZnO catalysts. They proposed that at low CO_2 concentrations, hydrogenation of a surface Cs formate was responsible for methanol synthesis. At high CO_2 concentrations, whole active surface of Cu/ZnO components was believed to be responsible for methanol synthesis with probable formation of Cs carbonate.

Monnier et al. (1984) found that stability of Cu(I) species in complexed Cu/Cr_2O_3 catalysts was independent of CO_2. They obtained a 30% decrease in methanol yield using complexed Cu(1)/Cr(1) catalysts at 270°C and 52 atm. Using temperature programmed desorption (TPD), they concluded that non-catalytic, competitive adsorption of CO_2 on Cu(I) sites inhibited methanol synthesis. Courty et al. (1984) found that CO_2 had little effect on Cu/Co/Cr/K catalysts. Sheffer and King (1988) observed that increasing CO_2 in the feed gas decreased catalyst activity and oxygenate selectivity of complexed Cu/Co/Cr/K catalysts. They obtained a 30% decrease in overall activity and oxygenate selectivity of complexed Cu(1)/Co(1)/Cr(0.8)/K(0.09) catalysts at 275°C and 50 atm.

Our results indicate that increasing the CO_2/CO ratio in the feed gas decreases the alcohol yield of unpromoted Cu(2)/Cr(1) and Cu(1.5)/ Co(0.5)/ Cr(1) catalysts by 35 and 45% respectively. Increase in CO_2/CO ratio increased the methanol yield by 7% using Cu(2)/Cr(1)/K(0.045) catalysts. These results are in agreement with results of previous studies undertaken by Monnier et al. (1984), Courty et al. (1984) and Sheffer and King (1988) using Cu/Co/Cr/K catalysts. Therefore we see a correlation between catalyst activity and selectivity to alcohol formation. Monnier et al. used TPD experiments using complexed Cu/Cr catalysts and concluded that CO_2 inhibited alcohol formation rates by competitive, non-catalytic adsorption on Cu(I) sites Cu/Cr catalysts.

Based on our experimental observations and comparing the results reported in the literature, we propose the following mechanism:

1. CO_2 in the feed gas is reversibly adsorbed at active Cu(I) and K^+ sites at low CO_2 concentrations. Therefore the alcohol formation rate would not be affected by small increases in CO_2 content.

2. CO_2 is irreversibly adsorbed on active Co and Cr sites favoring alcohol formation.

Based on the above hypothesis, we believe that the alcohol formation rate of unpromoted Cu/Cr and Cu/Co/Cr catalysts decreases due to non-competitive, irreversible adsorption of CO_2 on active Co and Cr sites favoring alcohol formation. The alcohol formation rate of Cu/Cr/K catalyst is not adversely affected by increase in CO_2 content because the loss in active Co and Cr sites due to irreversible adsorption of CO_2 is compensated by increase in alcohol formation on K^+ sites. Therefore it appears that the effect of CO_2 in the feed gas is strongly dependent on the catalyst composition and preparation method.

4.1.2 Effect of H_2/CO ratio. We studied the effect of CO/H_2 ratio on the activity of a series of complexed Cu/Co/Cr/K catalysts. The catalysts had molar compositions of Cu/Co/Cr/K = 2/0/1/0, 2/0/1/0.045 and 1.5/0.5/1/0 respectively. Our results led to the following observations:

1. Increasing the CO/H_2 ratio from 1.0 to 2.3 had a pronounced effect on the activity of unpromoted Cu/Cr and Cu/Co/Cr catalysts. The rate of CO conversion decreased by 43% for

Cu(2)/Cr(1) catalysts while it decreased by 84% for Cu(1.5)/Co(0.5)/Cr(1) catalysts. Increasing CO/H_2 ratio had little effect on the activity of Cu(2)/Cr(1)/K(0.045) catalysts.

2. Increasing the CO/H_2 ratio had a significant effect on the overall alcohol formation rate for unpromoted Cu/Cr and Cu/Co/Cr catalysts. The overall alcohol formation rate decreased by 12% for the Cu(2)/Cr(1) catalyst while it increased by 22% for the Cu(1.5)/Co(0.5)/Cr(1) catalyst. Increasing CO/H_2 ratio had little effect on the alcohol formation rate for the Cu(2)/Cr(1)/K(0.045) catalyst. For the Cu(2)/Cr(1) catalyst, methanol and ethanol formation rates decreased by 8% and 38% respectively. The rates of formation of i-butanol and n-butanol decreased by 8% and 50% respectively. The i-pentanol yield was not affected by change in CO/H_2 ratio while n-pentanol was not obtained at the lower CO_2 ratio. For the Cu(1.5)/Co(0.5)/Cr(1) catalyst, the rates of formation of methanol and ethanol increased by 96% and 27% respectively. No C_{2+} alcohol formation was observed at the higher ratio. Increasing CO/H_2 ratio had no significant effect on the alcohol formation rate for Cu(2)/Cr(1)/K(0.045) catalysts. The rate of formation of methanol increased by 8% while no higher alcohol formation was observed at the lower CO/H_2 ratio.

3. Increasing the CO/H_2 ratio had a significant effect on the hydrocarbon selectivity of unpromoted Cu(2)/Cr(1) and Cu(1.5)/Co(0.5)/Cr(1) catalysts. At the higher CO/H_2 ratio, hydrocarbon formation was not observed for Cu/Cr and Cu/Co/Cr catalysts. Hydrocarbon formation was not observed for K promoted Cu(2)/ Cr(1)/ K(0.045) catalysts for either CO/H_2 ratio.

Smith and Anderson (1983) studied the effect of CO/H_2 ratio on activity of coprecipitated $Cu/ZnO/K_2CO_3$ catalysts and found that increasing CO/H_2 ratio doubled isobutyl alcohol selectivity. For CO/H_2 ratio of 0.5, butanol selectivity was independent of (H_2 + CO) conversion, whereas at the higher CO/H_2 ratio of 2.0, butanol selectivity increased from 2 to 28% as reactant conversion increased from 7 to 45%. They believed that CO decreased the relative rate of hydrogenation of methanol precursor. The rate of hydrogenation of methanol appeared to be faster than formation of higher alcohols. Their results agreed with Graves (1931) mechanism which proposes chain growth by condensation of two lower alcohols. Secondary alcohols are believed to react only by the loss of the hydroxyl group.

Cao et al. (1988) have studied adsorption behaviour of a series of coprecipitated $Cu/Co/ZnO/Al_2O_3$ catalysts using IR and TPD techniques. They found that the surface of the reduced catalyst consisted of metallic Cu clusters containing isolated Co atoms. These Co atoms are believed to block active Cu sites for methanol synthesis but are capable of accomplishing elementary steps associated with Fischer Tropsch reactions. Co atoms are found to adsorb multiple CO molecules which was believed to enhance oxygenate formation by CO insertion reaction.

Vedage et al. (1985) studied the effect of CO/H_2 ratio on unpromoted Cu/ZnO and Cs promoted 0.4%CsOH/30%Cu/70% ZnO catalysts under reaction conditions of 288°C and 75 atm. Upon increasing CO/H_2 from 1.1 to 2.2, they found that methanol yield decreased by 50% while higher alcohol yield increased to a small extent. Decreasing CO/H_2 increased the rate of CO insertion. They proposed that higher alcohols are obtained by stepwise attachment of either the C or the O atom of an intact C-O bond of a C_1 intermediate to a growing alcohol chain. Based on their product compositions, they concluded that straight chain higher alcohols are formed at the lower CO/H_2 ratio of 1.1 while branched chain alcohols are obtained at the higher CO/H_2 ratio.

Courty et al. (1987) studied different alcohol synthesis catalysts and concluded that the optimum CO/H_2 ratio for maximum higher alcohol selectivity was dependent on catalyst composition and reaction conditions. They obtained optimum CO/H_2 ratios of 0.33-0.5, 1.0, 0.5-1.0, and 1.0 for Cr/Zn, Cu/Zn, Cu/Co and MoS_2 based catalysts respectively under different reaction

conditions. Higher CO/H_2 favored C_{2+} formation while CO/H_2 ratios smaller than 0.3 had detrimental effect on higher alcohol selectivity.

Sheffer and King (1988) found that increasing the CO/H_2 ratio from 0.5 to 1.0 did not affect the oxygenate activity of complexed Cu(1)/Co(1)/Cr(0.8)/K(0.09) catalysts under reaction conditions of 275°C and 50 atm. The overall activity increased by 18% and the aldehyde selectivity increased while alcohol selectivity decreased. Upon further increasing the CO/H_2 ratio to 2.0, they observed that the oxygenate activity and overall activity of the catalyst decreased by a factor of 3. The aldehyde selectivity increased significantly while the alcohol selectivity decreased.

Our results indicate that increasing the CO/H_2 ratio from 0.4 to 1.0 did not have any effect on the activity and selectivity of complexed Cu(2)/Cr(1)/K(0.045) catalysts. The activity of Cu(2)/Cr(1) catalysts decreased due to decrease in the alcohol and hydrocarbon formation rates. Increasing the CO/H_2 ratio had a marked effect on the activity and selectivity of Cu(1.5)/ Co(0.5)/ Cr(1) catalysts. The overall catalyst activity decreased due to disappearance of hydrocarbons at the higher $CO/_2$ ratio. The overall alcohol formation rate increased due to increases in methanol and ethanol formation rates but no higher alcohols were obtained at the higher CO/H_2 ratio.

Based on our results, we believe that CO/H_2 ratio of 1.0 suppresses hydrocarbon formation by decreasing the CO dissociation rate. For the Cu/Cr catalysts, increasing the CO content in the catalyst results in more active sites being blocked due to adsorption of CO molecules. In Cu/Co/Cr catalysts, Co metal is proposed to be capable of adsorbing multiple CO molecules, resulting in enhanced alcohol formation due to CO insertion (Cao et al. (1988)). We propose that CO reacts reversibly with active K sites. Therefore, changing the CO/H_2 ratio does not affect the alcohol formation rate of Cu/Cr/K catalysts.

From a comparison of our results with the results obtained in the literature, we conclude that there exists an optimum CO/H_2 ratio for obtaining maximum higher alcohol selectivity. The optimum ratio is found to be dependent on catalyst composition, preparation method, and reaction conditions.

4.1.3 Effect of Co/Cu ratio. We were interested in determining the effect of Co/Cu ratio on the activity and selectivity of Cu/Co/Cr catalysts. We studied catalysts having molar compositions of Cu(2)/Cr(1) and Cu(1.5)/Co(0.5)/Cr(1) respectively. The reaction conditions used were 250°C and 50 atm. We used two feed gas mixtures having molar compositions of $CO_2/CO/H_2$ = 0/30/70 and $CO_2/CO/H_2$ = 6/24/70. The results obtained for the CO_2-free feed gas are discussed first, followed by the discussion for feed gas containing CO_2.

We studied the effect of Co/Cu ratio on catalyst activity and selectivity using a CO_2-free feed gas containing $CO_2/CO/H_2$ = 0/30/70 vol% under reaction conditions of 250°C and 50 atm. From the results we made the following observations:

1. Increasing the Co/Cu ratio from 0.0 to 0.33 resulted in a decrease in the rate of CO conversion by 45%.

2. Increasing the Co/Cu ratio resulted in a significant decrease in the overall alcohol yield. The rate of formation of methanol decreased by 93%. The ethanol formation rate decreased by 23%. N-butanol and n-pentanol were not obtained at the higher Co/Cu ratio. The rates of formation of i-butanol and i-pentanol decreased by 58%.

3. Increasing the Co/Cu ratio resulted in an increase in selectivity to hydrocarbon formation. The methanation rate increased by 29%. The rates of formation of ethane and propane increased by 30% and 32% respectively. Butane was obtained at the higher Co/Cu ratio.

We studied the effect of Co/Cu ratio on the activity and selectivity of Cu/Co/Cr catalysts using a feed gas containing $CO_2/CO/H_2$ = 6/24/70 Vol%. The tubular reactor was maintained at 250°C and 50 atm. From our results we made the following observations:

1. Increasing the Co/Cu ratio from 0.0 to 0.33 resulted in a significant decrease in the catalyst activity. The rate of CO conversion decreased by 35%.

2. Increasing the Co/Cu ratio decreased the overall alcohol yield. The rate of formation of methanol decreased by 92%. Trace quantities of ethanol were obtained at the higher Co/Cu ratio of 0.33.

3. Increasing the Co/Cu ratio increased the catalyst selectivity to hydrocarbon formation. The rate of formation of methane, ethane and propane increased by 4%, 67% and 167% respectively. Butane was obtained at the higher Co/Cu ratio.

Spencer (1986) used ESCA and SIMS on $Cu/Co/ZnO/Al_2O_3$ catalysts and found that surface concentrations of Co were much higher than the bulk Co concentrations. They obtained negligible surface area using N_2O chemisorption technique. They proposed that surface of Cu crystallites was covered by an oxidic layer containing Co and support oxides which would prevent chemisorption by Cu-Co bonding.

Cao et al. (1988) studied coprecipitated Cu/Co/ZnO catalysts under reaction conditions of 290°C, 50 atm and feed gas (CO/H_2 = 1). They found that addition of 5% Co decreased methanol yield by an order of magnitude. Using infrared (IR) and temperature programmed desorption (TPD) studies they concluded that Co atoms are present on the surface of Cu clusters and block active Cu sites for methanol synthesis. They also found that Co sites were capable of adsorbing and dissociating multiple C-O bonds resulting in hydrocarbon formation by CO dissociation and higher alcohol formation by CO insertion reaction.

Courty et al. (1982) have studied coprecipitated Cu/Co/Cr catalysts under reaction conditions of 290°C and 60 atm for a feed gas containing CO/H_2 = 0.5. They found that small amounts of Co (<10%) promoted methanol synthesis. For Co/Cu ratio varying between 0.33 and 1.0, a mixture of light C_1-C_6 alcohols were obtained, with C_1-C_6 hydrocarbons obtained as byproducts. For catalysts containing more than 50% Co, Fischer-Tropsch catalysts promoting hydrocarbon formation were obtained. They proposed that Co must be partly combined in a spinel type structure in the precursor while the remaining Co was present either in the pure form or was alloyed with Cu.

Sheffer and King (1989) studied various Cu/Co/Cr/K catalysts and found that the activity and selectivity of Co was not dependent on the citrate complexation method of preparation. Co/Cr catalysts were found to form spinels and have low activity and were selective to hydrocarbon formation. Cu/Co catalysts formed a mixture of Co and Cu oxides upon calcination. They believed that Co was a necessary component for higher oxygenate formation in the Cu/Co/Cr catalysts.

Our results indicate that increasing the Co/Cu ratio from 0.0 to 0.33 results in a significant reduction in catalyst activity. Increasing the Co/Cu ratio reduced the catalyst selectivity to alcohols and resulted in an increase in the hydrocarbon yield for both CO_2 free and CO_2 containing feed gas compositions. Based on comparison of our results with previous studies undertaken by

Spencer (1986) and Cao et al. (1988) on Cu/Co catalysts described above, we believe that Co is present in large quantities on the catalyst surface, blocking active Cu sites for methanol and higher alcohol synthesis. Using N_2O chemisorption technique, we observed that the metal surface area of Cu(1.5)/Co(0.5)/Cr(1) catalyst decreased from 11.1 m^2/g to 3.5 m^2/g after activity tests. In contrast, there was no significant decrease in metal surface area of Cu(2)/Cr(1) catalysts which decreased from 4.7 m^2/g to 4.0 m^2/g after activity tests. Spencer obtained negligible surface area using N_2O chemisorption technique.

Cao et al. (1988) observed that addition of 5% Co to Cu/ZnO catalysts decreased the methanol yield by an order of magnitude. We have also observed that addition of 17% Co to Cu/Cr catalysts decreases the methanol yield by an order of magnitude. Since Co is capable of adsorbing multiple CO molecules (Cao et al.(1988)), we propose that increase in hydrocarbon formation is due to increase in CO dissociation rate and a decrease in higher alcohol formation is due to decrease in CO insertion rate.

4.1.4 Effect of K promoter. We were interested in determining the effect of K on the activity and selectivity of Cu/Cr catalysts. We studied catalysts having molar compositions of Cu(2)/Cr(1)/K(0.0) and Cu(2)/Cr(1)/K(0.045) respectively. The reaction conditions used were 250°C and 50 atm. We used two feed gas mixtures having molar compositions of $CO_2/CO/H_2$ = 0/30/70 and $CO_2/CO/H_2$ = 6/24/70. The results obtained for the CO_2-free feed gas are discussed first, followed by the results for feed gas containing CO_2.

We studied the effect of K on catalyst activity and selectivity using a CO_2-free feed gas containing $CO_2/CO/H_2$ = 0/30/70 vol% under reaction conditions of 250°C and 50 atm. From our results we make the following observations:

1. The K promoted Cu(2)/Cr(1)/K(0.045) catalyst had lower activity than the unpromoted Cu(2)/Cr(1) catalyst. The rate of CO conversion decreased by 57% for the K promoted catalyst.

2. The K promoted catalyst had lower overall alcohol yield than the unpromoted Cu/Cr catalyst. The rate of formation of methanol decreased by 20%. The rate of formation of i-pentanol decreased by 52%. Ethanol,i-butanol, n-butanol and n-pentanol were not obtained upon using the K promoted Cu/Cr/K catalyst.

3. The K promoted catalyst had significantly lower hydrocarbon selectivity. Methane and ethane were not obtained for the K promoted Cu/Cr catalyst. The rate of formation of propane decreased by 20%.

We studied the effect of K on the activity and selectivity of the Cu/Cr catalysts using a feed gas containing $CO_2/CO/H_2$ = 6/24/70 vol%. The reactor was maintained at 250°C and 50 atm. From our results we make the following observations:

1. There was no significant difference in the activity of the K promoted Cu/Cr catalyst compared to the activity of the unpromoted Cu/Cr catalyst. The rate of CO conversion increased by 5% for the K promoted catalyst.

2. The overall alcohol yield of Cu/Cr/K catalysts was higher compared to the overall alcohol yield for unpromoted Cu/Cr catalysts for a feed gas containing $CO_2/CO/H_2$ = 6/24/70 vol%. The rate of formation of methanol for the K promoted catalyst was greater than the unpromoted catalyst by 9%. Higher alcohol formation viz. ethanol, i-butanol and i-pentanol was observed for the K promoted Cu/Cr catalyst.

3. The overall hydrocarbon selectivity was lower for the K promoted Cu/Cr catalyst. Methane and ethane formation rates decreased by 20% and 5% respectively for the K promoted catalyst. The rate of formation of trace amounts of propane increased by 10% for the K promoted catalyst. Trace amounts of butane were also obtained.

We made a comparative study of catalysts having molar compositions of Cu(1.5)/Co(0.5)/Cr(1) and Cu(1.5)/Co(0.5)/Cr(1)/K(0.045). The effect of K on catalyst activity and selectivity using a CO_2-free feed gas containing $CO_2/CO/H_2$ = 0/50/50 vol% under reaction conditions of 250°C and 50 atm yielded the following observations:

1. The activity of the K-promoted Cu/Co/Cr catalyst was significantly greater than the activity of the unpromoted Cu/Co/Cr catalyst. The rate of CO conversion for the K promoted catalyst was three times the rate of CO conversion for the unpromoted catalyst.

2. We obtained a 100% increase in the overall alcohol yield on the K-promoted Cu/Co/Cr catalyst. The rate of formation of methanol decreased by 20%. The rate of formation of ethanol increased by 50%. Isobutanol, n-butanol, i-pentanol and n-pentanol were obtained only for the K-promoted Cu/Co/Cr catalyst.

3. Potassium had little effect on the selectivity to hydrocarbon formation. The rate of formation of trace amounts of propane increased by 28% for the K promoted catalyst.

We studied the effect of K on the activity and selectivity of the same catalysts using a feed gas containing $CO_2/CO/H_2$ = 6/24/70 vol%, for the same reactor conditions. This gave the following observations:

1. There was no significant difference in the overall activity of K-promoted Cu/Co/Cr/K catalyst compared to the activity of the unpromoted Cu/Co/Cr catalyst. The rate of CO conversion decreased by 4% for the K promoted catalyst.

2. The overall alcohol yield of Cu/Co/Cr/K catalysts was greater by 73% compared to the overall alcohol yield of the unpromoted Cu/Co/Cr catalyst. The rate of formation of methanol increased by 20%. The ethanol formation rate increased by 14%. K promoted higher alcohol formation (viz. i-butanol and i-pentanol).

3. The overall hydrocarbon yield of the K-promoted Cu/Co/Cr catalyst decreased by 14%. The methanation rate was not affected by K. The ethane and propane formation rates decreased by 26 and 44% respectively. No higher hydrocarbon formation was observed for the Cu/Co/Cr/K catalyst.

Discussion. Courty et al. (1982) proposed that alkali cation suppresses acidity by suppressing alcohol dehydration, possibly by modifying the electronic properties of Co. They found uncontrolled methanation for unpromoted Cu/Co catalysts below 290°C.

Smith and Anderson (1983) studied the effect of K on coprecipitated Cu/ZnO catalysts and obtained a twofold increase in i-butanol selectivity for a catalyst containing 0.5wt% K_2CO_3. Increasing K content decreased the BET surface area. The CO_2 uptake was found to be a measure of the alkali surface area. They concluded that maximum activity and selectivity were obtained for an alkali to metal surface area of 0.25.

Vedage et al. (1985) studied the effect of Cs on activity of coprecipitated CuO(30%)/ZnO(70%)/catalysts. Under reaction conditions of 235°C, 75 atm and using a feed gas containing $CO_2/CO/H_2$ = 0/30/70 vol%, they obtained a 48% increase in rate of CO conversion to methanol for the Cs promoted 0.4%CsOH/ 30%Cu/ 70%ZnO catalyst, compared to the unpromoted 30%Cu/ 70%ZnO catalyst. For a feed gas containing $CO_2/CO/H_2$ = 6/24/70 Vol%, they observed a 54% decrease in the rate of CO conversion to methanol for the Cs-promoted catalyst compared to the unpromoted Cu/ZnO catalyst. They observed that alkali hydroxides first occluded or agglomerated and then dispersed on the surface during tests. They believed that alkali hydroxides were more effective catalysts due to their low lattice enery resulting in their dispersion whereas alkaline earth metal hydroxides agglomerate. They proposed that the role of Cs was to increase the surface hydroxyl groups that react with CO to produce an intermediate formate species which was then hydrogenated to methanol and regenerated surface hydroxyls.

Sheffer and King (1989) studied the effect of K on unsupported Cu catalysts and observed that catalyst specific activity and BET surface area decreased with increase in K content. K was found to be present as K_2CO_3. They do not agree with the hypothesis of Vedage et al. (1985) that CO reacted with alkali hydroxide resulting in an intermediate formate species which was then hydrogenated to methanol. Instead they proposed that upon reduction, active Cu(I) sites were probably stabilized by phase formation of K with Cu in the form of $KCuCO_3$.

Sheffer et al. (1989) found that K increased sintering rate upon reduction. They observed a fivefold decrease in catalyst activity upon adding K to a Cu/Co catalyst. They obtained an active and selective methanol synthesis catalyst upon addition of K to a Cu/Cr catalyst. Since they did not observe any higher alcohol formation on Cu/Cr/K(0.064) catalyst, they discounted the theory that Cu(I)-Cr_2O_3 methanol sites were modified by K. Instead they proposed that Co was a necessary component for higher oxygenate formation in the Cu/Co/Cr system.

Sheffer and King (1988) studied the effect of K on Cu/Co/Cr catalysts and found that K suppressed methanation during startup, decreased activity, and increased aldehyde selectivity. They concluded that K diluted the catalyst surface since they did not observe any increase in average molecular weight of the products. They believed that K reduced the activity of Cu/Co/Cr catalysts due to an electronic effect resulting from electron donation to Co by K.

Our results indicate that overall activity of K promoted Cu/Cr catalysts is dependent on feed gas composition. For a CO_2-free feed gas, K inhibited methanol and higher alcohol formation rates. For a feed gas containing CO_2, we did not observe any significant effect of the K promoter. Our results are in agreement with Sheffer et al (1989)'s observations that K-promoted Cu/Cr catalyst decreased the catalyst activity and inhibited higher alcohol formation. Our experimental results are not in agreement with Vedage et al.'s (1985) observations that unpromoted catalysts are less active than alkali promoted catalysts for a CO_2-free feed gas. Our results are also not in agreement with Vedage et al's observations that the unpromoted catalysts are more active for methanol synthesis than the alkali promoted catalysts for a feed gas containing CO_2. We attribute the differences in our results to differences in our reaction conditions, catalyst compositions and catalyst preparation methods.

Our results also indicate that overall activity of K-promoted Cu/Co/Cr catalysts is dependent on feed gas composition. For a CO_2-free feed gas, K decreased methanol formation rate and increased higher alcohol formation rates. For a feed gas containing CO_2, K-promoted methanol and higher alcohol synthesis. K had a small inhibiting effect on the selectivity to hydrocarbon formation for CO_2-containing feed gas.

Sheffer and King (1988) obtained a 31% decrease in rate of CO conversion for the K promoted Cu(1)/ Co(1)/ Cr(0.8)/ K(0.045) catalyst compared to the activity of unpromoted Cu/Co/Cr catalyst under reaction conditons of 275°C, 50 atm and H_2/CO equal to 2. The oxygenate yield of the K promoted catalyst was greater than the oxygenate yield of the unpromoted catalyst by 7%.

Our experimental results are not in agreement with results obtained by Sheffer and King, since we observed that K promoted the activity of Cu/Co/Cr catalysts. We observed that K doubled the oxygenate yield. We attribute the differences in results to differences in reaction conditions, catalyst composition and catalyst preparation method.

Based on our experimental results, we propose that K inhibits activity and alcohol selectivity of Cu/Cr catalysts using a CO_2-free gas by blocking active Cu sites. The effect of K on Cu/Cr catalysts is not significant in the presence of CO_2 feed gas. For Cu/Co/Cr catalysts, Co inhibited alcohol formation and promoted hydrocarbon selectivity. Therefore, we believe that the role of K in Cu/Co/Cr catalysts is to compensate inhibiting effect of Co, possibly by an electronic interaction between Co and K as proposed by Sheffer and King (1989) and Courty et al. (1982). Our experimental findings also agree with Sheffer and King's observation that both Co and K are necessary for higher alcohol formation in Cu/Co/Cr/K catalysts.

A comparison of higher alcohol yields obtained for our complexed Cu/Co/Cr/K catalysts at reaction conditions of 250°C and 50 atm can by summarized as follows:

1. Maximum higher alcohol yield of 0.024 g/g/hr was obtained on the Cu(1.5)/Co(0.5)/Cr(1.0)/K(0.045) catalyst using a feed gas containing $CO_2/CO/H_2$ = 0/30/70 vol%. Selectivity to alcohols was 97% with higher alcohol selectivity being 66%.

2. Maximum methanol yield of 0.104 g/g/hr with selectivity of 65% was obtained on the Cu(2)/Cr(1) catalyst using a feed gas containing $CO_2/CO/H_2$ = 0/30/70 vol%. The higher alcohol yield was 0.019 g/g/hr for this catalyst and the overall alcohol selectivity was 77%.

3. We obtained minimum alcohol selectivity of 21% using unpromoted Cu(1.5)/Co(0.5)/Cr(1.0) catalyst using a feed gas containing $CO_2/CO/H_2$ = 0/30/70 vol%.

4.2 OXIDE COVERAGE MODEL

4.2.1 Model assumptions. In order to first correlate the results of different CO_2/CO ratios and different K loadings, we investigated a theoretical model showing the effect of oxygen coverage on the methanol yield. This model is based on the following assumptions:

1. The surface of K-promoted Cu catalysts consists of Cu sites (Θ_{Cu}), K sites (Θ_K) and perimeter sites(Θ_P):

$$\Theta_{Cu} + \Theta_K + \Theta_P = 1.0$$

2. Cu sites consist of vacant Cu sites (Θ_v), oxidized Cu sites (Θ_O) and carbonate sites formed by adsorption of CO_2 (Θ_{CO3}):

$$\Theta_v + \Theta_O + \Theta_{CO3} = \Theta_{Cu}$$

3. K sites consist of oxidized K sites (Θ_{KO}) and carbonate sites (Θ_{KCO3}):

$$\Theta_{KO} + \Theta_{KCO3} = \Theta_K$$

4. Perimeter sites consist of oxidized sites (Θ_{PO}) and carbonate sites (Θ_{PCO3}):

$$\Theta_{PO} + \Theta_{PCO3} = \Theta_P$$

5. Oxidized Cu sites (Θ_O) are obtained by oxidation of vacant sites (Θ_v) by CO_2:

$$\Theta_O = K_1 (P_{CO2}/P_{CO}) (\Theta_v)$$

where K_1 is the adsorption constant for oxidation of vacant Cu sites. P_{CO2} and P_{CO} are the partial pressures of CO_2 and CO respectively.

6. Some oxidized Cu sites are converted to carbonate sites upon increasing CO_2 concentration in the feed gas:

$$\Theta_{CO3} = K_2 (P_{CO2}) (\Theta_O)$$

where K_2 is the adsorption constant.

7. Oxidized K sites and perimeter sites may similarly be converted to carbonate sites:

$$\Theta_{KCO3} = K_2 (P_{CO2}) (\Theta_{KO})$$

$$\Theta_{PCO3} = K_2 (P_{CO2}) (\Theta_{PO})$$

Here we assume that the adsorption constant K_2 is same for both sites.

8. Methanol is formed on vacant Cu sites adjoining either oxidized Cu sites, oxidized K or perimeter sites:

$$r_{CH3OH} = k_1 (\Theta_v) [\Theta_O + \Theta_{KO} + \Theta_{PO}]$$

where k_1 is the rate per site at fixed reaction conditions.

4.2.2 Parameter Sensitivity. Using trial values of Θ_K and Θ_P, these equations are solved to obtain Θ_{Cu}, Θ_v, Θ_O, Θ_{KO}, Θ_{PO}, Θ_{CO3}, Θ_{KCO3}, and Θ_{PCO3}. Parameter sensitivity was determined by doubling one of the adsorption constants and determining the effect on the rate of methanol obtained for fixed value of K sites and perimeter sites ($\Theta_K + \Theta_P = 0.01$).

At low CO_2 concentrations, increasing K_1 results in an increase in the number of oxidized Cu sites and decrease in number of vacant Cu sites. Thus, rate of methanol synthesis increases. Upon increasing K_1, the maxima for methanol synthesis increases and shifts towards lower CO_2 concentrations. At higher CO_2 concentrations, increase in K_1 results in increase in number of carbonate sites and decrease in the number of oxidized sites and vacant sites. Therefore, rate of methanol synthesis decreases with increase in K_1 at higher CO_2 concentrations.

At low CO_2 concentrations, increase in K_2 does not affect the methanol synthesis rate since the number of carbonate sites are not significant. At high CO_2 concentrations, increase in K_2 results in an increase in the number of carbonate sites and a decrease in the number of vacant sites and number of oxidized sites. Thus, the carbonate sites block sites available for methanol synthesis leading to a decrease in rate of methanol synthesized.

Increasing the number of K or perimeter sites results in increase in the methanol synthesis rate for low CO_2 concentrations as more oxidized sites are available. At higher CO_2 concentrations, increase in the number of K or perimeter sites has little effect on the methanol formation rate due to increase in the number of oxidized Cu sites.

The oxide coverage model predicts that at low CO_2 concentrations, adding CO_2 to feed gas mixture results in an increase in the methanol yield for both the unpromoted and K promoted catalysts for both model parameters of K_1 and K_2 equal to 1.0 and the number of K and perimeter sites $(\Theta_K + \Theta_P) < 0.08$. The effect of CO_2 on the methanol yield is more pronounced for the unpromoted catalysts. This prediction is consistent with observations by Vedage et al. (1985) using unpromoted and Cs promoted Cu/ZnO catalysts.

We observe that our model also predicts a maximum on methanol synthesis rate for Cs promoted Cu/ZnO catalysts. The differences in the normalized methanol synthesis rates for Cu/ZnO/Cs catalysts in presence of CO_2 can be eliminated by assuming that the rate of carbonation of oxidized Cs sites is higher than the rate of carbonation of oxidized Cu sites. This would lead to usage of two adsorption constants for the carbonation reaction instead of the single adsorption constant K_2 currently used in the model.

We fitted our experimental results obtained using Cu/Cr/K catalysts using the oxide coverage model parameters. We observed that addition of CO_2 to the feed gas mixture decreased the activity of unpromoted Cu(2)/Cr(1) catalysts. Addition of CO_2 causes carbonation of oxidized Cu sites resulting in a decrease in methanol activity when the number of K and perimeter sites are 0.118. Therefore, we can conclude that addition of CO_2 does not have a promotional effect on the methanol synthesis rate for a catalyst containing sufficient number of oxidized K and perimeter sites.

We observed that addition of CO_2 to K promoted Cu/Cr catalysts had a small effect on the methanol yield. This experimental observation can be predicted by the model by assuming the Cu/Cr/K catalyst has sufficient number of oxidized K and perimeter sites. Therefore, increasing CO_2 concentration in the feed stream would have a very small effect on the methanol yield.

4.3 UNIFIED MODEL FOR ACTIVE SITES

The capstone of our work is the proposal of a unified model for active sites for alcohol synthesis using complexed Cu/Co/Cr/K catalysts. Our model is based on our experimental observations and a review of previous mechanisms for alcohol synthesis discussed above.

Role of copper sites. Methanol can be synthesized by hydrogenation of CO on active Cu(I) sites. Most discussions on the mechanism for methanol synthesis involve hydrogenation of an intermediate formate species on active Cu(I) sites. These sites are obtained by oxidation of metallic Cu sites in several ways. Support oxides viz. ZnO, Al_2O_3 and Cr_2O_3 can be used to oxidize metallic Cu perimeter sites. The role of Al_2O_3 and Cr_2O_3 is secondary, involving stabilization of coprecipitated $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ catalysts, respectively (Herman et

al., 1979). Active Cu(I) sites are stabilized in the chromite phase in Cu/Cr_2O_3 catalysts (Monnier et al., 1984).

Higher alcohols can also be synthesized on active Cu(I) sites. The mechanism for higher alcohol synthesis on alkali promoted Cu/ZnO catalysts was proposed to involve a stepwise attachment of either the C or the O atom of a C_1 intermediate to a growing alcohol chain. Straight chain alcohols are proposed to be obtained by CO insertion reaction while branched chain alcohols are proposed to be obtained by aldol condensation reaction (Vedage et al., 1985).

Role of CO_2. The promotional effect of CO_2 for methanol synthesis is unique for Cu/ZnO catalysts. CO_2 has been found to inhibit methanol synthesis on Cu/Cr_2O_3, Pd/SiO_2, Pt/SiO_2 and Ir/SiO_2 catalysts, possibly by noncatalytic, competitive adsorption on active Cu(I) sites. When present in small concentrations, CO_2 in feed gas oxidizes metallic Cu and maintains it in active Cu(I) state in $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ catalysts. However, when present in high concentrations, CO_2 inhibits methanol synthesis by blocking active Cu(I) sites in Cu/ZnO catalysts. CO_2 in the feed gas can also form carbonates on alkali promoted catalysts blocking active Cu(I) sites.

Role of alkali. Potassium stabilizes surface oxygen, thus creating partially oxidized Cu sites which are active for methanol synthesis. Potassium has been found to promote methanol synthesis on metallic Cu and coprecipitated Cu/ZnO catalysts. However, we found that K inhibits methanol formation on Cu(2)/Cr(1) catalysts possibly by blocking active Cu(I) sites.

On bulk Co Fischer-Tropsch synthesis catalysts, K_2O promotes the olefin yield (Dent and Lin, 1979). K_2CO_3 is also the most important promoter for Fe Fischer-Tropsch synthesis catalysts (Anderson, 1984). Activity of conventional fused or precipitated Fe catalysts passed over a maximum for a K/Fe ratio of 0.005-0.01 by weight (Anderson, 1984). Addition of K increases the average molecular weight of the product, the olefin/paraffin ratio, the oxygenate product yield. K also promotes the water gas shift reaction and the rate of carburization of Fe (Arakawa and Bell, 1983). Increase in K content increases the hard wax selectivity (Dry, 1981). Potassium was found to promote dissociation of strongly bound molecular CO state, α_3-CO, on clean Fe(100) surface resulting in formation of K_xO surface complex (Cameron and Dwyer, 1988).

Role of Co. Bulk Co catalysts are active for Fischer-Tropsch synthesis, resulting in hydrocarbon formation. Co catalysts are also active for methanol carbonylation, resulting in formation of oxygenates (viz. higher alcohols and acids). Co catalysts dissociate multiple CO molecules to form a surface alkyl intermediate and promote chain growth. Hydrogenation of alkyl intermediates results in hydrocarbon formation while CO insertion results in oxygenate formation.

In mixed Cu/Co catalysts, Co is present on surface of Cu clusters (Spencer, 1984, Cao et al., 1988). Higher alcohols can be synthesized by chain termination of alkyl intermediates formed on Co sites by CO insertion on neighbouring Cu atoms (Courty et al., 1982, Pan et al., 1988b). For mixed Co(3)/Cu(7) catalysts supported on Al_2O_3, no promotional effect of K or Na were observed (Yang et al., 1979). We believe this is possibly due to low K-Co interaction due to acidic nature of Al_2O_3 support resulting in more K bonded to the support. Activity of $K/Fe/Al_2O_3$ catalysts has also been found to increase with increase in K-Fe interaction (McVicker and Vannice, 1980).

Our results indicate that K promotes higher alcohol formation and inhibits hydrocarbon formation on Cu/Co/Cr/K catalysts. We propose that Co sites are possibly modified by neighboring K sites resulting in chain termination on K sites by CO insertion. This would cause increase in

higher alcohol yield and decrease in hydrocarbon formation on Cu/Co/Cr/K catalysts. This proposition is in contrast to the proposition by Cameron and Dwyer (1988) that K promotes α_3-CO dissociation on clean Fe(100) surface, resulting in formation of K_xO.

This conflict can be resolved by assuming that initially K promotes CO dissociation on clean Co surface, resulting in formation of K^+-O sites. After some time, all the K sites on the surface are oxidized. These sites are then unable to dissociate CO, and instead promote chain termination of alkyl intermediates by CO insertion. This leads to increased oxygenate formation, possibly aldehydes, and decreased hydrocarbon formation. The role of Cu would then be to hydrogenate aldehydes resulting in higher alcohol formation.

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