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Higher Alcohol and Oxygenate Synthesis over $Cs/Cu/ZnO/M_2O_3$ (M = Al, Cr) Catalysts

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Surface doping of $Cu/ZnO/M_2O_3$ (M = Al, Cr) catalysts prepared from hydrotalcite precursors with cesium ($Cs/Cu/ZnO/M_2O_3$) significantly enhanced the alcohol synthesis rate under higher alcohol synthesis conditions. With respect to the unsupported Cs/Cu/ZnO catalyst, the product selectivity of the $Cs/Cu/ZnO/Al_2O_3$ catalyst was shifted toward methanol, while the $Cs/Cu/ZnO/Cr_2O_3$ catalyst maintained a high selectivity toward C_2^+ alcohols. The presence of cesium in the $Cu/ZnO/M_2O_3$ catalysts inhibited the synthesis of dimethyl ether. Comparison of the product distributions obtained over the $Cs/Cu/ZnO/M_2O_3$ catalysts with those observed over the Cs/Cu/ZnO catalysts indicates that the function of the $Cs/Cu/ZnO/Cr_2O_3$ catalyst is similar to that of the Cs/Cu/ZnO in that higher alcohols are synthesized by a stepwise carbon chain growth via a unique aldol coupling with oxygen retention reversal mechanism. The Al_2O_3-based catalysts undergo complex structural changes that probably cause occlusion of the Cs dopant, thus resulting in low selectivity to higher alcohols while retaining high activity toward methanol.

INTRODUCTION

It has been shown that surface doping of Cu/ZnO catalysts with a submonolayer dispersion of cesium results in the promotion of methanol synthesis (*1–3*) as well as the water gas shift reaction (*2, 4*) under typical methanol synthesis conditions [523 K, 7.6 MPa, H_2/CO = 2.33, gas hourly space velocity (GHSV) = 6120 liters (STP)/kg cat/hr]. At the same time, the rates of the $C_1 \rightarrow C_2$ oxygenate synthesis processes that form ethanol and methyl formate were also enhanced (*1, 3*), although the methanol selectivity was maintained at greater than 98.9 mol% of the total oxygenate product. The mechanism of the $C_1 \rightarrow C_2$ steps over a 0.4 mol% Cs/Cu/ZnO catalyst was probed by injecting $^{13}CH_3OH$ into the $^{12}CO/H_2$ synthesis gas and following the flow of the isotopically labeled carbon into ethanol and methyl formate by ^{13}C nuclear magnetic resonance (NMR) analysis of the C_2 products (*3*). It was shown that the C_1 surface species formed from methanol was a precursor of the methyl group of methyl formate and of both the CH_3 and CH_2 groups of ethanol. Thus, the C–C bond in ethanol was made by coupling C_1 surface intermediates, and methyl formate was formed by methanol carbonylation and was not a precursor of ethanol.

To obtain insight into the mechanism of the synthesis of higher alcohols, e.g., the $C_2 \rightarrow C_3$ and $C_3 \rightarrow C_4$ steps and the linear vs branched carbon chain growth, over Cu/ZnO and 0.4 mol% Cs/Cu/ZnO catalysts, a ^{13}C-NMR study of the C_2–C_4 products formed under higher alcohol synthesis conditions [583 K, 7.6 MPa, H_2/CO = 0.45, and GHSV = 3260 liters (STP)/kg cat/hr] was carried out, as reported in the preceding paper (*5*). It was demonstrated that over both Cu/ZnO and Cs/Cu/ZnO catalysts, lower alcohols were incorporated into the higher alcohols via stepwise growth processes. Over the unpromoted Cu/ZnO catalyst, the

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dominant carbon chain growth process was a linear insertion chain growth, e.g.,

$$CH_3{}^{13}CH_2OH + CO/H_2 \xrightarrow[Cu/ZnO]{} CH_3{}^{13}CH_2CH_2OH. \quad (1)$$

However, carbon chain growth over the Cs/Cu/ZnO catalyst was dominated by β-carbon addition wherein the adding C_1 intermediate retained its oxygen, e.g.,

$$CH_3{}^{13}CH_2OH + CO/H_2 \xrightarrow[Cs/Cu/ZnO]{} {}^{13}CH_3CH_2CH_2OH. \quad (2)$$

This unique mechanism was termed *aldol coupling with oxygen retention reversal.*

Since practical industrial methanol synthesis catalysts are supported with Al_2O_3 or Cr_2O_3, the influence of these components on higher alcohol synthesis over Cs/Cu/ZnO/M_2O_3, where M = Al or Cr, was studied. The M_2O_3 can be a structural promoter by increasing the surface area and stability of the catalyst. However, the M_2O_3 component might also induce side reactions, e.g., formation of dimethyl ether and hydrocarbons, under the higher alcohol synthesis conditions. In addition, the components might exhibit inherent catalytic activity; e.g., alkali/ZnO/Cr_2O_3 is a higher alcohol synthesis catalyst (*6, 7*) at high temperatures (603–703 K) and pressures (9–18 MPa). Therefore, the purpose of the present investigation was to compare product distributions and rates for higher alcohol synthesis over the Cs/Cu/ZnO/M_2O_3 catalysts with those obtained over the previously studied (*5*) Cs/Cu/ZnO catalyst.

EXPERIMENTAL

Catalyst preparation. While the preparation of the binary Cu/ZnO = 30/70 catalyst by an initial precipitation procedure resulted in a single-phase aurichalcite-type [$Cu_{1.5}Zn_{3.5}(OH)_6(CO_3)_2$] precursor (*8*), precipitation of the Cu/ZnO/M_2O_3 catalyst precursors resulted in formation of a different hydroxycarbonate (*9–11*), which in this case contained single-phase hydrotalcite (*12*). Hydrotalcite is a naturally occurring mineral or synthetically prepared compound (*13*) having the typical composition $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, whereas the catalyst precursor prepared here contained (Cu,Zn) in place of the magnesium, and in the case of the chromium- and gallium-containing catalysts, Cr or Ga replaced Al. These synthetic catalyst precursors were isomorphous with the natural mineral. The single-phase precursor was prepared by the simultaneous addition of a Cu/Zn/M nitrate salt solution and a 1.0 *M* Na_2CO_3 solution to 1 liter of 1 *M* sodium acetate solution at 323 K that contained enough Na_2CO_3 to achieve a pH of 9.5. Continuous stirring and a pH of 9.5 were maintained during the 2-hr addition of the metal salt solution. After subsequent digestion for 30 min, the precipitate was allowed to settle and the supernatant was decanted. The precipitate was then washed three times by decantation with warm distilled water, filtered, and air-dried at ambient temperature. The hydrotalcite-like precursors used in the present investigation had the chemical composition $Cu_{2.4}Zn_{3.6}M_2(OH)_{16}CO_3 \cdot 4H_2O$ (M = Al, Cr, or Ga) and contained less than 0.02 wt% sodium. In each case, the dried precipitate was pelletized from a dense aqueous slurry by being pressed through a Teflon die, dried, and sieved to 0.85–2.0 mm in size, followed by stepwise calcination to 623 K to give the corresponding mixed oxides.

Cesium doping with CsOOCH was carried out by adding 2.5 g of the calcined pelletized catalyst to 25 ml of N_2-purged aqueous CsOOCH solution at 323 K. The solution was then evaporated to dryness under flowing nitrogen. After doping, all catalysts were recalcined at 623 K for 3.0 hr and loaded into the reactor for testing.

Testing of the catalysts and determination of the alcohol synthesis activity and selectivity. For the Cs/Cu/ZnO/M_2O_3 catalyts, 1.5 g of the pelletized catalyst was diluted with three times its volume of 3-mm Pyrex beads and centered in the fixed-bed continuous-flow 316 stainless-steel reactor.

Before testing, the catalysts were reduced in a flowing H_2/N_2 = 2/98 mol% mixture at 523 K and ambient pressure. The reduction was followed by monitoring the water content of the exit gas using gas chromatographic analysis and was terminated when a sudden drop in the production of water was observed.

After screening for methanol synthesis activity, catalytic activities and selectivities were obtained under the higher alcohol synthesis conditions of 583 K and 7.6 MPa with H_2/CO = 0.45 synthesis gas at GHSV = 5330 liters (STP)/kg cat/hr. The mode of operation, along with schematic diagrams of the two testing systems utilized, has been described previously (*5, 14, 15*). All experimental data were obtained under steady-state conditions that were usually maintained for ≈24 hr before changing the reaction conditions to obtain another set of data. The $Cs/Cu/ZnO/Ga_2O_3$ catalyst was not tested for higher alcohol synthesis because the catalyst underwent a physicochemical change during the Cs doping procedure and exhibited a lower methanol synthesis activity than did the Cs/Cu/ZnO catalyst.

The exit product mixture from the reactor was sampled every 20–60 min using an in-line automated heated sampling valve and analyzed by a Hewlett–Packard 5730A gas chromatograph that was coupled with a Hewlett–Packard Model 3388A integrator/controller. Reaction products were separated on Porapak Q columns and were identified by comparison of their retention times with those of known standards and also from their mass spectroscopic (MS) fragmentation patterns, as determined with a Finnegan 4021 GC/MS/Nova system. Coupled with the above on-line GC analyses was a more extensive analysis of the higher-molecular-weight liquid product that was collected in liquid nitrogen-cooled traps. This analysis was carried out with a film-type SPB-1 wide-bore Supelco 60-m × 0.75-mm i.d. capillary column (1.0-μm film thickness) contained in a Hewlett–Packard Model 5890 gas chromatograph. Reported thermal response factors (*16*) were utilized to correct for the different thermal conductivities of the reaction products except for hydrogen which was excluded from the compositional analyses.

Catalyst characterization. The catalysts were removed from the reactor under nitrogen and were routinely examined for surface area by gas adsorption (*17*) and for phase composition and crystallite size by X-ray powder diffraction under nitrogen in airtight cells (*18*). Surface areas were obtained by the BET method using argon (0.168 nm^2/Ar atom). For these determinations, samples were charged under N_2 into the Pyrex analysis bulbs, evacuated overnight, and subsequently heated under a dynamic vacuum of 10^{-5} Torr for 1 hr at 383 K prior to argon gas adsorption measurements at 77 K.

RESULTS

Using the experimental conditions employed with the Cs-promoted Cu/ZnO catalysts described in the previous paper (583 K, 7.6 MPa, H_2/CO = 0.45, flow rate = 8.0 liters/hr), the $Cs/Cu/ZnO/M_2O_3$ catalysts were tested for higher alcohol synthesis activity. In the case of the $Cs/Cu/ZnO/M_2O_3$ catalysts, 1.5-g samples were tested because of the lower bulk density of the Al_2O_3- and Cr_2O_3-supported catalysts rather than the 2.45-g portion previously used for the Cs/Cu/ZnO catalysts. This resulted in a higher effective GHSV over the Cs-promoted $Cu/ZnO/M_2O_3$ catalysts [5330 liters (STP)/kg cat/hr] than over the Cs-doped Cu/ZnO catalysts [3265 liters (STP)/kg cat/hr].

The initial selectivities toward particular groups of products and the percentages conversion of CO to all products over the $Cu/ZnO/Cr_2O_3$ catalysts doped with various levels of cesium are shown in Table 1. The corresponding product yields are given in Table 2. The following observations were made:

TABLE 1

Short-Term Testing Product Selectivities[a] for Cesium Formate-Promoted Cu/ZnO/Cr_2O_3 Catalysts Tested under Higher Alcohol Synthesis Conditions [583 K, 7.6 MPa, H_2/CO = 0.45, GHSV = 5330 Liters (STP)/kg cat/hr]

Catalyst	CO conversion (mol%)		CO_2-free selectivity (carbon atom%)				
	Total	CO_2-free	Alcohols	Alcohols + methyl esters	C_2^+ alcohols	Hydrocarbons	Dimethyl ether
Undoped Cu/Zn/Cr (28 hr)	20.10	13.77	76.11	81.89	22.69	9.36	5.26
0.8 mol% Cs/Cu/Zn/Cr (24 hr)	21.20	13.68	78.46	84.35	29.81	13.65	2.00
3.0 mol% Cs/Cu/Zn/Cr (20 hr)	21.96	14.47	79.44	86.59	36.72	10.58	—
5.0 mol% Cs/Cu/Zn/Cr (22 hr)	16.88	11.94	84.28	92.29	30.01	6.96	—

[a] The major products not included in these selectivities were the aldehydes, which constituted as much as 3.49 carbon atom% (over the undoped Cu/Zn/Cr catalyst) of the product mixture observed over these catalysts.

1. Doping of the ternary Cr_2O_3-containing catalyst with cesium increased the selectivity for higher alcohols, and the maximum selectivity was produced by Cs doping of approximately 3.0 mol%.

2. Alcohols most affected by cesium doping were 1-propanol, 2-methyl-1-propanol, and 2-methyl-1-butanol, while the yields of ethanol and 1-butanol were relatively unaffected by Cs doping, as was observed for the Cs-promoted binary Cu/ZnO catalyst.

3. Unlike the Cs/Cu/ZnO system, dimethyl ether was observed in the reaction

TABLE 2

Product Yields over Cesium Formate-Promoted Cu/Zn/Cr = 30/45/25 mol% Catalysts under Higher Alcohol Synthesis Conditions of 583 K and 7.6 MPa with H_2/CO = 0.45 Synthesis Gas at GHSV = 5330 Liters (STP)/kg cat/hr

Catalyst	Product yield (g/kg cat/hr)											
	CO_2	Water	Alkanes[a]	Dimethyl ether	Methanol	Ethanol	1-Propanol	2-Methyl-1-propanol	1-Butanol	2-Methyl-1-butanol	Methyl acetate	Others[b]
Undoped Cu/Zn/Cr	456	6.1	22.1	18.6	263	24.5	24.5	20.1	7.4	—	8.0	38.1
0.8 mol% Cs/Cu/Zn/Cr	532	6.8	27.5	6.0	202	23.9	20.5	25.2	7.5	0.7	5.6	19.7
3.0 mol% Cs/Cu/Zn/Cr	538	10.2	25.0	—	206	25.4	34.8	30.6	6.5	5.8	6.3	53.6
5.0 mol% Cs/Cu/Zn/Cr	360	5.4	15.1	—	239	22.7	36.1	19.2	5.5	—	5.8	35.4

[a] Alkanes = methane, ethane, and propane.

[b] Others = methyl esters, aldehydes, ketones, C_4^+ linear primary and secondary alcohols, C_4^+ branched primary and secondary alcohols, and methyl formate.

TABLE 3

Product Selectivities for Cesium Formate-Promoted $Cu/ZnO/Al_2O_3$ Catalysts Obtained after Testing for 24 hr under Higher Alcohol Synthesis Conditions [583 K, 7.6 MPa, H_2/CO = 0.45, GHSV = 5330 Liters (STP)/kg cat/hr]

Catalyst	CO conversion (mol%)		CO_2-free selectivity (carbon atom%)				
	Total	CO_2-free	Alcohols	Alcohols + methyl esters	C_2^+ alcohols	Hydrocarbons	Dimethyl ether
0.30 mol% Cs/Cu/Zn/Al[a]	14.12	11.48	90.44	93.50	10.46	6.50	trace
0.73 mol% Cs/Cu/Zn/Al[b]	13.79	11.57	91.11	94.12	5.96	5.55	0.33
2.5 mol% Cs/Cu/Zn/Al[c]	12.48	10.72	91.16	94.30	8.85	5.70	trace

[a] Obtained after testing for 114 hr under methanol synthesis conditions [523 K, 7.6 MPa, H_2/CO = 2.33, and GHSV = 10,000 liters (STP)/kg cat/hr].

[b] Obtained after testing for 141 hr under methanol synthesis conditons.

[c] Obtained after testing for 126 hr under methanol synthesis conditions.

product over the $Cs/Cu/ZnO/Cr_2O_3$ catalyst, and its yield decreased rapidly with increasing cesium loading of the catalyst.

4. Much higher levels of cesium doping were needed for maximum yields of higher alcohols on the $Cu/ZnO/Cr_2O_3$ catalyst than on the Cu/ZnO catalyst.

5. The overall yield of alcohols over the optimally promoted 3.0 mol% $Cs/Cu/ZnO/Cr_2O_3$ catalyst was nearly 310 g/kg cat/hr, which was appreciably higher than that observed over the 0.43 mol% Cs/Cu/ZnO catalysts [see Table 1 in the preceding paper (*5*)].

The surface areas of the tested Cr_2O_3-containing catalysts were in the range 80–86 m^2/g, and the surface areas of the previously tested (*3*) Cs/Cu/ZnO catalysts, 32–38 m^2/g.

Under the same experimental conditions, the $Cs/Cu/ZnO/Al_2O_3$ catalysts gave much higher total alcohol selectivities, as shown in Table 3, but lower levels of CO conversion. The enhanced CO_2-free carbon atom percent selectivity toward total alcohols was mainly a reflection of the higher methanol synthesis activity of the $Cs/Cu/ZnO/Al_2O_3$ catalysts, as demonstrated by a comparison of Table 4 with Table 2. It is also evident from this comparison that lower yields of the C_2^+ alcohols and alkanes were produced over the latter catalysts. Comparisons of the product yields and selectivities over the $Cs/Cu/ZnO/Al_2O_3$ catalyst with those over the $Cs/Cu/ZnO/Cr_2O_3$ catalysts

TABLE 4

Product Yields over Cesium Formate-Promoted Cu/Zn/Al = 30/45/25 mol% Catalysts after 24 hr under Higher Alcohol Synthesis Conditions of 583 K and 7.6 MPa with H_2/CO = 0.45 Synthesis Gas at GHVS = 5330 Liters (STP)/kg cat/hr

Catalyst	Product yield (g/kg cat/hr)									
	CO_2	Water	Alkanes[a]	Dimethyl ether	Methanol	Methyl formate	Ethanol	1-Propanol	2-Methyl-1-propanl	Methyl acetate
0.30 mol% Cs/Cu/Zn/Al	170.56	1.40	15.42	trace	383.92	6.74	17.58	6.84	8.55	5.76
0.73 mol% Cs/Cu/Zn/Al	154.87	2.32	14.03	1.22	436.05	9.46	13.87	3.12	3.58	4.09
2.5 mol% Cs/Cu/Zn/Al	118.83	1.49	13.94	trace	404.97	10.40	12.63	6.11	9.37	3.36

[a] Alkanes = methane and ethane.

clearly shows that replacing Cr with Al resulted in a poorer higher alcohol synthesis catalyst. The physicochemical reasons for the difference between the Al- and Cr-containing catalysts are associated with reconstitution of the hydroxycarbonate precursor upon doping of the $Cu/ZnO/Al_2O_3$ catalyst with cesium, and the results and conclusions will be presented elsewhere (*19*). The Cs-doped $Cu/ZnO/Cr_2O_3$ catalyst, on the other hand, gave rise to a product very similar to that of the Cs/Cu/ZnO catalyst, and in fact identical product distributions were obtained for these two catalysts with the appropriate choice of reaction conditions.

DISCUSSION

Comparisons of the Cs-promoted Cu/ZnO catalysts with the unpromoted Cu/ZnO catalyst [Table 1 in the preceding paper (*5*)] and of the $Cs/Cu/ZnO/Cr_2O_3$ catalysts with the unpromoted $Cu/ZnO/Cr_2O_3$ catalyst (Table 2) demonstrate that Cs is a promoter of the higher alcohol synthesis reaction over these catalysts. With the Al_2O_3-containing catalyst, however, the presence of Cs principally promoted methanol synthesis, which resulted in a higher C_1–C_4 alcohol yield but lower C_2^+ alcohol yield than the Cr_2O_3-supported catalyst and the Cs/Cu/ZnO catalyst. Using the data for the optimized catalysts, i.e., 0.4 mol% Cs/Cu/ZnO, 2.5 mol% $Cs/Cu/ZnO/Al_2O_3$, and 3.0 mol% $Cs/Cu/ZnO/Cr_2O_3$, this can be expressed by the following trends:

- C_1^+ alcohol rate: $Cs/Cu/ZnO/Al_2O_3 > Cs/Cu/ZnO/Cr_2O_3 > Cs/Cu/ZnO$.
- C_2^+ OH Selectivity: $Cs/Cu/ZnO \approx Cs/Cu/ZnO/Cr_2O_3 \gg Cs/Cu/ZnO/Al_2O_3$.

In regard to the formation of alkanes (HC) over these catalysts, the following order of selectivities (CO_2-free carbon atom percent) was observed:

- HC selectivity: $Cs/Cu/ZnO/Cr_2O_3 > Cs/Cu/ZnO > Cs/Cu/ZnO/Al_2O_3$,

where the CO_2-free and H_2O-free alkane selectivity over the $Cs/Cu/ZnO/Cr_2O_3$ catalyst corresponds to 6.3 wt%, that over the Cs/Cu/ZnO catalyst to 4.5 wt%, and that over the $Cs/Cu/ZnO/Al_2O_3$ catalyst to 3.0 wt%.

From the results presented in Tables 1 and 2, it is evident that doping the $Cu/ZnO/Cr_2O_3$ catalyst with cesium caused the rate of CO conversion to products and the selectivity to C_2^+ oxygenates to go through a maximum as a function of cesium concentration. A similar maximum was observed with the Cs-promoted binary Cu/ZnO catalysts, although at a lower cesium concentration (*5*). The maximum for the latter catalyst was attributed (*5*) to the bifunctional nature of these copper-based catalysts (*20, 21*). One function is the hydrogenation function of the Cu/ZnO portion of the catalyst and the second function is the basic site provided by the cesium ion and its counterion that executes various C–C and C–O bond-forming reactions. At high cesium loadings, the alcohol synthesis process is inhibited because the cesium blocks the hydrogenation sites on the catalyst surface. For both the $Cu/ZnO/Cr_2O_3$ and Cu/ZnO catalysts, cesium also suppressed the production of hydrocarbons [Table 2 in the present work and Table 1 in Ref. (*5*), respectively]. With the Cr_2O_3-containing catalyst, doping with cesium had the added advantage of increasing the catalyst stability and suppressing the synthesis of dimethyl ether, the formation of which had been recognized as a drawback to the use of chromia-based methanol synthesis catalysts (*22*). The synthesis of dimethyl ether over the undoped $Cu/ZnO/Cr_2O_3$ catalyst was undoubtedly due to the acidic nature of the chromia component that was effectively neutralized by the cesium doping. This explains the higher concentrations of the ce-

TABLE 5

Crystallite Sizes in Particular Crystallographic Directions Determined by X-ray Diffraction Line Broadening for the Hydrotalcite-like Precursors as Originally Formed and as Reconstituted during Aqueous Cesium Doping

Crystal direction	Crystallite size (nm)					
	Cu/Zn/Cr		Cu/Zn/Al		Cu/Zn/Ga	
	Original	Cs-doped	Original	Cs-doped	Original	Cs-doped
[003]	5.6	[a]	13.5	29.1	38.3	48.5
[015]	[b]	[a]	15.3	23.0	18.1	19.7
[110]	[b]	[a]	20.0	28.8	16.6	19.5

[a] Only very broad, weak peaks were observed.
[b] Very broad peak, crystallite size <5 nm.

sium promoter that were needed with the ternary $Cu/ZnO/Cr_2O_3$ catalyst to achieve optimum activity as compared with the binary Cu/ZnO catalyst.

The overall activity of the $Cu/ZnO/Al_2O_3$ catalyst for higher alcohol synthesis was found to be very low at 583 K, but a maximum in selectivity to alcohols and to oxygenates was observed with a doping level of approximately 2.5 mol% Cs. Doping this alumina-based Cu/ZnO catalyst with cesium tended to result in the re-formation of the original hydroxycarbonate precursor from the oxide, which correlated with the lower C_2^+ alcohol selectivity observed for these catalysts relative to the Cs/Cu/ZnO and $Cs/Cu/ZnO/Cr_2O_3$ catalysts that did not undergo this precursor reconstitution. This re-formation process resulted in an increase in the crystallite sizes of the Cs/Cu/Zn/Al catalyst precursor. It appears that much of the cesium is buried during this reconstitution and subsequent recalcination process, resulting in catalysts that are good methanol synthesis catalysts but poor higher alcohol synthesis catalysts because of the lack of high dispersion of C–C bond-forming centers. Although a wider scatter in the experimental results was obtained with the Al_2O_3-containing catalyst, perhaps because of the uncontrolled crystallite growth and burying of the cesium, the trends in decreasing yields of ethanol and methyl acetate with increasing Cs concentration were the same as those observed with the Cs/Cu/ZnO catalyst system (*5*).

Re-formation of the hydroxycarbonate precursor was also observed during preparation of the $Cs/Cu/ZnO/Ga_2O_3$ catalysts, and therefore those catalysts were not examined for higher alcohol synthesis activity, although they were tested under methanol synthesis conditions and observed to be poorer methanol synthesis catalysts than the unpromoted and Cs-promoted $Cu/ZnO/Cr_2O_3$ catalysts (*19*). Among the supported catalysts, only the Cr_2O_3-containing catalyst did not undergo precursor reconstitution and crystallite growth, as shown in Table 5, and was dopable on the surface by cesium. A stabilizing factor with the chromia catalyst might be the formation of a prespinel phase during the initial calcination at 623 K, which at higher temperatures would yield $CuCr_2O_4$ and $ZnCr_2O_4$. It has been demonstrated that a spinel-like phase was formed upon calcination of binary Zn–Cr coprecipitated precursors at 653 K (*23*).

CONCLUSIONS

Preparation of Cs-promoted $Cu/ZnO/Al_2O_3$ catalysts via a hydrotalcite-type precursor using the procedures employed here does not result in a good higher alcohol synthesis catalyst. However, this procedure can be used to prepare active and selective

$Cs/Cu/ZnO/Cr_2O_3$ catalysts that are not reconstituted into a precursor state during the Cs surface doping process. While the Cs dopant promotes C_2^+ alcohol formation and inhibits dimethyl ether synthesis over the $Cu/ZnO/Cr_2O_3$ catalyst, the production of hydrocarbons is higher over this catalyst than over the Cs/Cu/ZnO catalyst. Since the product distributions and trends in product yields as a function of cesium concentration are similar for the three catalysts, it is proposed that the higher alcohols are mechanistically formed in the same way over the Cs/Cu/ZnO and $Cs/Cu/ZnO/Cr_2O_3$ catalysts; i.e., the $C_1 \rightarrow C_2$ step proceeds via coupling of aldehydic-type species and the $C_2 \rightarrow C_2$ and $C_3 \rightarrow C_4$ steps occur predominantly by β addition.

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REFERENCES

1. Nunan, J., Klier, K., Young, C. W., Himelfarb, P. B., and Herman, R. G., *J. Chem. Soc. Chem. Commun.*, 193 (1986).
2. Bybell, D. G., Deutsch, P. P., Herman, R. G., Himelfarb, P. B., Nunan, J. G., Young, C. W., Bogdan, C. E., Simmons, G. W., and Klier, K., *Preprint Div. Pet. Chem. ACS* **31**(1), 282 (1986).
3. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C. W., and Herman, R. G., *J. Catal.* **113,** 410 (1988).
4. Klier, K., Young, C. W., and Nunan, J. G., *Ind. Eng. Chem. Fundam.* **25,** 36 (1986).
5. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C. W., and Herman, R. G., *J. Catal.* **116,** 195 (1989).
6. Fattore, V., Notari, B., Paggini, A., D'Adda, S., and Vincenzo, L., U.S. Patent 4,513,100 (April 23, 1985); assigned to Snamprogetti S.p.A.
7. Paggini, A., and Sanfilippo, D., *in* "Proceedings, AIChE National Meeting, New Orleans, LA, April 6–10, 1986.
8. Himelfarb, P. B., Simmons, G. W., Klier, K., and Herman, R. G., *J. Catal.* **93,** 442 (1985).
9. Herman, R. G., Simmons, G. W., and Klier, K., *in* "Proceedings, 7th International Congress on Catalysis" (T. Seiyama and K. Tanabe, Eds.), p. 475. Elsevier, Amsterdam, 1981.
10. Ruggeri, O., Tredici, A., Trifiro, F., and Vaccari, A., *in* "8th Pan-American Symposium on Catalysis, Huelva, Spain, 1982"; and Trifiro, F., Vaccari, A., Del Piero, G., Fattore, V., and Notari, B., *in* "Proceedings, 5th International Symposium on Heterogeneous Catalysis" (D. Shopov, A. Andreev, A. Palazov, and L. Petrov, Eds.), Vol. II, p. 303. Bulgarian Acad. Sci., Sofia, 1983.
11. Courty, P. and Marcilly, C., *in* "Preparation of Catalysts III" (G. Poncelet, P. Grange, and P. A. Jacobs, Eds.), p. 485. Elsevier, Amsterdam, 1983.
12. Busetto, C., Del Piero, G., Manara, G., Trifiro, F., and Vaccari, A., *J. Catal.* **85,** 260 (1984).
13. Reichle, W. T., Kang, S. Y., and Everhardt, D. S., *J. Catal.* **101,** 352 (1986).
14. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56,** 407 (1979).
15. Herman, R. G., *in* "Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals" (R. G. Herman, Ed.), p. 433. Plenum, New York, 1984.
16. Dietz, W. A., *J. Gas Chromatogr.* **5,** 68 (1967).
17. Herman, R. G., Pendleton, P., and Bulko, J. B., *in* "Advances in Materials Characterization" (D. R. Rossington, R. A. Condrate, and R. L. Snyder, Eds.), p. 109. Plenum, New York, 1983.
18. Bulko, J. B., Herman, R. G., Klier, K., and Simmons, G. W., *J. Phys. Chem.* **83,** 3118 (1979).
19. Nunan, J. G., Himelfarb, P. B., Herman, R. G., Klier, K., Bogdan, C. E., and Simmons, G. W., to be submitted.
20. Vedage, G. A., Pitchai, R., Herman, R. G., and Klier, K., *in* "Proceedings, 8th International Congress on Catalysis," Vol. II, p. 47, 1984.
21. Vedage, G. A., Himelfarb, P. B., Simmons, G. W., and Klier, K., *Amer. Chem. Soc. Symp. Ser.* **279,** 295 (1985).
22. Natta, G., Colombo, U., and Pasquon, T., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 5, Chap. 3. Reinhold, New York, 1957.
23. Del Piero, G., Trifiro, F., and Vaccari, A., *J. Chem. Soc. Chem. Commun.*, 656 (1984).