Characterization of Modified Fischer–Tropsch Catalysts Promoted with Alkaline Metals for Higher Alcohol Synthesis

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Received: 22 September 2011/Accepted: 1 January 2012/Published online: 14 January 2012 © Springer Science+Business Media, LLC 2012

Abstract Two series of Cu/Co/Cr modified Fischer– Tropsch catalyst promoted with Zn or Mn and an alkaline metal (Me: Li, Na, K, Rb, Cs) were prepared by co-precipitation method and tested for high alcohol synthesis (HAS) at one hour on-stream and at two temperatures, 300 and 350 °C. The results indicate that the best selectivity toward high alcohols depends on temperature and catalysts composition and is obtained as follows: a) at 300 °C over catalysts without Zn and containing K, Na and Rb; b) at 350 °C over catalysts without Zn and containing K; c) at 350 °C over catalysts containing Zn as well as Li and Cs.

Keywords Fisher–Tropsch modified catalysts · Hydrocarbon · Higher alcohol · Synthesis · Alkaline metals

1 Introduction

Fischer–Tropsch (F–T) hydrocarbon synthesis is an exothermic reaction over catalysts containing transition metals or their compounds consisting in adsorption of carbon monoxide (CO) on catalyst surface followed by its disproportionation in order to obtain an active form of carbon

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 Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México, D. F, México e-mail: salmon@unam.mx previous to its hydrogenation [1, 2]. The excess of oxygen is removes from the catalyst surface via CO_2 or H_2O [1–7]. This mechanism works well within a narrow temperature range, 500-700K, producing low-molecular-weight hydrocarbons and small amounts of high-molecular-weight hydrocarbons as well as oxygenates [3]. Production of higher molecular species by CO hydrogenation implicates a polymerization mechanism which is a chain growth reaction sequence of similar characteristics of F-T process. The polymerization products however, are unstable at the normal reaction temperature (> 500K), but they lasting at lower temperatures [3]. Promotion of F-T catalysts with alkali shows that the overall reaction rate and methane production dropped while the olefin-to-paraffin ratio and CO₂ production increased [8-10]. This implicates that alkali metal cations are acting as Lewis acid which is consistent with a mechanism called "reduced hydrogen mobility" [1].

Since hydrogenation of CO to hydrocarbon is thermodynamically more favorable than hydrogenation to alcohols, it is understandable that alcohol formation requires selective catalysts [11–14]. Therefore, a combination of the methanol synthesis catalysts (containing Cu) and the usual F–T catalysts containing transition metal oxides such as Co, Cr can theoretically work to produce high-molecularweight alcohols by CO hydrogenation [15]. Commercially, two categories of catalysts are available: modified methanol catalysts and, modified Fischer–Tropsch catalysts. Lower temperature Cu–Co based catalysts promoted with alkali and ZnO or MnO are more active and selective for HAS that Cu-free catalysts [16–23].

Most catalysts for methanol synthesis by hydrogenation of molecular CO contain Cu, Cu and Zn and the likely reaction mechanism consists in splitting of hydrogen molecules and activation of CO sigma bond followed by hydrogenation of CO molecule at the both ends [24]. High

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alcohols formation implicates a carbon chain growth mechanism referred to as oxygen retention reversal aldol condensation and centered on β -carbon addition [18, 24, 25]. Following this line of research, bimetallic Cu/Co alkalized catalysts have been developed by Institute Français du Petrole for higher alcohol synthesis. The product distribution is similar to that obtained over an F–T modified catalyst with ethanol as the main product [26–28]. Such improvement of the catalyst composition allows the adsorption of molecular CO on the Cu sites while cobalt main role is to suppress selectively the methanol production by modifying the electron environment of Cu. Additionally, promotion with MnO or ZnO contributed to improve the dispersion of Cu on catalyst surface, and also favored the production of C₂–C₄ olefins [29, 30].

As concerning alkalis, they are supposed to restrain alcohol dehydration and, therefore, favoring the formation of high oxygenates compounds [1]. However, the promotional effect of alkali on the catalytic activity it was found being uneven for alcohol synthesis. Depending on their amounts, Li and K can contribute to methanol production; Na may favor larger chain products; while Cs may reduce the total catalytic activity [8, 20, 22].

The mechanism for higher alcohol synthesis (HAS) is a combination of various mechanistic reaction paths with three dominant reactions: a) linear growth; b) β -addition or branched-primary alcohols formation; and c) α -addition or methyl esters formation [31].

The molecular weight distribution of straight alcohols is expected to follows a Schulz–Flory (SF) distribution [32–34]. Such distribution is usual in polymer chemistry but also was applied for the Fischer–Tropsch synthesis products molecular weight distribution as Anderson–Schulz–Flory (ASF) model suggesting that C–C bonds formation follows an infinitely diminishing geometrical progression pattern. However, if a system shows a non-ASF molecular weight distribution it may represent more complicated kinetic mechanism.

The objective of the present paper is to evaluate the performance of two series of F–T modified catalyst promoted with alkali for higher alcohol synthesis following a CO hydrogenation reaction at two temperatures, 300 and 350 °C, at one hour on-stream and at a fixed composition of the feed H_2/CO of 1:1 molar ratio. The ten catalysts having the following composition: CuCoCrMe and CuCoCrZnMe (Me refers to alkaline metals: Li, Na, K, Cs and Rb) were tested for HAS. Other published papers reporting HA synthesis results used higher ratio. The optimal ratio of H_2 to CO cannot be determined theoretically but the selectivity towards alcohols is not affected if the ratio is 2 or 1, as the catalyst activity drops for ratios lower than the unit [33].

2 Experimental Section

2.1 Synthesis of Catalysts

The synthesis of Cu–Co–Cr oxides doped with Me was carried out by co-precipitation method. Metal nitrates (Cu^{II}, Co^{II}, Cr^{III}) (from Aldrich) were contacted with a 0.66 M solution of (Me₂)CO₃ in aqueous solution and under controlled temperature (23 °C) until a pH 9.0 was reached [35]. The gel obtained was divided in five portions, filtered and dried at 80 °C, and further washed several times with demineralized water.

Each portion of the gel precipitate was mixed vigorously with the 2% wt of alkaline metal chloride solution of the respective alkaline metal (i.e. Li, Na, K, Rb, and Cs). Each sample was dried, extruded in 1/8 inch cylinders and finally calcinated at 500 °C for 4 h in static air atmosphere. The samples were coded as CuCoCrMe where Me indicates the wt% alkaline metal. The series of catalysts CuCoCrZnMe was synthesized in the same way by using zinc chloride solution, respectively.

2.2 Characterization Techniques

The chemical composition was determined by Atomic Absorption Spectroscopy in a Perkin Elmer S-2380 apparatus and presented in Table 1 in wt%.

Table 1	Catalysts	composition,
in wt%		

Catalyst	CuO	CoO	Cr2O3	ZnO	MnO	Na2O	Li2O	K2O	Rb2O	Cs2O
CuCoCrNa	28.10	43.32	25.01	0.00	0.00	2.07	0.00	0.00	0.00	0.00
CuCoCrLi	36.10	41.06	20.05	0.00	0.00	0.00	2.11	0.00	0.00	0.00
CuCoCrK	33.40	43.01	20.12	0.00	0.00	0.00	0.00	2.56	0.00	0.00
CuCoCrRb	30.00	41.05	20.74	0.00	0.00	0.00	0.00	0.00	2.17	0.00
CuCoCrCs	36.20	41.06	20.65	0.00	0.00	0.00	0.00	0.00	0.00	2.04
CuCoCrZnNa	25.91	24.82	12.82	32.31	0.00	3.80	0.00	0.00	0.00	0.00
CuCoCrZnLi	26.14	24.93	13.02	31.55	0.00	0.00	3.31	0.00	0.00	0.00
CuCoCrZnK	26.08	25.01	13.03	30.56	0.00	0.00	0.00	3.29	0.00	0.00
CuCoCrZnRb	26.12	24.05	13.05	32.62	0.00	0.00	0.00	0.00	3.12	0.00
CuCoCrZnCs	25.89	25.15	12.87	30.03	0.00	0.00	0.00	0.00	0.00	3.61

Specific surface area measurements were carried out in a Micromeritics Digisorb 2600 apparatus according to the method described in ASTM-D-3663. Textural properties are presented in Table 2.

2.3 Catalytic Activity

A stainless-steel fixed bed microreactor with 7 mm diameter and 15 cm length was used for testing the catalytic activity. The reactor temperature was monitored by two Chromel–Alumel thermocouples positioned at the center of the reactor and; the flow rate was monitored using a gas digital mass flowmeter. Previously to the test, a small amount of each catalyst (i.e. 0.2 g) was preheated at 500 °C. Helium (He) gas was used as carrier gas, at a flow rate of 30 mL/min. Analysis of the gas phase was carried out with a Hewlett-Packard 5890 GC, fitted with FID and

Table 2 Textural properties of catalyst

Catalyst	Specific area, m ² /g	Pore vol., cm ³ /g	Pore diam., Å
CuCoCrLi	60.71	0.41	270
CuCoCrNa	12.32	0.09	292
CuCoCrK	77.56	0.34	176
CuCoCrRb	96.83	0.39	232
CuCoCrCs	116.24	0.49	169
CuCoCrZnLi	102.4	0.467	210
CuCoCrZnNa	76.69	0.412	215
CuCoCrZnK	105.22	0.501	191
CuCoCrZnRb	136.42	0.578	187
CuCoCrZnCs	147.29	0.642	175

Table 3 Conversion and selectivity at 60 min on stream

an integrator (model HP-3392), and following a dynamic on-line sampling procedure. Products separation was achieved by using a 5 m \times 1/8 inch Poropak-Q column.

The operational parameters are summarized as follows: 0.2 g weight of catalyst; He (30 mL/min) as gas carrier and flow; pretreatment temperature was 400 °C; the reaction was carried out at two reaction temperatures: 300 and 350 °C; H₂/CO ratio was maintained constant at 1 mol/ mol; total pressure was 40 kg/cm²; GHSV was 7377 h⁻¹; and the stabilization time was at 60 min. Conversions and alcohols selectivity are presented in Table 3 and Table 4, respectively.

2.4 Statistic evaluation of data

Understanding the role of the catalyst composition on textural properties and their effect on reaction products at two temperatures entails a rather complicated task. A shortcut is proposed in order to find the obvious relationships between variables and measure it. Correlation is one of the most common and most useful statistic methods that give as a result a single number, a product-moment coefficient of correlation or Pearson's correlation coefficient, which describes the degree of linearity between two variables. This correlation coefficient, r, indicates the covariance degree between to two variables, x_i and x_j , linearly related and calculated as follows:

$$r_{ij} = \sigma_{ij} / \sqrt{\sigma_{ii} \sigma_{jj}} \tag{1}$$

where $\sigma_{ii} = E[(x_i - \mu_i)^2]$ and $\sigma_{jj} = E[(x_j - \mu_j)^2]$, are the matrix of standard deviation of x_i and x_j variables; $\sigma_{ij} = E[(x_i - \mu_i)(x_j - \mu_j)]$ is the matrix of covariance. The calculated values fall within the interval:

Catalyst Cor 300	Conversion at 300 °C, 60 min	Selectivit 60 min o	Selectivity at 300 °C, 60 min on stream, % mol		Alcohols to hydrocarbon	Conversion at 350 °C, 60 min	Selectivity at 350 °C, 60 min on stream, % mol			Alcohols to hydrocarbon
	on stream, % mol	Hydroc.	CO_2	Alcohols	ratio	on stream, % mol	Hydroc.	CO_2	Alcohols	ratio
CuCoCrLi	21.27	29.05	47.01	23.94	0.82	68.71	47.96	42.21	9.83	0.20
CuCoCrNa	6.76	33.44	29.59	36.96	1.11	47.467	21.02	66.36	12.62	0.60
CuCoCrK	7.49	13.28	73.41	13.31	1.00	56.192	21.71	67.63	10.66	0.49
CuCoCrRb	8.31	21.41	60.15	18.43	0.86	28.46	19.24	63.25	17.52	0.91
CuCoCrCs	42.08	23.86	64.16	11.99	0.50	60.358	24.65	62.96	12.39	0.50
CuCoCrZnLi	17.25	41.63	43.47	14.90	0.36	61.66	39.55	48.33	12.12	0.31
CuCoCrZnNa	13.29	30.04	65.46	4.51	0.15	56.929	17.20	57.97	24.83	1.44
CuCoCrZnK	25.48	55.65	39.25	5.10	0.09	57.962	19.79	67.46	12.75	0.64
CuCoCrZnRb	12.38	40.25	55.75	4.00	0.10	30.437	19.64	60.78	19.58	1.00
CuCoCrZnCs	23.61	25.50	57.17	17.33	0.68	63.062	25.31	61.05	13.64	0.54

Catalyst	Conversion at	Selectivity	at 300 °C				Conversion at	Selectivity :	at 350 °C			
	300 °C	C ₁ , Methanol	C ₂ , Ethanol	iC ₃ , i-Propanol	C ₃ , n-Propanol	C ₄ , Butanol	350 °C	C ₁ , Methanol	C ₂ , Ethanol	iC ₃ , i-Propanol	C ₃ , n-Propanol	C ₄ , Butanol
CuCoCrLi	21.27	71.32	21.32	0.00	4.07	3.29	68.71	61.68	19.23	13.46	3.02	2.61
CuCoCrNa	6.76	8.90	6.76	30.96	36.30	17.08	47.47	79.13	15.17	4.18	1.52	0.00
CuCoCrK	7.49	62.50	21.43	0.00	16.07	0.00	56.19	57.12	19.49	11.39	7.80	4.20
CuCoCrRb	8.31	40.99	30.63	8.11	13.06	7.21	28.46	44.04	35.50	13.96	6.50	0.00
CuCoCrCs	42.08	44.21	26.93	14.81	11.16	2.90	60.36	44.24	26.45	14.03	13.80	1.48
CuCoCrZnLi	17.25	84.49	6.46	2.74	4.14	2.18	61.66	0.00	40.61	7.42	35.37	16.59
CuCoCrZnNa	13.29	61.73	38.27	0.00	0.00	0.00	56.93	64.41	25.44	9.23	0.48	0.44
CuCoCrZnK	25.48	75.33	4.67	16.00	4.00	0.00	57.96	90.50	0.88	5.68	2.35	0.59
CuCoCrZnRb	12.38	35.29	59.80	4.90	0.00	0.00	30.44	36.74	33.95	18.60	6.51	4.19
CuCoCrZnCs	23.61	87.08	7.96	1.06	2.30	1.59	63.06	47.83	21.74	21.74	2.17	6.52

 $-1 \leq r_{ij} \leq +1 \tag{2}$

If r is close to zero, it means that the variables are not linearly correlated which doesn't implicate that the two variables are not correlated in a different way. If r is positive and close to +1, it means that both variable moves in the same direction (direct correlation). If r is negative and close to -1, it means that if one of the variable moves in one direction the other moves in opposite direction (inverse correlation) [36]. The correlation matrix between textural properties, alkaline metal molar composition and conversion at 300 and 350 °C as well as products selectivity is presented in Table 5.

3 Results and Discussion

3.1 Textural Properties

Relationship between composition and textural properties was explored in the first place and textural properties were plotted as a function of the alkaline metal molecular weight, following the order: Li, Na, K, Rb and Cs.

From Table 2, it is evident that the highest mean surface area value corresponds to CuCoCrZnMe catalysts set, 113.6 m²/g. Table 2 indicates that the calculated mean pore diameters for the catalysts series CuCoCrMe and CuCoCrZnMe are 228 Å and 196 Å, respectively. This table shows that the highest surface area corresponds to catalysts promoted with Cs. On the other hand, catalysts promoted with Na exhibit the lowest surface area and porous volume (44.5 m²/g and 0.251 m³/g, respectively) but they exhibit the highest pore diameter.

3.2 Conversion and Selectivity Towards Alcohol, Hydrocarbon and CO₂

Table 3 shows the overall conversion data and selectivity towards alcohol, hydrocarbons and CO_2 at 300 and 350 °C for the two sets of catalysts. At 300 °C, the best conversion was obtained over CuCoCrCs catalyst, while at 350 °C corresponds to CuCoCrLi. As concerning the alcohol, Na contributes to the highest selectivity independently of the temperature, as the oxygenate-to-hydrocarbon ratios indicated in Table 3 show. At 300 °C selectivity towards hydrocarbon is high for CuCoCrZnK catalyst, while at 350 °C this corresponds to CuCoCrLi.

Selectivity towards CO_2 is high over CuCoCrK independently on temperature. This indicates that oxygen elimination occurs via CO_2 , and hydrocarbon synthesis prevails over alcohols production [1].

Variables	Textural propert	ies		Alkaline metal composition, % mol					
	Specific area	Pore vol.	Pore diam.	Li	Na	K	Rb	Cs	
Conversion at 300 °C	0.45	0.51	-0.44	0.05	-0.31	-0.01	-0.34	0.58	
Hydrocarbons	0.11	0.19	0.06	0.23	-0.01	0.25	0.05	-0.27	
CO_2	0.41	0.35	-0.62	-0.33	-0.03	0.03	0.15	0.23	
Alcohols	-0.67	-0.69	0.76	0.17	0.04	-0.33	-0.26	0.02	
Methanol	0.47	0.63	-0.43	0.46	-0.29	0.27	-0.41	0.29	
Ethanol	0.27	0.24	-0.19	-0.30	0.14	-0.31	0.75	-0.22	
i-Propanol	-0.46	-0.58	0.40	-0.31	0.15	0.06	-0.08	-0.09	
n-Propanol	-0.72	-0.87	0.53	-0.23	0.17	0.01	-0.18	-0.16	
Butanol	-0.69	-0.79	0.76	-0.08	0.25	-0.34	-0.05	-0.13	
Conversion at 350 °C	-0.08	0.11	-0.07	0.42	0.02	0.16	-0.89	0.33	
Hydrocarbons	-0.13	0.09	0.24	0.81	-0.26	-0.15	-0.52	0.07	
CO_2	-0.02	0.04	-0.35	-0.12	0.07	0.48	-0.86	0.45	
Alcohols	0.05	0.19	-0.14	-0.06	0.74	-0.14	-0.39	0.14	
Methanol	-0.45	-0.37	0.27	-0.59	0.34	0.49	-0.27	-0.12	
Ethanol	0.30	0.20	-0.09	0.38	-0.09	-0.68	0.49	-0.02	
i-Propanol	0.71	0.69	-0.46	-0.20	-0.41	-0.36	0.44	0.63	
n-Propanol	0.20	0.14	-0.20	0.73	-0.34	-0.16	-0.07	-0.08	
Butanol	0.32	0.33	-0.23	0.76	-0.34	-0.15	-0.12	0.10	

Table 5 Correlation matrix between the textural properties, alkaline metal in mol %, and conversion and selectivity of the outlet gas at 300 and 350 °C (Highly correlated variables are marked with bold numbers.)

3.3 Correlation Coefficient Analysis

In an attempt to separate the effect of textural properties and each of the alkali on the alcohol synthesis we analyze the correlation coefficients from Table 5. The linear correlations, either positive or negatives are highlighted. As it can see from this table, textural properties (specific area and pore volume) show important, linear and positive correlation toward methanol and negative correlation toward the following alcohols selectivity at 300 °C: i- and n-propanol, and butanol. On the other hand, pore diameter correlates positively with alcohols and butanol selectivity and negatively toward CO_2 selectivity.

However, at 350 °C only i-propanol selectivity shows a linear and positive dependence on specific area and pore volume. The rest of the correlations between textural properties and F-T products are either negative or insignificant.

Positive and strong correlation coefficients show, therefore, that there is an upward and linear dependence of branched alcohols production on the catalysts specific area and pore volume at 350 °C, while at 300 °C, such dependence is negative. The effect of pore diameter on selectivity only seems to be important at 300 °C.

As concerning alkaline metals, Li shows strong and positive correlations towards hydrocarbons, n-propanol and butanol selectivity at 350 °C, and strong and negative correlation coefficient toward methanol selectivity at the same temperature; Na correlate positively with alcohol selectivity at 350 °C; K shows a negative correlation toward ethanol selectivity at 350 °C; Rb shows strong and positive correlation towards ethanol selectivity at 300 °C and a negative correlation towards conversion and CO_2 selectivity at 350 °C; Cs shows strong and positive correlations toward i-propanol at 350 °C.

3.4 Molecular Weight Distribution (MWD)

The products of the F–T reaction chain growth following a sequence that should obey the Schulz–Flory (SF) model for MWD [32]. This model obtained experimentally for polymerization reactions was applied also to fit the hydrocarbon MWD produced by the F–T synthesis and it is known as ASF model [34]:

$$\ln(M_n/n) = n\ln p + \ln[(1-p)/p]$$
(3)

where M_n is the molar fraction of the chain with *n* carbons; *n* is the number of carbon of the linear chain; and *p* is the probability factor of the chain growth [34]. The dependence of MWD on the carbon numbers of the product, *n*, is expressed by a plot of $log (M_n/n)$ against *n* and should have the form of a straight line.

The ASF plots of MWD for alcohols and for the sum of products—alcohols and hydrocarbons at 300 and 350 °C and for the catalysts CuCoCrMe and CuCoCrZnMe series, respectively are shown in Figs. 1 and 2.

As Figs. 1 and 2 show that only few of the MWD plots follow a linear path. Among them are the alcohols and total products obtained over CuCoCrRb and the alcohols produced over CuCoCrZnNa at 350 °C. For most of the products, there is a large deviation from the normally expected ASF distribution manifested either as a small deviation or as breaks on the linear MWD plots. In this case, the break of the propagation line corresponds to C_2 for products obtained over all catalysts at 300 °C and is more evident for CuCoCrK. However, this break is less evident for the products obtained at 350 °C and over Cu-CoCrZnMe catalysts, which indicate the importance of synthesis temperature in the reaction propagation. Alcohols



(a) 3.00

Fig. 1 ASF distribution of (**a**) linear alcohols and (**b**) total product at 300 °C; ASF distribution of (**c**) linear alcohols and (**d**) total product at 350 °C for CuCoCrMe catalyst series

Fig. 2 ASF distribution of (**a**) linear alcohols and (**b**) total product at 300 °C; ASF distribution of (**c**) linear alcohols and (**d**) total product at 350 °C for CuCoCrZnMe catalyst series

obtained over CuCoCrNa follows an MWD incremental path related to the formation of C_4 alcohols at 300 °C while alcohols produced over CuCoCrZnK show a similar path but for C_3 alcohol formation.

Deviation from the expected ASF MWD indicates the presence of different mechanism, which implicates independent active centers or a high degree of dispersion of the catalyst particles on the catalysts surface allowing the simultaneous formation of alcohols and hydrocarbons independently of the carbon number of the chain [34].

The mechanism for HAS is a combination of various mechanistic reaction paths with three dominant reactions: a) linear growth, l_i ; b) β -addition or branched-primary alcohols formation, b_i ; and c) α -addition or methyl esters formation, c_i [31]. According to Smith [31], and based on the assumptions that the alcohol synthesis is an irreversible first order reaction, the concentration of alcohols with n carbons can be calculated as the ratio of concentration of the alcohols containing n and (n-1) carbons (as those synthesized first).

If only linear and branched alcohol chains are produced, a kinetic model for linear alcohol distribution can be expressed using linear growth parameter, *l*, and *b*, the β -addition parameter for branched alcohols [22]. The molar ratio calculated as C_n/C_{n-1} should be proportional to the linear growth rate constant of the linear chain as another way to indicate the direction of the chain growth propagation. The C_n to C_{n-1} ratio are indicated in Table 6 and implicate linear and branched alcohols.

Table 6 shows that none of the ratios calculated as C_n/C_{n-1} follow a linear propagation path. Most of these paths have a break in the propagation chain with the formation of C_3 alcohols independently of the temperature. Among them, CuCoCrZnK is one of the catalysts that, at 350 °C, contribute to C_3 alcohols formation from C_2 , the alcohol first synthesized. However, only CuCoCrNa and at

Table 6 Alcohols molecular weight ratios as C_n/C_{n-1}

300 °C follows an incremental path toward to the formation of C_4 alcohols from C_3 .

Copper-based catalysts used for alcohol synthesis from $H_2/CO/CO_2$ are bimetallic catalysts promoted with other metals such as Co, Cr or Zn as well as with alkaline metals [20, 37]. Promotion with Cr_2O_3 or ZnO demonstrates an improvement of the textural properties of the catalysts [30]. However, the catalyst activity seems to depend mostly of the synergy between components rather than on the textural properties. For example, dispersion of Cu particles is uneven on catalysts surface independently of its amount as the particles growth is irregular affecting the textural properties of the catalyst in a no linear way [33]. The role of ZnO, a part of its contribution to improve the textural properties of the F-T catalyst and the CuO dispersion, seems to favors the formation of larger and stable C-C saturated chains, which means a lower production of CO₂ but this effect only is evident at 300 °C (see Table 3).

Catalysts containing ZnO exhibit larger surface areas and porous volumes than the rest of the catalysts: 113.6 m^2g^{-1} and 0.52 m^3g^{-1} , respectively. ZnO is an *n*-type semiconductor oxide contains lattice oxygen vacancies which are helpful to stabilize the Cu⁺ sites activity and, therefore, to enhance the activity of the catalyst [8]. This oxide was also related to Cu metal particles dispersion and it is a good hydrogenation catalyst [30]. Moreover, independently of the presence of ZnO, when the catalyst contains Cs the textural properties are improved; the mean values of surface area and porous volume are 117.3 m^2g^{-1} and 0.56 m^3g^{-1} , respectively. Surface area depends linearly on amount of ZnO but only to a certain critical amount of ZnO [29]. However, Table 5 shows that at 300 °C, the contribution of surface area and pore volume is negative for almost all products but methanol. Nonetheless, at 350 °C there is a linear correlation between these properties and branched alcohol formation.

Catalysts	300 °C			350 °C		
	C2/C1	(C3 + iC3)/C2	C4/(C3 + iC3)	C2/C1	(C3 + iC3)/C2	C4/(C3 + iC3)
CuCoCrLi	0.76	9.95	0.25	0.19	0.38	0.00
CuCoCrNa	0.30	0.19	0.81	0.31	0.86	0.16
CuCoCrK	0.34	0.75	0.00	0.34	0.98	0.22
CuCoCrRb	0.75	0.69	0.34	0.81	0.58	0.00
CuCoCrCs	0.61	0.96	0.11	0.60	1.05	0.05
CuCoCrZnLi	0.62	0.00	0.00	0.40	0.38	0.05
CuCoCrZnNa	0.08	1.07	0.32		1.05	0.39
CuCoCrZnK	0.06	4.29	0.00	0.01	9.11	0.07
CuCoCrZnRb	1.69	0.08	0.00	0.92	0.74	0.17
CuCoCrZnCs	0.09	0.42	0.47	0.45	1.10	0.27

3.5 Alkalis Effect

The alkali dopants acts as structural promoters used to modify the surface properties and the mobility of lattice oxygen. Moreover, such promotion affects the catalysts acidity, and cause a synergism between transition metal oxide phases increasing the oxygenate production [23, 38]. Alkalis were reported as promoters of selectivity towards iso-alcohols by depressing hydrocarbon formation and their effectiveness follows an increasing order: Cs > Rb > K> Na > Li, [39]. Dantas de Aquino [20] indicates that Li is an ideal promoter for alcohol synthesis in the presence of Cu oxide, especially for methanol production. Our results indicate that indeed, independently of the basic catalyst composition, Li contributes to n-propanol and butanol selectivity at 350 °C but also to hydrocarbon production. The highest selectivity towards hydrocarbons corresponds to CuCoCrZnLi at 300 °C and to CuCoCrLi at 350 °C.

Sodium as promoter may contribute to the growth of saturated chain and also activate oxygen elimination via H_2O followed oxygenates products [1–7]. This is confirmed by the low yields of CO_2 and the high amounts of methanol obtained at 300 °C over CuCoCrNa and at 350 °C over CuCoCrZnNa. Additionally, CuCoCrNa at 300 °C and CuCoCrZnNa at 350 °C show the highest selectivity towards alcohols, although Table 6 shows that selectivity in each cases are toward different products, n- and i-propanol at 300 °C and, methane at 350 °C.

Rubidium as promoter follows the ASF linear pattern for alcohols production as Figs. 1 and 2 shown. However, its contribution to HA production depends on temperature and the presence or absence of Zn as follows: the high alcohols production occurs over CuCoCrRb at 300 °C and high selectivity of i-propanol for CuCoCrZnRb at 350 °C.

Cesium-promoted catalysts contribute to stabilize the intermediate products on the catalyst surface since the metal oxide cannot accomplish it by itself [25]. It was reported to be the best promoter for HAS at high-temperature and on ZnO/Cr₂O₃ catalysts [39]. Incorporation of Cs is considered as an important element to stabilize the formyl intermediate species required for methanol coupling reaction pathway over CuO/ZnO/Al2O3 catalysts at low temperature [25, 31, 38]. Our results indicate that Cs promoted catalysts contribute to the highest CO conversion independently of the temperature and composition of the catalysts, as shown in Table 3. Apparently the C-C bond forming step is not activated sequentially since high amounts of hydrocarbon (i.e. methane) and CO₂ prevail at both synthesis temperatures and mostly branched alcohols are formed. Correlation coefficients from Table 5 show such linear dependence between Cs mol % and i-propanol selectivity.

Thermodynamic and kinetic studies claim that CO/H_2 synthesis of alcohols depends on reaction temperature and that high pressure and low temperature conditions only increase methanol production while high alcohols production occurs more readily at higher temperature [23]. In the case of Cu/Co, the real active phase for alcohol synthesis at temperatures below 350 °C is the cobalt carbide phase formed on catalyst surface but at higher temperatures, decomposition of cobalt carbide occurs simultaneous with catalyst deactivation [40].

Our results indicate that both methanol and high alcohols production increases when the temperature rises from 300 to 350 °C and especially on catalysts containing Zn. CO₂ production over catalyst promoted with Na and Li is low independently of catalysts composition and temperatures as a clear indication that, on such catalysts, most of the oxygen elimination occurs via H₂O, a required step to its inclusion at the end of the hydrocarbon chains. Therefore, high CO₂ and hydrocarbon productions indicate the prevalence of F-T catalyst behavior because the removal of oxygen from the surface occurs trough CO₂ rather than through water or oxygenates molecules [1]. When alcohols are the final products of CO hydrogenation, a different mechanism occurs: oxygen retention on the catalyst surface is followed by its mobility and inclusion as OH terminal at the end of the hydrocarbon chain is required [41]. Thus, the mechanism for HAS is a combination of various mechanistic reaction paths with three dominant reactions: a) linear growth; b) β -addition or branched-primary alcohols formation; and c) α -addition or methyl esters formation [31].

As oxygenate product distribution deviates from the ASF distribution linear pattern, as Figs. 1 and 2 shown, this indicates the presence of different and independent active centers or a high degree of dispersion of the catalyst particles on the catalysts surface allowing the simultaneous formation of alcohols and hydrocarbons independently of the carbon number of the chain [34]. Moreover, branched alcohol as final product indicates the prevalence of an isomerization reaction pathway. Based on the assumptions that the alcohol synthesis is an irreversible first order reaction, the concentration of alcohols with n carbons can be calculated based on the concentration of the alcohols containing n-1 carbons which are synthesized first. When the reaction is a polymerization sequence following a linear or a branched growth pathway the rate constant calculated as the ratio of C_n, as product, vs C_{n-1} , as reactant, should be > 1. The results in Table 6 show however that only few reactions follows such path and that direct reaction of CO is the predominant pathway for ethanol synthesis [25]. The alcohols ratio values indicate that even though the mechanism of HAS is different for each catalytic systems [31], it is also different when the same system is operating at different temperatures.

4 Conclusions

An effective approach to the nature of relationships between catalyst composition, textural properties and conversion are essential for the design of adequate HAS catalysts. The following general aspects were found out:

Textural properties are improved with the presence of ZnO and Cs, but the evidence of a direct relationship between these properties and any increment on alcohols selectivity is low.

The highest butane selectivity at one hour on-stream was obtained at 300 °C over CuCoCrNa catalyst and at 350 °C over CuCoCrZnLi. Therefore, the impact of alkali promotion on alcohols synthesis is uneven. The probability of side reactions is always open since the ASF analysis indicates breaks on the linear pattern of alcohol chains growth.

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