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Synthesis of higher alcohols with cobalt and copper based model catalysts: effect of the alkaline metals

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Abstract

The synthesis of higher alcohols, obtained from CO hydrogenation over transition metals, is an alternative for the production of chemical commodities and less pollutant renewable fuels nowadays. In this work, the influence of different alkali metals (Li, Na, K, Cs) over the formation of active phases of supported catalysts, based on cobalt and copper, as well as the performance of these solids in the reaction of CO hydrogenation under a 50 bar pressure were studied. The solids were prepared by continuous coprecipitation of sodium carbonate with metal nitrate solutions (Al–Co, Al–Cu or Al–Co–Cu) promoted with the alkali metals with dry impregnation. Characterization studies by atomic absorption spectrophotometry, BET, XPS and also the results of catalytic tests show that physico-chemical properties of the obtained catalyst are similar to those of the industrial catalyst used as reference (I). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alcohol synthesis; Al–Co–Cu; Al–Co; Al–Cu catalyst; Alkaline cations

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1. Introduction

The use of oxygenated compounds as automobile fuel has been limited to methanol, ethanol, *t*-butyl methyl ether, *t*-butyl ethyl ether, and the mixtures of C_1–C_5 alcohols. Although the direct use of such substances minimizes critical problems like the environmental contamination caused by hydrocarbons or the contamination of the gasoline due to the presence of water, this application considering a global scenery is still restricted due to the necessity of modifications in the project of conventional carburettors and injection systems.

It is known that the presence of C_2–OH in the gasoline improves simultaneously the volatility of the mixture, the water tolerance, and the solubility of hydrocarbons.

In order to accomplish the synthesis of higher alcohols, the ‘Institut Français du Pétrole’ (IFP) developed a generation of solid Co/Cu-based catalysts promoted with metals (Al, Zn) and alkalines [1].

The present study on higher alcohol synthesis, through the reaction $CO + H_2$ with solid catalysts type IFP, has the objective of studying the specific effects of alkaline promoters (Li, Na, K, Cs) on both the morphology and the catalytic behavior of such systems. With this purpose, models of catalytic systems of type Al–Co, Al–Cu, and Al–Co–Cu were prepared and alkalinized with the same atomic content for each alkaline metal analyzed.

2. Experimental

2.1. Catalyst preparation

Moisturized precursors were prepared following the methods patented by IFP [1]. The methodology

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consists basically of continuous coprecipitation of solutions of nitrates of the respective metals under controlled conditions [2] using aqueous solution of sodium carbonate (precipitant agent).

The coprecipitate was flushed continually with water in order to eliminate the excess of Na introduced with the carbonate. The moisturized precursors were dried in an oven, ground, and classified. The oxide precursors were prepared through the calcination of the respective moisturized precursors at 450°C for 3 h under continuous airflow of 17 ml/min.

The alkalization was carried out through dry impregnation of the oxide precursors using aqueous solutions of each alkaline carbonate. The alkalinized solids were dried at 120°C and calcined at 350°C, following the same procedures applied in the calcination of the moisturized precursors.

2.2. *Characterization of catalysts*

The specific surface areas of the oxide precursors were evaluated by BET method and the measures of adsorption of N_2 were carried out at -196°C. The moisturized precursors and non-alkalinized oxides were analyzed through X-ray diffraction (XRD) in order to identify the present phases. The X-radiation was generated by Cu-anticathode (Kα radiation).

Both the chemical composition of the surface and the atomic relations were analyzed through electronic spectroscopy for chemical analysis (ESCA) using radiation Al Kα ($h\nu = 1486.6\,\mathrm{eV}$).

The reduction of oxide phases was studied through temperature programmed reduction (TPR) using ca. 30 mg of solids in a ‘U’-type quartz reactor under a continuous flow of 17 ml/min of 2% H_2–98% N_2 mixture and a heating rate of 10°C/min from room temperature to 900°C.

2.3. *Catalytic tests*

The catalytic test started with the activation of the oxide precursors (100 mg) in a fixed-bed reactor, cooling from 500°C to room temperature under the flow of helium. Subsequently, the reactor was heated up to the reaction temperature of 250°C at a heating rate of 2°C/min and 50 bar of He. The reagent mixture ($CO+2H_2$) under the same pressure was fed to the reactor. The total reaction time of 10 h and the frequency of 2 h within the chromatographic analyses were allowed.

3. Results and discussion

The chemical compositions of the oxide precursors and of the industrial solid Al–Co–Cu (I) resulting from atomic absorption spectrophotometric analysis are presented in Table 1.

The atomic relation $(\mathrm{Co} + \mathrm{Cu})/\mathrm{Al}$ remained constant, showing a value of 0.51 for all the oxide precursors prepared. In the same way, the atomic relation alkaline/$(\mathrm{Co}+\mathrm{Cu})$ was equal to 0.2 for all alkalinized precursors allowing to compare the specific effects of each alkaline on the phases Co and/or Cu, since the number of atoms is the same. Results for the surface areas of the oxide precursors are presented in Table 2.

A comparison of the non-alkalinized solids indicates that Co-based systems present higher surface areas than the Cu-based solids. Thus, an increment of Cu content leads to a reduction of the surface area to the precursor. The alkalization with Li, Na, and K does not affect significantly the surface area, whereas the

Table 1
Nominal chemical compositions of oxide precursors

Series	Notation	Mass of the metal in the precursor (%)			
		Al	Co	Cu	Alcalino
Al–Co	Al–Co	26	29	–	–
	Al–Co–Li	26	29	–	0.63
	Al–Co–Na	26	29	–	2.0
	Al–Co–K	26	29	–	3.4
	Al–Co–Cs	24	27	–	11
Al–Cu	Al–Cu	25	–	30	–
	Al–Cu–Li	26	–	31	0.63
	Al–Cu–Na	26	–	30	2.0
	Al–Cu–K	25	–	30	3.4
	Al–Cu–Cs	23	–	28	11
Al–Co–Cu	Al–Co–Cu (I)[a]	27	15	16	–
	Al–Co–Cu	28	15	14	–
	Al–Co–Cu–Li	27	15	16	0.63
	Al–Co–Cu–Na	27	15	16	2.0
	Al–Co–Cu–K	26	15	16	3.4
	Al–Co–Cu–Cs	24	13	14	11

[a] Al–Co–Cu (I) — reference.

Table 2
Specific surface areas of the oxide precursor

Series	Specific surface area				
	Non-alkalinized precursor	Alkaline Li	Alkaline Na	Alkaline K	Alkaline Cs
Al–Co	230	226	212	210	176
Al–Co–Cu (I)	210	–	–	–	–
Al–Co–Cu	183	200	198	189	147
Al–Cu	127	127	130	125	64

addition of Cs promotes accentuated reduction. Such an effect may be related to the clogging of micropores caused by cesium carbonate.

The atomic relations metal/Al obtained through ESCA were compared to the ones calculated from global composition of the oxide precursors — bulk composition — and the results are shown in Table 3.

Analyzing the prepared solid Al–Co–Cu and the industrial Al–Co–Cu (I) of the same composition, both the surface atomic relations Co/Al and Cu/Al of these precursors are similar. The surface ratio Co/Al is smaller than the global relation to the non-alkalinized Al–Co and Al–Co–Cu.

This effect can be explained by preferential localization of Co-based oxide phases inside the pores, where the access of ESCA analysis is reduced. The addition of alkaline tends to diminish the relation Co/Al in the surface, this effect being more pronounced in the Cs case, a fact that can be related to the covering of Co-phases caused by promoters.

It is also observed that the surface ratio Cu/Al is inferior to the global one for Al–Cu and Al–Co–Cu systems. Therefore, similar to the oxide Co-phases, the oxide Cu-phases would be preferentially located inside the pores of the catalyst, even so the addition of alkaline increases significantly the relation Cu/Al in the surface. Consequently, the alkalization reduces the ratio Co/Cu on the surface of the solids (ca. 40% of the global ratio), emphasizing the hypothesis of preferential covering of the Co-phases caused by promoters.

The relation promoter/Al on the surface is close to the global one, except for Na, whose surface ratio is twice as much the global value. These results guide to the consideration of a possible preferential covering of one of the oxide phases caused by sodium addition.

In Fig. 1a, the solid Al–Co presents thin and relatively defined X-ray diffraction peaks, indicating the presence of a crystalline structure. The indexation of the present peaks suggests the yield of hydrotalcite-type phase [$Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$], where the ion Mg^{2+} was substituted for Co^{2+}.

Due to the larger and less intense peaks observed in Fig. 1b for solids Al–Co–Cu and in Fig. 1c for Al–Cu, the identification of the phases in comparison to the

Table 3
Comparison of surface (S) and global (G) metal/Al atomic relations

Precursor	Metal/Al atomic relation									
	Co		Cu		Na		K		Cs	
	G	S	G	S	G	S	G	S	G	S
Al–Co	0.51	0.19	–	–	–	–	–	–	–	–
Al–Co–Cu (I)[a]	0.25	0.12	0.25	0.15	–	–	–	–	–	–
Al–Co–Cu	0.25	0.14	0.25	0.13	–	–	–	–	–	–
Al–Co–Cu–Na	0.25	0.11	0.25	0.25	0.09	0.20	–	–	–	–
Al–Co–Cu–K	0.25	0.11	0.25	0.23	–	–	0.09	0.11	–	–
Al–Co–Cu–Cs	0.25	0.07	0.25	0.22	–	–	–	–	0.09	0.11
Al–Cu	–	–	0.51	0.35	–	–	–	–	–	–

[a] I: industrial.

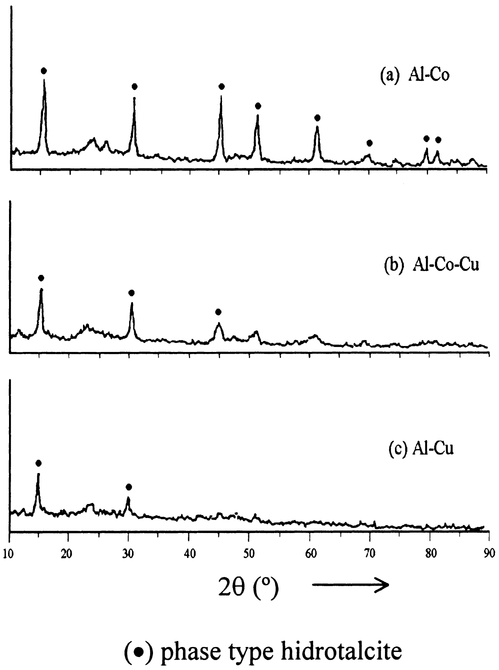


Fig. 1. XRD patterns of hydrated precursors.

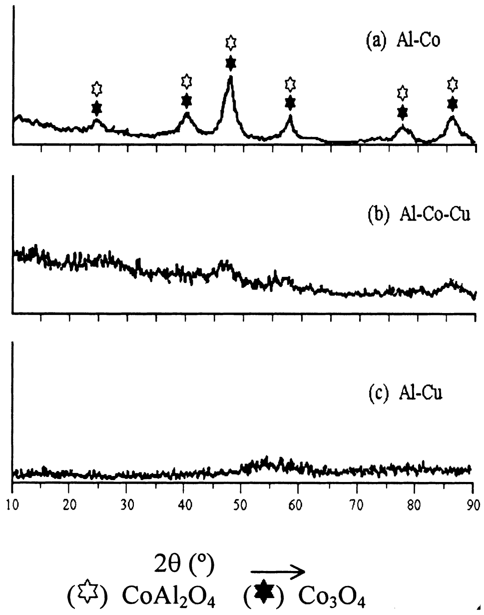


Fig. 2. XRD patterns of oxide precursors.

Al–Co solid is difficult. However, hydrotalcite-like structures seem to be present in such solids where the ion Mg^{2+} was substituted for Co^{2+} and/or Cu^{2+}. It can be inferred that the amorphous character in the hydrated precursors increases with higher Cu content. In the hydrated state, the precursor Al–Co (Fig. 2a) shows defined peaks after the calcination process (oxide-precursor). Indexing these peaks reveals the possibility of the existence of two oxide phase types for cobalt: Co_3O_4 and $CoAl_2O_4$. Analyzing Fig. 2b and c, referring to the oxide precursors Al–Co–Cu and Al–Cu, respectively, wide and non-intense peaks disable the identification of any present phases. Such results indicate high dispersion of oxide mixed phases, a fact that peculiarly regarding the solid Al–Co–Cu, could represent favorable conditions to yield bimetallic CoCu phases [3,4].

Alkalinized precursors were not displayed since the addition of alkalines did not present significant structural modification when compared to the diffractograms of non-alkalinized precursors.

In agreement with the results of XRD, the system Al–Co–Cu loses the crystallinity of hydrotalcite phase during the calcination.

Fig. 3 presents the TPR-profiles for oxide precursors in order to ease the observation of principal effects caused by alkaline addition on the reduction of the present oxide phases.

Series Al–Co (Fig. 3a and e): effect of alkalines on cobalt.

- Co_3O_4 and $CoAl_2O_4$ reducibility: Na $\approx$ K $>$ Li $\approx$ Cs.

Series Al–Cu (Fig. 3f and j): effect of alkalines on copper.

- CuO and $CuAl_2O_4$ reducibility: Li $\approx$ Na $\approx$ K $>$ Cs.

Series Al–Co–Cu (Fig. 3k and o): effect of alkalines on all present oxide phases.

- Mixed phase CuO and Co_3O_4 reducibility: Li $>$ Na $>$ K $>$ Cs.
- $CoAl_2O_4$ reducibility: Li $\approx$ Na $\approx$ K $\approx$ Cs.

The results of catalytic tests on hydrogenation of CO are presented in Tables 4–6 of product distribution representing the yield of alkenes, alkanes, and alcohols as a function of the number of carbon atoms

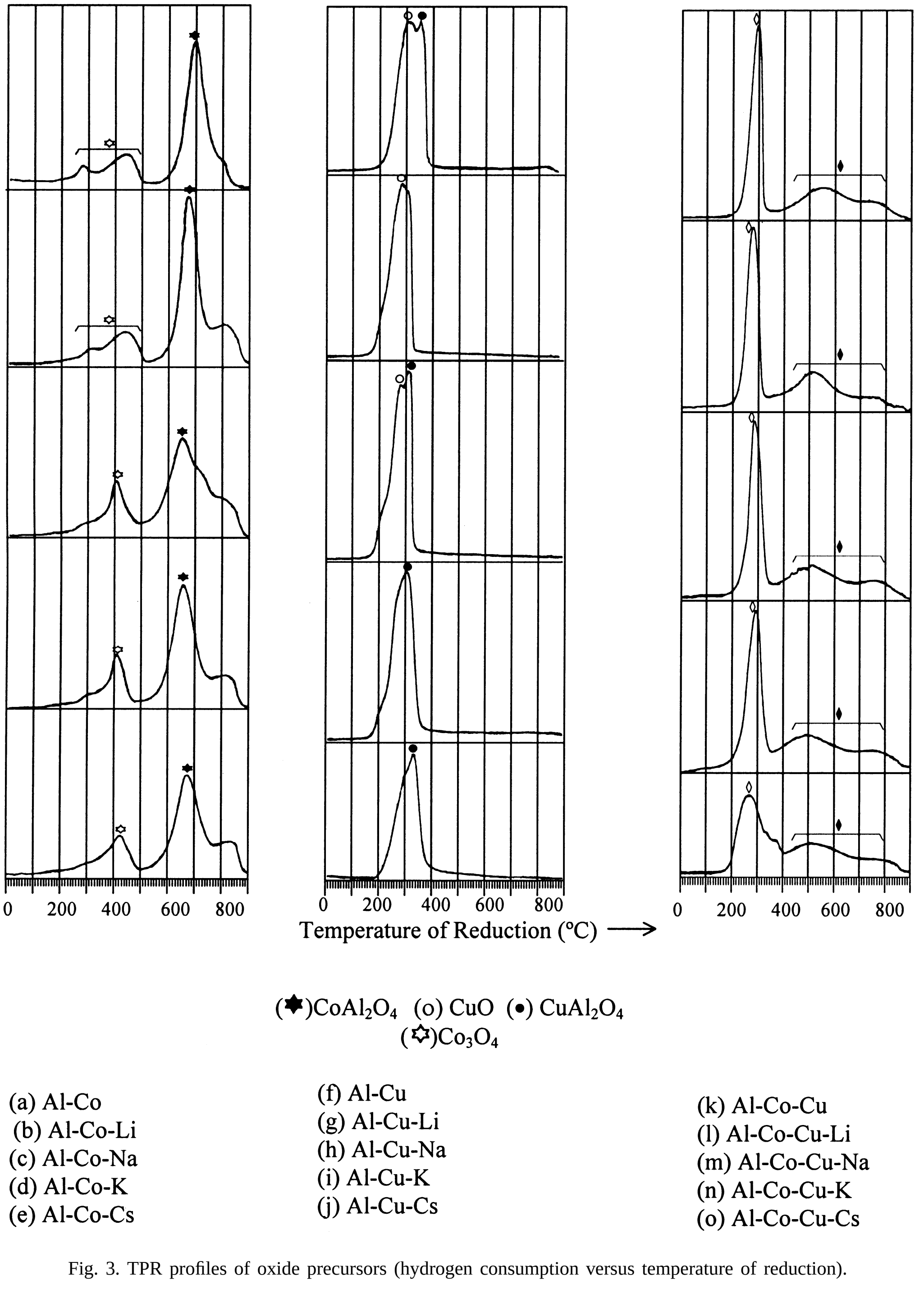


Fig. 3. TPR profiles of oxide precursors (hydrogen consumption versus temperature of reduction).

Table 4
Productivities of alkanes after 10 h reaction

Catalysts	Productivity $\times 10^4$ (g product/g catalyst h)				
	Methane	Ethane	Propane	Butane	Pentane
Al–Co–Cu (I)	1458.31	287.35	289.73	231.91	116.01
Al–Co–Cu	1324.04	275.62	252.14	223.49	203.24
Al–Co–Cu–Li	291.16	59.48	55.80	50.29	–
Al–Co–Cu–Na	126.62	14.85	14.50	13	–
Al–Co–Cu–K	63.71	5.75	5.68	4.11	–
Al–Co–Cu–Cs	81.93	7.01	8.09	6.51	4.01
Al–Co	4043.86	267.91	108.49	70.53	54.09
Al–Co–Li	5805.91	328.28	168.65	151.67	87.92
Al–Co–Cs	181.08	11.37	6.52	3.31	9.67
Al–Cu	13.34	–	–	–	–
Al–Cu–Li	12.69	–	–	–	–
Al–Cu–Cs	6.27	–	–	–	–

Table 5
Productivities of alcohols after 10 h reaction

Catalysts	Productivity $\times 10^4$ (g product/g catalyst h)				
	Methanol	Ethanol	Propanol	Butanol	Pentanol
Al–Co–Cu (I)	–	1283.34	395.53	–	–
Al–Co–Cu	464.03	1534.21	1298.89	561.8	299.41
Al–Co–Cu–Li	170.34	487.78	376.64	180.88	136.89
Al–Co–Cu–Na	132.34	115.89	100.96	–	–
Al–Co–Cu–K	44.49	14.55	–	–	–
Al–Co–Cu–Cs	43.50	–	–	–	–
Al–Co	–	–	–	–	–
Al–Co–Li	–	–	–	–	–
Al–Co–Cs	186.76	89.15	85.73	–	–
Al–Cu	2969.61	–	–	–	–
Al–Cu–Li	3553.37	9.88	–	–	–
Al–Cu–Cs	7380.18	62.56	–	–	–

Table 6
Productivities of alkenes after 10 h reaction

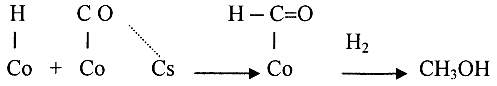
Catalysts	Productivity $\times 10^4$ (g product/g catalyst h)			
	Ethene	Propene	Butene	Pentene
Al–Co–Cu (I)	112.96	571.20	278.19	–
Al–Co–Cu	149.18	638.12	360.8	–
Al–Co–Cu–Li	50.22	180.57	109.06	79.99
Al–Co–Cu–Na	30.31	52.31	30.23	–
Al–Co–Cu–K	12.52	18.81	10.10	–
Al–Co–Cu–Cs	14.99	24.27	13.76	8.81
Al–Co	–	–	–	–
Al–Co–Li	19.74	119.76	84.52	46.96
Al–Co–Cs	16.52	14.01	5.52	22.55

in such compounds. For all tests carried out, the experimental conditions remained the same in order to favor the study of alkaline addition effects on catalytic properties of Al–Co, Al–Cu, and Al–Co–Cu systems.

Observing Table 4, the catalyst Al–Co leads to alkane production, substantially methane, suggesting that reactional paths of Fischer–Tropsch synthesis (chain growth) are secondary in relation to the methane yield reaction (surface carbon hydrogenation).

Comparing the product distribution for Al–Co system (Table 4) with the respective alkalinized catalysts, it may be inferred that the addition of lithium increases the methane yield. Such effect can be related to the appearance of secondary reactions like those of higher hydrocarbon hydrogenolysis. In the presence of Lewis acid the dissociation of CO is favored, therefore lithium can be an ideal promoter for CO dissociation, boosting the methane yield.

Cesium addition reduces drastically the total catalytic activity. The product distribution is very different from the one related to lithium addition disabling a reasonable comparison between the induced selectivity for these two alkalines (condition of isoconversion). The yield of alkenes, methanol, and higher alcohols in the presence of Cs suggests a possible carbonylation of CO (Tables 5 and 6). The yield of methanol can be a result of direct interaction of CO adsorbed on Co and Cs. A simplified scheme of electronic interaction in active sites Co–CO · · · Na was proposed by Cobo [5] and Sachtler [6].



The catalyst Al–Cu is selective for methanol yield (Table 5), evidencing the typical behavior of copper, a metal that either does not dissociate CO or dissociates in slight quantities. In this case, the small methane quantity yielded can be correlated to secondary reactions of methanol on Cu-metallic as exemplified:

$$CH_3OH + H_2 \rightarrow CH_4 + H_2O \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

$$CH_3OH + CO \rightarrow CH_4 + CO_2 \qquad (3)$$

Lithium addition on the catalyst Al–Cu results in augmentation of methanol yield and the cesium addition generates a considerable increment in the methanol production (Table 5).

Direct electronic interaction of alkaline and the CO molecule adsorbed on Cu could favor the hydrogenation of CO yielding methanol through a larger covering of the catalytic surface by CO.

Taking into account both alkalines used, Cs represents a less effective direct interaction easing hydrogenation of CO adsorbed due to its electronegative which is less intense than in the lithium atoms. However, the hypothesis of metal–alkaline electronic interaction cannot be set aside for these cases, since it can be influent on the strength of the metal–CO bond.

Since the goal of this study was to verify the influence of alkalines on the pair Co–Cu, only the systems Al–Co and Al–Cu alkalinized with Li and Cs were subjected to the reaction $CO + H_2$.

The catalysts of Al–Co–Cu series are presented in Tables 4–6 providing a base for comparison. It can be inferred that all catalysts of the series lead to simultaneous yield of alkanes, alkenes, and higher alcohols.

Solids Al–Co–Cu and Al–Co–Cu–Li are responsible for alkanes, alkenes, and higher alcohol production. The effect of Li is to promote selectivity for alcohol yield (methanol and C_2–OH) in detriment of hydrocarbon selectivity.

Although sodium addition if compared to the reference causes accentuated deactivation that is more pronounced for those compounds of larger chain, the relative selectivity for hydrocarbons and alcohols remains constant. It is also verified that an augmentation in the selectivity of CO_2 can be the resultant of the methanol reaction with CO (reaction (3)).

By adding K to the solid of reference, it is verified that a reduction in higher alcohol yield produces only methanol and ethanol (Table 5); it is also observed that there is a reduction in the hydrocarbon yield caused by accentuated deactivation of the catalyst in the beginning of the reaction. Potassium presents selectivity similar to the one of sodium, also generating high quantity of CO_2, a fact that can be explained by analogy to reaction (3), which also explains the methane yield.

Cesium addition reduces drastically the productivity of alkanes, alkenes, methanol, and higher alcohols, with similarity to the effects caused by potassium. The selectivity of CO_2 and hydrocarbons is increased, whereas the alcohol yield selectivity diminishes considerably.

Within the alkalines, Cs showed to be the worst alkaline additive for higher alcohol synthesis, however smaller addition of Cs can lead to satisfactory results. Cesium low efficiency is explained by the lack of direct interaction of this alkaline with CO, since Cs is a Lewis acid weaker than the others, presenting no tendency of attraction of the electron pair not linked to the oxygen atom.

4. Conclusion

Adding alkalines Li, Na, and K to the oxide precursors does not promote significant changes in the surface area and the addition of Cs leads to a significant reduction of this property.

The XRD spectra of hydrated precursors Al–Co, Al–Co and Al–Co–Cu demonstrate the existence of hydrotalcite-like phase, which by calcination at 723 K transforms into the phases Co_3O_4, $CoAl_2O_4$, CuO, $CuAl_2O_4$, and also a mixed phased CuO–Co_3O_4 for the precursor Al–Co–Cu.

TPR profiles evaluated show that the studied alkalines, particularly sodium, have promoting effects on the reduction of the oxide phases of Co and Cu.

Catalytic tests evidenced that the catalyst Al–Co–Cu–Li is more selective to higher alcohols and more stable along the reaction, whereas the catalyst Al–Co–Cu–Na is highly selective to higher alcohols only in the beginning of the reaction, showing high productivity.

Further Reading

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Acknowledgements

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