Co and La supported on Zn-Hydrotalcite-derived material as efficient catalyst for ethanol steam reforming

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Abstract

Four samples of Zn-hydrotalcite containing different amounts of Co (5, 10, 20, and 30 wt.%) have been synthesized and tested in the steam reforming of ethanol. The best results were obtained with the sample containing 20 wt.% of Co (20CoHT), with a complete conversion of ethanol and yields to hydrogen close to the equilibrium (73 mol.%). The physicochemical characterization of the samples by DRX, BET area and TPR indicates that the excellent performance exhibited by the sample containing 20 wt.% of Co is due to the higher percentage of reduced cobalt and lower crystallite size of metallic cobalt present in this sample (11 nm). Additional studies have been carried out to improve the stability of this catalytic material against deactivation by the incorporation of 1 wt.% of La. Stability studies were carried out using an industrial alcoholic waste as feed. Deactivation after 24 hours of reaction time was found lower for the catalyst containing La (20CoLaHT), confirming the positive effect of lanthanum on the catalytic stability. The results presented here show that it is possible to prepare a catalyst based on Co supported on Zn-hydrotalcite and promoted with La with improved ethanol conversion, high hydrogen selectivity, and high stability to produce hydrogen by the steam reforming of an industrial alcoholic waste without commercial value.

Keywords: Ethanol steam reforming, Hydrogen production, Hydrotalcite, LDHs, Cobalt catalyst, Alcoholic waste.

1. Introduction.

The search for an alternative energy source to our current energy system based on fossil fuels is one of the greatest challenges of our modern society. Among the different energy alternatives, hydrogen emerges with a great future [1-3]. Currently, hydrogen is not produced from renewable energy sources, representing an important drawback for its use as sustainable energetic alternative [4]. Thus, hydrogen should be produced from renewable energy sources such as biomass [5]. Particularly, the reforming of biomass derived compounds such as ethanol is considered an interesting option to produce hydrogen, because it can help to decrease the CO₂ emissions, reducing the greenhouse effect [6-8]. The steam reforming of ethanol (SRE) is a very active area of research [9-12]. However, the reforming of industrial alcoholic wastes has not been properly studied and they can be an interesting raw material suitable for hydrogen production. The use of ethanol or alcoholic wastes to produce hydrogen entails a series of environmental benefits compared with other fuels [13, 14]. In literature, many reviews about catalytic materials applied to SRE have been published recently [15-18]. Co-based catalysts are widely accepted for SRE, exhibiting high catalytic activity [10, 18-24]. However, the development of an optimal catalyst for the steam reforming of industrial alcoholic wastes has not been properly reported yet. The importance of using alcoholic wastes obtained from the wine industry to produce hydrogen is due to the fact that a very high percentage (65%) of world wine production is managed by European winegrowers [25]. The huge amounts of produced wine generate large amounts of solid and liquid wastes. The use of these liquid wastes in steam reforming reaction can be

an excellent solution for their properly treatment and for the simultaneous production of renewable hydrogen.

In the development of optimal catalysts in the steam reforming of alcohols, the support selection and the methods used in their synthesis are considered key factors for their catalytic performances. From a bibliographic search is observed how the scientific interest in layered double hydroxides (LDHs) materials as support of catalysts is recently increasing [26-37]. Moreover, positive feedback can be observed in the use of LDHs in SRE [38-41]. In this work, we have studied the catalytic activity of hydrotalcite-like materials containing Co in which the Mg has been substituted by Zn (Zn-Al hydrotalcite-like materials), since ZnO has been used with good results as support in the SRE [42-47]. One of the advantages is related to the ability of Zn to decrease the formation of CO, because ZnO favors water gas shift reaction (WGS) [48]. Another advantage is that the presence of Zn increases the reducibility of Co²⁺ [49]. In this study, the content of Co in Zn-hydrotalcite was first optimized. Next, La was added to the best Co-Zn-hydrotalcite catalyst as stability promoter because the addition of La reduces the production of coke during the steam reforming reaction, obtaining a more stable catalyst [50-55]. Finally, the new formulation containing La was tested in the steam reforming of an industrial alcoholic waste from the wine industry. The physicochemical characterization of the Zn-hydrotalcite-derived catalysts with Co and Co-La has been completed by XRD, BET surface area and TPR, finding interesting relationships with the catalytic results obtained in the steam reforming studies.

2. Experimental.

2.1. Preparation of catalyst.

Zn-Al hydrotalcite-derived catalysts containing Co and Co-La have been prepared by coprecipitation method. Two aqueous solutions, one acid and other basic, were initially prepared. The acid solution is formed by a mixture of Zn(NO₃)₂·6H₂O (≥97%, Sigma-Aldrich), Al(NO₃)₃·9H₂O (≥98%, Sigma-Aldrich) and Co(NO₃)₂·6H₂O (≥98%, Sigma-Aldrich) in the adequate proportion to obtain 5, 10, 20, and 30 wt.% of Co. The general formula of catalysts is [M(II)_(1-x)M(III)_x(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·mH₂O; where M(II) are Zn/Co and M(III) are Al/La according to each case, and Aⁿ⁻ is NO₃⁻. The ratio between trivalent metals and the sum of trivalent and divalent metals was 0.2. The basic solution is formed by a mixture of NaNO₃ (≥98%, Scharlab) and NaOH (≥98%, Scharlab). Both solutions were mixed using a syringe pump under constant stirring until obtaining a gel, which is deposited in a polypropylene bottle and kept in an oven at 333 K for 18 hours. After, the gel is filtered, washed and dried in an oven at 373 K overnight. Finally, it is calcined at 873 K in an oven for 3 hours obtaining the catalysts named as 5CoHT, 10CoHT, 20CoHT and 30CoHT. Following the same method is obtained the sample containing 1 wt.% of La (20CoLaHT) using La(NO₃)₃·6H₂O (≥98%, Sigma-Aldrich) as lanthanum precursor. The amount of Na⁺ in the catalysts is under 0.05 wt.%.

2.2. Characterization techniques.

The catalysts used in this study have been subjected to X-ray fluorescence (XRF) in a MiniPal4 apparatus (PANalytical) to determine the amount of Co and La. Moreover, the amount of Na⁺ was determined by atomic absorption spectrophotometry (AAS) in a Varian Spectra A-10 Plus apparatus. Textural properties were measured using an ASAP 2420 apparatus (Micromeritics) at 77 K. The X-ray diffraction has been carried out at room temperature in a Panalytical CubiX diffractometer using CuKα radiation. The identification of the crystalline phases has been carried out using the X'Pert HighScore Plus software. The reduction behaviors were studied by temperature programmed reduction (TPR) in Micromeritics Autochem 2910 equipment. The TPR experiments were carried out with the online analysis of the products evolved.

2.3. Catalytic study.

The reaction experiments were carried out in a continuous fixed bed reactor at atmospheric pressure, H₂O/EtOH molar ratio of 10, GHSV of 4700 h⁻¹ (EtOH+H₂O) and different reaction temperatures (673-873 K). The reactor was loaded with 0.3 mL of catalyst (~0.25 g), diluted with 3 g of carborundum (SiC). Before reaction the samples were reduced with H₂ flow (100 mL·min⁻¹) at 873 K for 2 h. The reaction compounds have been analyzed in a Varian 3800-GC equipped with two columns (TRB-5, L=30 m, DI=0.25 mm; CarboSieve SII, L=3 m, DI=2.1 mm) and two detectors, a thermal conductivity (TCD) and flame ionization (FID) using their corresponding standards.

An alcoholic waste supplied by Destilerías San Valero has been used in the last part of this paper to carry out the stability studies. The composition of this industrial alcoholic waste is shown in Table 1. The identification and quantification of impurities present in the alcoholic waste was carried out with a chromatograph (Shimadzu GC-17A) equipped with a PACKED injector, FID detector and steel packed column (VINICOL, L=2m, ID=2mm) using their corresponding standards. Stability tests with this alcoholic waste were carried out at atmospheric pressure, H₂O/EtOH contained in the alcoholic waste of 10 (molar ratio), GHSV of 4700 h⁻¹ (EtOH+H₂O) and 873 K.

Table 1. Composition of the industrial alcoholic waste used in the stability studies.

Compound	Concentration
Water	80.12 wt.%
Ethanol	19.64 wt.%
Impurities	0.24 wt.%
Acetaldehyde	2.17 mg/L
Methanol	115.88 mg/L
2-Propanol	17.15 mg/L
n-Propanol	847.47 mg/L
2-Butanol	870.72 mg/L
Isobutanol	41.89 mg/L
2-Methyl-1-Butanol	1.7 mg/L
SO ₂	10 mg/L

3. Results and discussion.

3.1. Characterization.

X-ray diffraction patterns of synthesized hydrotalcite-derived materials with different Co content are shown in Figure 1. All the diffraction peaks can be attributed to a typical hydrotalcite structure [56, 57], confirming that the catalytic materials have been correctly prepared.

Figure 1. XRD of hydrotalcite-like materials containing Co and La.

Once the correct synthesis of the catalysts was verified, the catalytic materials were calcined at 873 K to remove the precursor compounds used for the incorporation of Co and La. After calcination the catalysts were reduced in flow of H₂ at 873 K before reaction. Figure 2 shows the XRD of calcined and reduced catalysts. All the calcined materials (Figure 2, left) present similar XRD pattern with diffraction peaks corresponding to ZnO [Ref. code 01-089-0510], ZnAl₂O₄ [Ref. code 00-005-0669], and Co₃O₄ phases [Ref. code 00-042-1467] [58, 59]. For the catalyst containing La, reflections due to La₂O₃ phase or other

lanthanum phases were not observed in the calcined sample. This observation can be explained by the small amount of La in the sample (1 wt.%) and because it may be in an amorphous state [60].

Figure 2. (Left) XRD of Zn-hydrotalcite-derived materials containing Co and La calcined at 873K. (Right) XRD of Zn-hydrotalcite-derived materials containing Co and La calcined and after reduction at 873K.

For the reduced catalysts, the main peaks corresponding to the Co_3O_4 disappeared, appearing the diffraction peaks corresponding to the Co^0 phase [Ref. code 00-015-0806] (Figure 2, right). On the other hand, the diffraction peaks corresponding to the support (ZnO and ZnAl_2O_4) were also present in the reduced material. The crystallite size of metallic cobalt (Co^0) has been also determined from the XRD of the reduced catalysts using the Scherrer equation [61]. As it can be seen in Table 2, the average crystallite size of Co^0 increases with the load of Co. Specifically, the sample 5CoHT with 5 wt. % of Co presented the lowest size (7 nm), while the sample 30CoHT with 30 wt.% of Co presented the highest size (14 nm). This is an expected result if it is considered that increasing the load of Co, the sintering of the metallic phase is favored by the proximity between metallic crystallites.

Table 2 also shows the specific surface area and cobalt/lanthanum content for the different catalysts studied in this paper. As it can be seen, specific surface area decreases when Co or Co and La are incorporated. Initial specific surface area of $58 \text{ m}^2/\text{g}$ for the sample HT decreases to $25\text{--}40 \text{ m}^2/\text{g}$ when Co or Co and La are added. This decrease in area could be explained taking into account that cobalt in calcined samples is present as Co_3O_4 that has a very low surface area ($<1 \text{ m}^2/\text{g}$). The presence of Co_3O_4 will have a very low contribution to the total surface area of the final catalytic material. Thus, the cobalt incorporation would lead to a “dilution effect”, which could explain the reduction of the surface area detected [20].

Table 2. Co and La content, BET surface area, crystallite size of Co^0 determined by XRD and reduction degree for the catalysts studied in this work.

Sample	BET surface area (m^2/g)	Co/La composition determined by XRF, wt. %	Co^0 crystallite size determined by XRD (nm)	Reduction degree at 873 K, %
HT	58	-/-	-	-
5CoHT	35	5.1/-	7	96
10CoHT	36	10.0/-	10	92
20CoHT	35	20.5/-	11	86
30CoHT	38	29.2/-	14	71
20CoLaHT	25	20.1/0.9	12	69

The reduction properties of the calcined catalysts have been studied by temperature-programmed reduction (TPR). The reduction curves are shown in Figure 3. It is observed that all the catalysts present two main

reduction peaks. The first peak appears around 700 K and the second appears in a wider range of temperatures, between 850 and 950 K. These two peaks correspond to the reduction in two stages of Co_3O_4 oxide, which would be reduced first to CoO and then to Co^0 [49]. These results agree with the species observed in the XRD section of the catalysts calcined at 873 K and reduced with hydrogen at 873 K. Small changes can be found in the reduction temperature values for the second reduction peaks, suggesting that slight differences in the interaction between cobalt and support would be occurring in the different catalysts.

Figure 3. TPR profiles of the catalytic materials studied in this paper.

The reduction degree of the different catalysts has been also determined at 873 K. This temperature was used to reduce the calcined catalysts before starting the steam reforming studies. As it can be seen in Table 2, high reduction degrees are achieved for the samples containing low charge of Co. On the other hand, the presence of La does not seem to favor the reduction of Co at 873 K.

3.2. Catalytic activity.

In Figure 4 the values of ethanol conversion and hydrogen selectivity for the catalysts with different cobalt loadings are shown. The values given in this study were obtained after 5 hours of reaction, when stationary steady state was reached. In the experiments where temperature was varied, the activity at the first temperature tested (673 K) was measured again at the end of each experiment. In this way, it can be assured that the values for all the temperatures are reliable.

Initially, it was studied the effect of the cobalt content in the steam reforming of ethanol. Figure 4 shows the variation of the ethanol conversion with the amount of cobalt at 673 K. As it can be seen, the complete conversion of ethanol is obtained for loads of Co of 20 wt.% or higher. A combination of the low crystallite size of Co^0 (11 nm) and high reduction degree (86%) could explain the better catalytic results presented by the sample 20CoHT. Regarding the selectivity of hydrogen, it can be observed that the highest values are also obtained for the sample containing 20 wt.% of Co, remaining nearly constant for higher loadings. In summary, these results indicate that it could be prepared a Zn-hydrotalcite-derived catalysts containing 20 wt.% of Co with high ethanol conversion and hydrogen selectivity in the steam reforming of ethanol.

Figure 4. Conversion of ethanol and H₂ selectivity versus Co content. Reaction conditions: 673 K, H₂O/EtOH=10, GHSV= 4700 h⁻¹ and atmospheric pressure.

Products distribution have been also studied at 673 K and they are shown in Table 3. As it can be seen the catalyst containing 20 wt.% of Co produces the lowest amounts of CH₄, CO and other undesired byproducts (C₂H₄, CH₃COOH, C₂H₄O and C₃H₆O). It must be considered that the production of several of these byproducts can affect the stability of the catalyst since some of them (C₂H₄) are coke precursor.

Table 3. Products distribution for the ethanol steam reforming (selectivity values, mol %). Reaction conditions: 673 K, H₂O/EtOH = 10, GHSV = 4700 h⁻¹ and atmospheric pressure.

Catalyst	CH ₄	CO	CO ₂	C ₂ H ₄	CH ₃ COOH	C ₂ H ₄ O	C ₃ H ₆ O
5CoHT	6.9	5.4	3.5	0.4	0.2	34.0	0.9
10CoHT	6.6	2.3	17.1	0.3	0.3	3.3	0.2
20CoHT	5.0	1.2	19.5	0.2	0.2	0.2	0.1
30CoHT	5.3	1.4	21.7	0.4	0.4	0.5	0.2

Considering the excellent results obtained by the 20CoHT catalyst, it was decided to improve its catalytic stability incorporating La, a known stability promoter, which acts decreasing the coke deposition [50-55]. The catalyst 20CoLaHT containing 1 wt.% of La was prepared and tested in steam reforming of ethanol at different reaction temperatures. The results are shown in Table 4. In general, the two catalysts studied in this section present a high ethanol conversion values, with small differences between them. As it can be seen, a higher conversion of ethanol is exhibited by the sample containing La (20CoLaHT), with a complete conversion of ethanol in all the reaction temperatures here studied. Moreover, a higher hydrogen selectivity is also achieved, and a lower concentration of not desired byproducts is obtained, particularly at high reaction temperatures. These results suggest that the addition of La would have positive effects on the catalytic performance, improving the conversion of ethanol and decreasing the formation of undesired byproducts, such as C₂H₄, which is related to coke formation.

Table 4. Ethanol conversion and products distribution (selectivity values, mol%) obtained at different temperatures with the catalyst 20CoHT and 20CoLaHT. Reaction conditions: H₂O/EtOH = 10, GHSV = 4700 h⁻¹ and atmospheric pressure.

Catalyst	T ^a , K	% Conv.	CH ₄	CO	CO ₂	H ₂	C ₂ H ₄	CH ₃ COOH	C ₂ H ₄ O	C ₃ H ₆ O
20CoHT	673	99.0	5.0	1.2	19.5	73.6	0.2	0.2	0.2	0.1
	773	100.0	3.3	4.0	18.7	73.7	0.2	0.1	0.0	0.0
	873	100.0	4.0	4.6	18.4	72.8	0.1	0.1	0.0	0.0
20CoLaHT	673	100.0	5.9	1.0	18.5	74.6	0.0	0.0	0.0	0.0
	773	100.0	0.9	2.2	21.7	75.2	0.0	0.0	0.0	0.0
	873	100.0	1.1	3.0	20.8	75.1	0.0	0.0	0.0	0.0

20CoHT and 20CoLaHT have been also tested using an industrial alcoholic waste supplied by Destilerías San Valero. The composition of this waste was presented in Table 1. The catalytic results are presented in Table 5 and Figure 5. As it can be seen, both catalysts present similar catalytic activity with a complete conversion of ethanol and a high hydrogen selectivity over the entire range of temperatures here studied. The presence of impurities mentioned in Table 1 was not detected in the exhaust gas for any of the catalysts. Thus, they were completely reformed with both catalysts. It should be noted that 20CoLaHT presents slightly better catalytic results at high temperatures, similar to the catalytic behavior above described in the steam reforming of ethanol. Additionally, it was not detected the production of undesired byproducts such as C₂H₄, CH₃COOH, C₂H₄O and C₃H₆O for the sample containing La. Besides, deactivation of the sample containing La was not detected during the 24 hours of experiments, while the catalyst without La started to deactivate after 10 hours of reaction time (Figure 5), where a progressive drop in the ethanol conversion is observed.

Table 5. Catalytic results for the steam reforming of the alcoholic waste (conversion and selectivity values, mol %). Reaction conditions: H₂O/EtOH = 10, GHSV = 4700 h⁻¹ and atmospheric pressure.

Catalyst	T ^a , K	% Conv. EtOH	CH ₄	CO	CO ₂	H ₂	C ₂ H ₄	CH ₃ COOH	C ₂ H ₄ O	C ₃ H ₆ O
20CoHT	673	98.7	3.5	1.1	22.3	72.3	0.3	0.2	0.1	0.2
	773	100.0	1.0	2.7	21.1	74.7	0.2	0.2	0.0	0.1
	873	100.0	3.1	2.9	20.2	73.5	0.1	0.1	0.0	0.1
20CoLaHT	673	99.2	2.8	1.2	21.4	74.6	0.0	0.0	0.0	0.0
	773	100.0	0.9	2.8	21.2	75.1	0.0	0.0	0.0	0.0
	873	100.0	1.7	4.3	19.1	74.9	0.0	0.0	0.0	0.0

The acetaldehyde selectivity for 20CoHT also increased after 10 hours of reaction (from 0.0 mol% to 5.2 mol%), supporting also that deactivation of the catalyst is occurring [20,46]. Thus, the lanthanum addition seems to have a positive effect on catalyst performance improving the catalytic activity and avoiding the deactivation of the catalyst in the presence of the impurities contained in the alcoholic waste here used. Fatsikostas et al [62, 63] reported that the La incorporation improves the catalytic stability during the steam reforming of ethanol by the formation of La₂O₂CO₃ species, which react with surface carbon deposits. We have not detected the presence of these species by XRD or their decomposition products during the TPR studies. It is possible that the low concentration of La presents in our sample (<1 wt.%) could justify this fact.

Figure 5. Products selectivity and conversion of ethanol versus reaction time for 20CoLaHT and 20CoHT catalysts using alcoholic waste as feed. Reaction conditions: $\text{H}_2\text{O}/\text{EtOH}=10$, $\text{GHSV}= 4700 \text{ h}^{-1}$, atmospheric pressure and at 873 K.

Additional studies are being carried out to acquire more knowledge about the high catalytic performance and stability exhibited by the sample containing lanthanum. Specifically, it is being studied the influence of the La loading, superficial composition of the catalyst by XPS and the characterization of the fresh and of the used catalysts by IR and Raman spectroscopy.

All the results presented here show that it is possible to synthesize ethanol steam reforming catalysts based on Co supported on hydrotalcite-type material with high catalytic activity and hydrogen selectivity, which are able to reduce the formation of undesired byproducts (CO , CH_4 , C_2H_4 , CH_3COOH , $\text{C}_2\text{H}_4\text{O}$ and $\text{C}_3\text{H}_6\text{O}$) when industrial alcoholic waste is used as feed.

4. Conclusions.

Zn-hydrotalcite-derived material with different amounts of Co have been synthesized and tested in the steam reforming of ethanol. The catalytic results show that the sample containing 20 wt.% of Co presents the highest ethanol conversion values and hydrogen selectivity together with the lowest concentration of CO , CH_4 and other undesired byproducts (C_2H_4 , $\text{C}_2\text{H}_4\text{O}$, CH_3COOH , and $\text{C}_3\text{H}_6\text{O}$). This result could be explained by combining the small crystallite size of metallic cobalt present in this material together with its high reduction degree. It has been also seen that the addition of La increases the catalytic stability of this cobalt catalyst, keeping its ethanol conversion unaltered after 24 hours of reaction, when an industrial alcoholic waste containing several impurities is used as feed.

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