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Short Communication

Cobalt catalysts derived from hydrotalcite-type precursors applied to steam reforming of ethanol

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1. Introduction

Ethanol steam reforming (ESR, Eq. 1) has been suggested as an alternative route for H_2 production, since this reaction predicts a high yield of H_2 at low reaction temperatures.

$$\begin{array}{ll} C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 & \Delta H^0_{298K} = +174 \, \text{kJmol}^{-1} \\ \Delta G^0_{298k} = +65.5 \, \text{kJmol}^{-1} \end{array} (1)$$

In the literature, Rh, Co and Ni are described as promising metals for ESR catalysis [1]. Rh is the most active of these, but very costly, being a noble metal. Cheaper metals such as Ni and Co usually suffer deactivation by the deposition of carbon or sintering of the active phase [1]. The stability of such catalysts may be enhanced by careful choice of the constituents of the support and the method of preparation [2].

Hydrotalcites are known for their layered structure, which, on heat treatment, leads to a homogenous dispersion of the active phase [3]. Comas et al. [4] studied the performance of Ni–Al catalysts made from hydrotalcite-type precursors in the ESR reaction, carried out at 773 K, varying the molar ratio (R) of $H_2O:C_2H_5OH$ in the feed from 1 to 6. They reported that H_2 selectivity increased with rising R. The authors suggested that the increased H_2 selectivity could be related to the fine dispersion of Ni resulting from the method of preparation from hydrotalcite-type precursors.

Lucrédio et al. [5] tested catalyst precursors composed of Ni/Mg/Al oxides promoted with La and Ce in ESR reactions. The catalysts did not

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ABSTRACT

Catalysts derived from Co/Mg/Al hydrotalcite-type precursors modified with La and Ce were characterized by XANES and tested in ethanol steam reforming. The reaction data showed that, with a molar ratio of water: ethanol = 3:1 in the feed, addition of Ce and La favored acetaldehyde production. Increasing the water content (water:ethanol = 5:1) decreased the acetaldehyde formation by favoring the adsorption of water molecules on these samples, enhancing the acetaldehyde conversion.

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suffer significant carbon deposition throughout 6 h on stream and the reaction data showed that the addition of Ce and La resulted in greater H_2 production at 550 °C.

Considering the promising results obtained with hydrotalcitetype precursors, the goal of this paper was to assess the effect of Ce and La addition on the performance of cobalt catalysts derived from hydrotalcite-type precursors, Co/Mg/Al, in the ESR reaction.

2. Experimental

2.1. Synthesis

The preparation of the catalysts has already been described in detail in previous papers [6,7].

Briefly, the hydrotalcite-type precursors were prepared in two ways: the standard Co-LDH (layered double hydroxide) catalyst by the traditional technique of precipitation of carbonates and the promoted catalysts, LaCo-LDH and CeCo-LDH, by anion exchange of Mg/Al/Co with EDTA chelation complexes of La and Ce, to favor the transport of these cations into the hydrotalcite layers.

All hydrotalcites were calcined at 500 °C in air for 15 h. They were denominated Co, LaCo and CeCo.

2.2. Characterization

X-ray absorption near-edge structure (XANES) spectra at the Co K-edge were collected at the D04-XAFS1 beam line in the Brazilian Synchrotron Light Source Laboratory (LNLS), Brazil. The data acquisition system comprised three ionization detectors (incident I_0 , transmitted I_t and reference I_r). The reference channel was employed primarily for

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Table 1 Comparison between composition obtained by XPS (surface) and by EDS (bulk)^a.

Catalyst	Molar composition (XPS)					Molar composition (EDS)				
	Со	Mg	Al	La	Ce	Со	Mg	Al	La	Ce
Со	0.11	0.67	0.22	-	-	0.07	0.67	0.26	-	-
LaCo	0.17	0.67	0.12	0.04	-	0.08	0.76	0.15	0.01	-
CeCo	0.17	0.60	0.19	-	0.04	0.08	0.75	0.15	-	0.02
^a Lucrédio et al.[7].										

internal calibration of the edge positions, against a pure metal foil. Nitrogen filled the I_0 , I_t and I_r chambers, and a Si (111) single crystal was used as monochromator. The Athena computer package was used to analyze the XAS data.

2.3. Catalytic tests

The catalytic tests were performed at atmospheric pressure and 550 °C, in a fixed-bed tubular quartz micro reactor. The unused reactants and gaseous reaction products were analyzed in-line by gas chromatography (Varian, Model 3800), as described elsewhere [5].

Prior to the reaction, 150 mg of the catalyst, sieved in the range 60–100 mesh and freshly calcined, was introduced into the reactor and activated *in situ* by reduction in flowing H₂ (50 mLmin⁻¹) at 550 °C (heating rate 10 °Cmin⁻¹) for 1 h and then purged at 550 °C in a flow of pure N₂. The reaction was started in a hydrogen-free feed of water and ethanol. The catalysts were tested with two feeds: one with a molar ratio H₂O: ethanol = 3:1, flowing at 2.5 mLh⁻¹ (weight hourly space velocity,



Fig. 1. Normalized XANES spectra for (A) reference substances and (B) the catalyst samples Co, CoLa and CoCe compared with reference compound Co_3O_4 .

WHSV = 14.9 h⁻¹) for 6 h on stream, and the other with H₂O: ethanol = 5:1, flowing at 3.3 mLh⁻¹ (WHSV = 20.2 h⁻¹) for 3 h on stream. The H₂O: ethanol feed solution was driven by a piston pump, the flow of ethanol being fixed at 1.3 mLh⁻¹. The feed was vaporized in a preheating chamber (180 °C) before entering the reactor. At the end of the catalytic test, the feed was stopped and the system cooled with a flow of pure N₂. During the reaction, the liquid products were condensed in a cold trap kept at 0 °C. At the end of reaction, the condensed liquid



Fig. 2. Gaseous composition of products of ESR on (A) Co, (B) CoCe and (C) CoLa catalysts.

Table 2 Ethanol conversion and selectivity of acetaldehyde.

H ₂ O: ethanol	Time on stream (h)	Catalyst	Acetaldehyde (mol/mol EtOH _{converted})	Ethanol conversion (%)
3:1		Со	0.0040	97
(feed rate: 2.5 mLh ^{-1})	6 h	CoCe	0.0110	84
		CoLa	0.0476	63
5:1		Со	0.0155	85
(feed rate: 3.3 mLh^{-1})	3 h	CoCe	0.0005	89
		CoLa	0.0009	89

products were collected and analyzed by gas chromatography (Hewlett Packard 5890), with an HP-FFAP capillary column ($25 \text{ m} \times 0.2 \text{ mm i.d.}$) and FID detector. During the sample preparation, the solution was kept in a temperature lower than 10 °C, to avoid any liquid product evaporation.

The total ethanol conversion during the test was taken as the total volume of ethanol fed to the reactor minus the total volume of condensed ethanol, expressed as a percentage of the total fed volume. The selectivity of each product $(i = H_2, CH_4, CO_2, CO \text{ or } C_2H_4)$ was calculated by the following equation:

Selectivity of i = Molar flow of *i* produced/Molar flow of ethanol converted (2)

3. Results

The characterization of these catalysts is presented elsewhere by the authors [7,8]. Table 1 reproduces the molar composition of the catalysts [7] and according to this table, the concentrations of Co, La and Ce are higher on surface. According to the temperatureprogrammed reduction (TPR) and X-ray diffraction (XRD) analysis reported in these previous studies, the Co and Mg species are interacted strongly, probably in the form of a solid solution of CoO-MgO doped with $Al^{3\pm}$ cations [7,8]. In the Ce and La promoted samples, the analyses indicated the presence of Ce_2O_3/CeO_2 and La_2O_3 with no interaction with the support. The TPR results for the samples CoLa and CoCe showed reduction peaks shifted to lower temperatures, indicating that the presence of Ce and La had weakened the Cosupport interaction [7,8].

Fig. 1 presents the XANES spectra of the catalysts. For comparison, Fig. 1A shows the normalized Co K-edge XANES spectra of related reference materials: Co metal foil, CoAl₂O₄, Co₃O₄ and CoO. Fig. 1B shows the spectra of the oxide samples Co, CoLa and CoCe, plotted together with that of the reference compound Co₃O₄.

In Fig. 1A, a weak pre-edge peak (α) can be seen in the spectra for the reference substances, around 7.71 keV, which is attributed to the 1s-3d transition. The pre-edge region provides information about local geometry around the absorbing atom and depends on its oxidation state and bond characteristics. The pre-edge intensity is related to the symmetry and to the occupancy of the 3d shell. In the case of tetrahedral coordination, the 1s-3d transition, normally dipole-forbidden, becomes partially dipole-allowed due to the asymmetry and results in a weak pre-edge peak. With octahedral coordination, the pre-edge peak is absent or less intense, only appearing if thermal vibrations momentarily eliminate the center of symmetry and allow the 1s–3d transition [9,10]. Co₃O₄ has a spinel structure, with a third of the cobalt ions (Co²⁺) occupying tetrahedral sites and twothirds (Co³⁺) occupying octahedral sites. The pre-edge feature represents a superposition of the more intense tetrahedral peak and the weaker octahedral peak. CoAl₂O₄ also has a spinel structure, but here all the cobalt ions (Co^{2+}) occupy only tetrahedral sites, and the normalized absorption pre-edge (α) is more intense than that of Co₃O₄. CoO has only octahedral sites for Co, and therefore the pre-edge (α) feature is very



Fig. 3. Production of (A) H₂, (B) CH₄, (C) CO₂ and (D) CO in the ESR reaction with feed molar ratio = 3:1.

weak [11,12]. The oxide catalyst samples Co, CoLa and CoCe showed very weak pre-edge peaks, weaker than the reference compound Co_3O_4 (Fig. 1B), indicating Co ions in octahedral symmetry, as in CoO.

The XANES profile is affected by the oxidation state, the main absorption edge shifting to higher energy at higher oxidation states. The main absorption edge, or white line (β), is observed at 7.726– 7.727 keV in the samples Co, CoLa and CoCe. This is close to the value reported in the literature for CoO. Also, for the catalyst samples, the white line is appreciably more intense than for the reference compound Co₃O₄. The white line reflects holes in the d band: the more unoccupied the d band, the more intense is the white line absorption [13]. In these samples, the high intensity of the white line could be due to a strong interaction between Co and Mg, involving a charge transfer from the d band of Co to Mg, resulting in lower d occupancy and an increase in the intensity at the edge. The sample Co exhibited the most intense white line, possibly indicating a stronger Co-Mg interaction in this material. This would be consistent with the X-ray photoelectron spectroscopy (XPS) results presented elsewhere by the authors, which showed a charge transfer from Co to Mg in these samples, due to the solid solution formation as suggested by XRD and TPR results [7,8].

3.1. Catalytic tests

Fig. 2 plots the composition of the gaseous products against reaction time, the main products being H_2 , CH_4 , CO, CO_2 and C_2H_4 . It is seen in these profiles that the gaseous composition is practically the same for all catalysts. Note that C_2H_4 was observed at low levels, due to the weak acidity of the catalyst supports, which prevents the dehydration of ethanol to ethylene [3]. However, the sample CoLa presented a slight increase in the C_2H_4 formation with time on stream.

The rates of ethanol conversion at feed molar ratio H_2O :ethanol = 3:1 are presented in Table 2 and a decrease is observed on the addition of the rare earth metals, in the order: Co>CoCe>CoLa. This behavior is accompanied by the formation of acetaldehyde, in the liquid effluents, in the order: CoLa>CoCe>Co. Ethyl ether, acetone, ethyl acetate and acetic acid were observed in trace amounts. Also, carbon was deposited only in trace amounts.

The higher formation of acetaldehyde on catalysts CoLa and CoCe indicates that the basic additives stabilized the formation of adsorbed acetaldehyde. In the sample CoLa, the La³⁺ is the adsorption site for oxygen radicals [14] and in the present case it could favor the dissociative adsorption of ethanol (CH₃CH₂OH + O²⁻ \Rightarrow CH₃CH₂O⁻ + ⁻OH) with consequent dehydrogenation to acetaldehyde (CH₃CH₂O⁻ + ⁻OH \Rightarrow CH₃CHO + H₂ + O²⁻) [15].

The sample CoCe presented higher production of acetaldehyde, when compared to Co, but lower than CoLa. Ceria has high oxygen storage capacity and oxygen mobility that can favor the oxidation of acetaldehyde to acetate (CH₃CHO + $2O^{2-} \Rightarrow$ CH₃-COO⁻ + -OH + $2e^{-}$), which can then be decomposed to CH₄ and CO₂ or CO [15,16].

Fig. 3 shows the selectivity profiles of H_2 , CH_4 , CO and CO_2 during 6 h on stream. According to the data, the selectivity of H_2 , CH_4 and CO_2 are decreasing with the time on stream. Considering the low carbon deposition and the high values of ethanol conversion presented in Table 2, it can be inferred that this decreasing may be occurring due to a change in the selectivity of the reaction by the formation of liquid products or C_2H_4 , as observed for the sample CoLa, in Fig. 2.

Considering the selectivity, H_2 production follows practically the same curve on CoLa and CoCe catalysts, which presented higher H_2 selectivity than Co. The addition of La and Ce led to a higher CO₂ selectivity and reduced CH₄ selectivity relative to the Co catalyst, probably because the presence of the basic promoters Ce and La favored the activation of water or other oxygen compounds [8,17], thus promoting the steam reforming of methane (SRM: CH₄ + H₂O = CO + 3H₂) and the water gas shift reaction (WGSR: CO + H₂O → H₂ + CO₂).

To investigate further the role of the water in the catalyzed reactions, the H_2O :ethanol molar ratio in the feed was raised from 3:1 to 5:1, based

on the work of Mas et al. [18] which studied the ethanol conversion as a function of H_2O :ethanol molar ratio. The authors observed a maximum of ethanol conversion using a H_2O :ethanol molar ratio of 5:1 and suggest that there is a competition between ethanol and water adsorption for the active sites.

Table 2 also shows the ethanol conversion rates and the liquid product collected after 3 h of reaction with feed molar ratio H_2O : ethanol = 5:1. The other liquid by-products were observed only in trace amounts.

These data show that, the ethanol conversion was greater on the CoCe and CoLa catalysts than when the feed molar ratio of H₂O:ethanol was 3:1, while that on Co was lower. Also, acetaldehyde formation was



Fig. 4. Gaseous composition of products of ESR on catalysts (A) Co, (B) CoCe and (C) CoLa, with feed molar ratio of water:ethanol = 5:1.

strongly inhibited on the catalysts CoLa and CoCe and favored on the Co catalyst in the presence of excess water. The lower ethanol conversion on Co catalyst could be due to partial oxidation of the Co sites by the extra water and the increase in the acetaldehyde production due to a favoring of ethanol dehydrogenation (CH₃CH₂OH \leftrightarrows CH₃CHO + H₂) on the basic sites of the MgAl support.

Regarding the conditions used, the flow of ethanol was kept constant and the flow of water accelerated, leading to a shorter contact time. These conditions seem to have favored the adsorption of water on the samples CoLa and CoCe, leading to inhibition of acetaldehyde production [17,19]. The presence of these additives could favor the adsorption of H₂O and enhance the mobility of –OH on the surface and thus promote steam reforming reactions through an acceleration of the adsorption and dissociation of water molecules associated with CeO₂ and La₂O₃. The lower acetaldehyde formation could then be explained by promotion of acetaldehyde steam reforming (CH₃CHO + H₂O = CO₂ + CH₄ + H₂), which comprehends the two steps of reaction, the acetaldehyde decomposition (CH₃CHO = CH₄ ± CO) followed by WGSR (CO ± H₂O = H₂ ± CO₂) [20].

Fig. 4 shows the gaseous composition of the reaction products. The Co sample produced mainly H_2 and CO_2 , indicating SRM and WGSR. With regard to the addition of promoters, the CoCe catalyst showed a high content of CH_4 and CO_2 in the product gas composition, indicating the acetaldehyde steam reforming, while CoLa showed a high content of CO_2 and CO, indicating acetaldehyde steam reforming followed by SRM.

4. Conclusion

It has been demonstrated that Co/Mg/Al catalysts prepared via hydrotalcite-type precursors are active for ESR. The presence of the Ce and La promoters favored acetaldehyde production at the lower feed water content (H_2O :ethanol = 3:1). Increasing the water content and thus decreasing the contact time improved the catalytic performance of the samples modified with Ce and La and decreased their acetaldehyde

formation, probably by favoring the adsorption of water under these conditions.

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References

- K. Urasaki, K. Tokunaga, Y. Sekine, M. Matsukata, E. Kikuchi, Catal. Commun. 9 (2008) 600–604.
- [2] A.J. Vizcaíno, P. Arena, G. Baronetti, A. Carrero, J.A. Calles, M.A. Laborde, N. Amadeo, Int. J. Hydrogen Energy 33 (2008) 3489–3492.
- [3] A. Vaccari, Catal. Today 41 (1998) 53-71.
- [4] J. Comas, M.L. Dieuzeide, G. Baronetti, M. Laborde, N. Amadeo, Chem. Eng. J. 118 (2006) 11–15.
- [5] A.F. Lucrédio, J.D.A. Bellido, E.M. Assaf, Appl. Catal., A 388 (2010) 77-85.
- [6] A.F. Lucrédio, E.M. Assaf, J. Power Sources 159 (2006) 667-672.
- [7] A.F. Lucrédio, G. Jerkiewicz, E.M. Assaf, Appl. Catal., B 84 (2008) 106–111.
 [8] A.F. Lucrédio, G. Tremiliosi Filho, E.M. Assaf, Appl. Surf. Sci. 255 (2009) 5851–5856.
- [9] L.P.R. Profeti, E.A. Ticianelli, E.M. Assaf, Appl. Catal., A 360 (2009) 17-25.
- [10] L.P.R. Profeti, E.A. Ticianelli, E.M. Assaf, J. Power Sources 175 (2008) 482–489.
- [11] G. Jacobs, P.M. Patterson, Y. Zhang, T. Das, J. Li, B.H. Davis, Appl. Catal., A 233 (2002) 215–226.
- [12] G. Jacobs, Y. Ji, B.H. Davis, D. Cronauer, A.J. Kropf, C.L. Marshall, Appl. Catal. A 333 (2007) 177–191.
- [13] S.R. Bare, XANES Measurements and InterpretationDisponible on:, http://cars9. uchicago.edu/xafs_school/Material/Lectures/XANES%20Bare.pdf. 2010 Acess on: 23 nov.
- [14] T.L. Yang, L.B. Feng, S.K. Shen, J. Catal. 145 (1994) 384–389.
- [15] C. Resini, T. Montanari, L. Barattini, G. Ramis, G. Busca, S. Presto, P. Riani, R. Marazza, M. Sisani, F. Marmottini, U. Costantino, Appl. Catal., A 355 (2009) 83–93.
- [16] A. Yee, S.J. Morrison, H. Idriss, Catal. Today 63 (2000) 327–335.
- [17] D.L. Trimm, Catal. Today 49 (1999) 3-10.
- [18] V. Mas, M.L. Dieuzeide, M. Jobbágy, G. Baronetti, N. Amadeo, M. Laborde, Catal. Today 133 (2008) 319–323.
- [19] M.C., Sánchez-Sánchez, R.M., Navarro, J.L.G., Fierro, Int. J. Hydrogen Energy 32 (2007) 1462–1471.
- [20] J. Comas, F. Mariño, M. Laborde, N. Amadeo, Chem. Eng. J. 98 (2004) 61-68.