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Hydrogen production by steam reforming of ethanol Study of mixed oxide catalysts $Ce_2Zr_{1.5}Me_{0.5}O_8$: Comparison of Ni/Co and effect of Rh

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Abstract

One of the most interesting routes to produce energy from biomass is the production of hydrogen by bio-ethanol steam reforming. Deactivation, related to carbonaceous compounds deposition, is considered the principal inconvenience of the catalytic system based on transition metals supported on oxides. Carbon formation could be minimized using a support with good redox properties, a promoter, or enhancing the strong metal–support interaction. In this work, a catalytic system based on doped Ce–Zr mixed oxides with Co, Ni, Rh, Rh–Co or Rh–Ni is synthesized using a pseudo sol–gel method, characterized by X-ray diffraction (XRD) and thermo-programmed reduction (TPR), and evaluated as catalyst in the steam reforming of ethanol.

Ethanol steam reforming and physicochemical characterization were performed in order to understand the active phase and the role of the promoter on the catalyst reduction state, the catalytic performance and the carbonaceous deposits formation.

Keywords: Ethanol steam reforming; Deactivation; Carbon formation

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1. Introduction

The increase in global population with increasing global quality of life, has led to a great rise in world energy demand and therefore in the fuel consumptions. It is estimated that fossil fuel resources will not be sufficient to supply future energy requirements. At actual energy consumption levels, oil proven reserves are estimated at 40 years, 60 years for natural gas and 250 years for coal [1].

The above-mentioned situation associated with environmental restrictions impulses the investigations on alternative energies with high energetic conversion efficiency and lower environmental impact. In spite of the several disadvantages of hydrogen uses, i.e. storage and distribution difficulties, it has received special attention thanks to be considered a clean fuel. Among the various ways to produce hydrogen, the production from reforming of bio-ethanol, obtained by fermentation of vegetal biomass, is a favorable route due to its neutral contribution to the greenhouse gas emissions [2–5].

Various works on study of supported catalysts on oxides have been carried out using noble metals [6–8], cobalt [9,10] and nickel [11–13]. The supported-oxides transition metals have the inconvenient to produce carbonaceous compounds due to metal particle sintering.

Our approach to a catalytic system consists of the active phase integration into a support with high oxygen mobility, which would favor the strong metal–support interaction and consequently diminish the formation of carbonaceous deposits.

In previous works, we have studied Ce–Zr–Co fluorite type mixed oxides as catalysts for the hydrogen production by bio-ethanol reforming. This mixed oxides, in which the active phase (Co) has been inserted in the structure of the support [14–16],

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have high activity, high hydrogen selectivity and good stability. Nevertheless, the products distribution in gas phase changes with time on stream. Early, at total conversion, hydrogen, carbon oxides and methane are present as products. After, without a change in the conversion, the catalytic selectivity is modified and ethylene, acetaldehyde and acetone are present in the effluents. The deactivation is related to the formation of precursors of carbonaceous deposits [16].

In this paper we present the influence of the active phase integration on the catalytic behavior of trimetallic mixed oxides with formulae $Ce_2Zr_{1.5}Me_{0.5}O_{8-\delta}$ (Me = cobalt, rhodium, nickel) in ethanol reforming. Further, a trimetallic rhodium-doped Ce–Zr mixed oxide with a lower content ($Ce_2Zr_{1.5}Rh_{0.03}O_{8-\delta}$) and two tetrametallic mixed oxides in which the transition metal has been replaced partially by the noble metal, were prepared and studied as catalysts. In order to understand the influence of the active phase and the role of noble metal as catalytic promoter, the synthesized fresh mixed oxides were characterized by XRD and TPR and the carbonaceous deposits produced during the reaction were quantified by TPO.

2. Experimental

2.1. Preparation and characterization of the catalysts

Ce–Zr–Me mixed oxides were synthesized using the pseudo sol–gel method based on the thermal decomposition of metallic propionates [16]. The salts used were cerium(III) acetate hydrate, zirconium(IV) acetylacetonate, cobalt(II) acetate hydrate, nickel(II) acetate hydrate and rhodium(II) acetate. Mixed oxides prepared could be represented with the formulas:

$Ce_2Zr_{1.5}Co_{0.5}O_{8-\delta}$ (Co/CeZr)

$Ce_2Zr_{1.5}Ni_{0.5}O_{8-\delta}$ (Ni/CeZr)

$Ce_2Zr_{1.5}Rh_{0.5}O_{8-\delta}$ (9 Rh/CeZr)

$Ce_2Zr_{1.5}Rh_{0.03}O_{8-\delta}$ (0.5 Rh/CeZr)

$Ce_2Zr_{1.5}Rh_{0.03}Co_{0.47}O_{8-\delta}$ (Rh–Co/CeZr)

$Ce_2Zr_{1.5}Rh_{0.03}Ni_{0.47}O_{8-\delta}$ (Rh–Ni/CeZr)

The starting salts were dissolved separately in boiling propionic acid (0.12 mol L^{-1}). The solutions were mixed and the solvent was evaporated until obtaining a resin, which was calcined in air at 500 °C over 3 h (2 °C min^{-1}).

The crystalline structure of mixed oxides was determined by X-ray diffraction with Brucker D8 Advanced apparatus, Cu Kα radiation, in an interval $2\theta = 10^\circ$ up to $2\theta = 100^\circ$.

The reducibility was studied by thermo-programmed reduction (TPR) of a 0.05 g sample, in a hydrogen/argon mixture (52 mL min^{-1}, 3.85% (v/v)). The temperature was increased at 15 °C min^{-1} from room temperature to 900 °C.

2.2. Catalytic tests

The catalytic tests of ethanol steam reforming were carried out in a fixed bed reactor at atmospheric pressure.

Before the reaction, the mixed oxide (0.16 g) was reduced at 440 °C in a hydrogen flow (3 mL min^{-1}) over 12h. Then, the hydrogen flow was suspended, and an argon/nitrogen mixture (2.1 L h^{-1}, 4:1 M) was admitted until total hydrogen purge. Reactor temperature was increased to 540 °C, and the raction mixture of ethanol:water (0.9 L h^{-1} in gas phase, 1:5.95 M) was introduced. The space velocity (GHSV) was 26,000 h^{-1}.

The effluent mixture was analyzed on line by gas micro-chromatography with two channels (Poraplot Q; Molecular sieve 5 Å).

2.3. Carbon determination

The formation of the carbonaceous deposits was quantified by thermo-programmed oxidation (TPO) of a 0.05 g sample in an oxygen/helium mixture (50 mL min^{-1}, 10% (v/v)), heated from 25 to 900 °C at 15 °C min^{-1}. The gas effluents were followed by a quadrupole mass spectrometry.

3. Results and discussion

3.1. Characterization of catalysts: XRD

The structure of synthesized mixed oxides was studied by X-ray diffraction. Diffractograms obtained for the six fresh catalysts are presented in Fig. 1.

The synthesis process allows the crystallization of mixed oxides at the temperature of calcination (500 °C). In all diffractograms, we can observe diffraction lines at $d = 3.07$; 2.62; 1.88 and 1.60 nm that correspond to the pattern of diffraction of fluorite structure Ce–Zr. In the case of mixed oxides that contain nickel, the presence of two crystalline phases is observed. For the Rh–Ni/CeZr oxide, the presence of diffraction lines is clearly observed at $d = 2.42$; 2.09 and 1.48 nm, corresponding to NiO.

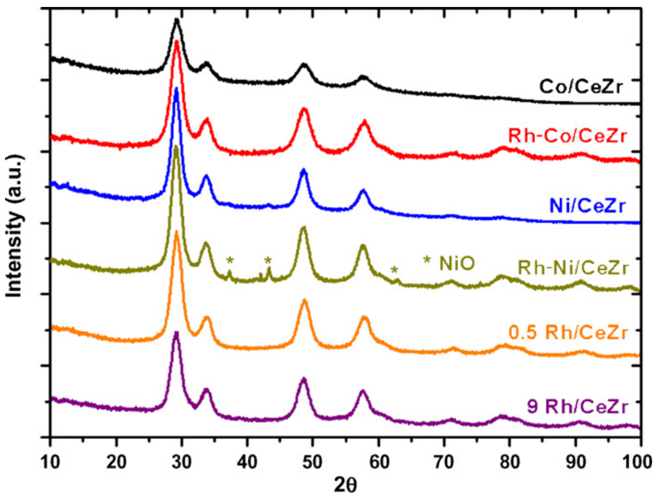

Fig. 1. Diffractograms of fresh mixed oxides Ce–Zr–Me.

In general, it is possible to be said that the preparation method is adapted for the mixed oxide synthesis of fluorite structure, depending on the nature of the metal to integrate in the structure. For cobalt and rhodium, both can be integrated to the structure of support Ce–Zr, obtaining a single crystalline phase. In the case of nickel, given its physicochemical properties, integration to the structure is more difficult. This rejection of nickel by the host structure (Ce–Zr), is more evident in the presence of a small amount of rhodium in mixed oxide, where two crystalline phases appear clearly in the pattern of X-ray diffraction.

3.2. *Characterization of catalysts: TPR*

In the ethanol reforming reaction, the state of reduction of the active phase and the catalyst in general has a great influence on the activity and catalytic stability. The presence of the active phase in metallic state and oxidized state confers greater stability to the catalyst. With the object of being able to relate these properties to the catalytic behavior, it is necessary to know the reducibility of the mixed oxides. In Fig. 2, thermograms of reduction of synthesized mixed oxides are presented.

From the analysis of the thermo-programmed reduction, the reduction pattern and the net hydrogen consumption can be established. For all synthesized oxides, independent of the metal, the reduction profile is similar; two zones of reduction are present, although at different temperatures for each mixed oxide.

The host structure of fluorite type, $Ce_2Zr_2O_8$, synthesized following similar routes of preparation reduced in two stages. First, it corresponds to reduction of Ce(IV) to Ce(III) at the surface (550 °C), and the second to the bulk reduction (850 °C). The presence of the transition metal or noble metal, changes the profile of reduction of the fluorite structure, diminishing the temperature of reduction. A similar phenomenon has been found for supported noble metal systems on CeO_2–ZrO_2 [17,18]. Therefore, if the temperature of reduction of the catalyst is equal to 450 °C, the reduction of mixed oxide is complex, the simultaneous reductions of the active phase and of a part of cerium of the host structure are encountered.

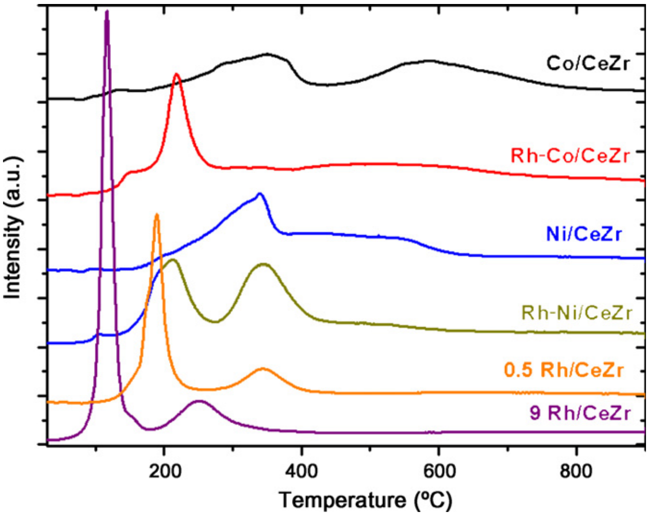

Fig. 2. Thermograms of hydrogen consumption in thermo-programmed reduction of mixed oxides Ce–Zr–Me.

For the oxides that contain only a transition metal (Co/CeZr and Ni/CeZr), the reduction proceeds in two stages, the first between 300 and 400 °C, and the second between 500 and 600 °C. The second stage of reduction appears at lower temperatures in the case of nickel, which can be correlated with the presence of nickel oxide in minor interaction with the host structure. For the cobalt integrated in the Ce–Zr oxide structure, the second stage of reduction proceeds at higher temperature.

The inclusion of a small amount of rhodium in the transition metal system has great influence in the profile of reduction of mixed oxide. For Rh–Co/CeZr and Rh–Ni/CeZr, it appears a zone of reduction at low temperatures (210–215 °C). This zone does not correspond solely to the reduction of rhodium since the area of the peak (proportional to the hydrogen consumption) corresponds to 25% of the total area, whereas, the content in rhodium is only 3%. It is interesting to observe that for the Rh–Ni/CeZr oxide, the second zone of reduction clearly appears far below (350 °C) of the Ni/CeZr system. Consequently, there is a part of the support that is reduced at lower temperature as a consequence of the rhodium presence along with the transition metal.

The catalysts containing only the noble metal (Rh/CeZr) present, the peaks of reduction is at the lowest temperatures. For greater rhodium content, the temperature of reduction is smaller. Therefore, it is evident that the presence of rhodium favors the reducibility of the support. This behavior has been attributed to a spillover effect of hydrogen, dissociated on the metal, and the surface of the support [19].

From the amount of hydrogen consumed in TPR knowing the total active metal content and that this one is reduced to the metallic state, the percentage of cerium reduction of the support can be calculated (Table 1).

From this calculation it is possible to demonstrate that the presence of rhodium favors the reducibility of cerium present in mixed oxide.

3.3. *Catalytic tests*

Previous experiments carried out in our laboratory on the ethanol reforming with mixed oxides Ce–Zr–Co as a catalyst have demonstrated that its partial reduction generates the phase Co^0/Ce–Zr–Co. This semi-reduced form of the catalyst turns out to be active and more stable than when the reduction is total

Table 1
Percentage of cerium reduced during TPR

Mixed oxide	$Ce^{IV} \rightarrow Ce^{III}$ (%)
Co/CeZr	23
Rh–Co/CeZr	28
Ni/CeZr	18
Rh–Ni/CeZr	29
9 Rh/CeZr	39
0.5 Rh/CeZr	29

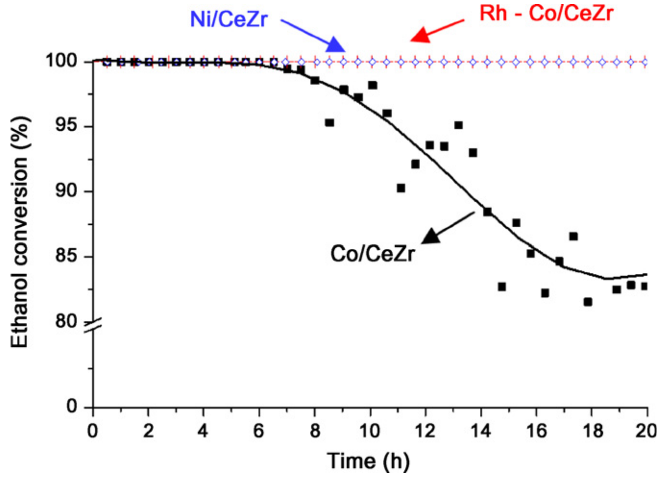

Fig. 3. Evolution of the ethanol conversion with time on stream for some catalysts.

(Co^0/Ce–Zr). This ''partial reduction'' corresponds to the minimum around 440 °C that can be observed in Fig. 2. With the intention of being able to compare all prepared mixed oxides in this work, the reduction *a priori* has been done at the same temperature (440 °C) and following the same procedure in all the cases.

The analysis of the effluent gases allowed us to follow the evolution of products with time on stream and the ethanol conversion.

In Fig. 3 appears the evolution with time of the ethanol conversion and in Table 2 is given the product distribution in the gaseous phase.

In the case of the Co/CeZr catalyst, it has been possible to observe a conversion of 100% during the 8 first hours of reaction. After 8 h, the conversion begins to diminish down to approximately 80% after 20 h on stream. During the time of total conversion (100%) the only products of the reforming reaction are H_2, CO_2, CO and CH_4, and later the formation of acetaldehyde, acetone and ethylene is detected [16].

The partial substitution of cobalt by a small amount of rhodium (Rh–Co/CeZr) remarkably improves the activity, the selectivity and the catalytic stability. Throughout the time of reaction, total conversion (100%) is observed and the formation of C_2H_4 is not observed.

For the mixed oxides that contain nickel and rhodium, the behavior is similar to that of the Rh–Co/CeZr oxide. The ethanol conversion is total, ethylene and oxygenated compounds are never detected over the test period. The product distribution stays constant during the time of reaction and is close to the equilibrium distribution anticipated by thermodynamic calculations, using the non-stoichiometric formulation also named the direct minimization of free energy method, using the same conditions of reaction for a mixture ethanol:water 1:6 M (ProSim Plus, Aspen Plus).

The product distribution in the gaseous phase presented in Table 2, allows the observation of the influence of the active phase on the catalytic selectivity. The catalysts that contain nickel and rhodium favor methane formation, between 3% and 5%. On the other hand, cobalt, although it presents minor selectivity towards hydrogen (63%), also presents the smallest methane formation, with 1% for cobalt only and 2% for rhodium–cobalt, as well as the greatest selectivity towards CO_2 (31%). May be in that case, a part of ethanol is consumed for the reduction of the catalyst, without any formation of hydrogen, this could explain the higher CO_2 production.

The relation between reaction products allows the observation that both nickel and rhodium favor CH_4 production at the expense of CO_2 production.

Table 2
Composition of the effluent after 6 h of reaction

Catalyst	H_2 (%)	CO_2 (%)	CO (%)	CH_4 (%)
Co/CeZr	63	31	5	1
Rh/Co/CeZr	66	27	5	2
Ni/CeZr	66	26	5	3
Rh/Ni/CeZr	64	26	5	5
9% Rh/CeZr	65	25	5	5
0.5% Rh/CeZr	66	24	5	5
Equilibrium composition[a]	68	22	6	4

[a] Calculated by the non-stoichiometric method of Gibbs free energy minimization.

3.4. Study of the carbonaceous deposits

The analysis of the catalytic behavior of Co/CeZr oxide suggests that the decrease of activity is accompanied by the by-product evolution (methane, ethylene, acetaldehyde). These compounds are considered intermediates of the reforming reaction and precursors of carbonaceous compounds [20–22]. For the mixed oxides with better stability, the ethylene production was not observed.

In order to determinate carbonaceous formation over the steam reforming reaction, catalysts have been analyzed by TPO. In Fig. 4 the signal of CO_2 ($m/z = 44$) production is presented as a function of temperature.

TPO profiles of the catalysts after ethanol steam reforming present two zones of oxidation at different temperatures. The zone of oxidation at lower temperature is associated to carbonaceous deposits in direct contact with the metallic

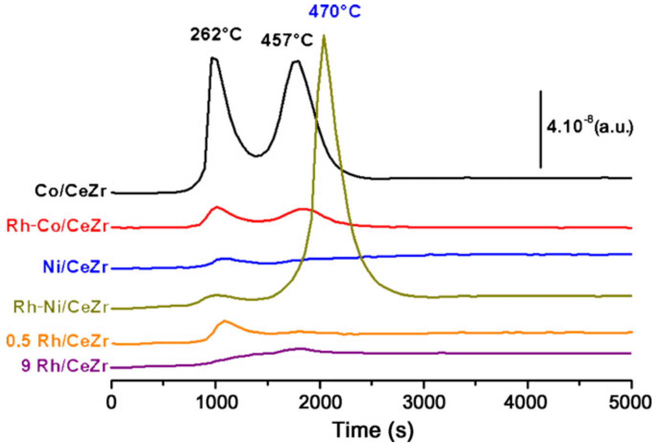

Fig. 4. TPO profiles of mixed oxides Ce–Zr–Me.

particle (superficial carbon) and the one at higher temperature is related to carbonaceous formations produced by carbenium ion mechanism (carbon filaments).

The TPO quantitative analysis shows an important carbon formation (≈8 μmol of C/mg of catalyst) on the Co/CeZr catalyst, of superficial and filamentous type. The addition of rhodium in cobalt doped Ce–Zr oxide diminishes the carbon amount formed on the catalyst until approximately 0.8 μmol of C/mg of catalyst, with the production of both types of carbonaceous compounds. That confirms that the deactivation of the catalyst is a consequence of the carbonaceous compounds formation that covers and/or destroys the catalytic active site.

In the case of the Ni/CeZr oxide, the carbon formation, mainly superficial, is very low (≈0.2 μmol of C/mg of catalyst). According to the literature, nickel activates the C–C bond and has a tendency to form great amounts of carbon. Nevertheless, due to the redox properties of the mixed oxide whose favor the activation of water in over-stoichiometric amounts, the gasification reaction the superficial carbon formed on the metallic particle is promoted and prevent its accumulation [23].

The rhodium addition has a negative effect on the nickel-doped Ce–Zr mixed oxide, increasing the amount of carbon deposits (≈4.5 μmol of C/mg of catalyst), mainly under carbon filament form. This result confirms the influence on the catalytic behavior of the degree of reduction of metallic phase and of the whole catalyst (support). For Rh–Ni/CeZr oxide, a large amount of NiO was evidenced (XRD), which is reduced in two steps at a lower temperature than reduction temperature (440 °C). Consequently, Rh–Ni/CeZr oxide is reduced deeper, resulting in a greater amount of metallic particles of larger size, in lower interaction with the support, favoring carbon filament formation, since the redox effect of the support is diminished in its oxidizing action [23].

Rhodium-doped Ce–Zr oxides (Rh/CeZr) present a low carbon formation (≈0.7 μmol of C/mg of catalyst). It is related to the powerful nature of Rh in breaking the carbon–carbon bond in ethanol [24] and to the redox properties of the mixed oxide [23]. A higher amount of rhodium does not have beneficial influence on the catalytic behavior in ethanol steam reforming reaction.

4. Conclusions

The method of preparation of the catalysts by pseudo sol–gel method, and mixed propionates decomposition, allows the synthesis of a mixed oxide Ce–Zr–Me, with cobalt, nickel and rhodium. The mixed oxides are precursors of efficient catalysts for ethanol conversion into hydrogen.

The use of the mixed oxide CeO_2–ZrO_2 as host structure and support, given its redox properties, diminishes the formation of carbonaceous deposits.

The only catalyst for which diminution of the catalytic activity has been observed, is the one obtained by doping with Co alone. The addition of a small amount of rhodium remarkably improves the stability of the cobalt catalyst, suppressing the formation of carbonaceous deposits.

The addition of rhodium to Ni/CeZr, leads to a rejection of nickel oxide by the host structure, and produces a mixed oxide of two crystalline phases. The reduction of this Rh–Ni/CeZr mixed oxide, in which the nickel is in lower support interaction, favors the carbon filament production and diminishes the redox support action.

The stability of the ethanol reforming catalyst is influenced by the active phase and support catalytic reduction states, and related to the carbonaceous compounds formation, whose type and amount have a large influence on the deactivation of the catalyst.

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