

The Efficiency of Co/CeO₂ Catalyst in Ethanol Steam Reforming Process

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A Co/CeO₂ catalyst for ethanol steam reforming process was prepared and characterized using different characterization techniques including X-ray diffraction, UV-Vis diffuse reflectance, FTIR spectroscopy, scanning electron microscopy (SEM), N₂ adsorption/desorption isotherms (BET) and thermal analysis method (TGA). The catalytic test in ethanol steam reforming process showed a high H₂ yield and almost complete ethanol conversion.

Keywords: ethanol, steam reforming, Co/CeO₂ catalyst

An alternative and promising way for production hydrogen, that is in attention of researchers worldwide, is the use of ethanol as raw material for steam reforming process.

It is a growing demand of the number of articles based on ethanol steam reforming process and different ways to find alternative renewable energy sources or environmental friendly fuels [1-4]. In the case of steam reforming the catalysts used are mainly Ni, Cu, Co and noble metal such Rh, Ru, Pd and Pt.

Although these catalysts present a good performance for steam reforming process their costs limits their large use. Cobalt on the other hand is less expensive and it has been reported in the literature to present good performance for this process mainly due to the capacity for C-C bond cleavage [5-7].

Different metal oxides have been used as support for Co catalysts in order to ensure a high surface area and a good thermal stability. Although almost all this supported cobalt catalysts present comparable activity, the mechanism of steam reforming process, involving the presence of different secondary products, is significantly different suggesting that this supports put their mark on the ethanol steam reforming process.

However, superior catalytic performance with good stability and high hydrogen production can be provided by supports with redox properties such as CeO₂. CeO₂ has a very high oxygen storage capacity this improving the resistance to coke deposition [8]. This increasing of oxygen mobility promotes gasification and oxidation of carbon deposits on the surface restoring the activity of the catalyst [9].

Wang et al. [10] studied the coke formation over Co/CeO₂ catalyst for steam reforming of ethanol. The authors get to the conclusion that when the reaction temperature is lower of 450°C, ethanol is dehydrogenated and/or dehydrated over Co/CeO₂ catalysts. When the reaction temperature increases appears the CO disproportionate reaction and cracking of CH₄. Finally at temperatures over 600°C, the authors confirm that coke formation is higher.

Wang et al. [11] studied the effect of ceria morphology. For steam reforming reaction, Co/CeO₂ (nanoparticles) was more active and exhibited superior anti-sintering ability, while Co/CeO₂ (nanorods) showed better anti-carbon deposition ability. They concluded that the morphology of ceria had effect on the catalytic performance of ceria supported cobalt catalyst for SRE (ethanol steam reforming) reaction, especially for anti-carbon deposition.

Song et al. [5] investigate the role of impregnation medium on the activity of ceria supported cobalt catalysts for ethanol steam reforming. The Co/CeO₂ catalyst prepared in ethanol medium presents higher catalytic performance compared to the one prepared in aqueous media.

From the characterization results, the authors discover the presence of oxygenated carbon species on the surface. These species are likely to play a role in the improved performance.

Lovon et al. [6] prepared by the polymeric precursor method Co/CeO₂ catalysts with different cobalt contents. The authors observed that the catalytic behavior could be influenced by the experimental conditions and the nature of the catalyst employed. The catalyst with the highest cobalt content showed the best performance in steam reforming process (SRE).

The objective of the present study was to prepare a bifunctional catalyst with lower cobalt content on a ceria support for efficient ethanol steam reforming to produce hydrogen. The catalyst was prepared through impregnation method. The catalytic behavior in the ethanol steam reforming process for hydrogen production was investigated by evaluating the effect of catalyst preparation.

Experimental part

Catalyst synthesis

Supported cobalt catalyst with 3wt% Co loading was prepared by impregnation method. Cerium (IV) oxide (nanopowder, Aldrich) was calcined at 550°C for 4 h in order to eliminate surface impurities. The synthesis started by dissolving about 7.4 grams of cobalt (II) nitrate hexahydrate in almost 25 mL of water followed up by a vigorous stirring up to complete dissolution. This solution was mixed with about 50 g of cerium oxide and then the content was dried at 100°C. Finally the prepared sample was calcined at 450°C under air flow for 3 h.

Catalysts characterization

XRD profiles were collected from 10 to 70° at a step of 2 s/step using Bruker D8 advance X-ray diffractometer equipped with a CuKα source (λ=1,5406 Å, 40 mA, 40 kV).

UV-Vis diffuse reflectance spectra were acquired with a JASCO 540V spectrophotometer in the 200-800 nm range. Magnesium oxide was the reference material.

The FT-IR measurements were performed with a Tensor 27 FT-IR Spectrometer Bruker, employing KBr pellet technique.

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Thermal analysis technique (TG-DTA) experiments were performed on a thermal analysis instrument SETARAM LABSYS EVO with a heating rate of 10°C/min in flowing air sample loading was typically 100 mg using an alumina crucible.

Adsorption/desorption isotherms provides data for the characterization of porous structure and pore size, pore volume and isotherm type which characterizes a specific structure. Nitrogen physisorption data were obtained on a Quantachrome Autosorb Automated Gas Sorption system at 77 K, after out-gassing at 473 K under vacuum.

The morphology of the sample was examined using a scanning electron microscope Quanta. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons.

Catalysts tests

Catalytic tests were carried out at atmospheric pressure in a fixed bed reactor, packed with 10 cm³ of catalyst placed in an oven at 300, 350, 400, 450 and 500°C.

Prior to reaction, the catalyst was treated under hydrogen atmosphere at 550°C for 6h. Water and ethanol were fed into the reactor using a Varian pump. Helium was used as carrier gas. The composition of gaseous effluent was analyzed in a gas chromatograph (Varian, 3800) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) connected in series. The chromatographic column is a Porapack-N column type.

The H₂ yield and ethanol conversion were defined as follows:

Ethanol conversion

$$X_{EtOH} = \frac{n_{EtOH_{in}} - n_{EtOH_{out}}}{n_{EtOH_{in}}} \times 100 \quad (1)$$

Hydrogen yield

$$\eta_{product} = \eta_{H_2} = \frac{g_{H_2}}{g_{mpreal}} \cdot 100 = \frac{\%H_2 \cdot g_{gas}}{g_{mpreal}} \quad (2)$$

where:

- X_{EtOH} - ethanol conversion
- n_{EtOH_{in}} - moles of ethanol in
- n_{EtOH_{out}} - moles of ethanol out of reactor
- η_{H₂} - yield of hydrogen
- g_{H₂} - mass of hydrogen
- g_{gas} - mass of gas produced in the experiments, g
- g_{mpreal} - real raw mass, g
- % H₂ - weight percent of H₂ obtained by chromatographic analysis of gas fraction (produced in reactor)

Results and discussions

Catalyst characterization

Catalyst prepared was characterized as mentioned before using various techniques, for better understanding the influence of structural characteristics on catalyst performances in the SRE process.

Figure 1 shows the XRD patterns of cobalt supported on ceria samples. Fluorite type CeO₂ was present in all the samples.

The crystalline structure type fluorite of CeO₂ is suggest by the main peaks at 2θ=28.75°, 33.13°, 47.50°, 56.25°, 76.25°, 79.37° attributed to a face centered cubic fluorite.

On the other hand it was observed that the peaks at 2θ=58.75° and 69.37° corresponds to the Co phase attributed to Co₃O₄ spinel.

Figure 2 presents the UV-VIS spectra for the samples. The two characteristics peaks for pure CeO₂ are 210 nm

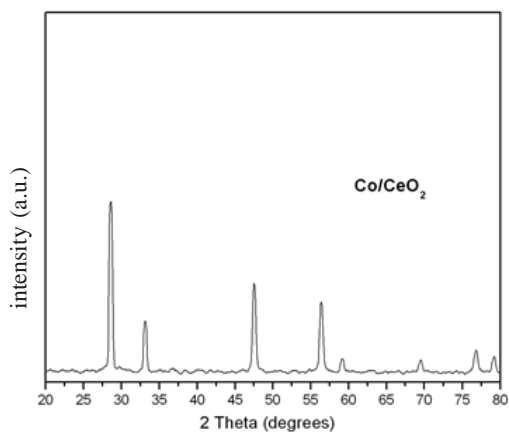


Fig. 1. XRD patterns of Co/CeO₂ catalyst

and 327 nm, attributed as f→d transitions of Ce³⁺ species, localized O-Ce charge transfer transition involving a number of surface Ce⁴⁺ ions and interband transitions in CeO₂, respectively. The absorption band at about 491.5 nm is due to transitions of octahedral Co³⁺, and the absorption band at 750 nm is due to transitions of tetrahedral Co³⁺. These bands indicate the formation of Co₃O₄ spinel represented by Co²⁺Co₂³⁺O₄²⁻.

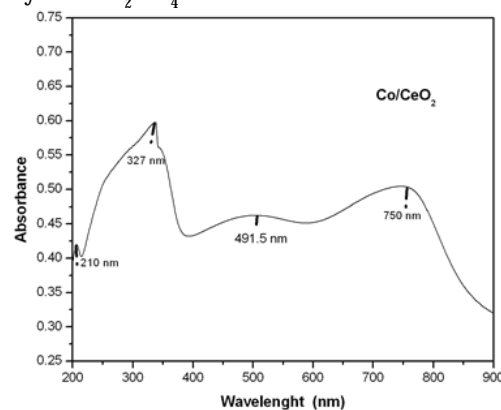


Fig. 2. UV-Vis spectra of Co/CeO₂ catalyst

Observing the FTIR spectra of the catalyst (fig. 3) we notice the presence of two bands located at 663.65 and 717.35 cm⁻¹ caused by the metal-oxygen typically vibration of the cubic structure of the Co₃O₄. The bands located at 2332.02 and 2661.98 cm⁻¹ can be attributed to the formation of ethoxide species.

The TGA profiles for Co/CeO₂ catalyst (fig. 4) shows the mass losses with several inflections due, first of water loss from cobalt hydrate and second to the nitrate anions decomposition, the nitrate was used as Co source (CoNO₃ · 6H₂O) in the impregnation process. The final loss was 2.5% of total mass of catalyst.

Figure 5 presents SEM images of the prepared sample. One can see the presence of agglomerates made of nanoparticles with average size between 20 and 30 nm. The SEM microphotograph shows typical hexagonal shaped particles for commercial cobalt oxide catalyst. The similar micrograph images were obtained for both ceria and cobalt promoted ceria catalysts, which confirms that the morphology remains unchanged even after cobalt loading. The SEM images also suggest the good dispersion of Co₃O₄ on ceria.

The specific surface area of the CeO₂ sample prepared in this work was 7.81 m²/g and for the catalyst Co/CeO₂ was 5.009 m²/g. A lowering of pore volume of ceria was observed, which is obviously due to impregnation of cobalt. This also suggests dispersion of cobalt oxide in the pores of ceria by using present method of synthesis. The pore volume for bare ceria and Co/CeO₂ was 0.06 and 0.04 cm³/g, respectively. This moderate reduction in surface area as

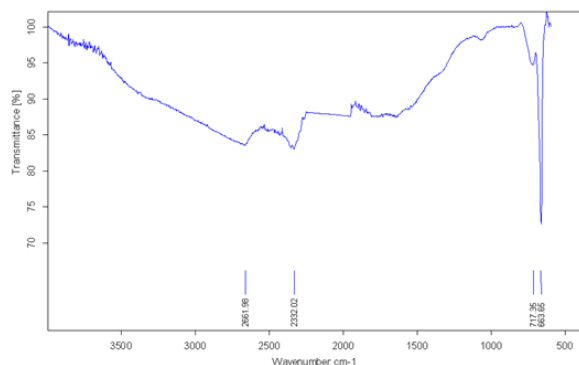


Fig. 3. FTIR spectra of Co/CeO₂ catalyst

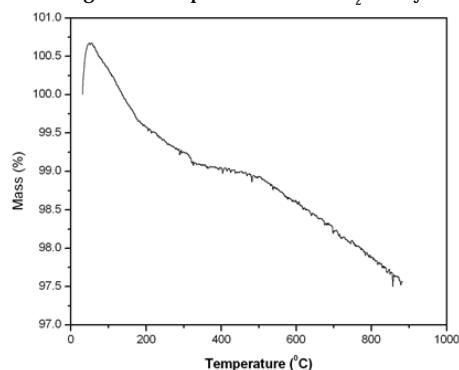


Fig. 4. TGA profile of Co/CeO₂ catalyst

Catalyst	Co/CeO ₂				
	300	350	400	450	500
Temperature (°C)					
EtOH conversion	71	72.3	75	80.2	82
H ₂ %	39.5	65.2	70.8	71	72.6
CH ₄ %	2.1	7.2	5.7	3.5	3.6
CO ₂ %	30.2	50.4	53	52.4	48.2
C ₂ H ₄ %	-	-	-	0.1	0.22
C ₂ H ₆ %	-	-	-	0.13	0.29
CO %	1.3	1.7	1.7	3.5	5.2
CH ₃ CHO %	15.8	-	-	-	-

well as pore volume is due to the dispersion of cobalt oxides in the pores of the ceria support.

Catalytic tests

The product distribution obtained for the catalyst Co/CeO₂ tested at five temperatures in the SRE process is presented in table 1.

At each temperature the catalyst, gave good yields in hydrogen and carbon dioxide and low yield in carbon monoxide and methane.

An important aspect is the secondary products distribution. It was observed the absence of the liquid product at temperatures above 350°C which means that acetaldehyde is transformed in methane and futher in hydrogen (see the mechanism presented in fig. 6). We note also the presence of small amount of by product as ethylene and ethane at higher temperatures. The presence of this secondary product suggests the involving of dehydration reaction in the reforming mechanism which can lead, further, to coke formation.

Anyway the catalyst remained active throughout the experiment maintaining a good ethanol conversion and hydrogen yield. Also, in this case, the yield in other byproducts remains at lower values.

Conclusions

In this study, prepared cobalt on CeO₂ catalyst prepared has been investigated for hydrogen production by the steam reforming of ethanol.

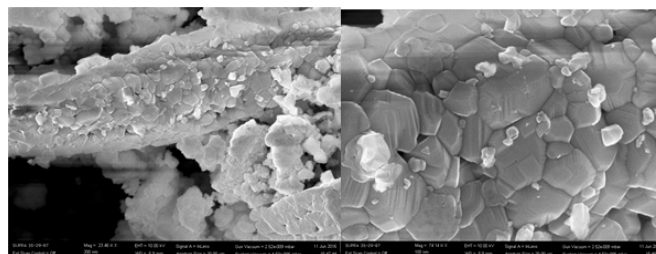


Fig. 5. Scanning electron micrographs of the Co/CeO₂

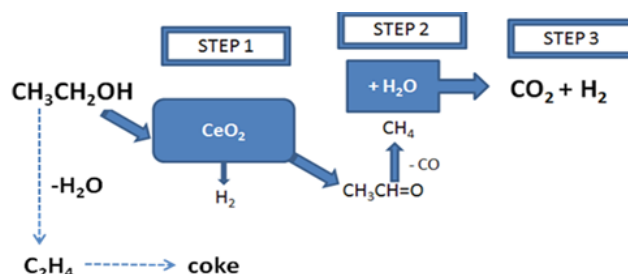


Fig. 6. The proposed mechanism for steam reforming reaction on Co/CeO₂ catalyst

Table 1
PRODUCT DISTRIBUTION OVER 3% Co/CeO₂
CATALYST AT VARIOUS TEMPERATURES. (C_{EtOH} = 10%,
WHSV=9h⁻¹)

This catalyst presents good properties for applications in the ethanol steam reforming process being effective for hydrogen production. It was found that CeO₂ support strongly influences the mechanism of the chemical process.

The results obtained from of the catalyst characterization showed the presence of oxygenated carbon species as possible acetate intermediates. These species appear to play an important role for improving the catalyst performance. Further researches are necessary to identify the exact importance of this impregnation phase medium.

References

1. BOGATU, L., CIUPARU, D., TANASESCU, C., Improving the Oxidation Stability and Biodegradability of Environmentally Friendly Lubricants, *Rev. Chim. (Bucharest)*, **61**, 2010, p. 1003
2. ZACCHERIA, F., MARIANI, M., PSARO, R., BONDIOLI, P., RAVASIO, N., Environmentally friendly lubricants through a zero waste process", *Applied Catalysis B: Environmental*, **181**, 2016, p. 581-586;
3. CURSARU, D., NEAGU, M., BOGATU, L., Investigations on the oxidation stability of biodiesel synthesized from different vegetable oils, *Rev. Chim. (Bucharest)*, **64**, 2013, p. 438
4. PERNA A., MINUTILLO M., JANNELLI E., Hydrogen from intermittent renewable energy sources as gasification medium in integrated waste gasification combined cycle power plants: A performance comparison, *Energy*, **94**, 2016, p. 457-465;

5. SONG, H., OZKAN, U.S., The role of impregnation medium on the activity of ceria-supported cobalt catalysts for ethanol steam reforming, *Journal of Molecular Catalysis A: Chemical*, **318**, 2010, p. 21-29;
6. LOVON, A.S.P., LOVON-QUINTANA, J.J., GIZELLE, I.A., VALENCA, G.P., et al., Preparation, structural characterization and catalytic properties of Co/CeO₂ catalysts for the steam reforming of ethanol and hydrogen production, *Journal of Power Sources*, **216**, 2012, p. 281-289;
7. MIHAI, S., NEGOIU, M., Synthesis and Characterization of Ni(II), Pt(IV), Pd(II), Co(II), Au(III), Cu(II) Complexes with Mixed Ligands, *Rev. Chim. (Bucharest)*, **60**, 2009, p. 222
8. GHITA, D., STANICA-EZEANU, D., ROSCA, P., VOICU, V., Steam Reforming of Bioethanol over Pt/CeO₂ Catalyst, *Rev. Chim. (Bucharest)*, **64**, 2013, p. 646
9. SONG, H., OZKAN, U.S., Ethanol steam reforming over Co-based catalyst: Role of oxygen mobility, *Journal of Catalysis*, **261**, 2009, p. 66-74;
10. WANG, H., LIU, Y., WANG, L., QIN, Y.N., Study on the carbon deposition in steam reforming of ethanol over Co/CeO₂ catalyst, *Chemical Engineering Journal*, **145**, 2008, p.25-31;
11. WANG, H., ZHANG, L., LI, M., LIU, Y., BAI, X., Co/CeO₂ for ethanol steam reforming: effect of ceria morphology, *Journal of rare earths*, **31**, 2013, p. 565-571.

Manuscript received: 3.11.2016