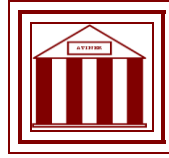


**Athens Institute for Education and Research
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**Hydrogen Production by Ethanol
Steam Reforming**

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Hydrogen Production by Ethanol Steam Reforming

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Abstract

The structure and surface properties of monometallic (Co or Ni) and bimetallic CoNi catalysts supported on MgAl₂O₄ for hydrogen production were studied applying different techniques for physicochemical characterization such as: XRD, TPR, XPS and XANES. The test reaction was ethanol steam reforming carried out at temperature interval of 250⁰-750⁰C and ratio H₂O/C₂H₅OH of 3/1. It was shown that the different behavior of catalysts in the C-C breaking depends mainly on the oxidation state of metal components. It was detected that the acetaldehyde production is large when the oxidation degree of metal components is maximum, i.e. the ethanol oxidative dehydrogenation takes place. Increasing the degree of metallic area in Ni and CoNi catalysts led to easily C-C bond cleavage, producing CO, CO₂ and H₂.

Keywords: Ethanol steam reforming, Hydrogen, CoNi catalysts, Characterization

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Introduction

Nowadays, the dependence on fossil fuels as energy sources has caused serious environmental problems, i.e. air pollutants and greenhouse gas emissions, and natural resource depletion. The need for renewable alternatives is becoming ever more urgent. Hydrogen has been identified as an ideal energy carrier to support sustainable energy development (Mattos *et al.*, 2012). Hydrogen can be used in a fuel cell to generate electricity with a high efficiency, since it is extremely clean as the only by-product is water. In order to support sustainable hydrogen economy, it is crucial to produce hydrogen cleanly and renewably. At present, steam reforming process of natural gas (CH₄) is the most commonly used and the most economically competitive method for hydrogen production. However, the natural gas, which is a kind of fossil fuel, provides the formation of a large amount of carbon dioxide emissions during the reforming processes. So, there is a growing interest in the search of effective alternatives to produce renewable hydrogen cleanly and safely. Among the various feedstock, ethanol is very attractive because of its relatively high hydrogen content, availability, non-toxicity, and storage and handling safety. Ethanol can be produced renewably by fermentation of biomass sources, such as energy plants, agro-industrial wastes, forestry residue materials, and organic fraction of municipal solid waste. The ethanol produced by this way is called as “bioethanol”. Therefore, ethanol steam reforming (ESR) is a promising method for hydrogen production from renewable resources.

One of the main challenges in ESR is the control of carbon deposition on the metal surface, which is a fundamental requirement for a stable and active catalyst. The use of suitable catalyst plays a crucial role in hydrogen production from ESR, since each catalyst induces different pathways in ethanol reforming. There is a fast deactivation of catalyst during ethanol reforming processes due to the carbon deposition over active metal phase. The active catalysts should maximize the hydrogen selectivity and inhibit coke formation as well as the CO production. It is well known that noble metal catalysts exhibit high catalytic activity in ESR (Cavallaro *et al.*, 2003; Fierro *et al.*, 2003). However, due to the high cost of noble metals the most commonly used catalysts in reforming processes for hydrogen production are Ni-based catalysts caused by their low cost and widely availability. In addition, the choice of Ni is the best one for hydrogen production by ESR since Ni has a high activity for C-C and O-H bond breaking and a high activity in hydrogenation facilitating the H atoms to form molecular H₂.

On the other hand, the selection of suitable support for catalyst and the methods of catalyst preparation significantly affect the catalyst activity. The most used support is γ -Al₂O₃ due to its high specific surface area and high thermal stability. But, alumina-supported Ni or noble metal catalysts deactivate very fast in SRE due to the acidic character of support that is favoring the ethanol dehydration to ethylene, which is a source for carbon formation. In terms of hydrogen production and long-term catalyst stability it was shown that

the addition of metal with basic nature to alumina can favor the ethanol reforming to hydrogen and suppress the carbon species formation. The development of bimetallic catalyst or alloy catalyst is also promising to enhance the hydrogen production and long-term Ni-based catalyst stability. It was shown (Batista *et. al.*, 2004) that Co catalyst studied in ESR reaction revealed lower hydrogenation activity of CH_x^* radicals at low reaction temperatures compared to that of Ni one due to the electronic properties of Co. In addition, Co has better ability to oxidize carbon deposits, which are accumulated during ethanol reforming. The modification of Ni catalyst by adding of Co could lead to increase of metal dispersion, degree of *reduction and/or to favor the proceeding of ethanol reforming to hydrogen at lower reaction temperatures and to suppress the carbon accumulation.

In the present work it was attempted the development of bimetallic CoNi catalyst supported on a basic support like MgAl_2O_4 for hydrogen production by ethanol steam reforming. Different techniques have been used for physicochemical characterization of the samples such as: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (TPR) and X-ray absorption near edge structure (XANES). Test reaction was ethanol steam reforming at different reaction temperatures.

Experimental

Sample Preparation

MgAl_2O_4 -supported CoNi catalysts were prepared by incipient wetness co-impregnation of MgAl_2O_4 with aqueous solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99%) and $\text{Co}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Aldrich, 99%) at 343 K. The samples were dried at 110°C and calcined at 550°C under synthetic air for 12 and 6 h, respectively. The MgAl_2O_4 support was prepared by a sol-gel method described in Ref. (Avila-Neto *et al.*, 2012). The samples were abbreviated as 8Co, 8Ni and 4Co4Ni, where the number represents the metal loading.

Sample Characterization

XPS

XP spectra of the samples previously reduced in the chamber at 750°C in flow of 10% H_2/He for 2 h were recorded with a SPEC SLAB II PHOIBOS HSA 3500 150 spectrometer containing nine detection channels and a hemispherical analyzer, employing Al *K α* radiation (1486.6 eV). The analyzer was operated in constant pass energy mode ($E_{\text{pass}} = 40$ eV). Binding energies (BE) were referenced to Al 1s core level of γ -alumina (121 eV). The vacuum level during the experiments was below 10^{-7} Pa.

XANES

Temperature resolved X-ray absorption near edge spectroscopy analysis in situ under H_2 atmosphere (H_2 -XANES) was performed at Co K edge (7709 eV) and Ni K edge (8333 eV) under a 5% H_2/He flow, heating from room

temperature up to 750°C K at 10°C min⁻¹, as the last temperature was kept for 1 h. D06A-DXAS beam line at Brazilian Synchrotron Light Laboratory was used. The samples were prepared as self-supporting pellets containing 60 mg of catalyst and placed into a tubular quartz furnace sealed with kapton refrigerated windows for the transmission measurements. The information about the oxidation state and the proportion of CoO, Co₂O₃, NiO and of Co and Ni metal evolution in the TPR experiments of the samples was achieved by the linear combination fitting (LCF) method.

TPR

TPR profiles of fresh samples were recorded on a Micromeritics AutoChem II 2920 with a thermo-conductivity detector (TCD). In order to remove surface contaminants, the sample (0.150 g) loaded in a quartz reactor was pretreated at 200°C in a He stream for 1 h. After cooling to r.t. a flow of 10% H₂/N₂ (30 ml/min) was passed through the sample and the temperature was raised up to 1000°C at a rate of 10 K/min while the TCD signal was recorded.

In the same TPR apparatus described above, N₂O titration was used to determine the area and dispersion of metallic particles. The samples were previously reduced up to 750°C in a 10% H₂/N₂ flow for 1 h and after that were cooled to 60°C in a N₂ flow and exposed to N₂O impulses (1 ml) for 5 min. The metallic area was calculated according the Ref. (Sato *et al.*, 2013).

Test Reaction

The steam of reforming of C₂H₅OH was carried out in a vertical fixed-bed reactor made of quartz tube under atmospheric pressure and at temperature interval 250° – 700°C with a molar ration of H₂O/C₂H₅OH=3/1. The catalyst sample was 120 mg. Before to each reaction test, the catalyst was reduced in situ by heating in a 10% H₂/N₂ flow at 750°C K at a rate of 10 K/min and maintaining the temperature for 1 h. The reaction products were analyzed in a gas chromatograph (VARIAN 3400CX) with a Chromosorb 102 packed column, while hydrogen was detected by mass spectrometry (Pfeiffer PrismaPlus).

Results and Discussion

Physicochemical Properties

Comparing the values of the average metallic area, dispersion and particle size of Co and Ni for reduced samples (at 750°C) obtained by N₂O chemisorption (Table 1) it can be concluded that the highest values are obtained for monometallic Ni catalyst in opposite to that observed for Co. It means that the MgAl₂O₄-supported Ni catalyst is well reduced. Adding of Co to Ni catalyst leads to a decrease of metallic area, as well as the size of metallic particles. This could be related to the presence of a high concentration of oxide

species in the bimetallic CoNi system under its treatment in a hydrogen atmosphere caused by some interaction between Ni and Co.

The intimate contact between Co and Ni is also supported by the results of XPS analysis of reduced monometallic and bimetallic catalysts. The values of BEs of Ni 2p_{3/2} and Co 2p_{3/2} core electrons and atomic XPS ratios of reduced samples are listed in Table 1. BEs of Ni 2p_{3/2} (855.48-855.98 eV) and Co 2p_{3/2} signals (780.83-781.05 eV) for oxide samples characterized Ni²⁺ and Co²⁺ ions, respectively. It should be noted that these values are higher compared to those characteristics of bulk NiO (854.5 eV) and Co₃O₄ (779 eV) (Andonova *et al.*, 2011). This one would be related to the strong interaction of the nickel and cobalt oxide species with the support surface as well as due to the interaction between Ni and Co in the case of bimetallic CoNi sample. Some displacement in the BEs is observed for reduced samples (Table 1). For bimetallic CoNi system the BE of Ni 2 p_{3/2} (852.84 eV) is higher compared to that of monometallic 8Ni (852.52 eV). In the same time, the BE value of Co 2p_{3/2} for bimetallic CoNi system (778.47 eV) is significantly lower relative to that of monometallic 8Co (781.76 eV). It means a deficient of electrons in the environment of Ni in opposite to that observed for Co, most probably, caused by the interaction between Co and Ni and alloy formation. The same phenomenon was observed by (Zhang *et al.*, 2009).

Table 1. Characteristics from N₂O Chemisorption, BE Values of Ni 2p and Co2p Signals for Co, Ni and CoNi Samples

Sample	Dispersion (%)	Metal area (%)	Particle size (nm)	Ni 2p _{3/2} (eV)	Co 2p _{3/2} (eV)
8Ni	16.6	8.83	6.1	852.5	-
4Co4Ni	13.6	7.29	7.4	852.8	778.5
8Co	1.4	0.79	-	-	781.8

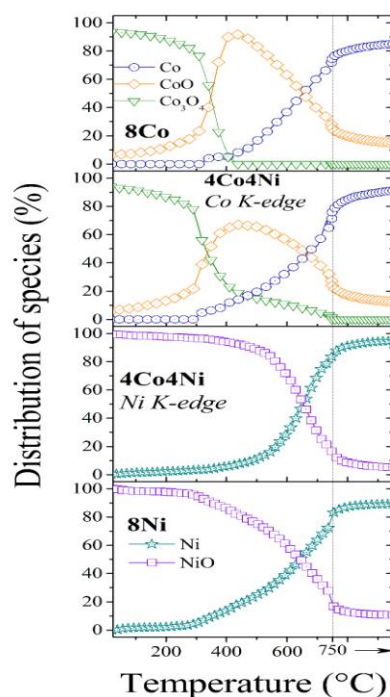
It should be noted that the XPS spectra (not shown) of reduced monometallic Co sample exhibited a major concentration of Co²⁺ species in comparison to that of Co⁰ that could be caused by the higher dispersion of the small cobalt particles in a strong interaction with support. The higher surface atomic XPS Ni/Co ratio for reduced bimetallic sample (2.8) than that of calcined sample (1.6) means a segregation of Ni on the Co particles and formation of a structure similar to *core-shell* type.

Additional insight regarding the influence of Co addition to MgAl₂O₄-supported Ni on the metal oxidation state was investigated by in situ temperature-resolved XANES spectroscopy at K-edge of Ni and Co during sample reduction in a hydrogen atmosphere up to 750°C. The percentage exchange of nickel and cobalt species in monometallic and bimetallic CoNi systems is shown in Fig. 1. It can be seen that at low reduction temperature there is no significant alteration in the percentage of Ni species for 8Ni sample. More visible change is observed above 300°C: the percentage of NiO species decreases with increasing the reduction temperature, while that of metallic Ni

component increases. The Ni oxide species on the surface of bimetallic CoNi system are characterized by a higher reduction temperature compared to that of Ni sample (above 400°C). The latter suggests that the presence of Co suppresses the reduction of Ni at lower temperatures. In addition, the latter stage of TPR experiments at higher reduction temperature (at 750°C) shows a higher fraction of reduced Ni species for CoNi in relation to that of 8Ni.

Despite the observed similarity in the percentage change of Co species for Co and CoNi samples there is an important difference related to the reducibility and reduction temperatures of the transformation of Co oxide species to metallic cobalt for both samples (Figure 1). For monometallic 8Co sample the percentage change of Co species under hydrogen treatment clearly demonstrates the two step reduction process of Co_3O_4 species to metallic Co^0 passing through the formation of CoO as an intermediate (Ji *et al.*, 2009). The reduction temperature of the first step transformation of Co_3O_4 to CoO is significantly lower for monometallic Co sample and finished at about 500°C. Above that temperature the formation of Co^0 is due to the reduction of CoO to Co^0 (second step). In the case of CoNi sample the presence of Co_3O_4 is observed up to a higher reduction temperature of 750°C, which is accompanied with a high fraction of metallic Co and with a decreased amount of CoO.

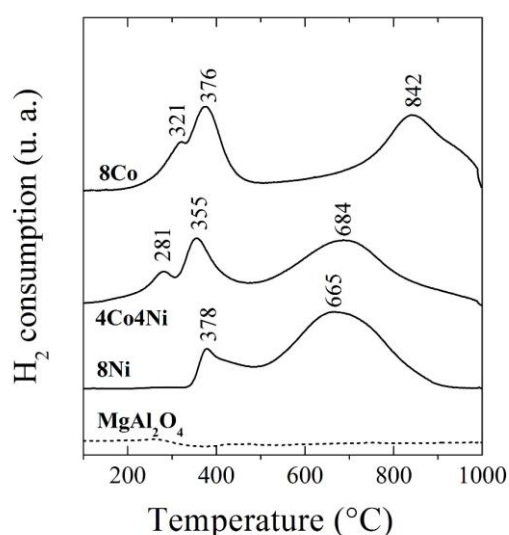
Figure 1. Percentage Change of the Ni and Co Species of the Samples during *in situ* XANES- H_2 at K-edge of Ni and Co



In addition, the fraction of metallic Co for this sample is high at lower reduction temperature interval (300-500°C) as well as at the end of reduction process. It can be concluded that more easy reduction of Co species to Co^0 is observed for bimetallic system. The directly transformation of Co_3O_4 species to Co^0 for CoNi is prevailing at higher temperature. It is important to note that fractions of metallic Co and Ni, as well as fractions of Co and Ni oxide species are observed for all samples at the end of reduction process at 750°C. The reducibility of Co and Ni for bimetallic system is improved, being confirmed by the higher fraction of metallic species at the end of reduction.

Information about the reduction of Co and Ni oxide species on the surface of MgAl_2O_4 support in monometallic and bimetallic systems was also obtained by the TPR. Fig. 2 shows the TPR profiles of Co, Ni and CoNi samples. The TPR profile of 8Ni exhibits a low temperature feature at 378°C as well as a strong asymmetric TPR signal with maximum at about 665°C due to the reduction of bulk NiO clusters weakly bound to MgAl_2O_4 surface and to the reduction of small NiO crystals in a strong interaction with support, respectively. It means a presence of Ni oxide species with different morphology on the surface of MgAl_2O_4 . The TPR profile of 8Co can be derived into two major features. The first peak at 376°C with a shoulder at 321°C can be related to a two-step reduction process of Co_3O_4 to metallic Co^0 passing through the formation of CoO as an intermediate that is similar to XANES results. The hydrogen consumption in the higher temperature region could be caused by the reduction of well dispersed Co oxide species in a strong interaction with support. Addition of Co to Ni sample leads to a visible change in the reduction profile of bimetallic 4Co4Ni system.

Figure 2. TPR Profiles of Monometallic and Bimetallic CoNi Catalysts

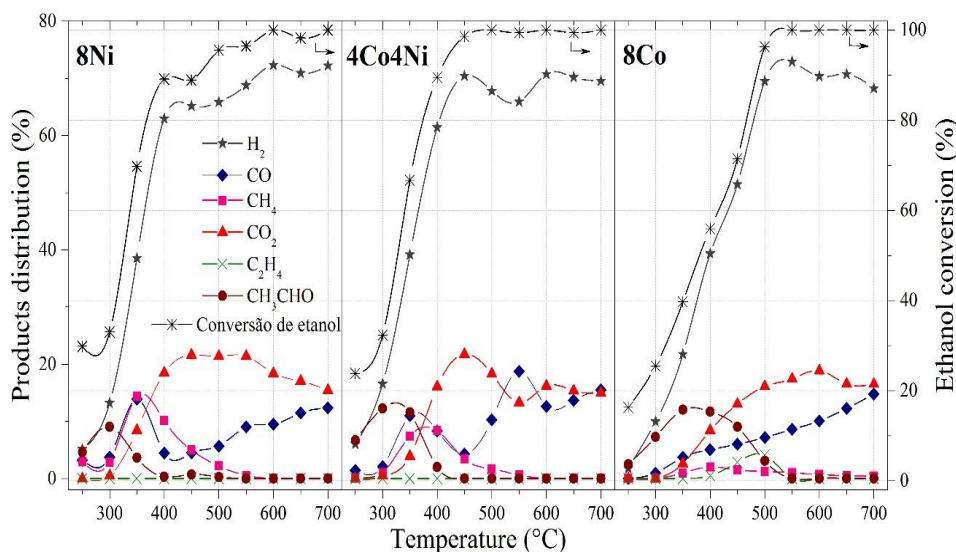


The initial stage of reduction of oxide species of CoNi sample is shifted to relatively lower temperatures than that of monometallic Ni and Co samples

(Figure 2). According to the results in the literature (Zhang *et al.*, 2008), the formation of Ni-Co-alloy during the reduction can be occurred. The latter facilitates the reduction process to proceed at lower temperature. In the same time the maximum of hydrogen consumption of CoNi sample in the higher TPR region is shifted to a higher value indicating a stronger interaction of the well dispersed Co and Ni species with support.

Catalyst Behaviors in ESR

Figure 3 shows the ethanol conversion and the products distribution as a function of reaction temperature in the interval of 250-700°C. From the Figure 3 it can be seen that the ethanol conversion for all samples increases with increasing the reaction temperature and the maximum conversion of ethanol to CO₂, CO and H₂ is achieved at 600°, 450° and 550°C for 8Ni, 4Co4Ni and 8Co samples, respectively. The reaction pathways of ethanol steam reforming at lower temperatures is strongly dependent on the capacity of the active metals for breaking the C-C bond in ethanol molecule. The results for Ni catalyst show that at low temperature of 300°C ethanol is first dehydrogenated with desorption of CH₃CHO and H₂. Increasing the temperature up to 350°C in parallel to a hydrogen abstraction from ethanol molecule, the C-C bond scission and decomposition of acetaldehyde is also observed, resulting in the formation of CH₄, CO and H₂ with a CO/CH₄ ration of about one. Over monometallic Co catalyst the relative abundant acetaldehyde at 300°C indicates that Co has weaker capability of breaking the C-C bond in ethanol molecule. Above this temperature products due to C-C scission begin to be observed. A low CO/CO₂ ratio up to 500°C is detected for Co catalyst that can be related to the presence of oxide Co species decreasing the ability of C-C breakage. The catalytic behavior of CoNi catalyst at lower temperatures is between those of the both monometallic catalysts (Figure 3). At lower temperatures acetaldehyde is mainly formed on the surface of bimetallic system, but in an amount much lower compared to that observed for Co catalyst that means a better reducibility of bimetallic catalyst.

Figure 3. Evaluation of Ethanol Conversion and Chemicals Products as a Function of Reaction Temperature

Above 300°C the behavior of CoNi is similar to that of Ni in spite of the lower amount of CH₄. Above 400°C the amount of CO₂ increases for all catalysts due to the activation of water and activation of water-gas shift reaction (WGSR) that leads to hydrogen production. However, over Co surface in spite of the formation of CO, CO₂ and H₂ in low concentration, a high amount of desorbed CH₃CHO is still present due to the high concentration of oxide species. Above 550°C an inversion in the CO₂/CO ratio is revealed for all catalysts, most probably caused by the reverse of WGSR.

Conclusions

Using MgAl₂O₄ as support for monometallic Co and Ni as well as for bimetallic CoNi catalyst can guarantee a high thermal stability of the catalysts. Addition of Co to Ni catalyst leads to: (i) alloy formation, which changes the electronic properties of bimetallic catalyst and (ii) improving the redox properties.

According to the thermodynamic calculations by (van Steen *et al.*, 2005) Co particles less than 4 nm are instable and can be easily oxidized in the presence of steam due to the increased free energy on the surface. This is in accordance with the loss of activity of 8Co catalyst under ESR process due to the decrease of the number of active centers (Figure 3). In the case of bimetallic CoNi catalyst the oxidation state of Co is stabilized to Co⁰ due the presence of alloy and the redox properties of catalyst are improved.

It is important to note that the formation of CH₄ is a very important point for ESR mechanism. The 8Ni catalyst demonstrates the highest activity to hydrogenation of CH_x radical caused by the C-C cleavage. Monometallic 8Co

catalyst leads to less methane formation due to the lower number of the active metallic centers. According to (Watwe *et al.*, 2000) the free energy for hydrogenation of CH_x species is low over Ni surface that support our conclusions. Increasing the reaction temperature leads to formation of products from the ethanol decomposition: H_2 , CO and CO_2 . It is important to note that for bimetallic catalyst the selectivity to H_2 production is higher as well as less carbon is formed. This means that the electronic properties of 4Co4Ni catalyst are more evident that leads to a more selective and stable catalyst.

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