

XANES and EXAFS study of supported CoNi catalysts for ethanol steam reforming

A. Braga¹, J. B. dos Santos¹, S. Damyanova^{2*}, J. M. C. Bueno¹

¹ Departamento de Engenharia Química, Universidade Federal de São Carlos, Box 676, 13565-905 São Carlos, SP, Brazil

² Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St. Block 11, 1113 Sofia, Bulgaria

Received October 10, 2015; Revised November 17, 2015

Monometallic nickel and cobalt and bimetallic CoNi catalysts supported on MgAl₂O₄ were synthesized. The electronic structure of the catalysts was characterized by in situ X-ray absorption near edge structure and extended X-ray absorption fine structure techniques. It was shown that the reduction of cobalt oxide species in Co-containing samples involved two reduction steps: the first one is reduction of Co₃O₄ to CoO and the second one is transformation of CoO to Co⁰. For the bimetallic CoNi system, there was a coexisting of Co³⁺, Co²⁺, and Co⁰, as the first step was completed at a higher reduction temperature of 750°C. The presence of cobalt in the bimetallic CoNi catalyst suppressed the reduction of nickel oxide species at lower temperatures. Different reaction pathways were running in parallel during ethanol steam reforming as revealed by product distribution changes as a function of reaction temperature. The last one was related to a change of the fractions of the oxidic and metallic Co and Ni species under reaction conditions. At a low reaction temperature of about 400°C, the highest selectivity to hydrogen was observed with the bimetallic CoNi catalyst due to an intimate contact between cobalt and nickel, which stabilizes catalytically active metallic centres.

Keywords: CoNi catalyst, hydrogen, ethanol steam reforming, XANES, EXAFS.

INTRODUCTION

Recent developments indicate that in the near future hydrogen will be used largely as a secondary energy carrier to produce electricity for mobile and small-to-medium scale stationary applications [1]. Hydrogen is an ideal energy carrier for sustainable energy development because the only product upon its burning is water. Hydrogen has the potential to solve two major challenges: restrict dependence on imported petroleum and reduce pollution and greenhouse emissions. Currently hydrogen is mainly produced from a fossil source (natural gas) that gives large amounts of CO₂ emissions. Developing technologies based on renewable resources have received much attention due to increasing costs of fossil resources, possibilities to carry out processes in more friendly conditions, and environmental appeal. Bioethanol, produced by biomass fermentation, is a promising feedstock for hydrogen production. Ethanol is advantageous over other conventional substrates because it is readily available, easy to obtain from biomass and to transport, CO₂ neutral and safe to handle. Ethanol steam reforming (ESR) (Eq. 1) is one of the possible industrial processes for hydrogen production:



Depending on catalyst used and operating conditions employed, several reactions may run in parallel, such as ethanol decomposition, dehydrogenation and dehydration, methane reforming, water-gas shift (WGS) and hydrogenation reactions producing acetaldehyde, hydrogen, methane, carbon oxides, and ethylene [2].

One of the major problems in ESR is coke formation on the catalyst surface, which may take place via several processes, such as ‘Boudouard’ reaction [3], methane decomposition, and cracking of ethylene produced by ethanol dehydration [4]. Carbon deposition can be avoided at high reaction temperatures (> 400°C), by using suitable catalyst, support, and promoter. However, high reaction temperatures enhance formation of by-product carbon monoxide, due to thermodynamically favoured reverse WGS and dry methane reforming. It is well known that CO concentration in PEM fuel cell systems should be reduced to less than 50 ppm [5].

Ethanol can also be reformed at low reaction temperatures (300–400°C) giving a gaseous mixture of H₂, CH₄, carbon monoxide, and carbon dioxide. CO content can be significantly reduced by involving a WGS activity function in the catalyst for-

* To whom all correspondence should be sent:
E-mail: soniad@ic.bas.bg

mulation or by a decrease of CH₄ selectivity by retarding CO methanation.

The mechanism of ethanol steam reforming has been extensively studied. Catalysts based on Ni, Co, Ir, Pt, Pd, Rh, and Ru dispersed on different supports, such as Al₂O₃, CeO₂, La₂O₃, ZrO₂, TiO₂, and MgO have been examined [6–9]. However, there are controversial opinions about the role of the surface oxidation state of metals in the different pathways of ESR reaction, carbon deposition, and catalyst deactivation [2]. It was proposed that some reaction pathways are favoured, depending on the nature of support, resulting in a different product distribution in the gas phase.

In this work, it was attempted to discuss the different reaction pathways of ESR over monometallic nickel and cobalt as well as over bimetallic CoNi catalysts as a function of metal composition and reaction temperature. MgAl₂O₄ was used as a catalyst carrier due to its high basicity. A detailed characterization of the samples was performed to point structural and electronic modification of MgAl₂O₄-supported nickel catalyst by cobalt addition. X-ray adsorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) methods were used for sample characterization.

EXPERIMENTAL

Sample preparation

MgAl₂O₄ carrier was prepared by sol-gel method described elsewhere [10]. MgAl₂O₄-supported nickel and cobalt catalysts were prepared by incipient wetness impregnation of carrier with aqueous solution of Ni(NO₃)₂·6H₂O (Aldrich, 99%) and Co(NO₃)₂·6H₂O (Aldrich, 99%), respectively. The obtained solids were dried and calcined in airflow at 110 and 500°C for 12 and 6 h, respectively. The total metal loading was 8 wt.%. The samples were labelled as 8Ni, 4Co4Ni, and 8Co, where numbers represent amount of respective metal.

Sample characterization

XANES analyses were performed at the K edge of Co (7709 eV) and Ni (8333 eV) using D06A-DXAS beamlines of Brazilian Synchrotron Light Laboratory at Campinas. Each sample was first crushed and sieved to particle sizes smaller than 20 μm and pressed into self-supporting pellets. Then the pellets were placed inside a tubular quartz reactor equipped with refrigerated kapton windows that were transparent to the X-ray beam. Temperature-resolved XANES spectra were acquired during reduction of the samples, which was achieved by heating at a rate of 10 deg.min⁻¹ from room temperature

to 750°C, with a holding time of 60 min, under a 200 ml.min⁻¹ flow of H₂/He (5 vol.%). Energy calibration of the XANES spectra was performed by means of open source ATHENA/IFEFFIT software. A linear combination analysis was performed using Co⁰, CoO, Co₃O₄, Ni⁰, and NiO references [10].

In situ XANES spectra at the K edge of cobalt and nickel catalysts under ethanol steam reforming conditions were realized. The reactor with samples reduced at 750°C was cooled to room temperature under He flow and then switched to a flow of 3.9 ml.min⁻¹ of ESR mixture (water/ethanol at a molar ratio of 3:1), diluted in 133 ml.min⁻¹ of helium. The samples were heated from room temperature to 750°C at 10 deg.min⁻¹ and the XANES spectra were acquired 10 min after reaching a steady state.

EXAFS analyses at the K edge of Co (7709 eV) and Ni (8333 eV) were performed at the D04B-XAFS1 beamlines of LNLS. A general description of these beamlines can be found elsewhere [11]. The samples placed in the quartz reactor were reduced under 200 ml.min⁻¹ flow of H₂/He (5 vol.%) by heating to 750°C at a heating rate of 10 deg.min⁻¹. The samples remained at the reduction temperature for 1 h followed by acquisition of EXAFS spectra at room temperature. Background subtraction, normalization, and alignment of the EXAFS data were performed by the ATHENA/IFEFFIT software [12]. Structural parameters were obtained from a non-linear least squares fitting of the EXAFS data processed by ARTE-MIS/IFEFFIT software [12]. Coordination numbers (CN) were fixed for all references (Co⁰, CoO, Ni⁰, and NiO) and floated for the samples. Average interatomic distance (R) and structural Debye-Waller factor ($\Delta\sigma_s^2$) values were allowed to float during the fitting. Table 1 provides fitting results of EXAFS spectra acquired at the K edge of Co and Ni of the samples reduced at 750°C.

Table 1. EXAFS parameters for reduced samples at 750°C.

Sample	Metal-metal		Metal-oxygen	
	CN	R(Å)	CN	R(Å)
Ni/NiO	12	2.48 ± 0.002	6	2.093 ± 0.003
Co/CoO	12	2.496 ± 0.003	6	2.130 ± 0.020
8Ni	9.6 ± 0.5	2.485 ± 0.001		
4Co4Ni	6.7 ± 0.3	2.481 ± 0.001	1.0 ± 0.1	1.949 ± 0.006
4Co4Ni	6.5 ± 0.6	2.485 ± 0.002	2.2 ± 0.9	1.978 ± 0.021
8Co	3.4 ± 0.2	2.490 ± 0.002	3.0 ± 0.2	1.973 ± 0.005

Ethanol steam reforming reaction

The steam reforming of C₂H₅OH was carried out in a vertical fixed-bed reactor made of quartz tube under atmospheric pressure at temperatures of 250–750°C with a molar H₂O to C₂H₅OH ratio of 3/1.

Catalyst loaded sample was 120 mg. Before reaction test, the catalyst was reduced in situ by heating at 750°C in a 10% H₂/N₂ flow at a rate of 10 deg.min⁻¹ and keeping the temperature for 1 hour. The reaction products were analysed by a VARIAN 3400CX gas chromatograph equipped with a Chromosorb 102 packed column, while hydrogen was detected by mass spectrometry (Preiffer PrismaPlus).

RESULTS AND DISCUSSION

XANES analysis

An insight regarding metal oxidation state of metal components in MgAl₂O₄-supported monometallic Co(Ni) and bimetallic CoNi samples was investigated by in situ temperature-resolved XANES spectroscopy at K-edge of nickel and cobalt during sample reduction under hydrogen atmosphere up to 750°C. The percentage change of nickel and cobalt species in monometallic and bimetallic CoNi systems is shown in Fig. 1. There is no significant alteration in percentage of Ni species in the Ni sample at a low reduction temperature (up to 300°C). A change that is more visible is observed above 300°C: the percentage of NiO species decreases on increasing the reduction temperature, while that of metallic nickel (Ni⁰) component is increased. The reduction of Ni oxide species on the surface of the bimetallic CoNi system is characterized by a higher reduction temperature compared to that of the Ni sample (above 400°C). The latter suggests that the presence of cobalt suppresses nickel oxide reduction at lower temperatures, which is possibly caused by coexistence of Co³⁺, Co²⁺, and Co⁰ ions (see below). This could be related to a strong interaction between nickel and cobalt, probably due to formation of a phase similar to NiCo₂O₄ [13].

The reduction process of cobalt oxide species involves two reduction steps, as seen in Fig. 1: reduction of Co₃O₄ to CoO and transformation of CoO to metallic cobalt (Co⁰). Co₃O₄ reduction to CoO for the Co sample is finished at 410°C with a maximum percentage of CoO (95%) achieved at this temperature. The maximum rate of transformation of Co₃O₄ to CoO started at the inflection point of the CoO percentage curve at 349°C (Fig. 1). The second reduction process of CoO to Co⁰ has occurred at a temperature higher than 410°C.

For the bimetallic CoNi sample, inflection point temperature decreases from 349 to 332°C (Fig. 1). There is a coexisting of Co₃O₄ → CoO and CoO → Co⁰ transitions. The maximum percentage of CoO (67%) occurs at 453°C accompanied with the presence of Co₃O₄ (18%). The first step of CoNi reduc-

tion is finished at a higher temperature of 750°C compared to monometallic Co (Fig. 1). It is interesting to note that both the CoO and Co⁰ species in the Co-containing samples are present at the end of reduction process (Fig. 1). In addition, the fraction of metallic Co in the monometallic Co is high at a lower reduction temperature interval (300–500°C) as well as at the end of reduction process.

Reduction of Co²⁺ species to Co⁰ for the bimetallic system starts at a lower temperature (300°C) if compared to the monometallic Co sample (360°C). The latter is due to H₂ activation over the surface of metallic nickel species as the hydrogen atoms are transferred to cobalt oxide by spillover effect. It can be concluded that Co oxide is more easily reduced to Co⁰ in the presence of nickel.

The percentage change of oxidic and metallic Co and Ni species in the monometallic and bimetallic systems as a function of reaction temperature up to 750°C during ethanol steam reforming reaction was analysed by in situ XANES-ESR at K edge of Ni and Co, as seen in Fig. 2. There is some equilibrium for Co⁰ and Co²⁺ species in the monometallic Co sample up to a reaction temperature of about 450°C and then the fraction of CoO species decreases at higher temperatures, while that of Co⁰ increases. For both Co-containing catalysts, CoO is present at the end of reaction, whereas with the Ni-containing samples a small portion of NiO is detected only for monometallic nickel. The Ni sample exhibits a high amount of metallic nickel species (80%) at the beginning of reaction, which reaches 100% with increasing the reaction temperature to 500°C. The behaviour of the bimetallic CoNi system is different in relation to the monometallic systems. At the beginning of reaction up to 200°C the fraction of nickel oxide species (35%) for CoNi is higher than that observed for monometallic Ni (16%), which indicates that metal particle oxidation takes place at low reaction temperatures in the presence of cobalt. Metallic nickel fraction in CoNi increases at the expense of cobalt oxide species at a reaction temperature over 300°C. Above 400°C the NiO in the bimetallic system is totally reduced to Ni⁰ (100%) (Fig. 2).

EXAFS analysis

Magnitudes of the Fourier transformation of each sample together with the corresponding fits are shown in Fig. 3. Results of the fitting analysis in terms of coordination number, CN, interatomic distance, R, for references and samples are summarised in Table 1. The absorption spectra (Fig. 3) indicate that supported nickel and cobalt oxide species are not fully reduced after reduction at 750°C.

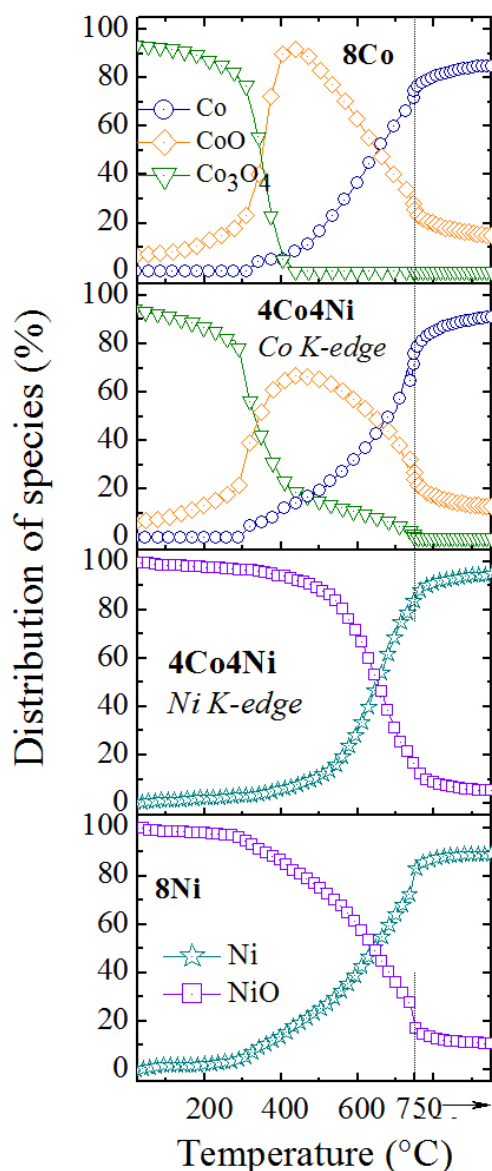


Fig. 1. Percentage change of species as a function of reduction temperature defined by in situ temperature-resolved XANES spectra of monometallic Co and Ni and bimetallic CoNi samples during reduction.

Both peaks of Co K-edge spectra at around 1.5 and 2.2 Å signify Co-O and Co-Co distances, respectively [14]. Peaks of Ni K-edge spectra at about 1.5 and 2.2 Å mean the atomic distance of Ni-O and Ni-Ni, respectively [15]. It should be noted that the values of the EXAFS parameters for references CoO, NiO, Co⁰, and Ni⁰ are in agreement with those reported in the literature. Values of interatomic distances $R_{\text{Ni-Ni}}$ and $R_{\text{Co-Co}}$ for reduced samples related to the Ni-Ni distance in bulk Ni⁰ and Co-Co distance in bulk Co⁰, respectively, indicate that the local structure of supported Ni and Co

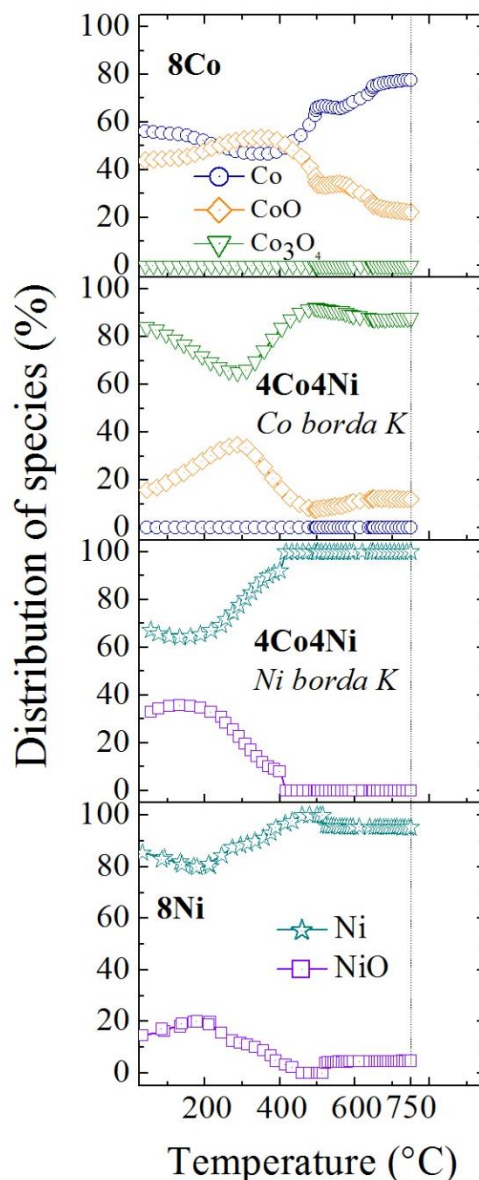


Fig. 2. Percentage change of species as a function of reaction temperature defined by in situ temperature-resolved XANES spectra of monometallic Co and Ni and bimetallic CoNi catalysts under ethanol steam reforming.

species is similar to that of the bulk samples. Co-Co and Ni-Ni atomic distances for the bimetallic CoNi system are lower compared to those of monometallic Co and Ni, which implies a strong interaction between the cobalt and nickel species. A decrease of the CN value from 9.6 to 6.7 for Ni and CoNi, respectively, is also evidence for a strong Co-Ni interaction. The highest CN value for the monometallic Ni sample is associated with Ni particle agglomeration on the MgAl₂O₄ support. The Ni-O bond distance for Ni was not found, since the EXAFS technique is limited to large particles.

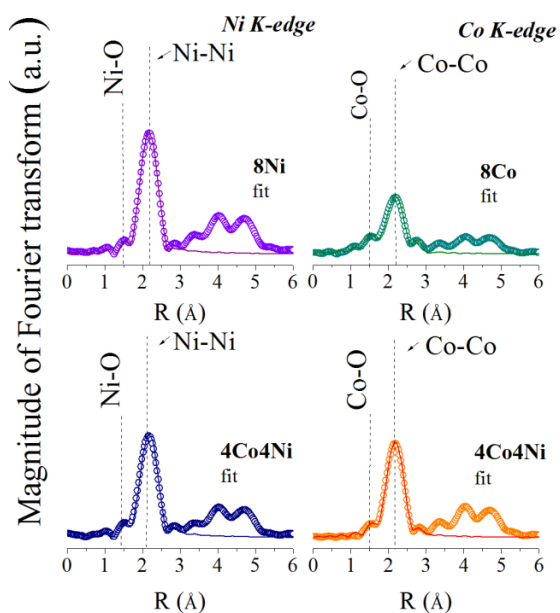


Fig. 3. EXAFS results at K edge of Co and Ni for reduced monometallic cobalt and nickel and bimetallic CoNi samples.

The Co sample has the smallest metallic nucleus revealed by the lowest CN value of Co-Co (3.4) (Table 1). In addition, the reduced monometallic Co catalyst possesses the highest oxidized surface shown by the highest CN value of Co-O (3.0, Table 1). The monometallic Co sample manifests the lowest Co-Co coordination number (3.4) to which cor-

responds the highest Co-O coordination number (3.0) that means more cobalt oxide species (Table 1). Changes in coordination number and interatomic distance of the bimetallic CoNi system relative to monometallic samples indicates a strong interaction between Ni and Co atoms that leads to a change of the electronic structure. It has been shown [16] that nickel species preferentially insert into octahedral sites in Co_3O_4 spinel structure resulting in formation of tetrahedrally coordinated cobalt species in a structure similar to NiCo_2O_4 spinel.

Catalytic test reaction

The effect of catalyst composition and metal component oxidation state on the catalytic performance of MgAl_2O_4 -supported monometallic Co and Ni and bimetallic CoNi catalysts at various reaction temperatures was studied by means of ESR. Results are summarised in Fig. 4, where ethanol conversion and products distribution as a function of reaction temperature are shown. For all samples ethanol conversion increased on increasing the reaction temperature, as the maximum value of 100% was reached for the bimetallic CoNi catalyst at a lower reaction temperature of 450°C accompanied by the highest selectivity to hydrogen (70%). Higher temperatures were required for monometallic 8Ni (600°C) and 8Co (500°C) to achieve conversions over 90%.

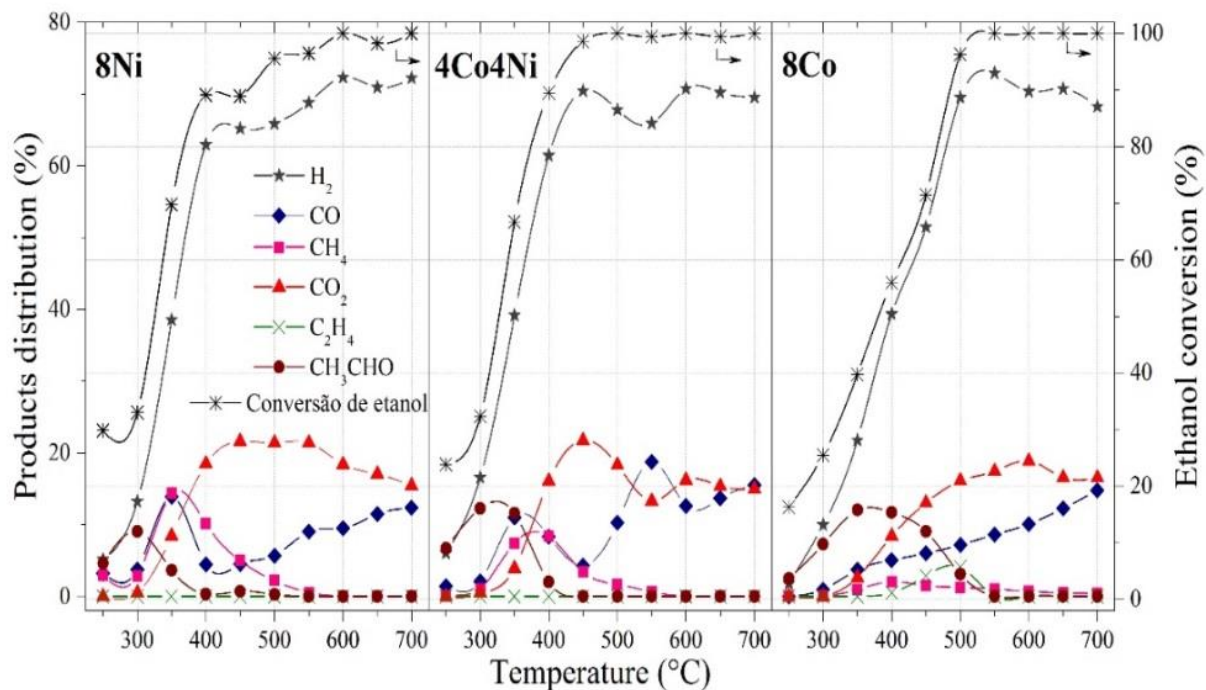
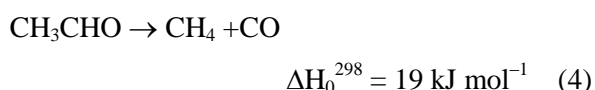
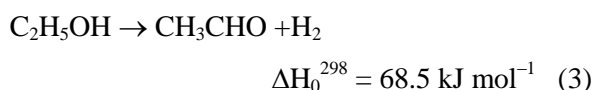
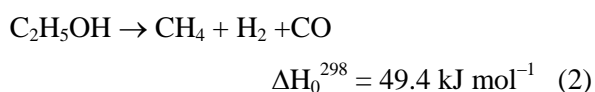
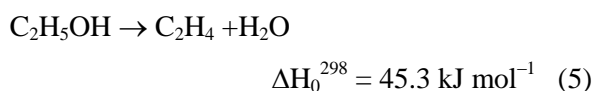


Fig. 4. Products distribution as a function of reaction temperature in ethanol steam reforming over monometallic cobalt and nickel and bimetallic CoNi catalysts.

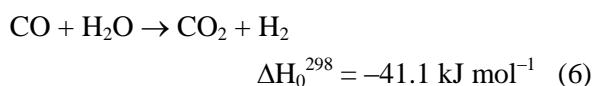
Reaction pathways of ethanol steam reforming at lower temperatures strongly depended on the capacity of the active metals to break the C-C bond in ethanol molecule. Over the Ni catalyst, at a low reaction temperature of 300°C ethanol was first dehydrogenated to acetaldehyde and hydrogen. By increasing the temperature up to 350°C, in parallel to hydrogen abstraction from the ethanol molecule, C-C bond scission and acetaldehyde decomposition were also observed resulting in formation of CH₄, CO, and H₂ at a CO to CH₄ ratio of about unity. The production of H₂, CH₄, and CO may be attributed to ethanol decomposition, which can occur either directly (Eq. 2) or via intermediate formation of acetaldehyde as a sum of reactions (Eq. 3) and (Eq. 4) [3]:



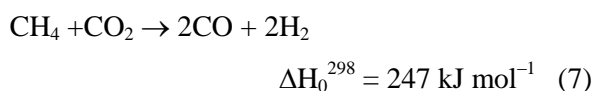
Traces of ethylene (< 0.05%) were detected as the formation of this product might take place via the dehydration reaction (Eq. 5):



CO selectivity for the Ni catalyst was comparable to that of hydrogen at 350°C, while at a higher temperature it decreased substantially. Contrary to this, raising the temperature above 400°C led to an increase in CO₂ production due to water-gas shift reaction (WGSR) (Eq. 6), the latter being caused by increased number of nickel metal centres, as seen in Fig. 2:



In the case of Ni catalyst, a maximal concentration of CH₄ may be associated with increasing the CO concentration up to 350°C, which indicates that ethanol decomposition reaction (Eq. 4) takes place on metallic nickel sites. Above 500°C, CH₄ is completely converted to CO and H₂ by dry methane reforming reaction (Eq. 7):



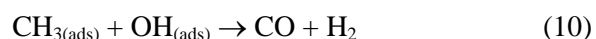
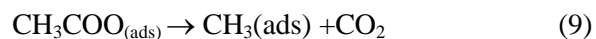
Detected decrease of CO₂ production at a temperature over 550°C can be related to occurrence of reverse WGSR. Above 500°C, H₂ and CO fractions continue to increase showing that ethanol steam reforming (Eq. 1) is dominating (Fig. 4).

Up to 300°C, the Co catalyst exhibits the formation of acetaldehyde and hydrogen products only, which is mainly due to the ethanol dehydrogenation, involving O-H bond cleavage in ethanol molecule (Fig. 3). Over Co surface, however, in spite of the low concentrations of produced CO, CO₂, and H₂ up to 400°C, a high amount of CH₃CHO is still present due to the high concentration of the cobalt oxide species that decrease catalyst ability for C-C bond breaking. As was suggested [17] both the Co⁰ and CoO species are active for partial oxidation of adsorbed ethoxide species to produce acetaldehyde. Above 400°C, there is an increase of the CO and CO₂ products formation that can be related to an increased fraction of metallic cobalt species. The latter is accompanied by a decrease in acetaldehyde formation. It should be noted that traces of CH₄ and C₂H₄ were formed at temperatures within 350–500°C (Fig. 4).

For the Co catalyst, increased concentrations of CO₂ and CO up to 500°C can mainly be attributed to formation of acetate species, which can be oxidized to carbonate species and after that decomposed to CO₂ or CO [18, 19]. It could be proposed that the produced acetaldehyde over the 8Co catalyst is oxidized by OH groups of support as well as by the metal oxide species to form surface acetate species (Eq. 8) in agreement with Refs. [18, 19].



According to Dömök *et al.* [19] the acetate species can be decomposed to CH_{3(ads)} species (eq. 9), which may further react with surface OH groups to produce CO and H₂ (Eqs. 9, 10):



The catalytic performance of the 4Co4Ni catalyst at lower temperatures is between that of the mono-metallic catalysts (Fig. 4). At lower temperatures acetaldehyde was mainly formed on the surface of the bimetallic system, however, its amount was much lower compared to that observed with the Co catalyst. This means a better reducibility of the bimetallic catalyst, as confirmed by XANES and EXAFS analyses. Above 300°C, the behaviour of CoNi is similar to that of Ni in spite of the lower amount of CH₄.

SUMMARY

The results show that applied MgAl₂O₄ carrier was a suitable support for the monometallic cobalt and nickel and bimetallic CoNi catalysts for ethanol steam reforming. XANES and EXAFS analyses show that introduction of nickel to a cobalt catalyst caused a change of the electronic structure and improved the redox properties.

The main difference in catalyst performance is related to variations of CH₃CHO, CH₄, CO, and CO₂ products distribution at different reaction temperatures. The results demonstrate that the main reaction pathway for ethanol steam reforming over supported catalysts at low temperatures (up to 400°C) is ethanol dehydrogenation to acetaldehyde, which is further decomposed to methane, hydrogen, and carbon dioxide. WGS and reforming reactions dominate at higher reaction temperatures (above 400–450°C).

Different catalyst performance can be related to differences in electronic properties. Dominating agglomerated nickel metal particles in the monometallic Ni catalyst are responsible for high activity in hydrogenation of CH_x radicals caused by C-C cleavage. In contrast to this, Co particles in the monometallic Co catalyst, probably smaller than 4 nm, could easily be oxidized by steam in ethanol steam reforming that causes a decrease of the number of active metal centres. The latter led to a lower catalyst capacity for C-C bond breaking and formation of acetaldehyde involving O-H bond scission. Introduction of nickel to cobalt catalyst caused a strong interaction between Co and Ni, which stabilized the oxidation state of cobalt to Co⁰ in the bimetallic CoNi catalyst under reaction conditions, thus stabilizing the highest hydrogen selectivity at a lower reaction temperature.

Acknowledgements: The authors kindly acknowledge FAPESP and project FNI E02/16 for financial support and Brazilian Synchrotron Light Laboratory for XAS beamline experiments.

REFERENCES

1. P. E. Dodds, I. Staffel, A. D. Hawkes, F. Li, F. Grünewald, W. McDowall, P. Ekins, *Int. J. Hydrogen Energy*, **40**, 2065 (2015).
2. D. Zanchet, J. B. O. Santos, S. Damyanova, J. M. C. Bueno, *ACS Catalysis*, **5**, 3841 (2015).
3. A. C. Basagiannis, P. Panagiotopoulou, X. E. Verykios, *Top. Catal.*, **51**, 2 (2008).
4. G. P. Szijjarto, A. Tompos, J. L. Margitfavi, *Appl. Catal. A: Gen.*, **1-2**, 417 (2010).
5. A. F. Ghenciu, *Curr. Opin. Solid State Mater. Sci.*, **6**, 389 (2002).
6. P. Ciambelli, V. Palma, A. Ruggiero, *Appl. Catal. B: Environ.*, **96**, 18 (2010).
7. Q. Shi, C. Liu, W. Chen, *J. Rare Earths*, **27**, 948 (2009).
8. A. Casanovas, C. Leitenburg, A. Trovarrelli, J. Llorca, *Catal. Today*, **138**, 187 (2008).
9. J. Sun, X.P. Qiu, F. Wu, W. T. Zhu, *Int. J. Hydrogen Energy*, **30**, 437 (2005).
10. C. N. Avila-Neto, J. W. C. Liberatori, A. M. da Silva, D. Zanchet, C. E. Hori, F. B. Noronha, J. M. C. Bueno, *J. Catal.*, **287**, 124 (2012).
11. H. C. N. Tolentino, A. Y. Ramos, M. C. M. Alves, R. A. Barrea, E. Tamura, J. C. Cezar, N. Watanabe, *J. Synchrotron Radiat.*, **8**, 1040 (2001).
12. J. Mustre de Leon, J. J. Rehr, S. I. Zabinsky, R. C. Albers, *J. Am. Chem. Soc.*, **113**, 5135, (1991).
13. S. Verma, A. Kumar, D. Pravarthana, A. Deshpande, S. B. Ogale, S. M. Yusuf, *J. Phys. Chem. C*, **118**, 16246 (2014).
14. Tae Hwan Lim, Sung June Cho, Hee Sung Yang, M. H Engelhard, Do Heui Kim, *Appl. Catal. A: Gen.*, **505**, 62 (2015).
15. J. Rosan, G. S. Hutchings, F. Jiao, *J. Catal.*, **310**, 2 (2014).
16. C. F. Windisch, C. J. Exarhos, R. R. Owings, *J. Appl. Phys.*, **95**, 5435 (2004).
17. E. Martono, J. M. Vohs, *J. Catal.*, **291**, 79 (2012).
18. S. M. Lima, A. M. Silva, L. O. O. Costa, G. Jacobs, B. H. Davis, *J. Catal.*, **268**, 268 (2009).
19. M. Dömök, M. Toth, J. Rasko, A. Erdöhelyi, *Appl. Catal. B: Environ.*, **69**, 262 (2007).

ИЗУЧАВАНЕ НА НАНЕСЕНИ CoNi КАТАЛИЗАТОРИ ЗА РЕФОРМИРАНЕ НА ЕТАНОЛ С ВОДНА ПАРА С ПОМОЩТА НА РЕНТГЕНОВА АБСОРБЦИОННА СПЕКТРОСКОПИЯ

А. Брага¹, Х. Б. Сантос¹, С. Дамянова^{2*}, Х. М. К. Буено¹

¹ Департамент по инженерна химия, Федерален университет на Сан Карлос, Сан Карлос, Бразилия

² Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България

Постъпила на 10 октомври 2015 г.; Преработена на 17 ноември 2015 г.

(Резюме)

Синтезирани са монометални никелови и кобалтови и биметални CoNi катализатори, нанесени върху носител MgAl₂O₄. Електронната структура на катализаторите е охарактеризирана *in situ* с помощта на рентгенова абсорбционна спектроскопия. Резултатите показват, че редукцията на кобалтово оксидни съединения в кобалт-съдържащи образци протича през два етапа: (а) редукция на Co₃O₄ до CoO и (б) трансформиране на CoO до Co⁰. Едновременно присъствие на Co³⁺, Co²⁺ и Co⁰ се наблюдава за биметална CoNi система, като първият етап приключва при по-висока температура на редукция. Присъствието на кобалт в биметален CoNi катализатор не позволява редукцията на никелово оксидни съединения да протича при по-ниска температура. Различни етапи на реакцията протичат едновременно по време на реформинг на етанол с водна пара, изразено чрез разпределението на реакционните продукти като функция от температурата на реакцията. Това се дължи на изменението на концентрациите на металните частици и кислород-съдържащи съединения на кобалта и никела в условията на протичане на реакцията. Биметален CoNi катализатор показва най-висока селективност по водород при ниска температура на реакцията (около 400°C), което се отдава на близкия контакт между кобалта и никела стабилизиращ активните метални каталитични центрове.