

## Study of CoNi catalysts for ethanol steam reforming

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The effect of Co addition to Ni-based catalysts on the change of their structure and electronic properties was studied, as well as how this change influences on catalytic properties in ethanol steam reforming. Two series of MgAl<sub>2</sub>O<sub>4</sub>-supported bimetallic CoNi catalysts with different metal loading of 8 and 15 wt% were prepared. The dependence of ethanol conversion and product distribution as a function of metal loading and temperature reaction was evaluated. Different techniques were used for physicochemical characterization such as: XPS, in situ XAS and HRTEM. Catalytic test was ethanol steam reforming carried out in a wide temperature region from 250° to 650°C. It was shown that a spinel-like Ni<sub>2</sub>CoO<sub>4</sub> was formed in oxide bimetallic CoNi systems, which leads to an alloy formation after reduction. The presence of alloy in bimetallic CoNi catalysts leads to different reaction pathways and to improving the catalyst stability.

**Key words:** CoNi catalysts, hydrogen, ethanol steam reforming, XPS, in situ XANES, TEM.

### INTRODUCTION

Great efforts are currently undertaken to produce hydrogen, for example, for fuel cell applications and for ammonia synthesis by heterogeneously catalyzed processes from renewable sources. This demand inspired studies of the dehydrogenation of oxygenated hydrocarbons. In particular, the light alcohol ethanol (“bioethanol”) is an important candidate as a chemical hydrogen carrier. It is well known that the surface properties of the metal and the oxide support, as well as the metal/oxide interface determine the formation and stability of the intermediates present in the ethanol transformation process. It is generally accepted that the primary step in alcohol activation is the formation of alkoxide [1]. Depending on the particular metal, dehydrogenation and C–C bond scission lead to the formation of alkoxide, aldehyde, acyl, and coke on the surface and mostly H<sub>2</sub>, CH<sub>4</sub>, CO, and aldehyde in the gas phase [2, 3]. Therefore, an efficient catalyst for hydrogen production from ethanol reforming has to dissociate the C–C bond at reasonably low temperatures, to maintain a low CO concentration and to be stable under catalytic reaction. Many studies have been focused on the ethanol steam reforming (ESR) over supported nickel, cobalt or noble metal catalysts. The major drawback of the catalytic systems is their deactivation caused by the coke deposition. It was shown [4] that the noble metals, like Rh and Ru can successfully break the C–C bond leading to less coke deposition and to formation of more stable catalysts.

However, alumina-supported Ni catalysts, due to their low cost and wide availability, as well as due to their capability of C–C bond capture, are the most used catalysts for reforming processes. In addition, ESR over nickel catalysts takes place at moderate temperatures. But, during the ESR the acidity of alumina favors the ethanol dehydration and thereby, increase the tendency for coke formation due to the polymerization of ethylene [5, 6]. In opposite to noble metals, the nickel particles tend to sinter under ESR reaction conditions. Therefore, to avoid the both, nickel metal sintering and alumina acidity, leading to carbon formation and catalyst deactivation, different supports and/or promoters have been added to nickel-based catalysts. For example, on ceria (CeO<sub>2</sub>) support, which is considered to be a basic support, the dehydration was limited and the coke formation was limited due to the redox properties of ceria [7]. Addition of Cu to Ni-based catalyst promotes the water gas shift reaction (WGSR) reaction, which is a site reaction of ESR, to produce hydrogen and to avoid the growth of nickel particles [8, 9].

The low-cost cobalt based catalysts are promising catalysts for ESR since they are very selective to H<sub>2</sub> and CO<sub>2</sub> because the reforming temperature can be as low as 623 K in such a way that WGSR occurs simultaneously with the steam reforming and, consequently the CO concentration is kept low. Recent studies suggested that the Co<sup>2+</sup> sites are the active centers in ESR, and the Co<sup>0</sup> sites are

responsible for coke formation [3,10]. However, other authors considered that the metallic cobalt plays a key role in ESR [11]. High-pressure X-ray photoelectron spectroscopic studies (HPXPS) demonstrated that during the ethanol reaction over Co/CeO<sub>2</sub>(111) model catalyst the amount of Co<sup>2+</sup> was decreased drastically with increasing the temperature, and at 600 K the majority of Co was metallic; this process was accompanied by the ceria reduction [12]. On the other hand, in-situ studies by FTIR with CO as a probe molecule suggested that the redox pair Co<sup>0</sup> ⇌ Co<sup>2+</sup> is responsible for the activity of cobalt in ESR [13]. Several strategies have been attempted to minimize the coke formation over Co-based catalysts under ESR conditions. It has been demonstrated [14] that alloying the cobalt with other metals promotes the redox pair Co<sup>2+</sup> ⇌ Co<sup>0</sup>, both in terms of lower cobalt reduction temperature, as well as a fast re-oxidation that results in a better catalyst stability.

The synergetic effect of the combination of two active elements like Ni and Co was investigated in the present work. It was attempted to discuss the effect of metal content on the change in the structure and electronic properties of MgAl<sub>2</sub>O<sub>4</sub>-supported monometallic Co and Ni and bimetallic CoNi catalysts with different metal loading under reductive atmosphere and ESR conditions. Different techniques were used for sample characterization such as: X-ray photoelectron spectroscopy (XPS), in situ X-ray adsorption near edge structure (XANES) and transmission electron microscopy (TEM).

## EXPERIMENTAL

### *Sample preparation*

Two series of MgAl<sub>2</sub>O<sub>4</sub>-supported monometallic Ni(Co) and bimetallic CoNi catalysts with different total metal loading of 8 and 15 wt.% were prepared by incipient wetness impregnation of the carrier with aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich, 99%) and/or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich, 99%). MgAl<sub>2</sub>O<sub>4</sub> carrier was prepared by sol-gel method described elsewhere [15]. The obtained solids were dried and calcined in air flow at 110° and 500°C for 12 and 6 h, respectively. The first series of samples was labeled as 8Ni, 4Co4Ni and 8Co and the second one as 15Ni, 7.5Co7.5Ni and 15, where the number represents the nominal content of each metal.

### *Sample characterization*

XPS of calcined and reduced samples were registered using SPECSLAB II Phoibos-HS 3500 150 analyzer, employing Al K $\alpha$  (1486.6 eV) radiation. Self-supported pellets of the samples were prepared and reduced in a pretreatment chamber at 750°C for two hours under hydrogen flow. The

spectra were fitted with CASA XPS software, with Shirley background subtraction, and using a convoluted Gaussian/Lorentzian function. Binding energies of Ni 2p, Co 2p, Al 2p and O 1s core electron levels were referred to the C<sub>1s</sub> level at 248 eV.

XANES analyses of the samples were performed at the K edge of Co (7709 eV) and Ni (8333 eV) using D06A - DXAS beamline of Brazilian Synchrotron Light Laboratory at Campinas. The sample was first crushed and sieved to particle sizes smaller than 20  $\mu$ m and pressed into self-supporting pellets. Then the pellets were placed inside a tubular quartz reactor equipped with refrigerated kapton windows transparent to the X-ray beam. In situ temperature-resolved XANES spectra were acquired during temperature programmed reduction (TPR) of the samples (XANES-TPR), which was achieved by heating from room temperature to 750°C, at 10°C/min, with a holding time of 60 min, under a 200 ml/min flow of H<sub>2</sub>/He (5 vol.%). Energy calibration of the XANES spectra was performed with open source ATHENA/IFEFFIT software. A linear combination analysis was performed using Co<sup>0</sup>, CoO, Co<sub>3</sub>O<sub>4</sub>, Ni<sup>0</sup> and NiO references [15].

In situ XANES spectra at the K edge of Co and Ni of the catalysts under ethanol steam reforming conditions were also realized (XANES-ESR). The reactor with previously reduced samples at 750°C under hydrogen stream was cooled to room temperature under a flow of helium. Then a flow of 3.9 ml/min of the ESR mixture (H<sub>2</sub>O/ethanol molar ratio of 3:1), diluted in 133 ml/min of He, was started. The samples were heated from room temperature to 500°C, kept for 30 min, and then more than 30 min at 550°C. The XANES spectra were acquired 10 min after reaching steady state. The reaction products were analyzed by mass spectrometry.

TEM images of reduced and spent catalysts were acquired in a Jeol 2010F microscope, with a Schotcky field emission gun operating with 200 kV of acceleration voltage. The bright field and high resolution images were acquired in a Gatan Tridien CCD detector (2k x 2k pixels). Scanning TEM (STEM) images in bright field and high-angle annular darkfield were obtained using a spot size of 1 nm. Energy filtered TEM (EFTEM) images were acquired in a Gatan Image Filter prism using the Ni and Co L<sub>2,3</sub> core-losses, and O and C K core -losses to generate the energy-filtered image.

Activity test of the catalysts in ESR was realized in a quartz reactor. After reduction of the samples at 750°C for 1 h under hydrogen stream, the reactor was cooled to r.t. and the mixture of H<sub>2</sub>O/ethanol in

molar ratio of 3/1 was past. The temperature was increased in steps of 50°C when the GC analysis was made. For stability test, the ESR stream was admitted at 550°C, the temperature at which the reforming reaction was at maximum, and kept for 6 h on steam in the same conditions of  $W_{\text{cat}}/F_{\text{EtOH}}$  and a mixture composition ( $W_{\text{cat}}/F_{\text{EtOH}} = 114.7 \text{ g}_{\text{cat}} \cdot \text{min} \cdot \text{g}_{\text{EtOH}}^{-1}$ ).

## RESULTS AND DISCUSSION

### XPS analysis

The BEs values of Co 2p<sub>3/2</sub> and Ni 2p<sub>3/2</sub> core electron levels, as well as the atomic XPS Ni/Co ratios for calcined and reduced monometallic and bimetallic CoNi samples with different metal loading are shown in Table 1. In addition, the average particle size of reduced catalysts at 750°C, defined by HRTEM, is included in the Table. 1. The XPS spectra (not shown) of calcined Ni-containing samples exhibited peaks of Ni<sup>2+</sup> accompanied with their satellites. The BE value of 855.48-955.51 eV of calcined monometallic Ni samples means the presence of Ni<sup>2+</sup> ions [16]. However, the addition of Co to Ni samples leads to the increase of BE values of Ni 2p<sub>3/2</sub> electrons for calcined bimetallic CoNi samples with different metal content by approximately of 0.5 eV (from Table 1). The observed phenomena should be explained by the presence of Ni ions in a more electron deficient environment, i.e. Ni<sup>3+</sup> ions could be existing. In opposite to that, the BEs of Co 2p<sub>3/2</sub> electrons for both bimetallic CoNi samples are shifted to lower BE values that suggests a higher concentration of Co<sup>2+</sup> in the spinel, more evidently for sample with the higher metal loading of 15 wt%. (Table 1). The shift in the BEs values of the calcined samples should be caused by the interaction between the components and support surface, as well as by the strong interaction between Co and Ni and formation

of some distorted structure like NiCo<sub>2</sub>O<sub>4</sub> spinel [17]. It was supposed [17] that this spinel could be formed by the insertion of Ni<sup>2+</sup> into octahedral sites in Co<sub>3</sub>O<sub>4</sub> spinel structure because the ion radius of Ni<sup>2+</sup> (0.069 nm) is larger than that of Co<sup>3+</sup> (0.055 nm).

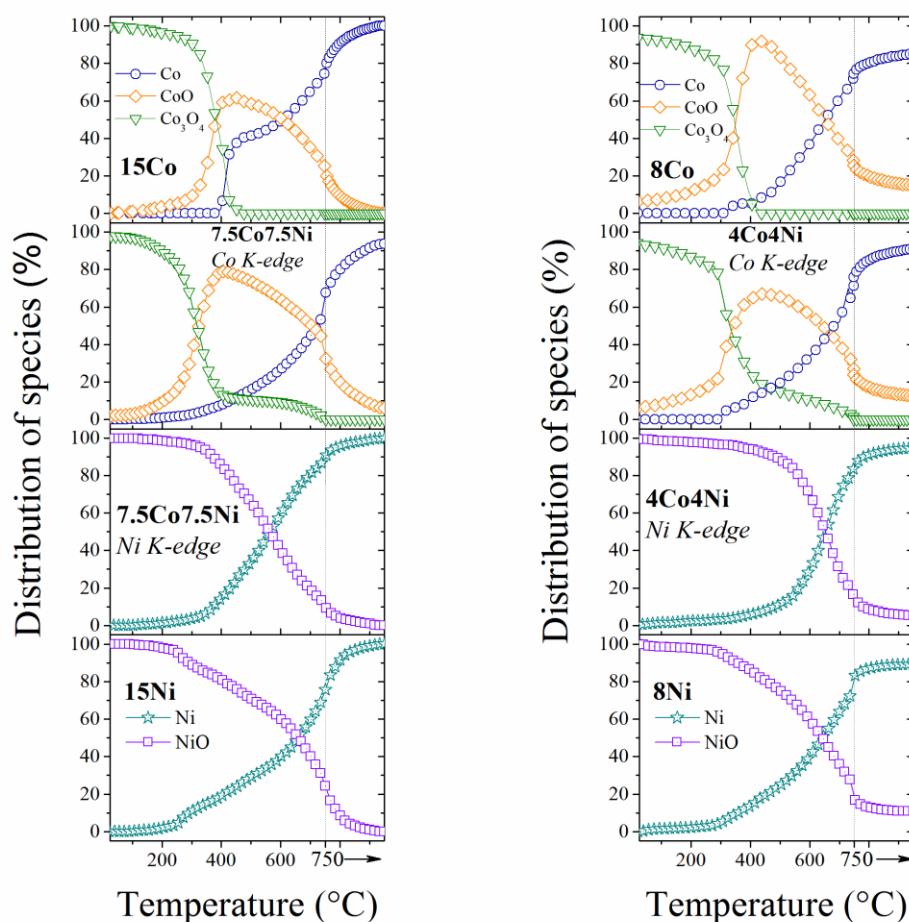
The XPS of reduced samples are more complex. With exception of the XPS of 8Co sample, all spectra exhibited components assigned to metallic Ni with BEs of 852.52-853.24 eV or metallic Co with BEs of 778.40-778.61 eV, as well as components of 2+ oxidation state. It means that the surface of reduced catalysts is still oxidized even after treatment in a hydrogen atmosphere at 750°C. The more difficult reduction of Co oxide species in these samples, probably is due to their metal dispersion (Fig. 1).

The observed shift in the BEs of reduced samples (Table 1) should be related to the electron interaction between Co and Ni that depends on the composition and metal loading. The shift of BE of Co 2p<sub>3/2</sub> for monometallic Co samples from 781.76 to 778.40 eV with the increase of Co content from 8 to 15 wt% should be connected with the increase of metal particle size (from 4.4 to 11 nm for 8Co and 15Co, respectively, Table 1), followed by the decrease of electron density and reduction of Co nanoparticles. After addition of Co to Ni catalysts the interaction between Co and Ni for reduced high metal-loaded sample of 15 wt% results in a decrease of BE of Ni 2p<sub>3/2</sub> and in a slight increase of BE of Co 2p<sub>3/2</sub>. In opposite to that, an increase of BE of Ni 2p<sub>3/2</sub> for low metal-loaded 4Co4Ni sample is observed, accompanied with the decrease of BE of Co 2p<sub>3/2</sub> (Table 1). 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 an alloy formation similar to that observed by other authors [18].

**Table 1.** Some physicochemical properties of the oxide and reduced monometallic and bimetallic CoNi catalysts

Sample	$D_{\text{metal}}^a$ , nm	Binding Energy, eV		Ratio
		Ni 2p <sub>3/2</sub>	Co 2p <sub>3/2</sub>	
<i>Calcined samples</i>				
8Ni		855.48	-	
4Co4Ni		855.98	780.83	1.6
8Co		-	781.05	
15Ni		855.51	-	
7.5Co7.5Ni		855.90	780.62	1.8
15 Co		-	779.71	
<i>Reduced samples</i>				
8Ni	5.2	852.52	-	
4Co4Ni	4.2	852.84	778.47	2.8
8Co	4.4	-	781.76	
15 Ni	16.8	853.24	-	
7.5Co7.5Ni	9.9	852.99	778.61	1.7
15Co	11.0	-	778.40	

<sup>a</sup>Average particle size or reduced catalysts defined by HRTEM



**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 with different metal loading during the TPR.

The XPS Ni/Co ratios values of both calcined bimetallic CoNi samples are approximately the same and are higher than 1, which means some enrichment of the surface with Ni. The reduction of bimetallic CoNi sample with the higher metal loading of 15 wt% does not change the atomic Co/Ni ratio in relation to that of the respective calcined sample (Table 2). However, the reduction leads to a significantly increase of the Ni/Co ratio of reduced bimetallic 4Co4Ni system (from 1.6 to 2.8, Table 2), which is almost in two times higher than that of the reduced 7.5Co7.5Ni (1.7). It suggests that the treatment of the bimetallic catalyst system with lower total metal loading of 8 wt% under hydrogen atmosphere leads to a re-dispersion of the small nanoparticles, which provokes a segregation of Ni at the surface and leaving Co in the interior, similar to formation of a *core shell* like structure, as the nickel possess a higher affinity to hydrogen than cobalt.

#### *In situ XANES-TPR*

The change of the oxidation state of metal components in both series of catalysts was investigated by in situ temperature-resolved XANES spectra at K-edge of Ni and Co registered during the TPR. The respective semi quantitative change in the percentage of different Co and Ni species as a function of reduction temperature up to 750°C is shown in Fig. 1. It should be noted that the fitting of XANES spectra of calcined Co-containing samples with a higher metal loading of 15 wt% showed mainly the presence of  $\text{Co}_3\text{O}_4$  species, whereas a mixture of 10% CoO and 90%  $\text{Co}_3\text{O}_4$  in the samples of 8 wt% was detected.

The reduction process of cobalt oxide species consists of two reduction processes, being seen in Fig. 1: the first process is the reduction of  $\text{Co}_3\text{O}_4$  to CoO and the second one is the transformation of CoO to metallic cobalt,  $\text{Co}^0$ . It is important to note that the second reduction process for monometallic

Co samples is occurred after finishing the first reduction process at about 400°C. However, for both bimetallic CoNi samples there is a coexisting of transitions  $\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$  and  $\text{CoO} \rightarrow \text{Co}^0$  in a wide temperature region. The reduction of  $\text{Co}^{2+}$  species to  $\text{Co}^0$  for bimetallic systems starts to occur at lower temperature, compared to that observed for monometallic Co samples (Fig. 1). The latter is due to the activation of  $\text{H}_2$  over the surface of metallic nickel species and the hydrogen atoms are transferred to cobalt oxide by spillover effect. It can be concluded that more easy reduction of Co oxide to  $\text{Co}^0$  is observed in the presence of nickel that is more visible for high metal-loaded bimetallic 7.5Co7.5Ni system. At the end of reduction process the monometallic Co catalyst with higher metal content of 15 wt% is totally reduced, whereas the low metal-loaded Co catalyst shows about of 15 wt.% CoO at 750°C (Fig.1).

The reduction of NiO species for both monometallic Ni samples is beginning at lower reduction temperature compared to that observed for the corresponding bimetallic CoNi samples with the same total metal loading (Fig. 1). In addition, there is no significant alteration in the percentage of Ni species of monometallic Ni samples at low reduction temperature (up to 250°-300°C). However, more visible change is observed at temperature higher than 300°C: the percentage of NiO species decreases with increasing the reduction temperature, while that of metallic nickel component ( $\text{Ni}^0$ ) increases, which is well visible for sample with a higher metal loading of 15 wt% (Fig. 1). The percentage of metallic nickel at the end of reduction of 15Ni is approximately of 100 %.

The reduction of NiO species to  $\text{Ni}^0$  for bimetallic CoNi samples is beginning at significantly higher temperatures compared to those of the corresponding monometallic Ni samples, which is more visible for 4Co4Ni (above 400°C, Fig. 1). This means that the presence of Co suppress the reduction of nickel oxide species in the bimetallic system, probably, due to the strong interaction between Co and Ni and formation of the phase similar to  $\text{NiCo}_2\text{O}_4$ .

It is interesting to note that the transition  $\text{Ni}^{2+} \rightarrow \text{Ni}^0$  for both bimetallic CoNi systems is occurred simultaneously with the reduction of  $\text{CoO}$  to  $\text{Co}^0$ . These dynamics suggest the interaction between the both metals cations, and the higher spinel content indicates a coexistence in the same crystallographic phase, like  $\text{Co}^{2+}_{\text{tet}}[\text{Ni}^{2+}\text{Co}^{3+}]_{\text{oct}}\text{O}_3^{2-}\cdot\text{O}$ , as was proposed by other authors [19, 20]. In addition, the shift of the values of reduction temperature of nickel oxide species to higher values with decrease of metal

content is a typical behavior of the small nanoparticles, which are highly reactive.

#### *In situ XANES-ESR*

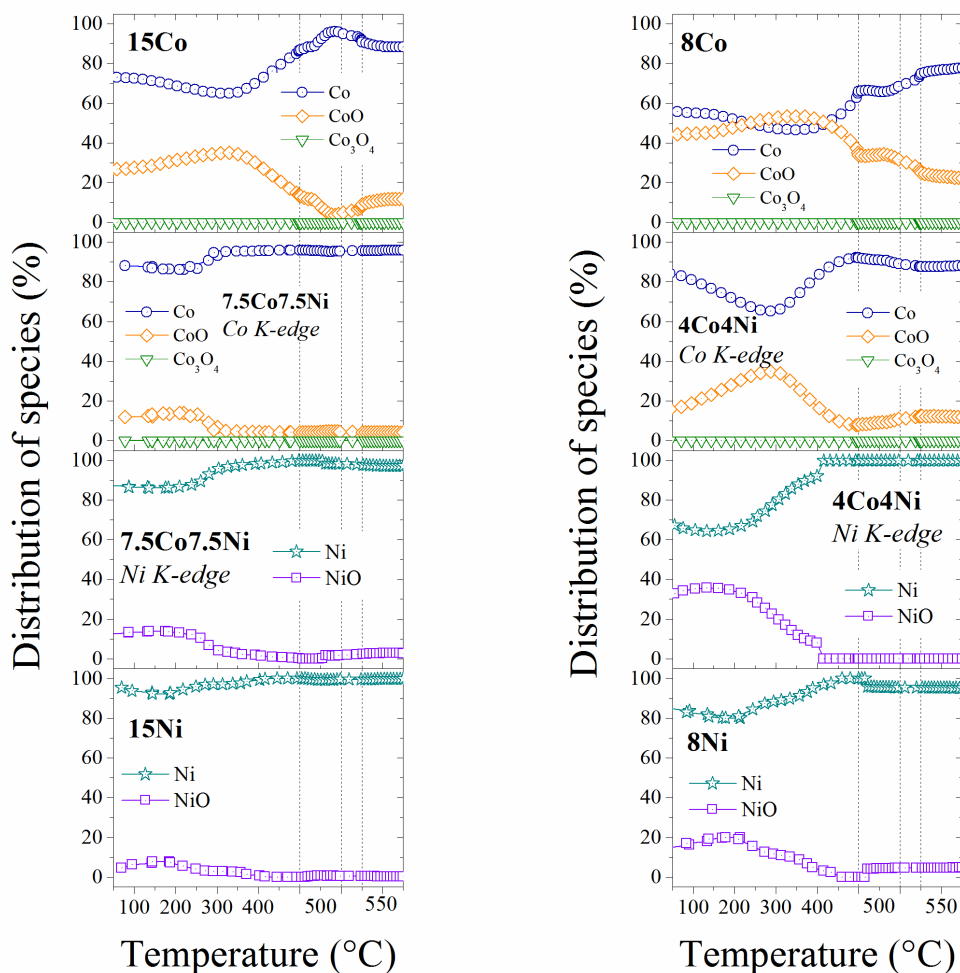
The change in the oxidation state of metal components (Co, Ni) of both series catalysts as a function of reaction temperature under ethanol steam reforming was evaluated by in situ XANES, being seen in Fig. 2. With exception of 15Co the degree of reduction of high metal-loaded samples (15Ni, 7.5Co7.5Ni) decreases slightly up to about 250°C with the admission of reactants and after that the particles became reduced again as the ethanol molecule activation is occurred. Monometallic 15Co catalyst continues to suffer oxidation up to 350°C followed by the surface reduction of  $\text{CoO}$  to  $\text{Co}^0$  when the atmosphere is turned more reductive (Fig. 2). The oxidation level of Ni particles for both monometallic Ni samples at low reaction temperatures up to around 200°-250°C is lower compared to that observed for bimetallic CoNi systems. This means that the monometallic Ni samples exhibit a higher number of metallic centers, more pronounced for high metal-loaded sample. However, addition of Co to Ni catalysts leads to an increase of the oxidation level of Ni particles, more visible for bimetallic CoNi system with lower total metal loading of 8 wt%. In addition, the presence of nickel oxide species in the low metal-loaded 8Ni and 4Co4Ni samples continue up to a higher reaction temperature of 500° and 400°C, respectively, as the concentration of NiO is much higher for the second one up to 250°C. Since an enrichment of Ni on bimetallic catalysts surfaces was detected by the XPS, especially in the case of 4Co4Ni sample (Table 1), it is reasonable a higher level of oxidation of Ni in relation to that of Co to be observed when  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$  mixture was admitted. Nickel oxide species are well reduced for all samples at reaction temperature above 450°-500°C, being seen in Fig. 2.

The oxidation level of Co particles for both monometallic Co catalysts is higher compared to that of bimetallic CoNi systems (Fig. 2), which can be related to the high affinity of Co to be oxidized. The low metal-loaded 8Co sample suffers a deep Co oxidation where some equilibrium of  $\text{Co}^0$  and  $\text{Co}^{2+}$  would be observed up to 450°-500°C. It is important to note that when Ni of both bimetallic CoNi samples is well reduced at 500°-550°C, Co is partially oxidized (around 5 % and 15 % of CoO for 7.5Co7.5Ni and 4Co4Ni, respectively, Fig. 2).

It is interesting to note that the oxidation level of Ni in bimetallic 4Co4Ni system is higher than that of Co at the beginning of reaction. Co is oxidized up to 300°C, whereas Ni reaches the maximum level of oxidation at about 150°-250°C and after that it starts

to be reduced (Fig. 2). It can be concluded that the oxidation level of CoNi catalysts up to about of 300-400°C with the high metal loading of 15 wt% is smaller than that of low metal-loaded samples (8 wt%), most probably, due to some reconstruction in

the particle size of catalysts under reaction conditions of ESR.



**Fig. 2.** The 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 with different metal loading under ethanol steam reforming.

#### Catalysts behaviors in ethanol steam reforming

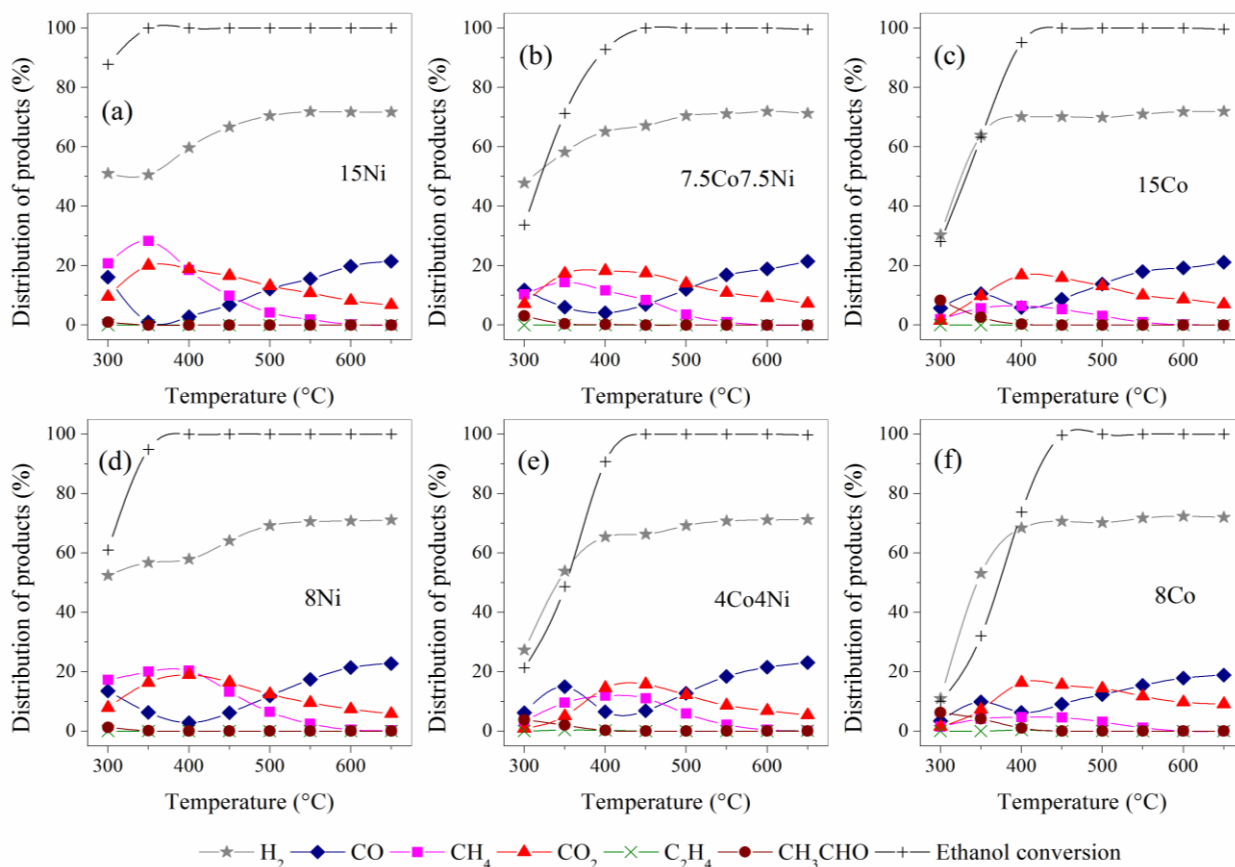
The evolution of the change of ethanol conversion and products distribution for both series of catalysts as a function of reaction temperature in ethanol steam reforming is shown in Fig. 3. Monometallic Ni catalysts at lower reaction temperature region of 300°-450°C produce methane in a great degree due to the hydrogenation of  $\text{CH}_x$  radicals formed by the C-C bond breakage of ethanol molecule. Ni catalyst with a high metal content of 15 wt% exhibits a higher percentage of  $\text{CH}_4$  at 300°-

350°C compared to that observed for low metal-loaded 8Ni. This can be related to the higher metallic character of 15Ni at low reaction temperatures, being seen in Fig. 1. In addition, up to 350°-450°C the methane formation is accompanied with the formation of  $\text{CO}_2$  in a great degree, which is probably caused by the occurring of the WGS, due to the increased degree of metallic character of nickel particles. However, above 500°C there is some inversion in the formation of  $\text{CO}_2$  and CO not only for both monometallic Ni catalysts, but for all other monometallic Co and bimetallic CoNi systems,

which can be a consequence of the reverse of WGSR. The highest selectivity to hydrogen for monometallic Ni catalysts is observed at about 350°C.

The high level of Co oxide species in both monometallic Co catalysts, more visible for 8Co, makes them less active in ethanol reforming reaction (Fig. 3). It was shown [21] that Co particles smaller than 5 nm are unstable and undergoes oxidation easily in the presence of water vapor. The addition of Co to Ni catalysts and the decrease of metal loading leads to less methane formation, which indicates that the methyl radicals formed by the C-C bond breakage are easily hydrogenated over metallic Ni sites. Acetaldehyde is the major product formed at low reaction temperature of 300°C due to the ethanol dehydrogenation, involving O-H bond cleavage of ethanol molecule, which is caused by the high concentration of Co oxide species detected by in situ XANES-ESR (Fig. 2). It is well known [22] that the presence of Co and CoO species are very active for the oxidation of the adsorbed ethoxide

species to produce acetaldehyde. For monometallic Co catalysts (Fig. 3) the activity to C-C bond cleavage accompanied with formation of CO, CH<sub>4</sub> and CO<sub>2</sub> is poorly observed at 300-350°C, more visible for low metal-loaded 8Co sample. The production of CH<sub>4</sub> is very low for Co catalysts, showing that the CH<sub>x</sub> radicals remain adsorbed and suffer successive dehydrogenation, in opposite to that observed for 8Ni. At 400°-450°C the high concentration of CO<sub>2</sub> for both Co catalysts accompanied with the highest degree of hydrogen production is due to the WGSR. At temperatures above 450°C there is some inversion in the ratio of CO/CO<sub>2</sub> that could be related to methane reforming with CO<sub>2</sub> [23]. The increase of the rate of C-C bond cleavage with the temperature should be provoked by the increased fraction of Co<sup>0</sup> (Figs. 1 and 2). The reforming reactions on monometallic Co catalysts dominate at temperature above 500°C and the high ethanol conversion is reached at higher temperatures than those for monometallic Ni-containing catalysts; H<sub>2</sub> yield also follows the same trend.



**Fig. 3.** Ethanol conversion and products distribution as a function of reaction temperature in ethanol steam reforming over monometallic Co and Ni and bimetallic CoNi catalysts with different metal loading.

The both bimetallic catalyst systems show an intermediate behavior between those of the bare Co and Ni. At low reaction temperature of 300°C acetaldehyde over CoNi catalysts is formed in a higher concentration than over monometallic Ni, but in a lower concentration than that on monometallic Co (Fig. 3). This is due to the better reducibility of Co and Ni sites of bimetallic CoNi catalysts as was observed by in situ XANES-TPR (Fig. 1). At temperatures above 300°C the route for bimetallic CoNi catalysts run like monometallic Ni ones, but the formation of CH<sub>4</sub> is lower. This suggests that the electronic modification caused by the Co-Ni interaction modifies also how the CH<sub>x</sub> radicals kept adsorbed on the surface.

The bimetallic CoNi catalysts revealed a high stability with time on stream under ESR reaction conditions at 650°C for 8 h. However, the HRTEM images of spent 4Co4Ni catalyst in Fig. 4 show the presence of carbon filaments, on the top of which the particle is situated that give accessibility of the reaction molecule to the catalytic active center. It is well known [24] that the carbon accumulation on the catalyst surface is a function of metal particle size. As was shown [24] the large metal particles in the reaction of methane reforming are encapsulated by carbon species; small nanoparticles due to its reactivity formed low carbon assemblies and the particles with medium size formed well defined carbon nanofilaments. The smallest nanoparticle size (4.2 nm) is detected for reduced 4Co4Ni catalyst (Table 1).

On the other hand, in the case of 4Co4Ni catalyst the electronic properties of the small nanoalloy

detected by the XPS analysis can make the surface oxygen more available to oxidize the carbon coming from the reforming reaction, and making by this way the catalyst more stable.

## CONCLUSIONS

The dependence of ethanol conversion and product distribution as a function of metal loading and temperature reaction was evaluated. The results show that MgAl<sub>2</sub>O<sub>4</sub> is a suitable support for monometallic Co and Ni and bimetallic CoNi catalysts for ethanol steam reforming. The both monometallic Ni systems exhibit the highest ethanol conversion at lower reaction temperature of about 350°C, accompanied with the highest methane yield due to the high metal character of catalysts. The high level of oxide species of monometallic Co catalyst with lower metal loading of 8 wt% makes them less active in reforming reaction at low reaction temperature. The addition of Co to Ni catalyst leads to alloy formation, which leads to the change of electronic properties of bimetallic CoNi catalysts revealed by the decrease of methane selectivity and increase of catalyst stability. The bimetallic CoNi systems exhibit different redox properties than monometallic catalysts, being easily oxidized than monometallic Ni and controlling better the oxidation level than monometallic Co.

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## ИЗСЛЕДВАНЕ НА КАТАЛИЗАТОР ОТ КОБАЛТ И НИКЕЛ ЗА СТИЙМ-РЕФОРМИНГ НА ЕТАНОЛ

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(Резюме)

Изследван е ефектът на добавен Со в Ni катализатори върху измененията в структурата и електронните свойства на катализаторите, както и върху тяхното каталитично поведение в реакцията паров реформинг на етанол. Получени са две серии биметални CoNi катализатори, нанесени върху носител MgAl<sub>2</sub>O<sub>4</sub>, с различно съдържание на металните компоненти в тях (8 и 15 тегл.%). Използвани са различни техники за тяхното физико-химично охарактеризиране: рентгенова фотоелектронна спектроскопия, *in situ* рентгенова абсорбционна спектроскопия и трансмисионна електронна микроскопия с висока резолюция. Каталитичният тест на образците е проведен в реакцията паров реформинг на етанол в широк температурен интервал от 250° до 650°С. Установено е, че шпинел подобна структура на Ni<sub>2</sub>CoO<sub>4</sub> се образува в оксидни биметални CoNi системи, което след редукция води до получаването на сплав. Присъствието на сплав в биметални катализатори е отговорна за високата им стабилност по време на протичане на реакцията.