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Magdalena Greluk, Marek Rotko, Sylwia Turczyniak-Surdacka

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Comparison of catalytic performance and coking resistant behaviors of cobalt- and nickel

based catalyst with different Co/Ce and Ni/Ce molar ratio under SRE conditions

Magdalena Greluk^{a,*}, Marek Rotko^a, Sylwia Turczyniak-Surdacka^b

^aDepartment of Chemical Technology, Faculty of Chemistry, Marie Curie-Sklodowska

University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland

^bBiological and Chemical Research Centre, University of Warsaw, 101 Żwirki i Wigury

Street, 20-089 Warsaw, Poland

*Corresponding author. Tel.: +48 81 537 55 14; fax: +48 81 537 55 65. *E-mail adress:* magdalena.greluk@poczta.umcs.lublin.pl (Magdalena Greluk).

Graphical abstract



Highlights

 Co(Ni)-support interaction decreases with increase in Ce amount above Co(Ni)/Ce=0.1

- Optimum Ce amount for performance in SRE corresponding to molar ratio metal/Ce=0.1.
- Ce amount influences on morphology of coke deposits of Ni catalysts.
- The Ni catalysts were more capable of cleaving the C–C bond in SRE than Co samples.
- The coke deposited on Co and Ni catalysts in SRE differs the type and morphology.

Abstract

A series of Co-xCe/CeO₂ and Ni-xCe/CeO₂ catalysts with different ceria amount introduced from Ce(NO₃)₃ × 6H₂O precursor, corresponding to Ce/Co(Ni) molar ratio from 0 to 1 were prepared by impregnation method. Among the tested catalysts, Co-0.1Ce/CeO2 and Ni-0.1Ce/CeO2 samples exhibited the smallest metal crystallites size, the strongest metal-support interaction, the best catalytic performance and the strongest resistance toward carbon deposition. Only an introduction of small amount of ceria from Ce(NO₃)₃ × 6H₂O precursor led to an increase in the number of active sites for breaking C-C and C-H bonds. Too high Ce/Co molar ratio caused rapid deactivation of cobalt-based catalysts because of faster coverage of active sites by encapsulating carbon. Whereas too high Ce/Ni molar ratio generated the thin and long carbon filamentous deposits causing the nickel-based catalysts deactivation including not only the coverage of nickel species by carbon but also limitation of the contact of reactants with nickel species.

Keywords:

Hydrogen production; Ethanol steam reforming; Cobalt; Nickel; Ceria

1. Introduction

Hydrogen may be produced by catalytic steam reforming of ethanol (SRE). An efficient catalyst for hydrogen production from ethanol has to dissociate the C—C bond, maintain a low carbon monoxide concentration by being a poison of platinum anodes in the low-temperature fuel cells and be stable under catalytic operation. In the literature, supported cobalt and nickel

catalysts have shown promising results in SRE due to their low cost, relatively high activity towards C-C bond cleavage and hydrogenation/dehydrogenation reactions. However, a drawback in their performance in this process is the formation of carbonaceous species. The conversion of ethanol and the product distribution is directly related to the catalyst composition and the operational conditions in the reaction system. The support acts as a dispersion medium, however, in most cases the nature of the support will influence the product distribution and the metal support interactions. An ideal support to SRE would not favour dehydration reactions (otherwise polymer formation may occur) and would have no (or mild) capacity for other C-C bond formation reactions (e.g., making higher unsaturated aldehydes by aldolization reactions) [1-5]. Moreover, there is some evidence that the use of reducible oxides, like CeO₂ can result in additional benefits when compared to ir such as Al₂O₃ or SiO₂. Ceria improves catalyst stability due to their high oxygen storage capacity (OSC) and oxygen mobility. The high oxygen-exchange capacity of ceria is associated with its ability to reversibly change oxidation states between Ce⁴⁺/Ce³⁺by reversibly storing/releasing oxygen. The easily accessible oxygen can react with carbon species as soon as it forms, and this process keeps the metal surface free of carbon, thus inhibiting deactivation. Moreover, support such as ceria is known to be highly active toward WGS, which promotes the reduction of carbon monoxide concentration in reformate. [2, 6, 7].

Generally, catalytic activity and coking resistant behaviors of catalysts are affected by their surface and structural properties, so that the methodology involved in the preparation step can lead to the obtainment of materials with important properties for applications in catalytic processes [8]. Various synthesis techniques have been used preparing Co/CeO₂ and Ni/CeO₂ catalysts for SRE process, the most commonly utilized ones being wet impregnation [3, 8-15], incipient wetness impregnation [8, 16, 17] and conventional co-precipitation [8, 18-20]. However, recent years have witnessed application of many novel synthesis techniques to

Co/CeO₂ and Ni/CeO₂ catalysts preparation for SRE reaction such as hydrothermal coprecipitation [21], hydrothermal ultrasonic-assisted co-precipitation [21], co-precipitation in reverse microemulsions [15, 17], solvothermal decomposition [17], colloidal crystal templating [17] or one-step polymerization [22]. The conclusion drawn from these papers is that SRE reaction on Co/CeO2 and Ni/CeO2 catalysts is mainly dependant on the active phase's particle and the interactions between the active metal and its support (SMSI) which offers a route to control the structural properties of supported metals and, hence, their activity, stability and resistance to carbon formation [20]. The form and degree of metal-support interaction depend on many factors, including the content of metal and preparation methods. According to Lovón et al. [23], the metal-support interactions strengthened with the increase of cobalt content of Co/CeO₂ catalyst from 5-20 wt.% resulted in better ethanol conversion, a higher hydrogen selectivity and better stability of the catalyst with the highest amount of cobalt. Also Carvalho et al. [24] observed that the enhancement of the metal-support interactions with increase of cobalt content of Co/CeO₂ catalyst from 5-20 wt.% led to the better catalytic performance of the catalyst containing 20 wt.% of cobalt amount in SRE reaction and a lower carbon deposition rate on it. Moreover, the increase of interaction between metal and support of Co/CeO₂ catalysts favoring the catalytic properties in SRE with the increase in cobalt content was also observed for the highest amount of metal ranging from 15-29 wt.% [25]. The enhancement of the metal-support interactions of Co/CeO₂ and Ni/CeO₂ catalysts for SRE reaction was also possible by using the proper preparation method to obtain materials. Song et al. [17] proposed novel synthesis techniques such as solverthermal decomposition, colloidal crystal templating and reverse microemulsion methods to prepare Co/CeO₂ catalysts and the superior performance in SRE reaction of the catalyst prepared by the last mentioned technique was attributed to the improved cobalt dispersion but also enhanced metal-support interaction and increased metal-support interface. The influence of

the preparation method on the strength of the metal-support interaction resulting in the catalyst properties in SRE reaction was also found for Ni/CeO₂ catalysts by Fang et al [8]. Coprecipitation method allowed to obtain the smallest sized NiO and CeO₂ nanoparticles which enhanced the interactions between the nickel and cerium species and not only led to very high activities but also meant that the stability was maintained due to the formation of the graphitic filamentous carbon, small and homogeneous in size compared to the filamentous carbon formed over the catalysts issued from the other preparation methods. Moreover, Fang et al. [8] demonstrated that the stronger metal-support interaction allowed to minimize the amount of carbon deposition on the catalyst surface during SRE process. Also Liu et al. [26] noticed dependence between the metal-support interaction and carbon formation on Ni-CeO_x catalyst in SRE reaction stating that a strong-metal interaction between nickel and ceria facilitated oxygen transfer and improved the oxidation of surface carbon. Moreover, the strong metalsupport interactions between nickel and ceria perturbed the electronic and chemical properties of nickel atoms reducing their ability to break C–O bonds. Thus, the nickel-ceria interactions substantially decreased the carbon monoxide methanation activity of nickel which is an important factor to take into account when dealing with the steam reforming of ethanol on Ni/CeO₂ catalyst as it was emphasized by Xu et al [27] and Zhou et al [28].

Inspired by the findings in the literature mentioned above, the idea of this work was to prepare Co/CeO_2 and Ni/CeO_2 catalysts exhibiting the strong metal-support interactions. It was assumed that the methodology used in their preparation, i.e. introduction of the metal active phase in the presence of ceria to the support allows to strengthen the metal-support interactions which stabilizes the loaded metal nanoparticles against thermal sintering during SRE reaction. It was also supposed that subsequent addition of cobalt/nickel and CeO₂ to the nano dispersed CeO₂ support allows to modify the surface and structural properties of the

obtained catalysts, leading to the improvement of their catalytic activities and coking resistance in SRE process.

With this aim, a series of Co/CeO₂ and Ni/CeO₂ (denoted as Co-xCe/CeO₂ and NixCe/CeO₂) catalysts with different Co/Ce and Ni/Ce molar ratio (x=0.1, 0.5 and 1) was prepared by co-impregnation method in the presence of CA and characterized. For comparison, the Co/CeO₂ and Ni/CeO₂ catalysts without ceria introduced from Ce(NO₃)₃ × $6H_2O$ precursor were prepared by impregnation method in the presence of CA and characterized. The amount of CeO₂ used as the support remained constant for all catalysts. A correlation between physicochemical properties of these catalysts and their catalytic performance in SRE reaction was investigated. Additionally, the deactivation behaviors of these catalysts were investigated. The knowledge of this relation will help not only to understand the effects of ceria promotion, but also to obtain the catalyst design concept. It is also an interesting comparison of catalytic performance and deactivation behaviors of cobaltand nickel based catalyst under SRE conditions.

2. Experimental

2.1. Catalysts preparation

The Co/CeO₂ and Ni/CeO₂ catalysts were prepared by impregnation of the commercial nano-dispersed ceria support (<25 nm, Aldrich) in the presence of CA as reported elsewhere [10-14]. The Co-xCe/CeO₂ and Ni-xCe/CeO₂) catalysts with different Ce/Co and Ce/Ni molar ratio (x=0.1, 0.5 and 1) were prepared by co-impregnation the commercial nano-dispersed ceria support (<25 nm, Aldrich) with a solution of Co(NO₃)₂ × 6H₂O, Ce(NO₃)₃ × 6H₂O and CA or Ni(NO₃)₂ × 6H₂O, Ce(NO₃)₃ × 6H₂O and CA (the molar ratios of Co + Ce/CA or Ni + Ce/CA was 1/1). After impregnation, the catalyst precursor was dried at 110°C for 12 h, then calcined at 500°C with the heating rate of 2°C min⁻¹ up to the calcination set point and maintained for 1 h at that temperature. The amount of the Co(NO₃)₂ × 6H₂O and Ni(NO₃)₂ ×

 $6H_2O$ precursors was adjusted to reach a corresponding nominal metal loading of 10 wt% in all catalysts. The cerium from Ce/Co or Ni/Ce molar ratio means that only cerium introduced was from Ce(NO₃)₃ × $6H_2O$ precursor. The amount of the commercial nano-dispersed ceria support used during the catalyst synthesis was fixed and equaled 10 g for all catalysts which means that the contribution of the commercial ceria decreased whereas contribution of ceria from Ce(NO₃)₃ × $6H_2O$ precursor increased with the increase Ce/Co or Ni/Ce molar ratio.

2.2. Catalysts characterization

Catalysts characterization was performed using the conditions reported in previous studies. The cobalt and nickel content in the catalysts was determined by X-ray fluorescence method using a Canberra 1510 fluorescence spectrometer. The X-ray powder diffraction patterns in Bragg-Brentano geometry were recorded on a Empyrean X-ray (PANalytical) diffractometer using Cu K α radiation (λ =0.154 nm). Textural properties of calcined catalysts were determined by nitrogen adsorption measurements at -196°C using ASAP 2420 (Micromeritics). Hydrogen chemisorption was measured in the ASAP 2020 apparatus (Micromeritics) These experiments were carried out on the samples after their reduction in hydrogen flow successively for 1 h at 500°C. Adsorption isotherms of hydrogen were obtained at 130°C. The amount of surface metal atoms was calculated from the amount of hydrogen chemisorbed, assuming that one hydrogen atom is adsorbed on the area occupied by one surface cobalt/nickel atom (the stoichiometry of chemisorption is Co(Ni)/H=1/1) and that the surface area occupied by one atom of hydrogen is equal to 0.065 nm^2 [9]. The total H₂ uptake was determined by extrapolation of the linear part of the isotherm to zero pressure. Reducibility of catalysts was investigated by the temperature-programmed reduction (TPR) experiment carried out with the AutoChem II 2920 (Micromeritics). The reduction profile was obtained by passing 5% H₂/Ar flow at the rate of 30 mL·min⁻¹ through 0.05 g (0.3-0.6 mm) of the catalyst. The temperature was increased from RT to 750°C at the rate of 10 °C min⁻¹. The

water vapour formed during the reaction was removed in a cold trap placed in front of the thermal conductivity detector. The susceptibility of active metal phase to its oxidation was investigated by the temperature-programmed oxidation (TPO) experiment carried out with the AutoChem II 2920 (Micromeritics) coupled with the quadruple mass spectrometer (HPR-20 with triple filter, Hiden Analitical). Prior to the main experiment, the catalyst sample (0.1 g, 0.3-0.6 mm) was treated with the 6% H₂/Ar mixture, at the temperature of 500°C for 1 hour and next it was cooled down to -70°C. The TPO measurement was performed using 5 %O₂/He and heating of the catalyst sample from -70°C to 600°C with the temperature ramp of 10° C×min⁻¹. In all cases, i.e. during the pre-treating and the main experiment, the total flow rate of the reaction mixture was 45 mL min⁻¹. Studies of the catalyst coking under the steam reforming of ethanol conditions were performed by the thermogravimetric method using the TG121 microbalance system (CAHN), under dynamic conditions in a quartz reactor with a continuous flow of ethanol-water vapours diluted with He at 420 °C. The molar ratio of H₂O/ethanol was equaled to 12/1 (ethanol concentration of 7.1 mol%). Prior to reaction, catalyst sample (0.01 g, 0.3-0.6 mm) was reduced by passing 10 % H₂/He flow at the temperature of 500°C for 1 hour. In all cases, i.e. during pre-treating and main experiment, the total flow rate of the reaction mixture was 70 mL min⁻¹. Quantification of the carbon formation rate (CFR) on catalysts was calculated according to the equation [29]:

$$CFR = \frac{m_{carbon}}{m_{usedcatalist} \times t}$$
(1)

where:

 m_{carbon} - is the mass of carbon deposited on the catalyst calculated from TG; $m_{usedcatalyst}$ - is the mass of the catalyst, t – is the time of the reaction of steam reforming of ethanol. SEM images were taken using a FIB-SEM Crossbeam 540 FEG (Zeiss) with an acceleration voltage of 1.8 kV. For SEM observations, the samples were prepared by drying the solution of

catalyst diluted in 98% ethanol dropped on carbon tape at room temperature. The TEM and STEM images of catalysts were obtained in scanning/transmission electron microscope TALOS F200X (FEI Company), equipped with field emission gun (X-FEG), HAADF detector and EDS spectrometer. Microscopic studies of the catalyst were conducted at an accelerating voltage of the electron beam equal to 200 kV. The mapping was conducted in the STEM mode by collecting point by point EDS spectrum of each of the corresponding pixels in the map. The collected maps were presented in the form of a matrix of pixels with the color mapped significant element and the intensity corresponding to percentage of the element.

2.3. Catalytic performance test

The reaction of ethanol conversion was performed in a Microactivity Reference unit (PID Eng & Tech.) under atmospheric pressure in a fixed-bed continuous-flow quartz reactor over the catalyst (0.3-0.6 mm) reduced in situ with hydrogen with a flow rate of 100 ml min⁻¹ at 500°C for 1 hour, prior to the reaction. The catalysts mass was selected as 0.05 or 0.1 g in order to reach space velocity equal to 120000 and 60000 ml/g h, respectively. The catalyst diluted at the weight ratio of 1/25 with the same size of quartz in order to avoid temperature gradients and hot spots. The aqueous solution of ethanol with molar ratio H₂O/ethanol of 12/1 or 4/1 corresponded to the constant ethanol concentration around 7.7 mol% was supplied by a $(H_2O/ethanol=12/1)$ and 2.21 controller (Bronkhorst) (5.20 g h^{-1} mass $g h^{-1}$ (H₂O/ethanol=4/1)) to a michrochannel evaporator (Fraunhofer-ICT-IMM) heated by a heating cartridge. The temperature was controlled with integrated K-type thermocouple (150°C). The reactant vapours were fed to the reactor at an actual flow rate of 100 mL·min⁻¹ without diluting with any inert gas in order to work in similar conditions expected in a real fuel cell for H₂O/ethanol molar ratio of 12/1 or at an actual flow rate of 38.5 mL min⁻¹ diluted with argon with the flow rate of 61.5 mL/min for H₂O/ethanol molar ratio of 4/1. The analysis of the reaction mixture and the reaction products (all in the gas phase) were carried out on-line

by means of two gas chromatographs. One of them, Bruker 450-GC was equipped with two columns, the first filled with a porous polymer Porapak Q (for all organics, CO_2 and H_2O vapor) and the other one – capillary column CP-Molsieve 5Å (for CH₄ and CO analysis). Helium was used as a carrier gas and a TCD detector was employed. The hydrogen concentration was analyzed by the second gas chromatograph, Bruker 430-GC, using a Molsieve 5Å, argon as a carrier gas and a TCD detector. Argon was used as an internal standard. In the case of the experiment with molar ratio H₂O/ethanol=12/1, argon was introduced out of the reactor. Because argon flow rate in each steam reforming test was fixed, based on the argon content in outlet, it was possible to calculate the selectivity to products in each experiment.

The conversion of ethanol (X_{EtOH}) and conversions of ethanol into individual carboncontaining products (X_{CP}) were calculated on the basis of its concentrations before and after the reaction:

$$X_{EtOH} = \frac{C_{EtOH}^{in} - C_{EtOH}^{out}}{C_{EtOH}^{in}} \times 100\%$$
(2)

$$X_{CP} = \frac{n_i C_i^{out}}{\sum n_i C_i^{out}} \times 100\%$$
(3)

where:

 C_{EtOH}^{in} - is the molar concentration of ethanol in the reaction mixture (mol%); C_{EtOH}^{out} - is the molar concentration of ethanol in the post-reaction mixture (mol%); C_i^{out} - is the molar concentration of carbon-containing product in the post-reaction mixture (mol%); n_i – is number of carbon atoms in carbon-containing molecule of the reaction product.

The selectivity of hydrogen formation was determined as:

$$H_{2} \text{selectivity} = \frac{C_{H_{2}}^{\text{out}}}{C_{H_{2}}^{\text{out}} + 2 \times C_{CH_{4}}^{\text{out}} + 2 \times C_{C_{2}H_{4}}^{\text{out}} + 2 \times C_{CH_{3}CHO}^{\text{out}} + 3 \times C_{(CH_{3})_{2}CO}^{\text{out}}} \times 100\%$$
(4)

10

where:

 C^{out} - is the molar concentration of the hydrogen-containing products in the post-reaction mixture (mol%).

Blank runs (without catalyst) have been performed in order to confirm complete vaporization of ethanol and water. These runs have been carried in an empty quartz reactor and with maintaining the same conditions as in the runs with catalyst. The quantitate analysis of the reaction mixture by means of Bruker 450-GC chromatograph confirmed that H_2O /ethanol molar ratio was equal to 12/1 or 4/1.

3. Results and discussion

3.1. Catalyst characterization

A summary of the physicochemical properties of the synthesized Co/CeO₂, CoxCe/CeO₂, Ni/CeO₂ and Ni-xCe/CeO₂ catalysts and CeO₂ commercial support are presented in Tables 1 and 2. It can be seen that the real content of cobalt or nickel was close to the nominal value of 10 wt.%. All catalysts had a medium BET surface area which was contributed to the support CeO₂. There is no clear dependence between BET surface area and the amount of ceria introduced from Ce(NO₃)₃ × 6H₂O precursor. However, the highest values of this parameter were obtained for catalysts with Ce/Co and Ce/Ni molar ratio equal to 0.5. All catalysts possessed a mesoporous structure but it was found that a pore size and pore volume slightly decreased with an increase in contribution of ceria introduced from Ce(NO₃)₃ × 6H₂O precursor. Two different techniques were used, hydrogen chemisorption (Table 1) and XRD line broadening (Table 2), to measure metal particle size. Average crystallite diameters estimated from these methods were found to be in poor agreement. Application of hydrogen chemisorption method gives data about the amount of metal atoms exposed on the sample surface [30]. Usually, the stoichiometry of the adsorption is assumed to be one hydrogen atom for one surface metallic atom. However, it is well known that the presence of

ceria in a system will cause problems with the estimation of metal dispersion by chemisorption-based methods. Particle size calculation is speculative because in the case of metal supported on ceria, it has been observed that the support is able to chemisorb large amounts of hydrogen via a spillover phenomenon [31]. The easier reduction of ceria in the presence of transition metal, such as cobalt and nickel, was repeatedly confirmed [11, 32-34] and explained on the basis of hydrogen dissociation at the metal surface and its subsequent spillover onto the ceria support. However, the cobalt and nickel crystallites size were determined by chemisorption method and presented in Table 1. Whereas table 2 lists the crystallite sizes calculated using the Scherrer equation for unreduced and reduced cobalt- and nickel-based catalysts. After reduction, the CeO₂ crystallite size remained unchanged for all catalysts in comparison with crystallite size of unreduced catalysts. In addition, all catalysts exhibited the similar CeO₂ crystallites size regardless of the amount of introduced CeO₂ from $Ce(NO_3)_3 \times 6H_2O$ precursor. No signals from a cobalt-containing phase were detected after reduction in the diffraction patterns of Co/CeO₂ and Co-0.1Ce/CeO₂ catalysts which indicates that it was well-dispersed. But the addition of a larger amount of CeO₂ from Ce(NO₃)₃ \times 6H₂O precursor led to an increase in the size of metallic cobalt crystallites to 14.4 and 17.4 nm for Co-0.5Ce/CeO₂ and Co-Ce/CeO₂ catalyst, respectively. In the case of nickel-based catalysts, metallic nickel crystallites of Ni/CeO₂ and Ni-0.5Ce/CeO₂ were comparable (d= ~10 nm) and metallic nickel crystallites of Ni-0.1Ce/CeO₂ catalyst were the smallest (d=7.2 nm) among all studied nickel-based catalysts. The increase of Ce/Ni molar ratio to 1 caused, however, a significant increase in the size of metallic nickel crystallites of Ni-Ce/CeO2 catalyst to 21.4 nm. These results differ from these obtained for Ni-xCe/MMT [35] and NixCe/SBA-15 [36] catalysts which indicated that nickel particles are smaller with the increase of the content of ceria promoter. However, Xiao et al. [37] also observed that only low amount of CeO₂ allowed to reduce nickel particle size and enhanced nickel dispersion of Co-

Ni/xCeO₂-Al₂O₃ catalyst whereas too high content of this promoter caused agglomeration of nickel particles. Moreover, the crystallites of NiO (before reduction) were mostly smaller than the metallic nickel crystallites (after reduction) suggesting that the reduction process increased the crystallite size by agglomeration or sintering of the active phase (Table 2) [4]. Whereas the cobalt species with exception of Co-0.5Ce/CeO2 catalyst undergone the re-dispersion under reduction conditions and the metallic cobalt particles become smaller in comparison with the size of Co₃O₄ crystallites (Table 2) [38]. Probably the bonding between cobalt species and surface cerium atoms became stronger and thus more stable upon reduction, which, in turn, led to the re-dispersion of metallic cobalt on ceria [38]. The XRD patterns of Co-xCe/CeO₂ and Ni-xCe/CeO₂ catalysts before and after their reduction with hydrogen at 500 °C (see Supporting Information, Figs. S1a-d and S2a-d) showed reflections related to fluorite face-centered cubic CeO₂ structure (JCPDS 34-0394). Moreover, the XRD patterns of unreduced cobalt-based catalysts promoted with CeO2 revealed reflection line at 20=36.8° attributed to cubic spinel Co₃O₄ (JCPDS 43-1003). In the diffraction pattern of unreduced Ni-0.1Ce/CeO₂ and Ni-0.5Ce/CeO₂ catalysts, signals of nickel-containing phase were not observed suggesting its small particle/crystalline sizes since the XRD technique presents limitations especially for crystalline sizes below 2-4 nm [20, 39] and metal loading smaller than 20 wt.% [39]. Only in the case of diffractograms of unreduced Ni/CeO2 and Ni-Ce/CeO2 catalyst, very broad and small diffraction reflections at 2θ =37.2 and 43.1° corresponding to cubic NiO phase (JCPDS 01-1239) were observed. The XRD patterns of all studied cobaltand nickel-based catalyst after their reduction with hydrogen at 500 °C for 1 hour confirm that the active phase precursors (Co₃O₄ or NiO) were reduced to metallic cobalt (JCPDS 01-1277) or nickel (JCPDS 01-1258). Lines characteristic of Co₃O₄ or NiO phases were no longer detected, suggesting that the Co₃O₄ or NiO reduction was complete. However, taking into account the results obtained by Xiao et al [40], the XRD technique could give false

information of particle size of the studied catalysts because cobalt/nickel nanoparticles could be partially or fully covered by ceria introduced from CeO₂ from Ce(NO₃)₃ × 6H₂O precursor. Moreover, detailed analysis of diffractograms revealed that there was no shift in characteristic reflection of CeO₂ neither to the higher nor to the lower angles after ceria introduction from Ce(NO₃)₃ × 6H₂O precursor which means that the interaction between Co₃O₄ and CeO₂ and NiO and CeO₂ was not enhanced. It was also confirmed by the calculation of the lattice parameter of CeO₂ (Table 2) which remained almost unchangeable for all catalysts. These results exclude solid solution formation in the studied cobalt-ceria and nickel-ceria systems

The morphological properties of promoted with ceria cobalt- and nickel-based catalysts were studied by high-resolution STEM-EDS analysis (see Supporting Information, Figs. S3-S8) which indicates the spatial distribution of the cobalt or nickel elements on the surface of ceria. For the Co-0.1/CeO₂ catalyst, cobalt species were mostly distributed on the surface of ceria (Fig. S3). For the Co-0.5Ce/CeO₂ catalyst there were areas where cobalt and cerium species did not overlap suggesting that cobalt was not located on the surface of ceria and remained unsupported. However, most of it was definitely supported (Fig. S4). Whereas in the case of Co-Ce/CeO₂ catalyst, the cobalt and cerium species were not in contact with each other, i.e. empty, wide areas of the ceria and isolated unsupported cobalt species were mainly found (Fig. S5). It means that the proposed method of the catalysts preparation indicates limitation to the amount of cerium precursor which can be introduced with cobalt precursor during co-impregnation the ceria support. This limitation was observed in a lesser degree for the considered nickel-based catalyst samples. Nickel species are mostly distributed over ceria support regardless of the amount of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor (Figs. S6-S8). However, small areas that the nickel was unsupported were also observed for Ni-0.5Ce/CeO₂ (Fig. S7) and Ni-Ce/CeO₂ catalysts (Fig. S8). The results obtained for both cobalt- and nickel-based catalysts suggest that preparation method shows a low repeatability

for catalysts with high amount of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor corresponding to Ce/Co(Ni) molar ratio higher than 0.5.

The reduction behavior of the ceria support and cobalt- and nickel-based catalysts was studied by H₂-TPR, as shown in Figs. 1a and b. The H₂-TPR profile of ceria showed peaks at two different temperature ranges. First peak at low temperatures ranging from 240 to 500 °C is assigned to the reduction of adsorbed and surface lattice oxygen of ceria. Whereas the second peak above 580 °C is due to the reduction of bulk CeO₂ [41-43]. In the case of CoxCe/CeO₂ catalysts (Fig. 1a), hydrogen consumption corresponding to first peaks below 200 °C is attributed to the removal of oxygen species adsorbed on ceria oxygen vacancies [11, 28] and the reduction peak centered at about 240 °C is due to the reduction of Co₃O₄ to CoO [44– 46]. Whereas the next peak appearing at temperature of about 290 °C – 300 °C is the result of the reduction of CoO that weakly interacts with ceria to metallic cobalt [45, 46] or the reduction of independent Co₃O₄ that weakly interacts with ceria directly to metallic cobalt [44]. This peak is small for both Co/CeO₂ and Co-0.1Ce/CeO₂ catalysts which suggests that these catalysts contain small amount of cobalt species that interact weakly with the support. But intensity of this peak increases with the increase of content of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor which is in good accordance with STEM-EDS data which indicated that amount of unsupported and isolated from ceria cobalt phase (weakly interacting with the support) increased with the increase of Ce/Co molar ratio. The next peak, with the maximum in the temperature range from 420 to 470 °C depending on the catalyst, is attributed to the reduction of cobalt oxide species which strongly interacted with the ceria and it probably overlapped with the surface reduction of ceria [44-46]. According to Wu et al. [47] and Luo et al. [44], however, surface ceria reduction is attributed to peak detected at lower temperature (240 °C) and overlapped with reduction of Co₃O₄ to CoO. Undoubtedly, the last peak above 580 °C observed in H₂-TPR profiles of Co-xCe/CeO₂ catalysts is specifically

related to bulk reduction of ceria [12, 25]. The same peak is also observed in H₂-TPR profiles of all considered Ni-xCe/CeO₂ catalysts and it is assigned the same process (Fig. 1b). Because the adsorbed oxygen molecules are very reactive oxygen species and ready to be reduced by hydrogen at low temperature, the peak located below 220 °C can be ascribed to the reduction of the adsorbed oxygen species in ceria oxygen vacancies [48]. The next broad peak in H₂-TPR profiles of Ni-xCe/CeO₂ catalysts in the temperature range from about 240 to 420 °C included the reduction of a dispersed NiO phase interacting weakly with ceria and step-bystep reduction of a well-dispersed phase interacting strongly with ceria [49]. However, it could not be excluded that surface ceria reduction also occurred in the discussed temperature range. As can be seen in both Fig. 1a and Fig 1b, the peak of reduction of a well-dispersed phase interacting strongly with ceria shifts gradually to lower value after increasing Ce/Co(Ni) molar ratio from 0.1 to 1, indicating weakened interaction between cobalt or nickel species and ceria at higher promoter content [49]. A summary of H₂-TPR results is shown in Table 3. The highest values of H/M and the hydrogen consumption were obtained for Co/CeO₂ and Ni/CeO₂ catalysts. These values were higher than the calculated ones for the reduction of Co₃O₄ or NiO to metallic cobalt or nickel, respectively (based on the cobalt/nickel amount calculated from XRF) which is typical of CeO₂ supported catalysts and is a consequence of the high hydrogen spillover rate and confirmation of surface reduction of ceria below 500 °C along with cobalt/nickel species reduction [50]. An examination of the data reported in Table 3 reveals a gradual suppression of hydrogen consumption with the increase of the ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor. The order in the H/M values is C_0/CeO_2 (2.91) > $C_0-0.1Ce/CeO_2$ (2.78) > $C_0-0.5Ce/CeO_2$ (2.74) > C_0-Ce/CeO_2 (2.71) and Ni/CeO₂ (2.30) > Ni-0.1Ce/CeO₂ (2.23) > Ni-0.5Ce/CeO₂ (2.07) > Ni-Ce/CeO₂ (2.03). Moreover, in the case of Co-0.5Ce/CeO2, Co-Ce/CeO2, Ni-0.5Ce/CeO2 and Ni-Ce/CeO₂, quite a good agreement between calculations of H/M values and their expectations

2.67 and 2.0 for Co-xCe/CeO₂ and Ni-xCe/CeO₂ catalysts, respectively can be noticed. Because the spillover phenomenon of hydrogen occurs when there is a direct interaction between the ceria surface and the transition metal, a gradual suppression of hydrogen consumption with the increase of the ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor is not surprising. The EDS maps (Figs. S4-S5 and S7-S8) show that there are areas of the lack of intimate contact between cobalt/nickel species and ceria in the case of catalysts with higher Ce/Co(Ni) molar ratio. Besides the intimate contact between metal dissociation source and ceria, the high dispersion and small size of metal particles are crucial to facilitate the hydrogen spillover. The well dispersed metal particles close to the ceria activate the hydrogen dissociation and by hydrogen spillover favors the reduction of ceria surface [51, 52]. Sermon and Bond [53] emphasized the importance of the degree of dispersion and contact of the catalyst phases in studies on hydrogen spillover and the confusion which can arise in comparing systems in which these parameters are unknown indicating that the extent of hydrogen spillover can be lesser in the catalysts where contact between the two phases is insufficient. Moreover, it should be remembered that spillover phenomena depends on many other factors such as the size of the ceria nanoparticle the stability of the Ce 4f levels [54], morphology of ceria [55], the hydroxylation of ceria surface [56], the dispersion state of ceria [57].

Literature data suggests that metallic nickel is the active phase for C-C bond cleavage [26, 27, 58]. There remains a disagreement on the role of metallic cobalt and CoO during SRE reaction. Numerous papers assumed that the metallic cobalt is the most active form of cobalt in SRE [16, 59-61] but the literature does not provide a definitive consensus on this issue. Recently, the ideas that Co^0/Co^{2+} ratio forms during SRE might favor different reaction paths has been gaining ground. According to Martono and Vohs [62, 63], metallic cobalt is most active for decomposition and decarboxylation reactions while CoO favors dehydrogenation of

ethanol to acetaldehyde. The similar conclusion were drawn by Passos et al [4] who also stated that the presence of CoO species plays a role in the selectivity towards ethanol dehydrogenation to acetaldehyde and formation of methane because of acetaldehyde decomposition. Karim et al. [52] found that metallic cobalt is active for water gas shift reaction whereas methanation increases if CoO phase becomes more predominant. Whereas Turczyniak et al. [12] showed that in the presence of metallic cobalt carbon monoxide is favored, while CoO species promotes carbon dioxide and acetaldehyde yields. The profiles of O₂-TPO for CeO₂, Co-xCe/CeO₂ and Ni-xCe/CeO₂ catalysts, depending on their composition, are presented in Figs. 2a and b. In case of both cobalt- and nickel-based catalysts a few oxidation peaks are observed. Because similarly to Luo et al. [44] studies, O₂-TPO profile of ceria indicates that there was no detectable oxygen consumption peak for pure ceria it could be supposed that all peaks observed in Figs. 2a and b result from oxidation of cobalt or nickel species. Moreover, Luo et al. [44] showed that for unsupported cobalt metal, a broad oxygen consumption peak occurs at 393 °C due to the oxidation of metallic cobalt to Co₃O₄. Results obtained by Sewell et al. [64], however, indicated that O₂-TPO profiles of unsupported cobalt metal are characterized by two oxygen consumption maxima at 298 and 583 °C corresponding to the sequential oxidation of metallic cobalt first to CoO and then to Co₃O₄. The maxima of the last peaks present in the O₂-TPO profiles of all ceria supported cobalt catalysts (Fig. 2a) are below 300 °C which indicates that interaction between cobalt species and ceria can contribute to easier oxidation of cobalt species as it was suggested by Luo et al. [44]. Furthermore, oxidation of cobalt species of ceria supported cobalt catalysts is rather complex as can be seen in Fig. 2a. As it was suggested by Greluk et al. [11], the first peaks can be attributed to oxidation of the surface layer of cobalt crystallites whereas a broad oxygen consumption peaks at higher temperature of Co-xCe/CeO₂ catalysts probably resulted from oxidation of metallic cobalt. The shift of high-temperature oxidation peaks towards

higher temperatures with the increase of ceria content introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor is related to the decrease of metal dispersion degree [44]. Metallic cobalt particles of Co/CeO₂ and Co-0.1Ce/CeO₂ catalysts oxidized more easily at low temperature than those of Co-0.5Ce/CeO₂ and especially of Co-Ce/CeO₂ catalysts because cobalt particles for the catalysts with lower amount of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor were smaller. It means that the higher dispersion of cobalt species corresponds to lower oxidation temperature of metallic cobalt [44]. According to Luo et al. [44], high cobalt dispersion can ensure a more profound contact and interaction between cobalt species and ceria, hence facilitating oxygen supply from ceria to cobalt species and promoting the oxidation of cobalt phase. The similar conclusions can be drawn for Ni-xCe/CeO₂ catalysts (Fig. 2b). In O₂-TPO profiles of these catalysts, there are also low-temperature peaks which can be attributed to oxidation of the surface layer of nickel crystallites and a broad oxygen consumption peaks at higher temperature resulted probably from oxidation of metallic nickel. The shapes of O₂-TPO profiles and the locations of oxygen consumption peaks for Ni/CeO₂, Ni-0.1Ce/CeO₂ and Ni-0.5Ce/CeO₂ catalysts are very similar (Fig. 2a) because the size of nickel crystallites of these catalysts is comparable as it was indicated by hydrogen chemisorption or XRD results (Tables 1 and 2). But the nickel crystallites of Ni-Ce/CeO₂ catalyst are much larger and its O₂-TPO profile differs from the remaining nickel-based catalysts. It is noticeable that it is more difficult to oxidize the nickel species of this catalyst.

3.2. Catalytic performance test of Co-xCe/CeO₂ and Ni-Ce/CeO₂ catalysts in SRE reaction

The activity test of $Co-xCe/CeO_2$ and $Ni-Ce/CeO_2$ catalysts in SRE reaction was evaluated by the reactants conversion and the selectivity to the products. To compare the catalytic properties of the catalyst and influence of ceria content on it, the condition of the process which was not to ensure complete ethanol conversion was chosen. Because space

velocity of 60000 mL/g h allowed 100 % ethanol conversion over nickel-based catalysts (see *Supporting Information*, Fig. S9), it was increased to 120000 mL/g h in case of catalytic tests for these catalysts by decreasing the catalyst mass. The comparison of catalysts at full conversion is meaningless because obtained results can be the consequence of an excess of contact time (i.e. of catalyst mass) for the test conditions selected. Therefore, it cannot be sait if the whole catalyst sample in the catalytic bed is really working or part of it cannot work because ethanol is exhausted before reaching it. It is also possible that an activity decay is not observed because, if catalyst amount is in excess, the decay is compensated by a higher amount of catalyst taking part in the reaction (without still reaching the total of the bed). The results obtained from catalytic tests at 420 °C for H₂O/EtOH molar ratio of 12/1 after 21 hours of SRE reaction over Co-xCe/CeO₂ and Ni-Ce/CeO₂ catalysts are shown in Figs. 3a and b (see also *Supporting Information*, Figs. S10 and S11).

As it was suggested by Song et al. [65], the first step of a typical reaction pathway for ethanol decomposition over cobalt sites involves the formation an ethoxy species through the dissociative adsorption of ethanol. The second step consists of eliminating hydrogen from the ethoxy intermediate which produces an aldehyde intermediate. Acetaldehyde can desorb to the gas phase, decompose to methane and carbon monoxide, or undergo further abstraction which leads to the formation of acetyl species [66]. This reaction pathways observed for ethanol adsorption over nickel sites are very similar. As demonstrated previously by Gates et al. [67], the decomposition of ethanol on the nickel surface forming these products occurs by a sequence of bond scission: (i) the scission of the H–O– bond of the ethanol molecule to form adsorbed ethoxy; (ii) the scission of the -C-H bond of the C-C bond of intermediate of acetaldehyde; (iii) the scission of C-C bond of intermediate of acetaldehyde; (iii) the scission of C-C bond of intermediate of acetaldehyde adsorbed to form adsorbed $-CH_3$ and -CO [68]. It is well known that the oxidation products, resulting from ethanol transformation (e.g. acetate) are present to greater

extent over metal oxide supported metals because of the availability of oxygen on surfaces of these materials [66]. Both acetaldehyde and acetyl species can be oxidized to acetate species by hydroxyl groups or by oxygen from the support. The acetate species can be further oxidized to carbonate species that decompose to give carbon dioxide. Finally, acetaldehyde can contribute to the formation of acetone through condensation of acetate or acetyl species. These reactions take place mainly over the support and depend on the nature of the metal oxide [66].

The discussion on results concerns only those obtained after 21 hours of the process and presented in Figs. 3a and b. With this aim, bar graphs were chosen because they are better for comparing the small differences in the data among the groups of Co-xCe/CeO₂ (Fig. 3a) and Ni-xCe/CeO₂ (Fig. 3b) catalysts. Using bar graphs (Figs. 3a and b) data can be shown in a clear manner and any differences in activity and selectivity to products of the catalysts during SRE process in dependence of ceria amount introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor can be noticed better. Moreover, error bars as graphical representations of the uncertainty were used on Figs. 3a and b to indicate the standard deviation in reported measurement. Usually the decreasing of catalyst stability is determined by measuring activity or/and selectivity as a function of time. The changes in trend over the time displayed as line plots (see Supporting Information, Figs. S10 and S11) are not discussed. However, the loss over time of catalytic activity and selectivity is observed in the case of all catalysts (see Supporting Information, Figs. S10 and S11) because of carbon formation (described in detail in the section 3.3). The time of 21 hours of SRE reaction was sufficient to observe the differences in catalytic performance between catalysts, although it was too short to obtain the steady state of the catalysts under SRE conditions. It means that the non-steady-state behavior caused by the deactivation of the catalyst is illustrated on Fig. 3a and b.

The increase of ceria amount introduced from Ce(NO₃)₃ × 6H₂O precursor does not have significant influence on the ethanol conversion over cobalt-based catalysts but slight differences in the selectivity to some products in dependence of the Ce/Co molar ratio after 21 hours of SRE process are observed (Fig. 3a). All cobalt-based catalyst, with the exception of Co-Ce/CeO₂ sample, exhibit a comparable selectivity to two most desirable products of the reaction, i.e. hydrogen (~75% for Co/CeO₂, ~76% for Co-0.1Ce/CeO₂, ~75% for Co-0.5Ce/CeO₂) and carbon dioxide (~39% for Co/CeO₂, ~41% for Co-0.1Ce/CeO₂, ~38% for Co-0.5Ce/CeO₂) after 21 hours of SRE process. The formation of these products is slightly lower only in the presence Co-Ce/CeO₂ catalyst (H₂ ~72%, CO₂ ~ 32%) (Fig. 3a). As it was reported by Zhang [69], in the case of ceria, water is chemisorbed on vacancies of its surface forming hydroxyls, which migrate through oxygen vacancies on the ceria surface. These oxygen species (including hydroxyls) originating from water can oxidize CO and CH_x to form H₂ and CO_x. Therefore, if there are sufficient oxygen species on the catalyst surface, the intermediate products can be fully converted to carbon dioxide and hydrogen by WGS reaction (reaction 1) [33]:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 (1)

All cobalt-based catalysts exhibit highest carbon dioxide formation (~39% for Co/CeO₂, ~41% for Co-0.1Ce/CeO₂, ~38% for Co-0.5Ce/CeO₂, ~32% for Co-Ce/CeO₂) in comparison with production of carbon monoxide (~6% for Co/CeO₂, ~5% for Co-0.1Ce/CeO₂, ~5% for Co-0.5Ce/CeO₂, ~7% for Co-Ce/CeO₂) after 21 hours of SRE reaction which suggests that WGS reaction is favored by cobalt-based catalysts supported on ceria and is consistent with conclusion of Marcos et al. obtained for Co/CeO₂ catalyst [3]. Also similarly to results obtained in this study, Marcos et al. [3] showed that high ethanol conversion of Co/CeO₂ catalyst was directed to the formation of acetaldehyde (~13% for Co/CeO₂, ~12% for Co-0.1Ce/CeO₂, ~16% for Co-0.5Ce/CeO₂, ~19% for Co-Ce/CeO₂) and acetone (~39% for

Co/CeO₂, ~36% for Co-0.1Ce/CeO₂, ~38% for Co-0.5Ce/CeO₂, ~37% for Co-Ce/CeO₂) after 21 hours of SRE process. According to Carvalho et al. [24], the formation of acetaldehyde in the presence of Co/CeO₂ catalysts suggests that the basicity of ceria (owing to their basic lattice O^{2-} sites on the surface) stabilized the adsorbed acetaldehyde. As it was explained by the authors [24], the oxygen radicals on the surface of ceria can favor the dissociative adsorption of ethanol (reaction 2) with consequent dehydrogenation to acetaldehyde (reaction 3) as follows:

$$C_2H_5OH + O^{2-} \rightarrow C_2H_5O^- + OH^-$$

 $C_2H_5O^- + OH^- \rightarrow CH_3CHO + H_2 + O^{2-}$

Because ethanol dehydrogenation to acetaldehyde is enhanced on the basic supports [70], also Sohn et al [71] suggested that this reaction mainly takes place on the reduced surface having Ce³⁺ sites, which are more basic. The results presented in Fig. 3a show that Co/CeO₂ and Co-0.1Ce/CeO₂ catalysts exhibit the lowest selectivity to acetaldehyde in comparison with two remaining cobalt-based catalysts with higher Ce/Co molar ratio. The selectivity to acetaldehyde is comparable for Co/CeO₂ and Co-0.1Ce/CeO₂ catalysts and slightly increases with the increase of ceria amount introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor. Barroso et al. [72] suggested that the highest formation of hydrogen and the lowest acetaldehyde production of ceria containing cobalt-based catalysts come out of the highest dispersion of cobalt in the presence of ceria. Also Marcos et al. [3] ascribed the higher hydrogen yield of the mixed Co/La₂O₃-CeO₂-SiO₂ with varied La₂O₃ and CeO₂ content to smaller cobalt species crystallite size, greater metal area and dispersion which meant more active sites available to react in comparison with the catalyst without mentioned promoters. Because in the case of considered Co-xCe/CeO₂ catalysts, only low Ce/Co molar ratio allows to improve cobalt dispersion (Table 1 and Table 2) leading to larger cobalt active phase for breaking C-C and C-H bonds, both Co/CeO₂ and Co-0.1Ce/CeO₂ catalysts indicated less selectivity to acetaldehyde after 21

(2)

(3)

hours of SRE process (Fig 3a). Because besides the presence of aldehyde among the products of SRE reaction over all studied Co-xCe/CeO₂ catalysts also acetone was detected in the significant amount, it suggests that cobalt-based catalysts are not very active in breaking C–C bonds at 420 °C. The presence of acetone which is formed either by coupling of two acetate molecules or the disproportionation of two acetyl species [66] is very undesirable because acetone can polymerize to produce carbon which would cause catalyst deactivation [73]. Since small amount of ethylene in the presence of all Co-xCe/CeO₂ (~1.5% for all catalysts) was also detected, it is likely that dehydration of ethanol occurred (reaction 4):

$C_2H_5OH \rightarrow C_2H_4 + H_2O$

The obtained results indicates that the lowest amount of C2 and C3 products was observed over Co-0.1Ce/CeO₂ catalysts which suggests that the presence of cobalt species with a small particle size and enhancement of metal-support interactions guarantee higher activity in C–C bond cleavages and is in good accordance with results obtained by Song et al [17] and Carvalho et al. [24]. The low selectivity to methane over all catalysts (~3% for all catalysts) after 21 hours of SRE process suggests that the Co-xCe/CeO₂ catalysts promoted the steam reforming of methane (reaction 5) [74]:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{5}$$

Both polimeryzation of ethylene (reaction 6) and methane dehydrogenation (reaction 7) are the possible routes for carbon deposition on cobalt-based catalysts. However, the carbon formation on the studied Co-xCe/CeO₂ catalysts because Boudouard reaction (reaction 8) cannot be excluded:

$$C_2H_4 \rightarrow coke$$
 (6)

$$CH_4 \rightarrow C + H_2$$
 (7)

$$CO \rightarrow C + CO_2$$
 (8)

(4)

According to Carvalho et al. [24]. both methane decomposition and/or the Boudouard reaction include hydrogen and carbon dioxide as by-products and their contribution can influence the high selectivity to mentioned products under SRE conditions over Co/CeO₂ catalysts. From the distribution of the main products (H₂, CO, CO₂, CH₄ and C₂H₄, acetaldehyde, acetone), it can be inferred that the predominant reactions are: the dehydrogenation of ethanol to acetaldehyde (reaction 9), followed by the complete acetaldehyde decomposition to carbon monoxide and methane (reaction 10) and/or decomposition of ethanol (reaction 11), followed by WGS reaction (reaction 1) and dehydration of ethanol (reaction 4). Moreover, aldol condensation reaction of acetaldehyde to acetone, carbon monoxide and hydrogen (reaction 12) occurred over the Co-xCe/CeO₂ under studied conditions rather than the steam reforming of acetaldehyde (reactions 13) as it is suggested by large amount of acetone detected among by-products of SRE reaction.

$C_2H_5OH \rightarrow CH_3CHO + H_2$	(9)
$CH_3CHO \rightarrow CH_4 + CO$	(10)
$C_2H_5OH \rightarrow CH_4 + CO + H_2$	(11)
$2CH_3CHO \rightarrow CH_3COCH_3 + CO + H_2$	(12)

 $CH_3CHO + H_2O \rightarrow 2CO + 3H_2 \tag{13}$

Regarding the products distribution, all Ni-xCe/CeO₂ catalysts displayed the same products as Co-xCe/CeO₂ catalysts but with different distributions (Fig. 3b). It suggests that ethanol transformations over Ni-xCe/CeO₂ catalysts proceeded through the same reactions as in the case of Co-xCe/CeO₂ catalysts. However, nickel displayed a higher activity for the methanation leading to increased methane selectivity which is highly undesirable since it consumes hydrogen [70] (reactions 14).

$$CO + 2H_2 \rightarrow CH_4 + H_2O$$
 (14)

The selectivity to methane was slightly lower for the Ni-0.5Ce/CeO₂ (~17%) and Ni-Ce/CeO₂ (~14%) catalysts among the studied nickel-based catalysts (~19% and for Ni/CeO₂ and ~23% Ni-0.1Ce/CeO₂) after 21 hours of SRE process (Fig. 3b) which indicates that methanation was suppressed in the presence of a high content of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor. Simultaneous increase of hydrogen and carbon monoxide production in the presence of the Ni-0.5Ce/CeO₂ (H₂ \sim 84%, CO \sim 8%) and Ni-Ce/CeO₂ (H₂ \sim 84%, CO \sim 15%) catalysts can suggests that catalysts with molar ratio of Ce/Ni above 0.5 promoted the steam reforming of methane (reaction 5) (H₂ ~75%, CO ~ 7% for Ni/CeO₂, H₂ ~81%, CO ~ 7% for Ni-0.1Ce/CeO₂.) It is in accordance with hypothesis that ceria promotes steam reforming reactions due to an improvement in the adsorption and dissociation of water molecules on the surface of catalyst [75]. But promotional effect of ceria on the reactions responsible for carbon formation, methane cracking (reaction 7) may not be excluded [29]. On the other hand, Xu et al. [27] proposed that the strong metal-support interactions between nickel and ceria perturb the electronic and chemical properties of nickel adatoms reducing their ability to break C-O bonds and substantially decrease the carbon monoxide methanation activity of nickel which suggests that methane production over Ni-0.1Ce/CeO₂ catalysts should be the lowest because it exhibited the highest nickel active phase dispersion (Table 1 and Table 2) and the strongest metal-support interactions (Fig. 1). However, the highest selectivity to methane ($\sim 23\%$) observed in the presence of this catalyst are in contradiction with this thesis. On the other hand, this catalyst allowed to significantly reduce acetaldehyde formation to ~8% in the comparison to other studied nickel-based catalysts after 21 hours of SRE process (~12% for Ni/CeO₂, ~14% for Ni-0.5Ce/CeO₂, ~17% for Ni-Ce/CeO₂) (Fig. 3b). Therefore, both high selectivity to hydrogen (~81%) and low selectivity to acetaldehyde (~8%) over Ni-0.1Ce/CeO2 catalyst could be ascribed to smaller nickel crystallite size with respect to other studied nickel-based catalysts (Table 2) due to the dispersing effect obtained by introduction

of low amount of ceria from Ce(NO₃)₃ \times 6H₂O precursor [34, 75]. Similarly as in the case of cobalt-based catalysts, a smaller crystallite size of nickel active phase (Table 2) results in enhanced metal-support interactions which leads to increase metal active sites for breaking C-C and C-H bonds and facilitates the ethanol conversion and other C2 intermediates. Also Ebiad et al. [76] ascribed superior activity of Ni/CeO₂-ZrO₂ catalyst containing 2% of the active phase to the small nickel particle size. The increase of nickel active phase dispersion and metal-support interaction obtained by introduction of CeO₂ to Al₂O₃-La₂O₃ support was also an explanation for the complete conversion of ethanol in SRE process in the presence of obtained Ni/Al₂O₃-La₂O₃-CeO₂ catalyst given by Osorio-Vargas et al. [29]. Similar conclusions were drawn for promoting effect of ceria in the case of SRE reaction over Ni-Ce/MMT [35] and CeNi/SBA-15 [36] catalysts. In the case of studied catalysts ethanol conversion after 21 hours of SRE process is the highest over Ni-0.1Ce/CeO₂ catalyst and it follows the order of Ni-0.1Ce/CeO₂ (~52%) > Ni/CeO₂ (~48%) ~ Ni-0.5Ce/CeO₂ (~47%) > Ni-Ce/CeO₂ (~43%) (Fig. 3b) which corresponds to the sequence in which nickel crystallites size of these catalysts increases (Table 2). In comparison to ethanol conversion obtained for Co-xCe/CeO₂ catalysts (Fig 3a and Fig. S9) under the same SRE conditions (for space velocity of 60000 mL/g h), the activity of Ni-xCe/CeO₂ catalysts (Fig. S10) is much higher. These results are in good accordance with those obtained by Zhang et al [77] which also indicated that Ni/CeO₂ catalyst had stronger capacity for breaking C-C bond in ethanol than Co/CeO₂ catalyst. Fig. 3a indicates that the conversion of Co-xCe/CeO₂ catalysts was directed to the formation of acetone which is also with good agreement with the results obtained by Zhang et al [77]. Whereas the production of this product in the case of Ni-xCe/CeO₂ catalysts (Fig. 3b) ,despite the two times higher space velocity (1200000 mL/g h), was rather small (~6% for Ni/CeO₂, ~3% for other nickel-based catalysts) indicating that these catalysts are more capable of cleaving the C-C bond than the studied cobalt-based ones which was also

confirmed by the lower selectivity to ethylene (<0.7% for all nickel-based catalysts) demonstrated by Ni-xCe/CeO₂ catalysts after 21 hours of SRE process. Because the NixCe/CeO₂ catalysts exhibited lower selectivity to C2 and C3 intermediates than the CoxCe/CeO₂ catalysts, more C1 products in their presence were produced. It is mainly carbon dioxide which was produced in much larger amounts than carbon monoxide indicating nickelbased catalysts' capability to facilitate WGS reaction (reaction 1). Since the highest CO₂/CO ratio of 8.7 is demonstrated over Ni-0.1Ce/CeO₂ catalyst after 21 hours of SRE process (Fig. 3b), it can suggest that WGS reaction was especially favored by the small addition of ceria from Ce(NO₃)₃ × 6H₂O precursor to nickel active phase which can be attributed to the strong interaction between nickel crystallites and ceria occurring in case of this catalysts as it was confirmed by TPR method (Fig. 1b).

It must be emphasized that all considerations about catalytic properties of $co-xCe/CeO_2$ and Ni-xCe/CeO₂ catalyst concern the state which was obtained after 21 hours of SRE process. Because both cobalt-and nickel-catalysts underwent gradual deactivation due to carbon formation (described in detail in the section 3.3) under SRE conditions, it is possible that observed dependence could slightly change with the further increase in time.

3.3. Analysis of the carbon deposits on the used Co-xCe/CeO2 and Ni-xCe/CeO2 catalysts

To examine the possible carbon deposition on the catalysts during SRE process, post reaction characterization experiments were performed. The amount of carbon deposition over the Co-xCe/CeO2 and Ni-xCe/CeO2 catalysts under SRE conditions at 420 °C for H₂O/EtOH molar ratio of 12/1 was determined by using TG analysis (Fig 4a and b and Table 4) whereas to investigate the structure and morphology of the carbonaceous materials deposited on the used catalysts exposed to SRE reaction during catalytic tests under mentioned conditions, the SEM (Fig. S12) and TEM analysis was examined (Figs. 5 and 6).

The redox properties of ceria and the high lability of lattice oxygen are among the most important factors contributing to carbon minimization by ceria as a promoter under SRE conditions. The highly mobile oxygen in ceria can instantaneously react with carbon species formed during the reaction and maintain a clean metal surface whereas the oxygen vacancies are readily replenished by steam from the feed [35, 75]. As it is suggested by Osorio-Vargas et al. [29] the oxygen lattice provided by ceria may oxidize the solid carbon according to the following reaction:

$$\mathbf{C}_{(s)} + \mathbf{O}_{(l)} \rightarrow \mathbf{O}_{(l-1)} + \mathbf{CO}$$

On the other hand, studies by Senanayake et al [78] indicate that the electronic perturbations between nickel and ceria can limit the ability of nickel to break C–O bonds which could probably suppress the activity of carbon monoxide disproportion to produce carbon deposits [66]. Whereas Yang [79] suggested that electrons released from the oxygen vacancies in ceria could migrate through the Ni-CeO₂ interface to the unfilled d-orbital of Ni⁰ and due to the electron-rich property of Ni⁰, decomposition of methane could be effectively inhibited. The conclusion of these studies concerning influence of ceria on the minimization of carbon during steam reforming reactions suggest that both these promoters reduce the rate of carbon deposition and accelerates the rate of carbon gasification [75].

The results obtained from the thermogravimetric studies (Fig. 4a and b and Table 4) seem to indicate that introduction of ceria from $Ce(NO_3)_3 \times 6H_2O$ precursor to cobalt- and nickel-based catalysts allow to minimize the amount of carbon formed on their surface under SRE conditions. However, the detailed analysis of the products distribution after 21 hours of this process (Figs 3a and b) and the SEM and TEM images (Figs. S12 and 5 and 6) rather suggests that only small amount of ceria corresponding to Co(Ni)/Ce molar ratio of 0.1 prevents the cobalt- and nickel-based catalysts from carbon accumulation.

(15)

In the case of Co-xCe/CeO₂ catalysts, there were great amount of acetone produced which can undergo an aldol condensation-type reaction according to reaction 16 [80-82]: $2CH_3COCH_3 \rightarrow CH_2COHCH_3 + CH_3COCH_3 \rightarrow (CH_3)_2C(OH)CH_2COCH_3 \rightarrow (CH_3)_2CCHCOCH_3 (MO) + H_2O \rightarrow oligomers$ (16)

Condensation reactions by attack of acetone enolate on adsorbed mesityl oxide (MO) and the resulting oligomers would yield polymerization products that can stay strongly held on the catalyst surface and lead to the formation of carbon deposits and deactivate the catalyst by blocking active sites [80-83]. A second source of polymeric carbon under SRE conditions except for the aldol condensation of acetone can stem from ethylene polymerization (reaction 6). Because ethylene was also produced over cobalt-based catalysts, it allows to suppose that Co-xCe/CeO₂ catalysts were mainly covered by polymeric carbon film. Although the possible route for carbon formation over cobalt-based catalysts as a result of methane dehydrogenation (reaction 7) and carbon monoxide disproportionation (reaction 8) could not be excluded, the carbon, which encapsulates the particles over Co-xCe/CeO2 catalysts resulting in their immediate deactivation, is mainly formed on the cobalt-based catalysts surface as the olymeric carbon, as it was suggested by Greluk et al. [84, 85]. And undoubtedly Fig. 5 demonstrated that graphitic carbon formed over Co-xCe/CeO₂ catalysts totally encapsulated a cobalt particles and thereby deactivated them. However, some not numerous short carbon filamentous with cobalt crystallites in their tips were also present (Fig. 5). According to Nolan [87], contrary to filamentous, encapsulating carbon is generated through the precipitation of several graphitic layers perpendicular to active phase crystallites, one by one, each layer wrapping the particle. Indeed, most of the carbon found on the used Co-xCe/CeO₂ catalysts was mainly graphitic (Fig. 5), i.e. the kind of carbon which has high trend for accumulation due to its low reactivity with surface oxygen species [87]. It is consistent with the data obtained from thermogravimetric studies (Fig. 4a) which shows that carbon formation was

initially high and with time the rate of deposition decreased because the majority of the active sites were becoming inactive suggesting formation of encapsulating carbon during the initial stage of reaction. The similar conclusions were drawn by Greluk et al. for Co/CeO₂ [84] and KCo/ZrO₂ [85] catalysts and by Alberton [88] for Ni/ α -Al₂O₃ catalyst. Because the largest amount of carbon was deposited over Co-0.1Ce/CeO₂ catalyst (Fig. 4a and Table 4) it shows that this catalyst remained active for the longest period i.e. the greatest number of active sites remained accessible for reactants with the studied time. Whereas very low value of carbon content was observed for Co-Ce/CeO₂ catalyst (Fig. 4a and Table 4) suggesting its rapid deactivation because of coverage of great number of active sites by encapsulating carbon. It explains the lowest ability to decompose C2 and C3 intermediated over Co-Ce/CeO₂ catalyst (Fig. 3a). The carbon blocked its active sites responsible for C–C breaking reaction.

In the case of Ni-xCe/CeO₂ catalysts, the SEM (Fig. S12) and TEM (Fig. 6) pictures of them after the 21 hours of SRE reaction confirm the formation of carbon filaments by precipitation of dissolved carbon at the rear side of metal crystallites causing the metal particles to have been detached from the support. It allowed active sites to remain exposed to the reactants for a longer period of time reaction which explains a good performance and incomplete deactivation of Ni-xCe/CeO₂ catalysts (Fig 3b) despite the presence of the great amount of carbon (Fig. 4b) [3, 89]. The filamentous carbon results from the methane decomposition (reaction 7) and carbon monoxide disproportion (reaction 8) reactions which are thermodynamically favorable under the SRE reactions conditions [90, 91]. Therefore, it is likely that carbon monoxide and methane are the major carbon precursor for Ni-xCe/CeO₂ catalysts with minor contributions of carbon from ethylene and acetone. It is in good agreement with the catalytic data presented in Fig. 3b. Much higher selectivity to carbon dioxide over nickel- than cobalt-based catalysts can be attributed to occurring to much larger extent WGS (reaction 1) but also Boudouard reaction (reaction 8) over Ni-xCe/CeO₂ than Co-

xCe/CeO₂ after 21 hours of SRE process. Similar explanation was proposed by Osorio-Vargas et al. [29] for high selectivity to carbon dioxide observed in SRE reaction for Ni/La₂O₃-Al₂O₃. Whereas high production of hydrogen over nickel-based catalysts can be the result of decomposition of methane (reaction 7) produced in a large amount. Because both the highest selectivity to hydrogen and the lowest selectivity to methane were obtained for Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂ catalysts, it could not be excluded that addition of ceria to nickel-based catalysts from $Ce(NO_3)_3 \times 6H_2O$ precursor promotes the methane decomposition (reaction 7) that leaded to the accumulation of carbon deposits as it was suggested earlier. On the other hand, the thermogravimetric studies (Fig. 4b and Table 4) shows that the less carbon was produced in the presence of these two catalysts with the high content of ceria promoter. It could suggest that these catalysts were more resistant to coking because the high oxygen storage and transport capacity of ceria enabled the mobile oxygen stored in ceria lattice to react with carbon species when it forms during the SRE reaction. The SEM (Fig. S12) and TEM (Fig. 6) images, on the other hand, revealed that a considerable amount of carbon was formed during 21 hours of SRE process on the surface of these catalysts which suggests that the results obtained by SEM (Fig. S12) and TEM (Fig. 6) techniques are in contradiction to these obtained by thermogravimetric method (Fig. 4b and Table 4). The deep study of TEM images (Fig. 6) helps to resolve this issue. Indeed, as it was suggested by SEM and TEM images, the amount of deposited carbon on Ni-0.5Ce/CeO2 and Ni-Ce/CeO2 catalysts was large but this carbon was less dense than those deposited on the nickel-based catalysts with lesser content of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor. Hence, carbon formed on Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂ catalysts weighed probably less than those on Ni/CeO₂ and Ni-0.1Ce/CeO₂ catalysts despite being produced in the large amount which can explain the results obtained by means of thermogravimetric method (Fig. 4b and Table 4). On the basis of these results it can be concluded that different morphology of carbon species is observed over

Ni-xCe/CeO₂ catalysts depending on Ce/Ni molar ratio. As it was observed in SEM (Fig. S12) and TEM (Fig. 6) images, not only density but also diameter of carbon filamentous formed on Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂ catalysts, are different from these obtained for the nickelbased catalyst with lesser amount of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor. Despite formation of carbon filaments on the surface of all studied Ni-xCe/CeO₂ catalysts the mean size of filaments on the catalysts with the highest content of ceria promoter, Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂, was larger than those on the other two catalysts. The filaments formed on Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂ catalysts exhibit very wide range of diameters with similar sizes of nickel crystallites on the tips. Besides thin filaments observed on the surface of all studied nickel-based catalysts, also thick filaments are deposited on Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂ catalysts. Moreover, the thick filaments are longer in comparison with thinner ones (Figs. S12 and 6) which allows to conclud that the more ceria is added to nickel-based catalysts from $Ce(NO_3)_3 \times 6H_2O$ precursor, the thicker and longer carbon filamentous deposits are formed on catalysts under SRE conditions. So far many authors [92-94] studied the influence of temperature of reaction on the morphology of carbon species deposited on nickel-based catalysts. However, there is a lack of this in literature, the studies concerning the different morphology of carbon filaments in dependence on the amount of added ceria promoter to nickel active phase. In case of all studied Ni-xCe/CeO₂ catalysts, the carbon is fibrous and grows in random direction and tends to take the form of loops (Figs. S12 and 6). But only for Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂ catalysts, many fibers of carbon are woven into each other randomly to become lumps. It is especially easily to notice in the case of Ni-Ce/CeO₂ catalyst. It allows us to speculate that deactivation of Ni-0.5Ce/CeO₂ and Ni-Ce/CeO₂ catalysts includes not only the coverage of nickel species by deposited carbon but also limitation of the contact of reactants with nickel species because of too crowded, thin filamentous carbon. The space limitations due to carbon with similar structure and

morphology was proposed as the one of the deactivation mechanisms of Ni/SiO₂ catalyst during decomposition of methane by Dong et. al [92]. Deactivation of Ni/CeO₂ and Ni-0.1Ce/CeO₂ catalysts likely occurred because a certain number of nickel active sites became covered by the carbon and stopped being exposed to the reactants and gas-phase intermediates. Because the thermogravimetric studies (Fig 4b and Table 4) show that intensity of carbon formation is significantly lower on Ni-0.1Ce/CeO₂ catalyst than on the Ni/CeO₂ catalysts, it can prove that addition of small amount of ceria from $Ce(NO_3)_3 \times 6H_2O$ precursor corresponding to Ni/Ce molar ratio of 0.1 inhibits the carbon formation. Thus, on the basis of these results, it can be concluded that only this small amount of ceria introduced from $Ce(NO_3)_3 \times 6H_2O$ precursor was able to supply oxygen in order to combust carbon deposits resulting in oxygen vacancies which are regenerated by dissociation of water. Thus, accumulation of carbon deposits on Ni-0.1Ce/CeO2 catalyst was minimized and resulted in a more stable catalyst under SRE conditions (Fig. 3b). The lower tendency of carbon formation of Ni-0.1Ce/CeO₂ catalyst can result from the strong interactions between nickel crystallites and the support as it was proved by TPR and TPO studies (Figs. 1b and 2b). Similar conclusions were drawn by Li et al. [35] for Ni-Ce/MMT catalyst used in SRE reactions and by Cao et al. [95] for Cu/CeO₂-ZrO₂ catalyst used in ethanol dry reforming. In contradistinction to carbon deposits on cobalt-base catalysts after SRE reaction which were mostly graphitic (Fig. 5), the carbon which was formed on nickel-based catalysts under SRE conditions was mainly amorphous (Fig. 6) which is rather reactive and can be removed from the catalyst surface. It only confirms the greater carbon contribution from carbon monoxide and methane by the Boudouard reaction and cracking on nickel-based catalysts because these reactions lead to formation of amorphous carbon species [96].

In most studies devoted to the SRE authors suggest that in line with coking, sintering of an active phase can be responsible for catalysts deactivation. However, one should keep in

mind that under SRE conditions cobalt/nickel crystallites underwent defragmentation by growing carbonaceous deposit [14] as well. In this study the size of cobalt/nickel particles was determined by scanning-transmission electron microscope measurements combined with EDS mapping. The distribution graphs of particles size and their average size was presented in *Supporting Information (Figs. S13 and S14)*. In the case of spent cobalt-based catalysts average crystallites size is rather comparable to the result obtained from XRD studies over pristine sample. In the case of nickel-based catalysts in most of mesh of the TEM cupper grid one can observe very small and dispersed nickel crystallites embedded in carbon nanotubes. Only occasionally crystallites between 20 and 70 nm appear. Authors suggests that in order to decide which phenomenon: sintering or fragmentation of nickel-based catalysts is more favored under the ESR, studies of more statistics have to be made, however, over the samples applied on TEM grids with carbon only continuous films.

3.4. Stability tests for Co-0.1Ce/CeO2 and Ni-0.1Ce/CeO2 catalysts

The long-term performance of Co-0.1Ce/CeO₂ and Ni-0.1Ce/CeO₂ catalysts in the SRE was evaluated at different temperatures for the H₂O/EtOH molar ratio of 4/1. The catalytic behaviour of these catalysts under SRE conditions is presented in Figs. 7a and b (see also *Supporting Information*, Figs. S15a-c and S16a-b) in terms of ethanol conversion and selectivity to products versus time. The temperature of 500 °C is sufficient to obtain complete ethanol conversion over Ni-0.1Ce/CeO₂ catalyst during 21 hours of SRE process. But the higher temperature of 540 °C is required in the presence of Co-0.1Ce/CeO₂ catalyst in order to attain 100% conversion of ethanol under this conditions. It means that capacity of the nickel active metal for breaking C–C bond in ethanol molecule is much stronger compared with cobalt active phase. In the case of both catalysts (Figs. 7a and b), hydrogen (~86% for Co-0.1Ce/CeO₂ and ~71% for Ni-0.1Ce/CeO₂) and carbon dioxide (~55% for Co-0.1Ce/CeO₂ and ~26%

for Co-0.1Ce/CeO₂ and ~12% for Ni-0.1Ce/CeO₂) and methane (~19% for Co-0.1Ce/CeO₂ and ~34% for Ni-0.1Ce/CeO₂) were the only by-products. A higher production of carbon dioxide than carbon monoxide over both cobalt- and nickel-based catalysts confirms that cobalt and nickel active phase participate in WGS reaction (reaction 1) for converting carbon monoxide to carbon dioxide. For the Ni-0.1Ce/CeO₂ catalyst, the formation of methane was more significant in comparison with results obtained over Co-0.1Ce/CeO₂ sample which is in good accordance with results of Manfro et al. [7] and Davidson et al. [74] who suggested that nickel species display a high activity for the methanation reaction (reaction 14). Because this reaction was favored over nickel-based catalyst, the selectivity to hydrogen and carbon monoxide was lower in its presence compared to results obtained for cobalt cobalt-based sample (Figs. 7a and b).

It very difficult to compare results of performance of catalysts in SRE reaction presented in the literature because the studies are carried out under different conditions (H₂O/EtOH molar ratio, feed composition, temperature, time-on-stream, metal active phase content) which influences activity, selectivity and stability of catalysts. However, the results of stability of different cobalt- and nickel-based catalysts in SRE reaction which were recently reported in the literature were summarized in Table 5. The conversions and catalysts' efficiencies expressed in terms of selectivity, yield or concentration of products are indicated. Similarly to the majority of the reported studies (Table 5), when the ethanol conversion is total, the only by-products formed over Co-0.1Ce/CeO₂ and Ni-0.1Ce/CeO₂ catalysts are carbon monoxide and methane. In comparison with results obtained for other catalysts, both Co-0.1Ce/CeO₂ and Ni-0.1Ce/CeO₂ exhibited very promising properties under SRE conditions. However, there are Co/CeO₂ and Ni/CeO₂ catalyst described in the literature which also allow to obtain satisfactory product distribution. For example, the Co/CeO₂ catalyst obtained by reverse microemulsion method by Song et al. [17] allowed to attain the

compete ethanol conversion for 120 hours at 400 °C, i.e. at temperature which is lower by 140 °C compared to that required for 100% ethanol conversion over Co-0.1Ce/CeO₂ sample. On the other hand, reported studies [17] were carried out at higher excess of water in the feed (H₂O/EtOH=10) which could promote steam reforming reactions and decrease the deactivation rate by inhibiting the carbon accumulation. Also Co/CeO₂ catalyst prepared by co-precipitation method by Wang et al. [18] exhibited very promising results in SRE reaction maintaining total ethanol conversion for 40 hours at temperature 500 °C at H₂O/EtOH molar ratio of 3 which is even slightly lower than those applied in these studies. A temperature of 500 °C was also sufficient to obtain very high values of selectivity to hydrogen and carbon dioxide over Co/CeO₂ prepared by co-precipitation method [90]. But not only much higher H₂O/EtOH molar ratio of 12 was used compared to these studies but also the content of cobalt active phase of 15 wt.% was almost twice higher than the amount of cobalt which the Co-0.1Ce/CeO₂ sample contains. On the other hand, despite high content of cobalt active phase of 20 wt.% and high temperature of SRE reaction of 600 °C, Co/CeO₂ catalyst obtained by polymeric precursor method [23] was stable for only 17 hours. After this time, conversion of ethanol drastically decreased from 100% to ~40% after 24 hours of SRE process. In the case of nickel-based catalysts, incipient wetness impregnation method of CeO₂ nanocubes with an aqueous solution of nickel salt gave Ni/CeO₂ material [2] which exhibited total conversion at 400 °C during 28 hours of SRE reaction at H₂O/EtOH molar ratio of 3. However, it must be noticed that concentration of ethanol of 2.5 mol% in described studies [2] was 3 times lower than the ethanol concentration which was used in these studies. Whereas Słowik et al. [14] tested Ni/CeO₂ catalyst obtained with impregnation method at the same concentration of ethanol of 7.7 mol% as it was used in this work. However, the excess of water in Słowik et al. studies [14] was high and corresponding to H₂O/EtOH molar ratio of 12. Under these

conditions, temperature of 420 $^{\circ}$ C was sufficient for stable work of obtained catalyst for 100 hours.

4. Conclusions

A series of Co-xCe/CeO₂ and Ni-xCe/CeO₂ catalysts with different content of ceria introduced from Ce(NO₃)₃ × $6H_2O$ precursor ranging from 0 to 1 corresponding to Co(Ni)/Ce molar ratio were prepared by conventional impregnation method with the presence of a citric acid to investigate the effect of ceria addition on the psychochemical properties and catalytic performance of obtained catalysts in the steam reforming of ethanol process.

The catalysts with the lowest studied content of ceria introduced from Ce(NO₃)₃ × 6H₂O precursor, i.e. Co-0.1Ce/CeO₂ and Ni-0.1Ce/CeO₂, exhibited the best performance in SRE reaction among cobalt- and nickel based samples, respectively. Firstly, a small crystallite size of active phase and stronger metal-support interactions obtained for this catalyst thanks to addition of optimum amount of ceria corresponding to Co(Ni)/Ce molar of 0.1 led to an increase in the number of metal active sites for breaking C–C and C–H bonds which facilitated the ethanol conversion and other C₂ intermediates. Secondly, this optimum amount of ceria introduced from Ce(NO₃)₃ × 6H₂O precursor allowed to especially facilitate WGS reaction and/or to promote activation of water to generate –OH groups which could react with intermediate species to produce carbon dioxide which resulted in the highest CO₂/CO ratio over Co-0.1Ce/CeO₂ and Ni-0.1Ce/CeO₂ catalysts.

The loss of activity of both cobalt- and nickel-based catalysts under SRE conditions was caused by formation of carbon deposits. The ethylene and acetone were the major precursors of carbon, which was mainly formed on the cobalt-based catalysts surface as the polymeric carbon, encapsulated the cobalt particles resulting their immediate deactivation. Whereas the filamentous carbon results from the methane decomposition and carbon monoxide disproportion reactions was mostly formed on the nickel-based catalysts. Moreover, the

carbon which was deposited on Co-xCe/CeO₂ differed from those formed on Ni-xCe/CeO₂ catalysts the order of graphitization. The carbon deposits on cobalt-base catalysts after SRE reaction were mostly graphitic and the carbon which was formed on nickel-based catalysts was mainly amorphous.

The Co-0.1Ce/CeO₂ and Ni-0.1Ce/CeO₂ catalysts exhibited the strongest resistance toward carbon deposition. The largest amount of ceria added to cobalt-based catalysts from Ce(NO₃)₃ × 6H₂O precursor caused their rapid deactivation because of faster coverage of great number of active sites by encapsulating carbon. Whereas the ceria content introduced from Ce(NO₃)₃ × 6H₂O precursor to nickel-based catalysts influenced the morphology of the carbon filamentous formed on their surface, i.e. a density, thickness and length. The more ceria was added to nickel-based catalysts from Ce(NO₃)₃ × 6H₂O precursor the thicker, longer and less dense carbon filamentous deposits were formed on catalysts under SRE conditions. It means that the addition of too large an amount of ceria to Ni-xCe/CeO₂ catalysts caused their deactivation including not only the coverage of nickel species by deposited carbon but also limitation of the contact of reactants with nickel species because of the too crowded, thick filamentous carbon.

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Fig. 1. Temperature-programmed reduction profiles of (a) Co-xCe/CeO2 and (b) Ni- xCe/CeO_2 catalysts.

Fig. 2. Temperature-programmed oxidation profiles of (a) Co-xCe/CeO₂ and (b) Ni-xCe/CeO₂ catalysts.

Fig. 3. Catalytic performance of (a) Co-xCe/CeO₂ ($H_2O/EtOH=12/1$, 60000 mL/g h) and (b) Ni-xCe/CeO₂ ($H_2O/EtOH=12/1$, 120000 mL/g h) catalysts in the ethanol steam reforming at 420 °C after 21 hours.

Fig. 4. Changes of Co-xCe/CeO₂ and Ni-xCe/CeO₂ catalysts weight under SRE conditions at 420°C (H₂O/EtOH=12/1, TOS=18.5 hours).

Fig. 5. TEM images of Co-xCe/CeO₂ catalysts after 21 hours of the SRE process (H₂O/EtOH = 12/1, T= 420° C, 60000 mL/g h).

Fig. 6. TEM images of Ni-xCe/CeO₂ catalysts after 21 hours of the SRE process (H₂O/EtOH = 12/1, T= 420° C, 120000 mL/g h).

Fig. 7. Stability tests of Co-0.1La/CeO₂ catalyst at temperature of (a) 460 °C and (b) 500 °C and Ni-0.1La/CeO₂ catalyst at temperature of (a) 460 °C under the steam reforming conditions (H₂O/EtOH=12/1, GHSV=60000 mL/g h, TOS=21 hours).













Fig. 5.



Fig. 6.

Journal Prevention





Catalyata	Active phase metal	Na	physisorption		H ₂ chemisorption	
Catalysis	content wt.%	D _p (nm)	V _p (mL/g)	S_{BET} (m ² /g)	$d_{\text{Co/Ni}}(nm)$	Dispersion (%)
Co/CeO ₂	8.1 ± 0.2	13.0	0.17	47.6	9.5	10.6
Co-0.1Ce/CeO ₂	8.3 ± 0.3	12.1	0.15	47.0	6.9	14.5
Co-0.5Ce/CeO ₂	8.0 ± 0.2	11.6	0.16	52.1	10.8	9.3
Co-Ce/CeO ₂	7.9 ± 0.2	9.9	0.12	49.7	19.5	5.1
Ni/CeO ₂	$9.0\ \pm 0.3$	10.9	0.16	52.0	6.4	15.8
Ni-0.1Ce/CeO ₂	8.7 ± 0.3	10.8	0.16	52.8	6.1	16.6
Ni-0.5Ce/CeO ₂	9.4 ± 0.3	8.5	0.15	64.8	7.1	14.2
Ni-Ce/CeO ₂	8.5 ± 0.3	9.6	0.12	46.9	8.8	11.5
CeO ₂ support	-	14.0	0.14	42.5	-	-

Table. 1. Physicochemical properties of CeO_2 support $Co-xCe/CeO_2$ and $Ni-xCe/CeO_2$ catalysts.

	I	Before reduction	After reduction		
Catalysts	d _{CeO2} (nm)	d _{Co3O4/NiO} (nm)	Lattice parameter (nm)	d _{CeO2} (nm)	d _{Co/Ni} (nm)
Co/CeO ₂	21.7	7.6	0.5409	22.0	-
Co-0.1Ce/CeO ₂	24.4	11.4	0.5410	24.2	-
Co-0.5Ce/CeO ₂	29.0	9.4	0.5410	29.1	14.4
Co-Ce/CeO ₂	27.1	18.5	0.5412	28.6	17.4
Ni/CeO ₂	22.1	4.2	0.5410	22.2	10.0
Ni-0.1Ce/CeO ₂	26.8	-	0.5410	26.4	7.2
Ni-0.5Ce/CeO ₂	26.8	-	0.5410	27.1	10.5
Ni-Ce/CeO ₂	25.5	7.8	0.5410	25.1	21.4
CeO ₂ support	22.2	-	0.5411	22.1	-

Table. 2. XRD characterization of Co-xCe/CeO $_2$ and Ni-xCe/CeO $_2$ catalysts.

Table. 3. Atomic ratio	(H/M) calculated from	hydrogen consumption	of H ₂ -TPR profiles (M
= Co or Ni).			

Catalyata	Theoretical H ₂	Theoretical H/M ^a	H ₂ -TPR peaks between 180-500 °C (Co-xCe/CeO ₂) 180-500 °C (Ni-xCe/CeO ₂)		
Catalysts	(mmol/gCo(Ni))		Experimental H ₂ consumption (mmol/g)	Experimental H/M ^a	
Co/CeO ₂	1.83		2.00	2.91	
Co-0.1Ce/CeO ₂	1.90	2.67	1.98	2.78	
Co-0.5Ce/CeO ₂	1.81	2.07	1.86	2.74	
Co-Ce/CeO ₂	1.79		1.82	2.71	
Ni/CeO ₂	1.53		1.76	2.30	
Ni-0.1Ce/CeO ₂	1.48	2.00	1.65	2.23	
Ni-0.5Ce/CeO ₂	1.60		1.62	2.07	
Ni-Ce/CeO ₂	1.45		1.50	2.03	

^aH/M shows the number of adsorbed H atoms/the total number of metal atoms.

Table. 4. Data for carbon formation rate on Co-xCe/CeO₂ and Ni-xCe/CeO₂ catalysts during steam reforming of ethanol reaction.

Catalysts	Carbon formation rate (mg/g h)	
Co/CeO ₂	32	
Co-0.1Ce/CeO ₂	31	
Co-0.5Ce/CeO ₂	29	
Co-Ce/CeO ₂	19	
Ni/CeO ₂	152	
Ni-0.1Ce/CeO ₂	52	
Ni-0.5Ce/CeO ₂	15	
Ni-Ce/CeO ₂	13	

Catalyst	Reaction conditions	Results	Ref.
Co/CeO ₂	500 °C,	$X_{EtOH} = 93\%$	[3]
(10 wt.% Co)	150 mg of catalyst,	Yield $_{H_{\gamma}} \sim 1.0 mol_{H_{\gamma}} / mol_{EtOH}$	
	$H_2O/EtOH = 3,$	Yield $c_{O_2} \sim 0.4 mol_{CO_2} / mol_{EOH}$	
	$FV_{H2O/EtOH} = 3.5 \text{ ml/h},$	Yield $_{CO} \sim 0.2 mol_{CO} / mol_{FCOH}$	
	TOS = 6 h	Yield $_{CH} \sim 0.4 mol_{CH} / mol_{FtOH}$	
		Yield $_{CH,CHO} \sim 0.03 mol_{CH,CHO} / mol_{EOH}$	
		Yield $(CH_3) = c_0 \sim 0.01 mol_{(CH_3)} = c_0 / mol_{(CH_3)}$	
		Yield $\sim 0.01 mol_{cu} \cos (m_{3})_{2} \cos (m_{2})_{2} \cos (m_{$	
		ETT CH ₃ COOH	
Co/CeO2	540 °C	Y = -100%	[11]
(10 wt % Co)	100 mg of catalyst	$X_{EtOH} = 100\%$	[11]
(10	$H_2O/EtOH = 9.$	Product distribution	
	10 mol% EtOH.	$H_2 \sim 74\%$	
	$FV_{H2O/EtOH} = 100 \text{ ml/min}$	$CO_2 \sim 19\%$ CO < 5%	
	(without any dilution	$CH_{4} < 3\%$	
	with inert gas)	+	
	60000 ml/g h,		
	TOS = 35 h		
Co/CeO ₂	400 °C,	$X_{EtOH} = 100\%$	[17]
(10 wt.% Co)	100 mg of catalyst,	Yield $_{H_{\gamma}} \sim 90\%$	
	$H_2O/EtOH = 10,$	Yield $_{CO_2} \sim 90\%$	
	7.5 mol% EtOH,	Yield $_{CO} < 4\%$	
	$GHSV = 10000 h^{-1},$	Yield $_{CH_{\star}}$ < 5%	
<u> </u>	TOS = 120 h		5103
$C_{03}O_4/CeO_2$	500 °C,	$X_{EIOH} = 100\%$	[18]
(10 wt.% Co)	150 mg of catalyst,	$S_{H_2} = 68\%$	
	$H_2O/EtOH = 3,$	$S_{CO_2} = 17\%$	
	40000 ml/g n,	$S_{CO} = 14\%$	
-	105 = 40 11	$S_{CH_4} = 2\%$	
Co/CeO_2	500 °C,	$X_{EIOH} = 100\%$	[90]
(15.2 wt.% Co)	100 mg of catalyst,	$S_{H_2} = 96\%$	
	$H_2O/EtOH = 12,$	$S_{CO_2} = 83\%$	
	7.7 mol% EtOH,	$S_{CO} = 11\%$	
	$FV_{H2O/EtOH} = 100 \text{ ml/min},$	$S_{CH_4} = 9.5\%$	
	(without any dilution with inert gas)		
	60000 m/g h		
	TOS = 23 h		
Co/CeO ₂	350 °C.	Product distribution	[97]
(15 wt.% Co)	200 mg of catalyst	$H_{\rm c} \sim 65\%$	[//]
(10	$H_2O/EtOH = 9.$	$CO_{2} \sim 20\%$	
	11000 ml/g h.	<i>CO</i> ⁻ ~ 4%	
	TOS = 16.5 h	$CH_4 \sim 3\%$	
		$(CH_3)_2 CO \sim 8\%$	

Table. 5. Comparison of results obtained for Co/CeO₂ and Ni/CeO₂ catalyst in SRE reactions.

Co/CeO ₂	500 °C,	$X_{FOH} = 98\%$	[22]
(20 wt.% Co)	150 mg of catalyst,	Yield $_{H_{\star}} \sim 1.6 mol_{H_{\star}} / mol_{FOH}$	
	$H_2O/EtOH = 3,$	Yield $_{CO} \sim 0.5 mol_{CO} / mol_{FOU}$	
	$FV_{H2O/EtOH} = 2.5 \text{ ml/h},$	$Vield \sim 0.1 mol_{2} / mol_{2} \sim 0$	
	TOS = 6 h	Yield $_{CO} \sim 0.3 mol_{CO} / mol_{EOH}$	
	END °C	CH_4 CH_4 EIOH	[22]
C_0/C_0^2	10 mg of ostalyst	$X_{EtOH} = 100\%$	[23]
(20 wl.% CO)	$H_{\rm LO}/{\rm EtOH} = 3.1$	$S_{H_2} = 70\%$	
	$H_2O/EtOH = 3.1,$ EV. = 30 ml/h	$S_{CO_2} = 15\%$	
	$T_{He} = 30 \text{ m/m},$ TOS = 17 b	$S_{CO} = 20\%$	
$C_{0} = 0.1 C_{e}/C_{e}O_{0}$	105 = 17 II 540 °C	V = -1000/	[this
(8.3 wt % Co)	100 mg of catalyst	$\mathbf{X}_{EtOH} = 100\%$ $\mathbf{S}_{etoH} = 260\%$	workl
(0.5 WL /0 CO)	$H_2O/EtOH = A$	$S_{H_2} = 80\%$	workj
	7.7 mol% EtOH	$S_{CO_2} = 53\%$	
	$FV_{U20/F+OU} = 38.5 \text{ m}/\text{min}$	$S_{CO} = 20\%$ S = -19%	
	$FV_{Ar} = 61.5 \text{ ml/min}$	$S_{CH_4} = 1770$	
	60000 m/g h		
	TOS = 21 h		
Ni/CeO ₂	400 °C,	$X_{\rm pow} = 100\%$	[2]
(9.9 wt.% Ni)	100 mg of catalyst,	Product distribution	
	$H_2O/EtOH = 3,$	H = 50%	
	2.5 mol% EtOH,	$H_2 \sim 30\%$ $CO_1 \sim 27\%$	
	$7.5 \text{ mol}\% \text{ H}_2\text{O},$	$CO^{2} < 1.6\%$	
	90 mol% N ₂ ,	<i>CH</i> ₄ < 21.4%	
	TOS = 28 h		
Ni/CeO ₂	420 °C,	$X_{FtOH} = 100\%$	[14]
(10 wt.% Ni)	100 mg of catalyst,	$S_{H_2} = 78\%$	
	$H_2O/EtOH = 12,$	$S_{CO_2}^{(2)} = 62\%$	
	7.7 mol% EtOH,	$S_{CO}^{1} = 6\%$	
	$FV_{H2O/EtOH} = 100 \text{ ml/min}$	$S_{CH_4} = 34\%$	
	(without any dilution		
	with inert gas)		
	60000 ml/g h,		
	TOS = 100 h		54.0.4
Ni/CeO_2	300 °C,	$X_{EtOH} = 100\%$	[104
(10 wt.% N1)	100 mg of catalyst,	$S_{H_2} = 28\%$	
	$H_2O/EtOH = 3,$	$S_{CO_2} = 8\%$	
	0.5 VOI% EtOH	$S_{CO} = 20\%$	
	1.5 VOI% H2U	$S_{CH_4} = 17\%$	
	$70 \text{ VOI}\% \text{ IN}_2$, CHSV- 15000 b ⁻¹	$S_{C_2H_4} = 0.270$ S - 7%	
	U = 15000 II, TOS - 1 h	$S_{CH_3CHO} = 7.70$ S = - Q%	
	100 - 1 11	$S_{(CH_3)_2CO} - 770$	5003
Ni/CeO_2	350 °C,	Product distribution	[98]
(15 wt.% N1)	200 mg of catalyst,	$H_2 \sim 60\%,$	
	$H_2O/EtOH = 9,$	$CO_2 \sim 20\%$, $CO \sim 5\%$	
	11000 ml/g n,	CU~ J70 CH~~15%	
	105 = 16.5 h		

Ni-0.1Ce/CeO ₂	500 °C,	$X_{FIOH} = 100\%$	[this
(8.7 wt.% Ni)	100 mg of catalyst,	$S_{H}^{EIOH} = 71\%,$	work]
	$H_2O/EtOH = 4,$	$S_{CO_2}^{H_2} = 54\%$	
	7.7 mol% EtOH,	$S_{CO}^{112} = 12\%$	
	$FV_{H2O/EtOH} = 38.5 \text{ ml/min},$	$S_{CH_4} = 34\%$	
	$FV_{Ar} = 61.5 \text{ ml/min},$		
	50000 ml/g n, TOS – 21 h		
	105 – 21 II		<u> </u>
			64