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Syngas production by catalytic reforming of renewables for power generation in solid oxide fuel cell

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Ni and Co as active metals, supported on Al_2O_3, ZnO and AlZnOx were tested in partial oxidation and the steam reforming processes. The effect of catalysts for syngas production by catalytic reforming of bioethanol and acetic acid for power generation of SOFC was studied. Single supported Ni or Co catalysts,showed high activity but different product distribution. The Al_2O_3 supported catalysts were quickly deactivated by carbon deposition because of ethylene and acetone formation over the strong acidic sites of alumina. The ZnO supported catalysts showed a remarkable higher syngas productivity compared to the Al_2O_3 supported samples. The catalysts supported over mixed oxide,showed higher activity in partial oxidation and the steam reforming in comparison to single oxide samples. In partial oxidation of ethanol NiAlZnOx sample was more active, however in steam reforming of acetic acid CoAlZnOx sample showed better performance. In-situ XRD study of ZnO and AlZnOx supported samples showed that both series have similar phase composition, which is determined by the properties of ZnO, especially its oxygen mobility at high temperature. Alloy structure formation and the reduction of active metals under the reaction conditions provided high performance of these catalysts in partial oxidation and steam reforming with high production to syngas.

1. Introduction

Fuel cells are considered as one of the most efficient and clean energy conversion devices for the future. Proton exchange membrane fuel cells (PEMFC) are a promising option for mobile auxiliary power units for transportation applications, while solid oxide fuel cells (SOFC) are used mainly for stationary combined heat and power generation [1, 2]. Whereas the PEMFC requires hydrogen of high purity as a fuel, one of the main advantages of SOFC technology is its high fuel flexibility. In fact, the high operation temperature of the SOFC (700 – 1000 °C) allows the direct fuel conversion to reformate consisting of H_2, CO, CO_2, CH_4 and steam by internal reforming of hydrocarbons [3]. High concentration of H_2 and CO is desired, since those are the compounds which are electrochemically oxidized inside the SOFC by the O^{2-} ions received from the electrolyte.

The direct use of hydrocarbons in SOFC introduces the problem of carbon deposition, which can be reduced or eliminated by rational choice of the fuel cell materials, the operating conditions, or the used fuel. The fuel has to be oxidized and both carbon-oxygen and hydrogen-oxygen bonds have to be formed. Oxygenated fuels contain these bonds already (for example, ethanol and acetic acid), and so may

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x react more easily. To investigate the effect of oxygenation level, oxygenated hydrocarbons as alcohols (bioethanol) and carboxylic acids (acetic acid) will be compared. The biofuels such as bioethanol or acetic acid are renewable, widely available and non-toxic liquids with high energy density. The fact that they can be produced globally from several biomass feedstock including sugar-cane and wheat, up to industrial or municipal wastes, make them both economically and environmentally attractive. The utilization of biofuels for power generation leads not only to a CO_2 neutral and sustainable technology, but also reduces the expenses for fuel transportation and storage.

While the conversion of ethanol to a hydrogen-rich fuel has been intensively studied [4], the use of acetic acid as a fuel for hydrogen generation has received little attention [5]. Different strategies have been proposed to produce hydrogen from oxygenated hydrocarbons, among them steam reforming (SR) and partial oxidation (POX). The SR provides higher efficiency and reformates quality, i.e. higher hydrogen production yield and lower rate of side reactions, but this process has some disadvantages as well, such as the high energy consumption. The POX - features fast start-up and response times because of the exothermic nature of the oxidation reaction. Additionally, the partial oxidation reaction can take place without any external heat source and water addition [4].

Using bioethanol partial oxidation was chosen as the most effective process for its conversion in SOFC, where air is used as oxidant agent of the fuel [2]. Using acetic acid as a fuel SR reaction is the most effective process for hydrogen production, with water as oxidant agent. Although the addition of water reduces dramatically the energy density of the fuel, it generally prevents carbon formation and improves the reforming, providing high hydrogen yields [3, 6-12].

Syngas production by POX and SR are performed by similar, but complex reaction pathway, including decomposition, oxidation reactions, as well as the waster-gas shift reaction. The obtained products depend on the selected reaction conditions and the choice of catalysts. The generation of H_2 and CO from oxygenated hydrocarbons requires a catalyst which facilitates the break of C-C, C-H and O-H bonds. Moreover the cleavage of C-O bonds and the hydrogenation of CO to alkanes have to be suppressed. It is known that substrates with C-H bonds which are activated by adjacent OH-groups can be selectively converted to H_2 and CO_2. However, the non-activated methyl group in both ethanol and acetic acid is more easily transformed to CH_4 [13]. Catalytic systems with different active metals have been studied for both processes. Supported noble metals were shown to have high activity, but high costs limit their application [14, 15]. Instead, it is more practical to achieve a cheap and effective catalyst for more economic benefits. Therefore, increasing attention has been focused on the development of non-noble metal catalysts, such as Co- or Ni-based materials. The nature of supports strongly affects the performance of Co- and Ni-based catalysts by influencing the crystallite size, reducibility and electronic structure of the samples and the strength of metal-support interaction [16-18].

The aim of the present study is to investigate the effect of catalysts for the syngas production by catalytic reforming of bioethanol and acetic acid for power generation in the SOFC. The low cost metals, nickel and cobalt, were used as active metals supported on inexpensive and thermally stable metal oxides such as aluminum or zinc oxides as well as binary mixed oxides ($AlZnO_x$). The performance of the Co- or Ni-based catalysts in the partial oxidation of bioethanol and the steam reforming of acetic acid was elucidated. The best catalysts have been characterized by in-situ XRD in order to examine the effect of the phase composition of the samples on the performance of the catalysts in the reforming reactions.

2. Results and Discussion

In Figs. 1A and 1B the catalytic performance over alumina oxide supported Co and Ni catalysts was presented as a function of temperature in reactions of EtOH PO and AcOH SR, respectively.

In partial oxidation of ethanol (Fig. 1A), Co and Ni catalysts completely converted bio-ethanol in the temperature range of 600-800°C. Over $NiAl_2O_3$ sample the main reaction at 600 °C was ethanol dehydration (Eq. 1) with ethylene formation of about 40 vol. %. Together with this reaction, partial oxidation (Eq. 2 and Eq. 3) and thermal decomposition (Eq. 4) reactions also occurred at 600 °C. With increasing the temperature hydrogen production increased while the ethylene formation decreased, meaning that PO reaction is more involved. Over $CoAl_2O_3$ catalyst at low temperature ethanol was mainly converted to ethylene via Eq. 1. With increasing the temperature together with the main products of the POE (H_2, CO and CO_2) methane was also observed. In partial oxidation of ethanol $NiAl_2O_3$ sample showed better performances, with 56% H_2 and 33% CO production at 800 °C, in comparison to $CoAl_2O_3$ sample with 35% H_2 and 20% CO.

$C_2H_5OH \rightarrow C_2H_4 + H_2O$ $\Delta H_R = 49$ kJ/mol (Eq. 1)
$C_2H_5OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2$ $\Delta H_R = -549$ kJ/mol (Eq. 2)
$C_2H_5OH + 0.5O_2 \rightarrow 2CO + 3H_2$ $\Delta H_R = 14$ kJ/mol (Eq. 3)
$C_2H_5OH \rightarrow CH_4 + H_2 + CO$ $\Delta H_R = 19$ kJ/mol (Eq. 4)

In the steam reforming of acetic acid (Fig. 1B) Ni-containing catalyst also showed considerably better activity in comparison to Co-containing sample. Very high conversion of acetic acid was observed over $NiAl_2O_3$ in the temperature range of 600-800 °C, while over $CoAl_2O_3$ sample only about 30 % conversion was detected. The main reaction over $NiAl_2O_3$ sample in the whole temperature range was steam reforming of acetic acid (Eq. 5). With increasing temperature the production of CO increased while CO_2 and H_2 production decreased. These trends show the implication of endothermic reverse water-gas shift (WGS, Eq. 6) reaction, where H_2 and CO_2 were consumed in order to form CO and H_2O.

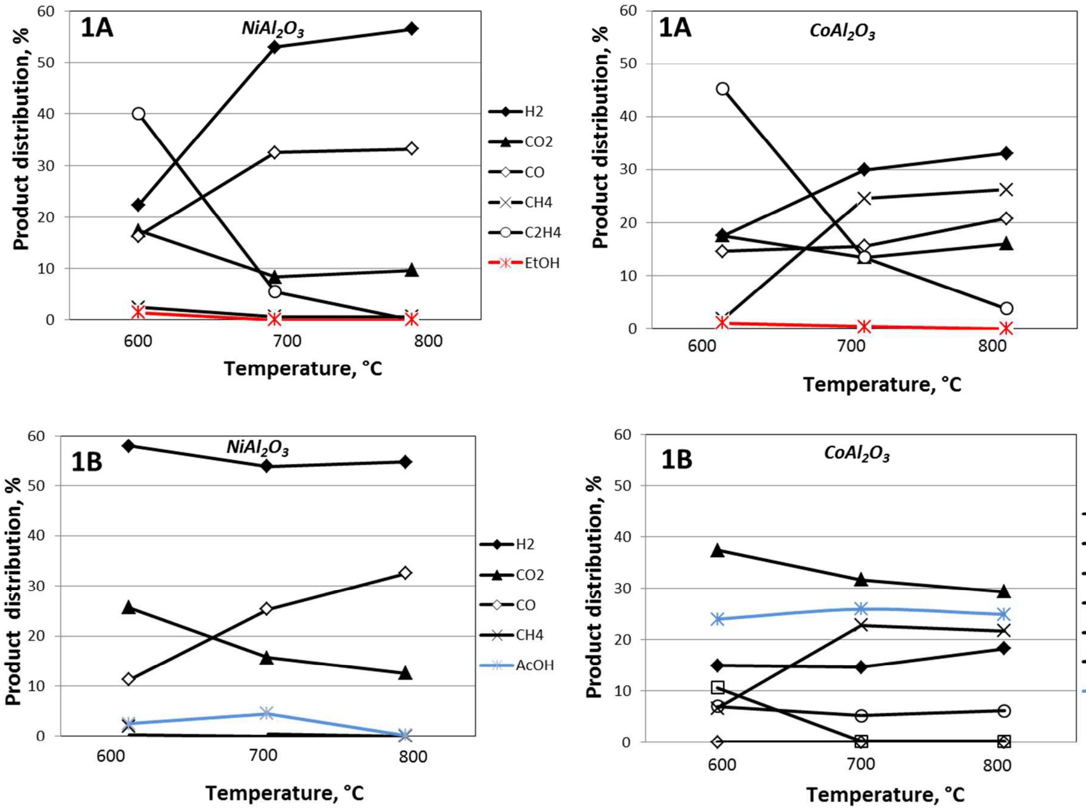

Figure 1. Catalytic performance on $NiAl_2O_3$ and $CoAl_2O_3$ in reactions of EtOH PO and AcOH SR.

$CH_3COOH(g)+2H_2O(g) \rightarrow 4H_2+yCO+zCO$ ΔH_R=172,6kJ/mol (Eq. 5)

$CO + H_2O \rightarrow CO_2 + H_2$ ΔH_R=41kJ/mol (Eq. 6)

The results reveal that the $CoAl_2O_3$ sample was not active in the selected temperature. At 600 °C, thermal decomposition of AcOH to methane, CO_2 and C_2H_4 (Eq. 7 and Eq. 8) was observed, as well as ketonization reaction (Eq. 9) forming acetone. At higher temperature steam reforming reaction occurred forming H_2 and CO_2 together with thermal decomposition reactions. Nevertheless at temperature higher than 700 °C the conversion of acetic acid was very low because the sample was quickly deactivated due to carbon deposition.

$CH_3COOH \rightarrow CH_4+CO_2$ ΔH_R=-33,5kJ/mol (Eq. 7)

$CH_3COOH \rightarrow C_2H_2, C_2H_4, C_2H_6, C_3H_4, C$ $\Delta H > 0$ (Eq. 8)

$2CH_3COOH \rightarrow CH_3COCH_3 + H_2O + CO_2$ ΔHr=16,7 kJ/mol (Eq. 9)

In Figs. 2A and 2B the catalytic performance over the zinc oxide supported Co and Ni catalysts was presented as a function of temperature in reactions of partial oxidation of ethanol and steam reforming of acetic acid, respectively.

In partial oxidation of ethanol (Fig. 2A), zinc supported Ni and Co catalysts show similar catalytic performance with complete ethanol conversion at selected temperatures. The main reaction over both catalysts was partial oxidation (Eq. 3) with production of H_2 and CO. At 600 °C CH_4 was formed via reaction of acetaldehyde decomposition (Eq. 10). The formation of acetaldehyde is promoted through the basic nature of ZnO at the lower temperature, as it was presented in detail in our preliminary work [20]. The amount of CH_4 formed over both catalysts was about 8 % and it did not change significantly with temperature. A part of produced CO was oxidized (Eq. 11) at low temperature forming CO_2. At higher temperature over both catalysts reverse WGS reaction occurred, consuming CO_2 and producing CO. It is interesting to note that the production of CO_2 for both catalysts at 800 °C was less than 9 %.

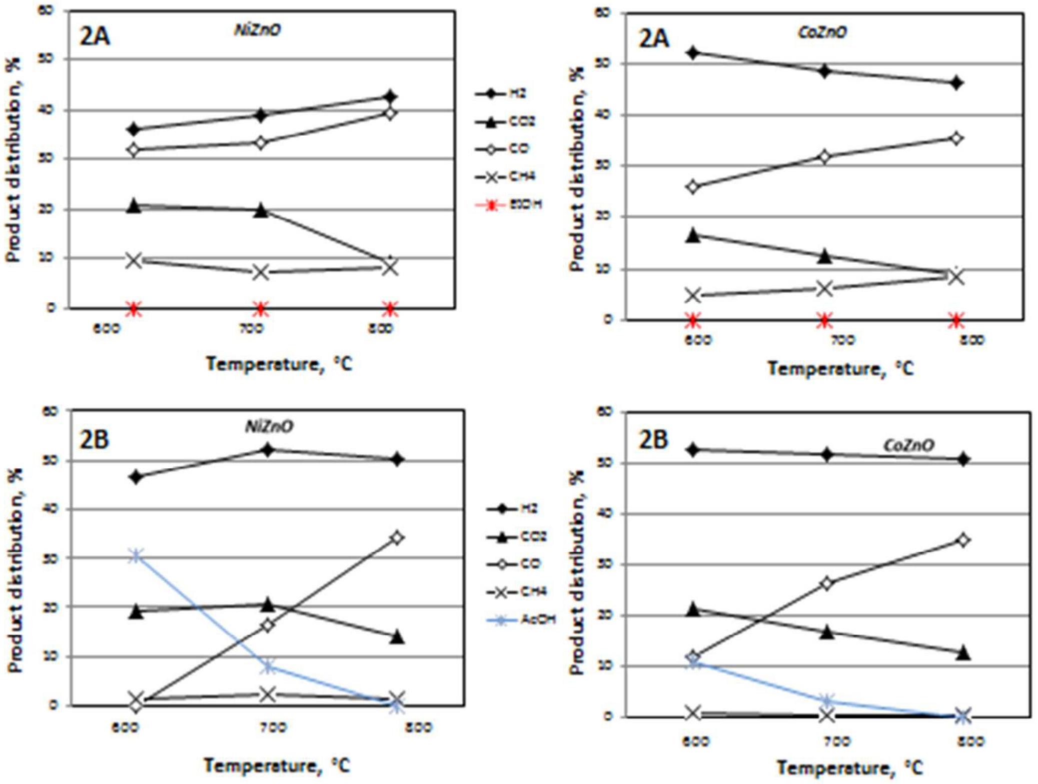

Figure 2. Catalytic performance on NiZnO and CoZnO in reactions of EtOH PO and AcOH SR.

$C_2H_4O \rightarrow CH_4 + CO \quad \Delta H_R = 19$ kJ/mol (Eq. 10)
$CO + ½ O_2 \rightarrow CO_2 \quad \Delta H_R = 173$ kJ/mol (Eq. 11)

In steam reforming of acetic acid (Fig. 2B), zinc supported Ni and Co catalysts showed similar catalytic performance with complete acetic acid conversion at 800 °C, but at 600 °C conversion was lower. In the selected temperature range the predominant reaction was steam reforming of acetic acid (Eq. 5) with the formation of H_2, CO, and CO_2 as main products. Less of 1 % CH_4 production was detected over both catalysts. With increasing temperature the conversion of acetic acid increased and reverse WGS (Eq. 6) reaction occurred.

Summarizing the results after screening catalytic tests in both systems, it should be emphasized that single supported Ni or Co catalysts, prepared by impregnation method, usually show high activity but different product distribution. The Al_2O_3 supported catalysts were quickly deactivat by carbon deposition because of ethylene and acetone formation over the strong acidic sites of alumina. The ZnO supported catalysts show a remarkable higher productivity to the main compounds compared to the Al_2O_3 supported samples. Ni was better promotor in both processes when it is supported on Al_2O_3, however Co was more active as a promotor on ZnO supported samples. It is noteworthy that in both PO and SR in the temperature range of 600-800 °C and over the active catalysts, the formation of byproducts was very small (less than 2%) and the formation of CO_2 also was less than 10%. These facts are important regarding the application of the catalysts in SOFC.

The adverse effect of the acidic nature of Al_2O_3 as a support can be reduced by using basic oxides such as ZnO, or adding basic species to the acidic support in mixing composition [21]. In our research a new approach was explored using $AlZnO_x$ mixed oxide support with amphoteric character and thermal stability, in order to improve the performance of Co- or Ni-based catalysts in both processes [18]. Our preliminary study of POX of ethanol over $AlZnO_x$ mixed support show that at 400 °C the main reactions were dehydrogenation to acetaldehyde and the further decomposition of acetaldehyde to hydrogen (the result was not present here) [18, 20]. Through this reaction pathway the ethylene formation is prevented, and therefore coke formation is reduced. These results focused our interest on using $AlZnO_x$ supported catalysts in SR of acetic acid, too.

In Figs. 3A and 3B the catalytic performance over the Ni(Co)$AlZnO_x$ mixed oxide catalysts was presented as a function of temperature in of partial oxidation of ethanol and steam reforming of acetic acid, respectively.

During the partial oxidation of ethanol mixed oxide supported catalysts showed high catalytic performance (Fig. 3A), achieving complete EtOH conversion in the whole temperature range of 600-800°C. Over the NiAlZnO$_x$ catalyst at 600 °C the highest hydrogen production (56 %) was obtained, whereas over CoAlZnO$_x$ catalyst 42 % of H_2 was produced. As byproduct only methane was formed over CoAlZnO$_x$, around 8 %, at the expense of hydrogen production. With increasing the temperature, the product distribution did not change dramatically, only small variation in the amount of the main products was observed, determinant by the parallel reverse WGS reaction [10, 18].

In steam reforming of acetic acid Co-containing catalyst showed better performance in comparison to Ni sample. Complete conversion of acetic acid was observed over CoAlZnO$_x$ catalyst in the temperature range of 600-800°C. However, over NiAlZnO$_x$ sample the conversion of AcOH was around 40 % at 600 and 700 °C, and at 800°C it was completely converted. The main reaction over both samples in the selected temperature range was steam reforming of acetic acid (Eq. 4). The production of CO increased while CO_2 and H_2 production decreased with increasing temperature over both catalysts, demonstrating the implication of reverse WGS (Eq. 5). As byproduct only methane was formed over both catalysts (less than 5%).

Summarizing the results after screening catalytic test over mixed oxide samples, prepared by citrate method, it should be emphasized that these catalysts usually showed higher activity in both POX and SR in comparison to single oxide samples. In POX of ethanol NiAlZnO$_x$ sample was more active while in SR of acetic acid CoAlZnO$_x$ sample show better performance.

Among the three series of catalysts, ZnO and AlZnO$_x$ supported samples were more stable with good performance for SR and POX processes. Over these catalysts at 800 °C not only EtOH and AcOH were completely converted, but also considerable amounts of H_2 and CO were produced, with only small amounts of CH_4 and CO_2. This implies that the ZnO and AlZnO$_x$ catalysts are greatly selective to the overall both reforming reactions. In order to gain an insight into the structural transformations occurring in these catalysts, the simulation of the reaction conditions was performed in the in-situ XRD set up. The reflection patterns of both Co and Ni samples are collected in the H_2/He flow from room temperature till 600 °C. After the reduction the sample was heated up to 800 °C under inert atmosphere (pure He). The difractograms were presented in Figs. 4 and 5 for ZnO and AlZnO$_x$ supported samples, respectively.

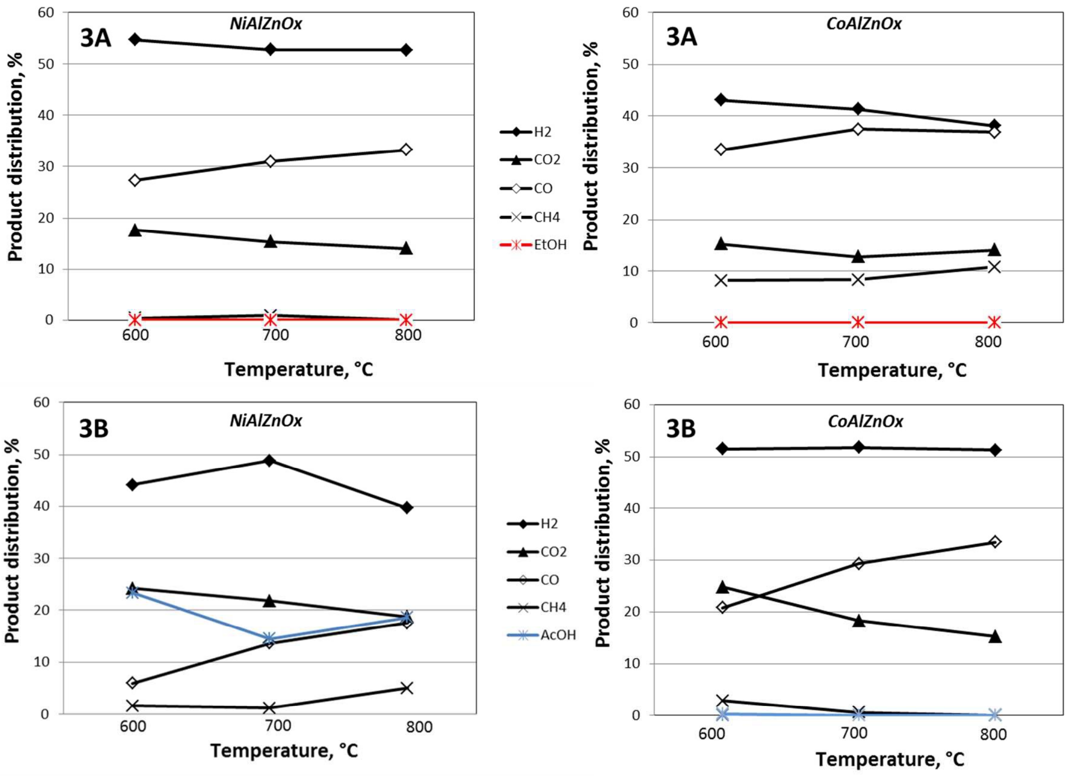

Figure 3. Catalytic performance on NiAlZnOx and CoAlZnOx in reactions of EtOH PO and AcOH

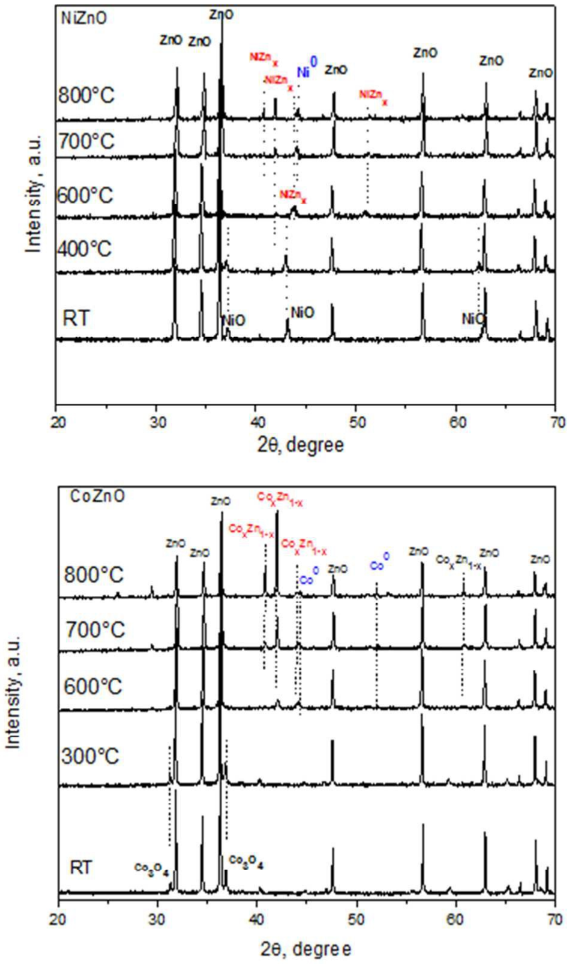

Figure 4. In-situ XRD analysis of NiZnO and CoZnO samples

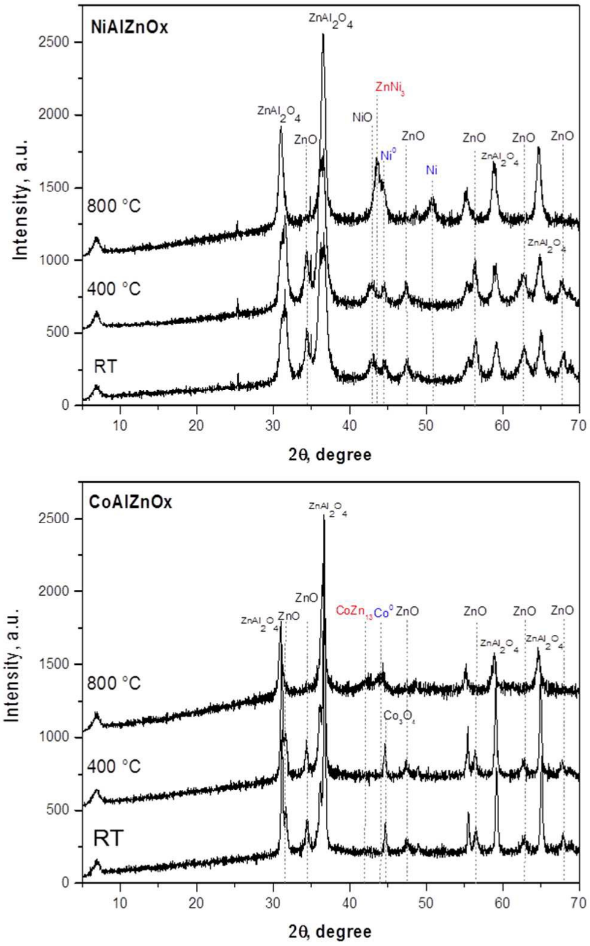

Figure 5. In-situ XRD analysis of NiAlZnO$_x$ and CoAlZnO$_x$ samples

For NiZnO sample the diffraction patterns at room temperature and at 400 °C were visibly identical. They showed intense and symmetric peaks of ZnO phase (2θ = 31.8°, 34.4°, 36.2°, PDF-No. [36-1451]) and reflections of NiO (2θ = 37.3°, 43.3°, 62.9°, PDF-No. [4-835]). CoZnO sample reveals the same reflections till the reduction at 300 °C, with characteristic peaks of ZnO and Co_3O_4 (2θ = 31.2°, 36.7°, 38.4°, 44.7°, 59.2°, PDF-No. 42-1467) phases. In samples the intense and symmetric peaks of ZnO phase remained in the whole temperature range. During the reduction of the samples till 600 °C the diffractograms showed structural changes in the composition of the catalysts. Metal oxides (NiO and Co_3O_4) were reduced to the metallic Ni°(2θ = 43.9° and 51.2°, JCPDS 70-1849) and Co^0 phases, respectively. After completing the reduction, together with metallic Ni and Co, metal alloy structure could be formed between Zn an Ni or Co, identified by the reflections at 44.00° and 51.2° for NiZnx and 42.03° for CoZnx alloys [23-25]. As temperature increased, and without submitting the sample to a H_2 flow, the peaks corresponding to the alloy structure are more intense, while the theta corresponding to metallic Ni and Co decreased. After this in-situ study it can be ensured that during the reaction, in the temperature range from 600 °C to 800 °C, MeZnO catalysts contained alloy crystals with variable composition. Alloys, together with metallic Ni or Co and ZnO phase, was the ones affecting the catalytic performance of ZnO supported catalysts. Fig. 5 shows the structural transformations occurring in NiAlZnOx and CoAlZnOx were performed in the in situ XRD setup. The patterns collected on both catalysts at room temperature and at 400° were visibly identical, showing reflections at 2θ = 31.2°, 36.8°, 55.7°, 59.3°, 65.3° (PDF-No. [5-669]) corresponding to $ZnAl_2O_4$ spinel phase and signals of ZnO (2θ = 31.8°, 34.4°, 36.2°, PDF-No. [36-1451]) and NiO or Co_3O_4 appear as well. After the reduction, and increasing the temperature up to 800 °C the ZnO phase is not detected in the catalysts. Nor the characteristic peaks of Co_3O_4 phase can be seen in CoAlZnOx sample. However, new lines appear at 43.8°, 47.2° and 51.0°, which might be attributed to alloy NiZnx and CoZnx phases. In addition, in both samples shoulders attributed to metallic Ni or Co were also observed. It is interesting to note that in NiAlZnOx sample reflections of NiO phase were detected even at 800°C, which indicates that nickel was not completely reduced under these conditions, whereas in CoAlZnOx sample cobalt was totally reduced to the metallic cobalt at 800°C.

To summarize, the in-situ XRD study of mixed samples helped to detect the structural changing in the composition, and it can be ensured that during the reactions, in the temperature range from 600 °C to 800 °C, MeAlZnOx catalysts contained alloy crystals and spinel phase, as well as metallic Ni or Co and NiO. Those phases were, therefore, the ones affecting the catalytic performance of mixed supported catalysts. In NiAlZnOx sample the presence of unreduced nickel in form of NiO determined the low activity of the sample in SR, however in reaction of POX, the existence of NiO has a positive effect on the performance of the sample. The absence of nickel, in the form of NiO, at high temperature on NiZnO sample, confirmed by in-situ XRD studding, determined significantly better catalytic preformats of this sample during the SR in comparison with Ni-AlZnOx sample in the same reaction condition, where this NiO has been established.

The morphological structure of NiAlZnOx as the best catalyst for POE and of CoAlZnOx as the best one for SR of AcOH before and after catalytic test is studied by TEM analysis. The results are presented in Fig 6.

The TEM images for both samples before catalytic test show well defined spherical particles with size 5-20 nm. Comparing the micrographs for both samples before and after catalytic test it can be seen an agglomeration of metal particles and formation of a thin film of carbon deposition. The deposited carbon is in graphite form, which does not affect the catalytic performance. The agglomeration and sintering of the active metal particles were the facts responsible of the deactivation of the catalysts.

In order to observe the quantity of deposited carbon, CHNS analysis of the best samples for both processes was done.

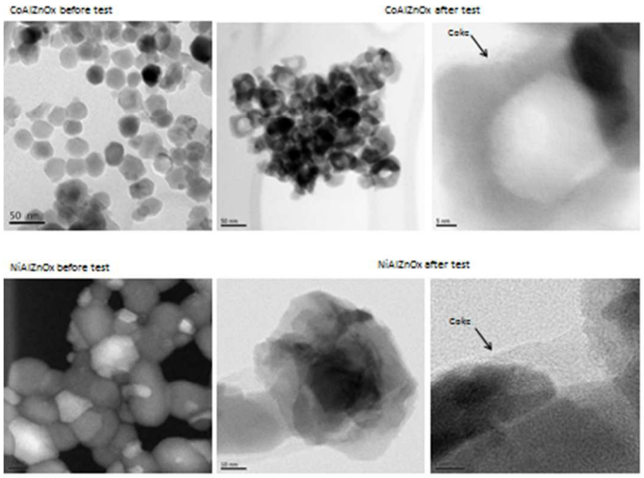

Figure 6. TEM images of CoAlZnOx, (SR of AcOH) and NiAlZnOx (POX of EtOH) before and after catalytic test.

CHNS elemental analysis was performed on the NiAlZnOx samples tested in POE reaction. Carbon content on catalyst was low, suggesting that the presence of oxygen in the feed strongly suppresses coke formation. The NiAlZnOx contained 0.05 wt% of carbon. These results demonstrate that the latter had more efficient mechanism of carbon removal than the former.

CHNS elemental analysis was performed on the CoAlZnOx sample tested in SR reaction. CoAlZnOx contained only 0,57% wt.% of carbon.

TEM and CHNS analysis of the best catalysts tested in POX and SR processes show, those samples were deactivated by agglomeration and sintering of active metals, not by cock deposition.

3. Experimental

a. Preparation and characterization of samples

The catalysts supported on single oxides – $NiAl_2O_3$, $CoAl_2O_3$, NiZnO and CoZnO – were prepared by impregnation method (IWI). Single oxides used as a supports were commercial γ-Al_2O_3 (Alfa Aesar) and ZnO (Alfa Aesar). The supports were impregnated with an aqueous solution of the active metal precursors - $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Merck). The amount of nitrates was calculated to yield the catalyst loading of 10 wt %. In a typical preparation, the powdered support was added to the aqueous solution of Co or Ni nitrate and stirred for 2.5 h at 60 °C. Then the water was vaporized in a rotary evaporator at 80 °C under vacuum. The samples were dried at 120 °C for 2 h and afterwards calcined at 700 °C for 2 h.

The catalysts supported on binary mixed oxides – $NiAlZnO_x$ and $CoAlZnO_x$ – were prepared by citrate sol-gel method (CM). Metal nitrate precursors – $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ (Merck) and $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich) – were dissolved in water and citric acid (Alfa Aesar) was added to the solution. After 30 min of mixing, the solution was concentrated in a rotary evaporator at 75 °C until viscous liquid was obtained. The substance was then dried in an oven at 120 °C for 16 h and calcined at 700 °C for 2 h in air flow. The molar ratio of Al/Zn was set to 0.73, the amount of Co and Ni precursors was calculated to yield the final content of the metal in mixed oxides at the level of 10 wt%. The amount of citric acid added was in a molar proportion equivalent to the amount of metal cations.

The physicochemical characterization of the samples was made by in-situ XRD method.

X-ray powder diffraction (XRD) measurements were carried out on a STADI P automated transmission diffractometer (STOE, Darmstadt) with CuKα1 radiation and Ge monochromatic. The patterns were collected in a 2θ range of 5 - 60° in 0.5° steps with a dwell time of 100 s and recorded with a STOE position sensitive detector. The phase analysis was performed with the program suite WINXPow (STOE&CIE) with inclusion of the Powder Diffraction File PDF2 of the International Center of Diffraction Data.

The in-situ XRD experiments were performed on X'Pert Pro (Panalytical, Almelo, the Netherlands), with CuK α1 radiation (Kα1 = 1.5418 Å, 40 kV, 40 mA) and a X'Celerator RTMS Detector. The samples were heated in 5 vol. % H_2/He to 600 °C at 10 K/min. After reaching 600 °C, the flow of H_2 was stopped and the sample was heated up to 800 °C under inert atmosphere (He). The phase analysis was carried out using the program suite WINXPow (STOE&CIE) as explained before.

The carbon content in the samples after the catalytic experiments was measured on Microanalyzer TruSpec Micro CHNS (Leco) equipped with a thermal conductivity detector; 10 mg of the sample were used for the measurement.

High Resolution Transmission Electron Microscopy (HRTEM) study was performed using a JEM-2100 (JEOL, Japan) operating at 200 kV accelerating voltage, equipped with an energy dispersive X-ray spectrometer (EDX) (Oxford, UK) for elemental identification. The powders were dispersed in isopropanol and sonicated to ensure homogeneous dispersion. A small drop of each suspension was deposited on a 200 mesh carbon-coated copper grid and introduced into the TEM column after complete solvent evaporation.

b. Catalytic test

Reforming reactions were carried out in a fixed bed flow reactor (i.d. 6 mm) in a temperature range of 600–800 °C at atmospheric pressure [19]. The operation temperature was regulated by a thermocouple inside the oven which was placed closed to the reactor. Activity tests were performed using 0.15 g and 0.20 g of catalysts for POE for SR, respectively. The samples were with a particle size range of 0.4–0.5 mm, which was chosen after preliminary mass transport experiments to minimize diffusional resistances. The catalyst was diluted by quartz chips at a volume ratio of 1:10 to avoid adverse thermal effects. Catalyst particles were placed in the middle of a quartz-glass fixed-bed reactor. The molar ratio of oxygen-to-ethanol of 0.75 for partial oxidation reaction was used. Environmentally sustainable bio-ethanol of 97 vol% purity (Richter GmbH) was used in all catalytic experiments. Ethanol was fed at a constant rate of 10 g/h to the evaporator heated to 120 °C and then mixed with an air stream (291 mL/min) and N_2 (100 mL/min). The gas hourly space velocity (GHSV), defined as the ratio of the total volumetric flow to the catalyst volume, was 35,000 h^{-1}. The S/AcOH molar ratio of 2/1 was used in steam reforming reaction. The latter solution was prepared by the dilution in water of technical grade acetic acid (80 vol. %), supplied by AppliChem, to 60 vol.%. AcOH During the reaction AcOH solution was fed at 10 g/h into an evaporator heated to 180 °C. Vaporized solution was then mixed with N_2 flowing at 100 mL/min. Gas hourly space velocity (GHSV) was in the range between 7400 and 10000 h^{-1}. Before each test, the catalysts were reduced at 600 °C for 60 min in a 20 vol. % H_2/N_2 mixture.

The catalysts were tested stepwise at target temperatures of 600, 700, and 800°C, maintaining the reaction for 2 h at each temperature to ensure that the system reached steady state [20].

The composition of the inlet and outlet gas mixtures was frequently analysed on-line using Shimadzu gas chromatographs equipped with FID and TCD detectors. The carbon balance calculated for each experiment was close to 1.

In order to evaluate the catalysts performance, the following parameters were calculated:

Product distribution: $P[\%]=[Fp_i/F_{tot\_out}] \times 100$

where Fp_i is the molar flow of component i at the outlet and F_{tot_out} is the total flow at the outlet.

Conclusions

Bio-ethanol partial oxidation and steam reforming of acetic acid are studied in this paper as reforming processes of renewables. The focus is given to catalysts development for syngas production by renewables for their application in SOFC. The catalytic performance of three series of samples containing low cost Ni and Co as active metals on Al_2O_3, ZnO and $AlZnO_x$ mixed oxide supports were explored in order to evaluate their ability to convert bio-ethanol and acetic acid. Adding oxygen to the feed (PO) improved the catalytic activity from the standpoint of conversion in comparison with adding water (SR). In SR, using a high concentrated acetic acid (steam/acetic acid=2/1 ratio) syngas production was favored at the expense of catalytic stability. Conversion and product distribution in SR determined more strongly from variation of temperature in comparison of PO. With both reforming processes high production to the desired H_2 and CO were achieved at high temperature.

In the case of Al_2O_3 supported samples both processes exhibited better performance over $NiAl_2O_3$ sample in terms of bio-ethanol and acetic acid conversion and selectivity to H_2 and CO in comparison with $CoAl_2O_3$. Acidic nature of alumina oxide promoted dehydration reaction in PO and ketonization in SR process, which affected the catalytic activity and stability as a preliminary step in deactivation of samples. The challenge of both PO and SR is carbon deposition on the catalysts, which can further deactivate the catalyst. In order to maximize the productivity and stability of the catalysts, suitable supports are required, i.e. ZnO and $AlZnO_x$ mixed oxide, which inhibit catalytic deactivation by reactions pathways. Regarding single oxide samples, ZnO supported catalysts showed a remarkable higher activity and stability compared to Al_2O_3 supported samples. CoZnO sample showed high activity in both processes, with full conversion of renewables at 800 °C and high production to syngas. NiZnO catalyst promoted the main products (H_2 and CO) production with increasing the temperature in both PO and SR. In SR over both samples the formation of byproducts was prevented, only small amount of CO_2 was observed. Generally, the $AlZnO_x$ supported catalysts showed higher activity in both PO and SR in comparison to single oxide samples. In PO of ethanol $NiAlZnO_x$ sample was more active, whereas in SR of acetic acid $CoAlZnO_x$ sample showed better performance. Complete conversion of renewables was detected in the temperature range of 600-800 °C, with high productivity of syngas. Over the best catalyst of each process the formation of CH_4 was prevented and the CO_2 was less than 9%.

In-situ XRD study of the catalysts supported on ZnO and $AlZnO_x$ showed similar phase composition for both series of samples, which were determined by the properties of ZnO. Alloy structure formation and the reduction of active metals under the reaction conditions provided high performance of these catalysts in PO and SR with high production to syngas.

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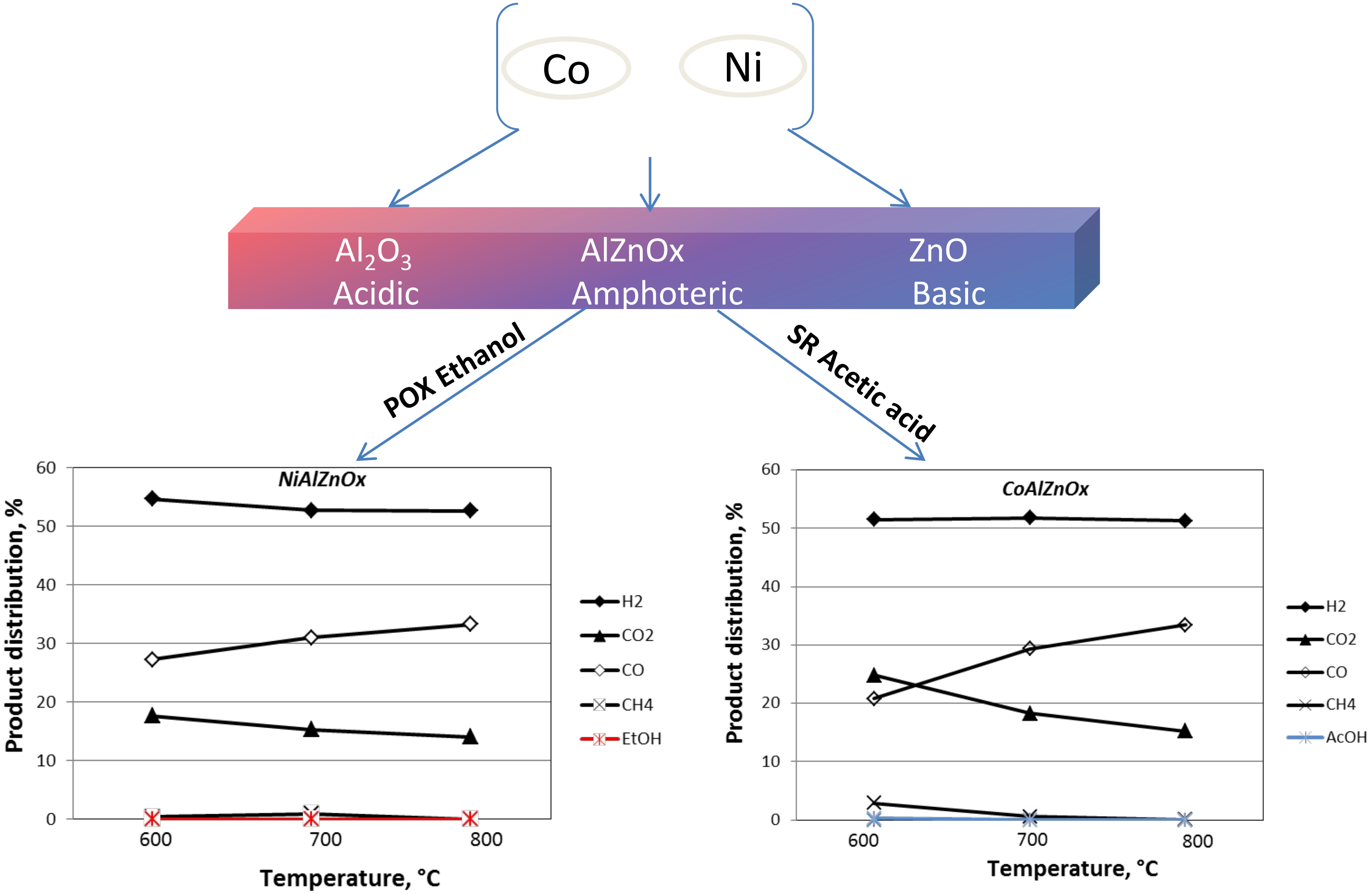
Co
Ni
Al_2O_3
Acidic
AlZnOx
Amphoteric
ZnO
Basic
POX Ethanol
SR Acetic acid
NiAlZnOx
Product distribution, %
60
50
40
30
20
10
0
600
700
800
Temperature, °C
H2
CO2
CO
CH4
EtOH
CoAlZnOx
Product distribution, %
60
50
40
30
20
10
0
600
700
800
Temperature, °C
H2
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AcOH