ORIGINAL PAPER

Synthesis, characterization and activity of Co and Ni catalysts supported on AlMe (Me = Zn, Zr, Ti) mixed oxides
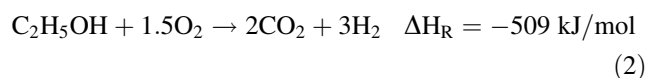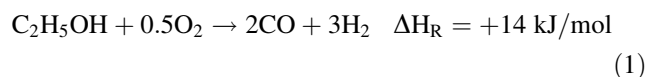
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Abstract Binary Al–Ti, Al–Zr and Al–Zn oxides, prepared by the sol–gel method were used as supports of catalytic systems. The catalysts were prepared by impregnation of these supports with the low cost Co or Ni nitrate salts and subsequent calcination at 700 °C. Catalysts have been characterized by S_{BET}, XRD and TPR techniques. The catalysts were tested in ethanol partial oxidation using a fixed-bed quartz reactor at atmospheric pressure and temperature at 600 °C. In test reactions a constant feed composition was used with O_2/EtOH molar ratio of 0.75 in nitrogen balance. The catalytic performance of the systems depends on type of support and type of promoter. Hydrogen and CO are the predominant products beside some by-products in different quantities (CO_2, methane, ethylene, acetaldehyde, acetone, acetic acid). The Co and Ni catalysts supported on AlZn binary oxide showed the highest selectivity to hydrogen and to carbon monoxide with full ethanol conversion. Selectivity of hydrogen follows the order of Co(Ni)AlZn > Co(Ni)AlTi > Co(Ni)AlZr. The best performance was obtained by NiAlZn catalyst with 89 % hydrogen selectivity.

Keywords Sol–gel mixed oxide · Low cost metals as promoters · Partial oxidation of ethanol · Hydrogen production

1 Introduction

Nowadays, 95 % of the hydrogen production comes from steam reforming of natural gas. The expected increased

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demand for hydrogen for fuel cell applications, however, dictates the development of new methods for hydrogen production, especially from bio-renewable feed stocks. The use of biofuels (bio-ethanol, glycerol, n-butanol and bio-methanol) for hydrogen production through different processes [steam reforming (SR), partial oxidation (PO), dry reforming (DR) or autothermal reforming (ATR)] has the significant advantage of being CO_2 neutral as carbon dioxide released into atmosphere during biofuel conversion was absorbed in the growth of biomass [1–4]. Among the liquid biofuels, ethanol is considered as the promising candidate for hydrogen sources [5]. Ethanol can be produced renewably from several biomass sources, including energy plants, waste materials from agro industries, organic fraction of municipal solid waste, etc. Therefore it is very reasonable to investigate different options of hydrogen production from bio-ethanol since supply and infrastructure for ethanol distribution is existing up today. Most of the research in hydrogen production by bio-ethanol reforming is under taken in development of catalysts for ethanol steam reforming but also hydrogen production by partial oxidation of bio-ethanol is an interesting application [6, 7]. The stoichiometry of this process is shown in Eqs. (1) and (2).

$$C_2H_5OH + 0.5O_2 \rightarrow 2CO + 3H_2 \quad \Delta H_R = +14 \text{ kJ/mol} \tag{1}$$

$$C_2H_5OH + 1.5O_2 \rightarrow 2CO_2 + 3H_2 \quad \Delta H_R = -509 \text{ kJ/mol} \tag{2}$$

Partial oxidation of ethanol exhibits fast start up and response times while potentially offering a more compact reactor design, desirable features for fuel cells in portable applications. Ethanol oxidation follows a very complex pathway, including several reaction intermediates formed and decomposed on both the supports and active metals

making up the catalytic systems [8–11]. In light of the above studies, it has been shown that the ethoxy species generated on the metal and on the support can be decomposed on the metal sites, forming CH_4, H_2, and CO, whereas parts of the ethoxy species generated on the support are further oxidised to acetate species, which decompose to CH_4 and/or oxidise to CO_2 via carbonate species. The obstacles for stable operation of ethanol partial oxidation are mainly coke formation and metal sintering. The acidic nature of Al_2O_3 support induces dehydration of ethanol to ethylene, leading to coke formation. Coke can destroy catalyst structure and occupy catalyst surface, thus considerably reduce catalyst activity. Moreover, coke formation on acidic supports is faster than dehydration occurs. This adverse effect can be reduced by using basic oxide as support or adding basic species onto the acidic support. The addition of the more basic support ZnO can significantly inhibit ethylene formation, greatly reducing coke formation. Recently, novel concept for using of mixed oxide support was proposed to improve catalyst stability [12]. Increasing the support surface area using a sol–gel method for preparation of mixed oxide supports led to improved catalyst stability and a lower coking rate. The higher oxygen/OH group mobility in the supports surface area promotes the mechanism of carbon removal, which in turn contributes to the high stability of Co or Ni catalysts. Otherwise, the morphological properties of materials are strongly influenced by the synthesis method, which strongly affect their performances and purposes.

Currently, the most important task is to identify effective, long-term stable catalysts for partial oxidation of ethanol. Experiments with low-cost base metals like nickel and cobalt on different supports showed great promise for ethanol conversion. Although, in general, supported noble metal catalysts are more active and stable during reforming reactions, supported nickel and cobalt catalysts are much more cost attractive. In this case, the support properties must be carefully tuned in order to minimise the extent of coke deposition that results in catalyst deactivation.

In this work, the preparation, characterization and catalytic activity of cobalt and nickel catalysts supported on alumina based mixed oxides in the ethanol partial oxidation are presented. As supports binary mixed oxides from AlZn, AlZr and AlTi, prepared by sol–gel method, were used. The influence of type of support is discussed as well.

2 Experimental

2.1 Catalyst preparation

The AlZn, AlZr and AlTi binary mixed oxides were prepared by sol–gel method using alkoxide precursors from Merck, 2,4-pentanedione (Alfa Aesar) as the complexion agent, and n-butanol as solvent. The amounts of alkoxide precursor, complexing agent, and water for hydrolysis are 2,4-pentanedione/alkoxides (mol/mol) = 0.5 for all oxides and water/alkoxides (mol/mol) = 10, 6.9, and 4.2, respectively. The molar ratios between metals were 1:1 for AlZn and AlZr mixed oxide and 2:1 for AlTi mixed oxide. The typical procedure for the synthesis of the mixed oxide is as follows: required amounts of the alkoxide precursors were dissolved in 200 mL of solvent under constant stirring until the solution became homogeneous ($\sim$0.5 h). Then, the complexing agent, 2,4-pentanedione was added (pH = 8). After stirring the solution at room temperature for five minutes the temperature was increased to 70 °C and hold for 10 min. Deionized water was added drop by drop to the hot solution to complete hydrolysis. After that stirring was continued for 1 h. The resulted mixture was cooled to room temperature and stored for 12 h. The solvents were removed at 110 °C by a vacuum evaporator. After drying, the materials were finely powdered and then calcined at 500 °C to remove the organic residues. The catalytic systems were prepared by incipient wetness impregnation of the binary mixed oxides with aqueous solution of cobalt and nickel (II) nitrate hexahydrate (Merck) at 60 °C. The resultant quantity of Co and Ni on the supports was 10 wt%. The excess water was removed in a rotating evaporator. The samples were dried at 120 °C for 6 h and calcined at 700 °C in Ar flow of 20 mL/min for 2 h.

The samples are named CoAlZn, CoAlZr, CoAlTi, and NiAlZn, NiAlZr, NiAlTi, respectively.

2.2 Catalyst characterization

All supports and catalysts were characterized using the following physicochemical methods.

Nitrogen adsorption–desorption isotherms were registered at −196 °C after drying and evacuation in a ASAP 2100 M device (Micromeritics). Samples were out gassed for 3 h at 300 °C in the degas station. The adsorbed nitrogen volumes were normalized to standard temperature and pressure. The specific surface area (S_{BET}) was calculated according to the standard BET method in the relative adsorption pressure (P/P_0) range from 0.05 to 0.3.

The X-ray powder diffraction measurements were carried out on a STADI P automated transmission diffractometer (*STOE*, Darmstadt) with CuKα1 radiation and Ge monochromatic. The pattern was scanned in the 2θ range of 5°–60° (step width 0.5, 100 s per step) and recorded with a STOE position sensitive detector. The samples were prepared to flat plates. The phase analysis was carried out with the *Win Xpow* software package, including the powder

diffraction file. The apparent size of crystallites in samples (spinel phases, nickel oxide and cobalt oxide) was calculated by the Scherrer's formula, $L = 0.9\lambda/\beta_{2\theta}\cos\theta_{max}$, where λ is the X-ray wavelength (1.54056 Å for the CuKα radiation), $\beta_{2\theta}$ is the width of the ZnAl$_2$O$_4$, NiO and Co$_3$O$_4$ diffraction peaks at half-height, and θ_{max} is the Bragg angle at the peaks maximum position.

Temperature programmed reduction (TPR) experiments were performed on 40–50 mg of all materials. The materials were loaded into fixed-bed continuous flow quartz reactors and heated to 900 °C at a 10 K/min rate in 5 % H$_2$/Ar gas mixture passed at a flow rate of 7 mL/min. Hydrogen consumption was monitored by the quadrupole mass spectrometer (Pfeiffer OmniStar).

The metal content of the calcined catalysts was determined by inductively coupled plasma optical emission spectroscopy (*ICP-OES, Varian 715-ES*).

2.3 Catalytic tests

The catalysts were tested in reaction of ethanol partial oxidation using a fixed bed reactor at atmospheric pressure and temperatures at 600 °C. The catalytic test was carried out using a constant feed composition with an O$_2$:Ethanol molar ratio of 0.75. A constant ethanol flow of 10 g/h was evaporated at 100 °C and then mixed with a gas stream of 291 mL/min air and N$_2$ as a balance. Space velocity (GHSV), i.e. the ratio of the total volumetric flow at reaction conditions to the catalytic volume, was 35.000 h^{-1}. The composition of the inlet and outlet gases were analysed on-line using *Shimadzu* gas chromatographs equipped with FID and TCD detectors.

To evaluate the performance of the catalytic systems, the conversions of ethanol [X$_{Ethanol}$ (%)] and selectivity to hydrogen [S$_{H2}$] and to carbon-containing products [S$_i$] are defined as follow:

Conversion of ethanol

$$X_{Ethanol}(\%) = \frac{F_{Ethanol\_in} - F_{Ethanol\_out}}{F_{Ethanol\_in}} \times 100$$

Selectivity to hydrogen

$$S_{H_2}(\%) = \frac{F_{H_2}}{n_i \times (F_{Ethanol\_in} - F_{Ethanol\_out})} \times 100$$

Selectivity to carbon-containing products

$$S_i(\%) = \frac{F_{carbon-containing\_products}}{n_i \times (F_{Ethanol\_in} - F_{Ethanol\_out})} \times 100$$

where F_{i_in} and F_{i_out} are the molar flow of the i species at the inlet and outlet of the reactor respectively, and n_i is the stoichiomeric factor between the carbon-containing products and ethanol.

3 Results and discussion

3.1 Physico-chemical characterisation

The chemical composition of the catalysts, expressed as weight percentages, as well as the textural properties of the calcined supports and catalysts are summarized in Table 1. Nitrogen sorption experiments performed on calcined catalysts showed that impregnation of the supports followed by calcination resulted in the loss of the surface area (Table 1). This loss can be justified considering that nonporous particles formed after the metal deposition and calcination steps block the pores of the porous supports. Pore volume decreases slightly by incorporation of the metal into the support. Otherwise, pore size increases after impregnation of the supports with Co and Ni. This effect is caused by the filling of the support pores by the active phase. The cumulative pore volume, however, did not show a substantial decrease upon impregnation suggesting that smaller pores blocked by introduced active metal oxide species comprised only a fraction of the total pore volume. Comparison of the S$_{BET}$ surface areas exhibit a clearly higher surface area of the AlTi support than the AlZr and AlZn mixed oxides due to a more amorphous structure, which has been described elsewhere [13].

Nitrogen isotherms of the supports and catalysts are similar and correspond of II type isotherms according to IUPAC classification [14]. Figure 1 show isotherms with different hysteresis loop. The shapes of hysteresis loops have often been identified with specific pore structures. The AlZn support exhibit H1 type of hysteresis, characteristic of the solids consisting of particles crossed by nearly cylindrical channels or constituted by aggregates (consolidated) or agglomerates (unconsolidated of spherical particles). For AlTi and AlZr samples exhibit type H4 loop of hysteresis is often associated with narrow slit-like pores, but in this case the Type II isotherm character is indicative of microporosity [15]. Table 1 document that all samples contain nano-size pores in the range of 5.3–1.3 nm, the highest being observed at AlZn mixed oxides.

The XRD patterns of the mixed oxide supports (binary AlMe (Me = Zn, Zr, Ti)) and the Co- and Ni-containing catalysts are displayed in Fig. 2a–c. The X-ray diffractograms of the AlZn and AlZr mixed oxides show intense and symmetric reflections of ZnAl$_2$O$_4$ spinel phase (2θ = 31.2°, 36.8°, 55.7°, 59.3°, 65.3°, PDF-No.[5-669]). The X-ray diffractogram of the AlTi mixed oxide show presence of amorphous phase. This is determined from temperature treatment of mixed oxide supports at 500 °C. The temperature for calcination was not high enough to form the typical clean crystal spinel structure.

Calcined nickel and cobalt catalysts supported on AlZn exhibit intense and symmetric reflections of ZnAl$_2$O$_4$

Table 1 Physico-chemical properties of the supports and catalysts

| Catalyst	Co(Ni) wt%	Crystallite size (nm)[a] Zn(Zr, Ti)Al$_2$O$_4$	Surface area[b] (m^2/g)	Pore volume[c] (cm^3/g)	Pore size[d] (nm)	T of phase reduction in TPR[e] (°C)			
						Co$_3$O$_4$	MeO	MeAl$_2$O$_4$ surface	MeAl$_2$O$_4$ spinel
AlZn		9.8	76	0.15	3.2	No reduction			
NiAlZn	9.8	7.2	44	0.14	4.1		450	545	633
CoAlZn	9.8	7.1	35	0.14	5.3	380	420	690	
AlZr		4.1	200	0.15	1.3	No reduction			
NiAlZr	9.8	Amorphous	140	0.12	1.7		440		730
CoAlZr	9.8	Amorphous	130	0.11	1.7	400		690	
AlTi		4.9	320	0.28	1.7				760
NiAlTi	9.8	Amorphous	140	0.20	2.2				700
CoAlTi	9.8	Amorphous	94	0.19	3.6		455		780

[a] Determined by XRD

[b] Specific surface area calculated by BET method at relative pressures p/p$_0$ = 0.05–0.30

[c] Total pore volume determined from isotherms at relative pressure p/p$_0$ = 0.995

[d] Average pore radius determined from BJH analysis of adsorption branch isotherms

[e] Temperature of maximal hydrogen consumption, temperature range 10–900 °C
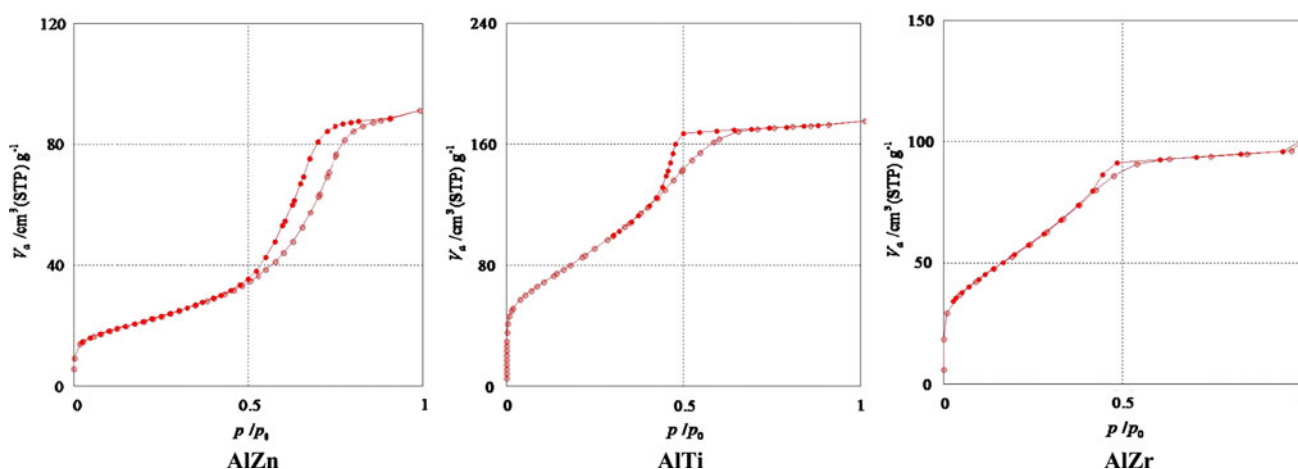
Fig. 1 Nitrogen isotherms of samples

spinel phase (PDF-No. [5-669]). It is also noteworthy that in calcined NiAlZn catalyst, peaks of NiO ($2\theta = 37.1°$, $43.1°$, $62.6°$, PDF-No. [89-7130]) are detected. Since reflections of NiAl$_2$O$_4$ are coincident with those of ZnAl$_2$O$_4$, the presence of the former cannot be ruled out. The ZnAl$_2$O$_4$ used as support is a highly stabilized spinel and the Ni impregnation was carried out in one step by impregnation method, consequently the stoichiometric NiAl$_2$O$_4$ formation ($2\theta = 31.4°$, $37.0°$, $45.0°$, $59.6°$, $65.5°$, PDF-No. [78-0552]) should be very low. However, nickel could be incorporated into the subsurface of the zinc spinel and a surface Ni compound related to Ni strongly interacting with the spinel matrix could be formed. In case of CoAlZn catalyst, ZnAl$_2$O$_4$ spinel phase was also formed upon calcination. However, cobalt oxide can not be seen on the

diffractogram since Co$_3$O$_4$ (PDF-No. [42-1467]) reflections coincide with those of ZnAl$_2$O$_4$ spinel phase.

The cobalt and nickel catalysts supported on AlZr and on AlTi mixed oxides (Fig. 2b and c are mostly amorphous, confirming a high dispersion of the species formed on the catalyst surfaces. Only in NiAlZr catalyst, clear peaks of NiO ($2\theta = 37.1°$, $43.1°$, $62.6°$, PDF-No. [89-7130]) are detected. However, the diffractogram of the AlZr support gives the evidence of the presence of spinel ZrAl$_2$O$_4$ phase formed at higher temperature for all AlZr based samples.

Reducibility of nickel and cobalt oxide species is a very important characteristic of the catalysts directly related to their activity and ability to self-activity under the reaction condition. TPR data of cobalt- and nickel-based catalysts
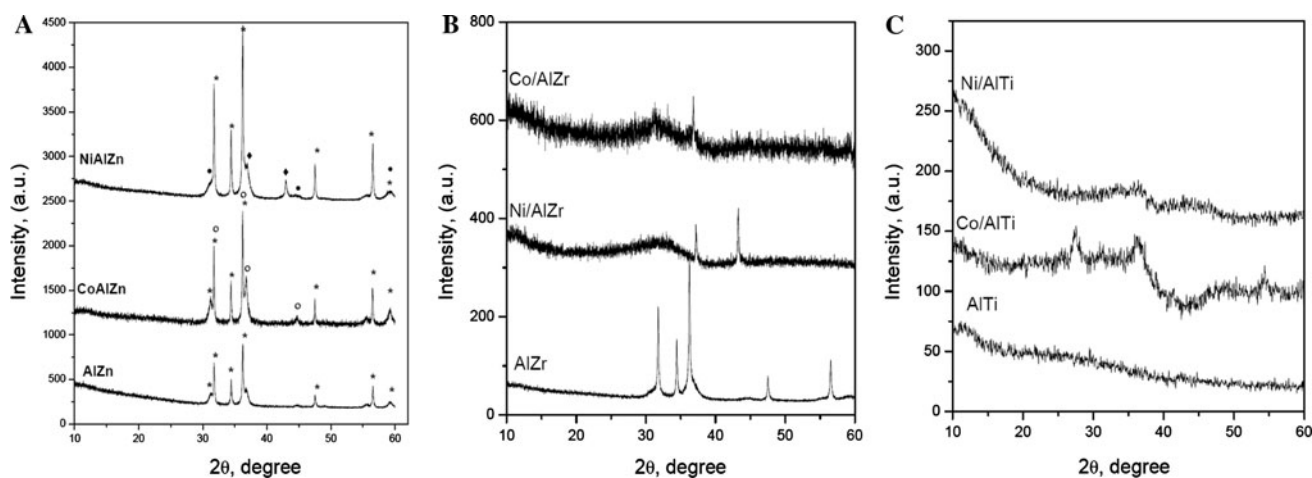
Fig. 2 X-ray diffractograms of the samples: **a** AlZn supported catalysts; **b** AlZr supported catalysts; **c** AlTi supported catalysts. A*sterisk*: $ZnAl_2O_4$ spinel phase; *circle*: Co_3O_4; *filled diamond*: NiO; *filled circle* $NiAl_2O_4$

are shown in Table 1. The temperature maximum from TPR analysis of catalytic systems are different from one another, which implies that Co and Ni reducibility are strongly influenced by the composition of the mixed oxide. For Co- and Ni-containing samples supported on AlZn mixed oxide TPR analysis presented three main reduction peaks. For CoAlZn catalyst the maxima of hydrogen consumption is close to 380, 420 and 690 °C, respectively. This implies a two-step reduction process of Co_3O_4, where the first peak at 380 °C is assigned to the reduction of Co^{3+} to Co^{2+} and the second peak at 420 °C corresponds to the reduction of Co^{2+} to metallic Co^0 as reported by different authors [16–18]. The high temperature peak at 690 °C is ascribed to the reduction of Co^{2+} species which are strongly interacting with $ZnAl_2O_4$ or forming $CoAl_2O_4$. A similar behaviour was reported by Barroso et al. [19] on CoZnAl catalysts prepared by the citric method. For NiAlZn catalyst the main peak appears with maxima close to 633 °C and has weak shoulders at 450 °C and 545 °C, respectively. A weak band at 450 °C should be assigned again to the reduction of NiO whereas the band centered at 545 °C suggests a strong interaction of Ni^{2+} species with the spinel phase (mainly NiO in agreement with XRD results and/or $NiAl_2O_4$). The high temperature of the main reduction peak at 633 °C indicates a strong interaction between Ni^{2+} species and spinel phase. The reducibility of Ni in NiAlZn catalyst is similar to that reported in literature for catalysts prepared by co-precipitation and sol–gel methods [20, 21].

For Co- and Ni-containing samples supported on AlZr mixed oxide analysis presented two main reduction peaks. For CoAlZr catalyst the main peaks show maxima close to 400 and 690 °C, respectively. The first peak at lower temperature is assigned to the reduction of Co^{3+} to Co^{2+}, whereas the second peak at 690 °C corresponds to the

reduction of Co^{2+} species (probably including in $CoAl_2O_4$ or CoO_x). For NiAlZr catalyst the main peaks appear with maxima close to 440 and 730 °C, respectively. The peak at 440 °C is indication of NiO forming. This temperature maximum is similar to that of NiAlZn sample, with lower variation of the temperatures probably determined from particle size. In XRD analysis of this sample the presence of NiO was indicating. The high temperature peak (730 °C) can be attributed to a strong interaction between nickel and the support [22, 23], promoted by the calcination temperature applied to the material.

TPR profile of AlTi supported catalysts shows a different behaviour. The main peak at around 760 °C was found in the support as well as in the catalysts suggesting the reduction of mixed oxide phase. The shoulder at 455 °C in CoAlTi sample is assigned to the reduction of $Co^{3+/2+}$ in CoO_x.

TPR results indicate that cobalt and nickel oxides exhibit strong interaction with binary mixed supports and this determined temperature maximum in catalysis profiles.

3.2 Catalytic activity

The activity of Co- and Ni-containing samples are tested in partial oxidation of ethanol. The reaction was carried out at constant conditions for all tests at atmospheric pressure, with O_2/C_2H_5OH molar ratio = 0.75, at constant flow rate (EtOH 10 g/h, Air 291 mL/min, N_2 100 mL/min) and temperature of 600 °C. The N_2 flow was used as the inert component and only decrease the partial pressures of the reactants and the products. The carbon balance was around 100 % for all samples.

Table 2 gives information on the bio-ethanol conversion and selectivity of the reaction over Co- and Ni-catalysts supported on different binary mixed oxides. An important question in using Co and Ni as the active metal is the effect

Table 2 Catalytic performance on partial oxidation of bio-ethanol over NiAlMe and CoAlMe catalysts

Catalysts	Ethanol conversion (%)	Selectivity (mol%)						
		H_2	CO	CO_2	CH_4	C_2H_4	C_2H_4O	CP*
AlZn	99.5	33.2	26	21.4	11	10	30	2
CoAlZn	100	79	76	22	2	0	0	0
NiAlZn	100	89	78	21	0.5	0	0	0
AlZr	47	3.8	14.7	5	7.2	30	32	8
CoAlZr	94	37	55	6	3.4	9	22	3.5
NiAlZr	90	44	81	4.9	4.2	9	21	2.2
AlTi	99	15.6	47.6	8.8	1.3	38	2	2.3
CoAlTi	100	45	64	16	2.5	15	1.5	1.5
NiAlTi	100	60	66	34	0	0	0	0.6

Reaction conditions: T = 600 °C; O$_2$/EtOH = 0.75; GHSV = 35.000 h^{-1}

CP*—carbon containing products (acetone, acetic acid)

of the support material, which is reported to make a dramatic difference in catalytic performance, including activity, selectivity and stability. In general, it can be observed that the catalytic activity and selectivity of reaction were determined by the composition of supports. The nature of supports strongly affects the products distribution of cobalt and nickel supported systems. The products detected were hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethylene (C_2H_4), acetaldehyde (C_2H_4O) and acetone and acetic acid [summarized in table as carbon containing products (CP*)].

If ethanol conversion and product distribution of different binary mixed oxide without active metal components are compared, one can see that the AlZn mixed oxide is the best material for hydrogen production. Barroso et al. [24] presented that aluminium spinels were very active in the catalytic conversion of ethanol at 500 °C. In our cases, a nearly complete initial ethanol conversion was obtained at 600 °C for AlZn and AlTi supports. For AlZr mixed oxide ethanol conversion is considerable slower (47 %). However, the product distribution depends strongly on the nature of divalent metal which determines the physicochemical properties of samples. The hydrogen selectivity follows the order of AlZn > AlTi > AlZr. The $ZnAl_2O_4$ spinel phase is characterized by high thermal resistance under reforming conditions which influenced the performance in hydrogen production.

Morphology and crystalline size seem to influence many properties of the catalysts. Thereby, larger support particles of AlZn, which were obtained by calcination of AlZn mixed oxide, favour the metal-support interactions. This is resulting in a decrease in metallic particle sizes, thus avoiding metal (Ni or Co) sinterization during the calcination step. Although strong metal-support interactions decrease the reducibility of metallic Co and Ni particles, these strong interactions produce higher values of exposed surface metallic active sites, which increase the catalytic performance. On the contrary, small particles of AlZr and AlTi increase the surface area, but favour the metal cations

mobility over the support surface, which allows the sintering of the metallic particles during the calcination process [25]. Metal sintering decreases metal exposure, and consequently, decreases the bio-ethanol conversion and hydrogen production.

While conventionally a metal oxide support is used in conjunction with Ni or Co to increase the surface area of the exposed metal, the support almost always plays a role in intermediate steps in ethanol reforming reactions. The support can often act as a site for reactant adsorption and consequently can induce side reactions in partial oxidation.
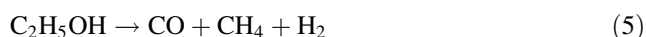
In this proposed system, bio-ethanol passes through the first active center ($ZnAl_2O_4$ spinel phase) at 300–400 °C to perform dehydrogenation to acetaldehyde and hydrogen, followed by acetaldehyde reforming or decomposition yielding hydrogen and CO. Ethylene formation can be prevented at 300–400 °C, thus reducing coke formation. The intermediate species are then passed through the second active center (Ni- or Co-based catalyst) to enhance hydrogen production. This concept offers an economical method to enhance hydrogen production and catalyst stability. This structure is confirmed by XRD and TPR analysis of catalysts supported on mixed oxides clearly showing that $ZnAl_2O_4$ spinel, $CoAl_2O_4$ or $NiAl_2O_4$ and NiO or Co_2O_3 are the active phases.

In addition, the improvement of the performance of the bimetallic catalysts is also due to structural and electronic effects, which arises from a strong metal–metal and metal–support interaction in the catalyst. Therefore synergetic effect between the metal and the support can increase activity of the catalyst for the oxidation reaction.

In general, it was observed that the Ni- and Co-based catalysts show similar activity. Full ethanol conversion was assured at 600 °C for Co- and Ni-based catalysts supported on AlZn and AlTi mixed oxides but for samples supported on AlZr oxide conversion was not completed. The role of promoters is clearly marked in product distribution for all catalysts. Accordingly, for the Co(Ni)AlZn catalytic system, after impregnation of supports with active components, the

main pathway of reaction is partial oxidation of ethanol (Eqs. 1 and 2) and the predominant products are H_2, CO and CO_2. Selectivity to CO was 76 and 78 %, respectively, and selectivity to CO_2 was around 22 %. CH_4 also was observed but with less than 2 % selectivity. The highest selectivity to hydrogen was obtained for the NiAlZn catalyst with 89 %. In contrast to reactions performed with the unpromoted AlZn, CP* products were not obtained when CoAlZn and NiAlZn were utilized as catalytic material.

For AlZr supported catalysts H_2 and CO were the main products, but hydrogen selectivity was only about 40 % because conversion of ethanol is not complete and quantity of acetaldehyde and ethylene were around 30 %. For Co(Ni)AlZr catalytic systems, together with the reaction of partial oxidation of ethanol whose products are H_2 ($\sim$40 %) and CO, dehydrogenation (3) and dehydration (4) of ethanol proceeded which main products are acetaldehyde and ethylene. Decomposition of ethanol (5) to CO and CH_4 also happens:

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \tag{3}$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{4}$$

$$C_2H_5OH \rightarrow CO + CH_4 + H_2 \tag{5}$$

For Co(Ni)AlTi catalyst systems results are different. Hydrogen selectivity was 45 % for CoAlTi sample and CO, CO_2 and ethylene were formed as main products. Base reaction pathways are ethanol decomposition (5) and dehydration (4). The selectivity of hydrogen increases to 60 % when nickel is utilized as promoter on AlTi support. For NiAlTi catalytic system predominant products are H_2, CO and CO_2 and the base reaction is partial oxidation of ethanol. The quantity of main CP* products decreased to 0.6 %.

In summary, the catalytic properties of supported low cost Co- and Ni-based catalysts for hydrogen production from partial oxidation of bioethanol depend on the type of used supports. The studies show that the best catalytic results were exhibited by Ni and Co supported on AlZn mixed oxide. The main problems during the catalytic partial oxidation of bio-ethanol for catalytic system supported on AlZr and AlTi mixed oxide are (1) sintering of active metal and catalyst poisoning by coke depositing at high temperature and (2) formation of acetaldehyde or ethylene. All these problems were found to be related to the physicochemical properties of the catalyst, which highly depend on the nature of supports and the type of metal precursors.

4 Conclusions

This study demonstrated that binary Al–Ti, Al–Zr and Al–Zn oxides, prepared by the sol–gel method and

subsequently impregnated with the low cost Ni or Co alts, can be used as catalysts for partial oxidation of bio-ethanol. The preparation method of binary mixed oxide led to the formation of spinel matrix $Zn(Zr,Ti)Al_2O_4$ in the supports. Nonstoichiometric Co_2O_3, NiO and $NiAl_2O_4$ were mainly formed and detected on the catalytic systems. We have shown that supports play an important role in partial oxidation of ethanol, as supports help in the dispersion of metal catalyst and may enhance metal catalyst activity via metal-support interactions.

At 600 °C full ethanol conversion was observed on AlZn and AlTi supported samples and a hydrogen and CO rich fuel gas was obtained. Selectivity to hydrogen follows the order Co(Ni)AlZn > Co(Ni)AlTi > Co(Ni)AlZr. The best catalytic performance was obtained by the NiAlZn catalyst with 89 % hydrogen selectivity.

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