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# Role of oxygen vacancies and $Mn^{4+}/Mn^{3+}$ ratio in oxidation and dry reforming over cobalt-manganese spinel oxides

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ARTICLE INFO	A B S T R A C T				
Keywords: Co-Mn spinel oxides Ethanol combustion Ethanol dry reforming Ethanol dehydrogenation	Spinel type cobalt-manganese oxides $Mn_xCo_{3-x}O_4$ (x = 0; 0.05; 0.10; 0.15) were prepared by co-precipitation method, from cobalt and manganese salts in the presence of ammonium carbonate. X-ray diffraction (XRD), texture measurements (BET/BJH), Fourier transform infrared spectroscopy (FT-IR), Scanning electron micro- scopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used for their characterization. Their catalytic behavior in ethanol combustion, dry reforming with $CO_2$ and dehydrogenation was investigated. The results showed that the cubic structure of $Co_3O_4$ , corresponding to spinel network, is not disturbed by adding man- ganese. Results obtained revealed that $Mn_{0.15}Co_{2.85}O_4$ catalyst, with the highest content of $Mn^{4+}$ cations in the octahedral sites and oxygen defects, display superior catalytic activity compared to the others. The apparent activation energies, calculated from Arrhenius plots, are as follows: $E_a$ combustion < $E_a$ non-oxidative dehydrogenation < $E_a$ dry reforming, showing that cobalt-manganese spinel type oxides are good candidates for combustion.				

# 1. Introduction

The use of advanced biofuels such as alcohols is advantageous, provided that volatile compounds like aldehydes, with harmful effects to human health, do not release by their combustion. The alcohols have been intensively studied as biofuels. Among them, methanol and ethanol were the most used as alternative fuels for internal combustion engines. Currently, the dominant liquid fuel is ethanol, which having the advantage to be obtained from renewable resources is used especially as fuel for transportation [1]. Ethanol, unlike to gasoline, is an oxygenated fuel by whose combustion no nitrogen oxides are emitted. Another fuel obtained from biomass is isopropanol, which is more soluble in diesel fuel than ethanol, making its use being more sustainable alternative [2].

Generally, the addition of oxygenates compounds such as  $C_1-C_4$  alcohols in gasoline prevent the ignition, increasing the octane number and also decreasing the toxicity of the exhaust gases [3]. According to the European Standard EN 228:2000 for the addition of alcohols in diesel fuel, the composition corresponds to 3% methanol, 5% ethanol and 10% isopropanol and isobutanol. Moreover, from their combustion, volatile compounds such as aldehydes and ketones, with harmful effects to human health, should not be released into the atmosphere. The catalysts used commonly for  $C_1$ - $C_4$  alcohols combustion are based on noble metals such as Pt, Pd, Rh, Ir supported on TiO<sub>2</sub> [4], bimetallic compounds Pt–Rh, Rh–Au, Rh–Pd, and Pt–Pd over CeO<sub>2</sub> [5], Rh-Ce [6], Pt, Rh, Ag oxides [7].

The noble metal based catalysts have a number of disadvantages including their high price, are partially deactivated as a result of coke deposition, and additionally, they are more active for dehydrogenation despite combustion.

Therefore, their replacement by mixed oxides, mainly perovskites type has been investigated. The advantages of these catalysts are resistance to poisoning and the low price. It is known that, the catalytic performances of these oxides are directly correlated with their surface area, the pore structure, the nature of oxygen species present on the surface and their reducibility [8]. These factors are remarkably influenced by the preparation method. Synthesis of ordered porous structure especially nanoporous one, lead to increased surface area. Another important factor to take into consideration in the combustion reaction is the catalyst stability [9], which has been studied to a lesser extent than the catalytic activity.

Catalysts based on  $Co_3O_4$  and  $Mn_3O_4$  on different supports have been intensively studied for the combustion of organic volatile compounds [10–14]. Cobalt oxides display higher oxidation potential

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Fig. 1.  $N_2$  adsorption-desorption isotherms and pore size distribution of  $Mn_xCo_{3-x}O_4$  (x = 0, 0.05, 0.1, 0.15).

Table 1Textural properties of Co-Mn oxides.

Sample	S <sub>BET</sub> (m²/g)	V <sub>micro</sub> (cm <sup>3</sup> /g)	V <sub>meso</sub> (cm <sup>3</sup> /g)	d <sub>meso</sub> a (nm)	Cell parameter (a) (Å)
Co <sub>3</sub> O <sub>4</sub>	21	0.0004	0.09	-	8.06
Mn <sub>0.05</sub> Co <sub>2.95</sub> O <sub>4</sub>	27	0.0005	0.20	34.5	8.08
Mn <sub>0.1</sub> Co <sub>2.9</sub> O <sub>4</sub>	37	0.0009	0.22	30.3	8.06
Mn <sub>0.15</sub> Co <sub>2.85</sub> O <sub>4</sub>	47	0.0007	0.23	20.5	8.07

<sup>a</sup> BJH Desorption average pore diameter.

relative to manganese oxides, but manganese has the advantage to transfer more electrons [15]. The reaction mechanism and kinetic parameters for catalytic VOC oxidation are currently intensively studied; a general conclusion regarding combustion over cobalt and manganese oxides has not been established.

Ethanol dry reforming with  $CO_2$  is an interesting task from socioenvironmental considerations, related to the reduction of greenhouse gases emissions. This reaction has many advantages such as the feedstock is renewable, biodegradable and easily transportable and in addition, the reaction is thermodynamically favorable at relatively lower temperatures (~ 300 °C) [16,17].

The studied reactions are:

Combustion:  $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 2H_2O \ \Delta H_{298} = -1271 \ kJ/mol$  (1)

Fig. 3. FT-IR spectra of Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> samples.

Dry reforming:  $C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2 \Delta H_{298} = 297 \text{ kJ/mol}$  (2)

Dehydrogenation:  $C_2H_5OH \rightarrow CH_3CHO + H_2 \Delta H_{298} = 71 \text{ kJ/mol}$  (3)



Fig. 2. (a) XRD patterns of Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> spinel oxides, (b) the variation of crystallite sizes and elastic strain with respect to manganese atomic composition.

Co3O4 ---- Mn0.05Co2.95O4 ---- Mn0.1Co2.9O4 ---- Mn0.15Co2.85

![](_page_2_Figure_2.jpeg)

Fig. 4. SEM images of Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> samples.

Table 1	2
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The EDX composition of Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> spinel oxides.

Catalyst	Wt (%)			At (%)			
	Со	Mn	0	Со	Mn	0	
$\begin{array}{c} Co_{3}O_{4} \\ Mn_{0.05}Co_{2.95}O_{4} \\ Mn_{0.1}Co_{2.9}O_{4} \\ Mn_{0.15}Co_{2.85}O_{4} \end{array}$	73.14 71.66 70.81 69.72	- 1.26 2.83 3.4	26.86 27.09 26.35 26.88	42.51 41.47 41.43 40.45	- 0.78 1.78 2.12	57.49 57.75 56.79 57.43	

The aim of the present work is to investigate the catalytic combustion of ethanol, dry reforming with  $CO_2$  and dehydrogenation, over mixed oxides based on cobalt and manganese and to study the influence of Mn/Co ratio over the structure and catalytic activity.

# 2. Experimental

## 2.1. Catalysts preparation

Cobalt-manganese mixed oxides, with formula  $Mn_xCo_{3-x}O_4$  (x = 0, 0.05, 0.1, 0.15) were synthesized by co-precipitation method. In this scope, (CH<sub>3</sub>COO)<sub>2</sub>Co-4H<sub>2</sub>O and (CH<sub>3</sub>COO)<sub>2</sub>Mn-4H<sub>2</sub>O were dissolved in water and homogenized by vigorous stirring for 30 min. Then, an excess of ammonium carbonate, in aqueous solution was added in drop over the previous solution, under stirring. The obtained pink precipitate was filtered, thoroughly washed with distilled water, dried at 60 °C for 24 h and calcined at 500 °C (5 °C/min) for 6 h.

## 2.2. Catalysts characterization

The crystalline phases present in the samples were determined with a PANalyticalX'Pert Pro MRD diffractometer using a Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.78897$ ). Data recording was made in the 2 $\theta$  range of 5–80° with a step size of 0.0251°.

The nitrogen adsorption-desorption isotherms, measured by a Micromeritics ASAP 2020, were used for the specific surface area calculation using Brunauer–Emmett–Teller (BET) mode. The total pore volume, the micropore and mesopores volume were calculated by a BJH (Barrett–Joyner–Halenda) method. The samples were degassed under vacuum at 200  $^{\circ}$ C for 8 h prior to measurements.

Scanning electron microscopy, using an XL-30 Environmental SEM, was used for morphological information about samples.

The X-ray photoelectron (XPS) measurements were obtained using a VG-220IXL spectrometer with a monochromated Al K $\alpha$  radiation (1486.6 eV, line width 0.8 eV) and energy resolution of 0.4 eV. The binding energy of C(1 s) at 284.8 eV was used as a reference. Spectra were deconvoluted using a CASAXPS software with the accuracy of 0.2 eV using the Shirley background.

Information about metal–oxygen bonds were obtained from Fourier transform infrared (FT-IR) using a Bruker IFS 66 V/S spectrometer, equipped with a diamond attenuated total reflectance (ATR) and spectra were recorded in the range of 400–4000 cm<sup>-1</sup> and a resolution of 4 cm<sup>-1</sup>.

#### 2.3. Catalytic activity test

The catalytic activity studies were carried out in a continuous-flow fixed bed reactor (8 mm i.d.) at atmospheric pressure. Temperature in the catalyst bed was monitored by electronic control. Ethanol vapors were generated using air as a carrier gas passed through a saturator, with a total flow rate of 50 ml/min at the inlet of the reactor. The catalyst amount was 0.2 g, the ethanol concentration 145 ppm and the temperature varied between 100–300 °C.

Ethanol dry reforming was perform at a  $CO_2$  flow rate of 50 ml/min and ethanol flow rate of 0.15 ml/min (molar ratio 1:1), while for the ethanol dehydrogenation a flow of 50 ml/min  $N_2$  was passed through a saturator with ethanol.

The reactant and the reaction products (after a stabilization time of 30 min) were analyzed using a GC K072320 Thermo-Quest gas chromatograph equipped with a FID detector.  $CO_2$  analysis was performed using a Thermo Finnigan Gas-Chromatograph equipped with a thermal conductivity detector (TCD) and an alumina column. The ethanol conversion was calculated as the percentage of the ethanol which reacted, after reaching the stationary regime, by the following relation:

# $X(\%) = [(A_i - A_f)/A_i] \times 100$

where: ' $A_i$ ' and respectively ' $A_f$ ' represent the ethanol chromatographic peaks areas before and after catalytic reaction.

![](_page_3_Figure_3.jpeg)

Fig. 5. XPS spectra of Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> samples (a-Co 2p, b- Mn 2p, c-O 1s).

Table 3The surface composition from XPS.

Catalyst At (%)		Co ratio Mn ratio		O (%)			Mn/Co			
	Со	Mn	0	$\mathrm{Co}^{3+}/\mathrm{Co}^{2+}$	$\mathrm{Mn}^{\mathrm{3+}}/\mathrm{Mn}^{\mathrm{4+}}$	O <sub>L1</sub>	O <sub>L2</sub>	O <sub>V</sub>	EDX	XPS
$\begin{array}{c} Co_{3}O_{4} \\ Mn_{0.05}Co_{2.95}O_{4} \\ Mn_{0.1}Co_{2.9}O_{4} \\ Mn_{0.15}Co_{2.85}O_{4} \end{array}$	43.9 42 43.1 41.3	- 1.1 1.7 3.6	56.1 56.9 55.2 55.1	0.92 1.44 4.29 1.40	- 1.27 0.78 0	52.5 53.4 51.3 46.4	- 2.7 4.1 8.9	47.5 43.9 44.6 44.7	0 0.02 0.04 0.05	0 0.03 0.04 0.09

#### 3. Results and discussion

# 3.1. Characterization of catalysts

 $\rm N_2$  adsorption-desorption isotherms of Co-Mn spinel type oxides, shown in Fig. 1, were plotted in order to determine the specific surface area and the pore distribution. All the samples with manganese exhibited type-IV isotherms, characteristic for mesoporous materials. The capillary condensation takes place at high relative pressure, respectively 0.75 - 0.8, corresponding to multilayer adsorption and capillary condensation in mesopores. The average pore size decreases with the manganese content increasing, from 34.5 to 20.5 nm (Table 1) and the size distribution is broad (Fig. 1). Co<sub>3</sub>O<sub>4</sub> sample reveals type II isotherm with H3 hysteresis loop, characteristic of macroporous materials. The volume of adsorbed nitrogen over this sample is much lower than the volume adsorbed over the others, the capillary condensation occurs at

 $P/P_0=0.9$  and this sample has a low porosity with a very broad pore size distribution.

The specific surface area for  $Co_3O_4$  is  $21 \text{ m}^2/\text{g}$ . The specific surface area is increased at  $27 \text{ m}^2$  /g,  $37 \text{ m}^2$  /g and respectively  $47 \text{ m}^2$  /g by manganese adding, the increase being directly proportional to its quantity.

The XRD patterns of synthesized  $\text{Co}_3\text{O}_4$  and  $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$  powders are depicted in Fig. 2a. All lines observed in figure are indexed to a cubic structure of  $\text{Co}_3\text{O}_4$ . No characteristic lines of CoO,  $\text{Co}_2\text{O}_3$  and, respectively, manganese oxides are present, which indicates a very good incorporation of manganese into the spinel network of  $\text{Co}_3\text{O}_4$ . The reflections at  $2\theta = 22$ , 36.6, 43.2, 45, 52.6, 65.7, 70.3 and 77.6° are attributed to the typical diffraction lines, corresponding to a face-centered-cubic phase of  $\text{Co}_3\text{O}_4$  spinel [18]. These were attributed to the diffraction of (111), (220), (311), (222), (400), (422), (511), and (440) crystal planes. The value of cell parameter "a" (Table 1) does not

#### Molecular Catalysis xxx (xxxx) xxxx

![](_page_4_Figure_3.jpeg)

Fig. 6. Catalytic performances in ethanol combustion over Mn<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> systems (a) and Arrhenius plots (b) (145 ppm of ethanol, 0.2 g catalyst, total flow rate 50 mL/min).

![](_page_4_Figure_5.jpeg)

Fig. 7. Correlation between ethanol conversion (300  $^\circ\text{C})\text{,}$  lattice strain and  $\text{Mn}^{4+}$  content.

change by addition of manganese, into the spinel structure of cobalt oxide.

The average crystallite size, calculated using Scherrer equation, has value of 19 nm ( $Co_3O_4$ ), 18 nm ( $Mn_{0.05}Co_{2.95}O_4$ ), 17 nm ( $Mn_{0.1}Co_{2.9}O_4$ ) and 15 nm ( $Mn_{0.15}Co_{2.85}O_4$ ), respectively.

For the purpose of crystal lattice deformations evaluation, the elastic strain of all catalysts has been calculated with the formula  $E = \beta/2 \cos \theta$  [19], where  $\beta$  is the full-width at half maximum (FWHM), and  $\theta$  is the diffraction angle, and the results compared with the crystallite size are shown in Fig. 2b. The elastic strain is directly proportional to amount of manganese and inversely proportional to crystallite size. The replacement of cobalt ions with manganese ions leads to network defects such as micro-straining in the lattice.

Fig. 3 displays the FT-IR spectra of  $Mn_xCo_{3-x}O_4$  samples. Three distinctive peaks are observed. The first, at 657 cm<sup>-1</sup>, that could be attributed to the stretching vibration of Co<sup>2+</sup>-O bond, with the cations placed in the tetrahedral position. The second peak, located at 553 cm<sup>-1</sup>, is attributed to the stretching vibration of Co<sup>3+</sup>-O bond, for

the cations located in octahedral position [20]. The last peak, located at  $515 \,\mathrm{cm}^{-1}$ , is attributed to  $\mathrm{Mn}^{3+(4+)}$ -O bond in octahedral position, whose intensity increased with the increase of manganese amount, therefore, it can be concluded that Mn cations are predominantly placed in octahedral positions.

The FT-IR spectra are in good agreement with XRD patterns which confirm the presence of a pure spinel structure.

The morphology of all samples is shown in Fig. 4, and EDX composition in Table 2. For manganese modified samples, an agglomeration of particles can be seen clearly, and also, the morphology of microsphere particles is very uniform, with a very narrow distribution, revealing flake-like spherical structures. From EDX composition has been evidenced that, only for the last sample, the atomic ratio between Co and Mn is equal with the experimental one. For other samples the Co/ Mn ratio is slightly lower than for the last sample. In addition, the Co/O ratio is very close to the experimental one.

The XPS spectra of all samples are shown in Fig. 5, while the XPS composition compared with EDX is shown in Table 3. All the binding energies (BEs) were corrected using C1 s as internal reference (set at 284.8 eV). The Co  $2p_{3/2}$  spectrum presents two spin–orbit doublets, characteristic to Co<sup>2+</sup> (781.2–781.9 eV) and Co<sup>3+</sup> (779.9–781.3 eV) and two shakeup satellites (785.7–789.7 eV) [15,21]. The characteristic peak of Co<sup>3+</sup> is shifted to higher values of energy in the presence of manganese, revealing that cobalt ions share the octahedral positions with manganese ions, leading to an asymmetry in the bond arrangement and an extra pressure on the  $Co^{3+}$  ions. The Mn  $2p_{3/2}$  spectrum presents a peak located at 641.6 eV characteristic to Mn<sup>3+</sup> [22], that has been observed only in the samples with 0.05 and 0.1 Mn, and a peak, in the range of 643.4–643.5 eV, corresponding to Mn<sup>4+</sup> (in all the samples). The spectrum of O1s could be fitted into two peaks, at 529.1-531.3 eV, attributed to lattice oxygen (OL1) and at 530.4-532.4 eV, characteristic for oxygen-deficient regions as undercoordinated lattice oxygen, O<sup>-</sup>, (O<sub>V</sub>) [23]. In the samples with manganese, an additional peak at 529.3-530.9 eV, attributed to manganese oxide lattice oxygen (O<sub>L2</sub>), is evidenced and its area increased at increasing in manganese loading. The interaction between Co and Mn leads to a change in coordination environment of oxygen and as a result, the O1 s peaks are shifted toward higher binding energy at increasing in manganese loading. The presence of surface oxygen vacancies plays a very important role in heterogeneous catalysis, being the active oxygen species, essential in redox reactions [24]. The atomic composition of elements in the subsurface layer, the ratio between Co and Mn ions and atomic ratio from XPS and EDX are listed in Table 3. In the samples with 0.05 and 0.1 Mn the atomic ratio Mn/Co is close to the

![](_page_5_Figure_3.jpeg)

Fig. 8. Effect of temperature on  $C_2H_5OH$ ,  $CO_2$  conversions and products composition (a), Arrhenius plot for ethanol dry reforming (b) on  $Mn_{0.15}Co_{2.85}O_4$  catalyst ( $CO_2$  flow rate 50 ml/min, ethanol 0.15 ml/min, molar ratio 1:1, 0.2 g catalyst).

![](_page_5_Figure_5.jpeg)

Fig. 9. Effect of temperature on ethanol conversion and products selectivities (a), Arrhenius plot of ethanol non-oxidative dehydrogenation (b) over Mn<sub>0.15</sub>Co<sub>2.85</sub>O<sub>4</sub> catalyst (145 ppm of ethanol, 0.2 g catalyst, total flow rate 50 mL/min).

stoichiometric value, whereas for the last sample the manganese oxides are concentered in the subsurface layer.

# 3.2. Catalytic activity

#### 3.2.1. Ethanol combustion

Cobalt-manganese oxides are nonstoichiometric oxides whose oxidation state changes almost continuously. Lattice oxygen may reduce the oxidation state of Mn and Co cations (from  $\text{Co}^{3^+}$  to  $\text{Co}^{2^+}$  and from  $\text{Mn}^{4+(3^+)}$ to  $\text{Mn}^{2^+}$ ) and leads to apparition of oxygen vacancies, which could be the active sites for oxidation reactions. Oxygen species, extracted from the lattice, also could act as oxidizing agents.

We discussed the potential applications of these catalysts in industry, taking into account their catalytic behavior in the combustion of volatile compounds. In this regard, the catalytic performances of cobaltmanganese oxides, with different Mn/Co molar ratios, were evaluated in ethanol combustion; the results are shown in Fig. 6(a). The curves of conversion as a function of reaction temperature were used for the catalytic activity assessment. The main products of reaction are CO<sub>2</sub> and H<sub>2</sub>O. The selectivity to acetaldehyde not exceeds 5%; therefore the catalytic activity was assessed by conversion to CO<sub>2</sub>.

At the same time, we also evaluated the effects of Mn doping on the  $Co_3O_4$  activity. The catalyst with higher manganese content presents better catalytic activity than catalysts with lower manganese content

and Co<sub>3</sub>O<sub>4</sub> sample. The temperature of T<sub>50</sub> (for a conversion of 50%) was selected as a parameter to evaluate the activity toward the ethanol oxidation. According to this parameter, the activities in ethanol combustion are as follows: Co<sub>3</sub>O<sub>4</sub> (218 °C) < Mn<sub>0.05</sub>Co<sub>2.95</sub>O<sub>4</sub> (193 °C) < Mn<sub>0.1</sub>Co<sub>2.9</sub>O<sub>4</sub> (182 °C) < Mn<sub>0.15</sub>Co<sub>2.85</sub>O<sub>4</sub> (167 °C).

At the increasing of Mn/Co ratio, an increase in  $Mn^{4+}$  content on the surface (XPS), in line with activity, has been observed. The presence of  $Mn^{4+}$  cations and oxygen vacancies is important since they act as active sites for ethanol combustion. The alcohol molecule is adsorbed on  $Mn^{4+}$  sites that are more easily reduced to  $Mn^{3+}$  than  $Co^{3+}$  could be reduced to  $Co^{2+}$ . At replacement of  $Co^{3+}$  cations in the octahedral position with  $Mn^{4+}$  cations, the oxygen contribute to the charge compensation (by reducing of  $Mn^{4+}$  to  $Mn^{3+}$ ), leading to emergence of the  $O^{2-}$  vacancy that is subsequently filled with  $O_2$  from air [25]. The placement of  $Mn^{3+}$  and  $Mn^{4+}$  cations in octahedral positions, as seen in the FT-IR spectra, provide more active catalysts, knowing that the cations in octahedral positions are more reactive than those in tetrahedral positions.

The apparition of oxygen vacancies, evidenced by increase of the lattice strain (XRD) with manganese content, is determined by the oxygen release. There is a good correlation between ethanol conversion,  $Mn^{4+}/Mn^{3+}$  ratio and lattice strain, as can be seen in Fig. 7. The presence of  $Mn^{4+}$  cations on the surface, at the same time with the presence of lattice defects, represents the essential factors for ethanol

![](_page_6_Figure_2.jpeg)

Fig. 10. Ethanol conversion in combustion, dry reforming and dehydrogenation over  $Mn_{0.15}Co_{2.85}O_4$  spinel oxide.

combustion.

Our results are in agreement with those reported by other researchers in alcohols combustion. Chen [9] noticed that Co–Cu–Mn (1:1:1)/ZSM-5 membrane/PSSF catalysts are active for isopropanol (T<sub>50</sub> at 200 °C), ethyl-acetate and toluene combustion. Bellal et all [26] also found that mixed iron-cobalt spinel oxides are active for ethanol combustion (T<sub>50</sub> is reached at 260–300 °C).

The catalytic performances in ethanol combustion could be evaluated from the activation energies. The apparent activation energies, calculated from the slopes of Arrhenius linear plots, (Fig. 6b) are, as follows: 48 kJ/mol for  $Co_3O_4$ , 43 kJ/mol for  $Mn_{0.05}Co_{2.95}O_4$ , 37 kJ/mol for  $Mn_{0.1}Co_{2.9}O_4$  and respectively 36 kJ/mol for  $Mn_{0.15}Co_{2.85}O_4$ . Similar values of the activation energy were obtained by Bellal [26] in the ethanol combustion over cobalt-iron spinel oxides.

#### 3.2.2. Dry reforming of ethanol with carbon dioxide

In the same time, ethanol dry reforming, in scope of the syngas production, represents an interesting method, since it uses as raw materials a renewable such as ethanol and undesirable such as  $CO_2$ . Syngas production, from methane and ethanol reforming with  $CO_2$ , is an important method through which the greenhouse gas reduction occurs [27]. Between the two methods, ethanol reforming is more attractive because the feedstock is renewable, nontoxic, easily transportable and in addition, energy consumption is lower compared to methane reforming.

In this scope, on the best catalyst of the studied series, namely  $Mn_{0.15}Co_{2.85}O_4$ , dry reforming of ethanol with carbon dioxide has been carried out and the results are shown in Fig. 8a. The influence of reaction temperature on the catalytic performance, in dry reforming of ethanol, has been investigated, using a stoichiometric CO<sub>2</sub>: ethanol ratio and temperature range from 200 °C to 450 °C. The ethanol and carbon dioxide conversions are improved significantly with increasing temperature; the ethanol conversion exceeds CO<sub>2</sub> conversion. Dry reforming reaction takes place in parallel with ethanol dehydrogenation to acetaldehyde, at temperatures below 350 °C.

The surface mobility of oxygen species and the cations redox ability are the key factors, in ethanol dry reforming, as it was observed by Kawi [17] and Lee [28]. Our catalyst presents the both features, especially the redox ability of  $Mn^{4+} \leftrightarrow Mn^{3+(2+)}$  and  $Co^{3+} \leftrightarrow Co^{2+}$  cations.

The hydrogen and carbon monoxide composition increased with increasing the reaction temperature. A similar behavior has been observed by Bahari [29,30] in ethanol dry reforming over Ce-promoted Ni/Al<sub>2</sub>O<sub>3</sub> and over La-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. The H<sub>2</sub>/CO ratio is very close to the stoichiometric value of 1:1, the highest H<sub>2</sub>/CO ratio (1.18) has been observed at 250 °C, probably due to the parallel reaction as ethanol dehydrogenation [31].

The apparent activation energy, from Arrhenius plot (Fig. 8b), of ethanol dry reforming reaction, has been determined to be 58 kJ/mol, much higher compared to the ethanol combustion, which means that in dry reforming, high temperatures are required for the catalyst activation.

# 3.2.3. Non-oxidative dehydrogenation of ethanol

In order to investigate the role of  $O_2$  in combustion and  $CO_2$  in dry reforming, we studied the ethanol conversion using  $N_2$  as diluent gas, on the same catalyst. The ethanol conversion and products selectivities are shown in Fig. 9a. The ethanol conversion is continuously increasing starting with the temperature of 100 °C up to 300 °C. Acetaldehyde, hydrogen, ethylene, water, methane and carbon monoxide are the reaction products, obtained from dehydrogenation, dehydration and decarbonylation of ethanol, respectively. The acetaldehyde selectivity reaches a maximum at 250 °C, while ethylene and methane selectivities have a slight decrease with the reaction temperature increasing.

The apparent activation energy of ethanol dehydrogenation is 40 kJ/mol, a value comparable to that obtained by Shan (45–49 kJ/mol) [32] in non-oxidative dehydrogenation of ethanol on Ni-Cu based catalysts.

As observed from Fig. 10 and from the values of apparent activation energies, the combustion proceeds under much milder conditions than dehydrogenation and dry reforming.

The apparent activation energies increase in the following order:  $E_a$  combustion  $< E_a$  non-oxidative dehydrogenation  $< E_a$  dry reforming, which means that the catalytic activity is decreased from combustion to dehydrogenation and dry reforming, respectively, as expected from thermodynamic data of (1)-(3) reactions.

Our results are comparable to the literature data on ethanol combustion [33] over cobalt-iron mixed oxides, where the ethanol conversion reaches 100% at temperatures above 300 °C; on ethanol dry reforming with CO<sub>2</sub> [34] using Cu-Ce-Zr-O catalysts, the ethanol conversion exceeding 50% only at temperatures above 550 C; and on ethanol dehydrogenation [35] over copper stabilized in Beta zeolite, the ethanol conversion having values of 30–70% at temperatures of 200–350 °C.

#### 4. Conclusions

The  $Mn_xCo_{3-x}O_4$  spinel oxides have been prepared by coprecipitation and investigated in combustion of ethanol, dry reforming with  $CO_2$  and in ethanol dehydrogenation.

The substitution of Co with Mn, in the cubic phase of spinel structure, leads to the appearance of network defects as micro-straining in the lattice (oxygen vacancies), observed from evaluation of lattice deformation where the elastic strain increases with Mn content increasing. The  $Co^{3+}$  cations are substituted by  $Mn^{3+}$  and  $Mn^{4+}$  cations in octahedral sites as can be observed from FT-IR. Moreover, a change of oxygen coordination environment, as a result of the interaction between Co and Mn, has been evidenced by the O1 s peak shifting toward higher binding energy with manganese loading increasing.

The presence of Mn<sup>4+</sup> cations on the surface and the presence of lattice defects represent the essential factors for ethanol conversion in combustion and dry reforming.

The catalyst is efficient for all three reactions, but in dry reforming and dehydrogenation, a high temperature is required for catalyst activation.

## **Declaration of Competing Interest**

There are no conflicts to declare.

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